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Preparation and characterization of poly(propylene carbonate)/montmorillonite nanocomposites by solution intercalation

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Abstract

Poly(propylene carbonate) (PPC) is a new biodegradable aliphatic polycarbonate. However, the poor thermal stability and low glass transition temperatures (T_g) have limited its applications. To improve the thermal properties of PPC, organophilic montmorillonite (OMMT) was mixed with PPC by a solution intercalation method to produce nanocomposites. An intercalated-and-flocculated structure of PPC/OMMT nanocomposites was confirmed by X-ray diffraction (XRD) and transmission electron microscopy (TEM). The thermal and mechanical properties of PPC/OMMT nanocomposites were investigated by thermal gravimetric analysis (TGA), differential scanning calorimetric (DSC), and electronic tensile tester. Due to the nanometer-sized dispersion of layered silicate in polymer matrix, PPC/OMMT nanocomposites exhibit improved thermal and mechanical properties than pure PPC. When the OMMT content is 4 wt%, the PPC/OMMT nanocomposite shows the best thermal and mechanical properties. These results indicate that nanocomposition is an efficient and convenient method to improve the properties of PPC.

Keywords: Poly(propylene carbonate) (PPC); Montmorillonite (MMT); Nanocomposites; Solution intercalation; Thermal and mechanical properties

1. Introduction

Biodegradable polymers, which could allow degradation under the natural environment, have gained considerable interests due to the urgent need for the development of green materials [1]. Poly(propylene carbonate) (PPC) is a new biodegradable aliphatic polycarbonate. Due to the utilization of carbon dioxide (CO_2) as one of the reaction components, the synthesis of PPC can largely exhaust CO_2 and subsequently efficiently reduce the amount of CO_2 released in atmosphere. PPC has a potentially wide range of applications, such as binder resins and packing materials. In addition, the ester bonds in the macromolecular backbone chains supply the molecular chain flexibility and good melt flow characteristics. However, the poor thermal stability of PPC has limited its applications [2].

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Polymer/layered silicate (PLS) nanocomposites are a novel class of polymeric materials [3]. Owing to the nanometer-sized dispersion of layered silicate in polymer matrix, PLS nanocomposites usually exhibit improved mechanical properties, thermal stability and gas barrier properties compared to the original polymers. Following the success of nylon–MMT nanocomposites, there has been a rapid expansion of interest in PLS nanocomposites. Clay is a kind of abundant natural resource which is a non-toxic and applicable component for food, medical, cosmetic, and healthcare recipients. In consideration of the environmental-friendly properties of both raw materials and products, the biodegradable polymer/clay nanocomposites are regarded as green materials and widely investigated [4–7].

Great efforts have been devoted to improve the deficient thermal property of PPC, including the chemical method such as coupling maleic anhydride (MA) to the end of PPC chains [8], and the physical method such as incorporating an environmentally acceptable filler [9–11]. However, for conventional PPC/filler composites, the high loading level of fillers leads to the deterioration of some properties, such as the high density and the loss of toughness. For PLS nanocomposites, a quite low filling addition will give material superior mechanical, thermal and processing properties. Xu et al. prepared intercalated-exfoliated PPC/OMMT (the product name is 20A) nanocomposites by direct melt blending in an internal mixer. The thermal decomposition temperature, storage modulus and Young's modulus of nanocomposites with even a low content of OMMT were much higher than those of PPC [12]. However, it was reported that some undesired problems such as thermal degradation of PPC and loss of mechanical property could happen during the melt compounding process of nanocomposites [13]. Du et al. prepared PPC/MgAl layered double hydroxide (PPC/MgAl-LDH) exfoliated nanocomposites by solution intercalation with cyclohexanone as solvent [14]. Compared to the pure PPC resin or the simple PPC/MgAl-LDH mixtures, the nanocomposites showed improved mechanical property and slightly enhanced thermal stability. However it was pointed out that the organic modified MgAl-LDH additive could catalyze the degradation of PPC resin. Zhang et al. prepared maleated poly(propylene carbonate) (PPC–MA)/OMMT nanocomposites by using commercial OMMT with and without hydroxyl groups (OH): Cloisite 30B (C30B) and Cloisite 20A (C20A). Through the reaction between hydroxyl groups (OH) of C30B and carboxyl groups (COOH) on the two ends of PPC–MA chains, the C30B can disperse more fully in matrix than C20A [15].

In this study, we prepared PPC/OMMT nanocomposites in order to improve the thermal stability of PPC. Solution intercalation method was used to avoid the thermal degradation of PPC which usually occurs during the melt blending. To improve the interaction between clay and polymer matrix, MMT was modified by cetyltrimethyl ammonium bromide (CTAB) before filled in PPC matrix. The structure of PPC/OMMT nanocomposites was elucidated by using X-ray diffraction (XRD) and transmission electron microscopy (TEM). The influences of OMMT on the thermal and mechanical properties of PPC/OMMT nanocomposites were investigated.

2. Experimental methods

2.1. Materials

PPC sample with a number-average molecular weight (M_n) of 27,000 was kindly provided by Changchun Institute of Applied Chemistry, Chinese Academy of Science. Inorganic MMT was supplied by Zhangjiakou Qinghe Chemical Plant Co. (China). Cetyltrimethyl ammonium bromide (CTAB) was purchased from Acros. Benzene (analytical grade) was purchased from Beijing Chemical plant. All the above chemicals were used as received without further treatment.

2.2. Preparation of OMMT

The OMMT was prepared by cation-exchange reaction with CTAB. Dried inorganic MMT (5.00 g) was dispersed and swelled in 500 ml of distilled water at 50 °C. To the stirred slurry, an aqueous solution of ammonium salt (CTAB, 2.73 g) in 30 ml distilled water was added dropwise. The solution was stirred at 50 °C for 8 h, and then stayed overnight. The white precipitate was collected, and washed thoroughly with distilled water until no Br ions could be detected by 1 wt% $AgNO_3$ solution. The received organic modified MMT was lyophilized and stored in a desiccator.

2.3. Preparation of PPC/OMMT nanocomposites

The PPC/OMMT nanocomposites were prepared by solution intercalation. First, a solution of a certain amount of OMMT dispersed in 25 ml benzene was sonicated for 10 min, and mechanically stirred for another 10 min. After then, the PPC was added to the above mentioned solution and continuously stirred for 3 h at 40 °C for polymer intercalation between silicate layers. The mixed solution was poured into a Petri-dish, and dried in a vacuum at room temperature to rapidly remove any remaining solvent. The thickness of the film was controlled by the concentration of the mixed solution and the area of the Petri-dish. After the solvent was completely removed, the composite film was taken out and dried for further analyses.

2.4. Characterization

X-ray diffraction (XRD) studies were performed on a Rigaku D/Max 2500 Diffractometer (40 kV, 200 mA, Cu Kα, $\lambda = 0.154$ nm) at ambient temperature with a 2θ range from 1.5° to 40°, at a scanning rate of 4°/min and a scanning step of 0.02°. The morphological analyses of nanocomposite samples were performed by transmission electron microscopy (TEM) on a Hitachi H-800 electron microscope. The samples for TEM analysis were sliced up using ultra microtome. The thermal stability of materials was measured by thermogravimetric analysis (TGA) on a Perkin–Elmer TGA-7. The samples were gradually heated at a rate of 20 °C/min from 30 to 500 °C under the protection of N_2 gas with a flow rate of 20 ml/min. The thermal properties and glass transition temperature (T_g) of nanocomposites were analyzed by a Perkin–Elmer DSC-7 differential scanning calorimeter thermal analyzer in a N_2 environment. The samples were heated at a rate of 20 °C/min from −30 to 70 °C, then quenched to −30 °C and finally heated again to 70 °C at a rate of 20 °C/min. The T_g was gotten from the second heating run. Tensile properties were tested on an INSTRON3365 electronic tensile tester with a computer controlling system. The testing specimen with a dimension of $5 \times 70 \times 0.1$ mm was cut from the films of PPC and composites. The rate of cross-head motion was 10 mm/min at 20 °C. Five specimens of each composition were tested, and the average values were reported.

3. Results and discussion

3.1. Characterization of nanocomposites

There are two complimentary techniques to characterize the structure of nanocomposites: X-ray diffraction (XRD) and transmission electron microscopy (TEM) [7], where the former reveals the change of *d*-spacing of clay gallery while the later shows the morphological structure of nanocomposites. Fig. 1 shows the XRD pattern of MMT before and after organic modification by surfactant CTAB. The original MMT shows a (001) diffraction peak at $2\theta = 7.1°$, which is corresponding to the *d*-spacing of 1.2 nm. After organic modification, the MMT which was denoted as OMMT shows a (001) diffraction peak at $2\theta = 4.4°$, which is corresponding to a larger *d*-spacing of 2.0 nm. The enlarged *d*-spacing values indicate the intercalation of alkyl ammonium within silicate layers. After organic modification, it was found that the organic modified MMT could not disperse well in water and finally precipitated. This phenomenon reveals that the surface of silicate platelets changed from hydrophilic one into hydrophobic one and this change is favorable for the interaction of organic polymer chains.

Fig. 2 shows the XRD patterns of PPC/OMMT nanocomposites with different clay contents. It was found that the initial diffraction peak (001) of OMMT shifted from $2\theta = 4.4°$ to a lower degree of diffraction angle after blending with PPC. This result is ascribed to the intercalation of PPC macromolecular chains into hydrophobic silicate layers, resulting in the enlargement of interlayer distance of OMMT. The (001) diffraction peak of PPC/OMMT nanocomposites with clay contents from 1 to 6 wt% located at $2\theta = 2.1–2.5°$, which indicates that the intercalation of PPC chains increases the d_{001} spacing of OMMT for about 2 nm. In the case of PPC/OMMT4% and PPC/OMMT6% nanocomposites, there are small peaks appearing at $2\theta = 4.6°$ corresponding to a *d*-spacing of 1.9 nm. This is

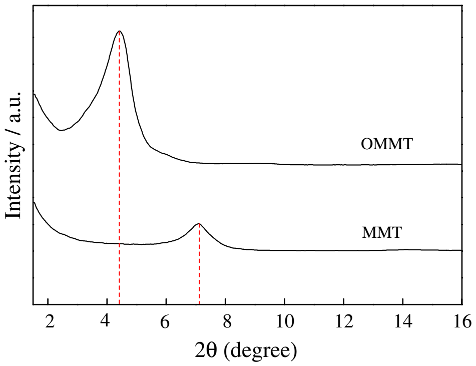

Fig. 1. XRD patterns of MMT before and after modification by CTAB. MMT: original; OMMT: after modification.

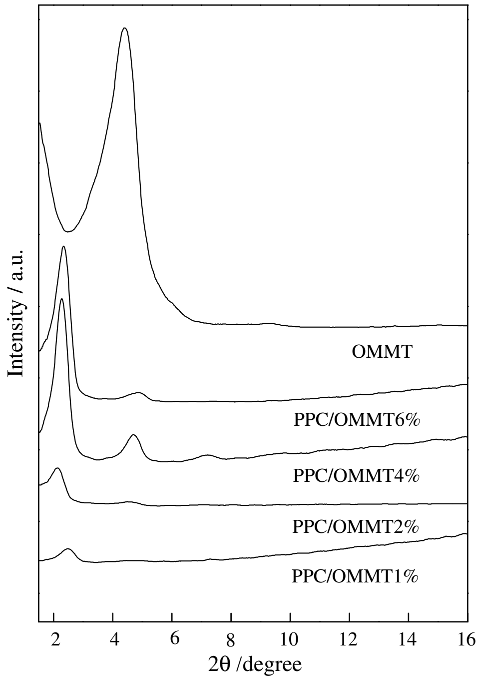

Fig. 2. XRD patterns of OMMT and PPC/OMMT nanocomposites with different OMMT contents. (The numbers *X* in PPC/OMMT*X*% refer to the weight percent of OMMT in nanocomposites.)

because of the hydroxylated edge–edge interaction of the silicate layers, which leads to the flocculation of stacked and intercalated silicate layers [5,7,16,17].

The morphological structure of PPC/OMMT nanocomposites was further analyzed by TEM. Depending on the strength of interfacial interactions between the polymer matrix and layered silicate, there are three types of thermodynamically achievable PLS nanocomposites: intercalated, intercalated-and-flocculated and exfoliated nanocomposites [7]. In the case of PLS nanocomposites, XRD may not reveal the real hybrid microstructures due to its problems such as weak diffraction intensity, bias toward the surface region, and poor peak resolution for those nanocomposites with low clay content [18] as well as the overlapping of diffraction patterns of exfoliated structure and intercalated structure [17,19]. In contrast to XRD, TEM can provide information in real space on morphology and spatial distribution of various phases for the better interpretation of XRD results. Fig. 3 is a typical TEM image of PPC/OMMT nanocomposites with clay content of 4 wt%. It clearly shows that OMMT has been delaminated into nano-scale layers and dispersed throughout PPC matrix. Therefore, combined TEM and XRD results, it could be concluded that the PPC/OMMT nanocomposites have an intercalated-and-flocculated structure.

3.2. Thermal properties

It has been known that the poor thermal stability and low glass transition temperature (T_g) of PPC have limited its application. Many efforts have been devoted to improve the thermal property of PPC. An effective method is to modify the PPC chain structure by adding maleic anhydride to the end of PPC molecular chain. In the case of PLS nanocomposites, the silicate layers can retard the thermal degradation of polymer due to its good thermal insulation effect. Furthermore, the PLS nanocomposites could be prepared more simply and conventionally compared to the chemical modification of PPC chains. Considering above mentioned, the PPC/OMMT nanocomposites were prepared to improve the thermal property of PPC.

Fig. 4 shows the thermal gravity analysis (TGA) and differential thermal analysis (DTG) of PPC/OMMT nanocomposites with different clay contents. Compared with pure PPC, the thermal stability of PPC/OMMT nanocomposites is improved due to the shielding effect of OMMT silicate layers, as shown in Fig. 4a and its inset. The TGA analysis data is summarized in Table 1. Here, the $T_{0.05}$ represents the onset temperature of thermal degradation when 5% weight lost, while $T_{0.5}$ is the temperature regarded as the midpoint of the

Fig. 3. TEM images of PPC/OMMT nanocomposites with 4 wt% OMMT content.

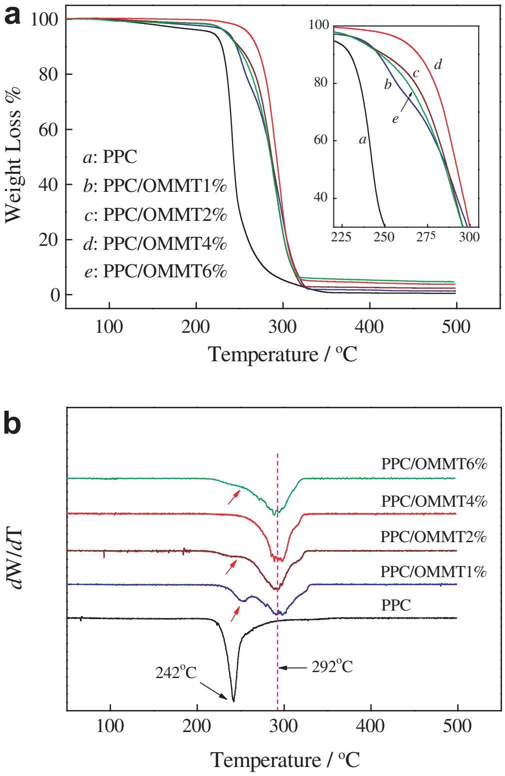

Fig. 4. TGA (a) and DTG (b) curves of PPC and PPC/OMMT nanocomposites with different OMMT contents.

degradation process when 50 wt% degradation occurred. As shown in Table 1, all the PPC/OMMT nanocomposites show an obviously higher thermal stability than pure PPC, and the PPC/OMMT with 4 wt% OMMT has the highest thermal stability. However, the thermal stability of nanocomposites decreases after OMMT content increases to 6 wt%. It was reported that the thermal decomposition behavior of a polymer is influenced by many factors, such as heating rate, surrounding atmosphere, sample weight and shape [20]. From the DTG results in Fig. 4b, it can be seen that the fastest thermal decomposition temperatures are improved after the addition of OMMT, and about 50 °C higher than that of PPC. The curves of nanocomposites become coarser and wider than that of pure PPC. The incorporation of clay into the polymer matrix would enhance its thermal stability by acting as a superior insulator. The silicate layers which uniformly disperse in matrix lead to the difficulty in heat conduction and acts as a mass transport barrier to the volatile products which generate during decomposition. Those functions of silicate layers will result in the lag, wide and coarse peaks of nanocomposites during decomposition. In addition to see the fastest thermal decomposition rate at 292 °C for all PPC/OMMT nanocomposites, a small peak around 251 °C was found for PPC/OMMT with OMMT contents as 1, 2 and 6 wt%, except PPC/OMMT with 4 wt% OMMT. This maybe ascribed to the uneven dispersion of OMMT when the clay content is too high or to the insufficient insulation function of OMMT when the clay content is too low. In both situations, the PPC/OMMT nanocomposites decompose early (around 251 °C, which is near the decomposition temperature of pure PPC).

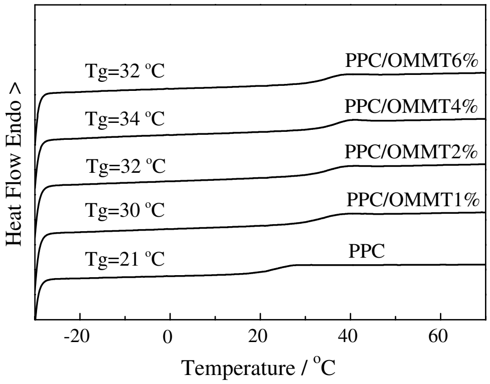

Fig. 5. DSC curves of PPC and PPC/OMMT nanocomposites with different OMMT contents.

The DSC traces of both PPC and PPC/OMMT nanocomposites are shown in Fig. 5. The pure PPC exhibits a glass transition temperature (T_g) at 21 °C. With the addition of OMMT, the glass transition temperatures of PPC/OMMT nanocomposites obviously increase, and the nanocomposites with OMMT content is 4 wt% shows the highest T_g at 34 °C, which is 13 °C higher than that of PPC. This is because of the strong interaction between the polymer and the nano-dispersed silicate layers, which restricts the segmental motion of PPC molecular chains.

Table 1
TGA results of PPC/OMMT nanocomposites

Materials	Pure PPC	PPC/OMMT1%	PPC/OMMT2%	PPC/OMMT4%	PPC/OMMT6%
$T_{0.05}$ (°C)	219	237	235	260	235
$T_{0.5}$ (°C)	243	287	287	293	286

The improvement of both the decomposition temperature and glass transition temperature of composites indicates that nanocomposition is an efficient way to increase the thermal stability of PPC.

3.3. Mechanical properties

In this work, the tensile strength and Young's modulus as representative mechanical properties were measured for the PPC/OMMT nanocomposites with OMMT contents from 0 to 6 wt%. Fig. 6 shows the mechanical properties of nanocomposites as a function of OMMT contents. It was found that both the tensile strength and Young's modulus of nanocomposites increased with clay addition. When the OMMT content is 4 wt%, the nanocomposite shows the highest tensile strength as 23.1 MPa which is about three times higher than that of pure PPC. At the same time, it shows the highest Young's modulus as 1.71 GPa, while the Young's modulus of PPC is 0.72 GPa. Further addition of OMMT such as the nanocomposites with 6 wt% OMMT leads to the decrease of mechanical properties. This is a characteristic behavior of PLS nanocomposites [7]. Nevertheless, all PPC/OMMT nanocomposites show improved mechanical properties than pure PPC in our experimental conditions.

The improvement of mechanical properties could be attributed to the nano-scale dispersion of OMMT in PPC matrix. The organic-modified MMT have strong interfacial interaction with the polymer matrix. These strong interaction and the excellent properties of clay lead to the significant increase in both thermal and mechanical properties of nanocomposites. As the clay content continuously increases, some silicate layers begin to aggregate. The formation of large silicate aggregates will effectively reduce the interfacial area between polymer and silicate layers. Furthermore, these aggregates will act as stress concentrators to diminish the mechanical properties of nanocomposites.

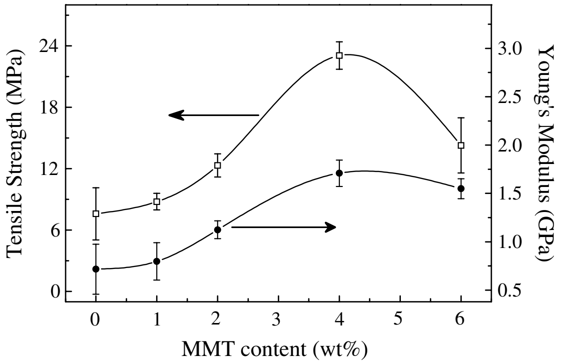

Fig. 6. Mechanical properties of PPC and PPC/OMMT nanocomposites with different OMMT contents.

4. Conclusion

PPC/OMMT nanocomposites were prepared by solution intercalation method. The nanocomposites have an intercalated-and-flocculated structure as revealed by TEM and XRD. The thermal stability, glass transition temperature and mechanical properties of PPC are improved by adding OMMT into PPC matrix. The PPC/OMMT nanocomposite with 4 wt% OMMT shows the best thermal and mechanical properties in our experiment conditions. When the OMMT content is 4 wt%, the nanocomposite shows the highest tensile strength as 23.1 MPa, which is about 3 times higher than that of pure PPC. Correspondingly, it also shows the highest thermal stability and the T_g is 13 °C higher than that of pure PPC. Those improvements could be attributed to the enough amount and good dispersion of OMMT in PPC matrix. The nanocomposition provides an efficient way to improve both the thermal and mechanical properties of PPC and consequently widely expands its application fields.

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References

[1] Okada M. Chemical syntheses of biodegradable polymers. Prog Polym Sci 2002;27:87–133.

[2] Peng SW, An YX, Chen C, Fei B, Zhuang YG, Dong LS. Thermal degradation kinetics of uncapped and end-capped poly(propylene carbonate). Polym Degrad Stabil 2003;80:141–7.

[3] Zhu J, Start P, Mauritz KA, Wilkie CA. Silicon-methoxide-modified clays and their polystyrene nanocomposites. J Polym Sci, Part A: Polym Chem 2002;40:1498–503.

[4] Chang JH, An YU, Cho D, Giannelis EP. Poly(lactic acid) nanocomposites: comparison of their properties with montmorillonite and synthetic mica (II). Polymer 2003;44:3715–20.

[5] Chen BQ, Evans JR. Poly(ε-caprolactone)-clay nanocomposites: structure and mechanical properties. Macromolecules 2006;39:747–54.

[6] Lim ST, Hyun YH, Choi HJ. Synthetic biodegradable aliphatic polyester/montmorillonite nanocomposites. Chem Mater 2002;14:1839–44.

[7] Ray SS, Okamoto M. Polymer/layered silicate nanocomposites: a review from preparation to processing. Prog Polym Sci 2003;28:1539–641.

[8] Lai MF, Li J, Liu JJ. Thermal and dynamic mechanical properties of poly(propylene carbonate). J Therm Anal Calorim 2005;82:293–8.

[9] Li XH, Meng YZ, Wang SJ, Rajulu AV, Tjong SC. Completely biodegradable composites of poly(propylene carbonate) and short, lignocellulose fiber hildegardia populifolia. J Polym Sci, Part B: Polym Phys 2004;42:666–75.

[10] Ge XC, Li XH, Zhu Q, Li L, Meng YZ. Preparation and properties of biodegradable poly(propylene carbonate)/starch composites. Polym Eng Sci 2004;44:2134–40.

[11] Li XH, Tjong SC, Meng YZ, Zhu Q. Fabrication and properties of poly(propylene carbonate)/calcium carbonate composites. J Polym Sci, Part B: Polym Phys 2003;41:1806–13.

[12] Xu J, Li RK, Meng YZ, Mai YW. Biodegradable poly(propylene carbonate)/montmorillonite nanocomposites prepared by direct melt intercalation. Mater Res Bull 2006;41:244–52.

[13] Xu J, Li RK, Xu Y, Li L, Meng YZ. Preparation of poly(propylene carbonate)/organo-vermiculite nanocomposites via direct melt intercalation. Eur Polym J 2005;41:881–8.

[14] Du LC, Qu BJ, Meng YZ, Zhu Q. Structural characterization and thermal and mechanical properties of poly(propylene carbonate)/MgAl-LDH exfoliation nanocomposite via solution intercalation. Compos Sci Technol 2006;66:913–8.

[15] Zhang ZH, Shi Q, Peng J, Song JB, Chen QY, Yang JL, et al. Partial delamination of the organo-montmorillonite with surfactant containing hydroxyl groups in maleated poly(propylene carbonate). Polymer 2006;47:8548–55.

[16] Ray SS, Yamada K, Okamoto M, Fujimoto Y, Ogami A, Ueda K. New polylactide/layered silicate nanocomposites. 5. Designing of materials with desired properties. Polymer 2003;44:6633–46.

[17] Tong X, Zhao HC, Tang T, Feng ZL, Huang BT. preparation and characterization of poly(ethyl acrylate)/bentonite nanocomposites by in situ emulsion polymerization. J Polym Sci, Part A: Polym Chem 2002;40:1706–11.

[18] Galgali G, Ramesh C, Lele A. A rheological study on the kinetics of hybrid formation in polypropylene nanocomposites. Macromolecules 2001;34:852–8.

[19] Vaia RA, Jandt KD, Kramer EJ, Giannelis EP. Microstructural evolution of melt intercalated polymer-organically modified layered silicates nanocomposites. Chem Mater 1996;8:2628–35.

[20] Lu XL, Zhu Q, Meng YZ. Kinetic analysis of thermal decomposition of poly(propylene carbonate). Polym Degrad Stabil 2005;89:282–8.