

Research Note

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Fine Dispersion of Hydrophobic Silicate Platelets in Anhydride-Cured Epoxy Nanocomposites

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Hydrophilic silicate platelets, prepared from the two-step process of exfoliation and extractive isolation of layered silicate clays, were allowed to react with an alkyl anhydride and convert into organic-platelet hybrids of hydrophobic property. The exfoliative process was developed previously to isolate the silicate platelets of different sizes, including the platelets from the naturally occurring montmorillonite and synthetic fluorinated mica. The introduction of the hydrophobic organics through ionic exchanging with the sodium ions on the platelet surface ($\equiv\text{SiO}^-\text{Na}^+$) was critical for rendering the silicate platelet in powder form and compatible with epoxy resin in curing into nanocomposites. The ultimate fine-dispersion of the hydrophobic platelets in epoxy matrices was observed by using transmission electron microscopy (TEM) and rendered the epoxies advanced high transparency, hardness, and particularly low coefficient of thermal expansion (CTE). The sustainable physical performance is suitable for the specific electronic applications such as encapsulation for light-emitting-diode devices.

Introduction

Recent research on the polymer/layered silicate nanocomposites has been actively pursued by introducing various intercalated^{1,2} and exfoliated^{3,4} organoclays into hydrophobic polymers. A number of disclosures have demonstrated the advanced properties of mixing smectite clays to the polymer matrices, such as in epoxy,⁵ nylon,⁶ polyamide,⁷ polyimide,⁸ and polyurethanes.⁹ In most cases, the layered silicate clays are required to be exfoliated into randomized platelets and finely dispersed in the organic polymers and consequently achieve high performances such as gas barrier,^{10,11} thermal stability,^{12,13} and mechanical strength.^{14,15}

The commonly utilized smectite clays such as the naturally occurring montmorillonite (MMT) and synthetic fluorinated mica consist of layered silicate platelets bound with ionic charges in primary stacks.^{16,17} The dimensions of platelets are polydispersed, ranging from approximately 80–100 nm for the natural Na^+ -MMT to 300–1000 nm for the synthetic mica.^{18–20} Because of the presence of ionic charges, these clays are hydrophilic and modifiable with organic quaternary salts through ionic-exchange reaction.^{21,22} After swelling in water, the cationic metal counterions in the silicate galleries may be replaced by the cationic surfactants. As a result, the organic intercalation generally widens the interlayer spacing and alters the dispersing properties from hydrophilic to hydrophobic. When mixing with hydrophobic polymers, nanocomposites could be prepared with the layered clays being randomized and homogeneously dispersed in polymer matrices. Exfoliation of the layered clays into random platelets is essential for improving the physical properties of the nanocomposites. However, in the process of blending with polymer substrates, the exfoliation and fine dispersion of layered clays may not be easily achieved.

Previously, we have demonstrated an exfoliative process that allows the randomization of the smectite layered structure by using polyamine quaternary salts and subsequent isolation of the randomized platelets in water suspension.^{19,23,24} During the process, the ionic charges of the neighboring platelets were redistributed or exposed easily with water or polar organics. Our previous studies had shown that the randomized platelets can be homogeneously mixed with the polar curing agent and improve epoxy property.²⁵ When blended with hydrophilic amine curing agent (Jeffamine T403) and cured with epoxy resin, the resulting polymer was found to have a significant improvement in hardness. However, the hydrophilic and ionically charged silicate platelets may not be compatible with the hydrophobic curing systems,^{26–29} such as phenol- and anhydride-types. These epoxy systems are important for the applications of printed wiring board (PWB), epoxy molding compounds (EMCs), and light-emitting-diodes encapsulation.

To demonstrate the possible mixing of the randomized platelets in a hydrophobic curing system, we selected the two-component system, anhydride curing agent in combination with an aliphatic epoxy resin, which is known for the transparency and suitability for the light-emitting diode (LED) encapsulation. We report here the process of converting the silicate platelets in water suspension into hydrophobic powder by reacting with the anhydride and subsequently curing with the epoxy resin. The property performances such as coefficient of thermal expansion (CTE), hardness, and transparency were characterized and correlated with the fine dispersion of platelets as observed by using transmission electron microscopy (TEM).

Experimental Section

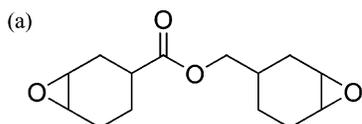
Materials. Sodium montmorillonite (Na^+ -MMT), with a cationic exchange capacity (CEC) of 115 mequiv/100 g, was obtained from Nanocor Co. The synthetic fluorinated mica (Mica, trade name as SOMASIF ME-100) having a cationic exchange capacity of 120 mequiv/100 g was obtained from CO-OP Chemical Co., Japan. The silicate platelets are polydispersed

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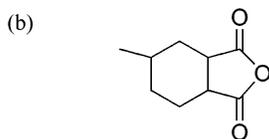
[†] National Taiwan University.

[‡] National Chung Hsing University.

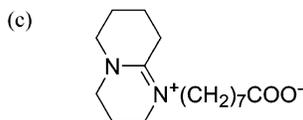
[§] Chinese Petroleum Corp.



3,4-epoxycyclohexylmethyl-3',4'-epoxycyclohexanecarboxylate (4221)



hexahydrophthalic anhydride (MHHPA)



1,8-diazabicyclo(5,4,0)-undecene-7 (DBU) octanoic acid salt (SA102)

Figure 1. Chemical structures of (a) 3,4-epoxycyclohexylmethyl-3',4'-epoxycyclohexanecarboxylate (4221), (b) hexahydrophthalic anhydride (MHHPA), and (c) 1,8-diazabicyclo(5,4,0)-undecene-7 (DBU) octanoic acid salt (SA102).

in their dimensions, estimated to be approximately 80–100 nm for Na^+ -MMT and 300–1000 nm for mica in an irregular shape. The aliphatic epoxy resin, 3,4-epoxycyclohexylmethyl-3',4'-epoxycyclohexanecarboxylate (Union Carbide ERL-4221 and abbreviated as 4221) with an epoxide equivalent weight (EEW) of 137, was purchased from Aldrich Chemical Co. The anhydride-type curing agent, methyl hexahydrophthalic anhydride (MHHPA) with an equivalent weight of 168, was purchased from Huntsman Chemical Co. The catalyst, 1,8-diazabicyclo-(5,4,0)-undecene-7-octanoic acid salt (code U-CAT SA102 and abbreviated as SA102), was purchased from San Apro Co. (Japan). These chemical structures of epoxy resin, curing agent, and catalyst are illustrated in Figure 1.

Preparation of Nanosilicate Platelets (NSP) Suspension in Water. Direct exfoliation of montmorillonite for preparing the random NSP platelets with the Mannich polyamine salts has been reported previously.^{19,24} The exfoliated platelets were isolated by using a two-phase extraction process from toluene/aqueous NaOH (10 wt %): suspension in methanol at 60 °C and extraction by agitating the slurry with water/toluene. After allowing the solution to settle, it separated into two layers. The upper layer containing mostly toluene and organics was removed. The bottom water phase contained the silicate suspension. The extraction process afforded silicate platelets in water (~10 wt %) and was characterized by X-ray powder diffraction (XRD), thermogravimetric analysis (TGA), TEM, atomic force microscopy (AFM), and pH analyses. The isolated silicate platelets are polydispersed in dimension and estimated at 80–100 nm in width dimension and 1 nm in thickness.

Preparation of Nanomica Platelets (NMP) Suspension in Water. By using similar experimental procedures as described for NSP preparation, the exfoliation of synthetic fluorinated mica to NMP by the hyperbranched polyamine salts³⁰ was performed. The nanomica platelets were dispersible in water (~10 wt %) and characterized by XRD, TGA, TEM, AFM, and pH analyses. The mica platelets are estimated to be 300–1000 nm in dimension and 1 nm in thickness.

Conversion of NSP or NMP Slurry in Water into MHHPA Anhydride Powders as Curing Agent. The typical process for converting the silicate/water suspension into a powder form of

hydrophobic platelets is described below. The water slurry of 10 wt % NSP (or 10 wt % NMP) in water suspension (20 g, CEC = 115 mequiv/100 g for NSP and 120 mequiv/100 g for NMP) was added with MHHPA (10 g, 59.5 mmol) in a round-bottomed flask, equipped with a magnetic stirrer. The gelled products were collected and subjected to an oven under a reduced pressure for 12 h at 80 °C and a freeze dryer for 48 h at -40 °C until dry. The powdered form of platelets, the silicate platelet/MHHPA hybrid, consists of 90 wt % of organics and 10 wt % of silicates (characterized by TGA) and was further characterized by using XRD analyses as shown in the Supporting Information Figure S1.

Preparation of NSP- or NMP-Epoxy Nanocomposites. The powdered form of the platelet/MHHPA hybrid with different amounts (0.01, 0.03, 0.05, and 0.07 g, platelet/MHHPA hybrids at the composition of 1/9 weight ratio) was mixed well and ground with the designated amount of MHHPA curing agent (5.51 g, 32.8 mmol) and epoxy resin 4221 (4.49 g, 16.38 mmol), at an equal equivalent ratio of epoxide/anhydride and added catalyst (SA102) of 0.5 phr (parts per hundred parts of resin). The mixtures were thoroughly stirred, degassed, and poured into a 1/8 in. thick flat aluminum mold to form a sample plaque or spin-coated on a copper surface to form a film. The curing samples were placed in an oven, and the temperature was programmed at 80 °C for 1 h and 150 °C for 2 h. The prepared epoxies were further characterized by using XRD analyses as shown in the Supporting Information Figure S2.

Characterization and Instruments. The X-ray powder diffraction (XRD) was performed on a Shimadzu 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 Bragg's equation ($n\lambda = 2d \sin\theta$). Thermogravimetric analysis (TGA) was measured by using a Perkin-Elmer Pyris 1 model at a heating rate of 10 °C/min from 100 to 850 °C under air flow. Thermal mechanical analysis (TMA), performed on a DuPont Instrument-TMA2940 at a heating rate of 10 °C/min under N_2 , was used to identify the coefficient of thermal expansion (CTE). Pencil hardness was measured according to the method of ASTM D 3363-74. Ultraviolet-visible (UV-vis) spectra measured a film thickness of 100 μm on a Perkin-Elmer Lambda 20 UV-vis spectrophotometer. Transmission electronic microscopy (TEM) was performed on a Zeiss EM 902 A at an acceleration voltage of 80 kV, and the sample 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 ~80 nm, 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.

Results and Discussion

Conversion of Hydrophilic NSP and NMP into Hydrophobic Powder. The nanosilicate platelets (NSP) and nanomica platelets (NMP), prepared from the exfoliation of sodium montmorillonite and synthetic fluorinated mica, respectively, are hydrophilic and dispersible in water owing to the presence of sodium ions ($\equiv\text{SiO}^-\text{Na}^+$) on the platelet surface. The inorganic silicate platelets are characterized as thin-platelet shape with a thickness of 1 nm, but in different width dimensions, approximately 80–100 nm for NSP and 300–1000 nm for NMP.^{18–20} The silicate platelets were modified to become hydrophobic in nature by reacting with organic alkyl anhydride through the ionic complexing with the $\equiv\text{SiO}^-\text{Na}^+$ functionalities

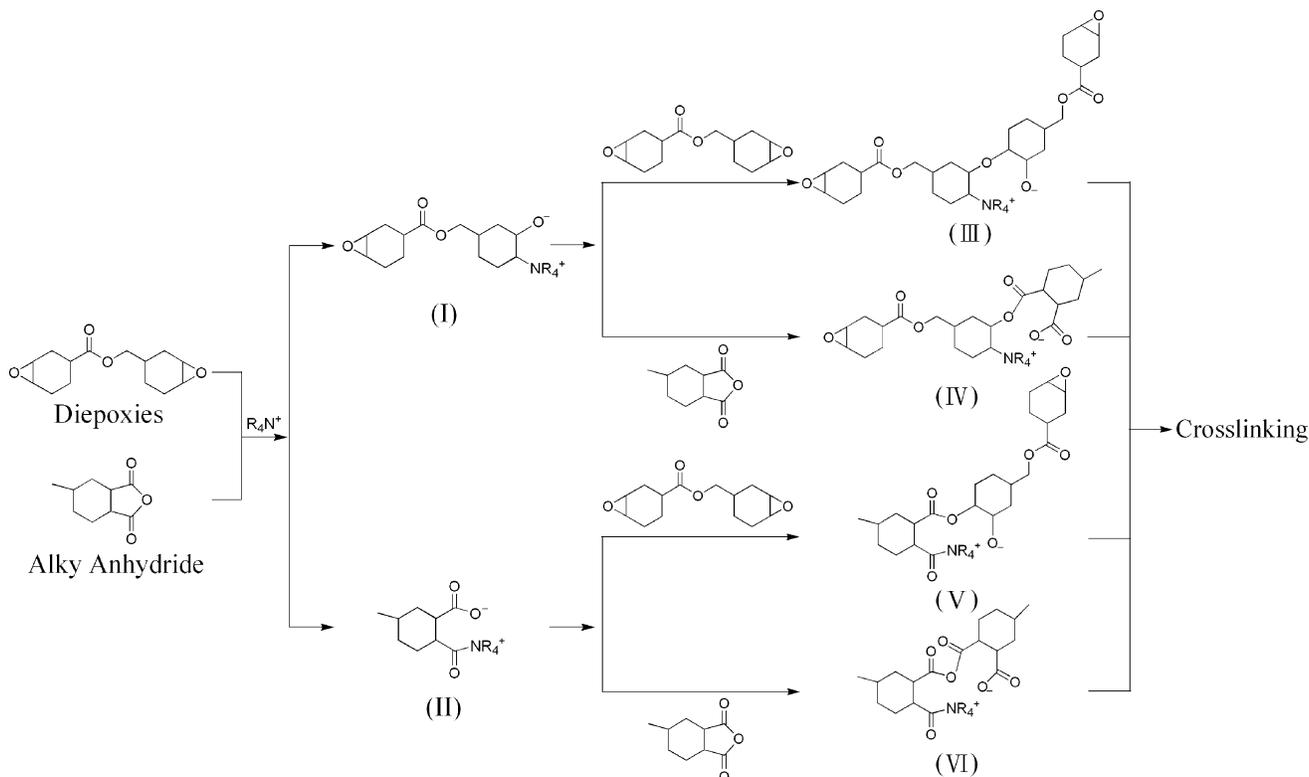
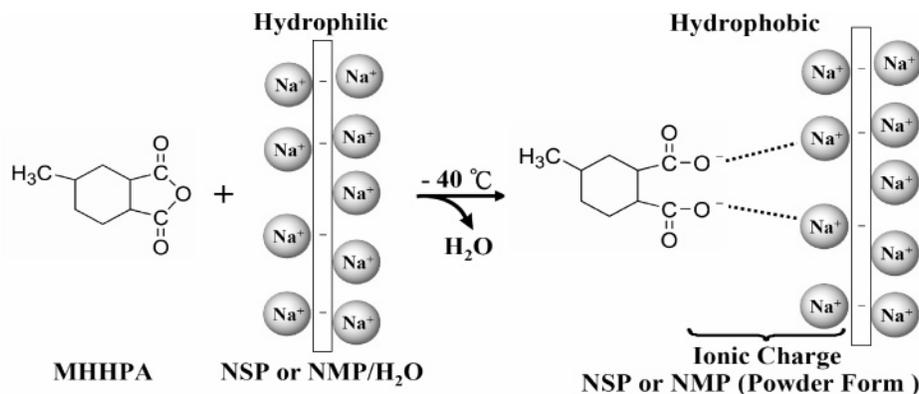


Figure 2. Curing mechanism of anhydride and aliphatic epoxy resin with amine salts as the catalyst.

Scheme 1. Conceptual Illustrations of Converting Ionic Silicate Platelet into Hydrophobic Powder by Complexing with Alkyl Anhydride



on the platelet. The alkyl anhydride (methyl hexahydrophthalic anhydride or MHHPA) was chosen because of its high latent curing ability with epoxy resin in the two-component epoxy system. The anhydride underwent a ring-opening reaction in water to form the carboxylate and subsequent association with the sodium counterions on the hydrophilic silicates, as conceptually described in Scheme 1. Experimentally, during the mixing of the anhydride with NSP or NMP in water suspension, a gelled product was obtained. The gel was subjected to a freeze-drying process to afford the powder form of the platelet/MHHPA hybrids with the composition of 1/9 weight ratio. The hybrids of powder form were found to disperse well in organic solvents and epoxy resin. The conversion from the hydrophilic platelets to the hydrophobic powder is essential for the epoxy compatibility.

Curing Reaction of Anhydride and Epoxy Resin. The use of alkyl anhydride as the epoxy curing agent was well-documented in the literature.^{31–33} However, the detailed mechanism involving the reaction of the anhydride-epoxy curing process was rather complicated.^{33–35} It generally required the

Table 1. Properties of Anhydride-Cured Aliphatic Epoxy Nanocomposites with Silicate Platelets

silicate platelets	loading ^a (wt %)	CTE ^b ($\mu\text{m}/(\text{m } ^\circ\text{C})$)	hardness ^c (H)	transparency ^d (%)
none	0	82	4	85
NSP	0.1	78	4	84
	0.3	65	5	81
	0.5	37	7	77
	0.7	34	7	72
NMP	0.1	71	4	84
	0.3	56	6	83
	0.5	36	8	80
	0.7	30	8	77

^a Calculated on the basis of silicates. ^b CTE = coefficient of thermal expansion, determined by TMA. ^c Pencil test. ^d Determined by using a UV–vis absorption method at 550 nm/T %.

amine salt as the catalyst to initiate the ring-opening reaction of either epoxide or anhydride reactive groups. The amine salts in catalytic amount could first react with epoxide or anhydride to afford the corresponding alkoxide (I) or acid salt (II), respectively. Both intermediates, RO^- and $RCOO^-$, are highly

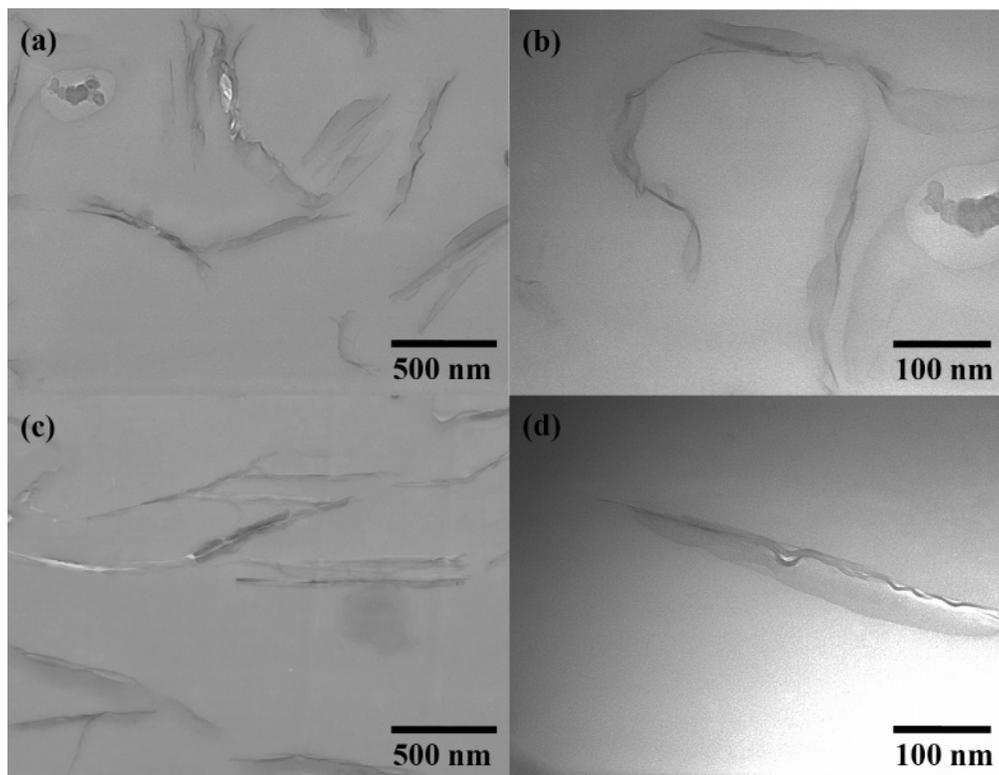


Figure 3. TEM micrographs of platelets in epoxies: (a and b) for NSP (0.5 wt %) and (c and d) for NMP (0.5 wt %) at different magnifications.

reactive for the subsequent ring-opening polymerization. According to the reaction scheme described in Figure 2, there are two routes for the propagation. The intermediate (I) may react with either anhydride or epoxide to form (III) and (IV), while the intermediate (II) will generate (V) and (VI). In the intermediates (III) and (V), the propagation proceeds with the formation of ether ($-C-O-C-$) linkages, while the ester ($-CO-O-$) linkages are formed via the (IV) and (VI) reactions. With the presence of diepoxides, the cross-linking may occur during the polymerization.

Preparation and Properties of Silicate Platelet–Epoxy Nanocomposites with the Addition of Platelet/MHHPA Hybrid. The selected epoxy system for preparing the silicate nanocomposites is comprised of two resin components, aliphatic diepoxide and anhydride curing agent at 1/2 molar ratio of epoxy/anhydride, and the catalyst (SA102) at the concentration of 0.5 phr. During the blending process, the silicates platelet/anhydride MHHPA powder was mixed with the anhydride curing agent first and then the epoxy resin. The loadings of silicate platelets were 0, 0.1, 0.3, 0.5, and 0.7 wt %. As summarized in Table 1, by adding 0.5 wt % of nanosilicates, the coefficient of thermal expansion (CTE) was significantly lowered from 82 to 37 $\mu\text{m}/(\text{m } ^\circ\text{C})$ for NSP and from 82 to 36 $(\mu\text{m}/\text{m } ^\circ\text{C})$ for NMP. This CTE decrease is leveled off at 0.5–0.7 wt %. The decrease in CTE implies the intensive interaction between the platelet surface with the polymer network, hindering the motion of network junctions. For a similar reason, the hardness was significantly enhanced from 4 to 7 H for NSP and from 4 to 8 H for NMP by adding only 0.5 wt % of platelets. The nanocomposites were also characterized by using an optical UV–vis spectroscopy. The material transparency was compared by determining the absorbance at 550 nm, with the result of dropping from the measurement of 85% to 77% for NSP addition and from 85% to 80% for NMP addition. The

transparency of 90% was maintained, indicating a fine dispersion of the platelets in the matrices without a serious light interference.

Fine Dispersion of Silicate Platelet NSP or NMP in Epoxies by TEM Observation. The material properties of CTE lowering and hardness enhancement, while maintaining the transparency, were attributed to the fine dispersion of randomized silicate platelets in hydrophobic epoxy matrix. The TEM micrographs in Figure 3 exhibit the morphologies of the exfoliated clay platelets at 0.5 wt % in the epoxies. At different magnifications, the distribution of platelets and the detailed shape of individual platelet, particularly the side-view pictures, are visualized. The homogeneity of individual platelet distribution in the anhydride-cured aliphatic epoxy matrix is shown in parts a and b of Figure 3 for NSP and parts c and d of Figure 3 for NMP. It is noteworthy that the platelets tend to form a lamellar structure and further stack into lengthy bilayer morphology, self-arranging from one lamella over another. From the side view, the lamellar orientation has extended to a length of 200–500 nm for NSP and to 300–1000 nm for NMP. The unique array of the platelet lamellae may be caused by the intensive ionic attraction to each other. Interestingly, it was noted that the homogeneity of the silicate platelet distribution in a lamellar manner is correlated well with the physical performance of the nanocomposite.

Conclusion

The hydrophilic silicate platelets were allowed to convert into hydrophobic powder form by reacting with an anhydride and were cured into a two-component epoxy system with anhydride curing agent and aliphatic epoxy resin. With high compatibility, the randomized platelets were homogeneously distributed in the epoxies and rendered the improved properties such as hardness increase from 4 to 8 and CTE decrease from 82 to 36 $\mu\text{m}/(\text{m } ^\circ\text{C})$ while maintaining the required transparency. Furthermore, the

morphology of the platelets arranged in a lamellar shape and well-distributed in epoxy matrix was observed by the TEM micrographs.

Acknowledgment

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Supporting Information Available: XRD analyses of the powder form of the silicate platelet/MHHPA hybrid and the epoxy nanocomposites with silicate platelets are included in the Supporting Information. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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