Effect of Reactivity of Organics-Modified Montmorillonite on the Thermal and Mechanical Properties of Montmorillonite/Polyimide Nanocomposites

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Montmorillonite/polyimide (3,3′,4,4′-benzophenone tetracarboxylic dianhydride-4,4′-oxy-dianiline, BTDA-ODA) nanocomposites displaying different morphological, thermal, and mechanical characteristics were synthesized by involving mono-, di-, and trifunctional group swelling-agent-modified montmorillonite and poly(amic acid). It was found that the dispersion of silicate layers in BTDA-ODA shifted from intercalated to exfoliated structures when the number of functional groups of the swelling agent increased to three as evidenced from X-ray diffraction and transmission electron microscopy studies. The improved morphology of the nanocomposites resulted in their enhanced mechanical and thermal properties. In particular, a 70% increase in Young's modulus, a 50% increase in the maximum stress, and a 30% reduction in the coefficients of thermal expansion for the case of BTDA-ODA nanocomposites containing 5 wt % trifunctional group swelling-agent-modified montmorillonite as compared to that of pure BTDA-ODA.

Introduction

Montmorillonite/polymer nanocomposites[1–16] have gained considerable interest in recent years owing to their enhanced stiffness, strength and barrier properties by containing only a few weight percentages of organics modified montmorillonite dispersed in the nanometer scale in the polymer matrix. Nature montmorillonite consisted of layered silicates carrying negative charges that formed ionic bonds with metal cations in the intergallery of the layered silicates. These silicates also contained dangling hydroxyl end groups on their surfaces.[17–20] The existence of ionic bonds and the ability of forming hydrogen-bonding with water made montmorillonite highly hydrophilic, and thus pure montmorillonite was difficult to be mixed with hydrophobic polymers. To improve the affinity of montmorillonite toward organic materials, it was necessary to modify montmorillinite by replacing the metal cations in the intergallery of silicates with various organic cation molecules. The modification serves two purposes. First, the space between the layered silicates increased and became more uniform after the intercalation by the organic cation molecule. Second, these small organic molecules bonded to silicates made montmorillonite more miscible with larger-sized polymer molecules. Hence, polymer molecules were allowed to enter the enlarged intergallery of silicates for further intercalation or exfoliation. The modification of montmorillonite is a prerequisite for creating the desired morphology of nanocomposites and consequently resulting in enhanced properties in polymer nanocomposites. These small organic molecules are termed swelling agents in this study.

The approach in several studies adopted swelling agents of different sizes suitable for intercalating the layered silicates from the viewpoint of a maximizing of intercalation without involving reactions of the swelling agents with the polymer matrix.[4–12] In our previous study,[21–24] we used a di-functional group swelling agent

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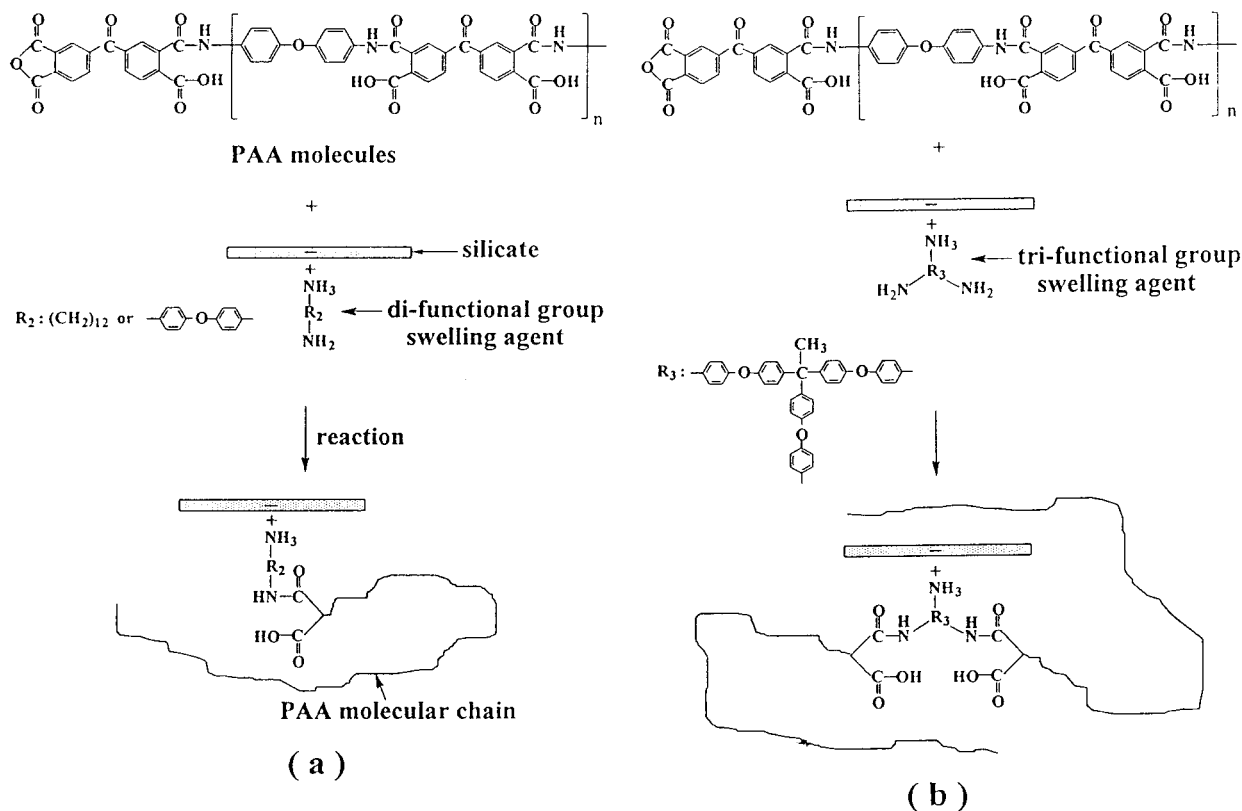(16) Giannelis, E. P. *Adv. Mater.* **1996**, *8*, 29.

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PAA molecules

+

silicate

di-functional group swelling agent

$R_2 : (CH_2)_{12}$ or

reaction

PAA molecular chain

(a)

+

tri-functional group swelling agent

$R_3 :$

(b)

Figure 1. Schematic drawings of (a) difunctional group ($-NH_2$) swelling agent and (b) trifunctional group swelling agent for intercalating layered silicates and reacting with poly(amic acid) molecules.

for modifying montmorillonite. In the present study, we would like to systematically investigate the effect of reactivity of the swelling-agent-modified silicates on the morphology and the physical properties of amorphous polyimide by using one-, two-, and trifunctional group swelling agents. The schematic drawings of the reaction of multiple-functional-group-swelling-agent modified silicates with the poly(amic acid) are presented in Figure 1. In Figure 1 (a), in the di-functional swelling agent case, one functional group ($-NH_2$) of the swelling agent formed an ionic bond with the negatively charged silicates, and the other functional group can react with poly(amic acid) containing dianhydride end groups. The resultant structure was that the modified silicate was situated at the end of the poly(amic acid) molecular chain. When the number of functional groups of the swelling agent increased to three, there are two functional groups available for reaction with two poly(amic acid) molecules, and the silicates could be situated in the middle of a longer poly(amic acid) molecule as shown in Figure 1 (b), resulting in a greater interaction force in achieving either intercalation or exfoliation of these layered silicates. The various swelling agents used in the present study are given in Table 1.

Experimental Section

Materials. Source clay Swy-2 (Wyoming Na$^+$-montmorillonite) was obtained from the Clay Minerals Depository at the University of Missouri, Columbia, MO. 1,1,1-Tri(4-hydroxy-

Table 1. Swelling Agents of Different Chemical Structures Used in Modifying Montmorillonite in This Study

Swelling Agent	Characteristic	Abbreviation
laurylamine $NH_2(CH_2)_{11}CH_3$	one functional group (aliphatic)	12CH$_3$
1,12-diaminododecane $NH_2(CH_2)_{12}NH_2$	di-functional group (aliphatic)	12NH$_2$
4,4′-oxydianiline $H_2N\!-\!\bigcirc\!-\!O\!-\!\bigcirc\!-\!NH_2$	di-functional group (aromatic)	ODA
4-(4-1, 1-di[4-(4-aminophenoxy)phenyl]ethylphenoxy)aniline[a]	tri-functional group (aromatic)	tri(NH$_2$)

[a] Synthesized in our lab.

phenyl)ethane, 1-fluoro-4-nitrobenzene, and tetrahydrofuran (THF) were obtained from Aldrich. Laurylamine (12CH$_3$), 1,-12-diaminododecane (12NH$_2$), 4,4′-oxydianiline (ODA), and

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3,3′,4,4′-benzophenone tetracarboxylic dianhydride (BTDA) were purchased from TCI in Tokyo, Japan. *N,N*-Dimethylacetamide (DMAc) was obtained from Tedia in Ohio.

Synthesis of 4-[4-[1,1-Di[4-(4-aminophenoxy)phenyl]-ethyl]phenoxy]aniline and Swelling-agent-modified Montmorillonite/PAA. 1,1,1-Tri(4-hydroxyphenyl)ethane (10 g), 13.9 g of 1-fluoro-4-nitrobenzene, 13.5 g of K_2CO_3, and 100 mL of DMF were put into a 500 mL three-neck flask. The mixture was stirred under nitrogen purge at room temperature for 24 h and then was poured into deionized water. After the precipitates was filtered and dried, 21.5 g of 1,1-di[4-(4-(nitrophenoxy)phenyl]-4-(4-nitrophenoxy)benzene [tri(NO_2)] was obtained. Then Pd/C (2.1 g) was added to a solution of tri-(NO_2) (21 g) in THF (100 mL), and the mixture was stirred vigorously at room temperature under hydrogen for 24 h. The 4-[4-[1,1-di[4-(4-aminophenoxy)phenyl]ethyl]phenoxy]aniline [tri(NH_2)] was obtained and then was filtered and dried. Swy-2 Na^+-montmorillonite having a cationic exchange capacity of 76.4 mequiv/100 g was screened with a sieve of 325 mesh to remove impurities. The detailed procedure for modifying montmorillonite with various swelling agents has been described elsewhere.[22] These montmorillonites (Mont) modified by $12CH_3$, $12NH_2$, ODA, and tri(NH_2) were termed $12CH_3$-Mont, $12NH_2$-Mont, ODA-Mont, and tri(NH_2)-Mont, respectively. Poly(amic acid) (PAA) was synthesized by reacting ODA with BTDA in DMAc as described elsewhere.[23] Swelling-agent-modified montmorillonite in PAA (2 and 5 wt %) was obtained by first mixing the proper weight of swelling-agent-modified montmorillonite in DMAc for 12 h and then adding the suspension to PAA/DMAc to form Mont/PAA in DMAc. The final solid content of PAA in DMAc was 16% . Imidization of Mont/PAA was carried out by putting the samples in an air-circulation oven at 100, 150, 200, and 300 °C for 1 h, respectively, and then at 400 °C for 5 min.

Characterization. The intrinsic viscosity of recovered PAA from Mont/PAA of different compositions was measured with a Ubbelohde capillary viscometers at 30 °C. The reverse ion-exchange reaction[25] was performed by putting 2 g of synthesized Mont/PAA in 30 mL of 5% LiCl/DMAc solution with stirring for 1 week at room temperature. The resultant solution was then centrifuged at 3000 rpm for 5 min to obtain the recovered PAA. X-ray diffraction study was carried out on a Mac Science M18 X-ray diffractometer (50 kV, 250 mA) with copper target and Ni filter at a scanning rate of 4 deg/min. The preparation of the samples for transmission electron microscopy (TEM) observation was described elsewhere.[23] The type of TEM used is JEOL-2000 FX. The thermal gravimetric and the thermal transition analyses of Mont/BTDA-ODA films were carried out with a Du Pont TGA 2950 and with a Du Pont DSC 2910 at a heating rate of 20 °C/min, respectively. The in-plane coefficients of thermal expansion (CTE) measurement of the samples was carried out by using a Du Pont 2940 probe at a heating rate of 5 °C/min and by taking average values between 50 and 250 °C. The tensile properties of Mont/BTDA-ODA films were measured according to the specifications of ASTM D882-88 at a crosshead speed of 2 mm/min with an Instron tester.

Results and Discussion

The wide-angle X-ray diffraction (WAXD) curves of swelling-agent-modified montmorillonite are presented in Figure 2. In Figure 2, a broad diffraction peak around $2\theta = 7.42°$ was displayed by pure montmorillonite, equaling a *d* spacing of 1.2 nm for the layered silicates in montmorillonite. For the $12CH_3$-Mont, a strong X-ray diffraction peak at $2\theta = 5.48°$ resulted from the diffraction of the (0 0 1) crystal surface of layered silicates, indicating that layered silicates have been intercalated by $12CH_3$ molecules to a *d* spacing of 1.6 nm. Strong

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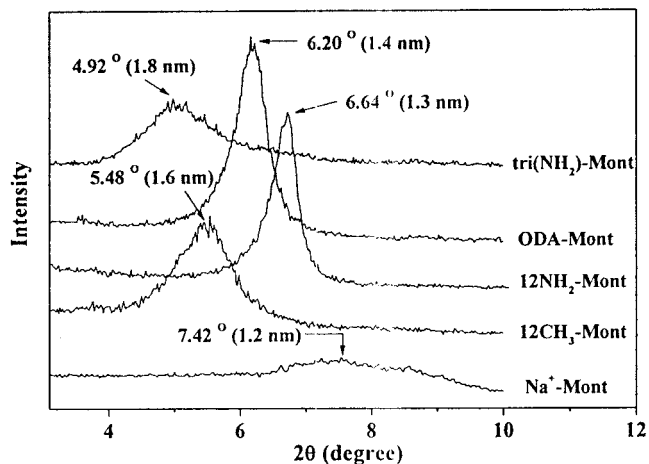

Figure 2. X-ray diffraction curves of pure montmorillonite and of swelling-agent-modified montmorillonite.

diffraction peaks at $2\theta = 6.64°$ and at $2\theta = 6.20°$ with corresponding *d* spacing of 1.3 and 1.4 nm were displayed in the case of $12NH_2$-Mont and ODA-Mont, respectively. For the tri(NH_2)-Mont case, a medium diffraction peak at $2\theta = 4.92°$ equaling a *d* spacing of 1.8 nm was observed. This indicated that the *d* spacing of the layered silicates in these swelling-agent-modified montmorillonite increased with the size of these swelling agents. The WAXD curves of BTDA-ODA films containing various 5 wt % swelling-agent-modified montmorillonite did not display any X-ray diffraction peak at $2\theta = 3\sim10°$. This implied that the *d* spacing between the layered silicates had been either intercalated to a distance of more than 3 nm or exfoliated in BTDA-ODA.

Direct evidence of this nanometer-scale dispersion of intercalated montmorillonite can be found in the transmission electron microscopy examination of the cross section of Mont/BTDA-ODA. Three cases of BTDA-ODA that containing 2 wt % modified montmorillonite but with different swelling agents were chosen for comparison, and their TEM micrographs are shown in Figure 3. In Figure 3a, in the one-functional-group swelling agent case, $12CH_3$-Mont/BTDA-ODA, there were intercalated silicate domains having a collection of 5−10 nearly parallel layered silicates with basal spacing about 3−6 nm. The thickness of the silicate layers (dark lines) was about 1.0 nm. For the aliphatic difunctional group swelling agent case, $12NH_2$-Mont/BTDA-ODA, the space between layered silicates was about 4−8 nm as shown in Figure 3b. In Figure 3c, for the aromatic trifunctional group swelling agent case, tri(NH_2)-Mont/BTDA-ODA, the space between layered silicates was between 6 and 12 nm, and the distribution of intercalated silicates became more homogeneous than that in the previous two cases, with a small portion of silicates exhibiting exfoliated structure. Hence, the extent of the dispersion of the silicates and the space between the silicates in BTDA-ODA films increased with the number of functional groups (or the reactivity) of the swelling agent. The difference in the morphology of the Mont/BTDA-ODA nanocomposites formed by swelling agents with different number of functional groups quite possibly affects their thermal and mechanical properties.

The thermal properties of Mont/BTDA-ODA nanocomposites at different compositions are given in Table

Coating Direction

$\longrightarrow$

(a)

(b)

(c)

30nm
⊢___⊣
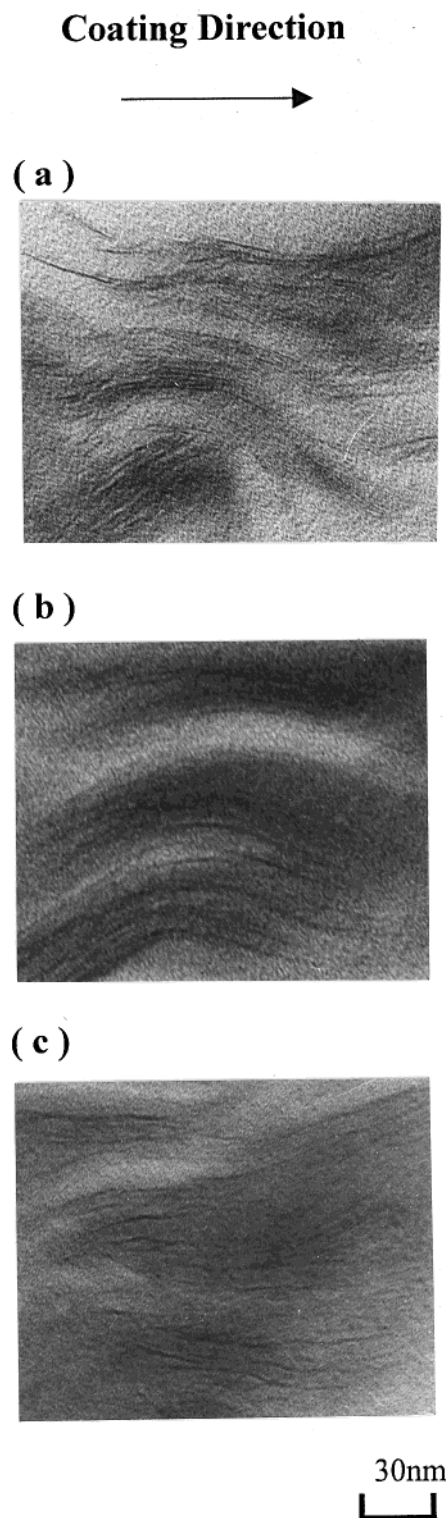
Figure 3. Transmission electron microscopy micrographs of the cross-section view of Mont/BTDA-ODA nanocomposite films containing 2 wt % of (a) 12CH₃-Mont, (b) 12NH₂-Mont, and (c) tri(NH₂)-Mont.

2. In Table 2, at 5 wt % montmorillonite concentration, the thermal degradation temperatures of 12NH₂-Mont/BTDA-ODA, ODA-Mont/BTDA-ODA, and tri(NH₂)-Mont/BTDA-ODA are 10, 18, and 24 °C higher than that of pure BTDA-ODA, respectively. Therefore, the extent of the thermal stability enhancement of BTDA-ODA by layered silicates also increased slightly with the number of functional groups of the swelling agents. The glass

Table 2. Thermal Properties of Mont/BTDA-ODA Nanocomposites and Intrinsic Viscosity of Recovered Poly(amic Acid) at Different Compositions

	contents of montrillonite (wt %)	decomposition temp[a] (%)	T_g (°C)	CTE[b] (ppm/°C)	intrinsic viscosity of recovered poly(amic acid) (dL/g)
pure BTDA-ODA	0	583	274.9	43.9	0.929
12CH₃Mont/ BTDA -ODA	2	594	274.4	38.2	0.925
	5	593	273.5	35.4	0.938
12NH₂Mont/ BTDA -ODA	2	593	275.7	36.3	0.957
	5	595	274.2	34.0	0.976
ODA-Mont/ BTDA-ODA	2	595	276.1	34.2	1.011
	5	601	280.3	31.5	1.032
tri(NH₂)-Mont/ BTDA-ODA	2	598	277.5	33.5	1.034
	5	607	281.8	29.3	1.056

[a] Temperature at 5% weight loss. [b] Averaged between 50 and 250 °C.

transition temperature (T_g) of BTDA-ODA films containing 5 wt % ODA-Mont and 5 wt % tri(NH₂)-Mont increased slightly as compared to that of pure BTDA-ODA. This small increase can be attributed to the higher molecular weight of BTDA-ODA in the ODA-Mont/BTDA-ODA and tri(NH₂)-Mont/BTDA-ODA cases and the restriction on the main-chain motion of BTDA-ODA molecules by these layered silicates. To verify whether the molecular weight of PPA in the nanocomposites increased due to the reaction with the swelling agent, a reverse ion exchange of Mont/PAA was carried out for getting rid of silicates. The PAA obtained after the reverse ion exchange was defined as "recovered" PAA. The intrinsic viscosity of recovered PAA is given in Table 2, and it was higher than that of pure PAA. Specifically, the intrinsic viscosity of recovered PAA from containing 5 wt % tri(NH₂)-Mont was about 14% higher than that of pure PAA (1.056 vs 0.929 dL/g), indicating that the molecular weight of recovered PAA was larger than that of pure PAA. This supported our argument that PAA has reacted with the swelling agent in montmorillonite. Moreover, in Table 2, the in-plane coefficients of thermal expansion (CTE) for Mont/BTDA-ODA decreased with either the increasing number of functional groups of the swelling agent or the increasing concentration of montmorillonite, with the largest reduction of 33% in the case of BTDA-ODA containing 5 wt % tri(NH₂)-Mont as compared to that of pure BTDA-ODA.

The tensile mechanical properties of these nanocomposites are given in Table 3. In Table 3, the Young's moduli of BTDA-ODA containing either 2 or 5 wt % 12CH₃-Mont, 12NH₂-Mont, ODA-Mont, and tri(NH₂)-Mont were much higher than that of pure BTDA-ODA, with the largest increase of 70% in the case of BTDA-ODA having 5 wt % tri(NH₂)-Mont (3.85 vs 2.28 GPa). Controlled experiments involving measuring the thermal and mechanical properties of blends of swelling agent and BTDA-ODA at the compositions corresponding to that in the nanocomposites were carried out to address the observed changes due to the possible cross-linking in the continuous polymer phase. Swelling agents 12NH₂, ODA. and tri(NH₂) were chosen because

Table 3. Mechanical Properties of Mont/BTDA-ODA Nanocomposites at Different Compositions

	contents of mont. (wt %)	modulus (GPa)	max. stress (MPa)	elongation (%)
pure BTDA-ODA	0	2.28	78.30	6.89
12CH$_3$Mont/BTDA-ODA	2	2.77	72.24	7.04
	5	2.68	59.18	3.42
12NH$_2$Mont/BTDA-ODA	2	2.81	78.80	5.30
	5	2.73	67.70	4.41
ODA-Mont/BTDA-ODA	2	2.97	82.55	9.00
	5	3.33	81.68	7.83
tri(NH$_2$)-Mont/BTDA-ODA	2	2.99	87.81	6.90
	5	3.85	120.43	7.27

Table 4. Thermal and Mechanical Properties of Blends of Swelling Agent and BTDA-ODA at Compositions Corresponded to the Cases of Modified-Mont/BTDA-ODA Nanocomposites

	contents of swelling agent (wt %)[a]	degradation temp (°C)	modulus (GPa)	max. stress (MPa)
pure BTDA-ODA	0	583	2.28	78.30
12NH$_2$/BTDA-ODA	1	578	2.18	64.26
ODA/BTDA-ODA	1	581	2.20	66.46
tri(NH$_2$)/BTDA-ODA	1	584	2.36	80.20

[a] The actual weight percentage of swelling agent present in the case of BTDA-ODA containing 5 wt % of swelling-agent-modified montmorillonite.

they are the most reactive ones. The thermal and mechanical properties of blends of BTDA-ODA/12NH$_2$, BTDA-ODA/ODA, and BTDA-ODA/tri(NH$_2$) are given in Table 4. As shown in Table 4, only small increases in the thermal and mechanical properties of BTDA-ODA occurred due to the presence of the trifunctional group swelling agent tri(NH$_2$). Therefore, the increase in the Young's modulus of Mont/BTDA-ODA nanocomposites could mainly be attributed to the stiffness of the silicate, but the extent of increase depends on the bonding between layered silicates and BTDA-ODA molecules or the reactivity of the swelling agent. Specifically, the greater the number of functional groups in the swelling agent, the higher the modulus of Mont/BTDA-ODA nanocomposites becomes. Additionally, swelling agents of aromatic structure performed better than swelling agent of aliphatic structure in enhancing the modulus of the Mont/BTDA-ODA nanocomposites. The maximum stress of BTDA-ODA containing 2 or 5 wt % 12CH$_3$-Mont or BTDA-ODA containing 2 or 5 wt % 12NH$_2$-Mont was lower than that of pure BTDA-ODA, probably

due to the low reactivity and the soft structure of 12CH$_3$ or 12NH$_2$ molecules. However, the maximum stress of BTDA-ODA containing 2 or 5 wt % ODA-Mont or BTDA-ODA containing 2 or 5 wt % tri(NH$_2$)-Mont was higher than that of pure BTDA-ODA. A rather large increase of 50% in the maximum stress was found for BTDA-ODA having 5 wt % tri(NH$_2$)-Mont as compared to that of pure BTDA-ODA. The elongation-for-break of Mont/BTDA-ODA for montmorillonite modified with aliphatic-series swelling agent decreased slightly as demonstrated in the cases of 12CH$_3$-Mont/BTDA-ODA and 12NH$_2$-Mont/BTDA-ODA in Table 3. For montmorillonite modified with aromatic-series swelling agent, the elongation-for-break of Mont/BTDA-ODA increased slightly as shown in the cases of ODA-Mont/BTDA-ODA and tri-(NH$_2$)-Mont/BTDA-ODA.

Concluding Remarks

Montmorillonite/polyimide (BTDA-ODA) nanocomposites were synthesized by use of reactive organic molecule-modified montmorillonite and poly(amic acid). The reactive organic molecules (swelling agents) containing multiple functional groups can be controlled in such a way that one of the functional groups formed an ionic bond with negatively charged silicates, and the rest of the functional groups in the swelling agent are available for further reaction with poly(amic acid) containing dianhydride end groups. In particular, if the total number of functional groups of the organic molecule (swelling agent) is equal to or more than three, it is quite possible that the modified silicates can react with two or more poly(amic acid) molecules, which generated much greater force for attaining an exfoliation of layered silicates than in the nonreactive swelling agent case. Hence, the improved morphology of montmorillonite/polyimide due to the intensive chemical bond between the swelling-agent-modified montmorillonite and the polymer molecules resulted in dramatically enhanced thermal and mechanical properties.

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