

Morphology and Properties of Silane-Modified Montmorillonite Clays and Clay/PBT Composites

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ABSTRACT: Commercially available organoclay (Clo-site 30B) was modified by using 3-aminopropyltriethoxysilane (APS) via a silylation reaction. Sodium clay (Clo-site Na) was treated by APS directly as a control. Such modified clays were further melt-compounded with polybutylene terephthalate (PBT). The morphology and properties of the modified organoclays were characterized with X-ray diffraction (XRD), transmission electrical microscopy (TEM), Infra-red spectroscopy, contact angle measurement, and thermogravimetric analysis (TGA). The effects of modified clays on the crystallization behavior of PBT were characterized by differential scanning calorimetry. The basal spacing of Clo-site Na was enlarged from 1.01 to 1.41 nm after APS treatment, indicating that the APS was intercalated into the clay inter-galleries as a monolayer. The basal spacing of Clo-site 30B

increased slightly after APS treatment, partially resulted from the reactions between the APS and hydroxyl groups on the intercalant of Clo-site 30B. Clo-site 30B was found to be exfoliated disorderly after melt-compounded with PBT. The APS-modified Clo-site 30B only dispersed as swollen elliptical clay aggregates, in which the silicate layers were orderly intercalated. TGA results showed that the decomposition temperature at 5% weight loss of Clo-site 30B was increased from 250 to 270°C after APS treatment. A significant increase in the degree of crystallinity of PBT was observed in the exfoliated PBT/30B composite. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 550–557, 2008

Key words: organosilane; clay; silylation; thermal stability; PBT

INTRODUCTION

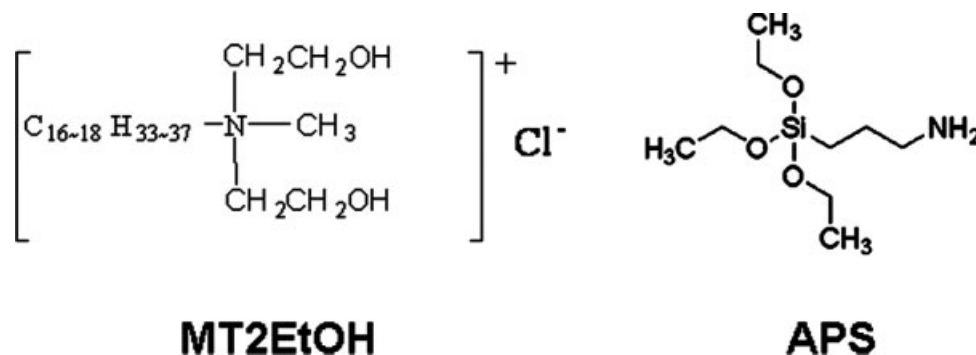
Thermal instability of conventional ammonium ion modified clays is a major limitation for melt-compounding of polymer/organoclay composites. The most often used alkyl ammonium surfactants are known to start degradation at temperatures between 180 and 200°C,¹ which is in the processing temperature range for most commodity plastics. The thermal degradation of ammonium also induces discoloration, molecular weight decrease, and reduction of mechanical properties of polymer/organoclay composites. To improve the thermal stability of organoclays for polymer processing phosphonium,^{2,3} imidazolium,⁴ pyridinium,⁵ and ionic liquid⁶ have been used for this purpose. Although these organic compounds can improve the thermal stability of organoclays to some extent, they are not as good as ammonium tallow salts in expanding clay interlayer and improving the compatibility with polymers. These

organic compounds also have limitations in availability and cost. Therefore, achieving a good compatibility and high thermal stability of organoclays for polymer processing is a key point in producing polymer/organoclay composites.

Montmorillonite clay belongs to the smectite group. It is composed of units made up of two silica tetrahedral sheets with a central alumina octahedral sheet.⁷ Montmorillonite has exchangeable interlayer cations, hydroxyl groups on the "broken" edge and Lewis and Bronsted acidity on the clay surface.⁸ Such structural features provide active sites for organic modification. In addition to the ion-exchange reaction with organic cations, the reactions involving organosilane compounds with silanol groups on the edge of the clay sheets are another possible way to modify the clays.^{9–13} Ruiz-Hitzky et al.⁹ first used organosilanes to modify layered silicates. They found that the grafting reaction mainly occurred at the external surface of the clay, and was highly dependent on the accessible surface area. Herrera et al.^{10,11} investigated the reactions of trifunctional and monofunctional vinyl alkoxysilanes with laponite clay. They quantified the grafted amount and chemisorbed organosilanes at saturation on the laponite clay surface and found that the

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Scheme 1 The molecular structures of MT2EtOH and APS.

monofunctional silane exhibited nearly no effect on the physicochemical properties of the clay, whereas grafting of the trifunctional silane resulted in decreased porosity, increased interlamellar distance, and higher hydrophobicity. Park et al.¹² found that external surface modification of laponite with octyltrimethoxysilane greatly enhanced the intercalation rate of hydrophobic molecules without any effects on the crystal structure and uptake capacity of laponite. He et al.¹³ reported that the grafting reaction between organosilane and layered silicates includes two steps. The silane molecules first intercalate into the clay interlayers followed by a condensation reaction between the silane molecules and clay layers. The arrangement of organosilane between the clay intergalleries was depended on the clay type. Most of these studies mainly focused on the synthesis of organosilane-clays and seldom reported the application of organosilane-clays in polymer processing. More importantly, the organosilane modification is an effective way to improve the thermal stability of clay.¹⁴

In this article, a commercial organoclay (Closite 30B) was treated by an organosilane (APS) via a silylation reaction. The Closite 30B is a kind of montmorillonite, modified with bis(2-hydroxyethyl) methyl hydrogenated tallow ammonium salt. Sodium clay (Closite Na) was also directly treated by APS as a control. The structure and surface properties of the obtained organoclays were studied in detail by using thermogravimetry (TGA), Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), transmission electrical microscopy (TEM), and contact angle measurement techniques. Furthermore, the obtained organoclays were melt-compounded with a high-temperature engineering plastic, polybutylene terephthalate (PBT), to evaluate the compatibility and thermal stability of the organoclays. The effects of organosilane modification on the morphology and crystallization behavior of PBT/organoclay composites were also investigated.

EXPERIMENTAL

Materials

Sodium montmorillonite clay with cation exchange capacity of 92 mmol/100 g was purchased from Southern Clay Products, Inc. (USA), under the trade name of Closite[®] Na. Closite[®] 30B with bis(2-hydroxyethyl) methyl hydrogenated tallow ammonium chloride (MT2EtOH) as an intercalant was purchased from the same company. 3-aminopropyltriethoxysilane (APS) and ethanol were purchased from Aldrich Chemical Company. The molecular structures of MT2EtOH and APS are shown in Scheme 1. All the chemicals were used as received.

PBT was obtained from Ticona Co., Ltd. (UK), with the trade name of Celanex[®] PBT. Its intrinsic viscosity is 0.70 dL/g, which was measured by using a Cannon-Ubbelohde viscometer at 20°C in phenol/1,1,2,2-tetrachloroethane (50/50 w/w) solutions of 0.5 g/dL concentration.

Preparation procedure

Before organosilane modification, Closite Na and Closite 30B were dried in a vacuum oven overnight at 100°C and 60°C, respectively.

About 1 g of clay (Closite Na or Closite 30B) was added into a 25 mL APS ethanol solution containing 1 g of APS. The mixture was refluxed for 6 h with constant stirring. The resulting product was washed thoroughly by ethanol/water solution to remove excessive silane coupling agent, then dried at 60°C for 24 h. The modified organoclays obtained were designated as APS/Na and APS/30B, respectively.

The modified nanoclays were melt-compounded with PBT in an internal mixer (HAAKE Rheocord 9000, Haake Co., Vreden, Germany) at 240°C and 60 rpm for 15 min to produce PBT/30B and PBT/APS/30B composites. The clay content is kept at 3 wt % for each sample.

TABLE I
Surface Energy of Water and Diiodomethane
Measured at 20°C¹⁵

Sample	γ^d (mJ/m ²)	γ^p (mJ/m ²)	γ (mJ/m ²)
Water	21.8	51.0	72.8
Diiodomethane	49.5	1.3	50.8

Characterization

XRD patterns of the clays, APS-modified clays, and the composites were recorded using Cu K α radiation ($\lambda = 0.1542$ nm) on a Bruker AXS, D8 Advance Diffractometer operating at 40 kV and 40 mA with a divergence slit of 1.0° and a 1.0° scatter slit between 1° and 10° (2θ) at a step size of 1°/min. FTIR spectra were recorded in the spectral range 4000 cm⁻¹ ~ 400 cm⁻¹ on a Perkin-Elmer FTIR spectrometer in air at room temperature. TGA was performed on a Setaram TGA 92 Thermobalance. The measurements were carried out under dry nitrogen atmosphere at a flow rate of 40 mL/min and a scanning rate of 10°C/min over the temperature range 20–800°C. The thermal gravimetric weight loss curve and the derivative of this curve were presented in each plot. The equilibrium contact angles of the clays were measured using a dataphysics OCA20 contact angle equipment (Dataphysics Instrument GmbH, Germany). Water and diiodomethane were used as testing liquids. The surface free energy of the clays was calculated by using the Owen-Wendt-Kaelble's equation¹⁵ and the data in Table I referred to Wu's results.¹⁶ The PBT/organoclay composites were microtomed with Reichert-Jung Ultracut-E into 60- to 80-nm thick slices. The slices were deposited on copper nets for TEM observations on a JEOL 2000FX with an acceleration voltage of 120 kV. The crystallization behavior of PBT and PBT/organoclay composites was analyzed with a differential scanning calorimeter (DSC, Paris 1, Perkin-Elmer Co., Norwalk, CT) under dry nitrogen atmosphere at a flow rate of 50 mL/min and a scanning rate of 10°C/min. Samples underwent the following temperature protocol: (a) heated to 280°C and kept isothermally for 5 min; (b) cooled to 20°C and kept isothermally for 5 min; and (c) heated to 270°C. The glass transition temperature (T_g) was obtained from the first scan, and the crystallization and melting behavior were obtained from the second cooling and heating cycle. The degree of crystallinity (X_c) of the sample was calculated according to eq. (1).

$$X_c (\%) = \frac{\Delta H_m}{\Delta H_m^0 (1 - \phi)} \times 100 \quad (1)$$

where ΔH_m is the measured heat of fusion for the sample, and ΔH_m^0 is the heat of fusion for 100% crys-

talline polymer. The symbol ϕ is the clay weight percent in polymer composites. According to previous studies, the heat of fusion of 100% crystalline PBT is 142 J/g.¹⁷

RESULTS AND DISCUSSION

Morphology of the organoclays

Figure 1 shows the XRD patterns of Cloisite Na and Cloisite 30B before and after organosilane modification. The observed characteristic diffraction peak correspond to the $d(001)$ plane reflection of the montmorillonite clay. The broad peak of $d(001)$ ($2\theta = 8.7^\circ$, $d = 1.01$ nm) of the Cloisite Na with weak intensity underwent obvious shift to smaller angles upon intercalation or silylation modification. The basal spacing for Cloisite 30B is 1.80 nm. The estimated intergallery height for Cloisite 30B is 0.83 nm, which is calculated from the thickness of a single montmorillonite layer of 0.97 nm.¹⁸ When a hydrocarbon chain stretches out, the covalent bond length of a $-\text{CH}_2-$ is 0.127 nm and the van der Waals' diameter of $-\text{CH}_3$ is about 0.3 nm.¹⁹ Hence, a lateral-bilayer arrangement is supposed for the intercalated MT2EtOH in Cloisite 30B intergalleries.^{20,21}

After silylation reaction, the basal spacing is increased from 1.01 to 1.41 nm for Cloisite Na and from 1.80 to 1.90 nm for Cloisite 30B, respectively (Fig. 1). The increase of the basal spacing of APS/Na indicates that APS was intercalated into the clay intergalleries. After hydrolysis, the height of the aminopropyl group of APS is about 0.40 nm, similar to that of the alkyl chain.²² Accordingly, the gallery height of 0.40 nm of APS/Na suggests that a lateral-monolayer of APS was formed between the intergalleries of clay. As for APS/30B, the intergallery height is slightly increased from 0.83 to 0.93 nm. The

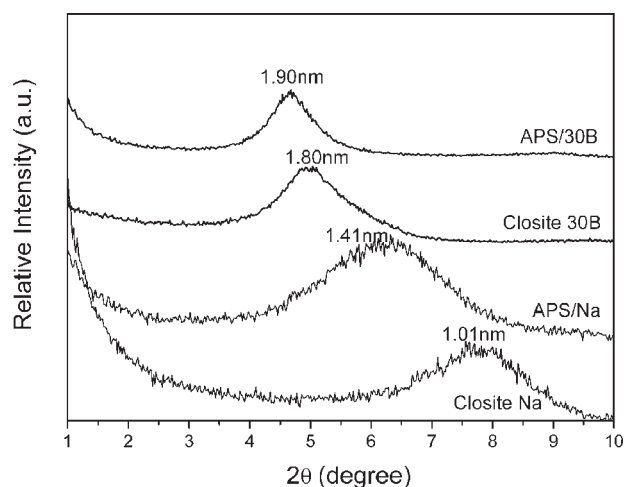


Figure 1 XRD patterns of clays before and after APS modification (the APS concentration is 100% of clay weight).

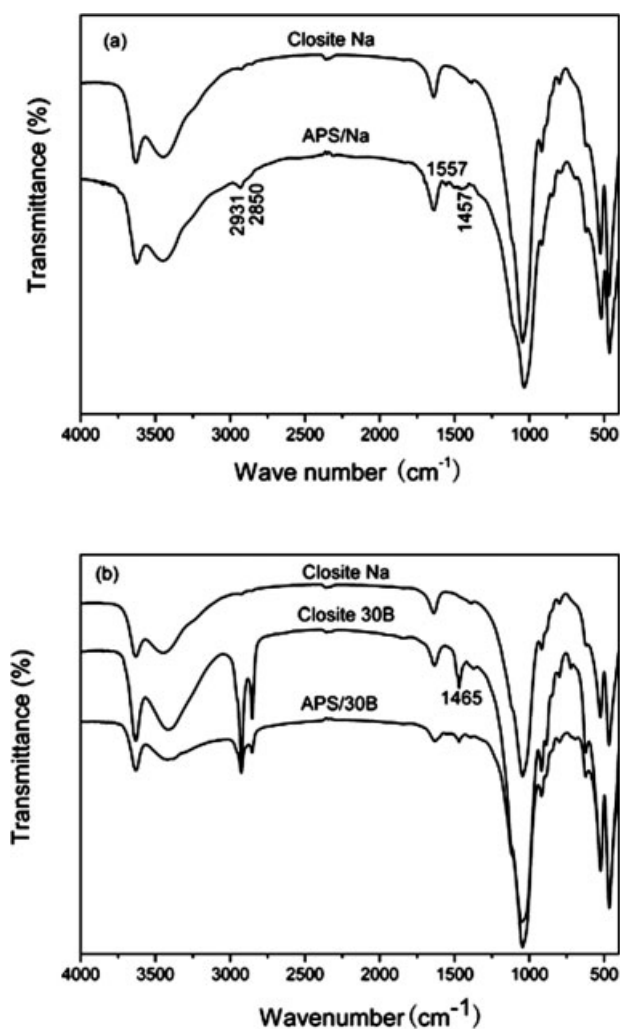


Figure 2 Infrared spectra of clays before and after organic modification.

surfactant in Closite 30B has two hydroxyl groups in the molecular chains. Therefore, the organosilane could react with both these hydroxyl groups and the Si—OH groups on the edge of silicate layers, which introduced one organosilane layer to enter into the clay galleries and mutual interlock with the alkyl ammonium chains, resulting in the increase of the *d*-spacing.

The FTIR spectra of clays with different treatments were shown in Figure 2. The characteristic vibration bands of various hydroxyl groups associated with octahedral cations, silicates, quartz, and water present in the Closite Na are exhibited in Figure 2(a). The peak at 3634 cm⁻¹ corresponds to the hydroxyl stretching that is bonded to the aluminum and magnesium in clay. The peaks at 3440 cm⁻¹ and 1638 cm⁻¹ are due to the —OH stretching and bending vibrations of the adsorbed water. The broad peak over the range from 1200 cm⁻¹ to 1000 cm⁻¹ with the peak maximum at 1035 cm⁻¹ is attributed to the

Si—O in plane stretching. The peak for Si—O bending vibration is observed at 529 cm⁻¹. The shoulder at 1113 cm⁻¹ shows Si—O out-of-plane stretching vibration. The bending vibrations of Al(Al)OH and Mg(Mg)OH are located at 916 cm⁻¹ and 800 cm⁻¹, respectively.²³ After modification with APS, new peaks at 2931 cm⁻¹ with a small shoulder at 2850 cm⁻¹ appeared in APS-Na, which are attributed to the asymmetric and symmetric stretching vibrations of the methylene groups. New peaks at 1557 cm⁻¹ with a broad shoulder at 1457 cm⁻¹ correspond to —NH₂ vibration. A small peak at 690 cm⁻¹ is because of the —CH out-of-plane deformation vibration.²⁴ These new peaks suggest that the APS reacted with the hydroxyl groups on the broken edges of the silicate layers or self-condense and form polysiloxane oligomers adsorbing on the silicate layers, which was observed by other research groups as well.²⁵ These peak intensities in APS-Na are very weak indicating a small loading of organosilane. This also indicates a low-reactive content of —OH groups on the sodium clay.

Strong vibration peaks at 2930 cm⁻¹ and 2847 cm⁻¹ for —CH stretching and at 1465 cm⁻¹ for —CH₂ bending in Closite 30B were observed in Figure 2(b), supporting the intercalation of alkyl ammonium ions between the silicate layers. The relative peak intensity (I_{3400}/I_{1035}) of Closite 30B is 1.23, which is much larger than that of APS/30B (0.35). This confirms that the hydroxyl groups of the intercalant reacted with APS through silylation reaction, resulting in the decrease of hydroxyl group content, i.e., the grafting of APS on Closite 30B was mainly formed through the reactions between the organosilane and hydroxyl groups in the hydrogenated tallow ammonium ions. The grafting of APS on Closite Na was produced by the reactions between the organosilane and Si—OH groups on the silicate edges.

Surface properties of the organoclays

Based on Fowkes' theory,²⁶ the surface-free energy of a solid (γ_s) includes two components as shown in eq. (2)

$$\gamma_s = \gamma_s^d + \gamma_s^p \quad (2)$$

in which γ_s^d is a dispersive component, attributed to London attraction. The γ_s^p is a specific (or polar) component, owing to all other types of polar interactions (such as hydrogen bonding and other weakly polar effects).

The surface free energy of the organoclays was measured by equilibrium contact angle method and determined based on the Owens-Wendt-Kaelble method¹⁵ as shown in eq. (3):

TABLE II
Surface Energy of Sodium Clay and Organoclays

Sample	θ_1 (water)	θ_2 (diiodomethane)	γ_s^d (mJ/m ²)	γ_s^p (mJ/m ²)	γ_s (mJ/m ²)
Closite Na	49.6	52	34.5	19.3	53.8
APS/Na	58.7	48.2	35.3	14.9	50.2
Closite30B	74.2	55.8	31.0	8.1	39.1
APS/30B	75.7	56.7	30.5	7.6	38.0

$$\frac{(1 + \cos \theta)\gamma_l}{2} = \sqrt{\gamma_s^d \gamma_l^d} + \sqrt{\gamma_s^p \gamma_l^p} \quad (3)$$

in which, θ is the contact angle of liquid on the solid, γ_l^d and γ_l^p are the dispersive and polar components of liquid's surface energy. The results are shown in Table II.

The surface free energy (γ_s) of Closite Na was reduced after APS modification, suggesting the existence of APS on the Closite Na surface and the Closite Na become more hydrophobic. The surface free energy of Closite 30B is much lower than that of Closite Na because of the absorption of ammonium tallo salt onto the clay surfaces. A further reduction in the surface-free energy for APS/30B, as compared with Closite 30B is mainly because of the grafting and absorption of the APS to/on the organoclay, which corresponds to the FTIR results (Fig. 2).

Thermal stability of organosilane modified clays

Figure 3 displays the TGA thermograms of various clays. The first weight loss below 100°C of the Closite Na is the loss of water molecules hydrating the inorganic cations and these physisorbed on the aluminosilicate surfaces. There was no further weight loss observed until the second weight loss of 5% between 500 and 700°C because of dehydroxylation of clay. However, a different TGA thermogram was demonstrated by the APS/Na clays. In addition to the weight losses around 100 and 600°C, a continuous weight loss of 10% in the temperature range of 100 ~ 600°C was displayed for APS/Na, representing the decomposition of the organosilanes absorbed and grafted on the silicate layers. Thermal decomposition of the ammonium surfactants in the organically modified clays was most likely responsible for the large drop in weight of 25% between 250 and 600°C for Closite 30B [Fig. 3(b)]. This mass loss was absent in the Na clay. About 20% weight loss was also observed in the thermogram for APS/30B at the same range of temperature because of the combined decomposition of ammonium ions and organosilanes.

DTG spectra of the various clays are also shown in Figure 3. In general, the exothermic peaks in the DTG involving weight loss, no weight change and weight gain are result from combustion, crystallization, and oxidation, respectively. Also, the endothermic peaks

involving weight loss indicate decomposition or dehydration. The endothermic peaks observed at 262, 407 and 577°C for APS/Na correspond to the physically adsorbed APS, the decomposition of the grafted APS, and the intercalated silane, respectively.²⁷ As shown in Figure 3(b), Closite 30B exhibits four DTG peaks in the temperature range of 200 ~ 600°C. The first weight loss at 278°C is attributed to the decomposition of the physically adsorbed ammonium ions. The following two overlapping peaks at 358 and 404°C are because of the decomposition of the intercalated ammonium ions. The decomposition peak at 576°C belongs to the dehydroxylation of the silicates. APS/30B showed similar DTG thermogram as APS/Na but higher weight loss because of the decomposition of

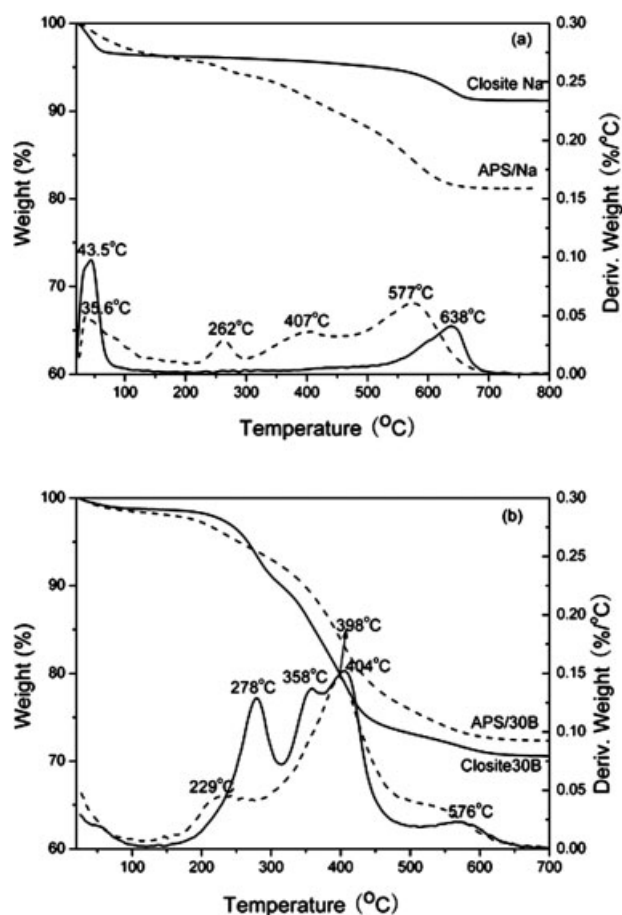


Figure 3 TGA curves of all kinds of clays before and after silylation.

TABLE III
TGA Data of Organoclays

Sample	T_5 (°C)	T_{max} (°C)	Weight loss at 700°C (%)
Closite Na	511	638	8.8
APS/Na	258	577	18.8
Closite30B	250	258	22.0
APS/30B	270	382	24.7

the ammonium surfactant. TGA results (Table III) also shows that the decomposition temperature at 5% weight loss (T_5) of APS/30B is 270°C which is 20°C higher than that of Closite 30B (250°C), i.e., the thermal stability of Closite 30B is improved by APS modification probably because of the formation of the condense product of organosilane as a coverage on the clay surface enhancing its thermal stability. It was found that the PBT/30B discolored severely from white to dark-gray during melt-compounding process, whereas the PBT/APS/30B did not change color after melt-compounding.

Morphology and properties of PBT/organoclay composites

To evaluate the effect of organosilane modification on the compatibility and thermal processing stability of organoclays, the Closite 30B with and without silane modification were melt-compounded with PBT. The morphology and dispersibility of the organoclays in PBT matrix are shown in Figure 4 and Figure 5 respectively. The characteristic (001) diffraction peak of Closite 30B was not be detected in the PBT/30B composites [Fig. 4(a)], which indicated that the Closite 30B lost its orderly layered structure and was exfoliated in the PBT matrix [Fig. 5(a)]. The carboxyl groups on PBT chains have strong interactions with the hydroxyl groups of the intercalant in Closite 30B, which makes it easier for PBT to intercalate and even exfoliate clay layers during melt-com-

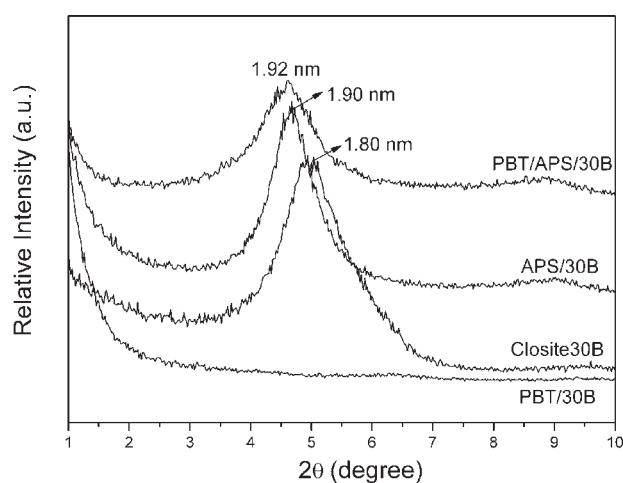
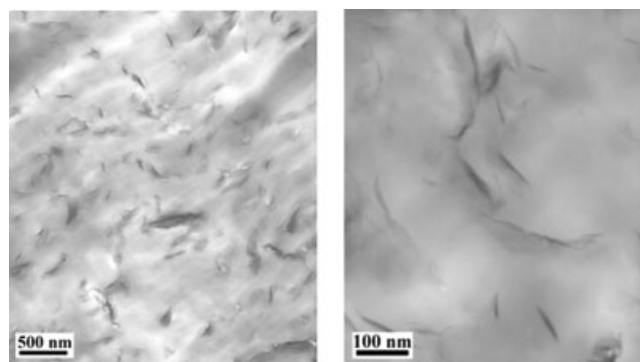
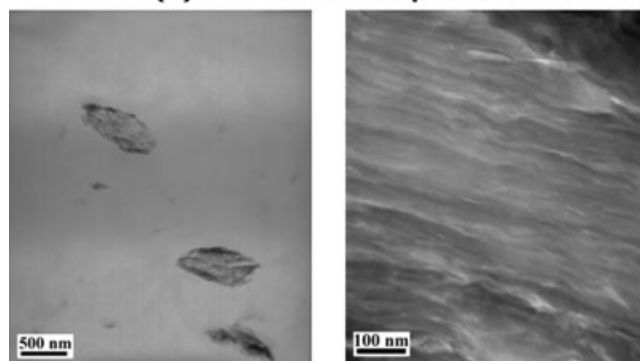


Figure 4 XRD patterns of PBT/organoclays composites.



(a) PBT/30B composites



(b) PBT/APS/30B composites

Figure 5 TEM pictures of PBT/organoclays composites.

pounding process. The basal spacing of APS/30B only showed a slight increase after melt-compounding with PBT, that is, the APS/30B still kept its original layered structures with a small expanded intergallery distance. It appears that the organosilane modification restricted the dispersion of Closite 30B in the PBT matrix. Besides the APS reacted with silanol groups on the broken edges and surface of clay, the condensation reactions of the APS can also form coverage on the clay surface and a linkage to bond adjacent clay layers altogether, which prevents the clay layers from peeling apart. Hence, the APS/30B clays were only dispersed as swollen elliptical particles in PBT matrix, as shown in Figure 5(b).

DSC results for the PBT/organoclay composites are given in Table IV and Figure 6(a,b). The degree of crystallinity X_c of the three samples was calculated according to eq. (1) on the basis of the data in Figure 6(a). All three samples exhibit two melting peaks in the DSC thermograms when heating at the rate of 10°C/min [Fig. 6(b)]. The double melting endotherms are because of the melting and recrystallization process during the DSC scan.²⁸ The glass transition temperature (T_g), crystallization temperature (T_c), melting temperature (T_m), and the supercooling degree ΔT ($\Delta T = T_m - T_c$) did not show

TABLE IV
DSC Results of PBT/Organoclay Composites

Sample	T_c (°C)	T_g (°C)	T_{m1} (°C)	T_{m2} (°C)	ΔT (°C)	ΔH_m (J/g)	X_c (%)
PBT	194.8	48.4	217.9	226.6	31.8	43.5	31.6
PBT/Closite30B	194.7	48.5	217.0	226.3	31.6	59.1	42.9
PBT/APS/30B	194.9	48.7	217.3	226.8	32.0	46.1	33.5

much difference among the samples as shown in Table IV. However, the degree of crystallinity of PBT/30B and PBT/APS/30B composites is higher than that of pure PBT, in particular, a significant increase of the crystallinity of 12% was observed for PBT/30B composite compared with PBT matrix. This indicates that the Closite 30B and APS/30B act as heterogeneous nucleation sites for PBT crystallization and enhance the degree of crystallinity. The Closite 30B disperses uniformly in nanoscale in PBT matrix providing more silicate layers as the heterophase nucleus.

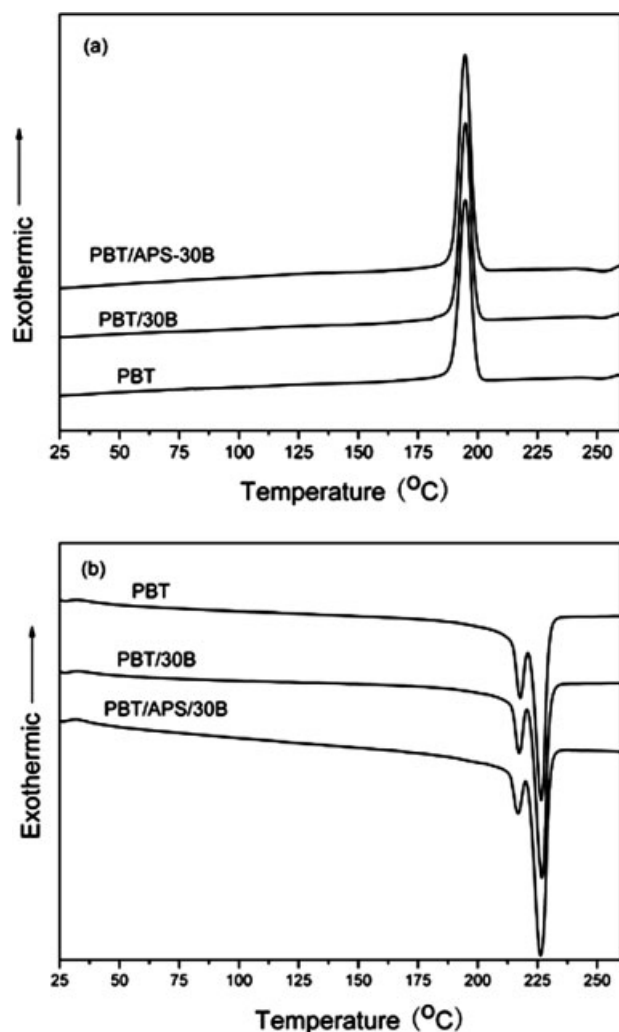


Figure 6 DSC thermograms of PBT and PBT/organoclay composites.

CONCLUSIONS

Sodium montmorillonite clay (Closite Na) and quaternary ammonium tallow ions intercalated clay (Closite 30B) were modified with APS via a silylation reaction. The basal spacing of Closite Na increased to ~ 0.4 nm after APS modification indicating that one layer of APS was intercalated into the clay galleries. A small increase of the basal spacing of Closite 30B was found after APS treatment, which was probably because of the grafting reaction between the silane groups of APS with the hydroxyl groups on the ammonium tallow ion chains of Closite 30B.

Closite 30B was exfoliated disorderly in PBT matrix after melt-compounding due to a strong interaction between the carboxyl groups of PBT and the hydroxyl groups on the ammonium tallow ion chains of Closite 30B. APS/30B dispersed as swollen elliptical particles in the PBT with slightly intercalation. Such poorly dispersible behavior was mainly attributed to the crosslink reactions between APS and silanol groups on the edge of clay sheets. The APS modification improved the thermal stability of the Closite 30B but played a small role in expanding clay intergalleries and facilitating the clay dispersion. A larger heterogeneous nucleation effect resulted from a better dispersion of Closite 30B in the PBT led to a significant increase of the degree of crystallinity of PBT/30B composite.

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