This is the published version:


Available from Deakin Research Online:

http://hdl.handle.net/10536/DRO/DU:30045112

Reproduced with the kind permission of the copyright owner.

Copyright : 2012, Nova Science Publishers
Chapter 8

ON TOUGHENING OF EPOXIES AND THEIR CARBON FIBRE-REINFORCED COMPOSITES

Jin Zhang*, Tong Lin and Xungai Wang
Centre for Material and Fibre Innovation, Deakin University,
Geelong, VIC 3217, Australia

ABSTRACT

Epoxy resins were introduced commercially in the late 1940s and have been used widely in industrial applications, including fibre-reinforced polymer matrix composites, adhesives and coatings. While epoxies have numerous advantages, they suffer from brittleness as a result of their high crosslink polymer structure. The present work is a brief review of the toughening methods used previously to improve the crack growth resistance of epoxies and their fibre reinforced composites. Toughening agents discussed include rubbers, inorganic fillers, thermoplastics and hyperbranched polymers. The chapter provides the state-of-the-art knowledge in this field as well as indicates the future directions towards improving the fracture toughness of epoxies.

1. INTRODUCTION

Epoxy resins are predominately used as matrices in aerospace polymer matrix composites, because of their excellent adhesion to carbon fibres, low shrinkage on curing, high chemical and corrosion resistances and good mechanical and thermal properties [1, 2]. However, their brittle nature resulted from the highly crosslinked structure limits their applications in high performance composites where superior impact resistance is critical. Modification of thermosetting epoxy matrices is crucial in material development aiming at reducing the delamination tendency of composite structures [3].

Many types of filler from inorganic materials, rubbers and thermoplastics have been used previously for toughening epoxy resins. Among them, thermoplastic shows great advantages,
since they can significantly toughen epoxies without compromising the thermal-mechanical properties, elastic modulus and yield stress, which is usually associated with rubber toughening [4]. For that reason, high performance thermoplastics have served as toughening agents for modifying brittle epoxies for over 20 years. Thermoplastic toughening is generally achieved through phase separation of an initially homogeneous thermoplastic/epoxy blend, which leads to the formation of different phase structures such as particulate (discrete thermoplastic particles dispersed in the epoxy matrix), co-continuous and phase inverted morphologies, depending on factors such as the composition of the initial blend, the cure temperature, the competition between the rate of cure and the rate of phase separation, and the diffusion rate [5, 6].

In this review, previous research on toughening of carbon/epoxy composites using thermoplastics, hyperbranched polymer and thermoplastic nanofibres is summarized. The phase morphology, thermal-mechanical property, toughening effect and mechanism are discussed for the toughening of multifunctional epoxies with different modifiers.

2. RUBBER AND INORGANIC TOUGHENING FILLERS

As early as the 1970’s, Sultan et al. [7] first reported their work on using a soft rubbery particulate phase to improve the crack resistance of epoxy resins. Two main methods have been used to apply rubber to epoxy, such as using reactive oligomers and preformed elastomeric particles. In the first approach, toughening is achieved by the generation of a second particulate phase during curing of an epoxy that contains initially dissolved reactive oligomer. Liquid rubber copolymers of butadiene-acrylonitrile with various functional end groups, including carboxyl-terminated group (CTBN) [8, 9], amine terminated group (ATBN) [10], epoxy terminated group (ETBN) [11], hydroxyl-terminated group (HTBN) [12] and vinyl-terminated group (VTBN) [13], have been intensely studied as modification agents. In the second approach, preformed elastomeric particles such as core-shell particles with a rubbery core and a glassy shell have been employed, where the particle size, volume fraction and handling characteristics can be better controlled [14]. Recent progress has been made when block copolymers are incorporated into rubber modifiers which can self-assemble into hierarchical nanostructures such as vesicles, spherical micelles and worm-like micelles [13, 15, 16]. This field of research requires further study to examine their applicability in toughening of epoxies.

A number of theories have been proposed to explain the toughening mechanism of rubber modification. Particle cavitations and shear yielding is the most accepted theory currently. The cavitations of rubber particles releases the hydrostatic tension in resin matrix, with the stress state between voids being converted from a triaxial to a more uniaxial tensile state, which is favourable for the initiation of shear bands [17]. Improved toughness is obtained through effective energy dissipation at the crack tip as a result of shear yielding.

Rubber modifiers are able to increase the fracture toughness of epoxies effectively. In contrast to unmodified epoxies, however, they also cause deterioration in other important properties, such as modulus and glass transition temperature of the modified epoxies. As an alternative, engineering thermoplastics demonstrates great advantages by enhancing the
fracture toughness as well as maintaining the desired properties, which is favourable when high thermal stability and toughness are both needed for industry applications.

Besides rubber, several inorganic toughening agents, such as glass beads, alumina, silica, barium titanate, dolomite, aluminium hydroxide have also been considered for toughening epoxies [18, 19]. To enhance the modulus, strength and toughness of rubber modified epoxies, inorganic fillers have been added to prepare hybrid systems. Recently, inorganic nanofillers have been widely investigated as the modifiers of epoxies. Polymer nanocomposites, as a new family of engineering materials, have attracted intense attention in both industry and research field. Depending on their nanostructures, nanofillers can be divided to three types. For example, montmorillonite clay falls into the two dimensional category [20], carbon nanotubes [21], carbon nanofibres and cellulose whiskers belong to the one dimensional nanofillers, and spherical silica nanoparticles are typical zero dimensional nanofillers. Apart from increased toughness in epoxies, significantly enhanced strength and modulus can be achieved, and new functionality may also be added to the system. Nanofillers constrain the matrix deformation less than the micro particles, because their smaller size allows them to integrate better into the polymer microstructure. They may influence the deformation of matrices on nano or micro scales, based on their more or less strong interaction with the matrices [22].

3. THERMOPLASTIC TOUGHENING AGENTS

Thermoplastic toughening has been widely used in aerospace industry because it enhances toughness without significantly compromising other desirable properties of epoxies such as high modulus and high glass transition temperature. The toughening result is achieved by phase separation of an initially homogeneous blend of thermoplastics and epoxies. The phase separation process of thermoplastic/epoxy blends has been studied extensively. Nucleation and growth (NG), spinodal decomposition (SD), or a mixed mode of both can occur during the separation process [5, 23]. When its concentration is low, the thermoplastic modifier tends to segregate from the matrix by the NG mechanism. For blends containing higher thermoplastic content, phase separation proceeds by more complex SD mechanism and leads to co-continuous or phase inverted morphology [24]. Different types of thermoplastics have been used as toughening agents in epoxies, including polyethersulphones [25, 26], polyetherimides [27], polyester [28], polyacryletherketone [29], and polyhydration [30].

3.1. The Influence of Processing Rates

The end mechanical properties are directly related to the phase behaviour of epoxy/thermoplastic blends. By controlling various parameters such as thermoplastic concentration, molar mass, curing temperature and reaction rate, it is possible to generate various phase morphologies, which result in different mechanical properties. Several studies have been conducted to investigate the influence of cure rate on the phase separation mechanism of thermoplastic modified epoxy systems. Jo et al. [31] applied a simulation approach to study the effect of reactivity on the phase separation behaviour. Girard-Reydet et
al. [32] selected cure temperature as a parameter to change the cure rate. Peng et al. [33] changed the cure temperature and the amount of cure agent to modify the cure rate. Zhang et al. [34-36] used heating rate as a variable to investigate the effect of cure rate on the cure kinetics and phase morphology of polyether sulphone (PES) modified multifunctional epoxies, triglyceridyl aminophenol (TGAP) and tetraglycidyl diamino diphenylmethane (TGDDM), cured with 4,4'-diamino diphenylsulfone (DDS). Thermoplastic/epoxy blends were prepared by solution casting from methylene chloride at room temperature. The blends were dried in a vacuum oven at 50 °C for 15 hours to remove the trace solvent. Polymer blends were cured with two heating rates, i.e. a low heating rate of 1.5 °C/min and a high heating rate of 10 °C/min. The cure temperature was 175 °C. The cure kinetics was investigated by performing real-time Fourier transform infrared spectroscopy (FTIR). The oxirane ring stretching mode at 908 cm⁻¹ was used for measuring the conversion of epoxy groups.

For a TGAP/PES/DDS (100/30/30 w/w) blend, the cure kinetics following with different cure schedules can be seen in Figure 1. The slow temperature rise (1.5 °C/min) resulted in a very slow epoxy conversion which can almost be seen as zero in the first 80 min. The epoxy conversion of the blend heated at 10 °C/min reached a plateau when it was heated for 40 min. The final conversion after the blend was heated at 175 °C for 60 minutes was 0.865 for the cure with the heating rate of 10 °C/min, but was 0.807 for the cure with lower heating rate.

![Figure 1. Cure kinetics followed with different cure schedules of the TGAP/PES/DDS (100/30/30) blend: I. heating stage (from 20 °C to 175 °C); II. isothermal curing stage (at 175°C) [34].](image)

The Tg vs conversion curve was followed by DSC which is shown in Figure 2. The Tg vs conversion relationship shows increase in the concentration of branching points and high-functional crosslink as a function of conversion [37]. The data points were simulated by using an MMF function within the sigmoidal regression models' family which is shown in equation 1:

\[ Y = \frac{ab + cx^d}{b + x^d} \]  

(1)
where \( a, b, c \) and \( d \) are fitting parameters. The initial formulation exhibits a shift in the baseline at \( T_{g0} = -24.9 \, ^\circ C \). \( T_g \) increases with cure time at the constant temperature \( (175 \, ^\circ C) \). After the blend is cured for 320 minutes, the \( T_g \) value increases to 194.8 \, ^\circ C \). The conversion of the specimens is defined by:

\[
\alpha = 1 - \frac{-\Delta H_R}{-\Delta H}
\]

where \( -\Delta H \) is the reaction heat for the initial formulation, and \( -\Delta H_R \) is the residual reaction heat measured from the partially cured specimens.

![Graph](image)

Figure 2. \( T_g \) as a function of conversion for the TGAP/PES/DDS (100/30/30) blend cured at 175\,^\circ C for different times. The solid line is the curve simulated using equation 1 (The values of the fitting parameters are: \( a = -28.45 \), \( b = 0.046 \), \( c = 213.77 \), and \( d = 2.84 \)) [34].

A phase contrast optical microscope was employed to investigate the morphology evolution. To slow down the phase separation process for observation, a specimen was chosen to be monitored at 160 \, ^\circ C \) (a heating rate of 10 \, ^\circ C/min was used to heat up the specimen). As shown in Figure 3, the blend remained homogeneous after 56 minute heating at 160 \, ^\circ C \). Phase separation started at 70 minutes. A co-continuous phase structure was observed at 72 minutes, indicating that the phase separation was likely to take place via a spinodal decomposition mechanism. As the curing reaction proceeded, the periodic distance of the co-continuous structure increased. The growing macrophases connected to each other to form larger phases. In the mean while, fine particles started to appear and dispersed in both the dispersed macrophase and the matrix macrophase. These visible particles imply that second and possibly third stage of microphase separation continued to proceed after the primary macrophase separation. At 79 minutes, the morphology was finally fixed in which the irregular macrophases dispersed in a continuous matrix macrophase.
Figure 3. The process of phase separation of the TGAP/PES/DDS (100/30/30) blend monitored by a phase contrast optical microscope at 160 °C [34].

Figure 4 shows the optical and SEM images for this blend cured with two different heating rates. Optical images provide a two-dimensional view of the phase structure. For comparison, an image processing software (ImagePro+ 4.5.1) was used to measure the domain size and the percent area occupied by the dispersed macrophases.
Figure 4. Optical and SEM morphologies of the cured TGAP/PES/DDS (100/30/30) blend. The SEM images were taken on the etched fracture surface: (a1 and a2) heating rate: 1.5 °C/min; (b1 and b2) heating rate: 10 °C/min [34].

Table 1. Comparison of macrophase size and distribution in the cured TGAP/PES/DDS (100/30/30) blend [34]

<table>
<thead>
<tr>
<th>Cure with a heating rate of 1.5°C/min</th>
<th>D$_{\text{mean}}$ (nm)</th>
<th>Area$_{\text{mean}}$ (μm$^2$)</th>
<th>Percentage area (%)</th>
<th>No. of dispersed macrophases</th>
<th>Size in length (μm)</th>
<th>Size in width (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average</td>
<td>9.67</td>
<td>107.80</td>
<td>14.94</td>
<td>202</td>
<td>12.30</td>
<td>8.08</td>
</tr>
<tr>
<td>Standard deviation</td>
<td>0.64</td>
<td>11.22</td>
<td>1.33</td>
<td>15</td>
<td>0.76</td>
<td>0.64</td>
</tr>
<tr>
<td>Cure with a heating rate of 10°C/min</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Average</td>
<td>11.41</td>
<td>162.75</td>
<td>18.74</td>
<td>167</td>
<td>14.60</td>
<td>9.35</td>
</tr>
<tr>
<td>Standard deviation</td>
<td>0.62</td>
<td>11.87</td>
<td>1.98</td>
<td>17</td>
<td>0.60</td>
<td>0.66</td>
</tr>
</tbody>
</table>

The results are shown in Table 1. With an increase in the heating rate, the number of the dispersed macrophases became smaller. However, the domain size becomes larger and the percent area occupied by the dispersed macrophases became larger as well. The reason is that when the system is cured under a linear rise of temperature, a slow temperature rise leads to longer curing time at lower temperatures [12]. The SEM images show a three dimensional view of the phase-separated structure. Since the thermoplastic phase was etched away, it can
be seen that there existed two different types of macrophases. The epoxy micro-particles within the PES-rich macrophase and the cavities in the epoxy-rich macrophase left by the PES-rich particles can be seen in these structures.

Figure 5 demonstrates the possible toughening mechanism in the TGAP/PES/DDS (100/30/30) blend. The material can be improved in its toughness by increasing the plastic deformation ability of the material. The idea is to initiate a very large number of small local yield events [38]. In this case, PES-rich particles were plastically stretched in the area of the crack tip to prevent premature crack propagation, hence increasing the toughness of epoxy. SEM images show the actual examples of the plastically deformed PES-rich particles which contribute to the toughening effect.

![Figure 5. Toughening mechanism as observed in the TGAP/PES/DDS (100/30/30) blend cured with the heating rate of 10 °C/min. The illustrative graph was redrawn from [38]. A and b in the SEM images correspond with a and b in the illustrative graph [34].](image)

SEM observation reveals that more and larger cavities were left in the blend when heating at a higher ramp rate. It suggests a more complete and higher degree of phase separation occurring in the rapidly heated blend. It has been found that phase separation is inhibited when the blend is of high viscosity which results in none or incomplete phase separation [24]. Significant decrease in the minimum viscosity has been demonstrated by applying a higher heating rate [39], which may assist with achieving a more complete phase separation.

For a TGAP/TGDDM/PES/DDS (90/10/30/30) blend, the cure kinetics at different heating rates is shown in Figure 6. The heating rate had a great influence on the cure process. At the low heating rate of 1.5 °C/ min, the cure reaction took place by two stages as evidenced by the two-step conversion rise monitored by FTIR. This is caused by the presence of more reactive tetrafunctional resin - tetraglycidylidaminoiphendiphenylmethane (TGDDM). Slower temperature ramp drove the possibility to separate particularly curing processes of
TGDDM and TGAP. The final epoxy conversion after the blend was heated at 175 °C for 60 minutes is 0.875 for curing with the heating rate of 10 °C/min, which was higher than 0.853 for curing with the heating rate of 1.5 °C/min. The Tg vs conversion curve is displayed in Figure 7. Tg increased from 20.7 °C to 178.8 °C with the increase in curing time from 0 minute to 320 minutes at 175 °C. A heating rate of 10 °C/min was used for the cures.

The cured TGAP/TGDDM/PES/DDS (90/10/30/30) blend showed a finer phase separation structure compared to the TGAP/PES/DDS (100/30/30) blend. The morphologies in Figure 8 display a co-continuous phase structure. The periodic distance of the macrophases for the blend heated at 10 °C/min was longer than that heated at 1.5 °C/min.

Figure 6. Cure kinetics following with different cure schedules of the TGAP/TGDDM/PES/DDS (90/10/30/30) blend: I. heating stage (from 20 °C to 175 °C); II. isothermal curing stage (at 175 °C) [34].

Figure 7. Tg as a function of conversion for the TGAP/TGDDM/PES/DDS (90/10/30/30) blend cured at 175 °C for different times. The solid line is the curve simulated using Equation 1 (the values of the fitting parameters are: a = -23.93, b = 0.015, c = 183.52, d = 2.02) [34].
The epoxy micro-particles within the PES-rich macrophase and the PES-rich particles within the epoxy-rich macrophase indicate further phase separation after the primary phase separation. The SEM images of the un-fractured surface for the fast heated specimen (after etching) show more cavities left due to the removal of PES-rich particles.

Similar phenomena were found on the aerospace composite system HexPly914. This commercial composite prepreg consists of carbon fibres (Torayca T300H) embedded within a blend of TGDDM (MY720) and TGAP (ERL0510) hardened with dicyandiamide (DICY) and/or DDS, to which is added a small percentage of PES. Due to the existence of residual carbon fibres, there were interferences in the conversion versus time curves shown in Figure 8. As for the sample heated at 1.5 °C/min, the epoxy conversion started to reach a plateau when the temperature increased to 175 °C. However, the epoxy conversion of the sample material heated at 10 °C/min seemed to keep increasing even after 60 minutes of curing at 175 °C. The final epoxy conversion after the sample was cured at 175 °C (for 60 minutes) was 0.849 for the rapidly heated material and was 0.595 for the slowly heated one. To ensure the complete cure of the HexPly914 composite, a post heat treatment at 190 °C for 4 hours is required.

![Figure 8. Cure kinetics following with different cure schedules of the T300/914 prepreg: I. heating stage (from 20 °C to 175 °C); II. isothermal curing stage (at 175°C) [34].](image)

Composite laminates laid up with the HexPly914 prepregs were cured at heating rates of 1.5 °C/min or 10 °C/min, followed by a post-curing treatment at 190 °C for 4 hours. SEM observation on the delaminated fracture surface reveals a connected-globule phase-separated structure (Figure 9).

The domain sizes of these microphases, i.e. epoxy globules, are quite uniform, around 0.88 µm for the fast heated specimen, which is slightly larger than those of the slowly heated specimen (0.80 µm).
Figure 9. SEM morphology of delamination fracture surface after etching treatment. Composite specimen HexPly914, cured with heating rates of (a) 1.5 °C/min and (b) 10 °C/min.

3.2. Interlayer Toughening by Using Thermoplastic Nanofibres

Two main strategies to toughen thermosetting matrix composites have been developed: blending a toughener with the matrix resin [40-42] or incorporating a discrete toughening interlayer between composite plies [43-45]. The addition of tougheners to the entire matrix resin could lead to the decrease in in-plane compression and shear strengths. The increased viscosity arising from the addition of tougheners could also reduce the processing ability of matrix resin. However, interlayer toughening is less likely to cause those issues, and it is thus used increasingly in the composite industry. Indeed, several interlayer toughening methods have been developed, such as using thermoplastic or thermosetting films [46, 47], porous membranes [48], and rubber and/or thermoplastic particles [49, 50]. Zhang et al. [51] used electrospun polyetherketone cardo (PEK-C) nanofibres to improve the interlaminar fracture toughness of carbon/epoxy composites. In this work, PEK-C nanofibres were directly deposited onto carbon fabrics. The effects of nanofibre diameter and interlayer thickness on the mode I delamination fracture toughness, flexural property and thermal mechanical properties of the resultant composites were examined.

Electrospun PEK-C nanofibres were obtained from PEK-C solutions with various PEK-C concentrations. The nanofibre morphologies are shown in Figure 10. It has been established that electrospinning a polymer solution could result in individual beads, beads-on-structure and bead-free fibres [52].
In the case of PEK-C solution, a similar trend on the fibre morphology was also observed. For example, electrospinning of 10 wt% PEK-C solution in N, N-dimethylformamide led to beads-on-string fibres. When the PEK-C concentration was larger than 20 wt%, bead-free uniform nanofibres were produced. With an increase in the PEK-C concentration from 20 wt% to 30 wt%, the average fibre diameter increased from 275 nm to 950 nm, respectively.

PEK-C nanofibres were directly electrospun onto dry carbon fabrics to form a randomly orientated nanofibre nonwoven membrane, and they served as an interlayer toughening agent for preparing carbon/epoxy composite laminates. To investigate the influence of fibre diameter on the mechanical performance of interlayer toughened composites, PEK-C nanofibres with average diameters of 450 nm, 750 nm and 950 nm were used. With an equal weight loading of PEK-C nanofibres on the carbon fabric, the effects of fibre diameter on the Mode I delamination fracture toughness and flexural properties were examined. To achieve approximately 0.44% weight fraction of PEK-C nanofibres in the composite laminates, the electrospinning time for different polymer concentrations varied. The average interlayer thickness of the cured composite laminates was 58 μm, 65 μm and 70 μm for the membranes with fibre diameters of 450 nm, 750 nm and 950 nm, respectively.

Figure 11a reveals the delamination resistance curves for both the control and the composite laminates modified by nanofibres with different diameters. For the control specimen, there existed a considerable scatter in the calculated critical strain energy release rate $G_{IC}$ from mode I double cantilever beam (DCB) tests, which was attributed to the $[0/90]_4$ carbon fibre orientation and the bonding stitches pre-existing in the carbon fabrics [53, 54]. Compared with the control, the PEK-C nanofibre modified composite specimens showed increased $G_{IC}$. The delamination resistance curves showed unstable crack growth and the
stick/slip fracture behaviour. The fluctuation of the delamination resistance curves became more significant as the fibre diameter increased.

Figure 11. Delamination fracture toughness of the composite specimens [51].

Visual detection was applied as the criteria to define the initiation of crack propagation. The strain energy release rates for crack initiation (\(G_{IC-INI}\)) and for crack propagation (\(G_{IC-PROP}\)) influenced by nanofibre diameter were compared and included in Figure 12a. The average \(G_{IC-INI}\) for the control specimen was 151 J/m², whereas the \(G_{IC-INI}\) value for the nanofibre-modified specimens with average fibre diameters of 450 nm, 750 nm and 950 nm was 249 J/m², 228 J/m² and 241 J/m², respectively, indicating increased \(G_{IC-INI}\) value for the nanofibre-modified composite specimens. The presence of nanofibre interlayer also led to increased average \(G_{IC-PROP}\). Here, since the weight loading of the nanofibres in the nanofibre-modified specimens was less than 1 wt% (around 0.4 wt%), the improvement in \(G_{IC-INI}\) and \(G_{IC-PROP}\) due to such a low interlayer weight loading is quite significant.

Figure 12. Mode I delamination fracture toughness and flexural properties of nanofibre modified composites as a function of (a) nanofibre diameter and (b) interlayer thickness. —— \(G_{IC-INI}\); —— \(G_{IC-PROP}\); —— elastic modulus (E¹*GPa); —— flexural strength (MPa). The dotted lines underneath different properties indicate the corresponding average data for the control composite specimen [51].

The effect of fibre diameter on the flexural strength and elastic modulus is also shown in Figure 12a. By comparison with the control specimen, the flexural strength of the nanofibre-modified specimens decreased slightly when the average nanofibre diameter increased from 450 nm to 750 nm. However, a noticeable decrease in the flexural strength was observed in
the specimen with a larger average fibre diameter (950 nm). Similarly, a considerable reduction in the elastic modulus was observed when coarse nanofibres (e.g. 950 nm) were employed as interlayers. This suggested that composites modified with finer nanofibres had greater improvement in the interlaminar property without compromising the in-plane performance of the toughened composites.

The interlayer thickness was adjusted through the electrospinning time. Here nanofibres with the average diameter of 950 nm were chosen. With an increase in the electrospinning time from 23 min, to 46 min and 68 min, the average interlayer thickness of the cured composite laminates changed from 40 μm, to 70 μm and 105 μm, which led to changes of the $G_{IC-\text{ini}}$ from $198 \text{ J/m}^2$, to $241 \text{ J/m}^2$ and $236 \text{ J/m}^2$ and the $G_{IC-\text{prop}}$ from $272 \text{ J/m}^2$, to $296 \text{ J/m}^2$ and $376 \text{ J/m}^2$. In comparison with the control specimens, whose $G_{IC-\text{ini}}$ and $G_{IC-\text{prop}}$ values are $151 \text{ J/m}^2$ and $207 \text{ J/m}^2$, respectively, the presence of nanofibre interlayer resulted in higher delamination fracture toughness (Figures 11b and 12b). It was also noted that the weight fraction of PEK-C in the cured composites was approximately 0.22 %, 0.44 % and 0.65 % for the laminates with an average interlayer thickness of 40 μm, 70 μm and 105 μm, respectively. The influence of interlayer thickness on the flexural properties is also shown in Figure 12b. Both the flexural strength and the elastic modulus showed a decreasing trend as the nanofibre interlayer thickness increased.

Figure 13a shows the morphology of the delaminated control specimen, and the phase morphologies of delaminated composite specimens toughened by PEK-C nanofibres with average diameters of 450 nm, 750 nm and 950 nm are shown in Figure 13b, 13c and 13e, respectively. In contrast to the control specimen, PEK-C-rich particulate phases with various sizes were shown on the delamination fracture surface of modified composites. Despite the equal weight loading of the PEK-C nanofibres, the size of PEK-C-rich phases and their distance increased with the increase in the fibre diameter.

It should be noted that the penetration of epoxy at room temperature did not lead to dissolution or “deterioration” of nanofibres and PEK-C nanofibres started dissolving into the epoxy resin as the curing temperature increased to 70 °C. However, the high viscosity of PEK-C retained the diffusion of dissolved PEK-C into the epoxy resin, which led to unique phase structure after curing. Coarser nanofibres caused higher local concentration of PEK-C in epoxy resin, resulting in larger PEK-C-rich particulate phases as revealed on the delamination fracture surface. The PEK-C-rich phases create stress concentrations at their equators and also act as sites for initiating shear bands. When the shear bands created by one toughener-enriched phase interact with another, they may stop propagating and keep the matrix yielding localized [18, 55]. Therefore the cracks were hindered intermittently by the PEK-C-rich phases and forced to propagate between two unstable jumps. The membrane composed of finer fibre diameters gave rise to reduced distance between the ductile PEK-C-rich phases, which assisted with maintaining a more stable crack growth during delamination. Analogous findings were reported where poly(acrylonitrile-butadiene-styrene) particles (ABS) particles were used for interlayer toughening of glass fibre/vinyl-ester resin composites [56]. By using particles with a similar size, the stability of crack propagation was improved by increasing the particle concentration in the interlayer. Figures 13d, 13e and 13f show the morphology of delamination fracture surface influenced by nanofibre interlayer thickness. Larger PEK-C-rich phases were observed to scatter on the fracture surface of thicker nanofibre interlayer.
Figure 13. SEM images of delamination fracture surface. (a) Control composite specimen; (b–f) nanofibre-modified composites; (b) fibre diameter: 450 nm, interlayer thickness: 70 μm; (c) fibre diameter: 750 nm, interlayer thickness: 70 μm; (d) diameter: 950 nm, interlayer thickness: 40 μm; (e) fibre diameter: 950 nm, interlayer thickness: 70 μm; (f) fibre diameter: 950 nm, interlayer thickness: 105 μm. The PEK-C-rich particulate phases have been removed by solvent DMF and are shown as dark holes in the images [51].

Figure 14 shows the tan δ curves for the control and PEK-C nanofibre-modified composite specimens. The control sample displayed a well-defined relaxation peak at 281 °C, which corresponds to the glass transition temperature of the epoxy resin. All the PEK-C nanofibre modified composites showed two separate glass transitions. The glass transition temperature for PEK-C powder was measured by differential scanning calorimetry (DSC), where T_g was determined from the midpoint of the slope change of the heat capacity plot of the second scan. A glass transition at 219 °C was obtained from the DSC curve. Since the T_g values measured by DSC are generally 20-30 °C lower than those measured by DMA at the same compositions, the relaxation peak at lower temperature shown in the tan δ curves of modified composites was attributed to the PEK-C-rich phase, which is T_{gPEK-C}. The relaxation peak at higher temperature displayed in the spectrum is ascribed to the glass
transition of the cured epoxy resin, which is $T_{gER}$. Figure 14a displays the tan $\delta$ curves influenced by the nanofibre diameter.

It is noted that there was almost no reduction or slight increase in $T_{gER}$ with the addition of PEK-C nanofibres. The peaks centred at 283 $^\circ$C, 280 $^\circ$C and 285 $^\circ$C correspond to the $T_{gER}$ for the composites modified by PEK-C nanofibres with average fibre diameter of 450 nm, 750 nm and 950 nm respectively. Similar shifts of relaxation peaks to higher temperature have been reported in the literature on the thermal mechanical properties of nanocomposites [57]. Nano-reinforcements have been shown to affect the segmental motions of polymer matrices when they are well dispersed [58].

The large surface areas of nanofibre membranes provide complete interaction with the epoxy matrix, which may prohibit the epoxy chains from moving freely as in the neat resin [59]. No noticeable shifts occurred in the relaxation peaks for the $T_{gPEK-C}$ as the average fibre diameter changed. It is also noticed from figure 15b that both the $T_{gER}$ and $T_{gPEK-C}$ reduced to lower temperatures as the thickness of PEK-C interlayers increased to 105 $\mu$m. This result indicates the level of interaction and compatibility between the PEK-C nanofibres and the epoxy resin deteriorated after the inclusion of nanofibre membranes increased to a certain extent.

![Figure 14. Tan $\delta$ traces of both control and nanofibre-modified composites [51].](image-url)
Figure 15. Phase structure of interlayer region of a nanofibre-modified composite specimen (average nanofibre diameter: 950 nm, average interlayer thickness: 105 μm). Optical micrographic (a) and SEM (b) images of interlayer region; (c–f) phase structures of the PEK-C-rich macrophases after etched with DMF; (d and f) are magnified images of the selected areas in (c and e); (g and h) phase structure of the epoxy-rich macrophase [51].

Figure 15 presents the phase structure of the interlayer region from PEK-C nanofibre modified carbon fibre reinforced TGAP/DDS epoxy matrix composites. Figure 15a is an optical micrograph for the cross section of a modified composite laminate. The bright part is a pre-inserted aluminium film, which was located in the midplane of composite laminate. A dark interlayer region composed of both an epoxy-rich macrophase and PEK-C-rich macrophases was found to be sited between the top [0°] and the bottom [90°] carbon fibre layers.

As shown in Figures 15 b–e, cylinder-shaped macrophase structures were observed to be embedded in the continuous epoxy resin. Figures 15 d–f are enlarged views of the PEK-C-rich macrophases showing a fibrous structure inside of the cylinder-shaped macrophase. Since the specimens have been etched with N, N-dimethylformamide, the PEK-C should be removed.
These fibrous structures could come from undissolved PEK-C nanofibres which were covered by cured epoxy resin. Figures 15 g and h show the morphology of a detached epoxy-rich macrophase from carbon fibre. It clearly indicated that the PEK-C-rich microphases (particulate phases) dispersed in the continuous epoxy-rich matrix.

4. HYPERBRANCHED POLYMERS AS TOUGHENING AGENTS

4.1. Introduction

Since being introduced theoretically by Flory in 1952 [60], hyperbranched polymers (HBP) reawakened the interests of many researchers in the early 1990's when Kim and Webster reported the reduced melt viscosity of polystyrene with the addition of a small amount of hyperbranched polypolyethylen [61]. The unique three-dimensional dendritic architecture of hyperbranched polymers leads to significant differences in properties from linear polymers, which result in unique physical and chemical properties. The potential applications of hyperbranched polymers cover versatile areas including conjugated functional materials, polymer electrolytes, supramolecular chemistry, coatings, nanomaterials, modifiers and additives [62, 63]. One of the most important properties of hyperbranched polymers is their low melt viscosities even for high molecular weights, resulting from a much lower degree of chain entanglement relative to linear polymers [64]. This characteristic has particular significance when HBP are used as additives to modify inherently brittle thermosets. Conventional modifiers such as rubber [10, 65] and thermoplastic [66-69] toughening agents are able to enhance the fracture toughness of unmodified thermosets, however, they tend to cause significant increase in the viscosity of the blends with the addition of only a relatively small amount. It is well known that liquid moulding technologies are economical alternatives to expensive autoclave processing of polymer matrix composites. Viscosity and resin flow are critical issues for obtaining good quality composite components. As a result, HBP are promising candidates for modifying thermosets with minimal decrease in processing-ability of the modified resins. A number of works reported the modification effect of hydroxyl and epoxy functionalised HBP on different epoxy resin formulations.

4.2. HBPs as Modifiers for Difunctional and Trifunctional Epoxies

Both hydroxyl and epoxy functionalised HBPs have been shown to significantly increase the toughness of less-reactive and lower crosslink-density difunctional epoxy resin systems such as the diglycidyl ether of bisphenol A (DGEBA) resin. Two hydroxyl functionalized hyperbranched polyester, Boltron H30 and H40, which have theoretically 32 primary hydroxyl end groups and 64 primary hydroxyl end groups per molecule respectively, were studied by Cicala et al. [70] for their modification result on a DGEBA epoxy (Epon 828) cured with 3, 3’ diamino diphenyl sulphone (DDS). The stress intensity factor $K_C$ for fracture toughness tests increased from $0.93 \text{ MPa} \sqrt{m}$ to $1.56 \text{ MPa} \sqrt{m}$ with 30 wt% H30 and to $1.67 \text{ MPa} \sqrt{m}$ with 30 wt% H40. All the blends studied, except at low percentages of H30, showed particulate morphologies and two relaxation peaks in the tan $\delta$ spectra. Two other
works also showed similar trends when a fifth generation hydroxyl functionalised HBP, Boltron G5, and an epoxidised HBP Boltron E1 were used as additives in DGEBA epoxy resins. The Boltron G5, Ratna and Simon [71] used for their study, was a fifth-generation Perstorp hyperbranched polyols which were developed on polyester chemistry and have an average of 128 –OH end groups per molecule and a theoretical molecular weight and polydispersity index of 14,000 g mol\(^{-1}\) and 2.0, respectively. It was noted that the HBP strongly enhanced the curing rate due to the catalytic effect of hydroxyl groups. The impact strength of the cured blends showed the most significant increase when the content of the HBP accounted for 20% of the blends, which was almost double the value of the unmodified epoxy system. The impact behaviour was explained by the phase separated morphology of the cured blends. Up to 10% of HBP, the globular HBP particles were dispersed in the continuous epoxy matrix and as the content of HBP increases, the connectivity between the dispersed HBP particles increased and the phase morphology became nearly co-continuous at higher concentrations. Varley [72] evaluated the effect of epoxy-terminated aliphatic polyester HBP as a low viscosity toughener for modifying the less-reactive DGEBA epoxy resin. The main advantage of using Boltron E1 is that it has minimal influence on processing parameters such as viscosity and gel time, while enhancing the fracture toughness by around 54% with 15 wt% addition of modifier. Similarly, particulate phase structure was formed from phase separation.

For the more reactive trifunctional epoxies, HBPs have also displayed good suitability as toughening agents. Ratna, Simon and Varley reported that the HBP Boltron G5 [73] and E1 [74, 75] modified triglycidyl p-amino phenol (TGAP) (MY0510, Ciba Speciality Chemicals) epoxy resins had 50% higher impact strength than unmodified epoxy resin with 20 wt% Boltron G5 and 100% higher impact strength than unmodified epoxy resin with 20 wt% Boltron E1. The smaller improvement of Boltron G5, in comparison with an 80% increase in \(K_{IC}\) of DGEBA using the same HBP, was believed to be caused by the single phase morphology due to the compatibility of Boltron G5 with TGAP epoxy resin. In contrast, the trifunctional epoxy resin modified with the epoxy-functionalised HBP showed a two-phase morphology, where globular HBP-rich particles dispersed uniformly in the continuous TGAP-rich matrix. The addition of Boltron E1 demonstrated little influence on gel time and vitrification time up to 10% of HBP content.

4.3. HBPs as Modifiers for Tetrafunctional Epoxies

Nevertheless, the modification effect of HBPs on the highly reactive and highly crosslinkable tetrafunctional epoxy resins have not been shown to be desirable. Varley tried to add HBP Boltron E1 into an epoxy resin based on triglycidyl methylene dianiline (TGDDM) (Araldite MY721, Ciba) and a cycloaliphatic diamine hardener [76]. Not only the E1 modified TGDDM exhibited decreased \(K_{IC}\), but also the TGDDM modified by other low viscosity additives such as carboxy-terminated polybutadiene, CTBN rubber (Goodyear, OH, USA) and the aminopropyl-terminated polydimethylsiloxane, PS510 (United Chemical Technologies, PA, USA), showed little toughening result. High service temperature and good chemical and water resistance provide tetrafunctional epoxies with great advantages in the application of aerospace polymer matrix composites. In fact, they have been used as matrix
materials for > 90% composites [77]. Modification of the brittleness of these highly crosslinked epoxies is crucial in material development aimed at reducing the delamination tendency of composite structures. Zhang et al. [78] modified a tetrafunctional epoxy resin tetruglicyldimethylene diamine (TGDDM) (Araldite MY720, Huntsman) with a fourth generation hydroxyl functionalised hyperbranched polyester (Boltorn H40, Perstop Speciality Chemicals, Sweden). The cure agent used was 3, 3′-diaminodiphenyl sulfone (DDS).

The DDS-cured epoxy/HBP blends displayed a decreased transparency and gradually became opaque with the increase of the HBP content, indicating the occurrence of phase separation. The DSC curves obtained for the DDS-cured neat epoxy resin and epoxy/HBP blends during the second heating scan are shown in Figure 16. The glass transition of the epoxy-rich phase, \( T_{gER} \), can be seen in all DSC curves. There was a reduction in \( T_{gER} \) with increasing HBP content, which may be caused by the residual miscibility between HBP and the crosslinked epoxy resin. The dilution effect of HBP might also produce an incomplete curing reaction, which resulted in a lower \( T_g \) for the crosslinked epoxy resin [79]. The glass transition of the HBP-rich phase \( T_{gHBP} \) was not detected by DSC for the blends with HBP content up to 20 part per hundred (phr). However, the cured blend with 30 phr HBP exhibited two separate glass transitions. The glass transition at higher temperature in the blend containing 30 phr HBP was associated with the cured epoxy phase (\( T_{gER} \)). The other at lower temperature was attributed to the HBP-rich phase (\( T_{gHBP} \)). The values for \( T_{gER} \) and \( T_{gHBP} \) measured by DSC are included in Table 2 along with the measurements carried out by DMA.

![Figure 16. DSC thermograms of the second run of the DDS-cured neat epoxy resin and epoxy/HBP blends [78].](image)

### Table 2. \( T_{gER} \) and \( T_{gHBP} \) for DDS-cured neat epoxy resin and epoxy/HBP blends measured by DMA and DSC [78]

<table>
<thead>
<tr>
<th>HBP (p.h.r)</th>
<th>( T_{gER} ) (DMA) (°C)</th>
<th>( T_{gER} ) (DSC) (°C)</th>
<th>( T_{gHBP} ) (DMA) (°C)</th>
<th>( T_{gHBP} ) (DSC) (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>245</td>
<td>216</td>
<td></td>
<td>237</td>
</tr>
<tr>
<td>---</td>
<td>-----</td>
<td>-----</td>
<td>---</td>
<td>-----</td>
</tr>
<tr>
<td>5</td>
<td>235</td>
<td>205</td>
<td></td>
<td>230</td>
</tr>
<tr>
<td>10</td>
<td>230</td>
<td>196</td>
<td></td>
<td>64</td>
</tr>
<tr>
<td>20</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>30</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 17 shows the dynamic mechanical spectra for the DDS-cured neat epoxy resin and epoxy/HBP blends with the HBP content of up to 30 phr. The DMA measurements of the cured epoxy/HBP blends with HBP content up to 20 phr exhibited storage modulus $G'$ close to the cured neat epoxy resin. $G'$ was not strongly influenced by the HBP content. A reduction in $G'$ at $\sim -40^\circ C$ was observed in the blend with 30 phr HBP content, which corresponds to the low-temperature thermal transition of HBP. The tan $\delta$ versus temperature curve for the cured neat epoxy resin displayed a well-defined relaxation peak at 245 $^\circ C$, attributed to its glass transition.

![Image](image.png)

**Figure 17.** Temperature dependence of a) storage modulus ($G'$) and b) tan $\delta$ of the DDS-cured neat epoxy resin and epoxy/HBP blends [78].

This relaxation peak shifted slightly to a lower temperature in the cured blends with increasing HBP content, a reduction from 237$^\circ C$ to 230$^\circ C$ for $T_{gER}$, corresponding to the increase of HBP content from 5 to 30 phr. It is noted from Figure 18b that a well-defined lower-temperature relaxation peak started to appear in the cured blend with HBP content of 15 phr. This indicates the existence of a HBP-rich phase in the cured blends. The relaxation peaks at around -50 $^\circ C$ are the $\beta$ relaxation peaks and those at around 60 $^\circ C$ are the $\alpha$ relaxation peaks of the HBP-rich phase. The values for $T_{gER}$ and $T_{gHBP}$ measured by DMA also can be found in Table 2. As expected, the $T_g$ values measured by DMA are generally 20 - 30 $^\circ C$ higher than those measured by DSC at the same composition. DMA is more sensitive to the detection of the HBP-rich phase; the two separate relaxation peaks in the tan $\delta$ spectra for cured blends with 15-30 phr showed the occurrence of phase separation. It was interesting to see that the glass transition temperature of the HBP-rich phase ($T_{gHBP}$) was decreased in the cured blends with addition of HBP. This result implies that the epoxy
resin dissolved in the HBP-rich phase was not sufficiently cured. The HBP-rich phase composed of HBP and some uncured and/or insufficiently cured epoxy resin thus had a reduced $T_g$ [64].

Analogous results have been shown in other researcher's work, such as toughening TGDDM (Araldite MY721, Ciba) using a hyperbranched epoxy-functional HBP Boltorn E1 [76]. Increasing additive content produced a gradual decrease in $T_g^{ER}$, resulting in a 24 °C reduction from the cured neat epoxy resin when 15 wt% HBP is used. In contrast, the $T_g^{ER}$ was almost unaffected when HBP was added into a difunctional epoxy DGEBA (DER 331, Dow) [76]. Previous work also supports unchanged $T_g^{ER}$ in the DDM-cured diglycidyl 1, 2-cyclohexanedicarboxylate (DGCHD) / Boltorn H40 blends with HBP content up to 30 wt% [64].

![Figure 18. Effect of HBP content on the fracture toughness and Young's modulus of DDS-cured neat epoxy resin and epoxy/HBP blends [78].](image)

The fracture toughness and phase structure were studied as a function of the modifier content. The $K_{IC}$ values as a function of the HBP content for the cured neat epoxy resin and epoxy/HBP blends are shown in Figure 18. The addition of HBP led to a 90% increase in the $K_{IC}$ values, from 0.503 $MPa \sqrt{m}$ for the cured neat epoxy resin to 0.956 $MPa \sqrt{m}$ for the cured epoxy/HBP blend with 30 phr HBP. Meanwhile, the Young's modulus of the cured epoxy/HBP blend showed limited decrease over that of the unmodified epoxy. The HBP modified tetrafunctional epoxy systems in this work exhibited significantly higher fracture toughness than thermoplastic modified tetrafunctional epoxies [80-82]. Fernandez et al. [80], added polyethersulfone (PES) into a DDM-cured TGDDM epoxy resin. However, no significant improvement was observed in fracture toughness after modification. The deficiency of modification was believed to be caused by the nanoscale phase separation. The high crosslink density of the tetrafunctional epoxy resin hindered the occurrence of higher enhancement in fracture toughness. Song et al. [83] used phenolphthalein poly(ether ether ketone) (PEK-C) to modify a DDM-cured TGDDM resin. The fracture toughness of
epoxy/thermoplastic blends showed a slight decreasing tendency, which was attributed to the reduced crosslink density of the epoxy network and the homogenous phase structure of the cured blend.

The morphology of the cured epoxy/HBP blends was investigated by SEM. Figure 19 presents the phase structures of the cured epoxy/HBP blends by cryogenically breaking the samples and then immersing in tetrahydrofuran (THF). Heterogeneous morphologies were observed for the cured blends with 10, 15, 20 and 30 phr HBP contents. In comparison with the DMA and DSC results, the cured blend with HBP content of 10 phr was also revealed to have a two-phase morphology. For the cured blend containing 5 phr HBP, a homogenous morphology was observed (Figure 19a). One of the most important criteria for obtaining increased fracture toughness in rubber or thermoplastic modified epoxy resins is a two-phase morphology after phase separation [84]. Similarly, with 5 phr HBP, no toughening result was shown. With the increase in the HBP content, a particulate morphology in which the discrete HBP-rich phases were dispersed in a continuous matrix of epoxy resin was obtained [85]. The discrete HBP-rich particles with an average size of less than 1 μm in diameter appear in the cured blend containing 10 phr HBP (Figures 19b and c).

Figure 19c is an enlargement to reveal the small HBP-rich particles which cannot be seen clearly in Figure 19b using the same scale as the other SEM micrographs. The toughening effect was not obvious for the cured blend with 10 phr HBP content despite the occurrence of phase separation. Inclusion of 15 phr HBP produced much more and larger HBP-rich phases with a bimodal particle size distribution, resulting in a 35% enhancement of $K_{IC}$. When the HBP content increased to 20 phr, the particle size ratio in the bimodal phase structure became higher (Figure 19e), leading to higher fracture toughness in the cured blend. Okamoto et al. [86] have studied the relationship between the Izod impact strength and the blend ratios of two different monomodal high impact polystyrene (HIPS) for two bimodal systems. They observed that the particle size ratio in the bimodal system affected the extent of the toughening effect. The greater the difference between the particle size of the constituent bimodal HIPS, the higher was the impact strength. The maximum toughening effect was demonstrated for the cured blend containing 30 phr HBP, when a uniform distribution of monomodal HBP-rich particles was achieved.

It has been noted that all the epoxy/HBP blends with HBP content from 10 to 30 phr experienced phase separation through the nucleation and growth (NG) mechanism [5, 24]. An important factor which may influence the phase behaviour of the epoxy/HBP blends needs to be considered: as a low viscosity modifier, HBP does not have the semi permeable characteristics required for mass transfer (usually, when the modifier is a viscous thermoplastic, the dispersed primary phase will continuously receive material from the continuous primary phase but not deliver species back [23]), which can be associated with significantly different thermodynamic simulations from thermoplastic modified epoxies.

For the cured blends containing 15 and 20 phr HBP, both phase structures displayed bimodal particle-size distributions (Figure 19d and e). The explanation could be based on the following: when the average distance between growing particles is high and the conversion rate is significantly high, concentration profiles of the modifiers become very sharp. The high supersaturation at these points (concentration excess with respect to equilibrium at the particular conversion level) causes a new nucleation process to occur. The different concentration profiles are repeated as the cure conversion proceeds, resulting in the bimodal
particle size distributions. However, the inclusion of higher HBP content (30 phr) gave rise to a reduced cure conversion rate when phase separation occurred, which may not be sufficient enough to initiate the second NG process. Under these conditions, the cured blend containing 30 phr HBP exhibited a monomodal particle size distribution (Figure 19f).

Figure 19. SEM micrographs of cryogenically fractured surfaces of DDS-cured epoxies with (a) 5, (b), (c) 10, (d) 15, (e) 20, (f) 30 phr HBP modifiers. The scale bars are 10μm except for the micrograph (c) which is 2μm [78].

Figure 20 presents the SEM micrographs on the fracture surfaces of the cured neat epoxy resin and the epoxy/HBP blends after single-edge-notch bending tests. For the neat epoxy resin (Figure 20a), the regularly oriented cracks were developed freely, indicating typical brittle characteristics of the fracture surface. The inclusion of 5 phr HBP did not change the
brittle nature of the fracture surface (Figure 20b), accounting for its unimproved fracture toughness. As it has been known earlier, phase separation occurred when the HBP content increased to 10 phr. Although the dispersed HBP-rich particles cannot be distinctly observed in Figure 20c, a great amount of tortuous and fine cracks appeared on the fracture surface, resulting from the formation of shear bands near the plastic HBP-rich particles. The plastic characteristic was further developed on the surface of the cured blend containing 15 phr HBP (Figure 20d). The dispersed HBP-rich particles created stress concentrations at their equators and also acted as sites for initiating shear bands. When the shear bands created by one particle interact with another, they may stop propagating and keep the yielding localised [18, 55]. More matrix yielding was induced locally surrounding the particles due to a larger number of dispersed particles.

Figure 20. SEM micrographs on $K_{IC}$ fracture surfaces of DDS-cured epoxies with (a) 0, (b) 5, (c) 10, (d) 15, (e) 20, (f) 30 phr HBP modifiers. The scale bars are 10μm [78].
Some cracks deviated from their original planes, leading to significantly increased surface area. All these factors contributed to more absorbed surface energy thereby increasing fracture toughness. For the cured blend containing 20 phr HBP (Figure 20e), the crack tips became obscured and large plastically deformed planes were aligned regularly on the surface. As the particle size ratio in the bimodal phase structure increased, the surface relief became more pronounced, which absorbed even more energy and led to a higher $K_{IC}$ value. The SEM micrograph for the 30 phr HBP blends (Figure 20f) showed distinctly different characteristics from the others. No more lengthy cracks could be detected. Extensive plastic deformation took place in the continuous matrix embedded with uniformly distributed HBP-rich particles with considerably high concentration. Apparently, the most surface energy was absorbed through this way, contributing to the highest $K_{IC}$ achieved among all the HBP modified epoxies in this study. In addition to the above observations, particle cavitations were present in all the investigated epoxy/HBP blends which experienced phase separation. The cavitated HBP-rich particles induced large stress concentrations, leading to extensive shear deformation. This high energy absorbing mechanism assisted with toughening the tetrafunctional epoxy resin more effectively [87].

![FTIR spectra](image)

Figure 21. FTIR spectra in the 3100-3800 cm$^{-1}$ region of the HBP (Bolton H40) and the DDS-cured epoxy/HBP blends [78].

Figure 21 shows the FTIR spectra of the HBP and the DDS-cured epoxy/HBP blends in the stretching region from 3100 to 3800 cm$^{-1}$. Two components can be seen from both the spectrum for the HBP and for the DDS-cured neat epoxy resin. For the cured epoxy resin, a broad band centred at 3389 cm$^{-1}$ is attributed to the self-associated hydroxyl groups (i.e., hydrogen bonded hydroxyl groups) and a shoulder centred at 3557 cm$^{-1}$ is assigned to non-associated, free hydroxyl groups [88]. For the HBP, a broad band centred at 3432 cm$^{-1}$ is attributed to the hydrogen bonded hydroxyl group and the shoulder centred at 3557 cm$^{-1}$ is assigned to free hydroxyl groups. The relative intensity of the free hydroxyl band to the hydrogen bonded hydroxyl band is the highest for the HBP, indicating the existence of a higher fraction of free hydroxyl groups in the HBP than both the cured neat epoxy resin and
the epoxy/HBP blends. The spectrum for the cured epoxy resin shows a reduced relative intensity of the free hydroxyl band to the hydrogen bonded hydroxyl band. The inclusion of HBP to the epoxy resin caused gradually decreased relative intensity of the free hydroxyl band to the hydrogen bonded hydroxyl band, which indicates the formation of hydrogen bonded hydroxyls in the cured epoxy/HBP blends. It can also be seen from Figure 21 that with the increase in HBP content, the associated hydroxyl band shifted to higher frequencies. However, the non-associated hydroxyl band did not move. The frequency difference between the non-associated hydroxyl absorption and the associated hydroxyl absorption ($\Delta \nu$) is a measure of the average strength of the intermolecular interactions [89]. This indicates that the average strength of the hydrogen bond in the cured blends ($\Delta \nu = 148$ cm$^{-1}$ for the cured epoxy/HBP blend containing 30 phr HBP) is lower than the hydrogen bond in the cured neat epoxy resin ($\Delta \nu = 168$ cm$^{-1}$).

**CONCLUSION**

In reviewing the research endeavour contributed to improving the fracture toughness of epoxies and their carbon fibre reinforced composites, this chapter has briefly summarised the main toughening agents used in the past. Rubbers were firstly accepted as effective modifiers to toughen epoxies and commercial adhesives and composite matrix resins based on these systems have been widely used. However, rubber toughening has its main disadvantages of lowering the modulus and glass transition temperatures of the host epoxy resin. Thermoplastic toughening was proposed to overcome this barrier by replacing rubbers by high performance thermoplastics, which have similar values of elastic modulus and yield stress as those of the epoxy network. This method has been successful to modify epoxies with higher crosslink-density; as a result, many aerospace composite systems nowadays are based on the thermoplastic toughened epoxy matrix resin systems. A key factor influencing the application of laminating resins is the processing-ability of the resin, i.e. the initial viscosity of the resin system. Both rubbers and high performance thermoplastics lead to significantly increased viscosity of the modified epoxy resins, resulting from their linear polymer structure which involves a high degree of polymer chain entanglement. As promising candidates for modifying epoxies with minimal decrease in processing-ability of the modified resins, hyperbranched polymers with unique three-dimensional dendritic polymer structures have attracted great attention. The low viscosity, high solubility and high degree of functionality of these hyperbranched polymers have been taken advantage of for the modification of epoxies.

Future research in toughening of epoxies should focus on improving the fracture toughness as well as maintaining the initial properties of epoxies. In the mean time, important parameters such as the size and distribution of the ductile secondary phases, the interfacial adhesion between modifier particulate phases and matrix, and the viscosity and resin flow should also be carefully controlled. Newly emerged areas include using rubbers incorporating block copolymers that are able to self-assemble into hierarchical substructures at nanometre scale. The work of utilizing nano-sized rubber modifiers is currently under investigation.
REFERENCES


