

Preparation and Properties of Polyacrylate/Clay Photocured Nanocomposite Materials

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A functionalized surfactant, GME-N-C₁₀ containing a C=C double bond, was synthesized to modify clays such as montmorillonite (MMT) and mica for the preparation of organic–inorganic composite resins via radical photoinduced polymerization. As revealed by X-ray diffraction (XRD) analysis of the organophilic samples, the synthesized surfactant was successfully intercalated into the layers of clay by its full molecular length and such an intercalation generated a paraffin-like structure in the modified clays. By forming the C–C bonds between surfactants and oligomers/monomers during subsequent radical photoinduced polymerization, the hybrid comprising organophilic clay/oligomers/monomers became an intercalated nanocomposite resin. The thickness of the dispersed lamellae was less than 100 nm, as revealed by transmission electron microscopy (TEM). For the composite sample containing 5.0 wt.% of organophilic clay, the decomposition temperatures raised at least 15 °C; the transmittance detected by UV–visible spectrometer showed a less than 15% loss in the visible light region but a satisfactory transparency was still retained, and the degree of moisture absorption decreased from 3.4% to about 1% due to dispersive organophilic clay in the polymer matrix.

Introduction

Nanocomposites are a new class of materials that may form by the hybridization of organic polymer and inorganic compounds as oxides, clays, etc. at a nanometer scale. In the past decade, utilization of inorganic nanoparticles as additives to enhance performance of polymeric materials has been widely reported,^{1–10} and related studies have attracted considerable attention from both theoretical and application points of view.^{4,11,12} Owing to the unique interfacial properties and phase morphology in the nanometer scale, the nanocomposites exhibit improved physical and chemical properties such as better mechanical and thermal properties,^{1,12–14} lower gas permeability,^{15,16} and higher fire retardation

capability.¹⁷ For instance, nylon-6 nanocomposite containing 4 wt.% of montmorillonite (MMT)^{1,13} possesses superior mechanical and thermal properties compared with additive-free nylon-6.¹⁶ Polymer comprising 7.5 vol % of the exfoliated 1-nm-thick silicate layers yielded a 10-fold increment on the mechanical strength.¹⁴ An exfoliated polymer–clay nanocomposite might lag the moisture diffusion inside so as to achieve the low permeation property.² In contrast to the former cases, kaolin, a nonswelling clay, had also been used to prepare nylon-6 composites but the enhancement in mechanical and thermal properties was limited due to the lack of nanometer-scale dispersion.^{18,19} Apparently, the dispersion morphology is the primary cause affecting the performance of nanocomposites.

The concept of nanocomposite has been successfully applied to various organics such as polyimide,^{1–2,5} epoxy,^{6,15} polysiloxane,¹⁰ polystyrene,²⁰ and polyacrylate,^{21–24} etc., and most of them were thermally cured, e.g., the nanocomposites

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based on polystyrene via radical thermal-cured polymerization.²⁰ With the advanced development of high quantum yield free radical photoinitiators, photocurable nanocomposites have become an attractive research topic due to their versatile applications.^{25–30} For instance, the preparation and characterization of organoclay–acrylic nanocomposite resins,²⁵ polyurethane–acrylate/silicate platelets nanocomposite,²⁶ and polymer films containing commercially available modified MMT²⁷ via photopolymerization have been reported by various research groups. Packaging of organic luminescence devices (OLEDs) requires sealing adhesives with low curing temperature, short curing time, and good moisture/oxygen barrier properties. Photocurable nanocomposite resin thus becomes a promising material for such an application.

In this article, we report the synthesis of the λ -shaped surfactant, preparation of photocured nanocomposite resins comprising well-intercalated polyacrylate–clays by interfacial chemical reactions via photopolymerization between surfactants/monomers or surfactants/oligomers and their property characterization. With the functional C=C groups and unusual geometry, this particular surfactant might effectively extend the lamellar spacing of clays and further provide fine dispersion of clays in polymer matrix.

Experimental Section

Materials. MMT powder (code PK802, provided by Pai Kong Ceramic Material Co.) with cationic exchange capacity (CEC) = 95 mEq/100 g, and mica powder with CEC = 60 mEq/100 g (termed Mica60 in this work) were adopted as the inorganic components of composite resins. Bisphenol A epoxy diacrylate (viscosity = 27.1 M mPa·s at 25 °C), glycidyl methacrylate ester, and dipentaerythritol pentaacrylate were purchased from Sartomer Co. The radical polymerization initiator, 1-hydroxycyclohexylphenyl ketone, was obtained from Chembridge International Co. Didecylamine, 3-(trimethoxysilyl)propyl methacrylate, and 2,3,4,5,6-pentafluorostyrene were purchased from Aldrich Chemical Co. The synthesized surfactant, GME-N-C₁₀, was prepared by the reaction of glycidyl methacrylate ester and didecylamine (molar ratio 1:1) in ethanol at 60 °C for 48 h. The product was distilled in a vacuum rotator at $T > 80$ °C to remove the ethanol completely, and its molecular structure was characterized by FTIR and ¹H NMR spectroscopy.

Cationic Exchanged Clays. Organophilic MMT and mica were prepared by cationic exchange in clay galleries in aqueous solution. Before cationic exchange, all clays were dried at 80 °C for 24 h to remove absorbed moisture. The GME-N-C₁₀ was first acidified by hydrochloric acid (HCl). The MMT and Mica60 were respectively added in 300 mL of distilled water and stirred for several hours to form a suspending solution. The acidified GME-N-C₁₀ was added

into the aqueous solutions containing clays in constant proportion and the mixture was stirred for 72–96 h to complete the cationic exchange. The cationic exchange clays were also extracted from above mixtures by a centrifuge. They were dried in a vacuum oven at 80 °C for at least 24 h to remove the residual solvent and then sent to an X-ray diffractometer for structure characterization.

Synthesis of Radical Photoinduced Polymerization Polymer–Clay Nanocomposites. The functional monomers, 15.0 wt.% dipentaerythritol pentaacrylate and 10.0 wt.% 2,3,4,5,6-pentafluorostyrene, were added in bisphenol A epoxy diacrylate. After complete mixing, 5.0 wt.% 3-(trimethoxysilyl)propyl methacrylate was next added and then stirred for 90 min to finish the preparation of pre-polymer. The desired amount of surfactant-modified clay was first swollen in ethanol by ultrasonic vibrator then the mixture was added into the pre-polymer. After stirring vigorously for 24 h to achieve the complete dispersion, previously added ethanol was removed as completely as possible by heating at 90 °C for more than 12 h. Finally, 5.0 wt.% of radical photoinitiators, based on the weight of oligomer, and the above mixture were sealed in amber sample vials and stirred in N₂ ambient at 40 °C for 90 min to prevent unexpected reaction.

Subsequent radical photopolymerization was carried out at room temperature. The pre-polymer layers of about 110 μ m thick were coated onto the glass substrates. The specimens were cured in an UV oven (CL-1000, UVP) in which the source of UV irradiation comes from an array of five 8-W dual bipin discharge tubes emitting UV light with wavelength ranging from 350 to 400 nm (peak wavelength at about 365–370 nm) to induce the photopolymerization. Total energy of the photopolymerization was about 6 joules/cm². After polymerization, the specimens were further cured at 80 °C for 1 h to complete the polymerization.

Characterization. Molecular structure of GME-N-C₁₀ surfactant was characterized by FTIR and NMR. The ¹H NMR spectrum was provided by Varian UnityInova 500 NMR with CDCl₃ as the sample solution. The FTIR spectra were obtained from a Nicolet Protégé 460 FTIR spectrometer. The X-ray characterization of modified clays and polymer–clay composites were carried out in a Siemens D5000 X-ray diffractometer using Cu K α ($\lambda = 1.5418$ Å) radiation and a scanning rate of 0.02°/sec. Thermogravimetric analysis (TGA) was performed within a DuPont 2950 TGA. The specimens were heated at a rate of 20 °C/min from 30 to 800 °C then an isothermal soak for 10 min in air atmosphere to calibrate the residual weight of clay; meanwhile, another thermal recipe with the heating rate of 10 °C/min from 30 to 800 °C was performed to determine the decomposing temperature (T_d). The TGA data were further transformed into differential thermogravimetry (DTG) curves to identify the bonding interactions between modified clays and polymer matrix. In-plane thermomechanical analysis (TMA) was carried out in a DuPont 2940 TMA at a heating rate of 10 °C/min from 30 to 200 °C to identify the coefficient of thermal expansion (CTE) of the composites. The microstructures of modified clays and polymer–clay composites were observed by using a JEOL 2000FX TEM operating at 200 kV. The transmittance of composite films was characterized by a HP8453 UV–visible spectrometer with scanning wavelength ranging from 190 to 1200 nm.

Results and Discussion

Synthesis and Characterization of GME-N-C₁₀ Surfactant. Surfactants play a very important role for clay exfoliation in polymer. They reduce the energy of the organic/inorganic interface so that various dispersion morphologies may be achieved in the polymer-based composites. Functionalization of surfactants further provides functional

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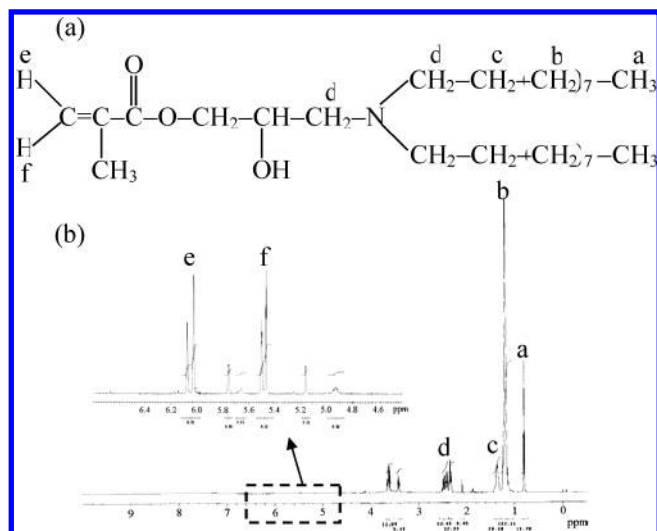


Figure 1. (a) Molecular structure of surfactant GME-N-C₁₀ synthesized in this work; and (b) ¹H NMR spectrum of GME-N-C₁₀ dissolved in CDCl₄.

groups to induce the polymerization. After cationic exchange reaction, the modified clays containing organophilic functionalized surfactants would polymerize with the oligomers and monomers. Moreover, via interacting with the organic material, the modified clays might disperse evenly to form exfoliated polymer-clay nanocomposites. Figure 1 shows the ¹H NMR spectrum of GME-N-C₁₀ synthesized in this work. A comparison of the NMR spectra of synthesized surfactant and its reactants revealed that the proton peaks of methyl (–CH₃) and methylene (–CH₂) among long alkyl chains appear near $\delta = 0.8$ and $\delta = 1.2$ for both specimens. The peaks corresponding to the proton resonance in C=C double bond of GME-N-C₁₀ and its reactants offer another evidential support. In general, identification of proton resonance in C=C double bond could be derived from the calculation of chemical shift related to the substituent constant (*Z*) effect. The calculation based on the *Z* effect for chemical shift of proton resonance in C=C double bond has been reported in the range of $\delta = 5.0$ – 7.0 .³¹ In the ¹H NMR spectra for reactants, there are two peaks between $\delta = 5.5$ to 6.5 : one is very close to $\delta = 5.5$ and the other is near $\delta = 6.0$. Similarly, in the NMR spectrum of GME-N-C₁₀, peak groups *e* and *f*, both comprising two peaks, locate at $\delta = 5.5$ and 6.0 , respectively. This provides evidence that the dodecylamine did react with glycidyl methacrylate ester to form the synthesized surfactants.

Figure 2 shows the FTIR spectrum of GME-N-C₁₀ surfactant. After synthesis, the surfactant was transparent yellow and its viscosity was similar to that of isopropyl alcohol at room temperature from their outward appearances. The ν_{C-H} of normal long alkyl chains bonded with nitrogen appears in the region of 3000 – 2840 cm^{–1}. Absorption of stretching hydroxyl groups generated by the epoxy/amine reaction occurs at the wavenumber of 3500 to 3220 cm^{–1},²⁰ and the other three stretching bands of C=O, C–N, and C=C of methacrylate groups appear near 1760 cm^{–1}, in the region of 1250 to 1020 cm^{–1} and at 1635 cm^{–1}, respectively.

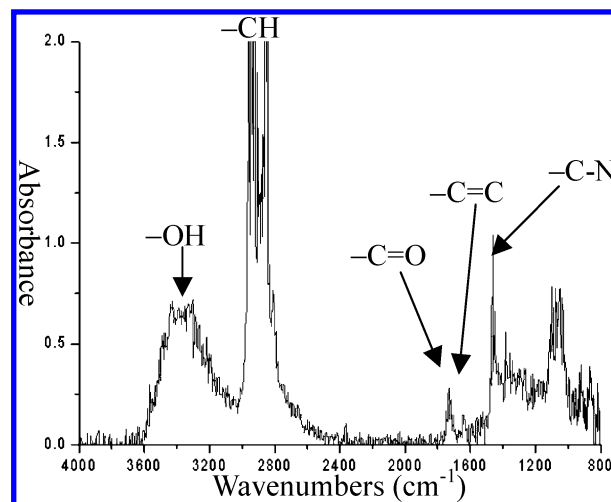


Figure 2. FTIR spectrum of GME-N-C₁₀.

Table 1. TGA Analysis of Clays Before and After Modification

	residual weight (%)		degree of modification ^a (%)
	before	after	
MMT	87.08	57.27	71.36
Mica60	92.70	71.22	81.33

^a Degree of modification was calculated according to following formula: $\{[(\text{residual weight before modification}) - (\text{residual weight after modification})] \div (\text{molar weight of surfactant})\} \times (1000 \div \text{CEC}) \times 100$.

The above NMR and FTIR analyses evidenced that our synthesis reaction did proceed to generate the surfactants with expected structure. We note that the huge absorbance difference between C=C double bonds and hydroxyl groups within surfactants might result from the incomplete removal of ethanol during synthesis.

Cationic Exchange of Clays by Surfactants. The result of TGA analysis for native and modified clays in ambient air is shown in Table 1. As expected, after cationic exchange the acidified surfactants were substituted for the cations in clays and intercalated into the lamellae. Less weight ratio was observed in all the modified clays after thermal decomposition. For instance, residual weight ratio of native MMT decomposed in air is about 87.08%, which is higher than that for modified MMT at about 57.27%. The degree of modification, or the modification ability of surfactants, represents the ratio of the amount of acidified surfactants intercalated into the lamellae during cationic exchange to the maximum amount of acidified surfactants that could be intercalated into the clays according to their CEC value. Our calculation revealed that both modified MMT and Mica60 have relatively high degrees of modification over 70%. Those results evidenced that the synthesized surfactants may effectively increase the *d*-spacing of clay lamellae with inherent steric hindrance.

Figures 3 and 4 depict the XRD patterns of the three types of clays before and after modification. The *d*₀₀₁ spacings calculated based on the XRD data are given in Table 2. The native clays consist of a lamellar structure formed by sharing the edges of two silica tetrahedral sheets of aluminum or magnesium hydroxide.³² In the inserted layers, cations within a few H₂O molecules induce hydrophilicity to the organic

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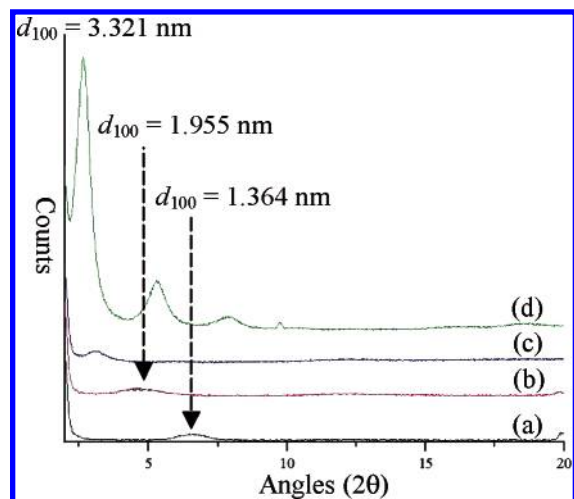


Figure 3. XRD patterns of (a) pristine MMT, (b) commercial clay (CL34), (c) composite resin containing 5.0 wt.% modified MMT, and (d) MMT modified by GME-N-C₁₀ (m-MMT).

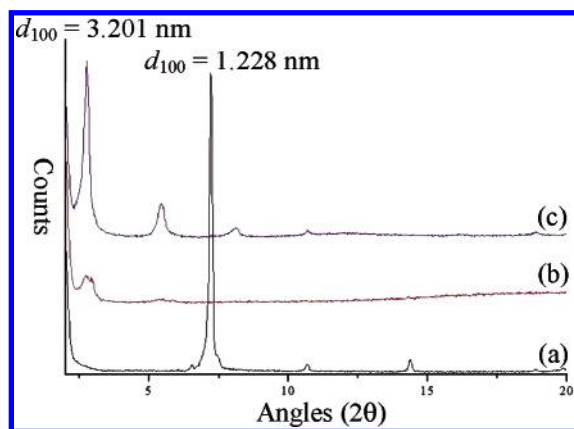


Figure 4. XRD patterns of (a) pristine Mica60, (b) composite containing 5.0 wt.% modified Mica60, and (c) Mica60 modified by GME-N-C₁₀ (m-Mica60).

Table 2. d_{100} Spacing of Modified Clays

	MMT (nm)	Mica60 (nm)
d_{001} calculated from 1st order diffraction peak	3.321	3.201
d_{001} calculated from 2nd order diffraction peak	3.347	3.249
d_{001} calculated from 3rd order diffraction peak	3.383	3.259
average value of d_{001}	3.350	3.236

polymer so that compatibility between them is always an interesting issue. After cationic exchange reaction, the modified clays dispersed in organic media. In Figure 3, the d_{001} spacing of native MMT is equal to 13.64 Å. This value was adopted to evaluate the degree of dispersion induced by the surfactants after cationic exchange reaction. As reported by Kornmann et al.,³³ the higher the value of d_{001} spacing of modified clays, the better the dispersion of clays in the organic polymer. It might also promote the separation of clay lamellae during the polymerization when the surfactant was attached to clays and monomers of polymers. For modified MMT, the (001) peak at $2\theta = 2.66^\circ$ indicated that it possesses a d_{001} spacing equal to 3.321 nm, which is larger than that of native MMT. Furthermore, the XRD peaks of

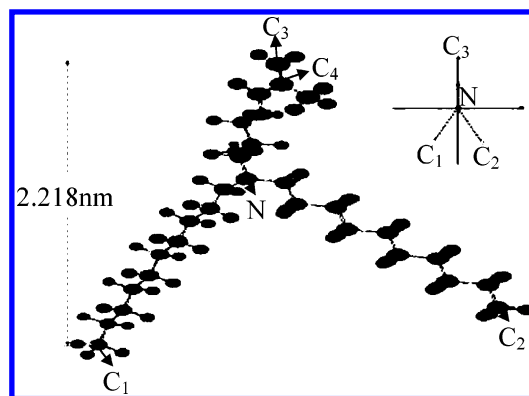


Figure 5. Schematic illustration of simulated GME-N-C₁₀ molecular structure. The sketch on upper-right corner is the planar projection of GME-N-C₁₀ used for further calculation, assuming that the N atom is on the origin in X-Y dimension and each molecular chain is treated as linear, ignoring molecular vibration.

Table 3. Simulated Chain Length of GME-N-C₁₀ Molecule

	distance (nm)
C ₁ -C ₂	1.5478
C ₁ -C ₃	2.0247
C ₂ -C ₃	1.8235
N-C ₁	1.2713
N-C ₂	1.2650
N-C ₃	0.6549

modified MMT show a better regularity after discovering similar d -spacing deduced from the 1st to 3rd diffraction peaks as indicated in Table 2. These facts imply the surfactant synthesized in this work not only effectively enlarged the lamellar spacing of MMT, but also formed a uniformly dispersive structure in MMT. Similar phenomena were also observed in organophilic mica, as shown in Figure 4. Fu and Qutubuddin²⁰ pointed out that the quaternary monomer could homopolymerize and copolymerize with other monomers due to the existence of C=C double bond. It may also intercalate into inorganic compounds possessing lamellar structure according to their XRD studies.

Figure 5 schematically illustrates the simulated molecular structure of GME-N-C₁₀. The chain-length information is given in Table 3. Further calculation based on data in Table 3 indicated that the distance from C₃ to the plane containing C₁-C₂ in GME-N-C₁₀ is about 2.2179 nm. To attract the negative charges in clays, the angle between the two long alkyl chains should be as large as possible to reduce the effect of steric hindrance; therefore, the linear length of surfactants intercalated in lamellar structure should be reduced slightly. It is known that the thickness of clay lamella is about 1 nm. Consequently, the sum of linear length of surfactant and thickness of clay lamella is about 3.2 nm, which is very much the same as the experimental results obtained by XRD. Furthermore, based on the XRD results and structure simulation, a paraffin-like structure³⁴ could be found in the organophilic clays as illustrated in Figure 6. Finally, because GME-N-C₁₀ contains two 10-carbon alkyl chains, the geometry of λ -shaped surfactant may make itself tougher than the ammonium salt of long alkyl containing 16–18 carbons.

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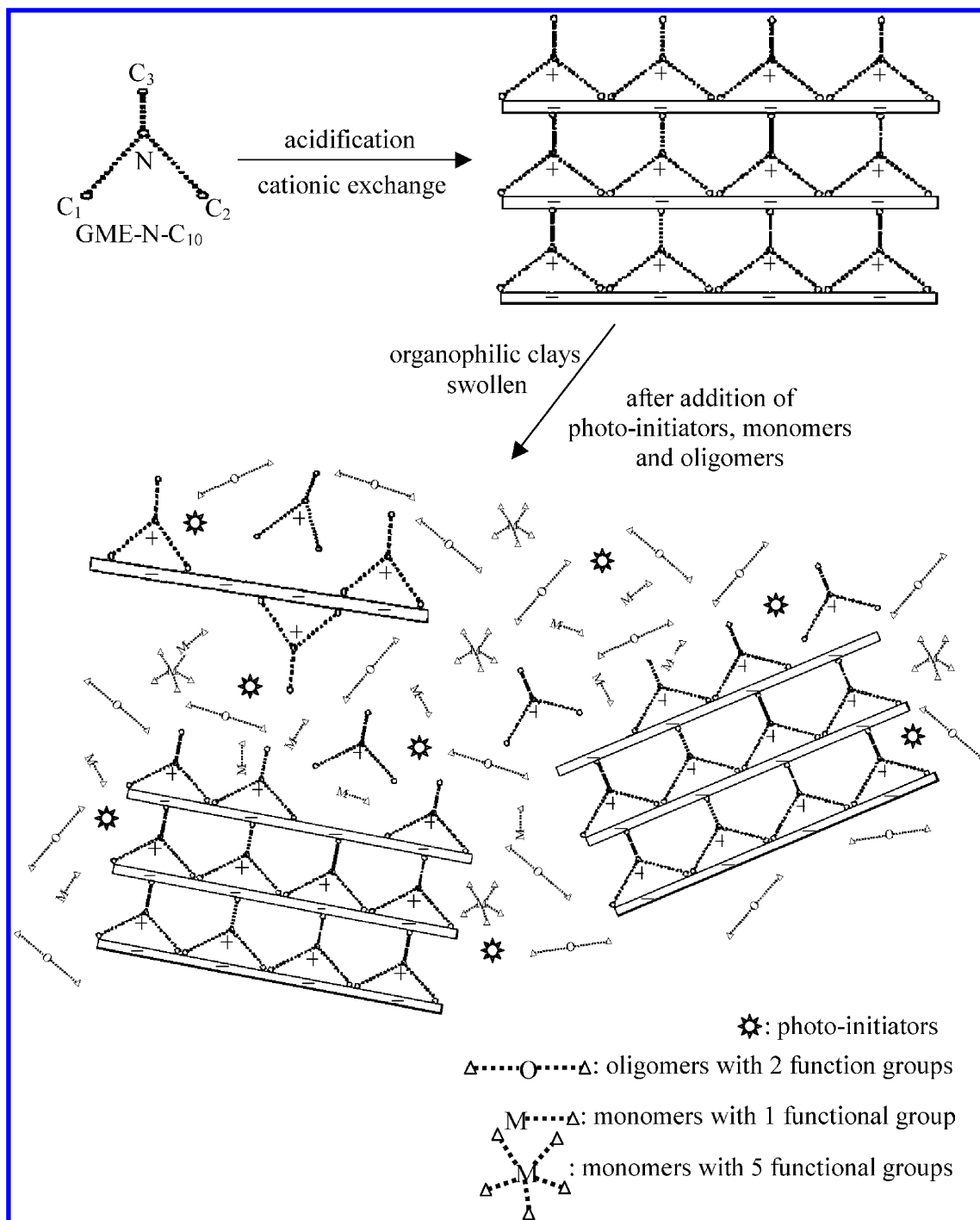


Figure 6. Expected schematic representation in the modification stage of clay lamellae by GME-N-C₁₀ and the clay lamellae attached with GME-N-C₁₀ after swollen in this work.

Microstructure. Figure 7 presents the DTG analysis of the reactivity between surfactants, surfactants and monomers, and surfactants and pre-polymer. It was deduced from the data obtained by TGA analysis in ambient air in order to calibrate the reactivity of surfactants during the radical photoinduced polymerization. As indicated by curves (a) and (b) in Figure 7, photoinduced polymerization caused a slight shift of the highest peak, and the polymerization induced new peaks at about 200 and 600 °C (curve (b)). The new peak at about 600 °C might correspond to the formation of C–C bonds between surfactants containing C=C double bonds due to copolymerization induced by the radicals

derived from the UV-breakage of photoinitiators.³⁵ Additionally, in the cured sample with monomers, the shift of the highest peak toward about 400 °C in curve (c) evidences the higher probability of C–C bonds formation between surfactants and monomers than that between surfactants. Hence, the functionalized surfactants, which are active during radical photoinduced polymerization, should be able to cross-link with pre-polymer and exfoliate the modified clays during subsequent process. Furthermore, the higher decomposition

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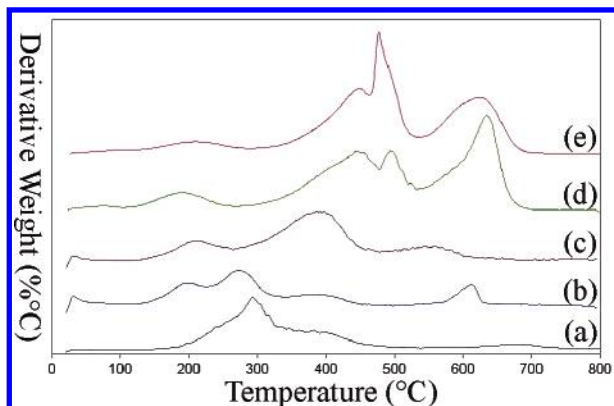


Figure 7. DTG analysis of (a) m-MMT without radical photoinduced polymerization, (b) m-MMT after polymerization, (c) the cured sample containing m-MMT and dipentaerythritol pentaacrylate, (d) pre-polymer, and (e) composite containing 5.0 wt.% m-MMT.

rate around 500 °C observed in curves (d) and (e) would indicate the occurrence of homopolymerization between surfactants and pre-polymer among composite resin.

Figure 8a shows the as-purchased MMT samples without modification and Figure 8b and c are the TEM micrographs of composite containing 5.0 wt.% modified MMT and its enlargement. The comparison between 8a and b indicates that the surfactants synthesized in this work could effectively provide the intercalation of clay in polymer. Furthermore, the MMT segments dispersed in polymer matrix are about 60–80 nm thick, as indicated by Figure 8c, and this corresponds to about 20–30 clay lamellae in each segment. The analyses above also indicate that ethanol added during the synthesis of surfactant is unlikely to be removed completely. With appropriate selection of solvent according to the solubility parameters, the organoclays should be able to achieve better exfoliation during swelling and photocured nanocomposites containing finely dispersed inorganic fillers could be obtained.

Thermal Properties. Figure 9 and Table 4 list the thermal properties of photocured nanocomposites prepared in this work. The 5.0% weight-loss decomposing temperature of pre-polymer is about 179 °C, and when 5.0 wt.% of modified MMT and Mica60 were added, the decomposing temperature (T_d) of composites raised at least 15 °C. The improvement of the thermal properties was attributed to the high thermal stability of clays and their interactions with the polymer matrix.^{36–39} Table 4 also lists the coefficient of thermal expansion values of pre-polymer and composites in the range of 40–90 °C. It can be seen that hybridization of modified clays increases the CTE of composites. One of the possible causes of this is that the van der Waals force between the two species bearing opposite charges would decrease as their distance increases.⁴⁰ As shown in Figure 5, because the two 10-carbon long chains connect to the N atom, the distance

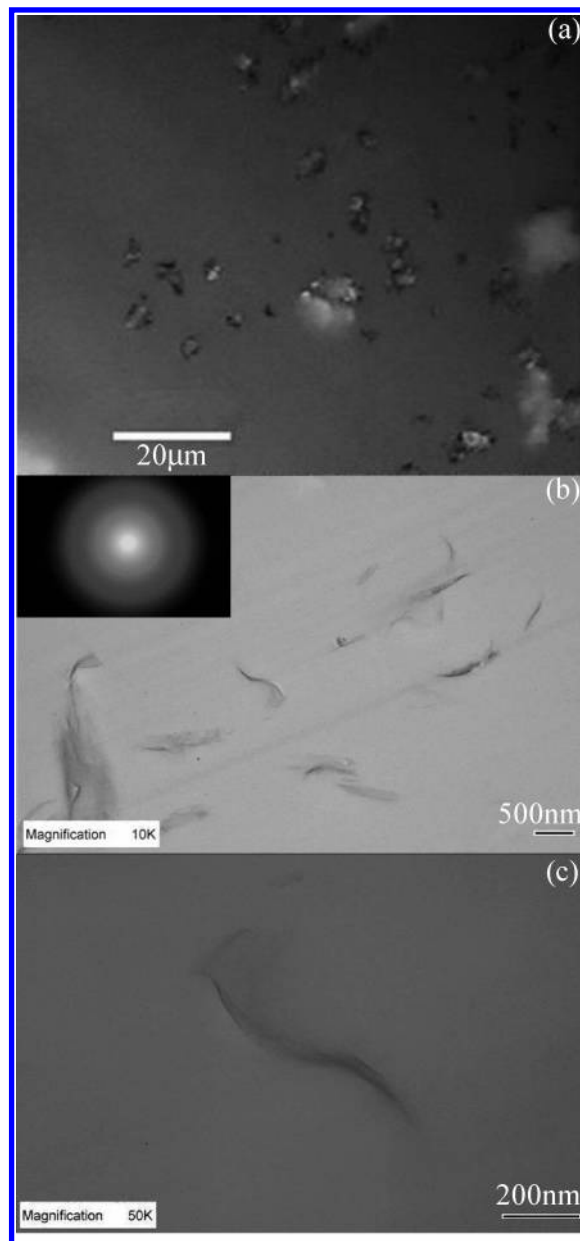


Figure 8. (a) Morphology of MMT before surfactant modification, (b) TEM micrographs of composite containing 5.0 wt.% m-MMT with corresponding electron diffraction pattern, and (c) enlargement of part of (b).

between the negative charge on clays and the ionized N atom on acidified surfactant increases so that the N^+ atoms are unable to reach to the surface of clays as much as they could even though those surfactants could be highly intercalated into clay lamellas according to the degree of modification listed in Table 1. The steric hindrance would decrease the attractive force and lead to some of surfactants attached to clays leaving their original sites, and remain free after swelling as shown in Figure 6. This phenomenon would decrease the interfacial area between the clay and polymer matrix,² thus increasing the CTE value of the composites. Besides, as mentioned above, ethanol molecules might residue in the lamellae of organophilic clays due to the incomplete removal of solvent, which may also cause the increase of CTE values of the composites prepared in this work.

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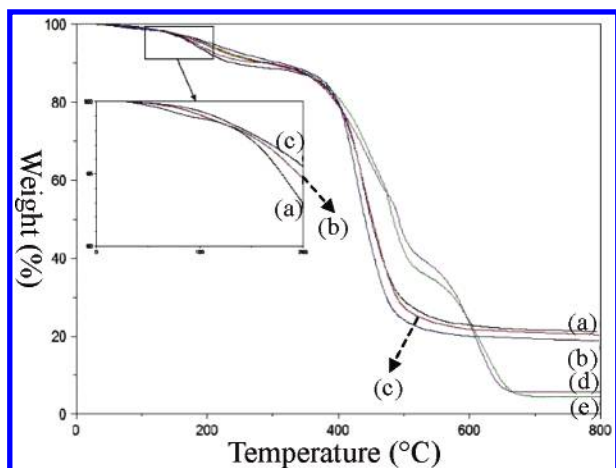


Figure 9. TGA thermograms of (a) pre-polymer under N_2 , (b) pre-polymer hybridized 5.0 wt.% m-Mica60 under N_2 , (c) hybridized 5.0 wt.% m-MMT under N_2 , (d) hybridized 5.0 wt.% m-Mica60 under air, and (e) hybridized 5.0 wt.% m-MMT under air.

Table 4. Thermal Properties of Composites

	T_d ($^{\circ}C$)	residual weight (%)	CTE_{40-90} ($^{\circ}C$)
pre-polymer	179		62.44
pre-polymer + 5.0 wt.% modified MMT	195	4.34	86.63
pre-polymer + 5.0 wt.% modified mica	209	5.81	85.12

Table 5. Optical Properties of Composites

	average transmittance in visible light region (%)
pre-polymer	88.68
pre-polymer + 5.0 wt.% modified MMT	76.60
pre-polymer + 5.0 wt.% modified mica	66.74

Optical Properties. Transmittances of pre-polymer and composites are given in Table 5. The transmittance of composites in the visible light region decreases due to the addition of opaque clays in polymer. The average transmittance decreases from 88.68 to 76.60% for the specimen containing 5.0 wt.% of modified MMT and to 66.74% for the specimen containing 5.0 wt.% modified Mica60. Since the sizes of modified MMT and mica are smaller than the wavelength of visible light, the composites might retain satisfactory transparency after hybridization.

Moisture Absorption. Table 6 shows that the moisture absorption reduces from 3.444% for pre-polymer to 1.304% for the specimen containing 5.0 wt.% of modified Mica60 and to 1.308% for the specimen containing 5.0 wt.% of modified MMT. Kojima et al.⁴¹ pointed out that nanocomposites have excellent resistance to moisture permeation

Table 6. Moisture Absorption of Composites

	moisture absorption (%)
pre-polymer	3.444
pre-polymer + 5.0 wt.% modified MMT	1.308
pre-polymer + 5.0 wt.% modified mica	1.304

because of a decrease in the diffusion coefficient compared with that of additive-free polymers. The increasing diffusion length due to the large aspect ratio feature of clay lamella should also benefit the moisture absorption.

Conclusions

A functionalized surfactant containing a C=C double bond was synthesized in this work to provide intercalation of clays in polymers. Molecular structure analyses indicated that the steric hindrance in surfactants induced a paraffin-like structure in the modified clays. The C=C double bonds in surfactants reacted with those in oligomers/monomers, even with others in surfactants, to form C-C covalent bonds during radical photoinduced polymerization so as to produce the nanocomposite resin. As revealed by TEM, the thickness of dispersed clay segments was about 60–80 nm, which corresponds to 20–30 clay lamellae in each segment. Microstructure analyses indicated that the intercalated nanocomposite resins consisting of organoMMT/oligomer/monomers were successfully prepared. Experimental analyses also indicated that the organic-inorganic composites prepared in this work possessed better thermal stability, satisfactory transparency, and low moisture absorption properties due to the nanometer-scale dispersion of modified clays in the polymer matrix. The incomplete removal of ethanol after the synthesis of surfactant and swelling of organoMMT and the long-chain feature of the surfactant synthesized in this work might result in the increase of CTE of the nanocomposites and hence further structure refinement of surfactant and appropriate selection of solvent according to the solubility parameters is required.

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