

Preparation and Characterization of Modified-Clay-Reinforced and Toughened Epoxy-Resin Nanocomposites

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ABSTRACT: Epoxy-clay nanocomposites were prepared by the dispersion of an organically modified layered clay in an epoxy resin (diglycidyl ether of bisphenol A) and curing in the presence of methyl tetrahydro acid anhydride at 80–160°C. The nanometer-scale dispersion of layered clay within the crosslinked epoxy-resin matrix was confirmed by X-ray diffraction and transmission electron microscopy, and the basal spacing of the silicate layer was greater than 100–150 Å. Experiments indicated that the hydroxyethyl groups of the alkyl ammonium ions, which were located in the galleries of organically modified clay, participated in the curing reaction and were directly linked to the epoxy-resin matrix network. Experimental results showed that the properties of epoxy were improved, evidently because of the loading of organically modified clay. The impact strength

and tensile strength of the nanocomposites increased by 87.8 and 20.9%, respectively, when 3 wt % organic clay was loaded, and this demonstrated that the composites were toughened and strengthened. The thermal-decomposition and heat-distortion temperatures were heightened in comparison with those of pure epoxy resin, and so were the dynamic mechanical properties, including the storage modulus and glass-transition temperature. Moreover, experiments showed that most properties of the composites were ameliorated with low clay contents. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 2649–2652, 2004

Key words: resins; clay; nanocomposites; reinforcement; thermal properties

INTRODUCTION

Composites are the inevitable development for materials in the 21st century. Nanocomposites are a relatively new class of materials, which are defined by the particle size of the dispersed phase having at least one dimension of less than 100 nm. In particular, nanostructured hybrid organic-inorganic composites have attracted considerable attention from both fundamental research and application points of view.^{1–3}

Polymer/layered-silicate nanocomposites are organic-inorganic nanocomposites that dramatically improve the performance properties of a polymer.⁴ One especially intriguing system, recently reported by Toyota researchers, is based on the delamination (exfoliation) of $[\text{H}_3\text{N}(\text{CH}_2)_{11}\text{COOH}]^+$ and clay in a semicrystalline nylon-6 matrix. The dispersion of 9.6-Å-thick clay layers significantly improved the tensile strength (107 vs 69 MPa), tensile modulus (2.1 vs 1.1 GPa), and heat-distortion temperature (152 vs 65°C) with respect to pristine nylon-6. The inorganic parti-

cles were the individual layers of clay, and they were used to modify the epoxy resin. Clay belongs to the general family of 2:1 layered silicates, the structure of which consists of two fused silica tetrahedral sheets of either aluminum or magnesium hydroxide. Although the natural forms of clay usually contain Na^+ or K^+ ions, ion-exchange reactions with organic cations (e.g., alkyl ammonium ions) can transform normally hydrophilic clay into a hydrophobic material.

In this study, inorganic clay was modified by organic cations, and then monolithic epoxy/exfoliated-clay nanocomposites were prepared via curing with methyl tetrahydro acid anhydride. Additionally, the microstructure and performance properties were investigated.

EXPERIMENTAL

Materials

Sodium clay was obtained from Hua-Shen Clay Co., Ltd. (He-Nan, China). Epoxy resin (E-51), that is, diglycidyl ether of bisphenol A with an average molecular weight about 380, was obtained from the Tianjin Institute of Synthetic Materials (Tianjin, China), and so was the tetrahydro acid anhydride used as a curing agent for the epoxy resin. The alkyl ammonium salt with hydroxyethyl groups was obtained from Tianjin Letai Chemical Co. (Tianjin, China).

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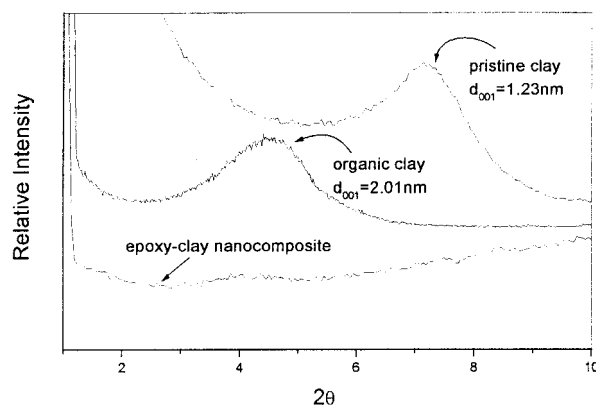


Figure 1 XRD patterns of clay and composites.

Sample preparation^{5,6}

First, the pristine clay was washed and purified. Then, a 500-mL quantity of 0.02M alkyl ammonium salt and 10 g of washed clay were heated at 70–75°C for 6 h. The cation-exchange clays were separated from the centrifuge, washed with a 1:1 ethanol/water mixture and deionized water until no chloride was detected with a 0.1N AgNO₃ solution, and dried *in vacuo*. The clay was then sieved to less than 400 mesh, and less than a 38.5- μ m fraction was collected.

Epoxy-resin/organic-clay mixtures were obtained through the mixing of the desired amount of clay with the epoxy resin at 75°C for 1–2 h and the addition of 1 equiv of tetrahydro acid anhydride. The mixtures were degassed for a short period of time and poured into a steel mold. The samples were cured at 85°C for 4 h, and this was followed by an additional 4-h cure at 145°C.

Measurements and characterization

X-ray diffraction (XRD) was performed at room temperature with a DMAX-RC diffractometer; the X-ray beam was nickel-filtered Cu K α_1 ($\lambda = 0.154$ nm) radiation operated at 50 kV and 180 mA. The data were obtained from 1 to 20° (2θ) at a rate of 1°/min. The dispersion of the clays in the epoxy matrix and nanofeatures were observed with an H-800 transmission electron microscope at 100 kV. The thermal analyses of the composites were performed with an SDT-2960 thermogravimetric analyzer and an XWB-300F heat-distortion-temperature analyzer. The mechanical measurements mainly included measurements of the impact strength and tensile strength. Additionally, the dynamic mechanical properties of the composites were measured with a DMA983 dynamic mechanical analyzer.

RESULTS AND DISCUSSION^{6,7}

Microstructure

The XRD patterns for pristine clay, organic clay, and tetrahydro acid anhydride crosslinked epoxy-clay composites with 3 wt % organic clay are shown in Figure 1. These XRD patterns reveal the changes in the clay basal spacing during the preparation process of the epoxy-clay composites. The characteristic diffraction peaks are at $2\theta = 7.2^\circ$ ($d_{001} = 1.23$ nm) and at $2\theta = 4.4^\circ$ ($d_{001} = 2.01$ nm) for pristine and organic clay, respectively. However, no diffraction peak was observed for the epoxy-clay composite. The results indicate that the intercalation of a long-chain organic cation expands the basal spacing of clay, whereas the basal spacing is greater than 8.824 nm ($2d \sin \theta = \lambda$ at $2\theta = 1^\circ$) for the epoxy-clay composite. Thus shows that a kind of intercalated-clay/epoxy-resin nanocomposite has been prepared.

A typical transmission electron microscopy (TEM) image of epoxy/intercalated-clay nanocomposites containing 3 wt % organic clay is shown in Figure 2. The light, white area is the epoxy matrix, and the black area is made up of the clay layers. The clay layers are irregularly separated by more than 100–150 Å of the epoxy matrix, and this is compatible with the XRD results.

An analysis of the TEM images and XRD patterns of the epoxy-resin composites formed with organic clay confirms that epoxy-resin/intercalated-clay nanocomposites have been achieved.



Figure 2 TEM image of a composite containing 3 wt % organic clay.

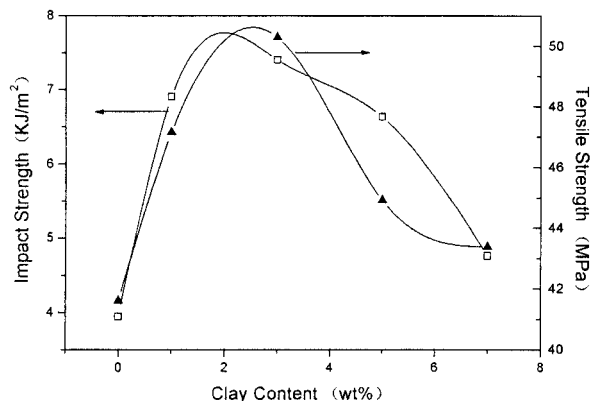


Figure 3 Impact strength and tensile strength of epoxy-clay nanocomposites.

Mechanical properties: impact strength and tensile strength

The mechanical properties of the epoxy-clay nanocomposites are shown in Figure 3. When the clay content was 3 wt %, the impact strength of the composites was improved by 87.8% (from 3.94 to 7.40 kJ/mol), and the tensile strength of the composites was enhanced by 20.9% (from 41.60 to 50.28 MPa), in comparison with the pristine epoxy resin. As a result, the loading of organic clay evidently ameliorates the mechanical properties of the epoxy-resin matrix, and the epoxy resin is toughened and strengthened with a low loading.

Thermal analysis: thermal-decomposition and heat-distortion temperatures

To determine the benefits of delaminated clay in the epoxy-resin matrix, we investigated the composite thermal properties, such as the thermal-decomposition temperature and heat-distortion temperature. The results for the heat-distortion temperature are shown in Figure 4, and the results for the thermal-decompo-

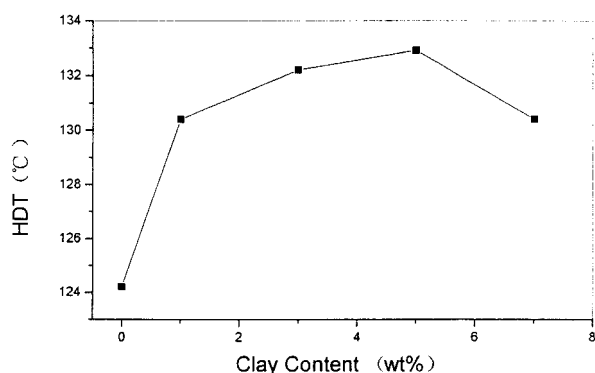


Figure 4 Heat-distortion temperature of epoxy-clay nanocomposites.

TABLE I
Effect of the Clay Content on the Maximum Decomposition Temperature of Epoxy-Resin Nanocomposites

	Content of organic clay (wt %)		
	0	3	5
Maximum decomposition temperature (°C)	348.1	357.9	372.8

sition temperature are shown in Table I.

The heat-distortion temperature of epoxy-clay nanocomposites increased from 124.2 to 132.9°C with a 5 wt % clay content. The thermal-decomposition temperature of the composites also increased from 348.1 to 372.8°C. Because the clay layer effectively restrains the diffusion of small molecules in the crosslinked epoxy-resin matrix, the thermal stability of the composite increases.

Dynamic mechanical properties

The dynamic mechanical properties of composites were also studied. The results are shown in Table II. The stiffness of clay in the epoxy matrix also affects the dynamic mechanical properties of the composites. When the temperature was lower than the glass-transition temperature (T_g), the storage modulus of the composite increased by 42.86% (from 2.17 to 3.10 GPa). When the temperature was higher than T_g , it increased by 229.8% (from 23.83 to 78.60 MPa). Furthermore, T_g increases from 132.4 to 147.1°C.

CONCLUSIONS

Polymer-silicate nanocomposites, which consisted of individual clay layers embedded within a crosslinked epoxy matrix, were prepared. The synthetic approach involved the delamination of organic clay within an epoxy resin, following by the curing of the crosslinked network. The separation of adjacent silicate layers by 100–150 Å or more was confirmed by XRD and TEM, with good wetting of the clay surface and the epoxy resin. The loading of organic clay evidently ameliorated the me-

TABLE II
Effect of the Clay Content on the Storage Modulus (E') and T_g of Epoxy-Resin/Clay Nanocomposites

	Content of organic clay (wt %)				
	0	1	3	5	7
E' ($T < T_g$) (GPa)	2.17	2.50	2.77	3.10	2.46
E' ($T > T_g$) (MPa)	23.83	44.00	52.01	78.60	56.32
T_g (°C)	132.4	143.5	146.0	147.1	145.9

T = temperature.

chanical properties of the epoxy-resin matrix and toughened and strengthened the epoxy resin during a low loading. Its thermal stability was increased, in comparison with that of the pristine epoxy resin, with a low content, and the dynamic mechanical properties, including the storage modulus and T_g , increased as well. The nanocomposites showed greater dynamic modulus reinforcement than conventionally filled epoxy resins with comparable filler loadings, and this may lead to wide applications as adhesives, coatings, electronics, structural materials, and so forth.

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