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On the Nature of Polyimide–Clay Hybrid Composites

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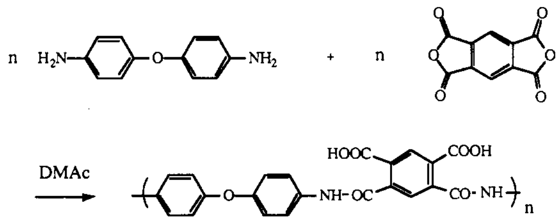
The reactions of chemically modified smectite clays and organic molecules typically afford intercalation compounds with well-defined compositions and basal spacings.[1] More recent studies of clay–organic reactions have led to the formation of true clay–polymer hybrid composites in which engineering polymers are encapsulated between smectite clay particles approximately 1 nm in thickness.[2–7] Semial work by Toyota researchers has led to the discovery of several nanoscale polymer–clay hybrid composites, including systems based on the dispersion of alkylammonium-exchanged forms of montmorillonite in semicrystalline nylon-6,[8–10] amorphous epoxide,[11] and polyimide[12,13] polymers.

The properties of polymer–clay hybrids are often far superior to those of pristine polymers and conventional composite materials. For instance, the addition of 4.7 wt % montmorillonite clay[14] to nylon-6 increased the tensile strength and modulus, respectively, from 68.6 MPa and 1.11 GPa for the pristine polymer to 97.2 MPa and 1.87 GPa for the composite. Also, the thermal and rheological properties of the nylon were improved significantly by nanocomposite formation. An increase in heat distortion temperature from 65 °C for nylon-6 to 152 °C for a nylon–clay hybrid was achieved at a 5 wt % clay loading.

Owing to their plateletlike morphology clay particles embedded in a polymer matrix should lower permeability and improve the barrier film properties of the polymer. Indeed, a significant reduction in the permeability of helium, oxygen, and water has recently been reported for polyimide–clay composites containing embedded organocation-exchanged forms of montmorillonite.[12,13] The rate of transport of a permeant molecule through a composite will be dependent upon the size, geometry, and orientation of the embedded phase in the polymer matrix. It has been suggested that nearly complete dispersion (exfoliation) of the 10-Å-thick clay layers is needed to optimize the aspect ratio of the particles, which in the case of montmorillonite can reach a value of 2000. However, relatively little is known concerning the extent of polyimide intercalation in organoclays.

In the present work we examine the intercalation of a polyamic acid in the galleries of a series of $CH_3(CH_2)_{n-1}NH_3^+$ montmorillonites and the subsequent conversion of the polyamic acid to polyimide. The results indicate that the polyimide intercalates in large part as a monolayer, regardless of the chain length of the initial clay exchange ion over the carbon number range $n = 4$–18. Although regular face–face layer aggregation is extensive even for a long-chain alkylammonium montmorillonite ($n = 18$), the composite exhibits impressive barrier film properties, as judged from CO_2 permeation measurements.

Homoionic $CH_3(CH_2)_{n-1}NH_3^+$ montmorillonites, where n = 4, 8, 12, 16, and 18, were prepared from Na^+–montmorillonite (CEC = 92 mequiv/100 g) by ion-exchange reaction with alkylammonium chloride or bromide salts in H_2O/EtOH solution.[15,16] Polymerization of 4,4′-diaminodiphenyl ether and pyromellitic dianhydride in dimethylacetamide (DMAc) afforded a 7 wt % polyamic acid solution:[17]



Polyamic acid–clay intercalates then were prepared by reaction at 25 °C of the desired organoclay with the polyamic acid solution. Allowing the polyamic acid–clay suspensions to dry on a clean glass plate afforded self-supporting films, which then were heated at 300 °C for 3.0 h to form the cured polyimide–clay hybrid composites:

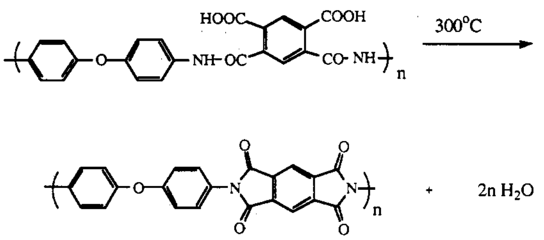


Figure 1A shows the XRD patterns for polyamic acid films containing 10 wt % of different $CH_3(CH_2)_{n-1}NH_3^+$ montmorillonites. For each organoclay the basal spacing is approximately equal to the clay layer thickness (9.6 Å) plus the chain length of the intergallery $CH_3(CH_2)_{n-1}NH_3^+$ cation. Basal spacings of 13.5–17.6 Å are observed for the pristine organoclays in the absence of intercalated polyamic acid, as expected for horizontal monolayer or bilayer orientations of the onium ions.[18] Thus, when the polyamic acid and DMAc enter the clay galleries, the onium cations

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(1) Theng, B. K. G. Formation and Properties of Clay–Polymer Complexes; Elsevier: New York, 1979.

(2) Kato, C.; Kuroda, K.; Misawa, M. *Clays Clay Miner.* **1979,** *27,* 129.

(3) Giannelis, E. P. *Chem. Mater.* **1990,** *2,* 627.

(4) Mehrotra, V.; Giannelis, E. P. *Solid State Commun.* **1991,** *77,* 155.

(5) Mehrotra, V.; Giannelis, E. P. *Solid State Ionics* **1992,** *51,* 115.

(6) Giannelis, E. P. *JOM* **1992,** *44,* 28.

(7) Messersmith, P. B.; Giannelis, E. P. *Chem. Mater.* **1993,** *5,* 1064.

(8) Fukushima, Y.; Inagaki, S. *J. Inclusion Phenom.* **1987,** *5,* 473.

(9) Fukushima, Y.; Okada, A.; Kawasumi, M.; Kurauchi, T.; Kamigaito, O. *Clay Miner.* **1988,** *23,* 27.

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

(11) Usuki, A.; Mizutani, T.; Fukushima, Y.; Fujimoto, M.; Fukumori, K.; Kojima, Y.; Sato, N.; Kurauchi, T.; Kamigaito, O. U.S. Patent 4,889,885, 1989.

(12) Yano, K.; Usuki, A.; Okada, A.; Kuraychi, T.; Kamigaito, O. *Polym. Prepr. (Am. Chem. Soc., Polym. Div.)* **1991,** *32,* 65.

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

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

(15) Lin, Chi-Li; Lee, T.; Pinnavaia, T. J. *ACS Symp. Ser.* **1992,** *499,* 145.

(16) Lee, T. Ph.D. Thesis, Michigan State University, 1992.

(17) Sroog, C. E.; Enerey, A. L.; Abramo, S. V.; Beer, C. E.; Edwards, W. M.; Oliver, K. L. *J. Polym. Sci., Part A: Polym. Chem.* **1965,** *3,* 1373.

(18) Lagaly, G. *Solid State Ionics* **1986,** *22,* 43.

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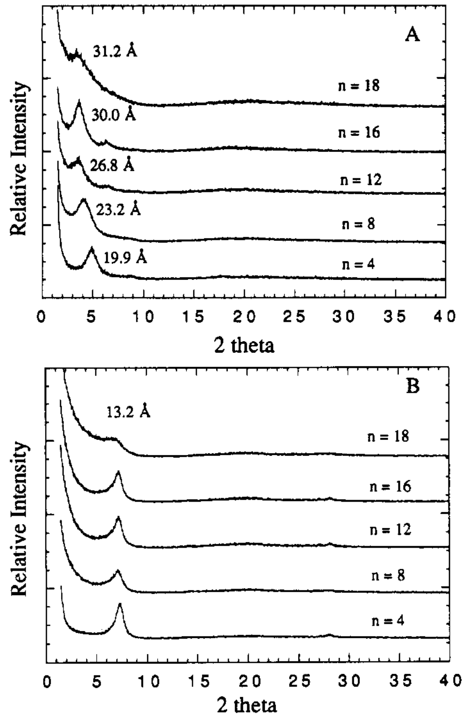

Figure 1. XRD patterns (Cu Kα) of polymer–$CH_3(CH_2)_{n-1}NH_3^+$ montmorillonites composites: (A) air-dried polyamic acid films and (B) polyimide films cured at 300 °C. The clay loading was 10 wt % for each system.

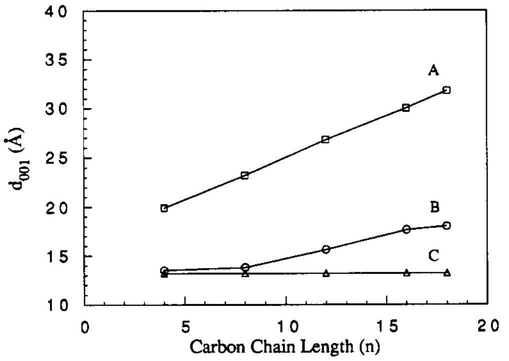

Figure 2. Dependence of the basal spacings of $CH_3(CH_2)_{n-1}NH_3^+$ montmorillonites on the carbon number, *n*: (A) clays dispersed in air-dried polyamic acid films, (B) air-dired pristine clays, and (C) clays dispersed in cured polyimide films. Curves A and C were obtained at clay loading of 10 wt %.

reorient from a horizontal to a vertical position relative to the silicate host layers. That is, the extent of gallery solvation by polyamic acid and DMAc is regulated by the chain length of the alkylammonium cation. There is no doubt that polyamic acid is co-intercalated along with DMAc, because the basal spacings are significantly larger than the spacings observed in the presence of DMAc alone.

Since the nuclearity of the intercalated polymer chain already is established at the polyamic acid stage, the clay galleries can not expand further upon thermal conversion of the polyamic acid to the polyimide. As shown by the XRD patterns in Figure 1 and by the plots of basal spacings vs alkylammonium ion chain length in Figure 2 (curves A and C) a 6.7–16.9-Å contraction in gallery height occurs upon transformation at 300 °C of the polyamic acid to the more rigid polyimide. The same contractions in basal spacings occur at 100 °C, a temperature well below that needed for polyimide formation. Thus, most of the gallery swelling for the air-dried polyamic acid–clay complex is attributable to the presence of intercalated DMAc. Eliminating the solvent at elevated temperature (~100 °C) leaves behind only a monolayer of polymer in the galleries, as judged from the basal spacing of 13.2 Å.

Significantly, the basal spacing of ~13.2 Å, which corresponds to a gallery height of ~3.6 Å, is independent of the initial onium ion chain length and *smaller* than the spacings for the starting alkylammonium montmorillonites (cf. Figure 2, curves B and C). This contraction in spacings cannot be due to the thermal decomposition of the gallery onium ions, because essentially identical values are observed for the polyamic acid intercalates dried at 100 °C, where the intercalated onium ions are stable. Also, the polyimide composites retain their 13.2 Å spacing even at 450 °C, whereas the pristine onium ion clays give collapsed (10 Å) spacings at this temperature. Hence, a polyamic acid monolayer and not onium ions is intercalated in the clay galleries upon thermal elimination of DMAc. The somewhat constrained gallery height of 3.6 Å suggests that the polymer adopts a flattened conformation and/or is keyed into the hexagonal cavities of the gallery surfaces.

The above XRD results demonstrate that much of the clay is retained in an ordered intercalated state upon hybrid composition formation. In contrast, previous studies[12,13] have reported the essentially complete exfoliation of $CH_3(CH_2)_{11}NH_3^+$ montmorillonite in a polyimide matrix using essentially the same chemistry and methodologies as the present work. The exfoliated state of the clay was considered to be important to the barrier film properties of the composite. To more fully characterize the particle texture of the materials prepared in the present work, TEM images were obtained on thin sections of the polyimide–clay hybrids formed from $CH_3(CH_2)_{17}NH_3^+$ montmorillonite. Both delaminated layers with more-or-less random separations of 30–100 Å and ordered aggregates with the layers separated by about 15 Å were observed. The ordered domains are in accord with the XRD results for a regularly intercalated phase. We conclude, therefore, that a major fraction of the clay indeed is embedded in the polymer matrix as an ordered intercalate, rather than as a completely exfoliated array of single layers.

Despite the presence of a substantial fraction of highly ordered clay aggregates, the hybrid materials of the present work exhibit impressive barrier film properties at low clay loadings. The data points in Figure 3 illustrate the nonlinear dependence of CO_2 permeability on clay loading for a series of composite films containing 0–7.4 vol % (0–15 wt %) $CH_3(CH_2)_{17}NH_3^+$ montmorillonite. Since non-permeable platey particles act as a barrier to gas diffusion by increasing the tortousity of the diffusion pathway,[19] the dependence of permeability on loading can be estimated from the equation

$$\frac{P_c}{P_p} = \frac{\phi_p}{1 + (W/2T)\phi_f}$$

where P_c and P_p is the permeability of the composite film and that of the unfilled (pristine) polymer, respectively, ϕ_p and ϕ_f are the volume fractions of polymer and filler, and W/T is the width-to-thickness aspect ratio of the filler. As indicated by the above equation, a large aspect ratio

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(19) Nielsen, L. E. *J. Macromol. Sci.* (*CHEM.*) **1967**, *A1*, 929.

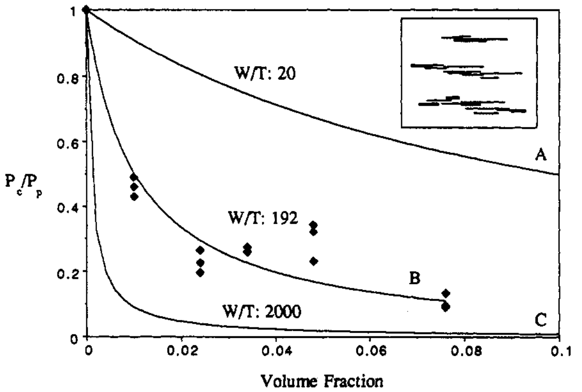

Figure 3. CO_2 permeability of polyimide–clay composites prepared by curing $CH_3(CH_2)_{17}NH_3^+$ montmorillonite–polyamic acid films at 300 °C. The measurements were performed on films of 2.5-cm diameter and 25-μm thickness. Curve B was generated by least-squares fitting of the permeability equation to the experimental data. Curves A and C are calculated for fillers with W/T aspect ratios of 20 and 2000, respectively. The inset illustrates a possible self-similar aggregation mechanism for the clay plates.

will dramatically decrease permeability, provided the particles can be oriented parallel to the surface of the film.

Curve B in Figure 3 represents the best fit of the permeability equation to the data, yielding a particle aspect ratio of 192. For comparison, curves A and C were generated assuming particle aspect ratios of 20 and 2000 for nonintercalated and completely exfoliated particles, respectively. The relationship between permeability and clay loading which we observe for our hybrid composites is quantitatively similar to the results of Toyota investigators, who also report an apparent aspect ratio of 200. These latter workers have concluded that the clay is completely exfoliated into 10-Å-thick layers. However, our results clearly show that the clay retains a crystallographically regular layer stacking order with a monolayer of polymer (*not* onium ions) intercalated between the layers. The retention of crystallographic order is in part a consequence of the unique intercalation mechanism, wherein the onium ions are displaced from the galleries and the polyamic acid becomes encapsulated upon removal of the DMAc solvent.

Previous work[20] on the barrier properties of polymer films containing conventional clay-type fillers (*e.g.*, talc, mica) has shown that the permeability decreases almost linearly with increasing filler loading, owing primarily to the low aspect ratio (<20) of the particles. The aspect ratio of the clay particles in our polymide composites is an order of magnitude larger than conventional clay-type fillers. On the basis of the linewidth of the 001 XRD lines, the scattering domain size along the stacking direction of the particles is ~276 Å, corresponding to ~20 layers/aggregate. This value, together with the aspect ratio, suggests an average lateral dimension of ~5.5 μm for the aggregates. The lateral size of montmorillonite single layers is typically much smaller, usually in the range 0.1–2.0 μm. This apparent contradiction in particle size may be explained by a self-similar clay aggregation mechanism. Van Damm et al.[21] have proposed that clays dispersed in liquid media can adopt fractal structures in which the face–face associated layers are slipped in staircaselike fashion (see inset, Figure 3). These self-similar structures can exhibit enhanced aspect ratios and give rise to 001 X-ray scattering in accord with the observations of the present work.

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(20) Bissot, T. C. *ACS Symp. Ser.* **1989**, *423*, 225.

(21) Van Damme, H.; Levitz, P.; Fripiat, J. J.; Alcover, J. F.; Gatineau, L.; Bergaya, F. In *Physics of Finely Divided Matter*; Boccara, N., Daoud, M., Eds.; Springer-Verlag: New York, 1985, 2/8–8/8.