

Study on the Dynamic Self-Organization of Montmorillonite in Two Phases

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ABSTRACT: Polycarbonate (PC)/acrylonitrile–butadiene–styrene (ABS) polymer alloy/montmorillonite (MMT) and nylon 6 (PA6)/ABS polymer alloy/MMT nanocomposites were prepared using the direct melt intercalation technique. Their structures were characterized by XRD and TEM. The results of TEM show that the silicate layers dispersed differently in two phases. In the PC/ABS/MMT nanocomposite, the silicate layers were self-organized in the ABS phase, whereas in the PA6/ABS/MMT nanocomposite, the silicate layers were dispersed in both phases but mainly in the PA6

phase. Furthermore, the PC/MMT nanocomposite was melt-mixed with pure ABS, and the changed morphology of the hybrid with the change of melt-mixing time was characterized by XRD and TEM, to study the dynamic self-assembly of clay layers in two phases. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 1457–1462, 2004

Key words: alloys; clay; nanocomposites; TEM; self-organization

INTRODUCTION

The field of polymer nanocomposites, especially polymer/clay nanocomposites, has stimulated fundamental and applied research because these nanoscale materials often exhibit physical and chemical properties that are dramatically different from those of conventional microcomposites.^{1–3} Moreover, they can provide a good model system for the studies of the phase behavior of a polymer–nanoparticle mixture as well as the polymer chain dynamics in the confined geometry.⁴ Although polymer/clay nanocomposites have been researched for decades, attention has seldom been focused on the morphology of silicate layers in polymer alloys. Lim and coworkers⁵ reported the preparation and interaction characteristics of OMT with a miscible polymer blend of poly(ethylene oxide) and poly(methyl methacrylate).

We synthesized acrylonitrile–butadiene–styrene (ABS)/montmorillonite (MMT) nanocomposites by the melt-mixing technique,^{6,7} and first reported the self-assembly of montmorillonite in polycarbonate (PC)/ABS alloys.^{8,9} Other reports on PC/ABS alloy,

ABS/clay, and PC/clay nanocomposites were published by Jang et al.,¹⁰ Huang et al.,¹¹ Choi et al.,¹² and Notomi et al.¹³ For two-phase immiscible polymer blend/clay nanocomposites, such as PC/ABS and PA6/ABS^{14,15} with OMT, the properties of the nanocomposites greatly depend on the morphology of clay in the polymer blend matrices, so it is worth evaluating the dispersion of clay in polymer blend/clay nanocomposites. In this work we synthesized PC/clay, ABS/clay, PC/ABS/clay, PA/clay, and PA/ABS/clay nanocomposites by the direct melt intercalation technique and studied the morphology of clay in these polymer matrices. The dynamic self-organization of the silicate layers in the two phases (PC/ABS) is also reported in this article.

EXPERIMENTAL

Materials

The materials examined in this study were PC (weight-average molecular weight, 65,000 g/mol; K-1300, Teijin Chemicals, Ltd., Hiroshima, Japan), ABS (acrylonitrile content, 25%; Qimei Stock Co., Taiwan), and nylon 6 (weight-average molecular weight 18,000 g/mol; UBE Industries, Yamaguchi, Japan). The original purified sodium montmorillonite (MMT; cation exchange capacity, 96 meq/100 g; interlayer spacing $d_{001} = 1.45$ nm) and organophilic montmorillonite (OMT; interlayer spacing $d_{001} = 2.4$ nm) were kindly provided by Keyan Co. (Hefei, China). OMT was prepared from MMT by ion-exchange reaction using hexadecyl trimethyl ammonium bromide (C16) in water according to the reported method.¹

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TABLE I
Summary of Polymer/Clay Compounds

| Compound | Melt-mixing time (min) | PC (wt %) | ABS (wt %) | OMT (wt %) | Main diffraction peak (d_{001}) (Å) |
|--------------|------------------------|-----------------|------------|------------|---|
| MMT | — | — | — | — | 15 |
| OMT | — | — | — | — | 24 |
| PC/5%OMT | — | 95 | — | 5 | 27.8 |
| PC/ABS/5%OMT | — | 57 | 38 | 5 | 29.2 |
| ABS/5%OMT | — | 95 | — | 5 | 33.5 |
| PC/ABS-1 | 1 | 60 ^a | 40 | — | 33.4 |
| PC/ABS-2 | 2 | 60 ^a | 40 | — | 33.4 |
| PC/ABS-5 | 5 | 60 ^a | 40 | — | 31 |
| PC/ABS-10 | 10 | 60 ^a | 40 | — | 30.3 |
| PC/ABS-20 | 20 | 60 ^a | 40 | — | 30.5 |
| PC/ABS-30 | 30 | 60 ^a | 40 | — | 30 |

^a PC/5%OMT.

Preparation of nanocomposites

Nanocomposites (Table I), PC/5%OMT, ABS/5%OMT, PC/ABS/5%OMT with the weight ratio of PC/ABS = 3/2 and PA6/5%OMT, PA6/ABS/5%OMT with the weight ratio of PA6/ABS = 3/2 were synthesized using the following procedure: OMT and polymer were mechanically mixed and then extruded by a twin-screw extruder (TE-35, Nanjing, China) at a rotational speed of 300 rpm. The temperature profiles of the barrel were 150–220–230–220°C from hopper to the die for PC/5%OMT, ABS/5%OMT, and PC/ABS/5%OMT, and 150–240–240–235°C for PA6/5%OMT and PA6/ABS/5%OMT. This extrudate was pelletized, dried, and pressed into a thin film for XRD testing.

To study the dynamic dispersibility of clay layers in two phases, PC/5%OMT nanocomposite made by twin-screw extruder was melt-mixed with pure ABS [weight ratio of (PC/5%OMT)/ABS is 3/2] at 225°C using a twin-screw mill at high speed (XK-160, Jiangshu, China) for 1, 2, 5, 10, 20, and 30 min to yield nanocomposites designated PC/ABS/OMT-*x*, where *x* is the mixed time.

Evaluation of dispersibility of the clay in polymers resin matrix

The dispersibility of the silicate layers in the PC, ABS, PA6, PC/ABS, and PA6/ABS alloys was evaluated using an X-ray diffractometer (XRD) and bright-field transmission electron microscopy (TEM). X-ray diffraction experiments were performed at room temperature by a Rigaku D/max-rA X-ray diffractometer (30 kV, 10 mA; Rigaku, Tokyo, Japan) with Cu ($\lambda = 1.54178 \text{ \AA}$) irradiation at the rate of 2°/min in the range of 1.5–10°. TEM specimens were cut from epoxy block with the embedded nanocomposites at room temperature using an ultramicrotome (Ultracut-1,

Emitech Ltd., Ashford, Kent, UK) with a diamond knife. TEM images were obtained by JEOL JEM-100SX (JEOL, Tokyo, Japan) with an acceleration voltage of 100 kV.

RESULTS AND DISCUSSION

Dispersibility of polymer/clay nanocomposite

Figure 1 shows the XRD patterns of the MMT, OMT, PC/5%OMT, PC/ABS/5%OMT, PC/ABS/5%OMT, ABS/5%OMT, PA6/5%OMT, and PA6/ABS/5%OMT. The peaks correspond to the (001) plane reflections of the clays. The average basal spacing of MMT increases by organic modification from 14.5 to 24 Å, when original MMT was modified by C16. The increased spacing suggests that the chain of C16 intercalates into the gallery of MMT and expands it. From the analysis of XRD patterns in Figure 1 and Table I, the d_{001} peaks of PC/5%OMT, PC/ABS/5%OMT, and ABS/5%OMT are 27.8, 29.2, and 33.5 Å, respectively,

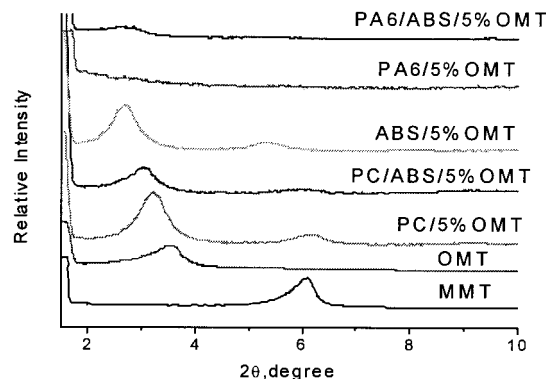


Figure 1 XRD patterns for MMT, OMT, PC/5%OMT, PC/ABS/5%OMT, ABS/5%OMT, PA6/5%OMT, and PA6/ABS/5%OMT.

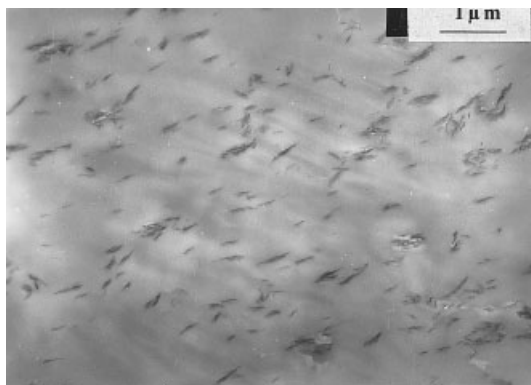


Figure 2 TEM micrograph of PC/5%OMT nanocomposite.

and have 4- to 10-Å gallery height increase compared to that of OMT, indicating an intercalated structure. The fact that the layer thickness of the nanocomposite ABS/OMT was larger than that of PC/OMT indicates a better compatibility or intercalation between OMT and ABS.⁵ The intergallery height of clay in PC/ABS/5%OMT (29.2 Å) ranged between that of PC/5%OMT (27.8 Å) and that of ABS/5%OMT (33.5 Å), indicating the clay layers in PC/ABS alloy may be intercalated by both ABS and PC molecular chains. Because intercalation between OMT and ABS is better than that of OMT and PC, we proposed that, in PC/ABS/5%OMT, it is mainly the ABS chains that intercalate into the interlayers OMT.

The loss of the d_{001} peak in PA6/5%OMT indicates an exfoliated structure and the broad d_{001} peak in PA6/ABS/5%OMT indicates an exfoliated intercalated structure. However, it is difficult for XRD to reveal definitive conclusions about the defined structure such as how many layers constitute multilayer stacks and which phase of the silicate layers is dispersed. Thus, TEM techniques are necessary to characterize the morphology of the composites.

In the TEM micrographs, PC/5%OMT (Fig. 2) and ABS/5%OMT (Fig. 3) are mainly made up of multi-

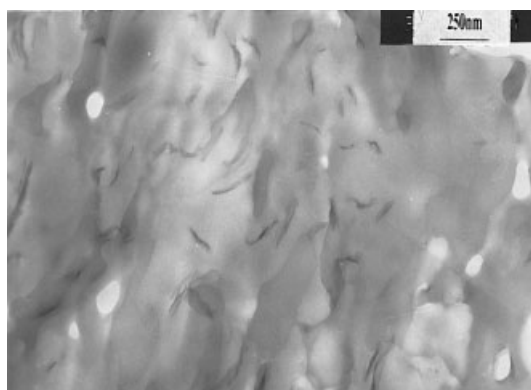


Figure 3 TEM micrograph of ABS/5%OMT nanocomposite.

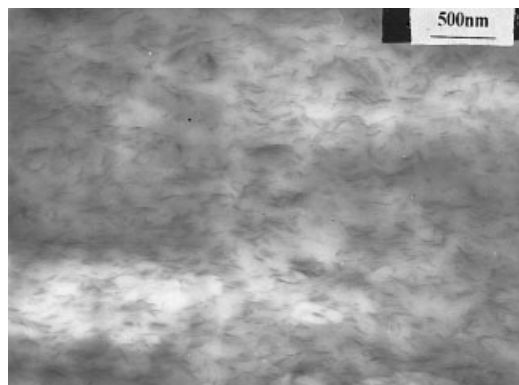


Figure 4 TEM micrograph of PA6/5%OMT nanocomposite.

layered stacks, about 50–100 nm in PC/5%OMT and about 10–30 nm in ABS/5%OMT. However, PA6/5%OMT (Fig. 4) shows well-dispersed delaminated structure with a visible single layer of silicate layers. The dispersibility of silicate layers decreases in the order PA6/5%OMT \gg ABS/5%OMT > PC/5%OMT. These results indicate that compatibility or interaction between polymer and OMT increases in the order PC < ABS \ll PA6. As we move along this series, the hybrid structure changes. From large multilayered stacks (PC/5%OMT) to small multilayered stacks (ABS/5%OMT) and to well-delaminated clay layers (PA6/5%OMT). In the TEM micrographs of PC/ABS/5%OMT and PA6/ABS/5%OMT [Fig. 5 and Fig. 6(a), (b), respectively], the gray continuous region corresponds to PC or PA6 phase and ABS appears as deep gray islands. The black lines correspond to clay layers. The TEM microcopy for PC/ABS/5%OMT nanocomposite (Fig. 5) shows that the clay layers were almost dispersed in ABS phase (deep gray islands). Moreover, in the interphase region, a higher density of dispersed clay particles is observed relative to the density inside the ABS phase, although in the PA6/

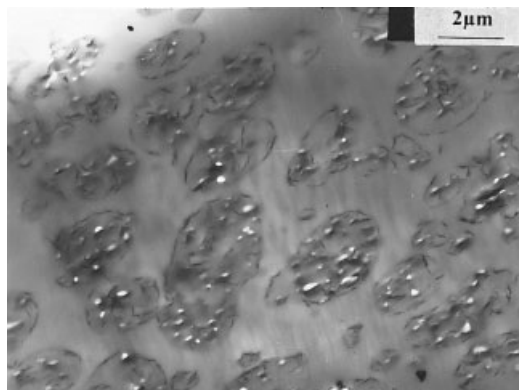
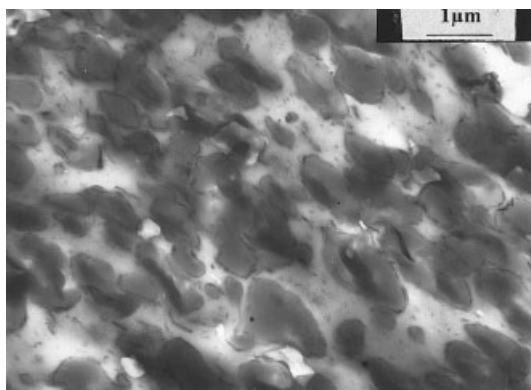
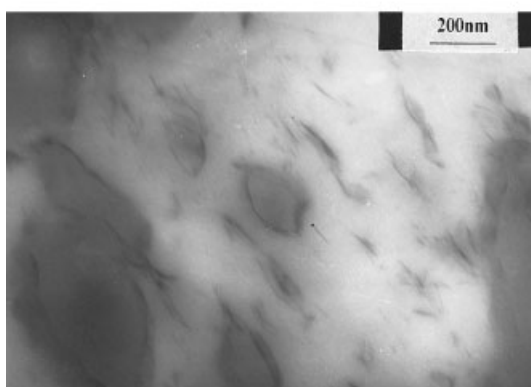


Figure 5 TEM micrograph of PC/ABS/5%OMT nanocomposite.



(a)



(b)

Figure 6 TEM micrographs of PA6/ABS/5%OMT nanocomposite: (a) low magnification; (b) high magnification.

ABS/5%OMT nanocomposite, the silicate layers were mainly dispersed in the PA6 phase as well as in the interphase region. The excess silicate layers in the interphase region are presumably the result of the segregation of the clay particles from the surface attributed to the surface tension or from the crystal growth front attributed to the exclusion.¹⁶ This segregation phenomenon is greatly dependent on the choice of polymers. The more compatible or the greater the intercalation of polymer with OMT, the more the density of clay layers is dispersed.

Study on the dynamic self-organization of clay in two phases

To study the dynamic dispersibility of clay layers in two phases, the PC/5%OMT nanocomposite was melt-mixed with pure ABS [the weight ratio of (PC/5%OMT)/ABS = 3/2] at 225°C using a twin-screw mill at high speed for 1, 2, 5, 10, 20, and 30 min to yield hybrids.

TEM micrographs of PC/ABS-1 (Fig. 7), PC/ABS-2 [Fig. 8(a), (b)], and PC/ABS-5 (Fig. 9) show that with the increase of melt-mixing time, the clay layers were

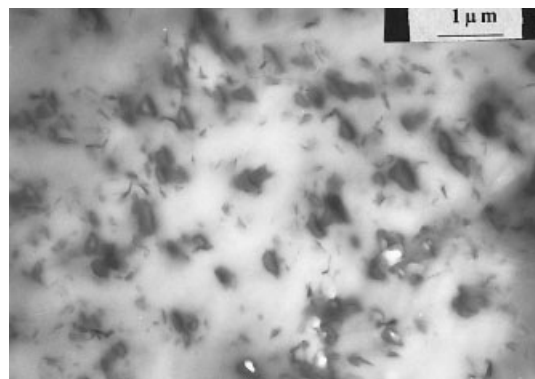
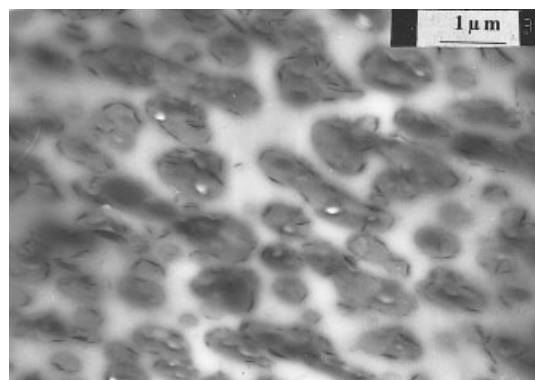
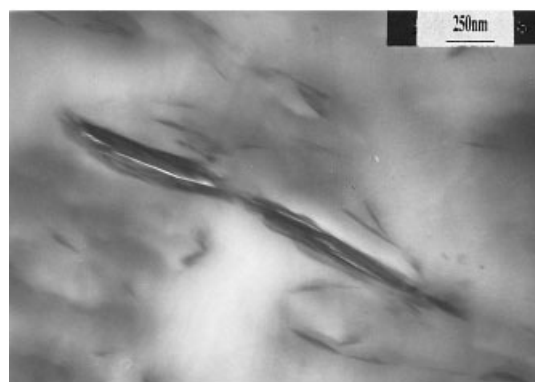


Figure 7 TEM micrograph of PC/ABS/OMT-1 nanocomposite.

self-organized from the PC phase to the ABS phase. Figure 10 shows the XRD patterns for PC/ABS-*x* and Table I gives the summary of the result of XRD. Figure 11 shows the scheme of self-assembly of clay layers in the PC/ABS alloy. When melt-mixing 1 min, most of the PC chains dispersed in the interlayer of clays were replaced by ABS chains deduced from the interlayer spacing increasing from 27.8 to 33.4 Å (Fig. 10). How-



(a)



(b)

Figure 8 TEM micrographs of PC/ABS/OMT-2 nanocomposite: (a) low magnification; (b) high magnification.

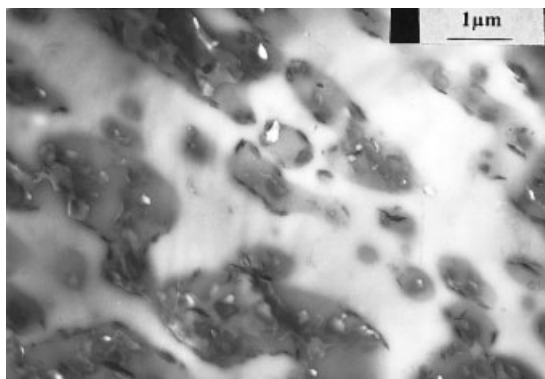


Figure 9 TEM micrograph of PC/ABS/OMT-5 nanocomposite.

ever, the clay layers were still maintained in the PC phase region (Fig. 7). After 2 min, ABS chains began to congregate into prominent gray islands [Fig. 8(a)] and the clay layers were transferred from the PC region to the ABS region, especially in the interphase region. However, it should be noted that there were still clay layers, which were dispersed in the PC phase [Fig. 8(b)]. When melt-mixing 5 min, almost all clay layers were transferred to the ABS phase, both the inside region and the interphase region (Fig. 9). In this process, the ABS phase islands increased and the d_{001} value of clays decreased from 33.4 to 31 Å. We ascribed the decrease of interlayer height of clay layers to the change of surrounding tension and clay layers were suppressed. When melt-mixing 10–30 min, the interlayer height of clays was suppressed at about 30 Å (Fig. 10).

It is well known that the presence of acidic or basic impurities will enhance the depolymerization of carbonic ester in PC.¹⁷ However, OMT can produce Lewis or Bronsted acid sites in the aluminosilicate when heated over 200°C,^{18,19} which have an enhance effect on the thermal degradation of PC. Thus, the self-organization of clay layers in ABS phase may be

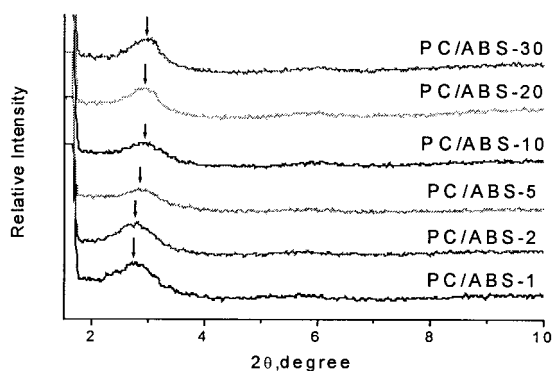


Figure 10 XRD patterns for PC/ABS- x ($x = 1, 2, 5, 10, 20, 30$ min).

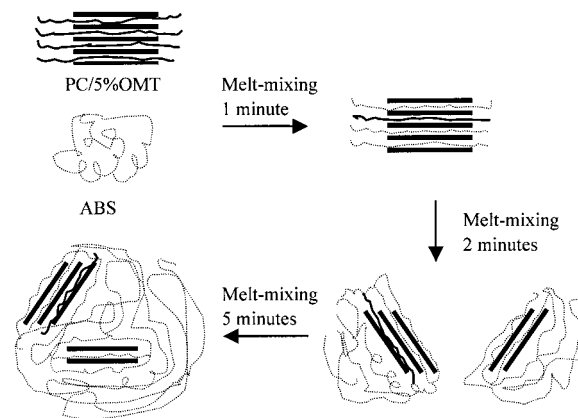


Figure 11 Scheme of dynamic self-assembly of clay layers in two phases.

helpful for avoiding the enhancing effect of clay on PC during decomposition and enhance the thermal stability of PC/ABS.

CONCLUSIONS

We first studied the dynamic self-assembly of clay layers in two phases by a melt-mixing technique. We found that the dispersed density of clay layers was greatly dependent on the compatibility between polymer and clay. In PC/ABS alloys, the clay layers were almost dispersed in the ABS phase and in PA6/ABS alloys, the clays were dispersed in both phases but mainly in the PA6 phase. However, in both alloys, the high clay density was observed in the interphase region. Thus, by choosing the proper polymer, we could realize the self-organization of clays from one phase to another phase.

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