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Montmorillonite intercalated by ammonium of octaaminopropyl polyhedral oligomeric silsesquioxane and its nanocomposites with epoxy resin

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Abstract

The octaammonium chloride salt of octaaminopropyl polyhedral oligomeric silsesquioxane (OapPOSS) was synthesized via the hydrolytic condensation of γ-aminopropyltrimethoxysilane in the methanol solution catalyzed by concentrated hydrochloric acid and was further used as the intercalating agent to modify sodium montmorillonite (MMT). X-ray diffraction (XRD) data indicate that the MMT was successfully intercalated by the ammonium of OapPOSS, as evidenced by the fact that the basal spacing of MMT galleries was expanded from 1.3 to 1.7 nm. The intercalation method used here introduced only the octaammonium POSS salt in contrast to the introduction of all hydrolyzed products from γ-aminopropyltriethoxysilane (APTEOS). The POSS-modified MMT was exploited to prepare the epoxy-MMT nanocomposites. Using a two-step technique, the disorderly exfoliated epoxy-MMT nanocomposites were obtained. XRD studies showed that the formation of the nanocomposites in all the cases with the disappearance of the peaks corresponding to the basal spacing of MMT. Transmission electronic microscopy (TEM) was used to investigate the morphology of the nanocomposites and indicates that the nanocomposites are comprised of a random dispersion of intercalated/exfoliated aggregates throughout the matrix. Differential scanning calorimetry (DSC) indicates that the glass transition temperatures of the as-prepared epoxy-MMT nanocomposites remained invariant in comparison with that of the control epoxy when the POSS-MMT content is less than 10 wt%. However, the nanocomposite containing 15 wt% of POSS-MMT displayed a decreased T_g, which could be attributed to the incomplete curing reaction resulting from the POSS-MMT loading. Thermogravimetric analysis (TGA) shows that the incorporation of POSS-MMT into epoxy networks displayed an apparent improvement in the thermal stability, and the char residue increased with increasing the concentration of POSS-MMT.

Keywords: POSS; Montmorillonite; Epoxy resin

1. Introduction

Polymer/inorganic nanocomposites have attracted considerable interest in the past decade [1–3]. Layered ceramics such as clay and montmorillonite consisting of stacked silicate layers with a typical thickness of 10 Å can be intercalated or exfoliated by organic polymers to form the nanocomposites [4,5]. It was reported that the incorporation of a small amount of layered inorganic to organic polymers (<10 wt%) can bring the significant improvement in the properties of materials. Since the poly(ε-caprolactam)/clay nanocomposites were first reported by Toyota in 1987 [6], a great number of polymer/layered silicate nanocomposite systems have been prepared [7–17]. Generally, the hydrophilic pristine layered silicates would be intercalated using organic ammonium via cation exchange reaction to improve the affinity of inorganic layered silicates with organic polymers. However, alkyl ammonia of low molecular weight are inherently thermally unstable, which greatly limits the processing of materials, especially at elevated temperatures.

Polyhedral oligomeric silsesquioxane (POSS) reagents, monomers, and polymers are emerging as a new chemical technology for the nano-reinforced organic–inorganic

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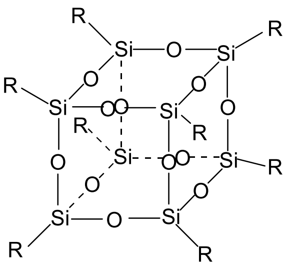
hybrids [18–24] and the polymers incorporating POSS monomers are becoming the focus of many studies due to the simplicity in processing and the excellent mechanical properties, thermal stability and flame retardation etc. [19–29]. The recent development of several families of functional hybrid reagents based on POSS affords a tremendous potential for modification of organic–inorganic hybrid polymers. The typical POSS monomers possess the structure of cube-octameric frameworks with eight organic corner groups, one or more of which is reactive or polymerizable (see Scheme 1). The excellent properties of POSS macromonomer and POSS-containing polymers inspires to prepare the functionalized POSS cages, which can be used as the intercalating agents of layered silicates to prepare the nanocomposites combining the two types of nanoreinforcement agents.

In this work, we explore to employ the use of octa(γ-aminopropyl) polyhedral oligomeric silsesquioxane (OapPOSS) to modify the pristine hydrophilic montmorillonite and subsequently to prepare epoxy-layered silicate nanocomposites. The gravimetric analysis (TGA) showed that OapPOSS is thermally stable up to ca. 300 °C [30,31]. The cubic POSS cages possess some important features, which make them the ideal pillaring agents for interactions with smectic montmorillonite. On the one hand, the ammonium ion salt of OapPOSS is fully water-soluble, which facilitates with the modification of sodium montmorillonite in the hydrophilic suspension. On the other hand, the γ-aminopropyl groups on the exterior of silsesquioxane core can endow POSS with organic affinity. For epoxy systems, OapPOSS could further take part in the formation of crosslinking network via the reaction between amine and epoxide groups. In the preparation of this manuscript, we have noted that a report on polystyrene-MMT nanocomposites mediated by isobutyl POSS amine appeared [32]. In this work, a monoamine-substituted POSS was used to intercalate sodium MMT.

In this communication, we present the synthesis and characterization of OapPOSS-intercalated montmorillonite and thereafter the POSS-modified MMT was employed to prepare the nanocomposites of epoxy resin. The morphology and thermal properties are addressed based on wide angle X-ray diffraction (XRD), transmission electronic microscopy (TEM), differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA).



Scheme 1. Structure of polyhedral oligomeric silsesquioxane (POSS).

2. Experimental

2.1. Materials and preparation of samples

γ-Aminopropyltrimethoxysilane (98%) was purchased from Guotai Huarong Organosilicon Co., Jiangsu province, China. The montmorillonite (MMT) used in this study was kindly supplied by Fenghong clay chemical Co. Inc., Zhejiang province, China. Before use, the raw montmorillonite was purified and then the highly hydrophilic suspension of sodium montmorillonite was used in this work. The Na^+-montmorillonite has a cationic exchange capacity of 110 meq per 100.0 g. The epoxy monomer, diglycidyl ether of bisphenol A (DGEBA), was purchased from Shanghai Resin Co., Shanghai, China and it has a quoted epoxide equivalence of 185–210. The curing agent was 4,4′-diaminodiphenylmethane (DDM), which is of chemically pure grade, obtained from Shanghai Reagent Co., China.

2.2. Synthesis of octaaminopropyl polyhedral oligomeric silsesquioxane (OapPOSS)

The OapPOSS was synthesized by following the literature methods [31,33]. Typically, to a flask equipped with a magnetic stirrer, 360 ml of methanol, 27 ml of concentrated hydrochloric acid (37%) and 15 ml (0.0838 mol) of γ-aminopropyltrimethoxysilane ($NH_2CH_2CH_2CH_2Si(OMe)_3$) were charged. The hydrolysis and rearrangement reaction was carried out for 6 weeks at room temperature and the microcrystalline precipitates were obtained. The product was collected (3.7 g, 30% yield) after filtration, washed with methanol and dried in a vacuum oven. FTIR (cm^{-1}) with KBr pellet: 3200–2800 (N–H in NH_3^+), 3000–2800 (C–H, in aliphatic aminopropyl), 1105 (Si–O–Si); ^{29}Si cross-polarization/magic angle spinning (CP/MAS) NMR (ppm, relative to Q_8M_8): δ −67.0 (s).

2.3. Preparation of montmorillonite mediated by OapPOSS

The pristine MMT (3.0 g) was dispersed in 300 ml deionized water at 80 °C. OapPOSS (6.0 g) were added to the MMT-water system with vigorously stirring for 24 h at 80 °C to afford a white precipitate. The precipitate was isolated by filtration and washed with water until no chloride was detected in the filtrate using 0.1 N $AgNO_3$ solution. The POSS-modified MMT was then dried at 80 °C in vacuo for 2 days. MMT-POSS together with the pristine MMT was subjected to the measurement of X-ray diffraction (XRD). Prior to use, it was ground with a mortar and a pestle and the fraction with the particle size smaller than

50 μm was collected. For brevity, the POSS-modified MMT was denoted as POSS-MMT.

2.4. Preparation of epoxy resin/POSS-MMT nanocomposites

The epoxy monomer, DGEBA was first mixed with the desired amount of POSS-MMT at 80 °C for 12 h with vigorously stirring until the homogenous system was obtained. A stoichiometric amount of curing agent (DDM) with respect of epoxide groups was added to the DGEBA/MMT-POSS mixture with continuously stirring and the ternary mixture of DGEBA, MMT-POSS and DDM was then transferred to a Teflon mold for curing. All the samples were cured at 80 °C for 2 h plus 150 °C for 2 h.

2.5. Measurement and techniques

2.5.1. Fourier transform infrared spectroscopy (FTIR)

The FTIR measurements were conducted on a Perkin–Elmer Paragon 1000 Fourier transform infrared spectrometer at room temperature (25 °C). The octaammonium chloride salt of OapPOSS was granulated and the powder was mixed with KBr pellets to press into the small flakes. The specimens were sufficiently thin to be within a range where the Beer–Lambert law is obeyed. In all cases, 64 scans at a resolution of 2 cm^{-1} were used to record the spectra.

2.5.2. Nuclear magnetic resonance spectroscopy (NMR)

The high-resolution ^{29}Si NMR spectra were obtained using the cross polarization (CP)/magic angle spinning (MAS) together with the high-power dipolar decoupling (DD) technique. The 90°-pulse width of 4.6 μs was employed with free induction decay (FID) signal accumulation, and the CP Hartmann–Hahn contact time was set at 3.5 ms for all the experiments. The rate of MAS was 4.0 KHz for measuring the spectra. The Hartmann–Hahn CP matching and dipolar decoupling field was 57 KHz. The time of recycle delay was set to be 10.0 s for the signal accumulation. The chemical shifts of all ^{29}Si spectra were determined by taking the silicon of solid Q_8M_8 relative to TMS as an external reference standard.

2.5.3. X-ray diffraction

X-ray diffraction (XRD) experiments were carried out on a Shimadzu XRD-6000 X-ray diffractometer with Cu ($\lambda=$ 0.154 nm) irradiation at 40 kV and 30 mA using a Ni filter. Data were recorded in the range of $2\theta=2$–15° at the scanning rate and step size of 1.0 (degree) $\times \mathrm{min}^{-1}$ and 0.02 (degree), respectively.

2.5.4. Differential scanning calorimetry (DSC)

The calorimetric measurement was performed on a Perkin–Elmer Pyris-1 differential scanning calorimeter in a dry nitrogen atmosphere. The instrument was calibrated with standard Indium. All the samples (about 10 mg in weight) were heated from -20 to 160 °C and the thermograms were recorded at a heating rate of 20 °C/min. The glass transition temperatures were taken as the midpoint of the capacity change.

2.5.5. Thermogravimetric analysis (TGA)

A Perkin–Elmer thermal gravimetric analyzer (TGA-7) was used to investigate the thermal stability of the nanocomposites. The samples (about 10 mg) were heated under N_2 atmosphere from ambient temperature to 800 °C at the heating rate of 20 °C/min in all cases. The thermal degradation temperature was taken as the onset temperature at which 5 wt% of weight loss occurs.

2.5.6. Transmission electronic microscopy (TEM)

Transmission electron microscopy (TEM) was performed on a JEM 1000GX-II (for lower magnification) and JEM-2010 transmission electron microscopes (for higher magnification respectively). The samples were trimmed using a microtome and the specimen sections (ca. 70 nm in thickness) were placed in 200 mesh copper grids for analysis.

3. Results and discussion

3.1. Preparation of MMT modified by ammonium OapPOSS

Octaaminopropyl polyhedral oligomeric silsesquioxane (OapPOSS) can be synthesized via the hydrolytic condensation of aminopropyltriethoxysilane (APTEOS) in ethanol–water solution [33–36]. The octameric oligomeric silsesquioxane can stably exist in the solution of 14:1 methanol–water solution while it is quite unstable after isolated [31,33]. Roziere et al. [34] and Petridis et al. [36] claimed that in the ethanol–water solution of all the hydrolyzed products of γ-aminopropyltriethoxysilane (APTEOS), both γ-Zirconium phosphate and clay were intercalated by OapPOSS. In comparison with OapPOSS, the ammonium of OapPOSS is quite stable and can be isolated with good purity. In this work, the use of the octaammonium chloride salt of OapPOSS was explored to carry out the cation exchange reaction with Na^+-MMT to obtain the intercalated layered silicate with the POSS compound. The ammonium chloride of octaaminopropyl polyhedral oligomeric silsesquioxane (OapPOSS) was prepared via hydrolytic condensation of γ-aminopropyltrimethoxysilane (APTMOS) catalyzed by hydrochloric acid according to the literature methods and then isolated [31, 33]. The isolated and purified product was subject to FTIR and NMR measurements. The FTIR spectrum of OapPOSS was presented in Fig. 1. The broad band in the range of 2800–3200 cm^{-1} is assigned to the stretching vibration of N–H in $-\mathrm{NH}_3^+$. It should be pointed out that the stretching vibration of aliphatic C–H also occurs in the range of

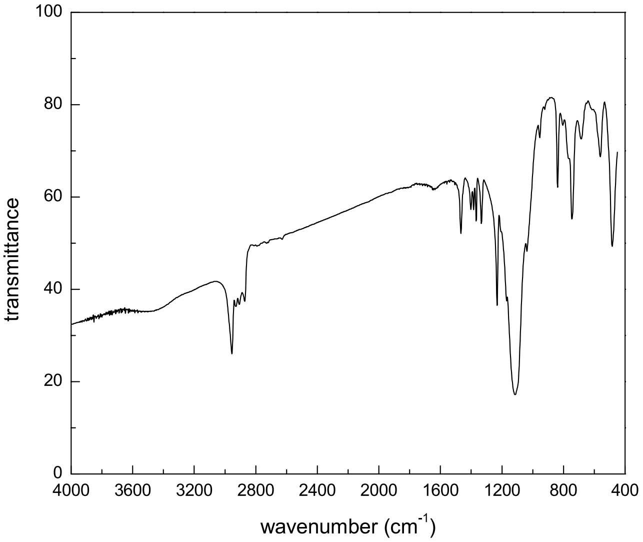


Fig. 1. The FTIR spectrum of OapPOSS.

2800–3000 cm^{-1}. The symmetrical Si–O–Si bonds in the silsesquioxane cages were characterized by the stretching bands at 1105 cm^{-1}. Shown in Fig. 2 is the ^{29}Si CP/MAS NMR spectrum of the POSS compound. A well-defined symmetric resonance was observed at -67.0 ppm, which was in a good agreement with the results of the literature [31,33], indicating that the OapPOSS was obtained and with quite good purity.

The solubility test shows that the ammonium of OapPOSS is fully water-soluble, which could facilitate the intercalation of MMT in the suspension of the hydrophilic Na^+-MMT. Therefore, the ammonium chloride of OapPOSS was exploited to carry out the cation exchange reaction with Na^+-MMT. Shown in Fig. 3 are the X-ray diffraction curves of Na^+-MMT and OapPOSS-modified MMT in the 2θ region of 1.5–10°. For Na^+-MMT, the Bragg diffraction peak was observed at $2\theta=6.7°$. The d-spacing in the (001) direction of the Na^+-MMT is calculated to be ~ 1.3 nm according to Bragg equation, which was taken as the basal spacing of galleries.

$$\lambda = 2d \sin\theta \qquad (1)$$

where λ is the wavelength of X-ray; θ is defined as the glancing angle of incidence and d the inter-planar spacing of MMT layers. For OapPOSS-modified MMT, it was observed that the diffraction peak of the (001) lattice shifted to the lower diffraction angle at $2\theta=\sim 5.3°$, which

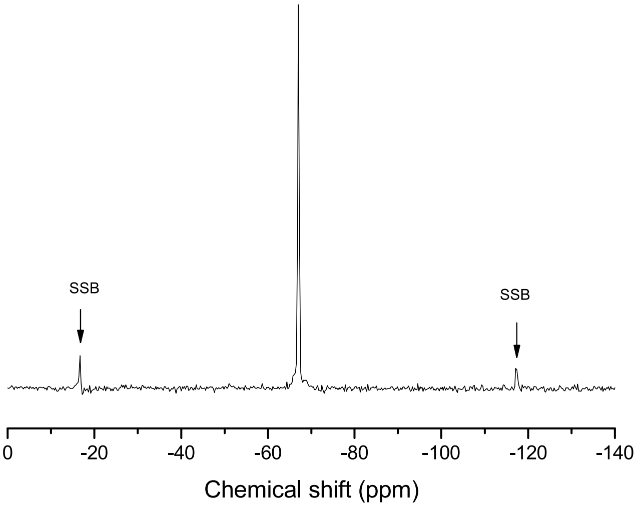


Fig. 2. The spectrum of ^{29}Si CP/MAS NMR of OapPOSS.

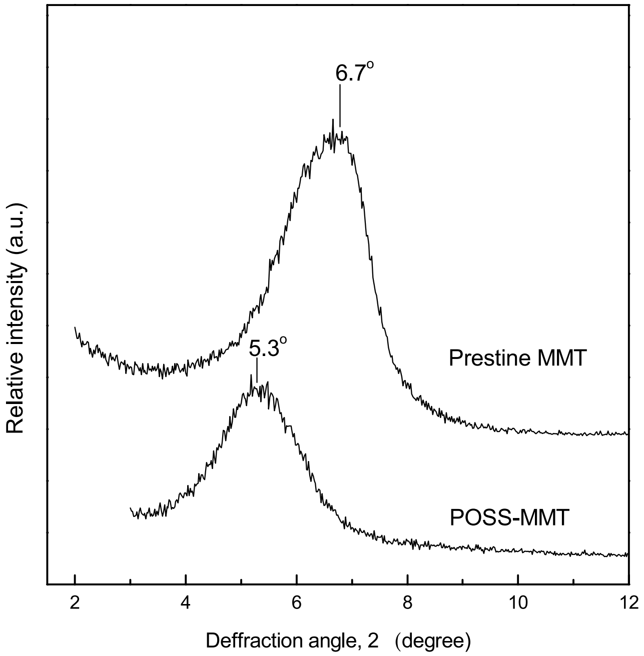


Fig. 3. Curve of thermogravimetric analysis (TGA) of POSS-treated MMT.

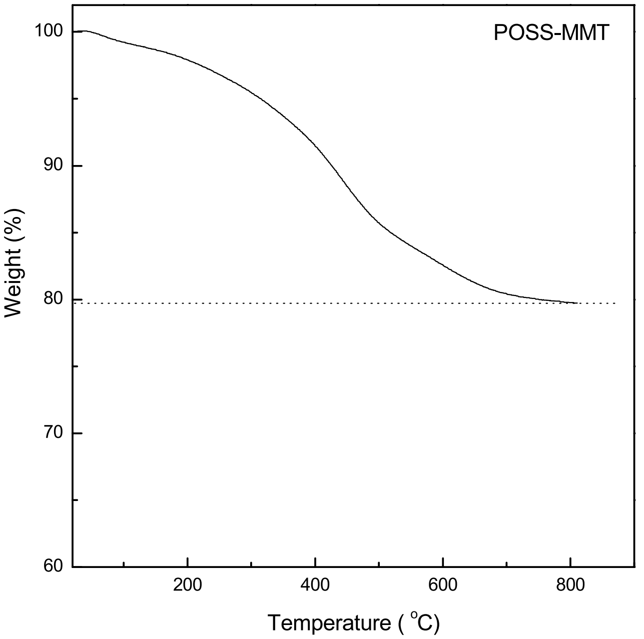
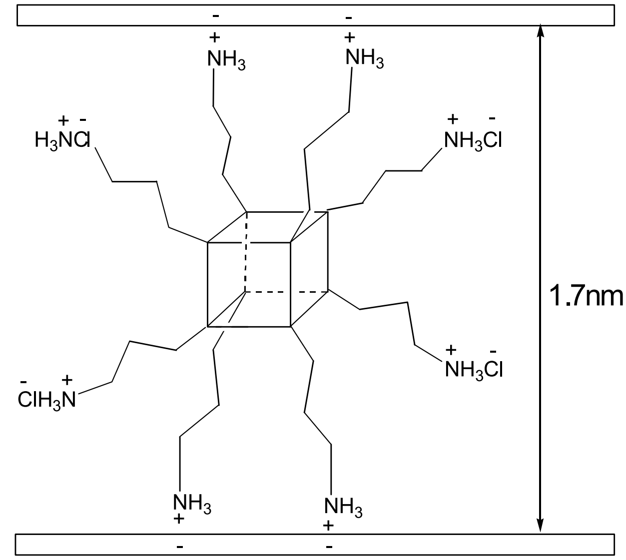


Fig. 4. XRD patterns of Na^+-MMT and OapPOSS-modified MMT in the 2θ region of 1.5–10°.

corresponds to the basal spacing of galleries of 1.7 nm. The increase in the basal spacing indicates that the MMT was efficiently intercalated by OapPOSS. Shown in Fig. 4 is the curve of thermal gravimetric analysis (TGA). From the TGA result, it is estimated that the organic portion of POSS-MMT is about 20.0 wt%. According to the standard cationic exchange capacity of MMT (110 meq/100 g), it is calculated that 100.0 g of MMT requires 16.1 g of octaammonium chloride salt of OapOSS for intercalation, which is much lower that the experimental value estimated from the organic portion of POSS-MMT, i.e. 33.8 g of octaammonium chloride salt of OapPOSS per 100 g of MMT. This result implies that only half of all NH_3^+ cites of octaammonium chloride salt of OapPOSS are interacting with negative charges in the alumnia-silicate sheets as shown in Scheme 2. It should be pointed out that the intercalation of MMT makes use of the preformed ammonium ion form of OapPOSS other than the ethanol–water solution of all the hydrolyzed products of γ-aminopropyltriethoxysilane (APTEOS) as reported in the previous literature [34,36]. The ammonium has been isolated from the products of all the hydrolytic condensation, which avoids that MMT was intercalated by any other incompletely condensed siloxane species. Therefore, it is plausible to propose that the intercalating agent is the completely condensed octameric oligomeric silsesquioxane. In terms of the XRD results, it is proposed that the flexible aminopropyl groups of cubic POSS must adopt a vertical orientation between the adjacent layers of MMT (See Scheme 2) [36].

3.2. Epoxy-MMT nanocomposites mediated by OapPOSS

The above MMT mediated by OapPOSS was used to prepare epoxy-MMT nanocomposites. Fig. 5 presents the X-ray diffraction curves for the POSS-mediated MMT and the epoxy-MMT nanocomposites containing 5, 10 and 15 wt% of MMT modified by POSS. It can be seen that the (001) diffraction peak of the POSS-modified MMT appears at $2\theta = 5.3°$, which corresponds to the characteristic basal spacing of $d = 1.7$ nm as calculated from Bragg's equation. The diffraction peaks are absent in the scattering curves for all the epoxy-MMT composites, irrespective of MMT concentration, suggesting that the MMT silicate layers are significantly delaminated, i.e. the nanocomposites were formed. It should be pointed out that the presence of order at the higher d-spacing (>6.0 nm or $2\theta < 1.5°$) could not be confirmed for the data.



Scheme 2. The arrangement of ammonium of OapPOSS in the gallery of MMT.

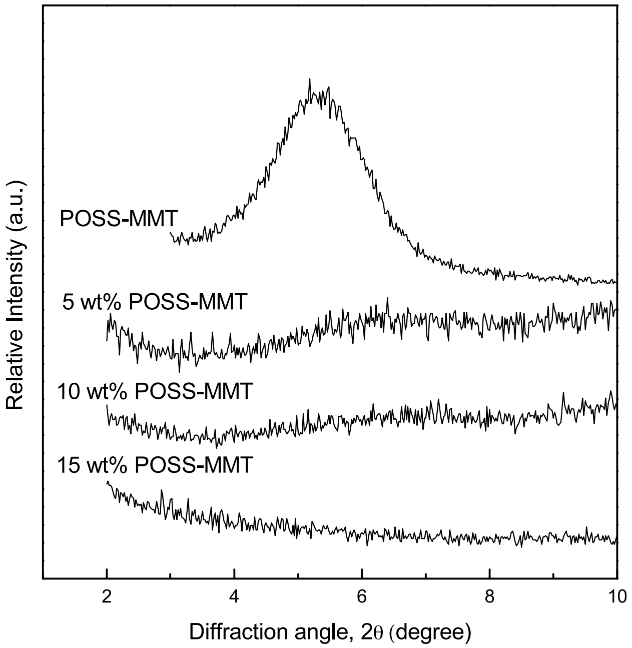


Fig. 5. XRD patterns of MMT intercalated by the octaammonium chloride salt of OapPOSS and its nanocomposites with epoxy resin.

Transmission electronic microscopy (TEM) allows the morphological analysis of the nanocomposites. Representatively shown in Fig. 6 are the TEM micrographs of the nanocomposites containing 10 wt% of MMT-POSS. The lower magnification micrograph, Fig. 6(A), shows that the MMT layers do not fill the full volume, suggesting that the platelet tactoids of MMT were dispersed in epoxy matrix at sub-micro-sized scale. A close observation of an area of platelet tactoid at higher magnification with high-resolution TEM reveals the individual platelets of MMT clearly separated by polymer matrix, i.e. some polymer has diffused between the some of the platelets (see Fig. 6(B)). It is evident that the morphology could be considered a mix of intercalated and exfoliated platelets, i.e. there are regions where the regular stacking platelet tactoids are maintained with polymer diffusing between the platelets of MMT, and also regions where MMT platelets were completely delaminated. It should be pointed out that the inorganic OapPOSS could be closely attached with the platelets of

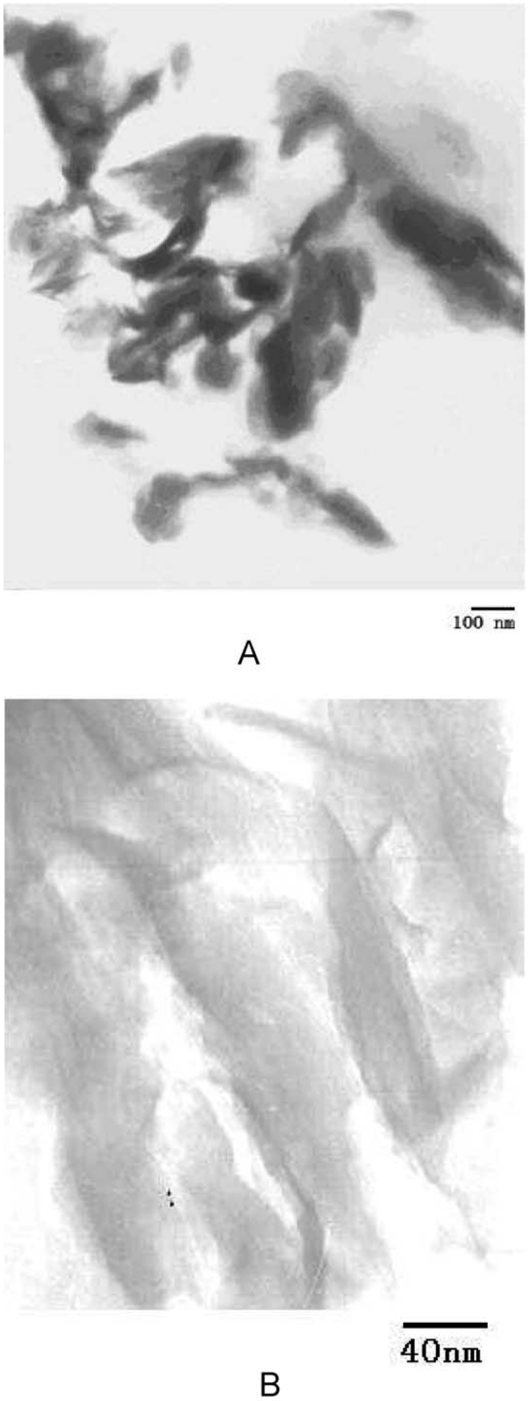


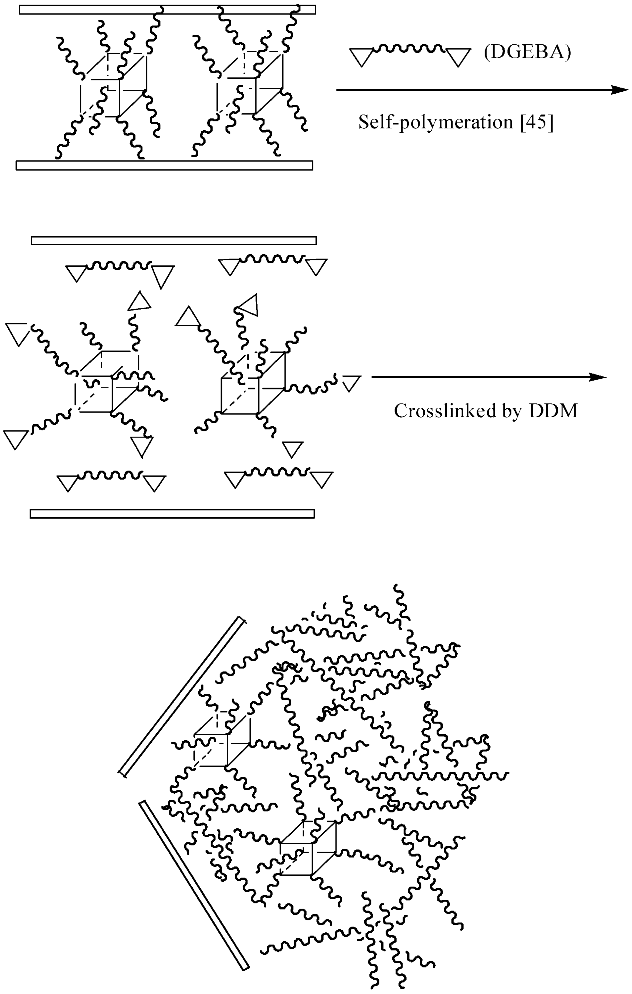
Fig. 6. Transmission electron microscopy (TEM) micrographs of epoxy-MMT nanocomposites containing 10 wt% POSS-MMT. (A) Micrograph at lower magnification; (B) micrograph at higher magnification.

clay and thus single clay platelets could not be clearly identified by TEM due to the close electronic densities between POSS and platelets of clay. It has been reported that for epoxy-clay nanocomposites, the orderly exfoliated morphologies were generally reported [37–43]. In the preparation of epoxy-clay nanocomposites, the curing reaction of epoxy was generally carried out under quiescent conditions and no external shear force was acted on clay layers and thus the intercalated or orderly exfoliated structures were generally obtained on epoxy-clay nanocomposites to date [44] unless the specific methods were used. More recently, Mai et al. [44] reported a novel technique to prepare the disorderly exfoliated epoxy-clay nanocomposites. By controlling the quantity of hydrochloric acid, only one amine function was protonated per *m*-xylylenediamine (MXD) and the modified MXD was used as the intercalating agent to prepare the organoclay (M-clay). The M-clay was then allowed to react with diglycidyl ether of bisphenol A (DGEBA) in an emulsion to prepare a DGEBA-modified M-clay, which then was used to blend with epoxy and 4,4′-diaminodipenylsulfone (DDS) agent for curing reaction. In the present work, the intercalating agent, octaammonium of OapPOSS endows the MMT the hydrophobic character, i.e. increases its organophilic nature. In the preparation of the nanocomposites, DGEBA was first mixed with the desired amount of MMT-POSS at 80 °C for 12 h with vigorously stirring until the homogenous system was obtained. During the pre-mixing procedure, the ammonium of OapPOSS in the galleries of MMT could act as the catalyst of self-polymerization of epoxy precursor [45] and could initiate the inter-layered self-polymerization of DGEBA, i.e. the MMT-POSS could be pre-intercalated by DGEBA. The pre-intercalation of DGEBA into POSS-MMT layers prior to curing reaction would facilitate the subsequent exfoliation of some MMT platelets (see Scheme 3). It has been shown that the formation of exfoliated clay nanocomposites is dependent on the nature of alkyl ammonia that were used as the intercalating agents of layered silicates [17] and the ammonium with long alkyl chains could allow more organic species to diffuse into the layer-galleries and progressively exfoliate the layered silicates. The subsequent polymerization could be a driving force to overcome the attractive electrostatic force between the negatively charged silicate layers and the gallery cations. Although the alkyl chains in the ammonium of OapPOSS are shorter, an OapPOSS has eight ammonium cations of aminopropyl groups. Therefore, the catalytic effect is pronounced; upon additional heating, further polymerization is catalyzed by the acidic primary amine and thus more epoxide and amine can enter the galleries, leading to the formation of an exfoliated nanocomposites.

3.3. Thermal properties of epoxy-MMT nanocomposites mediated by OapPOSS

3.3.1. Differential scanning calorimetry (DSC)

The epoxy-MMT nanocomposites mediated by ammonium of OapPOSS were subjected to thermal analysis. The DSC curves of the control epoxy and its nanocomposites with the MMT are presented in Fig. 7. The glass-to-rubber transition of the control epoxy occurs at 172 °C. With the addition of POSS-MMT to system, it is noted that the



Scheme 3. Formation of epoxy-MMT nanocomposites mediated by ammonium of OapPOSS.

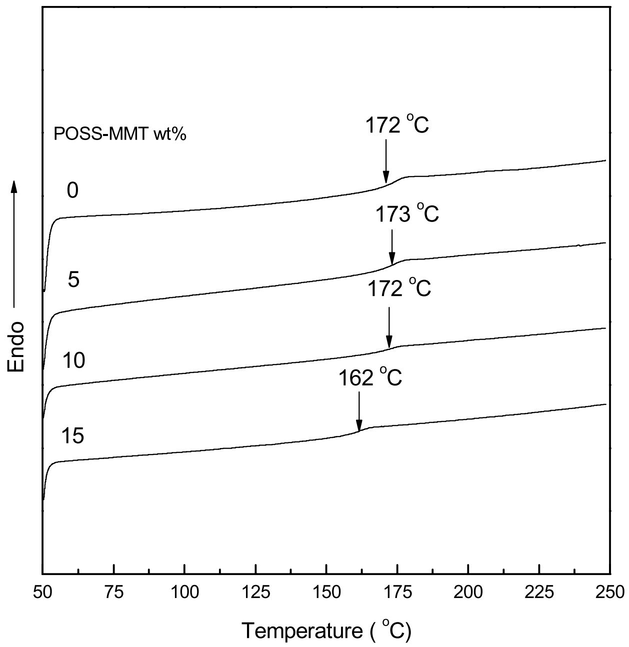


Fig. 7. DSC curves of the control epoxy and its nanocomposites with POSS-MMT.

glass transition temperatures (T_g's) almost remain invariant for the nanocomposites containing 5 and 10 wt% of POSS-MMT whereas the nanocomposite containing 15 wt% of POSS-MMT displayed the glass transition temperature lower than that of the control epoxy. In the hybrid system, the glass transition temperatures of materials could be affected at least by following two factors. On the one hand, there could be the nanoreinforcement effect of MMT layers together with the intercalating agent (viz. ammonium of OapPOSS), which were dispersed in the continuous epoxy matrix and restrict the motion of polymer chains and thus give rise to the increase in T_g. On the other hand, the glass transition temperatures (T_g's) of thermosetting nanocomposites could be affected by the crosslinking density of epoxy resin. In the present case, POSS-MMT was first allowed to mix with DGEBA at 80 °C for 12 h and the ammonium ion form of POSS-catalyzed homopolymerization of DGEBA could be initiated during this stage. This would consume a portion of epoxide groups. However, the stoichiometric quantity of the curing agent (DDM) added (versus DGEBA) initially requires that some remnant amine groups. These could exist in the system in the form of free ends, which could introduce free volume and lower the glass transition temperature. In addition, the decrease in T_g could also be related to the incomplete curing reaction resulting from the addition of POSS-MMT. It has been shown that low molecular organic modifier (viz. intercalating agent) has the effect of plasticization on epoxy network in epoxy-nanoclay systems [46]. However, in the present case, the decease in glass transition temperature for the nanocomposite containing 15 wt% of MMT-POSS was attributed to the incomplete curing reaction induced by the incorporation of MMT-POSS. It is proposed that the behavior of glass transition of the POSS-MMT containing hybrids are the comprehensive reflection of the above two factors, depending on the amount of POSS-MMT used in the composite system.

3.3.2. Thermogravimetric analysis (TGA)

TGA under a nitrogen atmosphere was applied to evaluate the thermal stability of the epoxy-MMT nanocomposites mediated by the ammonium of OapPOSS. Shown in Fig. 8 are the TGA curves of the nanocomposites, recorded in nitrogen atmosphere at 20 °C/min. Within the experimental temperature range, all the TGA curves displayed similar feature of degradation, suggesting that the existence of POSS-MMT did not significantly affect the degradation mechanism of the matrix polymers. The temperatures of degradation (T_d) were taken as the onset temperatures at which 5 wt% mass loss occurred. It is noted that the thermal stability of epoxy network is significantly reserved. The incorporation of POSS-MMT into epoxy networks displayed an apparent improvement in the thermal stability.

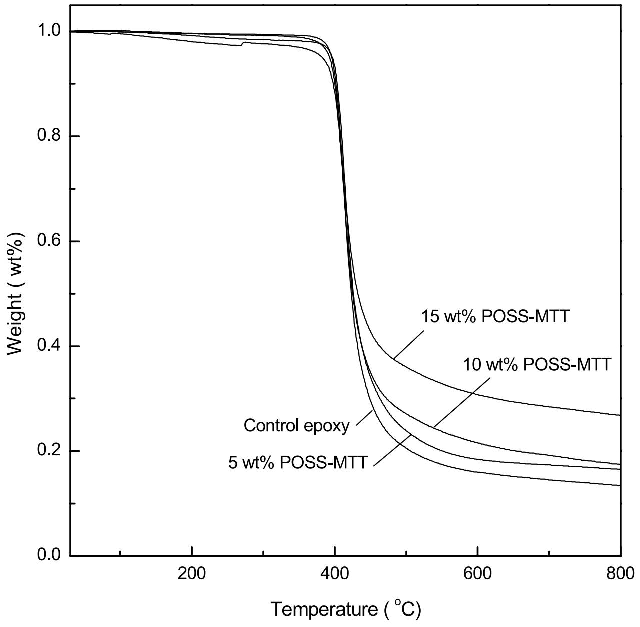


Fig. 8. TGA curves of the control epoxy and its nanocomposites with POSS-MMT.

The enhanced char yield was seen in the high temperature region. This effect was observed to be increasingly significant with increasing the concentration of POSS cages. It is plausible to propose that the improvement in weight retention is ascribed to POSS-MMT constituent, which was dispersed in the continuously epoxy matrix at the nanoscale. The higher char yields implied that there were fewer volatiles being released from the nanocomposites during heating. The layered silicates in the composites could act as an insulator and thus reduces the mass loss rate, i.e. improves flame retardence and thermal stability due to the properties of mass transport barrier [47]. In addition, the higher thermal stability of POSS also contributed the improvement in thermal stability of the nanocomposites [48].

4. Conclusions

The octaammonium chloride salt of octaaminopropyl polyhedral oligomeric silsesquioxane (OapPOSS) was synthesized via the hydrolytic condensation of γ-aminopropyltrimethoxysilane in the methanol solution catalyzed by concentrated hydrochloric acid. The isolated ammonium of OapPOSS was characterized by Fourier transform infrared spectroscopy (FTIR) and ^{29}Si cross-polarizations (CP)/magic angle spinning (MAS) nuclear magnetic resonance spectroscopy (NMR). The pre-formed POSS was further used as the intercalating agent to modified sodium montmorillonite (MMT). X-ray diffraction (XRD) results showed that the MMT was successfully intercalated by the ammonium of OapPOSS, i.e. the basal spacing of MMT galleries was expanded from 1.3 to 1.7 nm. The intercalation route is different from those previously reported in the ethanol–water solution of all the hydrolyzed products of aminopropyltriethoxysilane (APTEOS). The POSS-modified MMT was exploited to prepare the epoxy-MMT nanocomposites. Using a two-step method, the nanocomposites were obtained. XRD studies showed that the formation of the nanocomposites in all the cases with the disappearance of the peaks corresponding to the basal spacing of MMT. Transmission electronic microscopy (TEM) was used to investigate the morphology of the nanocomposites and indicates that the nanocomposites to be comprised of a random dispersion of intercalated/exfoliated aggregates throughout the matrix. Differential scanning calorimetry (DSC) indicates that the glass transition temperatures of the as-prepared epoxy-MMT nanocomposites mediated by POSS are identical with that of the control epoxy when the POSS-MMT content is less than 10 wt%. However, the nanocomposite containing 15 wt% of POSS-MMT displayed a decreased T_g, which was attributed to the incomplete curing reaction resulting from the POSS-MMT loading. Thermogravimetric analysis (TGA) shows that the incorporation of POSS-MMT into epoxy networks displayed an apparent improvement in the thermal stability, and the char residue increased with increasing the concentration of POSS-MMT.

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