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NANO-COMPOSITES: RELATIONSHIPS BETWEEN NANO-STRUCTURE AND MECHANICAL PROPERTIES: PHASE II

FINAL TECHNICAL REPORT
By

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Abstract

This work aims to understand and model the structure/property relationships of polymer nanocomposites, based upon thermosetting epoxy polymers that are widely used as adhesives and matrices for fibre-reinforced composites. The work concentrates on investigating the mechanical and fracture properties of multiphase materials (both bulk materials and reinforced fibre-composites), and on modelling the structure/property relationships of nanocomposites.

The present work shows that a substantial increase in toughness may be achieved when nano-SiO_2 particles are well dispersed in a hot-cured single-part epoxy polymer. Most importantly, the synergistic effect of having a multiphase structure based upon both nano-SiO_2 particles and rubbery particles is clearly demonstrated.

The use of nano-SiO_2 particles and rubbery particles to give ‘hybrid-toughened’ epoxy polymers is shown to give a range of novel matrices which lead to an increased delamination toughness of the resulting carbon-fibre reinforced-plastic (CFRP) composites. Also, it is noteworthy, that the presence of even a relatively high concentration of the nano-SiO_2 particles does not lead to a decrease in the modulus of the composite. Nor does it lead to a significant increase in the viscosity of the epoxy resin, which would preclude the use of low-cost manufacturing routes, such as a vacuum-assisted resin-transfer moulding (VARTM) process.

Keywords

Epoxy; Nanocomposite; Rubber; Hybrid Toughening; Fibre Composite; Fracture Toughness

Contents

1 Introduction

The use of polymeric adhesives can offer many advantages compared to the more traditional methods of joining such as bolting, brazing, welding, mechanical fasteners, etc. These include [1, 2] the ability to join dissimilar materials to give light-weight, but strong and stiff structures, such as honeycomb sandwich panels. In addition, polymeric adhesives may be used to join thin-sheet material efficiently which, due to its low bearing strength, cannot be readily joined by other methods. Further, adhesive bonding frequently represents the most convenient and cost-effective joining technique and, indeed, the bonding operation can often be readily automated. For these reasons, adhesive bonding is widely used in many industries, for example in the automobile, truck, aerospace, railway and electronic industries. Epoxy adhesives represent the most common type of *structural* adhesive; the term *structural* meaning that the polymerised (i.e. cured or hardened) adhesive possesses a relatively high modulus and strength so that a load-bearing joint is formed.

When polymerised, epoxy adhesives are amorphous and highly-crosslinked (i.e. thermosetting) materials. This microstructure results in many useful properties for structural engineering applications, such as a high modulus and failure strength, low creep, and good performance at elevated temperatures. However, the structure of such thermosetting polymers also leads to one highly undesirable property in that they are relatively brittle materials, with a poor resistance to crack initiation and growth. Nevertheless, it has been well established (e.g. [3-5]) for many years that the incorporation of a second micro-phase of dispersed rubbery particles into the epoxy polymer can greatly increase their toughness, without significantly impairing the other desirable engineering properties. Typically the rubber particles are about 1 to 5 μm in diameter with a volume fraction of about 5 to 20%. More recently there has emerged a new technology which holds great promise for increasing further the mechanical performance of such multiphase thermosetting polymers. Namely, via the additional formation of a nano-phase structure in the polymer, where the nano-phase consists of small rigid particles of silica [6].

We have previously shown [6] that the addition of low concentrations of nano-silica particles to a typical rubber-toughened adhesive, based upon a two-part epoxy formulation, may lead to very significant increase in the toughness of the adhesive, and also to increases in the glass transition temperature and the single-lap shear strength. The nano-SiO_2 particles had an average particle diameter of about 20 nm and were very well dispersed in the epoxy adhesive, and only a concentration of about 1% to 8 % by weight of such nano-particles were needed to achieve significant improvements in the mechanical and thermal performance of the two-part multiphase epoxy adhesive.

In the present work, for the first time, we report the substantial increase in toughness that may be achieved when such nano-SiO_2 particles are well dispersed in a hot-cured single-part epoxy polymer, and again the synergistic effect of having a multiphase structure based upon both nano-

SiO_2 particles and rubbery particles is clearly demonstrated in both bulk polymer and fibre composite materials. Achieving a relatively high toughness in a hot-cured single-part epoxy polymer represents a far greater challenge than in a two-part epoxy formulation. This is because the former invariably has a significantly higher glass transition temperature, T_g, and a lower molecular-weight between crosslinks; and both of these features inhibit the plastic deformation of the epoxy matrix which is a major toughening mechanism [4, 5, 7-9].

2 Rubber and Nanosilica-Modified Polymers

2.1. Introduction

Epoxy polymers, which are the basis for many structural adhesives, are amorphous, highly-crosslinked (i.e. thermosetting) and hence brittle materials. In the present work, for the first time, we report the substantial increase in toughness that may be achieved when nano-SiO_2 particles are well dispersed in a hot-cured single-part epoxy polymer, and the synergistic effect of having a multiphase structure based upon both nano-SiO_2 particles and rubbery particles is clearly demonstrated. It should be noted that achieving a relatively high toughness in a hot-cured single-part epoxy polymer represents a far greater challenge than in a two-part epoxy formulation. This is because the former invariably has a significantly higher glass transition temperature, T_g, and a lower molecular-weight between crosslinks; and both of these features inhibit the plastic deformation of the epoxy matrix which is a major toughening mechanism [4, 5, 7-9].

2.2. Experimental

2.2.1 Materials

The materials were based upon a one-component hot-cured epoxy formulation. The epoxy resin was a standard diglycidyl ether of bis-phenol A (DGEBA) with an epoxy equivalent weight (EEW) of 185 g/mol, 'Bakelite EPR 164' supplied by Bakelite AG, Duisberg, Germany. The nano-particles of silica (SiO_2) were obtained at a concentration at 40wt.% in this DGEBA epoxy resin: 'Nanopox F400' from Hanse Chemie, Geesthacht, Germany. The surface-modified SiO_2 nano-particles had an average particle size of about 20 nm, with a narrow range of particle-size distribution. This particle size of about 20 nm is created during a sol-gel manufacturing process [10], whereby the silica particles are formed *in-situ*, and the particle size and excellent dispersion of these SiO_2 particles remain unchanged during any further mixing and/or blending operations. Further, despite the relatively high SiO_2 content of 40wt.%, the nano-filled epoxy resin still has a comparatively low viscosity due to the agglomerate-free colloidal dispersion of the nano-particles of SiO_2 in the epoxy resin. The small diameter and good dispersion of the nano-particles of silica are clearly shown in Figure 1.

The reactive liquid rubber, which gives rise to the micrometre-sized spherical rubber particles upon curing of the formulation, was a carboxyl-terminated butadiene-acrylonitrile (CTBN) rubber. It was supplied by Noveon, Cleveland, USA, and was 'Hycar CTBN 1300x8' with a number-average molecular weight of 3,550 g/mol and an acrylonitrile content of 18wt.%. This was pre-reacted with the DEGBA resin to give a 40wt.% CTBN-epoxy adduct: 'Albipox 1000' from Hanse Chemie, Geesthacht, Germany.

The curing agent was an accelerated methylhexahydrophthalic acid anhydride, namely 'Albidur HE 600' supplied by Hanse Chemie, Geesthacht, Germany. The formulations were cured by firstly mixing together the simple DGEBA epoxy with given amounts of the nano-SiO_2 epoxy and CTBN-epoxy adduct, to give the required levels of added nano-SiO_2 and CTBN rubber. The value of the EEW of the blend was then calculated and the stoichiometric amount of the curing agent was added to the mixture, which was poured into release-coated moulds and cured for 1 hour at 90^oC, followed by a post-cure of 2 hours at 160^oC.

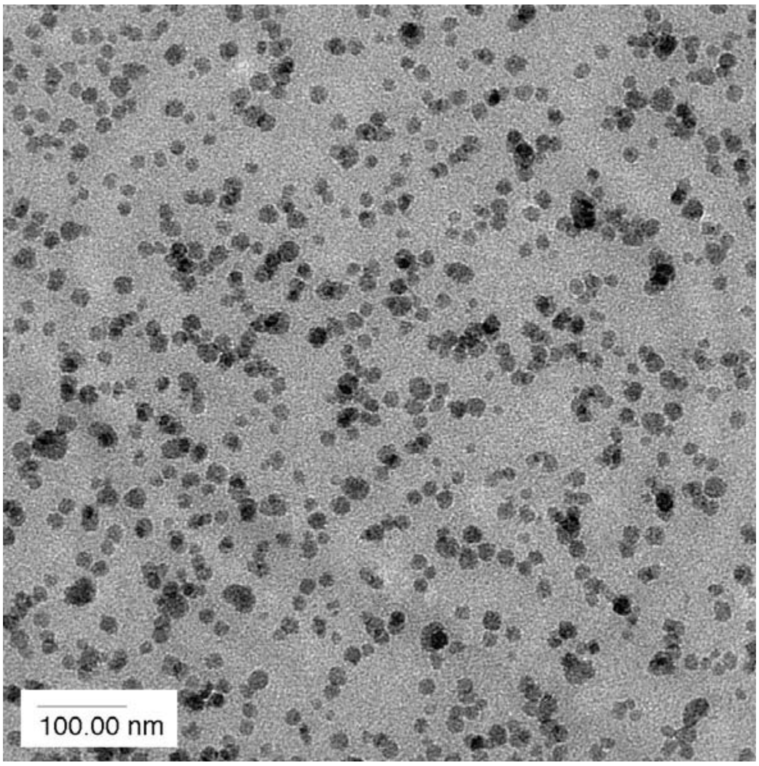

Figure 1. Transmission electron micrograph showing the excellent dispersion of the SiO_2 nano-particles in the epoxy resin.

2.2.2 Mechanical and Thermal Properties

The glass transition temperature, T_g, of the various formulations was measured using the method of dynamic mechanical thermal analysis (DMTA) at a frequency of 10Hz. The stress-intensity factor, K_{Ic}, at the onset of crack growth was measured according to the ISO test method [11]. The coefficient of variation in the values of K_{Ic} was $\pm 22\%$. The modulus, E, was measured at a displacement rate of 1 mm/min according to the ISO test method [12, 13]. The coefficient of variation in the values of E was $\pm$ 7.0%. The value of the fracture energy, G_{Ic}, was calculated from a knowledge of the values of K_{Ic} and E, using the relationship:

$$K_{Ic}^2 = \frac{EG_{Ic}}{1-\upsilon^2} \quad (1)$$

where υ is the Poisson's ratio and was taken to be 0.35 in value.

2.3. Results

2.3.1 Nano-phase Toughened Epoxy Polymers

The results for the thermosetting epoxy polymer containing only the *in-situ* formed nano-silica particles are shown in Table 1, with the results for the values of the fracture energy, G_{Ic}, as a function of the wt.% of nano-SiO_2 also given in Figure 2. The experimental scatter on the values of the glass transition temperature, T_g, of the polymers is typically $\pm 2^{o}$C, and thus the presence of the nano-SiO_2 particles would appear to have little effect on the value of T_g. However, the presence of the nano-phase particles does increase the modulus, E, of the polymer; with the value of E increasing steadily as the wt.% of the silica phase is increased. The value of the stress-intensity factor, K_{Ic}, at the onset of crack growth also increases steadily as the wt.% of the silica phase is increased. From Equation (1), the resulting value of the fracture energy, G_{Ic}, may be calculated and is shown as a function of the wt.% of added nano-SiO_2 particles in Figure 2. As may be seen, the inclusion of 4wt.% gives a significant increase in G_{Ic} from 103 J/m^2 to 291 J/m^2, but thereafter further increases in the concentration of the nano-SiO_2 phase produce a small, but steady, increase in the measured toughness.

Table 1. The formulations employed and their mechanical properties

Formulation		$T_g\left(^\circ C\right)$	$E\left(GPa\right)$	$K_{Ic}\left(MPa\sqrt{m}\right)$	$G_{Ic}\left(J/m^2\right)$
wt. % nano-SiO_2	**wt.% CTBN**				
0.0	0.0	143	2.96	0.59	103
4.0	0.0	137	3.20	1.03	291
7.8	0.0	136	3.42	1.17	352
11.1	0.0	141	3.57	1.18	343
14.8	0.0	138	3.60	1.29	406
20.2	0.0	138	3.85	1.42	461
0.0	0.0	143	2.96	0.59	103
0.0	9.0	127	2.44	1.11	444
2.3	9.0	133	2.66	1.17	453
4.5	9.0	135	2.77	1.70	918
9.0	9.0	129	2.79	1.76	977
10.5	9.0	126	2.80	1.99	1240
15.4	9.0	122	2.85	2.19	1480

2.3.2 Nano-phase and Rubber-phase (i.e. 'Hybrid') Toughened Epoxy Polymers

The results for the epoxy polymers containing both a nano-silica and a rubbery phase are also shown in Table 1 and in Figure 2.

We may firstly compare the data for the pure epoxy polymer, containing no toughening phase, to that of the epoxy polymer containing only the CTBN-adducted rubbery particles. (The rubbery particles are produced via a reaction-induced phase-separation, giving particles of about 1 to 5 μm in diameter, as is well documented for such materials [3, 9].) As expected the modulus, *E*, of the epoxy polymer falls with the addition of the CTBN rubber and the decrease in the value of the T_g indicates that some of the rubber remains dissolved in the epoxy-polymer phase. Of course, these relatively minor changes in these properties of the rubber-toughened epoxy polymer are more than compensated for by the significant increases in the values of K_{Ic} and G_{Ic}. Indeed, the value of G_{Ic} increases from 103 J/m^2 to over 400 J/m^2 due to the toughening mechanisms induced by the presence of the rubbery particles. Thus, compared to the pure epoxy polymer, with no dispersed rubbery phase, the rubbery particles greatly increase the toughness of the material via interactions of the stress field ahead of the crack tip and the rubbery particles which leads to greatly enhanced plastic deformation of the epoxy matrix [5, 9, 14].

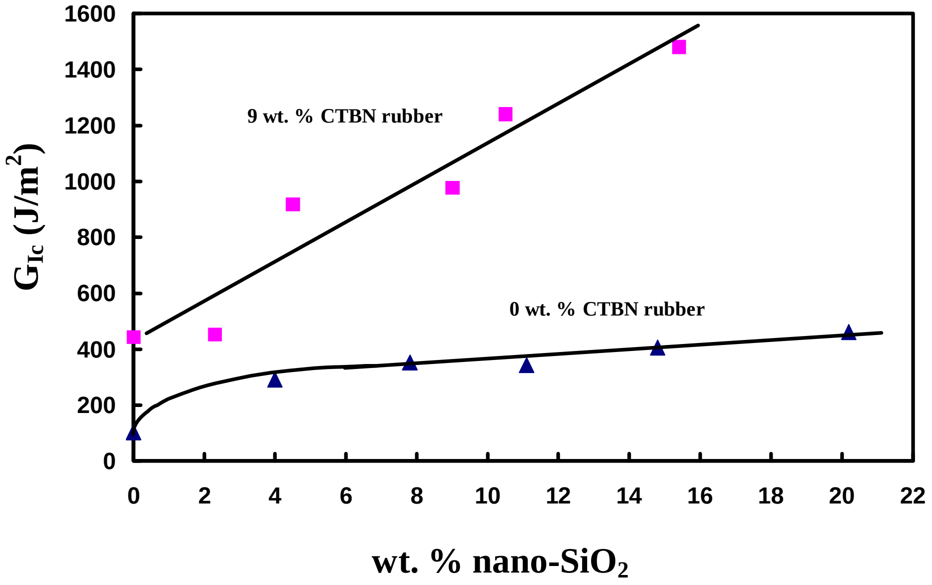

Figure 2. The fracture energy, G_{Ic}, versus the concentration of nano-SiO$_2$ particles.

Secondly, we may consider the effects of introducing both rubbery micrometre-sized particles and nano-SiO$_2$ particles into the epoxy polymer, to give a 'hybrid-toughened' polymeric material. Within experimental error there is no change in the T_g of the epoxy polymer containing 9wt.% CTBN and the various concentrations of the nano-SiO$_2$ particles, which suggests that the volume fraction of the rubbery-particulate phase which has formed is independent of the concentration of the nano-silicate phase present. Also, as would be expected, the modulus, *E*, of the polymer increases steadily as the wt.% of the silica nano-phase is increased.

However, the most dramatic changes in the mechanical properties are the very significant increases in the values of K_{Ic} and G_{Ic}. Indeed, the value of G_{Ic} increases from 103 J/m^2 for the pure epoxy polymer to over 1400 J/m^2 upon the formation of the 'hybrid' material containing both rubbery micrometre-sized particles and nano-SiO_2 particles. The major increases in the toughness of the 'hybrid' epoxy polymers as the concentration for the nano-phase is increased may clearly be seen in Figure 2. There is a linear increase in toughness as the wt.% of the nano-silica is increased. It is not immediately obvious why the additional presence of the nano-SiO_2 particles should further increase the toughness so markedly. Previous work on rigid fillers, but which were micrometres in size as opposed to be nanometres, has shown that the toughening mechanisms which are induced by the presence of the rigid particles may also involve enhancing the plastic deformation that occurs in the epoxy matrix [15]. However, other toughening mechanisms such as (a) crack deflection and crack twisting around the rigid particles [16] and (b) crack-front pinning by the rigid particles [17] may also be initiated. Future work will explore the detailed mechanisms of toughening which are initiated by the nano-particles. The understanding of these mechanisms may lead to even further increases in the mechanical performance of 'hybrid' epoxy polymers, containing a complex multiphase structure of nano- and micro-sized phase inclusions.

2.4 Conclusions

In the present work, for the first time, we report the substantial increase in toughness that may be achieved when nano-SiO_2 particles are well dispersed in a hot-cured single-part epoxy polymer. Most importantly, the synergistic effect of having a multiphase structure based upon both nano-SiO_2 particles and rubbery particles is clearly demonstrated. These multiphase 'hybrid' epoxy polymers would appear to have considerable potential for a wide range of applications, such as adhesives, composite matrices and electronic encapsulating resins, where a high toughness is often required but without any accompanying significant loss of other important properties such a modulus and thermal resistance.

3 Fibre Composites with Rubber and Nanosilica-Modified Matrix

3.1 Introduction

The amorphous and highly-crosslinked (i.e. thermosetting) microstructure of epoxy polymers results in many useful properties for structural engineering applications, such as a high modulus and failure strength, low creep, and good performance at elevated temperatures. For these reasons, epoxy polymers are frequently used as the matrices for fibre-reinforced materials. However, their structure leads to one highly undesirable property in that they are relatively brittle materials. Nevertheless, it has been well established for many years that the incorporation of a second micro-phase of a dispersed rubbery (e.g. [3-5, 8]) or a thermoplastic polymer (e.g. [18-20]) into the epoxy can increase their toughness, without significantly impairing the other desirable engineering properties.

More recently there has emerged a new technology which holds great promise for increasing further the mechanical performance of such multiphase thermosetting polymers. Namely, via the additional formation of a nano-phase structure in the polymer, where the nano-phase consists of small rigid particles of silica [6, 21] to give ‘hybrid-toughened’ epoxy polymers. This has been shown to not only increase further the toughness of the epoxy polymer but also, due to the very small size of the silica particles, not to lead to a significant increase in the viscosity of the epoxy. Both of these exciting and novel properties make the ‘hybrid-toughened’ epoxy polymers ideal matrices for relatively tough composite materials which may be produced by resin-transfer moulding (RTM), vacuum-assisted resin-transfer moulding (VARTM), etc. low-cost manufacturing processes. The initial results from such carbon-fibre reinforced-plastic (CFRP) composite materials produced via a VARTM process are reported in the present letter.

3.2. Experimental

3.2.1 Materials

The materials were based upon a one-component hot-cured epoxy formulation. The epoxy resin was a standard diglycidyl ether of bis-phenol A (DGEBA) with an epoxy equivalent weight (EEW) of 185 g/mol, ‘Bakelite EPR 164’ supplied by Hexion Speciality Chemicals, Duisberg, Germany. The nano-particles of silica (SiO_2) were obtained at a concentration at 40 wt.% in this DGEBA epoxy resin: ‘Nanopox F400’ from Hanse Chemie, Geesthacht, Germany. The surface-modified SiO_2 nano-particles had an average particle size of about 20 nm, with a narrow range of particle-size distribution. This particle size of about 20 nm is created during a sol-gel manufacturing process [10], whereby the silica particles are formed *in-situ*, and the particle size and excellent dispersion of these SiO_2 particles remain unchanged during any further mixing and/or blending operations. Further, despite the relatively high SiO_2 content of 40 wt.%, the nano-filled epoxy resin still has a comparatively low viscosity due to the agglomerate-free colloidal dispersion of the nano-particles of SiO_2 in the epoxy resin. The small diameter and good dispersion of the nano-particles of silica have been previously reported and shown [6, 21].

The reactive liquid rubber, which gives rises to the micrometre-sized spherical rubber particles upon curing of the formulation, was a carboxyl-terminated butadiene-acrylonitrile (CTBN) rubber. It was supplied by Noveon, Cleveland, USA, and was ‘Hycar CTBN 1300x8’ with a number-average molecular weight of 3,550 g/mol and an acrylonitrile content of 18wt.%. This was pre-reacted with the DEGBA resin to give a 40 wt.% CTBN-epoxy adduct: ‘Albipox 1000’ from Hanse Chemie, Geesthacht, Germany. The curing agent was an accelerated methylhexahydrophthalic acid anhydride, namely ‘Albidur HE 600’ supplied by Hanse Chemie, Geesthacht, Germany.

To determine the properties of the matrices, the formulations were cured by firstly mixing together the simple DGEBA epoxy with given amounts of the nano-SiO_2 epoxy and CTBN-epoxy adduct, to give the required levels of added nano-SiO_2 and CTBN rubber. The value of the EEW of the blend was then measured, via titration, and the stoichiometric amount of the curing agent was added to the mixture, which was poured into release-coated moulds and cured for 1 hour at 90^{o}C, followed by a post-cure of 2 hours at 160^{o}C.

The CFRP composite panels were manufactured by vacuum-assisted resin-transfer moulding (VARTM). The carbon fibre was an isotropic linen-weave fibre fabric arranged in a 0/90º pattern with a density of 168 g/m^2 and supplied by Lange-Ritter, Gerlingen, Germany. The average volume fraction of the fibres in the CFRPs was 26.5%. A thin film of poly(tetrafluoroethylene) (PTFE) was inserted into the fabric prior to resin infusion, along one side of the CFRP plate to a length of 35 mm, to act as a starter crack for the fracture specimens. It again should be emphasised that the lack of any significant increase in the viscosity of the epoxy resin, containing even 10.5 wt.% of the nano-silica, enabled this range of resins to be readily used in a VARTM manufacturing process.

3.2.2 Mechanical and Thermal Properties of the Bulk Matrices

The glass transition temperature, T_g, of the various formulations was measured using differential scanning calorimetry at a rate of 10^{o}C/minute. The stress-intensity factor, K_{Ic}, at the onset of crack growth was measured according to the ISO test method [11]. The coefficient of variation in the values of K_{Ic} was ±22%. The modulus, E, was measured at a displacement rate of 1 mm/min from uniaxial tensile tests, according to the ISO test method [12, 13]. The value of the fracture energy, G_{Ic}, was calculated from a knowledge of the values of K_{Ic} and E, using the relationship:

$$K_{Ic}^2 = \frac{EG_{Ic}}{1-\upsilon^2} \qquad (1)$$

where υ is the Poisson’s ratio and was taken to be 0.35 in value.

3.2.3 Mechanical Properties of the Carbon-fibre Reinforced-plastic Composites

Double cantilever beam (DCB) specimens were used to measure the interlaminar fracture energy, G_{Ic}(interlaminar), under Mode I loading conditions according to the ISO test method . The coefficient of variation in the values of G_{Ic}(interlaminar) was typically ±10%. The flexural modulus of the CFRP plates was measured according to the ASTM test method [22, 23], at a constant strain rate of 0.01min^{-1}.

3.3. Results

3.3.1 The Nano-silica phase and Rubber-phase (i.e. 'Hybrid') Toughened Matrices

The results for the epoxy polymers containing both a nano-silica and a rubbery phase are shown in Table 2. We may firstly compare the data for the pure epoxy polymer, containing no toughening phase, to that of the epoxy polymer containing only the CTBN-adducted rubbery particles, see Table 2. (The rubbery particles are produced via a reaction-induced phase-separation, giving particles of about 1 to 2 μm in diameter, as is well documented for such materials [3-5, 8].) As expected the modulus, E, of the epoxy polymer decreases with the addition of the CTBN rubber and the decrease in the value of the T_g indicates that some of the rubber remains dissolved in the epoxy-polymer phase. Of course, these relatively minor changes in these properties of the rubber-toughened epoxy polymer are more than compensated for by the significant increases in the values of K_{Ic} and G_{Ic}. Indeed, the value of G_{Ic} increases from about 100 J/m^2 to over 400 J/m^2 due to the toughening mechanisms induced by the presence of the rubbery particles. Thus, compared with the pure epoxy polymer, with no dispersed rubbery phase, the rubbery particles greatly increase the toughness of the material via interactions of the stress field ahead of the crack tip and the rubbery particles which leads to greatly enhanced plastic deformation of the epoxy matrix [4, 5, 8, 9].

Table 2. The formulations employed and the mechanical properties of the epoxy polymer matrices

Formulation		**T_g (°C)**	**E (GPa)**	**K_{Ic} (MPa√m)**	**G_{Ic} (bulk) (J/m^2)**
wt. % nano-SiO$_2$	**wt.% CTBN**				
0.0	0.0	143	2.96	0.59	103
11.2	0.0	142	3.63	1.23	363
0.0	9.0	126	2.44	1.11	443
2.3	9.0	133	2.66	1.71	964
4.5	9.0	135	2.77	1.70	917
9.0	9.0	129	2.79	1.76	973
10.5	9.0	126	2.80	1.99	1240

Secondly, we may consider the effects of introducing both rubbery micrometre-sized particles and nano-SiO$_2$ particles into the epoxy polymer, to give a multiphase 'hybrid-toughened' polymeric material. There are no significant major changes in the T_g of the epoxy polymer containing 9wt.%

CTBN and the various concentrations of the nano-SiO_2 particles, which suggests that the volume fraction of the rubbery-particulate phase which has formed is independent of the concentration of the nano-silicate phase present. Also, as would be expected, the modulus, E, of the rubber-particulate epoxy polymer increases steadily as the wt.% of the silica nano-phase is increased. However, it is noteworthy that the addition of the nano-silica phase to the rubber-particulate epoxy polymer never leads to a full recovery of the modulus, if the 'hybrid' polymers are compared with the pure epoxy polymer. However, the most dramatic changes in the mechanical properties are the very significant increases in the values of K_{Ic} and G_{Ic}. Indeed, the value of G_{Ic} increases from about 100 J/m^2 for the pure epoxy polymer to over 1200 J/m^2 upon the formation of the 'hybrid' material containing both rubbery micrometre-sized particles and 10.5 wt.% nano-SiO_2 particles. The major increases in the toughness of the 'hybrid-toughened' epoxy polymers as the concentration for the nano-phase is increased may clearly be seen from the data in Table 2.

3.3.2 The Carbon-Fibre Reinforced-Plastic Composites

The corresponding results for the CFRP laminates are shown in Table 3. As would be expected, the modulus of the CFRP laminates is essentially dominated by the presence of the carbon-fibre weave, giving a value of E of approximately 26 GPa. Considering the values of G_{Ic}(interlaminar), the presence of the nano-SiO_2 particles alone (at a concentration of 11.9 wt.%) has no significant effect on the delamination resistance, whilst the addition 9 wt% of CTBN rubber alone does lead to an increase in the toughness from 439 to 1050 J/m^2. However, the further addition of nano-SiO_2 particles to the rubber-toughened matrix, giving a range of 'hybrid-toughened' epoxy matrices, gives a further enhancement of the toughness, with a highest value of G_{Ic}(interlaminar) of 1320 J/m^2 being recorded.

Table 3. The formulations employed and the mechanical properties of the CFRP laminates

Formulation		***Modulus E***	**G_{Ic} (interlaminar)**
wt. % nano-SiO_2	**wt.% CTBN**	**(GPa)**	**(J/m^2)**
0.0	0.0	26	439
11.9	0.0	26	489
0.0	9.0	26	1050
2.3	9.0	26	1260
4.7	9.0	26	1080
7.2	9.0	26	1110
10.5	9.0	26	1320

The relationship between the values of G_{Ic}(interlaminar) of the CFRP laminates and G_{Ic} of the bulk matrices is shown in Figure 3. (Note that the wt.% of the nano-SiO_2 particles stated is the average value for some of the formulations given in Tables 2 and 3, since an exact correspondence between the composite and bulk matrix tests was not always experimentally obtained.) The results given in this figure clearly reveal the significant toughening of both the composite and bulk materials by the CTBN-rubbery phase being present in the epoxy polymer; and the further enhanced values of G_{Ic}(interlaminar) and G_{Ic} of the bulk matrices when the 'hybrid-toughened' epoxy polymers are employed. Thus, the synergistic effect of having a multiphase structure based upon both nano-SiO_2 particles and micro-sized rubbery domains is clearly demonstrated.

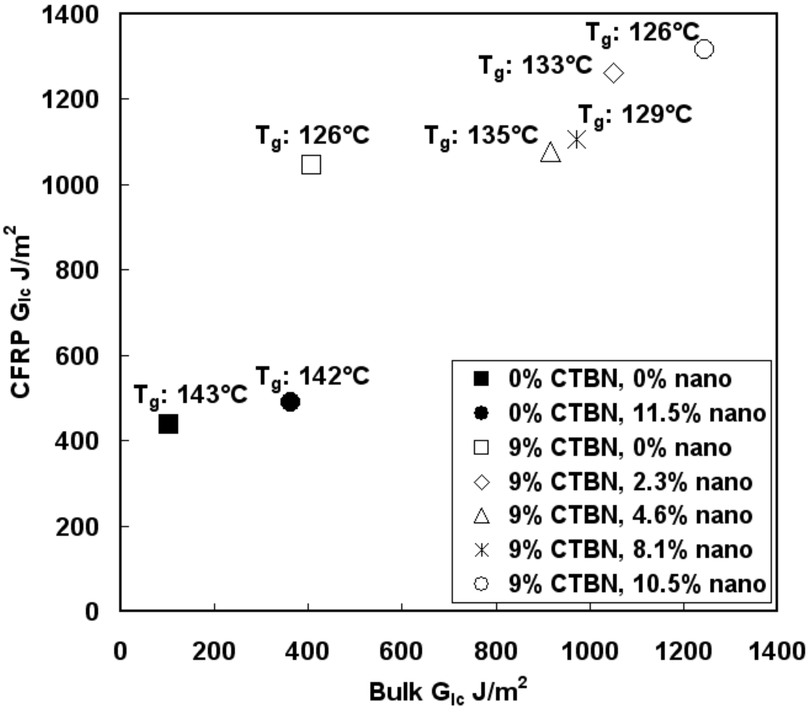

Figure 3. G_{Ic} (interlaminar) for the CFRP laminates versus G_{Ic} (bulk) for the matrices. Values of the T_g for the matrices are also shown.

3.4. Conclusions

The use of nano-SiO_2 particles and rubbery particles to give 'hybrid-toughened' epoxy polymers has been demonstrated to give a range of very novel matrices which lead to an increased delamination toughness of the resulting carbon-fibre reinforced-plastic (CFRP) composites. Also, it is noteworthy, that the presence of even a relatively high concentration of the nano-SiO_2 particles does not lead to a decrease in the modulus of the composite. Nor does it lead to a significant increase in the viscosity of the epoxy resin, which would preclude the use of low-cost manufacturing routes, such as a vacuum-assisted resin-transfer moulding (VARTM) process. Future work will explore the detailed mechanisms of toughening which are initiated by the nano-SiO_2 particles. Since, the understanding of these mechanisms may lead to even further increases in the mechanical performance of 'hybrid-toughened' epoxy polymers, containing a complex multiphase structure of nano- and micro-sized phase inclusions, and such increases may again be transferable to fibre-composite materials produced by relatively low-cost manufacturing routes.

4 Conclusions

In the present work, for the first time, we report the substantial increase in toughness that may be achieved when nano-SiO_2 particles are well dispersed in a hot-cured single-part epoxy polymer. Most importantly, the synergistic effect of having a multiphase structure based upon both nano-SiO_2 particles and rubbery particles is clearly demonstrated.

The use of nano-SiO_2 particles and rubbery particles to give ‘hybrid-toughened’ epoxy polymers has been demonstrated to give a range of very novel matrices which lead to an increased delamination toughness of the resulting carbon-fibre reinforced-plastic (CFRP) composites. Also, it is noteworthy, that the presence of even a relatively high concentration of the nano-SiO_2 particles does not lead to a decrease in the modulus of the composite. Nor does it lead to a significant increase in the viscosity of the epoxy resin, which would preclude the use of low-cost manufacturing routes, such as a vacuum-assisted resin-transfer moulding (VARTM) process.

These multiphase ‘hybrid’ epoxy polymers have considerable potential for a wide range of applications, such as adhesives, composite matrices and electronic encapsulating resins, where a high toughness is often required but without any accompanying significant loss of other important properties such a modulus and thermal resistance.

Future work will explore the detailed mechanisms of toughening which are initiated by the nano-SiO_2 particles. Since, the understanding of these mechanisms may lead to even further increases in the mechanical performance of ‘hybrid-toughened’ epoxy polymers, containing a complex multiphase structure of nano- and micro-sized phase inclusions, and such increases may again be transferable to fibre-composite materials produced by relatively low-cost manufacturing routes.

5 Proposed Future Work

- Ascertain impact resistance of the nano-toughened composites.
- Extend this to ballistic resistance.
- Investigate the fatigue performance of the nano-toughened polymers using a fracture mechanics approach.
- Study the use of carbon nano-tube mats as a toughening phase.

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