Novel Intercalated Nanocomposites of Polypropylene, Organic Rectorite, and Poly(ethylene octene) Elastomer: Morphology and Mechanical Properties

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ABSTRACT: The melt-blending method was applied to prepare ternary composites of polypropylene (PP), organic rectorite (OREC), and poly(ethylene octene) elastomer (POE) with a constant content of 2 phr (parts per hundred parts of PP) OREC and 5 or 15 phr POE (PRE25 and PRE215, respectively). At the same time, OREC/PP binary composites with a 2 phr loading of OREC (PR2) and POE/PP systems with 5 or 15 phr POE (E5 and E15, respectively) were prepared to investigate synergistic effects of OREC and POE. Scanning electron microscopy was used to study the distribution of OREC and POE in the matrix, X-ray diffraction (XRD) and transmission electron microscopy were used to investigate the intercalation performance of OREC in the composites, and polarized light microscopy (PLM) was used to observe the crystallization form and crystallite size. The mechanical properties and dynamic mechanical analysis were also measured. The PRE composites exhibited a multiphase structure, that is, a spherical texture of POE, a plate of clay, and a continuous phase of PP; a larger content of POE produced a larger size, a broader distribution of the spherical phase, and a better intercalation performance of the clay. The E systems were binary phases, that is, a spherical texture of POE and a continuous phase of PP. The crystallite size of the PRE composites was finer than that of pure PP according to XRD data, and this was confirmed by PLM. The impact strength and tensile elongation at break of the PRE composites increased dramatically in comparison with those of the PP, PR2, and corresponding E systems, and this indicated that POE and OREC had synergistic toughening and strengthening effects on PP. The storage modulus of PRE was higher than that of pure PP and lower than that of PR2. There were two glass-transition temperatures in the PRE systems according to the curve of tan δ; they represented those of pure PP and POE, respectively, and indicated that the PRE systems were physical mixtures. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 97: 1907–1914, 2005

Key words: elastomers; nanocomposites; poly(propylene) (PP); structure

INTRODUCTION

Polypropylene (PP) is widely used in packing, textiles, household goods, and automobiles because of its good processability, relatively high performance, great recyclability, and low cost. However, the usefulness of PP as an engineering thermoplastic is still limited by its low modulus and poor impact resistance, especially under extreme conditions such as low temperatures or high strain rates. There has been considerable commercial and scientific interest in the toughening of PP.[1,2]

Generally, an elastomer is used to improve the fracture toughness, which can be affected by morphological factors, including the domain size and size distribution, but it may sacrifice the modulus of poly-mers.[3–5] Inorganic fillers can enhance the stiffness and reduce costs but result in a decrease of toughness.[6] Recently, a lot of work has been done to enhance both the impact strength and modulus of polymers by nonelastomers, such as plastics and inorganic nanofillers.[7–9] The addition of an elastomer and a filler to a polymer matrix is a beneficial approach for overcoming drawbacks resulting from the addition of only an elastomer or a filler; the elastomer and inorganic filler are used to enhance the toughness and stiffness synergistically.[10,11]

Organic–inorganic nanocomposite materials have drawn a great deal of attention; among them, hybridized composites based on organic polymers and inorganic clay minerals are the most promising composites systems because the addition of clay minerals can be intercalated by the macromolecular chain and the obtained intercalated or exfoliated composites have high dimensional stability, stiffness, heat temperature, and, in some cases, impact-resistance properties. Rectorite (REC) is another kind of clay mineral with a structure and characteristics very similar to those of

montmorillonite (MMT). It is a sort of regularly inter-stratified clay mineral with alternating pairs of dioctahedral mica-like layers (nonexpansible) and dioctahedral smectite-like layers (expansible) existing in a 1:1 ratio. The exchangeable hydrated cations of Na^+, K^+, and Ca^{2+} lie in the interlayer region of 2:1 smectite-like layers, and this can make REC cleave easily between smectite-like interlayers, forming monolithic REC layers (2 nm thick). Therefore, the structure of REC, similar to that of MMT, gives it some excellent properties, such as good colloidal properties in water, high heat resistance, and good plastic index and processing properties, which may have many potential applications in industry, especially in the modification of polymers. Polar organic compounds or organic cations can be intercalated into the REC interlayer via an ion-exchange reaction and lead to an expanded gallery structure and organophilic layered structure. The resulting clay, that is, organic rectorite (OREC), can act as a nanoscale filler to modify polymer materials, such as thermoplastic polyurethane (TPUR) and PP, but the toughness of the resulting nanocomposites can only be enhanced slightly for PP because of its small polarity and poorly dispersed microstructure.[12–14] To obtain well-dispersed nanocomposites and excellent mechanical properties of PP composites, we have selected a poly(ethylene octene) elastomer (POE) and OREC to modify PP and have investigated the morphology, intercalation performance, and mechanical properties of ternary composites of PP, OREC, and POE with a constant content of 2 phr (parts per hundred parts of PP) OREC and 5 or 15 phr POE (PRE25 and PRE215, respectively).

Otherwise, the mechanical properties of modified PP are significantly affected by the crystalline structure and morphology of the semicrystalline polymer, which can be influenced by additional component and processing conditions.[15] Therefore, we have also investigated the crystallization morphologies.

EXPERIMENTAL

Materials

PP (T30S, common grade) was supplied by Fushun Petroleum Chemical Co. (Liaoning, People's Republic of China). REC, with a cation-exchange capacity of 40 mequiv/l00 g and a d-space of 2.2 nm, was obtained from the Hu Bei Zhongxiang Rectorite Mine (Hubei, People's Republic of China). OREC was prepared in our laboratory. Sodium REC was screened with a 300-mesh sieve to remove impurities. A certain amount of screened clay was suspended in deionized water in a glass vessel with a glass rod. Dodecyl benzyl dimethyl ammonium bromide, from the Xi'an Chemical Agent Factory (Xi'an, People's Republic of China), was dissolved in a certain amount of water and then added to

TABLE I
Composite Systems

	System[a]		
	PR2	PRE25	PRE215
POE (g)	0	5	15

[a] The content of OREC was 2 g; the content of PP was 100 g.

a suspended clay–water solution under continuous vigorous stirring for several minutes at room temperature. The mixture was transferred to a three-necked flask, heated to 85°C, and stirred for 5 h. The treated products were washed and filtered repeatedly to ensure the complete removal of bromide ions by the titration of an $AgNO_3$ solution. Thereafter, the product was dried *in vacuo* at 100°C for several hours. The d-space of OREC was 2.56 run, as measured by X-ray diffraction (XRD). POE (Wilmington, DE) was a commercial product of Dupont Dow Elastomers (DE) with the trade name Engage 8150. The other reagents were chemical-grade.

Preparation of the composites

The composites were obtained after the kneading of PP, OREC, POE, and necessary additives for 5 min at room temperature with a high-speed mixing machine (GH-10DY, Beijing Plastic Factory, Beijing, China) and the extrusion of the mixtures in a twin-screw extruder (PEL330, Brabender, Duisburg, Germany). The screw speed was set at 50 rpm, and the barrel temperatures were set from 170°C at the first barrel to 190°C at the last barrel. Table I shows the systems of the composites.

Characterization

The morphology of the PRE composites was characterized with scanning electron microscopy (SEM; 1000B, Armay, Tokyo, Japan) after the fracture was metalized. Wide-angle XRD measurements were conducted with an X-ray automatic generator (D/max-3C, Rigaku) made in Tokyo, Japan. The X-ray beam was derived from nickel-filtered Cu $K\alpha$ (λ = 0. 154 nm) radiation in a sealed tube operated at 40 kV and 40 mA, and the scan ranges of 2θ were 2–10 and 10–30°C at room temperature for intercalated and crystallization morphology analysis, respectively. The dispersion state and layered structure of the clay composites were inspected with a Hitachi H-800 transmission electron microscope (Osaka, Japan). The crystallization form and crystal size were investigated with a Nikon Eclipse E400POL polarized light microscope (Tokyo, Japan). The tensile strength and Izod impact strength tests were carried out on a ZMGi 250 machine
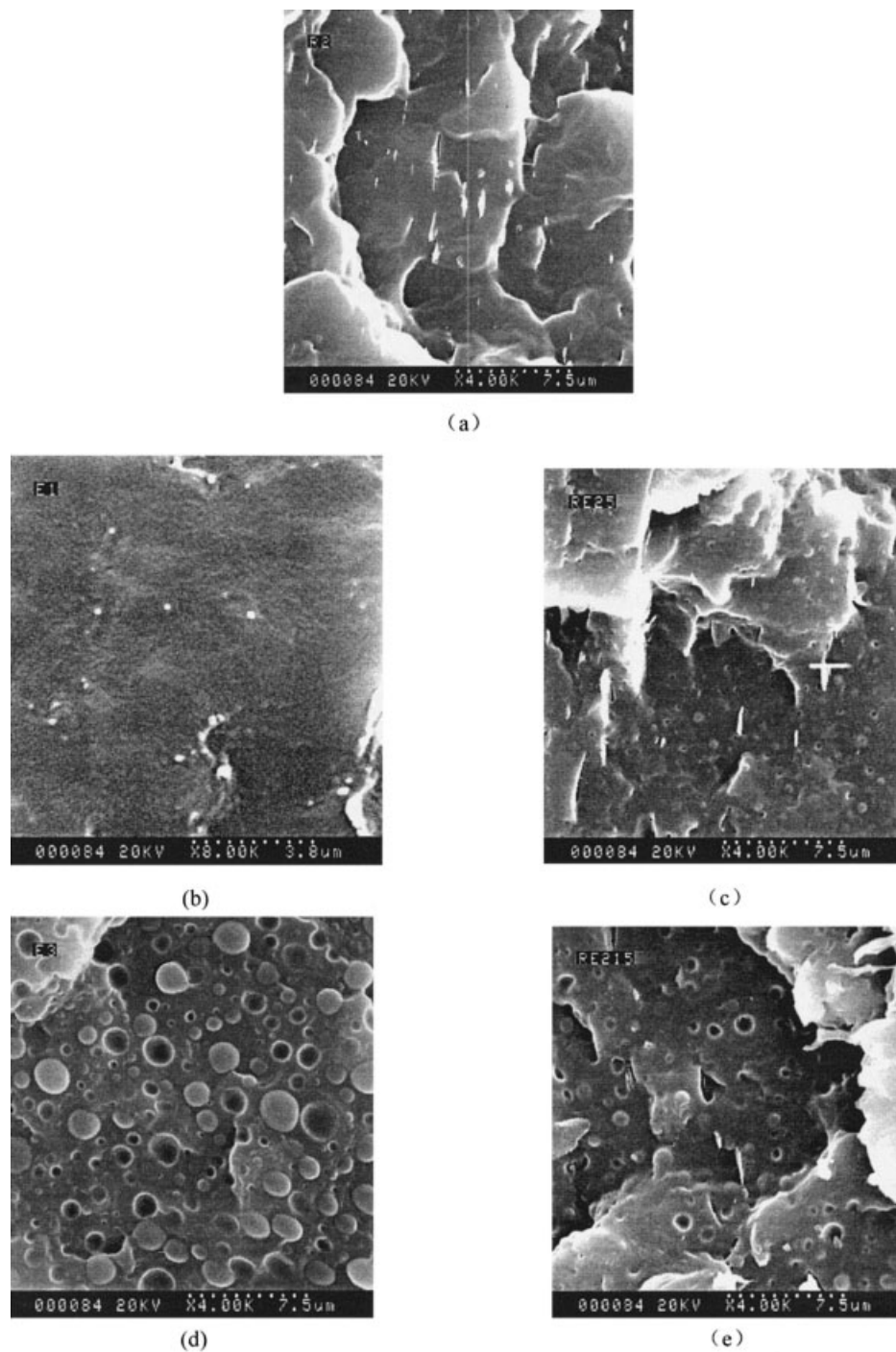
Figure 1 Morphology of the composites by SEM: (a) PR2, (b) E5, (c) PRE25, (d) E15, and (e) PRE215.

(Berlin, Germany) according to the specifications of ASTM D 638 and ASTM D 256, respectively. At least five tests were conducted for each group of specimens, and the reported values of the standard deviation are less than 10%. The thermal mechanical properties of the composites were determined with a dynamic mechanical analysis instrument (Q800, TA Co., New Castle, DE). The frequency was 1 Hz.

RESULTS AND DISCUSSION

Morphology of the composites observed by SEM

SEM observations show that the composites exhibit phase separations of the components (see Fig. 1). PP constitutes a continuous matrix in which a plate of and spherical POE are dispersed in PRE systems, whereas there is elastomer in the POE/PP systems with 5 or 15
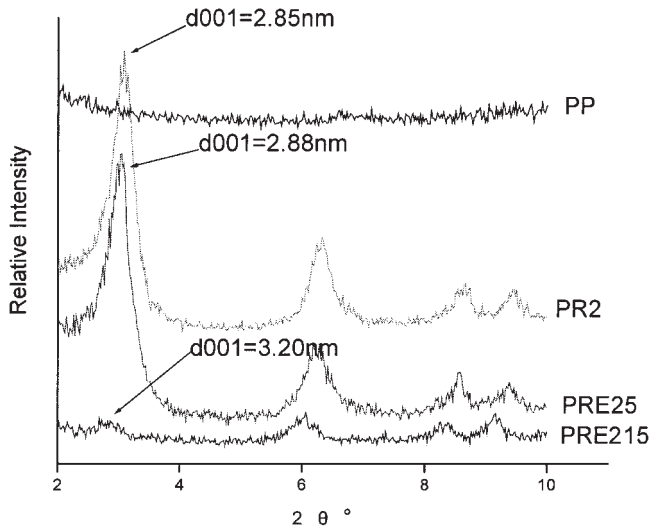
Figure 2 XRD patterns of modified PP.

(a)

(b)

phr POE (E5 and E15, respectively) and clay in the OREC/PP binary composites with a 2 phr loading of OREC (PR2). For the PRE systems, there are small aggregates as well as well-dispersed domains whose size and distribution correlate to the concentration of POE in the composites. Low concentrations of POE result in small dispersed domains and uniform distributions, whereas high concentrations result in large sizes and broad distributions. An appropriate size and broad distribution of POE may bring better properties to the final product.
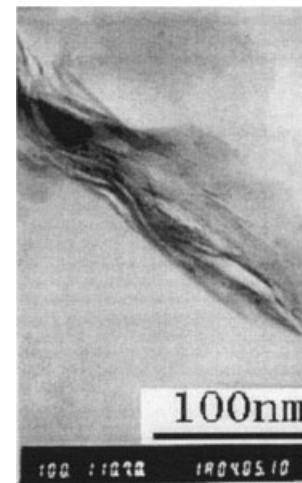
Intercalation performance of OREC in the composites

The basal spaces of OREC and the composites were estimated from the peak of the (001) plane in the XRD patterns. Figure 2 shows XRD patterns of the PP, PR2, and PRE systems in the range of 2–10°. No characteristic peaks appear in this range for pure PP. The relative intensity drops as the concentration of OREC decreases. In comparison with OREC (d_{001} = 2.56 nm), the basal spacing of OREC in PR2 is increased (d_{001} = 2.85 nm). The spacing of clay in the PRE25 systems is 2.88 nm, and in PRE215, it is 3.20 nm (larger than that of PR2); this indicates that the layered silicates are further intercalated or partially exfoliated with small clay loadings, and the larger content of POE can lead to better intercalation performance of OREC in PRE composites.
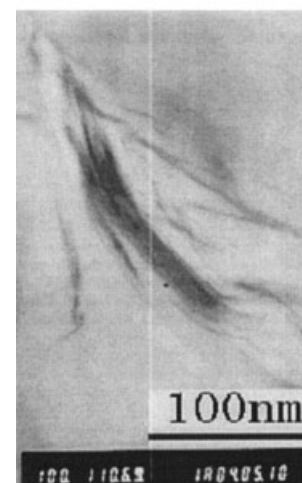
The PR2 and PRE composites were characterized by transmission electron microscopy (TEM) to search for possible phase separation. TEM micrographs of PR2 and PRE composites are shown in Figure 3: the dark lines are the sections of silicate layers. Obviously, OREC galleries are outward exfoliated. In the PR2 systems, the clay plate remains 50–60 nm in size, and

(c)

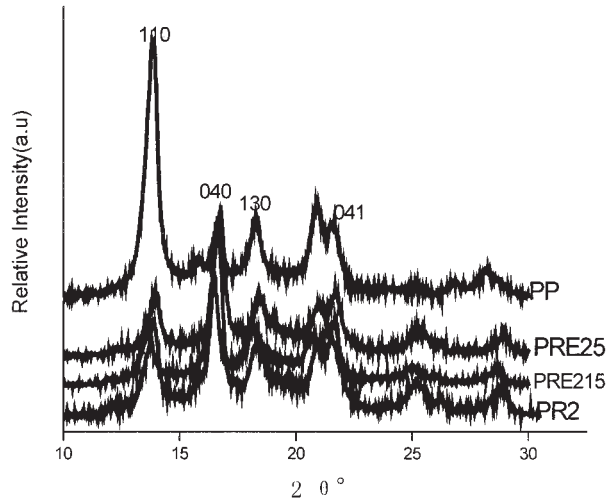**Figure 3** TEM of PRE composites: (a) PR2, (b) PRE25, and (c) PRE215.

Figure 4 XRD patterns of modified PP.

in the PRE215 system, the clay plate is 20–30 nm, so we can say that the intercalation performance of the PRE systems is better than that of the PR2 systems and OREC can be better intercalated with more POE in PRE systems, perhaps because the addition of POE can reduce the relative content of OREC.

Crystallization morphology of the composites

The crystalline form and crystal size of a semicrystalline polymer can influence its mechanical properties. Generally, PP can simultaneously crystallize into three crystalline forms, that is, the α, β, and γ forms. The α-phase crystallites are usually predominant in neat PP, whereas the β- and γ-phase crystallites may develop substantially under some special circumstances, such as the addition of a modifier or under high pressure, and this can be characterized by XRD. Figure 4 shows the XRD patterns of PP, PR2, and PRE systems in the range of 10–30°. The PR2 and PRE composites have a distribution for characteristic diffraction peaks that is similar to that of PP, exhibiting a monoclinic crystal form. However, the half-width of the (110) peak and consequently the POE microcrystal in the PRE and PR2 systems change in contrast to those of pure PP. The half-width of the (110) plane ($\beta 1$; rad) is listed in Table II.

The crystal size can be calculated according to the Scherrer equation:

$$D_{hkl} = \frac{K\lambda}{\beta \cos \theta}$$

where D_{hkl} is the size of the crystal (nm), λ is the length of the incident ray (nm), β is equal to ($\beta 1 - 0.2$) $\times$ $\pi/180°C$, θ is the diffraction angle (°), and K is a constant (0.9). The crystal sizes of the (110) plane of PP

and its composites calculated with this equation are also listed in Table II, which shows that the crystal size of the composites is reduced in comparison with that of PP.

The crystallization morphology of PP and its composites was observed by polarized light microscopy (PLM) after the samples were heated to 190°C under 10 MPa for 10 min with a pressure machine and then cooled naturally to room temperature (see Fig. 5). The crystalline forms of PP and modified PP show a spherulitic structure. The spherulite size of pure PP is much greater than that of the PRE and PR2 systems. An increase in the amorphous phase obviously occurs when the additional loading of POE is relatively high.

Effects of POE on the mechanical properties of the PR2 systems.

Figure 6 illustrates the effects of OREC and different amounts of POE addition on the mechanical properties of each composite. The impact strength and tensile elongation at break of the PRE systems increase with POE with a constant content of OREC. The impact strength of PRE215 is increased by 203.8 and 168.7% in comparison with those of pure PP and PR2, respectively, whereas the elongation is increased by 2021.8 and 663.6%. In addition, the impact strength and elongation at break of ternary PRE are higher than those of corresponding content binary systems modified by POE; that is, the impact strength of PRE215 is improved by 15.9%, and the elongation is improved by 46.6%, in comparison with E15; this suggests that the addition of POE and OREC can synergistically affect the toughness of PP.

The toughness improvement can be attributed not only to nanoscale layered clay and the distribution of POE but also to the crystal size of PP. On the basis of the microstructure and crystalline morphology mentioned previously, we can presume that although the pullout of clay from the matrix can help to improve the toughness, the larger spherical structure and broader distribution of POE can lead to a significant toughness improvement because craze initiation, craze growth, and craze termination are favored. For crystalline polymers, a toughness increase can also

TABLE II
XRD Data and Crystallite Size of the (110) Plane of PP and Modified PP

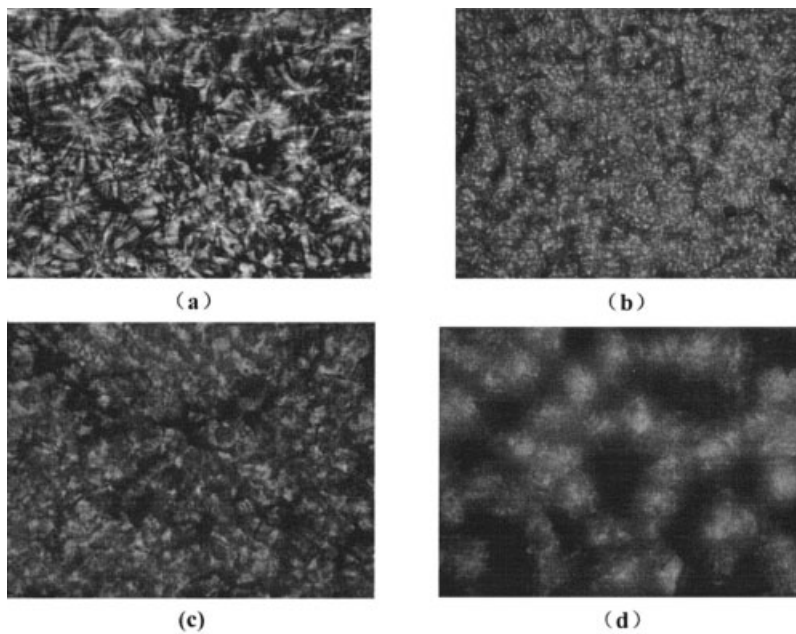|	System			
	PP	PR2	PRE25	PRE215
2θ (°)	13.94	13.90	13.94	13.62
$\beta 1$ (radian)	0.60	0.90	0.70	0.70
β (radian)	0.0070	0.012	0.0087	0.0087
D_{hkl} (nm)	19.95	11.64	16.05	16.04

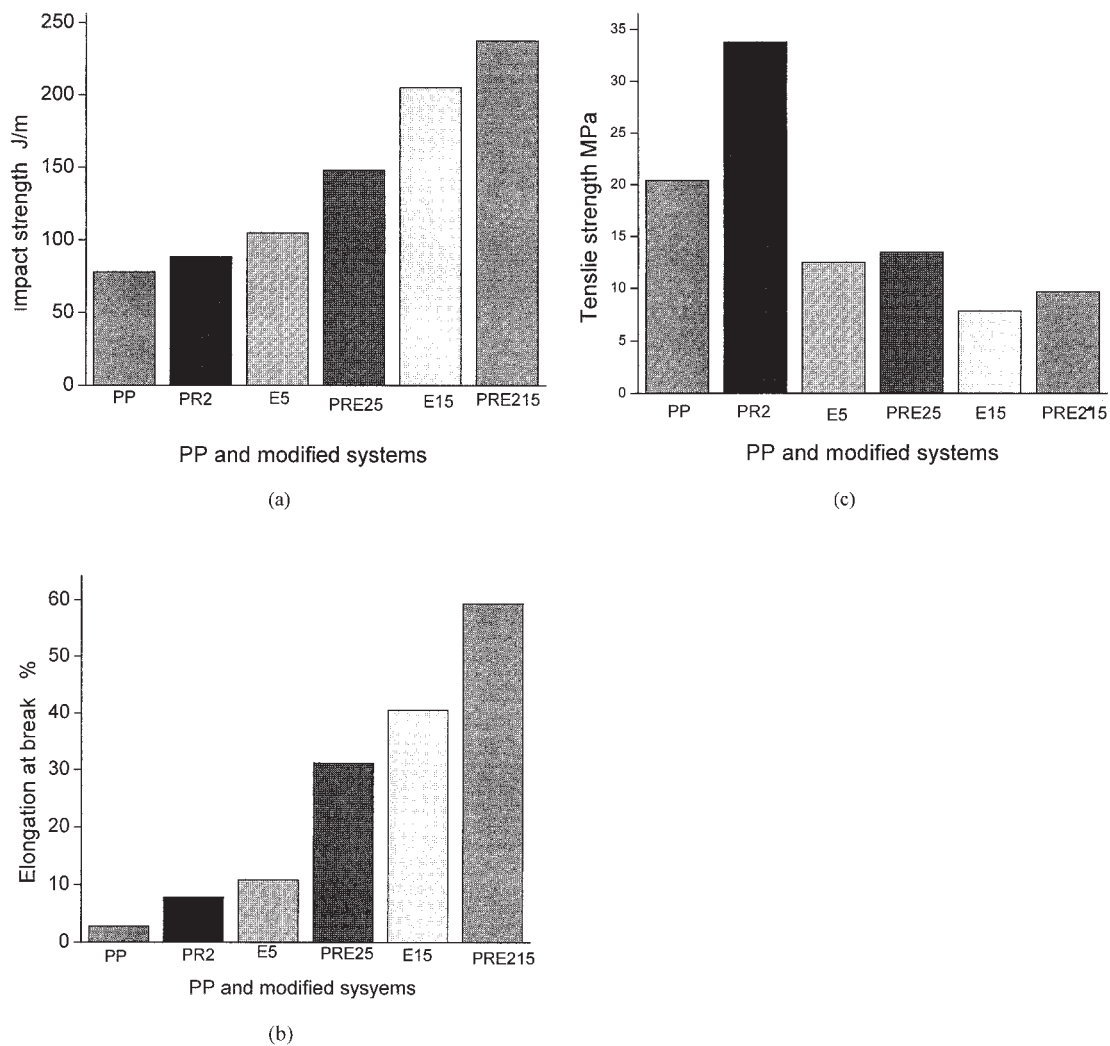**Figure 5** PLM images of PP and its composites: (a) PP, (b) PR2, (c) PRE25, and (d) PRE215.

Figure 6 Influence of POE and OREC on the mechanical properties of PR: (a) impact strength, (b) tensile elongation at break, and (c) tensile strength of PP and modified systems.
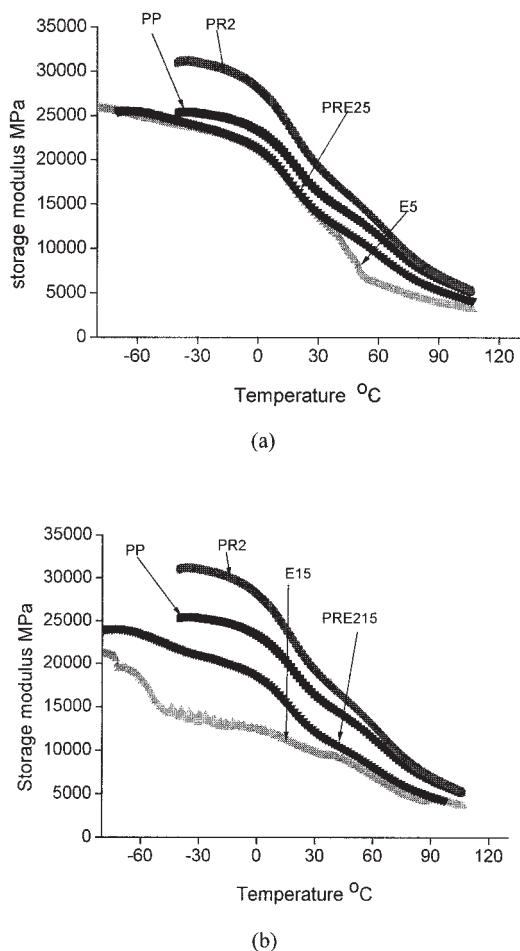
Figure 7 Storage modulus curves of modified PP: (a) PRE25, E5, PR2, and PP and (b) PRE215, E15, PR2, and PP.

benefit from a finer crystal size. Otherwise, the PP–additive interfaces are clearly visible, and spherical POE falls off from the matrix in addition to the pullout of clay in the PRE systems; this indicates that the interaction of PP between additives is necessary to obtain much more strength.

Figure 6(c) shows that the strength of PRE is higher than that of E at a constant content of POE despite the drop of the tensile strength of the PRE and E systems in comparison with neat PP; that is, the tensile strength of PRE215 is 22.6% higher than that of E15, although it is 52.7% lower than that of pure PP. This indicates that OREC can improve the tensile strength of the E systems.

Dynamic mechanical properties of PP and modified systems

The dynamic mechanical properties of the PR2, PRE25, and PRE215 systems are shown in Figures 7–9. The storage modulus as a function of temperature for PP and its nanocomposites is depicted in Figure 7. The storage modulus of the PR2 systems is higher than

that of the PP and PRE systems, whereas that of E5 and E15 is lowest; this indicates that the incorporation of OREC into the PP matrix remarkably enhances its rigidity and has good reinforcing effects, especially for lower temperatures and temperatures close to the glass-transition area.

Figure 8 shows the loss modulus evolution with the temperature. The loss moduli of PR2 and PP are close and higher than those of the PRE systems and corresponding binary E systems above the glass-transition temperature (T_g) of the PP matrix; this indicates that PR2 and PP consume more energy during the dynamic processes. For lower temperatures (below $-20°C$), the loss modulus of the composites is higher than that of pure PP, especially for the E systems. The loss modulus shows a marked drop when PRE25 and PRE215 are compared with PR2 and pure PP, whereas there is almost no change between the E15 and PRE215 systems and pure PP around T_g of the PP matrix.

In Figure 9, tan δ is plotted as a function of temperature for the composites. There are two T_g's in the PRE systems, representing those of pure PP and POE and indicating that the PRE systems are physical mixtures. The tan δ peak values of all the composites are higher

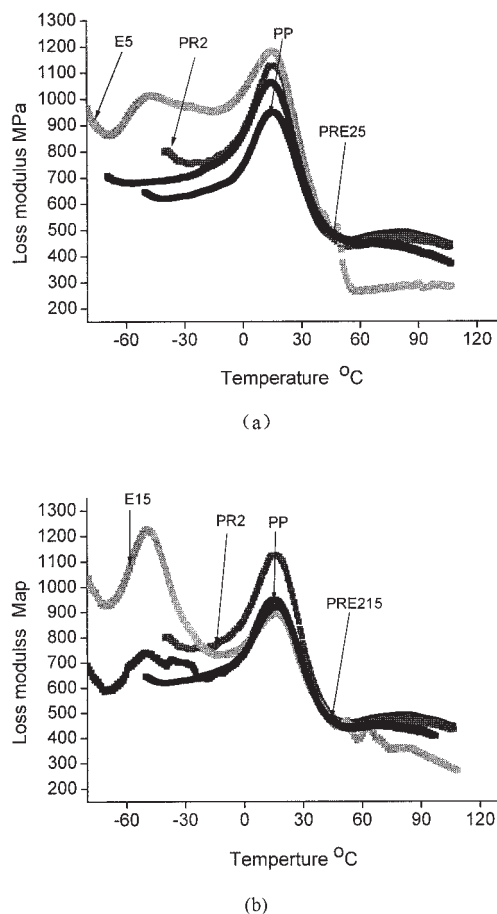**Figure 8** Loss modulus curves of modified PP: (a) PRE25, E5, PR2, and PP and (b) PRE215, E15, PR2, and PP.
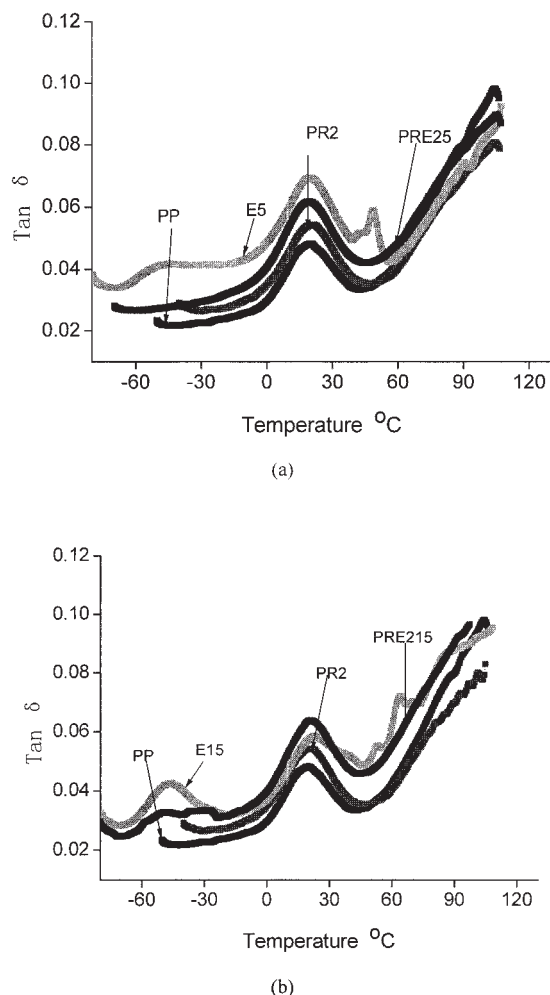
(a)

(b)

Figure 9 Tan δ curves of modified PP: (a) PRE25, PP, E5, and PR2 and (b) PRE215, PP, E15, and PR2.

than that of pure PP, and this may indicate that the interaction force between the molecule chains in the composites is increased. The tan δ curve of the POE-modified systems seems to be very complicated, and so it needs to be further discussed later.

CONCLUSIONS

PP/OREC/POE intercalated nanocomposites have been prepared via a melt-blending method. POE is well dispersed as spherical domains in the PP matrix, and a greater addition of POE can result in a larger and broader distribution in the matrix and make clay more effectively intercalated. The PRE composites exhibit a monoclinic crystal form, and the crystal size of the PP matrix in the composites is much smaller than that of pure PP. The impact strength and elongation of PRE increase in comparison with those of PP and PR2, and this indicates that POE and OREC have synergistic toughening effects on PP. The higher properties of the composites may be due to the broader distribution of POE domains, well-dispersed OREC, and fine crystallites of PP. The storage modulus of PRE is higher than that of pure PP and lower than that of PR2. There are two T_g's in the PRE systems, and they represent those of pure PP and POE, respectively, and indicate that the PRE systems are physical mixtures.

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