

NOTE

Preparation of Polyethylene–Clay Nanocomposites Directly from Na⁺ Montmorillonite by a Melt Intercalation Method

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ABSTRACT: Polyethylene (PE)/clay nanocomposites were prepared directly from Na⁺ montmorillonite by a melt intercalation technique, using hexadecyl trimethyl ammonium bromide (C16) as a reactive compatibilizer. Three other polymer–clay nanocomposites were also prepared by this new technique. Their structures were characterized by X-ray

diffraction and transmission electron microscopy. The mechanism of this new method was studied. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 2583–2585, 2003

Key words: clay; nanocomposites; polyethylene (PE); X-ray

INTRODUCTION

Recently, much attention has been paid to polymer nanocomposites, especially polymer-layered silicate nanocomposites, which represent a rational alternative to conventional filled polymers. Nanocomposite technology has been described as the next great frontier of material science because, by employing minimal addition levels (<10 wt %), nanoclays enhance mechanical, thermal, dimensional, and barrier performance properties significantly.¹

Traditionally, to facilitate the interaction of silicate layers with a polymer, the clay is modified with an alkylammonium salt (surfactant molecule), by a cation-exchange reaction, to make the hydrophilic clay surface organophilic. Although the modified clay is miscible for polar polymers such as nylon,² epoxy resin,³ polystyrene (PS),⁴ etc., the organically modified clay does not disperse well in nonpolar polymers, such as polypropylene (PP) and polyethylene (PE), because such nonpolar polymers are still too hydrophobic.⁵ Thus, a challenge exists to synthesize nonpolar polymer–clay nanocomposites. Initial attempts to create the nonpolar polymer–clay nanocomposites by simple melt mixing were based on the introduction of a modified oligomer to mediate the polarity between the clay surface and polymer,⁶ however, these techniques all used modified clay.

Recently, Alexandre and co-workers⁷ reported a novel technique for the preparation of ethylene vinyl acetate (EVA)–clay nanocomposites starting directly from natural (Na⁺-base) clay, using an ammonium salt with long alkyl chains as the polymer–clay reactive compatibilizer. In this communication, we report the synthesis of PE–clay nano-

composites starting directly from natural (Na⁺-base) clay and the study of the mechanism of this new method.

EXPERIMENTAL

Materials

High-density polyethylene (HDPE, PE-LA-50D12) was used as a model, and ethylene vinyl acetate (EVA, China), acrylonitrile butadiene styrene (ABS, PA-757), and high-impulsion polystyrene (HIPS, PS-LA-50012) were used as comparative polymers.

Purified sodium montmorillonite (MT, China) with cation-exchange capacity (CEC) of 96 meq/100 g and an interlayer spacing of $d_{001} = 15 \text{ \AA}$, was used as the nanofiller precursor. Several cation surfactants and anion surfactants [hexadecyl trimethyl ammonium bromide (C16), tetrabutyl ammonium bromide (C4), sodium stearate (18CNa, C₁₈H₃₅NaO₂), and sodium dodecyl sulfate (12CNa)] were chosen as clay/matrix reactive compatibilizers. A summary of the polymer–clay nanocomposites is given in Table I.

Evaluation of dispersibility of the clay in polymer matrix

Morphology studies were carried out on all compounds. X-ray diffraction (XRD) experiments were performed at room temperature with a Japan Rigaku D/max -rA X diffraction meter (30 kV, 10 mA), with Cu ($\lambda = 1.54178 \text{ \AA}$) irradiation at the rate 2°/min in the range 1.5–10°. Bright field transmission electron microscopy (TEM) specimens were cut from epoxy blocks containing the embedded HDPE nanocomposite powders at room temperature (10–15°C) with an ultramicrotome (Ultracut-1, U.K.) with a diamond knife. Thin specimens, 50–80 nm, were collected in a trough filled with water and placed on 200-mesh copper grids. TEM

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TABLE I
Summary of Polymer-Clay Compounds

Compound	Polymer (wt %)	Clay (wt %)	Compatibilizer (wt %)	Main Diffraction Peak (d_{001}) (Å)
1(a)	HDPE (95)	MT (5)		15.1
1(b)	HDPE (94)	MT (5)	C16 (1)	38.7–43.5
1(c)	HDPE (93)	MT (5)	C16 (2)	40.6
1(d)	HDPE (90)	MT (5)	C16 (5)	38.8
1(e)	HDPE (93)	MT (5)	C4 (2)	16.9
2(a)	EVA (93)	MT (5)	C16 (2)	39.9
2(b)	ABS (93)	MT (5)	C16 (2)	34.6
2(c)	HIPS (93)	MT (5)	C16 (2)	39.3
2(d)	HDPE (93)	MT (5)	18CNa (2)	40.9
2(e)	HDPE (93)	MT (5)	12CNa (2)	32.4

images were obtained by H-800 with an acceleration voltage of 100 kV.

RESULT AND DISCUSSION

For the sake of comparison, different contents of reactive compatibilizer (C16) were used to prepare HDPE-clay nanocomposites. Compounds 1(a), 1(b), 1(c), 1(d), and 1(e), filled with the same amount of inorganic compound (5 wt % MT) and different amounts of compatibilizers (C16 and C4), were prepared on a two-screw mill (HL-200, China) operating at 165°C for 10 min. The results in Figure 1 indicate that natural MT is immiscible with HDPE [compound 1(a), d_{001} = 15.1 Å]. The addition of as little as 1 wt % C16 resulted in a notable main diffraction peak at 38.7–43.5 Å [Fig. 1, compound 1(b)]. When 2 wt % C16 was added, the diffraction peak of MT disappeared and a sharp main diffraction peak at 40.6 Å, with second- and third-order diffraction peaks, appeared [Fig. 1, compound 1(c)]. However, when the content of C16 was increased to 5 wt %, the d_{001} did not increase but decreased slightly [Fig. 1, compound 1(d)]. This result indicates that the intercalation capability has a certain limit, which is similar to the results reported by Ki Hyun Wang.⁸

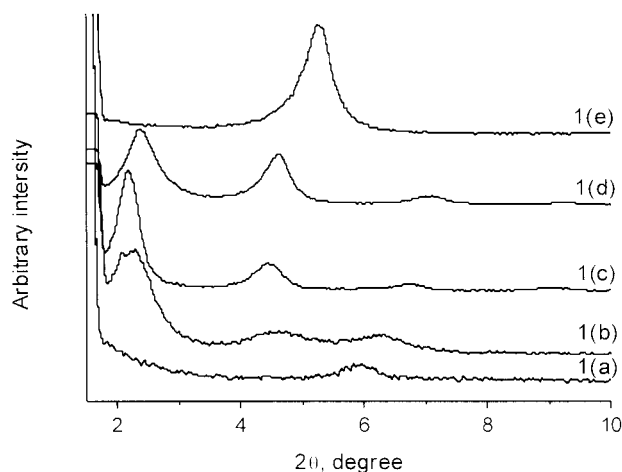


Figure 1 X-ray diffraction patterns of compounds 1(a) (HDPE + 5 wt % MT), 1(b) (HDPE + 5 wt % MT + 1 wt % C16), 1(c) (HDPE + 5 wt % MT + 2 wt % C16), 1(d) (HDPE + 5 wt % MT + 5 wt % C16), 1(e) (HDPE + 5 wt % MT + 2 wt % C4).

The TEM microscopy results for HDPE/MT/C16 [compound 1(d), Fig. 2] show that the distribution of layers is generally uniform, with the layered silicate forming ordered, intercalated tactoids containing many parallel silicate layers. This mesostructure can be considered as an intercalated nanocomposite. Primary particles composed of many silicate layers can be seen in the TEM image of HDPE-MT [compound 1(a), Fig. 3]. This situation corresponds to that of a conventional filled polymer in which primary particles measuring a few microns are dispersed in the matrix. The carbon chain length of surfactant also affects the morphology of the compound. When C4 was used as compatibilizer of the HDPE-clay nanocomposite, the d_{001} of compound 1(e) was 16.9, which is much less than that of compound 1(c). This result indicates that certain carbon chain lengths are needed to expand the layer of clay.

For the sake of comparison, four kinds of polymers were chosen as matrixes, including apolar HDPE, weakly polar HIPS, and polar copolymers EVA and ABS. Compounds 2(a), 2(b), and 2(c), filled with the same amount of inorganic compound (5 wt % MT) and compatibilizer (2 wt % C16), were prepared on a two-screw mill (HL-200, China) operating at 120°C [2(a)], 175°C [2(b)] and 170°C [2(c)] for 10 min. The XRD results (Fig. 4) show that the main diffraction peaks of the compounds decreased in the order d_{001} 1(c) > d_{001} 2(a) > d_{001} 2(c) > d_{001} 2(b). Assuming the values of d_{001} represent the degree of intercalation,⁸ this result indicates that polarity of the polymer is not a main factor in

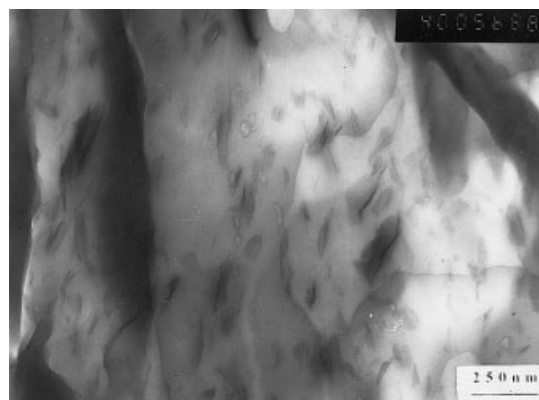


Figure 2 TEM of HDPE-MT-C16 [compound 1(d)] nanocomposite.

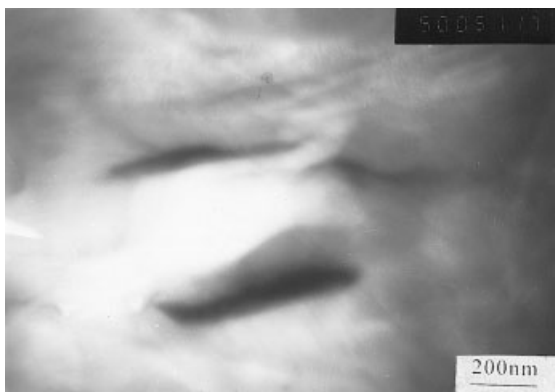


Figure 3 TEM of HDPE-MT [compound 1(a)] microcomposite (the montmorillonite only acts as filler and is not nano-dispersed in the polymer).

determining whether or not the polymer chain will favor intercalation.

This result also indicates that this mechanism of melting directly from natural clay and surfactant is different from that of other reports^{9, 10} that indicate that polar intercalation is more favorable than apolar intercalation. We deduce that the mechanism of mixing is as follows: during the process of melting, the surfactant first diffuses around the clay layers; then, by static adsorption, the surfactant intercalates into the silicate layers and expands them; and simultaneously, the chains of the matrix are introduced between the layers of the clay. A diagram of this kind of compound is shown in Figure 5.¹¹ To prove this hypothesis, two other anion surfactants (18CNa and 12CNa) were used as reactive compatibilizers for HDPE-clay nanocomposites. The mixing conditions for compounds 2(d) and 2(e) were the same as those for compounds 1(a)–1(e). The XRD results show that compounds 2(d) and 2(e) formed an intercalated structure, with $d_{001} = 40.9$ and 32.4 \AA , respectively. This result indicates that the surfactant adsorbs onto the layers of clay by static adsorption and expands the interlayer space.

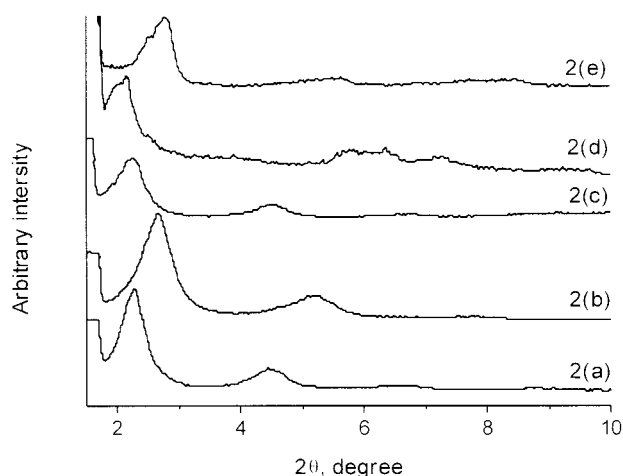


Figure 4 X-ray diffraction patterns of compounds 2(a) (EVA + 5 wt % MT + 2 wt % C16), 2(b) (ABS + 5 wt % MT + 2 wt % C16), 2(c) (HIPS + 5 wt % MT + 2 wt % C16), 2(d) (HDPE + 5 wt % MT + 2 wt % 18CNa), 2(e) (HDPE + 5 wt % MT + 2 wt % 12CNa).

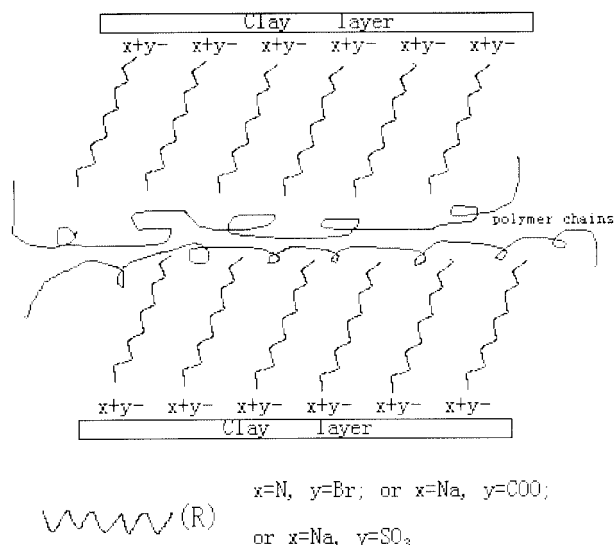


Figure 5 Structure of polymer-clay compound (R = surfactant chain; $x = N$ and $y = Br$, or $x = Na$ and $y = COO$, or $x = Na$ and $y = SO_3$).

CONCLUSIONS

This study has demonstrated the ability to prepare nonpolar HDPE-based nanocomposites by melt intercalation, starting with Na^+ montmorillonite and adding cation surfactant or anion surfactant as a reactive compatibilizer. The results indicate that the mechanism of this new technique is different from others reported in the literature. The proposed mechanism of this technique involves static adsorption of surfactant on the layers of clay and the resultant expansion of interlayer distance. The effect of cation exchange capacity on the intercalation with this new technique will be reported later.

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