

# Location of a Nanoclay at the Interface in an Immiscible Poly( $\epsilon$ -caprolactone)/Poly(ethylene oxide) Blend and Its Effect on the Compatibility of the Components

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**ABSTRACT:** Nanocomposites based on 80/20 and 20/80 (w/w) poly( $\epsilon$ -caprolactone) (PCL)/poly(ethylene oxide) (PEO) immiscible blends and organophilic layered silicates were prepared with melt extrusion. From transmission electron microscopy analysis, it was observed that the exfoliated silicate platelets were preferentially located at the interface between the two blend phases. When the blend-based nanocomposites were prepared via a two-step process in which the silicates were first premixed with the PEO component or with the PCL component, the silicate layers migrated from the PEO phase or PCL phase to the interface. The rheological behavior of the nanocomposites was also investigated. At low frequencies, the frequency

dependence of the storage modulus changed from a liquidlike behavior for the unfilled blend to a solidlike behavior for the nanocomposites, indicating the formation of a network structure as a result of exfoliation. From the scanning electron micrographs, a monotonic decrease of the PEO domain size in the 80/20 PCL/PEO blend was observed as a function of the organophilic clay content. Therefore, a clear emulsifying effect was induced by the organophilic layered silicates in the immiscible PCL/PEO blend. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 3125–3135, 2007

**Key words:** compatibility; immiscibility; morphology

## INTRODUCTION

Blending has now emerged as a major tool for obtaining new polymeric materials with desired properties. Because most homopolymer pairs are immiscible, they form phase-separated morphologies having poor mechanical properties. Physical compatibilization and reactive compatibilization are used to reduce the interfacial tension between the two phases and improve their interfacial adhesion. Effective compatibilizing agents should be able to minimize the interfacial tension and reduce the size of the dispersed phase. Block and graft copolymers with covalently connected immiscible blocks have demonstrated very effective compatibilization activity in immiscible blends.<sup>1–3</sup>

The addition of inorganic fillers to an immiscible polymer blend provides an alternative way to modify its interfacial properties. Studies on carbon black,<sup>4–8</sup>

fumed silicate,<sup>9–14</sup> and nanosize calcium carbonate<sup>15,16</sup> have revealed that the location of the filler particles at the interface in heterogeneous polymer blends and the interaction that develops with the blend components are of key importance for the emulsification of the filled blends. The use of mineral fillers as compatibilizers is more economical than the use of copolymers. For example, Krause<sup>17</sup> used a silica filler as a compatibilizer for immiscible polyolefin/polyacrylate and polyolefin/polymethacrylate blends. Voulgaris and Petridis<sup>18</sup> suggested that organoclays could also be used as emulsifiers for immiscible polymer blends. The emulsifying effect of dimethyldioctadecylammonium hectorite in polystyrene/poly(ethyl methacrylate) blends is an illustrative example among a series of reports on the subject.<sup>18–21</sup> However, the mechanism of the emulsification is not very clear. The localization of the clay particles in immiscible polymer blends remains an important topic for the understanding of the mechanism of emulsification.

Poly( $\epsilon$ -caprolactone) (PCL) and poly(ethylene oxide) (PEO) are immiscible polymer pairs.<sup>22</sup> The nanocomposites of either PCL<sup>23–27</sup> or PEO<sup>28–33</sup> with layered silicates have been extensively studied. The results show that both of them can have strong interactions with the organoclay and form an exfoliated nanostructure. Thus, PCL/PEO/clay combinations form a very good

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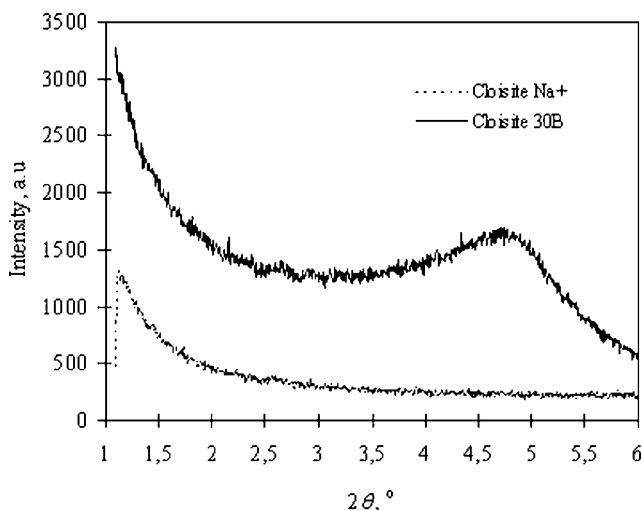


Figure 1 SAXS patterns of different clays.

model system for evaluating the emulsification activity of the clay.

The question considered here is the location of the filler in a binary immiscible blend in which the two components exhibit an exfoliating ability toward it. The ultimate purpose is to investigate the intercalation/exfoliation process in PCL/PEO immiscible blend nanocomposites prepared by melt extrusion as a function of the surface hydrophobicity of the layered silicates. Particular attention is given to the migration and location of the nanoclay at the PCL/PEO interface and its consequent emulsifying effect.

## EXPERIMENTAL

### Materials

The layered silicates were montmorillonites (MMTs) supplied by Southern Clay Products, Inc. (Texas). Two types of MMTs were used. Cloisite Na<sup>+</sup> is a natural unmodified MMT (MMT-Na) that contains exchangeable cations (primarily Na<sup>+</sup>). Its cation-exchange capacity is 92.6 mequiv/100 g of clay. The moisture content is less than 2 wt %. The weight loss on ignition is about 7 wt %, and the specific gravity is 2.86 g/cc. Cloisite 30B is an organoclay modified with a ternary ammonium salt, (C<sub>18</sub>H<sub>37</sub>)N<sup>+</sup>(C<sub>2</sub>H<sub>4</sub>OH)<sub>2</sub>CH<sub>3</sub>. After modification, the clays display hydrophobicity that enhances their intercalation with polymer matrices.

PCL was supplied by Solvay Interlox, Ltd. (UK). Its trade name is CAPA 6500, and it has a weight-average molecular weight of 50,000 g/mol and a melting temperature of 58–60°C.

PEO was supplied by Aldrich Co. Its molecular weight and melting temperature are 30,000 g/mol and 57–61°C, respectively.

### Composite preparation

The composites were prepared via melt mixing with a twin-screw miniextruder manufactured by DSM Co. The mixing was carried out for 10 min at a screw speed of 100 rpm and a temperature of 100°C. A nitrogen flow was continuously flushed into the chamber to prevent oxidative degradation. PCL, PEO, and the clay were fed into the miniextruder simultaneously. When the two-step process was considered, PCL or PEO was first premixed with the clay, and then the second polymer was added.

### Characterization

Small-angle X-ray scattering (SAXS) measurements were performed on a Rigaku Rotoflex RU2008 rotating-anode diffractometer (Rigaku Co., Tokyo, Japan) with Cu K $\alpha$  radiation having a wavelength of 1.54 Å and a nickel monochromator. The angular dependence of the intensity of the radiation was recorded with a goniometer. These data could be used to calculate the interlayer spacing ( $d$ ) through the Bragg equation:

$$\lambda = 2d \sin \theta$$

where  $\lambda$  is the wavelength of X-ray radiation (1.54 Å) and  $\theta$  is the reflection angle.

A Philips CM20 transmission electron microscope was used to examine the morphologies of the polymer/layered silicate composites. The extruded samples were cut to slices within the 50–100-nm thickness range with a Leica ultramicrotome (Vienna, Austria).

The phase morphology of the composites was also observed with a Philips XL20 scanning electron microscope. Samples of the blends consisting of a PEO dispersed phase were cryofractured in liquid nitrogen, and then the PEO phase was etched with distilled water for 2 days. When PCL formed the dis-

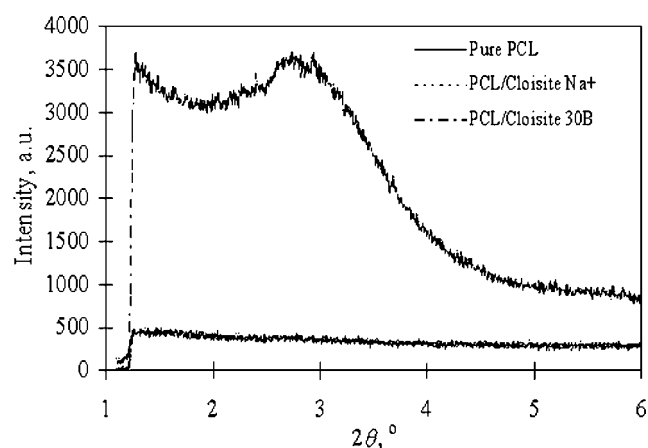
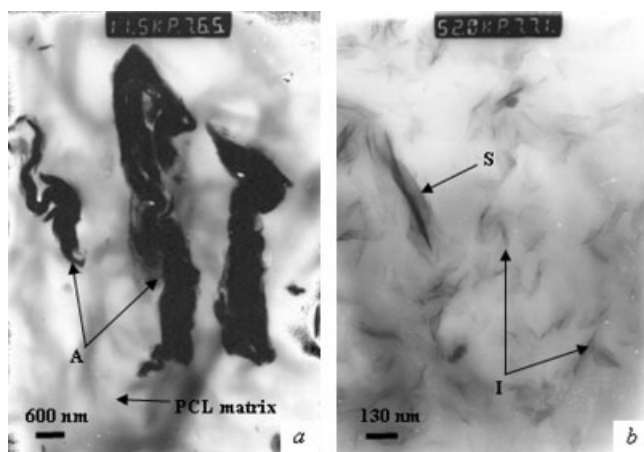


Figure 2 SAXS patterns of PCL and its composites with 5 wt % concentrations of different clays.



**Figure 3** TEM observations of (a) PCL/Cloisite Na<sup>+</sup> (95/5) and (b) PCL/Cloisite 30B (95/5) composites (I = individual layer; S = stack of layers; A = aggregate of clays).

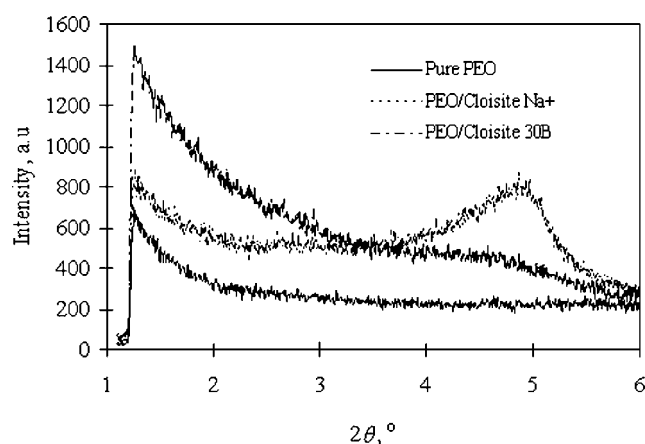
persed phase, the sample was dissolved in water, and the precipitates that consisted of PCL particles were filtered and collected on a flat surface for scanning electron microscopy (SEM) examination. All the samples were coated with gold before the SEM observations.

A dynamic stress rheometer with controlled stress was used to measure the rheological properties of the composites. The measurements were performed at 100°C in a frequency range from 0.03 to 10 rad/s. The storage modulus, loss modulus, and dynamic viscosity were recorded as functions of the frequency.

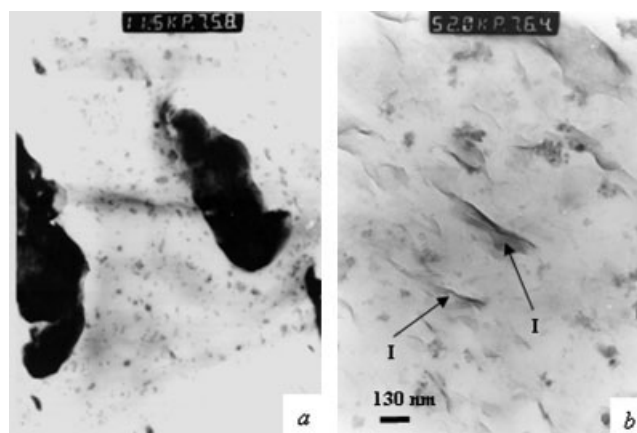
## RESULTS AND DISCUSSION

### Nanocomposites based on the homopolymers and clays

To probe the exfoliation of a filler in a polymer matrix, it is necessary to compare its crystalline characteristics, such as the long spacing, in its pure state

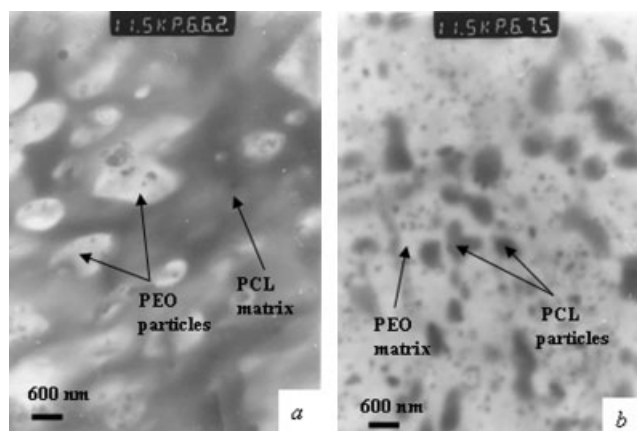


**Figure 4** SAXS patterns of PEO and its composites with 5 wt % concentrations of different clays.

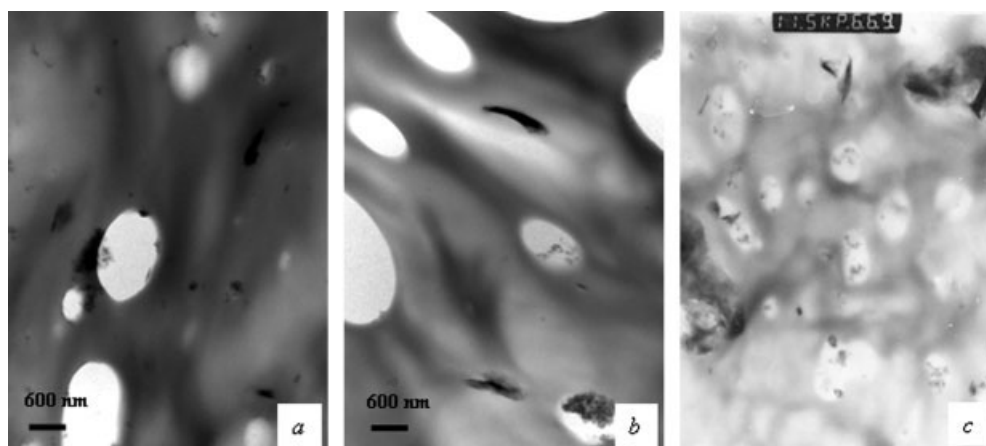


**Figure 5** TEM micrographs of (a) PEO/Cloisite Na<sup>+</sup> (95/5) and (b) PEO/Cloisite 30B (95/5) composites (I = individual layer; A = aggregate of clays).

and when it is exfoliated in the polymer matrix. The SAXS patterns of the hydrophilic (unmodified) and organophilic (modified) clays are displayed in Figure 1. No scattering peak is visible within the  $2\theta$  range of 0–6° when the unmodified Cloisite Na<sup>+</sup> is considered. According to Paul et al.,<sup>34</sup>  $d_{001}$  of the Cloisite Na<sup>+</sup> grade is 12.1 Å, which is too small to be detected in the SAXS range. In contrast, a clear scattering peak appears at  $2\theta$  of about 4.8 in the SAXS pattern of the organophilic clay (Cloisite 30B), which corresponds to a  $d_{001}$  value of 18.58 Å. When each of the two fillers is dispersed in the PCL, the SAXS patterns reveal that the pattern of a PCL composite containing 5 wt % Cloisite Na<sup>+</sup> is exactly the same as that of the pure PCL, indicating that no intercalation occurs when the unmodified clay is used (Fig. 2), whereas the X-ray diffraction trace of the PCL/Cloisite 30B mixture shows relevant peaks at  $2\theta = 2.9^\circ$ . This is a clear sign of a significant morphological change that the filler exhibits in the presence of the polymer matrix. This



**Figure 6** TEM micrographs of (a) 80/20 and (b) 20/80 PCL/PEO blends.



**Figure 7** TEM micrographs of the 80/20 PCL/PEO blends with (a) 1, (b) 2, and (c) 5 wt % Cloisite Na<sup>+</sup>.

morphological change is ascribed to exfoliation of the filler in the polymer matrix.

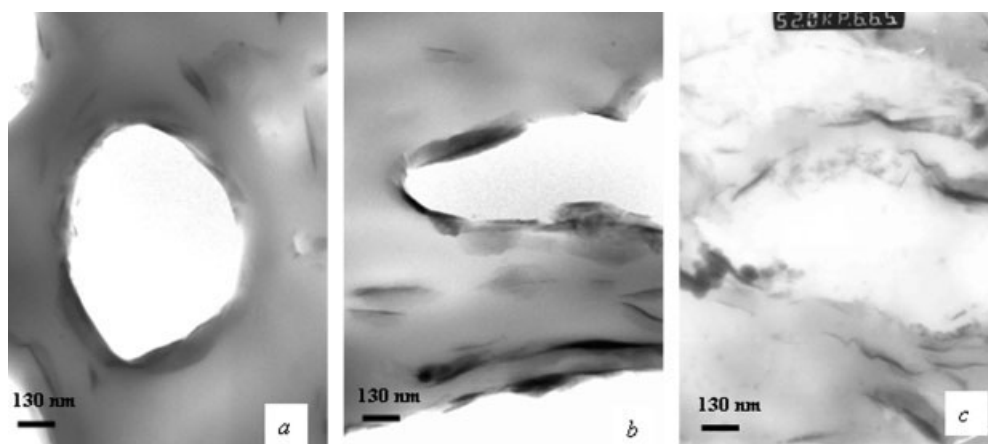
The transmission electron microscopy (TEM) micrographs of PCL composites containing 5 wt % concentrations of the hydrophobic or organophilic MMT, presented in Figure 3, support the SAXS data. As can be seen in Figure 3(a), mixing PCL with Cloisite Na<sup>+</sup> leads to a conventional microcomposite containing large-scale (micro)aggregations of the clay. In contrast, when the PCL is melt-mixed under the same mixing conditions with the organophilic MMT, Cloisite 30B, a nanocomposite is obtained having mainly exfoliated clay layers. Some partially exfoliated stacks are also observed [see the S symbol in Fig. 3(b)].

The composite containing 5 wt % hydrophobic or organophilic clay and having PEO as a matrix shows a scattering pattern in which a relevant scattering peak is visible at  $2\theta = 4.9^\circ$  when Cloisite Na<sup>+</sup> (hydrophilic) is considered (Fig. 4). The corresponding interlayer space is about 18.12 Å, which is significantly larger than that of the pure clay, indicating a clear intercalation process exhibited by the PEO chains into

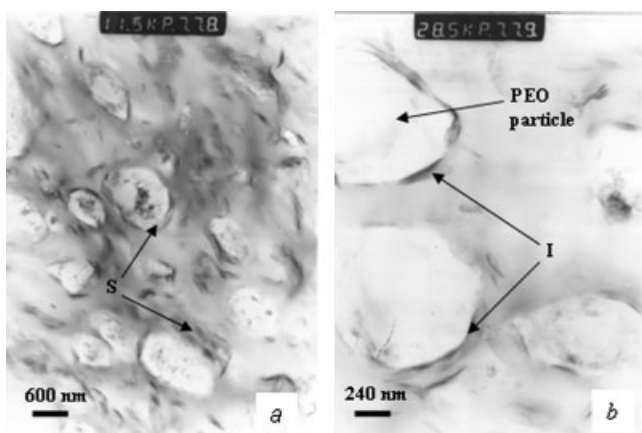
the gallery space of the hydrophilic clay. However, the TEM observations of this composite [Fig. 5(a)] show an aggregated structure of the clay, which indicates that the hydrophilic clays are only partially intercalated. The intercalation of PEO with the hydrophilic clay can be explained by the polar interactions between the ether groups (—O—) in the backbone of PEO chains and the hydroxyl groups present on the surface of the clay.

The SAXS curves of PEO/Cloisite 30B do not show any scattering peak as a result of a fully exfoliated structure. This morphological behavior is also confirmed by the TEM micrograph, which indicates a good dispersion of the individual silicate layers [Fig. 5(b)].

As the objective of this study was to determine whether the clay is located in the PEO phase, in the PCL phase, or at their interface in the PEO/PCL blend, TEM observations of the prepared composites were carried out. In Figure 6(a,b), the TEM micrographs of 80/20 and 20/80 (w/w) immiscible PCL/PEO blends without clay are shown. The two figures



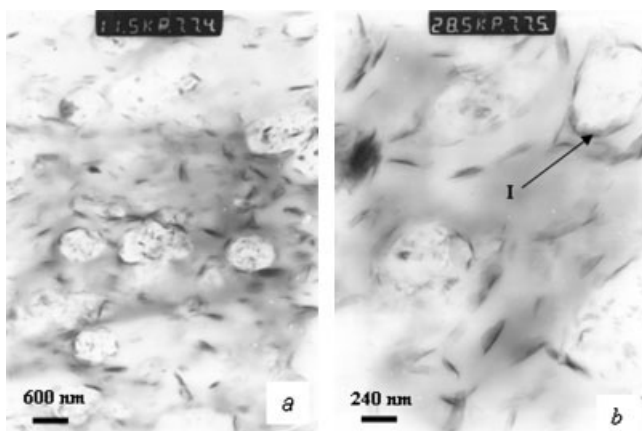
**Figure 8** TEM micrographs of the 80/20 PCL/PEO blends with (a) 1, (b) 2, and (c) 5 wt % Cloisite 30B.



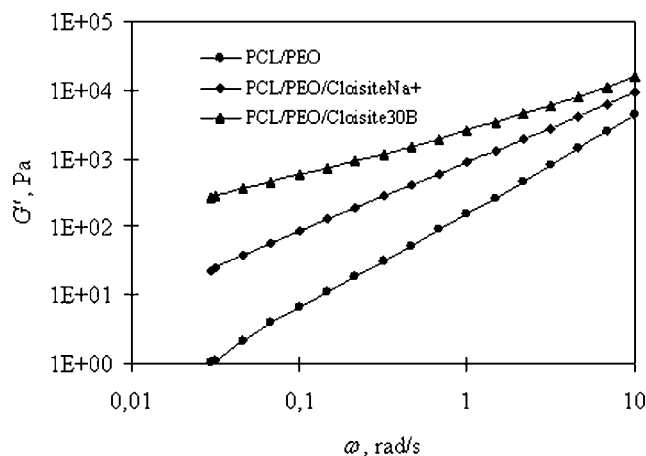
**Figure 9** TEM micrographs of the 80/20 PCL/PEO blends with 5 wt % Cloisite 30B, which were prepared by two-step melt extrusion. PCL was premixed with Cloisite 30B first and then mixed with PEO.

confirm the expected immiscibility between PEO and PCL. The bright parts represent the PEO phase, whereas the dark parts are ascribed to the PCL phase. Note that the PEO dispersed particles exhibit a smaller size in the PCL matrix than the PCL particles in the PEO matrix. This is mainly due to significant differences in their melt viscosities. How would the addition of each of the two types of clays, modified and unmodified, affect the phase morphology of PEO/PCL blends?

The TEM micrographs of the 80PCL/20PEO micro- and nanocomposites, presented in Figures 7 and 8, respectively, reveal micrometer-scale aggregates in the PCL/PEO/Cloisite Na<sup>+</sup> composite. As expected, this is ascribed to a lack of interaction between the hydrophobic polymers and the unmodified hydrophilic MMT Cloisite Na<sup>+</sup>. In contrast, as shown in the micrographs of Figure 8, PCL/PEO/Cloisite 30B nanocomposites contain both individual layers of clay

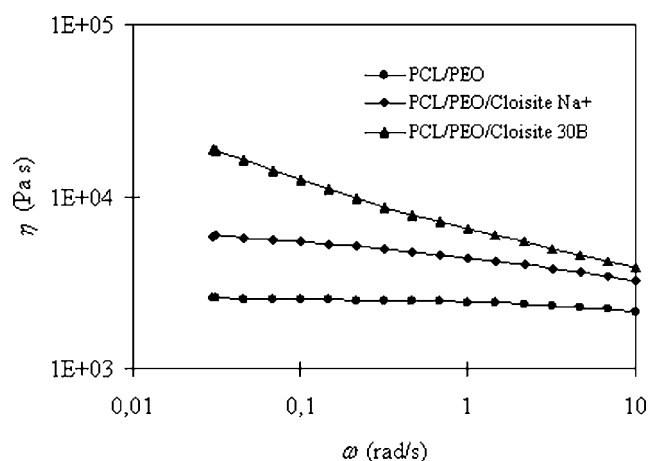


**Figure 10** TEM micrographs of the 80/20 PCL/PEO blends with 5 wt % Cloisite 30B, which were prepared by two-step melt extrusion. PEO was premixed with Cloisite 30B first and then mixed with PCL.

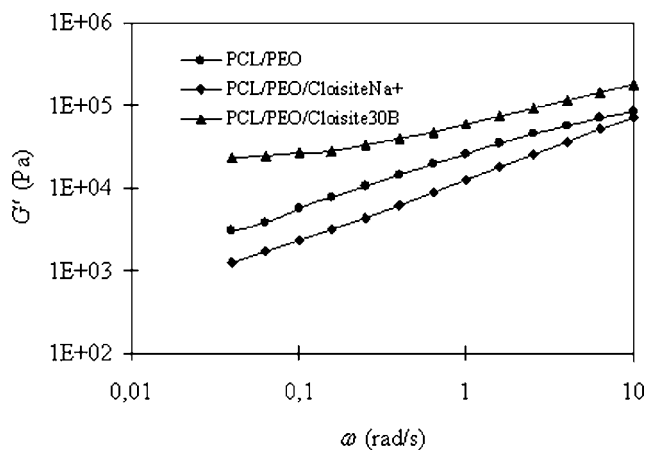


**Figure 11** Storage modulus ( $G'$ ) versus the frequency ( $\omega$ ) for an 80/20 PCL/PEO blend and its composites with 5 wt % Cloisite Na<sup>+</sup> and Cloisite 30B (100°C).

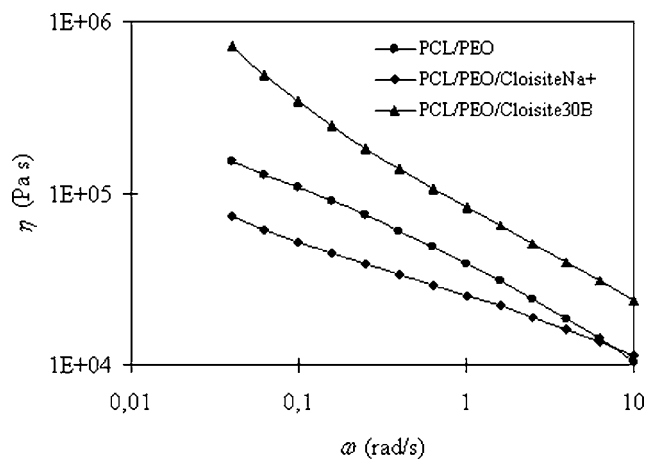
and stacks with differing extents of intercalation. The close observation of these pictures reveals that the clay is mainly located at the PCL/PEO interface. Note that as the concentration of the clay is increased from 1 to 5 wt %, the exfoliation is more pronounced than the intercalation, as indicated by the balance between the clay in the form of stacks and that in the form of individual layers. The location of the silicate layers at the interface in the immiscible PCL/PEO blends is due to differences in the interfacial tensions (which are not easy to measure) between the silicate and each of the two polymers in the composite. Similarly, the location of carbon black particles at immiscible blend interfaces was reported by Zakin et al.<sup>8</sup> These authors claimed that an increase in the interfacial tension associated with significant differences in the energies of the adsorption interaction between the polymers of the blend and the carbon black filler promotes an increase in their local concentration at the polymer-polymer interface.



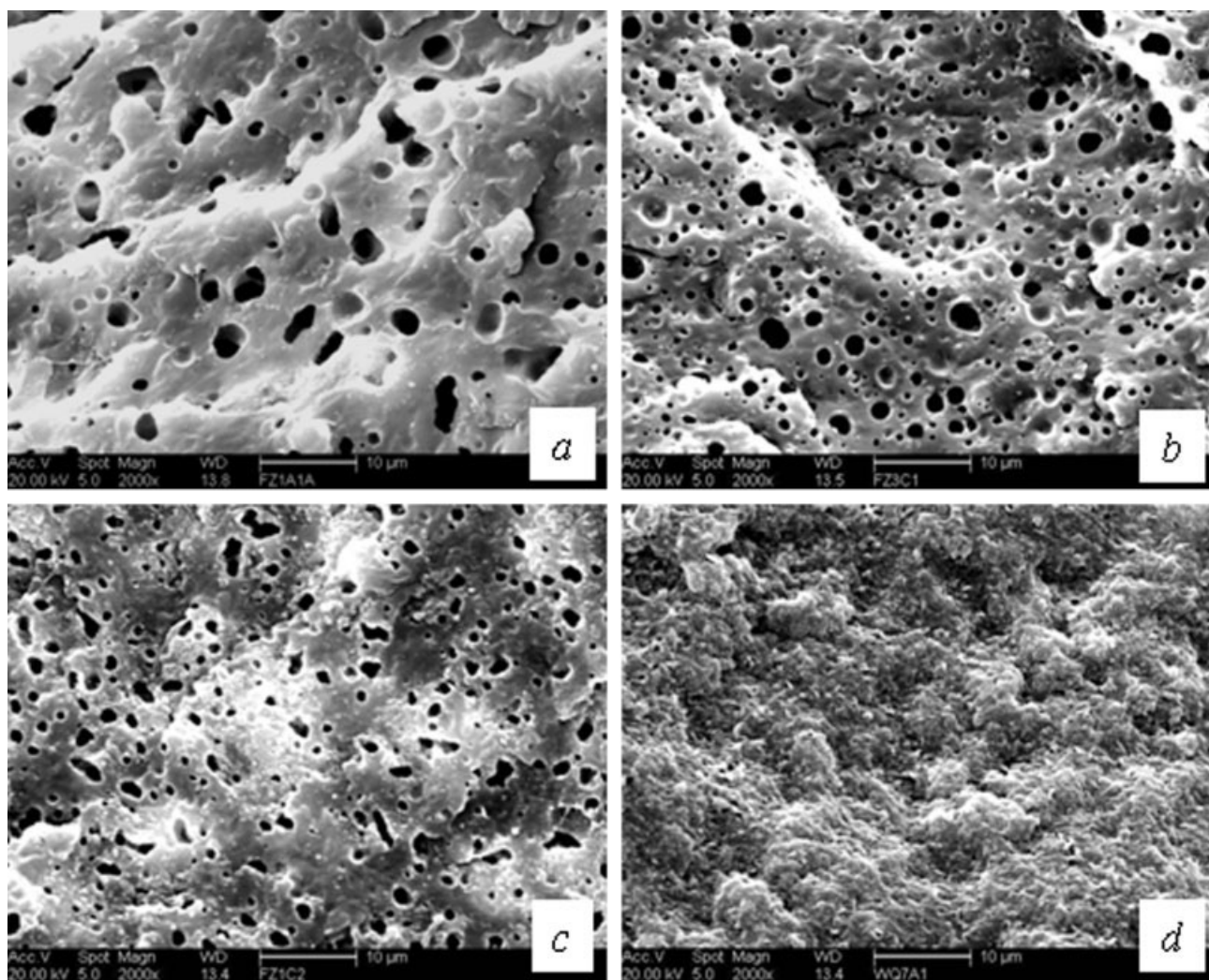
**Figure 12** Dynamic viscosity ( $\eta$ ) versus the frequency ( $\omega$ ) for an 80/20 PCL/PEO blend and its composites with 5 wt % Cloisite Na<sup>+</sup> and Cloisite 30B (100°C).



**Figure 13** Storage modulus ( $G'$ ) versus the frequency ( $\omega$ ) for a 20/80 PCL/PEO blend and its composites with 5 wt % Cloisite Na<sup>+</sup> and Cloisite 30B (100°C).

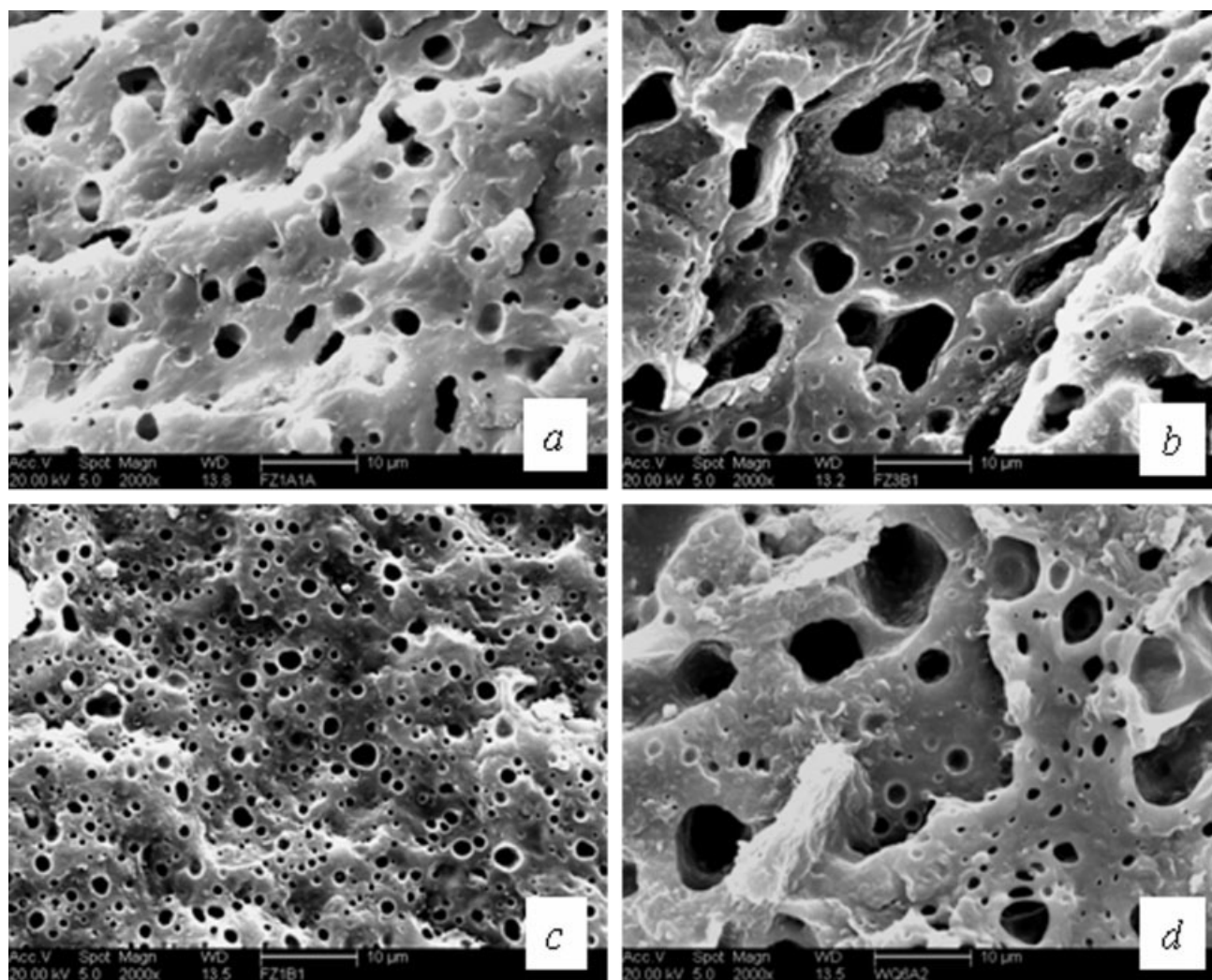


**Figure 14** Dynamic viscosity ( $\eta$ ) versus the frequency ( $\omega$ ) for a 20/80 PCL/PEO blend and its composites with 5 wt % Cloisite Na<sup>+</sup> and Cloisite 30B (100°C).



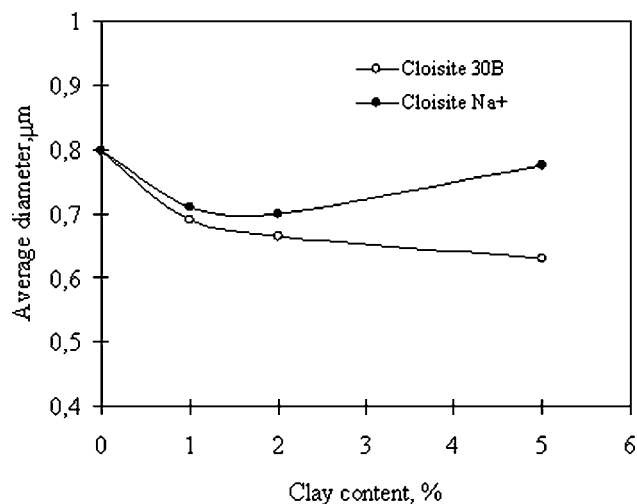
**Figure 15** SEM micrographs of (a) an 80/20 PCL/PEO blend and (b–d) its composites with (b) 1, (c) 2, and (d) 5 wt % Cloisite 30B.



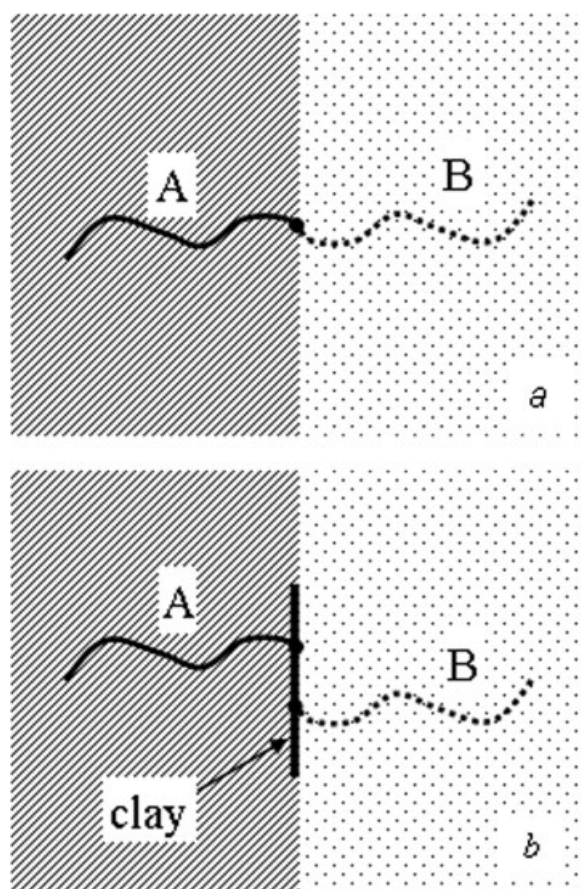


**Figure 16** SEM micrographs of (a) an 80/20 PCL/PEO blend and (b–d) its composites with (b) 1, (c) 2, and (d) 5 wt % Cloisite Na<sup>+</sup>.

To study the preferential location of the nanoclay at the polymer–polymer interface, the nanocomposites were prepared by a two-step process: premixing the whole amount of the clay with one of the two polymer components followed by the melt mixing of the resulting mixture with the second polymer component. The TEM micrographs presented in Figure 9 were obtained from an 80 PCL/20PEO composite containing 5 wt % Cloisite 30B prepared by first the premixing of the clay with the PEO minor phase and then the addition of the PCL matrix. Figure 10 was obtained from the same composite prepared by first the premixing of the clay with the PCL major phase and then the addition of the PEO minor phase. The two figures reveal that, independently of the mixing procedure used in both cases, the silicate layers diffuse and migrate from the premixed PEO domains or from the premixed PCL matrix to the PCL–PEO interface. The TEM micrographs of the 20/80 PCL/PEO micro- and nanocomposites containing 5 wt % Cloi-



**Figure 17** Effect of the hydrophobic and hydrophilic clay contents on the average diameter of the PEO phase.



**Figure 18** Comparison of the compatibilization mechanisms of (a) a diblock copolymer and (b) a clay platelet.

site  $\text{Na}^+$  and Cloisite 30B, which are not presented here, gave similar results. This morphological information confirms that the filler is more thermodynamically stable at the interface than in one of the two polymer phases. As could logically be expected, the kinetics of diffusion also affect the extent of the filler location at the interface. Note that in Figure 9, less filler is located in the PCL matrix, as initially the filler was premixed with the minor phase, whereas when it is premixed with the PCL matrix, the diffusion is slow, and a significant amount of the filler remains located in the PCL phase.

### Rheological behavior

The viscoelastic behavior of the investigated composites show interesting features with respect to the role of the exfoliation of the silicates and probably to their location at the interface. The storage modulus (Figs. 11 and 12) and dynamic viscosity (Figs. 13 and 14) versus the frequency of the blends and their composites with 5 wt % silicates reveal that the microcomposite containing hydrophilic MMT (Cloisite  $\text{Na}^+$ ) exhibits a normal response of a conventional filled thermoplastic polymer, with liquidlike behavior at low frequencies, that is, below 0.1 rad/s. The larger

values of the viscosity or the storage modulus of the microcomposites compared to those of the pure blend result from the positive contribution due to the incorporation of the filler.

In contrast, the storage modulus for the PCL/PEO (80/20 and 20/80) nanocomposites containing organophilic MMT (Cloisite 30B) increases in the frequency range of 0.03–0.1 rad/s. Furthermore, at low frequencies (corresponding to a regime in which the unfilled polymer exhibits a liquidlike Newtonian behavior), the storage moduli for these nanocomposites show a reduced frequency dependence, that is, solidlike behavior.

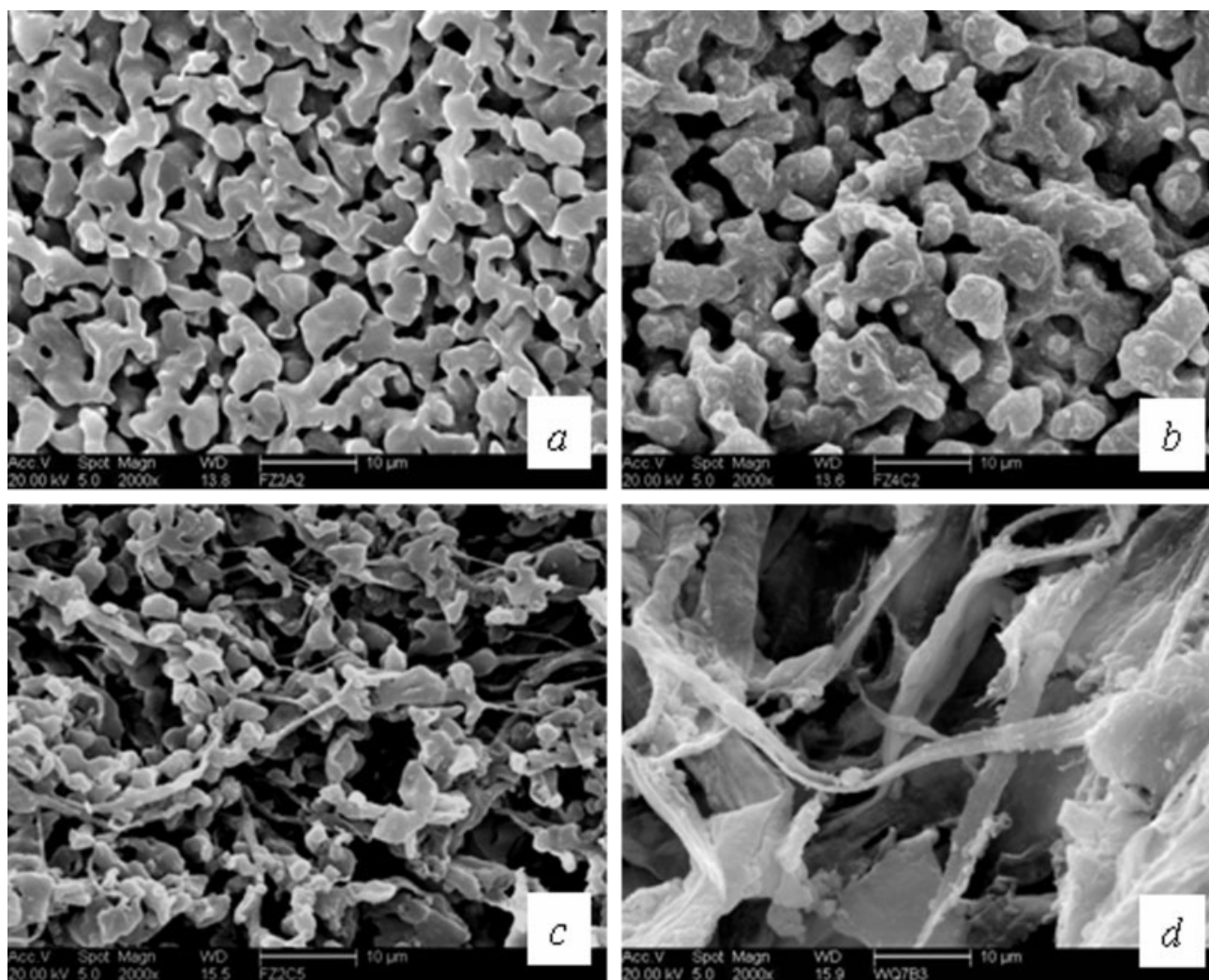
This is a clear indication of a long-time relaxation process resulting from enhanced levels of interactions between the silicates and the polymer components. At a given silicate loading (5 wt %), the liquidlike relaxation observed for the conventional filled composites (microcomposites) gradually changes to solidlike behavior for nanocomposites. This behavior can be attributed to the retardation of molecular relaxation processes induced by the confined geometric effect.<sup>35,36</sup> Solidlike behavior at low frequencies has recently been observed in both polycaprolactone and polyamide exfoliated nanocomposites having low silicate contents (3–5 wt %).<sup>37,38</sup> Similar behavior was also reported by Moussaif and Groeninckx<sup>39</sup> in poly(vinylidene fluoride)/poly(methyl methacrylate). This behavior was attributed to the percolation of a three-dimensional filler network structure comprising a random orientation of exfoliated layers. Our observations clearly indicate that the melt mixing of the organophilic MMT (Cloisite 30B) with the thermoplastic matrix leads to good exfoliation of the silicate layers in the matrix, resulting in the formation of a percolated network structure of the exfoliated layers. This is in good agreement with the morphological investigations.

The dynamic viscosity as a function of frequency for filled 80/20 and 20/80 PCL/PEO micro- and nanocomposites is given in Figures 12 and 14. Over the frequency range (0.02–10 rad/s), the viscosity of the nanocomposites is much higher than that of the microcomposites and the pure polymer matrix. At low frequencies ( $<0.1$  rad/s), the nanocomposites exhibit solidlike behavior, with a higher viscosity than that of the polymer matrix or that of the PCL/PEO/clay microcomposites. This enhancement of the dynamic viscosity arises from the exfoliation and dispersion of layered silicates in the polymer matrix leading to a network structure.<sup>40</sup>

### Emulsifying effect of the exfoliated clay

Recently, there has been growing interest in the emulsifying role that fillers can play in immiscible polymer blends. The role of organically modified layered sili-





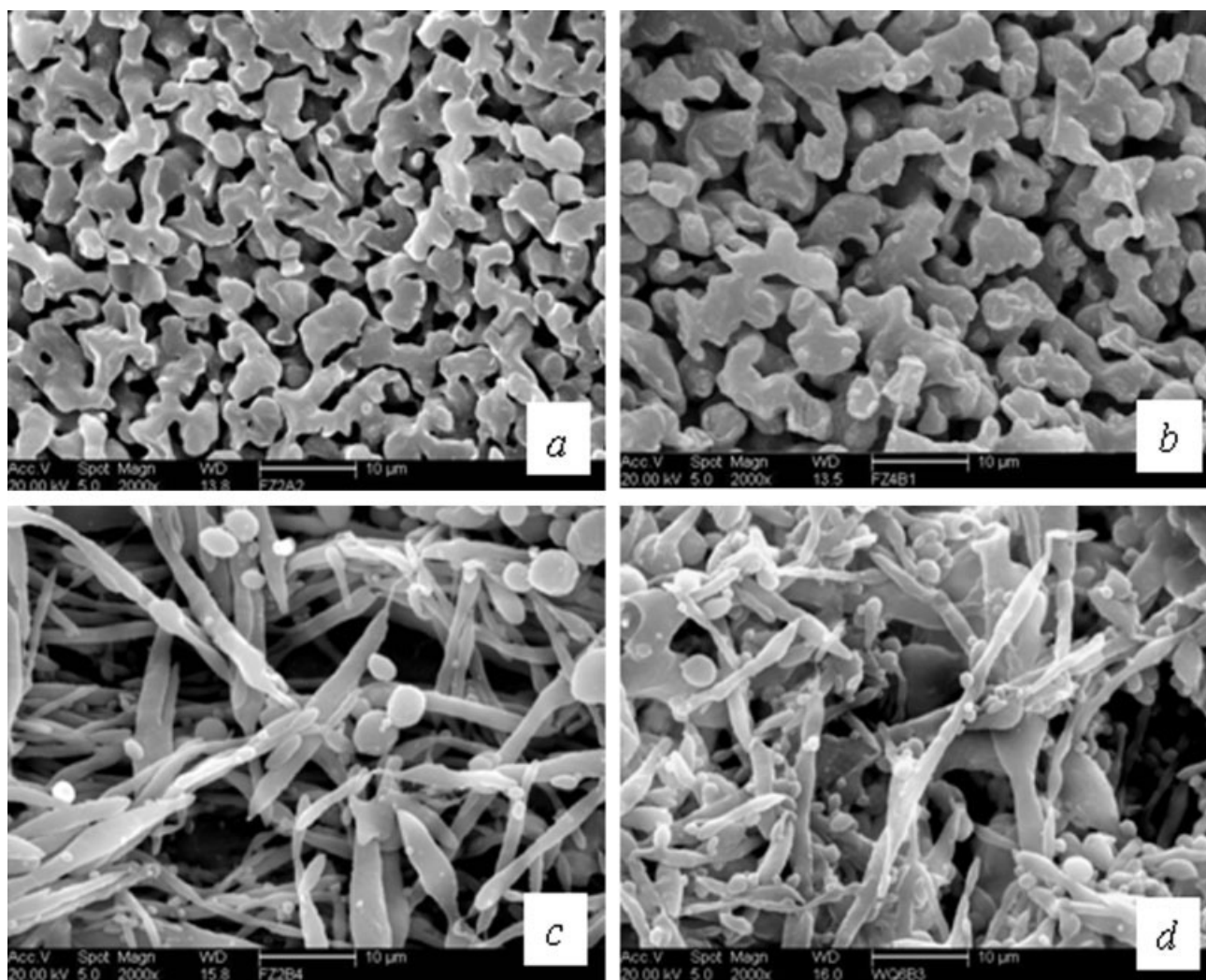
**Figure 19** SEM micrographs of (a) a 20/80 PCL/PEO blend and (b–d) its composites with (b) 1, (c) 2, and (d) 5 wt % Cloisite 30B. Parts c and d show the precipitates of the dissolved samples.

cate as a compatibilizer for immiscible polystyrene with polypropylene or polypropylene grafted with maleic anhydride was recently reported by Ray et al.<sup>41</sup> The effect of nanometer-sized silica particles on the flow-induced morphology of immiscible polymer blends was studied for a polydimethylsiloxane (PDMS)/polyisobutylene (PIB) model blend by Vermant et al.<sup>42</sup> A stable droplet/matrix microstructure was obtained for blends of 30% PIB and 70% PDMS or the opposite composition. The rheological measurements show that the silica particles altered the sensitivity of the dispersed phase/matrix microstructure to shear flow. Coalescence was suppressed or at least slowed down on a practical timescale, especially when PDMS was the matrix phase. Cryo-SEM allowed the observation of the accumulation of the particles at the interface. The authors proposed that blends stabilized by solid particles could provide an interesting alternative to blends compatibilized by block copolymers.

To distinguish the phases, the fractured samples were etched in distilled water for 2 days, which selectively removed the PEO; that is, the holes in the SEM images represent PEO domains.

The emulsifying effect of Cloisite 30B in the immiscible 80PCL/20PEO blend is evidenced via SEM observations, shown in Figures 15 and 16, of the composites with Cloisite Na<sup>+</sup> and Cloisite 30B, respectively. Upon the addition of the Cloisite 30B to an 80PCL/20PEO blend, a substantial decrease in the PEO domain size can be observed. The average diameter of the PEO dispersed phase is plotted as a function of the clay content in Figure 17. A monotonic decrease in the dimension of the dispersed PEO phase with increasing Cloisite 30B concentration can be observed up to 5 wt %, showing a typical emulsification curve.

In contrast, the effect of the hydrophilic Cloisite Na<sup>+</sup> is irregular. The PEO particles exhibit a broad size distribution. As expected, this might be a direct



**Figure 20** SEM micrographs of (a) a 20/80 PCL/PEO blend and (b–d) its composites with (b) 1, (c) 2, and (d) 5 wt % Cloisite Na<sup>+</sup>. Parts c and d show the precipitates of the dissolved samples.

result of a lack of interactions of the unmodified filler with the homopolymers. The formation of large domains might be due to the concentration of aggregated clays in PEO particles.

Figure 18 shows a schematic comparison of the compatibilization mechanisms of a clay platelet and a diblock copolymer. For a diblock copolymer, blocks A and B are compatible with phases A and B, respectively, and their connecting covalent link appears at the interface of the two phases. In the case of the clay, both polymers A and B have strong interactions with the exfoliated clay platelet, which is localized in the interface. The clay platelet plays the role of a coupling species between the two homopolymers.

In the opposite composition, that is, 20/80, in which the PCL is the dispersed phase, the phase morphology of the composite was found to be a cocontinuous type after the PEO major phase was removed by water. Figures 19 and 20 show SEM observations of the 20/80 PCL/PEO blend and its composites with

Cloisite Na<sup>+</sup> and Cloisite 30B, respectively. The phase continuity of the PCL phase was found to decrease gradually as a function of the clay content. At a concentration of 2 wt % Cloisite 30B, the sample was dissolved in water, and the precipitated PCL minor phase showed a quasicontinuous structure [Fig. 20(c)], indicating an emulsifying effect of the clay. When the clay content was increased to 5 wt %, the PCL phase became fiberlike.

It is interesting to note the phase morphology evolution of the 20/80 PCL/PEO blend composites with increasing Cloisite Na<sup>+</sup> content. The PCL phase evolved from a fully continuous structure to a sphere-like structure via an intermediate fiberlike shape.

## CONCLUSIONS

Nanocomposites based on 80/20 and 20/80 PCL/PEO immiscible blends and organophilic clay were studied and compared with organophobic clay. Both

one-step and two-step melt-extrusion processes showed that the organophilic layered silicates were finely exfoliated and preferentially located at the interface between the PCL and PEO phases.

The rheological behavior of intercalated/exfoliated PCL and PEO nanocomposites was also investigated. At low frequencies, the frequency dependence of the storage modulus gradually changes from liquidlike to solidlike behavior for the nanocomposites, indicating the formation of a network structure.

From the corresponding SEM micrographs, a monotonic decrease of the PEO domain size in an 80/20 PCL/PEO blend was observed with the increment of the Cloisite 30B content, indicating a clear emulsifying effect induced by the location of the clay at the PCL/PEO interface, and the continuity of the 20/80 PCL/PEO blend decreased with increasing clay content. Although there are various factors influencing the morphology of the composite, the emulsifying effect of organophilic layered silicates on immiscible PCL/PEO blends is evident.

## References

- Paul, D. R.; Bucknall, C. B. *Polymer Blends*; Wiley: New York, 2000.
- Shonaike, G. O.; Simon, G. P. *Polymer Blends and Alloys*; Marcel Dekker: New York, 1999.
- Utracki, L. A. *Polymer Blends Handbook*; Kluwer Academic: Dordrecht, 2002.
- Balazs, A. *Curr Opin Colloid Interface Sci* 2000, 4, 443.
- Marsh, P. A.; Voet, A.; Price, L. D.; Mullens, T. J. *Rubber Chem Technol* 1968, 41, 344.
- Sircar, A. K. *Rubber Chem Technol* 1981, 54, 820.
- Gubbels, F.; Jérôme, R.; Teyssié, P.; Vanlathem, E.; Deltour, R.; Calderone, A.; Parente, V.; Bredas, J. L. *Macromolecules* 1994, 27, 1972.
- Zaikin, A. E.; Mindubaev, R. Y.; Arkhireev, V. P. *Colloid J* 1999, 61, 464.
- Karim, A.; Liu, D. W.; Douglas, J. F.; Nakatani, A. I.; Amis, E. J. *Polymer* 2000, 41, 8455.
- Nesterov, A. E.; Lipatov, Y. S.; Horichko, V. V.; Gritensko, O. T. *Polymer* 1992, 33, 619.
- Lipatov, Y. S.; Nesterov, A. E. *Polym Eng Sci* 1992, 32, 1261.
- Nesterov, A. E.; Lipatov, Y. S. *Polymer* 1999, 40, 1347.
- Scherbakoff, N.; Ishida, H. *J Adhes* 1997, 64, 203.
- Zhang, Q.; Yang, H.; Fu, Q. *Polymer* 2004, 45, 1913.
- Gonzalez, J.; Albano, C.; Ichazo, M.; Diaz, B. *Eur Polym J* 2002, 38, 2465.
- Hrnjak-Murgic, Z.; Jelcic, Z.; Kovacevic, V.; Milna-Misak, M.; Jelencic, J. *Mater Eng* 2002, 287, 684.
- Krause, S. J. *Macromol Sci* 1972, 7, 251.
- Voulgaris, D.; Petridis, D. *Polymer* 2002, 43, 2213.
- Rafailovich, M.; Sokolov, J.; Zhu, S.; Chu, B. U.S. Patent 6,339,121 (2002).
- Giannelis, E. P.; Shah, D.; Schmidt, D. *Curr Opin Solid State Mater Sci* 2002, 6, 205.
- Ferreiro, V.; Douglas, J. F.; Amis, E. J.; Karim, A. *Macromol Symp* 2001, 167, 73.
- Qiu, Z.; Ikehara, T.; Nishi, T. *Polymer* 2003, 44, 3101.
- Alexandre, M.; Dubois, P. *Mater Sci Eng* 2000, 28, 1.
- Lepoittevin, B.; Devalckenaere, M.; Pantoustier, N.; Alexandre, M.; Kubies, D.; Calberg, J.; Dubois, P. *Polymer* 2002, 43, 4017.
- Kiersnowski, A.; Piglowski, J. *Eur Polym J* 2004, 40, 1199.
- Gorrasi, G.; Tortora, M.; Vittoria, V.; Pollet, E.; Lepoittevin, B.; Alexandre, M.; Dubois, P. *Polymer* 2003, 44, 2271.
- Lepoittevin, B.; Pantoustier, N.; Devalckenaere, M.; Alexandre, M.; Calberg, C.; Jérôme, R.; Henrist, C.; Rulmont, A.; Dubois, P. *Polymer* 2003, 44, 2033.
- Shen, Z.; Simon, G. P.; Cheng, Y. *Eur Polym J* 2003, 9, 1917.
- Shen, Z.; Simon, G. P.; Cheng, Y. *Polymer* 2002, 43, 4251.
- Chen, H. W.; Chang, F. C. *Polymer* 2001, 42, 9763.
- Aranda, P.; Ruiz-Hitzky, E. *Appl Clay Sci* 1999, 15, 119.
- Doeff, M. M.; Reed, J. S. *Solid State Ionics* 1998, 113, 109.
- Ogata, N.; Kawakage, S.; Ogihara, T. *Polymer* 1997, 38, 5115.
- Paul, M. A.; Alexandre, M.; Degée, P.; Henrist, C.; Rulmont, A.; Dubois, P. *Polymer* 2003, 44, 443.
- Peanasky, J.; Cai, L. L.; Granick, S.; Kessel, C. R. *Langmuir* 1994, 10, 3874.
- Granick, S.; Hu, H. W. *Science* 1992, 258, 1339.
- Galgali, G.; Ramesh, C.; Lele, A. *Macromolecules* 2001, 34, 852.
- Krishnamoorti, R.; Silva, A. S. In *Polymer-Clay Nanocomposites*; Pinnavaia, T. J.; Beall, G., Eds.; Wiley: New York, 2000; p 315.
- Moussaif, N.; Groeninckx, G. *Polymer* 2003, 44, 7899.
- Ren, J.; Silva, A. S.; Krishnamoorti, R. *Macromolecules* 2000, 33, 3739.
- Ray, S. S.; Pouliot, S.; Bousmina, M.; Utracki, L. A. *Polymer* 2004, 45, 8403.
- Vermant, J.; Cioccolo, G.; Nair, K. G.; Moldenaers, P. *Rheol Acta* 2004, 43, 529.