

## Tough Nanoparticle-Modified Polymers

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Abstract: A crosslinked epoxy polymer has been modified by the addition of nano-silica particles. The particles were introduced via a sol-gel technique which gave a very well dispersed phase of nano-silica particles which were about 20 nm in diameter. The glass transition temperature was unchanged by the addition of the nanoparticles, but both the modulus and toughness were increased. The fracture energy,  $G_{Ic}$ , increased from 100 J/m<sup>2</sup> for the unmodified epoxy to 460 J/m<sup>2</sup> for the epoxy with 20 wt. % of nano-silica. The microscopy studies showed evidence of debonding of the nanoparticles and subsequent plastic void growth of the epoxy polymer. A theoretical model of plastic void growth was used to confirm this mechanism. The cyclic-fatigue behaviour of the epoxy polymers has also been studied and the fatigue properties were clearly enhanced by the presence of the nano-silica particles. Indeed, it was found that the values of the strain-energy release rate at threshold,  $G_{th}$ , from the cyclic-fatigue tests increased steadily as the toughness,  $G_{Ic}$ , also increased, i.e. as the concentration of nano-silica particles was increased.

### 1. Introduction

Epoxy polymers are widely used for the matrices of fibre-reinforced composite materials and as adhesives. When cured, epoxies are amorphous and highly-crosslinked (i.e. thermosetting) polymers. 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 a 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 for many years that the incorporation of a second microphase of a dispersed rubber, e.g. [1-5], or a thermoplastic polymer, e.g. [6-7], into the epoxy can increase their toughness. However, the presence of the either of these phases typically increases the viscosity of the epoxy monomer mixture, and the presence of rubber particles reduces the modulus of the cured epoxy polymer. Rigid, inorganic particles have also been used [8-12], since these can increase the toughness and the modulus of the epoxy. However, these relatively large particles also significantly increase the viscosity of the resin, reducing the ease of processing. More recently, a new technology has emerged which holds considerable promise for increasing the mechanical performance of such thermosetting polymers. This is via the addition of a nano-phase structure in the polymer, where the nano-phase consists of small rigid particles of silica [13-15],

and the viscosity of the resin is not significantly affected by the presence of the nano-silica particles due to their very small diameter and lack of agglomeration [16]. The aims of the present work are to investigate the fracture and fatigue properties of epoxy polymer modified with *in-situ* formed nano-silica particles, and to establish the structure/property relationships and the toughening mechanisms.

## 2. Experimental Methods

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, Duisburg, Germany. The silica (SiO<sub>2</sub>) nanoparticles were supplied as a colloidal silica sol in the resin matrix, 'Nanopox F400', by Nanoresins, Geesthacht, Germany. The silica nanoparticles had a mean particle size of about 20 nm, with a narrow range of particle-size distribution; laser light scattering shows that almost all the particles are between 5 to 35 nm in diameter. The particle size and excellent dispersion of these silica particles remain unchanged during any further mixing and/or blending operations. The curing agent was an accelerated methylhexahydrophthalic acid anhydride, namely 'Albidur HE 600' supplied by Nanoresins, Geesthacht, Germany, the stoichiometric concentration being employed. The curing schedule employed was 1 hour at 90°C, followed by a post-cure of 2 hours at 160°C. Bulk sheets of unmodified epoxy and nano-silica modified epoxy were produced to determine the thermal (using differential scanning calorimetry (DSC) and differential mechanical thermal analysis (DMTA)) and the mechanical (i.e. tensile and fracture-mechanics) properties. The values of the stress-intensity factor,  $K_{Ic}$ , at the onset of crack growth were determined using ISO standard 13586 (2000) and were converted to values of the fracture energy,  $G_{Ic}$ , using the measured modulus, as described in the Standard. The cyclic-fatigue tests were conducted in displacement control, with a displacement ratio,  $\delta_{min} / \delta_{max}$ , of 0.5. Sinusoidal loading was used, with a frequency of 5 Hz. The rate of cyclic-fatigue growth per cycle,  $da/dN$ , was measured, following ASTM standard E647 (2000), as a function of the maximum strain-energy release rate,  $G_{max}$ , applied per cycle.

## 3. Results

Microscopy of the unmodified epoxy showed that a homogeneous thermoset was formed. For the nano-silica modified epoxy polymers, atomic force microscopy (AFM) and transmission electron microscopy (TEM) both showed that there was no agglomeration of the nano-silica particles, even at relatively higher volume fractions of nano-silica. Instead, the nanoparticles are well dispersed throughout the epoxy, as shown in Fig. 1.

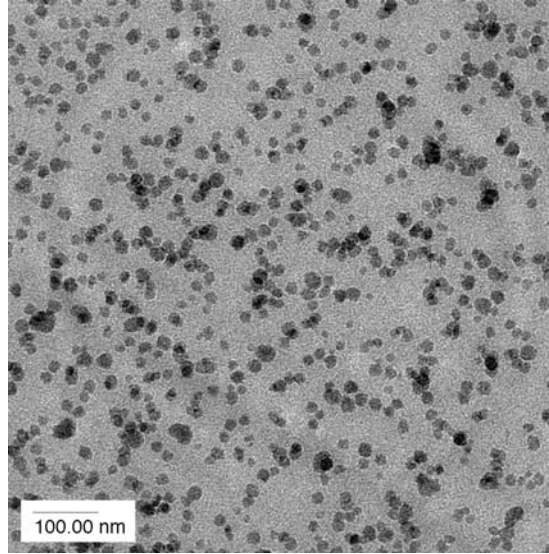


Fig. 1 Transmission electron micrograph showing the excellent dispersion of the nano-silica particles in the epoxy resin.

The properties of the thermosetting epoxy polymer containing the *in-situ* formed nano-silica particles are shown in Table 1. The experimental scatter on the values of the glass transition temperature,  $T_g$ , of the polymers is typically  $\pm 2^\circ\text{C}$ , and thus the presence of the nano-silica particles would appear to have no significant 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, as would be expected of course from adding relatively high modulus nano-silica 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. The resulting value of the fracture energy,  $G_{Ic}$ , is also shown as a function of the wt.% of added nano-silica particles in Table 1. As may be seen, the inclusion of about 20 wt.% gives a significant increase in  $G_{Ic}$  from  $103 \text{ J/m}^2$  to  $461 \text{ J/m}^2$ .

Table 1. Glass transition temperatures, modulus and fracture properties of the anhydride-cured epoxy containing nano-silica particles.

Nanosilica content (wt%)	Nanosilica content (vol%)	$T_g$ ( $^\circ\text{C}$ ) DSC	$T_g$ ( $^\circ\text{C}$ ) DMTA	$E$ (GPa)	$K_{Ic}$ ( $\text{MNm}^{-3/2}$ )	$G_{Ic}$ ( $\text{J/m}^2$ )
0	0	143	153	2.96	0.59	103
4.1	2.5	137	152	3.20	1.03	291
7.8	4.9	136	154	3.42	1.17	352
11.1	7.1	141	151	3.57	1.18	343
14.8	9.6	138	152	3.60	1.29	406
20.2	13.4	138	150	3.85	1.42	461

## 4. Toughening Micromechanisms

### 4.1 Introduction

The toughening mechanisms associated with micrometre-sized inorganic particles have frequently been shown to be due to debonding of the particles followed by plastic void growth, e.g. [11,12,17]. Indeed, Kinloch & Taylor [17] have also demonstrated that the voids around particles closed-up when the epoxy polymer was heated above its  $T_g$  and allowed to relax. The debonding process is generally considered to absorb little energy compared to the plastic deformation of the matrix. However, debonding is essential because this reduces the constraint at the crack tip, and hence allows the matrix to deform plastically via a void growth mechanism. High-resolution scanning electron microscopy (FEG-SEM) and AFM of a fracture surface of the polymer containing nano-silica showed the presence of voids around several of the nanoparticles. This shows that plastic void growth of the epoxy matrix, initiated by debonding of the nanoparticles, has also occurred in with these nano-sized inorganic particles. The diameter of these voids is typically 30 nm. These voids were also observed in the fracture surfaces of samples with different concentrations of nano-silica.

### 4.2 Modelling studies

Huang and Kinloch postulated that the fracture energy of a particle-modified polymer may be expressed [18] as:

$$G_{lc} = G_{lcu} + \Psi \quad (1)$$

where  $G_{lcu}$  represents the fracture energy of the unmodified epoxy, and  $\Psi$  represents the overall toughening contribution. They suggested that the overall toughening contribution,  $\Psi$ , was composed of contributions from particle bridging, localised shear banding in the epoxy matrix, and plastic void growth of the epoxy matrix which is initiated by cavitation or debonding of the particulate phase. However, for rigid spherical particles as used in the present work, microscopy studies have shown that bridging does not occur and that the plastic void growth mechanism seems to be by far the dominant toughening micromechanism. Thus, the relationship in Eq. (1) may be written:

$$G_{lc} \approx G_{lcu} + \Delta G_v \quad (2)$$

where  $\Delta G_v$  is the contribution to the increase in fracture energy from plastic void growth of the epoxy matrix. For simplicity, we will initially assume that the adhesion between the nano-silica and epoxy phases is relatively poor, and hence debonding will not contribute to the toughening effect. The contribution to the increase in fracture energy from the plastic void growth mechanism,  $\Delta G_v$ , is given [18] by:

$$\Delta G_v = (1 - \mu_m^2/3)(V_v - V_f)\sigma_{yc}r_{yu}K_{vm}^2 \quad (3)$$

where  $\mu_m$  is a material constant,  $V_v$  is the volume fraction of voids,  $V_f$  is the volume fraction of nanoparticles,  $\sigma_{yc}$  is the compressive yield stress of the unmodified epoxy polymer,  $r_{yu}$  is the radius of the plastic zone of the unmodified epoxy polymer, and  $K_{vm}$  is the maximum stress concentration factor of the von Mises stress in the plastic matrix. The value of  $\mu_m$ , which describes the pressure sensitivity of the material in the von Mises yield criterion, and was taken to be 0.2. The maximum stress concentration factor,  $K_{vm}$ , was found from a finite element analysis [19] to be 2.22 around a void in an epoxy matrix. The size of the plastic zone,  $r_y$ , ahead of the crack tip can be calculated assuming linear-elastic fracture-mechanics (LEFM) behaviour. Under plane-strain conditions and assuming that the zone is circular [18] as proposed by Irwin, for the unmodified epoxy  $K_{Ic} = 0.59 \text{ MNm}^{-3/2}$ ,  $\sigma_y = 61.1 \text{ MPa}$ , and hence  $r_{yu} = 5 \text{ }\mu\text{m}$ . Now, the use of Eq. (3) requires a knowledge of the volume fraction of voids; and it is difficult to measure this parameter accurately from the micrographs, since it is difficult to identify all the voids due to the resolution of the microscopes used. Nevertheless, a mean void diameter can be calculated from the features which are clearly voids. Analysis of micrographs of the polymer with 9.6 vol% nano-silica gave a mean void diameter of 30 nm, as noted above. Micrographs of the formulation containing 2.5 vol% nano-silica indicated an average void diameter of just below 30 nm. However, some voids up to 50 nm in diameter are observed in all formulations where micrographs from FEG-SEM analysis were available. The predicted toughening increment,  $\Psi$ , was calculated using Eqs. (1) to (3); assuming (a) that the measured toughening increment is entirely caused by plastic void growth (i.e.  $\Psi = \Delta G_v$ ), and (b) that all of the particles initiate the growth of voids which have a final diameter of 30 nm. For the epoxy with 9.6 vol % of nano-silica, the measured toughening increment is  $303 \text{ J/m}^2$  and the predicted toughening increment is  $394 \text{ J/m}^2$ . The toughening increment can also be predicted for the other formulations, for which detailed FEG-SEM images are not available, assuming that the average void diameter is constant and that all of the particles initiate void growth. The results are shown in Table 2 and, considering the simplifying assumptions made, the agreement between the measured and the predicted toughening increments is very reasonable.

Table 2. Measured and predicted toughening increments. Predicted values calculated using (3), assuming that  $\Psi = \Delta G_v$ . (Note  $G_{Icu} = 103 \text{ J/m}^2$ .)

Nanosilica content (wt%)	Nanosilica content (vol%)	Toughening increment, $\Psi$ ( $\text{J/m}^2$ )	
		Measured	Predicted
4.1	2.5	188	107
7.8	4.9	249	209
11.1	7.1	240	297
14.8	9.6	303	394
20.2	13.4	358	540

## 5. Cyclic-Fatigue Behaviour

Considering the cyclic-fatigue studies [20], Fig. 2 shows typical results for the unmodified epoxy polymer and for the material containing various concentrations of nano-silica particles. There are several noteworthy points. Firstly, for all materials there is a region where there is a linear relationship between the logarithmic crack growth rate per cycle,  $da/dN$ , versus the logarithmic maximum stress-energy release rate,  $G_{max}$ , applied per cycle in the fatigue tests, i.e. the ‘Paris Law region’. Secondly, for each formulation there is a clearly identifiable ‘threshold region’, i.e. a value of  $G_{max}$ , denoted  $G_{th}$ , below which no cyclic-fatigue crack growth will occur. This threshold value,  $G_{th}$ , is a very useful parameter for both (a) material development and selection, and (b) the design engineer. Thirdly, the cyclic-fatigue properties of the epoxy polymer are clearly enhanced by the presence of the nano-silica particles, and the value of  $G_{th}$  is increased significantly due to the addition of nano-silica.

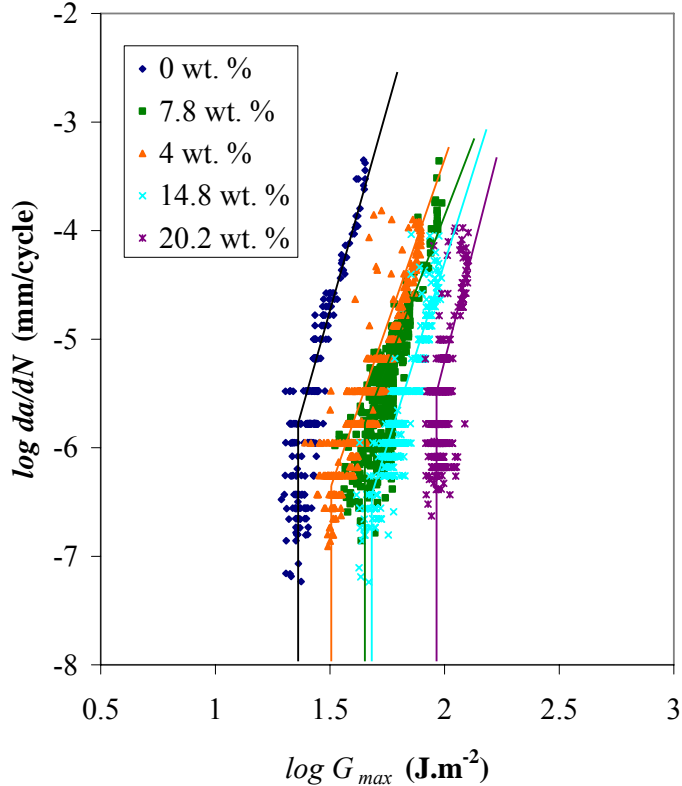


Fig. 3 Logarithmic crack growth rate per cycle,  $da/dN$ , versus logarithmic maximum strain-energy release rate,  $G_{max}$ , applied per cycle from the fatigue tests for the unmodified epoxy and nano-silica modified epoxies containing various levels of nano-silica particles.

Indeed, Fig. 3 shows the value of the maximum applied strain-energy release rate at threshold,  $G_{th}$ , from the cyclic-fatigue tests versus the fracture energy,  $G_{Ic}$ , for all the materials studied. It can be clearly seen that the value of  $G_{th}$  increases steadily as the toughness,  $G_{Ic}$ , also rises, i.e. as the concentration of nano-silica particles is increased.

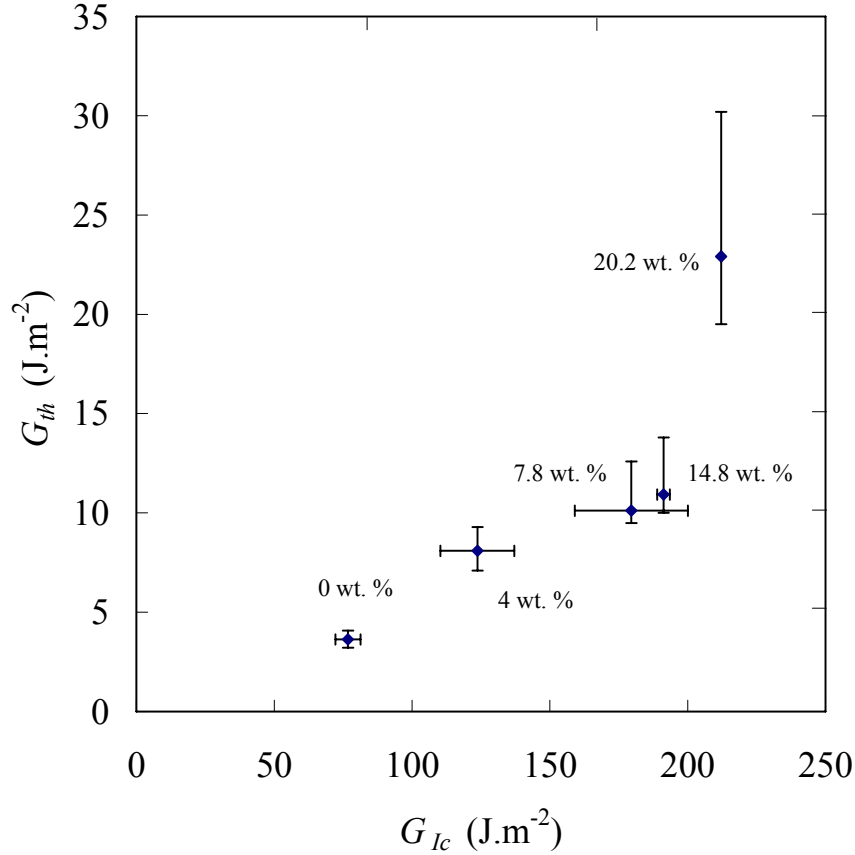


Fig. 4 Maximum strain-energy release rate at threshold,  $G_{th}$ , from the cyclic-fatigue tests versus the fracture energy,  $G_{Ic}$ .

## 6. Conclusions

An epoxy polymer containing nano-silica particles, which were approximately 20 nm in diameter, has been studied. These particles, produced via a sol-gel method, were well-dispersed through the epoxy matrix with no agglomeration being observed using transmission electron and atomic force microscopy. The addition of the nano-silica particles did not affect the glass transition temperature, but the addition of nanoparticles increased the modulus of the epoxy, as expected. The fracture toughness of the polymers was measured, and a  $K_{Ic}$  of  $0.59 \text{ MNm}^{-3/2}$  was recorded for the unmodified epoxy. Addition of the nano-silica particles increased the fracture toughness, with a maximum value of  $1.42 \text{ MNm}^{-3/2}$  being measured

for the epoxy with 20.2 wt.% of nanoparticles. The unmodified epoxy possessed a  $G_{Ic}$  of 103 J/m<sup>2</sup> and a maximum fracture energy of 460 J/m<sup>2</sup> was recorded for the modified epoxy containing 20.2 wt.% of nano-silica particles. Hence, there is a significant toughening effect due to the addition of the nano-silica particles. Observation of the fracture surfaces using scanning electron and atomic force microscopy showed nano-silica particles surrounded by voids, providing evidence of debonding of the nanoparticles and subsequent plastic void growth of the epoxy polymer. An analytical model of plastic void growth was used to confirm whether this mechanism could be responsible for the increased toughness. The mean void diameter was measured from the electron micrographs, and the model was used to predict the toughening increment, i.e. compared to the fracture energy of the unmodified epoxy. The predicted values were in good agreement with the measured values, indicating that debonding of the nano-silica particles and subsequent plastic void growth of the epoxy polymer were indeed the mechanisms responsible for the increase in toughness of the epoxy polymer upon addition of the nanoparticles. Finally, the cyclic-fatigue properties of the epoxy polymers have also been studied and they were clearly enhanced by the presence of the nano-silica particles. Indeed, it was found that the values of the strain-energy release rate at threshold,  $G_{th}$ , from the cyclic-fatigue tests increased steadily as the toughness,  $G_{Ic}$ , also increased, i.e. as the concentration of nanoparticles was increased.



## 7. References

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