

Thermally and Mechanically Enhanced Clay/Polyimide Nanocomposite via Reactive Organoclay

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High modulus and thermally stable clay/polyimide (pyromellitic dianhydride–4,4'-oxydianiline, PMDA–ODA) nanocomposites were synthesized from reactive organoclay and poly(amic acid). The reactive organoclay was formed by using *p*-phenylenediamine as a swelling agent for silicate layers of montmorillonite. The swelling process was first carried out through ion exchange between the onium of one amine end group of *p*-phenylenediamine and the sodium ion in montmorillonite. The other amine end group of *p*-phenylenediamine reacted with the dianhydride end group of poly(amic acid), producing an irreversible swelling. This irreversible swelling resulted in a nanostructured material containing intercalated nanometer silicate layers dispersed in PMDA–ODA as confirmed by both X-ray and transmission electron microscopy. The glass transition temperature and the thermal decomposition temperatures of this type of clay/PMDA–ODA are higher than that of pure PMDA–ODA. A 2.5-fold increase in the modulus of clay/PMDA–ODA film was obtained as compared to that of pure PMDA–ODA film. Both the maximum stress and the elongation-for-break of these clay/PMDA–ODA nanocomposites increased with the amount of organoclay. The maximum reduction in out-of-plane coefficient of thermal expansion of this type clay/PMDA–ODA was 50% as compared to that of pure PMDA–ODA.

Introduction

There has been considerable interest in the formation of clay/polymer nanocomposites in recent years due to the unique combination of advantageous properties of each component.^{1–3} The clay consisted of anionically charged layers of aluminum/magnesium silicates and small cations such as sodium or potassium located in silicate interlayer galleries.^{4–5} The basic idea for producing these nanocomposites was to render these silicate layers organophilic by first exchanging the interlayer cations with organic cation molecules and also swelling the inorganic lattice of clay in the presence of a polar solvent. Then, the enlarged interlayer spacing allowed polymer molecules to enter and to intercalate silicate layers. Due to the size of the polymer molecules, the interlayer distance of silicate can be increased to such an extent that exfoliated silicate layers in nanometer dimension might appear and be dispersed in the polymer matrix. These clay/polymer nanocomposites displayed unusual properties.

Since the development of clay/polyamide nanocomposite by Toyota's research group^{6–8} in 1990, a number

of clay/polymer nanocomposites have been investigated. In particular, clay/polyimide nanocomposites have also been developed by Yano^{9,10} and Lan et al.¹¹ from poly(amic acid) and montmorillonite. Their research had demonstrated 12-aminododecanoic and dodecylamine as effective swelling agents for montmorillonite for forming clay/polyimide nanocomposites, and they found that the incorporation of low concentrations of silicate sheets of montmorillonite lowered the thermal expansion and the gas permeation properties of polyimide films. In their approaches, the swelling agents, 12-aminododecanoic and dodecylamine, are basically nonreactive with the poly(amic acid) and remained in the clay/polyimide nanocomposites in a form of low molecular weight compound after imidization. This will have a negative impact on the thermal and the mechanical properties of clay/polyimide nanocomposites. In this study, a swelling agent that contains two amine functional groups was chosen. After converting one functional group of the swelling agent into a cation, this cation (functional group) can form an ionic bond with the negatively charged silicate layers, and the clay was intercalated by this swelling agent. The other functional group of the swelling agent can react with poly(amic acid) when poly(amic acid) molecules diffused into the

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(1) Theng, B. K. G. *The Chemistry of Clay-Organic Reactions*, Adam Hilger: Bristol, 1974.

(2) Ruiz-Hitzky, E. *Adv. Mater.* **1993**, *5*, 334.

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

(4) Wu, J.; Lerner, M. M. *Chem. Mater.* **1993**, *5*, 835.

(5) Ogawa, M.; Takizawa, Y. *Chem. Mater.* **1999**, *11*, 30.

(6) Usuki, A.; Kawasumi, M.; Kojima, Y.; Okada, A.; Kurauchi, T.; Kamigaito, O. *J. Mater. Res.* **1993**, *8*, 1174.

(7) Usuki, A.; Kojima, Y.; Kawasumi, M.; Okada, A.; Fukushima, Y.; Kurauchi, T.; Kamigaito, O. *J. Mater. Res.* **1993**, *8*, 1179.

(8) Kojima, Y.; Usuki, A.; Kawasumi, M.; Okada, A.; Fukushima, Y.; Kurauchi, T.; Kamigaito, O. *J. Mater. Res.* **1993**, *8*, 1185.

(9) Yano, K.; Usuki, A.; Okada, A.; Kurauchi, T.; Kamigaito, O. *J. Polym. Sci., Part A: Polym. Chem.* **1993**, *31*, 2493.

(10) Yano, K.; Usuki, A.; Okada, A. *J. Polym. Sci., Part A: Polym. Chem.* **1997**, *35*, 2289.

(11) Lan, T.; Kaviratna, P. D.; Pinnavaia, T. *J. Chem. Mater.* **1994**, *6*, 573.

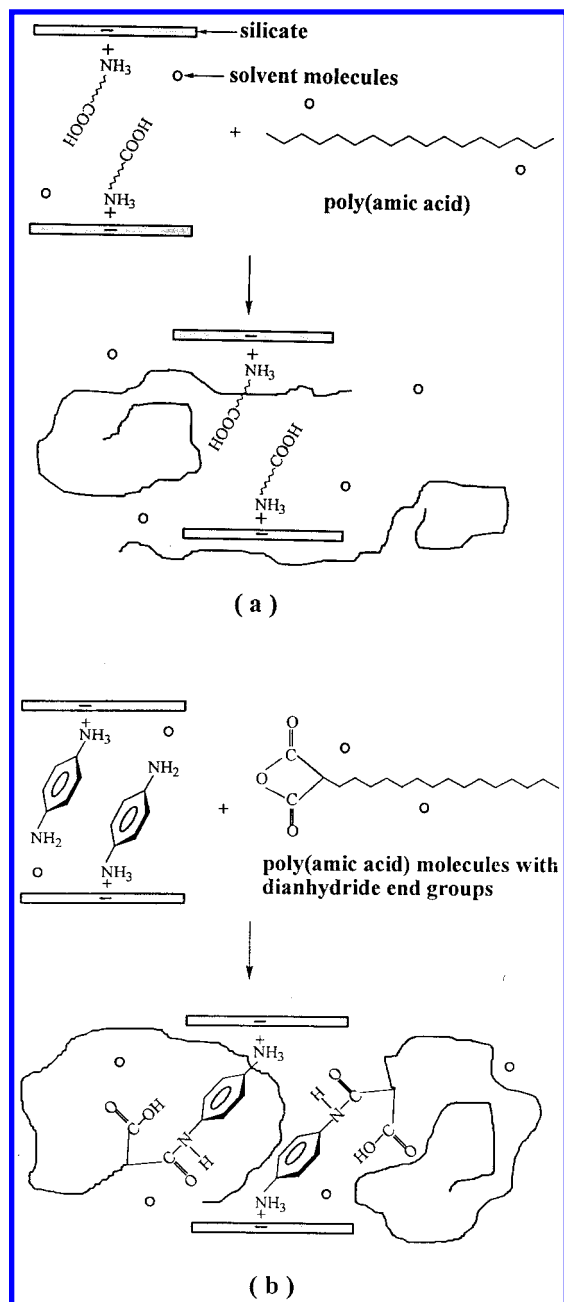


Figure 1. Schematic drawing of montmorillonite intercalated by poly(amic acid) and (a) nonreactive swelling agent containing one functional group NH_3^+ (reversible) and (b) reactive swelling agent having double functional groups NH_3^+ and NH_2 (irreversible).

space between the silicate layers of the montmorillonite. In this way, the swelling effect becomes more permanent due to the large poly(amic acid) molecules connected to the swelling agent. Moreover, thermally more stable and mechanically stronger nanocomposites are the result. The difference in these two ideas is illustrated in Figure 1a,b. In Figure 1a, one end group NH_3^+ replaced the original Na^+ and formed an ionic bond with the silicate layers, while the other end group COOH or CH_3 remains in its original state when the poly(amic acid) molecule entered or left the silicate layers gallery (reversible process). However, when the swelling agent having double NH_2 end groups was used, one end group NH_3^+ still formed an ionic bond with the silicate layers, but the other end group NH_2 of the swelling agent can react

with the dianhydride end group in poly(amic acid), as shown in Figure 1b. Therefore, the poly(amic acid) molecules will remain in silicate layers gallery. This makes the swelling an irreversible process.

With this approach in our laboratory, we have found a reduction of the activation energy for the imidization poly(amic acid) in the presence of organoclay dispersed on the nanometer scale.¹² The objective of this study was to further investigate the thermal, dynamic, and mechanical properties of this type of clay/polyimide nanocomposites.

Experimental Section

Source clay, Swy-2 (Wyoming Na^+ -montmorillonite), was obtained from the Clay Minerals Depository at the University of Missouri, Columbia, MO. *p*-Phenylenediamine was obtained from Janssen (Geel, Belgium). By screening Swy-2 Na^+ -montmorillonite with a 325-mesh sieve to remove impurities, one obtained a clay having a cationic exchange capacity of 76.4 mequiv/100 g. Ten grams of the screened montmorillonite was gradually added to a previously prepared solution of *p*-phenylenediamine (1.08 g dissolved in 1000 mL of 0.01 N HCl) solution and was vigorously stirred for 3 h at 60 °C. After the treatment, the montmorillonite suspension was repeatedly washed with deionized water. The filtrate was titrated with 0.1 N AgNO_3 until there was no AgCl precipitates to ensure a complete removal of chloride ions. Then, the filter cake was placed in a vacuum oven at 80 °C for 12 h of drying. The dried cake was ground and screened with a 325-mesh sieve. The powder obtained was termed organoclay.

Pyromellitic dianhydride (PMDA) was obtained from Chriskev. 4,4'-Oxydianiline was purchased from TCI (Tokyo, Japan). *N,N*-Dimethylacetamide was obtained from Tedia. Poly(amic acid) (PAA) was synthesized by putting 0.015 mol of 4,4'-oxydianiline (ODA) into a three-neck flask containing 32.92 g of *N,N*-dimethylacetamide (DMAc) under nitrogen purge at 25 °C. After ODA was completely dissolved in DMAc, 0.0151 mol of pyromellitic dianhydride (PMDA), which was divided into three batches, was added to the flask batch-by-batch with a time interval of 30 min between batches. After all the PMDA was dissolved in DMAc, the mixtures in the flask were stirred for 1 h, and a viscous poly(amic acid) solution was obtained. Different concentrations of organoclay in DMAc were prepared by putting 0.063, 0.125, 0.188, 0.314, 0.439, and 0.627 g of organoclay in 17.83 g DMAc, respectively, and by mixing each of them for 12 h. These organoclay suspensions were then mixed with the poly(amic acid) to obtain organoclay/poly(amic acid) in DMAc. The final solid content of poly(amic acid) in DMAc is 11%.

The organoclay/PMDA-ODA nanocomposite films were prepared by two different methods. The first method was spin-coating organoclay/poly(amic acid) (PAA) at 5000 rpm on glass slides. The second method was applying organoclay/PAA on glass slides with a doctor blade. These glass slides containing organoclay/PAA were put in a vacuum oven at 30 °C for 48 h before the imidization step. Imidization of organoclay/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 to ensure a complete imidization.

X-ray diffraction study of the samples was carried out by Mac Science M18 X-ray diffractometer (50 kV, 250 mA) with copper target and Ni filter at a scanning rate of 4°/min. The samples for transmission electron microscopy (TEM) study was first prepared by putting organoclay/PMDA-ODA films into epoxy capsules and by curing the epoxy at 70 °C for 24 h in a vacuum oven. Then the cured epoxies containing organoclay/PMDA-ODA were microtomed with Leica Ultracut Uct into 90-nm-thick slices in a direction normal to the plane of the films. Subsequently, a layer of carbon about 3 nm thick was

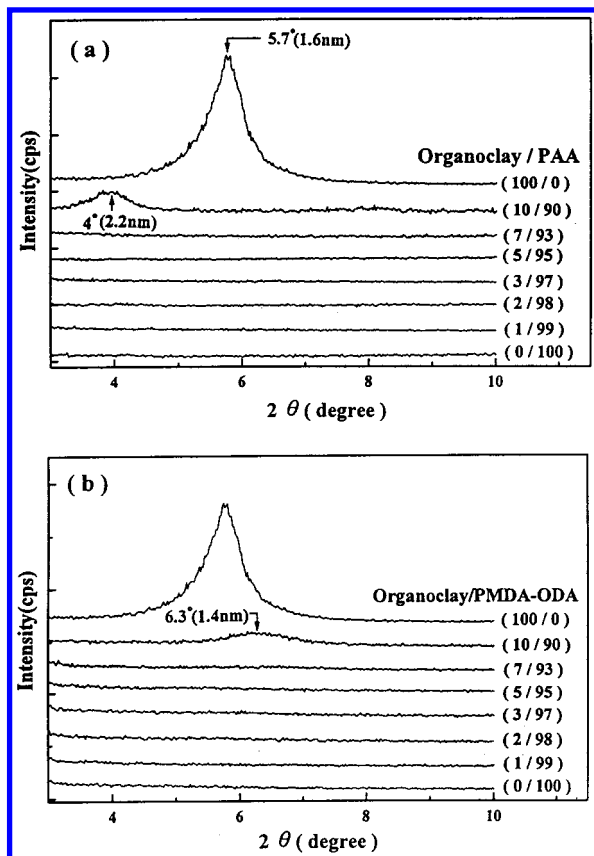


Figure 2. X-ray diffraction curves of different compositions of (a) organoclay/poly(amic acid) and (b) organoclay/PMDA-ODA films.

deposited on these slices that being on mesh 200 copper nets for TEM observation. The type of TEM used is JEOL-2000 FX, and its accelerated voltage was 200 kV. The dynamic mechanical analysis of organoclay/PMDA-ODA films was carried out from 45 to 480 °C with a DMA 2980 analyzer by Du Pont at a heating rate of 5 °C/min and at 1 Hz frequency. The glass transition temperatures of organoclay/PMDA-ODA films were determined from the in-plane thermal expansion measurement. The in-plane thermal expansion measurement at different temperature was carried out by using Du Pont 2940 probe, which provided 0.05 N tension force on the film, at a heating rate of 5 °C/min. The intersection points between the tangent lines of thermal expansion near the transition point were taken as the glass transition temperatures.

The measurement of out-of-plane coefficients of thermal expansion (CTE) of the samples was performed with a macroexpansion probe, which applied 0.05 N compression force on the film, at a heating rate of 5 °C/min. The tensile mechanical tests of organoclay/PMDA-ODA films were performed according to the specifications of ASTM D882-88 at a crosshead speed of 2 mm/min.

Results and Discussion

The X-ray diffraction curves of 1–10 wt % organoclay/PAA films are presented in Figure 2a. In Figure 2a, organoclay/PAA films did not show any diffraction peak in $2\theta = 3\text{--}10^\circ$ as opposed to the diffraction peak at $2\theta = 5.7^\circ$ (d spacing = 1.6 nm) for organoclay, indicating the possibility of having exfoliated silicate layers of organoclay dispersed in PAA. When the amount of organoclay increased to 10%, there was a small peak appearing at $2\theta = 4^\circ$, corresponding a d spacing of 2.2 nm. This implied that there is a small amount of organoclay that cannot be exfoliated in the PAA and

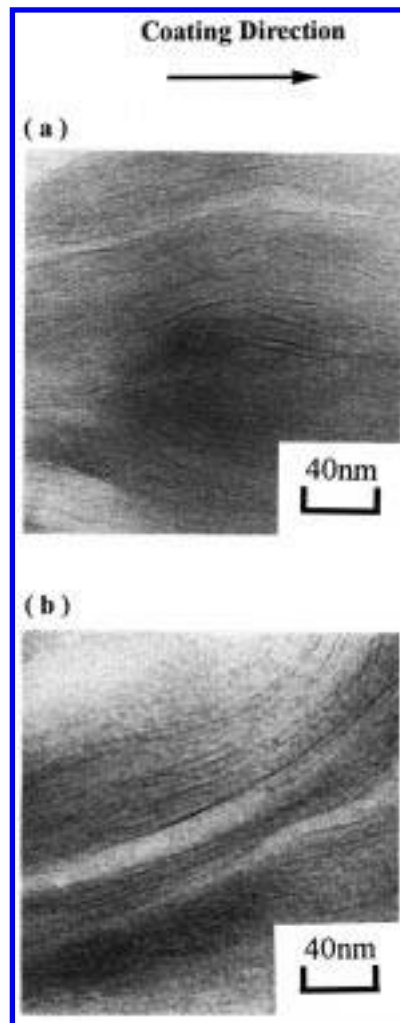


Figure 3. Transmission electron micrographs of the cross sectional view of organoclay/PMDA-ODA films containing (a) 2% organoclay and (b) 5% organoclay.

existed in the form of an intercalated layer structure as a result of swelling by poly(amic acid) molecules. After imidization, the wide-angle X-ray diffraction curves of organoclay/PMDA-ODA are similar to that of organoclay/PAA, except for the 10% organoclay/PMDA-ODA case, as shown in Figure 2b. In Figure 2b, there was a weak diffraction peak at $2\theta = 6.3^\circ$ (d spacing = 1.4 nm) for the case of 10% organoclay/PMDA-ODA. This shift from 2.2 to 1.4 nm in d spacing of the silicate layers after imidization can be explained by the fact that the PMDA-ODA molecules outside the silicate layers squeezed the silicate layers during the solvent removal process in imidization, causing a reduction in the space between the silicate layers. Further evidence of this nanometer-scale dispersion of intercalated silicate layers in PMDA-ODA can be supported by their TEM micrographs, as shown in Figure 3. In Figure 3, the thickness of the silicate layers of the organoclay (darker lines) was about 1 nm. In Figure 3a, the space between silicate layers appeared to range from 4 to 16 nm for 2% organoclay/PMDA-ODA, which is larger than the original 1.6 nm space between silicate layers in organoclay. This is direct evidence that these silicate layers have been intercalated in PMDA-ODA and a nanocomposite of silicate layers and PMDA-ODA has formed. When the amount of organoclay in PMDA-

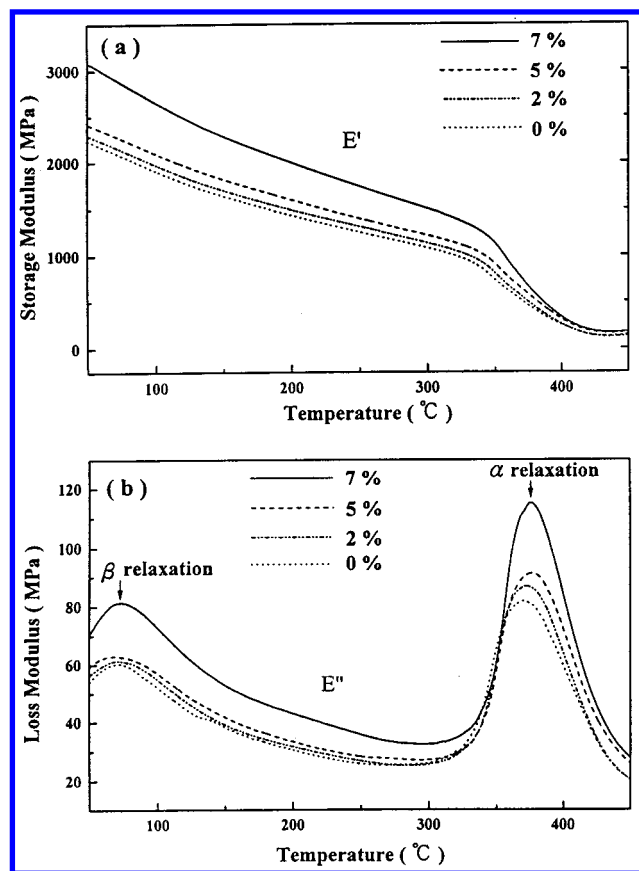


Figure 4. (a) the storage modulus and (b) the loss modulus of different compositions of organoclay/PMDA-ODA at different temperatures.

ODA increased to 5%, the space between silicate layers in PMDA-ODA was between 4 and 12 nm, slightly smaller than for the 2% organoclay/PMDA-ODA case, as displayed in Figure 3b.

The dynamic mechanical properties of pure PMDA-ODA and organoclay/PMDA-ODA nanocomposites are presented in Figure 4. In Figure 4a, the storage modulus of organoclay/PMDA-ODA nanocomposites increased with the amount of organoclay more distinctively in the temperature range between 50 and 300 °C than at near 400 °C. Specifically, at 50 °C, the storage modulus of 2% and 5% organoclay/PMDA-ODA was 2300 and 2400 MPa respectively, and they are larger than that of pure PMDA-ODA (2250 MPa). The largest increase in the storage modulus occurred at 50 °C, where the storage modulus of 7% organoclay/PMDA-ODA (3080 MPa) is 38% higher than that of pure PMDA-ODA. The storage modulus of organoclay/PMDA-ODA decreased near its transition temperature around 365 °C, but increased slightly due to the crystallization and the cross-linking of PMDA-ODA.¹³⁻¹⁵ The loss modulus of organoclay/PMDA-ODA also increased with the amount of organoclay, as shown in Figure 4b. Moreover, the loss modulus curves of organoclay/PMDA-ODA displayed two maxima at around 65 and 365 °C. The low-temperature one at 65 °C is caused by the rotation and/

Table 1. Glass Transition Temperature and Thermal Decomposition Temperature of Different Organoclay/PMDA-ODA

contents of organoclay (wt %)	T_g (°C)		decomposition temp ^a (°C)
	by DMA	by TMA	
0	369.9	365.7	618.0
1	372.0	368.2	625.7
2	372.3	368.9	630.5
3	374.7	369.1	637.0
5	375.6	369.7	642.9
7	376.4	369.2	643.1

^a Temperature at 5% weight loss.

or oscillation of the phenyl group of ODA,^{16,17} and was defined as the β relaxation or subglass transition. The high-temperature one at 365 °C is due to the backbone motion of PMDA-ODA molecules and was defined as α relaxation or the primary glass transition. The α relaxation or the glass temperatures of organoclay/PMDA-ODA are given in Table 1. In Table 1, the glass transition temperature measured by a dynamic mechanical analyzer increased slightly with the amount of organoclay in PMDA-ODA, indicating the restriction effect of the silicate layers on PMDA-ODA molecule motion. Furthermore, the largest increase in the glass transition temperature was 6 °C in the 7% organoclay/PMDA-ODA case, as compared to that of pure PMDA-ODA. Following a previous study,¹⁸ the glass transition temperatures of organoclay/PMDA-ODA measured by a thermal mechanical analyzer (TMA) were slightly smaller than that of organoclay/PMDA-ODA determined by DMA, but the dependency of the transition temperatures on the amount of organoclay is consistent in these two sets of data. This increase in T_g value of PMDA-ODA due to the presence of the intercalated silicate layer structures has not been reported in the literature. We are the first research group to report this phenomenon to our knowledge. This phenomenon can be interpreted as the motion of the polyimide molecules being retarded by the silicate layers when some portion of the space between the nanometer silicate layers was close to roughly 4 nm, as illustrated in the TEM micrographs in Figure 3. The decomposition temperatures of organoclay/PMDA-ODA increased with the amount of organoclay, with a maximum increase of 25 °C for 7% organoclay/PMDA-ODA as compared to that of the pure PMDA-ODA, as given in Table 1.

The tensile mechanical properties of organoclay/PMDA-ODA films processed by doctor blade and by spin-coating are given in Table 2. In Table 2, the Young's modulus of organoclay/PMDA-ODA increased with the amount of organoclay dramatically for the nanocomposite films processed with a doctor blade. In specific, the Young's modulus of 1% organoclay/PMDA-ODA was 1.2 GPa, which was 50% higher than the modulus of pure PMDA-ODA (0.8 GPa). When the amount of organoclay in PMDA-ODA reached 7%, a 2.5-fold increase in the modulus (2.8 GPa) and an 18% increase in the maximum stress were obtained as compared to that of the pure PMDA-ODA. Most

(13) Saini, A. K.; Carlin, C. M.; Patterson, H. H. *J. Polym. Sci., Part A: Polym. Chem.* **1993**, *31*, 2751.

(14) Cheng, S. Z. D.; Arnold Jr, F. E.; Zhang, A. Q.; Hsu, S. L. C.; Harris, F. W. *Macromolecules* **1991**, *24*, 5856.

(15) Cheng, S. Z. D.; Wu, Z. Q.; Eashoo, M.; Hsu, S. L. C.; Harris, F. W. *Polymer* **1991**, *32*, 1803.

(16) Bernier, G. A.; Kline, D. E. *J. Appl. Polym. Sci.* **1968**, *12*, 593.

(17) Perena, J. M. *Angew. Makromol. Chem.* **1982**, *106*, 61.

(18) Pottiger, M. T.; Coburn, J. C.; Edman J. R. *J. Polym. Sci., Part B: Polym. Phys.* **1994**, *32*, 825.

Table 2. Mechanical Properties of Different Organoclay/PMDA-ODA by Doctor Blade and Spin-Coating

contents of organoclay (wt %)	by doctor blade			by spin-coating		
	modulus (GPa)	max. stress (MPa)	elongation (%)	modulus (GPa)	max. stress (MPa)	elongation (%)
0	0.79	79.33	13.08	2.45	88.24	10.20
1	1.23	83.98	13.24	2.95	93.40	10.96
2	1.60	87.46	13.88	3.15	94.80	11.32
3	2.00	89.16	14.04	3.27	96.70	12.04
5	2.55	91.31	14.52	3.34	99.50	12.96
7	2.77	93.88	15.36	3.46	101.37	13.28

surprisingly, even the elongation-for-break of organoclay/PMDA-ODA increased slightly with the amount of organoclay, with a maximum increase of 17%. This phenomenon is absolutely impossible for inorganics-filled conventional polymer composites, where very low elongation-for-break was obtained (usually around 3%) as a result of added inorganics. The same kind of behavior was observed for the nanocomposite films processed with spin-coating. The maximum increase in modulus of organoclay/PMDA-ODA becomes considerably modest, but the modulus of 7% organoclay/PMDA-ODA was still 40% higher than that of pure PMDA-ODA. The large difference in the modulus of organoclay/PMDA-ODA films processed by doctor blade and by spin-coating can be attributed to the orientation of polyimide molecules. A large portion of these polyimide molecules and silicate layers are oriented in the plane direction of the film, as manifested in Figure 3, due to the high-shear spin-coating process. The maximum increases in the maximum stress and in the elongation-for-break of spin-coating processed organoclay/PMDA-ODA films were 15% and 30%, respectively, as compared to that of pure PMDA-ODA.

The dependency of the out-of-plane coefficients of thermal expansion (CTE) of organoclay/PMDA-ODA on the amount of organoclay is shown in Figure 5. The out-of-plane CTE of organoclay/PMDA-ODA decreased dramatically with the increasing amount of organoclay. For example, the out-of-plane CTE of pure PMDA-ODA and 1% organoclay/PMDA-ODA were 71.0 and 46.6 ppm/°C, respectively. As the amount of organoclay increased to 7%, the out-of-plane CTE of organoclay/PMDA-ODA was reduced to 36.5 ppm/°C, which is about one-half of the out-of-plane CTE of pure PMDA-ODA. This large reduction in CTE of PMDA-ODA owing to the presence of organoclay can be explained as follows. The amount of the reduction of thermal expansion by silicate layers depends on the orientation of polyimide molecules and the rigid nature of the silicate layers. Upon heating, the in-plane oriented polyimide molecules tend to relax in a direction normal to its original direction and therefore expand mainly in the out-of-plane direction.¹⁹⁻²³ The silicate layer was much more rigid than the polyimide molecules, and they do not deform or relax as the polyimide molecules do.

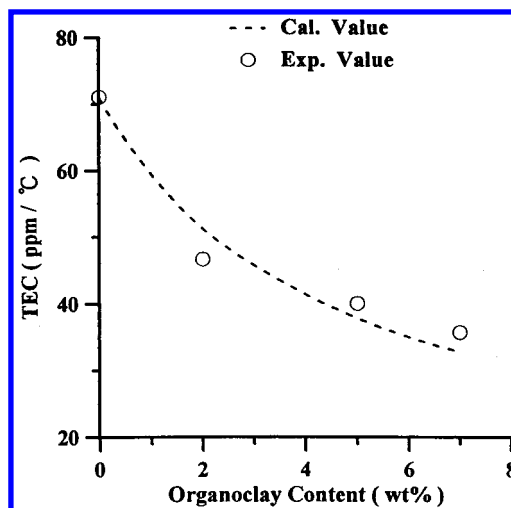


Figure 5. Out-of-plane coefficient of thermal expansion, averaged between 100 and 300 °C, of organoclay/PMDA-ODA films having different amounts of organoclay.

Moreover, the major portion of these nanometer silicate layers is parallel to the in-plane direction of the films. Consequently, the silicate layers exerted very effective retardation on the thermal expansion of polyimide molecules in the out-of-plane direction. The out-of-plane thermal expansion coefficients can be modeled by a simple empirical equation similar to the Gordon-Taylor equation,²⁴ which was derived for predicting the glass transition temperature in miscible blends. This empirical equation is used in this paper solely for the data-fitting purpose and is

$$\alpha = (\alpha_1 w_1 + K \alpha_2 w_2) / (w_1 + K w_2) \quad (1)$$

where α is the out-of-plane CTE of organoclay/PMDA-ODA nanocomposite films, α_1 is the CTE of bulk organoclay, α_2 is the out-of-plane CTE of PMDA-ODA, K is a constant, and w_1 and w_2 are the weight fraction of organoclay in PMDA-ODA. α_1 and α_2 are 12.5 and 71.0 ppm/°C, respectively. In Figure 5, the values calculated by eq 1 fitted the measured out-of-plane CTE of organoclay/PMDA-ODA films quite well, and the K value obtained is 0.04.

Concluding Remarks

The synthesis involving reactive organoclay and poly(amic acid) yielded a thermally stable and mechanically strong clay/polyimide nanocomposite. The reactive swelling agent organoclay may not be better than the nonreactive swelling agent regarding the effect of intercalating montmorillonite initially, due to the molecular size of the swelling agent. However, after reacting with the matrix polymer molecules, a permanent swelling can be produced. This permanent swelling is particularly advantageous when there was solvent involved in the dispersion of organoclay in polymer, as *N,N*-dimethylacetamide in case of poly(amic acid). Without the permanent swelling, the polymer molecules might slip out of the interlayer gallery of montmorillonite during the solvent removal process and reverse the swelling. This permanent swelling resulted in interca-

(19) Russell, T. P.; Guggen, H.; Swalen, J. H. D. *J. Polym. Sci., Part B: Polym. Phys.* **1983**, *21*, 1745.

(20) Numata, S.; Fujisaki, K.; Kinjo, N. *Polymer* **1987**, *28*, 2282.

(21) Jou, J. H.; Chung, C. S. *Macromolecules* **1992**, *25*, 6035.

(22) Boese, D.; Lee, H.; Yoon, D. Y.; Swalen, J. D.; Rabolt, J. F. *J. Polym. Sci., Part B: Polym. Phys.* **1992**, *30*, 1321.

(23) Struik, L. C. E., Ed. *Internal Stresses, Dimensional Instabilities and Molecular Orientations in Plastics*; John Wiley: New York, 1990.

(24) Gordon, M.; Taylor, J. S. *J. Appl. Chem.* **1952**, *2*, 495.

lated silicate layers in polyimide, even after imidization. Moreover, the original reactive swelling agent becomes a part of the polymer molecules, and it makes these nanocomposites more stable thermally and stronger mechanically.

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