

Effect of Polymerically-Modified Clay Structure on Morphology and Properties of UV-Cured EA/Clay Nanocomposites

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ABSTRACT: Bisphenol A epoxy diacrylate (EA)/clay nanocomposites were prepared by UV-curing from a series of styrene based polymerically-modified clays and EA resin. Effects of the chemical structure of the polymeric surfactants on the morphology and tensile properties of nanocomposites have been explored. X-ray diffraction and transmission electron microscopy experimental results indicated that surfactants having hydroxyl or amino group show better dispersion and some of the clay platelets were fully exfoliated. However, the composites formed from pristine clay and other polymerically-modified clays without hydroxyl or amino groups typically contained both intercalated tactoids and few collapsed clay particles with,

if any, exfoliated platelets. The tensile strength and the elongation at break of composites were greatly improved, where the organoclays dispersed well. Thermo gravimetric analysis and differential scanning calorimeter were carried out to examine the thermal properties of the composites. The results showed that the loading of polymerically-modified clays enhanced the thermal stability of EA/clay composites, and depressed the T_g of composites. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 116: 1278–1283, 2010

Key words: EA/clay composites; polymerically-modified clay; UV-curable

INTRODUCTION

Polymer layered silicate nanocomposites have attracted much attention as examples of developed polymer reinforcement nanotechnology for more than three decades; this interest is mainly driven by the promise of greatly enhanced properties, such as tensile strength, flammability resistance, and barrier properties due to the exfoliated clay platelets in matrices, such as nylon 6, polyimides, and epoxies without compromising other properties.^{1–9}

The UV-curing technology offers a number of advantages, namely, ultrafast curing, ambient temperature operations, spatial and temporal control of the process, minor emission of volatile organic compounds, and wide range of mechanical properties of the highly crosslinked polymer formed. It has found increasing applications especially in paint, ink, and

coating industries.^{10–13} However, in some cases such as printed circuits, patterning (video disk), sealants (encapsulation), and conformal coatings, it is required to prepare polymer films with higher glass transition temperature, good barrier properties, low shrinkage, flexibility, enhanced mechanical properties, thermal stability, and chemical resistance.^{12,14–16} These requirements make nanoclay reinforced polymers attractive.

To obtain true UV-cured clay nanocomposites, the exfoliated silicate platelets must be uniformly dispersed in the prepolymer. Although this is helped by treatment with alkyl ammonium salts to render the clay organophilic, the exfoliation is still difficult to achieve because of aggregation of the clays and the absence of shear as UV-curing progresses.^{17–19} Most of recent research work is focused on clay functionalization with reactive monomers, initiator, or both monomer and initiator to realize the exfoliation of the clay platelets through the *in situ* reactions happening between the layers.^{20–27} Functional groups such as acrylate, methacrylate, and benzophenones, among others have been used to expand the clay layers. Despite these modifications, nanocomposites with predominantly intercalated and only partially exfoliated structures have been obtained in these cases. To overcome the defects of

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present modified clays, a recent approach it to use polymerically-modified clays.^{9,28,29} The greatly expanded gallery and tunable properties of polymerically-modified clays will offer a platform for the formation of UV-cured nanocomposites.

The objective of this study is to explore the effect of polymerically-modified clay structures on the morphology and properties of UV-cured EA/clay nanocomposites. Various techniques including X-ray diffraction (XRD), transmission electron microscopy (TEM), and tensile testing were used to examine the morphologies and tensile behaviors of obtained nanocomposites.

EXPERIMENTAL

Materials

Bisphenol A epoxy diacrylate (EA) purchased from Sartomer Co., (Pennsylvania, USA) was used as telechelic oligomer. The reactive diluent, tripropyleneglycol diacrylate (TPGDA), was provided by UCB Co. (Shanghai, China), 4-methyl diphenyl ketone and triethanolamine were purchased from Huihong Chemical Reagent Co., (Changsha, China). Pristine sodium montmorillonite (Na-MMT) was provided by Zhejiang Fenghong Clay Chemicals Co., (Hangzhou, China) (cationic exchange capacity (CEC) = 90 meq/100 g). Acrylamide (AM), styrene (St), acrylic acid (AA), vinylbenzylchloride, methyl methacrylate (MMA), 30% trimethylamine aqueous solution, and *N,N'*-azobis(isobutyronitrile) (AIBN) were purchased from Shanghai Shanpu Chemical Reagent (Shanghai, China) and used without further purification. Tetrahydrofuran (THF) was purchased from Yueyang Chemical (Yueyang, China) and distilled before using.

Preparation of polymerically-modified clays

In general, the polymerically-modified clays were prepared by cation exchange of the sodium ions in the Na-MMT with the corresponding polymeric quaternary ammonium salts. The polymeric quaternary ammonium salts were prepared from the reactions of trimethylamine with the corresponding polymers, which were synthesized by free-radical copolymerization of styrene, monomers, and vinylbenzylchloride. The scheme for preparing polymerically-modified clays was reported in our previous work.³⁰ The structures of the polymeric surfactants and EA are shown in Figure 1.

The polymerically-modified clays were selected to explore the effects of the polymeric surfactants structures on the dispersion of clay particles in EA matrices. The only difference among this series of polymeric surfactants is that, in the preparation of these polymeric surfactants, the third monomer is methyl

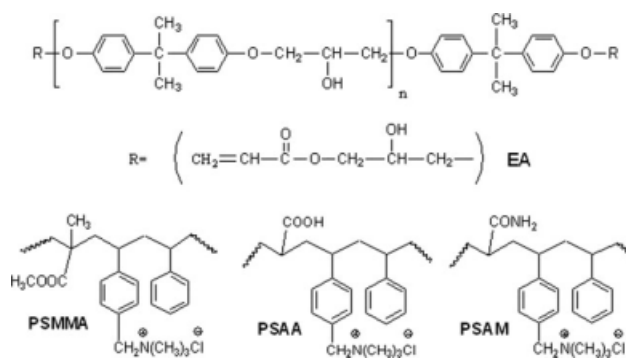


Figure 1 Structures of the oligomer surfactants and EA.

methacrylate, acrylic acid, or acrylamide. Their corresponding modified clays were denoted as PSMMA-clay, PSAA-clay, and PSAM-clay. The organic contents of these polymeric-modified clays were 56% for PSMMA-clay, 49% for PSAA-clay, and 55% for PSAM-clay, as calculated by Thermo gravimetric analysis (TGA) data.

Preparation of EA/clays UV-cured composites

Reactive diluent TPGDA (40 g) and polymerically-modified clays were added into 40 g of bisphenol A epoxy diacrylate (EA), and this mixture was stirred for 6 h to disperse the clay in the resin. Then 2.4 g of 4-methyl diphenyl ketone and 2.4 g of triethanolamine were added into the mixture. To avoid premature polymerization caused by light, the samples were wrapped by aluminum foils. After being homogenized with a high speed emulsifier at 20°C for 1 h and by sonication for 4 h, the sample was de-gassed under vacuum to remove the entrapped air. The clay loadings in these systems were 3 wt %. If a polymerically-modified clay with 50% of organic content was used, it means actually 6% of organic clay would be added in the system. Sample of pure EA was processed in the same way and used for comparison.

The resins were injected into a 2-mm thick organic glass gasket (length 150 mm × width 50 mm), sandwiched between two glass slides and PET films to allow easy removal of the samples. Samples were exposed to the UV radiation from a high pressure mercury lamp (output power of 600 W/cm²). The incident light intensity at the sample position was measured by radiometry to be 400 W/cm². A shutter was used to allow an accurate control of the exposure time of the sample by the light. Samples were exposed to the UV lamp for a total time of 2 min (1 min on each side) at ambient temperature.

Instrumentation

TGA was conducted from 30 to 800°C and 20°C/min scan rate on a Netzsch STA409PC instrument

(Bavaria, Germany) under nitrogen atmosphere. Differential scanning calorimeter (DSC) was performed on a TA Q20 series calorimeter (New Castle, USA) from 20 to 140°C under nitrogen atmosphere and 10°C/min scan rate. XRD patterns were collected from 1 to 10° using a step size of 0.02° on a Bruker-D8 instrument (Karlsruhe, Germany) using monochromatic CuK α radiation. TEM was performed on a JEOL-1230 instrument (Tokyo, Japan) under an accelerating voltage of 100 kV. The samples were ultra-microtomed with a diamond knife at room temperature to give thin sections, which were approximately 70 nm. The sections were transferred from the knife edge to 600 hexagonal mesh Cu grids. The tensile testing was carried out with a Kexin WDW3020 electronic universal testing machine (Changchun, China) according to GB1040-92 standards. The solvent-swelling properties of the modified clays were characterized using the method described in literature.³¹

RESULTS AND DISCUSSIONS

Swelling capacity of polymerically-modified clays

In general, the stability of dispersed clays is related to the swelling capacity of the clays in the solvent, and the morphology of cured composites is certainly related to the dispersion status of clays in the prepolymers.³² In this experiment it is important to form a stable suspension of clays because there is no extra-shear in UV-exposure period. The swelling capacities of clays used in this experiment were tested in the prepolymers. The X-ray patterns for the clays before and after swelling test are shown in Figures 2 and 3, respectively. The d-spacing of pristine

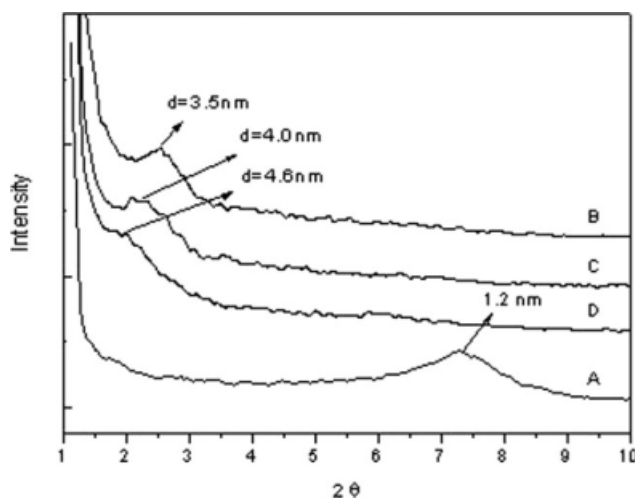


Figure 2 XRD patterns obtained from: A-pristine clay; B-PSAA-clay; C-PSMMA-clay; and D-PSAM-clay (before swelling).

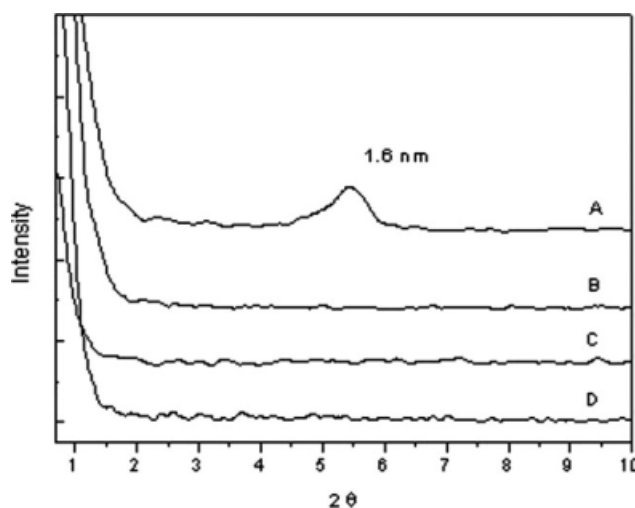


Figure 3 XRD patterns obtained from: A-pristine clay; B-PSAA-clay; C-PSMMA-clay; and D-PSAM-clay (after swelling).

clay has increased from 1.2 to 1.6 nm after being swollen in prepolymers as shown in Figures 2A and 3A. There is no obvious peak in the XRD patterns of polymerically-modified clays after being swollen in prepolymers as shown in Figure 3(B–D). This was taken as an indication that the prepolymers were intercalated into the layers of clays. The data also suggests that the swelling capacity of the clays is greatly dependent on the modifier used as shown in Figure 4. The swelling capacity testing results indicate that the polymerically-modified clays having hydroxyl (PSAA-clay) or amino groups (PSAM-clay) show better swelling capacity than that of clays with methyl methacrylate groups (PSMMA-clay); and all polymerically-modified clays show better swelling capacity than that of pristine clay. If one looks into the chemical structures of prepolymers and

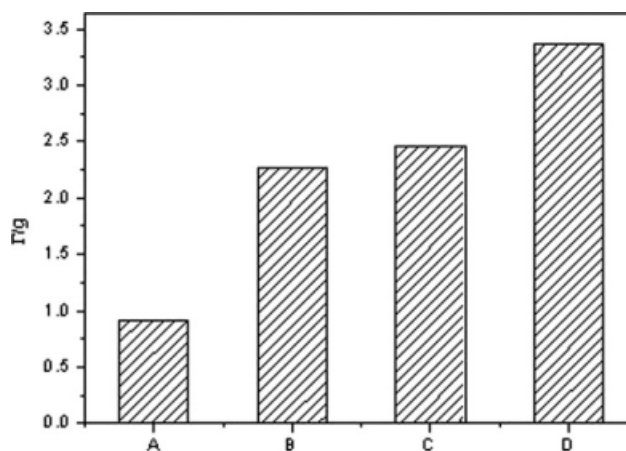


Figure 4 Swelling ability of clays in UV-curable resin: A-Pristine clay; B-PSMMA-clay; C-PSAM-clay; and D-PSAA-clay.

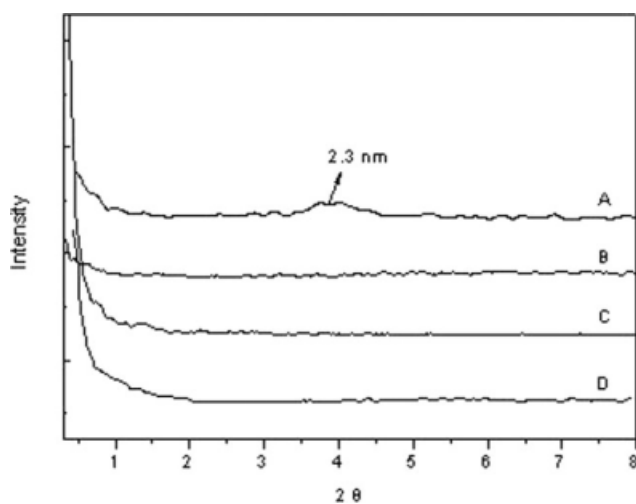


Figure 5 XRD patterns obtained from: A-EA/pristine clay; B-EA/PSAA-clay; C-EA/PSMMA-clay; and D-EA/PSAM-clay.

polymeric surfactants, a conclusion will be made that the difference in swelling capacity might be attributed to the hydrogen bonding formation between the modifiers and prepolymers.

Effect of polymerically-modified clay structures on the morphologies of formed nanocomposites

The structures of the polymeric surfactants used for the modification of clays in this experiment are expected to have effect on the morphology of the UV-cured EA nanocomposites. Figure 5 shows XRD patterns of EA/clay composites prepared from pristine clay and polymerically-modified clays. Apparently there is a peak in the XRD pattern of EA composites prepared from pristine clay at 2θ value of 3.8° , which corresponds to a d -spacing of 2.3 nm indicating that the polymers are further inserted into the gallery of clays after polymerization. The other three EA/clay UV-cured nanocomposites formed from polymerically-modified clays do not show any apparent diffraction peak as shown in Figure 5(B–D). These results suggest that the clay platelets are probably exfoliated or completely disordered. These results alone cannot confirm this premise as the observed absence of scattering could be due to geometry effects or lack of sensitivity at the low level of clay loading.

To confirm the structure of EA/clay and EA/polymerically-modified clay nanocomposites, TEM experiments were performed. TEM images of polymerically-modified clays and composites are shown in Figure 6. The composites formed from pristine clay contain many aggregates of clay as shown in Figure 6A1. Figures 6(B1–B3) show the morphologies of PSMMA-modified clay, and the low and high images of the nanocomposites formed from the

PSMMA-modified clays. It can be seen that most of the particles in the composites are much smaller than that observed in pristine clay-based composites, and that “tactoid” particles are still present; a comparison between the high images of PSMMA-modified clays and its EA composites shown in Figures 6(B1,B3) shows that the clay galleries are further expanded indicating the intercalation of polymers. Figure 6(C,D) showed the structures of EA nanocomposites formed using the PSAA and PSAM-modified clays. The clays in the composites are extensively dispersed as indicated in the low images. The high images shown in Figure 6(C3,D3) reveal that these composites are of exfoliated structure with some stacked-layers. In this experiment, the organic contents in all polymerically-modified clays are the same; the significant difference among them lies in the chemical structures of polymeric surfactants used in the modification of clays. There are hydroxyl and amide groups in the PSAA and PSAM surfactants which could form hydrogen bonding with the prepolymers. The hydrogen bonding may be the reason for the difference in morphologies of these clay composites.

Thermal analysis of EA/clay nanocomposites

The thermal stability of EA and its nanocomposites have been evaluated using TGA. The TGA traces obtained from pure EA and EA nanocomposites are shown in Figure 7. It shows that the small amount of clay loading in EA/clay nanocomposites can enhance the thermal stability of EA, and there is no significant difference among the nanocomposites. The experimental results indicate that morphological structures do not affect the thermal properties of nanocomposites at clay loading of 3%, and this is in agreement with what is usually seen for clay nanocomposites.³³

Figure 8 shows DSC patterns of pure EA and EA/clay nanocomposites. It is believed that the observed decrease in T_g for all nanocomposites can be attributed to lower crosslink density as reported in reference.³⁴ In the swelling capacity experiment, PSAA and PSAM-modified clays have shown stronger interactive attractions between the clays and prepolymers. This stronger interactive attraction may attribute to the observed difference in T_g of composites formed from different clays.^{35,36} The T_g of composites formed from PSAA and PSAM-modified clay are higher than either that of composites from PSMMA-modified clay or pristine clay.

Mechanical properties

Tensile properties of nanocomposites formed from different polymerically-modified clays are shown in

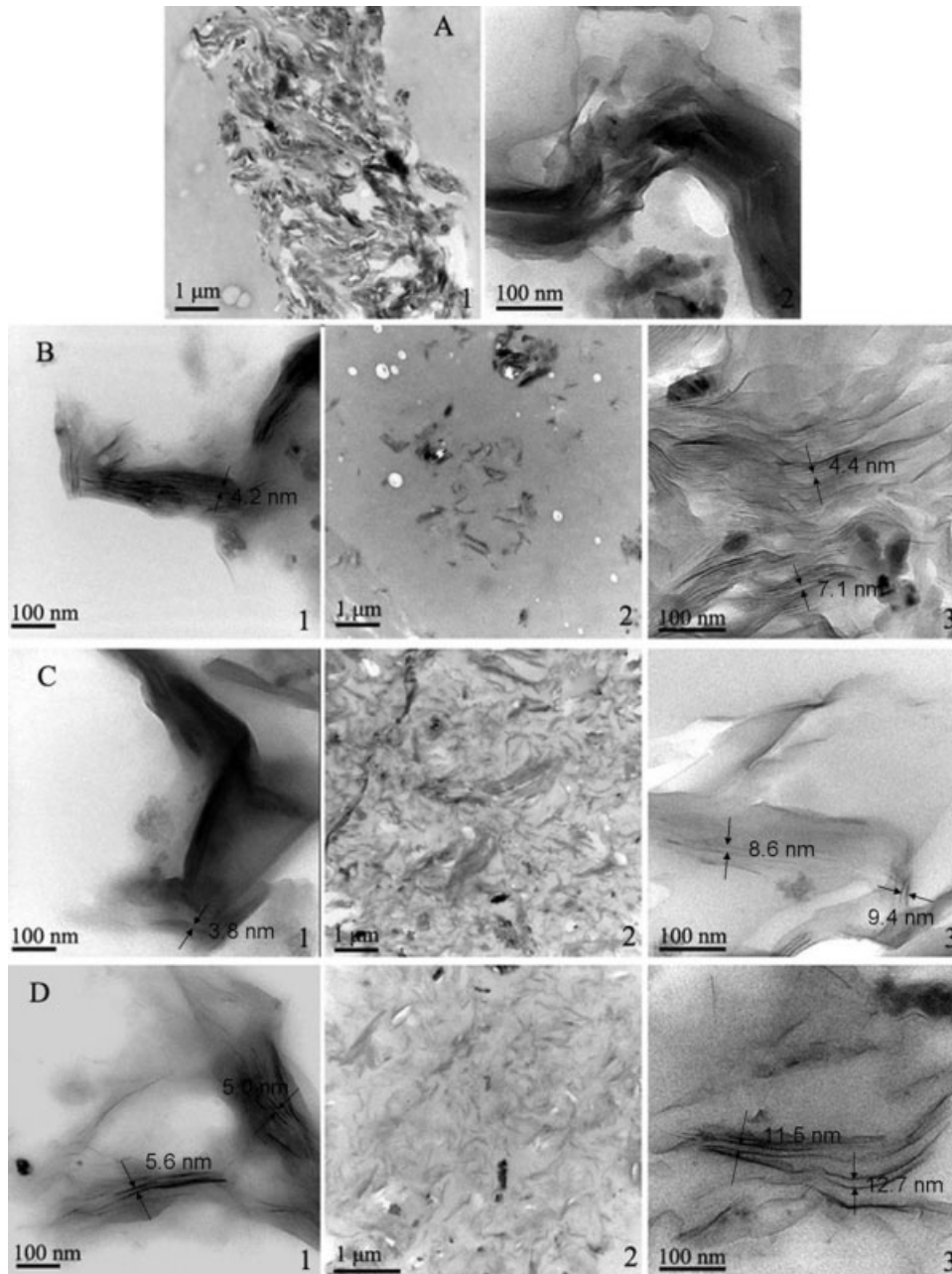


Figure 6 TEM images obtained from: A-EA/pristine clay; B-EA/PSMMA-clay; C-EA/PSAA-clay; and D-EA/PSAM-clay (left-low magnification, right-high magnification).

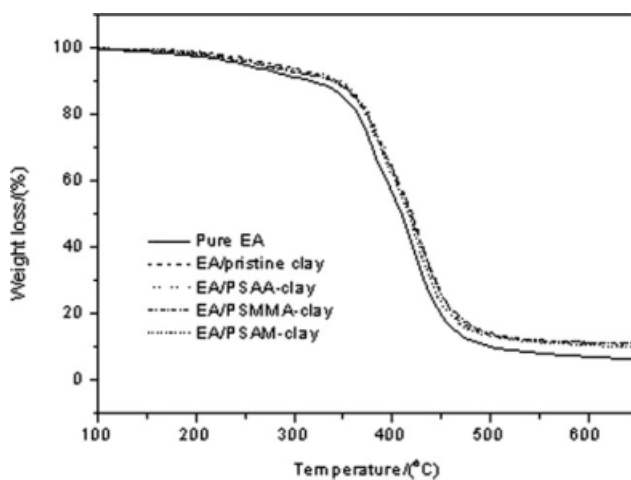


Figure 7 TGA traces obtained from pure EA and EA nanocomposites.

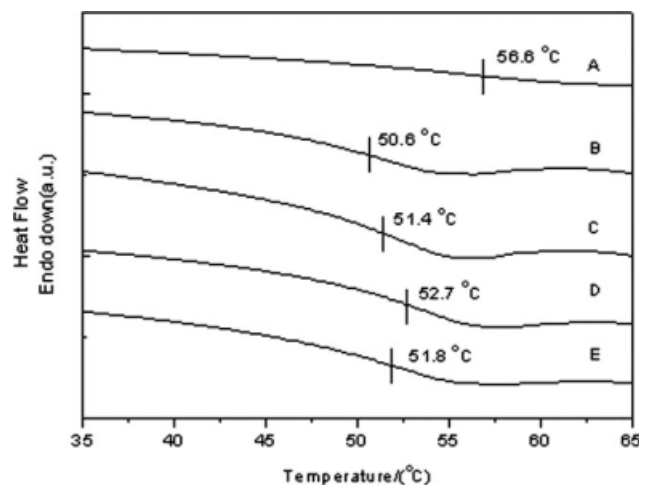


Figure 8 DSC traces obtained from: A-pure EA; B-EA/pristine clay; C-EA/PSMMA-clay; D-PSAA-clay; and E-EA/PSAM-clay.

TABLE I
Effect of Surfactant Chemical Structure on Mechanical Properties

Material	Tensile strength (MPa)	Elongation at break (%)	Elastic modulus (GPa)	Pencil hardness
Pure EA	22.3 ± 2.3	3.0 ± 0.5	2.0 ± 0.1	HB
EA/pristine clay-3%	22.1 ± 2.0	3.0 ± 0.5	1.9 ± 0.1	5H
EA/PSMMA-clay-3%	23.5 ± 1.2	2.6 ± 0.6	2.0 ± 0.1	5H
EA/PSAA-clay-3%	26.4 ± 2.2	2.9 ± 0.7	2.2 ± 0.1	5H
EA/PSAM-clay-3%	29.6 ± 1.2	4.4 ± 0.6	1.5 ± 0.1	5H

Table I. The experimental results indicate that the nanocomposites formed from the clays having hydroxyl or amino groups (PSAA and PSAM-modified clay) have significantly higher tensile strength and elongation at break than the ones formed from pristine clay or clays having methyl methacrylate groups. TEM experimental results show that nanocomposites based on PSMMA are of large aggregates, while nanocomposites based on PSAA and PSAM display better dispersion and exfoliated structures; Furthermore, DSC and swelling capacity tests have shown that PSAA and PSAM-modified clays have stronger interactive attractions with the EA matrix, which was attributed to hydrogen bonding resulting in a higher compatibility. The aforementioned two aspects have contributed to the high performance of nanocomposites formed from PSAA and PSAM-modified clays.

CONCLUSION

A comparative study on the morphologies and properties of EA/clay UV-cured nanocomposites prepared from different polymerically-modified clays has been performed. Experimental results have indicated that morphologies and tensile properties of the composites are dependent on the chemical structure of modifiers used in the preparation of clays. Polymerically-modified clays with hydroxyl and amide groups are promising additives for high performance UV-cured EA/clay nanocomposites.

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