An essential work of fracture study of the toughness of thermoset polyester coatings

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ABSTRACT

The fracture toughness of a range of thermoset polyester paints with different cross-link densities has been studied, using the essential work of fracture (EWF) method. The glass transition temperature, \( T_g \), of each of the materials was measured using differential scanning calorimetry, and found to lie between 8 and 46 °C. EWF tests were performed on the paint films at a range of temperatures around the measured glass transition temperature of each material. The essential work of fracture, \( W_{ef} \), at \( T_g \) was found to decrease with increasing cross-link density from around 20 kJ/m² at a cross-link density of 0.4 × 10^{-3} mol/cm³ to around 5 kJ/m² for cross-link densities of approximately 1 × 10^{-3} mol/cm³ or higher. A maximum in the essential work of fracture was observed at around \( T_g \) when \( W_{ef} \) was plotted versus temperature, which could be attributed to the effect of an \( \alpha \)-relaxation at a molecular level. The polyesters were found to be visco-elastic, and the applicability of the EWF test to the study of these visco-elastic thermoset materials is discussed.

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1. Introduction

Coil coating is the method of pre-painting metal sheets which are then stored in drums (coils) to be formed at a later stage. The coil coating process is continuous and includes the cleaning and pre-treatment of the metal strip as well as the application and subsequent curing of the coating, resulting in significant advantages both in terms of cost-reduction and in terms of reduced solvent emissions [1,2]. The method is particularly popular in the construction, electrical appliance and automotive industries and a number of different coating systems are used, including polyesters, polyurethanes and epoxies [1,2]. As the paint is applied before the forming stage in the manufacturing process, it is exposed to significant mechanical deformation during forming. Therefore it is imperative that the paint has the mechanical strength and toughness to withstand the applied deformation without cracking [2]. This has resulted in highly engineered coating systems that are in many ways similar to structural adhesives, for example the paints are generally based on thermoset polymer binders and are required to have excellent mechanical properties such as high strength and toughness. However, an important research question lies in the determination of the relationship between the mechanical properties of the paint and the formability of the coating when applied on a metal panel. Additionally, in order to design improved paint formulations, it is desirable to know the effect of microstructure (e.g. molecular weight, cross-link density, volume fraction and type of pigment etc.) on the mechanical properties, and subsequently on the formability of the paint.

Several research groups have investigated the tensile and dynamic mechanical properties of both industrial and artists’ paints [3–10]. The work required for the fracture of free-standing paint films in tension has also been considered [8]. However, relatively few studies have concentrated on directly measuring the fracture toughness of coatings [11–13]. Of these studies, some have focused on the toughness of the complete coating system (i.e. of the paint as applied on a substrate pre-coated with a layer of primer) [11,12], while others on determining the fracture toughness of the free-standing paint films [13]. The advantage of measuring the toughness of complete coating systems is that the results are easy to interpret from the industry’s point of view, as they provide a quick comparison between different systems. However, by using this method it is difficult to distinguish the contributions from different parts of the system (e.g. substrate, primer, top-coat) to the overall measured toughness. On the other hand, by measuring the toughness of the paint (top-coat) in isolation it is possible to obtain a property characteristic of this particular material. The
downside is that then further tests are required to study how this property correlates with the formability of the paint when applied on a substrate.

The present work uses the essential work of fracture (EWF) method to measure the toughness of a series of coil coatings based on different polyester resins and cross-linked with different amounts of hexa(methoxy)methylmelamine (HMMM). In particular, attention is given to the effect of cross-link density on the fracture toughness of the paints, while the effect of test temperature is also considered.

2. Essential work of fracture

2.1. General

In the case of brittle materials a linear elastic fracture mechanics (LEFM) approach is used to measure the fracture toughness, given in the form of a critical energy release rate, $G_c$, or critical stress intensity factor, $K_c$, of the material [14]. A basic assumption of this approach is that the sample behaves elastically, with plastic deformation taking place only in a relatively small region immediately surrounding the crack-tip. The method has been widely used for the characterisation of thermoset polymers and adhesives, such as epoxies and cyanate esters. These materials display a linear-elastic response in the bulk of the sample until fracture such that the plasticity is localised at the crack tip [14]. For materials that display elastic/plastic stress–strain behaviour, on the other hand, the method is not applicable as it tends to overestimate the energy required for fracture, due to its inability to account for energy lost in plastic deformation in the bulk of the sample (i.e. in parts of the sample far from where the fracture takes place) [15,16]. As paints are often required to operate at temperatures close to or even above their glass transition temperature ($T_g$), their mechanical response ranges from elastic-plastic, to visco-elastic and (at higher temperatures) rubbery. The visco-elastic nature of the materials discussed here has been discussed by the authors in a previous publication [17]. It is clear therefore that linear elastic fracture mechanics is not a suitable approach for measuring the fracture toughness of the materials at hand and a different methodology is required.

The essential work of fracture method was specifically developed for the evaluation of the fracture toughness of thin sheets that undergo significant plastic deformation prior to fracture. The method is based on the work of Broberg [15] and was later fully developed by Mai and Cotterell [16,18,19], who formulated the experimental procedure to separate between the essential, $W_e$, and the non-essential, $W_m$, components of the work of fracture. The former is the work consumed in the formation of the fracture surfaces and in plastic deformation in the area immediately surrounding the crack tip, while the latter accounts for energy dissipated in plastic (or more generally inelastic) processes in the bulk of the sample. The most popular specimen geometry is the double edge notch tensile (DENT) specimen, see Fig. 1(a), that results in Mode I crack propagation and rupture.

The total work supplied for fracture, $W_F$, can be written as the sum of its components as [16]:

$$W_F = W_e + W_m$$

(1)

An assumption is made at this point, that the essential component of the work is proportional to the cross-sectional area of the ligament, see Fig. 1. The non-essential component of the work is proportional to the volume of a region surrounding the ligament (referred to as the outer process zone), as shown by Eq. (2).

$$W_e = lw_e$$

$$W_m = \beta l^2 w_m$$

(2)

where $l$ is the ligament length, $t$ the sample thickness and $\beta$ is the shape factor of the outer process zone, for example for a circular outer process zone, $\beta = \pi/4$ [20]. Experimental determination of the process zone shape is possible through observation of stress whitening of the sample in the area surrounding the ligament [21,22]. Finally, in Eq. (2), $w_e$ is the essential and $w_m$ the non-essential specific (per unit surface and unit volume respectively) work of fracture.

If the total work of fracture is now normalised by $lt$, Eq. (1) becomes:

$$\frac{W_F}{lt} = \frac{W_e}{lt} = \frac{W_m}{lt} = \beta lw_{m}$$

(3)

Eq. (3) provides a strategy for the determination of $w_e$ by noting that if a series of samples with different ligament lengths are tested, then a plot of the total specific work of fracture, $W_F/lt$, versus ligament length, $l$, should give a straight line whose intercept with the $y$-axis is the essential work of fracture, $w_e$, and whose slope is equal to $\beta w_m$ (Fig. 1). In practice, a series of load versus displacement curves is obtained from the testing of samples with different ligament lengths, and in each case the value of $W_F$ is calculated as the area under the curve (Fig. 1(b)). These results are then re-organised as $W_F/lt$ versus $l$ and analysed according to Eq. (3), see Fig. 1(c). Note that as the samples are expected to fracture under identical stress states irrespective of ligament length (see also Section 2.2), the load–displacement traces are required to show self-similarity, i.e. to scale with ligament length while maintaining the same general shape (Fig. 1(b)). In fact the self-similarity of the load–displacement traces is perhaps the most commonly used criterion to determine the applicability of the EWF method.

2.2. Geometric restrictions

A number of restrictions apply regarding the geometry of the samples that are used in the EWF method. These restrictions are derived from three basic requirements: (a) that the ligament is fully yielded prior to fracture, (b) that the outer process zone is confined within the ligament and does not extend to the edges of the sample, and (c) that the fracture propagates under plane stress. The requirement for full yielding of the ligament prior to fracture usually leads to unrealistically high upper bound values for ligament length ($l > 100$ mm) [20]. On the other hand, a more realistic upper bound is provided by the requirement to confine plastic yielding within the ligament, giving values of $l \leq B^3/3$ [16], where $B$ is the sample width, see Fig. 1. This limit has been criticised as conservative by several researchers, and an upper bound of $l \leq B/2$ has been proposed [20,23]. Finally, the requirement for plane stress conditions prevailing in the fracture zone leads to a lower bound ligament, $l \geq 3t$. For thin films this can imply extremely small ligament values, for example in this study it would mean a minimum $l = 60–90$ $\mu$m. Apart from such low values being practically unobtainable, it has also been suggested that the transition from the required plane stress conditions to the undesired plane strain conditions actually takes place at significantly higher values of $l$. Such observations have resulted in a suggested lower bound value for the ligament, $l \geq 5$ mm [20]. The overall length, $l$, of the samples is not thought to affect the results, as long as it is sufficiently large compared to $l$.

2.3. Statistical analysis and data reduction

Apart from the requirement for self-similarity, a number of criteria are used to determine the applicability of the EWF method and the quality of the results. As the EWF is calculated from linear extrapolation of the $(l, w_e)$ data points, it is imperative to have a measure of the quality of the linear fit, and also of the
degree of certainty associated with the reported values. For this reason, the coefficient of correlation, $R^2$, and the standard errors (0.68 confidence level) from the least squares fitted line, as well as the standard errors of the intercept and the slope, are calculated. Williams and Rink [20] propose that $R^2$ values in excess of 0.98 are expected, while the standard error associated with the essential work of fracture should be lower than 0.1 $w_f$. It has been suggested that $w_f$ values lying more than two standard errors away from the best-fit line, should be discarded [20,24]. Further criteria for data reduction are set by consideration of the sample’s stress state during testing. From the assumption of full yielding of the ligament prior to fracture, it follows that the maximum stress during testing, $\sigma_m$, should be related to the yield stress of the material, $\sigma_y$, as, $\sigma_m = 1.15\sigma_y$. It is noted, however, that several groups have observed deviations from this behaviour, while a tendency for decreasing $\sigma_m$ with increasing $l$, is widely reported [21,24–27]. Because a criterion of $\sigma_m = 1.15\sigma_y$ could be considered as overly restrictive, an alternative criterion for data reduction has been proposed [20] that requires the maximum stress values measured for different values of $l$ to fall within 10% of the average maximum stress value, $\sigma_{m,avg}$, such that $0.9\sigma_{m,avg} < \sigma_m < 1.1\sigma_{m,avg}$.

3. Materials and manufacturing

The paints studied here were based on a polyester binder commonly used in the coil coatings industry (herein referred to as PE1), with a molecular weight of 4200 g/mol and an average of 3.6 OH sites available for cross-linking per chain. Hexa(methoxymethyl)melamine was used as the cross-linker, and was added to binder PE1 at concentrations of 5, 10, 20 and 30 wt% (denoted as paints PE1H5–PE1H30). Modifications of the basic binder were also explored (binders PE2–PE5). Details of the structures of the binders will be provided in a future publication, however for the purposes of the present study it will be assumed that the only difference between the binders lies in their molecular weight and the number of OH sites available for cross-linking.

4. Experimental procedures

The glass transition temperature, $T_g$, of the paints was determined by differential scanning calorimetry (Q2000 DSC, TA Instruments, USA). A mass of 5–10 mg of each material was placed in a hermetically sealed Al pan, and analysed in a heat–cool–heat cycle between −30°C and 100°C at 10°C/min. Dynamic mechanical analysis (DMA) was performed with a Tritic 2000 DMA (Triton Technologies, UK). Rectangular samples (approximately 5 mm × 15 mm, with a free length of 5 mm) were subjected to a sinusoidal tensile load, at a frequency of 1 Hz. A strain amplitude of around 0.1–0.2% was set, while the experiments were performed in ‘auto tension’ mode, meaning that an adjustable static load was applied on top of the dynamic load, to prevent the samples from
Table 2

Effect of the binder type and HMMM content on the glass transition temperature and cross-link density of the paints.

<table>
<thead>
<tr>
<th>Paint</th>
<th>$T_g$ [°C] (±2)</th>
<th>$\nu_e$ [10^-3 mol/cm³]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PE1H20</td>
<td>36</td>
<td>0.93 ± 0.06</td>
</tr>
<tr>
<td>PE2H20</td>
<td>46</td>
<td>0.74 ± 0.03</td>
</tr>
<tr>
<td>PE3H20</td>
<td>21</td>
<td>1.03 ± 0.10</td>
</tr>
<tr>
<td>PE4H20</td>
<td>17</td>
<td>0.47 ± 0.09</td>
</tr>
<tr>
<td>PE5H20</td>
<td>8</td>
<td>0.77 ± 0.01</td>
</tr>
<tr>
<td>PE1H5</td>
<td>28</td>
<td>0.44 ± 0.20</td>
</tr>
<tr>
<td>PE1H10</td>
<td>35</td>
<td>0.64 ± 0.02</td>
</tr>
<tr>
<td>PE1H20</td>
<td>36</td>
<td>0.93 ± 0.06</td>
</tr>
<tr>
<td>PE1H30</td>
<td>35</td>
<td>2.08 ± 0.16</td>
</tr>
</tbody>
</table>

The temperature was varied between −20 °C and 120 °C at a heating rate of 3 °C/min.

Rectangular samples were prepared for EWF testing, with dimensions of approximately 20 × 80 mm. To improve the grip of the samples within the tensile clamps, paper end-tabs (10 × 20 mm) were bonded to the samples with the use of a widely available cyanoacrylate adhesive. This resulted in a free-length between the clamps of L = 60 mm, see Fig. 1(a). A razor blade was used to notch the specimens, where care was taken to ensure that the notches were in the middle of the sample and directly opposite each other. The crack-tip radius is known to greatly influence $w_e$ [20,28], and this is why a new blade was used each time to notch the specimens, resulting in a crack tip diameter of the order of 1 μm (see Fig. 2). An Instron 4301 universal testing machine was used to perform the tests at a displacement rate of 5 mm/min. All tests were conducted inside an environmental chamber at controlled temperature and a relative humidity of 50%. Between eight and thirteen samples of each paint were tested, with ligament lengths ranging between 5 and 12 mm. It is recognised that a ligament of 12 mm is above the recommended upper bound of B/2, and in theory wider samples would need to be used to accommodate a sufficiently large range of ligaments. However, as a result of the curing procedure, the hardener contained both micrometre and millimetre sized holes, thus making it difficult to obtain defect-free 20 × 60 mm samples. The selected ligament range and sample size were found to provide a good compromise between EWF testing requirements and the limitations posed by the materials at hand.

5. Results and discussion

5.1. Thermal analysis

DSC and DMA were performed to obtain the glass transition temperature and cross-link density of the paints respectively. The $T_g$ values of the paints are given in Table 2, where the value of $T_g$ is seen to depend mainly on the polyester binder used. By comparison, the change in the concentration of HMMM has minimal effect. The main purpose for obtaining the $T_g$ values in this study was to enable the mechanical testing of the paints at equivalent temperatures with respect to $T_g$. DMA traces of the paints are shown in Fig. 3. The cross-link density, $\nu_e$, was calculated from the rubbery storage modulus, $E_e$, as obtained by DMA at 100−C as,

$$\nu_e = \frac{E_e}{3kT}$$

where $k$ is the ideal gas constant and $T$ is the temperature in Kelvin. The resulting cross-link densities are shown in Table 2. The density of the network increases with increasing concentration of the HMMM cross-linker (compare paints PE1H5–PE1H30). Changing the polyester binder can affect cross-link density as a result of changes in the molecular weight, the functionality and the packing ability of the chains. The effect of reducing the functionality while increasing the molecular weight of the polyester is seen for example in the case of PE4H20 which has the least dense network among the 20 wt% HMMM paints.

5.2. Applicability of the EWF method

Before presenting the results and discussing the effect of changing the formulation on the fracture toughness of the paints, it is important to address the issue of the method’s applicability to the study of the materials at hand. It is useful to consider first the tensile behaviour of the paints. A characteristic stress versus strain curve of paint PE1H20 loaded in tension at a temperature equal to its $T_g$ is shown in Fig. 4. The sample was stretched at a constant displacement rate of 5 mm/min up to a strain of 35%, at which point the cross-head movement was reversed and the load was removed. During the loading part of the cycle, the stress varies relatively linearly with strain up to approximately 2% strain, followed by an apparent yield point and what would appear to be plastic deformation. Upon unloading, however, it is clear that a larger portion of the strain is recovered than would be expected for elastic/plastic behaviour, i.e. the recovered strain is larger than the strain at the apparent yield point. Further, when the sample was removed from the tensile clamps and was left for an additional two hours inside the environmental chamber, complete strain recovery was observed. These findings show that the material behaviour beyond the initial linear part of the stress versus strain trace can be best characterised as inelastic rather than plastic. Notwithstanding differences in the exact amount of strain recovered at the end of the loading–unloading cycle, these findings were common for all paints discussed in this study. As the EWF method has been developed for elastic/plastic materials, a question regarding the applicability of the method arises. It was decided, however, to proceed with using the EWF approach, assuming that the basic premise of separating between the essential and non-essential components of the total work holds, only the non-essential work of fracture corresponds to...
5.3. EWF results – effect of the cross-link density

Example load versus displacement traces of paints PE1H20 and PE2H20 tested at $T_g$ (DSC) are shown in Fig. 5(a) and (b). For brevity the traces for the rest of the paints are not shown, as the curves in Fig. 5 can be used for a more general discussion that applies to the rest of the paints as well. It is seen that the load versus displacement traces of PE1H20 in Fig. 5(a) generally satisfy the requirement for self-similarity with changing ligament length. On the other hand, this is clearly not the case for the traces of PE2H20 in Fig. 5(b) (e.g. compare traces of $l=6.3$ mm and $l=6.2$ mm, or $l=11.6$ mm and $l=11.3$ mm). Upon investigating these results further it was found that the DENT samples of PE2H20 were obtained from two separate films of the paint. When the data were re-arranged into two separate plots with respect to the film used, it was found that in each case the traces displayed the desired self-similarity, see Fig. 5(c) and (d). The exact reasons for this discrepancy are not known, however, it would appear to be a result of the film-manufacturing process. First, it needs to be considered that during cure, the paints were inserted and removed from the oven manually. As the curing time was very short, small changes in the curing time caused by the operator could potentially result in paint films being cured to different extents. Second, micro-bubbles and holes were formed in the films as a result of both solvent evaporation and of ethanol emission as a by-product of the curing reaction. It is possible that changes in the amount of micro-defects present in different paint films slightly affected the EWF results. Further, it has been noted [29] that for sufficiently thin films (below around 200 μm) buckling in the transverse direction could affect the self-similarity of the load–displacement traces. The thickness of the films investigated here was around 20–30 μm and buckling was indeed observed in some cases. It has been proposed to use U-shaped clamps that constrain buckling in the transverse direction, although it is acknowledged that this would in turn result in a change in the applied stress field [29]. The use of this type of clamps for the testing of such thin specimens is worth investigating in the future. For the purposes of the present article, as there was no good reason to discard one or the other set of data, it was decided to use all PE2H20 traces to obtain $\sigma_m$, considering that the quality of the data will be reflected in the results of the statistical analysis.

Initial attempts to compare between the maximum stress during EWF testing and the tensile yield strength (results to be published), $\sigma_y$, of the paints, showed that $0.8\sigma_y \leq \sigma_m \leq 2.5\sigma_y$ depending on the formulation and ligament length. As an example, the yield stress of PE1H20 at $T_g$ along with $\sigma_m$ for different ligaments is shown in Fig. 6(a). However, it has already been discussed (see Section 2.3) that variations from the theoretical value of $\sigma_m = 1.15\sigma_y$ are widely reported. Alternatively, it was attempted to apply the requirement posed by Williams and Rink [20]
for $0.9\sigma_{m,\text{avg}} < \sigma_m < 1.1\sigma_{m,\text{avg}}$. Any load versus displacement trace giving $\sigma_m$ outside these boundaries should then be excluded. As an example $\sigma_m$ is plotted versus $l$ for the PE1H20 traces (Fig. 6(b)). Clearly, the data points fall close to the prescribed boundaries, however, strict application of the criterion would still lead to the exclusion of a significant number of samples. Similar conclusions were drawn across all paint formulations. As it was not possible to increase the number of samples in order to obtain enough valid data points that satisfied the $\sigma_{m,\text{avg}}$ criterion, it was decided to proceed regardless and expect that the statistical analysis should provide a measure for the quality of the results.

Plots of $w_f$ versus $l$ for samples tested at $T_s$ are shown in Fig. 7. For clarity, the data have been divided into two groups: one of the samples based on binder PE1 and cross-linked with different concentrations of HMMM, see Fig. 7(a), and one of the samples based on different binders and cross-linked with a constant concentration of HMMM of 20% by weight, see Fig. 7(b). A linear regression was performed on the data for each paint, and the best fit lines were plotted. The standard error of the regression was calculated in each case, and data-points lying more than two standard errors from the regression line were discarded. The regression was then repeated and the best-fit line was plotted through the data. The value of $w_f$ was obtained as the intercept of the best-fit line with the $y$-axis, while the slope of the linear regression gave the non-essential component of the work, $\beta w_{\text{in}}$. These values are given in Table 3 along with the associated standard errors. The high standard error values, as well as the low $R^2$ values are thought to be associated mainly with the quality of the samples. It has already been discussed that as a result of the curing process the paint films contained micron-sized holes and bubbles. As the exact concentration of such defects on each sample could not be controlled, it is thought that their presence results in a higher degree of uncertainty in the measured $w_f$ values. Small differences in the curing time between different films of the same paint could also affect results. Finally, it needs to be noted that as the films were very thin (20–30 $\mu$m) errors in the measurement of the thickness in the order of 1–2 $\mu$m could significantly affect the results. (Note that the width and length of each sample were measured with a digital vernier calliper to $\pm 0.01$ mm, and the thickness was measured with a digital micrometer to $\pm 0.001$ mm. At least three measurements were taken and mean values were calculated.)

Comparing the EWF results of the PE1-based paints with different concentrations of HMMM, the general trend is for the essential work of fracture to decrease with increasing concentration of the cross-linker, from approximately 19 kJ/m$^2$ in the case of PE1H5 to 4 kJ/m$^2$ for PE1H30. When a comparison is made between the different polyester binders, it is seen that the PE4-based paint has the largest fracture toughness (approx. 17 kJ/m$^2$), followed by PE3, while the fracture toughness of paints based on PE1, PE2 and PE5

**Table 3**

<table>
<thead>
<tr>
<th>$w_f$ [kJ/m$^2$]</th>
<th>$\beta w_{\text{in}}$ [MPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PE1H20</td>
<td>5.7 ± 1.0</td>
</tr>
<tr>
<td>PE2H20</td>
<td>4.4 ± 0.7</td>
</tr>
<tr>
<td>PE3H20</td>
<td>12.9 ± 1.4</td>
</tr>
<tr>
<td>PE4H20</td>
<td>16.9 ± 4.7</td>
</tr>
<tr>
<td>PE5H20</td>
<td>7.3 ± 3.8</td>
</tr>
<tr>
<td>PE1H5</td>
<td>19.4 ± 1.4</td>
</tr>
<tr>
<td>PE1H10</td>
<td>13.2 ± 1.9</td>
</tr>
<tr>
<td>PE1H20</td>
<td>5.7 ± 1.0</td>
</tr>
<tr>
<td>PE1H30</td>
<td>5.4 ± 0.8</td>
</tr>
</tbody>
</table>
was very similar at around 4–7 kJ/m². These results can be interpreted by considering the cross-link density of the paints. Fig. 8(a) shows that the essential work of fracture generally decreases with increasing cross-link density. This is not unexpected, as it is well-known that the fracture toughness of glassy polymers decreases as the degree of cross-linking increases, e.g. [30–32]. A smaller number of studies have focused on the relationship between toughness and cross-link density of polymer systems that show visco-elastic behaviour. Nevertheless, the available evidence (see [33–35]) supports the main findings of this study, i.e. an increase in cross-link density results in decreasing \( w_e \). On a microstructural level, the shortening of the chain segments between junction points will lead to a decrease in fracture toughness. Panico et al. [36] have provided a molecular dynamics study where the shift from a chain uncoiling-dominated failure mechanism to a chain-scission-dominated failure mechanism, with increasing cross-link density, is discussed. Chen and Wu [34] on the contrary suggest that \( w_e \) is a function of the elastic energy stored in chain segments at the moment of fracture. Therefore an increase in \( w_e \) with decreasing cross-link density is expected as a result of the greater number of C–C linkages per chain segment. This argument, however, appears to disregard that a significant amount of energy is dissipated in the inner process zone either plastically or viscoelastically, even though the authors acknowledge that stretched chain segments immediately around the crack tip will have to be plastically deformed prior to fracture [34]. Along these lines, \( w_e \) could be thought as comprising of two components: one related to the uncoiling of chains, and one related to the subsequent elastic stretching and rupture of covalent bonds. The relationship between fracture toughness and the viscous nature of the paints is highlighted when \( w_e \) is plotted against the maximum \( \tan \delta \) from DMA (Fig. 8(b)). Generally \( w_e \) increases with \( \max \tan \delta \), suggesting that energy dissipation in viscous processes is directly related to fracture toughness.

On the other hand, it is not clear which factor controls the variation of the non-essential work, \( \beta w_{em} \), between paint formulations. As \( \beta w_{em} \) reflects the fraction of the total work dissipated in inelastic processes within the sample, low values of \( \beta w_{em} \) signify that the material behaviour is elastic with little energy dissipation outside the fracture process zone. Along these lines it might be expected that increasing the cross-link density would result in a decrease in the value of \( \beta w_{em} \). However, this is not confirmed by the experimental data, as shown in Fig. 8(c), where no correlation between \( \beta w_{em} \) and cross-link density is seen. Furthermore, as a large viscous component would be reflected in a higher \( \tan \delta \) from DMA, it may be expected that \( \beta w_{em} \) will increase with the maximum value of \( \tan \delta \). However, this was not confirmed by the experimental findings, as shown in Fig. 8(d). Finally, in order to probe the relation between inelastic processes within the paints and \( \beta w_{em} \) directly, cyclic tests were performed (see Fig. 4) from which the ratio of the elastic (readily recoverable) energy, \( E_{el} \), over the total energy, \( E_{tot} \), was obtained. The resulting \( \beta w_{em} \) versus \( E_{el}/E_{tot} \) is shown in Fig. 8(e), where it could be argued that an increase in the elastic energy results in a decrease of the non-essential part of the work of fracture, however, the correlation is rather weak.

5.4 EWF results – effect of temperature

As the \( T_R \) of the paints is very close to room temperature, it is of great importance to study the effect of temperature on their fracture toughness. For this, additional tests were performed at \( T_R = -10^\circ \text{C}, T_R = -5^\circ \text{C} \) and \( T_R = +10^\circ \text{C} \) on paints PE1H5, PE1H10 and PE1H30. For brevity, individual load versus displacement and \( w_e \) versus \( f \) traces will not be plotted here. Instead, characteristic load versus displacement traces of paint PE1H5 at different temperatures are shown in Fig. 9. The same methods of data
over tests and reduction

Fig. 8. The essential work of fracture, $w_e$, and the non-essential component of the work, $\beta w_{in}$, versus cross-link density (a, c) and max tan $\delta$ (b, d). $\beta w_{in}$ versus ratio of elastic over total energy from cyclic loading (e).

reduction were used as outlined above. Plots of $w_e$ versus $T - T_g$ and $\beta w_{in}$ versus $T - T_g$ are shown in Fig. 10. Note that EWF testing of PE1H5 at $T_g - 10^\circ$C gave a negative $w_e$ value. This is considered unphysical and reflects the low toughness of the paint at this temperature combined with the uncertainty due to extrapolating from the measured data to find the y-axis intercept. Also, samples of PE1H30 failed in a brittle manner (within the initial linear part of the load versus displacement trace) at $T_g - 10^\circ$C and therefore these data were not considered further.

A clear maximum in the essential work of fracture is seen around $T_g$ for all three paints, while, $\beta w_{in}$ generally decreases with increasing temperature, see Fig. 10. It is worth noting that even though the maximum values of $w_e$ are strongly dependent on formulation, at both higher and lower temperatures the paints had similar toughness (i.e. at $T_g - 10^\circ$C and $T_g +10^\circ$C). Several studies have focused on the effect of temperature on the essential work of fracture. Hashemi and co-workers have investigated the fracture behaviour of several thermoplastics, and have generally found $w_e$ to remain unaffected by changes in temperature, while a maximum is reported in $\beta w_{in}$ versus temperature [21,23,37,38]. It is noted that these results were obtained at temperatures below the glass transition of the materials. Williams and Rink [20] claim that $\beta w_{in}$ is equal to $\sigma_y/2$. Considering that the yield strain of polymers is relatively unaffected by temperature compared to their modulus, it would be expected for the $\beta w_{in}$ versus temperature traces to follow the general shape
of the storage modulus curves from DMA. Qualitatively this is confirmed when comparing between Fig. 3 and Fig. 10. Kuno [39] found \( w_e \) to be independent of temperature below \( T_g \), but to decrease rapidly near the glass transition. Elsewhere [22,40,41] a maximum in \( w_e \) has been reported at temperatures where an \( \alpha \) or \( \beta \) relaxation takes place. Clearly, the effect of temperature on the essential work of fracture depends strongly on the material under investigation. An additional difficulty in explaining the current results comes from the fact that most of the published literature is on thermoplastic materials, whereas chemically cross-linked polymers are largely overlooked. Nevertheless, the position of the maximum in \( w_e \) at the \( T_g \) of the paints, suggests that the macroscopically observed fracture toughness is related to relaxation at a molecular level.

In trying to explain the effect of temperature on the essential work of fracture, several workers [21,23,37,38,40] have used a relationship, based on work by Cotterell and Reddel [16], that expresses \( w_e \) as a function of the crack opening displacement, \( \delta_c \), as:

\[
w_e = \frac{2}{3} \sigma_{m,\text{avg}} \delta_c
\]

(5)

where \( \sigma_{m,\text{avg}} \) is as defined previously, and the term 2/3 is related to the shape of the load–displacement trace which is assumed to be a parabola. Here this parabolic assumption appears justified at the lowest temperature (see \( T_g -10^\circ \) C trace in Fig. 9), however at higher temperatures a shape factor closer to 1 would seem more realistic (Fig. 9). To obtain the crack opening displacement, the maximum displacement, \( \delta_{\text{max}} \), for each sample is plotted versus \( l \). A linear regression is performed on the data, and \( \delta_c \) is determined as the intercept of the regression line with the \( y \)-axis.

It has been noted [38,40] that \( \sigma_{m,\text{avg}} \) and \( \delta_c \) move in opposite directions with temperature (\( \sigma_{m,\text{avg}} \) decreases with increasing temperature, whereas \( \delta_c \) increases with increasing temperature), and therefore it is the relative change of these two terms that dictates the effect of temperature on \( w_e \). Here, \( \sigma_{m,\text{avg}}, \delta_c \), and \( w_e \) were calculated using Eqs. (3) and (5) and are given in Table 4.

The general trend shown in Table 4 is for \( \sigma_{m,\text{avg}} \) to decrease and \( \delta_c \) to increase with increasing temperature, in agreement with results published elsewhere [38,40]. The essential work of fracture as calculated from Eq. (5) reaches a maximum at \( T_g \) which is in agreement with results obtained from Eq. (3), even though values obtained from Eq. (5) are significantly lower to those obtained from Eq. (3). The reasons for this discrepancy are unclear. It has already been suggested that the 2/3 factor in Eq. (5) is unrealistic at temperatures of \( T_g -5^\circ \) C or higher, and a value closer to 1 would better reflect the shape of the load–displacement curves. However, this still does not account for the difference in \( w_e \) values obtained from Eqs. (3) and (5). It is possible that the displacement as measured from the cross-head movement does not accurately capture the displacement in the area immediately surrounding the ligament.

An additional concern relates to the fact that the strain rate within the ligament will vary with ligament length, for constant cross-head displacement. Given the visco-elastic nature of these materials it may be expected that the different strain rates between ligaments could lead in errors in the measurement of \( w_e \). However, if changes in rate for different ligaments had a significant effect on the results, it would be expected that short ligaments and large ligaments would correspond to different types of load versus displacement traces. Additionally, such rate effects would be expected to lead to non-linear \( w_e \) versus \( l \) plots. In the present study, the self-similarity of the traces across ligament lengths as well as the linearity of the \( w_e \) versus \( l \) plots suggest that rate effects related to ligament length are not significant. The inclusion of such effects is recognised as a topic of interest for further study within a broader scope of including visco-elasticity in the standard methodology of the EWF test. Indeed, the visco-elastic nature of polymers is largely overlooked by the relevant EWF literature. The present paper serves to highlight visco-elasticity as an important factor affecting the fracture toughness of polymers and demonstrates the necessity for further analytical and experimental work on the fracture toughness of visco-elastic materials. In the future, tests where displacements are measured locally through digital image correlation and displacement rate is adjusted for the magnitude of strain inside the process zone, could help towards this direction and could explain the observed discrepancy in the results from Eqs. (3) and (5).

![Fig. 10. Essential work of fracture, \( w_e \), (a) and the non-essential component of the work, \( \rho w_{\text{non}} \), (b) versus temperature relative to \( T_g \).](image_url)
6. Conclusions

The fracture toughness of a series of thermoset polyester paint films was studied using the essential work of fracture method. The cross-link density of the paints was varied by changing the concentration of cross-linker, and the molecular weight and functionality of the polyester resin. The essential work of fracture, \( w_e \), was found to increase with decreasing cross-link density, from about 20 kJ/m\(^2\) at a network density of \( 0.4 \times 10^{-3} \text{ mol/cm}^3 \) to around 5 kJ/m\(^2\) at cross-link densities of \( 1 \times 10^{-3} \text{ mol/cm}^3 \) or higher. On the other hand, no clear correlation between the non-essential component of the work of fracture, \( \beta w_{\text{mm}} \), and cross-link density was found. When the effect of temperature was considered, \( w_e \) was found to reach a maximum value at the respective glass transition temperatures of the paints, while \( \beta w_{\text{mm}} \) generally decreased with increasing temperature. The effect of visco-elasticity on the fracture behaviour of polymers that are close to their \( T_g \) has been recognised, and the addition of visco-elastic effects to standard EWF methodology was highlighted as an area of particular interest for further investigation. Finally, the relationship between the fracture toughness of free-standing paint films, and the formability of the coating when applied on a metal substrate will be discussed in a future publication.

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References