THE MORPHOLOGY AND TOUGHNESS OF THERMOPLASTIC-MODIFIED EPOXY POLYMER WITH CARBON NANOTUBES OR SILICA NANOPARTICLES

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Abstract

The research carried out in this thesis was to investigate the effects of incorporating nanomodifiers into amine cured epoxy resin, with a second phase of thermoplastic.

The morphology and properties of the epoxy with various percentages of thermoplastic with reactive endgroups were assessed. As the percentage of thermoplastic was increased the morphology changed from spherical particulate, to co-continuous and finally phase inverted. The Young's modulus and 0.2% proof stress of the material were unaffected by the addition of the thermoplastic. The ultimate tensile strength (UTS) and fracture properties increased with increasing thermoplastic content.

Several methods of dispersion for the nanotubes were tested using different types of multiwalled carbon nanotubes. Sonicating non-functionalised Thomas Swan nanotubes into the epoxy gave the best dispersion. The dispersions were assessed using a greyscale analysis, and a quadrat analysis of transmission electron micrograph collages. Both methods gave comparable results. The addition of nanotubes to the blend was found to have no effect on the tensile or fracture properties of the polymer.

The addition of nanosilica to the blends was found to give an increase in Young's modulus but had no effect on the UTS, 0.2% proof stress or fracture properties. Plane strain compression tests were used to investigate why this epoxy was not toughened by the addition of nanosilica. These revealed that an epoxy which will toughen with the addition of nanosilica shows strain softening and significant shear band formation while the epoxy used throughout this thesis does not.

Finally the thermoplastic was used with different endgroups. Changing the endgroup from one reactive group to another had no effect on morphology, but resulted in a slight decrease in fracture properties. The unreactive endgroup had a significant effect on the morphology and resulted in general in an increase in fracture properties and a decrease in UTS.
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# Nomenclature

## Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>A.C.</td>
<td>Alternating current</td>
</tr>
<tr>
<td>AFM</td>
<td>Atomic force microscope</td>
</tr>
<tr>
<td>CT</td>
<td>Compact tension</td>
</tr>
<tr>
<td>D.C.</td>
<td>Direct current</td>
</tr>
<tr>
<td>DDS</td>
<td>Diaminodiphenylsulfone</td>
</tr>
<tr>
<td>DGEBA</td>
<td>Diglycidyl ether of bisphenol A</td>
</tr>
<tr>
<td>DGEBF</td>
<td>Diglycidyl ether of bisphenol F</td>
</tr>
<tr>
<td>DMA</td>
<td>Dynamic mechanical analysis</td>
</tr>
<tr>
<td>EDX</td>
<td>Energy dispersive X-ray</td>
</tr>
<tr>
<td>FEG-SEM</td>
<td>Field emission gun - scanning electron microscope</td>
</tr>
<tr>
<td>MCDEA</td>
<td>Amine curing agent</td>
</tr>
<tr>
<td>(4,4'-methylenebis-(3-chloro 2,6-diethylaniline))</td>
<td></td>
</tr>
<tr>
<td>MWNT</td>
<td>Multiwalled carbon nanotube</td>
</tr>
<tr>
<td>NS</td>
<td>Nanosilica</td>
</tr>
<tr>
<td>NT</td>
<td>Multiwalled carbon nanotube</td>
</tr>
<tr>
<td>PES</td>
<td>Poly (ether sulfone)</td>
</tr>
<tr>
<td>phr</td>
<td>Per Hundred Resin</td>
</tr>
<tr>
<td>PVA</td>
<td>Poly (vinyl alcohol)</td>
</tr>
<tr>
<td>SD</td>
<td>Standard deviation</td>
</tr>
<tr>
<td>SDS</td>
<td>Sodium dodecyl sulphate</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscope</td>
</tr>
<tr>
<td>SENB</td>
<td>Single edge notched bend</td>
</tr>
<tr>
<td>SWNT</td>
<td>Single walled carbon nanotube</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission electron microscope</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermal gravimetric analysis</td>
</tr>
<tr>
<td>TGAP</td>
<td>Triglycidyl aminophenol</td>
</tr>
<tr>
<td>TGDDM</td>
<td>Tetruglycidyl diamino diphenyl methane</td>
</tr>
<tr>
<td>TOM</td>
<td>Transmission optical microscopy</td>
</tr>
<tr>
<td>TP</td>
<td>Thermoplastic</td>
</tr>
<tr>
<td>UTS</td>
<td>Ultimate tensile strength</td>
</tr>
<tr>
<td>Vol</td>
<td>Volume</td>
</tr>
<tr>
<td>Wt</td>
<td>Weight</td>
</tr>
</tbody>
</table>
English Alphabet

A  Cross sectional area
a  Crack length for fracture tests
a_i  Half the length of an internal crack
a_c  Critical flaw size
B  Sample thickness for fracture tests
b_i  Width of narrow parallel-sided portion of tensile test specimen
b_o  Width at ends of tensile test specimen
E  Young's modulus
E_c  Young's modulus for the composite
E_f  Young's modulus for the filler
E_{flex}  Flexural modulus
E_m  Young's modulus for the matrix
E_{11}  Longitudinal Young's modulus
E_{22}  Transverse Young's modulus
G_c  Fracture energy
h  Thickness of tensile test specimen
K_c  Fracture toughness
K_Q  Trial K_c value
L  Initial distance between grips of tensile test specimen
l_i  Length of narrow parallel-sided portion of tensile test specimen
l_o  Overall length of tensile test specimen
n  Number of quadrats
P  Load
P_c  Load used from fracture test for calculating K_c
P_{max}  Maximum load during fracture test
P_Q  Load from fracture test where 5% compliance line crosses
R1  Thermoplastic with the reactive endgroup used most in this project
R2  Thermoplastic with the other reactive endgroup
r_1  Small radius of tensile test specimen
r_2  Large radius of tensile test specimen
S  Mean deviation for quadrat analysis
T_g  Glass transition temperature
U  Thermoplastic with the unreactive endgroup
V_f  Volume fraction of filler
W  Sample width for fracture tests
W_B  Energy to break
w/t  Particle aspect ratio for Halpin-Tsai
x  Equals a/W
\bar{x}  mean number of nanotubes per quadrat for quadrat analysis
Y(a/W)  Shape factor for K_c

Greek Alphabet

\varepsilon  Strain
\varepsilon_t  True strain
\zeta  Shape factor for Halpin-Tsai
\eta  Halpin-Tsai coefficient
\nu  Poisson's ratio
\sigma_c  Critical stress which causes fracture
\sigma_f  Stress factor taken from ultimate tensile strength
\sigma_t  True stress
\sigma_y  Yield stress
\Phi(x)  Factor for calculation of fracture energy
Chapter 1 Introduction

Epoxy polymers have been used widely as adhesives and as the matrix for fibre composites. In polymer form they provide good thermal stability and a high Young’s modulus which are desirable properties, and for application in composites, epoxy resins can have low viscosities which are essential for resin infusion. However the polymers tend to be brittle and much work has previously been carried out to find ways of increasing the toughness and fracture energy of epoxy polymers, e.g. [1-3].

Rubber has been found to effectively toughen epoxies but it also reduces the thermal stability and the Young’s modulus of the final polymer [4] which for some applications is not acceptable. Previous work has shown that epoxy / thermoplastic blends have better thermal stability and less of a reduction in Young’s modulus than the epoxy polymer with rubber [1]. For this reason thermoplastic is used in this work.

The addition of micron sized glass particles has also been found to increase the toughness of epoxy resins, but unfortunately it also increases the viscosity [5]. This increase in viscosity is a major limitation for the use of the epoxy in infusion techniques for making fibre composites. Nanomodifiers have more recently been investigated as it is thought they might provide an increase in toughness without such a large increase in viscosity [6], although only if the nanoparticles are well dispersed and do not agglomerate or entangle. However there is still much speculation about the mechanisms involved in nanoparticle toughening [7-9].

Carbon nanotubes were only discovered in 1991 [10] and since then there has been much speculation about possible uses for them. They have been found to have an exceptionally high modulus and strength, and in some cases the ability to conduct electricity [11]. The use of nanotubes in epoxy polymers has been investigated to increase a variety of mechanical and fracture properties, and also to turn the polymer into a conductor which would have a wide range of uses in anti-static applications [12].

The objectives of the work detailed in this thesis were to investigate the effects of adding a thermoplastic to an epoxy polymer, on the morphology, mechanical and fracture properties of the epoxy. Multiwalled carbon nanotubes were also to be added to the epoxy / thermoplastic blend. Firstly a dispersion method for the nanotubes had
to be decided upon and then methods for assessing the resulting dispersion were tested. After a dispersion method was chosen the multiwalled carbon nanotubes were added to the epoxy / thermoplastic blend, with the aim of increasing the fracture properties of the epoxy for eventual use in carbon fibre composites. Nanosilica particles were also to be added to the blend with the same aims.

This thesis starts with a literature survey in Chapter 2 which covers the use of epoxy resins for fibre composites and the work carried out previously into the use of thermoplastics to increase the toughness of the polymer. It also looks at the use of nanosilica particles in the toughening of epoxy polymers, and the properties of carbon nanotubes and their use in epoxy polymers. Discussion on methods of dispersing the nanotubes forms a significant portion of this chapter as understanding how to achieve a dispersion of the nanotubes within the polymer is thought to be important in understanding, and being able to reproduce, any mechanical or fracture results.

Chapter 3 gives details of the chemistry of the different epoxy resins, the curing agents and the thermoplastic which formed the epoxy and epoxy / thermoplastic blend. It also describes some properties of the nanotubes and the nanosilica. A variety of tests have been used to investigate the results of the addition of thermoplastic, nanosilica particles and multiwalled carbon nanotubes to the epoxy resin. Chapter 4 covers the experimental details for these testing methods. These included tensile tests to obtain the Young’s modulus, ultimate tensile strength and 0.2% proof stress. Fracture tests were carried out using compact tension or single edge notched bend specimens to determine the fracture toughness and fracture energy. To investigate the morphology of the polymers an atomic force microscope was used. A scanning electron microscope was used to image the fracture surfaces to identify the fracture and toughening mechanisms.

The above tests were carried out on the epoxy with five different percentages of thermoplastic, and Chapter 5 discusses the results. The five percentages the thermoplastic was added at range from 0 to 35 wt% and were used to cover the range of morphologies that the epoxy / thermoplastic blend can form once cured.

When dealing with nanotubes in the epoxy, one of the main problems is the dispersion of the nanotubes. Various aspects related to the dispersion are covered in Chapter 6. Two different methods were used for assessing the dispersion. One compared the greyscale histogram from images of thin sections of the bulk polymer. The other
method employed a quadrat analysis of a collage of transmission electron microscopy images. Having ascertained that the dispersion of the nanotubes was changing during the curing process a hot stage was used to examine the movement of the nanotubes during cure.

For the nanomodified polymers the thermoplastic was added at three percentages only, 0, 15 and 25 wt%. These were chosen to give a range of morphologies. The results of the tensile and fracture tests on the epoxy and thermoplastic blends with the nanomodifiers are covered in Chapter 7, with the results from the microscopy work.

Having found that the nanosilica particles do not lead to an improvement in fracture toughness and fracture energy in this epoxy, a small selection of samples of an epoxy, which has previously been found to have an increase in toughness with the addition of nanosilica, were made and tested. As expected for this second epoxy, an increase in fracture toughness and energy was seen with the addition of nanosilica. To investigate why one epoxy will be toughened by adding nanosilica when the main one used in this thesis will not, both epoxy polymers were tested in plane strain compression. The traces from the compression tests and the appearance of the shear bands formed in the samples have been used to formulate a hypothesis for why one epoxy will toughen while the other will not. The tests and result for this second epoxy and the plane strain compression test results are covered in Chapter 8.

The thermoplastic used was supplied in three batches, one main batch which was used for the majority of tests and two small batches which were used in the work recorded in Chapter 9. These smaller batches contained the same thermoplastic but with different endgroups. The effect of changing the endgroup on the thermoplastic was investigated in relation to the tensile and fracture properties, and the morphology.

Chapter 10 summarises the main findings from the preceding chapters and briefly describes some suggestions for future work which continues from the discoveries made during this project.
Chapter 2   Literature Review

2.1 Introduction

The work discussed in this thesis looks at various aspects of using a thermosetting polymer, epoxy, blended with a thermoplastic toughener, and the inclusion of nanomodifiers, carbon nanotubes and nanosilica, as additional tougheners. This survey looks at the literature available as a background to this work. It looks at the research performed using thermoplastics as tougheners, and more specifically at poly (ether sulfone) (PES) in thermosets such as epoxy. It also looks at various properties of carbon nanotubes and the properties they have been predicted to give to hybrids containing them. Literature on the actual properties found by experimentation and finally work done on the dispersion of nanotubes will be described. Previous work on the properties of hybrids containing nanosilica will also be explored.

2.2 The Origins of Fracture Toughness Testing

The failure of engineering materials is almost always undesirable. For this reason the study of fracture mechanics is important. Through the study of fracture mechanics a greater understanding of the causes of fracture can be developed and this can influence the choice of materials and the design of components. It can also be used as a means of analysing the properties of new materials so these materials can be tailored to have specific properties for specific uses.

The derivation of fracture toughness (\(K_c\)) and fracture energy (\(G_c\)) are covered in several elementary text books. The section below is adapted from the work by Callister [13].

The fracture of a solid requires the breaking of bonds between atoms, but back in the 1920s Griffiths found that the actual stress required to break a material is typically between 10 and 1000 times below the theoretical cohesive strength and that the cause of this are flaws in the materials which act as stress concentrations. He went on to propose that all brittle materials contain flaws and that fracture will occur when the
stress at the tip of a flaw exceeds the theoretical cohesive stress. The distribution of stresses around a crack tip are given by a stress intensity factor $K$, where $K$ is dependent on the size of the crack, the applied stress and the sample geometry.

When a crack propagates there is a release of elastic energy stored in the material from the elastic deformation it has undergone. Equally there is energy used up in the formation of new free surfaces and plastic deformation. The result of balancing these energies is the critical strain energy release rate $G_c$, which is given in Equation 2.1

$$G_c = \frac{\pi \sigma_c^2 a_i}{E}$$ \hspace{1cm} \text{Equation 2.1}

Where $a_i$ is one half the length of an internal crack, $E$ is the modulus of elasticity and $\sigma_c$ is the critical stress which will cause fracture.

Since $K$ is a measure of the stress at the crack tip, there is a critical value of $K$ for which the material will fracture. This is called $K_c$ and is given by Equation 2.2.

$$K_c = Y(a/w)\sigma_c\sqrt{\pi a}$$ \hspace{1cm} \text{Equation 2.2}

Where $Y(a/w)$ is a shape factor which is a function of the crack length and the geometry of the sample.

For thin samples, $K_c$ is found to be dependent on the specimen thickness, $B$. As $B$ increases a critical value of $B$ is reached beyond which $K_c$ is independent of thickness and this value of $K$ is known as the plane strain fracture toughness $K_c$. The higher the $K_c$, the more ductile the material and the less likely it is to undergo catastrophic failure.

The criterion for $B$ to give plane strain fracture toughness is given in Equation 2.3.

$$B \geq 2.5 \left( \frac{K_c}{\sigma_f} \right)^2$$ \hspace{1cm} \text{Equation 2.3}

The equations used in testing fracture energy and fracture toughness throughout this thesis are derived from these equations.
2.3 Epoxy Polymers

Epoxy resins are special types of polyether which have reactive epoxide endgroups. These endgroups allow the resin to be grafted onto other polymers and allow the resin to form cross-links, a process often referred to as curing [14]. The form of the epoxide endgroup is shown in Figure 2.1.

![Epoxide endgroup](image)

Figure 2.1: The epoxide endgroup.

Epoxy resins need at least two epoxy groups per chain, they are typically di-, tri- or tetrafunctional. The structures of three typical epoxy resins are shown in Figure 2.2 below [15].

![Chemical structures of three epoxy resins](image)

Figure 2.2: The chemical structures of three epoxy resins.
Cross-linking can be achieved in principle by using any di- or polyfuctional compound (hardener) which adds on to the epoxy groups. Cross-linking using amines is common. Figure 2.3 shows a generalised cross-linking reaction using amine.

![Cross-linking reaction diagram](image)

Figure 2.3: The cross-linking reaction of epoxy endgroups using amine.

Care must be taken when cross-linking reactions are taking place as they are exothermic, releasing 22-26 kcal per mole of epoxy groups [16]. The heat produced can cause burning and so samples are often kept small.

The properties of epoxy resins in the cross-linked state are generally considered very good, with high resistance to chemicals, temperature, solvents and moisture [16, 17]. This makes them suitable for a wide variety of uses including use in composites and protective coatings and as adhesives. The specific properties depend on several factors including [18]:

a) The type and amount of curing agent
b) The degree of cross-linking
c) The nature and amount of additives

The effect of too much curing agent can be to stop chain building at low molecular weight, leading to the polymer being brittle. Too little curing agent will not provide adequate cure [19]. A high degree of cross-linking will also lead to brittleness. Using a flexibiliser as an additive will reduce the degree of cross-linking thereby reducing the brittleness. Other additives include diluents, such as toluene, which reduce the
viscosity of the epoxy prior to curing, and are used in applications such as the impregnation of fibre mats. Fillers are also additives and their main role is to reduce shrinkage and cost but can also be used to improve heat resistance, moisture resistance, electrical conductivity or insulation depending to the exact filler [18].

Table 2.1 gives a variety of typical properties and Figure 2.4 shows the uses of epoxy resins in 1988 [18].

Table 2.1: Properties of a typical cross-linked epoxy. Taken from [18].

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glass transition temperature (°C)</td>
<td>120-190</td>
</tr>
<tr>
<td>Max Continuous Service Temperature (°C)</td>
<td>130</td>
</tr>
<tr>
<td>Specific Gravity</td>
<td>1.11-1.14</td>
</tr>
<tr>
<td>Thermal Conductivity (W/m*K)</td>
<td>0.88</td>
</tr>
<tr>
<td>Coefficient of Linear Thermal Expansion (1/Kx10^6)</td>
<td>11-13</td>
</tr>
<tr>
<td>Tensile Modulus (GPa)</td>
<td>2.1-5.5</td>
</tr>
<tr>
<td>Tensile Strength (MPa)</td>
<td>28-90</td>
</tr>
<tr>
<td>Compressive Strength (MPa)</td>
<td>241</td>
</tr>
<tr>
<td>Water Absorption (vol%)</td>
<td>0.05-0.2</td>
</tr>
<tr>
<td>Stability to Acids and Bases</td>
<td>Excellent</td>
</tr>
<tr>
<td>Stability to Solvents</td>
<td>Variable (less stable to Ketones and Halogenated Hydrocarbons)</td>
</tr>
</tbody>
</table>

Figure 2.4: Uses of epoxy resins in 1988 by end user. Data taken from [18].
Although the mechanical properties and chemical resistance of epoxy polymers are good, their high cross-link density makes them brittle. At low temperatures (below their $T_g$) epoxies will fail at very low strains, even before yielding. As the temperature approaches $T_g$ they yield first but will still not show necking and cold drawing [20]. This brittle nature with their poor resistance to crack propagation has led to the addition of a second particulate phase, commonly rubber, to toughen them.

The higher the functionality of the epoxy resin the more cross-linked it will be. While high cross-link density will give the resin high strength and high glass transition temperature, it will also make it more brittle. An alternative method of toughening resins, instead of using rubber, is to reduce the cross-link density [17]. However this has been found to reduce the stiffness, strength and heat resistance of the epoxy, which are some of the desirable factors [18].

### 2.4 Epoxy / Thermoplastic Blends

As detailed above, the properties of epoxy polymers include good thermal stability, relatively high modulus, solvent and creep resistance and excellent adhesion. They also have low ductility and poor fracture toughness [1, 21]. Toughening epoxy resins has been achieved with a variety of different materials such as rubbers, inorganic glasses, polyurethanes and acrylcs. Unfortunately these additives not only increase the toughness but reduce other desirable properties such as modulus or tensile strength [15].

Adding rubbers to toughen epoxies has been extensively tried and while this does have a toughening effect it also reduces the high temperature performance. This effect is the result of the low glass transition temperatures of rubbers in comparison to those of epoxy resins. Since thermal stability is an important factor in the use of epoxies, a lowering of the maximum use temperature is undesirable [22].

Toughening with thermoplastics has been suggested as a possible solution to this problem. McGrail et al [21] suggested that there is a limited choice of thermoplastics which have the required properties, and maintain the high glass transition temperature and modulus of the thermosetting epoxy resin. These are basically polyaromatics and polyamides. Of these groups poly(ether sulfone) (PES) has been the thermoplastic
used in many studies looking at the toughening of epoxy resins with thermoplastics, e.g.[1, 4, 23, 24].

Poly(ether sulfone) (PES) is a thermoplastic polymer with the structure shown below in Figure 2.5.

![Figure 2.5: The chemical structure of PES. Taken from [17].](image)

The properties of PES described in [25], include high tensile and impact strengths, plus good resistance to chemical attack, particularly from acids, alkalis, oils, greases, aliphatic hydrocarbons and alcohols. It has a low water absorption (about 2.3% at saturation) and electrically it is a good insulator. The properties reported are shown in Table 2.2.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific Gravity</td>
<td>1.37</td>
</tr>
<tr>
<td>Glass Transition Temperature (°C)</td>
<td>230</td>
</tr>
<tr>
<td>Coefficient of Linear Thermal Expansion</td>
<td>55</td>
</tr>
<tr>
<td>Thermal Conductivity (cal / cm. sec °C x10^-4)</td>
<td>3.2-4.4</td>
</tr>
</tbody>
</table>

### 2.4.1 Morphology

Early studies on the effects of introducing PES into epoxy resin found that when specimens of triglycidyl aminophenol (TGAP) epoxy, toughened with PES and hardened with diaminodiphenylsulfone (DDS), were examined under a scanning electron microscope, nodules were evident [23]. These nodules appear as small spherical lumps on the fracture surface, see Figure 2.6 for an example. These nodules increased in size with increasing PES concentration and it was concluded that the matrix was epoxy while the nodules contain cross-linked epoxy which had reacted with
the PES. When tetra glycidyl diamino diphenyl methane (TGDDM) was used in place of the TGAP no evidence of phase separation was seen at any percentage of PES.

Figure 2.6: Scanning electron micrograph of the fracture surface of an epoxy specimen containing 7 wt% PES showing 'nodules'. Taken from [23].

A more detailed study, including the changes in these 'nodules' as the percentage of PES increased, was carried out by Kinloch et al [1]. Triglycidyl aminophenol epoxy was used with DDS as a curing agent and a reactively terminated PES copolymer as toughener. They found that up to 8 parts per hundred resin (phr), about 5 wt%, the PES was soluble in the epoxy after curing, so a single phase microstructure was produced. Above 5 wt%, a second PES rich phase was seen in the form of particles between 0.2 and 0.4 μm diameter. Epoxy rich occlusions could also be seen within these particles. As more PES was added, the PES rich particles became larger and more elongated until at about 52 phr, (25 wt%), the phase became co-continuous. Once the PES content was higher than 83 phr, (35 wt%), a phase inverted structure was formed. Figure 2.7 shows the scanning electron micrographs of these different structures.
Figure 2.7: Microstructures of the epoxy resin / PES system showing a) particulate microstructure, b) “ribbon like” microstructure, c) co-continuous microstructure, and d) phase inverted microstructure. Taken from [1].

Dynamic mechanical thermal analysis showed that the glass transition temperature ($T_g$) of the TGAP epoxy blended with PES decreased as the percentage of PES increased up to the 5 wt% threshold. This was due to the PES having a lower $T_g$ than the epoxy. The $T_g$ of the cured epoxy, measured at 1 Hz, was 264 °C, while the $T_g$ of the PES was estimated at between 185 and 190 °C. Once the two phases separate the $T_g$ for the epoxy rich phase recovers to roughly the same value as for pure epoxy, indicating approximately complete phase separation. As the concentration of PES increases, the $T_g$ of the epoxy rich phase decreases and for the PES rich phase increases. This indicates that the amount of PES in the epoxy rich phase is increasing and so is the amount of epoxy in the PES rich phase. A graph of glass transition temperature against PES content is shown in Figure 2.8.
Hedrick et al [26] came to similar conclusions, namely that initially the uncured epoxy and thermoplastic form a homogeneous mixture. Upon curing the second phase will separate out. At low weight percentages (10-15% typically) this will happen as discrete spheres. At higher thermoplastic content (30-40%) phase inversion will occur and there will be spheres of epoxy resin in a thermoplastic matrix.

MacKinnon et al [27] also agree with these findings. They tested triglycidyl aminophenol epoxy with DDS as the hardener and Victrex 5003P, poly(ether sulfone) toughener. They found that while all of their samples showed a phase separated morphology, those below 20 wt% PES had a thermoplastic rich particulate phase, this morphology then changed to ribbon like, and at 20-25 wt% PES to co-continuous. Above this PES content a phase inverted structure was again seen with epoxy rich particles having a diameter of about 0.2 μm, while the diameter of the PES rich phase particles on initial phase separation was closer to 0.4 μm.

Control over the morphology of PES / epoxy blends has been achieved by using curing agents of different reactivity and by varying the curing temperature. This can accelerate the approach to the gel point and arrest the changes in morphology before complete phase separation takes place [22]. Another method of controlling the morphology is by varying the thermoplastic backbone [21], as changing the sulfone content of the backbone was shown to change the morphology from homogeneous, through thermoplastic particulate and co-continuous to phase inverted. Other methods...
of changing the morphology that have been suggested include changing the molecular weight and chemical inter-activity of the thermoplastic [21].

2.4.2 Properties

Early studies by Bucknall et al [23] and Raghava [24] found no significant effect on the mechanical properties of epoxy polymer with increases in the PES content. However more recent tests by other people have found a link between the fracture toughness, $K_C$, and fracture energy, $G_C$ and the thermoplastic content.

MacKinnon et al [27] found that increasing the amount of thermoplastic in the epoxy progressively decreases the flexural modulus, and also affected the yield strength. Initially the yield strength drops off rapidly with increasing thermoplastic content, but after 20 wt% this levels off and could be explained as a result of the continuous phase having become thermoplastic. The fracture performance shows very little change up to about 15 wt% content when the phases become co-continuous, but after this there is a clear increase in the $K_C$ and $G_C$ values.

One possible explanation for the results of Bucknall et al, which showed no effect of increasing PES content, is the lack of functional endgroups on their thermoplastic. McGrail and Street [21] investigated the effects of increasing the concentration of reactive endgroups, and their results clearly showed a large increase in $G_C$ as the percentage of functional endgroups increased, as shown in Table 2.3. These polymers were blended into a fixed epoxy formulation.

Table 2.3: Influence of polymer endgroups on the mechanical and fracture properties of PES / epoxy blends, taken from [21].

<table>
<thead>
<tr>
<th>Endgroup Molar Ratio</th>
<th>Flexural Modulus (GPa)</th>
<th>Yield Strength (MPa)</th>
<th>Fracture Energy $G_C$ (J/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unreactive 0</td>
<td>3.20</td>
<td>-</td>
<td>20</td>
</tr>
<tr>
<td>Reactive 26</td>
<td>3.27</td>
<td>160</td>
<td>80</td>
</tr>
<tr>
<td>Reactive 57</td>
<td>3.26</td>
<td>164</td>
<td>690</td>
</tr>
<tr>
<td>Reactive 96</td>
<td>3.16</td>
<td>169</td>
<td>920</td>
</tr>
</tbody>
</table>
The authors also investigated the effects on the fracture toughness and the morphology of changing both the sulfone content of the thermoplastic and the percentage of thermoplastic in the resin. They found that as the percentage of thermoplastic increased the morphology went from homogeneous, through thermoplastic particulate and co-continuous to phase inverted, while at the same time the fracture toughness increased. However the increase was most rapid through the change to co-continuous, as shown in Figure 2.9. Increasing the number of sulfone groups in the backbone of the PES also changed the morphology, from phase inverted through to homogeneous with a peak in fracture toughness in the co-continuous stage.

The effect of the thermoplastic molecular weight was also investigated and it was shown that the fracture toughness increased linearly as the molecular weight increased.

Figure 2.9: Fracture energy of epoxy versus thermoplastic structure (x) and content (o). Morphology is abbreviated as H - homogeneous, P - particulate, R - ribbon like, C - co-continuous, PI - phase inverted. Taken from [21].

MacKinnon et al [27] performed dielectric tests on a PES / TGAP blend. During these tests a high level of D.C. conductivity was initially observed and this reduced during the curing of the 30 wt% thermoplastic / epoxy blend. However significant D.C. conductivity was still evident in some of the fully cured samples.

Two other important properties of polymers are the gel time and the glass transition temperature. MacKinnon et al [27] found that the addition of the thermoplastic increased the gel time of triglycidyl aminophenol epoxy from 23.4 minutes with
20.6 wt% PES to 36 minutes with 39.1 wt% PES. The gel point was taken as the time when the viscosity reached 104 Pa s.

Lastly they looked at the effect on the glass transition temperature, $T_g$, and concluded that although the $T_g$ of the pure epoxy polymer was higher than that of the blend, (the $T_g$ of PES has been estimated as being between 185 and 190 °C), the $T_g$ of the blend was approximately constant with varying percentage of thermoplastic. The numerical value for $T_g$ of the cured mix was given as 237 °C while the range for the mix was 207-220 °C. The value for 0% PES and the upper limit of the range for the mix seem close together given the spread of values for the mix. This may be evidence of a true change in the $T_g$ or it could just be experimental error. When plotted the results could also be interpreted as a downwards slope, so $T_g$ decreases as the percentage of thermoplastic increases, see Figure 2.10. This decrease is also the trend predicted by the Fox-Flory rule of mixtures, although the experimental values are lower than the theoretically predicted values.

![Figure 2.10: Glass transition temperature versus the PES content in triglycidyl aminophenol epoxy with a trend line and the theoretical values calculated using Fox-Flory. Data taken from [27].](image)

Kinloch et al [1] carried out various mechanical tests on their triglycidyl aminophenol epoxy / DDS / PES blends, including ones to determine the flexural modulus and the fracture toughness. The flexural modulus was determined by using a three point
bending test at a rate of 0.5 mm/min. The results showed that the flexural modulus, $E_{\text{flex}}$, of the material undergoes a rapid decrease when the structure is homogeneous until the 8 phr (5 wt%) threshold, and then a slower but continuous decrease after phase separation occurs, see Figure 2.11.

![Graph showing flexural modulus versus thermoplastic content for epoxy / PES blends.](image)

Figure 2.11: Flexural modulus versus thermoplastic content for epoxy / PES blends. Taken from [1].

The fracture toughnesses, $K_C$, of the specimens were found using compact tension specimens, 20 mm x 20 mm x 3.5 mm. These were notched with a hacksaw and then gentle tapping of a razor blade into the notch caused a natural crack to grow. The tests were carried out at 0.5 mm/min. The $K_C$ curve for increasing PES content shows an initial decrease until phase separation occurs, indicating that the "single-phase microstructure of thermoplastic dissolved in epoxy polymer does not give any toughening effect", see Figure 2.12. After phase separation the $K_C$ curve increases smoothly with no discontinuities. The $G_C$ curve shows no initial decrease since both the $K_C$ and the modulus decrease, once again the curve is continuous with no discontinuities where the microstructure changes from particulate to co-continuous to phase inverted, see Figure 2.13.
Studies of the fracture surface showed no signs of cavitation, debonding of the particulate phase, or plastic yielding of the epoxy rich or PES rich phases which would have accounted for the increased toughening. The authors also noted that deflection of the crack was minimal. The increased toughness in the co-continuous and the phase inverted specimens could be explained by the necessity of the crack to go through the PES rich phase, and if the molecular weight has been increased by chain extension from the epoxy this would lead to increased toughness of this phase.

In the review by Hodgkin et al [15] four main parameters for the toughening of multiphase systems were identified. These were a) the size of the separated particles, b) the strength of the separated particles, c) the adhesion between the separated particles and the matrix, and d) the distribution of the particles within the matrix.
The use of reactive endgroups was also discussed and it was thought that these would increase toughness by achieving good interfacial bonding. By using reactive endgroups significant improvements to toughness were achieved by several researchers, including MacKinnon et al [4] who found that amine terminated PES provided the optimum fracture toughness. The molecular weight also played an important role, with the fracture toughness increasing with increased molecular weight.

Phenolic hydroxyl and aromatic amine functionally-terminated polysulfone with epoxy resin were used by Hedrick et al [26]. These were found to be miscible over all compositions prior to curing with the polysulfone forming a particulate phase in the epoxy matrix upon curing. The resultant network showed significantly enhanced fracture toughness over pure epoxy but the flexural modulus decreased. These results were explained by the ductile nature of the polysulfone rich composite particles perhaps resulting in crack pinning.

The molecular weight of the polysulfone oligomer also plays a significant role with higher molecular weights leading to higher fracture toughness [26]. The chemical linkage resulting from the functionalisation of the polysulfone was believed to be important for the improved impact strength. However when the epoxy was modified with a nonreactive polysulfone the fracture toughness was still seen to increase despite insufficient adhesion to allow ductile tearing or drawing of the polysulfone.

The conclusions drawn form the review by Hodgkin et al [5] include:
- Optimum toughness is achieved with a co-continuous or phase inverted morphology.
- Reactive endgroups in the toughening phase do not appear necessary to achieve good toughening.
- Thermoplastics toughen highly cross-linked epoxy resins more effectively than they do lower cross-link density materials
- Increasing the molecular weight of the thermoplastic increases the system toughness.
2.4.3 Epoxy Blends with PES

This section discusses the use of blends of two or more epoxy resins, with PES as a toughener.

Kinloch et al. [1] used triglycidyl aminophenol and diglycidyl ether of bisphenol F blended with DDS as curing agent and PES as a toughener. They carried out tests to investigate changes in morphology with increasing percentage of PES, and also to find the effect of this increase on the fracture toughness. It was found that the 8 phr (5 wt%) threshold discovered when only a single epoxy resin was used still existed. Above this value, PES rich particles were seen, but these were smaller than those in the single component system, and phase inversion was not seen at all. The two epoxies formed a single phase, with the T₉ being around 200 °C. The cured system containing the PES showed a broad tan δ peak between 170 °C and 230 °C. There was a steady decrease in the flexural modulus of the system and it was lower than that of the single component system.

The Gₐ and Kₐ values were shown to decrease initially in a similar way to the single component system and then increase after the formation of a phase separated system. However after about 50 phr (25 wt%) PES the two epoxy blended system shows lower values that the single epoxy system. Hence the addition of PES over 50 phr (25 wt%) has a greater effect in increasing the toughness of the single epoxy system than it does the two epoxy system.

MacKinnon et al. [4] also used triglycidyl aminophenol epoxy and diglycidyl ether of bisphenol F to form a blend with the diglycidyl ether of bisphenol F being the second epoxy component. They found that the introduction of the diglycidyl ether of bisphenol F caused a decrease in the yield strength at low thermoplastic content compared to the pure triglycidyl aminophenol epoxy samples. However, above 20 wt% thermoplastic the yield strengths of the systems are reasonably similar, indicating the dominance of the thermoplastic phase on the performance.
2.4.4 Summary

Epoxy resins have many excellent properties which make them ideal in a wide range of applications. Their good thermal stability, relatively high modulus, solvent and creep resistance and excellent adhesion are useful properties. Unfortunately they also have low ductility and poor fracture toughness. Toughening epoxy resins with thermoplastics has been suggested as a possible solution to this problem and poly(ether sulfone) (PES) has been the thermoplastic focused on.

It has been found that at very low weight percentages of thermoplastic, the PES was soluble in the epoxy after curing so a single phase microstructure was produced. As the amount of PES increased a second PES rich phase was seen with epoxy rich occlusions within these. As yet more PES was added the PES rich particles became larger and more elongated until eventually the phase became co-continuous. When the loading of PES was even higher a phase inverted structure was formed.

The morphology was generally agreed to affect the fracture toughness. Increasing the thermoplastic content increased the fracture toughness with optimum toughness being achieved in the co-continuous or phase inverted morphologies. Increasing the thermoplastic content was also found to reduce the flexural modulus and the glass transition temperature.

Adding functional endgroups to the PES in some work has been found to have no effect on the fracture toughness but in the majority of cases it has been seen to be beneficial. The use of a blend of two epoxy resins was also explored briefly and the findings in general showed a reduction in the desired effect over that of a single epoxy system. The yield strength was lower for the blend as was the fracture toughness at a given percentage of PES.
2.5 Nanosilica and its Composites

2.5.1 Nanosilica Particles

Nanosilica particles are spheres of SiO$_2$ with diameters in the order of nanometres. One of the most commonly used forms of nanosilica contains spheres of 20 nm diameter which have been formed using a sol-gel process and transferred into the epoxy resin without drying. These nanosilica particles have a small range of diameters and are well dispersed as a result of their silane treatment. Figure 2.14 shows a transmission electron microscopy (TEM) image of an epoxy containing these nanosilica particles from their manufacturer, Nanoresins, Germany.

![Transmission electron micrograph of dispersed nanosilica](image)

Figure 2.14: Transmission electron micrograph of dispersed nanosilica [28].

2.5.2 Mechanical Properties of Nanosilica / Epoxy Composites

Micron sized glass particles have long been seen as a method of toughening epoxies, and the more recent discovery of nanosilica particles has prompted researchers to explore the potential of nanosilica reinforced epoxy polymers.

In 2005 Kinloch et al [29] reported a significant increase in Young's modulus, fracture toughness and fracture energy for an anhydride cured DGEBA with the nanosilica dispersed in the epoxy through a sol-gel technique. The nanosilica was added up to 20.2 wt% and the Young's modulus was reported to increase from 2.96 to 3.85 GPa,
the fracture toughness increased from 103 to 461 J/m². Even at 20.2 wt% the composite was reported to have an agglomerate free colloidal dispersion which also gave the material a low viscosity.

Zhang et al [30] also investigated the effects of using nanosilica in epoxy composites. They used nanoparticles rather than micron sized particles as their high specific surface area promotes stress transfer from the matrix to the nanoparticles. This means that the required loadings are lower for nanofillers than microfillers which means several of the intrinsic merits of the neat resin are retained, such as low weight, processability and transparency. They used nanosilica particles formed in-situ through a sol-gel technique and an anhydride curing agent was employed. Up to 14 vol% nanosilica, the nanocomposite was optically transparent, and the glass transition temperature, modulus, microhardness and fracture toughness increase with increasing percentages of nanosilica. The Charpy impact resistance increased to a maximum at 3 vol% and the flexural strength was not affected by the addition of nanosilica. Figure 2.15 shows these results graphically.

![Figure 2.15: Testing results for nanosilica / epoxy composite. Taken from [30].](image)

### 2.5.3 Toughening Mechanisms

Although it is generally agreed that the addition of nanosilica can increase the fracture toughness and energy of epoxy resins, there have been no conclusions about the
toughening mechanisms. However several hypotheses have been put forward by different authors.

Zhang et al [30] suggested that the polymer in close proximity to the nanosilica may have different properties to the bulk polymer, and for nanosilica particles the interparticle spacing is sufficiently small that there would be a three-dimensional network of interphase. This would significantly affect the composite properties. The critical thickness of the interphase is thought to be approximately the same as the particle radius. They also suggest that the formation of ‘dimples’ on the fracture surface is a toughening mechanism as these are seen on the fracture surfaces of the epoxy with nanosilica, and the more nanosilica present the more dimples that are seen. Also seen on the fracture surfaces are river lines. These are only seen after crack initiation for pure epoxy and are associated with crack tip blunting, however they are also seen in the propagation region for the nanocomposites and here they are associated with high energy dissipation. Deflection of these river lines is thought to be an indication of crack pinning.

Another suggestion for the toughening mechanism was put forward by Johnsen et al [8]. Here they suggested that for crack pinning and crack deflection, the crack tip opening displacement needs to be less than the particle diameter, which is not the case where nanosilica particles are used. They also cast doubt on the three dimensional network of interphase being responsible for the toughening seen in their material, as this interphase would be expected to affect the glass transition temperature of the epoxy, and they reported no change in the glass transition temperature with the addition of nanosilica. Their suggestion for the toughening mechanism, instead, focused on the appearance of tiny voids (approximately 30 nm across) around the nanosilica particles when the fracture surfaces were examined with a field emission gun scanning electron microscope (FEG-SEM). The image of the voids is given in Figure 2.16. Using an analytical model by Huang and Kinloch, they showed that, assuming poor adhesion between particle and matrix, the toughening increment expected from the formation of 30 nm voids exceeds the actual improvement in toughness seen through experimentation. It is unlikely that all particles will grow voids so this overestimate is acceptable and therefore the growth of these voids theoretically could account for the increased fracture toughness and energy.
Chapter 2: Literature Review

A third suggestion for the toughening mechanism has been put forward by Ma et al [9]. They suggest that toughening is related to shear yielding. To investigate what was happening during fracture they used a sample with a crack in it which had been loaded to 80% of the critical load, so that a damage zone was formed. They found that this damage zone was between 100 and 200 nm in thickness and propagated at 90° to the applied load. They found no evidence of cavitation or debonding of the nanosilica particles. Their hypothesis is that the difference in Young's modulus and Poisson's ratio between the nanosilica and the epoxy causes stress fields to occur, these stress fields overlap and there is highly constrained development of local matrix yielding, forming this extremely narrow yielded zone.

It is clear from these three very different suggestions of toughening mechanisms that a definitive answer to the toughening mechanism which results in an increase in fracture toughness of epoxy with the addition of nanosilica, is still elusive.

2.6 Carbon Nanotubes

Carbon nanotubes were first reported by Iijima in 1991 [10]. They are finite carbon structures consisting of tubes of graphene sheets, see Figure 2.17. They come in two main forms, single walled tubes (SWNTs) which have only the one layer of graphene making up the wall and are open ended, and multiwalled (MWNTs) where several tubes are stacked one inside the other, each layer still being a single graphene sheet.
and the ends being covered by a cap. Figure 2.18 shows an image of a multiwalled nanotube.

Figure 2.17: A 3D image of a single walled nanotube. Taken from [31].

Figure 2.18: Transmission electron micrograph of a multiwalled nanotube with a spheroid of amorphous graphite on its surface. The concentric layers of tubes are typically separated by the order of 0.4 nm. Taken from [32].

Synthesis of nanotubes can be carried out by several different methods:

1. Carbon arc synthesis uses a reaction vessel with an inert gas flowing through it. Two graphite rods, one 6 mm and the other 9 mm in diameter are in the vessel and 18 Volts is applied between them (A.C. or D.C.). As the rods are brought closer together a discharge of carbonaceous material containing nanotubes will be deposited on the larger rod while the smaller rod is consumed. Ebbesen and Ajayan
used this method and discovered that the optimum pressure of the inert gas is 500 torr and that D.C. gives the highest yield.

2. Pulsed laser vaporisation, which uses pulses of laser energy, nanoseconds in duration. This energy is aimed at a carbon target containing small amounts of metals such as cobalt and nickel. This is done in a flow tube filled with argon, at high temperature and pressure. The nanotubes assemble themselves from the carbon vapour and condense on the cool walls of the flow tube [34].

3. Chemical vapour deposition, which involves placing a catalyst such as Fe₂O₃ in a furnace and heating it up to about 900 °C. A gas such as benzene, ethylene or methane is passed into the furnace, and as the gas decomposes, nanotubes form on the catalyst. Once the nanotubes have formed the gas is switched over to argon and the furnace cooled. This method has been shown to produce aligned nanotubes rather than rope bundles [35, 36].

The carbon-carbon bond is the strongest of all chemical bonds and while carbon fibres fall short of having their theoretical maximum properties (strength and stiffness) due to structural imperfections, the highly perfect structure of carbon nanotubes should give them a higher rigidity than any known material [33].

Measuring the exact properties of nanotubes has been challenging due to the size of the tubes. For example, an atomic force microscope has to be used to isolate a single nanotube and position it for testing. Indications to the properties have been concluded from the rarity of nanotubes fracturing even after grinding under a solvent. They must have a high Young’s modulus and a high breaking stress. Buckled nanotubes are more commonly seen. The stiffness of the nanotubes is thought to be related to the diameter, which explains why multiwalled nanotubes tend to be straight while single walled nanotubes tend to be curly.

Several papers have been published with different methods for calculating the properties of nanotubes. Treacy et al [37] measured the intrinsic thermal vibrations of nanotubes in a transmission electron microscope (TEM) to calculate the Young’s modulus of the nanotubes. Their results gave an average modulus of 1.8 TPa with a wide spread, from 0.40-3.70 TPa. These values are much higher than that of carbon fibres, the Young’s modulus of macroscopic vapour-grown carbon fibres being about
0.68 TPa. The predicted modulus of single walled nanotubes is higher than that of multiwalled nanotubes.

Wong et al [38] pinned multiwalled nanotubes onto a single crystal of MoS₂ and used an atomic force microscope (AFM) to locate and measure the nanotubes. Force displacement curves were measured at various points along the nanotubes and the average Young's modulus for 6 nanotubes was calculated as 1.28 TPa with a standard deviation of 0.59 TPa, and no dependence on the diameter of the nanotubes. They also found evidence of elastic buckling of the MWNTs with the average maximum bending stress being 14.2 GPa and a standard deviation of 8.0 GPa (taken just before buckling).

A device was built by Yu et al [39] which picks up and attaches the ends of MWNTs onto the tips of AFM cantilever probes. The nanotubes were then reported to have been stress loaded and observed in a scanning electron microscope (SEM). Their report was the product of testing 19 MWNTs. The nanotubes tended to break by the outermost layer failing first and the weak van der Waals forces allowed the inner layers to pull out before complete fracture. The tensile strength for the outer layer was measured between 11 and 63 GPa while the Young’s modulus varied between 270 and 950 GPa.

Research as reviewed by Xie et al [40] has been carried out to determine the properties of nanotubes and Table 2.4 summarises the results.
Table 2.4: Theoretical and experimental properties of carbon nanotubes. Taken from [40].

<table>
<thead>
<tr>
<th>Property</th>
<th>SWNT</th>
<th>MWNT theoretical</th>
<th>MWNT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific gravity</td>
<td>0.8 g/cm³</td>
<td>1.8 g/cm³</td>
<td></td>
</tr>
<tr>
<td>Elastic modulus</td>
<td>~1 TPa</td>
<td>~0.3-1 TPa</td>
<td></td>
</tr>
<tr>
<td>Strength</td>
<td>50-500 GPa</td>
<td>10-60 GPa</td>
<td></td>
</tr>
<tr>
<td>Resistivity</td>
<td>5-50 μΩ cm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Thermal conductivity</td>
<td>Theoretical</td>
<td>3000 W m⁻¹ K⁻¹</td>
<td></td>
</tr>
<tr>
<td>Magnetic susceptibility</td>
<td>Perpendicular with plane</td>
<td>22×10⁶ EMU/g</td>
<td>Parallel with plane</td>
</tr>
<tr>
<td>Thermal expansion</td>
<td>Theoretical</td>
<td>Negligible</td>
<td></td>
</tr>
<tr>
<td>Thermal stability</td>
<td>In air</td>
<td>In vacuum</td>
<td></td>
</tr>
<tr>
<td>Specific surface area</td>
<td></td>
<td>10-20 m²/g</td>
<td></td>
</tr>
</tbody>
</table>

One of the main problems with using carbon nanotubes is that they are difficult to separate. Two possible ways have been mentioned in Ehrenreich and Spaepen's book [41].

a) Changes to production by current density and rate of carbon vapourisation.
b) Chemically functionalise or modify the nanotubes.

SWNTs tend to group together into bundles, commonly described as ropes as shown in Figure 2.19. To transfer the required properties to the polymer it is thought these need to be broken up.
2.7 Epoxy Resin with Carbon Nanotubes

The excellent mechanical properties of nanotubes as detailed above have led people to believe they could be useful as a reinforcement for polymers. Hence many tests have been performed to determine the properties of nanotube reinforced polymers and methods of dispersion of nanotubes, since the current belief is that the full potential of these materials cannot be realised unless good dispersion is attained.

2.7.1 Mechanical Properties

Hsiao et al [43] investigated the effect of adding multiwalled carbon nanotubes (MWNTs) on the shear strength of epoxy adhesives. The MWNTs were dispersed in the epoxy resin, and this was then used to bond the two graphite fibre / epoxy composite adherends together, 1 and 5 wt% nanotubes were used. The specimens were prepared by adding 15 wt% acetone, surfactant, and nanotubes to the epoxy resin. The mixture was then sonicated for 20 minutes at room temperature to disperse the MWNTs and then placed in a vacuum chamber to eliminate any bubbles. The adherends were graphite fibre / epoxy composite laminates, and once bonded the samples were post-cured. The test was a single lap joint using either pure epoxy, epoxy with 1 wt% nanotubes or 5 wt% nanotubes as the adhesive. These samples were tested at a speed of 12.7 mm min⁻¹.
The results showed that the average shear strength of the lap joint specimens increased as the percentage of carbon nanotubes increased, particularly when the carbon nanotubes are first introduced, see Figure 2.20. The specimens were then examined under a scanning electron microscope (SEM) to try to establish the reason for the increase in shear strength and it was concluded that in the 5 wt% carbon nanotube specimens the load was transferred to the graphite fibres in the adherend while in the pure epoxy adhesive the failure occurred at the interface and no significant fibre fracture was seen.

![Figure 2.20: Average shear strength of the single lap adhesion specimens versus the weight fraction of MWNT in the epoxy / nanotube adhesive. Taken from [43].](image)

Lau et al [44] determined the hardness and flexural strength of pure epoxy and epoxy mixtures with varying amounts of MWNTs. These specimens were prepared by mixing the required amount of nanotubes with ethanol to form a solution, and this was then mixed with the epoxy resin. This mixture was sonicated for 2 hours to disperse the nanotubes and then left in a vacuum oven for 2 hours to remove any air bubbles. The hardener was added to the epoxy mixture in the ratio 1:0.23 and this new mixture was sonicated again for 1 hour to ensure uniform distribution.

After curing, the Vickers hardness was measured. The hardness of pure epoxy was found to be higher than that of all the samples with less than 1 wt% nanotubes, this was explained by the introduction of microvoids into the hybrid. The 2 wt% mixture was found to have a higher hardness than that of pure epoxy. The creation of a network of long nanotube reinforcements was used to explain this.
Flexural tests were carried out on a pure epoxy beam and on beams with 2 wt% carbon nanotubes. The fracture surfaces were then looked at using a SEM. The tests showed that the flexural strength for the pure epoxy beam was higher than that of the beams with carbon nanotubes in them. When examined under a SEM it was discovered that the nanotubes had been pulled out due to poor bonding between the matrix and the nanotubes and this could explain the result. It had been generally thought that using nanotubes would increase the tensile strength of composites.

The beams with 2 wt% carbon nanotubes were pre-treated at a range of temperatures, -180 °C, 20 °C and 70 °C by placing the beams in that temperature environment for 10 minutes prior to the test. The low temperature, -180°C, was achieved using liquid nitrogen, 20 °C is room temperature and placing the specimens in warm water created the 70 °C environment. It was found that the beams pre-treated at -180 °C fractured in a brittle manner with the nanotubes being aligned parallel to the fracture surface. Those pre-treated at 70 °C showed failure by a tough mode with the nanotubes being aligned perpendicular to the fracture surface and there was evidence of possible tensile breaking of some of the nanotubes. Figure 2.21 shows the results of the flexural strength tests.

![Figure 2.21](image)

Figure 2.21: Flexural strength test results of nanotube / epoxy beams treated at -180, 20 and 70 °C, and also for a pure epoxy beam. Deflection did not lead to rupture for the beam treated at 70 °C. Taken from [44].

Li et al [45] created carbon nanotubes by chemical vapour deposition using a quartz substrate, this was done to improve alignment, it also led to the nanotubes having a particularly high aspect ratio of between 1000 and 1000000. They were mixed with an epoxy resin, DGEBA, and the mixture was degassed in a vacuum oven at 130 °C for 1.5 hours before being cast and cured. In one sample the carbon nanotubes were untreated and in another they were treated with acid first, 35 wt% HNO₃ for 30 minutes.
Three types of specimen were produced; an epoxy control, epoxy with 0.5 wt% untreated carbon nanotubes and epoxy with 0.5 wt% acid treated carbon nanotubes.

These specimens were tested for various mechanical properties and the results are summarised in Table 2.5. It was found that the addition of carbon nanotubes improved the tensile strength, the flexural strength, the elongation at break and the impact toughness. The tensile and flexural moduli however remain unchanged. These effects were also seen with the acid surface treatment, the tensile strength, the flexural strength, the elongation at break and the impact toughness again increased while the tensile and flexural modulus still remained unchanged.

Table 2.5: Mechanical properties of epoxy control and 0.5 wt% nanotube / epoxy composites (nanotubes with and without acid treatment). Taken from [45].

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Tensile strength (MPa)</th>
<th>Tensile modulus (GPa)</th>
<th>Elongation at break (%)</th>
<th>Flexural strength (MPa)</th>
<th>Flexural modulus (GPa)</th>
<th>Impact toughness (N/mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>77</td>
<td>2.7</td>
<td>3.6</td>
<td>199</td>
<td>3.1</td>
<td>1.5</td>
</tr>
<tr>
<td>Untreated nanotubes</td>
<td>88</td>
<td>2.8</td>
<td>4.5</td>
<td>224</td>
<td>3.4</td>
<td>2.6</td>
</tr>
<tr>
<td>Acid treated nanotubes</td>
<td>96</td>
<td>2.7</td>
<td>7.0</td>
<td>244</td>
<td>3.1</td>
<td>2.8</td>
</tr>
</tbody>
</table>

Ganguli et al [46] have also recorded an increase in flexural strength through the addition of carbon nanotubes. Tetrafunctional epoxy resin was mixed with 1 wt% MWNT and dispersed using a dual axis centrifugal mixer (with a high speed (3500rpm) mixing arm rotating in the opposite direction to the basket containing the epoxy and MWNTs). DDS was added and the mixture was mixed for a further 30 seconds. Neat epoxy and epoxy with nanotube samples were cured.

The specimens were tested using the three point bend test, for flexural strength. The specimens where 1 wt% MWNT had been added showed that the strength increased from around 70 MPa (pure epoxy) to 170 MPa. The deflection also increased from 0.4 mm (pure epoxy) to 1 mm.

To compare the fracture toughnesses, single edge notch three point bend tests were carried out. The specimens had been notched using a 1 mm thick blade and the notch
length to specimen depth ratio was 45%. The results showed a threefold increase in the stress intensity factor when the 1 wt% MWNT were added, from 1.3 MPa.m$^{1/2}$ to 4.0 MPa.m$^{1/2}$. Therefore it was concluded there has been a significant improvement in both the toughness and the ultimate strength of the epoxy.

The storage modulus of hybrids containing high weight percentages of SWNTs has been investigated by Wang et al [47]. These specimens were prepared using a novel technique described in detail in section 2.7.3 and tested using a dynamic mechanical analyser operating in tension with the specimens being heated to 350 °C at a rate of 5 °C/min.

Although the storage modulus was found to be much higher for the hybrid than for the pure epoxy, a 349-492% increase depending on the SWNT loading, this is much lower than predicted by the rule of mixtures. Poor load transfer between nanotubes within ropes, and between the nanotubes and the matrix has been suggested as an explanation. It was also seen that the actual weight percentage of nanotubes had very little effect as the amount of nanotubes was varied between 28.1 and 39.1 wt%, see Table 2.6. The authors believe that the dispersion of the nanotubes may be of most importance since this affects the molecular interactions of the nanotubes and the matrix.

Table 2.6: Storage modulus test results for epoxy / nanotube samples with increasing SWNT loadings. Taken from [47].

<table>
<thead>
<tr>
<th>SWNT loading (wt%)</th>
<th>Storage Modulus (GPa)</th>
<th>Increase (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>2.55</td>
<td>0</td>
</tr>
<tr>
<td>28.1</td>
<td>11.45</td>
<td>349</td>
</tr>
<tr>
<td>31.3</td>
<td>15.10</td>
<td>492</td>
</tr>
<tr>
<td>37.7</td>
<td>13.49</td>
<td>429</td>
</tr>
<tr>
<td>39.1</td>
<td>13.24</td>
<td>419</td>
</tr>
</tbody>
</table>

Schadler et al [48] discussed the methods of load transfer from the matrix to the nanotubes and decided that there are three main possibilities, the first is micromechanical interlocking, which is thought to be unlikely with carbon nanotubes due to their atomically smooth surface. The second is via chemical bonding between the matrix and the nanotubes. The third is via weak van der Waals bonding. No reasoning for the suggestion of these three methods was given.
Tensile and compressive tests were carried out on epoxy and epoxy / MWNT samples. Schadler \textit{et al} [48] concluded that the addition of nanotubes increased the average modulus both in tension and compression, and that the compression modulus is significantly higher than the tensile modulus. The results are shown in Table 2.7, and although this trend can be seen the large scatter in the data makes the conclusions less clear.

Table 2.7: Tensile and compressive modulus of pure epoxy and epoxy / 5 wt\% nanotube hybrids. Taken from [48].

<table>
<thead>
<tr>
<th>Material</th>
<th>Tensile Modulus (GPa)</th>
<th>Compression Modulus (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure Epoxy</td>
<td>3.1±0.2</td>
<td>3.63±0.25</td>
</tr>
<tr>
<td>Nanotube hybrid</td>
<td>3.71±0.5</td>
<td>4.5±1.5</td>
</tr>
</tbody>
</table>

It was concluded that there was poor load transfer between the nanotubes and the matrix, for which there are two possible explanations. The first is that there is poor bonding between the matrix and the outermost nanotube layer, and the second is that there is poor bonding between the different layers in the MWNT, and whilst the load is transferred to the outermost layer the inner layers slip so the load is not transferred to them. They decided that the second of these two theories was more likely because it better explains the difference between the modulus in compression and tension. In compression the slippage of layers would be prevented by geometrical constraints and so the modulus would be expected to be higher than for tension.

While the theoretical properties of carbon nanotubes are excellent the likelihood is that these properties cannot be effectively transferred to hybrid due to poor bonding between the layers. For SWNTs the same effect may be seen due to the nanotubes being formed in ropes and the load will only be transferred to the tubes on the edge of the rope.

Detachment of nanotubes from the matrix has been seen as one of the failure methods of epoxy / nanotube hybrids. Cooper \textit{et al} [49] researched this area to determine the polymer / nanotube interfacial shear strength. Both MWNTs and SWNTs were tested. The nanotubes were dispersed using an ultrasonic processor, although the SWNTs still tend to form ropes. The pullout measurements were made by sliding a scanning probe microscope tip across a hole in the matrix spanned by a nanotube while monitoring the lateral force and position.
Cooper et al reported a variety of phenomena including pullout, bending, breaking and unsheathing of inner layers from the outer. Polymer damage was also reported although the specific type of damage was not mentioned. Table 2.8, taken from their paper shows the nanotube dimensions, work, pullout energy and shear strength calculations for the pullout specimens. It is mentioned that fibre stretching may have led to an overestimate of the energy.

Table 2.8: Experimental data for nanotube pullout in epoxy / nanotube hybrids. Taken from [49].

<table>
<thead>
<tr>
<th>Specimen Number</th>
<th>MWNT</th>
<th>SWNT rope</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diameter (nm)</td>
<td>8.2 11.0 24.0 13.4 13.4 24</td>
<td>11.6</td>
</tr>
<tr>
<td>Embedded length (nm)</td>
<td>484 256 2570 379 708 1870</td>
<td>193</td>
</tr>
<tr>
<td>Interfacial Area (m^2×10^{-14})</td>
<td>1.01 0.88 19.4 1.60 2.99 14.07</td>
<td>0.71</td>
</tr>
<tr>
<td>Max. Force (μN)</td>
<td>3.8±0.6 2.8±0.6 6.8±1.7 0.6±0.04 2.3±0.6 12.8±2.1</td>
<td>2.6±0.5</td>
</tr>
<tr>
<td>Work (J×10^{-15})</td>
<td>2.9 3.3 16 1.3 1.6 7.8</td>
<td>4.1</td>
</tr>
<tr>
<td>Shear Strength (MPa)</td>
<td>376±40 318±16 35±9 38±2 77±20 91±15</td>
<td>366±74</td>
</tr>
</tbody>
</table>

Only one of the SWNT ropes tested was pulled out, the others underwent fracture, the data for these specimens are shown in Table 2.9. Two values for cross-sectional area and breaking strength are given: the first, 'all', being for all of the nanotubes in the rope, the second, 'perim', uses only those nanotubes around the perimeter of the bundle since it has been suggested that only the outermost nanotubes in such bundles carry the load.

The breaking of the nanotubes rather than them being pulled out suggests that the force required to pull out the SWNTs is even greater than that required to break them.
Table 2.9: Experimental data for SWNT rope breaking in epoxy / nanotube hybrids. Taken from [49].

<table>
<thead>
<tr>
<th>Specimen</th>
<th>SWNT ropes</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>6</td>
</tr>
<tr>
<td>Diameter (nm)</td>
<td>15.6</td>
</tr>
<tr>
<td>Embedded length (nm)</td>
<td>568</td>
</tr>
<tr>
<td>Cross Sectional Area (m²×10⁻¹⁷)</td>
<td>A_\text{all}</td>
</tr>
<tr>
<td></td>
<td>A_\text{perim}</td>
</tr>
<tr>
<td>Max. Force (µN)</td>
<td>30.7±5.5</td>
</tr>
<tr>
<td>Work (Jx10⁻¹³)</td>
<td>14.6</td>
</tr>
<tr>
<td>Breaking Strength (GPa)</td>
<td>\sigma_\text{all}</td>
</tr>
<tr>
<td></td>
<td>\sigma_\text{perim}</td>
</tr>
</tbody>
</table>

Lourie and Wagner [50] explored the failure mechanism of carbon nanotube hybrids. They expected fracture of these composites to occur in a similar way to that of fibre-reinforced composites, by the combination of complex microdamage events such as fibre breakage, interface decohesion, or matrix failure.

They suggest that one possible path to failure for fibres is that scattered fibres throughout the composite break at weak spots along the fibre, the stress is then transferred through the matrix to local fibres which may then fail. Once clusters of adjacent fibres are broken and reach a certain size, catastrophic failure will result. Not all theories are transferable from fibres to nanotubes however, but they found the occurrence of random collapse sites along thinwalled nanotubes. This implies that the external force (compression) has been transferred to the nanotubes through the matrix, implying that the nanotube surface is not inert and one possible explanation of this is the strong curve of the surface of the graphene.

The results of their tests indicated that the “fundamental concepts pertaining to continuum mechanics of traditional fibre composites seem to possess some degree of validity at the nanometric level in the case of carbon-nanotube-reinforced polymers” [50].

The Young’s modulus is another important property and was investigated by Allaoui et al [51]. A relatively soft, ductile epoxy resin was used in this paper so that the influence
of the carbon nanotube addition on the stress-strain behaviour could be evaluated.

The epoxy resin was Bisphenol A-epichlorhydrine with two parts aromatic hardener triethylenetetramine. The MWNTs were dispersed in methanol solution using magnetic agitation to break up the aggregates which nanotubes tend to form. Once the methanol had been completely evaporated the nanotubes were added to the epoxy / hardener mixture and homogenized manually.

Samples were prepared with 1 wt% and 4 wt% MWNT, and were tested in tension. It was found that both the Young's modulus and yield strength were doubled from that of the epoxy matrix by the addition of 1 wt% MWNT, and were quadrupled with 4 wt%, see Figures 2.22 and 2.23. The stress of the composite was also normalised by dividing it by the stress of the pure epoxy at the same strain level, this showed that the reinforcement co-efficient for 1 wt% was approximately constant at about 2, and for 4 wt% it was closer to 2.5. The reduction in reinforcement efficiency for the 4 wt% hybrid was attributed to the presence of porosity and nanotube aggregates.

![Figure 2.22: Tensile stress versus strain for epoxy and epoxy / MWNT. Taken from [51].](image-url)
Improvements in mechanical properties, however, have not been reported by all researchers. Liu and Wagner [52] found no effect on the tensile properties of an amine cured DGEBA, with the addition of up to 1 wt% MWNT. The hypothesis put forward by the authors to explain this lack of increase in tensile properties of the epoxy, is that the nanotubes increase the activation energy of the curing reaction in the epoxy, thereby lowering the cross-link density, and this reduces the tensile properties.

Hernández-Pérez et al [53] have investigated the effect of aspect ratio of nanotubes on various properties of nanotube / epoxy composites. They found that the fracture properties, especially, were much improved for nanotubes with high aspect ratios. Nanotubes with low aspect ratios, around 50, showed very little improvement in fracture properties, although they were easier to disperse than the nanotubes with high aspect ratios.

### 2.7.2 Other Properties

Studies suggest that one of the uses of carbon nanotubes in a hybrid will be as a conductive filler, to allow for static discharge of the composite or for electromagnetic-radio interference protection. Percolation is the state required where a conductive path goes through the component. To achieve percolation in an insulating resin a three-dimensional network of conductive filler particles is needed. Percolation is characterised by a sharp drop in the electrical resistance. It is therefore important
when trying to achieve percolation with the lowest possible percentage of filler to have the filler well dispersed.

Sandler et al. [12] used shear intensive mechanical stirring to disperse carbon nanotubes, as discussed in more detail in the next section. They found that while the mechanical stirring led to a well dispersed system, low stirring rates and the addition of a hardener at the end of the process allowed aggregates to form. Only samples with the lowest weight loading of nanotubes (0.001 wt%) avoided any aggregates. Tests on the electrical properties of the specimens showed that sufficient conductivity is achieved at 0.005 wt% nanotube loading for the material to be used for anti-static applications. Figure 2.24 shows the effect on conductivity of nanotube weight loading. It was found that 0.005 wt% nanotube loading is sufficiently low that the processing behaviour and the surface finish of the samples is not adversely affected by the introduction of the nanotubes into the resin, a problem which occurs with other fillers requiring higher percentage weights.

![Figure 2.24: Conductivity of epoxy with different weight loadings of carbon nanotubes. Taken from [12].](image)

In the review paper by Moniruzzaman and Winey [54], they discuss several reports of improvements in conductivity with the addition of nanotubes. They concluded that the ability of the nanotubes to improve conductivity is strongly dependent on the dispersion and the length of the nanotubes. While functionalisation of the single walled nanotubes reduces their ability to conduct, it increases the ability of the composite to conduct since the benefits of improved dispersion outweighs the decrease in conductivity of the nanotubes.
2.7.3 Dispersion Techniques

One of the main problems with using carbon nanotubes is trying to achieve good dispersion. Hybrids using carbon nanotubes have been predicted to have excellent properties, but poor dispersion of the nanotubes within the polymer and the presence of entanglements or aggregates is one factor leading to drastic weakening of the hybrids [40]. Single walled nanotubes have a specific problem dispersing since they tend to form rope like bundles due to the strong van der Waals forces and they have a high surface area, a lack of functional sites and stable chemical characteristics [47].

Song and Youn [55] investigated the effects of dispersion on a variety of properties. They found that dispersion has little effect on the tensile modulus. The tensile strength of the composite is increased with increasing the percentage of well dispersed nanotubes, but with poorly dispersed nanotubes, the tensile strength decreases. This was explained as the result of the agglomerates causing cracks to initiate and then propagate. Elongation at break was also improved when the nanotubes were well dispersed over poorly dispersed.

Several different methods of dispersion have been tried by different people, and these were separated into three main categories by Xie et al [40]. These categories are in situ polymerisation, optimum physical blending, and chemical functionalisation.

In situ polymerisation improves the processability, electrical, magnetic, and optical properties of the carbon nanotubes. In this method the carbon nanotubes are ‘wrapped’ in a conjugated or conducting polymer. Little work was mentioned by Xie et al about the effect on dispersion of in situ polymerisation except that Tang and Xu [56] found that carbon nanotubes wrapped in poly(phenylacetylene) could be macroscopically processed and that the carbon nanotubes readily aligned in the direction of mechanical force when the solution they are in undergoes shearing.

Optimum physical blending can be as simple a treatment as using ultrasound or high speed shearing. An alternative approach is to use a surfactant, such as polyoxyethylene-8-lauryl, with epoxy / carbon nanotube hybrids. This works because of the strong van der Waals forces between the carbon of the carbon nanotubes and the hydrophobic segment of the surfactant, as well as the hydrogen bonding between the epoxy and the hydrophilic segment of the surfactant. Even with this Gong et al [57]
found that dispersion was not perfect. Xie et al believed that the use of surfactants along with melt blending is the most effective method of dispersion.

Sonication has been used in a variety of ways by different groups. Li et al [58] dispersed the tubes in sodium hydroxide (NaOH)-ethanol solution containing 150 g/l of NaOH in 80 vol% ethanol and 20 vol% water. During this treatment the aggregates swelled and softened and when sonicated for a few minutes they began to break up. After about 5 hours a black slurry was formed and this was filtered and washed thoroughly with a 1:5 water:ethanol mix until the filtered solution was pH neutral. It was then washed twice more with ethanol to remove any water. Finally it was either dried in a vacuum at room temperature or it was kept dispersed in ethanol.

Transmission electron microscope images showed that the SWNTs were mainly in 20-50 nm diameter bundles before the treatment. After treatment the average bundle diameter dropped to 8 nm. This occurred with little change to the tube length. It was also noticed that some of the catalytic iron particles were also removed from the SWNTs. Thermal gravimetric analysis (TGA) confirmed this, the iron oxide residue decreasing from 8.3% to 2.5% after treatment. TGA also showed that the weight loss peak was sharper for the treated nanotubes, and this was explained as the result of the higher surface area of the debundled tubes leading to more efficient combustion.

The treated nanotubes appeared to be more hydrophobic but were easily redispersed in organic solvents, even to the extent that in tetrahydrofuran it was claimed the nanotubes had been dispersed as individual nanotubes.

Sandler et al [11] also used sonication in ethanol. They dispersed between 0.0225 and 0.15 wt% of untreated carbon nanotubes in ethanol in an ultrasonic bath at room temperature for 1 hour. The ethanol based solution was then added to the resin and was stirred at 2000 rpm for 1 hour at a temperature of 80 °C. The mixtures were then placed in a vacuum oven to evaporate the ethanol at 80 °C for 1 hour and then they were stirred again at 2000 rpm for another hour. Finally the hardener was added and stirred for the last time at 2000 rpm for 15 minutes before being heated to harden them.

The resulting specimens were examined and it was found that while not all the entanglements had been broken up, the dispersion of nanotubes was improved over that without ultrasound treatment and intense stirring. Lau et al [44] prepared nanotube / epoxy mixtures, some of which were sonicated and others were not. They found that
the nanotubes in the unsonicated mixtures would be “agglomerated” together and this resulted in non-uniform distribution of the nanotubes. This problem was resolved by sonication.

A more sophisticated method of dispersion using sonication was attempted by Wang et al [47] and involved the nanotubes being formed into “buckypapers” (thin membranes of nanotube networks between 10 and 50 μm thick) which provided the reinforcement structure of the final nanocomposite. The SWNTs were first ground in a pestle and mortar with a little water to form a paste, which was sonicated. A surfactant and water were added and sonicated again for between 30 and 200 minutes. This produced a stable ink like suspension. The concentrations produced were 10 - 200 mg/l of SWNT. After filtering the suspension with the aid of a vacuum, the resulting buckypaper was washed with deionised water and dried, initially at room temperature and then in a vacuum oven.

The buckypapers were examined using a SEM to determine the structure and it was found that the SWNTs had formed ropes with average diameter between 30 and 60 nm, see Figure 2.25. These ropes had probably formed during the filtration. The rope size and the porous structure were uniform, indicating that good dispersion was achieved. Due to the nanoscale pore size of the buckypaper, a comparison had to be made between the size of the resin and curing agent molecules and the size of the pores. It was determined that both molecules could penetrate the nanostructure and form 3-D cross-linked networks.

The through thickness permeability of the buckypaper was determined to allow calculations of the resin infiltration time. The nanoscale of the pores in the buckypaper also caused problems, in that the viscosity of the resin was too high (2700 cP) for the resin to impregnate the buckypaper efficiently. The resin was diluted with acetone to lower its viscosity. After infiltration the buckypaper was soaked in the resin-curing agent system overnight. To create bulk samples several layers of infiltrated buckypaper were stacked together and cured.

The infiltration time for the resin was calculated at about 60 hours, during which time the resin / curing agent system would partly gel, increasing the viscosity and lengthening the time required. To decrease the viscosity acetone was added which lowered the viscosity to 100 cP. This takes the theoretical impregnation time to 2 hours, and during the experiments a time of 5 hours was used.
A simple mechanical mixing technique was tried by Ganguli et al [46], who achieved dispersion by using a dual axis centrifugal mixer. This was done for 1 minute before the hardener was added, and then for a further 30s after the hardener was added. When an unnotched fracture surface was examined with a SEM it was found that the nanotubes were well dispersed and that there was no evidence of agglomeration of nanotubes.

Calendering was a technique used by Fiedler et al [59] along with sonication and stirring. While sonication was found to leave agglomerates in this report, stirring and especially calendering gave good dispersion. Calendering involves using rollers, separated by a small gap, which rotate, applying a shear force to the resin in which the nanotubes are to be mixed. Initial dispersion occurs in the knead-vortexes and final dispersion occurs in the gap between the rollers. The gap used in this report was 5 μm.

Xie et al [40] suggest that chemical functionalisation is needed to achieve good dispersion. However before this can take place the carbon nanotubes need to be purified to remove impurities such as catalyst residuals, bucky onions and amorphous carbon. The SWNTs tend to form ‘ropes’ or bundles and these need to be disentangled or cut. There have been several different purification method tried.

1. MWNTS can be purified by simple oxidation. Ebbesen et al [60] put ground nanotubes in a furnace at 750 °C for 30 minutes and since the nanoparticles oxidise at a higher rate to the nanotubes, purification can be achieved. Whilst this method does work there are a couple of drawbacks. Firstly the caps of the nanotubes oxidise at a rate similar to that of the nanoparticles and so are removed by this process leaving
open tubes. Secondly the process destroys most of the nanotubes, giving only a 1% yield.

2. Since method 1 gives such a low yield, oxidation of the liquid-phase of the crude nanotube samples was tried by Hiura et al [61]. Potassium permanganate in acidic solution was found to be the best oxidant and after treatment the nanotubes had a higher dispersibility. The yield was improved over oxidation in air.

3. Oxidation by either of the above methods invariably damages the ends of the tubes and may even remove the outer layers of MWNTs. This is far from ideal so Bonard et al [62] investigated using sonication to suspend nanotubes in a surfactant. They did not find ethanol to be very effective but water-nanotube suspensions stabilised with sodium dodecyl sulphate (SDS) provided a stable suspension with few aggregates. Filtration was used to separate the carbon nanoparticles from the nanotubes. TEM indicated that the use of SDS and sonication does not damage the nanotubes at all.

4. A functional organic polymer, poly(m-phenylenevinylene-co-2,5-dioctyloxy-p-phenylenevinylene) can be used to coat nanotubes and nanoparticles. While this will suspend nanotubes indefinitely, amorphous graphite separates out leaving only a small percentage (about 5%) of the impurities dispersed. This occurs without damaging the nanotubes [63].

5. Liu et al [64] used a method involving refluxing in 2.6 M nitric acid and resuspending the carbon nanotubes in pH 10 water with surfactant followed by filtration with a cross-flow filtration system. This was also found to be effective without destroying the nanotubes.

Cutting or disentangling can be achieved easily by using sonication in an acid, such as concentrated sulphuric acid and nitric acid. Treatment following cutting with concentrated sulphuric acid and 30% aqueous hydrogen peroxide etches the carbon nanotubes, shortening them further [60].

Activation treatments such as oxidation of carbon nanotubes using oxygen, air, concentrated sulphuric acid, nitric acid and 30% aqueous hydrogen peroxide will form carboxylic acid and hydroxyl groups on the surface or in open ends [40].

Further activation can be achieved by converting these groups. The carboxylic acid groups can be converted into the corresponding chloride groups by reaction with thionyl chloride at room temperature [64]. Subsequent exposure to NH₂-(CH₂)₁₁-SH in toluene produces an amide linkage of the nanotubes to the alkanethiol CH₃(CH₂)ₙSH.
The hydroxyl groups can be converted into hydroxymethyl groups (-CH₂OH) by reaction with formaldehyde.

Guo et al [65] purified their nanotubes by warming them in a nitric acid bath to remove amorphous carbons and metal catalysts. The purified nanotubes were functionalised through sonication in a mixture of acids. The epoxy / nanotube composites were found to have a good dispersion and to give an increase in mechanical properties. These improvements were attributed to the purification and functionalisation.

Generally the species used in functionalisation becomes impurities in the final composite and so ideally the nanotubes will be functionalised with the matrix polymer. Lin et al [66] used poly(vinyl alcohol) (PVA) since it makes a good matrix polymer. They functionalised both MWNTs and SWNTs with PVA in carbodiimide activated esterification reactions. Since the PVA and functionalised nanotubes are both soluble in the same solvent, effective mixing is possible, and so a homogeneous dispersion is achievable. This backed up work by Mitchell et al [67] who found that 4-(10-hydroxydecyl)nitro benzoate-SWNTs, synthesised by in situ reaction of organic diazonium compounds, achieved a percolated structure in polystyrene at 1.5 wt% SWNTs, while for composites with unfunctionalised SWNTs percolation did not occur until twice this loading.

**2.7.4 Summary**

Carbon nanotubes have been shown to have superb theoretical properties, and despite the difficulties with measuring the actual properties, the data measured so far also attributes them with excellent strength and stiffness. Due to their graphitic structure they are also conductive. These properties have encouraged people to try to add them to polymers to improve the strength and fracture toughness of the polymers and to increase their conductivity.

It was found that the addition of carbon nanotubes improved the tensile strength, the flexural strength, the elongation at break and the impact toughness of epoxy resins. The tensile and flexural moduli however remain unchanged. Sufficient conductivity of epoxy resin for anti-static applications was achieved at low percentage weight of carbon nanotubes, so that the viscosity of the resin was not affected greatly. This has important implications for processing.
One of the main difficulties with using carbon nanotubes is the difficulty of dispersing the nanotubes within the polymer. Several different methods of dispersion have been tried by different people and these can be separated into three main categories: in situ polymerisation, optimum physical blending, and chemical functionalisation. Physical blending has been found to be fairly effective, with sonication being a common method. Chemical functionalisation has implications not only for the dispersion but also for bonding between the nanotubes and the polymer. No firm conclusions about the best method of dispersion have been put forward.

2.8 Conclusions

Blending thermoplastics with epoxy polymers to achieve increased fracture toughness has been found to be effective, with the morphology of the blend after curing being dependent on the weight percentage of thermoplastic. At low percentages a particulate structure is seen, changing to co-continuous and then phase inverted as the thermoplastic content increases.

Nanosilica has been incorporated into epoxy polymers and has been found to give an increase in fracture toughness and energy. There have been several suggestions for possible toughening mechanisms, none of which have been conclusively proven.

Carbon nanotubes have been added to thermosetting polymers in a different approach to increasing fracture toughness - with varied results. The nanotubes have been very difficult to disperse. Due to their size it is difficult to measure their properties, but the literature suggests that their exceptional strength and stiffness, combined with their conductivity and minimal effect on viscosity for processing could make them a useful addition to thermosetting polymers.
Chapter 3 Materials

3.1 Introduction

Details of the materials used during the following work are given below. This includes two epoxy systems and three different modifiers. The first epoxy system comprises a blend of two epoxy resins with an amine curing agent, and the second system is a single epoxy resin with an anhydride curing agent. The modifiers are a thermoplastic, and two nanomodifiers: nanosilica particles and multiwalled carbon nanotubes. These have been used to make epoxy / thermoplastic blends with varying percentages of thermoplastic and nanomodifiers.

3.2 Amine Cured Epoxy

The majority of the work was undertaken with the blend of two epoxy resins. Their structures are shown in Figures 3.1 and 3.2 below. They are a triglycidyl aminophenol (TGAP), (MY0510) and a diglycidyl ether of bisphenol F (DGEBF), (PY306). Both were manufactured by Huntsman.

Figure 3.1: Structure of triglycidyl aminophenol (TGAP) epoxy resin.
Chapter 3: Materials

PY306 has an epoxy content of 6.25 equivalents/kg, and MY0510 has an epoxy content of 10.3 equivalents/kg.

For this blend the curing agent was an amine hardener, 4,4'-methylenebis-(3-chloro 2,6-diethylaniline), (MCDEA) from Lonza Ltd, Switzerland, which is in powder form and has an active hydrogen content of 94.85 g/equivalent. The structure of MCDEA is shown in Figure 3.3.

These were used in a constant ratio by weight
1 PY306 : 1.17 MY0510 : 1.42 MCDEA [68]
This is just below stoichiometry, i.e. there is a slight excess of epoxy, as recommended by Cytec Engineered Materials [68].

3.3 Anhydride Cured Epoxy

As a comparison to the other system a diglycidyl ether of bisphenol A (DGEBA), (LY556) from Huntsman was also used. The anhydride curing agent, which was added
stoichiometrically, was accelerated with methylhexahydrophthalic acid anhydride, ‘Albidur HE 600’ supplied by Nanoresins, Geesthacht, Germany, which has an anhydride equivalent of 170 g/equiv. The structure of DGEBA is given in Figure 3.4

Figure 3.4: Structure of diglycidyl ether of bisphenol A (DGEBA) epoxy resin.

All further constituents for both the amine and anhydride cured systems are quoted in terms of weight percentage on epoxy and hardener, even when two extra constituents are added, see Equation 3.1.

\[
\text{wt\% (on epoxy + hardener)} = 100 \times \frac{\text{wt constituent}}{\text{wt (epoxy + hardener)} + \text{wt constituent}}
\]

Equation 3.1

3.4 Thermoplastic

The thermoplastic (TP) used in this work is from Cytec Engineered Materials. It is a Poly(ether sulfone) copolymer and is supplied in powder form. The exact structure is confidential, as are many of its properties, however it is known to have a glass transition temperature between 180 and 190 °C. The main batch of thermoplastic had reactive endgroups (R1). Two smaller batches with alternative end groups were also supplied, one was unreactive (U) and the other has a different reactive endgroup (R2).

3.5 Nanosilica

Nanosilica (NS), spheres of amorphous silica surface treated with epoxysilane, with an average diameter of 20nm, was supplied by Nanoresins, Germany. The nanosilica is
formed via a sol-gel technique. It was received dispersed at 40 wt% NS in the PY306, and at 40 wt% NS in the LY556, both of which are stable dispersions, and also received dispersed at 50 wt% NS in the PY306, which was a stable dispersion for only a short length of time. The nanosilica cannot be sourced dispersed in the MY0510 as it forms agglomerates and does not disperse [69]. An image of dispersed nanosilica is shown in Figure 3.5, and the particle size distribution can be seen in Figure 3.6.

Figure 3.5: A transmission electron micrograph of dispersed nanosilica [28].

![Transmission electron micrograph of dispersed nanosilica](image1.png)

Figure 3.6: Particle size distribution of nanosilica measured by small angle neutron scattering [28].

![Particle size distribution curve](image2.png)
3.6 Carbon Nanotubes

As discussed in Chapter 2, a singlewalled carbon nanotube is a sheet of graphene rolled up. A multiwalled carbon nanotube (NT) is in effect several single walled nanotubes one inside the other. An image of a multiwalled nanotube is given below in Figure 3.7.

![Figure 3.7: Transmission electron micrograph of a multiwalled nanotube with a spheroid of amorphous graphite on its surface. The concentric layers of tubes are typically separated by the order of 0.4nm [32].](image)

Multiwalled carbon nanotubes were received in two forms, dry, and pre-dispersed in the thermoplastic by Cytec via an ultrasonic horn. For the dry form, four different types of multiwalled carbon nanotubes were sourced. Thomas Swan & Co Ltd., County Durham supplied one type of chemical vapour deposition formed nanotubes which were not functionalised. These have the product reference P940 and have the following typical properties, average diameter of 10-12 nm, average length - microns, purity - 70-90% multiwalled nanotubes [70]. Figure 3.8 shows a transmission electron micrograph of these nanotubes.
Figure 3.8: Transmission electron micrograph of Thomas Swan multiwalled carbon nanotubes [70].

A second type were supplied by Ian Kinloch from Cambridge University. These had been grown on a plate and then had been cut from the plate leaving the nanotubes aligned. The third and fourth types were supplied by Nanocyl, Belgium. These had been produced by catalytic chemical vapour deposition. One type was supplied without functionalisation and is the 3100 series, the other type was supplied -COOH functionalised and is the 3101 series. Both of these series have the properties given in Table 3.1 below and a transmission electron micrograph is given in Figure 3.9.

Table 3.1: Properties of nanotubes supplied by Nanocyl, Belgium [71].

<table>
<thead>
<tr>
<th>Property</th>
<th>Unit</th>
<th>Value</th>
<th>Method of measurement</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average diameter</td>
<td>nanometre</td>
<td>10</td>
<td>Transmission Electron Microscopy</td>
</tr>
<tr>
<td>Length (average)</td>
<td>microns</td>
<td>0.1-10</td>
<td>Transmission Electron Microscopy</td>
</tr>
<tr>
<td>Carbon purity</td>
<td>%</td>
<td>&gt;95</td>
<td>Thermogravimetric Analysis</td>
</tr>
<tr>
<td>Metal Oxide (impurity)</td>
<td>%</td>
<td>&lt;5</td>
<td>Thermogravimetric Analysis</td>
</tr>
<tr>
<td>-COOH functionalisation (Nanocyl® 3101)</td>
<td>%</td>
<td>&lt;4</td>
<td>X-ray Photoelectron Spectroscopy</td>
</tr>
</tbody>
</table>
Figure 3.9: Transmission electron micrograph of Nanocyl 3100 series multiwalled carbon nanotubes [71].

Initial dispersion tests were carried out with all four types of nanotubes, but once a type which provided the best dispersion during these tests was ascertained, all further work focused on this type.

Two surfactants, FC-4430 and FC-4432, were also used during dispersion tests. These were both supplied by 3M and the main constituents are about 90% Fluoroaliphatic polymeric esters and 10% Polyether polymer.

Carbon nanotubes were also supplied dispersed in the thermoplastic at 1 wt%. The nanotubes were originally from Thomas Swan they were non-functionalised nanotubes.

3.7 The Formulations

The formulations used are given in the tables below, Tables 3.2 to 3.4.
Table 3.2: The formulations of the PY306 / MY0510, R1 ended thermoplastic plates with nanosilica and nanotubes which were produced and tested.

<table>
<thead>
<tr>
<th>Epoxy</th>
<th>Thermoplastic R1 (approximate)</th>
<th>Carbon Nanotubes</th>
<th>Nanosilica</th>
</tr>
</thead>
<tbody>
<tr>
<td>PY306 / MY0510</td>
<td>0 wt%</td>
<td>0 wt%</td>
<td>0, 2, 5, 10 and 15 wt%</td>
</tr>
<tr>
<td>PY306 / MY0510</td>
<td>15 wt%</td>
<td>0 wt%</td>
<td>0, 5.8, 10, 15 and 20 wt%</td>
</tr>
<tr>
<td>PY306 / MY0510</td>
<td>20 wt%</td>
<td>0 wt%</td>
<td>0 wt%</td>
</tr>
<tr>
<td>PY306 / MY0510</td>
<td>25 wt%</td>
<td>0 wt%</td>
<td>0, 2.7, 6.7 10 and 13.3 wt%</td>
</tr>
<tr>
<td>PY306 / MY0510</td>
<td>35 wt%</td>
<td>0 wt%</td>
<td>0 wt%</td>
</tr>
<tr>
<td>PY306 / MY0510</td>
<td>0 wt%</td>
<td>0.1, 0.178, 0.336 and 0.5 wt% (in epoxy)</td>
<td>0 wt%</td>
</tr>
<tr>
<td>PY306 / MY0510</td>
<td>15 wt%</td>
<td>0.1, 0.178, and 0.336 wt% (in epoxy)</td>
<td>0 wt%</td>
</tr>
<tr>
<td>PY306 / MY0510</td>
<td>25 wt%</td>
<td>0.1, 0.178, and 0.336 wt% (in epoxy)</td>
<td>0 wt%</td>
</tr>
<tr>
<td>PY306 / MY0510</td>
<td>15 wt%</td>
<td>0.1, 0.178, and 0.336 wt% (in TP)</td>
<td>0 wt%</td>
</tr>
<tr>
<td>PY306 / MY0510</td>
<td>25 wt%</td>
<td>0.1, 0.178, and 0.336 wt% (in TP)</td>
<td>0 wt%</td>
</tr>
</tbody>
</table>

Table 3.3: The formulations of the LY556 plates with nanosilica and nanotubes which were produced and tested.

<table>
<thead>
<tr>
<th>Epoxy</th>
<th>Thermoplastic</th>
<th>Carbon Nanotubes</th>
<th>Nanosilica</th>
</tr>
</thead>
<tbody>
<tr>
<td>LY556</td>
<td>0 wt%</td>
<td>0 wt%</td>
<td>0, 10 and 20 wt%</td>
</tr>
<tr>
<td>LY556</td>
<td>0 wt%</td>
<td>0.1 and 0.336 wt%</td>
<td>0 wt%</td>
</tr>
</tbody>
</table>
Table 3.4: The formulations of the PY306 / MY0510, U and R2 thermoplastic plates with nanosilica and nanotubes which were produced and tested.

<table>
<thead>
<tr>
<th>Epoxy</th>
<th>thermoplastic</th>
<th>Carbon Nanotubes</th>
<th>Nanosilica</th>
</tr>
</thead>
<tbody>
<tr>
<td>PY306 / MY0510</td>
<td>15 wt% U</td>
<td>0 wt%</td>
<td>0 and 10 wt%</td>
</tr>
<tr>
<td></td>
<td>15 wt% U</td>
<td>0.1 and 0.336 wt% (in epoxy)</td>
<td>0 wt%</td>
</tr>
<tr>
<td></td>
<td>15 wt% U</td>
<td>0.1 and 0.336 wt% (in TP)</td>
<td>0 wt%</td>
</tr>
<tr>
<td></td>
<td>25 wt% U</td>
<td>0 wt%</td>
<td>0 and 10 wt%</td>
</tr>
<tr>
<td></td>
<td>25 wt% U</td>
<td>0.1 and 0.336 wt% (in epoxy)</td>
<td>0 wt%</td>
</tr>
<tr>
<td></td>
<td>25 wt% U</td>
<td>0.1 and 0.336 wt% (in TP)</td>
<td>0 wt%</td>
</tr>
<tr>
<td></td>
<td>15 wt% R2</td>
<td>0 wt%</td>
<td>0 and 10 wt%</td>
</tr>
<tr>
<td></td>
<td>15 wt% R2</td>
<td>0.1 and 0.336 wt% (in epoxy)</td>
<td>0 wt%</td>
</tr>
<tr>
<td></td>
<td>15 wt% R2</td>
<td>0.1 and 0.336 wt% (in TP)</td>
<td>0 wt%</td>
</tr>
<tr>
<td></td>
<td>25 wt% R2</td>
<td>0 wt%</td>
<td>0 and 10 wt%</td>
</tr>
<tr>
<td></td>
<td>25 wt% R2</td>
<td>0.1 and 0.336 wt% (in epoxy)</td>
<td>0 wt%</td>
</tr>
<tr>
<td></td>
<td>25 wt% R2</td>
<td>0.1 and 0.336 wt% (in TP)</td>
<td>0 wt%</td>
</tr>
</tbody>
</table>
Chapter 4  Methods / Experimental

4.1 Introduction

Several different techniques were used in the manufacture of specimens, the tests carried out on these specimens and the microscopy work carried out to image them. These various methods are explained in this chapter.

4.2 Plate Manufacture

4.2.1 Amine Cured Epoxy System

4.2.1.1 Resin Preparation

The amine cured epoxy system described in section 3.2 used the constituents in the following ratio, 1 PY306 : 1.17 MY0510 : 1.42 MCDEA by weight. Typically 47.8 g PY306, 56.0 g MY0510 and 67.7 g MCDEA were used for a 190 x 110 x 5 mm plate. The two epoxies were put in a 600 ml Pyrex beaker and mixed briefly together using a spatula. The MCDEA was then added and the mix was placed in an oven at 120 °C and stirred for 1 hour at about 200 rpm with an overhead stirrer fitted with a radial flow impeller. This ensured that the MCDEA, which was added in powder form, dissolved fully into the epoxy. A cured sample was examined using a scanning electron microscope to check that no undissolved MCDEA could be seen, and it was found that this regime did fully dissolve the MCDEA. After the MCDEA had been dissolved into the epoxy the mix was ready to be formed into plates.

The plates were not only made with pure epoxy but also with various weight percentages of nanosilica, which was available dispersed in PY306. The constituents were prepared in an identical manner to above, with PY306 / 40 wt% nanosilica substituted for as much of the PY306 as needed to give the required nanosilica and PY306 content. For example, where 10 wt% nanosilica is required, 47.6 g of PY306 / NS is used, which gives 19.0 g nanosilica and 28.6 g PY306, 19.2 g of pure PY306 is added to make the total amount of PY306 up to the required 47.8 g.
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Carbon nanotubes were also incorporated into the epoxy. To limit the amount of nanotubes which were used smaller plates were made, 135 x 80 x 3 mm. For this 15.9 g PY306 and 18.7 g MY0510 were put in a 250 ml Pyrex beaker, the dry nanotubes were added to the mixed epoxy resins. The nanotubes were stirred in by hand and the beaker was placed in a Grant MXB6 ultrasonic bath for sonication. The bath was run continuously through the week and the mix was stirred thoroughly once each day by hand. The nanotubes were sonicated into the epoxy for approximately 120 hours. For each new plate a mix of resin with nanotubes in was sonicated. Immediately after the sonication had been completed 22.6 g MCDEA was added and stirred in as described above.

Plates were made incorporating the thermoplastic (a poly(ether sulfone) co-polymer). During the mixing process of the resin, after the two epoxies had been combined, the thermoplastic powder was added and this was stirred in using the mechanical stirrer at 650 rpm for at least 2 hours at 120 °C until all the thermoplastic had dissolved, then the MCDEA was added and stirred for 1 hour at 650 rpm. Epoxy / thermoplastic plates were made with a range of nanosilica (NS) and carbon nanotube (NT) percentages. If nanosilica was to be added then this was done as before, substituting the necessary amount of PY306 / nanosilica for some or all of the PY306 to give the required percentages. When nanotubes were to be added this was either done as described earlier by sonicating the nanotubes into the epoxy, before adding the thermoplastic. Alternatively the nanotubes were also supplied dispersed at 1 wt% in the thermoplastic and the thermoplastic was then added as usual to the epoxy mix, the thermoplastic / NT and thermoplastic were added in the necessary quantities to give the required percentages of NTs and thermoplastic. MCDEA was added as the final component for any plate and when thermoplastic was present was stirred in for 1 hour at 650 rpm and 120 °C. When 25 wt% thermoplastic or greater was required, the thermoplastic was added in 2 batches of approximately equal weight, each batch being stirred in for 2 hours at 650 rpm and 120 °C. The mix was allowed to cool overnight, re-heated the following day and then the MCDEA was added as described above.

4.2.1.2 Forming a Plate and Curing

The plates were made in picture frame moulds, as shown in Figure 4.1. These were used so that the material wastage was minimal and the plate would come out with a uniform thickness. Two different sizes of mould were used, final dimensions of a
standard plate are approximately $190 \times 110 \times 5$ mm, and to try to minimise the amount of nanotubes a smaller mould was used for plates containing nanotubes. These plates had a of size about $135 \times 80 \times 3$mm.

For both sizes of plate, the use of the picture frame moulds followed the same method. All parts of the mould were cleaned and coated in a layer of Frekote 700-NC from Loctite. The picture frame was clamped onto the base plate using G clamps and a silicone sealant such as Bostik Bond-flex 100HMA was used to seal the sides. The mould and its lid were pre-heated to 80 °C. If the resin had a low viscosity, once the resin and MCDEA were fully mixed, the mould was partially filled with the resin. The mould and the remaining resin in the beaker were placed in a vacuum oven to be degassed at 80 °C. Once this degassing had been completed the lid, which is not shown, was placed on the mould and the lid and mould were clamped together, again using G clamps. Extra resin was then poured into the mould from one side, so that the mould filled up to the top and the air could escape out the other side, without trapping air bubbles in the plate.

When thermoplastic and higher percentages of nanosilica were used the viscosity was sufficiently high that the resin was degassed in a vacuum oven at 100 °C in the beaker first. The resin was then transferred to the mould which was slightly overfilled and degassed again. Finally the lid was lowered from one side onto the mould to prevent air from becoming trapped. The lid was then clamped with the G clamps.

A thermocouple was placed in the resin in some of the first plates which were made to monitor the temperature in the resin to check that the plates were all cured at the same temperature and for the same length of time.
Once the moulds were full and had their lids clamped on they were cured in an oven. The schedules were worked out to allow the resin to be heated at 1 °C/minute and then held at 180 °C for 5 hours. The plates were allowed to cool to room temperature in the mould and then the plate was removed.

4.2.2 Anhydride Cured Epoxy System

Plate manufacture of the anhydride cured epoxy system followed a similar process to the amine cured system. 58.9 g LY556 was put into a Pyrex breaker, nanotubes were added and sonicated as above if required, or some of the LY556 was replaced by DGEBA with dispersed nanoparticles to give the required percentages of nanosilica and epoxy. 53.8 g HE600 hardener was added and stirred in at room temperature with an overhead stirrer fitted with a stainless steel, 3 blade propeller, rotating at 250 rpm, until the resins appeared fully mixed. This typically took 15 minutes. The mix was then poured into the small mould and degassed at 40 °C for no more than half an hour. Then the lid was clamped on and the mix was cured.

The cure cycle was:
Start at 50 °C, ramp to 100 °C at 1 °C/minute, dwell for 120 minutes, ramp to 150 °C at 1 °C/minute, dwell for 600 minutes, cool to room temperature in the oven before removing the plate from the mould.

Figure 4.1: The base plate and picture frame of the mould.
4.3 Mechanical Properties Testing

4.3.1 Tensile Tests

Tensile tests were carried out to comply with the standard BS EN ISO 527-2 using the sample geometry ‘5A’ as shown below in Figure 4.2 [72]. A minimum of four specimens were machined from plates of each material made and these were tested on an Instron 5584 or 4466 universal testing machine using the Bluehill software.

Figure 4.2: Tensile test specimen geometry [72].

Where

<table>
<thead>
<tr>
<th>Dimensions in millimetres</th>
</tr>
</thead>
<tbody>
<tr>
<td>$l_2$</td>
</tr>
<tr>
<td>12.5±1</td>
</tr>
<tr>
<td>25±1</td>
</tr>
<tr>
<td>4±0.1</td>
</tr>
<tr>
<td>8±0.5</td>
</tr>
<tr>
<td>12.5±1</td>
</tr>
<tr>
<td>50±2</td>
</tr>
<tr>
<td>≥2</td>
</tr>
</tbody>
</table>

An overall length of 75 mm was used for the specimens in this report, the thickness was either 5 or 3 mm depending on the thickness of the plate the samples were cut from. See Figure 4.3 for the setup in an Instron testing machine.
The tests were run at a cross-head speed of 1 mm/minute, at room temperature and an extensometer with a gauge length of 25 mm was used to record the strain in the central parallel section of the specimens.

The Young's modulus was calculated from the gradient of the stress versus strain plot once the initial load had been taken up. Figure 4.4 shows an example of the plot obtained from the testing. The average slope of the graph from 5 to 20 MPa was used for determining the Young's modulus. The region of the curve used does not include data from 0 to 5 MPa to avoid the first section of loading where the strain can be affected by the slack in the system. For this example the Young's modulus is 2.45 GPa and the ultimate tensile strength (UTS) is taken from the maximum stress.
4.3.2 Fracture Tests

Initially fracture tests were carried out using compact tension samples. However the results from single edge notch bend (SENB) samples were used for all later work as the samples use a smaller quantity of material and the results were found to be almost the same.

The specimens were machined out of the plates and the notch was added. This notch was then precracked by tapping a new, sharp, razor blade into the notch until a natural crack grew. The extent of this natural crack growth was difficult to see in some materials due to their opacity. The actual length of the precrack was measured after testing with a pair of vernier callipers and an optical microscope.

These tests were also carried out at room temperature, on Instron 5584 and 4466 testing machines, using the Bluehill software to collect data and carry out some calculations. The loading rate was 1 mm/min.
4.3.2.1 Compact Tension Tests

For compact tension the specimen geometry used is shown in Figure 4.5, and is in accordance with BS ISO 13586 [73]. The sample thickness (B) was determined by the thickness of the plates, and the size of the loading holes was set at 8 mm to fit with the loading pins and shackles available for use. To have the width (W) = 2B as suggested in the standard would have made the samples impractically small, so an arbitrary value was chosen which gave a suitable size of specimen and checks were carried out after testing to ensure that the plane strain criterion was met. All other dimensions were taken from W. The machine setup for testing compact tension specimens is shown in Figure 4.6.

Figure 4.5: Compact tension specimen geometry.

All dimensions in millimetres
The value of the fracture toughness, $K_c$, was calculated from the Equation below.

$$K_c = \left(\frac{P_c}{BW^{1/2}}\right) f(x)$$  \hspace{1cm} \text{Equation 4.1}

Where

- $P_c =$ load, either $P_{\text{max}}$ or $P_Q$ as appropriate,
- $B =$ specimen thickness,
- $W =$ specimen width,
- $a =$ crack length,

$$f(x) = \frac{(2+x)(0.886 + 4.64x - 13.32x^2 + 14.72x^3 - 5.6x^4)}{(1-x)^{3/2}}$$  \hspace{1cm} \text{Equation 4.2}

and $x = \frac{a}{W}$

The load used in $P_c$ is either the maximum load if the failure was brittle, or the intercept between the load line and a line drawn with a compliance 5% greater than that of the straight line section of the graph ($P_Q$). If the 5% line crosses the load line beyond the maximum load, then the maximum load is taken as $P_c$. If the 5% line crosses the load line before the maximum load then $P_Q$ is taken as $P_c$. Figure 4.7 shows this graphically.
Figure 4.7: Determination of $P_0$ [73].

If $P_{\text{max}} / P_0$ is less than 1.1 then $P_0$ can be used in the calculations of $K_Q$, however if $P_{\text{max}} / P_0$ is greater than 1.1, then $P_0$ cannot be used and the test is invalid.

$G_c$ was calculated from the area under the load-displacement graph using Equation 4.3.

$$G_c = \frac{W_B}{BW\Phi(x)}$$  \hspace{1cm} \text{Equation 4.3}

Where

$W_B =$ the energy to break (given by integrating the area under the load-displacement curve to $P_0$)

$B =$ specimen thickness,

$W =$ specimen width

and

$$\Phi(x) = \frac{A(1-x)}{B + 2A}$$  \hspace{1cm} \text{Equation 4.4}

$A = (1.9118 + 19.118x - 2.5122x^2 - 23.226x^3 + 20.545x^4)$  \hspace{1cm} \text{Equation 4.5}

$B = (19.118 - 5.0244x - 69.678x^2 + 82.16x^3)(1-x)$  \hspace{1cm} \text{Equation 4.6}
4.3.2.2 Single Edge Notched Bend Tests

For single edge notched bend (SENB) samples the basic conditions are the same, the $P_{\text{max}} / P_0$ condition still applies, but geometry is very different. It is shown in Figure 4.8, again it is in accordance with BS ISO 13586 and the sample thickness ($B$) was determined by the thickness of the plates, all other measurements were taken from the thickness [73].

![Figure 4.8: Single edge notched bend specimen geometry.](image)

The distance between the supports as shown below in Figure 4.9, was 40 mm and the displacement of the sample was measured with an extensometer attached to a sprung spacer which is located as shown in Figure 4.9.
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Sprung spacer with extensometer attached

Figure 4.9: Image of the SENB set up used.

To calculate the fracture toughness Equation 4.1 still applies, but for SENBs

$$f(x) = 6x^{1/2} \frac{1.99 - x(1-x)(2.15 - 3.93x + 2.7x^2)}{(1+2x)(1-x)^{3/2}}$$

Equation 4.7

Fracture energy is also calculated from Equation 4.3, but for SENBs Equations 4.8 and 4.9 must be used.

$$\Phi(x) = \frac{A + 18.64}{dA/dx}$$

Equation 4.8

$$A = \frac{16x^2}{(1-x)^3} \left(8.9 - 33.717x + 79.616x^2 - 112.952x^3 + 84.815x^4 - 25.672x^5 \right)$$

Equation 4.9

For both geometries to ensure the plane strain criterion was met it was checked that

$$B, a, (W-a) > 2.5(K_\sigma/\sigma)_o^2$$

Where

a is the crack length,
K_Q is the conditional or trial K_c value, and is equal to K_c if the above condition and the condition set on P_max / P_Q given above are both met, and

\( \sigma_y \) is taken from the maximum load from a tensile test as no clear yield is seen in these materials, they fracture first.

Indentation tests were carried out on each of the materials to account for displacement due to indentation of the specimens by the rig rather than displacement of the specimen. These tests were run on the same machine as the fracture tests, using unnotched samples and at a slower crosshead speed to try to get the loading rate about the same as it is for the fracture tests. For compact tension tests the machine set up is kept the same, but for SENB tests the two supports are moved as close together as possible to minimise bending of the sample. The tests were run until the maximum load seen during the fracture testing had been reached. The work done in indenting the material is given by the area under the force-displacement graph, this is calculated for each sample using the peak load and the area is subtracted from the area under the force-displacement graphs of each of the fracture tests.

Since tensile tests on these plates had also been carried out, the fracture energy G_c was also calculated from Equation 4.10 as a check on the accuracy of the test.

\[
G_c = \frac{(1 - \nu^2)K_c^2}{E} \quad \text{Equation 4.10}
\]

Where

\( G_c \) = the fracture energy,
\( K_c \) = fracture toughness,
\( E \) = Young's modulus,
\( \nu \) = Poisson's ratio, taken as 0.35 [1]

Between two and six specimens were tested for each type of material.

An example of the spreadsheet used to analyse a set of SENB specimens is given in Appendix 1.
4.3.3 Plane Strain Compression Tests

Plane strain compression tests were used to measure the modulus and yield stress of samples. The compression tests were carried out using a rig with two parallel platens 12 mm in width and longer than the specimens to be tested were wide. The specimens to be tested were 3 mm thick, 80 mm wide and 135 mm long, these were placed between the platens and the platens were loaded in compression with a crosshead speed of 0.1 mm/min (to give approximately the same extension rate, relative to the distance the displacement is over, as for the tensile tests carried out before). Five tests were carried out on each material leaving 12 mm between tests to minimise residual stress. The results were corrected for machine compliance which was measured by compressing the platens together with no sample in between them.

4.3.4 Dynamic Mechanical Analysis

Dynamic Mechanical Analysis (DMA) was carried out using a Triton Technology Tritec 2000 DMA, set up for dual cantilever bending. DMA measures the strain resulting from an applied stress which bends samples by moving the centre of a clamped specimen backwards and forwards at chosen frequencies and over a range of temperatures. This allows the glass transition temperature (T_g) to be determined. The samples used were 2 x 3 x 45 mm and were clamped at either end, 25 mm apart, with the centre of the clamped part of the specimen fixed in the grip which moves. The frequencies chosen for these tests were 1 and 10 Hz and the temperature range was from 25 °C, up to 200 °C. The glass transition temperature was identified as the peak in the Tan Delta trace.

4.4 Microscopy

4.4.1 Optical Microscopy

A Nikon Transmission Optical Microscope (TOM), an Optiphot II, was used to investigate the micron scale dispersion of nanotubes both in the uncured epoxy resin and the cured epoxy polymer. To examine the dispersion in the resin, a drop of the resin and nanotube mix was taken from the beaker that the nanotubes were being
mixed in, and this was placed on a microscope slide. A glass cover slip was placed over this and the sample was then examined through the microscope so any agglomerates could be seen. A graticule was used with each image to find the magnification.

To examine the cured polymers a section of the specimen, the thickness of the plate and approximately 6 mm square, was taken and bonded onto a glass slide with Araldite Instant Clear from Huntsman, Cambridge. The surface of each was then polished using a rotary plate polisher, starting with a 6 μm diamond solution, the finest solution used was a 1 μm diamond solution. The samples were then carefully cut off the slides with a hacksaw and bonded with M-bond AE10 from Vishay Measurements Group, polished sides down onto new slides. The samples were then ground down to about 70 μm thickness with a Struers grinder/polisher and polished again. Finally the samples were examined by eye and under the TOM to see the dispersion achieved.

A hot stage (Linkam THMS 600) was used to enable a visual assessment of the movement of the nanotubes during curing. A drop of the resin with curing agent and all relevant modifiers was placed in the hot stage between two thin glass discs. The hot stage was then programmed to run a cure cycle to mimic the temperatures the resin would experience during degassing and curing. While this was running images were taken using a camera at regular intervals.

4.4.2 Scanning Electron Microscopy

Scanning Electron Microscopy (SEM) was used to examine the fracture surfaces of the compact tension and single edge notched bend specimens. The first microscope used was a JEOL ‘JSM-5300’ scanning microscope, at an accelerating voltage of 20kV. The samples were sputter coated with gold before analysis to reduce charging on the sample surface. The second microscope used was a Hitachi S-3400N.

4.4.3 Atomic Force Microscopy

The specimens were prepared by taking the cured material and cutting off a small section, about 3 mm × 2 mm × 2 mm. This section was then shaped so that the top surface had an area about 1 mm × 1 mm and the sides sloped out to the full width of
the specimen. The specimens were mounted in an ultramicrotome from RMC Products and slices were cut off the surface first with a glass knife and then with a diamond knife, to give a smooth, flat surface. Initially samples were cut at -60 °C but the glass transition temperature of the thermoplastic was sufficiently high that it was found samples could be successfully cut at room temperature.

A MultiMode scanning probe microscope from Veeco was used for Atomic Force Microscopy (AFM) to investigate the morphology of the samples. The microscope was used in tapping mode, and height and phase images were taken. It also revealed the dispersion of the nanosilica and nanotubes. Fracture surfaces were also investigated using this technique.

### 4.4.4 Transmission Electron Microscopy

Specimens for Transmission Electron Microscopy (TEM) were prepared using the microtome. This was carried out in a similar way to the AFM samples except that the microtome was always used at room temperature and the sections cut from the specimens with the diamond knife were floated on water. Those sections with a thickness of about 90 nm were put onto a copper grid. The transmission electron microscope used was a JEOL 2000FX Mk2, used at 200kV. This was used to investigate the dispersion of individual nanotubes in the polymer. Overlapping images were taken to allow a collage to be assembled at a later date.
Chapter 5  Epoxy and Epoxy / Thermoplastic Blends

5.1 Introduction

The present chapter discusses the morphology and properties of epoxy and epoxy / thermoplastic (TP) blends, using the thermoplastic R1. Bulk plates were manufactured using epoxy with 0, 15, 20, 25 and 35 wt% R1. Tensile and fracture test specimens were cut from these plates and the Young’s modulus, fracture toughness and fracture energy were measured. Dynamic mechanical analysis was also undertaken to measure the glass transition temperature of the epoxy and thermoplastic phases in the blend.

Atomic force microscopy was used to investigate the morphology of the samples while scanning electron microscopy was employed to study the fracture surfaces of the specimens to compare with the fracture toughnesses and understand the mechanisms of fracture and toughening.

5.2 Microstructure

5.2.1 Epoxy

Pure epoxy specimens were microtomed and imaged using the atomic force microscope (AFM). This showed that the cut surface was devoid of any features, see Figure 5.1, indicating that the epoxy was a homogeneous thermoset polymer.
5.2.2 Epoxy and Thermoplastic

The micrograph of the epoxy and 15 wt% R1 specimen, given in Figure 5.2, clearly shows a spherical particulate morphology with spheres of thermoplastic about 1 μm in diameter. The thermoplastic is initially soluble in the epoxy but phase separates upon curing. There is no evidence of debonding of the thermoplastic particles during microtoming, which would be shown by holes on the side of the thermoplastic sphere where it has pulled away from the epoxy. This suggests that the thermoplastic is well bonded to the epoxy.

Figure 5.1: AFM image of the microstructure of a pure epoxy sample.

Figure 5.2: AFM image of the microstructure of 15 wt% R1 in epoxy showing a spherical particulate morphology.
In Figure 5.2 the image on the left shows the relative hardness of the phases, the lighter the colour the harder the phase. As can be seen above, the thermoplastic and the epoxy are of similar hardnesses and this can make distinguishing between the two difficult when the microstructure is complicated. The image on the right shows the relative heights of the two phases. While in theory the surface will be flat from the microtoming, in practice the different materials cut slightly differently and the phases can be identified from the height image where there is a height difference of approximately 10 nm. The thermoplastic is slightly higher than the epoxy and hence lighter in colour.

Increasing the percentage of thermoplastic to 20 wt% had no effect on the morphology. The thermoplastic still formed spherical particles of about 1 μm in diameter, as shown in Figure 5.3.

![AFM image of the microstructure of 20 wt% R1 in epoxy, showing a spherical particulate morphology.](image)

When the percentage of thermoplastic was increased to 25 wt%, the particles were no longer spherical, as shown in Figure 5.4. A co-continuous morphology with regions of epoxy and regions of thermoplastic was formed. In addition there is also some localised phase inversion with spheres of epoxy being seen in the regions of thermoplastic, these epoxy spheres have diameters of around 0.6 μm.
Figure 5.4: AFM image of the microstructure of 25 wt% R1 in epoxy showing the complex co-continuous / localised phase inverted morphology.

To complete this microstructural investigation a specimen with 35 wt% R1 was prepared. This was the highest percentage of thermoplastic it was possible to dissolve into the epoxy and form into usable plates, using the method employed in this work. This is due to the increasing viscosity which results from incorporating thermoplastic and prevents successful degassing during plate making. At 35 wt% R1 the morphology is fully phase inverted with the epoxy particles approximately 1 μm in diameter being entirely surrounded by a thermoplastic matrix as shown in Figure 5.5.

Figure 5.5: AFM image of the microstructure of 35 wt% R1 in epoxy showing a phase inverted morphology.
This range of morphologies agrees with previous work carried out by Kinloch and Yuen [1] which found the same progression from spherical particulate to co-continuous and finally to phase inverted for a similar material as shown in Figure 2.7 in the literature survey.

To calculate an approximate value for the percentage of thermoplastic which is phase separated in the plates, AFM images were imported into an image analysis program called 'blob analysis' in the package Global Lab image 2 by Data Translation Inc.. This was used to calculate the area fraction of thermoplastic in the epoxy. It can be assumed that the area fraction of a phase is equal to the volume fraction [74]. The results are summarised in Table 5.1. The images of 15, 20 and 35 wt% thermoplastic contained between 20 and 85 'blobs' depending on the scan size. Four images of 15 wt% R1 were analysed and the mean volume percentage was 14.5% with a standard deviation of 2.5%, indicating that the accuracy of the volume percentages are ± 2.5%.

Table 5.1: Percentage content of thermoplastic in specimens and the volume percentage contents of thermoplastic taken from 'blob analysis' of AFM images.

<table>
<thead>
<tr>
<th>Wt% R1</th>
<th>Vol% R1 (calculated from wt%)</th>
<th>Vol% R1 (from 'blob analysis')</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>13.5</td>
<td>14.5</td>
</tr>
<tr>
<td>20</td>
<td>18.1</td>
<td>19.2</td>
</tr>
<tr>
<td>25</td>
<td>22.8</td>
<td>33.1</td>
</tr>
<tr>
<td>35</td>
<td>32.3</td>
<td>46.2</td>
</tr>
</tbody>
</table>

The density of the thermoplastic in the epoxy was calculated by measuring the volume and the mass of samples with no thermoplastic, 20 and 35 wt% R1. The density of each sample was calculated, and hence the density of the thermoplastic for the 20 and 35 wt% R1 samples was found. From the two samples containing thermoplastic the density of the thermoplastic was averaged and this gave a value of 1.36 g/cm³. The density of the epoxy was 1.20 g/cm³. Using this density the volume percentages of thermoplastic in the samples in Table 5.1 were calculated.

While the 15 and 20 wt% R1 specimens had volume percentages from blob analysis similar to the added volume percentages, the 25 and 35 wt% R1 specimens had a much higher volume percentage from blob analysis than expected. This could indicate that the epoxy and thermoplastic are not fully phase separating where there is some
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phase inversion, leaving epoxy in the thermoplastic phase, or that the morphology is more complicated than initially supposed with small epoxy spheres separating out within the thermoplastic phase which are too small to be visible in the micrographs.

In general the mechanisms for forming spherical particulate and co-continuous structures are different [75], and this could help explain the amount of epoxy left in the thermoplastic for high percentages of thermoplastic. The spherical particulate morphology will typically be the result of a nucleation and growth process. Areas of high concentration of thermoplastic form, which are the nuclei; the regions around the nuclei are depleted of thermoplastic so thermoplastic diffuses in from the surroundings, and the nucleus grows depleting the region around it again. Hence regularly sized spherical particles which are evenly dispersed are formed. A second process, spinodal decomposition occurs when abnormal diffusion is seen and the thermoplastic moves to regions with higher concentrations of thermoplastic already in them. Spinodal decomposition is responsible for co-continuous morphologies [75, 76].

These two mechanisms can both occur in a sample, the phase separation may start as nucleation and growth and then change to spinodal decomposition, or vice versa, and this may result in the complex morphologies which have been seen at 25 wt% R1. The possibility of small nuclei of epoxy forming in the thermoplastic, and then the mechanism changing to give a co-continuous structure leaving very small spheres of epoxy which would be missed in the microscopy work, could explain the differences in the volume percentages of thermoplastic calculated for 25 and 35 wt% R1 samples from microscopy images and from the weight percentages. Another possibility is that the spinodal decomposition is not going to completion, preventing the epoxy and thermoplastic from fully separating out, leaving epoxy in the thermoplastic.

5.3 Mechanical Properties

5.3.1 Dynamic Mechanical Analysis

The glass transition temperatures \( T_g \) for the epoxy and epoxy / thermoplastic blends were measured using a Dynamic Mechanical Analyser. The \( T_g \) values were taken as the temperature at the peak tan \( \delta \), and are shown in Table 5.2 below. Four tests were run on specimens of the same material and the variation in these results indicates that the dynamic mechanical analysis (DMA) gives the \( T_g \) to an accuracy of \( \pm 0.8 \, ^\circ \)C.
Table 5.2: Glass transition temperature, $T_g$, results from DMA testing.

<table>
<thead>
<tr>
<th>Wt% R1</th>
<th>Wt% NS</th>
<th>$T_g$ (°C) at 1 Hz</th>
<th>$T_g$ (°C) at 10 Hz</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>193.9</td>
<td>201.4</td>
</tr>
<tr>
<td>15</td>
<td>0</td>
<td>197.1</td>
<td>203.1</td>
</tr>
</tbody>
</table>

The results for 1 Hz are displayed on the graph below, and the results for 10 Hz are similar to these. It was expected to see some effect of the thermoplastic on the tan δ curves in the form of a second peak or a broadening of the peak, however as can be seen from Figure 5.6 this is not obvious. Indeed there is very little difference between the data for the samples with and without thermoplastic.

If the thermoplastic had a significantly different glass transition temperature to the epoxy and had phase separated then a second peak would be expected at the $T_g$ of the thermoplastic as well as the main peak at the $T_g$ of the epoxy. If the two glass transition temperatures were relatively similar then a broadening of the peak would be expected. However, if the thermoplastic had remained in solution and had a lower $T_g$ than that of the epoxy then the peak would be expected to shift to a lower temperature. As can be seen in Figure 5.6, the addition of thermoplastic to the epoxy does not give any significant change in the peak. This indicates that the thermoplastic has a glass transition temperature which is within a few degrees of that of the epoxy, possibly slightly higher than the $T_g$ of the epoxy as the $T_g$ from the DMA test for the sample with thermoplastic in it was slightly higher than the $T_g$ for the epoxy sample. This agrees with the information given about the thermoplastic by Cytec. Hence no further DMA was performed on epoxy / thermoplastic blends. From Figure 5.6 it can also be seen that the storage modulus for the epoxy and the blend are approximately equal over the whole range of temperatures.
Figure 5.6: Modulus versus temperature for epoxy and epoxy / 15 wt% R1 specimens showing no effect from the addition of the thermoplastic.

5.3.2 Tensile Tests

Tensile tests were carried out for each of the formulations with increasing thermoplastic content. A typical trace for a tensile test on epoxy is shown in Figure 5.7.
Figure 5.7: Stress versus strain curve for an epoxy sample.

The curve shows an elastic region, the linear portion between 5 and 20 MPa, which was used to calculate the Young's modulus. The elastic region is followed by some plastic deformation. For this sample the ultimate tensile strength was 66 MPa and the Young's modulus was 2.6 GPa. An indication of where plastic deformation begins is taken from the 0.2% proof stress, to calculate this a straight line is drawn from the horizontal axis at 0.2% strain, with the same gradient as the Young's modulus. The stress at which this line and the experimental curve intersect is taken as the 0.2% proof stress. For this sample it is 43.9 MPa.

The Young's modulus, ultimate tensile strength and 0.2% proof stress were calculated for all formulations. The results for Young's modulus are shown in Figure 5.8 and indicate that the addition of 15 wt% R1 does not affect the Young's modulus, however there is a small jump in modulus between 15 to 20 wt% R1 and then the modulus stays approximately the same through 25 and 35 wt% R1.
Figure 5.8: The effect on Young's modulus of increasing the thermoplastic content.

With no initial information about the expected properties of the thermoplastic it is interesting to note that the Young's modulus does not change much with increasing thermoplastic content indicating that the modulus of the thermoplastic and the modulus of the PY306 / MY0510 epoxy mixture are similar.

The error bars for each data point show one standard deviation, all of the above deviations are within 10%, which for experimental data is considered typical.

The ultimate tensile strength (UTS) of the samples was also calculated, although it is recognised that the UTS is dependent on the surface finish of the samples as well as the material [77, 78]. All the samples were prepared in an identical manner so the surface roughness for each sample should be similar and therefore the UTS data for samples tested in this report should be comparable to each other. It was found that increasing the percentage of thermoplastic consistently raises the ultimate tensile strength. Figure 5.9 shows the effect on the UTS of increasing the percentage of thermoplastic.
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Figure 5.9: The effect on the ultimate tensile strength (UTS) of increasing the thermoplastic content.

There is a significant increase in the UTS with increasing thermoplastic content. This increase could indicate that the UTS of the thermoplastic is greater than that of the epoxy, and it is interesting to note that the changes in morphology do not seem to have any additional effect, although it is possible that some change in morphology is occurring at 20 wt% R1 which cannot be detected with the AFM and this is responsible for the changes in properties. A more in depth study of formulations around this percentage would be needed to confirm whether this was the case. It was also found that the amount of plastic deformation of the tensile specimens before break increased as the percentage of thermoplastic is increased, i.e. the material becomes less brittle. Figure 5.10 shows the typical stress strain curves of an epoxy sample with 35 wt% R1 compared to the pure epoxy sample which was given earlier in Figure 5.7. The 35 wt% R1 sample shows a distinct move towards greater plastic deformation and strain to failure which is expected as the matrix is thermoplastic at this point.
Figure 5.10: Stress versus strain curves comparing a pure epoxy sample with an epoxy sample with 35 wt% R1.

The Youngs' modulus, the UTS and the amount of plastic deformation may be increasing with the addition of thermoplastic, however the yield strength of the material is not increased by the addition of the thermoplastic as shown in Figure 5.11. Since true yield where the stress reaches a peak is not seen for these materials a 0.2% proof stress is taken, which gives an assessment of the point where the stress / strain curve deviates from linear for each sample.
Figure 5.11: 0.2% proof stress versus percentage thermoplastic showing no increase in yield with increasing percentage of R1.

Both an increase in the UTS and a reduction in the strain to failure of the epoxy with increasing thermoplastic content would be expected to result in an increase in toughness [79].

5.4 Fracture Properties

5.4.1 Fracture Toughness

Fracture tests were carried out using compact tension specimens, with samples of epoxy with 0, 15, 20, 25 and 35 wt% R1, in compliance with the requirements of linear elastic fracture mechanics. The fracture toughness, $K_c$, and fracture energy, $G_c$, were calculated as discussed in section 4.3.2. An example load versus displacement trace from a fracture test is given in Figure 5.12, which shows that the fracture was brittle. Most samples failed in this manner, but a couple showed slip / stick behaviour where the fracture arrested and initiated a couple of times. For these samples the $G_c$ and $K_c$ values were taken from the first initiation. The trace shows the take up of the load of the shackles used to hold the samples in the machine. This load is included in the result analysis as it is also carried by the samples.
Figure 5.12: Typical load versus displacement trace for compact tension test of an epoxy sample.

It was found that increasing the thermoplastic content increases both the fracture toughness and fracture energy as may have been expected from the tensile test results. Figure 5.13 below shows the results for these tests. The value of $K_c$ for the epoxy rose from 0.68 to 1.11 MPa.m$^{0.5}$ when 35 wt% R1 was added this is an increase of 63%. The value for $G_c$ rose from 214 J/m$^2$ for the epoxy to 531 J/m$^2$ when 35 wt% R1 was added, this is a 148% increase. Both of these rises are significant as the error bars do not overlap. It should also be noted that there is no step change in toughness as the morphology changes, the toughness gradually increases as the thermoplastic content increases.
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5.4.2 Fracture Mechanisms

To help explain the increase in fracture toughness and fracture energy, the fracture surfaces of the specimens after testing were investigated using a scanning electron microscope (SEM). This showed the morphology of the specimens again but also showed the roughness of the fracture surface and the path of the fracture. For all the micrographs the crack propagation direction is from left to right.

The SEM images for an epoxy specimen with no thermoplastic are shown in Figure 5.14. These show that the surface has a smooth and glassy appearance and is flat with very little plastic deformation. The mean fracture energy for the epoxy is 214 J/m² and the fracture toughness was 0.68 MPa.m⁰.⁵. This fracture toughness is typical for a brittle epoxy polymer. Work on a similar system carried out by Kinloch et al [1] using the same epoxies found a similar toughness. The fracture energy they found was approximately half the value found here but a different curing agent was used which explains this difference. The smooth surface is also typical of brittle failure, a rough surface will have a greater surface area and for a perfectly brittle material this would give a higher fracture energy. The white lines in the image at 250 times magnification
are known as river lines and are typically seen at the beginning of fractures in epoxies: they show where the crack front starts on different levels [80].

Figure 5.14: SEM images of an epoxy sample showing a relatively smooth surface, with little deformation, at 250, 1000 and 3000 times magnification.

The addition of 15 wt% R1 has only a very marginal effect on the fracture toughness. When a fracture surface was examined using the SEM the thermoplastic spheres seen in the AFM images are clear, and the microstructure seen in the SEM images of the fracture surfaces is the same as the microstructure seen in the AFM images.

The accepted toughening mechanisms of epoxy modified with thermoplastic involve crack deflection, particle bridging, and cavitation or debonding of the epoxy rich or thermoplastic rich phases [1, 81]. As seen in Figures 5.15 and 5.16 below none of these mechanisms are apparent when 15 wt% R1 is incorporated in the epoxy. The thermoplastic is well bonded to the epoxy, and there are no gaps round the particles or holes in the epoxy surface indicating debonding of particles. Similarly, there are no voids in the particles which would be seen if there was cavitation.
Figure 5.15: Scanning electron micrographs of the fracture surface of a 15 wt% R1 specimen, taken at 250, 1000, 5000 and 10000 times magnification.

It appeared that the crack front had run straight through the thermoplastic spheres during fracture, see Figure 5.16. Here the two images were taken from the same place on both halves of a fracture specimen. The thermoplastic spheres can be seen on both sides of the fracture, whereas if the crack had gone round the particles it would be expected to see the spheres on one side with holes on the other side where they had been before fracture.
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Figure 5.16: SEM images of both sides of a fracture surface at the same location showing the thermoplastic spheres on both sides, indicating that the crack front has passed straight through the spheres rather than being deflected round them. The brown and black arrow point to cracks, and the yellow, green and blue arrows point to thermoplastic spheres. There are two arrows of each colour, one on each image, indicating the same feature on both sides of the fracture surface.

The cracks do not appear to be deflected round the thermoplastic spheres, as they have passed straight through the sample almost unaffected by the thermoplastic and the thermoplastic is not greatly affected by the crack. However the fracture energy is increased from 214 J/m² for the epoxy to 244 J/m² when 15 wt% R1 is added. The surface of the sample is significantly rougher than that with no thermoplastic which could be seen as a sign of toughening, this roughness is most clearly seen in the white
lines which are seen on the surface. These river lines are commonly seen on surfaces following fast fracture [80] and are where the crack front is on several different levels. The AFM image of the fracture surface of a 15 wt% R1 sample shows some plastic deformation of the thermoplastic spheres by the presence of peaks in the fractured thermoplastic spheres, see Figure 5.17. These peaks are not in the centre of the spheres but drawn to the side in the direction of crack propagation. This deformation of the thermoplastic particles can help explain the small increase in fracture energy.

Figure 5.17: AFM image of the fracture surface of epoxy with 15 wt% R1 showing the spheres of thermoplastic having been plastically deformed.

The fracture surface of a sample containing 20 wt% R1 appears very similar to that for 15 wt%, see Figure 5.18, and the microstructure is the same. However this sample did show significant toughening, the fracture energy increased to 313 J/m². The surface of the sample appears rougher with far more white river lines where the fracture surface is on different levels and the energy needed to deform the material and create new
surfaces to give this roughness could partly explain the improvements in fracture properties.

Figure 5.18: Scanning electron micrographs of the fracture surface of a 20 wt% R1 specimen, taken at 250, 1000, 5000 and 10000 times magnification. The arrows point to peaks where the thermoplastic has plastically deformed during fracture.

From the images shown in Figure 5.18 it can also be seen that the secondary electrons highlight the high spots on the thermoplastic spheres, where the thermoplastic is plastically deformed to form peaks, offset in the direction of crack propagation. These peaks were not noticeable under the SEM for samples with 15 wt% R1 indicating that the spheres plastically deform to a greater extent with 20 wt% R1. The crack still seems to pass through the thermoplastic particles rather than being deflected around them but there are lines of disturbance running in the crack propagation direction, originating from the side of the thermoplastic particles, these are most clearly seen when using the backscatter detector for the microscope and can be seen in Figure 5.19 below. These 'tails' have been cited as evidence of crack pinning, where a crack has split to go round a particle and then rejoined behind the particle at which point the two cracks are on different levels resulting in the tail [82]. They can be seen in the 15 wt%
R1 samples as well as the 20 wt% sample, but they are far more pronounced and occur much more frequently in the sample with 20 wt%. This indicates that the particles are affecting the crack growth, and more so at the higher content which ties in with the fracture energies. The crack front may pass through the thermoplastic particle more slowly than through the epoxy and so the front still can end up on different levels at the other side of the particles and the tails are where these differences in levels occur.

Samples containing 20 wt% R1 or greater had too great a surface roughness to investigate with the AFM.

Figure 5.19: Backscattered electron micrograph of the fracture surface of a 20 wt% R1 sample showing the lines from the thermoplastic spheres running in the crack direction.

For samples containing epoxy and 25 wt% R1 the morphology had changed such that the morphology was co-continuous and the fracture surface was even rougher still. Hence it is more difficult to judge from the SEM images the effect on the crack of the thermoplastic regions. However the crack is seen to have gone through regions of thermoplastic rather than going round them. This is to be expected as the regions of thermoplastic are large and the crack would have to be deflected a long way to go round the regions, it is more likely that the crack would take the shorter route through the thermoplastic. If some epoxy has been left in solution in the thermoplastic, as indicated by the higher than expected volume percentage of thermoplastic from
microscopy images, then the thermoplastic will probably have been chain extended by the epoxy, which is likely due to the reactive endgroups on the thermoplastic. This chain extended thermoplastic could be tougher than the pure thermoplastic if the pure thermoplastic has a low molecular weight and as such is fairly brittle. Since the crack cannot go round these regions of thermoplastic because of their large size and co-continuous nature, but has to pass through them, then if the chain extended thermoplastic has an increased toughness, it would be expected that the toughness of the thermoplastic modified epoxy would increase [1]. The fracture energy of epoxy with 25 wt% R1 samples was found to be 454 J/m², approximately double the pure epoxy value.

Figure 5.20: Scanning electron micrographs of the fracture surface of a 25 wt% R1 specimen, taken at 250, 1000, 5000 and 10000 times magnification.

The SEM images for the 35 wt% R1 sample can be seen in Figure 5.21. Here the thermoplastic is phase inverted and this makes judging the effect of the thermoplastic on the crack growth harder still. However the roughness of the sample can be seen to have increased once again. This ties in with the further increase in fracture energy to 531 J/m², which is a significant increase in toughness from that of the pure epoxy. The
crack is passing through the thermoplastic matrix and through the epoxy particles, it is not being deflected round them. However the thermoplastic matrix is a lighter colour in the SEM images, which indicates that the thermoplastic is higher than the epoxy particles and hence must have plastically deformed during fracture.

![Figure 5.21: Scanning electron micrographs of the fracture surface of a 35 wt% R1 specimen, taken at 250, 1000, 5000 and 10000 times magnification.](image)

This steady increase in fracture energy with increasing thermoplastic content measured in the present work agrees with research by others on the toughness of thermoplastic modified epoxy where a steady increase in fracture energy was found as the percentage of thermoplastic was increased, [1, 27]. The percentage increases found by Kinloch et al for 83 phr of thermoplastic, approximately a 50% increase for $K_c$ and 100% for $G_c$ also agree reasonably well with the increases seen for 35 wt% R1 (approximately 89 phr) here. Whether the increase in toughness is the result of changes in the microstructure has been debated in the past by authors [4]. It is clear here that the increase in toughness seen is the result of the addition of the thermoplastic, rather than the change in microstructure, as the toughness increases from 15 to 20 wt% R1 although there is no change in morphology. This agrees with the general consensus [1, 27].
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Figure 5.22 shows the change in fracture energy against the percentage of thermoplastic added for both the epoxy system used throughout this thesis, and the work carried out using a different curing agent by Kinloch and Yuen [1], from this it can be seen that the epoxy system used in this work provides the larger increases in fracture energy. This change could be the effect of the curing agent as the epoxies were the same in both systems and the thermoplastic was similar, and it highlights the importance of the curing agent.

![Graph showing change in fracture energy against percentage of thermoplastic added]

**Figure 5.22**: Relative fracture energy versus the percentage of thermoplastic added for two systems, the one used in this thesis and the one used by Kinloch *et al* [1], where the main difference between the systems is the curing agent used. (Lines are simply to guide the reader).

Both systems have a spherical particulate morphology at low percentages and by 25 wt% both have changed to a co-continuous morphology. The system described throughout the present work is phase inverted by 35 wt% while the system used by Kinloch *et al* remains co-continuous.
5.5 Conclusions

The epoxy fracture surfaces were smooth and featureless. The addition of thermoplastic to the epoxy gives a spherical particulate morphology at 15 and 20 wt% R1, with spheres of thermoplastic which are approximately 1 μm in diameter and well dispersed in the epoxy. From comparisons of the percentage of thermoplastic spheres visible and the percentage of thermoplastic added to the material it can be deduced that all of the thermoplastic comes out of solution. At 25 wt% the morphology is co-continuous but the thermoplastic and the epoxy do not fully phase separate. The morphology is complex with small spheres of epoxy in the thermoplastic phase. The material is phase inverted at 35 wt% R1 and there is a large discrepancy between the percentage of thermoplastic which can be seen in the micrographs and the percentage which was added, indicating that there is a significant amount of epoxy in the thermoplastic.

DMA showed that the thermoplastic and the epoxy have very similar glass transition temperatures, which agrees with the information given by Cytec. There is no evidence of a second peak on the tan δ traces, nor is the epoxy peak broadened which would be expected if the thermoplastic had a T_g which was different from that of the epoxy.

The tensile tests show that the Young's modulus of the epoxy is only slightly increased by the addition of thermoplastic. However the UTS is increased. The stress versus strain traces show that the samples with high percentages of thermoplastic undergo greater plastic deformation than pure epoxy and have a greater strain to failure.

The fracture toughness and energy of samples increases with increasing percentages of thermoplastic. This is not the result of changes in morphology as there is an increase from 15 to 20 wt% R1 but there is no change in morphology. Examination of the fracture surfaces show that the higher the percentage of thermoplastic the rougher the surface which agrees with the increase in toughness. The spheres of thermoplastic can be seen to be pulled into peaks during the fracture. The exact mechanism for fracture at 25 and 35 wt% R1 is harder to deduce due to the complex morphology of the material, however there is no evidence of crack deflection, debonding or cavitation of the thermoplastic. This increase in toughness may be explained as an effect of the thermoplastic being chain extended by the epoxy therefore toughening the material.
Chapter 6  Nanotube Dispersion

6.1 Introduction

The first problem to overcome when working with carbon nanotubes is a means of dispersing them. Their high aspect ratio and surface area tend to result in them becoming highly entangled, agglomerated and difficult to disperse [83]. This Chapter records the work done for this thesis in choosing which dispersion method to use, and which type of nanotubes to use.

The second problem, having achieved a dispersion, is assessing how well dispersed the nanotubes are. This is especially important for choosing a method of dispersion, if it is not possible to tell whether one dispersion is better than another, how can it be decided which is the best method to use? Being able to assess the degree of dispersion is also important for comparisons with mechanical testing results, to see if the dispersion affects the properties. Two methods of assessing dispersion were used, one was a greyscale analysis and the other used a quadrat method.

6.2 Dispersion Methods

Before nanotubes were added to the epoxy and thermoplastic matrix for mechanical property testing it was important to carry out dispersion tests to determine the method to be used for attaining the best dispersion of the nanotubes in the resin, and a means of characterising this dispersion.

Dispersion was initially attempted with a mechanical stirrer and then a centrifugal mixer, but both of these were found to be unsuccessful as large agglomerates remained in the resin. A 40 W probe tipped sonicator from IKA Labortechnik, Germany was then used and this appeared to be more successful. An ultrasonic bath, Grant MXB series, was used for the following tests as this was more practical for the laboratories and it is believed that the effect of a bath sonicator and a horn sonicator are similar, although the bath requires longer times for sonication [84].
Four different types of multiwalled nanotubes were used for sonication testing to see if any dispersed more readily than the others. The four types were as follows:

1. Nanocyl non-functionalised
2. Nanocyl -COOH functionalised
3. Aligned (grown vertically on a surface to give alignment and then cut from the surface for use), see Figure 6.1.
4. Thomas Swan non-functionalised

Types 1 and 2 were obtained from Nanocyl S.A., Belgium, type 3 was supplied by Ian Kinloch from Cambridge University, and type 4 was obtained from Thomas Swan & Co Ltd., County Durham.

Figure 6.1: Scanning electron microscope image of aligned nanotubes [85].

### 6.2.1 Dispersion of Nanotubes in Resin

A sample of resin containing each of the types of nanotubes was made using 8.4g MY0510, 7.2g PY306 and as close to 0.0647g of nanotubes as possible, meaning the samples contained 0.25 wt% nanotubes. The resins and nanotubes were put into small Pyrex beakers, and stirred briefly with a spatula before being put in the ultrasonic bath. Four samples were sonicated together so the resulting dispersions could be
directly compared. Periodically a drop of the resin was removed from each beaker using a pipette and these drops were placed on glass microscope slides to inspect the dispersion using a transmission optical microscope. A glass cover slip was placed over each drop to reduce its thickness so that light could pass through it.

The images and descriptions below are representative of the final dispersions after 43 hours of sonication. The time of 43 hours was chosen as after that time no obvious improvement in dispersion could be seen by eye.

1. **Nanocyl non-functionalised nanotubes**

After sonication the resin in the beaker still had hard masses of undispersed Nanocyl non-functionalised nanotubes in the otherwise smooth resin when stirred. The image in Figure 6.2 is of a sample of the smooth resin. Very few hard, black agglomerates can be seen in the image but the nanotubes appear to have formed loose agglomerates as there are regions where there are no nanotubes and ‘drifts’ of nanotubes in other regions. The bulk resin was very black in appearance and was fairly viscous.

![Figure 6.2: Transmission optical micrograph of 0.25 wt% Nanocyl non-functionalised nanotubes in epoxy resin.](image-url)

2. **Nanocyl -COOH functionalised nanotubes**

The resin containing Nanocyl -COOH functionalised nanotubes was very smooth and had a low viscosity. When a drop was placed on the slide for examination under the transmission optical microscope it was a very light grey, but no undispersed nanotube masses were apparent. Given that the wavelength of visible light is about 500 nm it is
likely that if the nanotubes were very well dispersed the resin would appear light grey rather than dark grey or black as the nanotubes would be too small to diffract the light, so the light grey appearance of the resin is promising. Under the microscope only a few tiny black flecks, which are small nanotube agglomerates, were visible, as shown in Figure 6.3.

Figure 6.3: Transmission optical micrograph of 0.25 wt% Nanocyl -COOH functionalised nanotubes dispersed in epoxy.

3. Aligned nanotubes

The resin containing aligned nanotubes was mainly smooth with a medium viscosity but there were some undispersed nanotube masses in evidence when it was stirred, though not as many were found as in the Nanocyl non-functionalised nanotube mix. The slide sample was very dark grey. The TOM image in Figure 6.4 shows no small nanotubes masses but many darker regions where there is a higher density of nanotubes, these are loose agglomerates.
Figure 6.4: Transmission optical micrograph of 0.25 wt% aligned nanotubes dispersed in epoxy.

4. **Thomas Swan nanotubes**

When the resin with 0.25 wt% Thomas Swan nanotubes was stirred it was smooth with no undispersed nanotube masses and was of low-medium viscosity. The resin appeared a fairly dark grey on the slide and using the microscope the agglomerates shown below in Figure 6.5 could be seen.

![Image](image.png)

Figure 6.5: Transmission optical micrograph of 0.25 wt% Thomas Swan nanotubes dispersed in epoxy.

From these results it was decided to use the Nanocyl -COOH functionalised and the Thomas Swan nanotubes in further tests as these contained no undispersed nanotube masses and were relatively easy to source.
6.2.2 Effect of a Surfactant

6.2.2.1 Introduction

Following on from the sonication tests above, further tests were carried out to investigate the effect of surfactants. The surfactants used were FC-4430 and FC-4432 from 3M [86]. The main constituents of both are about 90% Fluoroaliphatic polymeric esters and 10% Polyether polymer. Two Nanocyl functionalised samples and two Thomas Swan nanotubes samples were prepared as before. Into one of the Thomas Swan and one of the Nanocyl functionalised samples, about 0.25 wt% of surfactant was added, 0.07g. The samples without surfactant were used to ensure identical conditions for a sample with and without surfactant for comparison purposes.

6.2.2.2 Surfactant FC-4430

These four samples were sonicated for 44 hours. For the Nanocyl functionalised sample without any surfactant the resin was smooth and had a low viscosity, it was a light shade of grey on the slide and was similar to what was seen in the last section for this type of nanotube. For the sample where the surfactant FC-4430 was added the resin was almost identical to the resin without surfactant. The resin containing Thomas Swan nanotubes had some undispersed nanotube masses, the resin was of medium viscosity and was very dark grey on the slide. This resin appeared to have slightly worse dispersion than was seen in the previous Thomas Swan sample. The sample with surfactant however was almost identical except that is had slightly fewer undispersed nanotube masses.

Images of these four samples can be seen in Figure 6.6. The Nanocyl -COOH functionalised samples appear to contain smaller nanotube agglomerates than the Thomas Swan samples, but within the same type of nanotubes there is no obvious difference between samples with and without FC-4430 surfactant.
6.2.2.3 Surfactant FC-4432

The tests for surfactant FC-4430 were repeated for surfactant FC-4432. Here the sonication time was 46 hours. As expected the Nanocyl functionalised nanotubes gave a moderately good dispersion with only a few small hard agglomerates and many tiny flecks which are tiny agglomerates. The sample with surfactant FC-4432 again appeared to give no significant improvement. As seen with the two Thomas Swan nanotube samples taken before, the resin was viscous and very dark coloured, with some nanotube masses. The sample examined with the transmission optical

Figure 6.6: Transmission optical micrographs of 0.25 wt% Nanocyl functionalised and Thomas Swan nanotubes, with and without surfactant FC-4430.
microscope shows some undispersed nanotube masses. The addition of FC-4432 surfactant to the Thomas Swan nanotubes made little difference, the dispersion is similar to that of the nanotubes without surfactant. The TOM images showing this are given in Figure 6.7.

Figure 6.7: Transmission optical micrographs of 0.25 wt% Nanocyl functionalised and Thomas Swan nanotubes, with and without surfactant FC-4432.

6.2.3 Analysis of Cured Samples

Assessing the dispersion of the nanotubes before curing is important, but assessing the dispersion of the nanotubes in the final cured sample is essential, as this is the dispersion which may affect the properties of the final polymer. If the nanotubes will
not disperse in the resin they will not be dispersed in the polymer, but even if they do disperse in the resin they may not remain dispersed when it is cured.

The cured nanotube samples were examined with the transmission optical microscope (TOM). Part of each cured epoxy / nanotube sample was cut, ground and polished to give a section of the sample about 70 µm thick bonded onto a glass microscope slide with both the top and the bonded sides polished. These samples were compared with both the naked eye and the TOM. The Nanocyl -COOH functionalised and Thomas Swan nanotubes were the two which were thought to give the best dispersion in the uncured resin and so these were the two samples which have been tested.

Using the naked eye it was clear that the nanotubes agglomerate on curing in the Nanocyl -COOH functionalised sample, as can be seen in Figure 6.8. The Nanocyl functionalised sample appeared fairly black in colour until the sample was ground to 70 µm. The nanotubes agglomerated and then sank to the bottom of the sample. This happened to be the side of this samples which was ground away to give the required thickness and so almost all the nanotubes were ground away leaving almost pure epoxy, hence the orange colour with only a few black flecks in it as shown in Figure 6.8a. The Thomas Swan sample has a better dispersion and so the samples appear as a more uniform grey, see Figure 6.8b.

![Image a) Nanocyl -COOH functionalised nanotubes](image1)
![Image b) Thomas Swan nanotubes](image2)

Figure 6.8: Transmission optical micrographs of the polished nanotube and epoxy samples showing where all the Nanocyl -COOH functionalised nanotubes agglomerated at the bottom of the sample and have been ground away, and the better dispersion of the Thomas Swan nanotubes.
The Nanocyl functionalised nanotubes were discounted at this point as their dispersion was by far the worst in the cured samples.

The cured samples with surfactants were also tested in this way but there was no noticeable improvement in the dispersion of the nanotubes in the cured polymer with the addition of surfactant. Hence the decision was taken not to use surfactants.

6.2.4 Formulations

For all further tests on nanotubes, the nanotubes used were supplied by Thomas Swan and no surfactants were used. Further tests on sonication were carried out. These involved putting a beaker of resin containing Thomas Swan nanotubes in the ultrasonic bath and running it continuously. Every few hours a small sample was removed from the beaker and was examined using the TOM. This revealed that 120 hours sonication in the ultrasonic bath gave the best dispersion, any additional sonication did not affect the dispersion.

Some of the Thomas Swan non-functionalised nanotubes were also supplied dispersed in the thermoplastic at 1 wt% and a second set of plates were made using the nanotubes in thermoplastic. Assessing the dispersion of the nanotubes in the thermoplastic was attempted using a TEM however it was unsuccessful.

Samples of epoxy, thermoplastic and nanotubes were made to the formulations given in Table 6.1 below.
Table 6.1: The formulations of epoxy, thermoplastic and nanotubes used.

<table>
<thead>
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<th>Wt% thermoplastic</th>
<th>Wt% nanotubes</th>
<th>Sonicated into epoxy</th>
<th>Dispersed in thermoplastic</th>
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<td>0</td>
<td>-</td>
</tr>
<tr>
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<td>0.1</td>
<td>-</td>
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6.3 Greyscale Analysis

Having decided on the methods of dispersion and the type of nanotubes to be used, plates of the above formulations were made and these were tested for their mechanical and fracture properties as discussed in Chapter 7. Sections of these materials were cut and observed using microscopy to see the effect of the thermoplastic and the percentage of nanotubes used on the dispersion. Details of the greyscale analysis for assessing dispersion are given in this section.

6.3.1 Sample Preparation

Samples of the cured polymer were prepared as for transmission optical microscopy. They were polished on one side, bonded onto a glass slide and then ground to approximately 70 μm in thickness and polished, as described in section 4.4.1. These sections were then photographed with a digital camera. The images were cropped to only show the sample and imported into an image analysis program, Corel Paint Shop
Pro, which gave a greyscale histogram of the picture. The histogram gave the number of pixels which had each shade of grey. The data from this greyscale histogram was used to calculate the standard deviation of the data from the mean shade of grey in the image. In theory, if the sample was perfectly dispersed, it would be expected that the image would be exactly the same shade of grey all over so there should only be the one very narrow peak on the histogram and the standard deviation would be zero. The less well dispersed the nanotubes are the broader the histogram will be and the greater the standard deviation.

6.3.2 Results

A couple of examples of the images and their resulting histograms are given in Figures 6.9 and 6.10 below, the complete set of images are given in Appendix 2. For each image the spread (the range of greyscale that the histogram covers) and the standard deviation of this data are calculated.

spread : 76 (55-131)
S.D. : 8.9

Figure 6.9: The photograph and histogram for a sample of 25 wt% R1, 0.178 wt% NT with the nanotubes sonicated into the epoxy.
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Figure 6.10: The photograph and histogram for a sample of 15 wt% R1, 0.178 wt% NT with the nanotubes dispersed in the thermoplastic.

From the above it can be seen that in the first sample the nanotubes appear to be well dispersed and there is a low standard deviation of 8.9. The sample in Figure 6.10 has a much higher standard deviation and the nanotubes appear far less well dispersed. The spread of the shades of grey is also much smaller for the image of the better dispersed sample.

Tests were carried out to investigate the effect of the thickness of the section on the results. Figures 6.11 and 6.12 show a sample of a similar formulation as Figure 6.10 but at two different thicknesses, 100 μm and 150 μm respectively. Here it can be seen that the thickness has a great effect on the standard deviation. The thicker the sample the better dispersed the sample appears. This is because the agglomerates at different levels in the sample overlap giving the appearance that the sample is evenly black. Therefore it is important for the section thickness to be the same if the results of several samples are to be compared.
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Figure 6.11: The photograph and histogram for a sample of 0 wt% R1, 0.336 wt% NT, with the nanotubes sonicated into the epoxy, ground to 100μm thick.

spread: 163 (12-175)  
S.D.: 29.7

Figure 6.12: The photograph and histogram for a sample of 0 wt% R1, 0.336 wt% NT, with the nanotubes sonicated into the epoxy, ground to 150μm thick.

spread: 111 (4-115)  
S.D.: 20.5

Table 6.2 gives the standard deviations and the spread of the greyscale histogram values for all the tested samples at 70 μm thick.
Table 6.2: Results for the greyscale analysis of the samples ranked in order of standard deviation.

<table>
<thead>
<tr>
<th>Greyscale rank (based on S.D.)</th>
<th>Wt% R1</th>
<th>Wt% NT</th>
<th>Method of dispersion</th>
<th>Standard deviation</th>
<th>Data spread</th>
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<td>0.1</td>
<td>R1</td>
<td>43.4</td>
<td>165</td>
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</table>

These results show a couple of trends, firstly the higher the thermoplastic content, the better the dispersion. Secondly, the samples with the nanotubes sonicated into the epoxy generally give lower standard deviations than the equivalent samples with the nanotubes dispersed in the R1. There is no obvious link between the percentage of nanotubes used and the resulting dispersion.

### 6.4 Quadrat analysis

The greyscale analysis only gives a measure of dispersion on a macroscale. It is possible that on a nanoscale the nanotubes are no longer in tightly knotted agglomerates, but rather just in regions where they are close together, and the greyscale analysis might not show this up. For this reason transmission electron microscopy (TEM) images were taken to investigate the dispersion on a nanoscale.
6.4.1 Method

It was decided to take a series of images of an area at a high magnification (80000 times) so that the nanotubes would be easily seen. However the loose agglomerates of nanotubes can be anything up to about 100 μm across. To achieve a representative sample covering a reasonably sized area, a collage was formed, such as the example in Figure 6.13. Typically a collage is made up of about 30 TEM images each with an image size of approximately 1.7 μm by 1.3 μm.

A quadrat method was employed to assess the degree of dispersion. The collage was divided up into a grid of small squares, approximately 70 nm by 70 nm, and the number of nanotubes within each of these squares was counted. Since the sections used for the TEM images were approximately 70 nm thick, some of the nanotubes were seen as small round circles if they were lying perpendicular to the cutting plane. However if they were lying parallel to the plane they are seen as long thin snake-like objects, see Figure 6.14. The nanotubes perpendicular to the plane would only be seen in one square while the nanotubes parallel to the plane would be seen in several squares. To account for this, each nanotube is only counted once, a nominal centre for each nanotube was found and the nanotube was only recorded as being in the square in which this centre lay.
Figure 6.14: TEM image of a sample of 15 wt% R1 with 0.178 wt% nanotubes dispersed in the thermoplastic, showing nanotubes parallel to the cutting plane which appear in more than one quadrat during analysis, and nanotubes perpendicular to the plane which appear as circles.

Also note that although the nanotubes were dispersed in the thermoplastic, they do not remain in the thermoplastic after it has been mixed with the epoxy and cured.

The data recording the number of nanotubes per square (or quadrat) was entered into a spreadsheet and from this the mean number of nanotubes per cell was calculated ($\bar{x}$). For each quadrat the variance of the number of nanotubes in that quadrat from $\bar{x}$ was calculated using Equation 6.1, and the mean of these variances was finally calculated.

$$\text{Variance} = (\text{Value in required cell} - \bar{x})^2$$  \hspace{1cm} \text{Equation 6.1}

To get an idea about the size of any agglomerates, the number of nanotubes in neighbouring cells were added together to create a new set of data. Initially 2 cells were added together, then 3, then 4 and so on up to 12 cells. The mean of the variances were calculated for each new set of data. The cells were added together in the $x$ direction and in the $y$ direction separately. This is demonstrated in Figure 6.15.
### Chapter 6: Nanotube Dispersion

**Figure 6.15: Spreadsheet showing how the means of the variances are calculated for the data from a 6 x 6 grid of quadrats, adding the cells together horizontally.**

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<th></th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
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<td>39</td>
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<td>=D3+E3+F3</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>=A4+B4+C4</td>
<td>=D4+E4+F4</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>41</td>
<td>=A5+B5+C5</td>
<td>=D5+E5+F5</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>42</td>
<td>=A6+B6+C6</td>
<td>=D6+E6+F6</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>43</td>
<td>=A7+B7+C7</td>
<td>=D7+E7+F7</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>44</td>
<td>mean</td>
<td>=average(A38:B43)</td>
<td>0.583</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>45</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>46</td>
<td>Variances</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>47</td>
<td>=(A38-C44)^2</td>
<td>=(B38-C44)^2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>48</td>
<td>=(A39-C44)^2</td>
<td>=(B39-C44)^2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>49</td>
<td>=(A40-C44)^2</td>
<td>=(B40-C44)^2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>=(A41-C44)^2</td>
<td>=(B41-C44)^2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>51</td>
<td>=(A42-C44)^2</td>
<td>=(B42-C44)^2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>52</td>
<td>=(A43-C44)^2</td>
<td>=(B43-C44)^2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>53</td>
<td>mean of variances</td>
<td>=average(A47:B52)</td>
<td>0.743</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Chapter 6: Nanotube Dispersion

Assuming perfect dispersion, it would be expected that the mean of the variances would be the same as the mean [87]. Hence if the mean variance is divided by the mean number of nanotubes per cell, this value (the mean deviation) would be expected to be unity. The mean deviation was calculated for each cell size and is plotted against cell size (one cell on its own, two cells added together etc). The closer to one that the mean deviation is the better the dispersion. The presence of any peaks in the trace this indicates the size of any agglomerates. Figure 6.16 shows an example of this data, where the mean deviation is plotted against cell size. The complete set of graphs are given in Appendix 3. The cells were combined in the x direction and the y direction separately so that if the nanotubes agglomerated to form long, thin agglomerates, the extent of these agglomerates would be seen in either the x or the y direction, whereas if only one direction had been used the agglomerate may only be accounted for through its narrow dimension, reducing its apparent size.

![Graph showing mean deviation vs cell size](image)

Figure 6.16: Example graph for quadrat results, data for a sample containing 25 wt% R1, 0.1 wt% nanotubes with the nanotubes dispersed in the thermoplastic.

The error bars are calculated using Equation 6.2 [87].

\[
\text{Error} = \frac{2 \times s^4}{n} \quad \text{Equation 6.2}
\]
Chapter 6: Nanotube Dispersion

Where $S^2$ is the mean deviation
and $n$ is the number of quadrats used.

The example in Figure 6.16 shows that the nanotubes were fairly well dispersed as the mean deviation is fairly close to 1 and is relatively independent of cell size. There might be some agglomeration around the cell size of 7 or 8 cells joined together, which in this case is about 0.6 $\mu$m, as indicated by the peaks.

### 6.4.2 Results

The complete set of graphs for mean deviation versus cell size are given in Appendix 3, and the results are summarised below in Table 6.3

### Table 6.3: Results for the quadrat analysis of the samples ranked in order of the mean deviation range.

<table>
<thead>
<tr>
<th>Quadrat rank (based on mean deviation range)</th>
<th>Wt% R1</th>
<th>Wt% NT</th>
<th>Method of dispersion</th>
<th>Mean Deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Minimum value</td>
</tr>
<tr>
<td>1</td>
<td>15</td>
<td>0.1</td>
<td>R1</td>
<td>1.0</td>
</tr>
<tr>
<td>2</td>
<td>25</td>
<td>0.178</td>
<td>Epoxy</td>
<td>1.4</td>
</tr>
<tr>
<td>3</td>
<td>25</td>
<td>0.336</td>
<td>R1</td>
<td>1.2</td>
</tr>
<tr>
<td>4</td>
<td>0</td>
<td>0.178</td>
<td>Epoxy</td>
<td>1.2</td>
</tr>
<tr>
<td>4</td>
<td>25</td>
<td>0.1</td>
<td>R1</td>
<td>1.2</td>
</tr>
<tr>
<td>6</td>
<td>25</td>
<td>0.178</td>
<td>R1</td>
<td>1.2</td>
</tr>
<tr>
<td>7</td>
<td>15</td>
<td>0.336</td>
<td>Epoxy</td>
<td>1.2</td>
</tr>
<tr>
<td>8</td>
<td>15</td>
<td>0.1</td>
<td>Epoxy</td>
<td>1.1</td>
</tr>
<tr>
<td>9</td>
<td>15</td>
<td>0.178</td>
<td>Epoxy</td>
<td>2.2</td>
</tr>
<tr>
<td>10</td>
<td>15</td>
<td>0.178</td>
<td>R1</td>
<td>1.7</td>
</tr>
</tbody>
</table>

From Table 6.3 it can be seen that in general the higher the percentage of thermoplastic the better the dispersion, and that the percentage of nanotubes has no clear effect on the dispersion.
6.4.3 Comparison of Greyscale and Quadrat Results

The quadrat ranking was then compared to the ranking from the grey scale analysis, to see if they provided similar results, Table 6.4 below shows the comparison.

The two methods rank the tested samples in an almost identical manner, with two exceptions. Firstly there is a slight variation in rank order when the values are close. Secondly, and more significantly, the grey scale analysis puts the sample containing 15 wt% R1 and 0.1 wt% nanotubes with the nanotubes sonicated into the thermoplastic in the last position, with the worst dispersion, while the quadrat analysis puts this sample in the first position with the best dispersion. This difference is thought to be the result of the different length scales that the tests work at. The greyscale analysis works at a macroscale (greater than 10 μm) and so all agglomerates will be seen, while the quadrat analysis works on a nanoscale (less than 10 μm). In general the quadrat analysis can still identify the degree of agglomeration. However in this case the agglomeration is sufficiently severe, with such large gaps between agglomerates, that the section tested for the quadrat analysis was a region without any agglomerates. This proposition is supported by the small number of nanotubes seen in the sample compared to the other samples with 0.1 wt% nanotubes. The 15 wt% R1, 0.1 wt% nanotube sample with the nanotubes dispersed in the thermoplastic contained an average of 0.0018 nanotubes per cell, while for the other samples with 0.1 wt% nanotubes, an average of 0.0102 and 0.0124 nanotubes per cell were seen. Hence only about 20% of the expected number of nanotubes were observed in this sample, indicating a poor dispersion and an incorrect quadrat ranking.

For all future tables this sample is removed from the quadrat ranking, and a corrected ranking is shown. The greyscale and quadrat rankings are compared in Table 6.4.
Table 6.4: Comparison of the rankings from greyscale analysis and corrected quadrat analysis.

<table>
<thead>
<tr>
<th>Rank</th>
<th>Values</th>
<th>Method of dispersion</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Corrected quadrat analysis</td>
<td>Greyscale standard deviation</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>8.9</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>16.3</td>
</tr>
<tr>
<td>3</td>
<td>3=</td>
<td>17.7</td>
</tr>
<tr>
<td>4</td>
<td>3=</td>
<td>20.1</td>
</tr>
<tr>
<td>5</td>
<td>6</td>
<td>20.7</td>
</tr>
<tr>
<td>6</td>
<td>5</td>
<td>23.8</td>
</tr>
<tr>
<td>7</td>
<td>7</td>
<td>27.2</td>
</tr>
<tr>
<td>8</td>
<td>8</td>
<td>29.4</td>
</tr>
<tr>
<td>9</td>
<td>9</td>
<td>41.9</td>
</tr>
<tr>
<td>10</td>
<td>N/R</td>
<td>43.4</td>
</tr>
</tbody>
</table>

*N/R: This is the result which comes from the tested area not being sufficiently large and so is not representative.

These results show that the greyscale analysis and the quadrat method are both good methods for assessing dispersion, although it is important with the quadrat analysis to ensure that the sampled area is sufficiently large, it may be best to use both methods to ensure that both the nano and the macroscales are covered.

The results show that the addition of thermoplastic reduces agglomeration, 25 wt% thermoplastic being more effective than 15 wt%. The amount of nanotubes added has no significant effect on the dispersion within the quantities tested. Whether the nanotubes are dispersed in thermoplastic or sonicated into the epoxy has a marginal effect. This can be seen in Table 6.5, by comparing samples where the only difference is the method of dispersion.
### Table 6.5: Comparison of dispersion of samples with the nanotubes dispersed in the epoxy and the thermoplastic.

<table>
<thead>
<tr>
<th>Wt% R1</th>
<th>Wt% NT</th>
<th>Method of dispersion</th>
<th>Greyscale rank</th>
<th>Corrected quadrat rank</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>0.178</td>
<td>Epoxy</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>25</td>
<td>0.178</td>
<td>R1</td>
<td>6</td>
<td>5</td>
</tr>
<tr>
<td>15</td>
<td>0.178</td>
<td>Epoxy</td>
<td>8</td>
<td>8</td>
</tr>
<tr>
<td>15</td>
<td>0.178</td>
<td>R1</td>
<td>9</td>
<td>9</td>
</tr>
<tr>
<td>15</td>
<td>0.1</td>
<td>Epoxy</td>
<td>7</td>
<td>7</td>
</tr>
<tr>
<td>15</td>
<td>0.1</td>
<td>R1</td>
<td>10</td>
<td>N/R</td>
</tr>
</tbody>
</table>

N/R: Not Representative

As can be seen for all three examples in Table 6.5 where the same formulation was used but the method of dispersing the nanotubes was different, the samples where the nanotubes were dispersed in the epoxy gave a better dispersion, but in some cases this is only a marginal difference.

Comparing the rankings for the samples where the difference is the percentage of nanotubes, such as with 25 wt% R1 with the nanotubes dispersed in the thermoplastic, the highest percentage of nanotubes was the best dispersed, then the lowest percentage and the middle percentage had the worst dispersion. Hence there is no obvious trend in the dispersion with the percentage of nanotubes.

### 6.5 Hot Stage Investigations

Considering samples where the nanotubes were sonicated into the epoxy, the nanotubes were sonicated for the same length of time for each sample, in the same ultrasonic bath, using the same quantity of epoxy, so there is no reason that the nanotube dispersion should vary from sample to sample. The epoxy nanotube mix was then removed from the ultrasonic bath and the thermoplastic and curing agent were added as required before curing. However the dispersion of the nanotubes changes somewhere between removing the epoxy and nanotube mix from the ultrasonic bath, and the final cured polymer. Having found that the amount of thermoplastic affects the
dispersion of the nanotubes in the final polymer, some tests were carried out with a hot stage so that the material could be observed during curing. The hot stage is shown below in Figure 6.17. This fits onto the optical microscope, and a drop of liquid can be placed in the hot stage and it is then programmed via a computer to run a cure cycle. While this cycle is taking place the material can be observed through the microscope.

Figure 6.17: Photograph showing the hot stage fitted to the microscope.

The cure cycle used was to heat the resin up to 90 °C at 10 °C/minute. It was then held at 90 °C for 30 minutes to simulate the degassing stage of the process of preparing samples, then finally the temperature was ramped at 1 °C/min to 180 °C. Several formulations were put through hot stage cure cycles, these include samples with 0.1 wt% nanotubes and 0, 15 and 25 wt% R1 with the nanotubes dispersed into the epoxy, and samples with the nanotubes dispersed in the thermoplastic.

A selection of the images taken during the cure cycles of each of the samples are given below. During the cure cycle the nanotubes move and it appears that the higher the percentage of thermoplastic the less movement is seen. Further, the higher the percentage of thermoplastic the higher the temperature at which the nanotubes start moving. It was also noted that as the percentage of thermoplastic increases the
viscosity of the resin also increases significantly. See Figure 6.18 below for the hot stage images of a sample of 0 wt% R1 and 0.1 wt% NT.

Figure 6.18: The hot stage images for samples with 0.1 wt% NT and 0 wt% R1, the nanotubes were sonicated into the epoxy. The images were taken at 22 °C, 50 °C, 90 °C and 180 °C. The arrows point to the nanotubes.

The first three images of Figure 6.18 were taken during the rapid ramp in temperature up to 90 °C. As the resin is heated up to 90 °C there is significant movement of the nanotubes showing that the nanotubes were mobile even at room temperature. By the time the resin reaches 90 °C the nanotubes have agglomerated to the maximum extent that they are going to and there is no further agglomeration seen during the dwell at 90 °C and the subsequent slow ramp to 180 °C. This can be seen since the third and fourth images are almost identical. It is thought that the ability of the nanotubes to move and agglomerate is related to the viscosity of the resin. When there is no thermoplastic in the resin, the resin has a relatively low viscosity.
The images taken with 15 wt% R1 can be seen below in Figure 6.19.

![Images of hot stage](image)

Figure 6.19: The hot stage images for samples with 0.1 wt% NT and 15 wt% R1, the nanotubes were sonicated into the epoxy. The images were taken at 30 °C, 90 °C, 90 °C + 30 mins, 140 °C and 180 °C.

The arrows point to large nanotube agglomerates which remain after the sonication.

The images above, in Figure 6.19, show that with 15 wt% R1 added there is very little agglomeration at low temperatures, some agglomeration can be seen at 90 °C but there is far more significant agglomeration between 90 °C and 140 °C. By the time 140 °C is reached however all the agglomeration that is going to occur has happened and the images at 140 and 180 °C are almost identical. The agglomeration seen does not seem as severe as it does with no thermoplastic so it is possible that this halting in agglomeration is not due to the nanotubes being fully agglomerated but rather that the
resin has reached its gel point and the nanotubes can no longer move. It is thought that the gel point is around 140 °C.

The processes of sonication and mixing in the thermoplastic and curing agent can trap air in the mixture, which is why there is a degassing phase in the process of manufacturing the plates. At 25 wt% R1 the mix is so viscous that air is trapped even in the small sample that is used for hot stage tests. The air bubbles can be seen in the images in Figure 6.20. As the resin is heated up the viscosity drops and as a result the air bubbles become fewer in number.

![Figure 6.20](image)

Figure 6.20: The hot stage images for samples with 0.1 wt% NT and 15 wt% R1, the nanotubes were sonicated into the epoxy. The images were taken at 90 °C, 90 °C + 30 mins, 140 °C and 180 °C. The arrows point to air bubbles.

As seen in Figure 6.20, the addition of 25 wt% R1 to the material has not only trapped air in the sample but it has also significantly decreased the degree of agglomeration. There is no obvious agglomeration even at 180 °C.

The images taken are in black and white rather than colour due to a different camera being employed for microscopy work. The microscope and hot stage themselves were unchanged.
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The images in Figure 6.21 show the agglomeration of nanotubes for a sample with identical composition to the sample given in Figure 6.19, with the difference that nanotubes are dispersed in the thermoplastic initially for this sample rather than being sonicated into the epoxy. As can be seen for the sample where the nanotubes were dispersed in the thermoplastic, the dispersion at 90 °C looks inferior to that where the nanotubes were sonicated into the epoxy. The majority of the agglomeration happens during the 30 minutes in which the resin is held at 90 °C, unlike the previous sample where agglomeration was found between 90 and 140 °C. Once again there is no obvious movement of nanotubes between 140 °C and 180 °C. The final dispersion of these two samples seems comparable.

Figure 6.21: The hot stage images for samples with 0.1 wt% NT and 15 wt% R1, the nanotubes were dispersed in the thermoplastic. The images were taken at 90 °C, 90 °C + 30 mins, 140 °C and 180 °C.
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Figure 6.22 shows the images from the sample with 0.1 wt% nanotubes and 25 wt% R1 with the nanotubes dispersed in the thermoplastic for a direct comparison with Figure 6.20. The sample given in Figure 6.22 shows that again the increase in the thermoplastic content to 25 wt% reduces the agglomeration. However the sample does show some degree of agglomeration between 140 and 180 °C in this instance which casts some doubt on the resin reaching its gel point at 140 °C. The result does confirm that the addition of thermoplastic decreases the degree of agglomeration seen and that the difference between the samples with the nanotubes sonicated into the epoxy and those where the nanotubes are dispersed in the thermoplastic are slight.

Figure 6.22: The hot stage images for samples with 0.1 wt% NT and 25 wt% R1, the nanotubes were dispersed in the thermoplastic. The images were taken at 90 °C, 90 °C + 30 mins, 140 °C and 180 °C. Red arrows point to air bubbles, white arrows point to nanotube agglomerates.
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6.6 Conclusions

Dispersion is one of main problems faced when working with carbon nanotubes. The results detailed above show that a good dispersion of nanotubes in epoxy can be achieved using an ultrasonic bath for around 120 hours. The addition of surfactants does not improve this dispersion significantly, nor does the use of functionalised nanotubes. The nanotubes found to give the best dispersion were those manufactured by Thomas Swan.

Having chosen a method for dispersion, assessing the dispersion was the next issue. Two methods were tried. One used images of 70 μm thick sections of the cured polymer to find the standard deviation of the shades of grey seen in the sample. The second method used a collage of TEM images and a quadrat method to find the deviation of the number of nanotubes per quadrat from the expected number. Both of these methods provided a ranking of the samples, and with only one notable exception these two rankings were almost identical. The exception was a sample which contained large agglomerates but due to the size and choice of area investigated, the quadrat method failed to indicate this. This exception shows the importance of using a sufficiently large, representative area for these methods of analysis. Using the two methods together will give a good measure of dispersion.

From analysing the dispersion it was found that whether the nanotubes were sonicated into the epoxy or dispersed in the thermoplastic made only a small difference, and that the percentage of nanotubes used had no effect, on dispersion. However, the amount of thermoplastic added significantly altered the dispersion. The higher the percentage of thermoplastic the better the final dispersion.

Investigations were carried out with a hot stage on an optical microscope so that the resin could be observed as it ran through a cure cycle. It was found that the nanotubes agglomerate during the cure cycle. The higher the percentage of thermoplastic the lesser the degree to which the nanotubes agglomerate and the higher the temperature needs to be before the nanotubes begin agglomerating. It is thought that this is due to the increase in viscosity of the resin with adding thermoplastic. The higher the viscosity the harder it is for the nanotubes to move through the resin, so the slower they move and the higher the temperature needs to be before the viscosity drops to a level at which the nanotubes can move. Once the resin reaches the gel point the
nanotubes can no longer move and the dispersion as it stands then is 'frozen'. The nanotubes in the resin with higher percentages of thermoplastic begin moving later, and move more slowly, so it is to be expected that the final dispersion is better.
Chapter 7 Nanomodified Epoxy and Epoxy / Thermoplastic Blends

7.1 Introduction

The addition of nanomodifiers to epoxy polymers and epoxy blends has been found to improve various properties of these materials including the fracture toughness and fracture energy, and to increase Young’s modulus [8]. This chapter covers the effect on the mechanical properties of the addition of two different nanomodifiers, nanosilica particles and multiwalled carbon nanotubes, to the epoxy / thermoplastic blend discussed in Chapter 5.

7.2 Nanosilica Modification

The PY306 / MY0510 epoxy blend, with 0, 15 and 25 wt% thermoplastic, was modified by the addition of nanosilica at various percentages, see Table 7.1 for the formulations used. The thermoplastic was only added up to 25 wt% as the nanosilica increases the viscosity to such an extent that it is too difficult to form useable plates at higher thermoplastic percentages. The addition of nanosilica has been found in previous research [88] to increase the fracture properties. However this is not true for all percentages of nanosilica in all cases [89]. One suggestion is that a good dispersion of the nanosilica is required to achieve toughening [30].
Table 7.1: The formulations of thermoplastic and nanosilica used.

<table>
<thead>
<tr>
<th>Wt% thermoplastic</th>
<th>Wt% nanosilica</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>0</td>
<td>2</td>
</tr>
<tr>
<td>0</td>
<td>5</td>
</tr>
<tr>
<td>0</td>
<td>10</td>
</tr>
<tr>
<td>0</td>
<td>15</td>
</tr>
<tr>
<td>0</td>
<td>20</td>
</tr>
<tr>
<td>15</td>
<td>0</td>
</tr>
<tr>
<td>15</td>
<td>5.8</td>
</tr>
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<td>15</td>
<td>10</td>
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<tr>
<td>15</td>
<td>11.6</td>
</tr>
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<td>15</td>
<td>14.9</td>
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<td>15</td>
<td>20</td>
</tr>
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<td>20</td>
<td>0</td>
</tr>
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<td>25</td>
<td>0</td>
</tr>
<tr>
<td>25.5</td>
<td>2.7</td>
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<tr>
<td>26.3</td>
<td>6.7</td>
</tr>
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<td>25</td>
<td>10</td>
</tr>
<tr>
<td>27.8</td>
<td>13.3</td>
</tr>
<tr>
<td>35</td>
<td>0</td>
</tr>
</tbody>
</table>

To investigate the effects of adding nanosilica to the epoxy / thermoplastic blends, the morphologies were examined using an atomic force microscope (AFM). Single edge notched bend and tensile tests were carried out on samples cut from plates of the materials.

7.2.1 Morphologies

The nanosilica (NS) was supplied well dispersed in the PY306. An AFM image of the nanosilica in PY306 which has been cured with MCDEA, but without any MY0510 or thermoplastic, is given in Figure 7.1. This shows the good dispersion of particles.
Figure 7.1: AFM image of the PY306 with 40 wt% nanosilica after curing with MCDEA.

The nanosilica was supplied dispersed only in the PY306 as the nanosilica will not form a stable suspension in MY0510 [69]. Although the manufacturers thought that the MY0510 was not able to support a dispersion of nanosilica even at the ratio of PY306 to MY0510 used in this project [69], the addition of the MY0510 does not appear to lead to agglomeration. The AFM image of the PY306 / MY0510 epoxy, with 15 wt% NS shows that the nanosilica remains well dispersed even at these percentages, see Figure 7.2.

Figure 7.2: AFM image of 15 wt% nanosilica in PY306 / MY0510 showing that the nanosilica particles are well dispersed.
The addition of the thermoplastic, however, stops the nanosilica from remaining dispersed. The addition of 15 wt% R1 to the epoxy leads to the agglomeration of the nanosilica, see Figure 7.3. The nanosilica appears to form small agglomerates, approximately 0.7 μm across. Many of these agglomerates touch the thermoplastic spheres. No nanosilica can be seen in the thermoplastic phase: it all remains in the epoxy phase.

![AFM image of a 15 wt% R1, 14.9 wt% NS in PY306 / MY0510 sample showing the thermoplastic spheres and the nanosilica agglomerates.](image)

**Figure 7.3**: AFM image of a 15 wt% R1, 14.9 wt% NS in PY306 / MY0510 sample showing the thermoplastic spheres and the nanosilica agglomerates.

The spheres of thermoplastic appear to stay the same size when nanosilica is added. The average size of the spheres (blobs) on 20 μm micrographs were measured for specimens with 15 wt% R1 and 0, 5.8 or 14.9 wt% nanosilica using the 'blob analysis' software. For 0 wt% R1 the mean blob diameter was 0.83 μm, while for 5.8 wt% and 14.9 wt% nanosilica it was 0.85 μm. Three images were used for the sample with 14.9 wt% nanosilica and the standard deviation of the blob diameters was 0.02 μm, so within this deviation the blobs are the same size for all three formulations. Although these blob diameters are not the true mean diameters of the thermoplastic spheres, as the sections seen as blobs will not all be from the centre of the spheres, the lack of change in the measured blob diameters indicates that the true sphere diameters are not changing either. However, the volume fraction of the thermoplastic spheres does seem to reduce more than would be expected given the change in nanosilica content, even when considering the statistical error margins as listed in Table 7.2. This decrease could be the result of the increased difficulty in identifying the thermoplastic
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spheres from the AFM images when the nanosilica is present. It is possible that a few spheres were missed which would result in the volume percentages appearing smaller than expected.

Table 7.2: Blob analysis results for volume percentage of thermoplastic which phase separates out into spheres.

<table>
<thead>
<tr>
<th>wt% R1</th>
<th>wt% nanosilica</th>
<th>vol% R1 calculated from wt%</th>
<th>vol% R1 from blob analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mean</td>
<td>Standard</td>
<td></td>
<td></td>
</tr>
<tr>
<td>deviation</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>0</td>
<td>13.5</td>
<td>14.5</td>
</tr>
<tr>
<td>15</td>
<td>5.8</td>
<td>13.1</td>
<td>11.0</td>
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<tr>
<td>15</td>
<td>14.9</td>
<td>12.6</td>
<td>10.2</td>
</tr>
</tbody>
</table>

It has been considered that the nanosilica may affect the thermoplastic spheres. The silane treatment on the nanosilica has epoxy endgroups so that when it is attached to the nanosilica it can make the nanosilica look as though it is coated in epoxy by 'hiding' the OH groups on the nanosilica. This acts to keep the nanosilica spheres dispersed in the epoxy rather than having them agglomerate, as it is the OH groups which cause the nanosilica to agglomerate [69]. If the silane treatment became detached from the nanosilica particles and was attracted to the thermoplastic, it could bond to the thermoplastic so the thermoplastic had epoxy endgroups. This could then affect the size of the thermoplastic spheres while at the same time, the removal of the silane from the nanosilica particles would leave the nanosilica prone to agglomerating. The agglomeration of nanosilica is seen but there is no evidence that the size of the thermoplastic sphere is affected.

When 25 wt% thermoplastic is added, the thermoplastic morphology becomes complex co-continuous as described in Chapter 5. The nanosilica still agglomerates in the epoxy phase. The agglomerates are 0.7 µm in diameter on average, and the size of the agglomerates does not seem to depend on the percentage of nanosilica or thermoplastic. The samples at approximately 25 wt% R1 do not all contain exactly 25 wt% R1. The two samples which do, contain 0 and 10 wt% nanosilica. A comparison of the morphologies of these two samples shows that the thermoplastic structure is not changed significantly by the addition of nanosilica, as shown in Figures 7.4 and 7.5.
Figure 7.4: AFM image of 25 wt% R1, 0 wt% nanosilica sample showing enlarged and elongated thermoplastic regions with localised phase inversion, but not a fully co-continuous morphology.

Figure 7.5: AFM image of 25 wt% R1, 10 wt% nanosilica sample showing enlarged and elongated thermoplastic regions with localised phase inversion, but not a fully co-continuous morphology. The nanosilica is agglomerated.

The morphology of the thermoplastic, however, does change as the percentage of thermoplastic is increased, even by a small amount. The structure becomes increasingly co-continuous, changing from elongated and enlarged regions of thermoplastic to a properly co-continuous structure. Compare the sample with 25 wt% R1 with 10 wt% NS in Figure 7.5 to a fully co-continuous morphology at 27.8 wt% R1,
13.3 wt% NS in Figure 7.6. The exact percentage of thermoplastic is clearly critical at around these percentages and a small change can significantly affect the morphology.

Figure 7.6: AFM image of 27.8 wt% R1 and 13.3% nanosilica in PY306 / MY0510 showing the co-continuous morphology of the thermoplastic and the nanosilica agglomerates in the epoxy.

One sample of 35 wt% R1 and 5 wt% nanosilica was made to test the morphology only. No mechanical or fracture testing was carried out using this formulation as the plates contained too much trapped air. The 35 wt% R1 sample gives a phase inverted structure, as discussed in Chapter 5. When the 35 wt% R1, 5 wt% NS specimen was analysed the thermoplastic structure was not changed. The nanosilica forms small agglomerates in the epoxy again. These agglomerates are still approximately 0.7 \( \mu m \) in diameter, see Figure 7.7.
Figure 7.7: AFM image of 35 wt% R1 and 5 wt% NS in PY306 / MY0510 showing the nanosilica agglomerates in the epoxy phase with phase inversion, the thermoplastic forms the matrix.

This agglomeration of the nanosilica was thought to be related to the mechanism by which the thermoplastic comes out of solution during curing to form a second phase. To test this theory a sample of epoxy with 25 wt% R1 and 5 wt% NS was prepared but not cured. The sample was microtomed at -60 °C and put straight in the AFM. Figure 7.8 shows a resulting image and it can be clearly seen that the thermoplastic is still in solution as there is no sign of phase-separation. However the nanosilica has already agglomerated. This indicates that the change from the thermoplastic being in solution to forming a second phase is not responsible for the agglomeration. Hence it is the presence of the thermoplastic which causes the agglomeration of the nanosilica.
7.2.2 Tensile Tests

Tensile tests have been carried out on samples of PY306 / MY0510, with 0, 15 and 25 wt% R1 and various percentages of nanosilica. The Young's modulus was measured and the results are shown in Figure 7.9. The addition of thermoplastic to the epoxy was discussed in Chapter 5, and it was found that the addition of the thermoplastic did not significantly increase the Young's modulus of the epoxy. From this graph it is clear that increasing the amount of nanosilica increases the Young's modulus, for any percentage of thermoplastic. The trend lines show even more clearly than was indicated in Chapter 5 that adding thermoplastic does not lead to a significant increase in the modulus. The slope of the trend lines show that the rate of increase in Young's modulus with nanosilica content is approximately constant and is not dependent of the percentage of thermoplastic.
This increase in Young’s modulus with the percentage of nanosilica is to be expected as the modulus of the nanosilica (70 GPa) is significantly higher than that of the epoxy (2.5 GPa). Various theoretical models have been created by previous workers to describe the change in Young’s modulus for a composite with two components. Two of these are the Halpin-Tsai and van Es models [90]. These models can be used to predict the modulus of a composite, \( E_c \), for a matrix and filler of known modulus, \( E_m \) and \( E_f \), with a known particle shape and volume fraction, \( V_f \). The matrix moduli are taken from the experimental values of Young’s modulus for the epoxy and for the epoxy with thermoplastic samples, the modulus of the nanosilica is taken as 70 GPa [91] which is the modulus of amorphous silica.

The Halpin-Tsai equation is given below.

\[
\frac{E_c}{E_m} = \frac{1 + \zeta \eta V_f}{1 - \eta V_f} \tag{7.1}
\]

Where \( \zeta \) is the shape factor, \( \frac{2w}{t} \),

\( w/t \) is the aspect ratio of the particles

and \( \eta \) is given by...
\[ \eta = \left( \frac{E_f}{E_m} - 1 \right) \left/ \left( \frac{E_f}{E_m} + \zeta \right) \right. \] 

Equation 7.2

While the Halpin-Tsai model takes the shape factor to be \( \frac{2w}{t} \) and therefore \( \zeta = 2 \) for a sphere, the difference for the van Es model is that here \( \zeta = \frac{2w}{3t} \), which gives a value of \( \frac{2}{3} \) for a sphere.

The density of epoxy was calculated from the mass and volume of a sample as 1.204 g/cm\(^3\). Similarly the density of epoxy with 15 wt% R1 was calculated as 1.225 g/cm\(^3\). The density of nanosilica was taken as 1.8 g/cm\(^3\) [91].

The following assumptions are made when using the Halpin-Tsai model [92].

1. the particles and the matrix are well bonded,
2. The particles and the matrix are both homogeneous,
3. Any interactions between the particles can be neglected.

The results of the models are given in Figures 7.10, 7.11 and 7.12 and show the epoxy and nanosilica, and the epoxy, thermoplastic and nanosilica composites, compared with the Halpin-Tsai and van Es models. From these it can be seen that the experimental tensile results generally fit the Halpin-Tsai model within reasonable error, whereas the van Es model gives an underestimate. The Halpin-Tsai model providing an acceptable fit to the experimental data, shows that the assumption of the modulus of nanosilica being 70 GPa is reasonable.
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4.5
0.5

• experimental, epoxy — Halpin-Tsai model

— van Es model

10
12
14
16
18
20

wt% nanosilica

Figure 7.10: Experimental and theoretical Young's modulus versus percentage nanosilica for PY306 / MY0510 epoxy with no thermoplastic showing a reasonable fit with the Halpin-Tsai model.

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Figure 7.11: Experimental and theoretical Young's modulus versus percentage nanosilica for PY306 / MY0510 epoxy with 15 wt% R1 showing a good fit with the Halpin-Tsai model.
Figure 7.12: Experimental and theoretical Young's modulus versus percentage nanosilica for PY306 / MY0510 epoxy with 25 wt% R1 showing a good fit with the Halpin-Tsai model.

The Halpin-Tsai model was originally created for macrocomposites, though it was found to give an overestimate in many cases and so the van Es model modified it to reduce the predicted values and give a better fit with experimental data. Halpin-Tsai predicts the modulus of the composites here reasonably well which indicates that the nanoscale of the nanosilica particles may have improved their ability to increase the Young's modulus. One of the assumptions made in the Halpin-Tsai model is that the particles are well dispersed and in the 15 and 25 wt% R1 samples the nanosilica clearly agglomerates. Because of this assumption it would be expected that the experimental modulus would be reduced relative to the predicted modulus, with agglomeration, and this is seen. For the well dispersed nanosilica the Halpin-Tsai model slightly under-estimates the Young's modulus, however when the thermoplastic was added the nanosilica agglomerates and the model becomes a much better estimate.

The ultimate tensile strength (UTS) of the nanosilica samples was also measured, although the UTS is known to depend on the surface finish [77, 78]. All the samples were prepared and treated the same so the results are compared here but the dependence on surface finish must be borne in mind. It was found that the UTS
increases with the percentage of thermoplastic but it does not vary with the addition of nanosilica. The results are shown in Figure 7.13, where the lines indicate the mean values of UTS for each of the percentages of thermoplastic.

Figure 7.13: Ultimate tensile strength (UTS) data from tensile tests showing no change in UTS with the addition of nanosilica.

Some previous studies have shown that the UTS is increased by the addition of small percentages of nanoparticles [93, 94]. However, from the results shown above the addition of higher percentages of nanosilica shows no improvement. Micron sized particles typically reduce the UTS because they act as flaws [95], and as the stress needed for a crack to propagate according to the Griffith criterion is related to the size of the flaws [79]. Hence it would be expected that the larger the particle the lower the stress at failure. Nanoparticles however are typically smaller than the inherent flaws found in epoxy and so will not affect the UTS as found here. The equation used for the Griffith criterion is given below.

\[ \sqrt{a_c} = \frac{\sqrt{E \times G / \pi}}{\sigma_f} \]  

Equation 7.3

Where \( a_c \) is the critical flaw size

For the unmodified epoxy \( E = 2.55 \) GPa
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\[ G = 214 \, \text{J/m}^2 \]
\[ \sigma_f = 65.2 \, \text{MPa} \text{ (taken from the UTS)} \]

This gives the critical flaw size as 40.5 \, \text{\textmu m} which is significantly larger than the size of the nanosilica particles (20 nm) and the agglomerates (0.7 \, \text{\textmu m}).

The yield stress of the samples shows no effect with either the addition of thermoplastic or nanosilica. Figure 7.14 shows the results for the yield stress, calculated using the 0.2\% proof stress.

![Graph](image)

Figure 7.14: 0.2\% proof stress results from tensile tests showing no increase in yield stress with the addition of nanosilica or thermoplastic.

### 7.2.3 Fracture Tests

The results of SENB tests on the PY306 / MY0510 blend with no thermoplastic are given below in Figures 7.15 and 7.16. These show that the addition of nanosilica does not increase the fracture toughness or fracture energy.
Figure 7.15: Fracture toughness of samples of epoxy with no thermoplastic and increasing amounts of nanosilica.

Figure 7.16: Fracture energy of samples of epoxy with no thermoplastic and increasing amounts of nanosilica.
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As shown above, if anything the addition of nanosilica may actually reduce the fracture energy slightly. However, the decrease is not significant as the error bars are sufficiently large that even the lowest value, for 20 wt% nanosilica, lies within the error of the epoxy sample with no nanosilica.

Research into nanosilica modification of epoxy resins has been carried out before using a diglycidyl ether of bisphenol A (DGEBA) with both an amine and an anhydride curing agent [88]. This work on DGEBA found an increase in fracture toughness with the addition of nanosilica in the anhydride system. The amine system was only tested with a CTBN rubber included, which caused the nanosilica to form large agglomerates, and no samples of well dispersed nanosilica in amine cured DGEBA were tested. For the agglomerated nanosilica in amine cured DGEBA no increase in toughness was seen. In the anhydride system the fracture energy increased for all percentages of nanosilica and rubber, although the nanosilica does not agglomerate except at high percentages. Whether the increase in fracture energy was related to the dispersion of the nanosilica has been discussed.

In this project the nanosilica remained well dispersed when there was no thermoplastic present. As soon as the thermoplastic is added the nanosilica agglomerates. If the increase in fracture energy was related to the nanosilica dispersion, it would be expected that there would be an increase in the fracture properties as the nanosilica content increases for the samples with no thermoplastic. As seen above this is not the case, there was no increase in fracture toughness.

Two sets of samples were made using the same DGEBA and anhydride curing agent as used by Mohammed [88] which showed that nanosilica could toughen epoxy. One set of specimens were made without any nanosilica and one with nanosilica to test if the increase in fracture toughness with the addition of nanosilica could be reproduced by the author of this thesis. The results are presented and discussed in full in Chapter 8, but they showed that when the DGEBA / anhydride system was used the nanosilica did result in an increase in toughness. The nanosilica particles for both systems are identical as they are formed by a sol-gel process before being added to the epoxy and they were supplied by the same manufacturer. It was decided that it could be a property of the epoxy which prevented toughening in the case of the PY306 / MY0510 system. To test this hypothesis plane strain compression tests on the DGEBA and the PY306 / MY0510 have been carried out, and are discussed in Chapter 8 with the fracture results from the DGEBA and DGEBA / nanosilica tests.
Given the agglomeration of the nanosilica with the addition of any thermoplastic, and the lack of toughening seen from samples of PY306 / MY0510 with no thermoplastic it was expected that the addition of nanosilica to samples with 15 and 25 wt% R1 would also result in no toughening. This was found to be the case, and the fracture toughness and fracture energy of these samples are given in Figures 7.17 and 7.18.

Figure 7.17: Fracture toughness of samples with 0, 15 and 25 wt% R1 and increasing amounts of nanosilica.
Figure 7.18: Fracture energy of samples with 0, 15 and 25 wt% R1 and increasing amounts of nanosilica.

The nanosilica appears to have no effect on the fracture properties of the PY306 / MY0510 and to help explain this, the fracture surfaces of all the samples were examined using the SEM. These images show no obvious increase in surface roughness as the percentage of nanosilica increases. Figure 7.19 shows images of the fracture surface from a sample with no thermoplastic and 5 wt% nanosilica, and Figure 7.20 shows the fracture surface of a sample with no thermoplastic and 20 wt% nanosilica. The resolution of the SEM is not good enough to see the nanosilica particles themselves but the morphology is known from the AFM images given earlier. For both fracture surfaces, other than the river lines which are commonly seen at the beginning of fracture in epoxies, there are no features visible. The fracture surfaces appear the same as the surface of the epoxy sample with no thermoplastic or nanosilica given in Chapter 5.

In all images the crack propagation direction is from left to right.
Figure 7.19: SEM images of the fracture surface of a SENB sample with no thermoplastic and 5 wt% nanosilica. Images taken at 500, 1000 and 5000 times magnification.
Figure 7.20: SEM images of the fracture surface of a SENB sample with no thermoplastic and 20 wt% nanosilica. Images taken at 250, 1000 and 5000 times magnification.

As discussed in Chapter 5, for a perfectly brittle material, the surface area of the fracture will affect the fracture energy. This is because energy is required to create new surface and the greater that surface is the greater the energy required. Here the material is not perfectly brittle but it is thought that a rougher surface, with greater surface area, is an indication of greater fracture energy.

When looking at samples containing thermoplastic, the nanosilica agglomerates can be seen in the SEM images as these are relatively large. To confirm that the features identified were nanosilica, energy dispersive X-ray (EDX) analysis was used to check the chemical composition of one agglomerate, see Figure 7.21. The samples were sputter coated in gold, so the gold peaks were expected. The epoxy is carbon based explaining that peak, as is the thermoplastic.
Figure 7.21: SEM image and corresponding EDX spectrum for a sample containing 15 wt% R1 and 20 wt% NS which is gold sputter coated, showing the agglomerate is formed of nanosilica.

The EDX results shown in Figure 7.21 demonstrate that where the agglomerate is there are significantly higher levels of silicon and oxygen, and a small decrease in the amounts of carbon and chlorine. The confirms that the agglomerate is nanosilica as the silica contains silicon and oxygen. Some carbon is present in the ‘agglomerate’ spectrum as there is epoxy in the agglomerate. The ‘not agglomerate’ spectrum includes silicon as some nanosilica particles will be present in the analysis volume. The sample is gold coated and there are equal amounts of gold seen in both spectrums.
When examining the surfaces of the nanosilica and thermoplastic fracture samples, again no increase in surface roughness can be seen with increasing the amount of nanosilica. Figures 7.22 and 7.23 show SEM images of the fracture surfaces for samples with 15 wt% R1 and 5.8 and 14.9 wt% NS. These micrographs show that the fracture surfaces appear almost identical in both samples. There is no obvious increase in surface roughness with the higher percentage of nanosilica, nor are there any other noticeable differences. As for the sample with 15 wt% R1 and no nanosilica which is discussed in Chapter 5, the fracture path goes through the thermoplastic particles and the fracture mechanisms are unchanged by the addition of the thermoplastic or the addition of the nanosilica.

Figure 7.22: SEM images of the fracture surface of a SENB sample with 15 wt% R1 and 5.8 wt% nanosilica. Images taken at 250, 1000 and 5000 times magnification.
Figure 7.23: SEM images of the fracture surface of a SENB sample with 15 wt% R1 and 14.9 wt% nanosilica. Images taken at 250, 1000, 5000 and 10000 times magnification.

The nanosilica agglomerates, into regions approximately 1 μm across, which can be seen in Figure 7.24. This morphology agrees with the morphology previously shown in the AFM images.
When 25 wt% R1 was added, as seen in Chapter 5, the morphology becomes far more complicated, and because of this it is much harder to differentiate between the nanosilica agglomerates and the thermoplastic particles. However large agglomerates of nanosilica were seen, up to 10 μm across. These were much larger than any of the agglomerates seen from the AFM images. It is not surprising that they were not seen in the AFM images as the AFM images only cover a small area, typically an area about 10 μm wide, while the SEM images can cover much greater areas, so occasional features are more likely to be captured by the SEM. There were not many of these large agglomerates but they were seen in several different 25 wt% R1 samples with different percentages of nanosilica indicating that they are significant and not an anomaly. There is no evidence from the fracture surfaces however that these large agglomerates have any effect on the fracture of the samples.

SEM images of the fracture surfaces of samples containing 25 wt% R1 and 2.7 and 10 wt% nanosilica are shown in Figure 7.25 and 7.26. The difficulty in identifying the nanosilica and the thermoplastic makes identifying differences in the fracture surfaces difficult. It is thought the increase in regions which appear lighter in colour is not the result of a less even fracture, and therefore a rougher surface, but that these are regions of thermoplastic or nanosilica, neither of which are clearly identifiable.
Figure 7.25: SEM images of the fracture surface of a SENB sample with 25 wt% R1 and 2.7 wt% nanosilica. Images taken at 250, 1000 and 5000 and 10000 times magnification.
Figure 7.26: SEM images of the fracture surface of a SENB sample with 25 wt% R1 and 10 wt% nanosilica. Images taken at 250, 1000, 5000 and 10000 times magnification.

7.2.4 Dynamic Mechanical Analysis

The glass transition temperatures ($T_g$s) for the plates were measured using a Dynamic Mechanical Analyser (DMA). The $T_g$s taken from the peak Tan δ are shown in Table 7.3 below. As mentioned in Chapter 4, four tests were run on specimens of the same material and the variation in these results indicates that the DMA gives the $T_g$ to an accuracy of ±0.8 °C
Table 7.3: Glass transition temperature results from DMA testing

<table>
<thead>
<tr>
<th>Wt% R1</th>
<th>Wt% NS</th>
<th>$T_g$ (°C) at 1 Hz</th>
<th>$T_g$ (°C) at 10 Hz</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>193.9</td>
<td>201.4</td>
</tr>
<tr>
<td>0</td>
<td>5</td>
<td>195.4</td>
<td>201.9</td>
</tr>
<tr>
<td>0</td>
<td>10</td>
<td>193.2</td>
<td>200.8</td>
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<tr>
<td>0</td>
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<td>192.2</td>
<td>198.9</td>
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<td>15</td>
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<td>203.1</td>
</tr>
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<tr>
<td>15</td>
<td>14.9</td>
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<td>200.8</td>
</tr>
</tbody>
</table>

The results for 1 Hz are displayed on the graph below, and the results for 10 Hz are similar to these. As discussed previously in Chapter 5 the addition of the thermoplastic does not affect the $T_g$, and from the graph below it can also be seen that the addition of nanosilica also does not affect the $T_g$ as has been reported by other work [8].

Figure 7.27: Glass transition temperature versus wt% nanosilica for epoxy and epoxy / 15 wt% R1, taken at 1 Hz.

Figure 7.28 shows a comparison of the traces from the DMA for samples with epoxy and no nanosilica, and samples with 10 wt% nanosilica. This shows that there is no
significant difference between the two traces, and that the nanosilica does not affect the traces when considering the T_g. This agrees with work carried out by Kinloch et al who also found that the addition of nanosilica does not affect the T_g [29].

Figure 7.28: Tan δ and modulus traces from DMA of samples with 0 and 10 wt% nanosilica with no thermoplastic, showing the nanosilica does not affect the T_g.

7.2.5 Conclusions

Atomic force microscopy showed that the nanosilica was well dispersed in the epoxy at all percentages when no thermoplastic was present. With thermoplastic in the material the nanosilica agglomerated. These agglomerates were in the epoxy phase, and no nanosilica was observed within the thermoplastic phase.

The addition of nanosilica to the epoxy and thermoplastic blend was expected to result in an increase in the Young's modulus, and to have no effect on the UTS as the particles are smaller than the inherent flaws in the material. The results from tensile tests showed that indeed the Young's modulus did increase with the addition of nanosilica and that this increase was well predicted by the Halpin-Tsai model. The
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UTS and the yield strength of the material were not affected by the addition of the nanosilica.

The fracture properties of the material were also not affected by the addition of nanosilica, neither fracture toughness nor fracture energy showed any increase despite nanosilica having produced an increase in fracture properties in some previous studies. A comparison between the materials used in the present work and those which have shown toughening in previous work is made in Chapter 8.
7.3 Carbon Nanotube Modification

Carbon nanotubes, as discussed in Chapter 2, are known to have a high tensile strength and Young's modulus [40]. It has been hoped that by incorporating multiwalled carbon nanotubes into the epoxy polymer and the epoxy / thermoplastic blend, a nanocomposite with superior properties will be formed. As some types of nanotubes are conductors it is possible that a polymer which includes nanotubes may also have a significant improvement in electrical conductivity.

7.3.1 Dispersion

The dispersion of the nanotubes was discussed in detail in Chapter 6 but is summarised briefly below for convenience.

The nanotubes were supplied in 4 different forms
1. Thomas Swan non-functionalised multiwalled nanotubes
2. Aligned multiwalled nanotubes supplied by Ian Kinloch from Cambridge University
3. Nanocyl non-functionalised multiwalled nanotubes
4. Nanocyl -COOH functionalised multiwalled nanotubes

These nanotubes were supplied dry, and tests were performed to establish the best way to disperse them in the epoxy. Following these tests it was found that the best dispersion of the nanotubes was achieved with the Thomas Swan non-functionalised nanotubes when sonicated into the epoxy using an ultrasonic bath for 120 hours. This was the process used to make the plates whose testing is detailed below.

Some of the Thomas Swan non-functionalised nanotubes were also supplied dispersed in the thermoplastic at 1 wt% by Cytec, and a second set of plates were made using these nanotubes.

Samples of epoxy, thermoplastic and nanotubes were made to the formulations given in Table 7.4 below.
Table 7.4: The formulations of thermoplastic and nanotubes used.

<table>
<thead>
<tr>
<th>Wt% thermoplastic</th>
<th>Wt% nanotubes</th>
<th>Sonicated into epoxy</th>
<th>Dispersed in thermoplastic</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
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</tr>
<tr>
<td>0</td>
<td>0.1</td>
<td>0.1</td>
<td>-</td>
</tr>
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<td>0</td>
<td>0.178</td>
<td>0.178</td>
<td>-</td>
</tr>
<tr>
<td>0</td>
<td>0.336</td>
<td>0.336</td>
<td>-</td>
</tr>
<tr>
<td>0</td>
<td>0.5</td>
<td>0.5</td>
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<td>-</td>
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<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>25</td>
<td>0.178</td>
<td>0.178</td>
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</tr>
<tr>
<td>25</td>
<td>0.336</td>
<td>0.336</td>
<td>0.336</td>
</tr>
</tbody>
</table>

The morphology of the thermoplastic is the same for the nanotube composites as it is for nanosilica composites. The nanotubes themselves were difficult to image with the AFM but Figure 7.29 below shows one of the AFM images where the nanotubes could be identified, they are the light flecks. The ability to see whole nanotubes would not be expected with the AFM as only the surface of the material can be imaged and typically only a short section of the nanotubes will be seen, unlike with the transmission electron microscope (TEM) where the image is taken through a thin section of the material so longer sections of the nanotubes are more common. Typically the nanotubes were easier to identify with the TEM and a TEM image of the same plate as Figure 7.29 is shown in Figure 7.30.
Figure 7.29: Two AFM height images of sample containing 15 wt% R1 and 0.178 wt% nanotubes initially dispersed in the thermoplastic, at 5 μm and 20 μm scans.

Figure 7.30: TEM image of sample containing 15 wt% R1 and 0.178 wt% nanotubes initially dispersed in the thermoplastic.

The dispersion of the nanotubes in the final material does vary quite significantly: it appears that the nanotubes are agglomerating during the cure cycle. It was found that the higher the percentage of thermoplastic the better the dispersion on both a macro
and a nanoscale. The 25 wt% R1 samples were typically better dispersed than the samples with 15 wt% R1 which in turn were better dispersed than those samples with no thermoplastic. The quantity of nanotubes in the samples did not seem to affect the dispersion. Whether the nanotubes were sonicated into the epoxy or dispersed in the thermoplastic initially does not seem to greatly affect the dispersion although there was a trend towards the nanotubes sonicated into the epoxy being slightly better dispersed.

The thermoplastic forms the same microstructure in the presence of the nanotubes as it did when no nanoparticles were present, and when nanosilica had been added. At 15 wt% R1 a spherical particulate morphology was formed with thermoplastic spheres approximately 1 μm in diameter, and at 25 wt% R1 a co-continuous morphology was seen.

### 7.3.2 Tensile Properties

Bulk plates have been made with epoxy, 0, 15 and 25 wt% R1 and nanotubes at various percentages as listed in Table 7.3 above. The nanotubes have been added either through sonication into the epoxy or were supplied blended into the thermoplastic. Tensile dumbbell specimens were made from these plates and have been tested. The modulus results are shown in Figure 7.31 below.
Chapter 7: Nanomodified Epoxy and Epoxy / Thermoplastic Blends

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Figure 7.31: Young's modulus of epoxy resin with increasing thermoplastic and nanotube content, the nanotubes were incorporated either into the thermoplastic, or into the epoxy by sonication.

Figure 7.31 shows that there is very little difference between the modulus of the polymer when the nanotubes are sonicated into the epoxy or when they are dispersed in the thermoplastic. It also shows that within the one standard deviation indicated by the error bars, there is no increase in Young's modulus through the addition of nanotubes.

To try to explain this lack of increase, the Halpin-Tsai model was used. The composite modulus was calculated with two values of shape factor, \( \zeta = 200 \) for \( E_{11} \) (longitudinal nanotube direction) and \( \zeta = 2 \) for \( E_{22} \) (transverse nanotube direction). These two composite moduli were combined as given in Equation 7.4 to give the modulus for a composite in which the nanotubes are randomly aligned [96].

\[
E_c = 0.184 E_{11} + 0.816 E_{22}
\]  
Equation 7.4

The predicted values show that some increase in Young's modulus would be expected even for such small amounts of nanotubes: see Figure 7.32 which gives the Halpin-Tsai model for a random orientation of nanotubes dispersed in epoxy with 25 wt%
thermoplastic. The Young’s modulus of a nanotube for use in this model was taken as 500 GPa, which falls within the range of moduli reported by Yu et al. [39]. A density of 1.8 g/cm$^3$ was taken from [40]. This density value assumes the nanotubes are not filled with epoxy, and since the nanotubes are multiwalled and should have end caps, this assumption seems reasonable.

Figure 7.32: Comparison of the Halpin-Tsai model to an experimental data point showing that the theoretical moduli of a composite with 0.336 wt% nanotubes and the experimental error bars of a 25 wt% R1, 0 wt% nanotube sample agree relatively well.

Again, as for the nanosilica samples, the UTS is in part dependent on the surface roughness of the samples to be tested. However all the samples were made with the same mould and machined in the same way so the results of each of the plates tested should be comparable with each other. The results are shown in Figure 7.33, it can be seen that the UTS is not affected by the addition of the nanotubes.
Figure 7.33: Ultimate tensile strength of samples of epoxy with thermoplastic and nanotubes showing no effect with adding the nanotubes.

The 0.2% proof stress has also been calculated, and these values are shown in Figure 7.34. Again the nanotubes do not affect the proof stress of the epoxy.
Chapter 7: Nanomodified Epoxy and Epoxy / Thermoplastic Blends

Figure 7.34: Yield stress calculated from the 0.2% proof stress of samples of epoxy with thermoplastic and nanotubes showing no effect with adding nanotubes.

The tensile properties of the epoxy are not affected in any way by the addition of the nanotubes. This can be explained by the very low weight loadings of nanotubes used, 0.5 wt% maximum. It is possible that higher weight loadings would give an increase in the tensile properties but the aim in this project was to achieve the properties required with low weight loadings.

It is also possible that the perfect graphite surface of the nanotubes makes it difficult for the epoxy to bond to them. No micromechanical interlocking will be possible but chemical and van der Waals bonding may be possible [48]. If the interface between the nanotubes and the epoxy is very weak then it would not be expected that the nanotubes take much of the applied load and therefore they would not increase the tensile properties [97].

7.3.3 Fracture Tests

Single Edge Notched Bend (SENB) specimens have been cut from the bulk plates and used to measure the fracture toughness: for the results see Figure 7.35.
Figure 7.35: Fracture toughness of epoxy resin with increasing thermoplastic and nanotube content. The nanotubes were incorporated either into the thermoplastic, or into the epoxy by sonication.

As for the nanosilica tests there is no clear increase in fracture toughness with adding nanotubes, if anything there is a decrease in the fracture toughness by adding nanotubes. There is also no clear difference between the nanotubes sonicated into the epoxy and those sonicated into the thermoplastic. The dispersion of the nanotubes does not appear to have a significant effect on the toughness.

The results for fracture energy show the same trends as fracture toughness. The addition of nanotubes does not lead to an increase in fracture energy and whether the nanotubes are dispersed in the epoxy or the thermoplastic does not affect the fracture energy. See Figure 7.36.
Figure 7.36: Fracture energy of epoxy with increasing thermoplastic and nanotube content, the nanotubes were incorporated either into the thermoplastic, or into the epoxy by sonication.

Given that the nanosilica discussed in the first half of this chapter also gave no increase in toughening it is not surprising that the nanotubes do not give an increase in toughness. The error bars for the nanotube specimens are always large and this could be related to the increased difficulty in preparing the samples. To precrack the SENB samples was particularly difficult due to the inability to see the progression of the natural crack through the sample and therefore it was difficult to ensure that the crack grew evenly and by the correct amount. Although the crack can be examined after testing, and improperly cracked samples were disregarded from the results, there is still an increased chance of results from samples with poor precracks being used. A second reason is that there are agglomerates of nanotubes left in some of the samples, as shown in the assessment of dispersion given in Chapter 6. These agglomerates will affect the fracture toughness as they can act as defects and so the fracture toughness of particular samples may depend on whether there were any agglomerates at the tip of the precrack.

To help explain the lack of toughening the fracture surfaces of the nanotube composites were examined with the SEM. Once again the fractures run from left to right in all the images.
When low percentages of nanotubes were used in epoxy samples no nanotubes were seen, see Figure 7.37. The fracture surface looked very similar to that of the sample of epoxy shown in Chapter 5.

At higher percentages the nanotubes are seen in the secondary electron images as bright flecks. This is because they project out of the surface of the sample, hence they charge more and so appear very bright and much larger in diameter than they really are, see Figure 7.38. It is possible that the nanotubes project out of the surface as they have been pulled out of the polymer. Alternatively it is also possible that the inner ‘tubes’ of these multiwalled nanotubes have pulled out of the outer tube in the fashion of a telescope, leaving the outer tube still firmly bonded to the polymer.

![SEM images of the fracture surface of a SENB sample of epoxy with 0.1 wt% nanotubes where the nanotubes were sonicated into the epoxy. No nanotubes are visible. Images taken at 250, 1000 and 3000 times magnification.](image)

**Figure 7.37**: SEM images of the fracture surface of a SENB sample of epoxy with 0.1 wt% nanotubes where the nanotubes were sonicated into the epoxy. No nanotubes are visible. Images taken at 250, 1000 and 3000 times magnification.
Figure 7.38: SEM images of the fracture surface of a SENB sample of epoxy with 0.5 wt% nanotubes where the nanotubes were sonicated into the epoxy. Images taken at 250, 1000, 3000 and 5000 times magnification. Blue arrows point to regions with loose agglomerates of nanotubes, the red arrows point to individual nanotubes.

Despite the addition of the nanotubes the fracture surfaces are very flat and smooth, indicating that the nanotubes have not increased the toughness of the material. There are very few river lines seen. The surfaces are sufficiently smooth and devoid of features that there is no obvious change in fracture mechanism associated with the addition of nanotubes.

The nanotubes in Figure 7.38 appear to be in loose agglomerates up to about 20 \( \mu m \) across, although these agglomerates often appear to join together to almost form a continuous network.

When 15 wt% R1 is added the nanotubes seem to be easier to identify even in small quantities as seen in Figures 7.39 and 7.40. They still appear as bright flecks. The nanotubes can either have been dispersed in the thermoplastic, as in Figure 7.39, or
sonicated into the epoxy, as in Figure 7.40. There are no obvious differences in the fracture surfaces between these two methods of dispersion.

Figure 7.39: SEM images of the fracture surface of a SENB sample of epoxy with 15 wt% R1 and 0.1 wt% nanotubes where the nanotubes were dispersed in the thermoplastic. Images taken at 250, 1000, 3000 and 5000 times magnification.
Figure 7.40: SEM images of the fracture surface of a SENB sample of epoxy with 15 wt% R1 and 0.1 wt% nanotubes where the nanotubes were sonicated into the epoxy. Images taken at 250, 1000, 3000 and 5000 times magnification. The arrow points to a large agglomerate.

As can be expected from the analysis of dispersion in Chapter 6 there are several tight agglomerates in the specimens, but as these are not the focus of this section and do not cover the majority of the fracture surface, most of the images at higher magnification were taken from the areas of the fracture surface which do not contain tight agglomerates.

The thermoplastic spheres are drawn into peaks on the right hand edge of the spheres. This is the same as was seen in samples with no nanoparticles. The nanotubes do not appear to affect the deformation of the thermoplastic, nor do they affect the river lines which look like the river lines in samples of epoxy with 15 wt% R1 and no nanoparticles.
Chapter 7: Nanomodified Epoxy and Epoxy / Thermoplastic Blends

Increasing the percentage of nanotubes to 0.178 wt\% also has no obvious effect on the fracture surfaces. Images of samples with 0.178 wt\% nanotubes can be seen in Figures 7.41 and 7.42.

Figure 7.41: SEM images of the fracture surface of a SENB sample of epoxy with 15 wt\% R1 and 0.178 wt\% nanotubes where the nanotubes were dispersed in the thermoplastic. Images taken at 250, 1000, 3000 and 5000 times magnification. A large, tight, agglomerate is indicated by the yellow arrow.

The large agglomerate shown in the 3000 times magnification image of Figure 7.41 does not appear to show any significant change in the fracture markings resulting from its presence. This is what would be expected since the nanotubes do not appear to affect any of the properties of the material.
Chapter 7: Nanomodified Epoxy and Epoxy / Thermoplastic Blends

Figure 7.42: SEM images of the fracture surface of a SENB sample of epoxy with 15 wt% R1 and 0.178 wt% nanotubes where the nanotubes were sonicated into the epoxy. Images taken at 250, 1000, 3000 and 5000 times magnification.

As expected with 25 wt% R1 the surface is very rough but the nanotubes can be identified as can the co-continuous thermoplastic morphology. The co-continuous nature of the thermoplastic is more obvious than it was for the samples with nanosilica as the nanotubes are incorporated at such a low weight percentage. As discussed in Chapter 6, the higher thermoplastic content has resulted in a reasonably good dispersion with few agglomerates visible, and those agglomerates that there are, tend to be smaller.

The fracture surfaces of all the nanotube composites with 25 wt% R1 appear the same as the sample in Chapter 5 with 25 wt% R1 and no nanoparticles. There are no significant differences.

Figures 7.43 and 7.44 below show the fracture surfaces of samples of epoxy with 25 wt% R1 and 0.1 wt% nanotubes, with the nanotubes dispersed in the thermoplastic and the epoxy respectively.
Figure 7.43: SEM images of the fracture surface of a SENB sample of epoxy with 25 wt% R1 and 0.1 wt% nanotubes where the nanotubes were dispersed in the thermoplastic. Images taken at 250, 1000, 3000 and 5000 times magnification.
Figure 7.44: SEM images of the fracture surface of a SENB sample of epoxy with 25 wt\% R1 and 0.1 wt\% nanotubes where the nanotubes were sonicated into the epoxy. Images taken at 250, 1000, 3000 and 5000 times magnification.

At 0.336 wt\% nanotubes and 25 wt\% R1 the morphology is still obvious but there is no real change in the surface from the 0.1 wt\% nanotube sample, there are no signs of the nanotubes forming large agglomerates as seen in Figures 7.41. There appears to be no change in fracture surfaces from samples with lower percentages of nanotubes. Figures 7.45 and 7.46 show the fracture surfaces of samples with 25 wt\% R1 and 0.336 wt\% nanotubes where the nanotubes were dispersed in the epoxy and the thermoplastic respectively.
Figure 7.45: SEM images of the fracture surface of a SENB sample of epoxy with 25 wt% R1 and 0.336 wt% nanotubes where the nanotubes were sonicated into the epoxy. Images taken at 250, 1000, 3000 and 5000 times magnification.
Throughout this microscopy work the addition of the nanotubes, at all the percentages used and via sonication into the epoxy or dispersion in the thermoplastic, have no noticeable effect on the fracture surfaces compared to the fracture surfaces with the same percentages of thermoplastic but no nanoparticles. The nanotubes have been shown earlier in the chapter to have no effect on the tensile properties and the fracture toughness and energy of these materials. It is therefore unsurprising that they do not seem to affect the fracture surfaces and fracture mechanisms.

To see if any differences can be noticed at a smaller scale a Field Emission Gun Scanning Electron Microscope (FEG-SEM) was used on the fracture surface of a sample to see if at higher magnification there was any evidence of nanotube pull-out, fracture or the middle tubes pulling out of the outer tubes as a telescope. It was also hoped that it would show if the nanotubes were sufficiently well bonded to the epoxy to be coated in epoxy which would help explain their increased apparent diameter in the SEM images given above. The FEG-SEM image of a sample of 15 wt% R1 and 0.178 wt% NT with the nanotubes dispersed into the thermoplastic is given in Figure 7.47.
Figure 7.47: FEG-SEM image of epoxy with 15 wt% R1 and 0.178 wt% NT where the nanotubes were dispersed in the thermoplastic. The arrow points to a hole where a nanotube could have been pulled out.

From Figure 7.47 it can be seen that a length of over 1 μm of some nanotubes can be seen sticking out of the surface of the sample, it also shows a hole where a nanotube might have been pulled out. However given the number of nanotubes seen sticking out of the surface, more than one hole would have been expected indicating that this is probably not the most common method of failure. The nanotubes appear to have a diameter of about 30 nm which is still greater than the stated average diameter of multiwalled nanotubes (10 nm), but the light colour indicates that the nanotubes are charging in this sample which would affect their apparent diameter. The dark patches on the epoxy polymer are where the polymer is burning as the nanotubes conduct the electrons from the beam down into the polymer. It is thought that the most likely mechanism for the nanotubes sticking out of the surface is that the end caps are broken either during the dispersion using ultrasonics, or during the testing, and the inner tubes are pulled out of the outer tubes. There are only weak van der Waals forces bonding the different layers of tubes together so very little energy would be
required to do this and as such it would not be expected to have a significant effect on
the fracture toughness or energy, or have a visible effect on the fracture surfaces. An
alternative explanation for the hole is that this is where the outer tube has been left in
the polymer, while the inner tubes have been pulled out of it completely.

7.3.4 Conclusions

The addition of nanotubes to the epoxy and thermoplastic has no effect on any of the
properties measured, the Young's modulus, ultimate tensile strength, 0.2% proof stress,
fracture toughness or fracture energy. For the Young's modulus this can be explained
as a result of the very low quantities used, as the Halpin-Tsai model predicts no
significant increase even at the highest weight percentage of nanotubes used.

If the outer tube or the end cap breaks, the inner tubes of the nanotubes may be pulled
out of the outer layers, and this may explain the lack of toughening seen for this
polymer with the addition of nanotube. However it must be remembered that the
addition of nanosilica does not affect the fracture properties of this specific mix of
polymers. It is therefore possible that it is the epoxy and thermoplastic which do not
allow for toughening and so it is not a surprise that the nanotubes do not give an
improvement either.
Chapter 8 DGEBA Tests and Compression Tests

8.1 Introduction

It has been found in the previous chapters that the nanosilica does not improve the fracture toughness or fracture energy for the samples of PY306 / MY0510 / MCDEA. Other researchers have found that nanosilica increased the fracture properties for a DGEBA / anhydride system [29, 98]. Tests were carried out to confirm that when using a DGEBA / anhydride system, an increase in fracture properties could be reproduced. This was confirmed, and then compression tests were carried out on bulk plates of the two epoxy systems to try to find the differences between the systems, as this will give the yield behaviour of the materials which cannot be seen in tensile tests due to premature fracture. It was hoped that any differences might help explain why one system will show toughening with the introduction of nanosilica while the other system will not. The DGEBA used for the fracture and tensile tests was LY556 from Huntsman and the curing agent was Albidur HE600 from Nanoresins, Germany.

8.2 Mechanical Tests and Fracture Tests

Plates were made of the LY556 system with no nanosilica, and 10 and 20 wt% nanosilica. These plates were made to the same dimensions as the samples of PY306 / MY0510 system. The test method and conditions for the LY556 system samples were also the same. The glass transition temperature for the epoxy polymer is 135 °C.

8.2.1 Fracture Tests

Fracture tests, using single edge notched bend samples, were carried out for the three formulations of the LY556 system and the results are shown in Figure 8.1 below.
Chapter 8: DGEBA Tests and Compression Tests

Figure 8.1: Fracture toughness and fracture energy results for LY556 system with increasing amounts of nanosilica showing a significant increase in both of these properties as the nanosilica is added.

A significant increase in the fracture properties was found when nanosilica was added to the LY556 system. This has also been seen by other researchers [98]. For 20 wt% nanosilica a 100% increase in fracture toughness was found and for fracture energy the increase was 176%. These values are comparable to the 73% increase in fracture toughness and 175% increase in fracture energy found by Sohn Lee [99].

These results show that it is possible for nanosilica to increase the toughness of some epoxy resins. It also shows that the lack of toughening seen in the PY306 / MY0510 system is not due to the testing methods used, as the same methods were used for testing both systems and the results for the one system show no improvement in toughness and the other system shows a significant increase in toughness. The fracture toughness and fracture energy for the LY556 with 0 wt% nanosilica are 0.53 MPa.m$^{0.5}$ and 80 J/m$^2$. For PY306 / MY0510 with 0 wt% nanosilica, the fracture toughness and fracture energy are 0.75 MPa.m$^{0.5}$ and 202 J/m$^2$ showing that the PY306 / MY0510 system is significantly tougher than the LY556 system.
8.2.2 Tensile Tests

Table 8.1 below shows the tensile results for both the LY556 and PY306 / MY0510 systems with 0, 10 and 20 wt% nanosilica. From this it can be seen that the addition of nanosilica increases the Young’s modulus of the LY556 system, but not to the same extent that it did for the PY306 / MY0510 system. Figure 8.2 shows the tensile results for the LY556 system graphically with the Halpin-Tsai and van Es models.

Table 8.1: The Young’s modulus for the PY306 / MY0510 and LY556 systems, comparing the percentage increase in modulus for the two systems with the addition of nanosilica.

<table>
<thead>
<tr>
<th>Wt% nanosilica</th>
<th>PY306 / MY0510 system</th>
<th>LY556 system</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Young’s modulus (GPa)</td>
<td>% increase</td>
</tr>
<tr>
<td>0</td>
<td>2.55</td>
<td>-</td>
</tr>
<tr>
<td>10</td>
<td>3.44</td>
<td>35</td>
</tr>
<tr>
<td>20</td>
<td>3.87</td>
<td>52</td>
</tr>
</tbody>
</table>

Figure 8.2: Young’s modulus results for LY556 system with increasing amounts of nanosilica, and the Halpin-Tsai and van Es models.
The increase in Young's modulus for this system is closer to the van Es model than it is to the Halpin-Tsai model. The Halpin-Tsai model gave a closer fit for the PY306 / MY0510 system. The Halpin-Tsai model predicts a higher composite modulus than the van Es model, therefore it can be seen that the PY306 / MY0510 system has its modulus increased to a greater extent than the LY556 system by the addition of nanosilica.

An example stress versus strain curve for LY556 is given in Figure 8.3. This shows that there was very little plastic deformation of the sample before failure.

![Stress versus strain curve for a sample of LY556 with 0 wt% nanosilica](image)

Figure 8.3: Stress versus strain curve for a sample of LY556 with 0 wt% nanosilica

The ultimate tensile strength (UTS) for the samples and the 0.2% proof stress were also calculated, these results have both been plotted on the graph in Figure 8.4. There is no apparent change in the UTS with the inclusion of, and increase in the percentage of nanosilica, however there is a noticeable increase in the proof stress. These results were compared to the results of Hsieh [100] and he also found no change in UTS with percentage of nanosilica but an increase in 0.2% proof stress.
Figure 8.4: Ultimate tensile strength (UTS) and 0.2% proof stress results for LY556 system with increasing amounts of nanosilica, showing no change in the UTS and a small increase in proof stress.

It must be remembered that the UTS is not only dependent on the properties of the material but also on the material’s surface finish. The plates from which the tensile samples for these tests were cut were made in the same mould and therefore in theory the surface roughness of samples for each formulation should be the same. However the large error bars are evidence that the surfaces were not exactly the same. The proof stress is not dependent on the surface finish and the data has extremely small error bars. These data clearly show a steady increase in proof stress with the addition of nanosilica. This is unlike the PY306 / MY0510 system which did not show any increase in proof stress.

Comparing the two systems it can be seen that the LY556 system does not show as great an increase in Young’s modulus with the addition of nanosilica as the PY306 / MY0510 system does, however it does give an increase in the proof stress and therefore in the point of yield which is not seen with the PY306 / MY0510 system. When considering the significance of these properties to the fracture properties, simplistically the fracture energy is related to the area under the load displacement graph. A smaller Young’s modulus and a lower yield stress would both tend to result in
a greater area under the graph, assuming that the value of $P_0$, the load the area is measured to, is not also decreased. Here we have a much smaller increase in Young's modulus with the addition of nanosilica, and only a small increase in proof stress indicating that the LY556 system may result in more of an increase in fracture energy than the PY306 / MY0510 system did. This assessment only holds true if the strain to failure is small, Figure 8.3 showed that there is very little plastic deformation during the tensile tests.

The reason for one system to result in improvements in fracture properties while the other system does not is the focus of the rest of this chapter, and to investigate this it was decided to carry out some plane strain compression tests since the tensile tests showed failure at low strains.

### 8.3 Plane Strain Compression Tests

Plates of the PY306 / MY0510 epoxy polymer, and the DGEBA / anhydride polymer, without nanosilica, were made to investigate possible differences in the properties of the two epoxy systems. These differences result in only one having an increase in fracture properties with the addition of nanosilica. These plates were then tested in plane strain compression using a rig with two, 12mm wide, parallel platens. The true stress versus true strain traces from these tests after the machine compliance has been accounted for are given below in Figure 8.5.

To calculate the true stress and strain the Equations 8.1 and 8.2 below are used [101].

- **True Stress**: $\sigma_T = \frac{P(1+\varepsilon)}{A}$  
  Equation 8.1

- **True Strain**: $\varepsilon_T = \ln (1 + \varepsilon)$  
  Equation 8.2

Where:  
- $P$ is the load  
- $A$ is the cross sectional area of the sample  
- $\varepsilon$ is the strain
As can be seen in Figure 8.5 the DGEBA system shows significant strain softening (a decrease in the stress after yield) while the PY306 / MY0510 system shows very little strain softening. This is not the same as necking as here true stress and true strain are considered. One hypothesis is that for a material which shows strain softening, during fracture the material reaches yield and where the nanosilica particles are, the nanosilica particles debond and the epoxy polymer forms small voids \[8\]. These voids are the result of plastic deformation around the nanosilica particles. This plastic void growth can occur because after yield, the stress needed for the strain to increase and plastic deformation to occur decreases. For both materials the stress field will be concentrated on the nanosilica particles and for the material which does not show softening, the material will withstand this stress. However the material which shows softening will become softer and this soft polymer around the particle will act as a soft particle or a void. This moves the stress concentration from the poles of the particle to the equator of the particles and gives an increase in the von Mises stress and therefore increases shear band formation, deformation and energy absorption. It is also possible that in this soft polymer around the nanosilica particles, voids may grow. The growth of a void and the formation of shear bands will require energy for the deformation of the matrix, this use of energy in deformation will lead to improvements in fracture toughness and energy. This is one hypothesis and further investigation needs to be
carried out to confirm the presence of voids and shear bands in materials which show toughening with nanosilica particles, and to show a lack of voids and reduced shear bands in materials which do not toughen, although the voids shown by Johnsen et al.[8] support this theory.

Shear band formation in the pure epoxy is one indication of a plastic's ability to plastically deform. Photos of the two epoxy samples were taken after compression tests and it can be seen in Figure 8.6 that the diagonal shear bands are much clearer on the DGEBA / anhydride sample than they are on the PY306 / MY0510 / MCDEA sample. This agrees with the hypothesis discussed above to try to explain the lack of toughening seen in samples made from the PY306 / MY0510 system.

Figure 8.6: Photos of the plane strain compression test samples showing extensive shear band formation in the sample of DGEBA / anhydride which can be toughened with the addition of nanosilica, and very little shear band formation in the sample of PY306 / MY0510 / MCDEA.
8.4 Conclusions

Through testing samples of a DGEBA / anhydride system for its mechanical properties it was found that the Young's modulus is increased by the addition of nanosilica, as is the proof stress, however the ultimate tensile strength is unchanged. The increase in Young's modulus is not as dramatic as the increase seen with the PY306 / MY0510 system. This, combined with the increase in proof stress which was not seen in the second system, are indications to the ability of this polymer to toughen where the second system does not.

Fracture tests confirmed the above thoughts with a 100% increase in fracture toughness and a 176% increase in fracture energy when 20 wt% nanosilica was added to the DGEBA / anhydride system. These increases are similar to the increases found by Sohn Lee [99] for the same system, indicating that it is not the test method employed by the author which explains the lack of toughening seen for the PY306 / MY0510 system.

To investigate differences in the two systems which could explain why the one system shows toughening and the other does not, plane strain compression tests were carried out on both epoxy systems. The compression tests showed that for the epoxy which toughens there is strain softening after yield, while for the PY306 / MY0510 system, no strain softening was seen. It is thought that this strain softening could result in increased plastic deformation, forming small voids around the nanosilica particles as reported by other researchers, this would result in higher fracture toughness and energy. Shear band formation is an indication of the ability of a material to plastically deform. The DGEBA / anhydride system showed considerable shear band formation while the PY306 / MY0510 / MCDEA system showed very little shear band formation. This reinforces the hypothesis about increased plastic deformation in the DGEBA / anhydride system being responsible for the increased fracture properties.
Chapter 9: Different Thermoplastic Endgroups

9.1 Introduction

The interaction between the thermoplastic and the epoxy is to some extent dependent on the endgroups on the thermoplastic. The majority of the work carried out in this thesis, and reported in Chapters 5, 6 and 7, used a reactive endgroup called R1. Two other endgroups were used for limited tests to investigate the effect of the endgroup on the morphology and properties of the final polymer and nanocomposite. One of these is an unreactive endgroup, U, the other is reactive but different to R1, and is called R2.

Plates using the thermoplastics R2 and U at 15 and 25 wt% were made with 10 wt% nanosilica and 0.178 wt% nanotubes. These plates were cut into samples for tensile and fracture testing, and for the nanosilica samples sections were examined with the atomic force microscope (AFM) to obtain the morphology.

9.2 Morphology

Small sections of each nanosilica composite were taken for use in the atomic force microscope (AFM). The images for the samples containing R1 are given here again for comparison with the images for samples containing U and R2.

It was found that the two thermoplastics with reactive endgroups gave similar morphologies, while the unreactive endgroups gave different microstructures to the two reactive endgroups. The morphology of samples made with U can be seen in Figures 9.1 and 9.2 below. Rather than forming a spherical particulate morphology at 15 wt%, some of the U forms large (7 μm) regions which means that the morphology is close to co-continuous, see Figure 9.1. These regions of U have epoxy particles in them, this localised phase inversion is also seen for R1 when it is co-continuous. At 25 wt% U the morphology is close to phase inversion, as shown in Figure 9.2. It appears the thermoplastic is not well bonded to the epoxy, in the height image there are dark lines...
around the left side of where the thermoplastic and epoxy phases meet, these are gaps where the thermoplastic has pulled away from the epoxy. The samples were prepared for the AFM by being cut with a diamond knife and the cutting direction is horizontal, it appears that the thermoplastic debonds and is pulled away from the epoxy during this cutting. This indicates that there is almost a complete lack of adhesion between the two phases.

Figure 9.1: AFM image of a sample containing 15 wt% U with 10 wt% nanosilica showing a partially co-continuous microstructure with localised phase inversion.

The debonding of the thermoplastic from the epoxy is not seen at 25 wt% U, but this could be the result of the change in microstructure. The thermoplastic is more ductile than the epoxy and where the thermoplastic forms particles within the epoxy, these particles can deform and pull away from the matrix. However for 25 wt% U the morphology is close to phase inverted, where the more ductile thermoplastic is the matrix with hard epoxy particles in it. As the thermoplastic deforms the epoxy particles are moved by the deformation rather than debonding.
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Figure 9.2: AFM image of a sample containing 25 wt% U with 10 wt% nanosilica showing how close to being phase inverted the morphology is.

For the same percentages of thermoplastic but using R1, and 10 wt% nanosilica, the morphologies were spherical particulate and co-continuous as discussed in Chapter 7. The images are repeated below in Figures 9.3 and 9.4 for convenience.

Figure 9.3: AFM image of a sample containing 15 wt% R1 with 10 wt% nanosilica showing the spherical particulate morphology.
Figure 9.4: AFM image of a sample containing 25 wt% R1 with 10 wt% nanosilica showing the co-continuous microstructure with localised phase inversion.

To complete the set of images, below in Figures 9.5 and 9.6 are the images for samples made using R2, these give the same microstructures as those samples made with R1. At 15 wt% R2 the morphology is spherical particulate and at 25 wt% R2 the morphology is co-continuous.

Figure 9.5: AFM image of a sample containing 15 wt% R2 with 10 wt% nanosilica showing the spherical particulate microstructure.
Figure 9.6: AFM image of a sample containing 25 wt% R2 with 10 wt% nanosilica showing the co-continuous microstructure.

The above micrographs show that the addition of U gives similar microstructures to those which would be expected for higher percentages of the reactive endgrouped thermoplastics, R1 or R2. The nanosilica in all samples forms small agglomerates in the epoxy, up to about 1 μm in diameter. The nanosilica does not appear to be affected by the changes in the endgroup.

9.3 Mechanical Tests

9.3.1 Tensile Tests

Tensile test specimens of each of the materials made with U and R2 were tested and the results are compared with the results for specimens made with R1. Figure 9.7 shows that there is no clear change in the Young's modulus with changing the endgroups.

The Young's modulus for samples with 15 wt% R1, 0 wt% nano is 2.6 ± 0.2 GPa. With the addition of nanotubes, and for all endgroups, the Young's modulus is about 2.8 GPa indicating no effect on the modulus of changing the endgroup or adding the nanotubes. For the addition of nanosilica, again there is no clear trend with changing the endgroups but the Young's modulus increases to about 3.2 MPa. The moduli for
samples with 25 wt% thermoplastic are the same as for the samples with 15 wt% thermoplastic.

Figure 9.7: Young's modulus results for samples with the three different endgroups.

The results for the ultimate tensile strength (UTS) of these samples show a much greater effect from changing the endgroups. While changing the endgroup from R1 to R2 has no significant effect, changing it to the unreactive endgroup, U, causes a significant decrease in the UTS. This can be seen in Figure 9.8 below. The UTS for samples with R1 and R2 is about 86 GPa and for samples with U it is between 30 and 70 GPa.
Figure 9.8: Ultimate tensile strength results for samples with the three different endgroups.

This decrease could be related to the weak epoxy / thermoplastic interface. The thermoplastic is so weakly bonded to the epoxy that it will not take any of the load and therefore the material is equivalent to the epoxy with holes in it. This results in a lower UTS as the load is only spread over the epoxy. The load per unit area of epoxy is greater for the polymer with U, than the load per unit area of epoxy for the material with a reactive endgroup on the thermoplastic, for the same applied load.

To complete this set of tensile data the 0.2% proof stress was calculated for each specimen. The results are given in Figure 9.9. Within the error bars all three have the same proof stress. However when 25 wt% U was used no 0.2% proof stress could be obtained as the material showed almost no plastic deformation. At 25 wt% U the matrix is the thermoplastic and for this formulation the material is far more brittle than it is for any other formulations. This was not what was expected since the thermoplastic would be expected to show more plasticity.
Figure 9.9: 0.2% proof stress results for samples with the three different endgroups. * specimens fractured too early for a 0.2% proof stress to be calculated.

Example stress versus strain curves for 15 wt% thermoplastic and 10 wt% nanosilica are given in Figure 9.10 to show the effects of the endgroups on the traces. The initial slopes and points at which the materials begin to yield are the same for all three traces, but the degree of plastic deformation varies, with U showing by a large degree the least deformation.
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9.3.2 Fracture Tests

Single edge notched bend (SENB) tests were carried out for the samples with R2 and U. These results are compared with the results for R1 in Figures 9.11 and 9.12 below. The fracture toughness and fracture energy for 15 wt% R1 with no nanoparticles are 0.69 MPa.m^{0.5} and 244 J/m^2, and for 25 wt% R1 with no nanoparticles, 0.96 MPa.m^{0.5} and 454 J/m^2.

Figures 9.11 and 9.12 show that in three out of the four formulations, using the thermoplastic with R2 endgroups led to a decrease in fracture toughness and fracture energy. When nanotubes were added the unreactive endgroup causes no change in fracture toughness and energy, but with nanosilica the unreactive endgroups led to a greater fracture toughness and energy, although the size of the error bars make the trends somewhat hard to be confident about. An increase in fracture energy and fracture toughness with U was not initially expected as the literature either reported a need for reactive endgroups to get an increase in toughness, or that endgroup reactivity makes no difference [4, 15]. However, since the unreactive endgroup is not
well bonded to the epoxy, it is possible that the areas where the thermoplastic are at 15 wt% debond, and then act as voids. These voids will allow plastic deformation to occur at the crack tip by reducing constraint, giving rise to an increase in fracture toughness and energy. At 25 wt% U the thermoplastic typically forms the matrix and assuming the thermoplastic deforms more than the epoxy, this would lead to a rise in the fracture toughness and energy. The unreactive endgroups at 25 wt% were found to lead to a decrease in plasticity from the tensile tests - this is plasticity for the polymer as a whole rather than the region in the order of microns around the crack tip. It is possible that the area around the crack tip could show increased plasticity, while a bulk tensile test sample shows a reduction in plasticity or fractures before significant plasticity can occur, although further research into this would be needed to confirm this theory.

Figure 9.11: Fracture toughness results for samples with the three different endgroups.
To investigate why these changes in fracture toughness and energy occur the fracture surfaces were examined using a scanning electron microscope.

9.4 Fracture Surfaces

The fracture surfaces of the SENB samples were investigated using the SEM. Figures 9.13 and 9.14 show the samples with 15 and 25 wt% R2 and 0.178 wt% nanotubes.

The fracture toughness and energy for the nanotube samples containing 15 wt% R2 are significantly lower than for the samples with R1. The fracture surfaces however appear to be the same, the thermoplastic is forming the same spherical particulate morphology. Also the thermoplastic spheres have been drawn into peaks before fracturing as seen for R1. The nanotubes appear to be in similar loose agglomerates in the epoxy.
Figure 9.13: SEM images of epoxy with 15 wt% R2 and 0.178 wt% nanotubes taken at 500, 1000, 3000 and 5000 magnification. The arrow points to where a thermoplastic sphere has been drawn to a peak before fracture.

Samples containing 25 wt% R2 with 0.178 wt% NT also give a decrease in fracture toughness and energy compared to samples with 25 wt% R1 and 0.178 wt% NT. The fracture toughness and energy decrease from 1.09 MPa.m^{0.5} and 386 J/m^2 to 0.95 MPa.m^{0.5} and 245 J/m^2 when the thermoplastic is changed from R1 to R2. When examining the fracture surfaces however there are no obvious differences between these two samples. SEM images for the fracture surfaces of the samples with R2 are shown below in Figure 9.14. The images of a sample with R1 and nanotubes was given in Figure 7.44. The thermoplastic is clearly forming a co-continuous morphology with epoxy spheres in the thermoplastic. The nanotubes are dispersed within the epoxy, and there are no obvious features to explain the decrease in fracture toughness and energy. To find a reason for the decrease in fracture toughness and fracture energy when R2 is used with nanotubes further tests would be required.
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Figure 9.14: SEM images of epoxy with 25 wt% R2 and 0.178 wt% nanotubes taken at 500, 1000, 3000 and 5000 magnification. The arrows point to nanotubes.

The fracture surface for the sample with 15 wt% R2 and 10 wt% NS, shown in Figure 9.15, has a similar appearance to that for 15 wt% R1 and nanosilica as given in Figure 7.22. The morphology is spherical particulate, although this was more clearly shown in the AFM images in Figure 9.3. The fracture surface shows that the thermoplastic is well bonded to the epoxy with no evidence of voids. The fracture path appears to be unaffected by the thermoplastic or the nanosilica.
Figure 9.15: SEM images of epoxy with 15 wt% R2 and 10 wt% nanosilica taken at 500, 1000, 3000 and 5000 times magnification.

SEM images of the fracture surface for 25 wt% R2 and 10 wt% NS are shown in Figure 9.16 below. These show a surface which is similar to that given in Figure 7.26 for a 25 wt% R1 and 10 wt% NS sample. This is to be expected, both endgroups are reactive and the fracture toughness and energy are the same for both samples. For 25 wt% R1 and 10 wt% NS the fracture toughness was 0.96 MPa.m$^{0.5}$ and the fracture energy was 295 J/m$^2$, for the samples with 25 wt% R2 these values are 1.1 MPa.m$^{0.5}$ and 306 J/m$^2$.

There are no obvious reasons for the general reduction in fracture toughness seen when the thermoplastic R2 is used rather than R1 especially when considering that all the tensile properties and the morphologies were unchanged.
Changing the thermoplastic to U has no significant effect on the fracture toughness and energy when nanotubes were added. The fracture toughness of the sample with 15 wt% R1 and 0.178 wt% NT is 0.85 MPa.m$^{0.5}$, and the fracture energy is 232 J/m$^2$. For the sample containing 15 wt% U and 0.178 wt% NT these values are 0.92 MPa.m$^{0.5}$ and 235 J/m$^2$. However as discussed in section 9.2 the morphology is different and compared with the AFM images, the larger areas which can be examined with the SEM show an increased complexity in the morphology.

At 15 wt% U, some of the thermoplastic forms spherical particles as seen for R1. See Figure 9.17. However there are also large sausage shaped regions of co-continuous thermoplastic, approximately 5 μm in diameter and up to 25 μm in length. Where these have fractured during the testing, spheres of epoxy can be seen inside indicating localised phase inversion. The fracture surface shows that the thermoplastic has been pulled away from the epoxy, with voids around some thermoplastic particles, and voids where both the small spheres of thermoplastic and large regions of phase inverted thermoplastic have come completely away from the epoxy. Clearly the thermoplastic is not well bonded to the epoxy. For the large regions of phase inverted thermoplastic, it can be seen that their sausage shaped appearance is the result of the epoxy and
thermoplastic debonding. When the material was cut in the microtome, these regions were sliced through and it would be expected to see an epoxy matrix with regions of thermoplastic showing localised phase inversion. This is what was seen in the AFM image in Figure 9.1.

Figure 9.17 shows the fracture surface of 15 wt% U and 0.178 wt% NT. As for the sample with 15 wt% U and 10 wt% NS there are small spheres of thermoplastic up to 4 μm in diameter, and large regions of thermoplastic which are phase inverted. The thermoplastic is poorly bonded to the epoxy as demonstrated by the voids where thermoplastic particles once were, and by the voids forming around thermoplastic particles which are still in place.

Figure 9.17: SEM images of epoxy with 15 wt% U and 0.178 wt% nanotubes taken at 500, 1000, 3000 and 5000 magnification. The arrow points to a nanotube.

When 25 wt% U is used with 0.178 wt% NT the morphology is clearly phase inverted, as shown in Figure 9.18, the thermoplastic is still not bonded to the epoxy and the epoxy spheres can be seen to have become detached from the thermoplastic. From the fracture toughness and energy results however it can be seen that there is no improvement in fracture properties from the use of U over R1 at 25 wt% just as there was no improvement at 15 wt%.
Figure 9.18: SEM images of epoxy with 25 wt% U and 0.178 wt% nanotubes taken at 500, 1000, 3000 and 5000 magnification.

When comparing the fracture toughness and energy for a sample of 15 wt% U with 10 wt% NS to the equivalent sample made with R1, the fracture toughness and energy can be seen to increase a little, from 0.82 MPa.m$^{0.5}$ and 168 J/m$^2$ for the sample with R1 to 0.97 MPa.m$^{0.5}$ and 214 J/m$^2$. This is the effect of debonding and void growth which can be seen in Figure 9.19.
Figure 9.19: SEM images of epoxy with 15 wt% U and 10 wt% nanosilica taken at 500, 1000, 3000 and 5000 times magnification. The black arrows point to voids where the thermoplastic has come away from the epoxy. The white arrow points to local phase inversion within a sausage shaped co-continuous region. The blue arrows point to thermoplastic spheres which clearly show voiding around them.

When 25 wt% U and 10 wt% NS was used the thermoplastic was as poorly bonded to the epoxy as it was for 15 wt% U. This is shown in Figure 9.20. The phase inverted morphology is also clearly shown, although the morphology appears to be very complicated. There appears to be a thermoplastic matrix in the main, epoxy particles in the thermoplastic, and sometimes thermoplastic particles in the epoxy particles. This level of complexity makes interpreting the fracture surface very difficult. Strands of thermoplastic can be seen projecting out of the surface and it is possible that these strands have been plastically deformed during the fracture process, before being broken. If this is the case, the debonding and void growth, and plastic deformation of these thermoplastic strands could help explain the increased fracture toughness and energy compared to samples made with 15 wt% U and 25 wt% R1.

The samples with U and nanotubes gave no increase in fracture toughness and energy over those with R1, but there was a significant increase for samples with U and
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nanosilica. From the images above it can be seen that the morphology for samples with nanotubes is slightly different to that for samples with nanosilica and it is thought that the change in morphology is responsible for this change in properties, especially where 25 wt% U is used, the morphology is closer to phase inverted for the nanosilica samples than for the nanotube samples. This completely thermoplastic matrix may be responsible for the increased toughness.

Figure 9.20: SEM images of epoxy with 25 wt% U and 10 wt% nanosilica taken at 500, 1000, 3000 and 5000 times magnification. The black arrow points to a plastically deformed thermoplastic strand and the white arrow points to thermoplastic spheres within epoxy particles in a thermoplastic matrix.

9.5 Conclusions.

Changing the endgroups on the thermoplastic from reactive to unreactive when adding it to epoxy nanocomposites not only has a significant effect on the morphology, but also affects the fracture and tensile properties of the polymer.
Changing the endgroup from one reactive group to another has no effect on the morphology, the thermoplastic still forms a spherical particulate morphology at 15 wt% and a co-continuous morphology at 25 wt%. It also has no effect on the tensile results with the Young’s modulus, UTS and 0.2% proof stress being unaffected. However using the thermoplastic R2 results in a significant decrease in fracture toughness and energy for most of the nanocomposites tested when compared to those using R1. There are no indications as to why this may be.

Using an unreactive endgroup has a noticeable effect on the morphology, the thermoplastic begins to become co-continuous at 15 wt% with some localised phase inversion within the thermoplastic. At 25 wt% the thermoplastic is phase inverted. It was also noted that the thermoplastic is not well bonded to the epoxy and the thermoplastic pulls away from the epoxy during testing, forming voids in many cases. The Young’s modulus is the same when using U as for R1, and this is expected as the debonding of the particles would not be expected to affect the Young’s modulus. However the UTS decreases, which could be an effect of the thermoplastic being detached from the epoxy and so the thermoplastic is not able to carry any of the applied load, increasing the load carried by the epoxy. The 0.2% proof stress is unchanged for 15 wt% U compared to 15 wt% R1 however there was insufficient plastic deformation when 25 wt% U was used for a 0.2% proof stress to be recorded. This could be the result of the effective increase in flaw size, as the material fractures before yield.

The fracture toughness and energy in general were increased when the thermoplastic was changed from R1 to U for nanosilica nanocomposites, and were unchanged for nanotube nanocomposites. There are no confirmed reasons why the nanosilica nanocomposites would show an increase in fracture properties with the use of U, while no increase is seen for nanotube nanocomposites, but the hypothesis is that it is the result of a change in morphology for nanotube composites compared to nanosilica composites. The increase seen for nanosilica composites could be related to the plastic deformation which appears to occur to the thermoplastic, and the debonding of the thermoplastic and void growth. This however does not explain why no increase is seen for the nanotube composites.
Chapter 10 Conclusions and Future Work

10.1 Conclusions

Epoxy polymers are used as adhesives and as matrices in glass and carbon fibre composites because of their high Young's moduli and good thermal stability. They also tend to have low fracture toughnesses. The work detailed in this thesis was carried out to investigate methods of toughening an epoxy polymer without reducing its thermal stability or Young's modulus. This was attempted through the addition of a thermoplastic and two different nanoparticles, nanosilica and multiwalled carbon nanotubes.

The epoxy used was a blend of a diglycidyl ether of bisphenol F and a triglycidyl aminophenol cured with an amine curing agent, MCDEA. The epoxy polymer had a glass transition temperature of around 190 °C. The thermoplastic has a similar glass transition temperature to the epoxy polymer.

The thermoplastic was added at five different percentages initially, 0, 15, 20, 25 and 35 wt%. These gave a range of morphologies from spherical particulate, through co-continuous to phase inverted. The addition of thermoplastic was found to have no effect on the Young's modulus as was hoped. It did however reduce the ultimate tensile strength. More importantly given the objective of this project, adding, and then increasing the percentage of thermoplastic increased the fracture toughness and fracture energy of the polymer. The fracture toughness increased from 0.68 MPa.m$^{0.5}$ at 0 wt% thermoplastic to 1.11 MPa.m$^{0.5}$ at 35 wt% thermoplastic, and the fracture energy rose from 214 to 531 J/m$^2$ for the same percentages of thermoplastic. The increase in fracture properties had no step changes at changes in morphology and the fracture surfaces showed that the fracture went straight through the polymer, deforming the thermoplastic but with no debonding. For the remainder of the thesis the thermoplastic was added at 0, 15 and 25 wt% so that spherical particulate and co-continuous morphologies were used. The thermoplastic was not used at 35 wt% for
Chapter 10: Conclusions and Future Work

further tests as the resin was too viscous to form usable plates after the addition of nanomodifiers.

The first problem with using carbon nanotubes is to find a way of dispersing them, and second, a method of assessing the dispersion is needed. For the epoxy system used in this project it was found that sonicating the nanotubes into the epoxy resin for 120 hours using an ultrasonic bath gave the best dispersion. The quality of the dispersion of the nanotubes in the final polymer was assessed using two methods. The first used thin sections and looked at the greyscale histogram for the sections, which examined the dispersion on a macroscale. The second method used a collage of transmission electron microscopy images of the polymers, and involved dividing the collage into quadrats. The number of nanotubes in each quadrat was counted and a statistical method was used to calculate the mean deviation, a measure of how close to random the dispersion is. It was found that when 10 different samples were tested with both of these methods and ranked, they gave almost identical results as long as a large enough area was used for the quadrat method. This ranking agreed with the appearance of the samples.

Having assessed the dispersion it was interesting to note that while the nanotubes should all have been equally well dispersed before the resin was cured, the final dispersion varied and the higher the thermoplastic content the better the dispersion. Samples of resin for several materials were cured in a hot stage on the optical microscope, so any movement of the nanotubes during cure could be seen. It was found that with no thermoplastic the nanotubes agglomerate at room temperature, before the cure cycle even starts, and as the thermoplastic content increases the temperature at which the nanotubes begin to agglomerate increases. The nanotubes stop agglomerating either when they have ‘fully’ agglomerated, or when the material reaches the gel point. The higher the thermoplastic content the higher the viscosity of the resin and the higher the temperature needed to reduce the viscosity to the level at which the nanotubes can agglomerate.

The addition of the nanosilica to the epoxy and epoxy / thermoplastic blends has given an increase in Young’s modulus from 2.6 GPa for 15 wt% R1 with 0 wt% NS to 3.8 GPa for 15 wt% R1 with 20 wt% NS. The increases seen for all three percentages of thermoplastic agree well with the modulus of the nanocomposites predicted by the Halpin-Tsai model. However it gave no increase in fracture properties, which was unexpected as nanosilica has been found to give an increase in fracture properties for
other epoxy polymers. The polymers containing nanotubes were also tested for mechanical and fracture properties. It was found that the addition of nanotubes had no effect on any of these properties, it is thought that the nanotubes are used in too small a quantity to affect the tensile properties (0.5 wt% was the highest percentage used) and since the nanosilica did not affect the fracture properties of this epoxy system there is no reason why the nanotubes would.

Samples of nanosilica nanocomposite were made using an epoxy (a diglycidyl ether of bisphenol A cured with an anhydride curing agent) which has previously been found to give an increase in fracture properties. These were tested to confirm that the test methods used in this project were not the reason that no increase in toughness had been seen for the main epoxy used. These tests showed an increase in fracture energy of 176% for 20 wt% nanosilica which agrees well with other researchers.

To investigate why one epoxy shows toughening with the incorporation of nanosilica particles while the other epoxy does not, bulk epoxy samples for both epoxies were tested in plane strain compression. From these tests it was found that the epoxy which will toughen exhibits strain softening and forms shear bands while the other does not. One hypothesis is that the ability of the epoxy to strain soften and form shear bands means that the material can form small voids around the nanoparticles during fracture. Forming these voids requires an energy input and hence the fracture energy and toughness is increased. If the material does not strain soften it does not form these voids and so does not show an increase in toughness.

Finally two different endgroups to the thermoplastic were tested. A second reactive endgroup had no effect on the morphology or tensile properties of the polymer but it did lead to a slight decrease in fracture properties, but the reasons for this remain elusive. The unreactive endgroup resulted in a decrease of the ultimate tensile strength which could be the result of the thermoplastic becoming detached from the epoxy during testing. It also resulted in an increase in the fracture toughness and energy when nanosilica was added. It is thought that this is the effect of the morphology for samples with U being different from the morphology of the material with the same weight percentage of R1.
10.2 Future work

It appears that while some epoxy polymers will toughen with the addition of nanosilica, others will not and the main areas for future research are related to this. The hypothesis put forward in this thesis is that the ability of an epoxy to be toughened by nanoparticles is related to the ability of that epoxy to form voids around these particles. Microscopy on a variety of samples which have shown toughening, and samples which have not, to identify any void growth would be very useful to help confirm this theory. It has also been suggested that the ability of a material to show strain softening and shear banding is related to the ability to show toughening. Further tests on other formulations to confirm a link between these properties and toughening is needed.

Having found that the epoxy used throughout this thesis will not show toughening it is unsurprising that no toughening is seen with the addition of nanotubes. Testing nanotubes in other epoxy systems which are known to show toughening would be important work for future investigations. This would be to see if nanotubes can toughen an epoxy and also to investigate the toughening mechanisms which occur in nanotube composites.

If the addition of nanotubes is found to improve the toughness of some epoxy polymers, it is important to find any relationship between the final dispersion of the nanotubes and the fracture toughness and energy of the final polymer. There is currently no standard method for controlling the dispersion of nanotubes, both the initial dispersion achieved and the agglomeration which occurs during curing need to be controlled and an effective method for doing this needs to be found. If epoxy resins with carbon nanotubes are to be used in carbon fibre composites, and the dispersion of the nanotubes is found to be important, then needing the viscosity of the epoxy to be high to prevent agglomeration will preclude the resin from being of any use, as it will not be able to infuse into the composite. A method of controlling the dispersion of nanotubes in a low viscosity resin will be needed. One possibility would be to investigate the effects of surface treatment of the nanotubes as this has been found to work for nanosilica.

Finally, having established an epoxy / thermoplastic / carbon nanotube system which has the required fracture toughness, fracture energy and tensile properties, tests will need to be carried out on the polymer to investigate the mechanisms involved in the
failure. Investigations should include whether the nanotubes are pulled out of the epoxy, and if so if they have a layer of epoxy coating them. It would also be interesting to see if the outer tube of the nanotubes is breaking and the inner tubes are pulling out in the way of a telescope. It would be useful to carry out mechanical and fracture tests on carbon fibre composites formed using this resin to ensure that these property improvements are transferred to the composite, and microscopy to see how these composites fail.
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Appendix 1: SENB Analysis

Single edge notched bend specimen analysis example. Analysis of sample 084-60-A, 25 wt% U, 10 wt% NS

Boxes highlighted in yellow need data to have imputed

| A  | B  | C  | D  | E  | F  | G  | H  | I  | J  | K  | L  | M  | N  | O  | P  | Q  | R  | S  | T  | U  | V  | W  | X  | Y  | Z  |
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</tr>
</tbody>
</table>

**Figure**

\[ y = 172.09x - 16.594 \]

\[ R^2 = 0.9986 \]
Summary of the repeat tests for 084-60-A showing all the data at the top, underneath the chosen data, leaving out sample 3 which did not comply with the requirement for $0.45 < \alpha/w < 0.55$.

|   | A | B | C | D | E | F | G | H | I | J | K | L | M | N | O | P | Q | R | S | T | U | V | V | X | Y |
| 1 |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |
| 2 |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |
| 3 |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |   |
| 4 | yield stress (MPa) | Slope (N/mm) | St offset (N/mm) | Indentation slope (N/mm) | Displacemen t @ PQ | Load @ PQ | Load @ Fq | PMAX/Fq | K | f(d) | 2.5[Ker] | A | dAnd | C | Cl | Co-Ci | U frac | U ind | U actual | G - Energy | G -LEFM method | E frac | E stiff |
| 5 | 45.00 | 172.09 | 163.49 | 907.00 | 0.40 | 36.73 | 36.73 | 1.00 | 1.20 | 0.75 | 1.77 | 0.26 | 31.32 | 190.76 | 0.01 | 0.00 | 0.00 | 4.07 | 0.73 | 3.34 | 426.35 | 359.25 | 2184.61 | 3910.67 |
| 6 |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |
| 7 | 45.00 | 176.13 | 167.32 | 907.00 | 0.36 | 36.44 | 36.44 | 1.00 | 1.23 | 10.09 | 1.88 | 0.26 | 33.49 | 203.86 | 0.01 | 0.00 | 0.00 | 2.92 | 0.46 | 2.44 | 422.85 | 381.31 | 2602.01 | 3963.00 |
| 8 | 45.00 | 143.32 | 136.16 | 907.00 | 0.39 | 29.12 | 29.12 | 1.00 | 0.87 | 0.77 | 0.94 | 0.28 | 20.28 | 154.47 | 0.01 | 0.00 | 0.01 | 3.12 | 0.46 | 2.62 | 232.67 | 191.76 | 1545.56 | 2256.09 |
| 9 | 45.00 | 162.99 | 154.84 | 907.00 | 0.38 | 36.22 | 36.22 | 1.00 | 1.16 | 9.19 | 1.87 | 0.27 | 27.71 | 163.44 | 0.01 | 0.00 | 0.01 | 4.10 | 0.71 | 3.28 | 440.02 | 338.52 | 1954.55 | 2752.19 |
| 10 | 45.00 | 180.57 | 171.54 | 907.00 | 0.35 | 34.04 | 34.04 | 1.00 | 1.27 | 10.82 | 2.00 | 0.24 | 38.33 | 233.84 | 0.01 | 0.00 | 0.01 | 3.67 | 0.55 | 2.92 | 420.86 | 406.19 | 2502.21 | 3843.28 |
| 11 |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |
| 12 |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |
| 13 | mean | 45.00 | 167.02 | 158.67 | 907.00 | 0.38 | 34.51 | 34.51 | 1.00 | 1.95 | 9.72 | 1.85 | 0.26 | 31.20 | 190.47 | 0.01 | 0.00 | 0.00 | 3.55 | 0.61 | 2.94 | 386.35 | 335.41 | 2257.79 | 3046.05 |
| 14 | Standard deviation | 0.00 | 14.75 | 14.01 | 0.00 | 0.02 | 3.20 | 3.20 | 0.00 | 0.16 | 0.90 | 0.41 | 0.02 | 5.13 | 30.82 | 0.00 | 0.00 | 0.05 | 0.54 | 0.12 | 0.42 | 58.92 | 54.16 | 567.54 | 613.60 |
| 15 |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |
| 16 |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |
| 17 | Selected data - samples complying with all the relevant conditions |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |
| 18 |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |
| 19 |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |
| 20 |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |
| 21 |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |
| 22 |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |
| 23 |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |
| 24 |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |
| 25 | mean | 45.00 | 172.95 | 164.2978 | 907.00 | 0.3738475 | 35.856373 | 35.856373 | 1 | 1.20 | 0.96 | 0.86 | 1.8284 | 226.944 | 0.01 | 0.00 | 0.00 | 3.66 | 0.64 | 3.02 | 462.57 | 371.18 | 2435.85 | 3256.287282 |
| 26 | Standard deviation | 7.49594 | 7.11463 | 0.020363431 | 1.2282419 | 1.228242 | 0.020363431 | 0.09473 | 0.69 | 0.14319 | 0.01 | 4.44 | 26.947 | 0.00 | 0.00 | 0.00 | 0.54 | 0.11 | 0.43946 | 53.71 | 20.727 | 467.026 | 455.3444621 |

Data highlighted in green, the final data used, values for $K_c$, $G_c$ calculated for $K_c$, and $G_c$ calculated from the energy method.
Appendix 2: Greyscale Results

Results from the greyscale analysis.

0 wt% R1, 0.1 wt% NT

spread: 140 (14-154)
S.D.: 29.9

0 wt% R1, 0.178 wt% NT

spread: 149 (9-158)
S.D.: 17.7
0 wt% R1, 0.336 wt% NT

spread: 163 (12-175)
S.D.: 29.7

0 wt% R1, 0.5 wt% NT

spread: 130 (4-134)
S.D.: 31.9
15 wt% R1, 0.1 wt% NT dispersed in thermoplastic

spread: 165 (7-172)
S.D.: 43.4

15 wt% R1, 0.1 wt% NT sonicated into epoxy

spread: 142 (24-166)
S.D.: 27.2
15 wt% R1, 0.178 wt% NT dispersed in thermoplastic

spread: 167 (9-176)
S.D.: 41.9

15 wt% R1, 0.178 wt% NT sonicated into epoxy

Spread: 156 (5-161)
S.D.: 29.4
15 wt% R1, 0.336 wt% NT sonicated into epoxy

spread: 173 (8-181)
S.D.: 20.7

Histogram

Display channel:
Greyscale
Value(s):
% in Range:
% Below:
% Above:
Mean: 52
Median: 48

25 wt% R1, 0.1 wt% NT dispersed in thermoplastic

spread: 152 (5-157)
S.D.: 20.1

Histogram

Display channel:
Greyscale
Value(s):
% in Range:
% Below:
% Above:
Mean: 63
Median: 60
25 wt% R1, 0.1 wt% NT sonicated into epoxy

![Histogram](image)

spread: 86 (82-168)
S.D.: 10.8

25 wt% R1, 0.178 wt% NT dispersed in thermoplastic

![Histogram](image)

spread: 144 (18-162)
S.D.: 23.8
25 wt% R1, 0.178 wt% NT sonicated into epoxy

spread: 76 (55-131)
S.D.: 8.9

25 wt% R1, 0.336 wt% NT dispersed in thermoplastic

spread: 168 (7-175)
S.D.: 16.3
25 wt% R1, 0.336 wt% NT sonicated into epoxy

spread: 152 (17-169)
S.D.: 20.1
Appendix 3: Quadrat Results

Graphs from quadrat analysis

0 wt% R1, 0.178 wt% NT

Mean deviation: 1.2-1.8, range: 0.6

15 wt% R1, 0.1 wt% NT dispersed in thermoplastic

Mean deviation: 1.0-1.3, range: 0.3
15 wt% R1, 0.1 wt% NT sonicated into epoxy

Mean deviation: 1.1-2.2, range: 1.1

15 wt% R1, 0.178 wt% NT dispersed in thermoplastic

Mean deviation: 1.7-12.1, range: 10.4
15 wt% R1, 0.178 wt% NT sonicated into epoxy

Mean deviation: 2.2-5.9, range: 3.7

15 wt% R1, 0.336 wt% NT sonicated into epoxy

Mean deviation: 1.2-2.1, range: 0.9
25 wt% R1, 0.1 wt% NT dispersed in thermoplastic

Mean deviation: 1.2-1.8, range: 0.6

25 wt% R1, 0.178 wt% NT dispersed in thermoplastic

Mean deviation: 1.2-1.9, range: 0.7
25 wt% R1, 0.178 wt% NT sonicated into epoxy

Mean deviation: 1.4-1.7, range: 0.3

25 wt% R1, 0.336 wt% NT dispersed in thermoplastic

Mean deviation: 1.2-1.7, range: 0.5