

Novel Organic Modification of Montmorillonite in Hydrocarbon Solvent Using Ionic Liquid-Type Surfactant for the Preparation of Polyolefin–Clay Nanocomposites

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ABSTRACT: The possibility of organic modification of montmorillonite (MMT) in hydrocarbon solvents by employing ionic liquid-type surfactants was investigated. As a first example, 1-methyl-3-tetradecylimidazolium chloride ($[\text{C}_{14}\text{mim}]^+\text{Cl}^-$) was used to treat pristine MMT in xylene. The dispersion of MMT in xylene was significantly improved, the collected organically modified MMT displayed a sufficiently enlarged interlayer spacing. The novel art of MMT organic modification is specifically advantageous to

the preparation of polyolefin-based nanocomposites. A polypropylene/MMT nanocomposite was exemplarily prepared by directly dissolving polypropylene in the MMT modification system and found to possess an excellent thermal stability. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 4314–4320, 2006

Key words: ionic liquid; polypropylene/MMT nanocomposite; thermal stability

INTRODUCTION

Since the invention of nylon/clay (usually montmorillonite, MMT) nanocomposites by Toyota researchers in the 1990s,^{1–3} the study of nano clay-reinforced polymer composites has been one of the most intensive research areas in both polymer and material science fields.^{4,5} This is because the introduction of a few weight percent of laminated nano clay fillers into a polymer matrix can drastically improve many of the polymer properties, such as modulus, strength, heat resistance, antflammability and antigas permeability, which are usually very difficult to access by traditional microscale inorganic fillers.

Polyolefins (polyethylene, PE, and polypropylene, PP, etc.) are among the most interesting polymers that are deemed to benefit the most from the formation of nanocomposites with clay due to their widespread applications. However, chemically nonpolar polyolefins are thermodynamically unfavorable for the nano dispersion of polar inorganic clay layers in

the polymer matrix. For such a reason, the preparation of a polyolefin-based nanocomposite is usually very difficult. To surmount the incompatibility between polyolefins and clay to render a successful preparation of polyolefin-based nanocomposites, most of the effective approaches^{6–9} involve the organic modification of clay by cationic organic surfactants to not only reduce the compatibility gap between polyolefins and clay but also enlarge the interlayer spacing of clay so as to facilitate both polymer (in the case of solution^{6–9} and melt intercalation^{10–13}) and monomer (in the case of *in situ* intercalative polymerization^{14–22}) intercalations. As a matter of fact, Manias²³ has even shown that a sole organic modification of clay by a proper surfactant (a mixture of hydrogenated and semifluorinated surfactants) adequately promoted the nano dispersion of clay in a polypropylene matrix. Conventionally, surfactant treatment of clay exercising ion-exchange reaction between the hydrated Na^+ or K^+ cations in the interlayer of clay and the cations of surfactants is carried out in water or other highly polar solvents due to the ionization demand of the surfactants. These highly polar solvents also provide suitable environments for clay to swell to achieve the best effect of organic modification. However, in the case of preparing nanocomposites based on polyolefins, no matter what kind of composite formation method (solution intercalation, melt intercalation, or intercalative polymerization) is adopted, such a surfactant treatment has to be followed by a thorough drying

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procedure before the organically modified clay can be brought into contact with polyolefin polymers or monomers to practice the composite preparation. Experimental results have shown that thus-obtained organically modified clay is actually very difficult to redisperse in a nonpolar environment due to the formation of ordered stacks of clay tactoids after removal of the highly polar medium.²⁴ It has been presumed that this may be one of the hurdles that prevent the property improvement of polyolefin/clay nanocomposites to be fully manifested.

Owing to the inherent ionic nature of ionic liquids, the ionic liquid-type surfactants can carry out effective ion-exchange reaction with ions in the interlayer of clay even in a nonpolar organic solvent, resulting in organically modified clay that is uniformly dispersed in the solvent. When the solvent adopted is able to dissolve polyolefins or use as polymerization medium in solution or slurry olefin polymerization, polyolefin polymers or monomers can be directly introduced into the dispersed organically modified clay/solvent system to practice the preparation of polyolefin/clay nanocomposites via either solution polymer intercalation or intercalative olefin polymerization. Because the organic treatment of clay and its subsequent combination with polyolefin polymers or monomers are allowed to complete in one pot, all the problems associated with an aqueous clay modification process including the difficulties in the redispersion of the organically modified clay will no longer exist. The obtained polyolefin/clay nanocomposites are expected to have better dispersion of clay and thus better property performances than those prepared from aqueously modified clay. Despite the fact that inorganic pristine clay cannot swell well in nonpolar organic solvents, the strong adsorption of ionic liquids by clay is still able to ensure a good contact between the surfactant and clay.^{25–28}

In this paper, we report a novel art of organic modification of clay that is specifically advantageous to the preparation of polyolefin-based nanocomposites. In this art, the surfactant treatment of clay is conducted in a common hydrocarbon solvent, such as xylene or toluene, with ionic liquid-type surfactants.

EXPERIMENTAL

Materials and instruments

The surfactant, 1-methyl-3-tetradecylimidazolium chloride ($[\text{C}_{14}\text{mim}]^+\text{Cl}^-$), was prepared following a procedure reported in literature.²⁹ The pristine sodium montmorillonite (Na-MMT), with a cation-exchange capacity of 90 meq/100 g, was kindly donated by Qinghe Clay. The commercial PP, PP-F401 ($M_w = 330,000$, $T_m = 164.5^\circ\text{C}$), was purchased from Petro-China Liaoyang Branch. Xylene was distilled over

CaH_2 and stored under nitrogen protection before use. Wide angle X-ray diffraction (WAXD) experiments were performed on a Bruker D8Discover diffractometer with GADDS as a 2D detector. The reflection peak positions were calibrated with silicon powder ($2\theta > 15^\circ$) and silver behenate ($2\theta < 10^\circ$). The 2D diffraction patterns were recorded in a transmission mode at room temperature. The air scattering was recorded and subtracted from the WAXD patterns. The ultrathin specimen for transmission electron microscopy (TEM) observation were mounted on 300 mesh copper grids and examined by a JEOL JEM-2010 TEM at an accelerating voltage of 200 kV. The thermal gravimetric analysis (TGA) experiments were performed using a Perkin-Elmer TGA-7 instrument with a heating rate of $20^\circ\text{C}/\text{min}$ under nitrogen flow.

Organic modification of MMT in xylene and preparation of the PP/*xo*-MMT nanocomposite

The organic modification of Na-MMT by $[\text{C}_{14}\text{mim}]^+\text{Cl}^-$ was carried out in xylene. Two parallel reactions were conducted. For either reaction, in a 500 mL three-necked round-bottom flask equipped with a condenser and a magnetic stirrer were added 100 mL of anhydrous xylene and 0.25 g of $[\text{C}_{14}\text{mim}]^+\text{Cl}^-$. After stirring at the ambient temperature for 5 min, a clear solution was formed, indicating the complete dissolution of $[\text{C}_{14}\text{mim}]^+\text{Cl}^-$ in xylene. Then 0.5 g of Na-MMT dried at 120°C for 8 h were introduced into the solution. The flasks were heated up to 50°C and kept at this temperature for 5 h with stirring. The content of one flask was poured into excess methanol and the precipitate was collected by filtration. After repeated washing with methanol and water and drying at 60°C for 8 h, 0.4 g of organically modified MMT (*xo*-MMT) were obtained and used for WAXD examination. To the other flask was added 9.5 g of PP pellets. Under the protection of N_2 , the flask was brought up to 140°C to have the PP dissolved. The clear solution was kept being stirred for 5 h, after which it was poured into excess methanol. The precipitate was filtered, washed with methanol several times and dried at 60°C under vacuum for 8 h to obtain 9.8 g of PP/MMT nanocomposite (PP/*xo*-MMT).

Organic modification of MMT in water and preparation of the PP/*ao*-MMT composite

The comparing PP/*ao*-MMT composite was prepared following the same procedure as PP/Na-MMT, except that the MMT was organically modified by $[\text{C}_{14}\text{mim}]^+\text{Cl}^-$ in water prior to the preparation of the composite. A standard ion-exchange procedure was employed to prepare the *ao*-MMT.²⁹ After the

ion-exchange reaction, the organically modified MMT was collected by filtration followed by repeated washing with water and drying at 60°C under vacuum for 8 h.

Preparation of the PP/Na-MMT composite

The comparing pristine Na-MMT-derived PP/Na-MMT composite was prepared as follows. In a 500 mL three-necked round-bottom flask equipped with a condenser and a magnetic stirrer were added 100 mL of anhydrous xylene, 0.5 g of Na-MMT, and 9.5 g of PP pellets. Under the protection of N₂, the flask was brought up to 140°C to have the PP dissolved. The clear solution was kept being stirred for 5 h, after which it was poured into excess methanol. The precipitate was filtered, washed with methanol several times, and dried at 60°C under vacuum for 8 h to obtain 9.7 g of composite (PP/Na-MMT).

RESULTS AND DISCUSSION

As a first example to demonstrate the feasibility of the novel clay organic modification art in the preparation of polyolefin/clay nanocomposites, we have carried out the organic modification of pristine Na-MMT in xylene with 1-methyl-3-tetradecylimidazolium chloride ([C₁₄mim]⁺Cl⁻), an ionic liquid having a long alkyl chain, which was followed by an *in situ* dissolution of isotactic polypropylene (*i*-PP) to prepare PP/MMT nanocomposites via solution polymer intercalation process. As illustrated in Figure 1, the formation of PP/MMT nanocomposite follows the same mechanism depicted in literatures.^{25–28} [C₁₄mim]⁺Cl⁻ was firstly dissolved in xylene to ion

exchange with Na⁺ and form intercalated [C₁₄mim]⁺-containing *xo*-MMT with increased interlayer spacing. Secondly, with the aid of the swelling effect of the solvent delaminated *xo*-MMT structures were formed and, upon the addition of PP at high temperature (140°C), exfoliated PP/MMT nanocomposites were fabricated.

Organic modification of MMT by [C₁₄mim]⁺Cl⁻ in xylene

In the beginning of the organic modification process, MMT particles were visible, the suspension was clearly composed by two phases, the clear solution and the solid particles. After stirring for a certain period, the boundaries between the solid particles and the solution became blurry, and the solution turned to be opaque. Continued stirring resulted in a colloid-like suspension without any visible solid particles, which indicated the completion of the organic modification process. A small portion of the stable suspension was then sampled out and deposited on a glass flake. Upon the solvent was evaporated, the residue was subjected to scanning electron microscopy (SEM) observation to shed light on the effect of the surfactant on the macroscopical dispersion of MMT in xylene. To give prominence to such an effect, pristine Na-MMT was also deposited from a xylene suspension free of any surfactants and subjected to SEM observation for comparison.

As shown in Figure 2(b), the deposited pristine Na-MMT from xylene exhibits agglomeration morphology, due to its poor dispersion in xylene. In sharp contrast, the [C₁₄mim]⁺Cl⁻-treated *xo*-MMT displays a uniform distribution on the glass flake, implying a good dispersion in xylene, which must

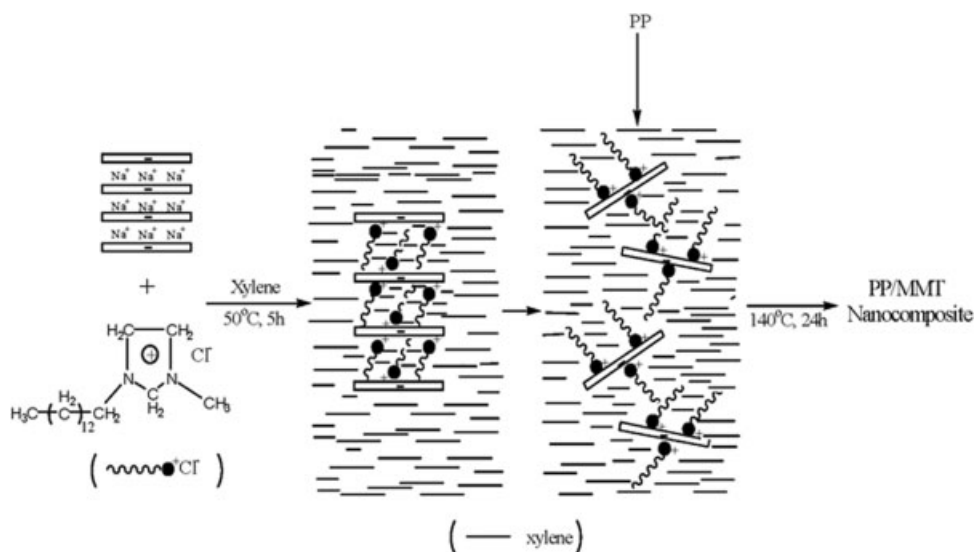


Figure 1 Schematic representation of the organic modification of clay in a hydrocarbon solvent for the preparation of polyolefin/clay nanocomposites.

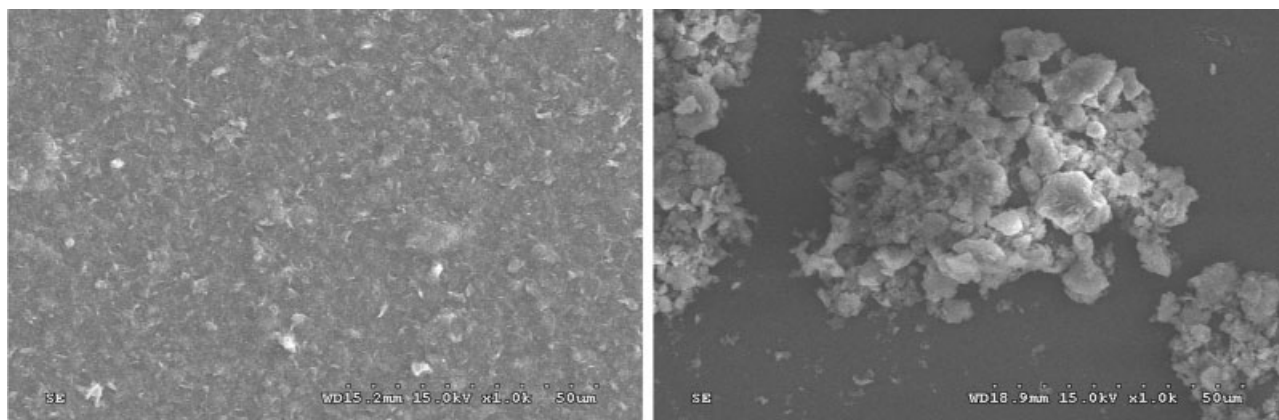


Figure 2 SEM photographs of (a) organically modified MMT (*xo*-MMT) by $[C_{14}mim]^+Cl^-$ and (b) pristine Na-MMT. Both samples were obtained by depositing from xylene.

be attributed to an effective organophilic transformation of the MMT surfaces caused by $[C_{14}mim]^+Cl^-$.

The dried *xo*-MMT was subjected to WAXD analysis. To give insight into the efficiency of the ion-exchange reaction between Na-MMT and $[C_{14}mim]^+Cl^-$ in xylene, the nonpolar organic solvent, a comparative experiment of MMT organic modification by the same amount of $[C_{14}mim]^+Cl^-$ was carried out in water following the conventional surfactant treatment procedure,³⁰ and the thus-modified MMT (*ao*-MMT) was also subjected to WAXD analysis.

Figure 3 compares WAXD patterns of pristine Na-MMT and the two organically modified MMT in different media, *xo*-MMT and *ao*-MMT. Pristine Na-MMT exhibits a primary silicate (001) reflection at about 7.1° [Fig. 3(a)], corresponding to an interlayer distance of 1.3 nm. After organic treatment in water by $[C_{14}mim]^+Cl^-$, the *ao*-MMT displays a (001) diffraction peak at 4.3° [Fig. 3(c)], corresponding to an interlayer distance of 2.1 nm. This value is consistent with those reported in literatures of organically modified MMT by typical alkylammonium surfactants having long alkyl chains.^{31,32} Our experiments using hexadecyltrimethylammonium chloride to treat Na-MMT in water also resulted in similar effect of MMT interlayer expansion. It is actually very interesting to note that *xo*-MMT shows a similar (001) diffraction peak at 4.3° in its WAXD pattern [Fig. 3(b)]. These results imply that ion-exchange reaction between Na-MMT and $[C_{14}mim]^+Cl^-$ indeed takes place in xylene and the organic modification of MMT in xylene using the ionic liquid-type surfactant $[C_{14}mim]^+Cl^-$ is as effective as that in water.

***In situ* preparation of PP/MMT nanocomposite via solution polymer intercalation**

As mentioned above, the unique aspect of the novel MMT organic modification in common hydrocarbon

solvents by using ionic liquid-type surfactants is that it enables the preparation of polyolefin-based nanocomposites to proceed *in situ* in the MMT modification system, and therefore avoids many problems caused by taking the organically modified MMT out and drying it before preparing the nanocomposites. To exemplify its advantages in the preparation of polyolefin-based nanocomposites, a PP/MMT nanocomposite was prepared via a solution polymer intercalation process by dissolving a predetermined amount of commercial *i*-PP *in situ* in the organically modified *xo*-MMT/xylene dispersion system to form a composite with 5.0 wt % of MMT loading (PP/*xo*-MMT). The structure and properties of this composite were compared with those of its two counterpart composites both with near 5.0 wt % of MMT loadings, one was prepared from the aqueously modified *ao*-MMT (PP/*ao*-MMT), the other was prepared from pristine

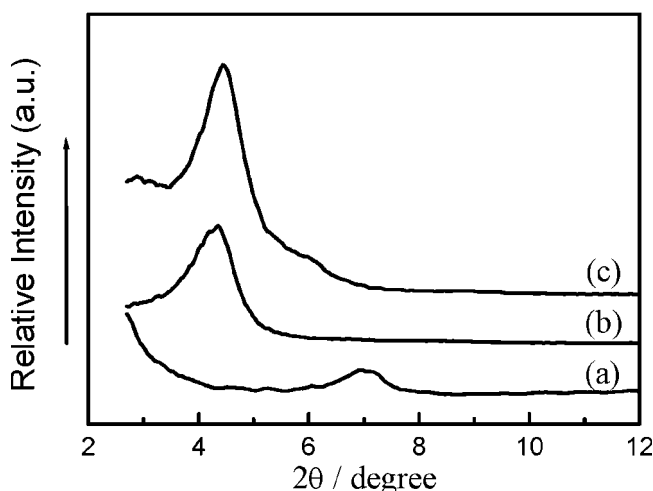


Figure 3 WAXD patterns of (a) pristine Na-MMT, (b) organically modified MMT by $[C_{14}mim]^+Cl^-$ in xylene (*xo*-MMT) and (c) organically modified MMT by $[C_{14}mim]^+Cl^-$ in water (*ao*-MMT).

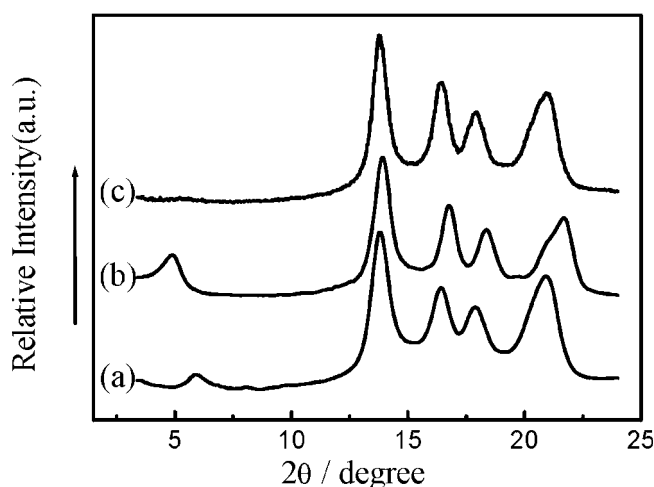


Figure 4 WAXD patterns of (a) PP/Na-MMT, (b) PP/ao-MMT and (c) PP/xo-MMT nanocomposites each with near 5 wt % of MMT loading prepared via solution polymer intercalation.

Na-MMT (PP/Na-MMT). Both composites were prepared following the regular solution polymer intercalation process by dispersing the respective MMT in the PP/xylene solution with vigorous stirring. Figure 4 compares WAXD patterns of the three composites. As expected, no significant intercalation of PP into the pristine Na-MMT occurred. The PP/Na-MMT composite still exhibits, in its WAXD pattern [Fig. 4(a)], a clear (001) diffraction peak at 5.9° , which corresponds to an interlayer distance of 1.5 nm. In this regard, it is obvious that a good exfoliation of MMT was achieved in the *in situ*-prepared PP/xo-MMT, without evident (001) diffraction peak observable [Fig. 4(c)]. The steadily dispersed xo-MMT in xylene with enlarged interlayer spacings and reduced surface energy must have allowed adequate intercalation of PP molecules into the interlayer of xo-MMT. On the other side, it is worthy to note that, although also prepared from organically modified MMT, the PP/ao-MMT composite whose preparation underwent a redispersion of dried, aqueously modified MMT in xylene still exhibits a clear (001) diffraction peak at 4.8° , corresponding to an interlayer distance of 1.7 nm, which is only slightly better than that of PP/Na-MMT.

The *in situ*-prepared PP/xo-MMT composite was further subjected to TEM analysis to visualize its nanostructure. Figure 5 exemplifies a representative observation site. In fact, the TEM picture we obtained may not present a satisfactory exfoliation of MMT layers in PP matrix which is expected on the basis of WAXD results. However, the well-exfoliated nanoscale (less than 10 nm) MMT platelets are indeed observed to disorderly disperse in the PP matrix. It's postulated that the inconsistency between the results

from TEM observation and WAXD measurement lies in the fact that in the preparation of TEM sample only a little amount of the as-prepared nanocomposites PP/xo-MMT was used in which even less MMT layers exist, thus hardly to truly reflect the panorama of the nanocomposites. However, WAXD characterization needs comparatively larger amount of the as-fabricated composites to prepare the sample and it gives a statistical result. Although the concrete reason for the discrepancy is unclear now, we think the result from WAXD is more convincing, i.e., exfoliated PP/xo-MMT nanocomposites were successfully prepared by this method.

The good dispersion of MMT resulted in greatly improved thermal stability of the composite. Figure 6 compares TGA curve of the *in situ*-prepared PP/xo-MMT composite [Fig. 6(d)], with those of PP/ao-MMT [Fig. 6(c)], PP/Na-MMT [Fig. 6(b)], and neat PP [Fig. 6(a)]. TGA experiments were conducted under N_2 flow. The *in situ*-prepared PP/xo-MMT composite with a 5 wt % of MMT loading shows an onset degradation temperature (T_d) of 484°C , $\sim 166^\circ\text{C}$ higher than neat PP ($T_d = 318^\circ\text{C}$), 62°C , and 66°C higher than PP/ao-MMT ($T_d = 422^\circ\text{C}$) and PP/Na-MMT ($T_d = 418^\circ\text{C}$), respectively. The temperatures of 25% weight loss ($T_{0.25}$) and 50% weight loss ($T_{0.5}$) for the four cases exhibit the same trend. The $T_{0.25}$

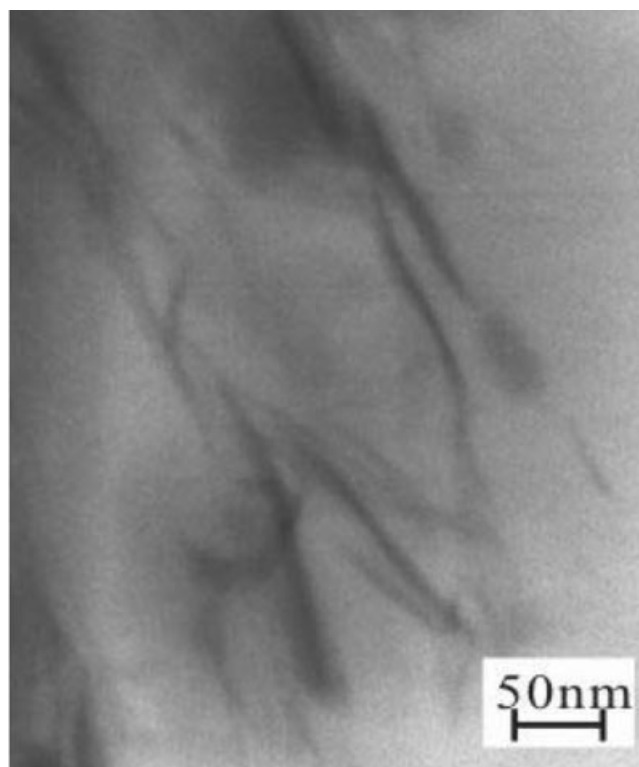


Figure 5 TEM image of PP/xo-MMT nanocomposite with 5 wt % of MMT loading prepared via solution polymer intercalation.

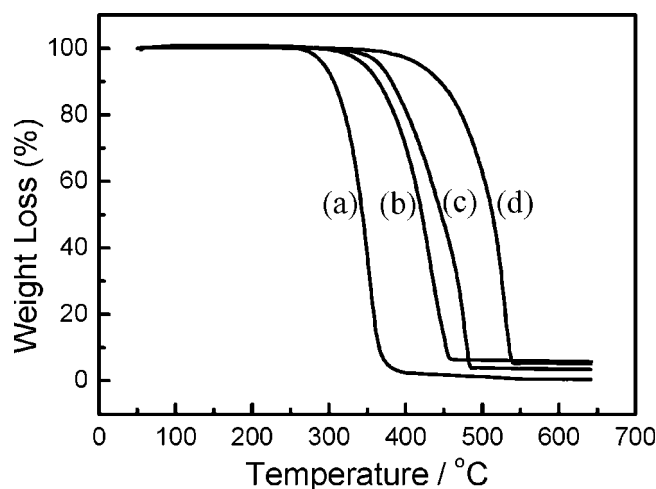


Figure 6 Comparison of TGA curves of (a) neat PP, (b) PP/Na-MMT, (c) PP/ao-MMT and (d) PP/xo-MMT nanocomposites each with near 5 wt % of MMT loading prepared via solution polymer intercalation.

increased in the same order as T_d , 326°C for neat PP, 394°C for PP/Na-MMT, 412°C for PP/ao-MMT, and 482°C for PP/xo-MMT composites. The $T_{0.5}$ increased from 344°C for neat PP, 421°C for PP/Na-MMT, and 447°C for PP/ao-MMT to 514°C for PP/xo-MMT composites. The well-dispersed xo-MMT in PP matrix functions effectively as an insulator and mass transport barrier to the volatile products generated during decomposition and contributes to the great enhancement of thermal stability of the composite. On the other hand, it is very interesting to note that the PP/ao-MMT composite exhibits only slightly higher onset degradation temperature than the PP/Na-MMT composite. Apparently, the efficiency of the MMT as a thermal stability enhancer is strongly determined by its degree of dispersion in the polymer matrix. In addition, the resultant PP/xo-MMT nanocomposite remained stable after thermal compression molding with a light transparent film obtained, whereas only fuscous semitransparent film was produced from the PP/Na-MMT composite under similar compression molding conditions. Both WAXD and TGA analyses confirmed the result as will be reported elsewhere.

CONCLUSIONS

In summary, we have demonstrated a novel organic modification of clay that can lead to the effective preparation of polyolefin/clay nanocomposites. The ionic liquid-type surfactant, 1-methyl-3-tetradecylimidazolium chloride, carried out effective ion-exchange reaction with Na-MMT in xylene, resulting in organically modified MMT with sufficiently

enlarged interlayer spacings. The subsequent dissolution of PP in the thus-formed organically modified MMT/xylene dispersion system rendered effective PP intercalation and promoted the *in situ* formation of PP/MMT nanocomposite with a very high T_d of 484°C.

Considering that the solvents used for the clay organic modification are also suitable for the Ziegler-Natta- or metallocene-catalyzed olefin polymerization, it is conceivable that an *in situ* intercalative polymerization of α -olefins will also benefit from the well-dispersed organically modified clay/solvent system to access polyolefin/clay nanocomposites with desirable performance. Furthermore, this novel approach is also applicable to the preparation of other types of polyolefin-based nanocomposites, especially ethylene-propylene random copolymer and syndiotactic polystyrene (s-PS) whose productions involve solution or bulk polymerization process.

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