

Mechanical Properties of Clay–Polyimide (BTDA–ODA) Nanocomposites via ODA-Modified Organoclay

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ABSTRACT: Clay–polyimide [3,3', 4,4'-benzophenone tetracarboxylic dianhydride–4,4'-oxydianiline (BTDA–ODA)] nanocomposites were synthesized from ODA-modified montmorillonite (organoclay) and poly(amic acid). The layered silicates of organoclay were intercalated by polyimide (BTDA–ODA), as confirmed by X-ray diffraction and by transmission electron microscopy, and the tensile mechanical properties of the nanocomposites were measured. It was found that the modulus and the maximum stress of these organoclay/BTDA–ODA nanocomposites were much higher than those of pure BTDA–ODA: a twofold increase in the modulus and a one-half-fold increase in the maximum stress in the case of 7/93 organoclay–BTDA–ODA. In addition, the elongation-for-break of organoclay/BTDA–ODA nanocomposites is even slightly higher than that of pure BTDA–ODA, which is a sharp contrast to that of conventional inorganics-filled polymer composites. © 2000 John Wiley & Sons, Inc. *J Polym Sci B: Polym Phys* 38: 2873–2878, 2000

Keywords: clay; polyimide; nanocomposites; tensile mechanical; modulus

INTRODUCTION

Clay–polymer nanocomposites have become an active field of research in recent years because of their unique microstructures and enhanced properties. Clay contains negatively charged layered silicates bonded by ionic bonding with metal cations such as Na^+ or Ca^{++} . The interaction of organoclay-modified layered silicates with polymers leads to two classes of nanocomposites. In the first class polymer chains are inserted between the silicate layers, generating ordered lamella with an interlayer distance of a few nanometers, denoted as intercalated nanocomposites. In the second class silicate layers of about 1 nm thick are exfoliated and dispersed in the polymer matrix, denoted as exfoliated nanocomposites. The nano-

meter scale interfaces between the silicate layers and the polymer matrix in these nanocomposites, resulting in much better additive properties than those of conventional composites. Clay–Nylon 6,^{1–3} clay–epoxy,^{4–6} clay–polyurethane,^{7–9} clay–polystyrene,¹⁰ clay–poly(ethylene terephthalate),¹¹ clay–poly(ethylene oxide),^{12,13} clay–polycaprolactone,¹⁴ and clay–poly(methyl methacrylate)¹⁵ have been developed by different research groups. Clay–polyimide [pyromellitic dianhydride–4,4'-oxydianiline (PMDA–ODA)] nanocomposites have also been formed through a two-stage polymerization process by Yano et al.^{16,17} and Lan et al.¹⁸ They used dodecylamine and 12-aminododecanoic acid in their studies as effective swelling agents for montmorillonite in forming clay/PMDA–ODA nanocomposites, whose films displayed reduced in-plane thermal expansion and lowered gas permeation as compared to those of pure PMDA–ODA films. However, they didn't report any mechanical or thermal properties of clay/PMDA–ODA in their studies.

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In our previous study,^{19,20} we used *p*-phenylenediamine, a swelling agent that contains two amine functional groups. After converting one functional group of the swelling agent into a cation ($-\text{NH}_3^+$), this cation formed an ionic bond with the negatively charged silicate layers of montmorillonite. The other functional group ($-\text{NH}_2$) of the swelling agent can react with the dianhydride end group of poly(amic acid) when the latter's molecules diffuse into organics-modified silicate layers. During the imidization process, swelling by the poly(amic acid) became permanent, even after the solvent was removed. In addition, the swelling agent became a part of the polyimide molecules, making these clay/ PMDA-ODA nanocomposite thermally more stable and mechanically stronger. In the current study we chose a swelling agent, 4,4'-oxydianiline diamine (ODA), that is also the monomer for the synthesis of polyimide constituted by 3,3', 4,4'-benzophenone tetracarboxylic dianhydride (BTDA) and 4,4'-oxydianiline (ODA). By using the same monomer, the miscibility between the organics-modified silicate layers and the poly(amic acid) can be improved further, and the probability of a reaction between the organoclay and the poly(amic acid) is increased, as shown in Figure 1. Hence, we expect a large improvement of their mechanical and thermal properties. Since BTDA-ODA is an amorphous polymer, the influence of the silicate layers on the mechanical and thermal properties of BTDA-ODA should become more pronounced than on that of semicrystalline PMDA-ODA.

EXPERIMENTAL

Source clay Swy-2 (Wyoming montmorillonite) was obtained from the Clay Minerals depository at the University of Missouri (Columbus, Missouri). 3,3',4,4'-Benzophenone tetracarboxylic dianhydride (BTDA) and 4,4'-oxydianiline (ODA) were purchased from TCI (Tokyo, Japan). *N,N*-Dimethylacetamide (DMAc) was obtained from Tedia (Ohio). By screening Swy-2 montmorillonite with a sieve of 325 mesh to remove impurities, clay with a cationic exchange capacity of 76.4 meq/100 g can be obtained. Ten grams of the screened montmorillonite was gradually added to a previously prepared solution of ODA (1.83 g dissolved in 1000 mL of 0.01N HCl), and it was vigorously stirred for 3 hr at 60 °C. After the treatment the montmorillonite suspension was

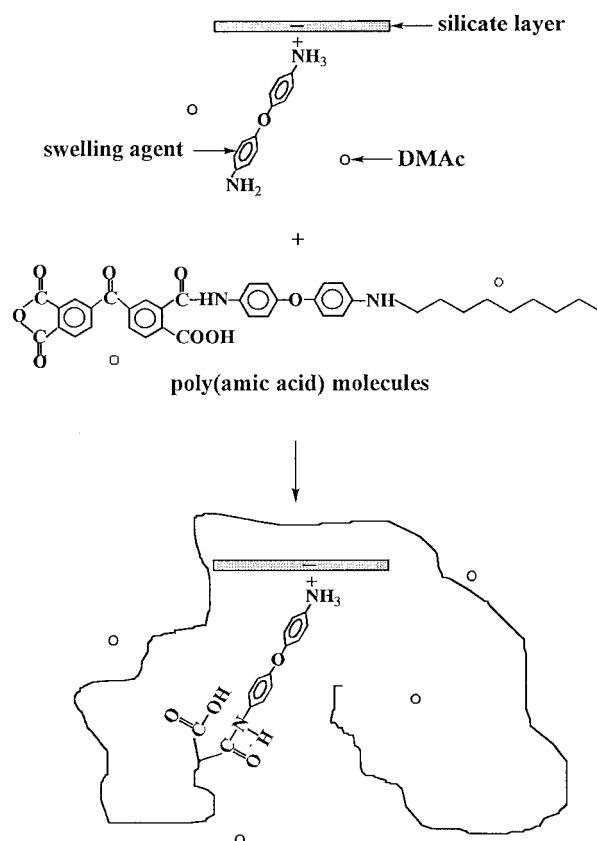


Figure 1. Schematic drawing of ODA-modified montmorillonite (reactive organoclay) and its intercalation by poly(amic acid).

repeatedly washed with deionized water. The filtrate was titrated with 0.1N AgNO_3 until there were no AgCl precipitates, ensuring a complete removal of chloride ions. Then the filter cake was placed in a vacuum oven at 80 °C for 12 h. The dried cake was ground and screened with a 325-mesh sieve. The powder obtained was termed organoclay. The ODA content in the organoclay was determined by thermogravimetric analysis (TGA) with a DuPont TGA 2950 at a heating rate of 20 °C/min from 30 to 1000 °C. The weight loss of the organoclay between 120 and 900 °C is assumed to be ODA and structural water in the organoclay.¹ The content of structural water in the montmorillonite was 5.41% as measured by TGA by heating the pure montmorillonite from 120 to 900 °C. The ion-exchanged fraction of montmorillonite in the organoclay was therefore 29.0% after comparing it to the CEC of the pure montmorillonite.

To synthesize poly(amic acid) (PAA), 0.0147 mol of ODA was put into a three-neck flask containing 24.62 g of DMAc under a nitrogen purge

at 25 °C. After the ODA was completely dissolved in the DMAc, 0.015 mol of BTDA divided into three batches was added to the flask batch by batch every 30 min. Once the BTDA was completely dissolved in the DMAc, the solutions were stirred for 1 h, producing a viscous PAA solution. To prepare organoclay in the DMAc at different concentrations, various quantities of organoclay—0.078, 0.156, 0.233, 0.389, and 0.545 g—were each added to 16.2 g of DMAc, and then each was mixed for 12 h. The organoclay suspensions were then mixed with the PAA to produce organoclay–PAA in DMAc. The final solid content of PAA in DMAc was 16%.

Using a doctor blade, organoclay–PAA was cast on glass slides, which then were put in a vacuum oven at 30 °C for 48 h. To imidize the organoclay–PAA, the samples were put in an air-circulation oven at 100, 150, 200, and 300 °C for 1 h and then at 400 °C for 5 min.

The intrinsic viscosity of pure PAA and recovered PAA at different compositions was measured with a Ubbelohde capillary viscometer at 30 °C. In order to performing the reverse ion exchange reaction,²¹ 2 g of the synthesized clay–PAA was added to 30 mL of 5% LiCl–DMAc solution, which was stirred for 1 week at room temperature. After the ion exchange, the solution was centrifuged at 3000 rpm for 5 min to obtain the recovered PAA.

X-ray diffraction study of the samples was carried out with a Mac Science M18 X-ray diffractometer (50 kV, 250 mA) with a copper target and an Ni filter, operating at a scanning rate of 4°/min. The samples for transmission electron microscopy (TEM) observation, done on a JEOL-

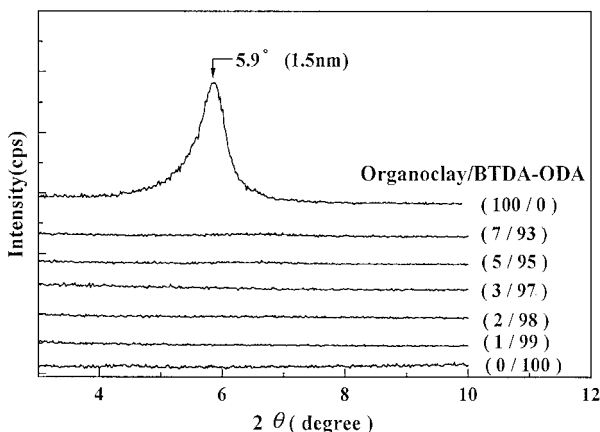


Figure 2. Wide-angle X-ray diffraction curves of organoclay/BTDA–ODA nanocomposites at different compositions.

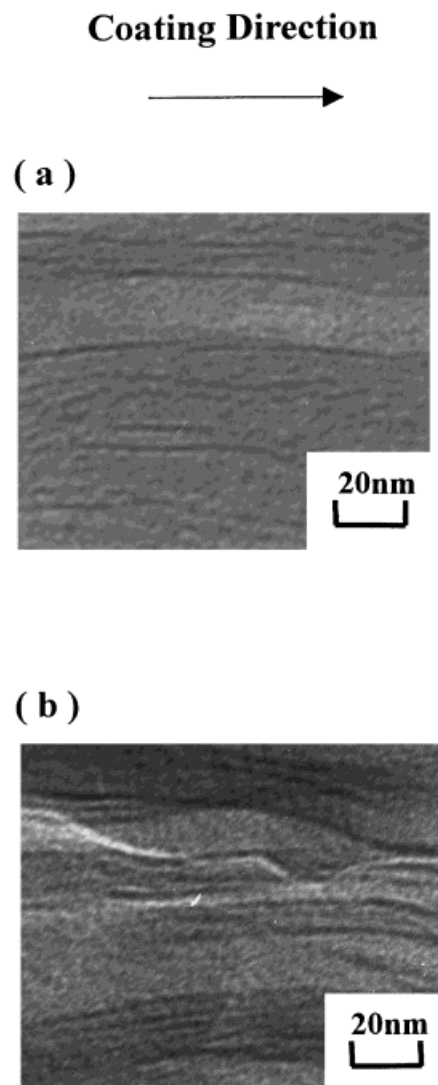


Figure 3. Transmission electron microscopy micrographs of the cross section view of (a) 3 : 97 organoclay/BTDA–ODA (b) 5 : 95 organoclay/BTDA–ODA nanocomposite films.

2000 FX at an accelerated voltage of 200 kV, were prepared by putting the organoclay/BTDA–ODA films into epoxy capsules and then curing the epoxy at 70 °C for 24 h in a vacuum oven. Subsequently, the cured epoxies containing the organoclay/BTDA–ODA were microtomed with a Leica Ultracut Uct into 90-nm-thick slices in a direction normal to the plane of the films. A layer of carbon about 1 nm thick was deposited on these slices, which were on mesh 200 copper nets for TEM observation. The thermal transitions of the organoclay/BTDA–ODA films were measured with a DuPont DSC 2910 differential scanning calorimeter (DSC) at a heating rate of 20 °C/min. The

Table I. Thermal Degradation Temperatures and Glass-Transition Temperatures of Organoclay/BTDA-ODA Nanocomposites as Well as Intrinsic Viscosity of Recovered Poly(amic acid) at Different Compositions

Contents of Organoclay (wt %)	Decomposition Temperature ^a (°C)	T_g (°C)		Intrinsic Viscosity of Recovered PAA (dL/g)
		By DSC	By DMA (α Relaxation)	
0	633	275.5	260.7	0.931
1	646	277.2	261.8	0.923
2	651	277.9	262.3	1.024
3	657	278.8	263.5	1.031
5	659	278.7	265.1	1.041
7	660	281.9	265.8	1.046

^a Temperature at 5% weight loss.

samples were first heated to 400 °C for 1 min and then quenched in liquid nitrogen to wipe out the thermal history. The DSC curve of the samples was obtained at the second heating. Thermogravimetric analysis of the organoclay/BTDA-ODA films was carried out with a DuPont TGA 2950 at a heating rate of 20 °C/min. The dynamic mechanical analysis of the organoclay/BTDA-ODA films was performed from 20 to 350 °C with a DuPont DMA 2980 analyzer at a heating rate of 5 °C/min and at a frequency of 1 Hz. The tensile properties of the organoclay/BTDA-ODA films were measured 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 organoclay and organoclay/BTDA-ODA at different compositions are shown in Figure 2. A strong peak appears at $2\theta = 5.9^\circ$ representing the diffraction from the (001) crystal surface of the 4,4'-oxydianiline-modified silicate layers of organoclay. The corresponding d-spacing for the peak in these silicate layers was 1.5 nm. There was no X-ray diffraction peak appearing at $2\theta = 3\text{--}10^\circ$ in the cases of 1–7% organoclay in the BTDA-ODA, indicating that these silicate layers of organoclay have been either intercalated to a distance of more than 3 nm or completely exfoliated in the BTDA-ODA. TEM micrographs (Fig. 3) provide additional evidence of this nanometer-scale dispersion of the intercalated silicate layers in the BTDA-ODA. In Figure 3 these dislike silicate layers have a diameter of

110 nm are 1.0 nm thick (the dark lines). The space between the silicate layers appeared to vary from 4 to 10 nm in the case of the 3/97 organoclay/BTDA-ODA. These spaces are larger than the original d-spacing (1.5 nm) between the silicate layers in organoclay. When the amount of organoclay in the BTDA-ODA was increased to 5%, the space between the silicate layers in the BTDA-ODA was between 4 and 8 nm, slightly smaller than that in the case of the 3 : 97 organoclay/BTDA-ODA case, as shown in Figure 3(b).

The thermal properties of these organoclay/BTDA-ODA nanocomposites and the intrinsic viscosity of the recovered PAA at different compositions are presented in Table I., which shows the thermal degradation temperatures of the organoclay/BTDA-ODA (at 5% weight loss) increased with the amount of organoclay, with a maximum increase of 27 °C in the case of the 7 : 93 organoclay/BTDA-ODA as compared to that of the pure BTDA-ODA. The intrinsic viscosity of the recovered PAA was slightly higher than that of the pure PAA, indicating the molecular weight of recovered PAA was slightly larger than that of pure PAA. Moreover, the glass-transition temperatures of organoclay/BTDA-ODA increased slightly with the amount of organoclay. The increase in the glass-transition temperature of organoclay/BTDA-ODA could be a result of two factors: a slightly higher molecular weight of polyimide in the nanocomposites because of the reactive organoclay and a retardation on the polyimide molecule main-chain motion by the silicate layers. In this case it seemed that the molecular weight of the polyimide was the dominating factor since the space between most silicate layers was

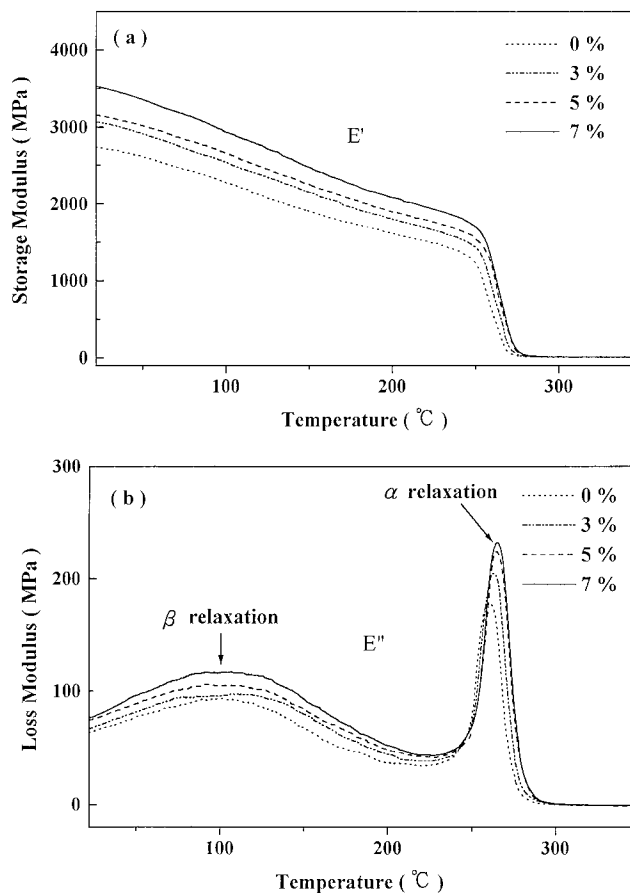


Figure 4. (a) The storage modulus, (b) the loss modulus of organoclay/BTDA-ODA nanocomposite films at different temperatures.

larger than 3 nm, as illustrated in the TEM micrographs in Figure 3.

The dynamic mechanical properties of pure BTDA-ODA and organoclay/BTDA-ODA nanocomposites at different temperature are shown in Figure 4. In Figure 4(a) the storage modulus of the organoclay/BTDA-ODA nanocomposites increased with the amount of organoclay in the temperature range of 20–250 °C. Specifically, the largest increase in the storage modulus of these nanocomposites was in the case of the 7 : 93 organoclay/BTDA-ODA (3.53 GPa) which is 30% larger than that of pure BTDA-ODA. The loss modulus of the organoclay/BTDA-ODA also increased with the amount of organoclay, as shown in Figure 4(b), in which the loss modulus of pure BTDA-ODA agrees with that reported by Gillham et al.²² A broad maximum at 110 °C and a sharp maximum at near 260 °C are displayed in the loss modulus curves of the organoclay/BTDA-ODA nanocomposites. The low-temperature one,

at 110 °C, is caused by the rotation and/or oscillation of the phenyl group of the ODA,^{23–25} and it was called β relaxation, or subglass transition. The β relaxation of the organoclay/BTDA-ODA at different compositions took place at the same temperature, indicating that either the rotation and/or the oscillation of the phenyl group of the ODA were not affected by the presence of silicate layers. The high-temperature one, at near 260 °C, results from the backbone motion of the BTDA-ODA molecules, and it was called α relaxation, or primary glass transition. The α -relaxation or glass-transition temperatures of organoclay/BTDA-ODA are given in Table I, showing that the α relaxation (the glass-transition temperature), measured by dynamic mechanical analyzer, increased slightly with the amount of organoclay in the BTDA-ODA. The largest increase in the glass-transition temperature was 5 °C, in the case of the 7 : 93 organoclay/BTDA-ODA as compared to that of the pure BTDA-ODA. The glass-transition temperatures of the organoclay/BTDA-ODA measured by DSC were slightly higher than that determined by DMA, but the dependency of the transition temperatures on the amount of organoclay is consistent in these two sets of data.

The tensile mechanical properties of the organoclay/BTDA-ODA nanocomposite films processed by a doctor blade are given in Table II, showing that the Young's modulus of the organoclay/BTDA-ODA increased sharply with the amount of organoclay. For instance, a twofold increase in the modulus of the 7 : 93 organoclay/BTDA-ODA (4.18 GPa) was found, as compared to that of the pure BTDA-ODA (1.35 GPa). These large increases in the Young's modulus of the BTDA-ODA depended on the orientation and the aspect ratio of the silicate layers. The average rate of increase in the modulus of these nanocom-

Table II. Mechanical Properties of Organoclay/BTDA-ODA Nanocomposites at Different Compositions Using a Doctor Blade

Contents of Organoclay (wt %)	Modulus (GPa)	Max. Stress (MPa)	Elongation (%)
0	1.35	75.26	7.04
1	1.78	75.67	7.24
2	2.30	88.50	7.36
3	2.66	93.74	7.88
5	3.22	105.44	8.16
7	4.18	113.66	8.42

posites was 0.4 GPa per wt % of the organoclay, which is much larger than that of conventional composites with platelike filler (about 0.03GPa/% loading).

The maximum stress of the organoclay/BTDA-ODA also increased with the amount of organoclay. When the amount of organoclay present in BTDA-ODA was 1%, the maximum stress of the organoclay/BTDA-ODA increased by 25% as compared to that of the pure BTDA-ODA. As the amount of organoclay increased to 7%, the maximum stress of the organoclay/BTDA-ODA was 113.66 MPa, a half-fold as compared to that of the pure BTDA-ODA (75.26 MPa). The elongation for break of organoclay/BTDA-ODA increased slightly with the amount of organoclay, with a maximum increase of 20% as compared to that of the pure BTDA-ODA. This is quite a contrast to conventional inorganics-filled polymer composites, where very low elongation for break is obtained (usually around 3%) as a result of added inorganics.

CONCLUSIONS

Organoclay/BTDA-ODA nanocomposites synthesized via ODA-modified organoclay display large increases in the modulus and in the maximum stress as compared to pure BTDA-ODA—a twofold increase in the modulus and a half-fold increase in the maximum stress in the case of 7 : 93 organoclay/BTDA-ODA. In addition, the elongation for break of the organoclay/BTDA-ODA nanocomposites is even slightly higher than that of pure BTDA-ODA, which is in sharp contrast to that of conventional inorganics-filled polymer composites.

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REFERENCES AND NOTES

- Usuki, A.; Kawasumi, M.; Kojima, Y.; Okada, A.; Kurauchi, T.; Kamigaito, O. *J Mater Res* 1993, 8, 1174.
- Usuki, A.; Kojima, Y.; Kawasumi, M.; Okada, A.; Fukushima, Y.; Kurauchi, T.; Kamigaito, O. *J Mater Res* 1993, 8, 1179.
- Kojima, Y.; Usuki, A.; Kawasumi, M.; Okada, A.; Fukushima, Y.; Kurauchi, T.; Kamigaito, O. *J Mater Res* 1993, 8, 1185.
- Wang, M. S.; Pinnavaia, T. J. *Chem Mater* 1994, 6, 468.
- Messersmith, P. B.; Giannelis, E. P. *Chem Mater* 1994, 6, 1719.
- Lan, T.; Kaviratna, P. D.; Pinnavaia, T. J. *Chem Mater* 1995, 7, 2144.
- Chen, T. K.; Tien, Y. I.; Wei, K. H. *J Polym Sci Polym Chem Ed* 1999, 37, 2225.
- Chen, T. K.; Tien, Y. I.; Wei, K. H. *Polymer* 2000, 41, 1345.
- Wang, Z.; Pinnavaia, T. J. *Chem Mater* 1998, 10, 3771.
- Noh, M. W.; Lee, D. C. *Polym Bull* 1999, 42, 619.
- Ke, Y. C.; Long, C. F.; Qi, Z. N. *J Appl Polym Sci* 1999, 71, 1139.
- Vaia, R. A.; Vasudevan, S.; Krawiec, W.; Scanlon, L. G.; Giannelis, E. P. *Adv Mater* 1995, 7, 154.
- Giannelis, E. P. *Adv Mater* 1996, 8, 29.
- Messersmith, P. B.; Giannelis, E. P. *J Polym Sci Polym Chem Ed* 1995, 33, 1047.
- Biasci, L.; Aglietto, M.; Ruggeri, G.; Giardelli, F. *Polymer* 1994, 35, 3296.
- Yano, K.; Usuki, A.; Okada, A.; Kurauchi, T.; Kamigaito, O. *J Polym Sci Polym Chem Ed* 1993, 31, 2493.
- Yano, K.; Usuki, A.; Okada, A. *J Polym Sci Polym Chem Ed* 1997, 35, 2289.
- Lan, T.; Kaviratna, P. D.; Pinnavaia, T. J. *Chem Mater* 1994, 6, 573.
- Tyan, H. L.; Liu, Y. C.; Wei, K. H. *Polymer* 1999, 40, 4877.
- Tyan, H. L.; Liu, Y. C.; Wei, K. H. *Chem Mater* 1999, 11, 1942.
- Meier, L. P.; Shelden, R. A.; Caseri, W. R.; Suter, U. W. *Macromolecules* 1994, 27, 1637.
- Bernier, G. A.; Kline, D. E. *J Appl Polym Sci* 1968, 12, 593.
- Perena, J. M. *Angew Makromol Chem* 1982, 106, 61.
- Arnold Jr., F. E.; Bruno, K. R.; Shen, D.; Eashoo, E.; Lee, C. J.; Harris, F. W.; Cheng, S. Z. D. *Polym Eng Sci* 1993, 33, 1373.
- Gillham, J. K.; Gillham, H. C. *Polym Eng Sci* 1973, 13, 447.