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Hot-cured epoxy-nanoparticulate-filled nanocomposites: Fracture toughness behavior

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ABSTRACT

This study focused on toughness behavior and mechanical properties of nanoparticles exerted of hot-cured epoxy resins. A comprehensive evaluation was carried out on series of nanocomposites containing varying amounts of nano-sized Al_2O_3 (nano-alumina) and nanoclay. Tensile strength and young's modulus of nanocomposite specimens was examined and compared with pure epoxy. Plane strain fracture toughness (K_{IC}) was calculated using single-edge-notch specimens that tested in three point bending condition. Results indicated that fracture toughness improves through increasing both alumina and clay nanoparticle content by several mechanisms. Finally, the fracture surfaces of nanoparticulate-filled epoxy nanocomposite specimens and mechanisms of toughening were observed by using field emission scanning electron microscope.

1. Introduction

Epoxy resins are being extensively used as matrix materials in high performance composites especially in automotive industries, electronics, marine, aerospace and structural applications. However, there are some limitations in these applications for epoxy composites especially hot-cured epoxy because of low toughness. Thus, a proper and adequate knowledge of toughness and fracture propagation is required in order to develop materials for high performance applications.

Many works have been done such as our previous works to improve the fracture toughness of epoxy resins by incorporating soft materials such as liquid or particulate rubber and proposed some toughening mechanisms based on fracture mechanics [1–4]. Nevertheless, these composites exhibit a lower strength and Young's modulus property. Beside this, it has been reported that second phase dispersion of a rigid filler into the matrix is a useful technique for toughening epoxy resins with possibility of increase the tensile strength and modulus of the epoxy over the original value. This increase is more pronounced if the strength and modulus values of the starting epoxy are low [5–7].

The utilization of nanoparticles as fillers in epoxy polymers has attracted considerable attention due to the improved mechanical, thermal, flame retardant and gas barrier properties of the resulting nanocomposites [6,8]. Generally, because of the extremely high surface to volume ratios and the nanometer size dispersion of nanoparticles in epoxy, they exhibit improved properties as compared to the pure epoxy. Furthermore, the surface-to-volume ratio of particles increases with decreasing particle size. On the nano-scale the fraction of atoms localized at the surface is much higher than on the micro-scale because of

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Nomenclature

a_0	crack length (mm)
b	width of specimen (mm)
K_{IC}	fracture toughness (MPa m$^{1/2}$)
P_c	loading (critical loading) determined from load–deflection curve (N)
E	tensile modulus (GPa)
υ	Poisson's ratio (–)
G_{IC}	strain energy release rate in mode I (Mode I fracture toughness) (N/m)

higher surface to volume aspect ratio of nano-particles. Therefore, the physical properties of particles of the same material can be different on the nano-scale, and they may even be dominated by quantum mechanical effects [9,10].

In rigid particle filled epoxies the toughening mechanism may comprise a combination of particle–matrix debonding, void formation around the particles, and subsequent yielding of the inter-particle matrix ligaments. Still so far, high material costs, complex processes and limitations in production technology hamper the production and the application of these nanocomposites on a large industrial scale. Specifically, there are still difficulties to distribute individual nanoparticles homogeneously in the matrix [9,11] and the maximum amount used is limited by the resulting deterioration in processing characteristics and fracture toughness [12].

Over the past 10 years, many other researchers have also attempted to improve the properties of epoxies using nanoclays [7,13]. Yasmin et al. [14] and Luo and Daniel [15] were using shear mixing to process epoxy-clay nanocomposites and obtained some improvement in elastic modulus and strength. Qi et al. [16] observed that while the addition of nanoclay significantly increased the elastic modulus and fracture toughness of diglycidyle ether of bisphenol A (DGEBA) epoxy resin, it also significantly reduced the failure strength and failure strain with increasing nanoclay level.

Lim et al. [17] studied the morphology, mechanical properties and fracture behavior of epoxy-alumina nanocomposites. It was found that the dispersion of the nano-sized alumina particle within the epoxy matrix mainly depends on the geometry of the particle. Mechanical characterization and fracture mechanics tests showed that the tensile modulus, tensile strength and fracture toughness were affected by the geometry of the particles. The fracture surface investigation showed that several toughening mechanisms, including particles pull-out, crack pinning, plastic yielding and deformation were the main factors for the increments of the fracture toughness of the epoxy-alumina nanocomposites. The nanostructured epoxy systems based on SBS epoxidized triblock copolymer and well-dispersed Al_2O_3 nanoparticles allowed an increase in fracture toughness maintaining the transparency and stiffness of neat epoxy [18].

In this paper, we investigated the effects of nano-sized particle addition on the mechanical properties and fracture toughness of hot-cured epoxy nanocomposites and tried to introduce mechanisms of toughening by fractography using field emission scanning electron microscope (FESEM). In addition, by using hot cured epoxy matrix with long-time pot life, we chose the optimized preparation process for nanocomposite specimens.

2. Experimental procedures

2.1. Materials

Three main constituents used as resin system, were DGEBA hot-cured epoxy resin (LY556), anhydride curing agent (Aradur 917) and imidazole accelerator (DY070) from Huntsman™, USA. Al_2O_3 nanoparticles with a particle size of 100 nm (GE6, Baikalox Co. Japan) and also Nanoclay (Cloisite 15A, Southern Clay Products, USA), which was natural montmorillonite modified with quaternary ammonium salt, were used as nanocomposite reinforcements. Table 1 shows the physical properties of the nanoparticles used as nanocomposites reinforcement.

2.2. Preparation of the nanocomposite specimens

A given amount of nanoparticles was dried up to 110 °C using a vacuum controlled oven and added to acetone. Then, the compound of nanoparticles with acetone placed in ultrasonic condition for 1 h for better distribution of nanoparticles. This

Table 1
Physical properties of nano-particles.

Physical properties	Nano-alumina	Nanoclay (Cloisite 15A)
Density (g/cm^3)	0.4	1.66
Surface area (m^2/g)	600	800
Particle size (μm)	0.1–0.2	2–13
d-spacing, d_{001} (Å)	–	31.5
Bulk elastic modulus (GPa)	300	6.5