Effect of bimodal particle size distributions on the toughening mechanisms in silica nanoparticle filled epoxy resin

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ABSTRACT

Epoxy formulations containing mixtures of two different size distributions of silica-based particles (micron-size and nanometer-size) were explored for possible synergistic toughening effects. The influence of bimodal particle size distribution and silica particle content on the glass transition temperature (T_g), coefficient of thermal expansion (CTE), Young's modulus (E), tensile yield stress (σ_y), and fracture toughness were investigated. Interestingly, fracture toughness improved by approximately 30% when mixtures of microparticles and nanoparticles were used. The origins for these improvements in toughness were explored using scanning electron microscopy (SEM) and transmission optical microscopy (TOM). These techniques revealed that the toughness improvements were due to the debonding of the microparticles and subsequent plastic void growth of the matrix, as well as more void growth due to a high fraction of debonded nanoparticles. The improvements in toughness were higher when the volume fraction of microparticles was less than the volume fraction of nanoparticles (overall filler content was fixed at 10 vol% in this study). The increased toughness in epoxies with mixtures of particles can be explained by summing the contribution of microparticle-induced matrix void growth, nanoparticle-induced matrix void growth and nanoparticle-induced matrix shear banding.

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1. Introduction

The fracture toughness of an unmodified epoxy can be enhanced with the addition of silica particles [1–11]. The size of the silica particles has been shown to dramatically affect the toughening efficiency. Interestingly, the toughening mechanisms in epoxies containing micron-size silica have been found to differ from epoxies containing nanometer-size silica particles [1–5]. For microparticles, the toughening mechanisms often involve particle bridging [6], crack pinning/bowing [7], and crack path deflection [8,9]. When nanoparticles are used as fillers for epoxy, there has been a lack of evidence to indicate that particle bridging, crack pinning and crack path deflection mechanisms occur [5,10]. Instead, particle–matrix debonding and matrix shear banding have been observed [5,11,12]. It is important to note that the majority of studies found in the literature has focused on the fracture behavior of epoxy resin containing a single particle size distribution i.e. the effect of bimodal particle size distributions on fracture toughness of filled epoxies has received relatively little attention.

The few studies that have considered the effects of multimodal particle size distributions on the fracture toughness of filled epoxies have found some interesting results. For example, Kwon et al. [13] studied the effect of mixtures of spherical silica particles (using 0.24 and 1.56 μm particle diameters) on the fracture toughness of an epoxy resin and reported that the increased fracture toughness is proportional to the volume fraction of a smaller, 0.24 μm diameter, silica particles. Greenwood et al. [14] reported a significant increase in mechanical properties of an epoxy filled with mixtures of two different particles and attributed these increases due to better particle dispersion due to the presence of large particles, which reduced nanoparticle agglomeration. Therefore, such studies show that the presence of a bimodal particle size distribution gives rise to synergetic toughening. However, the underlying reasons for these additional increases in toughness remain an enigma.

Several models have been developed to explain the possibility of synergistic toughening, i.e. the addition increase in toughness due to the interaction of particles and/or mechanisms. Observations of the toughening mechanisms in silica-filled polymers can be separated into two categories: those that occur in the crack wake and those that occur at or just ahead of the crack tip. Crack wake mechanisms include particle bridging [15] and crack path deflection [9]. These mechanisms shield the crack tip thus providing

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a toughening effect. The second category includes mechanisms occurring in a process zone near the crack tip such as plastic void growth and matrix shear banding [16,17]. Process zone mechanisms typically occur in direct proportion with the plastic zone size and contribute additively to the toughness [17]. Evans et al. [16] proposed that further improvements in toughness can be obtained by combining mechanisms that occur in the crack wake (specifically particle bridging) with those occurring in the process zone (plastic void growth and shear banding). Based on Evans's concept [16], this combination of mechanisms can provide a multiplicative effect.

Several researchers have challenged the multiplicative effect proposed by Evans [16,18]. For example, Huang and Kinloch [19] calculated the increase in fracture toughness by taking all the possible toughening contributions into consideration. Unlike the multiplicative model proposed by Evans, the toughness enhancement from crack wake mechanisms is simply added to the toughness induced by the zone-associated toughening mechanisms to obtain the total toughness. The model by Huang and Kinloch was developed for rubber toughened polymers but has been modified to predict the toughness in epoxies filled with silica nanoparticles. It is important to note that this model does not specifically model particle size and has not been used with a bimodal particle size distribution, which will be explored in this study.

In the current investigation, the fracture behavior of epoxies containing mixtures of two different size spherical, inorganic particles was studied as a novel approach to toughening epoxy systems. The results and conclusions derived from unimodal particle size systems are first considered and then evaluated for mixtures of micron- and nano-size particles (bimodal particle size distributions). Since the relatively large micron-size spheres can be effective bridging particles, it is of interest to assess whether the differences in toughening mechanisms will interact in a multiplicative or additive fashion.

2. Experimental

2.1. Materials

The epoxy matrix consisted of a standard diglycidyl ether of bisphenol A resin (DGEBA) (D.E.R. 331 Dow Chemical Company) and bisphenol A (Sigma–Aldrich). Note that bisphenol A acts as both a chain extender and as an accelerator. Bisphenol A was added in this study to prevent the large particles from settling. Particles with an average diameter of 42 μm (Potters Industry Spheriglass 2900 E-glass spheres) were used to represent the large particles that are effective bridging particles. Three different nanometer-size silica particles were also examined. Such particles are capable of inducing plastic deformation at the crack tip in ductile epoxies. The silica nanoparticles were received predispersed in DGEBA (three diameters: 170, 74, and 23 nm from the 3M Corporation). Piperidine (Aldrich) was used as a curing agent. Mixtures of two different size distributions of inorganic spheres were also examined in this study. Formulations for bimodal systems were prepared with different particle size compositions but the same total volume of micro/nanoparticles (concentration was fixed at 10 vol%). Five different ratios between micro-size and nano-size particles were studied. The formulations used in this study can be found in Table 1.

2.2. Sample preparation

The epoxy-based matrix was prepared by mixing the epoxy resin and 24 phr (part per hundred parts resin by weight) of bisphenol A at 180 °C under vacuum and then cooling the mixture down to 85 °C. The epoxy was then mixed together with the

Table 1
Fraction of nanoparticles investigated in the 10% filled epoxies studied.

Fraction of nanoparticles (Φ_f)	vol% of silica nanoparticles (V_{fn})	vol% of 42 μm particles (V_{fm})	Total vol% of fillers
0	0	10	10
0.25	2.5	7.5	10
0.50	5.0	5.0	10
0.75	7.5	2.5	10
1.0	10	0	10

appropriate amount of nanosilica-epoxy concentrate and/or glass-bead powder to obtain 10 vol% of reinforcement by mechanical stirring at 85 °C. After degassing under vacuum for 4 h, 5 phr of piperidine (curing agent) was added into the suspension and then agitated under vacuum for 10 min. The composites were then thermally cured at 160 °C for 6 h. The bulk density of the 42 μm particles was 2.4 g/cm^3, as listed from manufacturer. The density of composites was measured using a pycnometer. The calculated densities of the epoxy and the nano-SiO$_2$ were 1.16 g/cm^3 and 1.92 g/cm^3, respectively. Using the measured densities, the vol% of nano-SiO$_2$ was calculated since the weight percents are known.

2.3. Material characterization

A differential scanning calorimeter (DSC, TA Instruments model 2920) was used to measure the glass transition temperatures (T_g) of the nanocomposites. Samples of approximately 10 mg were sealed in aluminum pans and ramped from 25 °C to 160 °C under nitrogen gas at 10 °C/min.

Young's modulus (E) and yield stress (σ_y) of the particulate composites were measured using a screw-driven materials testing machine (Instron, universal type 5567) in tension. All the samples were machined into a dog-bone shape (Type V), with the following dimensions: 63.5 mm in length, 3 mm gage section width, and 3 mm in thickness. The tensile tests were conducted at a displacement rate of 5 mm/min at room temperature, according to the ASTM D638 standard test method.

Coefficient of thermal expansion (CTE) was investigated using a thermomechanical analyzer (TMA2940, TA Instruments). Sample dimensions of 3.0 mm × 3.0 mm × 3.0 mm were used and scans were taken from 25 °C to 160 °C at a heating rate of 2 °C/min. The CTE values were evaluated using TMA universal analysis software (version 2.6D) and calculated from the slopes of the critical T_g values to ±50 °C. All reported TMA data were collected from a second heating cycle in order to relieve residual stresses.

Fracture toughness was determined using a single-edge notch three-point-bend (SEN-3PB) test, in accordance to the ASTM D5045 standard. A pre-crack was made by lightly tapping a fresh razor blade between the adjoining plates with sample dimension of 75.6 mm × 12.7 mm × 6.36 mm, yielding a very sharp crack. The tests were performed at a rate of 1 mm/min and the span was set to 50.8 mm. Fracture toughness was determined in terms of the critical stress intensity factor (K_{IC}) using the relationship in equation (1) [20,21].

$$K_{IC} = Y \frac{6P_f S}{4tw^2} \sqrt{a} \tag{1}$$

where Y is the shape factor, P_f is the load at the break, S is the length of the span, and a is the crack length. The fracture energy (G_{IC}) was calculated by the following equation [21]:

$$G_{IC} = \frac{K_{IC}^2}{E} \left(1 - \nu^2\right) \tag{2}$$