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Exfoliation of smectite clays by branched polyamines
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Abstract

Exfoliation through an ionic exchange reaction of layered silicate clays, including synthetic fluorinated mica (Mica) and natural montmorillonite (MMT), were achieved by using polyvalent amine salts as the intercalating agents. The requisite polyamine was synthesized from the epoxy/amine coupling reaction, involving a trifunctional poly(oxypropylene)-triamine (*ca.* 440 g/mol M_w) and diglycidyl ether of bisphenol-A. The polyamine was a mixture of oligomeric adducts consisting of multiple amine functionalities and a branched backbone. Partial acidification by HCl addition generated a series of amine salts that affected the intercalation and the expansion of the silicate interlayer in the range of 15.2–60.0 Å XRD d spacing. At the specific acidified ratio ($H^+/amine = 1/3$ equiv ratio), the polyamine salts rendered the clay's layered structure into randomization. The result was confirmed by using XRD and transmission electronic microscopy (TEM). The hybrids of polyamines and Mica or MMT were blended into epoxy resins and cured into nanocomposites, which exhibited the improvements of thermal stability and hardness.

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1. Introduction

Organic modification of the naturally occurring smectite clays may lead these layered silicates to a variety of industrial applications including the uses as catalysts [1,2], adsorbents [3,4], biomaterial encapsulations [5,6], modified electrodes [7,8], and multilayer self-assembling substrates [9]. One of recent developments for utilizing the clay materials

is in the area of polymer/layered silicate nanocomposites [10]. In order to prepare a fine dispersion of silicates in hydrophobic polymers, organic surfactants are employed to improve their compatibility. The smectite clays, consisting of multiple-layered platelets in stacks and cationic metal ions in the interlayer spacing, are generally hydrophilic, easily swelled in water, but incompatible with most hydrophobic polymers. The organic modification through an ionic exchange reaction with organic quaternary salts, generally enlarge the clay layer spacing and organic compatibility. Conventionally, the organic cationic surfactants such as fatty

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ammonium salts [11–13], alkyl phosphonium salts [14–16], and polymeric ammonium salts [17–19] were used. The embedded organics may increase the clays' accessibility toward the incoming monomers or hydrophobic polymers. In the sequential process of preparing nanocomposites, the intercalated clays are *in situ* mixed and subsequently exfoliated into random platelets in the polymer matrices [20–22].

Among many kinds of smectite clays, montmorillonite (MMT) is the most studied and well characterized [23–26]. Similar to the montmorillonite clay, the synthetic fluorinated mica (Mica) has also a layered structure with ionic bridges in the primary stack, but with a larger platelet size than the Na^+ form of MMT. The difference is estimated to be 300–1000 nm for Mica platelet units and 80–100 nm for MMT [27–29]. The previous studies have shown that Mica can be intercalated with organic surfactants, as to the MMT modification, but in a different XRD basal spacing. A wide expansion of silicate spacing by using the series of poly(oxypropylene)-diamine salts (POP-amine) in the molecular weight range of 230–5000 g/mol has been achieved. However, the comparative results indicated a significant difference between the MMT and Mica intercalations with respect to the gallery expansion. For example, the use of the POP-amine of 5000 g/mol M_w could expand the interlayer structure of MMT up to 92.0 Å XRD d spacing, but only to 83.7 Å for Mica [27,30]. The difference was attributed to the platelet size and steric hindrance for organics to embedding into Mica. Further investigations on the polymeric intercalating agents have included PP-g-MA, SEBS-g-MA, and SMA grafting amines and the Mannich types of polyamines [31–34].

In the article, we design a new class of polyamines with a branched backbone and multiple amine functionalities for the clay exfoliation. The polyamines were prepared from the epoxy/amine coupling reaction of diglycidyl ether of bisphenol-A and POP-triamine of 440 g/mol M_w . It is anticipated that the multiplicity of polyvalent ionic sites will efficiently affect the clay modification. In this study, we compare the effectiveness of the polyamine salts on the MMT and Mica exfoliation. The polyamine modified silicates are further mixed and cured with an epoxy system to yield the MMT and Mica nanocomposites. The physical properties including thermal stability and hardness were measured and correlated with the platelet dispersion in the polymer matrix.

2. Experimental

2.1. Materials

The synthetic fluorinated mica (Mica, SOMASIF ME-100) is a layered silicate clay with chemical analyses of Si (26.5 wt%), Mg (15.6 wt%), Al (0.2 wt%), Na (4.1 wt%), Fe (0.1 wt%), and F (8.8 wt%) and a cationic exchange capacity (CEC) of 120 mequiv/100 g, obtained from CO-OP Chemical Co. (Japan). The Mica is possibly swelled and modified by organic amine salts. In contrast, the naturally occurring micas cannot be easily swelled or organically intercalated due to their high platelet size and the inherent hydroxyl cross-linking. Sodium montmorillonite (Na^+ -MMT), a layered silicate clay with a cationic exchange capacity (CEC) of 115 mequiv/100 g, was supplied from Nanocor Co. Poly(oxypropylene)-triamine (Jeffamine[®] T403, abbreviated as T403) with a molecular weight of 440 g/mol was purchased from Huntsman Chemical Co. or Aldrich Chemical Co. Diglycidyl ether of bisphenol-A (DGEBA, trade name BE-188) with an epoxy equivalent weight (EEW) of 188 was obtained from Nan-Ya Chemicals (Taiwan).

2.2. Preparation of polyamines

The typical experimental procedures for preparing the polyamines are described below. To a 50 mL three-necked and round-bottomed flask, equipped with a mechanical stirrer, a thermometer, and a heating mantle was placed with T403 (7.15 g) and DGEBA (2.85 g). The reactants were stirred by using a mechanical stirrer at room temperature. The progress of epoxy/amine reaction was monitored by FT-IR, showing the disappearance of 910 cm^{-1} epoxide absorbance during the process. The reaction was terminated after 4 h and the final product was recovered as a viscous, transparent liquid. The crude product after extracting out the unreacted T403 was analyzed by amine titration and GPC. The amine titration indicated the total-amine contents to be 4.8 mequiv/g. The GPC analysis identified two major peaks.

2.3. Intercalation and exfoliation of Mica with the polyamine salts

The ionic exchange reaction of Mica with a polyamine salt was performed according to the

procedures reported previously [30]. An example of a preparative procedure for preparing the Mica exfoliation is described below. Synthetic fluorinated mica (Mica, CEC = 120 mequiv/100 g, 1.0 g) was dispersed in 100 mL of deionized water at 80 °C by vigorously stirring. The prepared polyamines (4.80 g) and aqueous hydrochloric acid (35 wt%, 0.75 g) were mixed to form quaternary ammonium salts at room temperature and then poured into the Mica slurry in water. The mixture was continuously stirred at 80 °C for 3 h. The white precipitate was filtered, collected, and washed thoroughly with 40 mL of water/ethanol several times. The product was dried, pulverized into powder form and characterized by X-ray powder diffraction (XRD), thermal gravimetric analysis (TGA), and transmission electronic microscopy (TEM).

2.4. Intercalation and exfoliation of Na^+ -MMT

Procedures similar to that of the Mica exfoliation were carried out. Na^+ -MMT (CEC = 115 mequiv/100 g, 1.0 g) was dispersed in 100 mL of deionized water at 80 °C by vigorously stirring for overnight. The prepared polyamines (4.50 g) and aqueous hydrochloric acid (35 wt%, 0.71 g) were mixed to form quaternary ammonium salts at room temperature and then poured into the MMT slurry in water. The mixture was stirred at 80 °C for 3 h, filtered, collected, and washed thoroughly with 40 mL of water/ethanol several times. The product was dried, pulverized into powder form and characterized by XRD, TGA, and TEM.

2.5. Preparation of epoxy nanocomposites with the polyamine–Mica and MMT

Epoxy nanocomposites were prepared by first dispersing the designated amount of the polyamine–clay with additional curing agent T403 by mechanical stirring for 1 h at 70 °C and optionally stirred under ultrasonic vibration. To the polyamine modified clays (0.05, 0.07 or 0.1 g) were mixed with T403 (2.8 g, 6.3 mmol) and DGBEA (7.2 g, 20 mmol). The mixture was thoroughly stirred, degassed and poured into a 1/8-in.-thick flat aluminum mold to form a sample plaque. The curing process was conducted in an oven at the programmed conditions of 80 °C for 2 h and 120 °C for 2 h.

2.6. Characterization

Fourier transform infrared spectroscopy (FT-IR) was carried out using a Perkin–Elmer Spectrum One FT-IR spectrometer in the range of 400–4000 cm^{-1} . Samples were prepared by dissolving in THF and evaporated into thin film on a KBr plate. Amine titration was estimated by using ASTM D2073-92 method. Relative molecular weights were analyzed on a gel permeation chromatography (GPC), Waters apparatus (515 HPLC pump, 717 autosampler, 2410 refractive index detector). A set of Waters Stygel columns was used under a THF flow rate of 1.0 mL/min, calibrated by polystyrene standards. The X-ray powder diffraction (XRD) was performed on a Schimadzu SD-D1 diffractometer with a Cu target ($\lambda = 1.5405 \text{ \AA}$) at a generator voltage of 35 kV, a generator current of 30 mA, and a scanning rate of 2°/min. The d spacing ($n = 1$) was assigned on the basis of the Bragg's equation ($n\lambda = 2d\sin\theta$). The thermal analyses were analyzed by using thermal gravimetric analyzer (TGA), on a Perkin–Elmer Pyris 1 model. The organic weight was estimated from the weight losses by ramping the temperature from 100 to 850 °C at the rate of 10 °C/min in air. Transmission electronic microscopy (TEM) was performed on a Zeiss EM 902 A at an acceleration voltage of 80 kV, and the samples was cut into a wedge shape and then embedded in a polyethylene mold using epoxy resin. The specimen was trimmed into the shape of a trapezoid with a thickness of approximately 80 nm were microtomed at room temperature using a diamond knife on a Reichert-Jung Ultracut UCT, and collected on a 200 mesh carbon-coated Cu grid for the analyses. The glass transition temperature (T_g) was measured on Perkin–Elmer DSC 7, under the conditions of using a second heating scan at 10 °C/min from 25 to 200 °C. Pencil hardness was measured according to the method of ASTM D 3363-74.

3. Results and discussion

3.1. Preparation of the polyamines

The ionic exchanging agent was prepared from the amine/epoxy reaction of poly(oxypropylene)-tri-amine (T403) and diglycidyl ether of bisphenol-A (DGEBA), according to the reaction scheme and representative structures described in Scheme 1. This conventional amine/epoxy curing reaction may generate a cross-linked network. However,

Scheme 1. Representation of two possible polyamine structures from the amine/epoxy coupling reaction; the major product ($b = 1$; six amine functionalities) and the minor product ($b = 2$; nine amine functionalities).

when the molar ratio of the T403/DGEBA starting materials at 2/1 and 3/2, a non-gelled and THF-soluble adduct was obtained. The analysis by amine titration, GPC, and FT-IR indicated the product was a mixture of polyamines. The possible structures of the adducts are illustrated to represent the multiple amine functionalities, generally consisting of secondary amines ($-\text{CH}_2\text{NH}-$), primary amine terminals ($-\text{NH}_2$), poly(oxypolypropylene) segments and bisphenol-A linking sites. Besides two possible structures for the 2/1 T403/DGEBA adducts, other oligomers such as a dimer by linking the primary structure adduct with 1 mol of DGEBA may be existed.

3.2. Ionic exchange reaction and exfoliation of Mica and MMT by polyamines

The synthesized poly(oxypolypropylene)-polyamines/DGEBA products are hydrophobic and insoluble in water. When treating with hydrochloric acid, the hydrophobic polyamines were converted into the corresponding water-soluble amine salts. Partial acidification could control the multiplicity of the reactive sites for the ionic exchanging intercalation with clay. By adjusting the HCl/amine equivalent ratios, the intercalated clays were analyzed by XRD and TGA, with results summarized in Table 1.

The intercalation of Mica by the polyamines resulted the silicates of various XRD d spacing

(15.2–60.0 Å). Ionic exchange reaction under the condition of 1/1/1 molar ratio of polyamine/ H^+ /CEC, the silicate with a low 15.2 Å d spacing and 30 wt% organic fraction (TGA) was obtained. With increasing the acidification to the polyamine at the polyamine/ H^+ /CEC ratio of 1/2/1, the intercalation afforded a hybrid of 38.9 Å d spacing and an organic fraction of 58 wt%. A further increase in HCl equiv to 1/3/1 ratio could only shrink the spacing at 32.8 Å and *ca.* 50 wt% organic embedment. However, by maintaining the acidification ratio at polyamine/ H^+ = 1/2 but decreasing the Mica amount (i.e., polyamine/ H^+ /CEC at 1/2/0.5), the resultant hybrid had a further enlargement of d spacing at 60.0 Å and organic fraction of 68 wt%. For such a high platelet distance in the layered structure, it was noticed that their XRD peak patterns did obey the Bragg's equation ($n\lambda = 2d\sin\theta$), with the observed peaks to be $n = 2, 3$, and 4. However, the $n = 1$ peak was out of the detection limit in the wide-angle XRD measurement. On the basis of the Bragg's assignment, the assumption of the starting peak in a series of peak pattern was made to be an arbitrary n number. According to the corresponding n series and its $\sin\theta$, the correct peak pattern should follow the Bragg's equation to have a constant d value. In the example of Fig. 1, the assignment of the first peak to be $n = 2$, the following peaks $n = 3$ and 4 fitted well for the Bragg's equation to have the same d spacing (60.0 Å).

Table 1
Intercalation of Mica and MMT by polyamines of various multiple ionic sites

Intercalating agent	Polyamine/H ⁺ /CEC ^a (molar ratio)	d spacing (Å) ^b		Organics/Silicates (w/w) ^c	
		Mica	MMT	Mica	MMT
Polyamine	1/1/1	15.2	18.8	30/70	32/68
	1/2/1	38.9	38.2	58/42	58/42
	1/3/1	32.8	33.3	50/50	52/48
	2/4/1	60.0	Featureless	68/32	68/32
	3/6/1	Featureless	Featureless	76/24	76/24
None	–	12.6	12.4	–	–

^a Addition of HCl to polyamine; calculated on the basis of the titrated total-amine contents.

^b X-ray *d* spacing calculated on the basis of the Bragg's equation ($n\lambda = 2d \sin \theta$).

^c Measured by TGA from 100 to 850 °C at the rate of 10 °C/min in air.

Fig. 1. X-ray diffraction patterns of (a) polyamines/Mica and (b) polyamines/MMT with various polyamines/H⁺ ratios.

Furthermore, it is noted that the appearance of multiple peaks of Bragg's pattern implies that the organic intercalation is in high regularity for expanding the basal distance between each pair of the neighboring platelets.

It was observed that the polyamine intercalation could further increase the platelet distance to the extent of featureless XRD pattern (none of peaks) implying a possible exfoliation of the layered structure. This was occurred when using the excess amount of polyamine salts or the molar ratio of polyamine/H⁺/CEC = 3/6/1. Apparently, the polyamine was effective for the clay randomization. In order to generalize the effectiveness of the polyamine as an exfoliating agent, another clay (Na⁺-

MMT) was subjected to the ionic exchange reaction. Initially, it was found to have *d* spacing from 18.8 Å, 38.2 Å, and 33.3 Å at various polyamine/H⁺/CEC ratios of 1/1/1, 1/2/1, and 1/3/1. A featureless XRD pattern was observed at 2/4/1 ratio, under which condition the Mica intercalation yielded 60.0 Å *d* spacing. It appears that the designed polyamine is actually effective for both MMT and Mica clays for the exfoliation.

3.3. Mechanism for the exfoliation

Through the $\text{--NH}_3^+/\text{Na}^+$ exchange reaction, the polyamine salts may incorporate and tether onto the silicate platelet surface at multiple sites in the

silicate confinement. With varied acidification ratios, the polyamine salts may possess different conformations or molecular shapes within the inter-layer gallery. As illustrated in Fig. 2, the conceptual diagrams show the different distances between two neighboring silicate platelets generated by the same polyamines but with different HCl additions and the amount to CEC equiv; d spacing of 15.2 Å at 1/1/1 of polyamine/H⁺/CEC (Fig. 2a), 38.9 Å at 1/2/1 (Fig. 2b), 60.0 Å at 2/4/1 (Fig. 2c), and featureless at 3/6/1 (Fig. 2d). Furthermore, the trend of d spacing expansion is correlated to the amount of organic accumulation in the confinement, analyzed by TGA. The driving forces for the organic embedment may involve two types of bonding forces, ionic bridging of amine salts with platelet surface and self-aggregation of the hydrophobic polyamine backbones to generate a new phase through intermolecular non-covalent bonding. Ultimately, the

phase segregation of the intercalating organics overcomes the ionic attraction originally existed between the neighboring silicate platelets.

3.4. TEM evidence for the clay exfoliation

The exfoliation of the Mica by the polyamines is further evidenced by the TEM observation. Under the condition of polyamine/H⁺/CEC = 3/6/1, the hybrid exhibits a featureless XRD pattern, indicating a d spacing larger than 100 Å or beyond the detection limit. In the TEM micrographs (Fig. 3a and b), most of platelets appear to be well-dispersed and in a random distribution. There are few locations where existed 1–3 platelets in the manner of parallel alignment. By comparison, an intercalation of polyamine/H⁺/CEC = 2/4/1 and 60.0 Å d spacing exhibits the hybrid with their interlayer spacing in a highly regular or parallel structure (Fig. 3c and

Fig. 2. Conceptual illustration of polyamine intercalation and exfoliation of the silicate platelets (Mica), varied by using different molar ratios of polyamines/H⁺/CEC, at (a) 1/1/1 (XRD d spacing = 15.2 Å), (b) 1/2/1 (38.9 Å), (c) 2/4/1 (60.0 Å), and (d) 3/6/1 (XRD featureless or >100 Å).

Fig. 3. TEM micrographs of (a and b) exfoliated silicates (Mica) from polyamine/ H^+ /CEC = 3/6/1, with featureless XRD, (c and d) intercalated silicates by polyamine/ H^+ /CEC = 2/4/1, with XRD d spacing = 60.0 Å.

d). A rough estimation of 8–12 parallel platelets in a stack can be observed, with a distance between the neighboring platelets similar to the XRD measurement (60.0 Å). However, the length of these silicate stacks, in some cases, is extended into 1–2 μm which is longer than the primary structure as observed to be 300–1000 nm in Fig. 3a and 300–400 nm in Fig. 3b. The morphology is explained by the formation of a secondary structure from the primary stacks.

3.5. Properties of epoxy nanocomposites

The nanocomposites were prepared by mixing the polyamine modified Mica or MMT with the two-component system of epoxy resin/T403 amine. As summarized in Table 2, the properties of thermal decompositions of the epoxy nanocomposites were analyzed by thermal gravimetric analysis (TGA). With a 1 wt% loading of the polyamine/clay hybrids, the resultant materials exhibited a slow decomposition rate or delayed degradation temperature. For the measurement of the initial 5 wt% weight loss ($T_{5\text{wt}\%}$), the TGA trace indicated an

Table 2

Thermal and physical properties of polyamine modified clays cured with the epoxy resin and T403 curing agent into nanocomposites

Silicate platelets	Loading (wt%) ^a	$T_{5\text{wt}\%}$ (°C) ^b	T_g (°C) ^c	Hardness (H) ^d
None	0	337	71	2
Exfoliated Mica	0.5	344	81	6
	0.7	347	80	7
	1	355	78	7
	0.5	342	76	5
Exfoliated MMT	0.7	346	76	6
	1	348	75	6

^a Calculated on the basis of silicate weight.

^b $T_{5\text{wt}\%}$: temperature of weight loss at 5 wt%, measured by TGA from 100 to 850 °C at 10 °C/min in air.

^c Based on DSC measurements.

^d Pencil test.

increase from 337 to 355 °C for the Mica and from 337 to 348 °C for the MMT additions. The presence of silicate hybrids slightly enhanced the thermal stability of these epoxy nanocomposites. On the basis of DSC measurements, the epoxies exhibited a higher glass transition temperature (81 °C for Mica and 76 °C for MMT) than that of the pristine epoxy

Fig. 4. TEM micrographs of 1 wt% exfoliated platelets in epoxies, (a) exfoliated Mica in epoxies; (b) exfoliated MMT in epoxies, at different magnifications.

(71 °C). Apparently, the T_g was slightly affected by the initial 0.5 wt% loading but leveled off for the higher loadings. The most significant contribution for the platelet addition is the material hardness enhancement. By loading only 1 wt% of silicate platelets, the epoxy nanocomposites showed an increase of hardness from 2 H to 7 H for Mica and to 6 H for MMT. The enhancement is presumably affected by the intensive interaction between platelets and epoxies in the matrix.

3.6. TEM observation of the exfoliated clays in epoxies

The fine distribution of the exfoliated platelet in the epoxy matrix was evidenced by the TEM observation. In Fig. 4a and b, the homogeneous distribution of 1 wt% clay platelet in the amine-cured epoxy matrix loading is demonstrated. It is interestingly noted that, in Fig. 4a (Mica), the distribution of silicate platelets is actually in a parallel orientation rather than in a random single-platelet manner. By comparison, in the case of Fig. 4b (MMT), most of platelets are in a well-dispersed and random manner. It appears that the large platelets of Mica have a tendency for forming lamellar arrangements.

4. Conclusion

Layered silicates including the synthetic fluorinated mica and sodium montmorillonite were possibly exfoliated by using a synthesized polyamine with the controlled multiplicity of $-NH_3^+$ sites. The requisite polyamine was simply prepared from the Jeffamine T403/DGEBA coupling at a specific molar ratio. Their partially acidified polyamine salts

enabled to ionic exchange and randomize the clay layered structures, evidenced by XRD and TEM. The result of randomization was attributed to the presence of the multiple ionic sites tethering onto the silicate platelets and twisting their conformation in the clay confinement. The exfoliated Mica and MMT platelets were blended into epoxies to form nanocomposites with significant improvements in physical properties, particularly the hardness.

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