

Characterization of mechanical properties of epoxy nanocomposites using functionalized clays and layered double hydroxides

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Abstract

Tensile properties of epoxy nanocomposites using montmorillonites and layered double hydroxides (LDH) were measured to characterize a failure mechanism based on enhanced interfacial bonding between the functionalized clay and the epoxy matrix. Although alkylammonium exchanged montmorillonite-epoxy nanocomposites showed lower tensile properties than the neat epoxy, preliminary tensile test results of aminonaphthoic acid exchanged LDH-epoxy nanocomposites showed a similar tensile strength with the neat epoxy.

Introduction

Over the last few years, research on nanocomposites have focused on the use of aluminosilicate clays (montmorillonites) and layered double hydroxides (LDHs) as clay particles [1-6]. Despite efforts to exfoliate and intercalate clays into matrix systems, clay/epoxy nanocomposites generally exhibit reduced mechanical properties such as resistance to crack propagation compared to the neat epoxy matrix. Published results on LDH/epoxy nanocomposites also indicate a reduction in mechanical properties relative to the neat matrix system. Reduction of the mechanical properties on both montmorillonite and LDH/epoxy nanocomposites appear to be caused by poor dispersion of the particles and poor interfacial properties at clay boundary epoxy. To test this hypothesis the mechanical properties of functionalized clay-epoxy nanocomposites are discussed by addressing issues regarding degree of dispersion and adhesion at the clay-epoxy interface.

Experimental

Materials

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Sodium montmorillonite (Na⁺ Cloisite) and montmorillonite treated with dimethylbenzyltallow ammonium chloride (Cloisite 10A) were obtained from Southern Clay Products. Octadecylamine (CAS No. 124-30-1) was purchased from Aldrich, 12-aminolauric acid (CAS No. 693-57-2) was purchased from TCI America, and Jeffamine D2000 (CAS No. 9046-10-0) was purchased from Huntsman chemicals. Protonation of the octadecylamine and Jeffamine D2000 was done using reagent grade HCl acid (Mallinckrodt, CAS No. 7647-01-0).

All nitrate salts were used as purchased (magnesium nitrate, Aldrich, CAS No. 13446-18-9; zinc nitrate, Fluka, CAS No. 10196-18-6 and aluminum nitrate, Sigma Aldrich, CAS No. 7784-27-2). Sodium hydroxide (50 % w/w, Sigma Aldrich, CAS No. 1310-73-2) was used for the deprotonation of 2-naphthoic acid (Fluka, CAS No. 93-09-4) and 6-amino-2-naphthoic acid (Aldrich, CAS No. 116668-47-4) and for the LDH synthesis.

The diglycidyl ether of 1,4-butanediol (CAS No. 2425-79-8, Common name: DGEBD), the diglycidyl ether of bisphenol-A (CAS No. 25068-38-6, common name: DGEBA) and 1,3-phenylenediamine (CAS No. 108-45-2) were obtained from Sigma-Aldrich. These chemical structures are shown in Fig.1.

Preparation of C12 and C18-montmorillonite

Both octadecylamine and 12-aminolauric acid were protonated with HCl acid, and then subjected to mixing with suspensions of Na-montmorillonite. The functionalized montmorillonites were recovered by filtration, washed with deionized water, and then freeze dried.

Preparation of C18/D2000-montmorillonite

A mixture of protonated C18 and Jeffamine D2000 ($1/3 \times \text{Jeffamine D2000} + 2/3 \times \text{C18}$; molar ratio) was prepared in order to see if any fractional variations of mixed interlayer species will directly affect the adhesion/exfoliation process. A single protonation and double protonation procedure was used in an attempt to ensure that either one end or both ends of the Jeffamine molecule became protonated along with the octadecylamine. These functionalized products were prepared and recovered in a similar fashion as the C12 and C18-montmorillonite samples.

Preparation of the layered double hydroxides (LDHs)

The LDHs were prepared by precipitating solutions of magnesium nitrate and aluminum nitrate, or zinc nitrate and aluminum nitrate with sodium hydroxide ($0.2\text{M Mg}^{2+}/\text{Zn}^{2+}$; 0.1M Al^{3+}), such that the hydroxide concentration is six times the aluminum concentration, in both cases. This procedure produces the nitrate version of LDH, or the more commonly referred “parent LDH”. The nitrate was replaced by other negatively charged anions, through the process of anion exchange. The selected anions for this work included 2-naphthoate, 6-amino-2-naphthoate (6A2N), and a mixture of the two within the LDH interlayer ($2/3$ naphthoate : $1/3$ 6A2N; molar ratio). These anions were first deprotonated from their respective acids with sodium hydroxide.

The suspensions were subjected to overnight stirring under reflux conditions in the presence of a nitrogen blanket. The functionalized products were recovered by centrifugation, washed with deionized water then freeze dried.

Preparation of Montmorillonite-nanocomposites

The montmorillonite-nanocomposites were prepared by adding approximately 263 mg of functionalized montmorillonite (5 mass %) to an epoxy mixture containing a blend of DGEBA and DGEED. The clay/epoxy mixture was

stirred and placed in the $70\text{ }^{\circ}\text{C}$ vacuum oven for three hours, and then mixed with melted m-PDA. This clay/epoxy/m-PDA mixture was poured into the preheated silicone rubber mold, and the filled mold was immediately placed into a programmable oven preheated to $70\text{ }^{\circ}\text{C}$, then cured. In addition, nanocomposites with 2.5 mass % montmorillonites were also fabricated in similar method.

Preparation of LDH-nanocomposites

The LDH-nanocomposites were prepared by adding approximately 263 mg of functionalized LDH (5 mass %) to an epoxy mixture containing a blend of DGEBA and DGEED. The LDH was stirred for two hours with a mechanical stirrer, and then degassed in a $70\text{ }^{\circ}\text{C}$ vacuum oven for three hours. Melted m-PDA was then mixed into the LDH-epoxy mixture. The LDH/epoxy/m-PDA mixtures were then poured into a preheated silicone rubber mold, and the filled mold was immediately placed into a programmable oven preheated to $70\text{ }^{\circ}\text{C}$, then cured.

Characterizations and measurements

Tensile tests were carried out on the automated tensile testing machine reported in previous research [7]. Before testing, specimens were polished with emery papers No. 800, 1200 and 2400 to remove stress concentration sites at the edges of the sample. The specimen was loaded in tension by the sequential application of strain-steps. Strains at each step were calculated using the scanned images at each step. Each strain-step was applied to at a rate of $85\text{ }\mu\text{m/s}$ and the delay time between the strain-steps was 10min. The average deformation in the specimen during each strain-step was $85.7\text{ }\mu\text{m}$.

Results and discussion

In order to investigate the effect of the volume fraction of the clays, tensile properties using 2.5 mass% of clay-epoxy nanocomposites were also investigated as well as 5mass%. Fig.2 shows representative tensile behaviors of the neat epoxy and clay-epoxy nanocomposites with 2.5 mass % by applying the step loading. In this figure, the tensile strengths of clay-epoxy nanocomposites using Cloisite10A and C12 montmorillonite are lower than the neat epoxy. The ratio of brightness change of Cloisite10A epoxy

* Certain commercial materials and equipment are identified in this paper to specify adequately the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply necessarily that the product is the best available for the purpose.

nanocomposites taken by a digital camera under continuous illumination darkens with increasing deformation above 1% elongation, while C12 montmorillonite epoxy nanocomposites containing covalent bonds at the clay-epoxy interface show a constant light intensity until the fracture. This suggests that the darkening of the Cloisite10A epoxy nanocomposites is due only to clay-matrix debonding. Detailed results will be discussed in the presentation.

Conclusions

Mechanical properties of montmorillonite and LDH-epoxy nanocomposites were characterized in this study. Preliminary results showed tensile properties of Cloisite 10A/epoxy nanocomposites were not improved over that of the neat epoxy due to the poor interfacial adhesion. Despite the improved interfacial adhesion of C12 montmorillonite epoxy nanocomposites, the tensile properties were not improved and may be associated with poor dispersion of the nanoparticles. The process that nucleates the critical flaws will be the subject of future research

Table1. Description and sample identification of clays used as nanocomposites.

Clay	Organic modifier
Cloisite 10A	Dimethylbenzyltallow
C12-montmorillonite	12-aminolauric acid
C18-montmorillonite	Octadecylamine
C18/D2000-montmorillonite	Jeffamine D2000 + octadecylamine (d. and s. protonated)
Mg ₂ Al LDH	2-naphthoate
Mg ₂ Al LDH	6A2N
Mg ₂ Al LDH	2-naphthoate + 6A2N
Zn ₂ Al LDH	2-naphthoate + 6A2N
Zn ₂ Al LDH	2-naphthoate
Zn ₂ Al LDH	6A2N

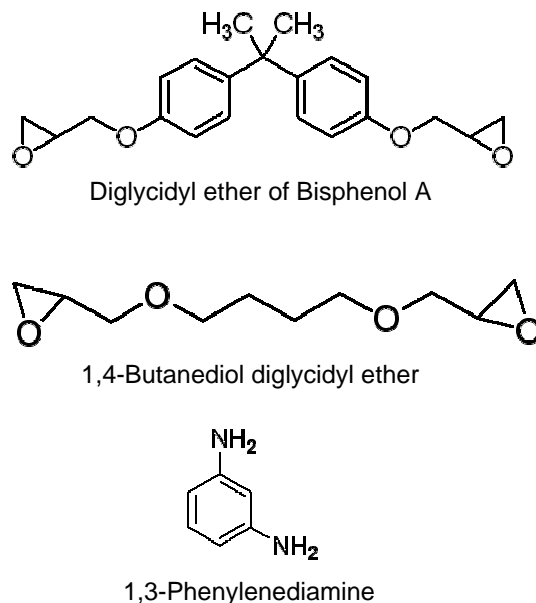


Figure 1. Chemical structures of the epoxy monomer DGEBA, DGEBD and curing agent m-PDA

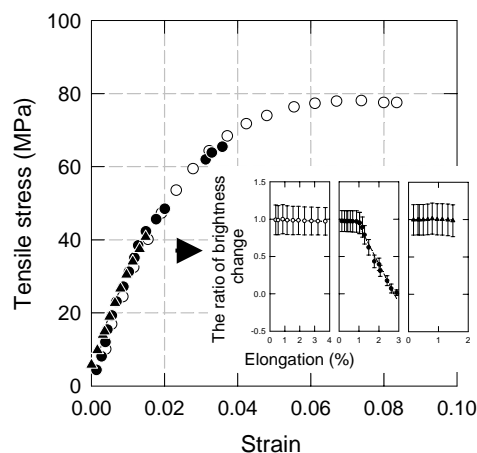


Figure 2. Tensile stress behaviors of clay and LDH nanocomposites. (O: neat epoxy, ●: epoxy with 2.5% mass fraction of Cloisite10A, ▲: epoxy with 2.5% mass fraction of C12 montmorillonite)

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