

On the Use of Nanoscale Materials to Toughen Model Epoxies

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ABSTRACT

A typical underfill resin consists of an epoxy matrix filled with micron-size silica particles to reduce thermal expansion. The fracture toughness of such resins plays an important role in the reliability of flip-chip packages. In this work, we will investigate the use of nanoscale materials to improve the fracture toughness of a model epoxy resin. A lightly crosslinked model epoxy system was chosen due to its “toughenability.” The toughening mechanisms are elucidated using a combination of electron and optical microscopy techniques. For epoxies toughened with soft, nanosize rubber particles, the toughening mechanism is rubber particle cavitation and matrix shear banding. The toughening mechanism when hard, nanosize silica particles are used involves particle matrix debonding and matrix shear banding.

1. INTRODUCTION

The outstanding merits of flip-chip technology have generated much research activity since its inception in the 1960s [1]. The use of epoxy-based, underfill resins to improve the reliability of flip-chip packages is widely known and a major concern in this technology is the fracture toughness of the underfill resin.

The fracture toughness of epoxy resins can be improved by the addition of soft, rubber particles or rigid, silica fillers [2-5]. Traditionally, the size of these types of additives/fillers has been on the micron scale, however, recent advances have led to additives/fillers with nanoscale dimensions. Recently, such additives have been shown to be effective in toughening epoxy resins [6, 7].

2. OBJECTIVE

The goal of this work is to evaluate the use of nanoscale additives to toughen epoxy resins. Particular attention will be given to understanding the mechanisms that impart improvements in fracture toughness.

3. EXPERIMENTAL APPROACH

Materials: A model epoxy system was used in this study: bisphenol A based epoxy (DER 331 resin from the Dow Chemical Co.) cured with 5 parts per hundred piperidine (Aldrich). The epoxy system was cured at 160 C for 6 hours.

Two types of copolymers were examined as toughening agents for the model epoxy system. The first copolymer was a carboxyl acid terminated random copolymer of poly(butadiene-co-acrylonitrile), which is commercially available as CTBN 1300x8. CTBN 1300x8 is a reactive liquid polymer. Such random copolymers result in 3-5 micron diameter rubber particles in the cured model epoxy system. The second type of copolymer consisted of a series of block copolymers from Arkema and are commercially available as Nanostrength® resins. These block copolymers have the ability to self assemble into nanometer size particles.

Nanosilica particles were provided by the 3M Corporation. Concentrates of nanosilica filled epoxy (bisphenol A based) were provided. Three different particle sizes were examined: 23, 74 and 170 nm in diameter.

Mechanical Characterization: A screw-driven universal testing machine was used (Instron, model 5567) to characterize the flaw tolerance of the various epoxies studied. Fracture toughness, K_{IC} , was measured according to ASTM D5045-99 standard method using a single-edge-notched, three-point-bend (SEN-3PB) test. The crosshead speed was 1 mm/min.

Fractography: Both electron and optical techniques were used.

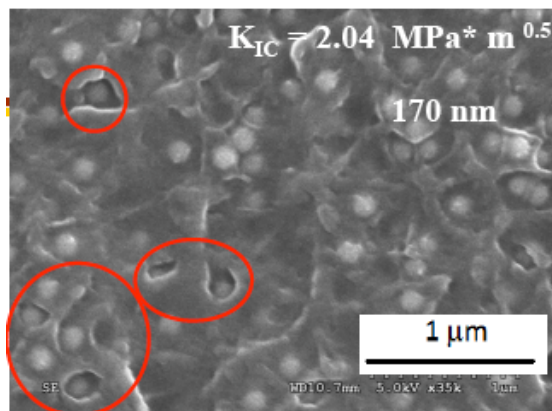
The fractured surfaces of the SEN-3PB specimens were examined using a field emission scanning electron microscope with an accelerating voltage

typically of 5kV. Fracture surfaces were coated with a thin layer of gold-palladium or Iridium to minimize charge build-up.

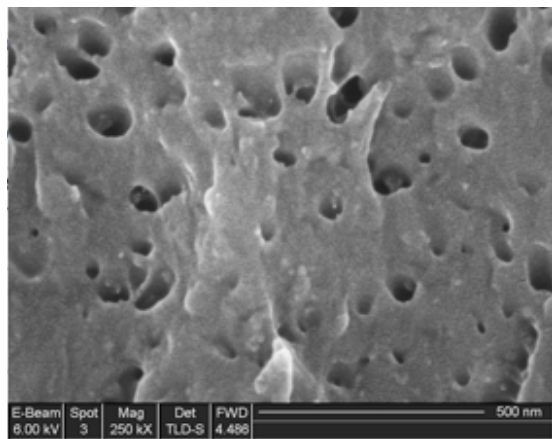
The subsurfaces of the SEN-3PB specimens were examined using an Olympus BH-2 optical microscope in transmission. Crossed polars were used to detect the birefringent shear yielded zones. All samples were petrographically polished to a thickness of ~ 75 microns.

4. RESULTS AND DISCUSSION

The fracture toughness of the neat resin is $1.1 \text{ MPa}\cdot\text{m}^{1/2}$. In the case of the nanosize rubber particles, the fracture toughness increased by more than $3 \text{ MPa}\cdot\text{m}^{1/2}$, i.e. nearly 4 times that of the neat epoxy. In the case of the nanosilica filled epoxies, the fracture toughness nearly doubled. More details will be presented.



(a)

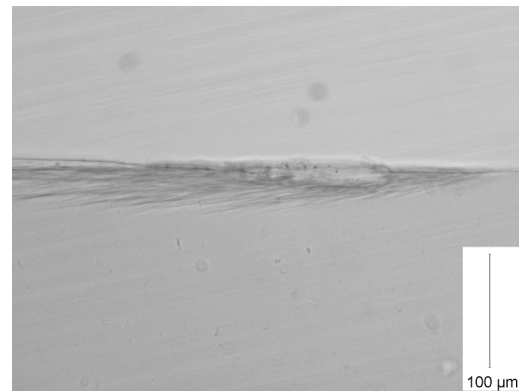


(b)

Figure 1: Fracture surfaces of a) nanosilica filled epoxy showing particle matrix debonding and b) SBM toughened epoxy showing rubber particle cavitation.

As mentioned in the experimental approach, both electron microscopy and optical microscopy were used to elucidate the toughening mechanisms. Figure 1 contains scanning electron micrographs of fracture surfaces taken from fracture toughness specimens. Note the presence of particle matrix debonding in nanosilica filled epoxies and particle cavitation in rubber-modified epoxies. Both of these micromechanical deformation mechanisms result in a damage zone at the crack tip. See Figure 2. The presence of these damaged regions results in a zone shielding mechanism that enhances toughness.

As expected, the size of the damage zones increases with increasing modifier/filler content. The size of the damage zone in nanosilica filled materials can be predicted using fracture mechanics. Interestingly, the tougher, SBM modified epoxies exhibit a much smaller damage zone than predicted which makes them prime candidates for toughening epoxies used in thin bondlines.



(a)



(b)

Figure 2: Subsurface damage zones for a) nanosilica filled epoxy and b) SBM toughened epoxy showing a damage zone consisting of dilational bands.

5. SUMMARY AND CONCLUSIONS

A brief overview of our work on nanoscale toughening agents for epoxy resins was given. More details will be shared during the presentation. Basically, nanosize fillers and modifiers can be used to effectively toughen epoxy resins. In some cases, the amount of toughness is greater than that of traditional modifiers. The ability of some of these modifiers to provide toughness with small damage zone size is of particular interest in applications where small bondlines are involved, i.e. for underfill resins in flip-chips.

Future work involves the characterization of other properties that are important in successful flip chip applications. Specifically, viscosity and CTE studies are underway.

6. ACKNOWLEDGEMENTS

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