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Toughening mechanisms in epoxy–silica nanocomposites (ESNs)

Y.L. Liang, R.A. Pearson*

Center for Polymer Science and Engineering, Lehigh University, 5 East Packer Ave, Bethlehem, PA 18015-3195, USA

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ABSTRACT

Two types of nanosilica (NS) particles with different average particle sizes (20 nm and 80 nm in diameter, respectively) were used to fabricate epoxy–silica nanocomposites (ESNs) in this study. No significant differences in fracture behavior were observed between the epoxies filled with 20 nm NS particles and the epoxies filled with 80 nm NS particles. Interestingly, both types of NS particles were found to be more efficient in toughening epoxies than micron size glass spheres. As with micron size glass spheres, the fracture toughness of the ESNs were affected by the crosslink density of the epoxy matrix, i.e. a lower crosslinked matrix resulted in a tougher ESN. The increases in toughness in both types of ESNs were attributed to a zone shielding mechanism involving matrix plastic deformation. Moreover, the use of Irwin's formalized plastic zone model precisely described the relationship between the fracture toughness, yield strength and the corresponding plastic zone size of the various ESNs examined.

1. Introduction

Rigid inorganic particles have been used to toughen epoxy resins for quite some time and such particles can provide modest improvements in fracture toughness [1–5]. In contrast to rubber-toughened epoxies, the use of inorganic rigid fillers provides toughened epoxies without a decrease in modulus [3]. Among the different types of inorganic fillers, micron size glass spheres have been a popular option since they are isotropic in shape, low cost, relatively stiff, and possess low coefficient of thermal expansion (CTE). CTE plays a critical role in alleviating the thermal stress between silicon chips and organic substrates when applied in microelectronic packaging [6].

Recently, a significant amount of fracture toughness improvement has been reported when mono-dispersed, non-agglomerated nanosilica (NS) particles, developed from sol–gel technology [7], are mixed into an epoxy resin [8–12]. The toughening mechanism of epoxy–silica nanocomposites (ESNs) proposed by Johnsen et al. [12] involves plastic void growth around debonded particles. Their quantitative model predicts that the improvement in fracture energy with increasing NS content and correlates well with experimental data. Interestingly, the effect of NS particle size and matrix crosslink density on fracture toughness has not been emphasized in the open literature. Also, it is of a great interest to enhance our comprehension of the toughening mechanisms in ESNs. In order to do so, a concise review of the toughening mechanisms in epoxy resins induced by micron-size glass spheres and nanometer-size silica is presented in the following paragraphs.

Researchers have used various models to predict the increases in toughness in filled epoxy systems including crack front pinning/particle bridging [13], crack path deflection [5], and microcracking [14]. Most glass bead filled epoxies systems possess several types of toughening mechanisms and the exact contribution of each type of toughening mechanism on the overall toughness is difficult to quantify. In the crack pinning concept [15], well-bonded inclusions locally pin the crack front and result in additional line tension in the crack front bowing between particles. Consequently, more energy is required to propagate the crack past inclusions. This model reveals that the relative improvement in the fracture toughness ($K_{\mathrm{composite}}/K_{\mathrm{matrix}}$) is a function of the filler volume fraction and particle diameter. On the other hand, for a weakly bonded inclusion, the crack front is deflected by the particle as a result of the tendency of crack to propagate towards the weak particle–matrix interface [5]. The fracture toughness improvement due to crack deflection is usually expressed as a function of fracture surface roughness as well as particle diameter. In the particle-induced microcracking concept [14], strain energy is absorbed when particles debond and concomitant matrix microcracking occurs. It is noteworthy that crack pinning and crack path deflection models predict increasing toughness with increasing particle size whereas the microcracking model favors smaller particles.

In contrast to the conventional wisdom obtained from previous micron-glass-sphere studies, Zhang [9] indicated that the advantages of ESNs are based on the larger amount of the interphase

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* Corresponding author. Tel.: +1 610 758 3857; fax: +1 610 758 4244.
E-mail address: rp02@lehigh.edu (R.A. Pearson).

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Table 1
The formulations of ESNs investigated in this work.

ESNs					
NS (g)	1.9	3.8	7.5	15.0	37.5
Epoxy (g)	141	138.6	136.3	127.5	107.3
Piperidine (g)	7.1	6.9	6.8	6.4	5.4
Total Weight (g)	149.9	149.3	150.6	148.9	150.2
NS Content (wt%)	1.3%	2.5%	5.0%	10.1%	24.6%
NS Content (vol%)	0.8%	1.6%	3.2%	6.6%	17.4%

polymer layer and a shorter interparticle distance. The surfaces of modified NS particles develop an interphase polymer layer around the inclusion, which exhibits dissimilar mechanical properties compared with bulk composites [16]. By increasing the NS fraction, the interparticle distance is diminished to a level where the properties of the interphase polymer layer become significant enough to affect the performance of the bulk materials. In Zhang's study [9], the fracture behavior and flexural modulus were considerably improved when interparticle distance is smaller than the particle diameter. According to Zhang, smaller NS particles are more efficient toughening particles than traditional micron size particles used in epoxy resins.

The objective in this study is to investigate the influence of nanosilica (NS) particle size and matrix crosslink density on the toughening efficiency of epoxy–silica nanocomposites (ESNs). In addition to quantify the toughness, the mechanisms responsible for increasing the toughness of ESNs are also explored.

2. Experimental approach

2.1. Materials

Two different size nanosilica (NS) particles, nominal 20 nm and 80 nm in diameter, were examined: 20 nm (Nanopox E430, Nanoresins) and 80 nm (3 M) NS particles were dispersed in diglycidyl ether of bisphenol A/F (DGEBA/F), and DGEBA epoxy resin as received, respectively. Both NS particles were supplied as concentrated dispersions, therefore, a DGEBA epoxy resin (DER331, Dow Chemical, Co.) was used to adjust the NS fraction from 0.8 to 17.4 vol%. The mixing process consisted of mechanical stirring (120 rpm) at 80 °C under a vacuum. After 4 h of mixing, 5 phr (per hundred parts resin) curing agent (piperidine, Aldrich) was added and stirred for another 10 min under atmospheric pressure. Then the mixture was poured out into a pre-heated steel mold with Teflon base release agent sprayed on it. The curing schedule for the study on the effect of NS particle size on mechanical properties was 160 °C for 6 h. However, in order to investigate the effect of matrix crosslink density, two other cure schedules (80 °C for 24 h and 120 °C for 16 h) were also applied and these results are discussed in Section 3.5.

The formulations of ESNs investigated are shown in Table 1. The volume fractions of NS particles were estimated according to the weight ratio of each component and the material densities obtained from the manufacturers and the reference (DGEBA: 1.16 g/cm^3; NS: 1.8 g/cm^3 [12], and piperidine: 0.86 g/cm^3). In order to simplify the calculation, it was assumed that the total volume of the ESN equals the sum of the volume from each component included in the blend.

2.2. Experimental methods

For the NS particle-dispersion study, the composite samples were sent to the Core Electron Microscopy Facility in UMass Medical School for transmission electron microscopy (TEM) investigation. The thickness of the TEM samples was maintained at 120 nm by cryomicrotoming at −10 °C.

The glass transition temperature, T_g, of cured epoxies was determined using the mid-point of the glass transition process according to the second scan from differential scanning calorimeter (DSC, model 2920, TA Instrument). The sample weight was 10–20 mg, and the heating rate was 10 °C/min.

A screw-driven material testing machine (model 5567, Instron) was used to characterize the mechanical properties of the materials studied under ambient temperature. Compression tests were conducted using ASTM D695 guidelines [17] with tetragonal shaped specimens of 5.0 mm × 5.0 mm × 10.0 mm and cross-head speed 1 mm/min. At least 5 samples for each formulation were tested. The compressive modulus and the yield stress were recorded for the calculations of the fracture energy and the plastic-zone size estimation. Note that we assumed that the compressive modulus is equivalent to the tensile modulus, i.e. Young's modulus.

The fracture toughness, K_{IC}, was measured according to ASTM D5045-99 guidelines under monotonic loading conditions [18]. A three point-bending (3PB) specimen was chosen with the following dimensions: 76.2 mm × 12.7 mm × 6.4 mm. At least 5 samples for

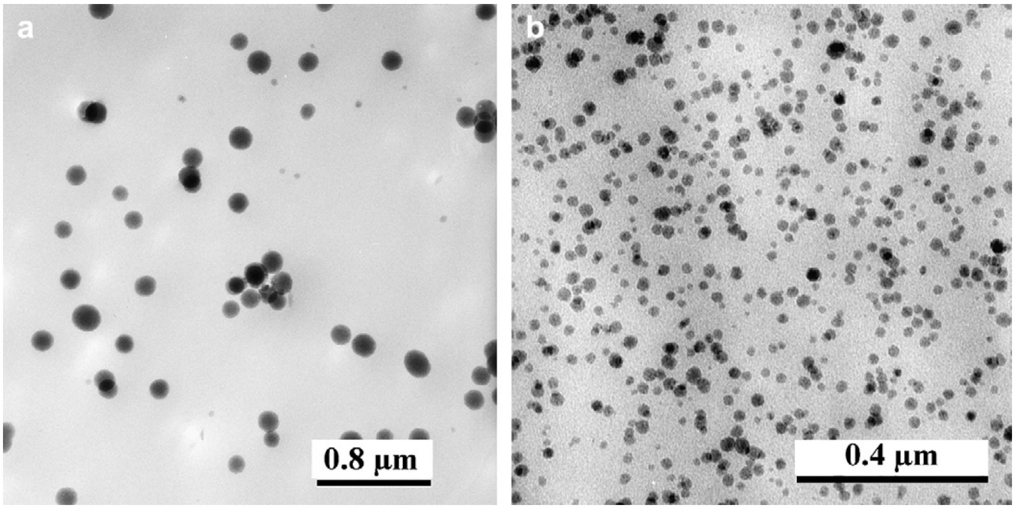

Fig. 1. TEM micrographs for particle-dispersion investigation in low NS content (3.2 vol %): (a) 80ESN, (b) 20ESN.