

Synthesis and Characterization of Poly(propylene)/Montmorillonite Nanocomposites by Simultaneous Grafting-Intercalation

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ABSTRACT: A novel process for the preparation of poly(propylene)/montmorillonite (PP/MMT) nanocomposites was developed via simultaneous solution grafting-intercalation in the presence of a reactive ammonium cation that can be grafted onto poly(propylene). Partially introducing this reactive cation into long alkyl ammonium modified MMT interlayers can transfer a conventional microcomposite into intercalated/exfoliated nanocomposites, which was evidenced by X-ray diffraction (XRD) and transmission electron microscopy (TEM). The PP chains were tethered onto the clay surface through the bridge of the reactive ammo-

onium cations, which can be characterized by FTIR. The bridged chemical bonding also results in a good interface adhesion between PP and MMT, as confirmed by SEM investigation. The enhanced thermal properties of PP/MMT nanocomposites were characterized by thermogravimetric analysis. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 94: 1018–1023, 2004

Key words: poly(propylene) (PP); montmorillonite; nanocomposites; simultaneous grafting-intercalation; interfaces

INTRODUCTION

In the past few years, polymer/clay nanocomposites consisting of layered silicates, such as montmorillonite (MMT), have attracted much attention from both industry and academia. This interest stems from the fact that nano-sized-layer-filled polymers can exhibit dramatic mechanical and thermal properties at a few weight percent of clay content because of strong synergistic effects between the polymer and the silicate layers on molecular or nanometric scale.^{1–4} This new technology has exploited extended industrial application fields for polar polymers such as polyamide 6.^{5,6}

Poly(propylene) (PP) does not contain any polar group in its backbone, making layered silicates difficult to be dispersed well in PP matrix even using clays modified with long alkyl (commonly C_{12–20}) ammonium (LAA). Even though there is more challenge in preparation of PP/clay nanocomposites (PPCN), *in situ* intercalative polymerization,^{7,8} solution intercalation,⁹ and melt intercalation^{10–13} have been successfully applied to prepare intercalated or exfoliated (delaminated) PPCN. Up to now, there have been two major approaches to preparing PPCN in polymer intercalation: (1) increasing the polarity of PP by func-

tionalizing PP via special synthetic methods or using modified PP compatibilizers containing maleic anhydride (PP-g-MA) or hydroxyl groups,¹⁰ which could bring about high-cost; or (2) decreasing the polarity of clay. Since using ordinary alkyl ammonium as clay modifier is not enough to disperse the clay in PP, Manias and coworkers introduced a semifluorinated alkyltrichlorosilane surfactant [CF₃-(CF₂)₅-(CH₂)₂-Si-Cl₃] to promote PP/MMT miscibility; however, the interaction between PP and MMT is still poor.¹¹ Recently, preparation of PPCN in the absence of compatibilizers has prevailed. Liu and Wu obtained intercalated PPCN by using a new kind of cointercalation organophilic clay.¹² The cointercalation monomer they used was unsaturated so that it could tether on the PP backbone by a grafting reaction. Tjong and coworkers reported the usage of maleic anhydride as both a reactive reagent and a swelling agent for the silicate.¹³ Both reports are consistent with the view that tethered polymer chains promote intercalation/exfoliation of clay. Besides these, a physical process assisted approach to produce PPCN by applying an electric field has been very recently proposed.¹⁴ We are aware of several reports that use reactive organic ammonium modifiers to produce tethered PMMA polymer chains to the silicate by *in situ* polymerization and get exfoliated structure.^{15–17} As far as we know, however, there is no experimental study to apply such modifiers to nonpolar polymer intercalation, especially to a polyolefin/clay system.

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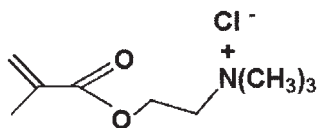


Figure 1 Chemical structure of META^+Cl^- used as reactive modifier for the MMT.

In this study, we describe a novel method to the synthesis of PPCN via simultaneous grafting-intercalation by introducing a reactive ammonium, [(2-methacryloyloxy)ethyl]trimethylammonium chloride (META^+Cl^-), to partially replace the long chain alkyl ammonium modifier without using any modified PP compatibilizer (e.g., PP-g-MA). To the best of our knowledge, this is the first report that produces tethered PP polymer chains to the silicate layers through ionic bonds by simultaneous grafting-intercalation. We also investigate the effects of the reactive modifier on the morphology and thermal properties of PPCN.

EXPERIMENTAL

Materials

Purified sodium montmorillonite (Na-MMT), with cation exchange capacity (CEC) of 85 meq/100 g, was produced by Qinghe Chemical Plant Co. (Zhangjiakou, Hebei, China). Additive-free isotactic PP powder (grade J 800, melt flow rate: 18 g/10 min) was manufactured by Yanshan Petrochemical Co. (Beijing, China). The LAA used in the preparation of organomontmorillonite (OMMT) is a mixture of dimethyldioctadecylammonium chloride (2C18) and dimethyldihexadecylammonium chloride (2C16) (the molar ratio of 2C18 to 2C16 is 75 : 25), purchased from Aokaide Chemical Plant Co. (Changzhi, Shanxi, China). The reactive organic modifier [(2-methacryloyloxy)ethyl]trimethyl ammonium chloride (META^+Cl^- , 75 wt % solution in water), with the chemical structure shown in Figure 1, was supplied by Xishan Chemicals Plant Co. (Wuxi, Jiangsu, China). All materials were used as received.

Preparation of OMMT

The preparation of OMMT was carried out by the cation-exchange reaction in distilled water. To a 1 wt % Na-MMT dispersion (2000 g) was added an aqueous solution containing 8.16 g LAA and 1.27 g META^+Cl^- (the molar ratio of LAA to META^+Cl^- is 70 : 30). The resultant mixture was stirred at 0°C for 3 h, followed by centrifugation and washed with distilled water until no Cl^- could be detected by an aqueous AgNO_3 solution, then dried under vacuum to yield an OMMT (Co-MMT) intercalated with both LAA and

META^+Cl^- . The same procedure was used to prepare another OMMT (LAA-MMT) intercalated with LAA alone.

Preparation of PP/OMMT composites

PP/Co-MMT nanocomposites were prepared by solution grafting-intercalation in the presence of Co-MMT. A 5% wt/vol solution of PP in xylene at its boiling point (138°C) was stirred for 30 min under flowing nitrogen gas until a transparent solution was created. Then a 2.5% wt/vol xylene suspension of Co-MMT, which was ultrasonically dispersed in advance, was added dropwise into the PP solution under continual stirring. The resultant suspension was allowed to react for another 2 h under nitrogen atmosphere and in the presence of dicumyl peroxide (DCP) as an initiator for the grafting reaction. At the end of the grafting reaction, a few thousand ppm of antioxidant, GX-2225 (Ciba Specialty Chemicals) was added to prevent degradation. The solvent was then evaporated for several hours in a fume hood at ambient temperature, until a very viscous gel was created. The gel was then dried in a vacuum oven at 80°C for up to 24 h to remove the residual solvent. The same procedure was also used to prepare PP/LAA-MMT composites in the presence of LAA-MMT. The weight ratios of PP to OMMT to DCP were fixed at 90 : 10 : 0.1. As a contrast, the virgin PP underwent the same procedure without any clay.

The injection-molded specimens were obtained by extruding the PP/MMT composites powder at $210 \pm 5^\circ\text{C}$ with a CS-183 MMX Mini Max Molder (Custom Scientific Instruments, Inc.). It was about 1.5 mm in thickness, 20–25 mm in length, and 4 mm in width.

Characterization

The XRD measurements were performed using a Rigaku D/max 2400 diffractometer (40 kV, 200 mA) with $\text{Cu K}\alpha$ radiation (0.154 nm) in the 2θ range from 1.5 to 40° with a step interval of 0.02° . The morphology of the fractured section of the specimens was observed by field emission scanning electron microscope (FE-SEM, JEOL model 6700F). The fractured section was obtained by breaking the injection-molded specimens in liquid nitrogen. TEM was carried out on a Hitachi H-800 apparatus using an acceleration voltage of 200 kV. Ultrathin sections of the injection-molded bars were prepared by cryogenic ultramicrotoming. TGA was performed from room temperature to 600°C on a Perkin-Elmer TGA 7 Series Apparatus with a heating rate of $20^\circ\text{C}/\text{min}$ under nitrogen atmosphere. FTIR spectra were obtained from a KBr disk using a Perkin-Elmer 2000 FTIR spectrometer in the range of 4000–400 cm^{-1} .

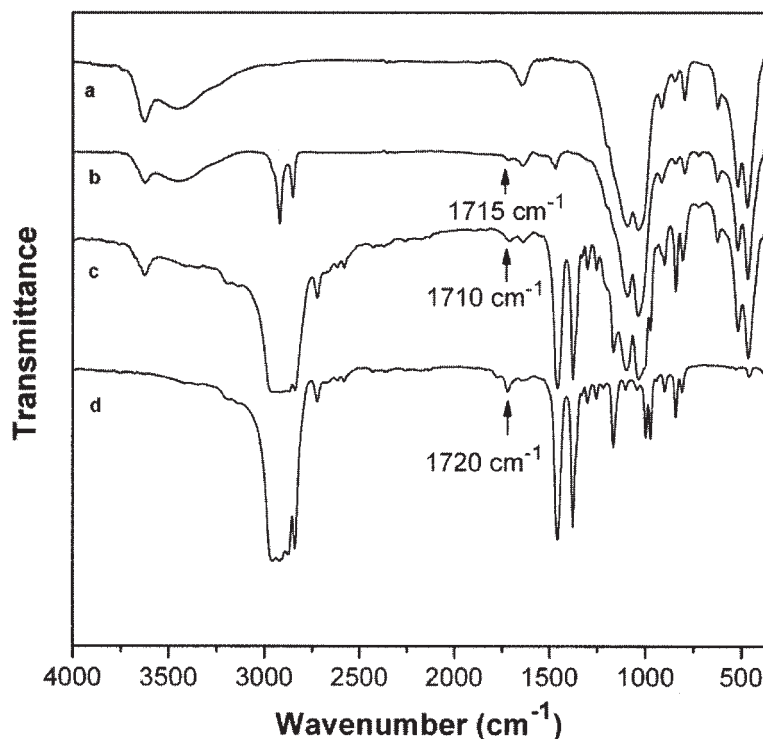


Figure 2 FTIR spectra of (a) Na-MMT, (b) Co-MMT, (c) PP/Co-MMT, and (d) extracted parts from PP/Co-MMT by 1,2-dichlorobenzene.

RESULTS AND DISCUSSION

Preparation of PP/MMT

Due to the incompatibility between hydrophobic polymers and hydrophilic pristine MMT, the modification of the organophobic MMT into organophilic characteristics is a critical stage in the preparation of polymer/clay nanocomposites. In this study, the modifier used to produce organophilic MMT is a reactive short chain alkyl ammonium, META^+Cl^- . Here we try to adopt this reactive modifier to prepare PPCN, because: (1) META^+Cl^- possesses a cationic group (ammonium cation) that can interact with the negatively charged MMT layer; and (2) META^+Cl^- contains reactive C=C double bond that can react with PP backbone by free radical grafting reaction.¹⁸ Considering the short chain length of META^+ , we organically modified MMT using a mixture of META^+Cl^- and the long chain alkyl ammonium, where the later modifier could widen the gap between MMT layers enough to allow PP chain intercalation.

Figure 2 shows the FTIR spectra of MMT and PP/MMT composites. A characteristic absorption band at around 1715 cm^{-1} (C=O stretching), corresponding to the ester group of META^+ , appears in the FTIR spectra of Co-MMT and PP/Co-MMT, suggesting the presence of META^+ in these substances (curve b and c in Fig. 2). To check out the presence of carbonyl groups, the PP/Co-MMT nanocomposites were subjected to a

Soxhlet extraction with 1,2-dichlorobenzene. The carbonyl absorption (shifted to approximately 1720 cm^{-1}) can be detected in the FTIR spectra of the extracted parts after being precipitated and washed with methanol (curve d in Fig. 2). Based on the above-mentioned results, we can conclude that META^+ had grafted onto PP chains in the presence of DCP during the grafting-intercalation process.

Structure of PP/MMT

Figure 3 presents the XRD patterns of Co-MMT, LAA-MMT, and their composites. The basal spacing of Co-MMT and that of LAA-MMT are 3.22 and 3.52 nm, respectively. The basal spacing of Co-MMT is lower than that of LAA-MMT, because of the lower content of LAA in Co-MMT as partial LAA were replaced by META^+ during the preparation of OMMT. In fact, the basal spacing is only 1.6 nm for the OMMT obtained by treating Na-MMT with abundant META^+Cl^- alone. The XRD pattern of PP/LAA-MMT (curve b in Fig. 3) shows a peak at $2\theta = 2.7^\circ$ ($d = 3.27\text{ nm}$), which is smaller than that of LAA-MMT (3.52 nm). This may suggest that no intercalation occurs to PP/LAA-MMT, which is probably just a conventional microcomposite as anticipated. However, the XRD curve of PP/Co-MMT (curve d in Fig. 3) shows a very weak and broad diffraction peak around $2\theta = 2.3^\circ$ ($d = 3.84\text{ nm}$),

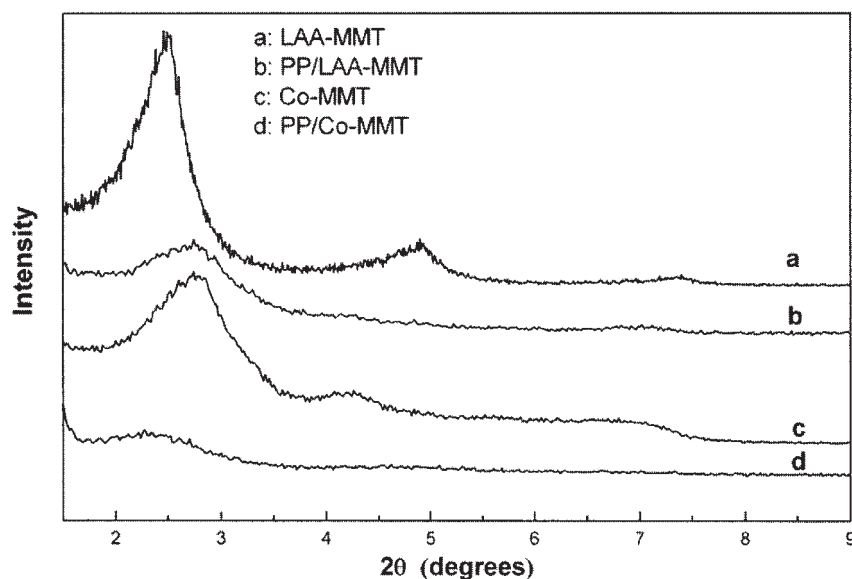


Figure 3 XRD patterns of LAA-MMT, PP/LAA-MMT, Co-MMT, and PP/Co-MMT.

indicating a disordered intercalated nanocomposite with a reduced extent of layer stacking.¹⁶

TEM was performed to examine morphology development of nanocomposites. Figure 4 shows TEM micrographs of PP/Co-MMT nanocomposites. The dark lines are the MMT layers perpendicular to the sample surface. Low-magnification TEM (Fig. 4a) shows the clay to be well dispersed throughout the PP matrix. At higher magnification, the TEM image (Fig. 4b) reveals that very thin and even single clay plates coexist with intercalated clay tactoids. This indicates that PP/Co-MMT nanocomposites are a mixture of intercalated and exfoliated structures.¹⁹ This is consistent with the result of XRD. It is quite likely that the grafting reaction between PP and META^+ is the driving force of such nanometer-scale dispersion, because no intercalation takes place in the PP/LAA-MMT system without META^+ .

Interfaces morphology of PP/MMT

The FE-SEM micrographs (Fig. 5) show the morphology of the section of cryogenically fractured specimens, revealing the undistorted view representative of the bulk material. Figure 5a (PP/LAA-MMT) presents a smooth surface with poor adhesion at the interface and some micron-scale MMT aggregates can be detected, which implies poor dispersion of the clay. In the meantime, PP/Co-MMT nanocomposites (Fig. 5b) display a very fine dispersion of nano-scale MMT particles (white strips) and a bumpy appearance with good interfacial adhesion. Furthermore, a higher magnification view of the PP/Co-MMT specimen (Fig. 5c) reveals that good adhesion exists between the uniformly dispersed MMT layers and the PP matrix. Sev-

eral rotund lacuna (marked with "L") and the peripheral protuberances (marked with "P") surrounding well-dispersed MMT layers in Figure 4c present this interface adhesion,¹³ which is absent in PP/LAA-MMT. This is a result of the favorable interaction of the MMT surface with PP matrix through the grafted META^+ .

It thus looks reasonable that PP chains were tethered to the clay layers through the bridge of the META^+ segment, which profoundly improved the dispersion of clay layers in the PP matrix. The grafting reaction could take place close to the entrance of the gallery or at the outer surface of the clay clusters at the first stage of the grafting-intercalation process. Then the tethered PP chain can act as a compatibilizer to help the PP chain penetrate into the clay gallery where further grafting reaction can take place between the PP chain and the META^+ on the clay surface, finally leading to the intercalated/exfoliated structure formation. This is somewhat similar to the PP/PP-g-MA/clay system, in which the PP-g-MA compatibilizer enhances dispersion of clay in the PP matrix.¹⁰ It should be noticed that, in this work, the grafting compatibilizer PP-g- META^+ was produced simultaneously in the intercalation of the PP chain.

Thermal stability of PP/MMT

Thermal stability of PP/MMT composites was measured on TGA in nitrogen atmosphere. The TGA curves are shown in Figure 6. A summary of the TGA data is given in Table I. Evidently, the onset temperature (T_{onset}) of degradation of PP/Co-MMT is 35°C higher than that of virgin PP and is about 10°C higher than that of PP/LAA-MMT. The maximum weight

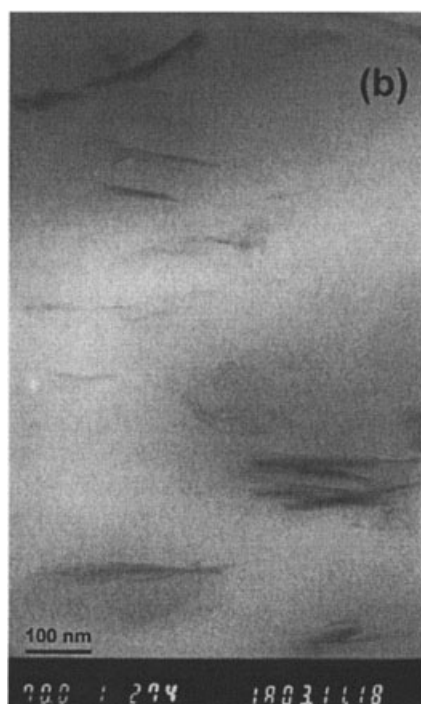
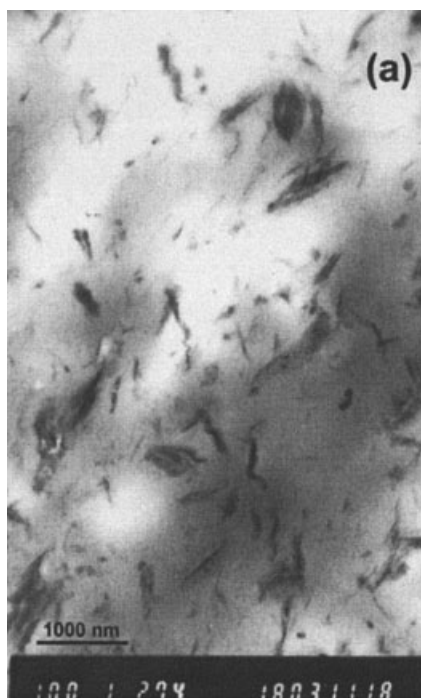


Figure 4 Representative TEM images of PP/Co-MMT nanocomposites.

loss temperature (T_{max}), the 5% loss temperature ($T_{-5\%}$), and the 10% loss temperature ($T_{-10\%}$) of PP/Co-Mt are also enhanced. This result shows that partially introducing the reactive $META^+$ into MMT interlayers can enhance the thermal stability of PP/MMT composites due to the better dispersion of the silicate layers in PP/Co-MMT nanocomposites than in PP/LAA-MMT microcomposites.

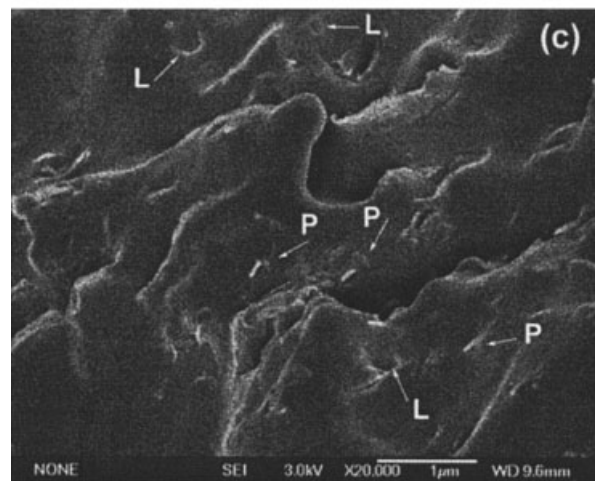
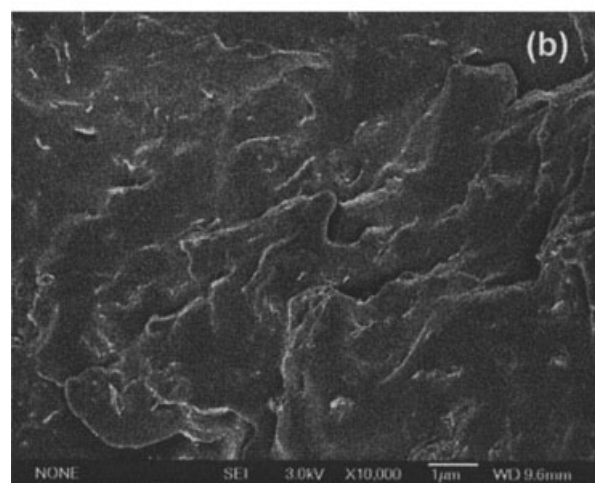
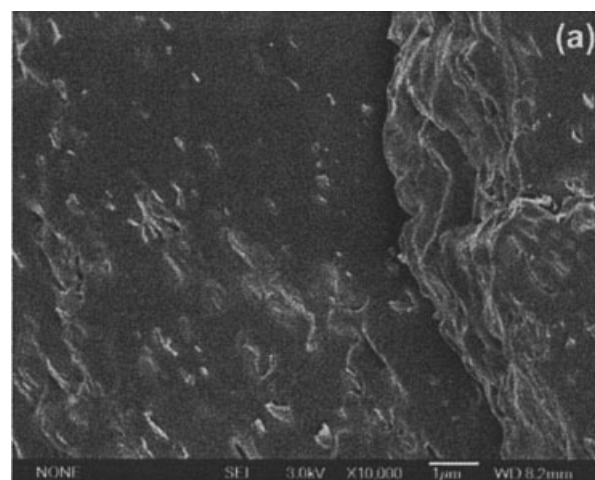


Figure 5 FE-SEM micrographs of the cryogenically fractured surfaces of (a) PP/LAA-MMT, and (b, c) PP/Co-MMT.

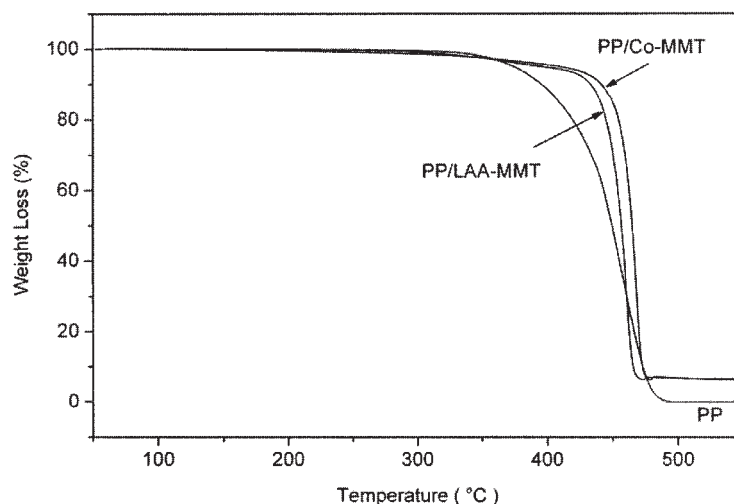


Figure 6 TGA curves of PP, PP/LAA-MMT, and PP/Co-MMT composites.

CONCLUSION

PP/MMT nanocomposites have been synthesized via simultaneous solution grafting-intercalation. Partially introducing a reactive META^+ cation into LAA modified MMT interlayers can improve the clay dispersion due to the strong interaction caused by the grafting reaction. The PP chains were tethered onto the clay surface through the bridge of the META^+ and simultaneously intercalated into the interlayer gaps leading to intercalated/exfoliated structure formation, which were evidenced by means of XRD and TEM. The bridged chemical bonding also results in a good interface adhesion between PP and MMT as confirmed by SEM. Moreover, TGA results indicate that the thermal stability of the PP/MMT nanocomposites is improved. This novel grafting-intercalation compounding method has presented a new approach to prepare

PP/clay nanocomposites without using any modified PP compatibilizer.

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TABLE I
Thermal Properties of PP and PP/MMT Composites

Sample	T_{onset} (°C)	T_{max} (°C)	$T_{-5\%}$ (°C)	$T_{-10\%}$ (°C)
PP	423	459	374	396
PP/LAA-MMT	449	460	395	433
PP/Co-MMT	458	468	409	441