THE MECHANICAL PROPERTIES OF POLYESTER-BASED COIL COATINGS. CORRELATIONS WITH CHEMICAL STRUCTURE

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Declaration of originality

I hereby declare that all material in this thesis is my own work except where clearly stated otherwise, in which case references are always provided.
Abstract

The present work studies the effect of changes in the formulation of coil coatings on their mechanical properties. The paint systems investigated were generally based on polyester binders that were heat-cured with hexa(methoxymethyl)melamine (HMMM). The chemical structure of the polyester, as well as the concentrations of the materials present in the formulations, was systematically changed and the mechanical properties of free-films of the paints were studied at a variety of different temperatures. Changes in the polyester back-bone resulted in significant changes in the glass transition temperature, $T_g$, of the paints. For example, the substitution of phthalic acid in the polyester, with iso-phthalic acid, resulted in a decrease in $T_g$ from 36 to 8 °C. At the same time, the respective effect on the mechanical properties was modest. On the other hand, changes in cross-link density resulted in dramatic changes in the mechanical properties of the paints. For example, the maximum strain at failure decreased from 180% to 30% when the concentration of the HMMM cross-linker in the paint was increased from about 5 wt% to about 30 wt%.

The effects of temperature and loading rate on the mechanical properties of the free-films of the paints were also investigated. Multi-frequency dynamic mechanical analysis (DMA) was used to obtain the correspondence between time and temperature, at low strains, in a quantitative way. This correspondence was extended to large strains, when tensile data under a range of different temperatures and loading rates were considered. Modelling studies were also performed, where a hybrid viscoelastic/hyper-elastic model was used to predict the tensile behaviour of the paints, with good agreement between the predictions and the measured data.

Finally, steel panels coated with a selection of the paint systems were tested in bending, using a T-bend test at 0T. An important finding was the increase in the amount of damage in the coating with time after bending, even though the panels were not deformed further. It was generally found that panels coated with paints which showed large values of strain to failure and toughness when tested as free-films, and also with little tendency for elastic recovery, suffered the least amount of damage when tested in bending.
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### Abbreviations

**AMP**: Amino methyl propanol  
**PE**: Polyester  
**BSE**: Back-scattered electrons  
**PET**: Polyethylene terephthalate  
**BSI**: British standards institution  
**PMMA**: Poly(methyl methacrylate)  
**DCB**: Double cantilever beam  
**PMT**: Peak metal temperature  
**DENT**: Double edge notch tension  
**PTFE**: Polytetrafluoroethylene  
**DMA**: Dynamic mechanical analysis  
**p-tsa**: P-toluene sulphonic acid  
**DSC**: Differential scanning calorimetry  
**RH**: Relative humidity  
**EB**: Electron beam  
**RMS**: Root mean square  
**EWF**: Essential work of fracture  
**SBR**: Styrene-butadiene rubber  
**HDAA**: Hexane diol diacrylate  
**SE**: Secondary electron  
**HMMM**: Hexa(methoxymethyl)melamine  
**SEM**: Scanning electron microscopy  
**IBOA**: Isobornyl acrylate  
**SENB**: Single edge notch bending  
**LEFM**: Linear elastic fracture mechanics  
**SENT**: Single edge notch tension  
**NPG**: Neopentyl glycol  
**TDCB**: Tapered double cantilever beam  
**PBT**: Poly(butylene terephthalate)  
**TTS**: Time-temperature superposition  
**PD**: Polydispersity  
**UV**: Ultra-violet  
**WLF**: Williams, Landel, Ferry
Greek alphabet

α: Breadth of Cole-Cole distribution of relaxation times

α₁, 2, 3, ... = Constants in Guth equation, eq. (2.66)

α₁: Shift factor

β: Refers to β (secondary)-transitions

β: Shape factor of outer process zone

β_L-N: Parameter in Lewis-Nielsen equation, eq. (2.76)

γ: Surface free energy

γ_B: Geometric factor in eq. (2.90)

δ: Phase angle

Δ: Displacement

δH: Activation energy

δa: Propagation length of crack

ε: Strain

ε_{c,e}: Ultimate strain of an elastic material with the Young’s modulus and failure stress of the composite

ε_{c,u}: Ultimate strain of composite

ε_D: Strain acting on dashpot

ε_{el}: Elastic component of strain

ε_{eng}: Engineering strain

ε_f: Strain to failure

ε_{m,e}: Ultimate strain of an elastic material with the Young’s modulus and failure stress of the matrix

ε_{m,u}: Ultimate strain of matrix

ε_{m}: Strain applied on matrix

ε_{max}: Maximum strain

ε_S: Strain acting on spring

ε_t: True strain

ε_y: Yield strain

ε’: In-phase component of strain

ε’’: Out-of-phase component of strain

ε₀: Instantaneous strain applied at t = 0

ζ: Shape factor in Halpin-Tsai equation, eq. (2.74)

ζ₁: Parameter in Sato-Furukawa equation, eq. (2.80)

ζ₂: Parameter in Sato-Furukawa equation, eq. (2.80)

η: Viscosity
\( \eta_{H,T} \): Parameter in Halpin-Tsai equation, eq. (2.74)

\( \vartheta \): Thickness

\( \lambda \): Stretch ratio

\( \lambda_{\text{lock}} \): Lock stretch ratio of chains

\( \lambda_1, \lambda_2 \text{ and } \lambda_3 \): Stretch ratios in the three principal dimensions

\( \mu \): Parameter in Lewis-Nielsen equation, eq. (2.76)

\( \mu_i \): Constants used in the Ogden equation, eq. (2.47)

\( \nu \): Poisson’s ratio

\( \nu_e \): Cross-link density

\( \nu_m \): Poisson’s ratio of matrix

\( \rho \): Density

\( \sigma \): Stress

\( \sigma_0 \): Time independent, strain dependant stress

\( \sigma_{c,u} \): Ultimate stress of composite

\( \sigma_D \): Stress acting on dashpot

\( \sigma_f \): Stress at failure

\( \sigma_I \): Stress applied on the \( i \)-th Maxwell element

\( \sigma_{\text{int},u} \): Strength of matrix-particle interface

\( \sigma_{m,u} \): Ultimate stress of matrix

\( \sigma_{\text{max}} \): Maximum stress

\( \sigma_s \): Stress acting on spring

\( \sigma_1 \): True stress

\( \sigma_y \): Yield stress

\( \tau \): Relaxation time

\( \tau_i \): Relaxation time of Maxwell element \( i \).

\( \tau_{m,u} \): Shear strength of the matrix

\( \tau^* \): Characteristic relaxation time

\( u_0 \): Extrapolated volume of one gram of polymer at a temperature of 0 K

\( u_{f,T} \): Free volume of one gram of polymer at a temperature \( T \)

\( u_T \): Volume occupied by one gram of a polymer at a temperature \( T \)

\( \varphi \): Volume fraction

\( \varphi_{\text{max}} \): Maximum volume fraction

\( \varphi^* \): Critical volume fraction of filler at which matrix behaviour changes from ductile to brittle
\( \psi \): Parameter in Sato-Furukawa equation, eq. (2.80)

\( \omega \): Oscillation frequency (DMA)

**Latin alphabet**

\( a \): Crack length

\( A \): Parameter in Doolittle’s equation, eq. (2.6)

\( a_{fr} \): Coefficient of friction

\( a_i \): Parameters used in the Ogden equation, eq. (2.47)

\( A_{P,A} \): Parameter in Papanicolaou and Bakos equation, eq. (2.89)

\( b \): Geometry parameter used in calculation of storage and loss modulus

\( B \): Parameter in Doolittle’s equation, eq. (2.6)

\( B_{P,A} \): Parameter in Papanicolaou and Bakos equation, eq. (2.89)

\( c \): Parameter of the generalized Cole-Cole distribution of relaxation times

\( C \): Compliance

\( C_f \): Moles of reactant with functionality

\( f \)

\( C_{ij} \): Constants in the general form of the continuum mechanics strain energy function

\( C_1 \): Constant in Williams-Landel-Ferry equation, eq. (2.7)

\( C_2 \): Constant in Williams-Landel-Ferry equation, eq. (2.7)

\( d \): Parameter of the generalized Cole-Cole distribution of relaxation times

\( E \): Young’s modulus

\( E' \): Storage modulus

\( E'' \): Loss modulus

\( E_c \): Young’s modulus of composite

\( E_e \): Equilibrium (rubbery) modulus

\( E_{m,d} \): Slope of the stress versus strain curve of the matrix material in the drawing region

\( E_m \): Young’s modulus of the matrix

\( f \): Functionality of reactant

\( f_{A,B} \): Force per unit area (Arruda-Boyce)

\( f_G \): Force per unit area (Gaussian)

\( f_i \): Predicted specific work of fracture from the linear regression for ligament length \( i \)
\( f_{\text{max}} \): Maximum force
\( f_{Ogden} \): Force per unit area (Ogden)
\( f_i \): Parameter in Clements and Mas equation, eq. (2.82)
\( G \): Shear modulus
\( G_c \): Critical energy release rate
\( G_E \): Shear modulus of composite
\( g_e \): Weighting of the equilibrium modulus
\( G_f \): Shear modulus of filler
\( g_i \): Weighting of the modulus of the \( i \)-th Maxwell element
\( G_m \): Shear modulus of matrix
\( h(\ln \tau) \): Distribution of relaxation times in logarithmic form
\( H(\tau) \): Distribution of relaxation times
\( I \): Moment of inertia
\( k \): Boltzmann’s constant
\( K_c \): Bulk modulus of composite
\( k_E \): Einstein coefficient
\( K_f \): Bulk modulus of filler
\( K_m \): Bulk modulus of matrix
\( k_{m,f} \): Relative change in matrix strength due to filler in Leidner-Woodhams equation, eq. (2.86)
\( l \): Ligament length
\( L \): Free length
\( l_{C-C} \): Length of C-C link
\( l_1, l_2, l_3 \): Stretch invariants
\( M_s \): Mean molecular weight of chains between cross-links
\( M_i \): Molecular weight of chain \( i \)
\( M_n \): Number average molecular weight
\( M_w \): Weight average molecular weight
\( n \): Number of C-C links between chemical cross-links
\( N \): Number of active chains
\( n_{P-B} \): Parameter in Papanicolaou and Bakos equation, eq. (2.89)
\( n_i \): Number of macromolecules of molecular weight \( M_i \)
\( P(r) \): Chain length distribution (eq. 2.23)
\( p_{fr} \): Fractional conversion of functional sites
\( p \): Pressure
\( P \): Load
**Nomenclature**

- $P_c$: Critical load
- $q$: Constant used in determination of critical load for buckling
- $r$: End to end length of a chain
- $R$: Ideal gas constant
- $r_s$: Stoichiometric ratio
- $R^2$: Coefficient of determination
- $s$: Time interval for application of a strain $\varepsilon(s)$
- $S$: Entropy
- $s_a$: Standard error of intercept of linear regression
- $s_b$: Standard error of slope of linear regression
- $S_{CF}$: Stress concentration factor
- $S_{ni}$: Breadth of log-normal distribution
- $s_{wrl}$: Standard error of residuals of linear regression
- $T$: Temperature
- $t$: Time
- $\tan\delta$: Tangent of phase angle between stress and strain (DMA)
- $T_{e}$: Temperature in the rubbery region
- $T_g$: Glass transition temperature
- $T_{g,end}$: End of glass transition
- $T_{g,onset}$: Onset of glass transition
- $T_{ref}$: Reference temperature
- $t_{ref}$: Reference time
- $t_T$: Time at temperature $T$
- $t_{T_ref}$: Time corresponding to reference temperature
- $U_1$: Work stored in the material elastically
- $U_2$: Work supplied to the material by an external force
- $w$: Width
- $W_{A-B}$: Arruda-Boyce strain energy function
- $w_e$: Essential work of fracture (specific)
- $W_e$: Total essential work of fracture
- $W_{el}$: Elastic part of work supplied to deform sample
- $w_e^*$: Plane strain essential work of fracture
- $W_f$: Total specific work of fracture
- $W_f$: Total work of fracture
- $W_G$: Gaussian strain energy function
$w_{inel}$: Specific inelastic work consumed in outer process zone

$W_{inel}$: Total inelastic work consumed in outer process zone

$W_{M-R}$: Mooney-Rivlin strain energy function

$W_{n-H}$: Neo-Hookean strain energy function

$W_{Ogden}$: Ogden strain energy function

$W_{tot}$: Total work supplied to deform sample

$z$: Parameter of the generalized Cole-Cole distribution
Coil-coating is the method where metal sheets (usually steel or aluminium) are pre-painted in a continuous process, before being formed into the desired shape of the end product. The method takes its name from the storage of the metal sheet in coils, both before and after the application of the paint. Coil-coated sheets are used in the automotive, construction and domestic appliances industries, offering significant advantages such as a reduction of costs and improved efficiency in the manufacturing process, compared to painting the finished product [1, 2]. Because the curing and drying of the paint are performed in a controlled way, generally inside a gas oven (see discussion below), an additional advantage of the method comes from the decrease in solvent emissions, which is gaining importance in recent years due to increasingly strict environmental regulations [3].

The coil coating process in its most popular form involves the application of wet paint through a set of rollers on a continuous metal sheet, and the subsequent heat-cure of the paint inside gas ovens operating at temperatures between 300 and 500 °C [1]. Alternative methods include the use of paint in powder form and the use of a radiation cure (instead of heat cure) method. Both of these methods have the advantage of the complete elimination of solvents from the paint formulation. Shortcomings of the radiation cure method are the often reported poor adhesion between the paint and the substrate, the poor formability of the cured paint, and the high capital costs [1, 4]. One disadvantage of the powder coating method is the associated reduction in the attainable line speed [1]. In the case of heat-cured liquid coil coatings, line speeds are generally between 20 and 200 m/min. Depending on line speed and oven
temperature, dwell times inside the oven can range between 15 and 60 sec [1, 5]. A schematic diagram of a coil-coating line is shown in Figure 1.1 where it is seen that the cleaning and surface treatment of the metal panel are also accommodated within the continuous coil-coating process.

Due to the nature of the forming method of the pre-painted panels, it is very important that the paint is able to withstand large mechanical deformations, without cracking or losing adhesion to the metal substrate. Therefore, paint manufacturers are faced with the challenge of providing products that show excellent formability as well as the usual qualities required from coatings, such as good appearance, weatherability, protection against corrosion etc. This has resulted in the development of highly engineered polymer-based coatings which can be treated similarly to structural adhesives, in that they require specific mechanical properties, such as stiffness, stress and strain to failure, and toughness. A wide range of paint systems based on a variety of binder resins, such as polyester, epoxy, acrylic and polyvinyl chloride (PVC) [1, 2, 5] is available for coil-coating applications. Among these systems, polyester binders are the most widely used, prominently in a cross-linked form where hexa(methoxymethyl)melamine (HMMM) is added as the cross-linker [5]. In this study the focus will be on polyester-based systems cross-linked either by heat cure with HMMM or by electron-beam cure.

![Figure 1.1. Schematic diagram of coil-coating line, source: [3].](image)

### 1.1 Aims and objectives

The primary objective of the present project was to investigate the effects on the mechanical properties from changes in the formulation of polyester-based paint-films. Such changes include the modification of the polyester binder, the use of different concentrations of HMMM cross-linker and catalyst, and the use of different cure
methods (heat cure versus electron-beam cure). Additionally, the effect of pigmentation was studied by considering both pigmented and unpigmented (clear) versions of the paints. As it is expected that pre-painted panels will be formed under a wide range of environmental conditions and deformation rates, a consideration of the effects of rate and temperature on the mechanical properties of the free-films of the paints is of particular interest, and a significant part of this work is dedicated to the study of these effects.

A second objective was to investigate the possibility of approximating the mechanical behaviour of the paint-films with the use of existing visco-elastic and rubber-elastic predictive models. On one hand, this treatment will enable the theoretical prediction of the paint properties at any temperature and loading rate, which is considered to be of great practical importance due to the resulting decrease in the amount of experimental tests required to characterise the materials. On the other hand, it is of interest to determine the visco-elastic and hyper-elastic constants of the paints. These can then be used in future work for the modelling of the deformation of coated panels, in the context of a finite element analysis.

A final objective of the project was to study the damage developing on coated panels under bending loads. Here, the scope was not only to correlate between changes in formulation and observed performance, but also to investigate which mechanical properties and which microstructural characteristics of the paint-films control the amount of damage on the surface of coated panels subjected to large deformations.

1.2 Thesis outline

In the following Chapters, the experimental results are grouped with respect to the affinity of the paint systems, in a way that in each Chapter there is one independent variable (for example the concentration of cross-linker), which will be responsible for changes in the mechanical properties of the paints. Due to the wide range of formulations and properties that were studied, it will not be attempted to give a comprehensive review of the published literature in a single separate Chapter. Instead the relevant literature will be presented and discussed for each group of formulations
separately, along with the experimental results. This facilitates a comparison between the results reported here and those reported in the literature. Modelling studies of the paint systems, and studies of coated panels tested in bending, are presented collectively for all formulations in an attempt to obtain general correlations and overall trends from the collected data. The outline of this thesis and a brief summary of each Chapter are given below.

Chapter 2 lays the theoretical basis required for the understanding of the discussions that will follow. This Chapter is divided in four Sections. In Section 2.1, a number of basic definitions integral to the study of polymeric materials (for example crystallinity, cross-link density etc.) are given. Section 2.2 offers an introduction to the response of polymeric materials to mechanical loads, with particular emphasis on the effects of temperature and loading rate. A selection of the available models that can be used to approximate the mechanical behaviour of polymers is also presented. In Section 2.3 the basic principles required for the understanding of fracture mechanics are given, where the focus is on the essential work of fracture method. Finally, Section 2.4 is concerned with the mechanical behaviour of particulate-filled composite materials, and more specifically with the prediction of the changes in the mechanical behaviour of polymers as a result of the addition of a second phase of filler particles.

In Chapter 3, the details of the formulations used in this work are given. This includes the chemical structure of the polyester binders as well as the concentrations of the materials present in the formulations. The methods used to manufacture the paints are presented, as well as the relevant cure schedules.

In Chapter 4, a description of the experimental methods that were used in this study is given, with details of the sample manufacturing processes and of the experimental set-up. Also given are details on the methodology followed for the analysis of the experimental results.

In Chapters 5 – 10, the experimental results are reported. All results are compared to those of the overall control formulation, which is based on a polyester that is widely used in coil-coating applications and is heat-cured with a commonly used amount of HMMM. Chapter 5 reports the results of the control paint along with two
formulations where the concentration of the monomers present in the polyester binder is systematically changed. As this is the first experimental Chapter in this thesis, several remarks are also made regarding the mechanical behaviour of polymers in general. Chapter 6 compares the results of the control paint to three formulations with a varying concentration of cross-linker (HMMM). In Chapter 7, the effects of the concentration of catalyst on the mechanical properties of the paints are considered, where two formulations (one with higher catalyst content and one with lower) are compared to the control paint. Chapter 8 reports the results of a linear (non-branched) version of the control paint. In Chapter 9, the results of two additional formulations are shown, where further modifications have been made to the chemical structure of the polyester. Of these two paints one is cross-linked with the standard heat-cure method while the other is cross-linked by the electron-beam cure method. Finally, in Chapter 10 the effect of pigment on the mechanical properties is reported by incorporation of 50 wt% of TiO₂ pigment in a selection of the formulations discussed previously.

In Chapter 11, a selection of the paints is used to demonstrate the correspondence between the effects of temperature and loading rate on the mechanical properties of the paint. By use of the time-temperature superposition principle the effects of temperature and loading rate are successfully predicted in both the small- and large-strain regime. Promising results are also obtained from the use of analytical models to predict the tensile behaviour of the materials.

Chapter 12 reports the results from the bending tests of steel panels coated with a selection of the paint formulations. Correlations are made between the mechanical properties of the paint films, the microstructure of the paints, and the observed damage on the coated surface of the panels.

In Chapter 13, the main conclusions of the present study are given and recommendations on future work are made.
Chapter 2. The mechanical properties of polymers and particulate-filled composites

2.1 An introduction to polymeric materials

The materials investigated in this study can be classified as either polymeric, in the case of unpigmented (clear) paints, or composite, in the case of paints also containing pigment. It becomes clear, therefore, that the present study will revolve around the properties of polymers, with the focus being on their mechanical properties. In that sense it is integral to the following discussions to give a number of definitions regarding the composition and the structure of polymeric materials, while a discussion on the properties of composite materials is given in Section 2.4. It is acknowledged that the subject of polymer properties is extremely broad and it would be beyond the scope of the present thesis to attempt a detailed introduction to the relevant topics. Instead, the focus here will be on providing these basic definitions that are necessary in the understanding of the discussions that follow, without going into details that are not relevant to this study. Sections 2.1.1 and 2.1.2 are informed by a number of texts that offer an introduction to polymer science [6-10].

2.1.1 General definitions

The term polymer (from the Greek words πολύς+μέρος) describes that which is made up of many parts. Thus polymers are constructed from the formation of covalent bonds (where valence electrons are shared) between repeating units, also known as monomers. This process is called polymerisation. The resulting polymer chain
The mechanical properties of polymers and particulate-filled composites may consist of one (homochain) or many (heterochain) types of atoms. The number of repeat units in a polymer chain will greatly influence the physical properties of the polymer. A commonly used example, to that effect, is the alkane series with a general formula $\text{H}(-\text{CH}_2-)_n\text{H}$, where $n$ denotes the number of repeat units. For $n \leq 4$ the polymer is in gaseous form, while for larger $n$ it becomes a liquid and eventually a solid for $n \geq 25$.

In reality polymers will contain chains of a range of different lengths, which can be considered to be distributed according to a probability density function. It follows that the molecular weight of the chains will also vary, and this is known as a molecular weight distribution. In practice, however, it is often useful to refer to a single value in order to describe the molecular weight of a polymer. The two most widely used definitions are the number average, $M_n$, and the weight average, $M_w$, molecular weight. It is noted that in the context of this study, the term molecular weight will always refer to the number average molecular weight, unless otherwise specifically noted. $M_n$ is calculated as

$$M_n = \frac{\sum n_i M_i}{\sum n_i} \tag{2.1}$$

where $n_i$ is the number of macromolecules of molecular weight $M_i$. The weight average molecular weight is given by

$$M_w = \frac{\sum w_i M_i}{\sum w_i} \tag{2.2}$$

where $w_i$ is the total weight of all chains with a molecular weight of $M_i$. It is also useful to have an idea of how uniform the molecular weight distribution is. A measure of this is the polydispersity, PD, of the polymer, that is obtained as the ratio $M_w/M_n$. When PD = 1 the molecular weight distribution is uniform, i.e. all chains have the same molecular weight, and the polymer is characterised as monodisperse.

Another distinction is between polymers that are formed from a single type of monomer and those which are the result of the combination of several monomers. The
The mechanical properties of polymers and particulate-filled composites

former are referred to as ‘homopolymers’ while the latter as ‘copolymers’. Depending on the arrangement of the different monomers along the polymer chain, copolymers can be further divided into random (where the monomers are randomly distributed), alternating (where the monomers are organised in an alternating fashion) and block copolymers (where the monomers form distinct blocks). These three different types of copolymers are schematically shown in Figure 2.1. The arrangement of atoms and groups along a chain is also important for polymer properties and constitutes the configuration of the polymer. In Figure 2.2 two different possible configurations of polystyrene are shown as an example. Clearly, for the configuration of a polymer chain to change, the breaking and reforming of covalent bonds is required. In addition, the spatial arrangement of the atoms in a chain (see Figure 2.3) is of interest, which results from the rotation of single bonds and is referred to as the conformation of the chain. Chain conformation can change when a sufficient amount of energy is supplied to the polymer and such changes can be very important for the macroscopically observed mechanical behaviour of polymers. Finally, so far polymer chains have implicitly been considered as linear, i.e. the backbone is assumed to be constructed of carbon atoms for example, with side groups (such as the benzene rings in the styrene molecule shown in Figure 2.2) connected to the backbone. An alternative is where entire chains are connected to the backbone to form branches of various lengths. Such polymers are referred to as ‘branched’.

Further to the above discussion regarding the configuration, conformation and linearity of individual chains, and since any given polymer will contain a large number of chains, it is important to consider also the interactions and arrangements of these chains with respect to each other. In the melt, chains are organised randomly, however, as the polymer enters the solid state different options exist. In one option, the random positioning of the chains in the melt is frozen to give an arrangement that is very vividly described by the popular ‘bowl of spaghetti’ metaphor. Polymers with such an arrangement of chains are called ‘amorphous’ (see also Figure 2.4 (a)). On the other hand, there also exists the possibility that, upon cooling from the melt, highly ordered, ‘crystalline’, regions will form inside the polymer, as shown in Figure 2.4 (b).
The degree to which polymers are crystalline or amorphous will again have a direct
effect on their physical and mechanical properties.

A–B–B–A–B–A–A–B (a) A–B–A–B–A–B–A–B (b) A–A–A–A–B–B–B–B (c)

Figure 2.1. Schematic of a random (a), alternating (b) and block (c) copolymer consisting of two
different monomers A and B.

Figure 2.2. Two different configurations of polystyrene: head to tail (a) and head to head (b).
Image recreated from [7].

Figure 2.3. Schematic of two different conformations ((a) and (b)) of the same polymer chain.

Figure 2.4. Schematic representation of amorphous (a) and crystalline (b) arrangements of
polymer chains.

2.1.2 Polymer networks

With polymers containing a large number of chains in close proximity, it is to be
expected that secondary bonds may form between the chains. However, of particular
interest is the case where primary bonds are formed between the polymer chains, to
give a three dimensional network. This procedure is known as cross-linking and is of
tremendous importance in polymer science and engineering, as it affects the
properties of polymer materials profoundly, making them suitable for a range of
highly-demanding and safety-critical applications. Cross-linking is also extremely
important in the context of this project, and its effects on the mechanical properties of the materials used are demonstrated and discussed throughout this thesis.

Generally speaking, cross-linking requires the mixing of two (or more) monomers, of which at least one has more than two functional sites available for the formation of primary bonds. In practice a polymer resin is mixed with a monomer or oligomer cross-linker, and links are formed between the functional groups of the two, resulting in a structure where the chains of the polymer resin are connected by molecules of the cross-linker in a permanent network. In the case of a perfect network, all chains are connected to the network and no dangling ends, loop-structures or unreacted chains are present (see Figure 2.5). By introduction of a mechanistic terminology, chains that have both ends connected to the network are also known as ‘elastically effective’ [11]. In that sense it is clear that a branch connected to the backbone is not elastically effective and does not contribute to cross-linking. Points where three or more elastically effective chains connect are referred to as ‘junction points’.

In dealing with cross-linked polymers it is very useful to have a measure of the degree to which they are cross-linked. To that extent, cross-link density can be defined as the number of moles of elastically effective network chains per unit volume of the polymer. Cross-link density is an experimentally determinable quantity as will be shown in Section 2.2.2.1. A theoretical calculation of the expected cross-link density, however, is also possible. A series of assumptions can be made that greatly simplify the calculations, i.e. that functional groups of the same type are equally reactive, that groups react independently and finally, that groups belonging to the same chain do not react with each other [12]. Further simplification is achieved if it is assumed that the reactants are in a stoichiometric ratio of unity (i.e. the total numbers of functional groups in the chains of the reactants are equal) and that cross-linking proceeds to completion (i.e. a perfect network is formed where all chains are elastically effective). Based on the above assumptions the cross-link density, \( ν_e \), of the resulting network is given by [11, 13]:

\[ \nu_e = \frac{2N}{M} \]

2. The mechanical properties of polymers and particulate-filled composites
where \( f \) is the functionality of each reactant, and \( C_f \) are the moles of reactant with functionality \( f \) per unit volume of the cross-linked polymer. The physical interpretation of equation (2.3) becomes clear if one considers that (since all chains are cross-linked and all functional sites have reacted) \( f \) is equal to the chain ends linked to junction points. Since each elastically effective chain has two chain ends, it follows that \( f/2 \) represents the number of elastically effective chains, which multiplied by \( C_f \) results in the number of moles of elastically effective chains per unit volume. As junction points with functionality of 2 or less are not elastically effective, the summation is performed for \( f \geq 3 \).

Hill [11] has proposed an extension of equation (2.3) allowing for incomplete reaction of the functional groups, provided that no completely unreacted chains remain in the network (i.e. each chain has at least one end connected to the network). To maintain the simplicity of the calculations he considered two cases separately: one where all junction points have a functionality of \( f \geq 4 \) and one where all junction points have a functionality of \( f = 3 \). For \( f \geq 4 \):

\[
\nu_e = \left(2p_{fr} - 1\right) \frac{1}{2} \sum_{4}^{\infty} fC_f
\]

while for \( f = 3 \):

\[
\nu_e = \left(3p_{fr} - 2\right) \frac{1}{2} \sum_{3}^{3} fC_f
\]

where \( p_{fr} \) represents the fractional conversion of functional sites, and the summation in equation (2.5) serves to acknowledge that even though all junction points are trifunctional, there may be several reactants with \( f = 3 \).

In practice none of equations (2.3)-(2.5) can provide an accurate picture for polymer networks, as they are based on assumptions that are not necessarily true in reality. A more general and realistic treatment is given by Miller and Macosko [12], which
comes, however, with a significantly higher level of complication in the required calculations. For the purposes of this study, equation (2.3) will be used to calculate the cross-link density of a perfect polyester-HMMM network where the two reactants are present at a stoichiometric ratio of unity.

![Schematic diagram of network of cross-links](image)

Figure 2.5. Schematic diagram of network of cross-links. Black circles correspond to junction points while the grey circle is not a junction point as one of the chains forms a loop structure. A dangling chain is noted with an arrow, while a completely unreacted chain is shown as the dashed line.

### 2.2 The mechanical behaviour of polymers

Having provided the basic definitions required for the understanding of the properties of polymeric materials in Section 2.1, their mechanical behaviour will be the main focus of Section 2.2. In particular, the dependence of polymer properties on temperature and time (visco-elasticity) will be at the centre of discussions in the following Sections. Depending on the test temperature and rate, polymer materials will behave in a glassy (brittle and time-independent), visco-elastic (ductile and time-dependent) or rubbery (hyper-elastic time-independent) manner. The change from glassy to rubbery behaviour, commonly referred to as the glass transition, constitutes perhaps the most important polymer property from a practical point of view, and is discussed in Sections 2.2.1.1 and 2.2.1.2.

The interchangeable effects of temperature and time on the mechanical response of polymers are discussed in Section 2.2.1.3, while simple mechanistic models are considered for capturing the dependence of small strain properties on time (visco-elastic case) in Section 2.2.1.4. The theories dealing with the strain-dependent (but time-independent) behaviour of rubbers are considered in Section 2.2.2, while visco-elastic and hyper-elastic models are combined in Section 2.2.3 to predict the large-strain tensile behaviour of polymeric materials.
2. The mechanical properties of polymers and particulate-filled composites

2.2.1 Time and temperature dependence of mechanical properties

It is well known (see for example standard textbooks such as [7, 10, 14]) that the mechanical properties of polymers are highly dependent on test temperature and time. This time and temperature dependence can be easily demonstrated by considering the tensile testing of a polymer at different temperatures (and a constant strain rate) or at different displacement rates (at constant temperature). Typical stress versus strain curves under such conditions are shown in Figure 2.6 (a), where the material behaviour is seen to change from brittle at low temperatures or high test rates (high failure stress, but low strain at failure) to ductile at high temperatures or low test rates (yielding and high strain at failure, but low failure stress).

Another popular experiment involves applying a constant displacement on a sample of the material and monitoring the change in the stress required for maintaining that displacement over time. This is known as a stress relaxation test. If the sample is of a time-independent material, no change in stress is expected. On the other hand a viscoelastic material will show a decrease in the required stress with time. This is shown in Figure 2.6 (b). In Figure 2.6 (c), the resulting relaxation modulus, measured simply as the instantaneous stress over the constant strain, is plotted versus time. Different regions are noted on the figure, i.e. the glassy region where the modulus is relatively independent of time, the transition region where the modulus decreases steeply with time and the rubbery plateau where again the modulus becomes independent of time. In the case of uncrosslinked polymers a fourth region follows the rubbery plateau where the modulus decreases once again, resulting in flow. Alternatively, a series of relaxation tests can be performed at different temperatures and the modulus can be measured after a predetermined constant period of time. If these measurements are then plotted versus temperature, Figure 2.6 (c) is obtained again where the x-axis is now in units of temperature instead of time.
2.2.1.1 Changes in modulus with time and temperature

Plots such as the one found in Figure 2.6 (c) are very important as they provide the position of the glass transition region along the temperature or time axis. Similar plots are used for example for the determination of the glass transition temperature from DMA or DSC data [15, 16] (albeit in the latter case it is not a mechanical property that is being monitored but rather the heat capacity of the sample). For the following discussion, the change in relaxation modulus with temperature will be considered, but it is noted that similar conclusions can be drawn by consideration of the relaxation modulus versus time. In explaining the concepts of the glass transition, the classic texts by Ferry [17] and Aklonis and MacKnight [18] are closely followed.

In Figure 2.6 (c) four different regions are shown. In the glassy region the modulus is slowly decreasing with increasing temperature as a result of molecular motion being severely hindered. At these low temperatures small-scale side-group motions can
result in stress relaxation. Such phenomena are referred to as secondary, or $\beta$, transitions [10]. At higher temperatures the relaxation modulus shows a dramatic decrease that for amorphous polymers can be several orders of magnitude. The temperature range over which this relaxation takes place is known as the glass transition region. The drop in modulus inside the glass transition is associated with an increase in the vibrational motion of the chains that now have sufficient energy for short range diffusion, i.e. it is now easier for short segments of the molecules to rearrange themselves, resulting in lower energy conformations of the chains and therefore in a relaxation of the applied stress.

When the temperature is increased further, the chains have enough mobility for any short range conformational changes to happen instantly (at infinitely short times). The material is relaxed at the time scale of observation and that is reflected in a constant relaxation modulus. That this modulus is not zero has to do with the fact that even though short range motion takes place readily, long range diffusion of molecular chains is hindered due to interactions between the chains. For a cross-linked polymer these interactions are in the shape of primary bonds and therefore the relaxation modulus will maintain a more or less constant value until chemical degradation of the material starts. On the other hand, in the case of thermoplastic polymers the interactions between chains are mainly in the form of physical entanglements. Therefore with increasing temperature large scale diffusion of chains is possible, leading to polymer flow. This is seen in Figure 2.6 (c) as the dotted line in the flow region.

2.2.1.2 Theories of the glass transition

It is obvious, from the above, that the change in polymer properties with temperature and time is at least qualitatively linked to the ease with which the molecules can move. Various theories have sought to interpret visco-elasticity in a more quantitative manner. These are usually classified as free volume, thermodynamic and kinetic theories [17, 18]. Of these three main approaches, free volume, presents a relatively simple explanation of visco-elasticity providing justification for many of the specific
observations associated with the glass transition, and will be briefly discussed here. However, it needs to be noted that the thermodynamic and kinetic theories also predict many aspects of polymer behaviour successfully. For example, the measurement of glass transition by DSC is based directly on the application of thermodynamic considerations.

The free volume approach can be traced back to Doolittle’s [19] treatment of the viscosity of polymer liquids. He proposed a relationship of the form:

\[ \eta_T = A \exp \left( B \frac{u_0}{u_{f,T}} \right) \]  

(2.6)

where \( \eta_T \) is the viscosity of the melt at a given temperature, \( u_0 \) is the (extrapolated) volume of one gram of the polymer at a temperature of 0 K and \( u_{f,T} \) is the free volume of one gram of the polymer at the measurement temperature. The free volume represents the ‘empty’ space that is not occupied by the polymer chains, and can be defined as \( u_{f,T} = u_T - u_0 \), where \( u_T \) is the volume occupied by 1 gram of polymer at a temperature, \( T \). \( A \) and \( B \) are constants specific to each polymer.

The extension of Doolittle’s free volume concept to the description of the visco-elastic properties of polymers is based on the idea that the mobility of polymer chains depends on the free volume available in the material. This is formally stated by Turnbull and Cohen [20, 21] who argued that molecular motion can only take place in the presence of sufficiently large voids which the molecule will occupy upon moving from its initial position. In that sense, the problem of the glass transition is reduced to explaining the temperature dependence of free volume, and the reader is referred to the original article [21] where this dependence is formally shown.

However, possibly, the most alluring aspect of the free volume theory is its success in describing the effects of a wide range of variables such as pressure, isothermal contraction, molecular weight, incorporation of diluents in polymers etc. on the glass transition [17]. Regarding the effect of molecular weight on free volume, for example, a decrease in free-volume can be expected with increasing molecular weight of the polymer. This is a result of the greater number of chain-ends present in polymers of a
lower molecular weight. Since chain ends are locations of imperfect packing for the polymer chains, an increase in their number will lead to an increase in the free volume available. Experimentally, a decrease in the specific volume and an increase in the glass transition temperature with increasing molecular weight was observed by Fox and Flory in [22]. It is therefore possible to attribute the observed dependence of glass transition on molecular weight to the respective correlation between the latter and free volume.

2.2.1.3 Time-temperature superposition

Up to now, a correspondence between the effects of temperature and time on the properties of polymers has been implied (see for example Figure 2.6 (c)). In this Section, this correspondence is considered in a more quantitative way. An example will be considered of a series of relaxation tests performed at different temperatures. In every case the relaxation modulus is monitored in the time interval between 0.1 and 10 s. The expected behaviour is for the relaxation modulus to decrease with time during each test, and for this decrease to initially become faster with increasing temperature through the glass transition, and to slow down again substantially upon a further increase in temperature which will bring the material into its rubbery region. These results can be plotted in a common graph as in Figure 2.7 (a), where the arrow points towards increasing testing temperature. The next step involves selecting one of the relaxation modulus isotherms as a reference and then seeking to shift the rest of the curves along the time axis, in order to produce a smooth curve similar to the one found in Figure 2.6 (c). This curve is usually referred to as a master-curve or master-plot. The results of such a shift are shown in Figure 2.7 (b) where the reference isotherm is noted as the dotted line in both graphs (a) and (b).

The above treatment of the data from relaxation experiments results in an impressive broadening of the time scale of the experiment. By using data at various temperatures, the experimental time-scale at the reference temperature is extended by nearly fifteen orders of magnitude. Therefore, the great importance of time-temperature
superposition lies in its ability to predict the material properties as times that would otherwise be either too short or too long for experimental observation.

For an analytical expression of the shifts required to obtain the master-plot in Figure 2.7 (b), Williams, Landel and Ferry [23] proposed a simple equation as:

$$\log \alpha_T = \frac{C_1(T - T_{ref})}{C_2 + T - T_{ref}}$$

where $C_1$ and $C_2$ are constants, $T_{ref}$ is the reference temperature that is used to shift the isotherms (customarily taken at $T_g$), and $T$ is the temperature of the isotherm being shifted.

$\alpha_T$ is the shift factor along the time axis, required for a smooth superposition of the isotherm at $T$ with respect to the isotherm at $T_{ref}$. It follows that:

$$\alpha_T = \frac{t}{t_{ref}}$$

where $t_{ref}$ is the time corresponding to the reference isotherm and $t$ is the time corresponding to the shifted isotherm.

Figure 2.7. Isotherms of relaxation modulus versus the logarithm of time for the isotherms (a) and master-plot of relaxation modulus versus time where the isotherms were shifted along the time axis with respect to a reference temperature (dotted isotherm in (a)) (b).
Equation (2.7) can be shown [17, 23] to be equivalent to the Doolittle equation (equation (2.6)). In that sense the Williams, Landel and Ferry (WLF) approach is directly related to the free volume theory discussed in the previous Section. Regarding the constants $C_1$ and $C_2$, these were initially thought to take values universally applicable to any polymer, as $C_1 = 17.44$ and $C_2 = 51.6$ [23]. Physically, $C_1$ is related to the free volume available in the polymer at $T_g$, while $C_2$ is related to the thermal expansion coefficient at the same temperature. Fox and Flory [22] and Fox and Loshaek [24] reported that, except for the case of very low molecular weight polymers, free volume at $T_g$ is approximately independent of molecular weight. This finding has been used to justify the universal value of $C_1$. However, the idea of universally applicable WLF constants has since been discarded, and Ferry [17] recommends that the constants are experimentally determined for each polymer tested.

The WLF equation describes the behaviour of polymers at temperatures between $T_g$ and $T_g + 100$ °C [17]. For temperatures below $T_g$ the free volume is more or less constant and changes with time very slowly. Therefore relatively large motions of chains as those associated with the glass transition are now hindered. Instead relaxation takes place through localised motions of side groups or even within the back-bone chains of the polymer [18]. These motions are better described through an activation energy approach and an Arrhenius type relationship is used for the prediction of the shift factors required for the construction of the master-plot in the glassy region. This is expressed as [10, 18]:

$$
\log \alpha_T = \frac{\delta H}{R} \left( \frac{1}{T} - \frac{1}{T_{ref}} \right) \frac{1}{2.303}
$$

(2.9)

where $\delta H$ is the activation energy required for the relaxation and $R$ is the ideal gas constant (taken as 8.314 J/(molK)).

The experimentally determined shift factors obtained from the time-temperature superposition (TTS) performed in Figure 2.7 are plotted along with the Arrhenius and WLF predictions ($C_1$, $C_2$ and $\delta H$ were determined by optimization of equations (2.7) and (2.9) against the experimental $\alpha_T$) in Figure 2.8. It is seen that the Arrhenius
prediction overestimates the required shifting of the data at high temperatures, while at low temperatures the WLF prediction rises sharply, again overestimating the values of $\alpha_T$ required for TTS.

Figure 2.8. Arrhenius and WLF predictions for shift factors ($\alpha_T$) based on the data shown in Figure 2.7.

2.2.1.4 Mechanical analogues of the visco-elastic behaviour of polymers

The time and temperature dependent behaviour of polymers has been shown so far to be a result of molecular mobility, and has been explained on the basis of the free volume theory. In trying to predict the response of visco-elastic materials to applied loads and strains the use of various mechanical analogues has been proposed. These analogues offer phenomenological predictions of the material behaviour and should not be expected to yield information about physical processes in a micro-structural level, at least directly. Nevertheless, they provide valuable tools for the modelling of the mechanical behaviour of polymers and for this a presentation of the basic concepts related to such models, is necessary here. Various text books cover the topic and the discussion below is informed by the texts of Ferry [17], Aklonis and MacKnight [18] and Wineman and Rajagopal [25].

For the construction of visco-elastic models, the polymer behaviour is considered to be the result of the superposition of elements that behave either in a purely elastic way (i.e. as Hookean springs) or in a purely viscous way (i.e. as Newtonian fluids). For a Hookean spring the stress is a linear function of strain, while for Newtonian fluids
stress is linearly proportional to strain rate. These relationships are shown in equations (2.10) and (2.11) respectively:

\[ \sigma(t) = E \varepsilon(t) \]  
\[ \sigma(t) = \eta \frac{\varepsilon(t)}{dt} \]

where \( \sigma(t) \) and \( \varepsilon(t) \) are the stress and strain applied on the material as functions of time, \( t \), \( E \) is the Young’s modulus of a material behaving like an ideal spring and \( \eta \) is the viscosity of a Newtonian fluid.

Perhaps the simplest mechanical analogue that can give a sufficiently good prediction of polymer behaviour is that of a Hookean spring connected in series with a viscous element, customarily represented by a dashpot. This is referred to as a Maxwell element and is shown in Figure 2.9, where the subscripts \( S \) and \( D \) denote the spring and dashpot respectively. If a tensile deformation is now applied to the Maxwell element, the total strain can be expressed as:

\[ \varepsilon(t) = \varepsilon_s(t) + \varepsilon_d(t) \]  
\[ \sigma(t) = \sigma_s(t) + \sigma_d(t) \]

while the stress applied to each part of the element is equal to the total stress:

Substitution of equations (2.10) and (2.11) into equation (2.12) and (2.13) and differentiation with respect to time gives:

\[ \frac{\varepsilon(t)}{dt} = \frac{1}{E_s} \frac{\sigma(t)}{dt} + \frac{\sigma(t)}{\eta} \]

where the total strain on the element is expressed as a function of the total stress, the spring modulus and the dashpot viscosity.
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Figure 2.9. Schematic diagram of a Maxwell element under a tensile load, where the stresses and strains acting on each part of the element are noted.

Now a stress relaxation experiment can be considered where a step strain, $\varepsilon_0$, is instantaneously applied to the Maxwell element, at $t = 0$ and the resulting stress, $\sigma(t)$, is monitored. Substituting $\varepsilon(t) = \varepsilon_0$ in equation (2.14) and integrating to find $\sigma(t)$ gives:

$$\sigma(t) = \varepsilon_0 E_s \exp\left(-\frac{E_s}{\eta} t\right)$$

(2.15)

where the ratio $\eta/E_s$ is a material parameter, referred to as the relaxation time, $\tau$. Therefore, equation (2.15) can be rewritten as:

$$\sigma(t) = \varepsilon_0 E_s \exp\left(-\frac{t}{\tau}\right)$$

(2.16)

For the physical significance of the relaxation time, $\tau$, consider that the higher its value the slower the decrease of the relaxation stress with time. For a given relaxation time, $\tau$, at $t = \infty$, the stress tends asymptotically to zero. On the other hand, at $t = 0$, it is easily seen that equation (2.16) reduces to Hooke’s law for a linear elastic solid. In other words at the instant when the step-strain is applied, it is only the spring of the Maxwell element that is under load.

An alternative to the basic Maxwell model is when the Maxwell element is combined with a spring in a parallel arrangement (see Figure 2.10), known also as the standard linear solid model. The relaxation stress now becomes:

$$\sigma(t) = E_e \varepsilon_0 + \varepsilon_0 E_s \exp\left(-\frac{t}{\tau}\right)$$

(2.17)

where $E_e$ is the Young’s modulus of the added spring. It is immediately obvious that with this new arrangement the relaxation stress will not reduce to zero at very long times but will rather assume a constant equilibrium value of $E_e\varepsilon_0$. Plots showing the
ratio of relaxation stress, $\sigma(t)$, over the initial stress, $\sigma(0)$, as predicted by the Maxwell element and by the Maxwell element connected in parallel with a spring are shown in Figure 2.11. For the construction of the plots a relaxation time of $\tau = 1$ s was assumed, along with $E_e/(E_s+E_e) = 0.1$.

The variation of the relaxation modulus with time can be obtained from equations (2.16) or (2.17) simply as, $\sigma(t)/\varepsilon_0$. From a practical point of view, the model of a Maxwell element in parallel with a linear spring is an improvement to the simple Maxwell model, since it was seen in Section 2.2.1.1 that both thermoplastic and thermoset polymers present a rubbery region (the former due to entanglements of chains inhibiting flow and the latter due to primary bonds connecting the chains). However, in the case of real polymers it is to be expected that relaxation will not take place as a result of a single mechanism, and from that point of view it is unrealistic to expect polymer behaviour to be fully described by a single relaxation time [17]. To address this issue one option is to consider a material model that, instead of single relaxation time, incorporates a continuous distribution of relaxation times. This can be written as:

![Figure 2.10. Schematic diagram of a Maxwell element connected in parallel with a spring.](image)

![Figure 2.11. Plots showing the stress relaxation of a Maxwell element and of a Maxwell element connected in parallel with a Hookean spring.](image)
where $E(\tau)$ is the modulus of the Maxwell element corresponding to relaxation time $\tau$. Equation (2.18) can be rewritten by considering that at the limit $t = 0$ it has to be $\sigma(0) = E(0)\varepsilon_o$, as:

$$\sigma(t) = E_e\varepsilon_o + \varepsilon_o\left[E(0) - E_e\right]\int_0^\infty H(\tau)\exp\left(-\frac{t}{\tau}\right)d\tau$$

(2.19)

where $H(\tau)$ is the distribution of relaxation times of the material. It is worth noting that $E(0)$ corresponds to the glassy modulus of the material. Because the relaxation of a material can be plotted over many decades of time, for presentation purposes the logarithm of time is often used, as in Figure 2.7 (b). Therefore by setting $h(\ln\tau) = \tau H(\tau)$, equation (2.19) becomes:

$$\sigma(t) = E_e\varepsilon_o + \varepsilon_o\left[E(0) - E_e\right]\int_{-\infty}^\infty h(\ln\tau)\exp\left(-\frac{t}{\tau}\right)d(\ln\tau)$$

(2.20)

A question now arises regarding the nature of the distribution of relaxation times. The hypothesis that $h(\ln\tau)$ follows a normal distribution has been widely used in the literature [26-28]. Thus, $h(\ln\tau)$ takes the form:

$$h(\ln\tau) = \frac{1}{\sqrt{2\pi S_n}} \exp\left[-\frac{1}{2} \left(\frac{\ln\tau - \ln\tau^*}{S_n}\right)^2\right]$$

(2.21)

where, $S_n$ determines the breadth of the distribution and $\tau^*$ represents the characteristic relaxation time (with $\ln\tau^*$ corresponding to the mean value of the distribution).

On the other hand, Cole and Cole [26] observed the dielectric relaxation of a range of polymers and found that an excellent fit to the experimental data could be obtained if the relaxation times followed a distribution of the form:
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\[ h(ln \tau) = \frac{\sin(\alpha \tau)}{2\pi \left\{ \cosh(\alpha \ln(\tau / \tau^*)) + \cos(\alpha \tau) \right\} } \]  

(2.22)

where \( \alpha \) determines the breadth of the distribution and it takes values between 0 and 1, with 1 corresponding to a single relaxation time.

The log-normal and Cole-Cole distributions are plotted in Figure 2.12 (a). Clearly, the two distributions are similar in shape (the parameters \( S \) and \( \alpha \) were chosen to highlight this equivalence). Another useful observation is that both distributions are symmetric with respect to the characteristic relaxation time, \( \tau^* \) (taken as \( \tau^* = 1 \) s in this example). However such symmetry need not be the case, as discussed in [28-30]. Friedrich and Braun [29] proposed a generalised form of the Cole-Cole model, that allows for greater flexibility in the shape of the distribution of relaxation times. This is expressed as:

\[ h(z) = \frac{1}{\pi} \frac{z^{c-d} \left\{ \sin((d-c)\pi) + z^c \sin(d\pi) \right\} }{1 + 2z^c \cos(c\pi) + z^{2c}} \]  

(2.23)

where, \( z = \tau/\tau^* \), and \( c \) and \( d \) are parameters that determine the shape of the relaxation, where \( c \leq d \leq 1 \). In the special case where \( c = d \) equation (2.23) reverts to the simple Cole-Cole behaviour, with \( \alpha = c = d \). An example of how the shape parameters affect the generalized Cole-Cole distribution is shown in Figure 2.12 (b). The full line represents the case of \( c = d = 0.6 \) and is therefore identical to the Cole-Cole curve shown in Figure 2.12 (a).

So far, three different continuous distributions of relaxation times have been presented, which are used to approximate the relaxation behaviour of polymers. However, even though these models are successful in fitting to the experimental data their physical significance is questionable. Indeed, Cole and Cole [26] as well as Friedrich and Braun [29] note the lack of physical justification behind equations (2.22) and (2.23) respectively. Tschoegl [31], states that such models represent essentially curve-fitting equations and warns against treating the associated parameters as material constants. Further, it makes sense that, since the macroscopic relaxation of a
polymer is the result of a finite number of relaxation processes, the distribution of relaxation times should also be formed of discrete values.

The notion of a discrete distribution of relaxation times can be accommodated by considering a mechanical analogue where a Hookean spring is arranged in parallel with \( N \) Maxwell elements that are also arranged in parallel [25]. This generalised Maxwell model is shown in Figure 2.13. The stress relaxation of the material, now becomes:

\[
\sigma(t) = E(0) \varepsilon_0 \left[ g_e + \left(1 - g_e \right) \sum_{i=1}^{N} g_i \exp \left( -\frac{t}{\tau_i} \right) \right]
\]  

where \( \tau_i \) is the relaxation time of element \( i \), \( g_e = E_e/E(0) \) and \( g_i = E_i/E(0) \). These are the weighting of the equilibrium spring and of the Maxwell elements used in the model, and correspond to the discrete distribution of relaxation times of the material. The values of \( g_i \) can be obtained by fitting equation (2.24) to experimental relaxation data.

Thus far it has been shown that the relaxation of stress of a polymer in response to a step-strain can be described through either equation (2.20) (continuous distribution of relaxation times) or equation (2.24) (discrete distribution of relaxation times). However, the application of strain instantaneously is an unattainable scenario in reality. On the contrary, in practice, a strain rate will be applied on the material before the desired strain is reached and subsequently held constant for the stress relaxation experiment.

![Figure 2.12](image-url)

**Figure 2.12.** Log-normal and Cole-Cole (a) and generalised Cole-Cole (b) distributions of relaxation times for \( \tau^* = 1 \). The parameters \( S_n = 2 \) for the log-normal distribution and \( \alpha = 0.6 \) for the Cole-Cole distribution where chosen so as to demonstrate the similarities in the predictions of the two models. The parameters \( c = d = 0.6 \) in the generalised Cole-Cole distribution correspond to the simple Cole-Cole prediction for \( \alpha = 0.6 \).
To that extent, consider a strain history applied to a polymer sample over a time interval \( s \) in \([0,t]\). This strain history can be expressed as an infinite series of infinitesimal strain steps as:

\[
\varepsilon(s) = \varepsilon(t_0) + [\varepsilon(t_1) - \varepsilon(t_0)] + \ldots + [\varepsilon(t_k) - \varepsilon(t_{k-1})] + \ldots + [\varepsilon(t_n) - \varepsilon(t_{n-1})]
\]

(2.25)

For the application of such a strain history on a continuous arrangement of Maxwell elements in parallel (equilibrium element has been omitted) Wineman and Rajagopal [25] give the relaxation stress as:

\[
\sigma(t) = \int_0^t E(t-s) \frac{d\varepsilon}{ds} ds
\]

(2.26)

where \( E(t-s) \) is the function of the relaxation modulus of the sample within the time interval \( s \).

By addition of the equilibrium element and considering a discrete distribution of relaxation times over \( N \) Maxwell elements, then equation (2.26) becomes:

\[
\sigma(t) = E(0)\varepsilon(s)g_s + \left[ E(0) - E(0)g_s \right] \sum_{i=1}^{N} g_i \exp \left( -\frac{t-s}{\tau_i} \right) \frac{d\varepsilon}{ds}
\]

(2.27)

which is essentially equation (2.24) expressed for any strain history rather than just for a step-strain. Thus, equation (2.27) provides an analogue that can be used to fit directly to experimental data.
2.2.2 Time-independent behaviour (rubber elasticity)

So far, the focus has been mainly on the time and temperature-dependent behaviour of polymers. However, as seen in Figure 2.6 (c) for relaxation modulus, polymer properties can be considered as practically independent of both time and temperature within the glassy and rubbery regions. Of particular interest here is the time independent stress response of a polymer to an applied strain. In the case of glassy time-independence this is given simply by Hooke’s law (equation (2.10)). In the following, the case of rubbery time-independence is considered, and more specifically the stress-strain response of rubbery polymers.

An important characteristic of rubbery materials has to do with their ability to recover from practically any amount of strain that they are subjected to (assuming that no flow occurs during the application of strain). A characteristic stress versus strain curve of a rubbery material is shown in Figure 2.14. The material response is linearly elastic (follows Hooke’s law) at small strains (up to less than 1%) and becomes non-linear at higher strains. Linear or lightly cross-linked rubbers will reach strains in the order of hundreds of percent. Of interest is also an upward shift of the stress versus strain plot of rubbers in the high strain region and towards the point of rupture. The above characteristics of rubber elastic behaviour are generally described by thermodynamic and chain-statistics considerations, but continuum mechanics approaches are also available. A review of the available theories on rubber-elasticity is given in the classic text by Treloar [32] and also by Boyce and Arruda in [33], while Treloar et al. [34] offer a useful discussion on the subject with an emphasis on the continuum mechanics approach.

![Figure 2.14. Characteristic stress versus strain plot of rubbery polymer.](image)
2.2.2.1 Chain-statistics approach

For amorphous rubbers, in the absence of external restraints, rotations around C-C bonds lead to a kinked conformation of the molecular chains [32]. The length of such chains (i.e. the distance between chain-ends) is clearly less than the length of the stretched linear chains. Upon application of a macroscopic deformation on the material, the uncoiling of the chains and the subsequent change in their conformations result in changes to the entropy of the system and to the macroscopically observed stress versus strain response. Integral to all statistical theories of rubber elasticity are expressions for the length of the unstretched polymer chains. As a number of conformations are available to each chain, the chain length is a statistical quantity. The treatment of chain-length as a Gaussian distribution will be considered, first, and other available models will be discussed subsequently. These discussions are largely based on the texts by Treloar [32, 35], Ward [10] and Boyce and Arruda [33] unless noted otherwise.

In the Gaussian approach, the chain length distribution, \( P(r) \), for a certain chain is:

\[
P(r) = 4\pi \left( \frac{3}{2\pi nl_{C-C}^2} \right)^{3/2} r^3 \exp\left( -\frac{3r^2}{2nl_{C-C}^2} \right)
\]

(2.28)

where \( r \) is the end to end length of the chain, \( n \) is the number of C-C links in the chain between chemical cross-links and \( l_{C-C} \) is the length of these links. The root mean square of \( r \) is customarily used as a measure of the average length of the unstretched chain [33]. This is obtained as:

\[
\text{RMS}(r) = l_{C-C} \sqrt{n}
\]

(2.29)

i.e. the length of the average chain in a rubber is proportional to the square root of the number of links in the chain, assuming that the probability distribution of the chain-lengths follows a Gaussian distribution.

Upon stretching (i.e. uncoiling) of the polymer chains, the available conformations (and therefore the conformational entropy) decrease. Now consider, the application of
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a principal stretch state \((\lambda_1, \lambda_2, \lambda_3)\) on a unit cube of a rubber containing \(N\) active chains, where \(\lambda_1, \lambda_2\) and \(\lambda_3\) denote stretch in the three principal directions. The term ‘active chains’ is used here to signify chains that are part of the rubber network, i.e. chains that lie between junction points. For a Gaussian distribution of chain lengths, the total entropy change due to the application of this stretch state is given as:

\[
\delta S = -\frac{1}{2} Nk \left( \lambda_1^2 + \lambda_2^2 + \lambda_3^2 - 3 \right)
\]  

(2.30)

where \(k\) is Boltzmann’s constant.

From equation (2.30) the (Gaussian) strain energy function can then be obtained as:

\[
W_G = -T\delta S = \frac{1}{2} NkT \left( \lambda_1^2 + \lambda_2^2 + \lambda_3^2 - 3 \right)
\]  

(2.31)

where \(T\) is the absolute temperature of the system.

Considering the case of uniaxial tension of a unit cube of rubber along the 1 direction, and assuming incompressibility, \(\lambda_1 = \lambda\) and \(\lambda_2 = \lambda_3 = \lambda^{-1/2}\). Therefore equation (2.31) becomes:

\[
W_G = \frac{1}{2} NkT \left( \lambda - \frac{2}{\lambda} - 3 \right)
\]  

(2.32)

By taking the derivative of \(W_G\) with respect to \(\lambda\), the force acting per unit area of undeformed cross-section of the cube is obtained as:

\[
f_G = NkT \left( \lambda - \frac{1}{\lambda^2} \right)
\]  

(2.33)

and true stress is easily found to be:

\[
\sigma = f_G \lambda
\]  

(2.34)

Therefore, based on equation (2.33) the stress versus strain behaviour of a rubber is described, by knowledge of only one material characteristic: the number of active chains in a unit volume of the material. The importance of this statement lies in the
fact that the response of a rubber to an external load is independent of the chemical structure of its molecules and depends only on the network characteristics of the material, in other words on the density of cross-links.

Just as important is the observation [32, 35] that the quantity $NkT$ is equal to the initial shear modulus, $G$, of the rubber:

$$G = NkT \quad (2.35)$$

By consideration of the relationship between $N$ and the mean molecular weight of (active) chains, $M_e$, equation (2.35) can be rewritten in the form:

$$\nu_e = \frac{\rho G}{M_e R T} \quad (2.36)$$

where $\nu_e$ is the cross-link density of the rubber, $\rho$ is its density and $R$ is the gas constant. Equation (2.36) is the standard relationship used to obtain the cross-link density of polymers from the measured shear modulus when they are in the rubbery region. This is of great significance, and is indeed very widely used, as knowledge of the micro-structure of cross-linked polymers can be obtained by a rather simple mechanical test on a bulk sample of the material.

Equation (2.32) provides a good representation of the behaviour of rubbers in uniaxial loading at relatively small strains. However as the chain length, $r$, approaches the maximum chain length, $n\ell_{CC}$, $P(r)$ deviates significantly from the Gaussian distribution. This deviation becomes clear at fractional chain extensions, $r/n\ell_{CC}$, larger than approximately 0.3 [35]. To rectify this discrepancy models based on non-Gaussian distributions of chain lengths were proposed (see [32] for a review of non-Gaussian models proposed early on). One disadvantage of these efforts was their significantly increased complexity. Attempts to deal with this complexity have been made by considering unit cells of the material containing a small number of chains in regular arrangements. A common characteristic of such models has been the consideration of chain locking stretch, which represents the ratio of chain length when the chain is fully extended over the initial length of the chain. Taking into account that the fully
extended length of the chain is $n_l - C_C$, along with the average initial chain length as given by equation (2.29), then the lock stretch ratio takes the form:

$$\lambda_{lock} = \sqrt{n}$$

(2.37)

In a relatively recent approach, Arruda and Boyce [36] proposed an eight chain model, where the chains are placed so that they are linked at the centre of a cube with their other ends stretching to the eight corners. The geometry of the model means that the junction point at the centre of the cube remains at a fixed position during deformation and that all chains are subjected to the same stretch. The resulting form for the elastic strain energy involves the inverse of the Langevin function and an approximation of the latter as a series expansion is required, giving:

$$W_{A-B} = NkT \left[ \frac{(I_1 - 3)}{2} + \frac{(I_1^2 - 9)}{20\lambda_{lock}^2} + \frac{11(I_1^3 - 27)}{1050\lambda_{lock}^4} + \frac{19(I_1^4 - 81)}{7000\lambda_{lock}^6} + \frac{519(I_1^5 - 243)}{673750\lambda_{lock}^8} \right]$$

(2.38)

where the energy function now depends on the lock stretch, $\lambda_{lock}$, and the stretch invariant $I_1$ is:

$$I_1 = \lambda_1^2 + \lambda_2^2 + \lambda_3^2$$

(2.39)

where $\lambda_1$, $\lambda_2$ and $\lambda_3$ are the stretch of the cube in each of the three principal directions.

For the case of uni-axial tension and assuming incompressibility ($\lambda_1 = \lambda$ and $\lambda_2 = \lambda_3 = \lambda^{-1/2}$), in analogy to the Gaussian case of equation (2.33), the force acting on a unit cross-section of the cube is obtained by differentiation of equation (2.38) with respect to $\lambda$ as:

$$f_{A-B} = 2NkT(\lambda - \lambda^{-2}) \left( \frac{1}{2} + \frac{2I_1}{20\lambda_{lock}^2} + \frac{33I_1^2}{1050\lambda_{lock}^4} + \frac{76I_1^3}{7000\lambda_{lock}^6} + \frac{2595I_1^4}{673750\lambda_{lock}^8} \right)$$

(2.40)
In the Arruda-Boyce model the quantity $NkT$ is related to the initial shear modulus of the rubber as [37]:

$$G = NkT \left(1 + \frac{3}{5\lambda_{lock}^2} + \frac{99}{175\lambda_{lock}^4} + \frac{513}{875\lambda_{lock}^6} + \frac{42039}{67375\lambda_{lock}^8}\right)$$ (2.41)

Predictions of the stress-stretch behaviour of a rubber with initial shear modulus of $G = 1$ MPa are shown in Figure 2.15, according to the Gaussian and Arruda-Boyce models of rubber elasticity. Clearly, the Gaussian model fails to predict the upward turn of the stress-strain curves at high strains. The Arruda-Boyce model on the other hand, succeeds at capturing the expected S-shape of the stress versus strain curves of rubbers. The effect of the choice of the lock-stretch ratio, $\lambda_{lock}$, is also shown in Figure 2.15, where it is clearly shown that as $\lambda_{lock}$ is reduced, equation (2.40) starts to deviate from Gaussian behaviour at lower strains.

![Figure 2.15. Force per unit area versus stretch plots according to the Gaussian and the Arruda-Boyce models of rubber elasticity, for a rubber with initial shear modulus of $G = 1$MPa.](image)

**2.2.2.2 Continuum mechanics approach**

Contrary to the chain-statistics models discussed in the preceding Section, continuum mechanics models are not based on micro-structural considerations. Instead they attempt to describe the behaviour of rubbers in a purely phenomenological manner, treating the rubbery material as a continuous medium that possesses certain properties responsible for its mechanical behaviour. Continuum mechanics models generally express strain energy as a function of the three principal stretches, by using the so-called stretch invariants:
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\[
\begin{align*}
I_1 &= \lambda^2 + \lambda_2^2 + \lambda_3^2 \\
I_2 &= \lambda_1^2 \lambda_2^2 + \lambda_2^2 \lambda_3^2 + \lambda_3^2 \lambda_1^2 \\
I_3 &= \lambda_1^2 \lambda_2^2 \lambda_3^2
\end{align*}
\]  
(2.42)

For incompressible materials \(I_3 = 1\) and for the case of uni-axial tension \((\lambda_1 = \lambda)\) equation (2.42) becomes:

\[
\begin{align*}
I_1 &= \lambda^2 + 2\lambda^{-1} \\
I_2 &= 2\lambda + \lambda^{-2}
\end{align*}
\]  
(2.43)

The strain energy function can then be expressed in its general form as, [35]:

\[
W = \sum C_{ij} (I_1 - 3)^j (I_2 - 3)^j
\]  
(2.44)

where \(C_{ij}\) are constants.

One of the simplest forms of equation (2.44) for \(I = 1, j = 0\) is the so-called neo-Hookean function:

\[
W_{n-H} = C_{10} (I_1 - 3)
\]  
(2.45)

It is easy to see that the neo-Hookean model is equivalent to the Gaussian prediction for strain energy (equation (2.31)), with \(C_{10} = 0.5NkT\). In that sense, the observations made for the Gaussian model and its lack of applicability at large strains are also valid for equation (2.45). Another special form of equation (2.44) is the Mooney-Rivlin equation, that was originally derived by Mooney [38] as:

\[
W_{M-R} = C_{10} (I_1 - 3) + C_{01} (I_2 - 3)
\]  
(2.46)

which also takes into account the second stretch invariant, \(I_2\).

Clearly, further refinement of the prediction for \(W\) is possible by incorporating an increasing number of terms from equation (2.44). Several examples of this approach are given by Treloar in [35], where he offers the criticism that such models often lack physical justification and can be seen as curve-fitting functions akin to fitting polynomials on experimental sets of stress versus strain data. A departure from the
formulation of most continuum models has been suggested by Ogden [39], who
derived a formula for strain energy not as a function of the stretch invariants, but
rather directly as a function of the principal stretches. The Ogden equation takes the
form:

$$W_{\text{Ogden}} = \sum \frac{\mu_i}{a_i} \left( \lambda_1^3 + \lambda_2^3 + \lambda_3^3 - 3 \right)$$ (2.47)

where incompressibility is assumed, and $a_i$ and $\mu_i$ are constants that are related to the
initial shear modulus, $G$ as:

$$\sum \mu_i a_i = 2G$$ (2.48)

Ogden reported a good fit with experimental data in various loading modes for $i \geq 3$.
For the case of uni-axial tension, taking the derivative of equation (2.47) with respect
to $\lambda$, the force acting on a unit cross-section of the material is obtained as:

$$f_{\text{Ogden}} = \sum \mu_i \left( \lambda^{(1-1)} - \lambda^{(0.5a_i+1)} \right)$$ (2.49)

When only the first term of the Ogden model is used, and taking into account equation
(2.48), equation (2.49) becomes:

$$f_{\text{Ogden}} = \frac{2G}{a} \left( \lambda^{(1-1)} - \lambda^{(0.5a_i+1)} \right)$$ (2.50)

In Section 11.4 the three term form of the Ogden model (equation (2.49)) will be used
to fit the tensile data of a selection of the paints used in this study.

### 2.2.3 Non-linear visco-elasticity

In Section 2.2.1.4 the case of linear visco-elastic material behaviour was discussed, and
mechanical analogues were presented that provide a satisfactory prediction of the
change in material properties with time. These discussions were based on the
assumption that material properties depend only on time, and are independent of the
applied strain. In reality this assumption holds only for small applied strains, usually
not higher than around 1%. As a result, the treatment presented in Section 2.2.1.4 is generally inadequate to describe the mechanical behaviour of polymers throughout the full stress versus strain curve. A comparison between the tensile curves of a visco-elastic material with a known distribution of relaxation times, as obtained experimentally and from equation (2.27) is shown in Figure 2.16. Clearly, the prediction based on linear visco-elasticity fails to capture the characteristic S-shape of the stress versus strain curve beyond the initial linear region.

Beyond the linear visco-elastic region the response of polymers is both time and strain-dependent. This idea was stated early on by Guth et al. [40] who proposed that the total stress relaxation of a polymer can be expressed as the product of a time-dependent and a strain dependent component:

\[ E(t, \varepsilon) = E(\varepsilon)E(t) \]  

(2.51)

A treatment of non-linear visco-elasticity that uses equation (2.51) makes the assumption that the effects of time and strain are separable, i.e. that the component \( E(\varepsilon) \) is independent of time, and similarly that \( E(t) \) is independent of strain. A discussion of this assumption as well as a proposed experimental methodology for its evaluation is given by Smith [41]. Now consider an equivalent form of equation (2.27) as:

\[ \sigma(t) = \sigma_0 g_e + \int_0^t \sum_{i=1}^N g_i \exp\left(-\frac{t-s}{\tau_i}\right) d\sigma_i ds \]  

(2.52)

Figure 2.16. Plot showing comparison between tensile stress versus strain data as obtained from experiment and from equation (2.27).
This can be written more simply as:

$$\sigma(t) = \sigma_0 g_e + \sum_{i=1}^{N} \sigma_i(t)$$  \hspace{1cm} (2.53)

On the basis of the assumption that strain and time effects are separable; \(\sigma_0\) in equations (2.52) and (2.53) represents the strain dependent (time-independent) component of stress. For a linear elastic solid this is simply given by Hooke’s law, while for a material following rubber-elastic behaviour \(\sigma_0\) is given by any appropriate formula, as given in Section 2.2.2. Depending on the exact form of \(\sigma_0\), the integral in equation (2.52) may or may not have a closed-form solution. For the more general case where no closed-form solution exists, an approximation method is required. Here the approximation derived by Goh et al. [42] is followed, where:

$$\sigma_i(t_{n+1}) = \exp \left( -\frac{\delta t}{\tau_i} \right) \sigma_i(t) + g_i \frac{1 - \exp \left( -\frac{\delta t}{\tau_i} \right)}{\delta t / \tau_i} \left[ \sigma_0(t_{n+1}) - \sigma_0(t_n) \right]$$  \hspace{1cm} (2.54)

So finally equation (2.53) becomes:

$$\sigma(t_{n+1}) = g_e \sigma_0(t_{n+1}) +$$

$$\sum_{i=1}^{N} \exp \left( -\frac{\delta t}{\tau_i} \right) \sigma_i(t) + g_i \frac{1 - \exp \left( -\frac{\delta t}{\tau_i} \right)}{\delta t / \tau_i} \left[ \sigma_0(t_{n+1}) - \sigma_0(t_n) \right]$$  \hspace{1cm} (2.55)

In most practical cases the stress at \(t = 0\) is known (for example \(\sigma(0) = 0\)), so the stress at any point in time can be easily calculated from equation (2.55).

### 2.3 Fracture mechanics of polymers

In the previous Sections, the problem of the mechanical response of polymer materials to applied loads and displacements was discussed. The influence of temperature, loading-rate and polymer micro-structure was outlined, and, for certain cases,
theoretical treatments that enable the prediction of this mechanical response were presented. However, little mention has been made of the mechanisms that control the fracture of polymers, and in the following the fracture mechanics background relevant to the characterisation of the materials investigated in this study will be presented. That is to say that, acknowledging the broadness of the subject, the focus in the following will be strictly on polymers, and more specifically on polymers that at the point of fracture are subject to bulk inelastic deformation (i.e. they operate outside the linear elastic regime).

There are various approaches to the fracture of polymers, that Kinloch and Young [43] summarise as molecular, statistical and continuum. From an engineering point of view, the continuum mechanics approach, which regards materials as a continuum of specific physical properties, is by far the most popular and will be the main focus of this discussion. The basis of (continuum) fracture mechanics is attributed [43, 44] to Griffith [45], who noticed that, for a material containing a crack of length \( a \), the propagation of the crack by \( \delta a \) results in a decrease of the potential energy stored in the material. The ‘lost’ energy being the energy consumed for the formation of two new surfaces at the crack-tip. Below, the basic concepts of linear elastic fracture mechanics (LEFM) are presented, that follow directly Griffith’s original ideas. Additionally, the background for a non-linear inelastic fracture mechanics approach, and more specifically the essential work of fracture (EWF) approach, is presented; as such treatment is more pertinent to the materials of interest in this study.

### 2.3.1 The linear-elastic case

Griffith’s criterion can be expressed for a crack propagating by a length \( \delta a \) in a solid of thickness, \( \vartheta \), in energy terms, as [43, 44]:

\[
\frac{1}{\vartheta} \frac{\delta U}{\delta a} \geq 2\gamma
\]  

(2.56)

where \( \gamma \) is the surface free-energy of the material and \( \delta U \) is the change in the total energy available to the system, given by:
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\[ \delta U = U_2 - U_1 \]  

\( U_2 \) is the work supplied to the material by an external force and \( U_1 \) is the energy stored in the material elastically.

The formulation of equation (2.56) implies that the energy supplied for the formation of new surfaces must be at least equal to double the material surface free energy. In practice, however, a much larger amount is seen to be required for the propagation of cracks, due to two principal reasons [43]. First, the surface free energy reflects only the energy associated with the breaking of secondary bonds, where clearly for fracture to occur covalent bonds also need to be broken. Second, even if the assumption for elasticity holds in the bulk material, a plastic zone is expected to develop in the vicinity of the crack tip, resulting in additional energy dissipation. Note that this zone is assumed to be sufficiently small for the general elasticity assumption to still hold. Taking these observations into account the fracture criterion can be re-written as [43, 44]:

\[ \frac{1}{\theta} \frac{\partial U}{\partial a} \geq G_c \]  

(2.58)

where the critical energy release rate, \( G_c \), now includes all energy losses associated with the propagation of a crack by a unit length.

So far the assumption of a material behaving elastically in the bulk has been made, with no distinction between linear and non-linear elastic behaviour, i.e. equations (2.56) - (2.58) are valid for both linear and non-linear elastic materials. The case of linear elasticity is of great importance as the LEFM theory is widely used for the characterisation of brittle and structural adhesives, such as epoxies (for example see [43, 46]). Thus, assuming linear-elasticity, the external work supplied to the material \( (\delta U_2) \) and the change in the elastically stored work \( (\delta U_1) \) can be re-written respectively as:

\[ \delta U_2 = P\delta \Delta + \frac{1}{2} \delta P \delta \Delta \]  

(2.59)

and,
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\[ \delta U_1 = \frac{1}{2} \left( P + \delta P \right) \left( \Delta + \delta \Delta \right) - \frac{1}{2} P \Delta \]  

(2.60)

where \( \Delta \) is the displacement, \( P \) is the applied load, and \( \delta \Delta \) and \( \delta P \) are the changes in the displacement and the load respectively, required for the propagation of the crack by \( \delta a \). The corresponding load versus displacement curve is shown in Figure 2.17 where the external work done, \( \delta U_{ext} \), is shown.

By combination of equations (2.58) - (2.60), the critical energy release rate for a unit length propagation of the crack, can be written as a function of the compliance, \( C = \Delta / P \), as [43, 44]:

\[ G_c = \frac{P_c^2 \delta C}{2b \delta a} \]  

(2.61)

where \( P_c \) is the critical load required for crack propagation.

For the experimental determination of \( G_c \), a variety of geometry-specific solutions of equation (2.61) have been developed for a wide range of specimen geometries, each addressing specific testing requirements. Examples of specific geometries used in the LEFM approach include the double cantilever beam (DCB), the tapered double cantilever beam (TDCB) and the single edge notch bend (SENB) specimens [43, 44]. However, as the LEFM approach is not applicable for the materials considered here (or more precisely is not applicable at the temperature of interest for the materials) these geometry-specific solutions will not be discussed further. Instead, the focus is shifted to the case when the assumption of linear elasticity is not valid, but rather extensive inelastic deformation takes place in the bulk of the material together with crack propagation.
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2.3.2 The inelastic case - Essential work of fracture (EWF)

As noted in the previous Section, the elastic case of fracture mechanics acknowledges the existence of a plastic zone surrounding the crack-tip, but assumes this zone to be sufficiently small so that the general requirement for elasticity prevailing in the bulk of the sample is satisfied. In the case of materials showing inelastic behaviour, however, the LEFM approach can no longer be considered valid. The term inelastic is used here as opposed to plastic, in recognition of the capacity of polymers for delayed recovery from large ‘plastic’ deformations. In the inelastic case, a large portion of the work supplied in breaking the sample is neither stored elastically nor consumed in the creation of new surfaces, but is rather dissipated through inelastic processes in the bulk of the sample [47, 48]. Such an idea forms the basis for the essential work of fracture approach and was first formally expressed by Broberg [47, 49, 50], who distinguished between an end-zone (inner process zone) immediately surrounding the crack-tip, in which the fracture event takes place, and a surrounding plastic zone (outer process zone) that essentially buffers the amount of energy being transferred to the inner process zone.

Cotterel, Mai and co-workers [48, 51, 52] extended Broberg’s concept to formulate the essential work of fracture (EWF) approach for measuring the toughness of thin sheets...
(i.e. the sample is assumed to be under plane stress) undergoing inelastic deformation. Single and double edge notched tension sample geometries (SENT and DENT respectively) are used in the EWF method with the DENT geometry being the most widely used. The EWF method has been used mainly in the determination of toughness in a crack opening mode (Mode I), where a tensile displacement is applied on the notched sample, resulting in opening of the crack faces and subsequently in crack propagation, although in principle the method should also be applicable in shearing, out-of-plane tearing and mixed-mode crack propagation [52-54].

A central assumption of the EWF method is that that the sample must be fully yielded before fracture. In practice yielding will take place in the ligament region of the sample (see Figure 2.18 for a schematic of the ligament, \( l \)). This means that yielding is indeed extensive (compared to the small size of the inner process zone), but at the same time it is confined within the ligament of the sample [48]. In Figure 2.18, the inner and outer process zones are shown for a DENT sample tested in EWF (tensile mode), where the sample width, \( w \), the crack length, \( a \), and the ligament, \( l \), are also shown. It needs to be noted that even though the outer process zone is circular in Figure 2.18, this serves for illustration purposes only and in reality it can also be approximated as elliptical or diamond shaped [53].

For a given sheet thickness, if the specific essential work of fracture (i.e. the work consumed inside the inner process zone per unit area of ligament) is assumed to be constant, it follows that the total essential work of fracture must be proportional to ligament length [48]:

\[
W_e = l \theta w_e
\]  

(2.62)

where \( W_e \) is the total essential work consumed in the inner process zone, \( w_e \) the specific essential work of fracture (\( w_e = W_e/l\theta \)) and \( \theta \) is the sample thickness.
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Figure 2.18. Schematic diagram of DENT sample in tension where the inner and outer process zone are shown. Also noted are the sample width, $w$, the two cracks with length, $a$, and the ligament, $l$.

On the other hand, the non-essential part of the work consumed in the outer process zone is proportional to the size of this zone, i.e. it is proportional to $l^2$ according to:

$$W_{inel} = \theta \partial l^2 w_{inel}$$  \hspace{1cm} (2.63)

where $W_{inel}$ is the total work consumed in the outer process zone, $w_{inel}$ is the specific work consumed in the outer process zone ($w_{inel} = W_{inel}/l\theta$) and $\theta$ is a factor related to the shape of the outer process zone. For a circular shape it follows $\theta = \pi/4$.

The total work consumed during the fracture of the sample, $W_f$, is by definition the sum of the essential and non-essential works of fracture given in equations (2.62) and (2.63). This can be expressed per unit area of crack growth (specific total work, $w_f = W_f/l\theta$), with the help of equations (2.62) and (2.63) as:

$$w_f = w_e + \theta w_{inel} l$$ \hspace{1cm} (2.64)

Equation (2.64) is very important in the determination of the EWF from experimental data as it means that if the specific total work of fracture, $w_f$, is plotted versus ligament length, $l$, the result should be a straight line whose intercept with the y-axis is the essential work of fracture, and whose slope is a function of the non-essential part of the total work. This extrapolation to $l = 0$ is shown schematically in Figure 2.19.

At this point it needs to be stressed that the essential work of fracture, as measured from the method outlined above, concerns a material of a particular thickness, that is
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$w_e$ is thickness dependent [48, 52, 55]. Indeed, Mai and Powell [55] argued that an increase in specimen thickness will result in a higher value of $w_e$, while similar results have been reported by Arkhireyeva and Hashemi [56]. A second point that bears attention is that the method requires the ligament to be in a state of plane stress. Effectively this means that there is a minimum ligament length that can be used, below which the stress state changes from plane stress to plane strain, and the EWF method is no longer applicable.

From an experimental point of view, the implication of this transition is that below the limiting value for $l$, the linearity of the $w_f$ versus $l$ plot is no longer maintained and a distinct change in the slope is seen (see Figure 2.19). The ligament length at which the plane stress-plane strain transition occurs has been defined as $l \leq 3\theta-5\theta$ [48, 52]. This limit, however, has been found to vary with material [54], while it has been shown (e.g. in [57]) that in some cases the $w_f$ versus $l$ plot starts to deviate from linearity at ligament lengths much greater than $3\theta-5\theta$. For these reasons, in practice, the minimum ligament length is usually chosen to be larger than that dictated by the plane stress requirement (see also Section 4.4.1). If the intercept of the best fit line between the plane strain points with the $w_f$ axis is taken, a plane strain essential work of fracture, $w_e^*$, is obtained, that additionally is shown to be independent of sample thickness [55, 58]. Despite the advantage of $w_e^*$ in being thickness independent (and therefore a better defined material property), work on this concept has been rather limited. This is not least due to the impractically short ligaments required, especially for the thinnest of the films tested with the method (for example for a 30 μm thick film, ligament lengths smaller than 150 μm would be required to satisfy an $l \leq 5\theta$ requirement) [59].

Finally, as well as a minimum length requirement for the ligament, there exists also a maximum length beyond which the EWF is not applicable. The maximum is dictated by two conditions: that the ligament is fully yielded and that the yielding remains confined within the ligament area and does not extend to the edges of the specimen [48, 52, 58]. Usually, the second condition results in a smaller maximum value for the ligament and on that basis, a ligament of length, $l \leq w/3$ was initially suggested even though more recently it has been argued that the above limit is rather conservative.
and larger values of \( l \) (in the region of \( w/2 \)) have been suggested [56, 59, 60] (see also Section 4.4.1).

The clear dependence of the results obtained with this method on the sample geometry makes direct comparison between data collected by different groups of researchers rather difficult. However, in terms of providing a comparison between the different systems investigated in this study the EWF method is considered very useful, since all samples had comparable thickness and the same range of ligament lengths was used in every case.

Figure 2.19. Schematic plot of the total specific work of fracture, \( w_f \), versus ligament length, \( l \), where the plane strain to plane stress transition is shown. The intercept of the best fit line of the data collected at ligament lengths, \( l \geq 3\theta - 5\theta \) with the \( y \)-axis gives the specific essential work of fracture under plane stress conditions (\( w_e \)). The intercept with the \( y \)-axis of the best fit line to the data collected at \( l \leq 3\theta - 5\theta \) corresponds to the plane strain specific essential work of fracture (\( w_e^* \)).

2.4 The mechanical properties of particulate-filled polymers

So far, discussions have been focused on the properties of polymeric materials. However, due to the fact that in most practical applications paints will also contain a second inorganic phase of pigment or filler, a discussion on composite materials and their properties is also required. By definition, composite materials consist of two or more distinct phases or constituents. Matthews and Rawlings [61] state two further requirements; firstly, that the constituents are present at reasonable proportions (as an example they mention a volume fraction of more than 5%) and secondly, that the constituents have noticeably different properties. Generally speaking, of the two phases in a composite, one will be the continuous phase (normally present at a higher
volume fraction than the other) and this phase is referred to as the matrix. A discontinuous distinct phase inside the matrix constitutes the filler phase.

Metals, polymers and ceramics have all been widely used to create composite materials, but of most interest here is the case of composites consisting of a polymer matrix reinforced with a second ceramic phase. With respect to the filler geometry, composites are most frequently classified as either particulate-filled or fibre filled. From the point of view of the systems discussed in this study, the paints that contain TiO$_2$ pigment particles can be considered as particulate-filled composites and therefore a presentation of the theory developed for describing the behaviour of composite materials is necessary.

A multitude of properties - such as the mechanical, optical and electrical properties - of the homogeneous matrix can be affected by the addition of the filler phase. Here, of interest are changes induced on the mechanical properties, and more specifically on the stiffness, tensile strength and strain at failure of the matrix. The following discussion aims to present the basic theories associated with the prediction of the mechanical behaviour of composite materials. The focus will be on models and material systems relevant to this study. For further information, the reader is referred to the original texts cited in the following sections, as well as to a number of excellent reviews on the subject [14, 62-64] and to the references therein.

### 2.4.1 Composite stiffness: suspensions and case of incompressible matrix

A lot of the models dealing with the stiffness of composite materials originate from the relationship developed from Einstein for the viscosity of suspensions of rigid spherical particles [14, 65], presented here as given by Nielsen and Landel [14]:

\[ \eta = \eta_1 \left(1 + k_e \varphi \right) \]  

(2.65)
where \( \eta \) and \( \eta_1 \) are the viscosities of the suspension and the suspending liquid respectively, \( \varphi \) is the volume fraction of the filler and \( k_E \) is the Einstein coefficient, taking a value of 2.5 in the original Einstein model.

A shortcoming of the Einstein equation (equation (2.65)), is that it is only valid for very small filler concentrations, where no interaction between the particles is possible [14]. An exact estimate of what constitutes a ‘very small concentration’ of filler is not given in the literature, however, it is indicative that for the derivation of equation (2.65) Smallwood [65] considered a single spherical particle inside a rubber matrix. Guth [66] presented a generalised form of equation (2.65), as:

\[
\eta = \eta_1 \left( 1 + a_1 \varphi + a_2 \varphi^2 + a_3 \varphi^3 + \ldots \right)
\]  

(2.66)

where the term \( a_1 \) is equal to the Einstein coefficient, \( k_E = 2.5 \), and accounts for the effect of individual particles on the viscosity of the suspension, while the terms of higher order represent interactions of two, three, etc. particles. Clearly, Einstein’s equation, is a special case of equation (2.66) where terms of an order higher than 1 have been dropped.

Guth reports that the \( a_2 \) term was calculated to take a value of 14.1 and thus the second order approximation of equation (2.66) becomes:

\[
\eta = \eta_1 \left( 1 + 2.5 \varphi + 14.1 \varphi^3 \right)
\]  

(2.67)

Another formula for the viscosity of suspensions with a high content of filler particles was developed by Mooney [67], where the term ‘high’ is used in contrast to the infinitely small concentration of filler assumed in the Einstein equation. In the Mooney equation a crowding factor was used to account for increases in viscosity at high volume fractions. Here, the Mooney equation is given as found in [14]:

\[
\eta = \eta_1 \exp \left( \frac{k_E \varphi}{1 - \varphi / \varphi_{\text{max}}} \right)
\]  

(2.68)

where \( \varphi_{\text{max}} \) is the maximum volume fraction that the filler can have in the suspension and is the reciprocal of the crowding factor that was used in the original article by
Mooney. Values of $\phi_{\text{max}}$ are given in [14] ranging between 0.74 for hexagonal close-packing of the filler particles to 0.37 for randomly close-packed agglomerates of particles.

So far the effect of particle concentration on the viscosity of suspensions has been considered. For composite systems where the matrix is an incompressible elastomer with a Poisson’s ratio of $\nu = 0.5$, and additionally the stiffness of the filler particles is much greater than that of the matrix, the composite moduli (bulk, shear or Young’s modulus) display the same behaviour with filler volume fraction as viscosity [14, 66]. Thus, for the Young’s modulus of the composite:

$$\eta \frac{E_c}{\eta_1 E_m}$$

(2.69)

where $E_c$ and $E_m$ are the Young’s moduli of the composite and the matrix respectively.

Based on equation (2.69), equations (2.65)-(2.68) can be rewritten for the Young’s modulus of composite materials simply by substitution of the suspension and suspending liquid viscosities, $\eta$ and $\eta_1$, with the Young’s moduli of the composite, $E_c$, and the matrix, $E_m$. It is noted, however, that where the matrix has a Poisson’s ratio, $\nu$, less than 0.5 or where the matrix and filler have similar values of stiffness, equation (2.69) is no longer valid.

### 2.4.2 Composite stiffness: general case of compressible matrix

Clearly, for a multitude of engineering applications models are required that can account for solid matrices with a Poisson’s ratio lower than 0.5. Two important approaches early on were the self-consistent model developed by Hill [68] and Kerner’s model [69].

Hill considered the case of ellipsoidal inclusions surrounded by a medium having the properties of the composite. For the specific case of spherical particles distributed in the matrix so that the overall composite is isotropic, he was able to obtain relationships for the shear and bulk moduli of the composite as,
The mechanical properties of polymers and particulate-filled composites

\[
\frac{1}{K_c + \frac{4}{3}G_c} = \frac{\varphi}{K_f + \frac{4}{3}G_c} + \frac{1 - \varphi}{K_m + \frac{4}{3}G_c}
\]

(2.70)

and

\[
\frac{\varphi K_f}{K_f + \frac{4}{3}G_c} + \frac{(1 - \varphi)K_m}{K_m + \frac{4}{3}G_c} + 5 \left( \frac{\varphi G_m}{G_c - G_m} + \frac{(1 - \varphi)G_f}{G_c - G_f} \right) + 2 = 0
\]

(2.71)

where \(K_c, K_f\) and \(K_m\), and \(G_c, G_f,\) and \(G_m\) are the bulk and shear moduli of the composite, the filler and the matrix respectively.

The Kerner model on the other hand considered spherical grains, each surrounded by a medium with the properties of the matrix, while surrounding the encapsulated grain is a homogeneous medium with the properties of the composite. Additionally, the filler is assumed to be distributed in such a way that the composite as a whole is isotropic. The formulas for the bulk and the shear modulus of the composite follow:

\[
K = \frac{K_f \varphi}{3K_f + 4G_m} + \frac{K_m (1 - \varphi)}{3K_m + 4G_m}
\]

(2.72)

\[
G_c = \frac{\varphi G_f}{(7 - 5\nu_m)G_m + (8 - 10\nu_m)G_f} + \frac{1 - \varphi}{15(1 - \nu_m)}
\]

(2.73)

where all notation is as defined previously, and \(\nu_m\) is the Poisson’s ratio of the matrix.

Building on the above theories, Halpin and Tsai developed much simpler relationships for the elastic constants of composite materials [70]. The Young’s modulus of an isotropic composite, containing spherical particles, was shown to be:

\[
E_c = \frac{1 + \xi \eta_{H-T} \varphi}{1 - \eta_{H-T} \varphi} E_m
\]

(2.74)
where $\eta_{H-T}$ is:

$$\eta_{H-T} = \frac{E_f / E_m - 1}{E_f / E_m + \zeta}$$

(2.75)

and $\zeta$ is a shape factor that depends on the geometry of the filler. From [70, 71], $\zeta = 2w/\theta$, where $w$ is the width and $\theta$ the thickness of the reinforcement. For spherical particles (where the aspect ratio is equal to 1), $\zeta = 2$.

Lewis and Nielsen [72] and Nielsen [73] expanded on the ideas of the Halpin-Tsai model. They proposed a relationship that also takes into account the maximum volume fraction of the filler, $\varphi_{max}$, that appeared in the Mooney model (see equation (2.68)) as well as the Einstein coefficient, $k_E$. The Lewis-Nielsen equation takes the form:

$$E_c = \frac{1+(k_E-1)\beta_{L-N}\varphi}{1-\beta_{L-N}\mu\varphi}E_m$$

(2.76)

where $\beta_{L-N}$ is:

$$\beta_{L-N} = \frac{E_f / E_m - 1}{E_f / E_m + k_E - 1}$$

(2.77)

and $\mu$ is:

$$\mu = 1 + \frac{1-\varphi_{max}}{\varphi_{max}^2} \varphi$$

(2.78)

Later, McGee and McCullough proposed another equation for the calculation of $\mu$. Nielsen and Landel [14], however, note that this alternative equation will yield values very similar to equation (2.78) for volume fractions of filler up to around 0.5. The McGee and McCullough equation for $\mu$ is presented here as given by Nielsen and Landel [14]:

$$\mu = 1 + \frac{1-\varphi}{\varphi_{max}^2} \left[ \varphi_{max} \varphi + (1-\varphi_{max})(1-\varphi) \right]$$

(2.79)
Regarding the Einstein coefficient, $k_E$, in equations (2.76) and (2.77), this takes the value of 2.5 in the original treatment of the viscosity of suspensions by Einstein, that assumed dispersed particles of filler inside a suspending liquid. However, in the presence of aggregates of the filler particles, an increase in $k_E$ is expected as noted by Gillespie [74] and by Lewis and Nielsen [75]. A value of 4.77 was reported for agglomerates of spherical particles in a cubic packing [75], and of 6.76 for randomly packed agglomerates [14]. All of the above values for $k_E$ correspond to the case of filler particles suspended in an incompressible medium (i.e. $\nu_m = 0.5$). A decrease in the Einstein coefficient is expected when the Poisson’s ratio is smaller than 0.5, and in [14] $k_E$ is given for different values of Poisson’s ratio. For a $\nu_m = 0.35$ which can be considered to be a good approximation for the Poisson’s ratio of glassy polymers, it is given that, $k_{E,0.35}/k_{E,0.5} = 0.867$. Finally, $k_E$ will decrease when slippage is observed at the particle-matrix interface [14, 76]. For the case of dispersed spheres in an incompressible medium, $k_E$ will fall from 2.5 for the case where there is no slippage at the interface, to 1 if there is slippage.

Sato and Furukawa [77] attempted to explicitly model the effect of adhesion between filler and matrix on the stiffness of the composite, for an incompressible elastomeric matrix containing spherical inclusions. They proposed that composite stiffness is a function of the degree of particle-matrix adhesion and derived the following relation:

$$\frac{E_c}{E_m} = \left(1 + \frac{1}{2} \frac{\phi^{2/3}}{1-\phi^{1/3}}\right)(1-\psi\zeta_1) + \zeta_2 \frac{\varphi\left(1-\varphi^{1/3}\right)}{(1-\varphi^{1/3})^2}(1-\psi\zeta_1) - \frac{\varphi^{2/3}}{1-\varphi^{1/3}} \frac{\psi\zeta_1}{\varphi} \tag{2.80}$$

where $\psi$ is:

$$\psi = \frac{\varphi}{3} \left(1+\frac{\varphi^{1/3}-\varphi^{2/3}}{1-\varphi^{1/3}+\varphi^{2/3}}\right) \tag{2.81}$$

and $\zeta_1$ and $\zeta_2$ are parameters associated with the quality of adhesion between the particles and the matrix, and with the number of chain ends adhering to the rigid particles respectively. It is noteworthy that equation (2.80) predicts a decrease in
2. The mechanical properties of polymers and particulate-filled composites

Young’s modulus for the case of no adhesion between matrix and particles ($\zeta_1 = 1$). However, this neglects the fact that even in the case of no adhesion, some stress transfer to the particles is expected to occur through contact with the surrounding matrix. This in turn would act to mitigate, to some extent, the decrease in Young’s modulus due to the particles acting as holes in the matrix.

Finally, it needs to be noted that the theories discussed within this Section, all assume that the matrix behaves as an elastic solid. A treatment where the matrix is considered to be a visco-elastic medium has been presented by Clements and Mas [78]. For the case of spherical particles in a visco-elastic matrix, their model takes the form [78, 79]:

$$E_c(t) = E_m(t) \left( 1 + 2.5 \frac{\varphi}{1 - f_1 \varphi} \right)$$

(2.82)

where $f_1$ is an empirical parameter associated with the degree of interaction between the filler particles, and the composite ($E_c(t)$) and matrix moduli ($E_m(t)$) are now expressed as functions of time, $t$. It is obvious that for $f_1 = 0$ (no interaction between the filler particles) the Clements and Mas treatment reduces to the standard Einstein equation (equation (2.65)) for the viscosity of suspensions, with $k_E = 2.5$.

2.4.3 Ultimate properties (stress and strain)

So far, the effect of the filler on the elastic stiffness of a composite material has been considered, i.e. the material was assumed to be under minimal levels of strain. It is also of interest, however, to determine how the incorporation of a filler affects the ultimate properties of a polymer matrix. A number of theories exist for the prediction of the failure strength and strain of composites. However, it needs to be stressed that these are not nearly as universal as the theories on stiffness. This is because of a number of factors (such as the degree of filler/matrix adhesion, filler size and filler dispersion) which affect the large strain properties to a greater extent than small strain properties [14, 62].

Indeed, Fu at al. [63] reviewed a number of publications with experimental data on the strength of particle-filled composites. They reported a very wide range of behaviours,
where the composite strength increased, decreased or was unaffected by the incorporation of the filler particles. It is outside the scope of this text to provide a full list of the existing theories on the ultimate properties of composites. Instead, a selection of the available theories will be presented and their main assumptions will be discussed in order to highlight the main factors that need to be taken into account when considering the failure strength of particulate-filled composites.

2.4.3.1 The Nielsen model: cases of perfect particle/matrix adhesion or no adhesion

Nielsen [80], expanded on some ideas by Smith [81] regarding the yield strength of elastomers filled with spherical particles in a close-packed cubic arrangement. He proposed that in the case where there is perfect adhesion between filler and matrix, the ultimate strain as a function of filler volume fraction should take the form:

\[
\varepsilon_{c,u} = \varepsilon_{m,u} \left(1 - \varphi^{1/3}\right) \tag{2.83}
\]

where \(\varepsilon_{c,u}\) and \(\varepsilon_{m,u}\) are the ultimate strains of the composite and the matrix respectively.

The prediction of equation (2.83) for failure strain is plotted against the volume fraction of the filler particles in Figure 2.20. A sharp decrease is seen at low filler concentration that levels off as the volume fraction increases further. Interestingly, Nielsen [14, 80] predicts that in the case where the filler/matrix interface is weak, the decrease in strain with filler content will be more gradual, with values of \(\varepsilon_{c,u}/\varepsilon_{m,u}\) generally lying above the curve in Figure 2.20.

To derive the failure strain of the composite in the case of no adhesion, Nielsen assumed that the particles act as holes which take none of the load applied on the composite. He then calculated the failure strength of the composite as:

\[
\sigma_{c,u} = \sigma_{m,u} \left(1 - \varphi^{2/3}\right)S_{cf} \tag{2.84}
\]
where \( \sigma_{c,u} \) and \( \sigma_{m,u} \) are the failure stresses of the composite and the matrix and \( S_{CF} \) is an empirical stress concentration factor that will take a suggested value of 0.5 [80].

Then if the response of the composite is assumed to be elastic, its failure strain can be determined by a simple application of Hooke’s law, as:

\[
\varepsilon_{c,u} = \frac{\sigma_{c,u}}{E_c} \tag{2.85}
\]

where the Young’s modulus of the composite, \( E_c \), can be calculated from any of the models presented in the previous Sections (Nielsen [80] suggests using the Sato-Furukawa model, equation (2.80), that accounts for the effect of interfacial strength on the elastic modulus).

However, equation (2.85) has very limited applicability due in part to the uncertainties associated with the calculations (determination of stress concentration factor and also calculation of the Young’s modulus) and more importantly due to the assumption that the material will operate in the linear-elastic regime.

Generally speaking, the decrease in failure strain with the incorporation of filler particles is expected. For the case of good adhesion this becomes clear by considering that the rigid particles will take a very small fraction of the total applied strain on the composite. Therefore, at any given time the matrix will be under a strain that is higher than the one that is macroscopically observed. Assuming that the failure strain of the matrix material is not influenced by the presence of the filler, the composite will fail at an overall strain that is lower than the failure strain of the matrix. On the other hand, when adhesion is weak or non-existent the particles can be thought to act as holes, reducing the effective cross-section of the sample and acting as sites of stress concentration. As a result of this stress concentration, the failure strain of the composite sample will again be lower than that of the unreinforced matrix. As discussed above, according to Nielsen [80] the decrease in failure strain is smaller in the case of weak adhesion than in the case of good adhesion.
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Equations (2.83)-(2.85) fail to include a number of factors that are expected to affect the failure strain of composites, such as particle size, particle dispersion, interfacial strength etc. For this reason various other models have been developed on the prediction of failure strain and strength seeking to address these issues.

2.4.3.2 Further developments in predicting the ultimate properties of particulate-filled composites

Leidner and Woodhams [82, 83] also considered two distinct cases for the effects of spherical particles in a polymer matrix; one of no adhesion and one where some degree of adhesion exists. Contrary to the treatment by Nielsen, in the case of no adhesion, they acknowledged that some stress transfer takes place from the matrix to the particles. This is due to the fact that as the polymer cools down from its melt state, its much higher thermal expansion coefficient compared to that of the rigid filler particles will lead to the development of a compressive load exerted to the particles. Therefore, under a mechanical load, stress transfer will take place from the matrix to the inclusions through friction (Figure 2.21(a)), and the following equation is derived:

\[
\sigma_{\text{e,\nu}} = 0.83 \rho a_{fr} \phi + k_{m,f} \sigma_{m,\nu} (1 - \phi)
\]

(2.86)

where \( \rho \) is the pressure applied from the matrix on the particles due to shrinkage from cooling down from the melt, \( a_{fr} \) is the coefficient of friction and \( k_{m,f} \) is the relative...
change in the matrix strength due to the presence of filler. The latter is related to the diameter of the particles, \(d\), as \(k_{mf}(d) = f(d^{-1/2})\) [83].

When there is some degree of adhesion the load is transferred from the matrix to the particles, through both shear and normal stresses acting on the interface (see Figure 2.21 (b)). The failure strength of the composite now becomes:

\[
\sigma_{c,u} = \left(\sigma_{int,u} + 0.83\tau_{m,u}\right)\varphi + \sigma_{int,u}S_{CF}(1 - \varphi) \tag{2.87}
\]

where \(\sigma_{int,u}\) is the strength of the interface, \(\tau_{m,u}\) is the shear strength of the matrix and \(S_{CF}\) is a stress concentration parameter reflecting the increased stresses acting at the interface compared to the rest of the matrix. Note that equation (2.86), when there is no adhesion, predicts a decrease in strength with volume fraction, whereas equation (2.87) predicts the composite strength will increase with volume fraction of filler when the particles are bonded to the matrix.

Based on equations (2.86) and (2.87), Leidner and Woodhams were also able to derive a relationship for the failure strain of the composite for the general case where the material behaves in a non-linear fashion [82]. For this, they made the assumptions that the non-linear behaviour of the composite is entirely due to the matrix and that, for a given volume fraction, the ratio of the stress taken by the composite over the stress taken by the matrix will be constant irrespective of the strain that is applied to the composite. The authors note that the first assumption is expected to hold well for the case of good adhesion between filler and matrix. However, as discussed by Smith [81] when dewetting of the particles is possible, non-linearity is enhanced as a result of the processes for void nucleation and growth. The second assumption will hold in the elastic region, due to \(E_c/E_m\) also being constant (i.e independent of strain) for a given volume fraction. However the extension of this assumption beyond the linear region is questionable.
The mechanical properties of polymers and particulate-filled composites

Figure 2.21. Schematic diagrams of a composite containing a single particle under tension, for the case where there is no adhesion between particle and matrix (a) and for the case where the particle is bonded to the matrix (b). In the diagrams the matrix is in light grey while the particle is in dark grey colour.

Nevertheless, the proposed equation for predicting the failure strain of composites takes the form [82]:

$$\varepsilon_{c,u} = \frac{\varepsilon_m}{\varepsilon_{m,e}} \varepsilon_{c,e}$$

where $\varepsilon_m$ is the strain applied to the matrix at a stress equal to the stress carried by the matrix at the point of failure of the composite. This stress is simply the second term of the right hand side of equations (2.86) and (2.87). $\varepsilon_{m,e}$ is the failure strain of an elastic material with the Young’s modulus and failure stress of the matrix. Similarly, $\varepsilon_{c,e}$ is the failure strain of an elastic material having the Young’s modulus of the composite (calculated according to any equation in Sections 2.4.1 and 2.4.2) and the strength of the composite taken from equations (2.86) and (2.87).

Interestingly, the Leidner and Woodhams prediction for the failure strain of composites is not in agreement with Nielsen’s theory for a smaller decrease in ultimate strain with decreasing strength of the particle/matrix interface. Instead, according to equation (2.88), the decrease in failure strain is similar whether there is good or no adhesion, with a somewhat greater decrease in the case of no adhesion.

Papanicolaou and Bakos [84] provided an alternative to the Leidner and Woodhams model for the tensile strength of particulate filled composites. The main difference in their model was the introduction of empirical parameters to account for particle/matrix adhesion and the degradation of matrix strength due to the presence of particles. The latter does not refer strictly to stress concentrations around the
The mechanical properties of polymers and particulate-filled composites

particles, but could also include chemical degradation of the matrix during the manufacturing stage due to the presence of the filler. They proposed the following equation for the failure stress of the composite:

\[
\frac{\sigma_{c,\mu} - \sigma_{m,\mu}}{\sigma_{m,\mu}} = A_{p,B} (B_{p,B} - 1) \varphi^{n_{p,B}}
\]

(2.89)

where \(A_{p,B}, B_{p,B}\) and \(n\) are empirical constants. The parameters \(A_{p,B}\) and \(n_{p,B}\) are related to the degree of adhesion between filler and matrix and to the change in the strength of the matrix due to the presence of the filler respectively. Values of \(A_{p,B} = 1\) and \(n_{p,B} = 1\) represent the case of perfect adhesion and no degradation in the matrix strength due to the inclusion of particles. \(B_{p,B}\) is a parameter related to the ratio \((E_f - E_m)/E_m\).

Note that equation (2.89) predicts a decrease in composite strength with increasing volume fraction of the filler. This is in contrast to the Leidner and Woodhams equation for the case of good adhesion where an increase in composite strength is seen with \(\varphi\).

Finally, Bazhenov et al [85] considered the case of composites where the matrix is a polymer capable of undergoing large deformations, and additionally shows a distinct drawing region in its stress versus strain curve under tensile loading. They observed that, during the drawing part of the deformation, a significant amount of void nucleation takes place around the particles. Experimentally, a gradual decrease in failure strain and in the extent of the drawing region were seen up to a certain critical volume fraction of particles, followed by a steep drop in the value of failure strain, where the samples were found to break before any cold drawing could occur. Based on these observations they described the addition of particles in a polymeric matrix in terms of a ductile to brittle transition in the mechanical behaviour of the polymer. They predicted the failure strain up to the critical volume fraction, where the material behaviour changes from ductile to brittle, as:

\[
\varepsilon_{c,\mu} = \varepsilon_{m,\mu} - \frac{\gamma_B \sigma_{m,\mu}}{E_{m,d}} \varphi^{2/3} + \frac{\sigma_{m,\mu}}{E_{m,d}} \varphi
\]

(2.90)

where \(\gamma_B\) is a geometric factor taking the value of 1.2 for spheres, and \(E_{m,d}\) is the slope of the stress versus strain curve of the matrix material in the drawing region.
The critical volume fraction, $\phi^*$, was given as:

$$
\phi^* = \frac{1}{\nu^3} \left( 1 - \frac{\sigma_{m,d}}{\sigma_{m,u}} \right)
$$

(2.91)

where $\sigma_{m,d}$ is the drawing stress of the matrix, i.e. the more or less constant stress in the drawing part of the stress versus strain curve. $\phi^*$ determines the highest volume fraction of reinforcement for which equation (2.91) is applicable and also the volume fraction at which the ductile to brittle transition takes place.

2.5 Chapter summary

In Section 2.1 a general introduction to polymer materials was given, with the focus on providing definitions for a number of polymer properties (such as molecular weight, branching, the configuration and conformation of polymer chains etc.) that are useful for the discussions to follow. The concept of a polymer network was also introduced and theoretical calculations of cross-link density were presented.

In Section 2.2, an introduction to the mechanical behaviour of polymeric materials was given. The focus of the discussions was on the time and temperature dependent nature of polymer materials. The transitions in the mechanical behaviour of polymers as a result of changes in temperature and time scale were presented, with the focus being on the glass transition. Additionally, the effects of time and temperature were shown to be equivalent and this was expressed quantitatively through the WLF and Arrhenius equations, which enable the prediction of material properties at time-scales that would be practically impossible to achieve experimentally. Mechanistic analogues were presented that can be used to predict stress relaxation for time-dependent materials. The concept of a distribution of relaxation times was introduced and different forms of such distributions were given. The case of time-independent, strain-dependent material behaviour was also considered and in particular the case of rubber elasticity. The main theories of rubber elasticity were discussed and formulas giving predictions of stress as a function of strain for rubber-elastic materials were presented. Finally, the case of non linear visco-elastic materials was considered. The response of
such materials to mechanical loads is a function of both time and strain, and a hybrid time-dependent/rubber-elastic model was presented that will be used in Chapter 11 to model the tensile response of the materials studied here.

In Section 2.3 a very basic introduction to the fracture mechanics theory was presented. The discussion focused on these aspects of the theory relevant to the present study, i.e. for polymers that can be treated as continuum bodies supplied with a uniform set of properties. The main considerations of the linear elastic fracture mechanics approach were discussed and the distinction was made between the elastic case, where the bulk of the material behaves as an elastic continuum, and the inelastic case, where extensive energy dissipation takes place in the bulk of the material. The discussion of the inelastic case focused solely on the essential work of fracture (EWF) approach which has found significant application in the experimental determination of the toughness of polymer films that present global yielding before fracture. The main theoretical considerations and experimental requirements of the method were discussed with an emphasis on specimen geometry and its effects on the results obtained.

Finally, in Section 2.4 the effect of rigid filler particles on the stiffness and strength of polymers was discussed. Numerous models exist that deal with these issues and here only a few representative theories were presented. Generally, the predictions using theories on composite stiffness agree reasonably well with the experimental data, and have been successful at incorporating the effect of various factors such as particle shape, dispersion and particle/matrix adhesion. On the other hand, theories relating to the ultimate properties of composites are much less universally applicable. This is due to a number of factors that will influence the large strain behaviour of composites. From the discussion on the available models, the strength of adhesion of the particles to the matrix appears to be the single most important parameter determining the ultimate properties of composites. Other factors affecting composite strength include particle size, shape and dispersion as well as any degradation of matrix properties due to the presence of inclusions.
Chapter 3. Materials and manufacturing

Chapter 2 served to provide a theoretical basis for the discussions that will follow on the mechanical properties of polyester-based coil coatings. In the present Chapter details are given regarding the formulation and manufacturing of the materials. All the paints considered in this study were invariably based on polyester binders. In every case the paints were also cross-linked either by heat-cure with hexa(methoxymethyl)melamine or by an electron-beam cure method. In the following Sections, particular emphasis is placed on the chemical structure of the polyester binders, on the chemistry of the cross-linking process and on the curing of the materials. Also the methods used in the preparation of samples for mechanical testing are detailed.

3.1 Polyester binders

All paint formulations examined in this study were based on polyester binders. Polyesters generally comprise of alternating units of saturated or unsaturated acids and glycols [86]. On an industrial scale they are produced either by direct esterification of carboxyl groups with hydroxyl groups or by a transesterification reaction or finally by reaction of polyfunctional hydroxy compounds with anhydrides. The third method is considered to be the most widely used in the preparation of polyester binders for the coatings industry [87]. This involves a two-step reaction where the anhydride first reacts with the polyfunctional compound, followed by esterification of the carboxyl groups. A common application is the building of polyester molecules by reaction of phthalic acid anhydride with the tri-functional glycerol, see Figure 3.1.
In the present study, a polyester resin commonly used in the coil-coating industry was used as the basic binder system. This contains four different monomers as building blocks - two different acids (adipic and phthalic), a di-ol (neopentyl glycol, NPG) and a tri-ol (referred to as T1 throughout this thesis) the structure of which will not be revealed by request of Becker Industrial Coatings. The extra hydroxyl of T1 is thought to act as a branching point and therefore the polyester is considered to be branched. This binder will be used as the control material throughout the project and will be referred to as PE1. Using the composition of PE1 as the basis, different binders were developed to study the effect of the chemical structure of the binder on the mechanical properties of the paint films. One variation concerned the relative concentrations of adipic and phthalic acid in the polyester macromolecule. Thus a binder with decreased (PE2) and one with increased (PE3) adipic acid content were prepared, where the relative concentrations of the polyols remained the same as for the control polyester. Practically this means that PE3 has a more linear macromolecule than PE1, with less of the bulky benzene rings present in the phthalic anhydride, while the opposite is true when comparing between PE2 and PE1.

![Chemical structure of polyester](image)

Figure 3.1. Two step reaction for the production of polyester from phthalic anhydride and glycerol.
A further variation of the initial polyester involved the elimination of the tri-ol from its backbone leading to a non-branched version of PE1. This is because the extra OH is now removed and therefore there are no sites available to act as branching points on the chains. This polyester will be referred to as PE4. A greater departure from the control binder is polyester PE5. In this case, part of the phthalic acid was substituted by its isomer, iso-phthalic acid, leaving the relative concentration of adipic acid unchanged. Additionally two extra di-ols were added, which will not be revealed and will be referred to as D1 and D2. As a result, the relative concentration of the tri-functional T1 is reduced and therefore the degree of branching of this polyester is expected to be smaller than for the control binder. Finally, a variation of PE5 was produced where an acrylate (no further information was supplied by Becker Industrial Coatings) was added so that the resin can be cured with UV-radiation. This will be referred to as PE6. The compounds that were used as the building blocks of the resins are listed in Table 3.1. The main characteristics, average molecular weights and polydispersities of all binders are shown in Table 3.2.

<table>
<thead>
<tr>
<th>Monomer</th>
<th>Chemical structure</th>
<th>IUPAC name</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adipic acid</td>
<td><img src="image" alt="Adipic acid" /></td>
<td>hexanedioic acid</td>
<td>-</td>
</tr>
<tr>
<td>Phthalic acid</td>
<td><img src="image" alt="Phthalic acid" /></td>
<td>benzene-1,2-dicarboxylic acid</td>
<td>-</td>
</tr>
<tr>
<td>Iso-phthalic acid</td>
<td><img src="image" alt="Iso-phthalic acid" /></td>
<td>benzene-1,3-dicarboxylic acid</td>
<td>-</td>
</tr>
<tr>
<td>Neopentyl glycol</td>
<td><img src="image" alt="Neopentyl glycol" /></td>
<td>2,2-dimethylpropane-1,3-diol</td>
<td>-</td>
</tr>
<tr>
<td>T1</td>
<td>N/A</td>
<td>N/A</td>
<td>Undisclosed tri-ol</td>
</tr>
<tr>
<td>D1</td>
<td>N/A</td>
<td>N/A</td>
<td>Undisclosed di-ol</td>
</tr>
<tr>
<td>D2</td>
<td>N/A</td>
<td>N/A</td>
<td>Undisclosed di-ol</td>
</tr>
<tr>
<td>Unknown acrylate</td>
<td><img src="image" alt="Unknown acrylate" /></td>
<td>N/A</td>
<td>General chemical structure given</td>
</tr>
</tbody>
</table>
### Table 3.2. Main characteristics of different polyester binders used in the study showing composition, number average molecular weight and glass transition temperature as measured by differential scanning calorimetry.

<table>
<thead>
<tr>
<th>Binder</th>
<th>Acids</th>
<th>Poly-ols</th>
<th>$M_n$ [g/mol]</th>
<th>Polydispersity</th>
<th>$T_g$ [°C]</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>PE1</td>
<td>Adipic (16 wt%) Phthalic (42 wt%)</td>
<td>NPG (37 wt%) T1 (5 wt%)</td>
<td>4200</td>
<td>6.9</td>
<td>15&lt;sup&gt;1&lt;/sup&gt;</td>
<td>Control</td>
</tr>
<tr>
<td>PE2</td>
<td>Adipic (12 wt%) Phthalic (46 wt%)</td>
<td>NPG (37 wt%) T1 (5 wt%)</td>
<td>3400</td>
<td>8.7</td>
<td>22&lt;sup&gt;1&lt;/sup&gt;</td>
<td>Decreased linearity</td>
</tr>
<tr>
<td>PE3</td>
<td>Adipic (24 wt%) Phthalic (34 wt%)</td>
<td>NPG (37 wt%) T1 (5 wt%)</td>
<td>4600</td>
<td>5.1</td>
<td>2&lt;sup&gt;1&lt;/sup&gt;</td>
<td>Increased linearity</td>
</tr>
<tr>
<td>PE4</td>
<td>Adipic (16 wt%) Phthalic (42 wt%)</td>
<td>NPG (42 wt%)</td>
<td>8400</td>
<td>2.2</td>
<td>15&lt;sup&gt;1&lt;/sup&gt;</td>
<td>No branches</td>
</tr>
<tr>
<td>PE5</td>
<td>Adipic (17 wt%) Phthalic (17 wt%) Iso-phthalic (23 wt%)</td>
<td>NPG (19 wt%) T1 (3 wt%) D1 (6 wt%) D2 (15 wt%)</td>
<td>2200</td>
<td>2.7</td>
<td>-11</td>
<td></td>
</tr>
<tr>
<td>PE6</td>
<td>Adipic (15 wt%) Phthalic (16 wt%) Iso-phthalic (21 wt%)</td>
<td>NPG (18 wt%) T1 (3 wt%) D1 (5 wt%) D2 (14 wt%)</td>
<td>2000</td>
<td>2.2</td>
<td>N/A</td>
<td>+ 7 wt% unidentified acrylate</td>
</tr>
</tbody>
</table>

Note: <sup>1</sup>Values measured by author, all other values provided by BIC.

### 3.2 Cross-linker for heat-cure

Coil coatings based on polyester binders are customarily cross-linked at high temperatures with hexa(methoxymethyl)melamine (HMMM). In the coatings industry the term melamine is often used to describe such cross-linkers even though melamine-formaldehyde represents a more accurate term for this class of materials. In the simplest case, the amino compounds of the melamine are reacted with formaldehyde (HCHO) to produce a methylolated compound at the end of a multi-step reaction, as shown in Figure 3.2 (a). Alternatively, the methylol groups can be replaced by alkyl groups through a reaction with an alcohol (see Figure 3.2 (b) for example), which can improve the compatibility of the cross-linker with the polyester and also increase its chemical stability (longer pot life of the paint) [88-90].

During cure, the methoxy groups of the melamine formaldehyde react with the hydroxyl groups present in the polyester, emitting methanol (see Figure 3.3). The number of functional sites (methoxy groups for the cross-linker and hydroxyl groups for the binder) dictates the theoretical maximum cross-link density of the coating. On
an industrial level the cross-linking reactions take place at elevated temperatures resulting in very fast curing rates further enhanced by the presence of catalysts (see Section 3.3).

In this study a commercial hexa(methoxymethyl)melamine (Cymel 303, Cytec Industries USA) was used, with a number average molecular weight, $M_n = 390 \text{ g/mol}$. This resin is considered to be fully methylated, i.e. all six of the amino groups of the melamine are thought to be substituted with functional methoxymethyl groups. In practice such a high degree of functionality is very difficult to achieve as methylolation becomes more and more difficult with the progress of the melamine-formaldehyde reaction.

![Figure 3.2](image.png)

Figure 3.2. Formation of a methylol melamine from the reaction of melamine with formaldehyde (a) and of hexa(methoxymethyl)melamine (HMMM) from the alkylation of the methylol melamine (b).

![Figure 3.3](image.png)

Figure 3.3. Reaction between hydroxyl group of polyester and methoxymethyl group of HMMM.
Additional groups (other than methoxymethyl) are also contained in HMMM resins including NCH$_2$OH, NH, NCH$_2$OCH$_2$OCH$_3$ and NCH$_2$OCH$_2$N. These groups can be important in controlling properties such as the tendency for self-condensation between HMMM molecules. For example NCH$_2$OCH$_2$N will tend to form a bridge between two melamine rings resulting in oligomeric structures considered to be present to varying degrees in most commercial HMMM resins [91]. Self-condensation can also take place during the curing reaction, creating a second melamine network inside the cured paint. The presence of such networks can greatly affect the physical and mechanical properties of the coating. Again the type of groups present in the HMMM molecule will influence the degree of self-condensation as well as the rate of the cross-linking reaction [92].

Since no specific information was provided on the composition of the HMMM resin used here, it will be assumed that this is monomeric with the general chemical formula found in Figure 3.2 (b). However, as it recognised that the theoretical value of six functional sites per molecule is unrealistic, a slightly more conservative estimate for five functional groups per molecule will be assumed [93]. For the calculation of the amount of cross-linker required to create a perfect PE-HMMM network, knowledge of the functionality of the polyester resin is also required. Hydroxyl groups available for cross-linking can be found at the two ends of the polyester chain, either as part of the carboxyl groups of the acid monomers or as part of the glycols. For those polyester resins which contain tri-ol monomers in their backbone, additional functional sites are provided by the free OH of the tri-ol, or in the case where this has reacted to give a branch to the backbone chain, an additional functional site will be at the free end of the branch. As the concentration of tri-ol in the polyester resins is known, the total number of functional sites per polyester chain (functionality) can be calculated. The functionalities of the polyester resins are shown in Table 3.3. The required concentrations of HMMM for cross-linking, so that neither of the reactants is in excess, (stoichiometric ratio, $r_S$, equal to unity) are also shown in Table 3.3.

In industrial applications it is standard practice to use excess HMMM to achieve a fully cross-linked network due to the short curing times and the expected less than theoretically possible functionality of the melamine [93]. For the purposes of this
study, binders PE1, 2, 3, 4 and 5 were combined with HMMM at a binder to cross-linker ratio of 80:20 by weight (this concentration is customarily used in an industrial scale) to produce cross-linked paints. These are paints PE1H20, PE2H20, PE3H20, PE4H20 and PE5H20 as shown in Table 3.4. To study the effect of the degree of cross-linking on the mechanical properties of the paint, three additional concentrations of HMMM (95:5, 90:10 and 70:30) were added to the basic binder PE1 (PE1H5, PE1H10 and PE1H30 respectively as shown in Table 3.5). It is noted that the above concentrations refer to the binder:HMMM ratio in the solid cured film, that is after all the solvents present have evaporated during the curing process.

Table 3.3. Number of tri-ol monomers and number of functional sites per chain of binders PE1-PE5. The stoichiometric amount \( (r_S = 1) \) of HMMM required for the cross-linking of each polyester is also shown.

<table>
<thead>
<tr>
<th>Binder</th>
<th>Number of tri-ol monomers</th>
<th>Functionality</th>
<th>PE:HMMM by weight ( (r_S = 1) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>PE1</td>
<td>1.6</td>
<td>3.6</td>
<td>94:6</td>
</tr>
<tr>
<td>PE2</td>
<td>1.3</td>
<td>3.3</td>
<td>93:7</td>
</tr>
<tr>
<td>PE3</td>
<td>1.7</td>
<td>3.7</td>
<td>94:6</td>
</tr>
<tr>
<td>PE4</td>
<td>0</td>
<td>2</td>
<td>98:2</td>
</tr>
<tr>
<td>PE5</td>
<td>0.5</td>
<td>2.5</td>
<td>92:8</td>
</tr>
</tbody>
</table>

Table 3.4. Formulations with different binder structures.

<table>
<thead>
<tr>
<th>Formulation</th>
<th>Binder</th>
<th>Binder: HMMM by weight</th>
<th>HMMM: p-tsa by weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>PE1H20</td>
<td>PE1</td>
<td>80: 20</td>
<td>98:2</td>
</tr>
<tr>
<td>PE2H20</td>
<td>PE2</td>
<td>80: 20</td>
<td>98:2</td>
</tr>
<tr>
<td>PE3H20</td>
<td>PE3</td>
<td>80: 20</td>
<td>98:2</td>
</tr>
<tr>
<td>PE4H20</td>
<td>PE4</td>
<td>80: 20</td>
<td>98:2</td>
</tr>
<tr>
<td>PE5H20</td>
<td>PE5</td>
<td>80: 20</td>
<td>98:2</td>
</tr>
</tbody>
</table>

Table 3.5. Formulations with varying HMMM content, based on binder PE1.

<table>
<thead>
<tr>
<th>Formulation</th>
<th>Binder</th>
<th>Binder: HMMM by weight</th>
<th>HMMM: p-tsa by weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>PE1H20</td>
<td>PE1</td>
<td>80: 20</td>
<td>98:2</td>
</tr>
<tr>
<td>PE1H5</td>
<td>PE1</td>
<td>95: 5</td>
<td>98:2</td>
</tr>
<tr>
<td>PE1H10</td>
<td>PE1</td>
<td>90: 10</td>
<td>98:2</td>
</tr>
<tr>
<td>PE1H30</td>
<td>PE1</td>
<td>70: 30</td>
<td>98:2</td>
</tr>
</tbody>
</table>

3.3 Radiation curing

An alternative to the traditional heat-curing procedure is offered by radiation curing. The term can refer to ultra-violet (UV), electron beam (EB), infra-red, radio frequency,
gamma ray or microwave curing. Commercially, UV and EB curing are the most relevant methods, with UV curing being the most widespread [89]. Here, EB curing was used to study the effects of the method on the mechanical properties of paint.

Both EB and UV curable paints usually consist of the resin (typically an oligomer or pre-polymer) and a reactive monomer solvent. The pre-polymer will typically contain either some degree of unsaturation or cyclic structures that can be subject to ring opening. The UV or EB radiation is absorbed by the unsaturation or the cyclic structures leading to the creation of radicals and subsequent polymerisation of the resin. However, on exposure to UV radiation, coatings will not generally yield enough reactive groups, and therefore the presence of photo-initiators that will absorb the UV light and form free radicals is required. On the other hand, the higher energies associated with the EB method mean that no such initiators need to be used in this case. An additional disadvantage of the UV method is its poor performance in curing pigmented systems, due to absorption of wavelengths in the UV region by the pigment.

With respect to the systems used in this study the inclusion of the unidentified acrylate in resin PE6 (see Table 3.1 for general chemical structure) will provide the free radical required for polymerisation of the binder. Advantages of using acrylates instead of other types of unsaturations, include the high reactivity of the acrylate double bond, their non-yellowing behaviour during cure and the wide range of available acrylate monomers offering different functionalities and chain lengths [89].

Typically, radiation-curable formulations will also contain monomers that can serve both as diluents and as polymerization/ cross-linking sites during cure. The advantage of using such monomer diluents comes from the elimination of solvents from the paint formulation (and therefore the elimination of solvent emissions during the curing process). For the purposes of this study isobornyl acrylate (Aldrich, USA) monomer, also referred to as IBOA, was used. IBOA is mono-functional and therefore cannot act as a cross-linking agent, its role being restricted to reducing the viscosity of the paint. IBOA was added to binder PE6 at a 50:50 ratio by weight to produce formulation PE6EB which practically is the EB-cured equivalent of formulation PE5H2O (Table 3.6).
Table 3.6. Paints prepared with use of heat-cure method and with EB-cure method.

<table>
<thead>
<tr>
<th>Formulation</th>
<th>Binder</th>
<th>Binder: HMMM by weight</th>
<th>HMMM: p-tsa by weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>PE5H20</td>
<td>PE5</td>
<td>80:20</td>
<td>98:2</td>
</tr>
<tr>
<td>PE6EB</td>
<td>PE5</td>
<td>N/A</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(50:50 by wt IBOA added)</td>
<td></td>
</tr>
</tbody>
</table>

3.4 Catalyst, solvents and flow agents

In practical applications, the cross-linking reactions between the polyester binder and the HMMM take place in the presence of catalysts. The choice of catalyst will affect both the rate of the curing reaction and the properties of the final product. Most commonly, p-toluene sulphonlic acid (p-tsa) is the catalyst used in the coatings industry [89, 94]. To achieve good stability of the paint and subsequently a longer shelf life, p-tsa is added to the paint formulation as its amine salt, i.e. in a solution with alcohol, stabilised with 2-amino-2methyl propanol (AMP) dispersant. For the purposes of this study p-tsa was used at a 98:2 (HMMM: p-tsa) ratio by weight, for all HMMM-cured formulations. To study the effects of catalyst concentration on the paint properties additional formulations were prepared containing 99.5:0.5 and 97:3 ratios of HMMM: p-tsa (formulations PE1H20C0.5 and PE1H20C3 respectively, see Table 3.7). The AMP-blocked p-tsa was prepared in the facilities of Becker Industrial Coatings, UK. No catalyst was used in the case of EB-cured formulations.

Solvents are important components in paint formulations, affecting not only the rheological behaviour (and therefore the ease of application) of the coating but also its stability and ageing behaviour [95] (in the case where the solvent has not fully evaporated during cure). The rate of solvent evaporation will affect the flow properties of the paint and it is not uncommon for two different solvents to be used (e.g. by combining a highly volatile with a less volatile one) resulting in better control of the solvent evaporation process [95]. For the formulations studied here, equal amounts of two different solvents were used, their concentration in the uncured paint formulation depending on the relative concentration of binder:HMMM and the presence of pigment. The names of the solvents will not be revealed by request of Becker Industrial
Coatings. As discussed earlier, for the EB-curable system the use of solvents was not required.

Finally, coating formulations usually contain flow (or levelling) agents to improve their rheological characteristics during application, and to eliminate common problems such as poor levelling and sagging that often appear when the paint is applied on vertical surfaces. Disparlon L-1984 (Kusumoto Chemicals Ltd, Japan), a commercially available flow agent, was used here at a concentration of approximately 0.3 wt% in the un-cured paint formulations. This is considered to evaporate completely during curing of the coating. In the case of the EB-cured paint a different levelling agent was used in BYK-UV 3500 (BYK-Chemie GmbH, Germany). As EB-curing takes place at room temperature the flow agent does not evaporate but is rather integrated in the cured coating due to its acryl functionality [96]. 0.2 wt% of BYK-3500 was added to the EB-cured formulations.

<table>
<thead>
<tr>
<th>Formulation</th>
<th>Binder</th>
<th>Binder: HMMM by weight</th>
<th>HMMM: p-tsa by weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>PE1H2O</td>
<td>PE1</td>
<td>80: 20</td>
<td>98: 2</td>
</tr>
<tr>
<td>PE1H20C0.5</td>
<td>PE1</td>
<td>80: 20</td>
<td>99.5: 0.5</td>
</tr>
<tr>
<td>PE1H20C3</td>
<td>PE1</td>
<td>80: 20</td>
<td>97: 3</td>
</tr>
</tbody>
</table>

### 3.5 Pigments and added particles

Pigments are solids of organic or inorganic nature, that are insoluble in the material they are incorporated and are not affected by it, either physically or chemically. The addition of pigments aims to alter a multitude of properties of the base material, ranging from optical (e.g. colour and opacity), to mechanical (reinforcement, hardness) and application-specific such as fire retardance and corrosion resistance [97]. Inorganic pigments have been in use since pre-historic times and include a wide range of materials such as carbonates, oxides, carbon and metals. Among these, titanium dioxide (TiO₂) is of great importance due to its overall excellent properties (for e.g. opacity, chemical resistance, heat stability and dispersability [97, 98]).
TiO$_2$ is a white pigment and commercially it is found in one of two different crystal forms, anatase and rutile. Both forms have a tetragonal unit cell; however rutile presents significantly closer atomic packing leading to a higher density and greater stability. Of the two, rutile is the form of greatest interest in coatings [98, 99].

One of the main concerns with the use of TiO$_2$ pigment is ‘chalking’. The term describes a condition where loose pigment makes its appearance on painted surfaces as a white powder that resembles chalk. The origin of chalking lies in the degradation of the paint due to oxidation from exposure to UV radiation. In principle, TiO$_2$ pigments will offer a degree of protection against UV exposure as they absorb light in the ultraviolet region. At the same time, however, they are thought to catalyze the oxidation reaction of the binder material especially in the presence of moisture [99]. The rutile form of TiO$_2$ generally behaves better, and is thus preferred for exterior use, but for the elimination of the problem it is necessary to subject the pigment to a relevant surface treatment. Such treatments include the coating of the TiO$_2$ pigment with thin layers of alumina and silica.

Another important aspect regarding pigments is their dispersability. Generally any pigment is thought to come in an agglomerated form and dispersion largely entails breaking down these agglomerates to (theoretically) single particles [97]. The size of a single crystal TiO$_2$ particle is around 200 - 300 nm, but realistically a paint will contain agglomerates much bigger than that. To achieve better results a mill is often used to process the paint, as simply stirring the pigment into the paint will generally result in large agglomerates [99].

For the purposes of this study Kronos 2310 (Kronos Worldwide Inc., USA) TiO$_2$ pigment of the rutile form was used. The surface of the pigment is treated with oxides of aluminium, silicon and zirconia to improve the chalking resistance of the paint. The density is given by the supplier as 4 g/cm$^3$. 50 wt% (in the solid film) of Kronos 2310 was added to a selection of the formulations detailed previously (see Table 3.8) in order to investigate the effect of pigment on the mechanical properties of the paints.
### 3. Materials and manufacturing

#### Table 3.8. Formulations containing 50 wt% Kronos 2310 TiO₂ pigment.

<table>
<thead>
<tr>
<th>Formulation</th>
<th>Binder</th>
<th>Binder: HMMM by weight</th>
<th>HMMM: p-tsa by weight</th>
<th>Kronos 2310 wt% (solids)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PE1H20Ti</td>
<td>PE1</td>
<td>80: 20</td>
<td>98: 2</td>
<td>50</td>
</tr>
<tr>
<td>PE2H20Ti</td>
<td>PE2</td>
<td>80: 20</td>
<td>98: 2</td>
<td>50</td>
</tr>
<tr>
<td>PE3H20Ti</td>
<td>PE3</td>
<td>80: 20</td>
<td>98: 2</td>
<td>50</td>
</tr>
<tr>
<td>PE4H20Ti</td>
<td>PE4</td>
<td>80: 20</td>
<td>98: 2</td>
<td>50</td>
</tr>
<tr>
<td>PE5H20Ti</td>
<td>PE5</td>
<td>80: 20</td>
<td>98: 2</td>
<td>50</td>
</tr>
</tbody>
</table>

#### 3.6 Preparation of paint formulations

The preparation of the paint formulations used in this study was performed at the facilities of the long-term development department of Becker Industrial Coatings. The same procedure was used for mixing all of the clear formulations. First, the polyester resin was mixed with the correct amount of melamine formaldehyde cross-linker and the mix was stirred with an electric stirrer for approximately twenty minutes. Subsequently, the levelling agent, the catalyst and the two solvents were added and the mixture was stirred again for an additional thirty minutes (see Figure 3.4 (a)).

In the case of pigmented (white) formulations, after the initial dispersion of HMMM in the polyester, the pigment powder was gradually added to the mix and was then left to stir for a period of another thirty minutes. At this point, the dispersion of the pigment was checked with the use of a Hegman gauge [100] (see Figure 3.4 (b)). For this, with the use of a palette knife, the paint is drawn down a metallic bar fitted with a groove of decreasing depth. As this depth changes from 30 μm to 0 μm pigment particles (agglomerates) of decreasing size get stuck in the groove and become visible. In this study good dispersion was assumed when the bulk of the visible particles were in the part of the groove with depth less than 5 μm. In the case where agglomerates larger than 5 μm were observed, the paint was stirred again until the desired level of pigment dispersion was achieved. The rest of the materials were then added to the mix and were stirred for another thirty minutes as for the clear formulations. After preparation, both clear and white paints were stored in epoxy-lined steel cans.
3.7 Preparation of free-films and coated steel panels

Free-films of the paint formulations were prepared by application of the paint on polytetrafluoroethylene (PTFE)-coated steel panels with the use of a wire-wound coating bar, also known as a draw-down bar (Figure 3.4 (c) and (d)). The advantage of using such a bar (compared, for example, to simply drawing down with a palette knife) is that a pre-specified amount of wet paint is laid evenly on the substrate producing films of repeatable thickness. Depending on the width and depth of the grooves on the bar, different film thicknesses can be achieved. The thin layer of PTFE coating on the steel panels ensures that the adhesion between the paint and the substrate is poor so the cured paint film can be removed easily and with minimal damage. The thickness of
the PTFE-coated panels was 300 μm, while to ensure similar curing conditions for all paint films their dimensions were kept constant at approximately 137x185 mm.

The different paint formulations were also applied on primed steel panels with the aim to test the formability of the paint. The panels were pre-primed by the supplier with a high molecular weight polyester with no further details given. The thickness of the panels was measured to be around 470 μm with a width of 150 and a length of 250 mm.

For the HMMM-crosslinked formulations, after the application of the paint, both the PTFE-coated and the primed panels were inserted into a gas oven for curing. To determine the time and temperature required for curing of the paint, an empty panel fitted with a self-adhesive temperature sensor (see Figure 3.4 (e)) was first put in the oven for different time intervals and in each case the temperature on the surface of the panel was recorded. This temperature is usually referred to as the peak metal temperature (PMT) of the panel.

For the purposes of this study a PMT of 232°C was used as the target temperature thought to produce a satisfactory degree of cross-linking. To achieve this target temperature the oven was set to 265°C throughout this project. Interestingly, the time required to reach the PMT of 232°C during the course of the project appeared to fluctuate between 30 and 35 s in the case of PTFE-coated panels, and 35 to 40 s in the case of primed panels. The longer dwell times for the primed panels reflect their larger thickness as well as width and length compared to the PTFE-coated ones.

Regarding the observed fluctuations in dwell times, it is expected that differences in the temperature of the environment surrounding the oven and of the steel panel itself will influence the time required to achieve the desired PMT. Both PMT [101-103] and dwell time [101, 102, 104] have been shown to affect the micro-structural (e.g. cross-link density and extent of HMMM self-condensation) and mechanical properties of coatings. However, since this project did not aim to study directly the effect of curing-conditions on paint properties, and since in any case the fluctuations in dwell-times were considered to be small, it was decided that all formulations would be cured to the same PMT and the above mentioned differences in bake time would be ignored.
After curing, the panels were withdrawn from the oven and placed briefly on a magnetic plate with a large heat capacity to cool down. They were then stored at room temperature and continued cooling at a slower rate.

The EB-cured paint, PE6EB, was mixed and applied on PTFE-coated and primed panels as detailed above, but was prepared for the author in the facilities of Becker Industrial Coatings, France. A radiation dose of 5 Mrad was used for the cure of the paint [105].

3.8 Chapter summary

In this Chapter, the materials that will be investigated in this study as well as the methods used in the manufacturing of these materials were outlined. The chemical compositions and molecular weights of the polyester resins which were used to make the paint systems were given. A description of the cross-linking reactions between the polyester resins and the curing agent, HMMM, was also given with emphasis on the functionalities of the reactants. The amount of HMMM used in the curing of the paints was systematically varied and the relevant formulations were presented. Additionally, one formulation was prepared that was EB-cured and therefore did not contain HMMM. The curing of paint systems with HMMM, takes place in the presence of a catalyst (p-tsa). Three different formulations were prepared where the polyester and the concentration of HMMM remained constant but the catalyst concentration was varied. In order to study the effect of pigment on the mechanical properties of the paints, 50 wt% of TiO₂ was added to a selection of the formulations. Finally, the methods used in the preparation (mixing, dispersion of pigment) application (application with use of draw-down bar, types of substrates) and curing (cure temperature and time, radiation dose) of the paint formulations were stated.
Chapter 4. Experimental methods

In the following, the various experimental methods used in this project will be presented along with the main calculations required to analyse the experimental data.

4.1 Differential scanning calorimetry (DSC)

Differential scanning calorimetry (DSC) is a very popular method used to observe phase transitions (such as the glass transition, melting, crystallization etc.) in polymers. It is based on the principle that phase transitions result in changes of the polymer’s heat capacity, and therefore by measuring heat capacity the aforementioned transitions can be detected [17].

Practically, a polymer sample is placed in a small pan which is positioned on a heat-sensitive sample holder inside the DSC furnace unit, while an empty reference pan is also placed on an identical holder. The furnace is then heated to the desired temperature at a specified temperature rate. As the sample goes through a phase transition heat is either emitted or absorbed, resulting in a temperature difference between the holder and the furnace. The differential heat flow between the sample pan and the reference pan can then be determined and is used to detect a transition in the sample, such as the glass transition [15, 106].

Customarily, the output of a DSC experiment is a specific heat flow (the measured heat flow divided by the weight of the sample) versus temperature plot, where the various transitions can generally be observed as exothermic (i.e. the sample emits heat) or endothermic (i.e. the sample absorbs heat) peaks. An example of an exothermic
transition in polymers is crystallisation, while melting is endothermic [15]. The glass transition on the other hand is a more subtle transition and is observed as an endothermic step in the heat flow vs temperature diagram (see Figure 4.1). Determination of the glass transition has been the main interest in performing DSC in this study. The glass transition temperature \((T_g)\) was measured as the midpoint of the transition region according to the specifications found in [107]. For this, tangents to the heat flow versus temperature trace are drawn before and after the step-change of the glass transition and also within the glass transition step (dashed lines in Figure 4.1). The intersections of the tangents are then used to determine the onset and end glass transition temperatures as shown in Figure 4.1. The mid-point glass transition is obtained as the point on the heat flow versus temperature trace where the heat flow value is in the middle between the heat flow measured at the onset and that measured at the end of the glass transition.

For the purposes of this project, a TA Q2000 Differential Scanning Calorimeter (TA Instruments, USA) was used. The samples were first cooled to the desired starting temperature, at -30 °C. After an isothermal period of two minutes at the lowest temperature, a constant heating rate of 10 °C/min was applied, up to the highest temperature, which was chosen as 100 °C. The sample was then cooled again down to the lowest temperature and subsequently the heating ramp was repeated for a second time. The choice of the temperature range was made so that the heat flow trace before and after the glass transition would be sufficiently long, thereby facilitating drawing the tangent lines that are required for the determination of \(T_g\). The weight of the samples varied between 5 and 10 mg and was measured prior to testing to an accuracy of 0.01 mg. The pans used were made of aluminium. The glass transition measurements from the second heat are quoted, as the first heat served to erase any thermal history of the samples.
Figure 4.1. Graph of specific heat flow vs temperature from DSC experiment on sample of polyester coating. The glass transition region is seen as a step change in the heat flow. The dashed lines correspond to the tangents drawn for the determination of the onset, midpoint and end glass transition temperatures. The dotted line simply denotes the mid-point of the specific heat flow change between the onset and the end of the glass transition.

4.2 **Dynamic mechanical analysis (DMA)**

DMA is another technique used to characterise transitions in polymers. Compared to DSC it provides more information on the effect of micro-structural characteristics on the mechanical properties of the material.

The method involves the application of an oscillatory stress, $\sigma(t)$, to a small sample of the material while the corresponding strain is recorded. Specimens can be loaded in a number of ways including tension, compression and flexure. For the case of a sinusoidal stress applied on a material sample, the stress at any time, $t$, is given by:

$$\sigma(t) = \sigma_{\text{max}} \sin(\omega t)$$  \hspace{1cm} (4.1)

where $\sigma_{\text{max}}$ is the maximum stress and $\omega$ is the oscillation frequency.

The resulting strain can be thought to consist of two components, one ($\varepsilon'$) that is in phase with the applied stress and another ($\varepsilon''$) that is offset by 90°. Because of this, the total strain will be out of phase with the applied stress by an angle $\delta$ and the individual strain components become [17]:

$$\varepsilon' = \varepsilon_{\text{max}} \sin \delta$$  \hspace{1cm} (4.2)

$$\varepsilon'' = \varepsilon_{\text{max}} \cos \delta$$  \hspace{1cm} (4.3)
where \( \varepsilon_{\text{max}} \) is the maximum strain. In Figure 4.2 an applied sinusoidal stress and the resulting strain response in the case of a visco-elastic material are shown, where the phase difference between the stress and the strain is also noted.

From these data, the storage modulus, \( E' \) (elastic part), and loss modulus, \( E'' \) (viscous part) are calculated. The first of the two moduli is a measure of the material’s ability to return energy stored as elastic deformation, and the second is a measure of energy lost towards molecular rearrangements. \( E' \) and \( E'' \) can be shown [17] to be:

\[
E' = \frac{f_{\text{max}}}{b \Delta_{\text{max}}} \cos \delta \tag{4.4}
\]

\[
E'' = \frac{f_{\text{max}}}{b \Delta_{\text{max}}} \sin \delta \tag{4.5}
\]

where \( f_{\text{max}} \) and \( \Delta_{\text{max}} \) are respectively the force and displacement of the sample at the peak of the sine wave and \( b \) is a geometry parameter. A useful measure of the degree to which a material deviates from elasticity (behaves in a viscous way) is the ratio \( E''/E' \), also known as the loss factor which according to the above equations is equal to the tangent of the phase between stress and strain (\( \tan \delta \)).

Dynamic mechanical analysers usually provide the options of either stress or strain control. Under stress control a set (but oscillatory) stress is applied on the sample whereas in strain control it is deformation that is maintained, and changes in the corresponding stress are recorded. DMA also gives the user the opportunity to observe the material response either over a range of temperatures or over a range of frequencies.

![Figure 4.2. Response of a visco-elastic material to a sinusoidal stress, where the phase angle, \( \delta \), between the stress and the strain is noted.](image-url)
4.2.1 Determination of glass transition and crosslink density

The most common application of DMA is where the sample is subjected to a sinusoidal deformation at a constant frequency while the temperature changes at a constant rate. In this way, the storage and loss moduli and tanδ are monitored over a desired range of temperatures enabling the detection of transitions in that region. Generally speaking, transitions due to relaxations will appear on the output graph as drops in the value of the storage modulus (or increases for loss modulus) and subsequently peaks in the case of tanδ. Tanδ maxima are used to identify the temperatures at which different transitions take place [16]. Here the determination of glass transition was of particular interest. Several definitions of the glass transition can be used [16] and the relevant British standard [108] recommends the use of the inflection point of the storage modulus versus temperature, noting that this usually also coincides with a maximum in the loss modulus trace. Here it was chosen to use the temperature corresponding to the maximum value of tanδ (see Figure 4.3) as the glass transition temperature, \( T_g \), on the grounds of the greater popularity of this method in the literature (for example [92, 101, 104, 109, 110]).

Additionally, it is well known [17, 18] that the modulus measured in the rubbery plateau region of thermoset polymers is directly linked to their crosslink density. Here, the rubbery modulus was used to determine the cross-link density of the paint samples according to:

\[
\nu_e = \frac{E_e}{3RT_e}
\]

(4.6)

where \( \nu_e \) is the crosslink density, \( E_e \) the rubbery modulus, \( R \) is the Avogadro constant and \( T_e \) the temperature in the rubbery region. The above equation is based on considerations regarding the structure of rubber networks and has been discussed in more detail in Section 2.2.2.1.
4.2.2 Special considerations in the testing of thin films

Generally, DMA analysers will provide the user with various loading-mode options, such as bending (single and double cantilever, 3 point bending), shear and tension. The geometry of thin paint films means that the only available option is tension. Although bending methods are more popular with bulk samples, the resulting bending stiffness for the paint films is lower than what most modern DMAs will accurately analyse. The experimental challenges and considerations associated with the testing of thin films using DMA are outlined in the excellent chapter by Duncan [111].

In the tensile geometry, the sample is subjected to alternating compressive and tensile deformation at a pre-specified frequency and its properties are measured as described in Section 4.2. The maximum dynamic strain at the compressive and tensile parts of the loading cycle is set by the user, usually to values inside the linear visco-elastic part of the material behaviour. During the compressive part of the cycle there exists the possibility of buckling the sample. This will influence the results by generally underestimating the stiffness (storage modulus) of the material. This problem is exacerbated with decreasing thickness and increasing length of the sample, as the critical buckling load, $P_c$, for a rectangular element under compression is given by:

$$P_c = \frac{\pi^2 EI}{(qL)^2} \quad (4.7)$$

![Figure 4.3. Graph of storage modulus, loss modulus and tanδ versus temperature also showing the glassy and rubbery region of the material with respect to the storage modulus curve.](image-url)
where \( I = \frac{1}{12}w\theta^3 \) is the moment of inertia of the element, \( E \) is its Young’s modulus, \( q \) is a constant equal to 0.5 when both ends of the element are fixed, \( L \) its free length, \( w \) its width and \( \theta \) its thickness.

To ensure that the sample is not buckled, a static force needs to be applied on top of the dynamic force operating during the experiment. In addition, it is necessary that the static force is maintained higher than the dynamic force throughout the experiment (thereby ensuring that the sample is not allowed to go into compression). Most DMA analysers accommodate this requirement by operating at a fixed ratio of static to dynamic stress. This way, the static stress is kept higher than the dynamic stress for the duration of the experiment and also decreases with the stiffness of the sample (following the decrease in the dynamic stress) so as to avoid excessive straining of the sample in the visco-elastic and rubbery regions. Usually, the static to dynamic stress ratio is chosen to be in the range between 1.1 and 1.5.

Another problem associated with the testing of thin films using DMA, is that in the visco-elastic and rubbery regions the total force (static plus dynamic) applied on the sample frequently lies below the lower bound of the analysing capability of the DMA. In this study, a Tritec 2000 DMA (Perkin Elmer, USA) was used, which offers the option of a smoothly changing static to dynamic force ratio that maintains the applied force within the analyser’s capability for the duration of the experiment. Practically, the ratio is maintained more or less constant in the glassy region and starts to increase as the sample enters the visco-elastic region where the sample stiffness drops significantly. This is shown in Figure 4.4 where storage modulus and the ratio of static to dynamic stress are plotted versus temperature for a sample of PE1H20 tested using DMA.

An often overlooked effect of this gradual increase of the static to dynamic force ratio is the fact that outside the glassy region the sample is subjected to total strains that can be multiple times higher than the dynamic strain set by the user. The danger here is for the strain to exceed the limit where linear visco-elasticity is applicable. Generally, this is a very difficult to point to address and at the very least it needs to be considered as one of the possible limitations in the testing of thin films. Nevertheless, certain observations are worth making here.
The results towards the end of the glass transition or in the rubbery region are not significantly affected by the choice of strain amplitude. This is demonstrated in Figure 4.5 where data from tensile tests on samples of PE1H20 at three different temperatures are shown (the $T_g$ of PE1H20 was measured from DSC as 36 °C). At the lowest temperature of 45 °C the stress versus strain plot shows a clear yield point and therefore the choice of strain-range for the calculation of the tensile modulus will greatly affect its value. At higher temperatures, however, the stress-strain trace is practically a straight line up to strains of approximately 15 to 20%, see the 55 °C and 65 °C data in Figure 4.5. This means that the choice of strain range will not significantly affect the calculation for the modulus, for as long as the strain does not exceed the limit of the linear region. When this observation is combined with the DMA data shown in Figure 4.4, it is seen that the increase in the static to dynamic stress ratio takes place at temperatures where the linearity of the stress-strain response is maintained up to high levels of strain. Therefore, the increase in the total applied strain at high temperatures is not expected to significantly affect the DMA results.

In any case, this increase in the total strain at high temperatures needs to be kept in mind in the analysis of DMA data from samples with such low stiffness. Generally, dynamic strains in the order of 0.1 to 0.2 % are applied to ensure that the total strain remains in the initial linear region of the stress vs strain curve throughout the entire range of testing temperatures.
4. Experimental methods

4.2.3 Experimental settings of DMA

For the purposes of this study, a Tritec 2000 DMA (Perkin Elmer, USA) was used. Cooling was provided by liquid nitrogen that was fed by an external dewar to the furnace of the DMA. This operation was manually controlled by the user, i.e. a pump supplied a constant flow of liquid nitrogen and the user was required to stop the operation of the valve when the desired temperature was reached. The DMA also offered no control of humidity conditions during testing.

Single frequency runs at 1 Hz were performed between -50 and 120 °C at a heating rate of 3 °C/min, in order to obtain the glass transition and rubbery modulus of the samples. The heating rate of 3 °C/min is somewhat higher than the recommended rate of 2 °C/min according to the relevant British standard [112]. This choice is justified by the small size of the samples (which means that their thermal inertia will be minimal) and by the existing literature on the dynamic mechanical analysis of paint films where heating rates from 3 °C/min [92, 104, 109] up to 10 °C/min [113] have been used. The time-dependant nature of the properties of the paints was investigated in multi-frequency scans where the samples were subjected to alternating frequencies of 0.1, 1 and 10 Hz at temperatures between -50 and 120 °C at a temperature rate of 2 °C/min. Ideally multi-frequency scans should be performed under isothermal conditions [112]. This point is easily understood by considering that the application of a temperature ramp will result in the sample being loaded in each of the multiple frequencies at different temperatures. Clearly, the faster the applied temperature ramp, the larger the resulting temperature gradient between frequencies. In the present study, it was
not generally possible to maintain iso-thermal conditions, as the DMA was not fitted with an automatic cooling source and therefore it was not possible to maintain a constant temperature below ambient. However, it is noted that the low heating rate used means that only a small temperature difference exists between measurements at different frequencies.

In the case of both single and multi-frequency tests the dynamic strain was set to approximately 0.1 to 0.2%. In every case, a small preload of 0.4 N was applied on the samples at the beginning of the experiment and the loading mode was set to ‘auto-tension’, which meant a changing ratio of static to dynamic stress throughout the experiment. Rectangular samples were used, approximately 5 mm in width with a free length of about 5 mm.

### 4.3 Tensile testing and environmental control

Tensile tests on free films of the paint were performed with the use of an Instron 4301 (Instron, USA) bench-top testing machine with a 100 N load-cell according the relevant BSI standards [114, 115]. The samples were deformed until failure at a constant displacement rate with the use of lightweight aluminium tensile clamps. Tests were performed at a displacement rate of 5 mm/min. Additionally, the effects of rate on the mechanical properties of the paints were studied by subjecting the control formulation (PE1H20) to displacement rates of 0.05, 0.5 and 50 mm/min. It is noted here that as the material deforms, the applied constant displacement rate corresponds to a decreasing strain rate. In terms of characterising the material properties the application of a constant strain rate would be preferable, however the testing machine did not provide this option. The repeatability of the tests was generally satisfactory and was found to largely depend on the careful control of the environmental conditions outlined in Section 4.3.2. At least four samples were tested for each loading condition, which was found to provide sufficiently accurate data.

One concern regarding the quality of the experimental data has to do with the fact that the displacement of the cross-head had to be used to measure the displacement of the sample. This was necessary as the nature of the samples prohibited the use of
strain gauges or a clip-gauge extensometer. Generally, the displacement of the crosshead would be expected to be larger than that of the sample, due to also including the compliances of the various parts of the testing machine and the experimental rig. However, the compliance of the thin polyester samples was considered to be much higher than the compliances of the various parts of the experimental set-up and therefore any difference between the displacements of the sample and the cross-head should be negligible. Previously, the same experimental set-up had been used for the testing of paint films and the cross-head displacement was used to measure the strain with good results [116].

The accuracy of the measurement of strain from the cross-head displacement was investigated by testing a sample in tension, where two horizontal lines were drawn on its surface and their distance was monitored with a digital camera throughout the test. The strain acquired optically was then compared to the one obtained from cross-head displacement, as:

\[ \varepsilon_{\text{eng}} = \frac{\Delta}{L} \]  

(4.8)

where \( \varepsilon_{\text{eng}} \) is the engineering strain applied on the sample (the distinction between engineering and true strain is made in Section 4.3.3), \( \Delta \) is the displacement of the cross-head and \( L \) is the initial length of the sample.

As seen in Figure 4.6 the optically measured strain and the strain measured from the cross-head displacement are fairly similar, even though the strain measured optically was found to be somewhat higher. Still, this difference was not considered to be big enough as to warrant the use of the significantly more time-consuming optical method for the measurement of strain. In the following, the strain is calculated from the recorded displacement of the cross-head of the tensile machine.
4. Experimental methods

Figure 4.6. Comparison of strain as measured by optical method to strain measured from the displacement of the cross-head of the testing machine.

4.3.1 Sample preparation

For the preparation of tensile samples, the paint films were first removed from the PTFE-coated panels by carefully pulling from one end (at 180° with respect to the substrate) with the help of a razor blade (Figure 4.7 (a)). Rectangular samples were then cut to a width of approximately 6 mm and a length of 60 mm (Figure 4.7 (b)). To achieve a better grip within the tensile clamps during testing, paper end-tabs (approximately 10x10 mm) were bonded to each end of the samples with the use of a cyano-acrylate adhesive (Figure 4.7 (c)). Care was taken to ensure that no excess adhesive wetted the sample outside the end-tabs as this was observed to cause the sample to fail at this point. The free-length of the samples between the end-tabs was approximately 40 mm. The width and length of each individual sample were measured with a digital vernier calliper to an accuracy of ± 0.01 mm and the thickness was measured with a digital micrometer to an accuracy of ± 0.001 mm. In each case, at least three measurements were taken and average values were calculated.

A point that is worth noting is that the general quality of the film samples was found to vary. Perhaps the most significant problem came from the presence of holes in the films. Large holes (with diameters of several mm) were frequently observed as a result of the poor wetting of the paint on the PTFE-coated panels. This issue was easily addressed by cutting samples from parts of the films with no such holes. However, much smaller holes, in the micrometre range, were also observed (this is frequently referred to as micro-pinning). These holes are a result of the evaporation of solvents as
well as the emission of methanol during cure. Practically, the existence of these microholes could not be addressed as they were a product of the curing procedure itself and the issue is acknowledged here as a limiting factor in the accuracy of measurements.

![Images of paint film peeled off PTFE-coated panel, cutting of sample from film, bonding of paper end-tab on sample]

Figure 4.7. Paint film peeled off PTFE-coated panel (a), cutting of sample from film with the use of razor blade (b), and bonding of paper end-tab on sample with use of cyano-acrylate adhesive (c).

4.3.2 Environmental control

One of the aims of this study was to investigate the temperature dependence of the mechanical properties of the paints. Also, it has been shown [110, 116-118] that the relative humidity (RH) of the testing environment will have a very significant influence on the properties of thin paint films. Since the present study did not aim to study the effect of humidity on the samples, all tests were performed under an arbitrarily chosen 50% RH. An experimental chamber developed by a previous researcher at Imperial College London (see [116] for a detailed description) was used to simultaneously control the temperature as well as the relative humidity (see Figure 4.8).

Prior to testing, all samples were left in the environmental chamber for an equilibration period of 10 min. The temperature was controlled to an accuracy of ± 0.5 °C and the relative humidity to ± 1% RH. It needs to be noted that the control of relative humidity at near-freezing temperatures was very difficult and generally it is
thought that reliable control was achieved only down to temperatures of about 10 °C. Below this temperature the % RH tended to rise sharply, and generally it proved impossible to keep the RH below approximately 60%. As a result, tests at temperatures below 10 °C will not be considered to have been performed under controlled humidity conditions.

![Environmental chamber](image)

Figure 4.8. Environmental chamber used for the control of temperature and humidity fitted on a bench-top Instron 4301 testing machine.

### 4.3.3 Analysis of results

The output of the tensile tests was load versus displacement of the crosshead. The engineering stress was obtained by dividing the load by the initial cross-sectional area of the sample. Likewise, the engineering strain was obtained as the displacement divided by the initial gauge length.

As the strain increases, the lateral contraction of the sample means that the instantaneous cross-section is smaller than the initial one and therefore the engineering stress underestimates the actual stress applied. Assuming incompressibility for the samples, the engineering stress can be transformed to the true stress, $\sigma_t$, as:

$$\sigma_t = \sigma_{\text{eng}} \left(1 + \varepsilon_{\text{eng}}\right)$$

(4.9)

where $\sigma_{\text{eng}}$ is the engineering stress and $\varepsilon_{\text{eng}}$ the engineering strain.
Similarly to the distinction between engineering and true stress, a distinction can be made between engineering and the true instantaneous strain. The latter is given as a function of engineering strain as:

\[ \varepsilon_t = \ln(1 + \varepsilon_{\text{eng}}) \]  

(4.10)

The experimental results here will be presented in terms of true stress and engineering strain, referred to as simply ‘stress’, \( \sigma \), and ‘strain’, \( \varepsilon \). The use of engineering instead of true strain was preferred simply because the former is more widely used in the literature, especially when relatively brittle polymers are used. For the remainder of this Section the type of stress and strain will be explicitly specified where necessary.

From the experimentally obtained true stress versus engineering strain data, the Young’s modulus of each sample was calculated as the slope of the initial linear part of the tensile curve, between strains of approximately 0.2 and 0.8 %. Yield stress is defined in [114] as the stress at which ‘an increase in strain occurs without an increase in stress’, which could practically be determined as the point where the slope of the stress versus strain trace becomes zero. Alternative definitions include the determination of yield stress as that corresponding to a particular strain [114] (where a previous knowledge of the approximate yield strain is required) or the use of Considere’s construction to determine a yield point [119]. According to the latter method, a tangent line is plotted from -100 % true strain to the true stress versus strain curve, and the point where the two intercept is taken as the yield point (see Figure 4.9). This method implicitly makes the assumption of a maximum present on the engineering stress versus strain curve, i.e. the yield point as defined by this method is thought to coincide with the formation of a neck on the sample.

For the materials tested in this study, the shape of the engineering stress versus strain curves changed drastically at temperatures from approximately 15 °C below to 15 °C above the glass transition (see Figure 4.10 (a)). For temperatures up to \( T_g \) the engineering stress reached either a maximum or a plateau at about 1 to 2 % strain. For these cases, the above definitions of the yield point can be applied. On the other hand, at temperatures in the range of \( T_g \) to \( T_g +10 \) °C, the engineering stress increased throughout the experiment but there was a distinct decrease in the slope of the tensile
curve, again at strains around 1 to 2 %. In the latter case, since no local maximum in the engineering stress is observed, the applicability of the above definitions of yield is questionable. At even higher temperatures, the stress versus strain curve was found to remain linear up to the point where the material began to strain harden. For this latter case no yield point could be determined.

As a result, an alternative method for determining the yield point was used here, that would be applicable to the entire range of test temperatures for which a yield point could be determined. Tangents are drawn to the initial linear part of the true stress versus engineering strain curve and also to that part of the curve where the slope changes for the first time (note that at even higher strains, above approximately 20 %, the slope is found to change again but this is a strain hardening effect not related to yield). The intersect of the two lines is used to define the yield strain on the x-axis. The stress at the point where a vertical line from the intersection cuts the true stress versus engineering strain curve is then taken as the yield stress. An example of the method is presented in Figure 4.10 (b) where the dashed lines are tangents to the stress versus strain plot and the dotted lines serve to note the yield stress and strain.

![Figure 4.9](image-url)  
**Figure 4.9.** Example of determination of yield point with the use of Considere’s construction. The dashed line is drawn from a strain of -100 % on the x-axis, tangent to the true stress versus strain curve and the point of intersection is considered as the yield point of the sample. The dotted lines note the resulting yield stress and strain.
4.4 Fracture toughness testing (essential work of fracture)

To study the fracture behaviour of the paints, the essential work of fracture (EWF) approach was employed. The same experimental set-up was used as outlined in Section 4.3, and the testing guidelines given in [60] were used in conducting the experiments. The double edge notched tension (DENT) sample geometry was used and samples were loaded in tension until failure, at a displacement rate of 5 mm/min. The load-displacement traces were recorded and were afterwards used to determine the total amount of work supplied for tearing the samples (see 4.4.2). Control of environmental conditions was achieved as detailed previously in Section 4.3.2.

4.4.1 Sample preparation

For the preparation of DENT samples, rectangular strips, approximately 80 x 20 mm, were cut from free-films of the paints. A notch was then made on each side of the strip, halfway along the strip’s length. A schematic diagram of a DENT sample is shown in Figure 4.11, where the two notches are seen and also noted are the distance between the notches (ligament, \( l \)), the sample width, \( w \), and the free length of the sample, \( L \). As it is important for the notches to lie exactly opposite one another and to be perpendicular to the edge of the sample, the notches were pre-drawn on the sample with the use of a pen. A new razor blade was then pushed on top of the drawn marks to create the two notches. At this point, end-tabs were bonded to the two ends of the sample leaving a free length, \( L \), of 60 mm.

---

Figure 4.10. Characteristic tensile curves at three different temperatures around \( T_g \), where yield is seen either as a maximum or as a mere change in slope of the stress versus strain trace (a). In (b) an example is given of the method used to determine the yield point in this study.
Regarding the size of the notch, this is thought as a factor that will greatly influence the results obtained with the essential work of fracture (EWF) method [59, 60]. Clutton [60] reports values of essential work of fracture ranging from 20 kJ/m² when polyethylene terephthalate (PET) samples were notched with the use of a scalpel (notch radius around 1 μm), to 58 kJ/m², when a die punch was used instead (notch radius of about 50 μm). Here, a sample was notched and was subsequently observed in reflected light using a ‘Carl Zeiss AXIO Scope’ optical microscope. Images at x100 and x1000 magnification are shown in Figure 4.12. The crack-tip is denoted by the arrows on the two images, and its size was measured to be in the order of a few micrometers, which satisfies the recommendation by Williams and Rink [59] that the notch-radius of EWF samples should be 15 μm or smaller.

The distance between the tips of the two notches is known as the ligament, \( l \). This was measured with the use of a travelling microscope. For each testing temperature several samples were tested with varying ligament lengths ranging from 5 mm to 12 mm. In [60] it is recommended that ligament lengths are chosen so that:

\[
\max(3\theta, 5mm) \leq l \leq \frac{w}{2}
\]  

(4.11)

where \( \theta \) is the thickness and \( w \) the width of the sample. It is recognised that at the longer ligaments the guideline for a maximum ligament length smaller than half the width of the sample is violated. For the materials used in this study however, it proved extremely difficult to find continuous regions of films with no holes where samples could be cut from. This meant that a compromise had to be made in obtaining the largest possible sample that was free of holes and also as wide a distribution of ligament lengths as possible.

Additional issues were the presence of bubbles and micropinning in the samples. These issues were a result of the evaporation of solvents and methanol during cure. Also, in order to obtain enough samples for EWF testing, it was necessary to prepare samples from more than one films of each formulation. This resulted in variations in the thickness of the samples and also in the amount of bubbles present on the sample surface. The existing literature, on the other hand, has focused primarily on...
thermoplastic materials (compare for example the number of references given for thermoplastic systems to that of cross-linked systems in the review article by Barany et al. [53]), that could generally be considered as defect free and that were usually of significantly greater (in the hundreds of μm or mm range) and more precisely controlled thickness. It is clear, therefore, that the use of the EWF approach in this study presents challenges that are related to the quality of the samples, which can affect the repeatability of the tests and result in a greater degree of scatter in the data than what is usually reported in the literature. This is discussed further in the relevant sections of this thesis where the EWF results for each paint-system are presented.

![Schematic diagram of EWF sample](image)

Figure 4.11. Schematic diagram of EWF sample, where the ligament length, , free length, , and width, , are shown. Also shown are the end-tabs as the grey areas at the top and bottom of the sample.

![Optical microscopy images](image)

Figure 4.12. Optical microscopy images showing notch on EWF sample of PE1H20Ti at x100 (a) and x1000 (b) magnification, where the arrows point to the crack-tip.
4.4.2 Analysis of results and data reduction

Typical load-displacement data at various ligament lengths are shown in Figure 4.13 (a). The total work supplied for fracturing the sample at each ligament length, $W_f$, can then be calculated as the area under the respective load-displacement curve. This is done by assuming the total area to be divided into a series of trapezoids. The sum of the areas of the trapezoids will then give the total area under the load-displacement curve, and consequently the total work supplied for the fracture of the sample. Subsequently the total specific work of fracture for each ligament length is obtained as:

$$w_f = \frac{W_f}{\delta l}$$  \hspace{1cm} (4.12)

The values of $w_f$ can then be plotted versus ligament length. When the EWF method is applicable, the data points should fall approximately on a straight line as shown in Figure 4.13 (b). If a linear regression is performed between these points, the best-fit line is given as:

$$w_f = w_e + \beta w_{inel} l$$  \hspace{1cm} (4.13)

where the essential work of fracture, $w_e$, is the intercept of the linear regression line with the y-axis, while the slope of the linear regression provides a measure of the work that was consumed in inelastic (viscous) processes during testing, $w_{inel}$. $\beta$ is a shape factor associated with the plastic zone around the crack.

A characteristic of the EWF method is the self similarity of the load-displacement traces for samples of different ligament lengths. This means that upon increasing the ligament length an increase in the maximum load and the maximum displacement is seen, while the general shape of the load-displacement curve remains the same. The self similarity of the EWF results is also used as a criterion for the applicability of the method, e.g. [60, 120, 121]. Generally, for the materials tested here, self-similarity was found to be satisfied. In certain cases individual samples showed load-displacement curves markedly different to those observed from the rest of the samples of the same formulation. These odd samples were discarded from any further analysis.
Another criterion suggested [59, 60] to determine the applicability of the EWF method states that the maximum stress, $\sigma_{\text{max}}$, observed during the tearing of DENT samples should be related to the yield stress as obtained from a tensile test, $\sigma_y$, as:

$$\sigma_{\text{max}} = 1.15\sigma_y$$  \hspace{1cm} (4.14)

This is commonly referred to as the Hill criterion, as equation (4.14) was originally proposed by Hill in 1952 [122]. In practice, even though equation (4.14) serves as a good approximation for $\sigma_{\text{max}}$, round-robin results have revealed discrepancies regarding the exact relationship between $\sigma_{\text{max}}$ and $\sigma_y$ [60]. In the literature, values of $\sigma_{\text{max}}$ both higher [54, 123] and lower [124, 125] than $1.15\sigma_y$ are observed, while $\sigma_{\text{max}}$ is seen generally to decrease with increasing ligament length. When it was attempted to apply this criterion on the data obtained in this study, it was found that generally the maximum stress values lay above $1.15\sigma_y$. The ratio of $\sigma_{\text{max}}/\sigma_y$ was found to vary between different formulations with values in the range between around 2.5 and 0.8.

Alternatively, it was attempted to compare the measured tensile yield stress to a yield stress obtained from the EWF data, $\sigma_{Y_{\text{EWF}}}$, calculated in the same way as the tensile yield stress (calculation for $\sigma_y$ discussed in Section 4.3.3). The $\sigma_{Y_{\text{EWF}}}$ values were found to compare somewhat better with $\sigma_y$ than the $\sigma_{\text{max}}$ values from EWF, with the ratio $\sigma_{Y_{\text{EWF}}}/\sigma_y$ again depending on formulation, and taking values between 1.4 and 0.6. An example of the above observations is shown in Figure 4.14 (a), for samples of PE1H20 tested with the EWF method at $T_g$ (35 °C).
Clearly both the $\sigma_{\text{max}}/\sigma_y$ and the $\sigma_{y,EWF}/\sigma_y$ ratios show significant scatter, especially when data from different formulations are considered. Potential reasons for a high degree of scatter in data obtained from the same formulation, are the presence of defects in the samples and the use of different batches of material (for example the samples used in the tensile testing of the paints were obtained from different paint-films than the samples tested in EWF), as was already mentioned in Section 4.4.1. In addition, the load versus displacement traces of different formulations tested in EWF were found to be significantly different is shape. This is shown in Figure 4.15 for samples of PE1H5, PE1H30 and PE3H20, where in each case the ligament length was 12 mm and all tests were performed at $T_g$. The resulting load versus displacement traces are seen to be significantly different. PE1H30 quickly reaches a maximum load and breaks. On the other hand PE2H20 shows a characteristic kink in its load versus displacement trace beyond the linear region, with the load then passing through a maximum and finally decreasing until fracture. Finally, in the case of PE1H5, after an initial decrease in the slope of the load versus displacement trace, the load continues to increase through what could be identified as an extensive strain hardening region, before it reaches a maximum shortly after which the sample breaks. From the above, it follows that the mechanisms associated with fracture are expected to be quite different in each case, and this is thought to be reflected in the large scatter in the $\sigma_{\text{max}}/\sigma_y$ and the $\sigma_{y,EWF}/\sigma_y$ values, when data from all formulations are considered.

In view of the difficulties in applying a yield stress criterion for data reduction, it was proposed [59, 60] to calculate the average value of the maximum stress, $\bar{\sigma}_{\text{max}}$, from EWF tests and then discard data points outside the limits $0.9\bar{\sigma}_{\text{max}}$ to $1.1\bar{\sigma}_{\text{max}}$. The choice of limits is considered arbitrary but is thought to improve the quality of the EWF data. The comparison of $\sigma_{\text{max}}$ values obtained for PE1H20 with the above limits is shown in Figure 4.14 (b). It is clear that, even though the maximum stress values are close to the $0.9\bar{\sigma}_{\text{max}}$ to $1.1\bar{\sigma}_{\text{max}}$ range, a strict application of the criterion would result in the exclusion of half the available data points. Generally, similar observations could be made by considering the EWF data of any other formulation tested in this study.

From the above discussions it can be appreciated that the application of any of the stress criteria for the validity of EWF data would result in discarding a large number of
test specimens. This would increase significantly the amount of materials required and was considered as practically impossible within the time-constraints of this project. Instead, it was chosen to include in the analysis all samples that satisfied the self-similarity criterion and whose resulting total specific work of fracture lay within a certain distance from the regression line (see following Section for the latter approach). Any variations in the fracture behaviour of samples are then thought to be reflected in the statistical analysis of the results and more specifically in the uncertainty regarding the values of the intercept and the slope of the regression line.

Figure 4.14. In (a) the maximum stress and the yield stress obtained from EWF tests of PE1H20 at $T_g$ are compared to the yield stress observed from tensile samples of the same formulation at the same temperature. In (b) The maximum stress values, $\sigma_{\text{max}}$, from EWF tests of PE1H20 at $T_g$ are compared to the average value of the maximum stress $\bar{\sigma}_{\text{max}}$.

Figure 4.15. Load versus displacement traces of samples of PE1H5, PE1H30 and PE3H20. In each case the ligament length was 12 mm and the testing temperatures were equal to the respective $T_g$s of the paints.

4.4.3 Statistical analysis

As the analysis of the EWF data requires the extrapolation of the specific work of fracture values to a ligament of zero length, an assessment of the quality of the linear
regression is necessary. A widely used measure of the quality of a linear regression is the coefficient of determination, $R^2$, defined as [126, 127]:

$$R^2 = 1 - \frac{\sum (w_{f,i} - f_i)^2}{\sum (w_{f,i} - \bar{w}_f)^2}$$  \hspace{1cm} (4.15)

where $w_{f,i}$ is the specific work of fracture corresponding to ligament length $i$, $f_i$ is the predicted specific work of fracture from the linear regression for ligament length $l_i$, and $\bar{w}_f$ is the average value of the specific work of fracture. Values of $R^2$ close to 1 signify a good fit of the linear regression to the experimental observations.

It would also be useful to have a measure of the uncertainty associated with the determination of the extrapolated $w_e$ value. The origin of this uncertainty can be appreciated by considering that if one or more data points were excluded from Figure 4.13 (b) (or conversely if more points were included) then the intercept of the linear regression with the y-axis would be expected to change. The uncertainty in the determination of the intercept can be calculated as the standard error, $s_o$, of the intercept [126, 127]:

$$s_o = s_{w/l} \sqrt{\frac{\sum i_i^2}{n \sum (l_i - \bar{l})^2}}$$  \hspace{1cm} (4.16)

where $n$ is the number of observations, $\bar{l}$ is the average ligament length, and $s_{w/l}$ is the standard error of the residuals, $(w_{f,i} - f_i)$ calculated as:

$$s_{w/l} = \sqrt{\frac{\sum (w_{f,i} - f_i)^2}{n - 2}}$$  \hspace{1cm} (4.17)

Similarly to the intercept, there is also uncertainty in the value of the slope of the linear regression, $\theta_{w_p}$. The standard error of the slope, $s_b$, is [126, 127]:

$$s_b = \frac{s_{w/l}}{\sqrt{\sum (l_i - \bar{l})^2}}$$  \hspace{1cm} (4.18)
Williams and Rink [59] state that a standard error of the intercept of up to 0.1 $w_e$ is considered to be acceptable. They also suggest that only $w_{ij}$ values within two standard errors from the regression line should be included in the analysis. This will be followed here and values of $w_{ij}$ outside this range will be discarded when analysing the data.

### 4.5 Stress relaxation and cyclic loading

For the investigation of the visco-elastic nature of the coatings, additional tests were performed where a sample was either left to relax at a constant strain or left to recover from high strains after initial loading. The testing machine and environmental set-up as well as the preparation of samples were as detailed in Section 4.3 for both types of tests.

In the case of stress relaxation, the samples were deformed to a strain of approximately 1%, at which point the cross-head was stopped. Subsequently, the change of the stress required to maintain that constant deformation was monitored versus time. The displacement rate at the initial part of the experiment was set to 50 mm/min. Stress relaxation is ideally a step-strain experiment, i.e. an infinite initial strain rate would be desirable to ensure no relaxation takes place before the peak strain is reached. Obviously an infinite strain rate cannot be achieved. An additional limitation came from the fact that the crosshead movement needed to be manually stopped by the user at the desired displacement. The displacement of 50 mm/min was thought to provide a good compromise of a relatively fast initial loading part that would also give time for the user to stop the cross-head movement.

Cyclic loading tests were also performed on samples. For these, the sample was loaded to a certain displacement at a displacement rate of 5 mm/min. The maximum strain in these tests was chosen to be after the yield point of the material, but before the corresponding fracture strain of the particular formulation. Upon reaching the maximum strain, the cross-head movement was reversed (the unloading rate was the same as the loading rate at 5 mm/min). The test was stopped when the load returned to zero and the residual strain at this point was recorded. The sample was
subsequently removed from the clamps and was left in the environmental chamber for a period of two hours. It was then removed from the chamber and the gauge length was measured with a digital vernier calliper.

4.6 T-bend tests

T-bend tests are widely used in the coil-coating industry for quality control of coated panels and are a variation of the mandrel bend test that is described in [128]. In the mandrel bend test a panel is bent around a mandrel until the two surfaces of the panel are parallel. The bent side of the sample can then be observed for the presence of cracks.

On the other hand, T-bend tests do not require the use of a mandrel, and the sample is bent around a rectangular spacer instead. In the most frequent application the sample is first bent with no spacer until its two surfaces touch. A second bend can then be made where the ‘spacer’ is simply the thickness of the sample. Customarily, the first spacer-less bend is referred to as 0T bend, the next 1T etc. (see also Figure 4.16). In this method the sample is bent in two stages. First, it is pre-bent in a sheet metal folder to an angle larger than 90°. At a second stage the two surfaces of the sample are compressed until they touch. The method is outlined in [129].

For the purposes of this study, T-bend tests were performed under controlled temperature and relative humidity conditions. The coated steel panels were first cut into strips with dimensions approximately 20 x 10 mm using a bench-top, hand-operated shear. The sample was then inserted in the environmental chamber for a period of approximately 10 minutes. It was then taken out and was pre-bent approximately in half parallel to its short side, using a bench-top sheet metal folder, to an angle of 135°.

Subsequently, the sample was returned to the environmental chamber where it was left for another ten minutes before it was compressed between two stainless steel compression platens. A 5 kN load-cell was used and the cross-head was stopped when the load reached 3 kN. At this load, a good contact between the two surfaces of the
sample was observed in every case. All tests were conducted to 0T as the focus was in comparing between the performance of different formulations. Subsequent bends to 1T, 2T etc. would only result in a decreasing amount of cracks on the sample surface [130].

After being compressed, the sample was removed from the chamber and the bent surface was observed using an optical microscope to identify any cracks. It was then returned to the chamber for a period of two hours before it was observed again using the optical microscope. This second stage intended to reveal the effect of time on the quality of the bent surface.

![Diagram](a) ![Diagram](b) ![Diagram](c) ![Diagram](d)

Figure 4.16. Schematic diagram of panel bent to 0T ((a) and (b)) and subsequently to 1T ((c) and (d)).

### 4.6.1 Observation of bent surfaces using optical microscopy

For the examination of bent panels the optical microscope was employed at a x50 magnification. Several images of the bent surfaces of the samples were recorded digitally and these images were later used to determine the area fraction of cracks present on the samples.

In the case of pigmented formulations, the coated panels were placed directly under the optical microscope and observed for cracks in the paint. In the case of clear formulations, however, cracks were not clearly visible. To address this issue a penetrant technique was employed. First, a blue whiteboard marker was used to colour the bent surface, which was subsequently wiped with a dry paper towel. As a
result, the ink of the marker was removed from the coated areas on the panel surface but remained inside the areas where the coating had cracked. This technique created enough contrast for the cracks to be readily observable using the optical microscope. The colouring and wiping procedure was repeated twice for each sample before observation. To demonstrate the applicability of the technique, it was also employed for a white sample (PE1H20Ti). A representative image obtained during this check is shown in Figure 4.17. It is seen that the marker has successfully coloured the outlines of the cracks present on the surface, and therefore it is expected that the method should give a sufficiently good estimate of the cracks present on panels coated with clear formulations. A characteristic image of a clear panel tested in bending is shown in Figure 4.17 (c), where the bent surface has been subjected to the penetrant technique described above.

Figure 4.17. Bent surface of steel panel of PE1H20Ti after T-bend test at room temperature: (a) observed under microscope as is and (b) observed after being subjected to the penetrant technique. In (c) a typical micrograph is shown of a bent clear panel (PE1H30 tested at Tg) where the penetrant method has been applied to the bent surface.
4.6.2 Analysis of results

The captured images of the panel surfaces were analysed to measure the area fraction of cracks present. The measurement of area fraction of cracks was performed with the use of a widely available open-source software (ImageJ). As the measurement was automated through the software’s ‘Analyze Particles’ built-in function, it was found that it was generally necessary to increase the contrast between cracked and non-cracked regions. To achieve this, images were first modified in freely distributed imaging software GIMP where the cracks were painted in black (see Figure 4.18). To increase the accuracy in colouring the cracked areas, the images were magnified as necessary in GIMP.

The modified images were then opened in ImageJ, and the software could now successfully distinguish between cracked and non-cracked regions. The area fraction of cracks on each image was then obtained directly in the output of the ImageJ analysis. Since several images were captured of each sample along its bent surface, the average area fraction of cracks was calculated and is quoted as the measure of the panel’s performance in T-bend under the specified conditions. The variation in the area fraction of cracks along the sample is expressed as the resulting standard deviation of the area fraction values. It needs to be recognised that the step of colouring the cracks in GIMP is a source of potential error. However, because the same procedure was carried out for all samples and by the same user, it is thought that any uncertainty due to this procedure should be the same for all samples. Therefore, even if a small error is introduced in the absolute value of the area fraction of cracks, this method is not expected to significantly affect the comparison between samples.
4.7 Scanning electron microscopy (SEM)

SEM was employed for the observation of cross-sections of pigmented samples in order to characterise the quality of dispersion of the pigment particles. This microscopy method uses a beam of high energy electrons in a vacuum environment to scan the sample surface. The electrons are produced from a heated filament cathode made of tungsten, which is chosen due to its high melting point [131]. As the beam hits the sample it interacts with the atoms on the surface, producing the information that is then translated to a visual image of the surface. This information comes in the form of secondary and back-scattered electrons (SE and BSE respectively). The latter are high energy electrons that are reflected away from the sample’s surface as a result of interactions with the nuclei of the atoms on the surface. Secondary electrons on the other hand are low energy and are ejected from the specimen’s atoms as a result of inelastic collisions with the beam electrons.

Polymeric samples need to be coated with an electrically conductive material before inspection under SEM, to prevent the development of a static charge on the surface, which would obscure the obtained image. Typically the coating is a thin layer of gold applied by a sputtering technique. Because of the vacuum conditions inside the SEM chamber, samples need to be bonded on the sample holder and this is done by using a double-sided conductive tape.
The scanning electron microscope used in this study was a Hitachi S-3400N. The microscope was operated in secondary electron mode, at an accelerating voltage set at 15 kV, under vacuum environment. Typical magnifications used were between x4000 and x8000. For the preparation of samples for observation, cross-sections were exposed by quickly pulling a strip of film apart by hand. The samples were then placed in a sample holder (gripping stub, Agar Scientific, UK) and were sputter-coated with gold for 20 seconds at 40 mA before being inserted in the microscope chamber.

4.8 Chapter summary

A range of experimental methods were employed to characterise the materials investigated in this study. The thermal and thermo-mechanical properties of the paints were studied with the use of differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA). Tensile testing was employed to obtain such properties as the Young’s modulus, the yield stress, and the stress and strain at the point of failure over a wide range of temperatures and at conditions of controlled relative humidity. For the study of the fracture behaviour of the paints, the essential work of fracture (EWF) method was used. Additional mechanical tests included stress relaxation and cyclic loading of samples. These tests supplied information on the visco-elastic properties of the paints. Coated panels were subjected to T-bend tests under controlled temperature and relative humidity conditions, and optical microscopy was employed to determine the area fraction of cracks induced in the coating. Finally, cross-sections of pigmented formulations were studied using scanning electron microscopy in order to determine the quality of dispersion of the pigment particles.
Chapter 5. Experimental results of paints based on binders with different adipic:phthalic acid concentrations

For the remainder of this thesis, the results obtained from the mechanical testing of the materials outlined in Chapter 3 will be presented. Here, the results from the mechanical and thermo-mechanical testing of formulations PE1H20, PE2H20 and PE3H20 are discussed. PE1H20 will serve as the control formulation based on a polyester binder with 16:42 relative content of adipic:phthalic acid by weight. PE2H20 and PE3H20 are based on polyester binders containing 12:46 and 24:34 adipic:phthalic acid respectively. Hence, PE2H20 has the lowest adipic acid content in its backbone, with the concentration of adipic acid increasing via PE1H20 to PE3H20. All three formulations were heat-cured with HMMM (PE:HMMM= 80:20 by weight).

5.1 Differential scanning calorimetry

In Figure 5.1 the DSC data obtained for the three formulations are shown. The resulting glass transition temperatures were found to be 36 °C for PE1H20 (the overall control formulation in this study), 46 °C for PE2H20 and 21 °C for PE3H20 (see also Table 5.1). Clearly, an increase in the adipic acid content results in a considerable decrease of the glass transition temperature. This was expected as the linear adipic acid is thought to act as a plasticiser for the coating by increasing chain flexibility.
Experimental results of paints based on binders with different adipic:phthalic acid concentrations

Figure 5.1. Heat flow vs temperature DSC plots for PE1H20 (a), PE2H20 (b) and PE3H20 (c). The glass transition temperatures of the formulations are noted on the plots.

Table 5.1. DSC results for formulations PE1H20, PE2H20 and PE3H20.

<table>
<thead>
<tr>
<th>Formulation</th>
<th>T_{g,midpoint} (DSC) [°C] (±2)</th>
<th>T_{g,onset} (DSC) [°C] (±2)</th>
<th>T_{g,end} (DSC) [°C] (±2)</th>
<th>T_{g,onset} - T_{g,end} (DSC) [°C] (±2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PE1H20</td>
<td>36</td>
<td>30</td>
<td>46</td>
<td>16</td>
</tr>
<tr>
<td>PE2H20</td>
<td>46</td>
<td>38</td>
<td>53</td>
<td>15</td>
</tr>
<tr>
<td>PE3H20</td>
<td>21</td>
<td>16</td>
<td>26</td>
<td>11</td>
</tr>
</tbody>
</table>

In the case of PE1H20 and PE2H20 a clear difference between the 1\textsuperscript{st} and 2\textsuperscript{nd} heat traces can be observed (see Figure 5.1 (a) and (b)). A steep drop in the heat flow with a clear local endothermic peak at temperatures near T_{g} is observed during the first heat of the samples. This drop is much less pronounced during the second heat and no endothermic peak is observed. This is attributed to enthalpy relaxation taking place as the paint is cooled from its cure temperature through T_{g} to room temperature. Generally for polymers, during storage of samples (assuming storage temperatures below T_{g}) the relaxation continues and its rate increases as the storage temperature approaches the glass transition temperature. This procedure is also known as physical ageing [132]. Even though a detailed study of physical ageing is outside the scope of this study, a qualitative discussion here is necessary in order to explain the observed differences between the DSC traces of the different formulations.

The endothermic peak in the heat flow observed in the 1\textsuperscript{st} heat DSC curves of aged samples corresponds to an enthalpy increase that seeks to balance the enthalpy relaxation during the ageing period. Because physical ageing is a reversible process its
Effects are completely eliminated on heating the sample above its glass transition temperature, hence the difference between the first and the second DSC heats. Qualitatively, the greater the difference between the first and second heat traces, the greater the enthalpy relaxation or the degree of physical ageing of the sample. Generally, samples that have had more time to relax, or that have been kept at temperatures closer to $T_g$ (resulting in higher relaxation rates) are expected to produce more pronounced peaks (e.g. see [133-135]). For a discussion on physical ageing more specifically relevant to organic coatings the reader is directed to the very comprehensive review paper by Perera [132].

For the purposes of this study the samples were kept at room temperature, which was found to range between approximately 20 and 26 °C throughout the year. In the case of PE3H20 the storage temperature was at or above the paint’s glass transition and hence no physical ageing phenomena were expected to occur. It was therefore not surprising that no enthalpy increase peak was observed during DSC testing of this sample.

On the other hand, it is a bit more difficult to explain the apparent greater enthalpy relaxation in the case of PE2H20 when compared to PE1H20. Even though no quantitative analysis was attempted, qualitatively this point is clearly supported by the difference in the shapes of 1st and 2nd heat curves of the two formulations. According to the above discussion it would seem that PE1H20 being stored at a temperature closer to its $T_g$ (36 °C) should present greater enthalpy relaxation and therefore a more pronounced difference between 1st and 2nd heat.

A possible explanation for the trend observed between the PE1 and the PE2-based paints could be linked to the difference in molecular packing between the two formulations. Van der Linde et al. [136] reported an increase in enthalpy relaxation rate when comparing between polyester powder coatings based on terephthalic (TPA) and iso-phthalic acid (IPA). This observation was attributed to a more dense molecular packing (i.e. less free volume) in the case of the TPA-based coating.

A similar argument could be drawn here for the comparison between PE1H20 and PE2H20. The more linear (lower phthalic acid content) PE1H20 will produce a more
dense molecular structure resulting in lower enthalpy relaxation rates when compared to the higher phthalic acid content PE2H20. Another explanation could be given from considering the molecular weights of PE1 and PE2, which are 4200 and 3400 g/mol respectively (see Table 3.2). Generally, a decrease in the enthalpy relaxation rate has been found with increasing molecular weight (see for example, [133] and [137]) again providing an explanation for the observed greater degree of physical ageing in the case of PE2H20.

5.2 Dynamic mechanical analysis

Representative plots of dynamic mechanical data from samples of PE1H20, PE2H20 and PE3H20 are presented in Figure 5.2. Clearly an increase in the phthalic acid content of the polyester binder results in a shift of both the storage modulus and the tanδ curves towards higher temperatures. The broadness of the glass transition region appears to be more or less the same for all three formulations as demonstrated by the tanδ data. Finally, the storage modulus in the rubbery region is approximately the same for all three formulations although somewhat lower in the case of PE2H20.

In Table 5.2, average values of the glass transition temperature, the rubbery modulus and the crosslink density (taken from equation (4.6)) are presented. The trend in the $T_g$ values is the same as observed from the DSC results, although $T_g$ as determined by DMA is in every case higher than the measured value from DSC. Indeed differences in the range of 10 – 30 °C are reported in the literature when the glass transition temperatures as measured by DSC and DMA are compared (see for example [16, 138]). The higher values obtained from DMA measurements are thought to be the result of the different criteria used for the determination of $T_g$ (mid-point of heat flow shift for DSC versus position of tanδ peak for DMA) as well as due to the different nature of the experiments to begin with (in DSC a very small sample is subjected to a heating rate whereas in DMA a much larger sample is subjected to a simultaneous thermal and mechanical loading).
5. Experimental results of paints based on binders with different adipic:phthalic acid concentrations

Despite the clear change in the glass transition temperature with varying adipic:phthalic acid ratio, there appears to be little difference between the systems’ network properties. The rubbery modulus and hence cross-link density are very similar (considering also the experimental error margins) for systems PE1H20 and PE3H20 and only slightly lower for PE2H20.

This small reduction in cross-link density for the high phthalic acid content system could perhaps be explained by a less close-packed molecular structure argument, as for the observed enthalpy relaxation discussed in Section 5.1. An alternative explanation could lie in a steric hindrance effect due to the increased number of benzene rings present in the high phthalic acid content PE2 binder. It can thus be proposed that the bulky phthalate monomers make it more difficult for nearby...
5. Experimental results of paints based on binders with different adipic:phthalic acid concentrations

hydroxyl groups on the polyester to react with the methoxymethyl groups of HMMM resulting in a lower cross-link density for formulation PE2H20. In any case the close values of cross-link density for the three systems were to be expected, as all three have the same cross-linker content and also the same number of functional groups per chain.

5.3 Tensile testing

The main results from tensile testing of formulations PE1H20, PE2H20 and PE3H20 are presented in this Section. In Figure 5.3, representative stress versus strain curves are shown at various testing temperatures. It is seen that temperature has a profound effect on the mechanical properties of the formulations as the material behaviour changes from brittle to rubbery within 30 °C. Furthermore, due to the relatively low glass transition temperatures of the paints, this 30 °C range is clearly within their expected service temperatures. This is of great interest from a practical point of view as it means that the same paint will have completely different mechanical properties at different times of the year or at different geographical locations.

The main tensile properties of the paints are shown in Figure 5.4, where the x-axes of the plots show the difference between the testing temperature and each formulation’s Tg. All three formulations were tested over a similar range of temperatures around their glass transition from about 40 °C below Tg to between 5 and 30 °C above Tg. The Young’s modulus changes as expected with temperature (see Figure 5.4 (a)), producing S-shaped curves very similar to the storage modulus curves obtained from DMA. Failure stress and yield stress both decrease with temperature. However, in the case of failure stress the rate of this decrease seems to show three distinct regions, see Figure 5.4 (c). At low temperatures, where the paints are in the glassy region, failure stress decreases slowly with temperature. This is followed by a much more rapid decrease in the visco-elastic region and finally the decrease rate is slowed down again as the material enters the equilibrium rubbery region. These distinct regions are not clearly observed in the case of yield stress, as the paints yielded only in the visco-elastic region. At low temperatures failure occurred before any yielding while at higher
temperatures no yielding could be observed as the rubbery stress versus strain curves were linear throughout the entire strain range.

Figure 5.3. Representative tensile stress versus strain curves at various temperatures around $T_g$ (from DSC) for formulations PE1H20 (a), PE2H20 (b) and PE3H20 (c).

Figure 5.4. Plots of Young’s modulus (a), strain at failure (b), stress at failure (c) and yield stress (d) versus the difference of testing temperature from $T_g$ (DSC) for formulations PE1H20, PE2H20 and PE3H20.
The failure strains (Figure 5.4 (b)) of the paints also showed behaviour typical for polymers tested around the glass transition. In the glassy region samples failed at low strains, generally below 2%. Then a dramatic increase is observed at temperatures between 10 and 5 °C below T_g. Maximum strains of about 50 to 60% were observed for all formulations when tested at around T_g to T_g+10°C the. When tests were carried out at even higher temperatures above T_g the failure strain was found to once again decrease (see PE1H20 data in Figure 5.4 (b)).

The effect of temperature (and time) on the failure strain of polymers has been extensively studied by Smith early on (see for example [139-141]) and the results presented in this study are in agreement with findings in his work. Of particular interest here is the observation that at least in terms of the strain to failure there exists an optimum operating temperature which is close to the T_g of the formulation.

Harwood and Payne [142] studied the behaviour of different rubbers with varying degrees of cross-linking at a wide range of temperatures and reported a correlation between the ability of the material to dissipate energy and its strain to failure. This maximum energy dissipation occurs at temperatures around the glass transition of the polymer and more specifically it can be thought to take place at the temperature where the damping factor (tanδ) reaches its maximum value.

From the data obtained for PE1H20 a clear maximum for the failure strain is observed at about 10 °C above T_g as measured by DSC, while a similar conclusion is drawn from the data for PE3H20. In both cases this temperature lies well below (14 °C and 13 °C respectively) the maximum tanδ temperature as measured by DMA, and in that sense it seems that the maximum in the failure strain occurs at a somewhat lower temperature than expected. Additionally, the maximum failure strain of PE2H20 is observed at even lower temperatures at 1°C below its glass transition temperature by DSC.

It should be noted here that two factors could artificially move the tanδ maximum to higher temperatures when comparing tensile with DMA data. First, the strain rate applied to the DMA samples was slightly higher than the initial strain rate applied to the tensile samples (0.004 to 0.008 s^-1 in the case of DMA versus 0.002 s^-1 for tensile
tests). Second, the tensile samples were tested under isothermal conditions whereas the DMA samples were subjected to a temperature ramp. However, both of these differences in experimental procedure are expected to have negligible effect on the measured properties.

In comparing between the three formulations it appears that they have fairly similar tensile properties despite the different chemical structures of their binders. The Young’s modulus plots of PE1H20 and PE3H20 are essentially identical while that of PE2H20 seems to be moved very slightly towards lower temperatures (Figure 5.4 (a)). In any case this shift along the temperature axis is well within the uncertainties associated with the measurement of $T_g$ and the testing temperature. The failure strains of all three formulations were also found to be very similar, with a maximum failure strain of about 50% to 60% in every case (Figure 5.4 (b)). When the tensile strength results are compared, generally PE3H20 showed the highest values and PE2H20 the lowest, even though some scatter in the data exists (Figure 5.4 (c)).

In terms of yield strength, in the temperature range investigated here, PE3H20 showed the highest values. Between PE1H20 and PE2H20 the former appears to have a greater yield strength at temperatures close to or greater than $T_g$, a trend that is reversed when the low temperature data are considered. To illustrate this point, Figure 5.4 (d) is re-plotted in Figure 5.5 where the y-axis is now in logarithmic scale.

For the apparent increase in yield strength with higher adipic acid concentrations, an explanation can be given by considering the molecular structures of the formulations on the basis of a free volume argument. The more linear (higher concentration of adipic acid) binder, PE3, will result in a material with less free volume than the low adipic acid content PE2, while PE1 is expected to fall between the other two formulations. The effect of free volume and molecular packing on the yield strength and generally on the mechanical properties of polymers has been discussed as early as 1968 in an extensive review paper by Boyer [143] and in [144-146]. Generally, denser molecular arrangements are expected to lead to a higher yield strength [145]. Therefore, the observed increase in yield strength with adipic acid content seems to be a result of an increase in molecular packing.
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Figure 5.5. Yield stress versus the difference of testing temperature from $T_g$ (DSC) for formulations PE1H20, PE2H20 and PE3H20, where the yield stress is plotted in logarithmic scale.

5.4 Essential work of fracture (EWF)

In Figure 5.6, typical load-displacement curves of double edge notched tensile (DENT) samples of formulations PE1H20, PE2H20 and PE3H20 are presented. Tests were performed near the respective $T_g$s (DSC) of the paints (at 21 °C in the case of PE3H20, 35 °C in the case of PE1H20 and 48 °C for PE2H20).

First, the question of the validity of the experimental data needs to be addressed. In the case of PE1H20 and PE2H20 a satisfactory degree of self-similarity is found. For PE3H20, however, this was not quite the case as can be seen for example from examination of the curves for ligament lengths of 11.6 and 11.3 mm (see Figure 5.6 (c)). For the preparation of DENT samples of PE3H20 two different films of this formulation were used. The load versus displacement curves obtained from the testing of samples of each film are plotted in Figure 5.7. In each of these cases the self-similarity of load versus displacement traces for different ligament lengths is evident. This would indicate a possible difference in the curing process of the two films that led to the observed difference in the load versus displacement traces of the DENT samples. Interestingly, when the data from the two films were analysed separately, very similar values for the essential work of fracture were obtained in both cases (12.6 and 13.1 kJ/m$^2$). Based on this finding it was decided that both sets of data would be considered valid and the essential work of fracture would be calculated from the linear regression of the total specific work of fracture of all samples.
5. Experimental results of paints based on binders with different adipic:phthalic acid concentrations

Figure 5.6. Load versus displacement curves for different ligament lengths (shown on the graphs in mm) of DENT samples of PE1H20 tested at 35 °C (a), PE2H20 tested at 48 °C (b) and PE3H20 tested at 21 °C (c).

By looking at Figure 5.8 (a), the specific work of fracture values appear to generally have a clear linear correlation with the ligament length, which is another important pre-requisite for the EWF method to be valid. Generally, $R^2$ values in excess of 0.98 are reported in the literature [59]. Here, the quality of the fit of the linear regression to the experimental data seems to be not as good, with $R^2$ ranging from 0.89 to 0.94. This is attributed to the quality of the samples (bubbles and micro-pinning due to evaporation of solvents and methanol during cure) and the errors arising from measuring the thickness of the samples as well as the ligament lengths. In Section 4.4.3 it was demanded that for data points to be included in the analysis, their distance from the linear regression line (residual), must be less than two standard errors. The ratios of the residuals over the standard error of the linear regression for each formulation are shown in Figure 5.8 (b)-(d). Clearly, in every case the residuals are contained with ±2 standard errors and thus all data shown were included in the analysis.
5. Experimental results of paints based on binders with different adipic:phthalic acid concentrations

Figure 5.7. Load versus displacement curves of DENT samples of PE3H20 cut from two different films of the paint. Clearly the curves are self-similar with ligament length in each case.

Figure 5.8. In (a) the specific work of fracture versus ligament length is shown for paints PE1H20, PE2H20 and PE3H20 where the linear regression lines are also plotted. In (b), (c) and (d) the ratios of the linear regression residuals over the standard error of the residuals are shown, for formulations PE1H20, PE2H20 and PE3H20 respectively.

When the results for the three formulations are compared, it is clearly seen that PE1H20 and PE2H20 returned very similar EWF values at about 5 kJ/m², while the essential work of fracture for PE3H20 was markedly higher at about 12 kJ/m² (see Figure 5.9 (a) and Table 5.3). Additionally, the slope of the regression lines, indicative of the magnitude of the inelastic part of the total work supplied for the fracture of the samples increases from 0.75 MPa in the case of PE1H20 to 1.32 MPa for PE2H20 and 1.86 MPa for PE3H20 (see Figure 5.9 (c) and Table 5.3). The above data suggest that an
5. Experimental results of paints based on binders with different adipic:phthalic acid concentrations

increase of the adipic acid content in the polyester backbone, results in an increase in the inelastic part of the total work supplied for the fracture of the coating and also in an increase in the essential work of fracture of the coating. This is further discussed in Section 5.5.

![Figure 5.9. Essential work of fracture (a) and $\beta_{w_{inel}}$ values (b) for formulations PE1H20-PE3H20.](image)

Table 5.3. Essential work and inelastic component of fracture of formulations PE1H20-PE3H20. All formulations tested at their respective glass transition temperatures.

<table>
<thead>
<tr>
<th>Formulation</th>
<th>$w_{e} \text{[kJ/m}^2\text{]}$</th>
<th>$\beta_{w_{inel}} \text{[MPa]}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PE1H20</td>
<td>$5.7 \pm 1.0$</td>
<td>$1.32 \pm 0.13$</td>
</tr>
<tr>
<td>PE2H20</td>
<td>$4.4 \pm 0.7$</td>
<td>$0.80 \pm 0.08$</td>
</tr>
<tr>
<td>PE3H20</td>
<td>$12.9 \pm 1.4$</td>
<td>$1.86 \pm 0.17$</td>
</tr>
</tbody>
</table>

5.5 Strain and recovery tests

A test to investigate the nature of the strain post-yield was performed, where samples of each formulation were deformed up to a strain of approximately 15% and were subsequently unloaded down to zero load at which point the residual strain was recorded. The samples were then removed from the clamps and kept in the environmental chamber for a period of two hours at which point their length was re-measured. In each case the temperature inside the chamber was maintained equal to the $T_g$ of the formulations. The resulting stress versus strain traces are shown in Figure 5.10.

In all cases the recovered strain upon unloading exceeded the yield strain of the sample. This practically means that, at $T_g$, the post-yield behaviour of the paints cannot be regarded as plastic but rather as visco-elastic, i.e. with time the samples are expected to recover at least part of their post-yield deformation. Indeed, when the
length of the samples was re-measured two hours after testing, no residual strain was seen. This is an important result from a practical point of view as it means that in the case of coated panels undergoing large deformations, the paint will tend to return to its original dimensions and thus retract from the panel surface potentially leading to cracks at a time after the initial panel-shaping process.

When a comparison between the three different formulations is made, it is seen that samples based on binders with adipic:phthalic acid ratio of 24:34 and 16:42 by weight (binders PE3 and PE1 respectively) show approximately the same amount of recovery upon unloading. This is seen both from the ratios of recoverable strain over the maximum strain, $\frac{\varepsilon_{el}}{\varepsilon_{max}}$, and from the fractions of elastic work over the total work supplied for the deformation, $\frac{W_{el}}{W_{tot}}$, of the systems (see Table 5.4). On the other hand, PE2H20 (Ad:Phth= 12:46) recovered a much greater part of the total applied strain and a bigger part of the total work supplied for deformation was stored elastically and was returned upon unloading.

Generally, the degree of elasticity (and therefore the tendency for recovery) of thermoset polymers is expected to correlate well with the density of their network of cross-links (see also Section 6.5 and discussion therein). In that sense it would be expected that all three formulations would show approximately the same extent of elastic recovery, since their cross-link densities were found to be similar. This is indeed the case for paints PE1H20 and PE3H20 (see Table 5.4), however the high phthalate content PE2H20 shows a much greater elastic component. This difference is even more pronounced considering that based on the somewhat lower cross-link density of this paint a smaller (not larger) elastic component would be expected. Nevertheless, this apparent greater elasticity of PE2H20 agrees also with the observation from EWF data for a smaller inelastic component of this formulation when compared to PE1H20 and PE3H20.

Even though the origins of this behaviour are not entirely clear, a possible explanation can be put forward by consideration of the composition of the macromolecules of each of the three binders used for the formulations considered here. At high adipic acid content the polyester molecules are long and flexible, favouring chain
Experimental results of paints based on binders with different adipic:phthalic acid concentrations

disentanglement when a tensile load is applied macroscopically on a sample of the material. On the other hand, at high concentrations of phthalate in the polyester macromolecules, chain mobility is expected to be reduced as a result of the bulky benzene groups present in phthalic acid. A bigger part of the total deformation will then come from the stretching of primary bonds along the polyester chains. Upon unloading the energy (strain) stored in the stretched bonds will be recovered as these bonds assume their original lengths.

The above mechanism appears to explain the observed greater tendency for recovery from post-yield strains for formulation PE2H20. Based on the same arguments it would be fair to expect that the strain recovery results of PE1H20 and PE3H20 would follow a similar trend. In practice this was not found to be the case, with the two formulations showing approximately the same amount of recoverable strain (note, however, that from EWF results the inelastic component of PE3H20 is indeed higher than that of PE1H20). The reasons for this discrepancy are not clear. The existence of a critical concentration of phthalate in the polyester, where the recovery changes from being governed mainly by cross-link density to being governed by the deformation mechanisms of polymer chains, can neither be ruled out nor proven by the data presented here.

![Figure 5.10. Stress vs strain traces of strain and recovery tests on formulations PE1H20, PE2H20 and PE3H20. Tests performed at the respective glass transition temperatures of the formulations, as measured by DSC.](image)
5. Experimental results of paints based on binders with different adipic:phthalic acid concentrations

Table 5.4. Yield strain, recovered strain, ratio of elastic strain at unloading over maximum strain and ratio of elastic work over work supplied to maximum deformation, for formulations based on binders with varying adipic acid: phthalic acid ratio.

<table>
<thead>
<tr>
<th>Formulation</th>
<th>Ad:Phth (wt)</th>
<th>Yield strain, %</th>
<th>Recovered strain ($\varepsilon_{el}$), %</th>
<th>$\varepsilon_{el}/\varepsilon_{max}$</th>
<th>$W_{el}/W_{tot}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PE1H20</td>
<td>16:42</td>
<td>1.6</td>
<td>3.8</td>
<td>0.26</td>
<td>0.10</td>
</tr>
<tr>
<td>PE2H20</td>
<td>12:46</td>
<td>2.0</td>
<td>6.1</td>
<td>0.41</td>
<td>0.27</td>
</tr>
<tr>
<td>PE3H20</td>
<td>24:34</td>
<td>1.4</td>
<td>4.2</td>
<td>0.28</td>
<td>0.11</td>
</tr>
</tbody>
</table>

5.6 Chapter summary

Paints based on polyester binders containing different ratios of adipic:phthalic acid and cross-linked with HMMM at an 80:20 PE:HMMM ratio by weight were examined and their mechanical and thermo-mechanical properties were reported. A rise in the glass transition temperature of the paints was seen, from both DSC and DMA results, with increasing phthalic acid content. On the other hand, the cross-link density of the cured formulations remained relatively unaffected. This was expected due to the curing conditions (amount of cross-linker, PMT and dwell time) being the same for all three paints.

From the analysis of data obtained from tensile testing, all three formulations showed similar values of Young’s modulus and failure strain, when results were compared at temperatures equally removed from the respective $T_g$ of each paint. Between $T_g$ and $T_g +10^\circ C$ a maximum (approximately 50 to 60 % strain) was seen in the failure strain versus temperature plots of all formulations. In terms of yield and tensile strength, PE3H20, the formulation with the highest adipic content, generally returned the highest values. An essential work of fracture approach was used to determine the dependence of toughness on the chemical structure of the paints. The high adipic acid content formulation (PE3H20) showed the highest values of essential work of fracture and was also the formulation with the greatest amount of energy consumed in inelastic deformation around the fracture zone.

Finally, strain and recovery tests were performed at the $T_g$ of the formulations, where samples were loaded to a strain of 15% and then unloaded at the same displacement rate. In every case, the recovered strain was higher than the measured yield strain which proves that post-yield deformation cannot be thought as plastic but rather as
5. Experimental results of paints based on binders with different adipic:phthalic acid concentrations

non-permanent inelastic. Of note is that for all formulations all strain was found to be recovered when the length of the samples was measured again approximately two hours after testing. Of the three paints, PE2H20 showed the fastest recovery. This was explained as a result of its high phthalic acid content favouring a mechanism of stretching of primary bonds instead of chain disentanglement.

In total, the change in the adipic:phthalic acid concentration is expected to affect the performance of painted panels mainly as a result of the observed change in $T_g$, since the mechanical properties of the free films were found to be similar. This is confirmed in Chapter 12 where it is seen that when panels of the three paints were tested in bending at their respective $T_g$s, they all suffered approximately the same amount of damage.
Chapter 6. Results for paints based on binder PE1 with varying content of HMMM

In this section the experimental results obtained from the testing of free films of formulations based on binder PE1 and cross-linked with HMMM are presented. Binder: crosslinker ratios of 95:5, 90:10, 80:20 and 70:30 by weight (paints PE1H5, PE1H10, PE1H20 and PE1H30 respectively) were used, and the effects of the cross-linker concentration on the mechanical properties of the paint were investigated.

6.1 Differential scanning calorimetry

Heat-flow versus temperature plots obtained from DSC are presented in Figure 6.1 for all four formulations. From the mid-point glass transition temperatures of the paints noted on each plot it can be seen that PE1H10, 20 and 30 share the same $T_g$ of about 35 °C while this value is lower in the case of PE1H5 at 28 °C. In Table 6.1 the onset and end temperatures of the glass transition are also given.

An increase in the glass transition temperature is observed when the cross-linker content is increased from a PE:HMMM ratio of 95:5 to a ratio of 90:10 by weight. Further increases in the cross-linker content have no effect on the glass transition temperature of the paint. The reason for this initial increase in $T_g$ followed by an apparent plateau with increasing cross-linker content is not clear, and this behaviour will be discussed further in Section 6.2 where the DMA results for these formulations are presented.
6. Results for paints based on binder PE1 with varying content of HMMM

Table 6.1. DSC results for formulations based on PE1 cross-linked with varying HMMM content.

<table>
<thead>
<tr>
<th>Formulation</th>
<th>$T_g$ midpoint (DSC) [°C] (±2)</th>
<th>$T_g$ onset (DSC) [°C] (±2)</th>
<th>$T_g$ end (DSC) [°C] (±2)</th>
<th>$T_g$ onset - $T_g$ end (DSC) [°C] (±2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PE1H5</td>
<td>28</td>
<td>23</td>
<td>31</td>
<td>8</td>
</tr>
<tr>
<td>PE1H10</td>
<td>35</td>
<td>30</td>
<td>42</td>
<td>12</td>
</tr>
<tr>
<td>PE1H20</td>
<td>36</td>
<td>30</td>
<td>46</td>
<td>16</td>
</tr>
<tr>
<td>PE1H30</td>
<td>35</td>
<td>28</td>
<td>45</td>
<td>18</td>
</tr>
</tbody>
</table>

Figure 6.1. Heat flow vs temperature DSC plots for PE1H5 (a), PE1H10 (b) PE1H20 (c) and PE1H30 (d). The glass transition temperatures of the formulations are noted on the plots.

On the other hand, a clear broadening of the glass transition region is observed with increasing melamine content. This is seen from the difference between onset and end temperatures of the glass transition shown in Table 6.1. Similar effects on the DSC trace from an increase in the concentration of the cross-linking agent have been reported, e.g. in [136, 147] where it is noted that the cause for such behaviour could either be an increase in cross-link density or the formation of a second network by the excess cross-linker.

The difference in shape of the 1$^{st}$ and 2$^{nd}$ heat traces observed in every case signifies that physical ageing took place during the storage period of the materials. Qualitatively speaking, based on the observed difference between the two heats for coatings PE1H10, PE1H20 and PE1H30, it appears that the degree of physical ageing decreases with the melamine content of the formulations. For the paint with the lowest HMMM content however, the difference between 1$^{st}$ and 2$^{nd}$ heat is small and clearly much less pronounced than for PE1H10 and PE1H20.
A decrease in enthalpy relaxation (physical ageing) with cross-link density is reported in the literature [136, 147]. This fits well with the observations for systems PE1H10-30. It would therefore be expected that PE1H5 would show evidence of even greater enthalpy relaxation, which is not the case as discussed above. The explanation for this could lie in the lower glass transition temperature (28 °C) of PE1H5. As mentioned in Section 5.1, generally an increase in the ageing temperature results in faster enthalpy relaxation and therefore a greater degree of physical ageing, as long as the ageing temperature is below \( T_g \). Here, with the storage temperature ranging from 20 to 26 °C this condition is satisfied. However, this range is very close to the formulation’s \( T_g \) and indeed well within the glass transition region (glass transition onset temperature is measured to be 23 °C for PE1H5).

Alves et al [147] point out that in cases where the ageing temperature is so close to \( T_g \) the rate of enthalpy relaxation is very fast. However, the enthalpy difference between the equilibrium state above \( T_g \) and that corresponding to the ageing temperature is small. Thus, for a given ageing time, as the temperature increases from the glassy region towards \( T_g \) there exists a temperature where the maximum degree of physical ageing is observed. The proximity of the storage temperature to the formulation’s \( T_g \) is thought to explain therefore the apparent smaller degree of physical ageing in the case of PE1H5.

### 6.2 Dynamic mechanical analysis

The traces of the storage modulus and \( \tan \delta \) versus temperature are presented in Figure 6.2. An increase in the glass transition temperature, as measured by the \( \tan \delta \) maximum, from 49 °C to 56 °C is observed when the binder: cross-linker ratio changes from 95:5 to 90:10. As the HMMM content is further increased to 80:20 the \( T_g \) reaches 60 °C while upon a further increase to 70:30 no further change in the glass transition temperature is observed. Similar results were obtained from DSC where all formulations were found to have approximately the same glass transition temperature at about 35 °C except for the low HMMM content formulation, PE1H5, with \( T_g \) = 28 °C.
A steady increase in the rubbery modulus was observed with melamine content, from 4.7 MPa for formulation PE1H5 to 19.8 MPa in the case of PE1H30 (see Table 6.2). From the theory of rubber elasticity this directly translates to an equal in magnitude increase in the measured cross-link density. There is also broadening of the tanδ peak, clearly seen when a comparison between the lowest and highest melamine content formulations is made (Figure 6.2 (b)). This observation fits well with the data obtained from DSC. Interestingly, in the case of PE1H30 the tanδ trace appears to be asymmetric with respect to its peak and clearly skewed to the right on the temperature axis. The effects of HMMM content on the shape of the glass transition are further discussed in Section 6.2.1.

![Figure 6.2](image-url)

Figure 6.2. Plots of storage modulus (a) and tanδ (b) versus temperature of representative samples of PE1H5, PE1H10, PE1H20 and PE1H30.

<table>
<thead>
<tr>
<th>Formulation</th>
<th>$T_g$ (DMA) [°C]</th>
<th>Max tanδ</th>
<th>Rubbery modulus [MPa]</th>
<th>Cross-link density [$10^{-3}$ mol/cm$^3$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PE1H5</td>
<td>49 ±2</td>
<td>2.10 ±0.09</td>
<td>4.7 ±1.6</td>
<td>0.44 ±0.20</td>
</tr>
<tr>
<td>PE1H10</td>
<td>56 ±1</td>
<td>1.68 ±0.01</td>
<td>6.0 ±0.2</td>
<td>0.64 ±0.02</td>
</tr>
<tr>
<td>PE1H20</td>
<td>60 ±2</td>
<td>0.94 ±0.02</td>
<td>8.7 ±0.6</td>
<td>0.93 ±0.06</td>
</tr>
<tr>
<td>PE1H30</td>
<td>59 ±2</td>
<td>0.54 ±0.03</td>
<td>19.8 ±1.4</td>
<td>2.08 ±0.16</td>
</tr>
</tbody>
</table>
In the case of PE1H10 a peak is observed on the tanδ trace between 35 and 40 °C. Such local maxima can signify the presence of a second phase inside the sample going through its T_g. However, here this is thought to be an artefact of the experimental process, and more specifically due to failure of the instrument to maintain a static to dynamic stress ratio higher than unity. This means that the sample is susceptible to buckling during the negative part of the strain cycle, which in turn will result in underestimation of the sample’s stiffness (seen in Figure 6.2 (a) as a steep drop in storage modulus of PE1H10 just before 40 °C).

To demonstrate the above point, the tanδ trace of formulation PE1H10 is plotted versus temperature in Figure 6.3, along with the ratio of static to dynamic stress. The horizontal line marks the point where the ratio of static to dynamic force is equal to one. Clearly, the dent in the tanδ plot occurs in the temperature range where the static to dynamic force ratio falls below unity.

![Figure 6.3. Plot of tanδ and of ratio of static to dynamic force versus temperature for PE1H10. The horizontal line signifies where the static to dynamic force ratio is equal to unity.](image)

### 6.2.1 Effect of HMMM content on cross-link density and on the nature of molecular network

When a comparison between the four formulations is made, the increase in cross-link density as measured from the value of the rubbery modulus has already been mentioned. At a micro-structural level, however, it is unclear whether only one network is present in the formulations or rather the measured properties reflect the influence of two separate networks, one of polyester cross-linked with melamine and one of self-cross-linked HMMM. The following discussion aims at shedding some light on the nature of the network at a micro-structural level.
Already since the 1950’s (see [24] and references therein) it was widely observed that the introduction of chemical cross-links resulted in an increase of the glass transition temperature of polymers, and also that there generally exists a linear relationship between \( T_g \) and cross-link density in thermoset systems. Since then, a positive correlation between cross-link density and \( T_g \) has been reported in numerous articles and for a wide variety of polymer systems [148-152]. In this light, an increase in \( T_g \) with cross-link density would be expected for the formulations studied here as well.

However, this does not appear to be the case. From DSC data the glass transition temperature is seen to reach a plateau for the three highest HMMM content formulations (see Section 6.1), and from DMA data there is no change in the glass transition temperature between formulations PE1H20 and PE1H30. Cook and Delatycki [149] reported a maximum in the glass transition temperature with cross-linker concentration which they attributed to an increase in the length of the ‘cross-linking bridges’ in the presence of excess cross-linker and to the possibility of the formation of a second phase (copolymer effect). Shefer and Gottlieb [150] also reported a maximum in \( T_g \) with cross-linker concentration, suggesting that in the presence of excess cross-linker unreacted chain ends will have a diluent effect in the network thereby increasing the free volume and subsequently decreasing \( T_g \). In both cases the maximum in \( T_g \) appeared at a stoichiometric ratio of resin:cross-linker, \( r_S = 1 \), i.e. when there is just enough cross-linker for the full development of a network of cross-links. It is also noted that this maximum in \( T_g \) coincided with a maximum in the cross-link density for \( r_S = 1 \). It is necessary therefore to consider the stoichiometry of the formulations studied here, in order to obtain a better understanding of the results presented.

The required amount of melamine to achieve a fully cross-linked PE1 network (stoichiometric ratio equal to unity) was calculated at 94:6 PE1:HMMM by weight (see Table 3.3). This calculation was based on functionalities of 3.6 for the resin and 5 for the hardener, taking into account their respective molecular weights. It follows that coating PE1H5 contains slightly less than the required amount of cross-linker to form a fully developed network, PE1H10 has a small excess of cross-linker but is relatively close to a stoichiometric ratio of \( r_S = 1 \), and PE1H20 and PE1H30 contain a significant
Results for paints based on binder PE1 with varying content of HMMM

excess of cross-linker. For the stoichiometric concentration of HMMM (PE1:HMMM = 94:6) the theoretical cross-link density of a perfect polyester-HMMM network was calculated as 0.9 x10^{-3} mol/cm^3 according to equation (2.3) (for a discussion on the assumptions made for the derivation of equation (2.3) see Section 2.1.2). The calculated value of cross-link density is shown in Figure 6.4 along with the experimentally determined values for the PE1-based formulations.

Two points are worth noting when considering the evidence presented thus far. First, the increase in the measured cross-link density is continuous with increasing HMMM content, and this increase is not accompanied by a similar increase in T_g (see Figure 6.4 and Tables 6.1 and 6.2). Second, the measured cross-link density is lower than the calculated value for formulations PE1H5 and PE1H10, approximately equal to the calculated value for PE1H20 and much larger than the calculated value for PE1H30.

Regarding the first point, based on the discussions above, the formulations would be expected to show a maximum in both T_g and cross-link density at a ratio of binder to cross-linker between 95:5 and 90:10, which clearly is not the case. Safranski and Gall [153] and Ortega et al. [154] investigated the properties of some (meth)acrylate networks and reported an increase in cross-link density with cross-linker content accompanied by a decrease in T_g. This was attributed to the formation of a second network (of the cross-linker) that on one hand increased the overall cross-link density of the material and on the other decreased the overall glass transition temperature through a copolymer effect due to its low T_g. Similar results had also been presented earlier in [155]. Therefore, it can be argued that the increase in the measured cross-link density at HMMM concentrations higher than stoichiometrically required, could be explained as a result of the formation of a second network of self condensed HMMM. However, the speed of the curing process which was used in the present study could mean that, at the stoichiometric ratio, there is insufficient time for cross-linking reactions to proceed to completion. Thus, the continued increase in cross-link density with HMMM content at stoichiometric ratios higher than unity could also be explained as the result of more HMMM molecules being available to react in the limited amount of time of cure.
Regarding the second point, a comment is due on the comparison between the measured and the calculated values of the cross-link density. In theory, the value calculated from equation (2.3) should correspond to the maximum cross-link density of a perfect PE1-HMMM network, at a HMMM concentration of 94:6. However, formulations PE1H5 and PE1H10 have cross-link densities much lower than the calculated value, while the measured value was similar to the calculated when a significant excess of HMMM was present (PE1H20). This could be explained again as a result of the limited time available for cure, i.e. it is possible that the dwell time was insufficient for the formation of a perfect network of polyester and HMMM when the stoichiometric ratio was close to unity. Of interest, however, is the comparison between the calculated and the measured value of cross-link density in the case of PE1H30. In this case, the experimentally observed cross-link density is much higher than the prediction according to equation (2.3). As equation (2.3) assumes that a perfect network of the reactants is formed, it follows that the calculated value presents an upper limit for cross-link density. Therefore, the higher measured value for PE1H30 cannot be explained unless the formation of a second network of self-condensed HMMM is considered.

In the literature, the development of a second network of HMMM, when an excess of the latter is present in the paint formulation, is very well documented (see for example [91, 101-103, 156, 157]). Of particular interest are studies that have used thermomechanical methods to demonstrate the presence of this second network. Gamage et al. [101] reported that the $T_g$ measured by DSC reached a maximum and then dropped to a plateau with increasing HMMM content, whereas DMA showed that $\tan \delta$ became broader and its magnitude decreased with increasing melamine content until two low peaks could be clearly observed. These two distinct peaks were attributed to the presence of two different networks, one of melamine co-condensed with polyester and one of self-condensed melamine. It is noteworthy that the two separate glass transitions were only distinguishable from the DMA data, whereas DSC only detected one broad transition.
6. Results for paints based on binder PE1 with varying content of HMMM

Figure 6.4. Cross-link density for the four formulations with varying HMMM content. The horizontal line represents the calculated cross-link density for a stoichiometric ratio, $r_s = 1$ (PE1:HMMM = 94:6).

For the materials studied here, a broadening of tanδ was observed with increasing HMMM content. Although this could be attributed to the presence of inhomogeneities in the material (e.g. a second phase of self-condensed HMMM), it could also be a direct result of the increasing cross-link density, as shown by a number of studies focusing on both mechanical and dielectric relaxation [158-162]. Generally, the underlying mechanisms responsible for this broadening effect are not entirely understood (see discussions in [158-162]), however, explanations have been put forward that correlate the increase in the width of the relaxation to an increasing level of inhomogeneity in the degree of constraint posed to chain segments from the junction points. Simply put, the motion of segments near junction points will be highly constrained while the motion of segments removed from the junction points (for e.g. segments in the middle of a chain between two junction points) will be relatively unaffected by the cross-linking [160]. As the cross-linking increases, a distribution of constraint level along the chains is introduced, resulting in the observed broadening of the relaxation.

With respect to the rubbery modulus, Gamage et al. [101] reported a clear increase when excess HMMM was used (i.e. $r_s > 1$), which they attributed to the additional cross-linking taking place between the HMMM molecules. These results are clearly very similar to those shown in the present study, and are related to the hypothesis presented earlier, that the cross-link density of PE1H30 would not have been possible unless a second network of self-condensed HMMM had formed. A potential problem in the above argument lies in the measurement of cross-link density from the rubbery
modulus value according to equations (2.36) and (4.6). As discussed in Section 2.2.2.1, equation (2.36) is derived under the assumption that the chain lengths of the polymer follow a Gaussian distribution. Roland [162] argues that such an assumption cannot be considered valid at high cross-link densities and that in such a case the portion of short network chains take a disproportionately large part of the applied stress. The end result of this deviation from Gaussian behaviour is the overestimation of cross-link density as measured from the rubbery modulus [162].

In light of the above discussions, the DMA data collected in the present study provide some evidence for the existence of a separate HMMM network in the paints, but generally this evidence is not conclusive. As discussed, the broadening of the tanδ could serve as an indication but certainly not as definite proof of the formation of a second network of self-condensed HMMM. The observation of a distinct second peak on the tanδ traces would provide more direct evidence of a second network, however, in every case only a single tanδ maximum was found. To that extent, the asymmetry around the tanδ peak of PE1H30 could suggest that a second unresolved maximum exists to the right of the observed $T_g$. Finally, the presence of self-condensed HMMM could be inferred by the cross-link density measured for formulation PE1H30, which could not be justified by considering a sole polyester-melamine network. However, it cannot not be ruled out that this high value could be an artefact of the measurement method.

**6.3 Tensile testing**

Characteristic stress versus strain curves of formulations PE1H5-PE1H30 are shown in Figure 6.5. The typical behaviour for polymers is observed for all formulations, with the tensile behaviour changing dramatically in the range from about 20 °C below $T_g$ to 5 °C above $T_g$. In comparing between the four formulations, the most striking result appears to be the significant decrease in failure strain with increasing HMMM content.

A summary of the tensile properties of paints with varying melamine content is presented in Figure 6.6. The plots of Young’s modulus versus temperature difference from $T_g$ (Figure 6.6 (a)) show the typical transition from glassy to visco-elastic and
rubbery behaviour that is to be expected from polymeric materials. The breadth of this transition increases with increasing HM MMM content, a finding that fits very well with the DMA data in Section 6.2.

Figure 6.5. Representative tensile stress versus strain curves at various temperatures around \( T_g \) for formulations PE1H5 (a), PE1H10 (b), PE1H20 (c) and PE1H30 (d).

Figure 6.6. Plots of Young’s modulus (a), strain at failure (b), stress at failure (c) and yield stress (d) versus the difference of testing temperature from \( T_g \) (DSC) for formulations PE1H5, PE1H10, PE1H20 and PE1H30.
The failure strain (Figure 6.6 (b)) also follows behaviour typical of polymers, with a sudden and significant increase at temperatures just below $T_g$, a subsequent maximum between approximately 5 and 10 °C above $T_g$, and finally decreasing values at higher temperatures. In the glassy region all four formulations broke at more or less the same strain. At higher temperatures, however, a clear negative correlation between HMMM content and failure strain exists.

The decrease in failure strain with cross-link density was first observed for elastomers and is discussed in a variety of publications [140, 163-166]. These studies found the maximum extensibility of a polymer chain to be in direct proportion to the length (or rather to the number of covalent bonds) between two cross-linking junction points. The ultimate properties of highly cross-linked glassy polymers have also been studied and a similar decrease in failure strain with cross-link density was found [153, 154, 167].

Recently, molecular dynamics have been employed to study the effect of cross-link density on the failure of plastics [168]. The failure of systems of higher cross-link density was found to involve an increased number of chain scissions, and at the same time the contribution of other energy dissipating mechanisms such as chain disentanglement and the growth of micro-voids (both important for thermoplastics) was suppressed by the permanent network of cross-links. Although, an investigation into the exact micro-structural causes of the dependence of failure strain on cross-link density was beyond the scope of this study, it is clear that the data presented for systems PE1H5 to PE1H30 fit very well with published results in the literature.

Failure stress decreases with temperature for all formulations, although a change in the slope of the data is observed, with the drop being more gradual at temperatures above $T_g$ (Figure 6.6 (c)). When a comparison between the systems is attempted a dependence of failure stress on cross-link density is observed, more prominently when the systems with the minimum and maximum HMMM content are examined. Clearly, the failure stress of PE1H30 is greater than that of PE1H5 throughout the entire temperature range. On the other hand, the failure stress of PE1H30 is generally higher than the failure stresses of PE1H10 and PE1H20 (although the difference in the values
now is less pronounced) for testing temperatures up to $T_g$ while at higher temperatures no significant trend is observed with HMMM content.

Similar points can be made when looking at the plot of yield stress versus temperature (Figure 6.6 (d)). The yield stress of the formulation with the highest melamine content (and cross-link density) is significantly higher than that of the low cross-link density coating, while the values of two intermediate formulations fall in the middle of the two extremes with no clear trend between them.

The literature on the effect of cross-link density on the failure strength of polymers appears to be varied. Taylor and Darin [166] as well as Bueche [169] reported that the engineering tensile strength of GRS-elastomers showed a clear maximum with cross-link density. On re-analyzing the data by Taylor and Darin, Smith and Chu [165] noted that the true tensile strength varied inversely with cross-link density. Epstein and Smith [163] expressed doubts on the existence of a relationship between cross-link density and tensile strength as they found strength to be highly dependent on viscoelastic parameters. A similar result was proposed from examination of original data in [165]. More recently [154], the study of highly cross-linked (meth)acrylate systems showed that generally the tensile strength first decreased at low values of cross-link density and then increased with cross-link density at higher values.

In terms of the yield stress, generally a positive correlation with cross-link density is expected by a simple consideration of the dependence of free volume on cross-link density [151] and the fact that yield strength increases with decreasing free volume [143, 145]. This argument fits well with the results shown in the present Chapter. Deviations from this trend have been reported in the literature, when various epoxy systems were studied inside the glassy region. Levita et al. [170] found yield strength to be independent of cross-link density, while in [171, 172] it was shown to decrease as the network density increased. Mayr et al. [173] reported an increase in yield strength with cross-link density and argued that any different trends should be attributed each time to the specific network characteristics and chemistry of the system at hand. Indeed, Georjon and Galy [171] found that due to the specific nature of the epoxy
network they studied, an increase in cross-link density resulted in higher values of free volume as well, and as a consequence in lower yield strength.

6.4 Essential work of fracture (EWF)

The load-displacement traces of DENT samples of PE1H5, PE1H10, PE1H20 and PE1H30 tested at the respective glass transition temperatures of the formulations are shown in Figure 6.7. Note that the scales on the axes of the plots are different in order to maintain clarity of the experimental data in each case. To demonstrate the markedly different behaviour of the four formulations, the traces at a ligament length of approximately 10 mm are plotted in a single graph in Figure 6.8.

Regarding the self similarity of the traces, an obvious departure from the rule is found in the case of PE1H5 (compare for example the trace for ligament length 11.54 with that for 11.31). However, again (see also Section 5.4) it was possible to split the data into two groups (Figure 6.9), this time according to the date of testing, with samples of l= 4.80, 8.81 and 11.31 mm having been tested a few days after the rest of the samples. The above three samples were also prepared from a different film of the paint compared to the rest.

Differences in the load-displacement traces of DENT samples as a result of coming from different films have already been highlighted in Section 5.4. Regarding the date of testing of the samples, this should not make a difference in the results since the tests are in every case performed under controlled conditions of temperature and humidity inside a chamber. A change in the storage conditions is possible, even though the equilibration time of at least ten minutes inside the testing chamber before testing should alleviate any such differences. In that sense, it seems more likely that the observed two distinct groups of data are a result of the different films used in each case. Since no good reasons for discarding one group or the other were found, both sets of data were used in the analysis that follows.
6. Results for paints based on binder PE1 with varying content of HMMM

Figure 6.7. Load vs displacement curves of DENT samples of PE1H5 tested at 28 °C (a) and PE1H10 (b), PE1H20 (c) and PE1H30 tested at 35 °C (d). The ligament lengths noted on figures are in mm. Note that for clarity the axes are not of the same scale.

Figure 6.8. Load- displacement traces of samples with varying HMMM content tested at their respective $T_g$s and at ligament lengths of approximately 10 mm.
Results for paints based on binder PE1 with varying content of HMMM

Figure 6.9. Load versus displacement curves of DENT samples of PE1H5. Graph (b) shows test results of samples cut from a different panel and tested three days after traces in graph (a) were obtained. Clearly the traces are self-similar with respect to ligament length in each case.

In Figure 6.10 (a) the specific work of fracture at $T_g$ of all formulations is plotted against ligament length together with the regression lines used in determining the essential work of fracture ($w_e$) and the inelastic component of the total work required for tearing the samples ($\beta w_{inel}$). The $R^2$ values are also given on the graph. Clearly, the quality of the linear regression fit for three out of four formulations is far from excellent. It was decided to proceed with the analysis of the results, however, on the basis that any scatter in the data should be taken into account by consideration of the relevant standard error. The ratio of the residuals over the standard error of the linear regression is shown for paint systems PE1H5, PE1H10 and PE1H30 in Figure 6.10 (b)-(d), while the respective plot for PE1H20 has already been shown in Figure 5.8 (b). In each case the residuals were within two standard errors from the regression line.

In Figure 6.11 (a), a clear dependence of $w_e$ on HMMM content (and therefore cross-link density) is shown, see also Table 6.3. On the other hand from Figure 6.11 (b) and the values in Table 6.3, no obvious trend is observed in the dependence of the inelastic component of the total work on wt% HMMM. On the effect of cross-link density on the toughness of thermosets the literature has focused in the past on glassy polymers or rather on polymers that are inside the glassy region at the test temperature. Bos and Nusselder [174] studied the fracture behaviour of model triisocyanate-poly(propylene glycol) networks and found the toughness to be inversely related to the cross-link density of the resulting networks. Similar results were also reported in [172] and [170]
for epoxy systems, although in the latter case an effect of the crack-tip radius on the correlation between cross-link density and toughness was observed.

Figure 6.10. In (a) the specific work of fracture versus ligament length is shown for paints PE1H5, PE1H10, PE1H20 and PE1H30 where the linear regression lines are also plotted. In (b), (c), and (d) the ratios of the linear regression residuals over the standard error of the residuals are shown, for formulations PE1H5, PE1H10, and PE1H30 respectively.

Figure 6.11. Essential work of fracture (a) and $\beta_{w\text{inel}}$ values (b) for formulations PE1H5-PE1H30.

Table 6.3. Essential work and inelastic component of fracture of formulations PE1H5-PE1H30. All formulations tested at their respective glass transition temperatures.

<table>
<thead>
<tr>
<th>Formulation</th>
<th>$w_e$ [kJ/m$^2$]</th>
<th>$\beta_{w\text{inel}}$ [MPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PE1H5</td>
<td>19.4 ±1.4</td>
<td>0.82 ±0.18</td>
</tr>
<tr>
<td>PE1H10</td>
<td>13.2 ±1.9</td>
<td>0.89 ±0.22</td>
</tr>
<tr>
<td>PE1H20</td>
<td>5.7 ±1.0</td>
<td>1.32 ±0.13</td>
</tr>
<tr>
<td>PE1H30</td>
<td>5.3 ±1.0</td>
<td>0.76 ±0.09</td>
</tr>
</tbody>
</table>
According to molecular dynamics simulations presented in [168], the embrittlement of a glassy polymer in the presence of chemical cross-links can be attributed to a change in the failure mechanism that favours chain scissions instead of a more energy consuming chain uncoiling process. Indeed, Sambasivam et al. [175] experimentally observed an increase in chain scissions with cross-link density for photopolymerised polystyrene and PMMA. They reported however an initial increase in fracture toughness at low cross-link densities that was followed by a decrease at higher degrees of cross-linking. It is possible that such a maximum is not observed in the present study simply because HMMM was not used at low enough concentrations and therefore the lowest cross-link density was still higher than the maximum fracture toughness point.

On the other hand, studies correlating the cross-link density and fracture toughness of ductile or visco-elastic materials by use of the EWF approach have been limited. Nevertheless, the evidence presented in the literature (see [176, 177]) supports the findings of this study, i.e. a decrease in $w_e$ is observed with increasing cross-link density. Regarding the correlation between cross-link density and the inelastic part of the total work supplied for fracture, Fayolle and Verdu [176] reported a decrease in $\beta w_{inel}$ with degree of cross-linking. Here, although the formulation with the highest cross-link density (PE1H30) has the lowest value of $\beta w_{inel}$, for the rest of the formulations there is no clear correlation, with PE1H5 and PE1H10 having similar inelastic components and PE1H20 showing the highest value amongst the four paints.

### 6.4.1 Essential work of fracture (EWF)- Effect of temperature

To investigate the effect of temperature on the fracture properties of the paints, formulations PE1H5 and PE1H10 were tested at temperatures 10 and 5 °C below $T_g$ and at 10 °C above $T_g$. PE1H30 was also tested at $T_g$+10 °C and $T_g$-5 °C. Attempts to test PE1H30 at the lowest temperature ($T_g$-10 °C) were also made, but the samples failed in a brittle manner and therefore the EWF approach was not applicable. The load vs displacement curves from these tests can be found in Figures 6.12- 6.14.
6. Results for paints based on binder PE1 with varying content of HMMM

Figure 6.12. Load vs displacement curves for PE1H5 (a) and PE1H10 (b) tested at 10 °C below $T_g$ (at 18 and 25 °C respectively). Note that for clarity the x-axes are not of the same scale.

Figure 6.13. Load vs displacement curves for PE1H5 (a), PE1H10 (b), and PE1H30 (c) tested at 5 °C below $T_g$ (at 23 °C for PE1H5 and 30 °C for PE1H10 and PE1H30).
6. Results for paints based on binder PE1 with varying content of HMMM

Figure 6.14. Load vs displacement curves for PE1H5 (a) PE1H10 (b) and PE1H30 (c), tested at 10 °C above $T_g$ (at 38 °C for PE1H5 and 45 °C for PE1H10 and PE1H30).

Regarding the quality of the collected data, the load vs displacement curves of the formulations at each temperature show a satisfactory degree of self-similarity (see Figures 6.12-6.14). Again some scatter in the data does exist which can largely be attributed to the use of samples cut from different films of the paint (see Figure 6.15). Generally, the specific work of fracture increases linearly with ligament length (Figure 6.16). The $R^2$ values of the fit of the linear regression to the experimental data can be found on the relevant graphs. To preserve the continuity of text here, the ratios of the residuals over the standard errors of the linear regression for each paint system and temperature are given in the Appendix. In every case the residuals were found to be less than two standard errors away from the regression line.

The quality of the linear regression is the worst for samples of PE1H10 tested at $T_g+10$ °C (45 °C), as seen by comparison of the $R^2$ values of the different sets of data. Due to constraints of time and material availability it was not possible to test more samples and potentially improve the quality of the data. The low correlation between ligament length and specific work of fracture in this case is brought to the attention of the
reader, however it will not be considered to signify a more fundamental inapplicability of the EWF method for the particular formulation and testing temperature. Instead, the low $R^2$ value is thought to be a result of the small number of samples tested, and of the difficulties associated with the testing of the paint films used in this study with the EWF method.

In Figure 6.17 (a) the essential work of fracture of formulations PE1H5, PE1H10 and PE1H30 is plotted versus temperature. For the paints with 95:5 and 90:10 PE:HMMM ratio by weight a clear maximum is observed at temperatures between 5 °C below $T_g$ and $T_g$. At both lower and higher temperatures the essential work of fracture decreases. In the case of PE1H30 a clear decrease in EWF is observed at the temperature above $T_g$, but the presence of a maximum at $T_g$ cannot be conclusively supported due to lack of data at more temperatures below the glass transition. Also, as shown in Figure 6.17 (b) the inelastic component of the work supplied for fracture of the paints ($\beta w_{\text{inel}}$) decreases with temperature in every case (with the exception of PE1H10 between temperatures $T_g - 10 °C$ and $T_g - 5 °C$). The values of the essential work of fracture along with the inelastic components of the work of fracture are also given in Table 6.4.

Figure 6.15. Load vs displacement curves for PE1H5 tested at 10 °C below $T_g$ where the two graphs (a) and (b) correspond to samples cut from two different films of the paint.
6. Results for paints based on binder PE1 with varying content of HMMM

Figure 6.16. Specific work of fracture vs ligament length for formulations PE1H5, PE1H10 and PE1H30 at test temperatures 10 °C below \( T_g \) (a), 5 °C below \( T_g \) (b) and 10 °C above \( T_g \) (c). Note that for clarity the y-axes are not of the same scale.

Figure 6.17. Essential work of fracture (a) and inelastic component of the work of fracture (b) vs temperature difference from \( T_g \) for formulations PE1H5, PE1H10 and PE1H30.

Table 6.4. Essential work and inelastic component of fracture of formulations PE1H5-PE1H30 tested at \( T_g -10 \) °C, \( T_g -5 \) °C and \( T_g +10 \) °C.

<table>
<thead>
<tr>
<th>Formulation</th>
<th>( T_g -10 ) °C</th>
<th>( T_g -5 ) °C</th>
<th>( T_g +10 ) °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( w_e ) [kJ/m²]</td>
<td>( \delta w_{inel} ) [MPa]</td>
<td>( w_e ) [kJ/m²]</td>
</tr>
<tr>
<td>PE1H5</td>
<td>-2.6 ±2.8</td>
<td>3.74 ±0.32</td>
<td>21.7 ±2.8</td>
</tr>
<tr>
<td>PE1H10</td>
<td>1.1 ±2.0</td>
<td>2.62 ±0.23</td>
<td>7.4 ±3.5</td>
</tr>
<tr>
<td>PE1H30</td>
<td>4.2 ±1.3</td>
<td>0.55 ±0.38</td>
<td>1.6 ±0.2</td>
</tr>
</tbody>
</table>
It is noted that the analysis of the data of PE1H5 at $T_g-10^\circ C$ resulted in a negative value for $w_e$. This is not considered to have any physical significance and the negative value is treated here as simply an indication of the low, close to zero essential work of fracture required to break the paint towards the glassy region. Of interest is the fact that any difference between the $w_e$ values of the different formulations is more pronounced when these are compared at $T_g$. At higher temperatures $w_e$ was more or less the same for all paints and it looks like a similar trend holds at temperatures below $T_g$ even though the negative value in the case of PE1H5 and the lack of data for PE1H30 obscure this argument.

On the dependence of the essential work of fracture on test temperature, the available literature is not extensive and the reported results are often contradictory. Hashemi [121] reports that for poly(butylene terephthalate) (PBT) films the essential work of fracture remained constant up to a certain temperature after which it decreased. No mention of the $T_g$ of the thermoplastic was given. On the other hand, on investigating the fracture properties of semi-crystalline poly(ethylene terephthalate) films (PET) Arkhireyeva and Hashemi [123] reported that the EWF was constant up to the polymer’s glass transition temperature, at which point it increased to a maximum value at about $T_g+25^\circ C$ only to decrease again at higher temperatures. The same group [124] in a later article on the fracture behaviour of an amorphous PET reported a constant value of EWF up to $T_g$ while disputing the validity of the EWF method at higher temperatures (although the grounds for this were not clearly given). Similarly, Chen and Wu [177] showed the essential work of fracture of thermoset polyurethanes to be independent of the test temperature for temperatures below $T_g$. Finally, a maximum in $w_e$ at $T_g$ is reported by Ferrer-Balas et al. in [178] for a polypropylene homopolymer.

A better agreement between different publications is obtained when the effects of temperature on $\beta w_{inel}$ are considered. In [123, 124, 178] the inelastic component of the fracture work is shown to increase up to a maximum value at $T_g$ and then decrease at higher temperatures. This is not the case in the present study where $\beta w_{inel}$ generally decreases constantly with temperature, in the range between $T_g-10^\circ C$ and $T_g+10^\circ C$. 

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Providing a molecular explanation for the observed dependence of the fracture properties of the paints on temperature is not easy, especially since the evidence in the literature is scarce and to some extent contradictory. The lack of essential work of fracture studies on cross-linked polymers also makes it difficult to compare findings presented here to results published elsewhere.

### 6.5 Strain and recovery tests

The ability of the formulations to recover from large deformations and its correlation to the HMMM content (and therefore cross-link density) were investigated. Samples were deformed to a strain of approximately 15% and then unloaded as described in Section 4.5. All samples were tested at their glass transition temperatures and the full stress vs strain traces obtained can be found in Figure 6.18.

Clearly, the strain recovered upon unloading increases with the cross-link density of the formulations. Of note is also that in every case the recovered strain is higher than the strain at yield point. This means that the even though, based on the shape of the stress vs strain curves, a yield point can be determined, this does not fit well with the traditional definition of yield as the onset of plastic deformation. Further to that, the length of the samples was measured again after they were left to recover at the test temperature and relative humidity for a further two hours. It was found that all samples invariably returned to their original length. These findings agree well with what was reported in Chapter 5, where the properties of formulations PE1H20, PE2H20 and PE3H20 were examined. At this point it can be stated that the post-yield behaviour of the coating systems studied here cannot be considered as plastic. Rather the terms visco-elastic or inelastic are thought to better describe the stress versus strain behaviour of the paints beyond the yield point.

In Table 6.5 the ratio of the recovered (elastic) strain upon unloading over the maximum strain, $\varepsilon_{el}/\varepsilon_{max}$, is given. A clear increase is observed with cross-link density, meaning that the greater the extent of the network of cross-links, the higher is the fraction of strain that is recovered. Similarly, when the ratio of the elastic over the total supplied work, $W_{el}/W_{tot}$, is considered, an increase is observed with cross-link density.
density. Thus, for higher cross-link density the readily recoverable ‘elastically stored’ energy increases.

Indeed, it is to be expected for energy to be stored in the elastically effective cross-links of the polymer network, and for this energy to increase as the number of cross-links increases. Roland [179, 180] presented data showing an increase in the recovered strain upon unloading with cross-link density for styrene-butadiene rubbers. Similarly, a negative correlation between time required for full recovery and cross-link density is reported in [181], while in [182] an increase in recoverable energy is reported with degree of cross-linking.

![Stress vs strain traces of strain and recovery tests on formulations PE1H5, PE1H10, PE1H20 and PE1H30.](image)

**Figure 6.18.** Stress vs strain traces of strain and recovery tests on formulations PE1H5, PE1H10, PE1H20 and PE1H30.

<table>
<thead>
<tr>
<th>Formulation</th>
<th>Yield strain, %</th>
<th>Recovered strain ($\varepsilon_{el}$), %</th>
<th>$\varepsilon_{el}/\varepsilon_{max}$</th>
<th>$W_{el}/W_{tot}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PE1H5</td>
<td>0.6</td>
<td>2.8</td>
<td>0.18</td>
<td>0.06</td>
</tr>
<tr>
<td>PE1H10</td>
<td>1.1</td>
<td>3.6</td>
<td>0.23</td>
<td>0.09</td>
</tr>
<tr>
<td>PE1H20</td>
<td>1.6</td>
<td>3.8</td>
<td>0.26</td>
<td>0.10</td>
</tr>
<tr>
<td>PE1H30</td>
<td>1.9</td>
<td>4.7</td>
<td>0.32</td>
<td>0.14</td>
</tr>
</tbody>
</table>

**6.6 Chapter summary**

The mechanical and thermo-mechanical properties of paint formulations containing different ratios of PE1:HMMM were examined. With increasing HMMM content the glass transition of the paints was found to consistently broaden although its position – after an initial increase– did not change significantly. From DMA data a clear increase
in cross-link density was observed with higher HMMM content. Based on the cross-link density measured for formulation PE1H30 an argument for the existence of two separate networks (one of co-condensed HMMM with polyester and one of self-condensed HMMM) was made, even though the evidence cannot be considered conclusive.

In terms of tensile properties, the most striking difference between the formulations is the much higher failure strain observed as the melamine content decreased. This was explained as a direct effect of the lower cross-link density of these formulations. A decrease with cross-link density of the essential work of fracture required to tear the paints was also observed when samples were tested at their respective glass transition temperatures. The temperature dependence of the essential work of fracture was also studied for formulations PE1H5, PE1H10 and PE1H30. A maximum in $w_e$ was generally observed approximately at $T_g$.

The nature of strain beyond yield was also investigated, where samples of the four paints were loaded until 15% strain and then unloaded at the same displacement rate. The recovered strain when the load reached zero was higher than the yield strain in every case and the degree of recovery was found to increase with cross-link density. Upon inspecting the samples again after two hours no signs of residual strain were found, as samples had returned to their original gauge length. These findings clearly showed that the post-yield behaviour of the paints studied here is best described as inelastic rather than plastic and that the elastic component increases with cross-link density.

Changes in cross-link density were seen in this Chapter to have a profound effect on the mechanical properties of the paint films. This is a point that is further discussed in the following Chapters. As a result the cross-link density is also expected to affect the formability of coated panels. In Chapter 12, a clear improvement is shown in the performance of coated panels in bending when the cross-link density of the coating is reduced.
Chapter 7. Results of formulations with varying catalyst content

To investigate the effect of catalyst concentration on the mechanical properties of the paints, two variations of the standard PE1-based, HMMM-cross-linked system, PE1H20 (PE:HMMM=80:20, HMMM:p-tsa=98:2), were prepared, with HMMM:p-tsa contents of 99.5:0.5 (PE1H20C0.5) and 97:3 (PE1H20C3). The experimental results for paints PE1H20C0.5 and PE1H20C3 are presented here and compared to those of the control formulation, PE1H20.

7.1 Differential scanning calorimetry

The onset, mid-point and end values of the glass transitions of formulations PE1H20C0.5, PE1H20C3 and PE1H20 are shown in Table 7.1, while the heat flow versus temperature traces of the paints are given in Figure 7.1. Clearly, the change in catalyst content has no effect on the glass transition temperature of the paints. However a modest increase in the broadness of the transition is seen, from 13 °C in the case of PE1H20C0.5 to 17 °C for PE1H20C3. This broadening of the glass transition could be an indication of an increase in cross-link density, but this will need to be confirmed from the DMA data given in Section 7.2.
Table 7.1. DSC results for formulations PE1H20C0.5, PE1H20C3 and PE1H20.

<table>
<thead>
<tr>
<th>Formulation</th>
<th>$T_g$, midpoint (DSC) [°C] (±2)</th>
<th>$T_g$, onset (DSC) [°C] (±2)</th>
<th>$T_g$, end (DSC) [°C] (±2)</th>
<th>$T_g$, onset - $T_g$, end (DSC) [°C] (±2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PE1H20C0.5</td>
<td>35</td>
<td>30</td>
<td>43</td>
<td>13</td>
</tr>
<tr>
<td>PE1H20C3</td>
<td>36</td>
<td>30</td>
<td>47</td>
<td>17</td>
</tr>
<tr>
<td>PE1H20</td>
<td>36</td>
<td>30</td>
<td>46</td>
<td>16</td>
</tr>
</tbody>
</table>

Figure 7.1. Heat flow vs temperature DSC plots for PE1H20C0.5 (a) and PE1H20C3 (b), while the trace of PE1H20 is also shown for comparison (c). The glass transition temperatures of the formulations are noted on the plots.

7.2 Dynamic mechanical analysis

Characteristic traces of storage modulus and tanδ of PE1H20C0.5, PE1H20C3 and PE1H20 are shown in Figure 7.2. The main results from the DMA testing of the formulations are shown in Table 7.2. As was also shown from DSC data, the glass transition temperature remains essentially unaffected by the catalyst content of the paints. The maximum of the tanδ, on the other hand, appears to be directly related to the concentration of the catalyst, increasing from 0.80 in the case of PE1H20C3, through 0.94 for PE1H20, to 1.46 for PE1H20C0.5. As the height of the tanδ has been shown to be inversely correlated with cross-link density (see for example the comparison of the varying HMMM-content systems in Section 6.2), this finding could be thought to serve as an indication of an increasingly dense elastic network with the addition of p-tsa. The latter point is, however, only partially confirmed from the rubbery modulus of the formulations, since the low catalyst content paint is seen to
have the lowest modulus at 6.7 MPa while the moduli of PE1H20C3 and PE1H20 in the rubbery region were rather similar at 8.2 and 8.7 MPa respectively.

Regarding the effect of the catalyst concentration on the network properties of HMMM-cross-linked systems, it is known that shorter bake times and lower temperatures are required, for the same degree of cross-linking, when an increasing amount of catalyst is used [91, 183]. When the cure schedule is maintained constant but the amount of catalyst is increased a maximum cross-link density is reported to be obtained at an optimum catalyst concentration, while lower degrees of cross-linking result from the use of either lower or higher concentrations of catalyst [183]. Additionally, a higher catalyst content is reported to result in an increase in the extent of self-condensation of HMMM inside the paint network [156]. Here, within the limited range of catalyst concentrations examined, the cross-link density appears to modestly increase when the catalyst content in HMMM is raised from 99.5:0.5 to 98:2, at which point the density of cross-links reaches a plateau when the p-tsa content is increased even further to 97:3. Regarding the possibility of an increase in the extent of a self-condensed HMMM network with catalyst content, as discussed in Section 6.2.1 this could be manifested in DMA data either as a second peak in the tanδ versus temperature trace or as higher than theoretically possible (under the assumption for a perfect PE-HMMM network) rubbery modulus. Such effects were not observed here, and therefore, even though the presence of a second network of self-condensed HMMM cannot be ruled out, the collected DMA data do not suggest an effect of the catalyst content on the extent of self-condensation in the paints.
Results of formulations with varying catalyst content

Figure 7.2. Storage modulus (a) and tanδ (b) versus temperature of representative samples of PE1H20C0.5, PE1H20C3 and PE1H20.

Table 7.2. DMA results for paints PE1H20C0.5, PE1H20C3 and PE1H20.

<table>
<thead>
<tr>
<th>Formulation</th>
<th>$T_g$ (DMA) [°C]</th>
<th>Max tanδ</th>
<th>Rubbery modulus [MPa]</th>
<th>Cross-link density [10$^{-3}$ mol/cm$^3$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PE1H20C0.5</td>
<td>58 ±0</td>
<td>1.46 ±0.00</td>
<td>6.7 ±0.0</td>
<td>0.71 ±0.00</td>
</tr>
<tr>
<td>PE1H20C3</td>
<td>60 ±1</td>
<td>0.80 ±0.01</td>
<td>8.2 ±0.3</td>
<td>0.87 ±0.03</td>
</tr>
<tr>
<td>PE1H20</td>
<td>60 ±2</td>
<td>0.94 ±0.02</td>
<td>8.7 ±0.6</td>
<td>0.93 ±0.06</td>
</tr>
</tbody>
</table>

7.3 Tensile testing

The results from the tensile testing of the formulations are shown in Figure 7.3. No significant differences in the Young’s moduli of the paints are seen, except for the glassy values of PE1H20C3 that were found to be somewhat lower than the respective values of PE1H20C0.5 and PE1H20. In terms of failure strain all three paints showed comparable maximum values at temperatures between $T_g$ and $T_g$+10 °C. The low catalyst content formulation had a slightly higher maximum failure strain than the other two paints, but when the error bars are also considered this difference is seen to be only marginal. With respect to failure and yield stress, the formulations had very similar values at temperatures higher than approximately $T_g$-10 °C. At lower
temperatures, the high catalyst content PE1H20C3 had the lowest yield and failure stress values, while the results for PE1H20C0.5 and the control PE1H20 were similar (with very slightly higher values for the low catalyst content paint).

The similar tensile results of the paints with varying catalyst content were expected, as they all shared the same polyester backbone, the same HMMM content and their cross-link densities as measured by DMA were generally comparable, with PE1H20C0.5 giving a somewhat lower value than the other two formulations. The failure strain results reflect the cross-link density values, where PE1H20C0.5 had a slightly higher maximum failure strain, while this was very similar for the other two formulations. The lower yield and failure stresses measured for PE1CH20C3 cannot be readily explained by differences in chemical or network structure, as these were fairly similar among the formulations. Of interest is to note the lower Young’s modulus of PE1H20C3 in the glassy region. Generally, no significant correlations were found between the glassy modulus and the microstructures of formulations, at least within the range of chemical and network structures investigated in this study.

Taking into account the above observations, it is suggested that the observed differences between PE1H20C3 and the two lower catalyst-content formulations are not intrinsic to the materials, but are related to differences in the geometry of the samples. An increase in the catalyst concentration results in faster curing of the paint. A consequence of this faster curing is that the methanol which is produced from the cross-linking reaction has less time to escape and becomes trapped in the cured film as bubbles. In Figure 7.4 SEM images from the surfaces of the formulations are shown, where it is clearly seen that the high catalyst content formulation contains the largest amount of bubbles, while only a few bubbles are seen on the surface of the control formulation, and almost none on PE1H20C0.5. The increased number of bubbles present in the samples of PE1H20C3 is therefore thought to be responsible for the apparent lower Young’s modulus, yield and failure stress of the formulation.

As the varying catalyst-content formulations were not found to differ drastically, either structurally or from the point of view of their mechanical properties, it was decided not to perform any further tests, such as EWF or strain and recovery, on them.
7. Results of formulations with varying catalyst content

Figure 7.3. Plots of Young’s modulus (a), strain at failure (b), stress at failure (c) and yield stress (d) versus the difference of testing temperature from $T_g$ (DSC) for formulations PE1H20C0.5, PE1H20C3 and PE1H20.

Figure 7.4. Series of three SEM images characteristic of formulations PE1H20C0.5 (a), PE1H20 (b) and PE3H20C3 (c). The SEM was operated in secondary electron mode at 15 kV.
7.4 Chapter summary

The effects of catalyst concentration on the properties of paint films were investigated for three formulations with a PE1:HMMM content of 80:20 and HMMM:p-tsa contents of 99.5:0.5, 98:2 (the overall control formulation) and 97:3. The three paints had the same glass transition temperatures as measured both from DSC and from DMA. The cross-link density of the low catalyst-content paint was found to be somewhat lower than that of the other two paints, which were found to be similar, but all three values were generally comparable. This result was reflected in the maximum failure strain observed from tensile testing of the formulations where a small increase was seen in the case of the paint with the low concentration of p-tsa. The lower values of Young’s modulus, yield stress and failure stress in the case of the catalyst-rich PE1H20C3 were explained as resulting from an increase in the amount of bubbles present in this formulation.

From these results it can be proposed that changes in catalyst content are not expected to affect the performance of coated panels, except by introduction of defects (micro-bubbles) due to the increased speed of cure at high catalyst concentrations.
Chapter 8. Results of paint based on linear binder, PE4

The experimental results from the testing of formulation PE4H20 are presented here. Polyester binder PE4 is based on binder PE1 where the triol in the latter’s back-bone has been eliminated resulting in a polyester with linear, as opposed to branched, chains. An additional effect of the elimination of the triol from the polyester is the reduction of its functionality. Each chain of PE1 contains approximately 1.6 monomers of the triol. Along with the two chain-ends this means that a total of 3.6 OH functional sites exist which are available for cross-linking on each chain of binder PE1 (see Table 3.3). When no triol monomers are present, as in the case of binder PE4, this means that the functionality of the polyester now reduces to 2. As binder PE4 also has a higher molecular weight than PE1 (8400 g/mol versus 4200 g/mol), it is expected that for the same amount of cross-linker (and ignoring any self-condensation effects) the cross-link density of a PE4-based paint will be lower than that of a PE1-based paint. This is an important point to remember when comparing between the PE1 and PE4 paints, as differences in their properties may come as a result of both their different polyester back-bones and of the differences in their networks of cross-links. In the following, the mechanical and thermo-mechanical data collected for PE4H20 will be compared to those of formulations based on binder PE1 in an attempt to investigate the effects of the elimination of the triol monomer on the properties of the paint.
8.1 Dynamic mechanical analysis

As the cross-link density of formulation PE4H20 is of particular interest, the DMA results will be presented first. In Figure 8.1 traces of storage modulus and tanδ are plotted versus temperature for PE4H20, while for comparison data of formulations PE1H20 (the overall control formulation) and PE1H5 (the low cross-link density PE1-based paint) are presented. When compared to formulations PE1H20 and PE1H5, a decrease in the glass transition temperature is seen for the linear paint. The maximum tanδ falls between the values for the two PE1 formulations, while the rubbery modulus of the PE4-based samples was found to be very similar to that of PE1H5. The glass transition temperature, maximum tanδ and cross-link density of PE4H20 are shown in Table 8.1, where the respective values of PE1H5 and PE1H20 are also given for comparison.

From the DMA data it is clear that the elimination of the triol from the back-bone resulted in a decrease of the rubbery modulus of the paint and hence of the measured cross-link density, see Table 8.1, when the two paints with an 80:20 PE:HM MMM content by weight are considered. Of interest is the shoulder on the right of the glass transition on the tanδ versus temperature plot of PE4H20 (Figure 8.1 (b)). In Section 6.2 a similar shoulder on the tanδ trace of PE1H30 was explained as potentially signifying the presence of a second network of self-condensed HM MMM. The content of HM MMM required for a stoichiometric ratio of unity with PE4 was calculated to be approximately 98:2 by weight (where functionalities of 2 and 5 where assumed for PE4 and HM MMM respectively, and the molecular weights were as given in Section 3.1). Comparing the above value with an HM MMM content of 94:6 required for stoichiometry in the case of PE1-based paints, it is clear that for the same content of HM MMM, PE4H20 contains a greater excess of HM MMM than PE1H20. As a result, it could be expected that PE4H20 should also have a more developed network of self-condensed HM MMM than PE1H20, and this seems to provide a satisfactory explanation for the presence of a shoulder on the tanδ trace of PE4H20 but not on that of PE1H20. When the theoretical cross-link density of a paint based on PE4 and cross-linked with HM MMM at stoichiometric ratio of unity was calculated, it was found to be about 0.13x10⁻³
mol/cm$^3$. The measured value of $0.47 \times 10^{-3}$ mol/cm$^3$ suggests the presence of a self-condensed network of HMMM, similarly to the discussion for PE1H$30$ in Section 6.2.1.

On the other hand, the cross-link density of the linear paint is comparable to that of the low melamine content formulation, PE1H$5$. However, the latter contains less HMMM than stoichiometrically required for the development of a full PE-HMMM network and therefore the extent of self-condensation of cross-linker molecules is expected to be minimal. The greater structural homogeneity of this formulation is reflected in its sharp and high tan$\delta$ peak and in the absence of a shoulder in the tan$\delta$ trace. It can be suggested therefore that even though the measured cross-link densities of PE4H$20$ and PE1H$5$ are very similar, the resulting networks are expected to be quite different.

Figure 8.1. Plots of storage modulus (a) and tan$\delta$ (b) versus temperature of representative samples of PE4H$20$, and PE1H$5$ and PE1H$20$.

<table>
<thead>
<tr>
<th>Formulation</th>
<th>$T_g$ (DMA) [$^\circ$C]</th>
<th>Max tan$\delta$</th>
<th>Rubbery modulus [MPa]</th>
<th>Cross-link density [$10^{-3}$ mol/cm$^3$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PE4H$20$</td>
<td>36 ±2</td>
<td>1.29 ±0.16</td>
<td>4.3 ±0.9</td>
<td>0.47 ±0.09</td>
</tr>
<tr>
<td>PE1H$5$</td>
<td>50 ±1</td>
<td>2.10 ±0.09</td>
<td>4.7 ±1.6</td>
<td>0.44 ±0.20</td>
</tr>
<tr>
<td>PE1H$20$</td>
<td>60 ±2</td>
<td>0.94 ±0.02</td>
<td>8.7 ±0.6</td>
<td>0.93 ±0.06</td>
</tr>
</tbody>
</table>
8.2 Differential scanning calorimetry

Traces of heat flow versus temperature of PE4H20, and of PE1H5 and PE1H20, are shown in Figure 8.2. As with the DMA data, the linear paint has the lowest glass transition temperature at 17 °C, followed by PE1H5 and PE1H20. As expected no signs of physical ageing are seen for PE4H20, as its $T_g$ lies below the storage temperature. Regarding the width of the glass transition, this is similar for the two low cross-link density paints, at 7 and 8 °C for PE4H20 and PE1H5 respectively, while the transition is clearly broader in the case of PE1H20. Interestingly, the shoulder on the right of the glass transition seen from DMA data is not observed on the DSC traces. This echoes the results obtained for PE1H30 where the asymmetry seen on its tanδ trace was not reflected in the DSC data of the formulation.

![Figure 8.2. Heat flow vs temperature DSC plots for PE4H20 (a), PE1H5 (b) and PE1H20 (c). The glass transition temperatures of the formulations are noted on the plots.](image)

### Table 8.2. DSC results for formulations PE4H20, PE1H5 and PE1H20.

<table>
<thead>
<tr>
<th>Formulation</th>
<th>$T_{g, \text{midpoint}}$ (DSC) [°C (±2)]</th>
<th>$T_{g, \text{onset}}$ (DSC) [°C (±2)]</th>
<th>$T_{g, \text{end}}$ (DSC) [°C (±2)]</th>
<th>$T_{g, \text{onset}} - T_{g, \text{end}}$ (DSC) [°C (±2)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PE4H20</td>
<td>17</td>
<td>13</td>
<td>20</td>
<td>7</td>
</tr>
<tr>
<td>PE1H5</td>
<td>28</td>
<td>23</td>
<td>31</td>
<td>8</td>
</tr>
<tr>
<td>PE1H20</td>
<td>36</td>
<td>30</td>
<td>46</td>
<td>16</td>
</tr>
</tbody>
</table>
8.3 Tensile testing

The results from the tensile testing of formulation PE4H20 are shown in Figure 8.3, where again the values for PE1H5 and PE1H20 are also shown for comparison. With respect to Young’s modulus, all three formulations returned similar values in the glassy region, while through the glass transition the moduli of PE4H20 were fairly similar to those of PE1H20.

In terms of failure strain, a maximum was observed for PE4H20 at a temperature approximately 10 °C above \( T_g \). The maximum value of failure strain was about 180 %, which is very close to the maximum observed for PE1H5 and much higher than the respective value for PE1H20. Recall from the data presented in Section 6.3 and from the relevant discussion therein, that generally a negative correlation is observed between cross-link density and failure strain. In that respect, it is possible to explain the high failure strain values of PE4H20 as resulting from the formulation’s low degree of cross-linking, i.e. PE4H20 has a similar cross-link density to PE1H5 and hence the similar values of the failure strains of the two formulations.

On the other hand, the yield stress of PE4H20 cannot be explained on the basis of its cross-link density. In Section 6.3 it was proposed that the yield stress would be expected to increase with cross-link density. In the literature, the effect of branching on the mechanical properties of polymers has been studied predominantly for thermoplastics with varying degrees of crystallinity (see for example [184, 185]). In these studies, a decrease in yield stress was observed with branching. However, this was also connected to a decrease in the degree of crystallinity that was a direct result of the introduction of branching. For the purposes of the present study, the increased yield stress of PE4H20 could perhaps be explained by a decrease in the available free volume in the absence of branches. In other words, the elimination of the tri-ol from the polyester back-bone could be thought to introduce two competing mechanisms regarding yield stress. On one hand, the lowering of the cross-link density tends to decrease the yield stress, while on the other, the reduced free volume of its more compact, linear structure, will tend to increase the yield stress of the paint. Similar comments can be made for the failure stress of PE4H20 that remains higher than that
of PE1H5 throughout the entire test temperature range. It appears that the elimination of branches from the polyester backbone results in a higher level of stress required for flow of the polymer up to the breaking point (see also Figure 8.4). Finally it needs to be acknowledged that the possible effects of the presence of a second highly cross-linked network of HMMM have been excluded from the above discussion. This is not to say that a possible influence of this heterogeneity on the mechanical properties of the paint is ruled out. However, due to the difficulty in defining this second network precisely (for example the extent of self-condensation, size of self-condensed HMMM regions, connectivity to the primary network etc. are unknown), any discussion of its effects on the properties of the paint would be highly speculative.

Figure 8.3. Plots of Young’s modulus (a), strain at failure (b), stress at failure (c) and yield stress (d) versus the difference of testing temperature from \( T_g \) (DSC) for formulations PE4H20, and PE1H5 and PE1H20.
Figure 8.4. Stress versus strain traces of formulations PE4H20 and PE1H5 tested at $T_g + 3^\circ C$ and $T_g + 2^\circ C$ respectively.

### 8.4 Essential work of fracture

Samples of PE4H20 were tested with the EWF method at $T_g$. A total of 17 samples were tested, taken from three separate films of the paint. The resulting load versus displacement plots from each film are shown in Figure 8.5. Clearly, in each case the condition for self-similarity of the traces is satisfied. However, when comparing between films, the load versus displacement plots are seen to be quite different. It has not been possible to explain the reason for this discrepancy. Mild differences in the load versus displacement traces of DENT samples obtained from different films of the paints have been reported before in this study (see Sections 5.4 and 6.4). Such is the case when comparing between Figure 8.5 (a) and (b). However, the traces of the third film, in Figure 8.5 (c) are very obviously removed from those of the other two films. The two films used in Figure 8.5 (a) and (b) were manufactured on the same day at the facilities of Becker Industrial Coatings. The film in Figure 8.5 (c) was manufactured separately, under the same conditions (see Section 3.7 for cure conditions), but at a later time. DSC and DMA results, however, showed no significant differences between the batches cured on the two different days (see Figure 8.6). As no good reason was found to discard any particular group of samples it was decided to use data from all three films in the following analysis.
Figure 8.5. Load versus displacement data at different ligament lengths, from three different films of formulation PE4H20 tested with the essential work of fracture method. Tests were performed at $T_g$.

Figure 8.6. Heat flow (2nd heats) (a) and storage modulus (b) traces of PE4H20 samples from batches cured on two different days. Batch A corresponds to the EWF data shown in Figure 8.5 (a) and (b) and batch B to the data shown in Figure 8.5 (c).

The values of the specific work of fracture of paint PE4H20 against ligament length are shown in Figure 8.7 (a), where again the respective values for PE1H5 and PE1H20 are shown for comparison. The $R^2$ value for the PE4H20 is considered to be low, however this has already been discussed to be a common problem for most formulations tested in EWF, and is thought to be addressed to some extent by consideration of the corresponding standard error. For the elimination of outliers, the usual method of discarding any data points more than two standard errors away from the linear regression was employed. The agreement to the best fit line is seen from Figure 8.7 (b) to be worse at longer ligament lengths, however no points were found to lie outside
the two standard errors band. The essential work of fracture of formulation PE4H20 was found to be 16.9 ±5.3 kJ/m² compared to 19.4 ±1.4 kJ/m² for PE1H5 and 5.7 ±1 kJ/m² for PE1H20 (Figure 8.7 (c)). The inelastic component of the total work was the highest for the linear formulation at 3.8 ±0.5 MPa followed by 1.3 ±0.1 MPa for PE1H20 and 0.8 ±0.2 MPa for PE1H5. The large error bars associated with PE4H20 are, as discussed, a result of the significant scatter in the data for this particular formulation.

Keeping in mind the high level of uncertainty associated with the \( w_e \) value of the linear paint, it still appears to be clearly higher than the respective value for PE1H20, see Figure 8.7 (c). On the other hand, the overlapping error bars make a comparison with PE1H5 difficult. It seems that the essential work of fracture of PE1H5 lies at the higher end of possible values for PE4H20. The data therefore appear to generally agree with the hypothesis proposed in this study for a negative correlation between essential work of fracture and cross-link density. Regarding the effect of branching on the essential work of fracture, again the focus in the literature is on semicrystalline thermoplastic systems where generally the density and length of branches are reported to be positively correlated with the EWF [53, 186]. However due to the very different microstructure of such systems compared to the materials considered in this study, a direct comparison between results is not possible. Instead, the \( w_e \) value of PE4H20 appears to be explainable through the effect of cross-linking on the toughness of polymers, i.e. it is proposed that the higher toughness of PE4H20 compared to the control paint system, PE1H20, is a result of its lower cross-link density.

The measured \( \beta w_{inel} \) value for PE4H20 is not readily explainable. In Section 6.4 it was shown that a consideration of cross-link density alone does not provide sufficient justification for the observed trends in the inelastic part of the work of fracture. Here it is seen that the linear paint, PE4H20, has a much larger \( \beta w_{inel} \) value than the PE1-based paints (see Figure 8.7 (d)). A hypothesis can be put forward connecting the high \( \beta w_{inel} \) value in the case of PE4H20 to a more compact molecular arrangement which comes as a result of the absence of branches. A similar argument was used in Section 8.3 to explain the higher yield stress of PE4H20. With respect to the inelastic part of the work of fracture it is proposed therefore, that the decreased free volume of PEH20 means
that a larger part of the total work is consumed in yielding the ligament, which experimentally is translated in a higher value for $\beta_{w_{inel}}$.

![Graph](image)

Figure 8.7. Specific work of fracture of PE4H20, PE1H5 and PE1H20 versus ligament length with linear regression lines plotted (a), ratio of the linear regression residuals over the standard error of the residuals for formulation PE4H20 (b), and essential work of fracture (c) and $\beta_{w_{p}}$ values (d) for paints PE4H20, PE1H5 and PE1H20.

Table 8.3. Essential work and inelastic component of fracture of formulations PE4H20, PE1H5 and PE1H30. All formulations tested at their respective glass transition temperatures.

<table>
<thead>
<tr>
<th>Formulation</th>
<th>$w_{e}$ [kJ/m$^2$]</th>
<th>$\beta_{w_{inel}}$ [MPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PE4H20</td>
<td>16.9 ±5.3</td>
<td>3.8 ±0.5</td>
</tr>
<tr>
<td>PE1H5</td>
<td>19.4 ±1.4</td>
<td>0.8 ±0.2</td>
</tr>
<tr>
<td>PE1H20</td>
<td>5.7 ±1.0</td>
<td>1.3 ±0.1</td>
</tr>
</tbody>
</table>

8.5 Strain and recovery

The fraction of recoverable elongation and elastic energy in the total elongation and energy supplied during a tensile test have already been shown to depend upon the extent of chemical cross-linking of the paints (see Section 6.5). The strain and recovery trace of a sample of PE4H20 tested at $T_g$ up to a strain of 15 % is shown in Figure 8.8, where the traces of PE1H5 and PE1H20 are also shown for comparison. PE4H20 recovers approximately 2.1 % strain, which is higher than its strain at the yield point, that was found to be about 1.1 %. Also, upon re-examining the sample two hours after
testing, the total amount of strain was found to be recovered. These observations were in-line with what was found for other systems and fit well in the general picture, that the strain beyond the yield point is not truly plastic, but rather recoverable with time.

In comparing between the formulations, the behaviour of PE4H20 is more similar to that of PE1H5. This is seen from the traces in Figure 8.8 and also from the values of elastic strain and recoverable work of the formulations, shown in Table 8.4. The ratio of elastic (recovered upon unloading) over maximum strain is the lowest for PE4H20 at 0.14, followed by 0.18 for PE1H5 and 0.26 for PE1H20. Similarly, the ratio of recoverable work over the total work supplied for the deformation of the samples increases from 0.05 in the case of PE4H20 to 0.10 in the case of PE1H20. These data suggest that the controlling factor for the recovery behaviour of the linear formulation is its low cross-link density, which results in a lower capacity for storing deformation elastically.

![Figure 8.8. Strain and recovery traces of formulation PE4H20 and of formulations PE1H5 and PE1H20. Tests performed at the respective T_g s of the formulations.](image)

<table>
<thead>
<tr>
<th>Formulation</th>
<th>Yield strain, %</th>
<th>Recovered strain ((\varepsilon_{el})), %</th>
<th>(\varepsilon_{el}/\varepsilon_{max})</th>
<th>(W_{el}/W_{tot})</th>
</tr>
</thead>
<tbody>
<tr>
<td>PE4H20</td>
<td>1.1</td>
<td>2.1</td>
<td>0.14</td>
<td>0.05</td>
</tr>
<tr>
<td>PE1H5</td>
<td>0.6</td>
<td>2.8</td>
<td>0.18</td>
<td>0.06</td>
</tr>
<tr>
<td>PE1H20</td>
<td>1.6</td>
<td>3.8</td>
<td>0.26</td>
<td>0.10</td>
</tr>
</tbody>
</table>
8. Results of paint based on linear binder, PE4

8.6 Chapter summary

In the preceding paragraphs the results from the mechanical testing of the paint based on the linear (non-branched) polyester PE4 were presented. These results were directly compared to the results of the overall control formulation PE1H20 and of the low HMMM content PE1H5. The latter was found to have a similar cross-link density to PE4H20 while the control material had a more dense network of cross-links. In general, properties such as the maximum strain at failure, the essential work of fracture at $T_g$ and the recoverable work obtained from strain and recovery tests were found to be explained well as results of the low cross-link density of the PE4-based formulation. On the other hand, the high yield and failure stress observed for PE4H20 did not agree with the general picture for the effects of cross-link density on these properties. Such discrepancies were explained as potentially deriving from a decrease in free volume due to the elimination of branching from the polyester chains.

Based on the above observations, it would be expected that steel panels coated with paint PE4H20 will have similar performance as panels coated with the low cross-link density PE1H5. This is confirmed in Chapter 12 where, generally, a negative correlation is shown between panel performance and cross-link density, irrespective of other differences in the chemical composition of the paints.
Chapter 9. Results of paints based on binders PE5 and PE6

In the following, the experimental results for the paints based on polyester binders PE5 and PE6 are given. Polyester binder PE5 is a modification of PE1 where the phthalic acid monomers of its backbone have been largely substituted with isophthalic acid. Additionally the neopenthy glycol and tri-ol contents have been reduced by approximately half in favour of two different di-ols (see Table 3.2 for more details on polyester composition). The molecular weight of this binder is 2200 g/mol compared to 4200 g/mol for PE1, while each chain is expected to contain on average 2.5 functional sites for cross-linking with HMMM (see Table 3.3 and relevant discussion in Section 3.2). The required PE:HMMM content by weight, for a fully cross-linked network of PE5-HMMM, was calculated to be approximately 92:8 and therefore paint PE5H20 (PE:HMMM=80:20) contains again a significant excess of cross-linker.

Regarding paint PE6EB, it is known that polyester binder PE6 is based on PE5 with the addition of an unknown acrylate. As the exact structure of the binder has not been revealed, not much can be inferred about the cross-linking process and the expected density of the network of cross-links of the paint. The addition of the mono-functional reactive diluent IBOA is expected to have a negative effect on cross-link density. Indeed, the mono-functional IBOA has been used instead of di-functional diluents such as hexane diol diacrylate (HDAA) in an attempt to reduce the cross-link density of radiation-cured systems, thereby improving their formability [4, 187].
9.1 Differential scanning calorimetry

The heat flow versus temperature traces of formulations PE5H20 and PE6EB are shown in Figure 9.1, where the trace of the control formulation is also shown for comparison. The $T_g$ values as well as the widths of the transitions of the formulations are shown in Table 9.1. The much lower $T_g$ of PE5H20 when compared to the $T_g$ of paint PE1H20 (8 °C versus 36 °C) follows the respective trend when a comparison is made between the two neat resins (-11 °C for PE5 versus 15 °C for PE1 as seen in Table 3.2). This decrease in the glass transition temperature is explainable as a result of the substitution of the phthalic acid monomers along the polyester macromolecule in favour of the more linear iso-phthalic acid and of the lower molecular weight of the PE5 resin. The similar increase in $T_g$ from the neat resins to the cured PE5H20 and PE1H20 suggests that the cross-link densities of the paints should be comparable.

Regarding formulation PE6EB, its midpoint glass transition was determined to be 16 °C. What is striking is the broadness of the transition, measured at 39 ±7 °C. Despite the quite large associated error, see Table 9.1, it is seen that even in the lower range of possible values, the glass transition of PE6EB is much wider than that of any of the HMMM cross-linked paints. The reasons behind this apparent widening of the glass transition are not clear at this point. Generally, both an increase in the heterogeneity of the system and an increase in its cross-link density will result in a broader transition, but from DSC data alone no direct evidence in support of either of the two mechanisms can be given.
9. Results of paints based on binders PE5 and PE6

Figure 9.1. Heat flow vs temperature DSC plots for PE5H20 (a) and PE6EB (b), while the trace of PE1H20 is also shown for comparison (c). The glass transition temperatures of the formulations are noted on the plots.

<table>
<thead>
<tr>
<th>Formulation</th>
<th>( T_g ), midpoint (DSC) [^{\circ}C]</th>
<th>( T_g ), onset (DSC) [^{\circ}C]</th>
<th>( T_g ), end (DSC) [^{\circ}C]</th>
<th>( T_g ), onset - ( T_g ), end (DSC) [^{\circ}C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PE5H20</td>
<td>8 ± 2</td>
<td>3 ± 2</td>
<td>14 ± 2</td>
<td>11 ± 2</td>
</tr>
<tr>
<td>PE6EB</td>
<td>16 ± 2</td>
<td>-1 ± 4</td>
<td>38 ± 5</td>
<td>39 ± 7</td>
</tr>
<tr>
<td>PE1H20</td>
<td>36 ± 2</td>
<td>30 ± 2</td>
<td>46 ± 2</td>
<td>16 ± 2</td>
</tr>
</tbody>
</table>

9.2 Dynamic mechanical analysis

Characteristic traces of storage modulus and tan\( \delta \) versus temperature of formulations PE5H20 and PE6EB, and of PE1H20, are shown in Figure 9.2, while the main DMA results are shown in Table 9.2. In comparing the DMA data of PE5H20 and PE1H20 the most striking difference is the much lower \( T_g \) in the case of PE5H20, at 27 \(^{\circ}C\) versus 60 \(^{\circ}C\) for PE1H20. This result is in line with the DSC results reported in Section 9.1. The somewhat lower rubbery modulus of PE5H20 signifies a less dense network of cross-links for this formulation, although the resulting values are in any case comparable (0.77x10^{-3} versus 0.93x10^{-3} mol/cm\(^3\) for PE1H20). The higher tan\( \delta \) peak of PE5H20 is also thought to reflect this difference in cross-link density.
9. Results of paints based on binders PE5 and PE6

Figure 9.2. Storage modulus (a) and tanδ (b) versus temperature of representative samples of PE5H20, PE6EB and PE1H20.

<table>
<thead>
<tr>
<th>Formulation</th>
<th>T_g (DMA) [°C]</th>
<th>Max tanδ</th>
<th>Rubbery modulus [MPa]</th>
<th>Cross-link density [10^{-3} mol/cm^3]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PE5H20</td>
<td>27 ±0</td>
<td>1.19 ±0.01</td>
<td>6.9 ±0.2</td>
<td>0.77 ±0.01</td>
</tr>
<tr>
<td>PE6EB</td>
<td>59 ±4</td>
<td>1.05 ±0.19</td>
<td>4.8 ±3.3</td>
<td>0.52 ±0.36</td>
</tr>
<tr>
<td>PE1H20</td>
<td>60 ±2</td>
<td>0.94 ±0.02</td>
<td>8.7 ±0.6</td>
<td>0.93 ±0.06</td>
</tr>
</tbody>
</table>

With respect to formulation PE6EB, the position of the tanδ peak was found to be at the same temperature as for the control PE1H20. This result was not expected as it does not agree with DSC results for the formulations, where the T_g's were found to be very different. Of note is also the broad shoulder on the left of the tanδ peak, that was observed for all samples of PE6EB tested in DMA. In that light, it seems that the discrepancy between the DSC and DMA data could be explained as a result of the very broad transition in the case of PE6EB, and the positioning of the T_g at different temperatures within the transition depending on the method of measurement.

Regarding the cross-link density of the EB-cured system, this is seen to be lower than both the PE5 and the PE1-based heat-cured paints, although the associated uncertainty severely obscures this result. In any case, however, it can be suggested
that the cross-link density of PE6EB does not exceed, and is most likely lower than, that of the control formulation.

In general, the testing of PE6EB samples in DMA proved to be quite problematic and the reproducibility between different samples was relatively poor, as reflected in the large margins of error for the PE6EB DMA results. This was rather surprising as, despite the difficulties associated with the testing of thin films in DMA (see for example Section 4.2.2 for relevant discussion), the reproducibility of DMA results in this study has generally been satisfactory. The reasons for the particular difficulty in the DMA testing of EB-cured samples based on polyester PE6 are not clear.

**9.3 Tensile testing**

The main tensile properties of formulations PE5H20, PE6EB and PE1H20 are shown in Figure 9.3. A note needs to be made here that, in general, the EB-cured formulation displayed very poor wetting of the PTFE-coated panels, which resulted in paint films with many millimetre-sized holes. This meant that it was very difficult to obtain continuous samples for tensile testing of this particular formulation. It was chosen therefore to reduce the gauge length from 40 mm to 20 mm in the case of PE6EB samples, decreasing at the same time the applied displacement rate by half in order to maintain a constant strain rate.

In comparing between the formulations, no significant differences are seen in their Young’s modulus values, over the temperature range considered, apart from PE6EB having a clearly lower modulus at the top-end of the temperature range (see Figure 9.3 (a)). With respect to failure strain, a moderate increase is seen when values for PESH20 and PE6EB are compared to those for the control formulation (Figure 9.3 (b)). This increase in failure strain is in line with the decrease in cross-link density reported in Section 9.2. The failure stress of the formulations, shown in Figure 9.3 (c) was generally similar, except for the greater values measured for PESH20 around its glass transition temperature. This is linked to the higher failure strains of this formulation in the same temperature range that result in a greater degree of strain-hardening at the point of failure.
Finally, regarding the yield stress of the formulations, PE5H20 gave clearly higher values compared to both PE1H20 and PE6EB, as seen in Figure 9.3 (d). As discussed for the PE4-based paint in Section 8.3, this result is in contrast to what was expected as a consequence of the different cross-link densities of two formulations. Again, however, the observed yield stress values could be thought to result from a free-volume consideration where the more linear (and hence compact) backbone of the PE5 polyester is responsible for the higher yield stress of the PE5-based paint. On the other hand, the EB-cured paint appears to have a yield stress similar to that of the control formulation, but in that case it is much more difficult to justify the observed values as a great deal of uncertainty is associated with this formulation's microstructure, its cross-link density and even its glass transition temperature.

### 9.4 Essential work of fracture

The results from the essential work of fracture testing of PE5H20 are shown here and are compared to those of the PE1-based formulation. Due to the poor quality of the PE6EB films, it was not possible to prepare samples big enough to test in EWF. Samples
prepared from three different films of PE5H20 were tested at $T_g$ and the resulting load versus displacement traces are shown in Figure 9.4. The condition for self-similarity of the traces is generally satisfied, even though some degree of scatter is seen between samples coming from different films but also to some extent between samples of the same film (see for example traces for $l = 10.4$ mm and $l = 8.5$ mm in Figure 9.4 (a) and (b) respectively).

The resulting values of the total specific work of fracture are plotted against ligament length in Figure 9.5 (a). Clearly, the data point at $l = 9.6$ mm lies much lower than the rest of the data. This is confirmed in Figure 9.5 (b), where the ratio of the residuals over the standard error of residuals is shown, and the $l = 9.6$ mm point is seen to be about 2.5 standard errors below the linear regression. Therefore, according to the statistical treatment for outliers presented in Section 4.4.3 the point at $l = 9.6$ mm is discarded. The revised scatter of $w_f$ versus ligament length for PE5H20 is shown in Figure 9.6 (a) along with the respective values for PE1H20. Also, the residuals plot for the new set of data is given in Figure 9.6 (b), where it seen that now the value at $l = 12.0$ lies more than two standard errors away from the best fit line. However, this time the point will not be discarded, as in the methodology given in Section 4.4.3, as well as in the review of the EWF method given by Williams and Rink [59], it is prescribed that only one round of elimination of outliers can be performed. Nevertheless, it is interesting to note that if the point at $l = 12.0$ mm was indeed excluded, the resulting $w_e$ would drop from its current value at $7.3 \pm 3.6$ kJ/m$^2$ to $4.9 \pm 1.6$ kJ/m$^2$. This is indicative of the sensitivity of the results to the data reduction process and is thought to be addressed to an extent by consideration of the standard error associated in the calculation of $w_e$. 
Comparing between the results of the PE5 and the PE1-based formulations, it is seen that, when uncertainties are also considered, the two systems had similar EWF values, at 7.3 ±3.6 kJ/m² for PE5H20 versus 5.7 ±1 kJ/m² for PE1H20, see Table 9.3. PE5H20 was found to have a somewhat lower cross-link density than PE1H20, however the difference in the two values was rather small. In that sense, it seems reasonable that the EWF values of the paints are in the same range. On the other hand, the plastic component of the total work, $\beta \text{w}_{\text{inel}}$, is very clearly much higher in the case of PE5H20 at 4.44 ±0.38 MPa, compared to 1.32 ±0.13 MPa for PE1H20 (see Table 9.3). It has already been shown for the systems with varying adipic:phthalic acid content and for the systems with varying HMMM content that there is no obvious correlation between $\beta \text{w}_{\text{inel}}$ and cross-link density. On the other hand, an increase in $\beta \text{w}_{\text{inel}}$ has been shown when changes in the polyester composition result in a more linear and more compact backbone. This is manifested in the reported values in Section 5.4 (where the PE1 to PE3-based paints are compared) and in Section 8.4 (where PE4 is compared to PE1). In that light, the higher $\beta \text{w}_{\text{inel}}$ value measured for PE5H20 seems explainable as a result of the compositional differences of the two polyesters, i.e. the substitution of part of the
phthalic acid with isophthalic acid and part of the triol with a diol in polyester PE1 to produce the more ‘linear’ PE5.

Figure 9.5. Specific work of fracture versus ligament length (a) and ratio of residuals over standard error (b) for formulation PE5H20 tested at 8 °C, where all samples have been included in the analysis.

Figure 9.6. Specific work of fracture versus ligament length for formulations PE5H20 (after the elimination of outliers) and PE1H20, where both formulations were tested at their respective $T_g$ (a). In (b) the ratio of the residuals over the standard error of the residuals is plotted for formulation PE5H20, where outliers have been discarded through a first round of data reduction.

Table 9.3. Essential work and inelastic component of fracture of formulations PE4H20, PE1H5 and PE1H30. All formulations tested at their respective glass transition temperatures.

<table>
<thead>
<tr>
<th>Formulation</th>
<th>$w_e$ [kJ/m$^2$]</th>
<th>$\Delta w_{inel}$ [MPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PE5H20</td>
<td>$7.3 \pm 3.6$</td>
<td>$4.44 \pm 0.38$</td>
</tr>
<tr>
<td>PE1H20</td>
<td>$5.7 \pm 1.0$</td>
<td>$1.32 \pm 0.13$</td>
</tr>
</tbody>
</table>

9.5 Strain and recovery tests

A sample of PE5H20 was subjected to a strain and recovery cycle at $T_g$. The elastic parts of the strain and supplied work were measured and are compared here with the respective values of formulation PE1H20. It was attempted to also test a sample of PE6EB at a temperature equal to its $T_g$ (DSC), but this failed at a much lower strain,
approximately 7 % (see also Figure 9.3 (b) where it is shown that PE6EB reached its maximum failure strain at about 20 °C above Tg as measured by DSC). Taking into account, as well, the uncertainty in the Tg value for this particular formulation, it was considered that it would be very difficult to obtain any meaningful comparison between the systems, and it was therefore chosen not to include strain and recovery data of PE6EB.

From the stress versus strain trace of PE5H20 in Figure 9.7 and from the data shown in Table 9.4, it is seen, that as was the case for all systems investigated in this study, the PE5-based paint recovered a greater amount of strain upon unloading than what would be expected if the strain post-yield was indeed plastic (the recovered strain was 2.4 % versus a yield strain of 1.7 %). Additionally, as expected, the entire amount of strain was found to be recovered upon re-examination of the sample two hours after testing. When a comparison is made between the two formulations, it is seen that PE5H20 recovers much less of the applied strain upon unloading, with the elastic part of the strain being 16 % of the total strain in the case of PE5H20 and 24 % for PE1H20. Similarly, the portion of the recoverable work was 6 % and 10 % for the PE5 and the PE1-based paint, respectively.

So far, a positive correlation between cross-link density and the capacity for storing energy elastically has been proposed. In that sense, it is to be expected that PE5H20 should be less elastic than PE1H20 as a result of its somewhat lower cross-link density. It needs to be acknowledged, however, that a cross-link density argument might not fully explain the difference in the strain and recovery data of the two formulations. The $\epsilon_{ev}/\epsilon_{max}$ and $W_{ev}/W_{tot}$ values of PE5H20 match very closely to the respective values of PE1H5 (see Table 6.5). However, as PE1H5 is of a lower cross-link density than PESH20 (0.44x10^{-3} versus 0.77 x10^{-3} mol/cm^3), it would be expected for the $\epsilon_{ev}/\epsilon_{max}$ and $W_{ev}/W_{tot}$ values of PE5H20 to lie somewhere in-between the respective values of the PE1-based formulations. The smaller than expected elasticity of PE5H20 could perhaps be explained by consideration of the more linear nature of its polyester back-bone favouring chain disentanglement and thus resulting in a reduction in the magnitude of retractive forces acting on the chains upon unloading. A similar observation was made when the high in phthalic acid formulation, PE2H20, was found to have a much larger
9. Results of paints based on binders PE5 and PE6

capacity for storing work elastically, than would be expected from considering its cross-link density (see Section 5.5).

Figure 9.7. Stress vs strain traces of strain and recovery tests on formulations PE5H20 and PE1H20.

Table 9.4. Yield strain, recovered strain, ratio of elastic over maximum strain and ratio of elastic work over work supplied to maximum deformation for formulations PE5H20 and PE1H20.

<table>
<thead>
<tr>
<th>Formulation</th>
<th>Yield strain, %</th>
<th>Recovered strain ($\varepsilon_{el}$), %</th>
<th>$\varepsilon_{el}/\varepsilon_{max}$</th>
<th>$W_{el}/W_{tot}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PE5H20</td>
<td>1.7</td>
<td>2.4</td>
<td>0.16</td>
<td>0.06</td>
</tr>
<tr>
<td>PE1H20</td>
<td>1.6</td>
<td>3.8</td>
<td>0.26</td>
<td>0.10</td>
</tr>
</tbody>
</table>

9.6 Chapter summary

Polyester binder PE5, a more linear, low-$T_g$ version of binder PE1, was cross-linked with HMMM (PE:HMMM=80:20) and its properties were determined and compared to those of the control formulation, PE1H20. An additional formulation was tested that was based on binder PE6, which was essentially identical to PE5 but also contained an undisclosed acrylate. A reactive diluent, IBOA, was added to binder PE6 at a 50:50 concentration by weight and the formulation was electron beam (EB)-cured.

Between formulations PE5H20 and PE1H20, the paint based on the more linear PE5 was found to have a substantially lower glass transition temperature as seen both by DSC and by DMA. The cross-link densities of the two paints were comparable, with that of PE5H20 being somewhat lower. In terms of tensile properties, a small increase in failure strain was seen for PE5H20 as well as a clear increase in yield stress. The former was explained in the context of the cross-link densities observed, while a free-volume
effect was proposed for the justification of the latter. The two formulations were found to have similar EWF values, however the in-elastic component of the total work of fracture was found to be clearly higher in the case of PE5H20. This could also be connected to the smaller capacity of PE5H20 for storing energy elastically, as observed from strain and recovery tests.

Regarding the EB-cured formulation, PE6EB, the determination of its glass transition temperature proved to be problematic, as the transition was found to be very broad and the $T_g$ values obtained from DSC and DMA were not in agreement. Significant scatter was found in the cross-link density values obtained from DMA. It seems, however, the cross-link density of PE6EB does not exceed (and most probably lies below) that of PE1H20. From tensile tests the maximum failure strain of PE6EB was found to be similar to the respective value for the PE5-based formulation and somewhat higher than the value for PE1H20. Due to the poor quality of the PE6EB films it was not possible to test this formulation in essential work of fracture.

From the free-films results that were presented above, it is expected that panels coated with paint PE5H20 will have similar formability as panels coated with formulation PE1H20 (notwithstanding any difference in performance arising from the lower glass transition temperature of the PE5-based paint). As a result it was not attempted to test panels coated with formulation PE5H20. On the other hand, the behaviour of PE6EB free-films is thought to be poorly understood and therefore it is difficult to correlate between the properties of the free-films and the performance of panels coated with this formulation. For this reason it was not attempted to test EB-cured panels in this study.
Chapter 10. Effect of pigment on the mechanical properties of the paints

In this section the mechanical and thermo-mechanical properties of coatings based on binders PE1 to PE5 and cross-linked with HMMM at a binder:HMMM ratio of 80:20 by weight are compared to the mechanical properties of the same coatings that also contain 50 wt% of TiO$_2$ pigment. The results are presented separately for each binder in paragraphs 10.1 to 10.5, while a more in-depth discussion on the effect of pigment on the mechanical properties of the paints (regardless of binder composition) is attempted in 10.6.

10.1 Effect of pigment: Binder PE1

DSC results for samples PE1H20 (unpigmented) and PE1H20Ti (pigmented) can be found in Figure 10.1. No change in the mid-point glass transition is observed with the addition of pigment. However, it seems that the presence of pigment results in a narrower transition region, since the difference between the onset and end values of glass transition decreases from 16 °C in the case of PE1H20 to 10 °C for PE1H20Ti (see also Table 10.1 in Section 10.6.2).

Similar results were obtained from dynamic mechanical analysis (see Figure 10.2 and also Table 10.2 in Section 10.6.2). The position of the tanδ maximum is the same for both the pigmented and the clear paint. The difference between the onset and the end glass transition however decreases from 32 °C to 20 °C with the addition of pigment. At the same time, a clear increase in the tanδ maximum is observed from 0.94 for the
unpigmented to 1.50 for the pigmented formulation, while the storage modulus of the white films remains higher for the entire temperature range with a value of 20.2 in the rubbery region versus 8.7 MPa for the clear films.

The results from the tensile testing of formulations PE1H20 and PE1H20Ti are compared in Figure 10.3. The Young’s modulus of the white coating is between 2 and 2.5 times higher than that of the clear in the glassy region. However, as the temperature is increased towards the visco-elastic region of the materials, the moduli of the two coatings become very similar. This could be attributed to the sharper glass transition in the case of the white paint, already observed from the DSC and DMA results and seen also as a steeper slope of the Young’s modulus versus temperature plot of PE1H20Ti at temperatures between about \( T_g - 10 \) °C to \( T_g + 10 \) °C. The effect of the addition of pigment on the stiffness of paints (and indeed on all the main mechanical and thermomechanical properties) is discussed further in Section 10.6.

![Figure 10.1](image-url)  
Figure 10.1. Heat flow vs temperature DSC plots for PE1H20 (a), PE1H20Ti (b). The glass transition temperatures of the formulations are noted on the plots.

![Figure 10.2](image-url)  
Figure 10.2. Plots of storage modulus (a) and tanδ (b) versus temperature of representative samples of PE1H20 and PE1H20Ti.
In terms of failure strain, the addition of pigment resulted in lower values in the glassy region while at higher temperatures the two systems failed at similar strains (Figure 10.3 (b)). On the other hand, the failure stress clearly increased for the pigmented formulation (Figure 10.3 (c)), both in the glassy region (although the error bars make this increase only marginal) and even more so in the visco-elastic region. The latter is due to the apparent greater degree of strain hardening in the case of the white samples, as shown in Figure 10.4. Finally an increase in yield stress is observed with the addition of pigment as seen in Figure 10.3 (d) (again these results will be discussed further when data of all formulations are considered in Section 10.6).

The load vs displacement traces from testing of DENT samples of PE1H20Ti are shown in Figure 10.5 (a) (the respective curves of PE1H20 can be found in Section 5.4). The traces appear to be self-similar with respect to ligament length. In Figure 10.5 (b) the specific works of fracture for both the clear and the white paint are plotted vs ligament length. The ratio of the residuals over the standard error of the regression is shown in Figure 10.5 (c), while the respective plot for PE1H20 can be found again in Section 5.4. From extrapolation of the data in Figure 10.5 (b) to zero ligament length, the $w_e$ value for PE1H20Ti was found to be $13.7 \pm 1.5 \text{ kJ/m}^2$ compared to $5.7 \pm 1 \text{ kJ/m}^2$ for PE1H20Ti. Clearly, the addition of pigment leads to an increase in the toughness of the paint at $T_g$. At the same time the inelastic part of the work of fracture also increased from $1.32 \pm 0.13$ to $1.98 \pm 0.17 \text{ MPa}$ with the addition of pigment.
Figure 10.3. Plots of Young’s modulus (a), strain at failure (b), stress at failure (c) and yield stress (d) versus the difference of testing temperature from $T_g$ (DSC) for formulations PE1H20 and PE1H20Ti.

Figure 10.4. Tensile stress versus strain curves at 30 °C (a) and 35 °C (b) for formulations PE1H20 and PE1H20Ti. Of interest is the higher degree of strain hardening in the case of the pigmented formulation.

Figure 10.5. Load versus displacement curves of DENT samples of PE1H20Ti where ligament lengths are given in mm (a) and plot of specific work of fracture versus ligament for PE1H20 and PE1H20Ti (b). In (c) the ratio of the residuals over the standard error of the regression is shown. Tests performed at 35 °C.
10.2 Effect of pigment: Binder PE2

The addition of pigment to the formulation based on binder PE2 did not affect its glass transition temperature as measured by DSC, when the uncertainty in the results is taken into account (see Figure 10.6 and Table 10.1). Also, both paints have equally broad transitions with the difference between onset and end $T_g$ (DSC) being 15 °C.

The glass transition temperature as measured by DMA was also found to be unaffected by the presence of pigment, at 70 °C. The width of the glass transition was found to decrease slightly with the addition of pigment, but when uncertainties are also taken into account this decrease is seen to be only marginal (Table 10.2). The storage modulus in the rubbery region was found to be 17.2 MPa for the white coating compared to 6.3 MPa for the clear (see Figure 10.7). Finally an increase in the tanδ maximum is observed for the pigmented formulation from 1.13 to 1.36, see Table 10.2.

Figure 10.6. Heat flow vs temperature DSC plots for PE2H2O (a), PE2H20Ti (b). The glass transition temperatures of the formulations are noted on the plots.

Figure 10.7. Plots of storage modulus (a) and tanδ (b) versus temperature of representative samples of PE2H2O and PE2H20Ti.
An increase in Young’s modulus by 2 to 2.5 times is observed (Figure 10.8(a)) for the pigmented paint in the glassy region. As the test temperature approached $T_g$, however, the Young’s moduli of the two formulations fall on more or less the same line against temperature difference from $T_g$. The strain to failure (Figure 10.8 (b)) was lower for the white coating throughout the entire temperature range, while no effect of pigment on failure or yield stress (Figure 10.8 (c) and (d) respectively) was found when the associated error bars were also taken into account.

In Figure 10.9 tensile stress versus strain traces of the two formulations at 45 °C and 50 °C are shown. A higher degree of strain hardening is seen in the case of PE1H20Ti. This however does not result in markedly higher failure stresses in the visco-elastic region (as for example in the case of binder PE1) due to the decrease in failure strain with the addition of pigment. In Figure 10.10 (a) load versus displacement traces from the EWF testing of PE2H20Ti samples are shown. The traces are seen to satisfy the condition of self similarity. The specific work of fracture versus ligament length is shown in Figure 10.10 (b) and in Figure 10.10 (c) the residuals of the regression are given, where they are shown to be within two standard errors from the regression line for all ligament lengths (for the residuals of PE2H20, see Section 5.4). The essential work of fracture required for the tearing of samples of PE1H20Ti was measured to be $10.1 \pm 1.0 \text{ kJ/m}^2$. 

Figure 10.8. Plots of Young's modulus (a), strain at failure (b), stress at failure (c) and yield stress (d) versus the difference of testing temperature from $T_g$ (DSC) for formulations PE2H20 and PE2H20Ti.
versus 4.8 ±0.7 kJ/m² for PE1H20. On the other hand, $\beta w_{inel}$ was almost the same for the white and the clear paint, at 0.90 ±0.11 and 0.76 ±0.08 MPa respectively.

Figure 10.9. Tensile stress versus strain curves at 45 °C (a) and 50 °C (b) for formulations PE2H20 and PE2H20Ti.

Figure 10.10. Load versus displacement curves of DENT samples of PE2H20Ti where ligament lengths are given in mm (a) and plot of specific work of fracture versus ligament length for PE2H20 and PE2H20Ti (b). In (c) the ratio of the residuals over the standard error of the regression is shown. Tests performed at 48 °C.

10.3 Effect of pigment: Binder PE3

DSC data from formulations PE3H20 and PE3H20Ti are shown in Figure 10.11. Clearly there is no change in the glass transition temperature as a result of the addition of
pigment. There is however an apparent increase in the width of the glass transition from 10 °C in the case of the clear paint to 16 °C in the case of the white (Table 10.1).

Dynamic mechanical analysis showed a slight decrease in glass transition temperature with the addition of pigment, from 44 to 41 °C that falls however well within experimental error (see Table 10.2). The difference between the onset and end values of the glass transition is very similar in both cases at approximately 30 °C, while there is a slight increase in the tanδ maximum (from 1.08 to 1.18) and a significant increase in rubbery modulus (from 9.3 to 16.3 MPa) with the addition of pigment. Representative storage modulus and tanδ curves of formulations PE3H20 and PE3H20Ti are shown in Figure 10.12.

Results from the tensile testing of PE3H20 and PE3H20Ti are shown in Figure 10.13. The presence of the pigment results in an increase of the glassy modulus of PE3H20 by 1.6 to 1.9 times. In the visco-elastic region the modulus decreases in both cases at the same rate while it generally remains higher for the white formulation. The strain to failure of PE3H20Ti generally remained somewhat lower compared to that of its clear counterpart throughout the entire testing temperature range.

![Figure 10.11. Heat flow vs temperature DSC plots for PE3H20 (a), PE3H20Ti (b). The glass transition temperatures of the formulations are noted on the plots.](image)

![Figure 10.12. Plots of storage modulus (a) and tanδ (b) versus temperature of representative samples of PE3H20 and PE3H20Ti.](image)
In terms of failure stress, there exist two distinct regions in Figure 10.13 (c). At relatively low temperatures the pigment seems to have no significant effect on the failure stress, while at higher temperatures the latter was found to be higher in the case of the white paint. This can be explained again as a result of the greater tendency of the pigmented formulation to strain harden (see Figure 10.14). The yield stress remained unaffected from the presence of pigment (Figure 10.13 (d)).

Load versus displacement curves from testing PE3H20Ti with the EWF method as well as a comparison of the results from clear and white samples are shown in Figure 10.15 (a) and (b). The ratio of the residuals over the standard error of the regression of PE3H20Ti data is plotted versus ligament length in Figure 10.15 (c), where it is shown that this ratio was always lower than 2. The addition of pigment does not seem to affect $w_e$ in this case as it was found to be $12.2 \pm 1.7 \text{ kJ/m}^2$ for the white compared to $12.9 \pm 1.4 \text{ kJ/m}^2$ for the clear paint. On the other hand, the inelastic part of the work required for tearing the samples increased with the addition of pigment ($2.57 \pm 0.19 \text{ MPa}$ for PE3H20Ti compared to $1.86 \pm 0.17 \text{ MPa}$ for PE3H20).
10. Effect of pigment on the mechanical properties of the paints

No effect on the glass transition temperature was found as a result of the addition of pigment to formulation PE4H20 as shown in Figure 10.16. The width of the transition was also found to remain unaffected at 7 °C in both cases (Table 10.1). Analysis of the DMA results (shown in Figure 10.17) revealed a small increase in the temperature of the tanδ peak from 35 to 40 °C for the white paint. The difference between $T_{g,\text{onset}}$ and
\[ T_{g, \text{end}} \] was similar for both paints at 22 °C for PE4H20Ti and 19 °C for PE4H20. An interesting observation is that at high temperatures the clear paint was found to have a somewhat higher rubbery plateau, and additionally the lack of a clear rubbery plateau for PE4H20Ti, as storage modulus continued to decrease (albeit it at a slower rate) throughout what should have been the rubbery region. Finally, as was the case in all previous comparisons between clear and white samples, the addition of pigment resulted in an increase in the \( \tan \delta \) maximum, in this case from 1.24 to 2.08 (see Table 10.2).

The tensile properties of PE4H20Ti, along with these of PE4H20, are shown in Figure 10.18. In the glassy region, the Young's modulus of the white paint is about 2 times higher than that of the clear, while at higher temperatures the two formulations behave in a similar manner. The failure strain of PE4H20Ti was generally found to be lower than the failure strain of PE4H20 throughout the entire testing range. An exception to this, are the values at about 15 °C above \( T_g \) and beyond. Whereas the failure strain of the clear formulation reaches a maximum at about \( T_g +10 \) °C and then drops considerably, in the case of the white paint it appears to reach a wide plateau between 10 and 30 °C above \( T_g \).

![Figure 10.16](image_url) Heat flow vs temperature DSC plots for PE4H20 (a), PE4H20Ti (b). The glass transition temperatures of the formulations are noted on the plots.

![Figure 10.17](image_url) Plots of storage modulus (a) and \( \tan \delta \) (b) versus temperature of representative samples of PE4H20 and PE4H20Ti.
In line with the rest of the results on the pigmented formulations, the stress at failure of PE4H20Ti is significantly higher than that of PE4H20 at temperatures above $T_g$, a result of the greater strain hardening in the presence of pigment particles (Figure 10.19). Finally, there seems to be no significant difference between the yield stress of white and clear samples.

Characteristic load versus displacement plots of DENT samples of formulation PE4H20Ti are shown in Figure 10.20 (a). Some variation in the shape of the plots exists, which can be attributed partly to the samples coming from different films of the paint. The reason for this remains unclear, and as there was no justification for keeping certain sets of plots instead of others it was decided to use all available data for the determination of $w_e$. 

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**Figure 10.18.** Plots of Young’s modulus (a), strain at failure (b), stress at failure (c) and yield stress (d) versus the difference of testing temperature from $T_g$ (DSC) for formulations PE4H20 and PE4H20Ti.

**Figure 10.19.** Tensile stress versus strain curves at 20 °C (a) and 25 °C (b) for formulations PE4H20 and PE4H20Ti.
The specific work of fracture versus ligament length for PE4H20Ti is shown in Figure 10.20 (b) along with the respective values for the clear paint. The residuals from the linear regression of the PE4H20Ti data are shown in Figure 10.20 (c) and it is seen that in every case the condition that they remain within two standard errors from the regression line, is satisfied (the residuals for PE4H20 are given in Section 8.4). The addition of 50 wt% TiO\textsubscript{2} pigment does not seem to affect the toughness of the PE4-based formulation considerably, resulting in a $w_e$ value of 12.8 ±4.0 kJ/m\textsuperscript{2} that compares with 16.9 ±4.7 kJ/m\textsuperscript{2} in the case of the clear samples. In terms of the inelastic component $\beta w_{\text{inel}}$, again no significant effect due to the presence of pigment was found with values of 4.6 ±0.5 MPa for the white samples and 3.8 ±0.5 MPa for the clear. The similar fracture behaviour of the two paints is also illustrated by the fact that their specific work of fracture versus ligament length traces generally overlap.
10.5 Effect of pigment: Binder PE5

The DSC results from formulations PE5H2O and PE5H20Ti once more showed no effect of pigment on the glass transition temperature of the paint (see Figure 10.21). The width of the glass transition was also practically the same for both formulations at about 10 °C (Table 10.1).

The glass transition temperature as measured by DMA (see Figure 10.22) was found to be 26 °C for the white paint compared to 27 °C for the clear, and the difference between end and onset values was measured at approximately 20 °C in both cases. A marginal increase in the tanδ maximum was observed from 1.19 to 1.23 with the addition of pigment. Finally, the rubbery modulus was found to be 18.4 MPa for PE5H20Ti compared to 6.9 MPa in the case of PE5H20 (see Table 10.2).

An increase in the glassy modulus by about 1.8 times is observed with the addition of pigment to PE5H20 (see Figure 10.23 (a)), where at higher temperatures the clear and the white modulus versus temperature traces converge and fall more or less on the same line. In comparing between the failure strains of the formulations there does not seem to be any significant difference. Above Tg, the clear films generally reached somewhat higher elongations, but this observation is well within experimental error as seen by the error bars in Figure 10.23 (b).

The failure stress is similar for both systems at low temperatures, and becomes significantly larger for the pigmented system at temperatures above Tg where strain hardening takes place (see Figure 10.23 (c) and Figure 10.24). No effect on the yield stress was found with the addition of pigment.

![Figure 10.21. Heat flow vs temperature DSC plots for PES5H2O (a), PES5H20Ti (b). The glass transition temperatures of the formulations are noted on the plots.](image-url)
10. Effect of pigment on the mechanical properties of the paints

Figure 10.22. Plots of storage modulus (a) and tanδ (b) versus temperature of representative samples of PE5H20 and PE5H20Ti.

Figure 10.23. Plots of Young’s modulus (a), strain at failure (b), stress at failure (c) and yield stress (d) versus the difference of testing temperature from Tg (DSC) for formulations PE5H20 and PE5H20Ti.

Figure 10.24. Tensile stress versus strain curves at 10 °C (a) and 15 °C (b) for formulations PE5H20 and PE5H20Ti.
10.6 Effect of pigment: A comparison between all systems

In the following paragraphs the results obtained for all formulations containing TiO$_2$ particles will be discussed collectively in an attempt to determine general trends regarding the effect of pigment on the mechanical properties of the paint.

10.6.1 Dispersion of pigment

As discussed in the following sections, the degree of dispersion of particulate fillers in polymer matrices will affect the composite properties [14, 63, 188]. For this reason cross-sections of films of all pigmented formulations were examined using a scanning electron microscope (Hitachi S-3400N, Japan). SEM micrographs are shown in Figure 10.25.

As it is expected that different films of paint, or even different parts of the same film, may show somewhat different micro-structure, a quantitative comparison between formulations will not be attempted. For the purposes of the discussion that follows it is sufficient to observe that the dispersion of the pigment varies from single particles (the nominal diameter of 300 nm provided by the manufacturer was confirmed by SEM observations here), to small agglomerates of up to 5 particles (see for example the agglomerates noted on image of PE1H20Ti in Figure 10.25 (a)), to larger agglomerates consisting of up to around 20 particles (see agglomerate noted on image of PE5H20Ti, Figure 10.25 (e)).
10.6.2 Effect on glass transition and dynamic properties

Both the DSC and DMA results presented in Sections 10.1 to 10.5 showed that generally no change in the glass transition temperature of the paint is observed due to the presence of pigment (see Tables 10.1 and 10.2 and Figure 10.26). Regarding the width of the glass transition, this remained unaffected in most cases with the exception of formulation PE1H20Ti where it decreased with the addition of pigment as seen both from DSC and DMA, and from the Young’s modulus versus temperature results.
The effect of pigment on the mechanical properties of the paints

Generally, the effect of pigmentation on the glass transition of coatings depends on the nature of both the pigment particles and of the carrying vehicle (binder and cross-linker) [188-190]. The microstructure of a polymer reinforced with inorganic particles is expected to consist of three distinct regions: one of bulk polymer material, one of pigment, and one of an inter-phase of adsorbed binder that forms around the pigment particles. If the glass transition temperature of this inter-phase is different to that of the bulk polymer, this difference is expected to be reflected as a change in the \( T_g \) of the composite system [189]. In the majority of cases an increase in glass transition temperature is expected as a result of the decreased mobility of polymer segments in the interface layers due to interactions with the solid inorganic particles [188, 190].

However cases where the glass transition temperature of the polymer is not affected (or is even reduced) by the addition of filler are also known. Kraus and Gruver [191] attributed this to an increase in free volume for particulate filled polymers due to the different thermal expansion coefficients of the polymer matrix and the inorganic reinforcement. As a result of this difference, internal stresses develop in the polymer when cooling down from high temperatures and through \( T_g \) to the glassy region. These stresses are therefore responsible for a relative increase of the free volume of the filled material, which in turn results in a decrease in the \( T_g \) of the material (at least in the regions adjacent to the filler particles).

Table 10.1. DSC results for clear and pigmented formulations based on binders PE1 to PE5.

<table>
<thead>
<tr>
<th>Formulation</th>
<th>( T_g, \text{midpoint (DSC)} ) [°C] (±2)</th>
<th>( T_g, \text{onset (DSC)} ) [°C] (±2)</th>
<th>( T_g, \text{end (DSC)} ) [°C] (±2)</th>
<th>( T_g, \text{onset} - T_g, \text{end (DSC)} ) [°C] (±2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PE1H20</td>
<td>36</td>
<td>30</td>
<td>46</td>
<td>16</td>
</tr>
<tr>
<td>PE1H20Ti</td>
<td>35</td>
<td>29</td>
<td>29</td>
<td>10</td>
</tr>
<tr>
<td>PE2H20</td>
<td>46</td>
<td>38</td>
<td>53</td>
<td>15</td>
</tr>
<tr>
<td>PE2H20Ti</td>
<td>48</td>
<td>41</td>
<td>56</td>
<td>15</td>
</tr>
<tr>
<td>PE3H20</td>
<td>21</td>
<td>16</td>
<td>26</td>
<td>11</td>
</tr>
<tr>
<td>PE3H20Ti</td>
<td>22</td>
<td>16</td>
<td>32</td>
<td>16</td>
</tr>
<tr>
<td>PE4H20</td>
<td>17</td>
<td>13</td>
<td>20</td>
<td>7</td>
</tr>
<tr>
<td>PE4H20Ti</td>
<td>18</td>
<td>14</td>
<td>21</td>
<td>7</td>
</tr>
<tr>
<td>PE5H20</td>
<td>8</td>
<td>3</td>
<td>14</td>
<td>11</td>
</tr>
<tr>
<td>PE5H20Ti</td>
<td>9</td>
<td>4</td>
<td>14</td>
<td>10</td>
</tr>
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</table>
Table 10.2. DMA results for clear and pigmented formulations based on binders PE1 to PE5.

<table>
<thead>
<tr>
<th>Formulation</th>
<th>( T_g, \tan \delta_{\text{max}} ) (DMA) [°C]</th>
<th>Max ( \tan \delta )</th>
<th>( T_g, \text{onset} - T_g, \text{end} ) (DSC) [°C]</th>
<th>( E_{\text{rub}} ) [MPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PE1H20</td>
<td>60 ±1</td>
<td>0.94 ±0.02</td>
<td>32 ±5</td>
<td>8.7 ±0.5</td>
</tr>
<tr>
<td>PE1H20Ti</td>
<td>59 ±2</td>
<td>1.50 ±0.12</td>
<td>20 ±1</td>
<td>20.2 ±4.6</td>
</tr>
<tr>
<td>PE2H20</td>
<td>71 ±1</td>
<td>1.13 ±0.04</td>
<td>24 ±1</td>
<td>7.0 ±0.1</td>
</tr>
<tr>
<td>PE2H20Ti</td>
<td>70 ±1</td>
<td>1.36 ±0.06</td>
<td>21 ±1</td>
<td>17.2 ±0.8</td>
</tr>
<tr>
<td>PE3H20</td>
<td>44 ±3</td>
<td>1.08 ±0.02</td>
<td>29</td>
<td>9.3 ±0.9</td>
</tr>
<tr>
<td>PE3H20Ti</td>
<td>41 ±2</td>
<td>1.19 ±0.01</td>
<td>30</td>
<td>16.3 ±2.0</td>
</tr>
<tr>
<td>PE4H20</td>
<td>35 ±1</td>
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<td>19 ±1</td>
<td>4.0 ±0.7</td>
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<tr>
<td>PE4H20Ti</td>
<td>40 ±2</td>
<td>2.08 ±0.14</td>
<td>22</td>
<td>3.5 ±1.6</td>
</tr>
<tr>
<td>PE5H20</td>
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<td>1.19 ±0.01</td>
<td>21 ±2</td>
<td>6.9 ±0.2</td>
</tr>
<tr>
<td>PE5H20Ti</td>
<td>26 ±0</td>
<td>1.23 ±0.00</td>
<td>20 ±1</td>
<td>18.4 ±1.1</td>
</tr>
</tbody>
</table>

Figure 10.26. Glass transition temperatures as measured by DSC (a) and DMA (b) for clear and pigmented paints based on polyester binders PE1 to PE5 and cross-linked with melamine at a relative PE:HMMM concentration of 80:20 by weight.

Even though the above argument could explain the lack of effect of pigment on the glass transition temperature of the paints whose \( T_g \) is above room temperature (PE1H20 and PE2H20) it cannot explain why this is the case also for paints whose \( T_g \) lies lower than RT (PE4H20 and PE5H20). In the latter case the difference in the thermal expansion coefficients of the polyester matrix and TiO\(_2\) remains, however any stresses developing due to this difference should readily relax at normal storage conditions.

Another way that the presence of pigment can affect the glass transition of thermoset polymers is if it has some influence on cure. Zosel [192] notes that a shift in \( T_g \) can be used as indication of the pigmentation interfering with the cross-linking process of paints. To that extent, the addition of 50 wt% TiO\(_2\) particles to the paints studied here appears to leave the structure of their chemical networks unaffected as the \( T_g \)s of the clear and white films were found to be equal within experimental error.
Of note is also the increase in the maximum of tan\(\delta\) for the white formulations (see also Figure 10.27). This increase was most pronounced in the case of PE1H20 (from 0.94 to 1.50) and of PE4H20 (from 1.24 to 2.08). This is contrary to the commonly observed decrease in the maximum tan\(\delta\) for particulate filled composites [72, 193], and pigmented paints in particular [113, 190]. Nielsen and co-workers [72, 76] investigated the dynamic properties of butadiene-acrylonitrile rubber/glass bead composites and found a significant amount of additional damping taking place in cases where there was poor adhesion between matrix and particles or in the presence of agglomerations of particles. Similar results were reported in [194] where an epoxy/glass bead system was studied. However, this additional damping was observed as a smaller than expected decrease in the tan\(\delta\) peak rather than as an increase in tan\(\delta\).

Akay et al. provide a rare study [195] where an increase in tan\(\delta\) is observed with the addition of pigment, in the case of a HMMM cross-linked acrylic system with added TiO\(_2\) particles that had been surface-treated with Al\(_2\)O\(_3\). At the same time a decrease of the glass transition temperature was reported. Of note is that Akay et al. report that when paints containing untreated TiO\(_2\) particles were tested, the expected dynamic mechanical behaviour was seen with a decrease in tan\(\delta\), while \(T_g\) remained unaffected by the presence of pigment.

![Figure 10.27. Max tan\(\delta\) for clear and pigmented paints based on polyester binders PE1 to PE5 and cross-linked with melamine at a relative PE:HMMM concentration of 80:20 by weight.](image-url)
As mentioned in Section 3.5, the TiO$_2$ particles used here had been surface treated with Al$_2$O$_3$, SiO$_2$ and ZrO$_2$. Based on the above discussion, a hypothesis could be put forward that the surface treatment of the pigment resulted in relatively poor adhesion between particles and matrix, and that this was the reason for the increase in the tan\(\delta\) maximum from the DMA data. However, it is acknowledged that the results presented so far do not offer conclusive evidence for such an effect of the surface-treatment of the pigment. For that, further studies would be required using pigments with different surface treatments, and preferably at different volume concentrations as well.

10.6.3 Effect on stiffness

To determine the reinforcing effect of the pigment, the ratio of the modulus values of clear and white formulations was taken at temperatures both below and above \(T_g\). A comparison in the transition region was not attempted due to the sensitivity of results to temperature.

In the glassy region, the ratio of Young’s modulus of white over that of clear paints was taken at testing temperatures more than 15 °C below \(T_g\), and the average value is quoted here. The stiffness of the paints was shown to increase with the addition of pigment by a factor of 1.7 to 2.2 at low temperatures. These results were compared to predictions from models that consider the effect of the inclusion of a rigid inorganic phase in a polymer matrix.

Two of the available models were used, the Halpin-Tsai and the Lewis-Nielsen model (see equations (2.74) and (2.76)). The particular equations have been used in the past by the author to predict the change in stiffness of an epoxy matrix with the addition of rubber micro-particles [196]. For both models, knowledge of the Young’s modulus of the rigid inclusions was required. This was taken from the literature [197] as 283 GPa. For the matrix modulus, values from clear films at testing temperatures below \(T_g - 15^\circ C\) were used, and subsequently the average value of \(E_c/E_m\) in the glassy region was calculated. The volume fraction of the pigment in the paint was calculated as approximately 21% in every case, based on densities of 4000 kg/m$^3$ for the TiO$_2$ pigment and of 1060 kg/m$^3$ [105] for the clear paint-films. A shape factor, \(\zeta\), appears in
the Halpin-Tsai model that is related to the aspect ratio of the reinforcement. For spherical particles, as is the case in this study, this is set to 2 [70, 71].

The Lewis-Nielsen model makes use of a maximum volume fraction of the added particles, \( \varphi_{max} \). This takes values between 0.37 for randomly close-packed agglomerated particles, to 0.63 for good dispersion with random close-packing and 0.74 for hexagonal close packing with no agglomerates [14].

Finally, the Einstein coefficient, \( k_E \), in the Lewis-Nielsen model depends on the shape and dispersion of the particles, their adhesion to the polymer matrix as well as the Poisson’s ratio, \( \nu \), of the matrix. For well-dispersed spherical particles a value of \( k_E = 2.17 \) is given in [73], where a Poisson’s ratio of 0.35 was assumed as typical for polymers in their glassy state [14]. This \( k_E \) value assumes no slippage between matrix and particles and is expected to drop to 0.87 in the case of perfect slippage (again \( \nu = 0.35 \) is assumed). When agglomerates of particles are present, \( k_E \) is expected to increase in proportion to the agglomerate size and inversely to the packing order up to a value of 6.76 for randomly packed large agglomerates in an elastomer (\( \nu = 0.5 \)) matrix [14, 75]. Taking into account the Poisson’s ratio of the paints in their glassy region (\( \nu = 0.35 \)) this value becomes 5.86. Lee and Nielsen [76] note that slippage between the matrix and the agglomerates or between the particles comprising the agglomerates will again reduce the Einstein coefficient, even though no quantitative estimate for this decrease is given.

Here calculations were performed under three different scenarios for the glassy paints. First, randomly dispersed close packed particles were assumed with no slippage, which resulted in \( k_E = 2.17 \) and \( \varphi_{max} = 0.63 \). For the case where slippage occurs between the matrix and the particles, the Einstein coefficient was taken as 0.87. Finally, for random close-packed agglomerates adhering perfectly to the matrix, the maximum volume fraction became 0.37 and \( k_E = 5.86 \).

The predicted values of \( E_c/E_m \) from the Lewis-Nielsen model along with the experimental results are shown in Figure 10.28. The Halpin-Tsai prediction was essentially identical to the Lewis-Nielsen one for the case of well dispersed particles with good adhesion to the matrix (\( k_E = 2.17, \varphi_{max} = 0.63 \)) and is therefore not plotted in
order to maintain the clarity of the graph. Clearly the scenario for randomly close packed particles with poor adhesion to the matrix underestimates the stiffening effect of the pigment, while the assumption for close packed agglomerates perfectly bonded to the matrix overestimates it considerably. A better fit is obtained for the case of well dispersed particles perfectly bonded to the polyester.

In practice as was seen in Section 10.6.1, small clusters of particles are present in the paints meaning that the maximum volume concentration value should fall between 0.37 and 0.63, while the Einstein coefficient will be between 2.17 and 5.86 assuming good adhesion between the pigment and matrix. A less than perfect adhesion between particles and matrix was indicated by examination of maximum tanδ values in Section 10.6.2, which would suggest that a small value of $k_E$ should be used. However, this cannot be further quantified since the exact extent of slippage is not known, and neither is the reduction in $k_E$ due to slippage for agglomerated particles.

Also of interest was a comparison between the stiffness of the clear and white paints in the high temperature equilibrium region. In the case of unfilled thermoset polymers, the modulus in the rubbery plateau is a very important property as it can be correlated directly to the cross-link density of the material. For filled polymers, however, the rubbery modulus is greatly affected by the properties of the filler. In a variety of publications [188, 192, 198] it is suggested that the effect of particulate reinforcements in the rubbery region is more pronounced than in the glassy region, i.e. that $E_d/E_m$ in the rubbery region is higher than the respective ratio in the glassy region. Hagan et al. [198] report a modulus enhancement by a factor of 10 in the rubbery region for 20 vol% of TiO$_2$ pigment in a latex paint, which rose up to a factor of about 100 for a 40% concentration by volume. The respective values in the glassy region were approximately 1.6 and 2.5.
Effect of pigment on the mechanical properties of the paints

Figure 10.28. Graph showing experimentally observed increase in glassy modulus with 50 wt% pigment (bars) along with predictions from the Lewis-Nielsen model under three different scenarios regarding pigment dispersion and adhesion between pigment and matrix.

For the purposes of the present study the rubbery storage moduli (obtained from DMA) of clear and pigmented formulations were compared to investigate the reinforcing effect of TiO₂ particles at high temperatures. The stiffness of the formulations was found to increase by a factor of 1.8 up to 2.7, except in the case of PE4H₂O where the pigment seemed to have no reinforcing effect in the rubbery region (a small decrease was observed actually but it is difficult to place too much significance on this result due to the lack of a well-defined rubbery plateau for these formulations).

The $E_c/E_m$ values in the rubbery region are plotted along with those in the glassy region in Figure 10.29.

Clearly, even though there is generally a small increase in the reinforcing effect of the pigment in the rubbery region, the $E_c/E_m$ values in both cases are fairly similar and certainly no dramatic effects of temperature, as reported elsewhere, are seen here. In [192] and [116] it is proposed that the existence of an interphase surrounding the particles and its increased influence at high temperatures are responsible for the great increase in the stiffness of particulate filled polymers in the rubbery plateau. Hagan et al. [198] also proposed a mechanism where the pigment particles acted as anchor points between chains, thereby creating a network in the polymer matrix similar to a network of chemical cross-links which significantly increased the stiffness of the matrix at high temperatures.
10. Effect of pigment on the mechanical properties of the paints

Figure 10.29. Increase in Young’s modulus in the glassy and in the rubbery region for paints containing 50 wt% pigment.

For the materials studied here, recall from the discussion in Section 10.6.2 that the tanδ results presented therein could suggest poor adhesion between the TiO₂ particles and the polyester matrix, i.e. a weak interphase layer around the pigment. Therefore a lack of a fully developed interphase could explain also the relative insensitivity of the reinforcement factor to changes in temperature. On the other hand, for the highly cross-linked systems presented in this study, it is considered unlikely for the inter-particle distance to be smaller than the length between cross-links. Therefore pigment particles are not expected to act as bridges between chains and increase the effective network density or at least to the same extent as for the high molecular weight systems studied elsewhere [116, 198]. In all, even though initially the results on the reinforcing effect of pigment in the rubbery region seem to contradict those reported in the literature, they appear to be justifiable when taking into consideration the experimental findings reported here and the micro-structural characteristics of the particular systems. More specifically the degree of adhesion between particles and matrix will be further investigated in the following Sections.

10.6.4 Effect on large strain properties

For all the formulations examined in this study, the ultimate strain decreased with the addition of pigment. This can be explained by considering the difference in stiffness between the matrix and the TiO₂ particles. The rigid TiO₂ particles will only take a very small part of the total strain applied on the composite system which means that a higher fraction of the total strain is sustained by the polyester matrix. Thus for the same amount of macroscopically observed strain the actual elongation of the polymer
is greater in the case of filled than for unfilled polymers, and therefore the observed failure strains of the composite material will be lower than those of the matrix.

On the basis of the above argument Nielsen [80] attempted to quantify the decrease in ultimate strain by considering two scenarios; one where the particles are perfectly bonded to the matrix and one where there is no adhesion between the matrix and particles. For the case of good adhesion, a simple relationship is given for strain at failure (see equation (2.83)), as a function of volume fraction of particles. When debonding of particles is possible the decrease in failure strain with added filler is expected to be less pronounced [14, 80].

In Figure 10.30 the ratio of the failure strain of white samples over that of clears is plotted against test temperature for all formulations and for test temperatures 10 °C below $T_g$ or lower. Even though in theory there is no reason not to expand the comparison to higher temperatures, this was not attempted as in the visco-elastic region mechanical properties are very sensitive to changes in temperature and therefore a comparison between results would be less straightforward. The Nielsen model prediction from equation (2.83) is also plotted.

Despite there being some scatter in the data in Figure 10.30, certain observations can be made. Firstly, the white paint based on binder PE2 consistently showed the greatest decrease in ultimate strain compared to the clear. The higher than unity values in the case of the PE5 formulations are considered suspect. Under certain conditions, for example when rigid particles are responsible for additional plastic deformation mechanisms in brittle matrices, an increase in the failure strain with filler content is indeed reported [199, 200]. However, no apparent reason exists of why this should be the case for the white films based on PE5 and not for the rest of the formulations. Finally, the prediction from equation (2.83) falls on the lower limit of the failure strain of the pigmented formulations, where an assumption was made for perfect bonding between the matrix and the particles.
Figure 10.30. Ratio of failure strain of white paints over failure strain of clear paints at different testing temperatures and comparison with prediction based on assumption of perfect adhesion of the particles to the matrix. Paints are based on binders PE1 to PE5.

As discussed in Section 2.4.3.1, Nielsen [14, 80] has proposed that a smaller decrease in the failure strain is to be expected in the case of weak adhesion. Experimental evidence for such an effect has been reported by Boluk and Schreiber [201], who found that for composites of chlorinated polyethylene containing TiO$_2$ particles, the failure strain was inversely correlated to the degree of adhesion between the particles and the matrix. On that basis it could be argued that the higher $\varepsilon_{c,u}/\varepsilon_{m,u}$ values reported here could indicate a weak particle-matrix interface. However, other researchers (see [82] and also Section 2.4.3.2 of this study), have derived predictions that give similar reductions for failure strain irrespective of the strength of the interface. In light of the above discussion, it is suggested that the failure strain data presented here provide an indication but cannot be thought as sufficient evidence of a weak particle-matrix interface in the pigmented formulation.

Regarding tensile strength, in a comprehensive review paper Fu et al. [63] discuss three factors that influence the strength of particulate filled composites; namely particle size, particle volume fraction and degree of adhesion of the particles to the matrix. For the results presented here, of greater interest is the influence of filler-matrix adhesion. Generally, well bonded particles to the matrix will have a reinforcing effect, resulting in strength equal to or greater than that of the bulk polymer. Conversely, the strength of the composite will decrease as the adhesion becomes worse. For coatings, this was demonstrated in a study [202] on acrylic/melamine top-coats where different pigments and surface treatments were used to vary the adhesion between matrix and particles. The main reinforcing mechanism was found to
be crack-pinning, i.e. bowing of the crack front as it is impeded by rigid impenetrable particles, which was negatively affected by both poor adhesion of the particles to the matrix and by the formation of agglomerates.

The above discussion on the reinforcing effect of rigid inclusions in polymer matrices has been based mainly on the study of glassy polymers (see [63] and references therein). Also of interest, however, is the distinctive change in behaviour when the paints were tested at higher temperatures, i.e. the much higher strength shown by pigmented formulations in this region. This has already been linked (see Sections 10.1 to 10.5) to an apparent increase in the degree of strain hardening for the TiO\textsubscript{2} paints. Bueche [203] proposed for the increase in tensile strength of carbon black and silica modified SBR vulcanizates, a mechanism where the redistribution of stresses due to the breaking of a single chain is affected by the presence of the filler particles ultimately resulting in a higher strength for the composite material. Once more, the above argument is based on an assumption of good adhesion between the pigment particles and the polymer matrix.

Regarding the energy consumed by the tearing of pigmented samples, it is shown in Figure 10.31 as well as in Table 10.3 that no uniform trend exists for all formulations. For paints based on binder PE1 and PE2 an increase in the essential work of fracture is seen with the addition of pigment, while no effect is observed in the case of PE3 and PE4 (also considering the associated error bars). Regarding the inelastic component of the work of fracture this seems to increase with the addition of pigment for all formulations, even though again some scatter in the data exists obscuring the results.

In trying to explain the observed fracture behaviour of the paints, a difficulty lies in the relative lack of published data on particulate reinforced polymers undergoing large inelastic deformations. For glassy polymers reinforced with rigid inclusions, an increase in toughness has been reported that has often been attributed to a crack pinning mechanism [63]. Regarding the effectiveness of the particles at toughening the matrix, it is reported that matrix-particle adhesion is of little importance for brittle matrices but this importance increases with the increasing ductility of the matrix [63, 204]. In the latter case the toughness is seen to drop with decreasing degree of adhesion.
between the particles and matrix as the poorly bonded rigid inclusions reduce the
effective cross-section of the sample. Experimentally, a decrease in the impact
toughness of the composite compared to that of the bulk material is shown in [205] as
a result of the poor adhesion between the nano-silica filler material and the nylon 6
matrix used.

When it comes to materials more relevant to the present study, the effect of pigment
on the toughness of coatings has been found to depend on the strength of the
adhesion between particles and matrix [202], and on the dispersion of the particles
[202, 206]. An improvement of particle-matrix adhesion increases the toughness of the
paint, while the presence of large agglomerates tends to decrease it.

If an overall trend can be drawn from the essential work of fracture data shown in this
study, this would be that the addition of TiO₂ particles did not result in a decrease of
the fracture toughness of the paints. The toughness was either improved or remained
 unaffected. Based on this observation and on the preceding discussion, it would seem
that at least some degree of adhesion exists between the pigment and the cross-linked
polyester. Especially since toughness would already be expected to decrease due to
the presence of agglomerates, clearly shown on the SEM micrographs in Section
10.6.1. On the other hand, an increase in the inelastic component of the total work is
shown with addition of pigment. This observation fits well with the trend observed in
the tanδ maxima obtained from DMA, which was attributed to additional energy-
damping mechanisms possibly due to the presence of a weak matrix/particle
interphase.

![Figure 10.31. Essential work of fracture (a) and inelastic component of work (b) for clear and pigmented paints based on binders PE1 to PE4.](image-url)
10. Effect of pigment on the mechanical properties of the paints

Table 10.3. Essential work and inelastic component of fracture for clear and pigmented versions of formulations based on binders PE1-PE4. All formulations tested at their respective glass transition temperatures.

<table>
<thead>
<tr>
<th>Formulation</th>
<th>$w_e$ [kJ/m$^2$]</th>
<th>$\theta w_{inel}$ [MPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PE1H20</td>
<td>5.7 ±1.0</td>
<td>1.32 ±0.13</td>
</tr>
<tr>
<td>PE1H20Ti</td>
<td>13.7 ±1.5</td>
<td>1.98 ±0.17</td>
</tr>
<tr>
<td>PE2H20</td>
<td>4.4 ±0.7</td>
<td>0.80 ±0.08</td>
</tr>
<tr>
<td>PE2H20Ti</td>
<td>10.2 ±1.0</td>
<td>0.90 ±0.11</td>
</tr>
<tr>
<td>PE3H20</td>
<td>12.9 ±1.4</td>
<td>1.86 ±0.17</td>
</tr>
<tr>
<td>PE3H20Ti</td>
<td>12.2 ±1.7</td>
<td>2.57 ±0.19</td>
</tr>
<tr>
<td>PE4H20</td>
<td>16.9 ±5.3</td>
<td>3.8 ±0.54</td>
</tr>
<tr>
<td>PE4H20Ti</td>
<td>12.8 ±4.0</td>
<td>4.58 ±0.46</td>
</tr>
</tbody>
</table>

10.6.5 Strain and recovery tests

Strain and recovery tests were performed on samples of all pigmented formulations at $T_g$, to study the effect of pigment on the ability of the paint to recover from post-yield strains. In Figure 10.32 the obtained stress versus strain traces are shown, and are compared to the respective traces of the clear paints. As with all the clear formulations, the recovered strain in the case of pigmented samples was found to be higher than the yield strain, while in every case no residual strain was observed two hours after testing. When comparing between pigmented and clear paints, the ratios $\varepsilon_{el}/\varepsilon_{max}$ and $W_{el}/W_{tot}$ of the white samples are seen to follow closely those of the clears (see Figure 10.33), and the general impression is that the pigment does not have a great effect on the tendency of the paints for elastic recovery. If a comparison is made between individual pairs of formulations (e.g. PE1H20 versus PE1H20Ti etc.), the trend in Figure 10.33 (b) appears to be for a small decrease in the ability of the paints to store energy elastically ($W_{el}/W_{tot}$ decreased in all cases except PE3H20 with the addition of pigment). The results for the amount of recovered strain, seen in Figure 10.33 (a), are more ambivalent; with an increase in $\varepsilon_{el}/\varepsilon_{max}$ with pigment in two cases (PE2H20 and PE3H20), and a decrease for the other three pairs of paint. The results of the strain and recovery testing of the pigmented formulations are given in Table 10.4, where the respective results from the clear paints are also shown for comparison.
10. Effect of pigment on the mechanical properties of the paints

Figure 10.32. Strain and recovery traces for clear and pigmented formulations based on binders PE1-PE5 (plots (a)-(e)).

Figure 10.33. Ratio of recovered to total strain, $\varepsilon_{el}/\varepsilon_{max}$, and ratio of elastic to total supplied work, $W_{el}/W_{tot}$, for clear and pigmented formulations based on binders PE1-PE5.
10.6.6 Cyclic loading and particle-matrix adhesion

Following the discussions in previous Sections, regarding the degree of adhesion between the pigment particles and the polyester matrix, it was decided to perform a number of additional tests in an attempt to obtain a better understanding of the issue. Smith [81] used dilatometry to investigate the debonding of carbon-black particles from a rubber matrix. He found an increase in the volume of the composite sample which he attributed to the formation and subsequent expansion of cavities around particles no longer adhering to the matrix. An alternative approach involves stretching the composite sample up to different strains, then unloading back to zero load and finally re-loading. If debonding between particles and matrix has occurred, the re-loading part of the stress versus strain data is expected to show softening of the material, which should be evident from a decrease in the slope of the initial linear part of the stress versus strain curve. This softening due to damage in the particle-matrix interface is a special case of what is commonly referred to as the Mullins effect (for a review see [207]).

Here, samples of both pigmented and clear films were stretched at $T = T_g$, up to various strains chosen to correspond to 15, 30 and 60% of the strain at failure observed from tensile tests at the same temperature. In some cases, additional higher strains were attempted that approached the failure strain of the formulation. After each strain
increment the samples were unloaded and subsequently were immediately reloaded up to the next strain increment. The Young’s modulus was measured from the initial linear part of each loading cycle and a comparison was made between the value of the first cycle and this of subsequent cycles. The stress versus strain curves obtained can be found in Figure 10.34.

From the analysis of data presented in Figure 10.34 an increase was found in the Young’s modulus when comparing the initial loading cycle to subsequent cycles. This increase was also more or less independent of the number of cycles that the sample was subjected to, i.e. the Young’s moduli measured for all cycles after the initial one were approximately the same. Thus, an average value from all cycles beyond the first loading was calculated. The ratio of this average value over the initial Young’s modulus is plotted in Figure 10.35.

Regarding the observed increase in the Young’s modulus of pre-strained samples, this can be attributed to the stretching of the polyester chains during the first cycle. This conclusion is reached by looking at the data obtained from clear samples. For the white paints, both the stretching of chains and the debonding of pigment particles from the polyester matrix can affect the Young’s modulus of the stress versus strain curve, albeit towards opposite directions. Therefore, even though the total effect is for an increase in Young’s modulus for pre-stretched samples, it cannot be ruled out that some debonding occurred but was overshadowed by the stretching of the chains. Interestingly, the increase in stiffness is similar for both bulk and composite samples (except in the case of samples based on binder PE5 where the white shows a markedly greater increase). This might suggest that no additional mechanisms, such as particle debonding, are in effect during the cyclic loading of the pigmented samples, but it can hardly be regarded as sufficient evidence.

In an attempt to isolate the effect of pigment-matrix adhesion from that of chain pre-stretching an additional test was performed. For this, samples of PE1H20 and PE1H20Ti were stretched at $T_g$ (35 °C) to about 35% strain. They were subsequently unloaded, removed from the tensile clamps and left to relax, inside the environmental chamber, until the residual strain was zero. The samples were then left for an additional period
of time (approximately five hours) outside the environmental chamber before being tested again in tension at 35 °C and 50% RH. The resulting stress versus strain traces from these tests are presented in Figure 10.36.

In terms of Young’s modulus this is seen to decrease in the case of the clear sample (from 280 to 188 MPa), whereas an increase is seen for the white paint (from 406 to 550 MPa). Of interest is that, beyond the initial linear region, in both cases a decrease in the stress required for a given level of strain is seen. To verify these results the tests were repeated. The stress versus strain curves in each case were almost identical to those presented in Figure 10.36 and thus are not presented here. The only difference in that second set of tests was that now a slight decrease in the Young’s modulus of the white sample from 565 to 525 MPa was observed. Thus, a comparison between the first and second load Young’s modulus values did not appear to give conclusive evidence of either debonding or good adhesion between the matrix and particles.

At this point, it was decided to focus on the post-yield behaviour of the paints, that in every case showed a clear softening effect (Mullin’s effect). Roland [180] commented on the behaviour of cross-linked rubbers subjected to multiple loading cycles, that unless cross-links break during the initial cycles no strain softening is expected to be observed in subsequent loadings. In this light, the undisputed softening observed in the case of the clear, PE1H20, will be attributed to damage sustained by the elastic network during the first loading of the sample. On the other hand, the strain softening observed by looking at the data from the pigmented formulation, could again be the result of two different mechanisms; i.e. the breaking of cross-links as in the case of the clear or the de-bonding of TiO$_2$ particles from the polymer matrix, a process that would be unique for the white formulation. Interestingly, the clear sample showed greater softening around the yield region while at higher strains both formulations suffered similar degrees of reduction in stress. This would seem to suggest that no significant additional damage takes place in the presence of the TiO$_2$ particles.
10. Effect of pigment on the mechanical properties of the paints

Figure 10.34. Cyclic loading of clear and pigmented samples based on formulations PE1 to PE5 (plots (a) to (e)).

Figure 10.35. Relative increase in Young’s modulus for subsequent cycles after initial loading of clear and pigmented samples based on binders PE1 to PE5.
10. Effect of pigment on the mechanical properties of the paints

Figure 10.36. Cyclic loading where samples were left to relax between first and second load for formulations PE1H20 (a) and PE1H20Ti (b). Tests performed at 35 °C.

10.7 Chapter summary

A comparison between the mechanical properties of pigmented and clear paint films was attempted in the preceding paragraphs. For this purpose, 50 wt% TiO$_2$ particles were added to formulations based on different polyester binders cross-linked with HMMM at a 80:20 PE:HMMM ratio. The dispersion of pigment was shown to vary from individual particles to agglomerates of up to around twenty particles.

The addition of pigment to the paints generally had no effect on the glass transition temperature or the width of the glass transition region. However, a clear increase in $\tan\delta$ was observed from DMA for pigmented paints. This was attributed to a possible weak interphase between particles and polyester matrix, resulting in additional energy damping.

The stiffness in the glassy region increased by around 1.7 to 2.3 times with the addition of pigment. A similar (if slightly higher) increase was seen in the rubbery region. The relative insensitivity of the stiffening effect on temperature served also as an indication of a weak or poorly developed interphase. The ultimate strain was found to decrease for the pigmented samples, throughout the entire temperature range. When these results were compared with predictions from a model where a perfect adhesion between matrix and particles is assumed, the model generally appeared to underestimate the ultimate strain of the composite materials. The tensile strength on the other hand remained unaffected in the glassy region, and actually increased at temperatures above $T_g$ with the addition of pigment. Finally, the essential work of
fracture required for the tearing of samples either increased or was left unaffected by
the addition of the TiO$_2$ particles.

In order to further investigate the matrix-particle adhesion, samples were subjected to
multiple cycles of strain, where they were stretched up to a certain point, unloaded
and immediately reloaded up to the next strain step. It was hypothesized that for
pigmented samples, the Young’s modulus would decrease for subsequent cycles after
the initial loading, due to debonding of the particles. However, this was not observed
experimentally, and on the contrary an increase of the Young’s modulus after the
initial loading was seen for both bulk and composite samples. This was attributed to a
stiffening effect due to the stretching of chains after the initial loading.

It was then decided to conduct a cyclic loading experiment, where sufficient time was
allowed between the two loadings for the samples to return to their original length
and relax completely. These tests showed strain softening beyond the yield point for
both the clear and the white samples. Although in the presence of pigment such an
observation would suggest the occurrence of damage between particles and matrix,
the similar behaviour of the clear film showed a cross-link breaking mechanism to also
be in effect. It was therefore not possible to prove the existence of a weak, prone to
de-bonding, interface between the TiO$_2$ particles and the polyester matrix.

In general the addition of 50 wt% TiO$_2$ particles was not found to have a significant
effect on the mechanical properties of the paints. In that respect, it may be expected
that panels coated with clear and pigmented versions of the paints will suffer similar
amounts of damage. This is shown in Chapter 12, where discrepancies between the
expected and the observed performance of (white) coated panels are also discussed.
Chapter 11. Time dependence and modelling of the mechanical response of the paints

In the following, the focus will be on one hand on determining the correspondence between temperature and time effects on the (small and large-strain) mechanical properties of the paints, and on the other hand on predicting the stress versus strain behaviour of the paints over the entire strain-range of a tensile test. For the former, multi-frequency DMA tests will be employed to demonstrate the superposition of time and temperature effects on small-strain properties and to determine the shift factors required for this superposition. Tensile tests at different displacement rates and temperatures will be conducted on samples of the control formulation, PE1H20, in an attempt to investigate the possibility of extending the use of these shift factors to large strains as well. Relaxation tests are used to determine the distributions of relaxation times of the materials.

Regarding the second objective set in this Chapter, the prediction of the tensile stress versus strain behaviour of the paints is of great importance, as the results obtained here could be used in the future in the context of a finite element analysis to simulate the behaviour of coated panels under deformation. The model used to predict the tensile behaviour of the paints contains a visco-elastic and a hyper-elastic component as discussed in Section 2.2.3. For the visco-elastic part of the model the parameters calibrated at small strains with the use of DMA and relaxation tests will be used. The hyper-elastic component will be of the three-term Ogden form (see equation (2.49)) and the relevant parameters are calibrated against experimentally obtained tensile data of the paints.
Due to time constraints it was not possible to apply these treatments to every system investigated in this study. Instead it was chosen to use a selection of the clear paints, namely PE1H10-30 and PE4H20, and the pigmented formulations PE1H20Ti and PE4H20Ti. These particular formulations were chosen as they were found to cover a wide range of mechanical behaviours that could additionally be explained as resulting from differences in cross-link density. However, it is noted that, in principle, there is no reason why the following discussions could not be also extended to the rest of the formulations investigated in this study.

11.1 Time dependence of mechanical properties (small strains) - DMA

The small-strain time dependence of the behaviour of the paints was studied with the use of multi-frequency DMA. The objectives were first to demonstrate this time dependence, and second to obtain the shift factors required for the superposition of time and temperature effects on material properties. The procedure followed in analysing the multi-frequency DMA data will be presented here in detail for the control formulation, PE1H20, whereas only the main results will be presented for the rest of the formulations. For the experimental settings used in the multi-frequency DMA tests the reader is referred to Section 4.2.3, while a discussion on time-temperature superposition is given in Section 2.2.1.3.

In Figure 11.1 multi-frequency storage modulus and tan\(\delta\) data of PE1H20 are plotted versus temperature. As expected the behaviour of the paint is seen to be independent of the loading-rate both in the glassy and in the rubbery region. In the transition region on the other hand, the dependence of both storage modulus and tan\(\delta\) on frequency is clear, and is seen as a shift of both traces towards higher temperatures with increasing frequency. The glass transition temperature (taken at the maximum of tan\(\delta\)) changes from 52 °C at 0.1 Hz, to 57 °C at 1 Hz and 63 °C at 10 Hz.
11. Time dependence and modelling of the mechanical response of the paints

The storage modulus data in Figure 11.1 (a) can then be re-organised in the form of isotherms versus the inverse of frequency, that corresponds to the time required for the completion of one loading cycle. Therefore, three different times, 0.1, 1 and 10 s, correspond to a particular temperature. The plot of the storage modulus isotherms is given in Figure 11.2 (a). These data were then shifted with respect to the 35 °C isotherm to produce a master-plot of storage modulus extending over many decades of time (see Figure 11.2 (b)). For the construction of the master-plot the isotherms were shifted according to:

\[
\log t_{\text{ref}} = \log t_T + \log \frac{1}{a_T}
\]  

(11.1)

where \(t_{\text{ref}}\) is the new time resulting from the shifting of the isotherm at \(T\) with respect to the reference temperature \(T_{\text{ref}}\). \(t_T\) is the time corresponding to the isotherm at \(T\) before the shift, and \(a_T\) is the shift factor. Here, \(T_{\text{ref}} = T_g\) was chosen in every case.

The experimentally obtained shift factors for PE1H20 are plotted in Figure 11.3 (a). These data can then be fitted with equations (2.7) and (2.9) in order to obtain the material parameters \(\delta H\), \(C_1\) and \(C_2\). \(\delta H\) is obtained directly by fitting the Arrhenius equation to the \(a_T\) versus temperature plot for \(T < T_g\). For \(C_1\) and \(C_2\) a plot of \(-(T-T_g)/\log(a_T)\) versus \(T-T_g\) needs to be made first, for \(T > T_g\) (Figure 11.3 (b)). The data points on this plot should approximately fall on a straight line if the material follows the WLF equation [27]. The WLF constants can then be obtained by observing that \(C_1\) is equal to the reciprocal of the slope of the line and \(C_2\) is obtained as the product of \(C_1\) times the intercept.
11. Time dependence and modelling of the mechanical response of the paints

Figure 11.2. Isotherms (a) and master-plot (b) of storage modulus versus the logarithm of time.

Figure 11.3. Logarithm of experimental shift factors versus $T - T_g$ where the predictions of the Arrhenius and WLF equations are shown (a) and plot of $-(T - T_g)/\log(a T)$ versus $T - T_g$ used for the determination of the WLF constants.

From the above method a $\delta H$ value of 405 kJ/mol was found, while $C_1$ and $C_2$ were determined as 47 and 240 K respectively for PE1H20. In Figure 11.3 (a) it is clearly seen that the Arrhenius equation provides a good fit to the experimental shift factors at temperatures below the $T_g$ of the formulation, but fails to predict the shift at temperatures higher than $T_g$. The opposite is true for the WLF fit to the data, which improves at temperatures above the glass transition. Moreover, it is seen that the prerequisite for linearity in Figure 11.3 (b) is satisfied.

The Arrhenius and WLF constants were determined likewise for a selection of the formulations investigated in this study and the results are given in Table 11.1. Knowledge of the time-temperature superposition (TTS) constants for these formulations means that their mechanical behaviour can now be predicted over a wide range of loading rates and temperatures, provided that it is given at a reference temperature or loading rate. At this point a comment regarding the precision in the determination of the TTS constants needs to be made, with respect to the practical difficulties arising from the multi-frequency DMA testing of thin polymer samples.
In Figure 11.4 the multi-frequency storage modulus data of sample PE1H10 are shown, along with the resulting master-plot of storage modulus versus time. The main concern is the sharp step-decrease in storage modulus between approximately 30 and 40 °C. This is not a unique feature of the multi-frequency DMA data. It was also shown for the single-frequency DMA data of PE1H10, and was attributed to a temporary decrease of the static to dynamic force ratio below unity. However, whereas this does not affect the single-frequency results significantly, it can have a bigger effect on the construction of the storage modulus master-curve and subsequently on the determination of the TTS constants. Generally, where such irregular storage modulus traces were obtained, the test was repeated in an attempt to alleviate the problem. This was not possible in the case of PE1H10, however, and it was decided to perform the time temperature superposition acknowledging this short-coming in the testing procedure. As will be shown below, it was possible to consider the TTS data collectively for all the formulations, and therefore the influence of the uncertainty in the data of PE1H10 on the collectively determined shift factors is minimal.

In Figure 11.5 (a) it is shown that despite the differences in the values of the TTS constants for each formulation, a plot of the experimentally obtained shift factors versus T-Tg reveals the shift factors to be fairly similar irrespective of the particular formulation. Based on this observation it seemed reasonable to attempt to determine the ‘average’ TTS constants collectively from all formulations instead of focusing on each one specifically. To achieve this, $\delta H$ was optimised simultaneously for all formulations, while a collective plot of $-(T-T_g)/\log(\alpha_T)$ versus T-Tg was created for the determination of the WLF constants, $C_1$ and $C_2$ (see Figure 11.5 (b)).

The resulting TTS constants based on all available data were $\delta H = 395$ kJ/mol, $C_1 = 17$ and $C_2 = 76$. This method of calculation of the TTS constants has the disadvantage that subtle differences in the $\alpha_T$ values of the different samples could potentially be lost. On the other hand, this averaging method could actually improve the estimate of the constants in those cases where the experimental data appear erroneous, as seen for formulation PE1H10. In any case, the very close $\alpha_T$ values of the different formulations with respect to T-Tg warrant the use of such ‘global’ constants.
Table 11.1. Arrhenius (δH) and WLF (C₁ and C₂) time-temperature superposition constants for selected paint formulations.

<table>
<thead>
<tr>
<th>Formulation</th>
<th>δH [kJ/mol]</th>
<th>C₁</th>
<th>C₂</th>
<th>Formulation</th>
<th>δH [kJ/mol]</th>
<th>C₁</th>
<th>C₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>PE1H20</td>
<td>405</td>
<td>47</td>
<td>240</td>
<td>PE1H20Ti</td>
<td>370</td>
<td>17</td>
<td>80</td>
</tr>
<tr>
<td>PE4H20</td>
<td>355</td>
<td>14</td>
<td>51</td>
<td>PE4H20Ti</td>
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<td>12</td>
<td>48</td>
</tr>
<tr>
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<td>12</td>
<td>48</td>
<td></td>
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<tr>
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<td>161</td>
<td></td>
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</table>

TTS constants based on all available data

<table>
<thead>
<tr>
<th></th>
<th>δH [kJ/mol]</th>
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<th>C₂</th>
</tr>
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<td></td>
<td>395</td>
<td>17</td>
<td>76</td>
</tr>
</tbody>
</table>

Figure 11.4. Plot of storage modulus versus temperature obtained from multi-frequency DMA test of formulation PE1H10 (a) and master plot of storage modulus versus the logarithm of time after the application of time-temperature superposition for the same formulation (b).

Figure 11.5. Logarithm of experimental shift factors versus T-T_g (a) and plot of -(T-T_g)/log(α) versus T-T_g used for the determination of the WLF constants (b). Data from all formulations tested in multi-frequency DMA are shown.

Another concern regarding the DMA multi-frequency testing method is that the data were not collected under isothermal conditions, but under a 2 °C/min ramp. As explained in Section 4.2.3 this was necessary due to the lack of automated control of the cooling apparatus connected to the DMA, which made it impossible to maintain iso-thermal conditions at temperatures below ambient.
To investigate the effect of the temperature ramp on the results, a sample of PE1H20 was tested in multi-frequency DMA at temperatures ranging from about 10 to 120 °C at temperature steps of 5 °C. Between temperatures, a temperature ramp of 1 °C/min was applied and at each temperature the sample was kept at isothermal conditions for 3 minutes before the actual data collection. For the 3 lowest temperatures the conditions were only nearly isothermal and an increase in temperature of about 0.2 °C was found between the 0.1 Hz measurement and the 10 Hz measurement. At temperatures above ambient, precise control of temperature was achieved and conditions were found to be iso-thermal. The storage modulus and tanδ versus temperature plots obtained from this test are shown in Figure 11.6.

The glass transition temperature is now seen to change from 50 °C at 0.1 Hz to 55 °C at 1 Hz and 60 °C at 10 Hz. The somewhat lower values compared to the non-isothermal results were expected, as the application of a temperature rate in DMA is known to increase the observed T_g. Following the same procedure as previously, a master-plot of storage modulus versus time was created from the isothermal data (Figure 11.7). When a comparison is made between the isothermal and non-isothermal master-plot, the two are seen be in very good agreement, although a somewhat smoother overlap was achieved from the isothermal test. The shift factors from the two tests are compared in Figure 11.7 (b) and again they are seen to be in good agreement, while the TTS parameters were calculated as $C_1 = 19$, $C_2 = 68$ and $\delta H = 450 \text{ kJ/mol}$ in the isothermal case. Based on these data it is concluded that the choice of non-isothermal conditions for the multi-frequency DMA tests should not influence the values of the TTS parameters significantly.

Figure 11.6. Storage modulus (a) and tanδ (b) versus temperature, obtained from iso-thermal multi-frequency DMA test of formulation PE1H20.
11.2 Time dependence of mechanical properties (small strains) - Relaxation

In the preceding Section the small strain time-dependent properties of the paints were examined with the use of multi-frequency DMA, with the focus being on the correspondence between time and temperature on material behaviour. Here, the dependence of properties on the variable of time will be examined more directly through relaxation experiments (for a description of the experimental procedure see Section 4.5). Tests were performed at two temperatures, i.e. T_g-15 °C and T_g. The experimentally obtained relaxation data at T_g were then fitted with the prediction from equation (2.55) where \( \sigma_0 \) was set to follow purely elastic (\( \sigma_0 = E(0)e \)) instead of hyper-elastic behaviour as discussed below. After the distribution of relaxation times was determined, it was shifted according to the Arrhenius equation to fit the relaxation data at T_g-15 °C, where the ‘global’ \( \delta H \) value from Section 11.1 was used.

Regarding the decision to neglect the contribution of non-linear effects in the calibration of the distribution of the relaxation times, the choice was made in view of the relatively small strains involved in the relaxation experiments. Upon initial attempts to model the relaxation behaviour by including a hyper-elastic component it was found that the latter had a negligible contribution to the prediction at such low strain. It was assumed therefore that the material behaviour at a strain of approximately 1 % could reasonably be regarded as strain-independent and therefore
it should be possible to describe the behaviour of the material by ignoring any effects of hyper-elasticity.

For the modelling of the relaxation behaviour according to equation (2.55), knowledge of the instantaneous modulus $E(0)$ as well as of the rubbery weight factor $g_e$ is required. The latter is calculated simply as $E_e/E(0)$ where $E_e$ is the rubbery modulus. The instantaneous modulus will be taken as the Young’s modulus in the glassy region as measured from tensile testing. More specifically, for each formulation, the average of the modulus values at temperatures 15 °C below $T_g$ or lower is calculated. For the rubbery modulus the values obtained from single frequency DMA will be used. These experimentally obtained constants are shown in Table 11.2. The weights, $g_i$, are then the parameters to be optimised. For the optimisation, 18 relaxation times were used with a spacing of one order of magnitude between them. The optimization process was performed using the solver routine in Excel by minimizing of the relative square error between the model prediction and experimental data.

Upon initial attempts to model the relaxation behaviour of the paints it was found that the solver would converge to slightly different solutions depending on the initial values used in the optimization. Furthermore, due to the random shape of the distribution of relaxation times it was not easy to compare between formulations. For these reasons it was decided to constrain the weights, $g_i$, to conform to the generalised Cole-Cole distribution given in equation (2.23). This meant that the general shape of the distribution of relaxation times was now constrained and the number of optimisation parameters reduced to just two, namely $c$ and $d$ in the generalized Cole-Cole equation (Table 11.2). The experimental relaxation data along with the predictions from equation (2.55) are shown in Figure 11.8 ((a) and (c)). The resulting distributions of relaxation times are also shown (Figure 11.8 (b) and (d)). A first comment concerns the generally good agreement between the model and the experimental data. It needs to be noted that if it is chosen to optimise the weights $g_i$ without constraining the shape of the distribution, the agreement can be further improved. However, for the reasons mentioned above, it is decided to keep the generalised Cole-Cole distribution of relaxation times, especially since this is found to fit the data reasonably well.
In comparing between the different formulations it is interesting to note that the relaxation behaviour generally reflects the observations from the single-frequency DMA testing of the samples. For the formulations with varying HMMM content the relaxation clearly takes place over a broader range of times as the concentration of HMMM increases. This becomes particularly obvious from examination of the respective distributions of relaxation times that is in direct analogy to the tan\(\delta\) versus temperature traces obtained from DMA. Similarly, the addition of pigment to formulation PE1H20 results in a narrower distribution of relaxation times. On the other hand, the width of the transition does not appear to be affected by the addition of pigment to PE4H20, an observation that again agrees with the findings from DMA.

Table 11.2. Visco-elastic constants used in the modelling of the relaxation behaviour of selected paint formulations.

<table>
<thead>
<tr>
<th>Formulation</th>
<th>(E(0)) [MPa]</th>
<th>(E_e) [MPa]</th>
<th>(c)</th>
<th>(d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PE1H20</td>
<td>2070</td>
<td>9</td>
<td>0.47</td>
<td>0.51</td>
</tr>
<tr>
<td>PE4H20</td>
<td>1900</td>
<td>5</td>
<td>0.64</td>
<td>0.68</td>
</tr>
<tr>
<td>PE1H10</td>
<td>2440</td>
<td>6</td>
<td>0.60</td>
<td>0.63</td>
</tr>
<tr>
<td>PE1H30</td>
<td>2180</td>
<td>20</td>
<td>0.27</td>
<td>0.31</td>
</tr>
</tbody>
</table>

Figure 11.8. Relaxation data obtained experimentally and from equation (2.55) for formulations PE1H10, PE1H20, PE1H30 and PE1H20Ti (a), and PE4H20 and PE4H20Ti (c). Also shown are the resulting distributions of relaxation times in (b) and (d).
Having calibrated the distribution of relaxation times against experimental data at \( T_g \) it was sought to obtain a prediction of the relaxation behaviour at a testing temperature of \( T_g - 15 \, ^\circ\text{C} \). For this, the weights, \( g_i \), were kept as obtained from the calibration at \( T_g \) while the relaxation times \( \tau_i \) were shifted according to the Arrhenius equation with \( \delta H \) equal to the global value of 395 kJ/mol. The result of this shift of the relaxation times is shown in Figure 11.9 for the control formulation, PE1H20. The effects of lowering the testing temperature on the relaxation behaviour, and more specifically on the agreement between the model and experimental data are shown in Figure 11.10.

In every case lowering the temperature to \( T_g - 15 \, ^\circ\text{C} \) (formulation PE4H20Ti was tested at \( T_g - 10 \, ^\circ\text{C} \), as the samples broke below 1 % strain at lower temperatures) resulted in higher peak stresses on the relaxation curves while the time required for relaxation was significantly prolonged. Regarding the use of the shifted relaxation times to predict the low temperature behaviour, it is seen that the agreement with the experimental data varies. Qualitatively the shifting of the distribution of \( g_i \) values towards longer times does result in an increase in the peak stress and in a slower relaxation of the applied stress. However, from a quantitative point of view, good agreement between model and experiment is seen only towards the longest relaxation times of formulations PE1H20, PE1H30, PE1H20Ti and PE4H20Ti (Figure 11.10 (b), (c), (e) and (f)), while agreement is poor in the case of PE1H10 and PE4H20 ((a) and (d)).

![Figure 11.9. Plot showing distribution of relaxation times as obtained at 35 °C (approximately \( T_g \)) and shifted to 20 °C (approximately \( T_g - 15 \, ^\circ\text{C} \)) according to Arrhenius equation, with \( \delta H = 395 \, \text{kJ/mol} \).](image-url)
Figure 11.10. Comparison of experimentally observed and theoretically predicted stress relaxation at $T_g-15$ °C for formulations PE1H10 (a), PE1H20 (b), PE1H30 (c), PE4H20 (d), PE1H20Ti (e) and at $T_g-10$ °C for PE4H20Ti (f). The experimental relaxation data at $T_g$ are also shown for comparison.

The reasons for the discrepancies between the experimental data and the model predictions are not clear. Changing the value of the Arrhenius parameter, $\delta H$, was attempted, but this was not found to improve the results significantly. The underestimation of the peak stress that was common for all formulations was found to be addressed if a higher $E(0)$ value was chosen. However, it is not considered desirable to treat these material constants as optimization parameters, and thus these attempts at improving the fit of the model will not be discussed further.

Regarding the better fit of the model at longer times, this could be a result of the temperature chosen for the calibration of the relaxation times, and of the limitations
imposed by the sampling rate of the tensile machine. The experimental time range between $10^{-1}$ and $10^4$ s at $T_g$-15 °C corresponds to times between $3.8 \times 10^{-5}$ and $3.8 \times 10^0$ s at $T_g$ when an Arrhenius relationship is assumed with $\delta H = 395$ kJ/mol. However, practically, it was not possible to obtain data at times shorter than $10^{-1}$ s due to the limitations imposed by the instrumentation used. Therefore, the poor fit of the model to the experimental data at $T_g$-15 °C, at times shorter than $10^2$ s could be attributed to the poor calibration of the relaxation times in the glassy regime. On the other hand, times longer than $10^2$-$10^3$ at $T_g$-15 °C correspond more closely to the range used for calibration of the model at $T_g$, and therefore the prediction is improved.

11.3 Time dependence of mechanical properties (large strains) – Tensile tests of PE1H20 at different displacement rates

So far the time-dependence of the small strain mechanical properties of some of the paints investigated in this study has been considered. In this section, the attention is shifted to large strain properties and the effect of time. For this purpose, tensile tests at different loading rates and testing temperatures were performed on samples of the control formulation, PE1H20. More specifically tests were performed at 15, 25, 35 and 45 °C, at displacement rates of 0.05, 0.5 and 50 mm/min (approximately equivalent to strain rates of $2.1 \times 10^{-5}$ to $2.1 \times 10^{-2}$ s$^{-1}$), while the tensile data collected at each temperature at 5 mm/min (as reported previously) are also used. Due to time-constraints it was not possible to perform these tests on the rest of the formulations, but it is considered that there is no evidence to suggest that the conclusions derived from the testing of PE1H20 could not be applied to other formulations as well.

To demonstrate the effect of displacement rate on the tensile behaviour of the paint, stress versus strain curves of PE1H20 at 25 °C and at four different rates are shown in Figure 11.11. As expected a transition from glassy to visco-elastic behaviour is seen with decreasing displacement rate, which is similar to the transition observed when the temperature is increased for a given displacement rate. Of interest is to see whether a time temperature superposition can be applied to the data from tensile testing, where the TTS constants will be as determined in Section 11.1 and the 35 °C
11. Time dependence and modelling of the mechanical response of the paints

isotherm will be used as the reference. In Figure 11.12 isotherms of Young’s modulus versus the logarithm of time at which the modulus value was measured are shown. As the modulus was determined over an interval between strains from about 0.2 to 0.8 %, the time required to reach a strain of 0.5 % is used as an approximation of the time at the point of measurement.

In Figure 11.12 (b) the results of shifting the Young’s modulus isotherms using the TTS constants obtained in Section 11.1 (where an Arrhenius relationship was assumed for the temperatures below \( T_g \) and a WLF relationship for the temperatures above \( T_g \)) are shown. Clearly, the resulting master-plot does not provide a perfect overlap of the isotherms. However, considering that the calibration of the TTS constants and the shifted data correspond to two separate types of tests the result is considered rather satisfactory.

Given the encouraging result from the shifting of the small-strain tensile data, it was tempting to apply the same approach to the large strain properties of the paint, i.e. its failure stress and strain. In Figures 11.13 (a) and (c), isotherms of failure strain and failure stress are shown. The time on the x-axis now represents the time to failure of the samples. The results of the superposition of isotherms with respect to the data at 35 °C, once again using the TTS constants obtained from multi-frequency DMA, are shown in Figures 11.13 (b) and (d). In both cases the result of the superposition is a relatively smooth master-curve that is clearly of the same shape as the respective curves obtained from tensile tests of PE1H20 at a constant displacement rate and at various temperatures.

This is considered as a result of great practical importance as it means that the TTS constants, calibrated in the small-strain regime from a single multi-frequency DMA sample, can be used to predict the large strain properties of the paint over a wide range of temperatures and rates. It also shows that findings obtained within the linear visco-elastic region of material behaviour can prove to be meaningful also at much higher strains where linearity cannot be assumed.
Figure 11.11. Stress versus displacement traces from tensile tests of PE1H20 at 25 °C at various displacement rates (as shown on graph).

Figure 11.12. Isotherms of Young’s modulus versus the logarithm of time at which it was measured (a), and master-plot of Young’s modulus created by using the shift factors determined from multi-frequency DMA data where the isotherm at 35 °C was used as reference (b).
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11.3.1 Failure envelopes and effect of cross-link density

An alternative way of presenting the correspondence between time and temperature effects on the ultimate properties of polymers is in the form of failure envelopes, as initially proposed by Smith [140]. Failure envelopes are based on the observation that the failure stresses and strains of a polymer, obtained under a wide range of temperatures and loading rates, create a single envelope that is characteristic of the material. This is shown in Figure 11.14 where the stress at failure has been normalised with respect to the formulation’s $T_g$. Following the failure envelope clock-wise from the top left corner demonstrates the effect of increasing the test temperature, $T$, or decreasing the loading rate on the ultimate properties of the paint. The shape of the envelope shows that with increasing temperature or decreasing strain rate the failure stress decreases continuously, while the failure strain first increases up to a maximum value and then decreases.
Figure 11.14. Plot of the logarithm of failure stress, \( \sigma_f \), normalised by \( T_g/T \) versus the logarithm of failure strain, \( \varepsilon_f \), for formulation PE1H20.

Of note is also the approach of Landel and Fedors [208] who investigated the effect of cross-link density on the failure envelopes of rubbers. For this they modified Smith’s failure envelope by also normalizing the failure stress with the cross-link density of the polymer. Interestingly, they found the ultimate properties (in the form of failure envelopes) to be largely independent of chemical structure and to depend mainly on the density of cross-links. That is, formulations of the same cross-link density are expected to share the same failure envelope. Following these ideas, the failure envelopes of all the clear formulations used in this study are plotted in Figure 11.15.

It is acknowledged that the available points are too few, especially in the high temperature/slow rate region (except perhaps in the case of PE1H20). However, some remarks can be made. It is seen that, at least qualitatively, formulations of similar cross-link densities have similar failure envelopes. This is manifested for example by observation of the failure envelopes of the low cross-link density formulations PE4H20 and PE1H5, and when these are compared to the failure envelope of the high cross-link density PE1H30. Regarding the shape of the envelopes, according to the work in [208], they are expected to converge to a single line at high temperatures and rise towards a point of maximum failure strain as the temperature is decreased. The rise is steeper and the maximum failure strain larger as the cross-link density decreases, while the failure envelope of low cross-link density polymers remains higher than that of high cross-link density polymers in the low-temperature region. Even though the lack of available data at high temperatures makes it difficult to comment on the convergence
of the failure envelopes to a single curve, it is seen that the turning point (point of maximum $\varepsilon_f$) is moved to a higher position and to the right with increasing cross-link density, and that $\sigma_f T_g/(\nu_e T)$ at low temperatures increases with decreasing cross-link density. These observations fit very well with the findings of Landel and Fedors [14, 208].

Figure 11.15. Plot of the logarithm of failure stress, $\sigma_f$, normalised by $T_g/(\nu_e T)$ versus the logarithm of failure strain, $\varepsilon_f$, for the clear formulations investigated in this study. In parentheses are the cross-link densities of the formulations with units of $10^{-3}$mol/cm$^3$.

### 11.4 Modelling of the tensile stress versus strain behaviour

In Section 11.2 the small strain relaxation behaviour of a selection of the paints was approximated with the use of a visco-elastic model. The main scope of this approach was the calibration of the distributions of relaxation times of the materials. Here, the hybrid visco-elastic/hyper-elastic form of equation (2.55) will be used in the prediction of the large strain tensile behaviour of the paints. Before proceeding with the comparison between theoretical predictions and experimental data, however, a check needs to be performed regarding the validity of the approach. More specifically, in Section 2.2.3 it was stated that for equation (2.55) to be applicable, the effects of time and strain on the stress-strain behaviour of the material need to be separable. Smith [41] proposed that where this is the case, iso-strain plots of the logarithm of stress versus the logarithm of time should lie parallel to each other.

For the purposes of this study, iso-strain stress versus time curves were constructed from tensile data of PE1H20 collected at different testing rates and at different...
11. Time dependence and modelling of the mechanical response of the paints

Temperatures. Strain values in the range between 0.4 and 20 % were chosen arbitrarily and the corresponding values of stress and time required to reach each strain were recorded. The results of this procedure are shown in Figure 11.16 for four different temperatures. Generally, the resulting plots are seen to be parallel to each other, suggesting good applicability of equation (2.55), with some deviation observed towards short times (see for example Figure 11.16 (a)). A shortening of the distance between the iso-strains can be interpreted as a manifestation of a yield point (see plots for 2.1 and 2.5 % strain at 15 °C in Figure 11.16 (a)) or of an extended strain softening/cold drawing region (see long-time data on plots of 2.1 to 20 % strain at 25 °C and short-time data between 5 and 20 % strain at 35 °C in (b) and (d) respectively).

Figure 11.16. Iso-strain plots of stress versus time where the axes are in logarithmic scale. Data obtained at 15 (a), 25 (b), 35 (c) and 45 °C (d).
Returning to the prediction of the tensile behaviour of the paints, equation (2.55) contains two components; a linear visco-elastic and a hyper-elastic one. Regarding the linear visco-elastic part of the model, the instantaneous and rubbery moduli are taken as shown in Table 11.2, while for the distribution of relaxation times a generalised Cole-Cole form is assumed with $c$ and $d$ as obtained from the calibration of relaxation data in Section 11.2. A shift of the relaxation spectrum, using the TTS constants obtained in Section 11.1, was performed as necessary where the test temperature was different to the reference temperature used in the calibration of the relaxation times distribution.

For the hyper-elastic part of equation (2.55), the Ogden model in its 3-term form, was found to provide a good fit to experimental data. The fit was performed again with use of the Solver routine in Excel by minimisation of the relative square error between model and experiment, and the $\alpha_i$ and $\mu_i$ terms of the Ogden equation were used as the optimization parameters. As stated in Section 2.2.2.2, the $\alpha_i$ and $\mu_i$ terms are directly related to the shear modulus of the material according to equation (2.48), which is added to the Solver routine as a constraint. As no directly measured value of shear modulus was available for the paints investigated in this study, an assumption was made that the Young’s modulus, $E$, is related to the shear modulus, $G$, as $E = 3G$. This assumption implies a Poisson’s ratio of 0.5 [44] (incompressibility) and is already built-in to the model, as the Ogden equation is derived for incompressible materials.

Upon initial attempts to calibrate the Ogden parameters it was found that at low temperatures (at $T_g$ or lower) the agreement between the model prediction and experimental data was rather poor beyond the initial linear part of the stress-strain trace. This reflected the inability of the model to capture the material behaviour in the presence of a pronounced yield point. A similar observation has been made in the literature by Hagan and co-workers [116, 198, 209]. For this reason, the calibration of the hyper-elastic part of equation (2.55) was performed by simultaneously optimizing the fit of the model to experimental data at $T_g+5$ and $T_g+10$ °C (or at the next closest available temperatures in each case).
In Figure 11.17 the fit of the model to experimental data at about $T_g$, $T_g+5$ and $T_g+10$ °C is given for the clear formulations PE1H10, PE1H20, PE1H30 and PE4H20, and for the pigmented formulations PE1H20Ti and PE4H20Ti. In the case of PE1H20 the experimental data and model prediction are also given at $T_g+20$ °C (the Ogden constants were still calibrated at $T_g+5$ and $T_g+10$ °C however). The Ogden parameters for each paint are given in Table 11.3.

A justification is required for the choice to present the fit between model and experiment separately for small strain and large strain data in Figure 11.17. This is due to the fact that small strain agreement predominantly depends on the visco-elastic part of the model, i.e. the distribution of relaxation times and the shift factors, while at larger strains the influence of the hyper-elastic part becomes increasingly important. To demonstrate this last point, the model prediction for paint PE1H20 based on the Ogden equation, is compared to the prediction in the case where the hyper-elastic component in equation (2.55) is completely ignored and $\sigma_0$ is set to follow Hooke’s law, i.e. $\sigma_0 = E(0)\varepsilon$. The comparison is shown in Figure 11.18. The two predictions are seen to be in perfect agreement up to strains of approximately 2 % and in very good agreement up to 5 % strain (Figure 11.18 (a)). The effects of the choice of form of the strain-dependent part of equation (2.55) are seen at larger strains (Figure 11.18 (b)), where the prediction based on a Hooke’s law type strain-dependence clearly fails to capture the characteristic strain-hardening shape of the stress-strain curves of the polymers above $T_g$. Finally, a comment is due regarding the noise in the model trace of stress versus strain. This is due to the presence of the experimentally obtained stretch ratio, $\lambda$, in the calculation of $\sigma_0$ in the Ogden equation (equation (2.49)). The recorded displacement of the testing machine crosshead did not increase continuously but was rather found to fluctuate slightly as a result of the limitations of the operating software in the accurate recording of data. This fluctuation in the displacement output is therefore reflected in the noise seen in the predicted stress versus strain curves in Figure 11.17.
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11. Time dependence and modelling of the mechanical response of the paints

Figure 11.17. True stress versus true strain plots obtained both experimentally and from equation (2.55) for formulations PE1H10 ((a) and (b)), PE1H20 ((c) and (d)), PE1H30 ((e) and (f)), PE4H20 ((g) and (h)), PE1H20Ti ((i) and (j)) and PE4H20Ti ((k) and (l)) at different temperatures. Plots (a), (c), (e), (g), (i) and (k) show the agreement between model and experiment at small strains while plots (b), (d), (f), (h), (j) and (l) offer a comparison over the entire strain range.

Table 11.3. Ogden parameters of formulations PE1H10-30, PE4H20, PE1H20Ti and PE4H20Ti calibrated with the use of tensile data at approximately $T_g+5\,^\circ C$ and $T_g+10\,^\circ C$.

<table>
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<tr>
<th>Formulation</th>
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<th>$\alpha_1$</th>
<th>$\mu_2$</th>
<th>$\alpha_2$</th>
<th>$\mu_3$</th>
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<td>PE1H10</td>
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<td>-53</td>
<td>-12.23</td>
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<td>-613</td>
<td>-6.54</td>
</tr>
<tr>
<td>PE1H30</td>
<td>3106</td>
<td>-1.52</td>
<td>218</td>
<td>-1.54</td>
<td>-613</td>
<td>-10.60</td>
</tr>
<tr>
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<td>-0.03</td>
<td>-20.20</td>
</tr>
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<tr>
<td>PE4H20Ti</td>
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<td>-3.73</td>
<td>728</td>
<td>0.84</td>
<td>-2414</td>
<td>-5.62</td>
</tr>
</tbody>
</table>
Figure 11.18. Comparison, at small (a) and large strains (b), between the predictions from equation (2.55) when $\sigma_0$ follows the three-term Ogden model and when it follows Hooke’s law for linear-elastic materials. The comparison was performed using the Ogden and visco-elastic parameters of paint PE1H20.

Regarding the agreement between the model predictions and experimental data shown in Figure 11.17, in almost every case, it is seen to be very good for strains up to 5 % irrespective of the testing temperature. This finding implies that the visco-elastic part of the model works well, i.e. that the distribution of relaxation times obtained from relaxation tests as well as the shift factors obtained from multi-frequency DMA can be used to give meaningful predictions of the tensile behaviour at small strains. At larger strains the quality of the fit is seen to depend on temperature. Generally a good fit is obtained for temperatures of $T_g+5$ °C or higher, while around $T_g$ (the lowest temperature used in the comparison) the fit to experimental data becomes progressively worse as the strain increases. Data at lower temperatures than $T_g$ are not shown as it is expected that the good agreement at small strains should continue, while at larger strains the prediction will be further and further away from the experimental data with decreasing temperature. These observations are similar to findings in [116] where the discrepancy between model and experiment at low temperatures and high loading rates was attributed to the formation of a neck instability in the samples. Here, no pronounced necking was observed during testing, however it does seem that the fit is worse in those cases where there is a clear yield point followed by a sharp decrease in the slope of the stress versus strain trace (e.g. 35 °C data in Figures 11.17 (d) and (f)).
With respect to the different formulations, PE1H30 (Figure 11.17 (e) and (f)) is clearly the one where the worst agreement between the model and experimental data is seen. This is the formulation with the highest cross-link density and the highest yield strength, and whose behaviour seems to be further from the behaviour expected from rubbers (after the yield point the stress almost reaches a plateau and only a mild increase in stress is seen up to the point of fracture). In that sense, again, the poor agreement in the case of PE1H30 appears to be related to the inability of the model to capture behaviour that involves a clear yield point followed by a region of strain softening/cold drawing.

A comment is also due regarding the values of the Ogden parameters shown in Table 11.3. Ideally, relationships between both the visco-elastic and hyper-elastic terms and the chemical structure (here cross-link density is of greater interest) of the paints should be obtained. For the visco-elastic part of the model this appears to be possible, if from a qualitative point of view. An increase in cross-link density should result in a higher value of the rubbery modulus and a broadening of the distribution of relaxation times, while it is not expected to significantly affect the glassy modulus and the TTS shift factors (as previously shown). When the hyper-elastic terms are considered, however, it is very difficult to observe any correlations based on the data available here. Generally, it was found that the values obtained from the Solver optimisation depended strongly on the initial values used to start the iteration procedure and that very similar fits could be obtained using different sets of parameters. This is shown in Figure 11.19 where the model prediction for formulation PE1H20Ti based on the Ogden parameters given in Table 11.3 (parameter set A), is compared to the prediction obtained using a different set of parameters (parameter set B). The two sets are presented together in Table 11.4. It is evident that two completely different sets of Ogden parameters result in approximately the same prediction of the paint’s tensile behaviour, and therefore the hyper-elastic terms cannot be considered to be unique for the material. It is recognised that this presents a shortcoming of the model at this stage. A possible solution to the problem of uniqueness of the Ogden parameters could be through the incorporation of other types of loading (such as compression, shear, bi-axial etc.) in the calibration procedure. This was also the method used for the
calibration of the Ogden constants in the original article by Ogden [39]. For the experimental data that are available here, the good agreement with the model predictions is considered encouraging, and warrants further research to obtain the unique hyper-elastic parameters of the materials.

Regarding the pigmented formulations, it would be desirable to be able to modify the visco-elastic and hyper-elastic parameters of the model as obtained for the clear formulation, to account for the effect of pigment. The difficulties in assigning a physical meaning to the Ogden parameters have already been discussed above and, at least within the confines of this project, it is not considered possible to predict the effect of pigment on their values. For the visco-elastic part, Hagan [116] proposed that where the enhancement of modulus due to the presence of pigment is similar throughout the entire temperature range, the visco-elastic component of the pigmented formulation can be obtained by using the same distribution of relaxation times as for the clear and multiplying the glassy, $E(0)$, and rubbery, $E_r$, modulus by a reinforcing factor taken from one of the available theories from 2.4 (e.g. Halpin-Tsai, Lewis-Nielsen etc.). However, in Section 11.2 it was shown that the assumption of a unique distribution of $g_i$ values for clear and pigmented versions of the paint is not necessarily true, as indeed in the case of PE1H20 and PE1H20Ti the addition of pigment is seen to drastically reduce the width of the distribution. It seems therefore that this treatment lacks the desired generality that would enable its use between different paint systems, even if the need to calibrate the hyper-elastic part of the model separately in each case is accepted, and for these reasons will not be pursued further.

Figure 11.19. Prediction of equation (2.55) for the tensile behaviour of paint PE1H20Ti using two different sets of Ogden parameters (shown in Table 11.4)
Time dependence and modelling of the mechanical response of the paints

Table 11.4. Two sets of Ogden parameters used for the prediction of the tensile behaviour of PE1H20Ti.

<table>
<thead>
<tr>
<th></th>
<th>( \mu_1 )</th>
<th>( \alpha_1 )</th>
<th>( \mu_2 )</th>
<th>( \alpha_2 )</th>
<th>( \mu_3 )</th>
<th>( \alpha_3 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Param. set A</td>
<td>3080</td>
<td>-6.27</td>
<td>728</td>
<td>3.20</td>
<td>-2414</td>
<td>-8.21</td>
</tr>
<tr>
<td>Param. set B</td>
<td>1389</td>
<td>7.58</td>
<td>11938</td>
<td>0.56</td>
<td>-2318</td>
<td>6.22</td>
</tr>
</tbody>
</table>

11.5 Chapter summary

The small-strain time-dependence of the mechanical properties of the paints was investigated with the use of multi-frequency DMA testing and relaxation tests. From the multi-frequency DMA results it was possible to obtain the shift factors required for the superposition of temperature and rate effects on the mechanical properties of the polymers. The shift factors were shown to be independent of the specific formulation examined and a single set of shift factors was found to capture the correspondence between temperature and time for all formulations. Relaxation tests at each formulation's glass transition temperature were used for the determination of the distribution of relaxation times of the paints. A correlation between cross-link density and the broadness of the distribution was shown. When the shift factors were used to predict relaxation at a lower temperature the results were encouraging, even though it is acknowledged that in some cases significant discrepancies between predictions and experimental results are seen.

The correspondence of time and temperature effects on the large strain properties of the paints was investigated with tensile tests of the control formulation PE1H20 conducted at different temperatures and displacement rates. It was shown that the use of the shift factors determined at small strains from DMA could be extended to large-strain data, and relatively smooth master plots of failure strain and failure stress versus time were created. The equivalent effects of loading rate and temperature were demonstrated by the construction of a single failure envelope for PE1H20 that extends over a wide range of temperatures and displacement rates. Finally, a hybrid visco/hyper-elastic model was used to predict the tensile behaviour of the paints. For the visco-elastic part of the model, the parameters calibrated from relaxation (distribution of relaxation times) and multi-frequency DMA (shift factors) were used. For the hyper-elastic component, the three-term Ogden equation was calibrated
against experimental data of the paints. The fit of the model to experimental data was generally very good and the method shows promise, especially at higher temperatures where the behaviour of the paints approximates that of rubbers. A significant shortcoming of the model is that it was not possible to correlate between the microstructural characteristics of the paints and the resulting parameters in the Ogden equation. This could possibly be addressed by calibrating the model against data from different types of tests (such as shear and bi-axial tension).

The results obtained in this Chapter could be of great importance in future studies on the performance of coated panels. The TTS constants could be used for the prediction of temperature and loading-rate effects on the amount of damage that is observed on coated surfaces. Also, the visco-elastic and hyper-elastic constants that were determined here, can be used in the context of a finite element analysis of the deformation of coated panels. For the latter, however, additional testing to determine the adhesion between the coating and the substrate would be required.
Chapter 12. Results of T-bend tests of coated panels

In this section, the results obtained from the T-bend testing of coated steel panels are presented. Comments on the relationship between the mechanical properties (and chemical structure) and panel performance are made. The effect of time is taken into account by examination of panels both immediately after testing and after an additional two hour period.

Steel panels were coated with paints PE1H5-PE1H30, plus PE2H20, PE3H20 and PE4H20. Pigmented versions of the paints based on binders PE1-PE4 were also used. The panels were cured to a PMT of 232 °C. They were subsequently tested in T-bending (0T) at the respective glass transition temperatures of the paints and at a relative humidity of 50% RH. This point is considered an important contribution of the present study to the existing literature on the formability of coated panels. A number of publications exist on the subject [130, 210-213], however in every case tests were performed at room temperature, even though the T_g's of the investigated systems were different. It is therefore difficult to distinguish between the effect of composition and that of the relative difference between test temperature and T_g on test performance. By testing all panels at the respective T_g's of the paints this issue is believed to be addressed and any observed differences in performance should be directly attributable to microstructure and the mechanical properties of the paints.

Immediately after testing, samples were removed from the environmental chamber and images of the bent surfaces were taken under an optical microscope to observe any damage created by the test. Samples were then left for an additional two hours in
the environmental chamber, at which point they were re-examined with the use of optical microscopy. The two hour interval between first and second observation was chosen for two main reasons. First, from relaxation and from strain and recovery tests, samples were found to have completely relaxed/recovered within a period of two hours. Second, a two-hour interval was found to be sufficiently long for clear changes to be observable on the panels and at the same time it was short enough for the testing to be practically feasible within the time constraints of the project. A detailed description of the experimental procedure is given in Section 4.6.

The results for paints with varying melamine content, varying adipic to phthalic acid ratio, with or without branching, and with or without pigment are shown in Sections 12.1-12.4. In Section 12.5 a general comment is made on the effect of chemical structure on the performance of the coated panels, and the fundamental free-film mechanical properties that control the T-bend behaviour of the coatings are discussed.

12.1 Formulations with varying wt% of HMMM

Representative optical microscopy images of the bent surfaces of PE1H5, PE1H10, PE1H20 and PE1H30 are shown in Figure 12.1. For comparison, images are shown of samples both immediately after testing and after the samples were left in the environmental chamber for an additional period of two hours. It is noted that, unless specifically mentioned the pairs of images taken at different times should not be considered to be from the same location on the sample surface. Additionally, these are representative images and it is acknowledged that areas of both higher and lower crack concentrations are expected to exist on the surface of the samples.

The results from the testing of steel panels coated with paints PE1H5-PE1H30 are shown in Figure 12.2. The y-axis represents the mean area fraction of cracks measured on the sample surface, and it therefore follows that the height of the bars is inversely related to the performance of the panels. The black bars represent the area fraction of cracks that was observed immediately after testing (short time data), whereas the white bars represent the area fraction of cracks that was measured after the samples were left inside the environmental chamber for an additional two hours (long time data).
Results of T-bend tests of coated panels

The error bars on the graph represent the standard deviation of the measured area fraction of cracks along the surface of each sample.

From observation of Figures 12.1 and 12.2 certain remarks can be made regarding the performance of steel panels coated with paints that contain different concentrations of HMMM. First, the quality of the bent panels generally decreases with increasing HMMM content, and consequently with cross-link density (see Section 6.2 for the cross-link densities of the formulations presented here). For the short time results it is the high melamine content paint (PE1H30) that behaves the worst, while the other formulations show similar behaviour. For the long time results the low HMMM content formulation (PE1H5) showed the least damage, and paints PE1H20 and PE1H30 showed the most. Second, the quality of the panels clearly deteriorates with time. It is noted that, upon visual inspection several days after the tests, the damage on the samples was found to be even more severe.

Regarding the correlation between T-bend performance and the cross-link density of the paints; to an extent this issue has been addressed in the literature previously. Massingill et al. [211] studied the T-bend performance of some epoxy coatings cross-linked with varying amounts of curing agent. They found that, generally, the T-bend performance improved initially with the addition of hardener only to deteriorate above a certain critical concentration (reported as between 5 to 10 wt% depending on the epoxy). A decrease in performance with cross-linker content was also reported in [213]. It needs to be noted again, however, that the above studies do not take into account a possible temperature effect on the performance of the panels, as tests were performed at room temperature irrespective of the $T_g$s of the formulations.

Further, it is noted that neither of the above studies makes explicit mention of the relationship between cross-linker content and cross-link density, thus making it difficult to establish a correlation between the density of the elastic network and the performance of coated panels in T-bend testing. Additionally, no mention is made of the glass transition temperature of the paints, and therefore it is not possible to isolate the influence of the hardener from temperature effects arising from changes in $T_g$ due to the different hardener concentrations.
Figure 12.1. Representative images of steel panels coated with paints PE1H5 ((a) and (b)), PE1H10 ((c) and (d)), PE1H20 ((e) and (f)) and PE1H30 ((g) and (h)) and tested in T-bending. Images in the left column were taken immediately after testing while images in the right column were obtained after samples were left in the environmental chamber for an additional two hours. Circled is a crack on the surface of PE1H30 as observed immediately after the test (g) and then two hours later (h).
12. Results of T-bend tests of coated panels

Figure 12.2. Area fraction of cracks measured from examination of T-bend specimens of PE1H5, PE1H10, PE1H20 and PE1H30 at Tg. Measurements performed both immediately after testing and after a period of approximately two hours. Error bars signify the variation of area fraction of cracks along the observed surface of the samples.

Kojima and Watanabe [210], on the other hand, investigated the formability of epoxy-coated steel panels as a function of the cross-link density of the paints. They found that generally more damage was observed on the panel surface with increasing cross-link density of the paint except for the formulations with the lowest densities of cross-links where this trend was reversed. Again, however, no information was presented regarding the Tg of the formulations and therefore an influence of temperature on the results cannot be ruled out.

Nevertheless, despite the problems in interpreting data presented in the literature, an overall trend can be drawn of T-bend performance initially improving with increasing cross-link density, reaching a maximum and subsequently deteriorating at higher degrees of cross-linking. These observations generally fit well with the results presented in this study, even though here the T-bend performance was seen to more or less deteriorate continuously with increasing cross-link density.

A question that remains to be answered concerns the determination of the fundamental mechanical properties of the paint films that control the performance of coated panels when tested in bending. In a series of papers, Ueda et al. [130, 214, 215] have attempted to provide an answer as to what are the paint properties that determine the formability of pre-painted steel sheets. They reported [130] that the formability of coated panels in bending, correlates mainly with the strain at failure of the paint, i.e. paints with high failure strains will perform better in T-bend tests. They also proposed that, in the case of deep-drawing, failure strain is no longer the sole
factor determining formability, but the ability of the paint to store energy elastically also plays an important role. More specifically it was argued that energy stored elastically during deep drawing tests caused delamination and the formation of wrinkles. It was thus concluded [214, 215] that low cross-link density paints with little capacity for storing energy elastically and high failure strain would behave better in both bending and deep drawing tests.

A link between the curing process and the performance of coated panels in bending has been provided by Kim and Nairn [216]. They conducted 4-point bending experiments on different kinds of substrates coated with automotive clearcoats and reported an increase in the number of cracks observed with bake-time. Although no specific mention of cross-link density is made in their study, it is thought that their findings fit well with those by Ueda et al. [130, 214, 215], as cross-link density is expected to increase with curing time. Another important finding of the Kim and Nairn [216] study is the dependence of the in-situ toughness of the coating, i.e. the toughness of the coating applied on a substrate as opposed to the toughness of a free-film of the paint (see also [217]), on the type of substrate used. When steel substrates were compared to polymeric substrates, an increase in crack density was seen when using the steel substrate for the same coating.

With respect to the results shown in the present study, the relationship between failure strain in the visco-elastic region and cross-link density has been discussed extensively throughout Chapters 5-10. Similarly, the essential work of fracture was found to generally vary inversely with cross-link density at T_g. Finally, a positive correlation between cross-link density and elastically stored energy has also been shown for formulations PE1H5-PE1H30 (Section 6.5). In Figure 12.3 the short and long time T-bend data are plotted versus the failure strain at T_g ((a) and (b)), versus the essential work of fracture at T_g ((c) and (d)), versus the cross-link density ((e) and (f)), and versus the ratio of elastic to total work obtained from strain and recovery tests at T_g ((g) and (h)). Where no data were available at the glass transition temperature, data from the closest test temperature to T_g were used (in every case this was no more than ±2 °C from T_g). In the plots a high area fraction of cracks indicates poor performance of the coated panel.
12. Results of T-bend tests of coated panels

Figure 12.3. Area fraction of cracks measured from examination of T-bend specimens of PE1H5-PE1H30 at \( T_g \) versus: failure strain at \( T_g \) ((a) and (b)), essential work of fracture at \( T_g \) ((c) and (d)), cross-link density ((e) and (f)) and ratio of elastic to total work from strain and recovery experiments at \( T_g \) ((g) and (h)). Graphs in the left column correspond to damage observed immediately after testing while graphs in the right column correspond to damage observed after samples were left in the environmental chamber for an additional two hours.

By looking at Figure 12.3, a first observation would have to be that the short-time performance of the panels seems to be much more insensitive to changes in formulations and mechanical properties than the long-time performance. Focusing on the long-time results, excellent negative correlations are seen between area fraction of cracks and failure strain (Figure 12.3 (b)) as well as essential work of fracture (Figure 12.3 (d)). Additionally, deterioration in panel performance in bending was also
observed with increasing cross-link density and capability for elastically storing energy. At this point, a hypothesis will be put forward that based on the available literature as well as on data presented in this study paints with high strains to failure, high values of essential work of fracture and reduced capability for storing energy elastically will give panels with better performance in bending. This hypothesis will be further discussed in the following sections.

A note also needs to be made regarding the quality of the short-time data presented. Even though these data are thought to have been collected immediately after the testing of panels, they do not constitute instantaneous observations of the damage at the completion of the test. In reality, some time will have passed between testing and observation using the microscope, as samples need to be removed from the environmental chamber, transferred to the microscopy room, prepared for observation with the use of a penetrant method and finally placed under the microscope for observation. In addition, the actual capturing of the images will take some time and in that sense, as samples are ‘scanned’, images are not only from different areas of the samples but also from different points in time.

As an increase in damage with time is clearly observed, differences in the amount of time required for the above procedure could also lead to artificially different results. On the other hand, this is not as great a concern for the long-time measurements, because it is thought that within two hours most of the damage will already be present and that at longer times the rate of increase in the amount of cracks will be much slower. This is supported by strain and recovery data at $T_g$, where in every case within two hours all strain was shown to have been recovered (from a maximum of 15%), and by relaxation experiments at $T_g$ where most of the relaxation is shown to have been completed within two hours from the application of the strain.

Regarding the observed deterioration of the appearance of the bent surfaces with time, this is considered to be a finding of great importance. From a very practical point of view, this could mean that coated parts could pass quality control checks immediately after being formed only to fail at a later date as a result of the initial deformation. In trying to link this increase in damage with time, to the free-film results
presented earlier, it is thought that this increase is related to the fact that the post-yield deformation of the paints was shown to be not permanent (plastic) but rather inelastic or visco-elastic.

The inelastic nature of the paint behaviour at large strains means that the coating will have the tendency to retract to its original unstrained condition after the T-bend test is completed. This recovery, however, is not allowed to take place due to the adhesion between the coating and the steel panel, leading to the build-up of stresses. These in turn lead to the propagation of existing defects (see circled defect in Figure 12.1 (g) and (h)) and to the formation of new ones (compare Figure 12.1 (c) and (d), and Figure 12.1 (e) and (f)).

In comparing between the four different formulations discussed here, the amount of damage two hours after the initial observation is the smallest in the case of paint PE1H5, followed by PE1H10. Panels coated with PE1H20 and PE1H30 had the worst performance with time (see Figure 12.2). It seems therefore that an increase in cross-link density has a detrimental effect on panel performance at sufficiently long time periods (Figure 12.3 (f)). The reason for this is believed to lie in the capacity of high cross-link density polymers to store energy elastically inside their network of cross-links (Figure 12.3 (h)). Evidence of the relationship between cross-link density and elastically stored energy has been presented in this study in Section 6.5.

To further demonstrate the influence of elastically stored energy on the deterioration of panel performance over time, the fraction of ‘new’ damage (that is long time damage minus initial damage) in the total amount of damage measured two hours after the initial observation, was calculated. This was then plotted against the ratio of elastic to total work from stain and recovery experiments. The result is shown in Figure 12.4. Even though some scatter in the data exists, the trend generally is for time to have a more detrimental effect on panel performance (more ‘new’ damage occurs) for those panels coated with paints with high capability for storing energy elastically.
12. Results of T-bend tests of coated panels

Figure 12.4. Fraction of damage incurred to the samples between initial and second measurement in the total amount of damage observed in second measurement (two hours after testing) versus ratio of elastic to total work from strain and recovery tests.

12.2 Formulations based on polyesters with varying ratio of adipic to phthalic acid

The results from the T-bend testing of panels coated with formulations PE2H20 (low adipic acid content) and PE3H20 (high adipic acid content) are presented here, and comparisons with PE1H20 (intermediate adipic acid content) are made. In Figure 12.5 representative images of bent surfaces of steel panels coated with formulations PE2H20 and PE3H20 are shown. For images of PE1H20 the reader is referred to Figure 12.1 (e) and (f). The area fraction of cracks on the bent samples is given in Figure 12.6.

By examination of Figures 12.5 and 12.6 it becomes immediately obvious that, as also shown in the previous Section, the increase in the area fraction of cracks with time is dramatic. When a comparison between the formulations is made for samples observed immediately after testing, PE3H20 performed the worst with an area fraction of cracks around 5%, while PE1H20 and PE2H20 were almost damage-free. With respect to the long-time results, PE2H20 panels suffered the greatest damage, followed closely by PE1H20 and PE3H20.
Results of T-bend tests of coated panels

Figure 12.5. Representative images of steel panels coated with paints PE2H20 ((a) and (b)) and PE3H20 ((c) and (d)) tested in T-bending. Images in the left column were taken immediately after testing while images in the right column were obtained after samples were left in the environmental chamber for an additional two hours.

Figure 12.6. Area fraction of cracks measured from examination of T-bend specimens of PE1H20, PE2H20 and PE3H20. Measurements performed both immediately after testing and after a period of approximately two hours. Error bars signify the variation of area fraction of cracks along the observed surface of the samples.

Generally, it appears that the variation in the ratio of adipic:phthalic acid did not have a great impact on the performance of coated panels in bending. By contrast a variation in HMMM content was shown to have a much greater influence on panel performance. As discussed in Section 12.1, performance is expected to be negatively influenced by increasing cross-link density, but to improve with increasing failure strain.
and essential work of fracture. The group of paints discussed here have similar cross-link densities and failure strains, and in that sense the general finding that they performed similarly in bending seems justified (see Figure 12.7 (a)-(d)). On the other hand, PE3H20 was found to require a clearly higher work of fracture to break (see Section 5.4), and for this reason it would be expected to give panels of a superior performance in bending. This is confirmed by neither the long-time data nor the short-time data, where on the contrary PE3H20 coated panels were found to suffer the greatest amount of damage (Figure 12.7 (e) and (f)).

Figure 12.7. Area fraction of cracks measured from examination of T-bend specimens of PE1H20, PE2H20 and PE3H20 at Tg versus: cross-link density ((a) and (b)), failure strain at Tg ((c) and (d)), essential work of fracture ((e) and (f)). Graphs in the left column correspond to damage observed immediately after testing while graphs in the right column correspond to damage observed after samples were left in the environmental chamber for an additional two hours.
Regarding the effect of time on the appearance of the bent panels, a correlation between the increase in the observed damage and the ability of the paints to store energy elastically was proposed in Section 12.1. Here, the long time damage as well as the increase in damage with time were found to be almost unaffected by the tendency of the paints for elastic recovery (see Figure 12.8). Generally, the long time behaviours of panels coated with paints with varying adipic acid content in their polyester backbone were similar.

![Figure 12.8](image-url)

**Figure 12.8.** Area fraction of cracks measured from examination of T-bend specimens of PE1H20, PE2H20 and PE3H20 at T_g (a) and fraction of damage incurred to the samples between initial and second measurement (b), versus: ratio of elastic to total work from strain and recovery experiments.

### 12.3 Formulations based on polyester with branched (PE1) and linear (PE4) back-bone

Images of a bent panel coated with formulation PE4H20 are shown in Figure 12.9. The area fraction of cracks observed both immediately after the test and two hours after initial observation is given in Figure 12.10. As discussed in Section 8.3, the mechanical properties and especially the failure strain measured for free films of formulation PE4H20 are largely explained by its low cross-link density (and not necessarily by the lack of branching per se). For this reason T-bend results are compared both with the overall control formulation, PE1H20, and with the low cross-link density PE1-based paint, PE1H5.
12. Results of T-bend tests of coated panels

Figure 12.9. Representative images of steel panel coated with paint PE4H20 tested in T-bending at Tg. Image on the left was taken immediately after testing while image on the right was obtained after the sample was left in the environmental chamber for an additional two hours.

Figure 12.10. Area fraction of cracks measured from examination of T-bend specimens of PE1H5, PE1H20 and PE4H20. Measurements performed both immediately after testing and after a period of approximately two hours. Error bars signify the variation of area fraction of cracks along the observed surface of the samples.

From the images in Figure 12.9 and from the results presented in Figure 12.10, it is seen that the induced damage from bending is minimal and does not increase significantly with time for the panel coated with paint PE4H20. By comparing the performance of PE4H20 with PE1H5 and PE1H20, it is seen that the paint based on the linear polyester behaves similarly to the low HMMM content low cross-link density PE1H5, while the control PE1H20 suffered much greater damage. It appears therefore that it is cross-link density that affects the performance of panels in bending the most and not the concentration of cross-linker. More specifically, it was proposed in Sections 6.2.1 and 8.1 that the existence of a second network of self-condensed HMMM is highly probable for formulations containing HMMM at stoichiometric ratios larger than unity. This is the case for PE1H20 and PE4H20, while for the low HMMM
12. Results of T-bend tests of coated panels

PE1H5 the extent of any HMMM-HMMM network is expected to be negligible. In that sense, it seems that it is the overall cross-link density of the paint that controls the performance of coated panels and not the presence of HMMM-rich areas with a high density of cross-links.

Indeed, from observation of Figure 12.11 it is seen that the data fit the proposed hypothesis for an improvement in performance in bending with lower cross-link density, higher failure strain and higher essential work of fracture. These trends are clearer in the case of the long time data than for these data obtained immediately after bending the panels. Regarding the increase in the observed damage with time, this is seen to be similar for PE1H5 and PE4H20, which were found to have a smaller capability for storing energy elastically, where the more elastic PE1H20 suffered much greater damage with time (see Figure 12.12).

Figure 12.11. Area fraction of cracks from examination of T-bend specimens of PE1H5, PE1H20 and PE4H20 at Tg, versus: cross-link density ((a) and (b)), failure strain ((c) and (d)), and essential work of fracture ((e) and (f)). Graphs in the left column correspond to damage observed immediately after testing while graphs in the right column correspond to damage observed after samples were left in the environmental chamber for an additional two hours.
12. Results of T-bend tests of coated panels

Figure 12.12. Long-time area fraction of cracks measured from examination of T-bend specimens of PE1H5, PE1H20 and PE4H20 at T_g (a) and fraction of damage incurred to the samples between initial and second measurement (b), versus: ratio of elastic to total work from strain and recovery tests at T_g.

12.4 Effect of pigment

So far panels coated with clear paints were examined, and the influence on T-bend panel performance, of changes in HMMM content and in the polyester back-bone was discussed. In this section, the effect of pigment is addressed by consideration of results obtained from the testing of panels coated with PE1H20Ti, PE2H20Ti, PE3H20Ti and PE4H20Ti. Representative images of the bent surfaces of the panels coated with white formulations are shown in Figure 12.13. The results obtained from white panels are compared to those of the respective clear formulations in Figure 12.14, where data have been split into two graphs to maintain clarity.

Generally, the behaviour of white panels is seen to follow closely that of the clears. A small improvement with the addition of pigment is seen in the-long time behaviour of PE1H20, while in the case of paint based on binder PE2 the addition of pigment resulted in a clear deterioration of short-time performance and also somewhat greater damage in the long-time measurement. Paints based on binder PE4 both had excellent performance. The one case where the addition of pigment was seen to have a very clear influence on panel performance was when comparing between the white and clear paint based on binder PE3. In this case, the amount of damage was significantly lower for the panel coated with the white formulation.
Figure 12.13. Representative images of steel panels coated with paints PE1H20Ti ((a) and (b)), PE2H20Ti ((c) and (d)), PE3H20Ti ((e) and (f)) and PE4H20Ti ((g) and (h)) and tested in T-bending. Images in the left column were taken immediately after testing while images in the right column were obtained after samples were left in the environmental chamber for an additional two hours.
Figure 12.14. Area fraction of cracks measured from examination of T-bend specimens of PE1H20, PE1H20Ti, PE2H20 and PE2H20Ti (a) and of PE3H20, PE3H20Ti, PE4H20 and PE4H20Ti (b). Measurements performed both immediately after testing and after a period of approximately two hours. Error bars signify the variation of area fraction of cracks along the observed surface of the samples.

The lack of effect of pigment on the performance of panels coated with paints based on binders PE1, PE2 and PE4 might suggest that the mechanical properties of free films would also remain unaffected with the addition of pigment. However this was not necessarily the case. The white films based on binders PE1 and PE2 had significantly higher values of essential work of fracture when compared to the respective clear films. On the other hand, the failure strain of PE1H20Ti at \( T_g \) was somewhat higher than that of PE1H20, and the opposite was true for PE2H20 and PE2H20Ti. In both cases the ability of the paint to store energy elastically decreased slightly with the addition of pigment. For paints based on PE4, the addition of pigment resulted in a significant reduction in failure strain at \( T_g \) while the essential work of fracture was left practically unaffected. Again the fraction of energy stored elastically under tensile deformation decreased somewhat with the addition of pigment.

In trying to explain the improved behaviour of the white PE3-based paint, again, an increase in failure strain and essential work of fracture might have been expected. This however was not found to be the case since the addition of pigment did not affect the essential work required for the fracture of free films although it caused the failure strain to decrease somewhat. Regarding the ability of the paint to store energy elastically, this was found to increase (but not greatly) with the addition of pigment.

From the above discussion it is clear that the effect of pigment on the performance of panels in bending cannot be fully explained by the mechanical properties of free films.
reported previously in this study. When a comparison is made between the four white formulations, a decreasing trend in damage suffered by the panels is observed with increasing failure strain, while panel performance appears to be unaffected by the essential work of fracture of the paints (Figure 12.15 (a)-(d)). On the other hand, a good correlation is seen between long-time panel performance and the ratio of elastic to total energy obtained from strain and recovery tests (Figure 12.15 (e)).

Figure 12.15. Area fraction of cracks measured from examination of T-bend specimens of PE1H20Ti, PE2H20Ti, PE3H20Ti and PE4H20 at T_g, versus: failure strain at T_g ((a) and (b)), essential work of fracture ((c) and (d)) and ratio of elastic to total energy from strain and recovery experiments ((e)). In (f) the fraction of damage incurred to the samples between initial and second measurement is plotted versus the ratio of elastic to total work from strain and recovery experiments at T_g.
12.5 Correlations between free-film properties and performance of coated panels in bending

So far the effects of a series of changes in paint formulation on the performance of coated panels in bending have been considered. These changes included variations in the amount of cross-linker used for curing the paint, variations in the relative concentrations of monomers present in the polyester chains and the addition of pigment particles. Based on the data presented thus far, correlations have been proposed between certain mechanical properties of the paint free-films and the quality of coated steel panels subjected to bending.

In this Section these results will be considered collectively, based on the premise that if such correlations are to have a general validity they should be observed irrespective of the particular structural characteristics of the paints. For this, the area fraction of cracks of the clear formulations is plotted versus cross-link density in Figure 12.16 (a) and (b), and the area fraction of cracks of both clear and pigmented paints is plotted versus strain at failure and essential work of fracture in Figure 12.16 (c)-(f). Both short- and long-time data are considered for these plots. To study the effect of time on panel performance, the long-time area fraction of cracks and the fraction of damage that was suffered by the panels between the short- and long-time measurement, are plotted in Figure 12.17 versus the ratio of elastic to total work obtained from strain and recovery tests at \( T_g \). On the plots linear regression lines are also drawn, to serve as guidance for observed correlations between data. This does not imply, however, that linear correlations are proposed, the regression lines are rather used to help in the visualisation of trends.

An increase in the observed damage is seen with cross-link density when long time data from clear paints are considered. The area fraction of cracks initially increases sharply and then appears to reach a plateau with cross-link density. When the long-time data from all the formulations tested in bending are plotted, a clear decrease in the observed damage is seen both with increasing failure strain and with increasing essential work of fracture, even though some scatter in the data exists. So far it seems therefore that the proposed hypothesis, for an improvement in panel performance in
bending with decreasing cross-link density and increasing failure strain and essential work of fracture, works sufficiently well.

By examination of Figure 12.16, a general observation would be that the long-time performance of panels correlates better with the paint-film properties than the short-time performance. It was also consistently shown in the preceding Sections that the increase in damage with time is of paramount importance when the performance of panels is considered. Indeed when samples were re-observed two hours after testing and initial observation, in most cases the initial damage constituted only a small fraction of the total damage observed.

Figure 12.16. Area fraction of cracks measured from examination of T-bend specimens of PE1H5-PE1H30, PE2H20, PE3H20 and PE4H20 at Tg, versus cross-link density ((a) and (b)) and area fraction of cracks measured from examination of T-bend specimens of clear and white paints based on binders PE1-PE4 versus: failure strain ((c) and (d)) and essential work of fracture ((e) and (f)) at Tg. Graphs in the left column correspond to damage observed immediately after testing while graphs in the right column correspond to damage observed after samples were left in the environmental chamber for an additional two hours.
Results of T-bend tests of coated panels

Figure 12.17. Long-time (a) and short-time (b) area fraction of cracks measured from examination of T-bend specimens of clear and white paints based on binders PE1-PE4 versus the ratio of elastic to total work from strain and recovery tests. In (c) the fraction of damage incurred to the samples between initial and second measurement in the total amount of damage observed in second measurement (two hours after testing) is plotted against the ratio of elastic to total work from strain and recovery tests. All data were obtained at the respective $T_g$s of the paints.

In that light, the importance of determining the property that controls the long-time damage of coated panels is seen to be paramount. It has already been proposed here that this delayed cracking effect is related to the tendency of the paint to recover from large strains, or equivalently to the paint’s capacity for storing energy elastically. In Figure 12.17 (a), the area fraction of cracks measured from the bent surfaces of all samples, two hours after initial observation, is plotted against the ratio of elastic to total work obtained from strain and recovery tests. Despite the significant differences between the formulations used, an almost linear correlation is observed. Clearly, the more ‘elastic’ the paint, the worse the behaviour of the respective coated panel in bending. For comparison the short-time damage of the paints is also plotted in Figure 12.17 (b) versus the strain and recovery results. In this case no significant trend is observed. This supports the argument that the elasticity of paint films affects primarily the long-time behaviour of coated panels. Finally in Figure 12.17 (c) the fraction of damage that was developed between the short- and the long-time measurement is presented versus the elasticity of the paints. The significant scatter in Figure 12.17 (c)
could be attributed to the large room for error associated with the measurement of the short-time damage area (see relevant discussion in 12.1). Nevertheless, a clear trend is observed where the amount of damage developed between observations increases with the capacity of the paints for storing energy elastically.

12.6 Chapter summary

Panels coated with clear formulations PE1H5-PE1H30, PE2H20, PE3H20 and PE4H20 as well as with white formulations PE1H20Ti, PE2H20Ti, PE3H20Ti and PE4H20Ti were tested in bending at their respective glass transition temperatures. The scope of these tests was to identify correlations between the performance of coated panels in bending and the microstructure or mechanical properties of free films. The effect of time on the appearance of tested panels was studied by observing the bent surfaces of the samples both immediately after testing (short-time results) and then an additional two hours after the initial observation (long-time results). A clear increase was seen in the observed amount of damage with time.

From the point of view of microstructure, it was cross-link density that was found to have the greatest influence on the performance of the coated panels, with an increase in the area fraction of cracks observed, with increasing cross-link density. This was seen to be the case more clearly when considering the long-time results. On the other hand, changes in the polyester backbone and the addition of pigment were, generally, not found to have a great effect on coated panel performance.

In terms of establishing relationships between the free-film mechanical properties and the performance of coated panels in bending, the area fraction of cracks on coated panels was seen to decrease with increasing failure strain and essential work of fracture of the paint films. These correlations, however, were again more obvious when the long time bending data were taken into account. This could perhaps be explained from a greater sensitivity of results on time, in the short-time range.

For the deterioration of panel appearance with time, a damage mechanism was proposed where cracks are created due to the tendency of the coating to retract from
its deformed state. As this strain recovery process is suppressed by the adhesion on the plastically deformed steel panel, stresses are created that eventually lead to the tearing of the coating. The extent of this delayed damage was seen to correlate very well with the degree of elasticity of the free-films (taken as the ratio of elastically stored work to total work supplied for the deformation of samples) from strain and recovery data reported earlier in this study. It is therefore proposed that the performance of coated panels in bending is largely and negatively influenced by the tendency of the paint for elastic recovery which in turn depends on the paint’s cross-link density.

Finally, it is recognised that several factors affecting the performance of coated panels in practical applications were not considered here, and would need to be investigated in future studies. Such factors include weathering effects where changes in temperature, humidity as well as absorption of UV-radiation are expected to affect the service life of the products. Also, a more detailed study into the formation of damage on the panels is required. Here, cracks were considered to appear on the coating (top-coat) as a result of Mode I fracture. However, the effect of the adhesion between top-coat and primer and the possibility of damage forming in the primer first and then propagating into the top-coat were not considered. In the future, a more detailed study into the fracture mechanisms that take place during the bending of coated panels is needed.
Chapter 13. Conclusions and future work

13.1 Conclusions

The primary aim of this work was to establish the effects of changes in the formulation of thermoset polyester-based coil-coatings on their mechanical properties. The basic formulation was based on a widely used polyester binder containing two different acid monomers (adipic and phthalic acid), a di-ol (neopentyl glycol) and an undisclosed tri-ol. The formulation was then heat cured with hexa(methoxymethyl)melamine (HMMM) resulting in a cross-linked paint with a glass transition temperature, $T_g$, of approximately 35 °C. Variations of the control formulation were prepared where the structure of the polyester back-bone was altered, the concentrations of the cross-linker and the catalyst were varied, and the effect of pigment was studied by considering both clear and titanium dioxide, TiO$_2$, pigmented versions of the paints. An electron-beam (EB)-cured system was also prepared to determine the effects of the choice of curing method on the mechanical properties of the paint.

A second objective was to quantitatively predict the effects of temperature and loading rate on the mechanical properties of the paint, and to predict the stress versus strain response under a tensile deformation at any temperature or loading rate. Multi-frequency dynamic mechanical analysis (DMA) was used to calibrate the Arrhenius and Williams-Landel-Ferry (WLF) constants that are required for time-temperature superposition (TTS). For the prediction of the tensile response of the materials, a hybrid visco-elastic/hyper-elastic model was used in conjunction with the TTS constants.
The above studies were performed on free-films of the paints. However, ultimately, it is important to know how the paint will perform when it is applied on a substrate that is subjected to a mechanical deformation. Steel panels were coated with a selection of the paint systems and tested in bending (T-bend, 0T). Of interest in this work was not only to determine the effect of paint formulation on the amount of damage incurred on the panel surface, but also to establish which are the mechanical properties and the microstructural characteristics that control the formability of the coating.

In the following, the main conclusions of this work are summarised.

**13.1.1 The effect of paint formulation on the paint’s mechanical properties**

Several modifications of a paint formulation commonly used in the coil-coating industry were prepared. A common finding for all formulations was the paramount effect of temperature on their mechanical properties. The Young’s modulus was seen to decrease by three orders of magnitude within a temperature range of 40-50 °C, while the failure strain increased from around 2% to values as high as 180% at temperatures close to the $T_g$ of the paints. It follows therefore that, irrespective of formulation, the single most important factor controlling mechanical behaviour is the test temperature, or for a given test temperature, it is the formulation’s $T_g$. A second general observation that is common for all formulations studied in this project, is the ability of the paints to completely recover from large (post-yield) deformations, within a time-period of two hours, when tested at their respective $T_g$s. This means that the deformation of the paints beyond the yield point cannot be considered strictly as plastic but is in fact inelastic, i.e. it is recoverable with time. This point is thought to be important in explaining the performance of coated panels in bending (see 13.1.3). Keeping in mind the above observations, which were common for all paint systems, the following discussions focus on the conclusions from the comparison between the properties of the different paints.

In a first modification two binders were used, one with a higher and one with a lower ratio of adipic:phthalic acid, compared to the control formulation. These results are
reported in Chapter 5. A clear positive correlation was obtained between the phthalic acid content and the $T_g$ of the cured paint. This was expected as a result of the decrease in chain mobility from the presence of the bulky benzene rings in phthalic acid. However, when the tensile properties of the paints were examined at temperatures equally removed from $T_g$, these were not found to be significantly affected by the changes in the polyester backbone. Higher values of the essential and of the inessential work of fracture of the formulation with the highest adipic acid content (PE3H20), were attributed to the increased linearity of the chains of this formulation which favours energy consuming mechanisms such as chain disentanglement prior to fracture.

A further modification of the control formulation consisted of varying the amount of cross-linker (Chapter 6). When HMMM was used at concentrations higher than PE:HMMM = 90:10 by weight, the $T_g$ of the paint remained unaffected by the cross-linker concentration. On the other hand the cross-link density increased continuously with HMMM content. In particular it was suggested that the cross-link density measured for the formulation PE1H30 (PE:HMMM = 70:30), provides indirect evidence for the existence of a second network of self-condensed HMMM in the paint. Similar results have also been reported elsewhere [101]. The increase in HMMM content (and cross-link density) was found to have a dramatic effect on the maximum failure strain as observed at temperatures between $T_g$ and $T_g+10 \, ^\circ C$, with values of the maximum failure strain decreasing drastically with cross-link density from around 170% in the case of the 95:5 paint to around 30% for the 70:30 one. Similar conclusions were reached from the fracture testing of the paints, where the essential work of fracture, $w_e$, was seen to decrease with cross-link density, from 19.4 ±1.4 kJ/m$^2$ to 5.3 ±1.0 kJ/m$^2$ as the cross-linker content increased from 95:5 to 70:30 (paints PE1H5-PE1H30). The decrease in failure strain and essential work of fracture with increasing cross-link density was attributed to a change in the fracture mechanism, with chain scissions becoming more prominent than chain disentanglement and void nucleation as the crosslink density increased [168, 175]. Lastly, a good correlation was obtained between the amount of recoverable strain and the cross-link density, when samples were unloaded from strains of approximately 15%.
A study of formulations with catalyst content both lower (HMMM:p-tsa = 99.5:0.5) and higher (97:3) than the control formulation (98:2), showed no effect on $T_g$, while a small decrease in cross-link density was seen for the low catalyst content formulation, see Chapter 7. The tensile properties generally remained unaffected by the catalyst content, which was to be expected as a result of the formulations having similar chemical and network characteristics.

On the other hand, when the polyester backbone was modified to eliminate the tri-ol monomers, which act as branching points, the change in the properties of the paint was dramatic (Chapter 8, paint PE4H20). The $T_g$ by differential scanning calorimetry (DSC) decreased to 17 °C, compared to 35 °C for the control formulation. At the same time, the cross-link density decreased significantly to a value very similar to that of the low HMMM content formulation, PE1H5. The decrease in cross-link density with the elimination of the tri-ol was explained to be a result of the reduction in the functionality of the polyester. Interestingly, as with the high HMMM content paint, the measured cross-link density of PE4H20 was higher than the theoretical prediction, suggesting the presence of a self-condensed HMMM network. In terms of mechanical properties, the maximum strain to failure increased significantly when compared to the control formulation (approximately 180% versus 45%). Similar findings were obtained for the essential work of fracture, which was seen to increase to 16.9 ±5.3 kJ/m$^2$ for the un-branched formulation, compared to a $\omega_e$ of 5.7 ±1.0 kJ/m$^2$ for the control. An important observation was that the maximum strain to failure as well as the essential work of fracture of paint PE4H20 compared closely to the respective values of the low HMMM-content paint. It was therefore proposed that the differences between the mechanical properties of the linear paint and those of the control can be explained, to an extent, as a result of the lower cross-link density of the linear paint. It is noted, however, that the yield stress of the linear formulation was higher than would be expected from its cross-link density. This was explained as a result of the greater molecular packing achieved in the absence of branching.

Another modification of the polyester back-bone involved the substitution of part of the phthalic acid monomers with iso-phthalic acid, along with the substitution of part of the alcohols with two different di-ols (Chapter 9, paint PE5H20). These changes
resulted in a significant reduction in the paint’s $T_g$ along with a smaller decrease in the cross-link density. In terms of mechanical properties, the increase in the maximum failure strain for the PE5-based formulation (around 80% for PE5H20 compared to 45% for PE1H20) is thought to reflect the paint’s lower cross-link density compared to the control, while the higher yield stress of PE5H20 was attributed to the more linear backbone of this paint.

An EB-cured version of the PE5-based paint was also studied (Chapter 9, paint PE6EB). The EB-cured paint showed a remarkably broad glass transition region, while its $T_g$ could not be determined with certainty, as the DSC and the DMA values compared differently with the rest of the formulations (by DSC the $T_g$ of PE6EB was found to be 20 °C lower than that of the overall control PE1H20, while by DMA the two paints shared the same $T_g$). At the same time, the cross-link density of the formulation was found to be lower than the respective values of PE5H20 and PE1H20, but the large associated error reduces the certainty of this comparison. When the tensile properties of PE6EB are considered, the maximum strain to failure was found to compare very well to the respective value of PE5H20, being somewhat lower than the maximum failure strain of PE1H20. This could be explained as a result of the lower cross-link density of formulation PE6EB when compared to that of PE120.

Finally, in Chapter 10, the effect of pigment on the properties of the paints was investigated by adding 50 wt% of TiO$_2$ particles to paints based on binders PE1-PE5. The addition of pigment was not found to have any effect on the glass transition temperatures of the paints. This was in contrast to the general trend reported in the literature for an increase in the $T_g$ of polymers with the addition of a second inorganic phase [188, 190]. It was also interesting that, from DMA data, an increase was seen in the magnitude of the tan$\delta$ peak for the pigmented formulations. This could serve as an indication of weak adhesion between the pigment particles and the polyester matrix, as discussed in Section 10.6.2. The Young’s modulus of the pigmented paints was found to increase by approximately a factor of 2 in the glassy region, and by a factor of around 2.3 in the rubbery region. Again this finding was in contrast to a higher stiffening effect of the pigment in the rubbery region, which is commonly reported in the literature [188, 192, 198]. When the failure strain of the paints was considered, the
pigmented formulations were found to break at lower strains than their clear counterparts. However the magnitude of this decrease was smaller than the prediction from Nielsen’s equation (equation (2.83)), which again could suggest a less than perfect adhesion between the pigment particles and the matrix. In terms of fracture toughness, \( w_e \) either remained unaffected by the presence of pigment or increased, suggesting that additional mechanisms for energy absorption take place in the presence of the pigment particles. Finally, when the formulations were subjected to cyclic loading, in an attempt to observe the formation of damage around the particles through a softening effect; the results were not conclusive, as both the clear and the pigmented samples showed similar amount of softening.

13.1.2 Modelling studies

In Chapter 11, a selection of the paints were tested using multi-frequency DMA in order to study the effect of loading rate on the small-strain mechanical properties. In every case master curves of storage modulus versus time were obtained, and from the respective shift factors it was possible to obtain the time-temperature superposition (TTS) constants of the paints. An interesting observation was that the shift factors were very similar for all the paints, and thus it was possible to obtain a single set of TTS constants. The correspondence of the effects of time and temperature in the small strain region is very well established in the literature [17]. However, from a practical point of view, it was of great interest to use the TTS constants obtained from small strain data to create master-plots of large strain properties, such as the stress and strain at failure. For this, the control formulation, PE1H20, was tested in tension at four different temperatures and loading rates. It was shown that by using the TTS constants from multi-frequency DMA, smooth master-plots of both stress and strain at failure were obtained. This finding is of great importance as it enables the prediction of the failure properties of the paints outside the range of temperatures and loading rates that are readily available from laboratory testing.

Data from relaxation tests (small strains) at \( T_g \) were fitted with a visco-elastic model to obtain the distributions of relaxation times of the paints. These were then used in a
13. Conclusions and future work

A hybrid visco-elastic/hyper-elastic model was used to fit the tensile stress versus strain traces of the formulations. The tensile traces were obtained at $T_g$ or higher temperatures and the TTS constants were used to shift the relaxation times accordingly in every case. For the hyper-elastic part of the model, the Ogden equation was used. The fit of the model to the experimental data was very good in every case, for strains up to around 5%. At these relatively low strains it was found that the visco-elastic part of the model dictated the quality of the fit. At larger strains the relative contribution of the hyper-elastic part became increasingly important. Generally, good results were also obtained at these large strains, with the fit being worse in those cases where a clear yield point existed on the tensile curve. One shortcoming of the model was that the Ogden parameters were not unique for each formulation, but they were found to depend on the initial values used in the optimisation procedure. Nevertheless, the method showed great promise, and the ability of the model to describe the experimental data was clearly demonstrated.

13.1.3 T-bend tests of coated steel panels

T-bend tests to $0^\circ$T (180° fold without spacer) were performed on steel panels coated with paints of a varying HM MMM content (PE1H5-PE1H30), of a varying ratio of adipic:phthalic acid (PE2H20, PE3H20) and of a non-branched back-bone structure (PE4H20). Panels coated with pigmented versions of the paints were also tested (PE1H20Ti-PE4H20Ti). Perhaps the most significant conclusion from the T-bend testing of the panels was the dramatic increase in the amount of damage observed on the bent surface with time. For example the area fraction of damage in the case of PE2H20 increased from approximately 0% immediately after testing to about 45% two hours later. It was proposed that this behaviour is related to the tendency of the paints to recover from large strains (as shown from strain and recovery tests of free films of the paints), which resulted in the development of tensile stresses in the coating layer of the bent panels. This increase in damage with time is of great importance from a practical point of view, as it means that parts can pass a quality control check immediately after forming, only to fail at a later stage without being subjected to any additional deformation.
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Generally, the damage on the coated panels was seen to increase with decreasing strain to failure and with decreasing toughness of the paints. An excellent correlation was also seen between the ability of the paints to store energy elastically, as measured from strain and recovery testing of free-films, and the long-time damage on the panels. Since the strain to failure and the fracture toughness of the paints have been shown to decrease with increasing cross-link density, while the ability for elastic recovery generally increases with cross-link density; it follows that panels coated with paints of a higher degree of cross-linking are expected to perform worse in T-bend tests. The above conclusions are in general agreement with findings reported in the literature [130]. An important contribution of the present study was the testing of all panels at the respective Tgs of the paints, as opposed to room temperature which is the common practice in the literature [130, 210-212]. In this way the effect of temperature on the test results was eliminated, highlighting the relationships between the mechanical properties (and the microstructure) of the paints and the performance of coated panels under mechanical deformation, as discussed above.

13.2 Recommendations for future work

This project has contributed a significant amount of experimental work in the field of coil-coatings with an emphasis on the correlations between paint microstructure and mechanical properties. In many cases, however, the collected data suggest interesting routes for additional work that could not be performed within the present project. In the following, a number of recommendations for future work are made.

13.2.1 Cross-link density and nature of formed network

A central finding of this work was that within the range of molecular structures studied, cross-link density was the microstructural characteristic with the greatest influence on the mechanical properties of the paints. However, in every case, changes in cross-link density were a result of differences in the chemical formulation of the paints (for example in the case of paints with varying cross-linker content). Cure studies, where changes in cross-link density would come as a result of changes in the
cure time and temperature, would eliminate possible effects of composition on the properties of the paint, and would provide a direct relationship between the observed mechanical properties and degree of cross-linking.

Throughout this thesis, the possibility of a second network of self-condensed HMMM being present in the paints has been suggested from indirect observations, such as the unexpectedly high cross-link densities of formulations PE1H30 and PE4H20. However, direct observation of such areas of self-condensed HMMM would be required to prove their existence. This can be achieved with the use of confocal Raman microscopy, which has already been employed to identify HMMM-rich areas in similar paint systems [218]. Additionally, the paints in this study were considered as homogeneous, and only the average cross-link density, as measured from DMA, was used to explain the observed mechanical properties. The mapping of a second network of HMMM would facilitate a better understanding of the effect of microstructure on the mechanical properties of the paint.

### 13.2.2 The effect of pigment on the mechanical properties of paints

In general, the addition of 50 wt% pigment to a selection of the formulations was not found to affect the properties of the paints significantly. However, it is recognised that the scope of this study was rather limited, as only one concentration of pigment was used. The effect of pigment could be better characterised if a range of concentrations were used, in order to obtain clear correlations between mechanical properties and particle volume fraction. Also of interest would be to determine the effect of the adhesion between pigment and matrix on the mechanical properties of the paints. For this, pigments with different surface treatments would be required, leading to a systematic variation of the expected degree of adhesion.

### 13.2.3 Heat-cure versus radiation-cure

Studies in this work have largely focused on traditional polyester-based heat-cured paint systems, with only one paint being cured with the use of EB radiation. Also, the
obtained results from the EB-cured paint could not always be explained properly (for example the width of the glass transition that was much greater compared to the rest of the formulations) and suffered from a great degree of uncertainty such as in the case of the measured cross-link density. Fracture testing of the EB-cured formulation was not possible due to the poor quality of the films. It is thought therefore that the results presented here are not sufficient to characterise the effect of EB-curing on the properties of the paint, and further studies are suggested. It is recommended that such studies should include the use of a range of radiation doses for curing, to study the effect on the cross-link density of the paint. It would also be of interest to substitute the mono-functional IBOA with a poly-functional diluent, as this is again expected to affect the network characteristics of the cured paint (see [4]). Finally, the amount of holes present in free films of the EB-cured paint needs to be significantly decreased, if samples are to be obtained for testing in essential work of fracture. A decrease in the viscosity of the paint could improve the wetting of panels, resulting in fewer holes in the cured film. As EB-cured paints do not contain solvents, the viscosity could be reduced by increasing the concentration of the reactive diluents (which would also change the composition of the cured product) or by heating the paint before application on the panel.

13.2.4 Modelling studies

The modelling of the mechanical response of the paints generally produced very encouraging results, as the effects of time, temperature and strain were predicted with the use of time-temperature superposition and models of visco-elasticity and hyper-elasticity. By fitting such models to the experimental data it was possible to determine a number of material constants, such as the distribution of relaxation times and the hyper-elastic (Ogden) parameters. The next step would be to establish relationships between these material constants and the paint formulation, so that the mechanical behaviour of the paint can be predicted directly from knowledge of its microstructure. In the case of relaxation times such a correlation is already possible, from a qualitative point of view, as it was shown that the width of the distribution increases with cross-link density. On the other hand, it was not possible to obtain a unique set of Ogden
parameters for each formulation. As discussed in Chapter 11, this could potentially be addressed by using a number of different loading modes to fit to the model, such as biaxial tension, shear and large strain relaxation.

In terms of establishing links between the microstructural characteristics and the macroscopically observed mechanical properties, molecular dynamics studies show great potential. Young’s modulus values from this study (paint PE4H20) were used for the experimental verification of a molecular dynamics model [219], showing good agreement between the model and the experimental results. In the future, molecular dynamics could be used to greatly improve the understanding of polymer behaviour (for example relaxation, yield, strain hardening etc.) and the effect that chemical structure has on this behaviour.

13.2.5 Studies of coated panels

The present work has provided correlations between the cross-link density, the failure strain, the essential work of fracture and the amount of damage observed on coated panels subjected to bending, where the test temperature was always equal to the $T_g$ of the paint. Future work would also need to consider cupping tests of the coated panels. It is known that different failure modes are involved in bending tests and in cupping tests [130, 220], and it has been proposed [130, 214, 215] that different paint properties could be responsible for the performance of coated panels in each case. It is also suggested to perform tests at temperatures both higher and lower than the $T_g$ of the paints, to study the effect of temperature on the amount of damage induced on the panels. Additionally, the increase in damage with time can be further considered by extending the observation to longer time periods, for example from the current period of 2 hours, to 20 or 200 hours. The effects of the choice of primer and substrate were not taken into account in the present study, although it is recognised that they are expected to affect the results (see [117, 216]). In that light, future work would need to include the study of different (or no) primers, as well as different types of panels (e.g. aluminium or even polymeric). Finally, a logical next step of the modelling studies presented here, would be the implementation of these results in a finite
element analysis context, aiming to study the deformation of coated panels. This is expected to decrease the required amount of experimental testing and help in the understanding of the failure mechanisms involved.
References


References

96. BYK, Data sheet S212, Issue 07/08, BYK-Chemie GmbH: Wesel, Germany.
117. Foster, G. M., Mechanical properties of coil coatings under controlled humidity. PhD in Engineering. 2005, University of Exeter, UK.


164. Smith, T., *Ultimate tensile properties of elastomers. IV. Dependence of the failure envelope, maximum extensibility, and equilibrium stress-strain curve on*


Plots of the ratio of the residuals over the standard error of the residuals, obtained from the EWF testing of formulations PE1H5, PE1H10 and PE1H30 at test temperatures of $T_g-10\,^\circ C$, $T_g-5\,^\circ C$ and $T_g+10\,^\circ C$ are shown here.

Figure A-1. Ratio of the residuals over the standard error of the regression for formulations PE1H5 (a) and PE1H10 (b) tested at $T_g-10\,^\circ C$.

Figure A-2. Ratio of the residuals over the standard error of the regression for formulations PE1H5 (a), PE1H10 (b) and PE1H30 tested at $T_g-5\,^\circ C$. 
Figure A-3. Ratio of the residuals over the standard error of the regression for formulations PE1H5 (a), PE1H10 (b) and PE1H30 tested at $T_g+10\,^\circ\mathrm{C}$. 