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ORIGINAL PAPER

Effect of silane functionalization of montmorillonite on epoxy/montmorillonite nanocomposite

Yoon Young Choi · Se Hyoung Lee · Sung Hun Ryu

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Abstract Mechanical and dynamic mechanical properties of various montmorillonite (MMT)/epoxy nanocomposites were investigated. 3-aminopropyltriethoxysilane functionalized MMT was compared with commercial pristine MMT and ammonium salt substituted MMT. Qualitative evidence of silane functionalization was confirmed by FT-IR. XRD and TEM were used to characterize the degree of intercalation of MMT in epoxy nanocomposite. Tensile stress and elongation of MMT/epoxy nanocomposite were improved significantly by the silane functionalization of MMT. Dynamic mechanical analysis showed that silane functionalization of MMT resulted in active interactions between MMT and epoxy.

Keywords Montmorillonite · Epoxy · Silane · Nanocomposite

Introduction

Layered silicates like montmorillonite (MMT) have received much attention as a reinforcing material for polymers because of their potentially high aspect ratio and unique intercalation/exfoliation characteristics [1, 2]. Such clay minerals with proper exfoliation can lead to platelets with high stiffness and strength dispersed in polymer matrix [3, 4]. As a relatively new kind of composite material, layered silicate reinforced polymer nanocomposites have great potential on many applications since they show a great improvement on properties compared to the conventional mineral composites, even with a small amount of silicate [5, 6]. These superior properties include improved tensile strength and modulus [7–9], reduced

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Y. Y. Choi · S. H. Lee · S. H. Ryu (✉)
College of Engineering, Industrial Liaison Research Institute, Green Energy Center,
Kyung Hee University, Yongin, Kyunggi-Do, Korea
e-mail: shryu@khu.ac.kr

gas permeability [10], increased thermal stability [11], and enhanced flammability [12, 13].

Epoxy resin exhibits an attractive combination of stiffness, strength, high heat distortion temperature, creep resistance, thermal and environmental stability. They are widely applied as binders for coating, adhesive, and composites [14, 15]. Addition of organically modified MMT to the epoxy matrix in the nano-scale dispersion can further improve the properties of epoxy resins [16, 17]. Epoxy/layered silicate nanocomposites are generally prepared using amine derivatives as hardeners [18]. Lu et al. [19] reported that the exfoliating ability of the organoclays in epoxy resin is determined by the nature of the clays and the curing agent used. Chin et al. [20] found that, for the *m*-phenylene daimine (MPDA)-cured epoxy systems, exfoliated nanocomposites are formed with epoxy cured with less than an equimolar concentration of MPDA or with autopolymerization of the epoxy without curing agent, whereas the intercalated structure was only observed with large excess curing agent. Messersmith and Giannelis [21] reported that the glass transition temperature of epoxy/clay nanocomposite is higher than that of epoxy matrix. The mechanical and barrier properties of epoxy/layered silicate nanocomposites are largely dependent on the degree of intercalation/exfoliation of the layered silicate in the polymer matrix. Pinnavaia et al. [22, 23] studied the effect of organo-surfactant chain length on the delamination of epoxy/clay nanocomposites and they found that tensile strength and Young's modulus increased with the increment of organo-surfactant chain length and the loading content. However, modification of MMTs using traditional modifier, such as long-chain alkylammonium, is a physical modification and it cannot provide the chemical interaction between polymer and MMTs which can induce high mechanical properties, such as tensile strength and toughness. Recently silane was used to functionalize the MMT [24–26]. Herrera et al. [25] reported the influence of silane functionalized clay on the properties of water based polymer/clay nanocomposites. It has been reported that amine is highly reactive epoxy and its reaction resulted in improved mechanical properties.

In the present work, epoxy nanocomposites using aminosilane functionalized MMT has been prepared and characterized mechanical and dynamic mechanical properties of epoxy/MMT nanocomposites. Commercial ammonium salt modified MMT was compared to investigate the influence of chemical interaction between aminosilane functionalized MMT and epoxy on the properties.

Experimental

Materials

Commercial grade MMT, Cloisite $\mathrm{Na}^{\oplus}$ and $15\mathrm{A}^{\mathrm{TR}}$, were purchased from Southern MMT Products Inc., USA. Cloisite $15\mathrm{A}^{\mathrm{TR}}$ was modified with ammonium salt. 3-aminopropyltriethoxysilane was obtained from Aldrich Chemical Company Inc., USA. Epoxy resin used in this work was diglycidyl ether of bis-phenol A (DGEBA) with the epoxy equivalent value of 180–190 g/eq (YD-115, Kukdo Chemical Co., Korea). The curing agent used was amine hardener (G-A0533) procured from

Kukdo Company, Korea. Amine hardener (G-A0533) was polyamidoamine (PAA) with amine hardener equivalent value of 95–115 g/eq.

Nanocomposite preparation

Cloisite Na$^{\oplus}$ (P-MMT), Cloisite 15A^{TR} (O-MMT) or silanized MMT (S-MMT) was incorporated at various concentrations (2, 6 or 10 wt%) relative to the epoxy. Aminosilane functionalized MMT was prepared with distilled water as a dispersing medium and detailed procedure was described in previous work [26]. Acetone was used as a solvent to facilitate the mixing. Weight ratio of epoxy (DGEBA)/hardener (PAA) was 2:1. DGEBA and MMT with solvent were mixed for 3 h at 25 °C using mechanical stirrer. Then hardener was added and mixed for 5 min. Mixture was dried for 3 h at 25 °C under vacuum to remove the solvent. The epoxy nanocomposites were then cured for 12 h at 110 °C using PTFE molds.

Characterizations

Degree of intercalation/exfoliation was evaluated using X-ray diffractometer (XRD). X-ray diffraction patterns were obtained by M18XHF-SRA diffractometer with CuKα radiation (Macscience Inc.) and it was scanned from 1.5° to 10° with 1°/min scanning speed. The dispersibility of MMT in the nanocomposite was observed directly using transmission electron microscopy (TEM, JEM-2100F, Jeol). Fourier transform infrared spectroscopy (FT-IR 2000, Perkin Elmer) was used in the range of 400–4,000 cm^{-1}. Dynamic mechanical analysis was carried out using DMA 2980 (TA Instrument) in the temperature range of 25–170 °C with a heating rate of 2 °C/min. The frequency was 1 Hz and amplitude was 5 microns. Tensile strength and elongation were measured using tensile tester (Tensilon/UTM-III, Toyo-Baldwin) and crosshead speed was 50 mm/min. Test specimen was prepared by pressing at 170 °C for 1 min. 10 different specimens were used to obtain the properties and results were quite reproducible.

Results and discussion

Figure 1 shows the FT-IR spectrum of the P-MMT and S-MMT. Typical characteristic peaks of P-MMT are observed, such as 3,634 cm^{-1} for hydroxyl stretching that is bonded to the aluminum and magnesium [Al(Mg) OH or Al(Al) OH], broad peak over the range of 1,200–1,000 cm^{-1} with the peak maximum at 1,035 cm^{-1} for Si–O stretching of silicates present in P-MMT and the bending vibrations of Al(Al) OH and Mg(Mg) OH occurs at 916 and 800 cm^{-1}, respectively. New peak at 2,930 cm^{-1} with a small hump around 2,850 cm^{-1} that are due to the –CH asymmetric and symmetric stretching of –CH_2 groups confirms the presence of the silane on the surface. Also, new peaks at 1,566, 1,496 and at 690 cm^{-1} that corresponds to the –NH_2, –CH_2 bending

Figure 2 shows the XRD patterns of MMTs and epoxy nanocomposites with P-, S- or O-MMT. Interlayer distance of P-, O-, S-MMT is 12.8, 32.1, 20.8 Å,

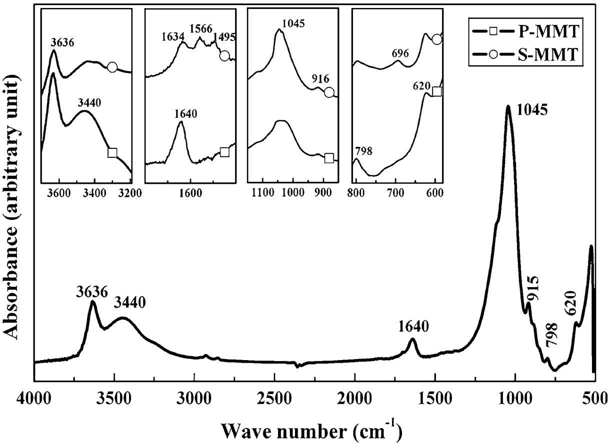

Fig. 1 FT-IR spectra of P-MMT and S-MMT vibrations and –CH out of plane deformation further support the successful grafting of silane onto the P-MMT

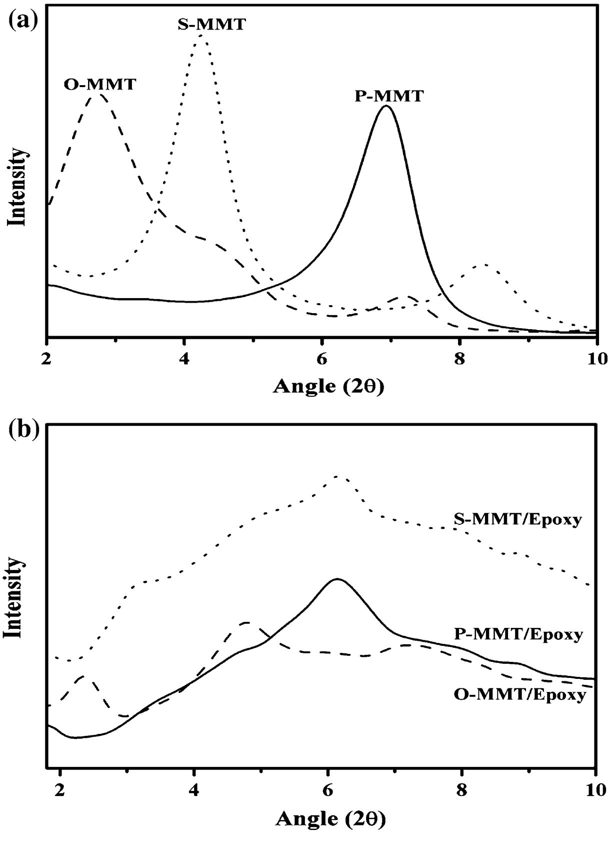

Fig. 2 XRD patterns of **a** MMTs and **b** 6 wt% MMT/epoxy nanocomposites

respectively. In epoxy/MMT nanocomposites it clearly shows that (001) peak of nanocomposites shifts to the lower angle which indicates intercalation behavior is occurred and it is attributed to the intercalation of epoxy molecules into MMT layers. Epoxy molecules penetrate into layers between MMT platelets and try to separate platelets during curing reaction by the formation of polymer. Interlayer distance of P-, O-, S-MMT/epoxy nanocomposites is 14.4, 38.25 and 28.0 Å, respectively. High interlayer distance of MMT encourages diffusion of polymer molecules and finally it results in high interlayer distance in polymer/MMT composites. The order of interlayer distance of nanocomposites is same as that of MMTs. Transmission electron micrographs of nanocomposites are shown in Fig. 3. The dark lines are the MMT layers in a matrix. O-MMT and S-MMT/epoxy nanocomposites (Fig. 3b, c) show intercalated structure with uniform interlayer. From TEM micrographs the interlayer distance of O-MMT/epoxy nanocomposite is measured as 34.2, while S-MMT/epoxy nanocomposite shows 20.7–27.9 Å. It is found that interlayer distance values from XRD and TEM are quite close. It is interesting that 20.7 Å in TEM micrograph is same as the interlayer distance of S-MMT itself and it indicates that no intercalation is occurred. Some layers with 20.7 Å in S-MMT/epoxy nanocomposite can be related to the structural characteristics of S-MMT. Ryu et al. [26] reported that the interaction between 3-aminopropyltriethoxysilane and the edge of MMT platelets was of less significant due to low wetting phenomena and thereby made the silane to diffuse into layers of

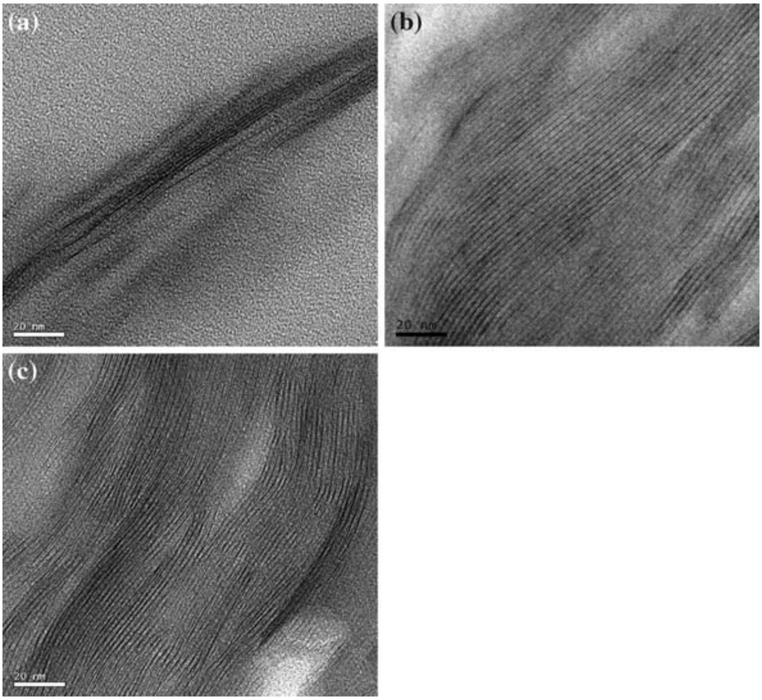

Fig. 3 TEM photographs of epoxy nanocomposites with 6 wt% **a** P-MMT, **b** O-MMT and **c** S-MMT

the platelets in water. It was expected to have grafting of silane between the platelets as observed by He et al. [24] and the possible S-MMT structures are proposed by Ryu et al. [26]. Thus, silanes grafted between platelets and edges can restrict the separation of platelets during curing reaction as shown in Fig. 4, while P- or O-MMT can separate as much as it can. This can induce the similar interlayer distance of S-MMT/epoxy nanocomposite compare to S-MMT itself. From XRD and TEM results, tactoid structures of MMT also exist with in S-MMT/epoxy nanocomposite. Even though it is not shown here, the change of amount of S-MMT did not show a significant change in XRD patterns and TEM micrographs. Silanization of MMT also improves the mechanical properties of nanocomposite. Figure 5 shows the tensile stress–strain behavior for 6 wt% MMT content. S-MMT nanocomposite shows highest elongation and tensile stress values, while P-MMT nanocomposite shows lowest values. Tensile stress and elongation also varies with content of MMT. As shown in Fig. 6, tensile stress increases with increasing amount of S-MMT, while elongation shows maximum value at 6 wt% and then decreases at 10 wt%. The area under stress–strain curve is useful indicator for the toughness of material and Fig. 7 shows the toughness of nanocomposites. It is quite evident that the toughness of S-MMT at high concentration of MMT is much higher than that of P-MMT or O-MMT nanocomposite. This behavior can be attributed to

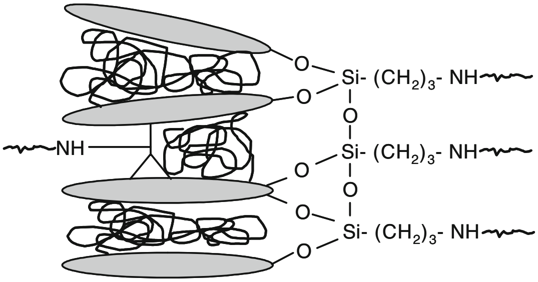

Fig. 4 Proposed schematic diagram of interaction of epoxy molecules with S-MMT

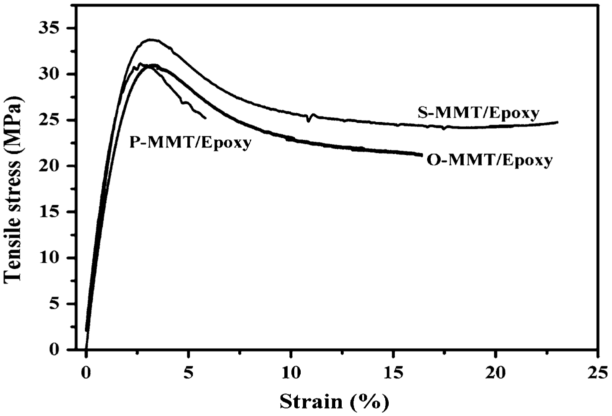

Fig. 5 Stress–strain diagram of various epoxy nanocomposites with 6 wt% MMT

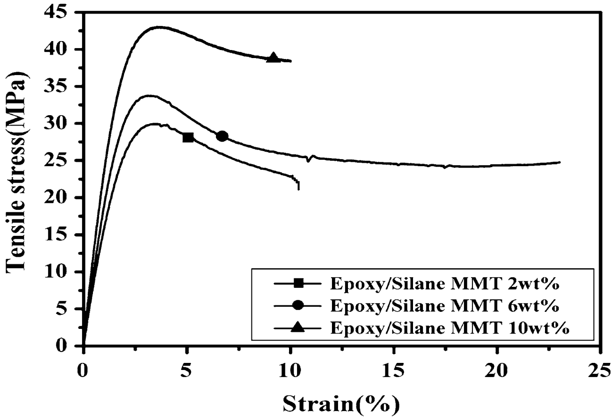

Fig. 6 Stress–strain diagram with various amount of S-MMT

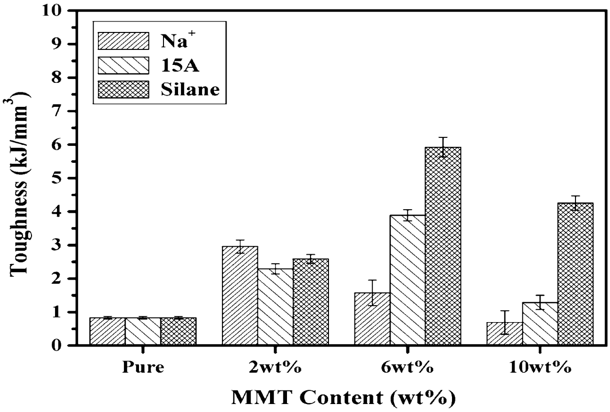

Fig. 7 Toughness of epoxy nanocomposites with different types of MMTs

the chemical interaction between grafted silanes of S-MMT and epoxy molecules while O-MMT and epoxy molecules has physical interaction. Grafted silanes in S-MMT have free end amine groups and those can react with epoxy molecules. Through this interaction S-MMTs can be chemically interconnected with polymer molecules which results in the improved interfacial characteristics between S-MMT and epoxy molecules and it induces high toughness of nanocomposite.

Interfacial characteristics of nanocomposite can be well described by dynamic mechanical analysis. The variation of tan δ of nanocomposites with 6 wt% MMT is shown in Fig. 8 and it is found that intensity and peak position of tan δ depends on the type of MMTs. It is observed that T_g of P-, O- and S-MMT/epoxy nanocomposite is 70.3, 71.4 and 72.0 °C, respectively. It has been reported that the addition of MMT resulted in the increase of T_g of nanocomposite and this behavior is attributed to the restricted segmental motions of molecules in the epoxy-MMT interfaces of intercalated MMT layers [8]. For P-MMT or O-MMT/epoxy

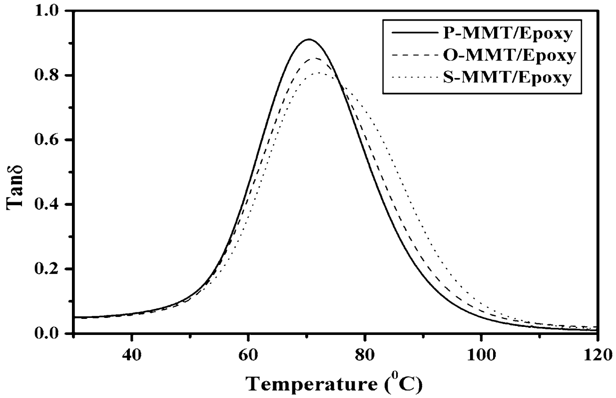

Fig. 8 Variation of tan δ of epoxy nanocomposites with different types of MMTs (6 wt% MMT)

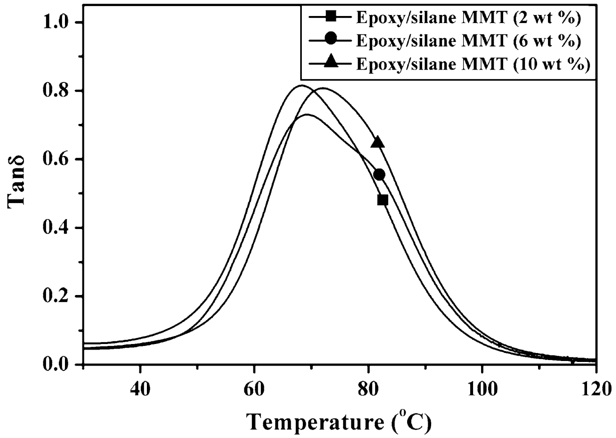

Fig. 9 Variation of tan δ with various amounts of MMTs

nanocomposite restriction of segmental motion of molecules is merely due to physical reasons. In S-MMT/epoxy nanocomposite, however, some epoxy molecules were connected chemically to the S-MMTs as shown in Fig. 4 and it may induce further molecule restriction. Polymer-filler friction, where there is essentially no adhesion at the interface and excess damping in the polymer near the interface because of induced thermal stresses or changes in polymer conformation, results in a high value of tan δ. This means if there is a good interaction between MMT and epoxy molecules and MMTs are well dispersed in the epoxy matrix, there should be a decrease in the damping factor. Thus, the variation of tan δ in Fig. 8 gives a clue that improved interfacial behavior exists between S-MMT and epoxy molecules through chemical interactions. Figure 9 shows that peak position of tan δ shifts to higher temperature with increasing amount of S-MMT and it can be attributed to the more restriction of molecules with increasing amount of S-MMT.

Conclusions

MMT was functionalized with 3-aminopropyltriethoxysilane and its epoxy nanocomposite was investigated. It is observed that MMT was successfully functionalized with silane using water as a solvent and its interlayer distance was increased due to functionalization. XRD results showed that intercalation was occurred for P-, O- and S-MMT/epoxy nanocomposites and it was confirmed by TEM. Tensile elongation and toughness of S-MMT/epoxy nanocomposite was improved significantly and it was attributed to the chemical interaction between epoxy molecules and amine groups of grafted silane on MMT, while P- or S-MMT caused physical interaction with epoxy. Chemical interaction in S-MMT/epoxy nanocomposite induced the restriction of molecular motion and increase of T_g was observed.

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