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Thermal Stability and Fracture Toughness of Epoxy Resins Modified with Epoxidized Castor Oil and Al_2O_3 Nanoparticles

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This study examined the effects of the epoxidized castor oil (ECO) and Al_2O_3 content on the thermal stability and fracture toughness of the diglycidylether of bisphenol-A (DGEBA)/ECO/Al_2O_3 ternary composites using a range of techniques. The thermal stability of the composites was decreased by the addition of ECO and Al_2O_3 nanoparticles. The fracture toughness of the composites was improved significantly by the addition of ECO and Al_2O_3 nanoparticles. The composite containing 3 wt % Al_2O_3 nanoparticles showed the maximum flexural strength. Scanning electron microscopy (SEM) revealed tortuous cracks in the DGEBA/ECO/Al_2O_3 composites, which prevented deformation and crack propagation.

Key Words : Epoxy resins, Al_2O_3 nanoparticles, Epoxidized castor oil, Thermal stabilities, Fracture toughness

Introduction

Epoxy resins are used widely in non-structural (coatings, flooring, and painting) and structural (casting, tooling, and matrices for advanced composites) applications owing to their outstanding mechanical performance, good chemical and electrical resistance, and superior dimensional stability.[1-3] On the other hand, cured epoxy resins are inherently brittle on account of their high crosslinking density, which makes them unsuitable for many engineering applications requiring high toughness.[4-6]

Epoxy ternary composites have attracted increasing attention because of the possibility of improved toughness. Ratna *et al.* reported the preparation of epoxy nanocomposites using the diglycidyl ether of bisphenol A (DGEBA) epoxy resins, functionalized hyperbranched polymer, and clay.[7] These nanocomposites exhibited higher impact strength than neat DGEBA. Li *et al.* prepared and characterized epoxy resin composites modified with SiO_2 nanoparticles and silane.[8] They reported an increase in the impact strength of epoxy resin-based composites with increasing SiO_2 content. Park *et al.* reported the thermal stability and the impact and flexural properties of epoxy resins/epoxidized castor oil (ECO)/$CaCO_3$ ternary systems. The impact strength of these ternary systems was improved by the addition of ECO and $CaCO_3$ nanoparticles.[9]

In the present study, ECO and Al_2O_3 nanoparticles were used as modifiers to increase the toughness of diglycidylether of bisphenol-A (DGEBA) epoxy resin. The DGEBA/ECO/Al_2O_3 ternary composites were characterized by thermogravimetric analysis (TGA), dynamic mechanical analysis (DMA), mechanical testing, and scanning electron microscopy (SEM).

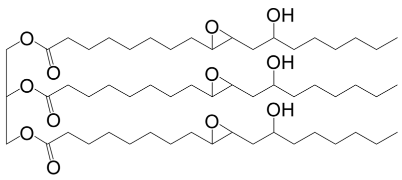
Experimental

Materials. The diglycidylether of bisphenol-A (DGEBA) (E-51, epoxide equivalent weight (EEW): 185-208 g/eq, Feichengdeyuan Chem. of China) was used as the epoxy monomer. Epoxidized castor oil (ECO, EEW: 510-520 g/eq, Mn: 1411 g/mol, Mw: 1518 g/mol; ECO/BPH, T_g: 38 °C, T_{d5}: 351 °C.) was synthesized using the method reported elsewhere.[10] *N*-Benzylpyrazinium hexafluoroantimonate (BPH), which was used as a thermally latent initiator, was synthesized using a general method reported in elsewhere.[11] Al_2O_3 nanoparticles (α-Al_2O_3, particle size: 80 nm, specific surface area: 10 m^2/g) were supplied by Nanjing High Technology Nano Material Co. of China. Figure 1 shows the chemical structures of ECO and BPH.

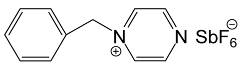
Sample Preparation. The weight content of Al_2O_3 nanoparticles was varied from 1 to 4 wt %, and the weight content of ECO and BPH was 20 wt % and 1 wt %, respectively. The desired amounts of DGEBA, ECO, and Al_2O_3 nanoparticles were mixed at 80 °C for 1 h, followed by the addition of BPH. The resulting mixture was stirred for 30 minutes followed by sonication for 10 minutes using an ultrasonicator. The bubble-free mixture was poured into a preheated mold that had been sprayed with a mold release agent. Curing was performed at 120 °C for 1 h, 160 °C for 2 h, and 200 °C for 1 h in a convection oven.

Characterization and Measurements. The thermal stability of the DGEBA/ECO/Al_2O_3 composites was evaluated by TGA (NETZSCH TG 209 F3) from 30 to 800 °C at a heating rate of 10 °C/min under a nitrogen atmosphere.

The tan δ was determined by dynamic mechanical analysis (RDS-II, Rhemetrics Co.). The samples, 2 mm × 12 mm × 35 mm in size, were tested in a three point bending mode



Epoxidized castor oil (ECO)



N-Benzylpyrazinium hexafluoroantimonate (BPH)

Figure 1. Chemical structures of the materials used.

ranging from 35 to 250 °C at a heating rate of 5 °C/min and a frequency of 1 Hz.

The critical stress intensity factor (K_{IC}) was characterized by single edge notched (SEN) testing in three-point bending flexure. The three-point bending test was performed on a universal testing machine (Instron Model 1125) according to ASTM E-399. The sample size for these tests was 5 × 10 × 50 mm^3. The flexural tests were performed according to ASTM D790-86 under a three-point bend configuration The sample size was 2 × 25 × 50 mm^3. The fracture surfaces after the K_{IC} tests were examined by field emission scanning electron microscopy (FE-SEM, S-4300/HITACHI).

Results and Discussion

Figure 2 shows the thermal stability of the DGEBA/ECO/Al_2O_3 ternary composites, as determined by TGA. The thermal stability factors, including the initial decomposing temperature (the temperature of 5% weight loss, T_{d5}) and char at 800 °C, were determined from the TGA thermograms.[12-14] Table 1 lists the thermal stability factors of the composites as a function of the Al_2O_3 content. The T_{d5} value of the composites was decreased by the addition of ECO and nano-Al_2O_3. This might be due to the lower crosslinking density of the composites, which resulted from the higher EEW of ECO. On the other hand, the T_{d5} value of the composites was similar to that of the DGEBA/DDM systems.[15]

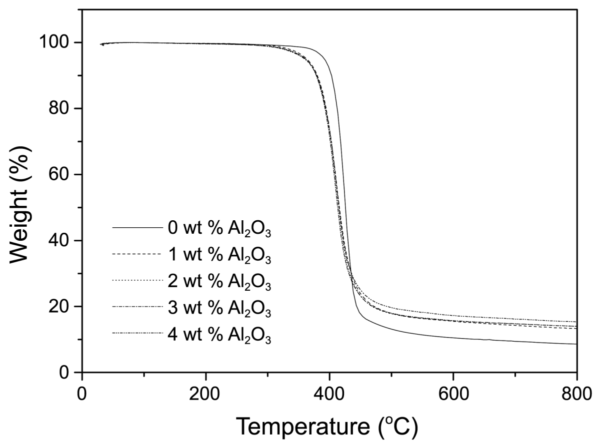


Figure 2. TGA thermograms of DGEBA/ECO/Al_2O_3 composites.

Table 1. Thermal stability of DGEBA/ECO/Al_2O_3 composites obtained from TGA thermograms

Al_2O_3 content (%)	ECO content (wt %)	$T_{5\%}$ (°C)	Char yield (%) at 800 °C
0	0	391.4	8.6
1	20	363.4	13.3
2	20	361.1	14.0
3	20	361.1	14.0
4	20	359.8	15.5

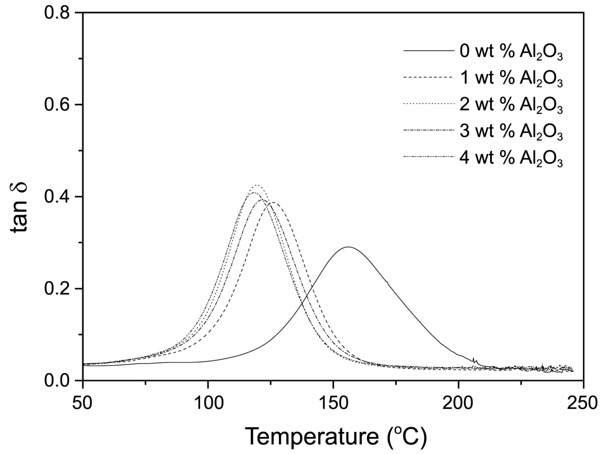


Figure 3. tan δ of DGEBA/ECO/Al_2O_3 composites as a function of Al_2O_3 content.

The char yield of the composites at 800 °C increased with increasing Al_2O_3 content. Chen *et al.* reported a similar observation with epoxy/γ-aluminum oxide nanocomposites.[16]

The glass transition temperature (T_g) of the DGEBA/ECO/Al_2O_3 composites was examined by DMA. Figure 3 shows the tan d of the composites as a function of temperature. The T_g values were derived from the DMA results by examining the α-relaxation temperatures. The T_g value of the composites decreased by approximately 30 °C compared to the neat epoxy resins. This might be due to the increased motion of macromolecule segments in the composites caused by the addition of larger soft segments of ECO in the epoxy resins.[17]

The fracture toughness of the DGEBA/ECO/Al_2O_3 composites was examined by critical stress intensity factor (K_{IC}) measurements. For the three-point flexural test, the K_{IC} value was calculated using the following equation:[18-20]

$$K_{IC} = PBW^{1/2}Y \tag{1}$$

where P is the rupture force (in kN), B the specimen thickness (in cm), W the specimen width (in cm), and Y the geometrical factor.

Figure 4 shows the K_{IC} values of the composites as a function of the nano-Al_2O_3 content. The K_{IC} value of the composites was improved significantly by the addition of ECO and Al_2O_3 nanoparticles. The neat DGEBA was quite brittle, exhibiting a K_{IC} value of 0.47 MPa·m$^{1/2}$. In contrast, the K_{IC} values were 0.62 MPa·m$^{1/2}$ for the composite containing 2 wt % Al_2O_3 nanoparticles and 20 wt % ECO

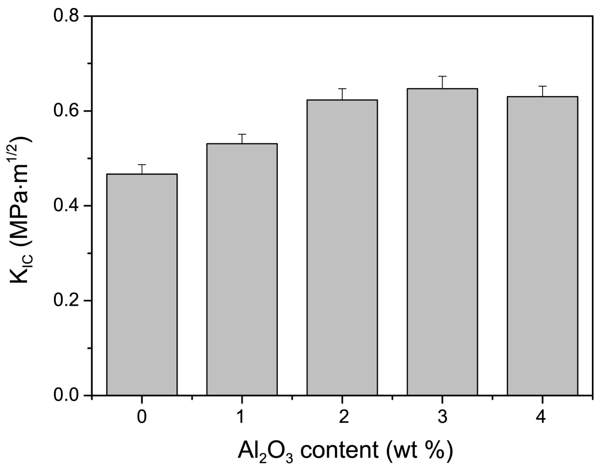


Figure 4. Toughness properties expressed in terms of the K_{IC} as a function of Al_2O_3 for DGEBA/ECO/Al_2O_3 composites.

(32% higher), and 0.65 MPa·m$^{1/2}$ for the composite containing 3 wt % Al_2O_3 nanoparticles and 20 wt % ECO (38% higher). This suggests that the flexible properties of the network structure are improved by the presence of soft segments of ECO in the epoxy resins.[17] The toughness was also attributed to the enhanced interfacial adhesion between the Al_2O_3 nanoparticles and epoxy matrix. Wang *et al.* reported a similar observation using polyglycidyl methacrylate-grafted Al_2O_3 particles.[21]

The mechanical properties of the DGEBA/ECO/Al_2O_3 composites were examined by measuring the flexural strength (σ_f) and elastic modulus (E_b). The σ_f and E_b values were determined using a three-point bending test, and calculated using the following equations.[22,23]

$$\sigma_f = \frac{3PL}{2bd^2} \tag{2}$$

$$E_b = \frac{L^3}{4bd^3} \cdot \frac{\Delta P}{\Delta m} \tag{3}$$

where P is the applied load (in N), L the span length (in mm), b the width of specimen (in mm), d the thickness of the specimen (in mm), ΔP the change in force in the linear portion of the load-deflection curve (in N), and Δm the change in deflection corresponding to ΔP (in mm).

Figure 5 shows the effects of the Al_2O_3 content on the σ_f and E_b values of the composites. The σ_f values of the composites increased with increasing Al_2O_3 content to 3 wt % (Figure 5(a)). This suggests that the mechanical properties of the composites were improved by the dispersion of Al_2O_3 nanoparticles in the epoxy matrix.[24] The elastic modulus of the composites was constant, as shown in Figure 5(b). Omrani *et al.* reported a similar observation using epoxy/Al_2O_3 hybrid composites.[25]

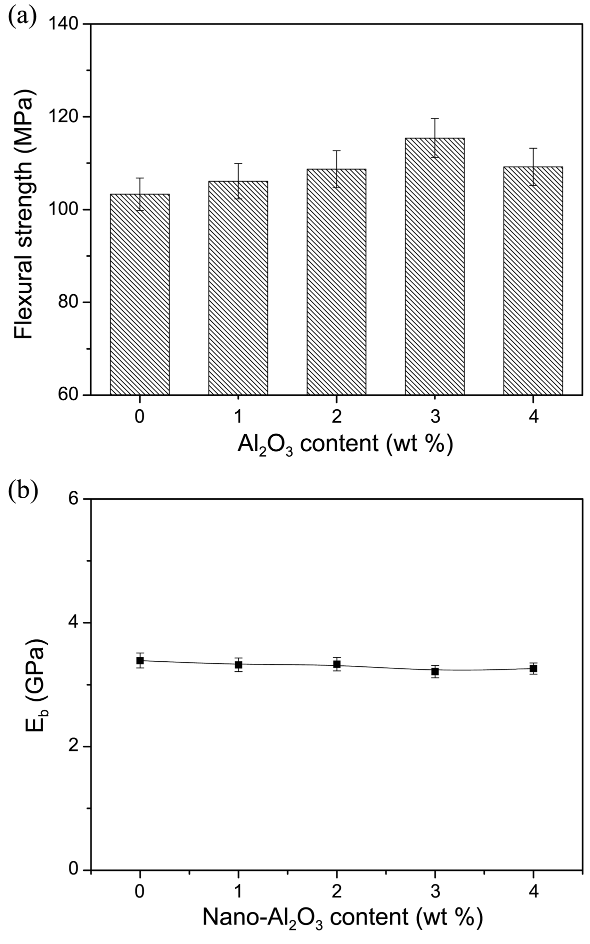


Figure 5. (a) Effect of Al_2O_3 content on flexural strength and elastic modulus of DGEBA/ECO/Al_2O_3 composites. (b) Revise "Nano-Al_2O_3 content (wt %) to "Al_2O_3 content (wt %)".

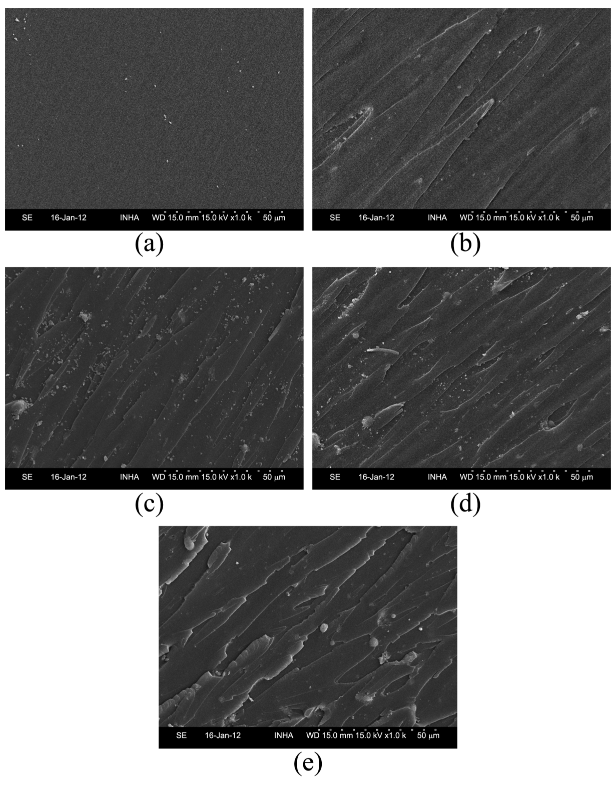


Figure 6. SEM micrographs of DGEBA/ECO/Al_2O_3 composites after K_{IC} tests with: (a) 0 wt %; (b) 1 wt %; (c) 2 wt %; (d) 3 wt %; (e) 4 wt % Al_2O_3 nanoparticles (magnification of 1000).

The fracture surfaces of the neat epoxy and epoxy composites after the K_{IC} tests were examined by SEM, and the SEM photographs are shown in Figure 6. The neat epoxy resins displayed a smooth surface, indicating brittle fracture surface (Figure 6(a)). In contrast, the composites containing ECO and Al_2O_3 nanoparticles showed tortuous cracks that resisted deformation and crack propagation, which was attributed to its good fracture toughness, as shown in Figure 6(b-e). The Al_2O_3 nanoparticles are embedded in the epoxy resin matrix. Hence, the primary crack might detour around the Al_2O_3 nanoparticles or the crack tips are blunted by these nanoparticles.[26]

Conclusions

This study examined thermal stability and fracture toughness of the DGEBA/ECO/Al_2O_3 ternary systems by TGA, DMA, universal testing machine, and SEM. The thermal stability and glass transition temperature of the composites were decreased by the addition of ECO and Al_2O_3 nanoparticles, whereas the fracture toughness of the composites was improved significantly. This was supported by SEM, which indicated the present of tortuous cracks that preventing deformation and crack propagation in the composites. The composite containing 3 wt % Al_2O_3 nanoparticles showed the maximum flexural strength.

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