

The effect of silica nano particles and rubber particles on the toughness of multiphase thermosetting epoxy polymers

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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. 1–3] for many years that the incorporation of a second microphase 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 1–5 μm in diameter with a volume fraction of about 5–20%. 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 nanophase consists of small rigid particles of silica [4].

We have previously shown [4] that the addition of low concentrations of nano-silica (SiO_2) 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 1–8% by weight of such nano particles was needed to achieve significant improvements in the mechanical and thermal performance of the two-part multiphase epoxy adhesive. In the present paper, 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. 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 [2, 3, 5–7].

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 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 [8], 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 nanofilled 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 Fig. 1.

The reactive liquid rubber, which give rises to the micrometer-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 1300 \times 8' with a number-average molecular weight of 3550 g/mol and an acrylonitrile content of 18 wt.%. This was pre-reacted with the DGEBA resin to give a 40 wt.% CTBN-epoxy adduct: 'Albipox 1000' from Hanse Chemie, Geesthacht, Germany.

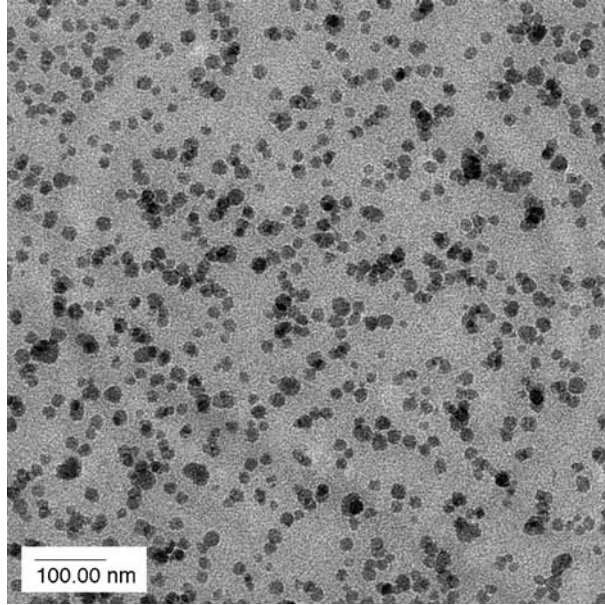


Figure 1 Transmission electron micrograph showing the excellent dispersion of the SiO₂ nano particles in the epoxy resin.

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-SiO₂ epoxy and CTBN-epoxy adduct, to give the required levels of added nano-SiO₂ 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 hr at 90 °C, followed by a post-cure of 2 hr at 160 °C.

The glass transition temperature, T_g , of the various formulations was measured using differential scanning calorimetry at a rate of 10 °K/min. The stress-intensity factor, K_{Ic} , at the onset of crack growth was measured according to the ISO test method [9]. 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 [10, 11]. The coefficient of variation in the values of E was $\pm 7.0\%$. The

value of the fracture energy, G_{Ic} , was calculated from the knowledge of the values of K_{Ic} and E , using the relationship:

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

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

The results for the thermosetting epoxy polymer containing only the *in-situ* formed nano-silica particles are shown in Table I, with the results for the values of the fracture energy, G_{Ic} , as a function of the wt.% of nano-SiO₂ also given in Fig. 2. The experimental scatter on the values of the glass transition temperature, T_g , of the polymers is typically ± 2 °C, and thus the presence of the nano-SiO₂ particles would appear to have little effect on the value of T_g . However, the presence of the nanophase 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, as would be expected of course from adding relatively high modulus silica nano particles to an epoxy polymer. 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-SiO₂ particles in Fig. 2. As may be seen, the inclusion of 4 wt.% gives a significant increase in G_{Ic} from 103 to 291 J/m², but thereafter further increases in the concentration of the nano-SiO₂ phase produce a small, but steady, increase in the measured toughness.

The results for the epoxy polymers containing both the nano-silica and the rubbery phase are also shown in Table I and in Fig. 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 I. (The rubbery particles are produced via a reaction-induced phase-separation, giving particles of about 1–5 μ m in diameter, as is well documented for such materials [1, 7].) As expected

TABLE I The formulations employed and their mechanical properties

Formulation		T_g (°C)	E (GPa)	K_{Ic} (MPa \sqrt{m})	G_{Ic} (J/m ²)
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

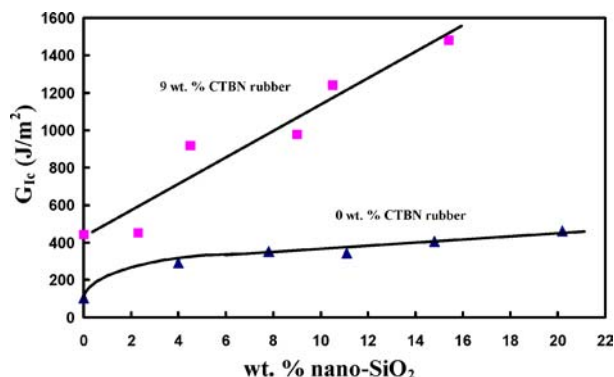


Figure 2 The fracture energy, G_{Ic} , versus the concentration of nano-SiO₂ particles.

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 103 J/m² to over 400 J/m² 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 [2, 3, 7].

Second, we may consider the effects of introducing both rubbery micrometer-sized particles and nano-SiO₂ 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 9 wt.% CTBN and the various concentrations of the nano-SiO₂ 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 nanophase 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 103 J/m² for the pure epoxy polymer to over 1400 J/m² upon the formation of the 'hybrid' material containing both rubbery micrometer-sized particles and nano-SiO₂ particles. The major increases in the toughness of the 'hybrid' epoxy polymers as the concentration of the nanophase is increased may clearly be seen in Fig. 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-SiO₂ particles should further increase the tough-

ness so markedly. Previous work on rigid fillers, which were micrometers in size as opposed to be nanometers, 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 [12]. However, other toughening mechanisms such as (a) crack deflection and crack twisting around the rigid particles [13] and (b) crack-front pinning by the rigid particles [14] 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.

In the present paper, for the first time, we report the substantial increase in toughness that may be achieved when nano-SiO₂ 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-SiO₂ 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 as modulus and thermal resistance.

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