



# The modelling of the toughening of epoxy polymers via silica nanoparticles: The effects of volume fraction and particle size<sup>☆</sup>



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## ABSTRACT

Silica nanoparticles possessing three different diameters (23, 74 and 170 nm) were used to modify a piperidine-cured epoxy polymer. Fracture tests were performed and values of the toughness increased steadily as the concentration of silica nanoparticles was increased. However, no significant effects of particle size were found on the measured value of toughness. The toughening mechanisms were identified as (i) the formation of localised shear-band yielding in the epoxy matrix polymer which is initiated by the silica nanoparticles, and (ii) debonding of the silica nanoparticles followed by plastic void growth of the epoxy matrix polymer. These mechanisms, and hence the toughness of the epoxy polymers containing the silica nanoparticles, were modelled using the Hsieh et al. approach (Polymer **51**, 2010, 6284–6294). However, it is noteworthy that previous modelling work has required the volume fraction of debonded silica particles to be measured from the fracture surfaces but in the present paper a new and more fundamental approach has been proposed. Here finite-element modelling has demonstrated that once one silica nanoparticle debonds then its nearest neighbours are shielded from the applied stress field, and hence may not debond. Statistical analysis showed that, for a good, i.e. random, dispersion of nanoparticles, each nanoparticle has six nearest neighbours, so only one in seven particles would be predicted to debond. This approach therefore predicts that only 14.3% of the nanoparticles present will debond, and this value is in excellent agreement with the value of 10–15% of those nanoparticles present debonding which was recorded via direct observations of the fracture surfaces. Further, this value of about 15% of silica nanoparticles present debonding has also been noted in other published studies, but has never been previously explained. The predictions from the modelling studies of the toughness of the various epoxy polymers containing the silica nanoparticles were compared with the measured fracture energies and the agreement was found to be good.

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## 1. Introduction

Epoxy polymers are widely used in many different engineering applications, such as coatings, adhesives and matrices in composite materials. For example, as coatings, such polymers are employed widely for applications requiring good ultra-violet light protection or high-scratch resistance. Their insulating properties, good temperature resistance and ease of processing also allow epoxy polymers to be used extensively in the electronics industry for applications in printed circuit boards and encapsulated electrical components [1]. Furthermore, the use of adhesive and composite materials based on epoxy polymers is widespread in the aerospace, automobile and wind-energy industries due to their structural efficiency [2,3]. Indeed, their outstanding temperature resistance and durability to weathering, fuel, de-icing fluids, etc. leads to them invariably being the preferred materials, compared to acrylics and

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polyurethanes, for external aerospace applications [1–3]. Epoxies are amorphous, highly cross-linked, thermosetting polymers which exhibit good elevated temperature resistance and low creep. However, their high cross-link density causes them to be relatively brittle polymers, and this limits their application as structural materials, as they have a poor resistance to the initiation and growth of cracks. Thus, improvements in their fracture performance are highly sought after by industry [3]. The addition of silica nanoparticles has been shown to improve these properties without adversely affecting the thermo-mechanical properties of the epoxy polymer [4–8]. Another advantage [5,6,8–10] is that due to their very small size, and hence large number, then a relatively low volume fraction of such nanoparticles can induce relatively extensive toughening of the epoxy polymer. Furthermore, the particles are sufficiently small such that when resin transfer moulding manufacturing processes are employed they are not filtered-out of the matrix by the fibre preforms when added to the matrices for fibre-reinforced composite materials [7,9]; where they improve both the fracture and fatigue resistance of the composite material.

Johnsen et al. [10] ascertained that a major toughening mechanism arose from plastic void growth of the epoxy matrix polymer around debonded silica nanoparticles. Liang and Pearson [11] extended these ideas to show that plastic shear-banding in the epoxy matrix polymer also contributed to the toughening of such modified epoxy polymers. These toughening mechanisms were then implemented into a mathematical model proposed by Hsieh et al. [12,13] and such a model was used to predict successfully the fracture energy,  $G_C$ , of epoxy polymers toughened via the addition of silica nanoparticles. Further, Giannakopoulos et al. [14] and Chen et al. [15] have shown that this theoretical model also applies to the toughening of epoxy polymers via rubbery core–shell nano-sized particles. Interestingly, Giannakopoulos et al. [14] also reported that, within experimental error, there was little effect of particle diameter on the increase in toughness resulting from the addition of the core–shell particles, within the range of 100–300 nm.

In the present study, the Hsieh et al. [12,13] model will be used to predict the fracture energy of nanoparticle-modified epoxy polymers, where rigid, amorphous silica nanoparticles of three distinct sizes have been used, at various concentrations, to modify the epoxy polymer. Further, the previous work discussed above required high-resolution scanning-electron microscopy of the fracture surfaces to be undertaken after the fracture test had been conducted in order to identify the quantitative details of the toughening mechanisms that were required in the predictive mathematical model. The present work develops a new approach which enables the modelling results to be deduced from the basic properties of the polymer, i.e. before any fracture tests are undertaken.

## 2. Experimental

### 2.1. Materials

The epoxy resin consisted of a standard diglycidyl ether of bisphenol A (DGEBA) (DER331 resin, Dow Chemical Company, USA) with an equivalent molecular weight of 187 g/mol. The three different sizes of silica nanoparticles were employed which possessed average particle diameters of 23 nm, 74 nm, and 170 nm, respectively, and were surface modified by an organosilane via a sol–gel process. They were supplied pre-mixed in a silica-DGEBA master-batch for each particle size by the 3M Company, USA. Piperidine (Sigma–Aldrich, USA) was used as the curing agent. The required volume fraction of silica nanoparticles was achieved by blending the silica-DGEBA master-batch with the pure DGEBA, mixing at 85 °C using a mechanical stirrer, and then degassing for

4 h. The silica nanoparticle-epoxy blend was then mixed with five weight percent of piperidine, degassed for a second time and then poured in a release-coated steel mould and cured at 160 °C for 6 h. As expected, the viscosity of the epoxy resin/curing agent mixture increased at higher loadings of silica nanoparticles. However, the basic epoxy resin/curing agent mixture possessed a relatively low initial viscosity and the increase in viscosity upon addition of the higher concentrations of silica nanoparticles was not considered to be an important aspect of the production of the cast sheets via pouring into, and then curing in, the steel mould. The same batch of material was used as for previous studies [16]. In Ref. [16] transmission electron microscopy images were given which showed that a good dispersion of silica nanoparticles in the epoxy polymer was achieved, although at the very highest concentration of silica nanoparticles a small degree of agglomeration was observed. The density of the composites was measured using a pycnometer and the calculated densities of the epoxy polymer and silica nanoparticles were 1.16 g/cm<sup>3</sup> and 1.92 g/cm<sup>3</sup>, respectively. Using the measured densities, the volume fraction of the silica nanoparticles was calculated from the known weight percentages. This confirmed that the volume fraction of silica nanoparticles was as stated. A glass transition temperature of 80 °C was measured for the epoxy polymer using differential scanning calorimetry, and this value was unaffected by the addition of the silica nanoparticles [16].

### 2.2. Material characterisation

The Young's modulus,  $E$ , and yield stress,  $\sigma_y$ , of the unmodified and silica nanoparticle-modified epoxies were measured using uniaxial tensile tests. The bulk polymer samples were machined into a dog-bone shape with dimensions of 63.5 mm long by 3 mm thick, and 3 mm wide in the gauge section. They were tested at a constant displacement rate of 5 mm/min at room temperature, according to the ASTM-D638 (Type V) standard test method [17], with a minimum of five replicate samples per material type. It should be noted that since the present epoxy polymers are all relatively brittle materials it was not possible to obtain meaningful values of the strain to break from uniaxial tensile tests: any such data would be very dependent upon the sample preparation technique employed and will inevitably exhibit a relatively high degree of scatter. Indeed, for these reasons plane-strain compression tests have been undertaken of the unmodified epoxy polymer to ascertain the overall yield behaviour of the material, since as expected it failed around the yield point when uniaxial tensile tests were undertaken. The plane-strain compression tests were conducted as described previously [13].

The fracture toughness,  $K_{IC}$ , was measured using a single-edge notch bend (SENB) test, in accordance with the ASTM-D5045 standard [18]. Sample dimensions of 75.6 mm × 12.7 mm × 6.36 mm and a constant displacement rate of 1 mm/min were used. A pre-crack was made by lightly tapping a fresh razor blade into the machined notch, yielding a very sharp natural crack tip. The mean and standard deviation values of the fracture toughness were ascertained, using a minimum of five replicate samples for each material. The fracture energy,  $G_C$ , was calculated from the values of the fracture toughness, Poisson's ratio and Young's modulus [19].

The fracture surfaces of the SENB samples were studied using scanning electron microscopy. High-resolution scanning-electron microscopy was performed using an electron microscope equipped with a field-emission gun (FEG-SEM); a Carl Zeiss Leo 1525 with a Gemini column was used, with a typical accelerating voltage of 5 kV. All samples were coated with an approximately 5 nm thick layer of chromium before imaging. The FEG-SEM images were used to study the debonding and any subsequent plastic void growth of the polymer. The fraction of silica nanoparticles that debonded

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