

PREFERENTIAL INTERCALATION BEHAVIOR OF CLAY AND ITS EFFECT ON THE THERMAL DEGRADATION IN IMMISCIBLE PP/PS BLENDS

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Abstract The typical immiscible PP/PS blend based clay nanocomposites were prepared *via* melt blending. The dispersion of clay was determined by X-ray diffraction (XRD) and transmission electron microscopy (TEM). Thermal stability and dynamic mechanical properties were measured by thermogravimetric analysis (TGA) and dynamic mechanical analysis (DMA), respectively. Preferential intercalation behavior of clay in PP/PS blends was found. The dispersion of clay is significantly influenced by the polarity of PP and PS, meanwhile the location of clay can be controlled by the alternation of the polarity of PP and PS through chemical modification. The clay migrates from PS phase to PP phase with the improvement of the polarity of PP. However, when the PS is sulfonated, clay migrates back to the dispersed PS phase again. The dispersion and location of clay have profound influence on the thermal and dynamic mechanical behavior of PP/PS blends. The better the dispersion of clay in either continuous phase or disperse phase, the higher the thermal stability of the blends. Besides, samples with clay located in the continuous phase can display the best strengthening effect.

Keywords: Clay; Nanocomposites; Poly(propylene); Polystyrene.

INTRODUCTION

Nanocomposites based on polymer blends are attracting increasing attention among scientists because the compounding may lead to a new kind of high performance material, which combines the advantages of polymer blends with the merits of polymer nanocomposites^[1–8]. A great deal of work focus on improving the performance of composites or studying the compatibilization effect of clay in the immiscible polymer blends^[9–15].

For polymer/clay nanocomposites, the clay dispersion plays a critical role in improving their macroscopic properties. When clay is introduced into the polymer blends, the location of clay is an interesting issue worthy being investigated. The clay is prone to dispersing in certain phase or in the interface of the polymer blends. The selective dispersion of clay is generally described as its “preferential intercalation” behavior^[16]. In several previous literatures the preferential intercalation behavior was discussed^[16, 17]. Choi *et al.*^[16] investigated the preferential intercalation of clay in miscible polymer blends of poly(methyl methacrylate) (PMMA)/poly(ethylene oxide) (PEO). They found that PMMA had better affinity for clay than PEO, and clay was located in the PMMA phase. Another typical example was the clay nanocomposites based on the immiscible polyamide 6 (PA6)/polypropylene (PP) and acrylonitrile-butadiene-styrene (ABS)/PA6 blends^[18–20]. In these immiscible polymer blends clay was located exclusively in the PA6 phase that has higher polarity than that of PP and ABS resins.

So far, all the previous work focused on the compatibilizing effect of clay on polymer blends. Beside, at least one polar component was included in the blending systems. Further researches need to be done on the

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preferential intercalation of clays in the immiscible polymer blends including two non-polar components such as PP/PS. On the other hand, the influence of the preferential intercalation of clay on the macroscopic properties of the blends should be investigated.

In this work, as a model system, the typical immiscible PP/PS blends based clay nanocomposites were prepared *via* melt blending. The polarity of PS and PP was modified by sulfonation and grafting of maleic anhydride (MAH) groups, respectively. The influence of component polarity on the preferential intercalation behavior was investigated by altering the polarity of PP and PS components. The influence of the preferential intercalation of clay on the macroscopic properties including thermal stability and dynamic mechanical properties was discussed.

EXPERIMENTAL

Materials

The polypropylene (T300, isotactic homopolymer, $M_w = 3.33 \times 10^5$ and $M_n = 8.06 \times 10^4$) used in this study was purchased from Sinopec Shanghai Petrochemical Co., China. The Polystyrene (666D, density = 1.05 g/cm^3 , $M_w = 3.10 \times 10^5$, $M_n = 8.70 \times 10^4$) was obtained from Yanshan Petrochemical Co., China. The commercial organophilic clay, provided by Zhejiang Huate Co., China, was obtained by a cation exchange reaction between Na-montmorillonite (110 mmol/100 g cation exchange capacity) and octadecyl trimethyl ammonium salt. All the other chemicals including 1,2-dichloroethane, dicumyl peroxide (DCP), sulfuric acid and maleic anhydride (MAH) were reagent-grade products and used without further purification.

Specimen Preparation

Preparation of maleic anhydride grafted polypropylene (PPMA) was carried out by melt grafting in a Thermo Haaker Rheomix at 160°C with a screw speed of 60 r/min. Before compounding, MAH and DCP were dissolved in acetone and then mixed with PP particles. After the acetone volatilized, MAH and DCP adhered onto the particles homogeneously. The grafting degree measured by the method reported in Ref. [21] was 3.79 wt%.

Preparation of sulfonated polystyrene (sPS) was carried out by sulfonating PS with sulfuric acid in a dichloroethane solution following the procedure of Makowski and colleagues, and the sulfonation degree was 0.43 wt% determined according to the method given in Ref. [22].

The formulations of clay with different PP/PS blends (as shown in Table 1) were prepared *via* melt compounding at 160°C in the Thermo Haaker Rheomix with a screw speed of 60 r/min, and the mixing time was 6 min for each sample. Before mixing, all the polymers and clay were dried in a vacuum oven at 80°C for at least 12 h. The compounded samples were transferred to a mold and preheated at 180°C for 3 min, and pressed at 14 MPa, then successively cooled to room temperature while maintaining the pressure to obtain the composite sheets for further measurements.

Table 1. Formulations of PP/PS, PP/PS/clay, PP/sPS/clay, PP/PPMA/PS/clay, PP/PPMA/sPS/clay systems

Sample	PP	PPMA	PS	sPS	Clay
PP/PS	80	—	20	—	—
PP/PS/clay	80	—	20	—	4
PP/sPS/clay	80	—	—	20	4
PP/PPMA/PS/clay	64	16	20	—	4
PP/PPMA/sPS/clay	64	16	—	20	4

Characterization

X-ray diffraction

Wide-angle X-ray diffraction (WAXD) was used to examine the dispersion of clay in the composites. WAXD was carried out by using a Rigaku X-ray generator (Cu $K\alpha$ radiation with $\lambda = 0.154 \text{ nm}$) at room temperature. The diffractograms were obtained at the scattering angles from 0.5° to 10° , at a scanning rate of $2^\circ/\text{min}$.

Transmission electron microscopy

The transmission electron micrographs were obtained with a JEM-1200EX electron microscope to examine the locations and dispersion states of clay in the blends. The blend samples for TEM observations were ultrathin-sectioned using a microtome equipped with a diamond knife. The sections (200–300 nm) were cut from a piece of about 1 mm × 1 mm, and they were collected in a trough filled with water and placed on 200 mesh copper grid.

Contact angle measurements

The polarity of pure and modified polymers was measured using the water contact angle on an OCA20 system (Dataphysics, Germany) equipped with video capture at 25°C.

Thermogravimetric analysis

Thermogravimetric analysis (TGA) experiments were taken in a TA SDT Q600 thermal analyzer from 60°C to 600°C using a scanning rate of 10 K/min under air and N₂, respectively.

Dynamic mechanical analysis

Dynamic mechanical properties were measured with a DMA Q800 (TA Corp.) in the stretching mode. The dynamic storage and loss moduli were determined at a frequency of 10 Hz and a heating rate of 3 K/min as a function of temperature from –50°C to 150°C.

RESULTS AND DISCUSSION

The Intercalation of Clay

X-ray diffraction, XRD, provides information on the changes of the inter-layer spacing of the clay upon the formation of nanocomposites. The formation of an intercalated structure should result in a decrease in 2θ , indicating an increase in the d-spacing; the formation of a delaminated structure usually results in the complete loss of regularity between the clay layers, and no peak can be seen in the XRD trace^[23].

Figure 1 shows the XRD profiles of original clay, organoclay, PP/PS/clay, PP/sPS/clay, PP/PPMA/PS/clay and PP/PPMA/sPS/clay systems. The (001) diffraction of organoclay was at $2\theta = 4.7^\circ$, corresponding to an interlayer spacing of 1.89 nm. After the addition of 4 phr organoclay to PP/PS blend, the characteristic (001) peak of the clay was split up into two peaks at 2.4° and 4.8° (corresponding to the basal spacing of 3.72 nm and 1.82 nm), respectively. The increased spacing indicated that some polymer chains intercalated into the clay galleries, forming an intercalated structure. The peak observed at $2\theta = 4.8^\circ$ resided at an angle very close to the one for the bulk clay, which was more likely due to the unintercalated clay layers.

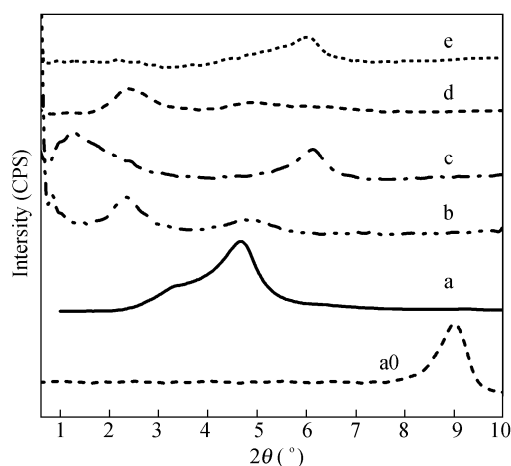
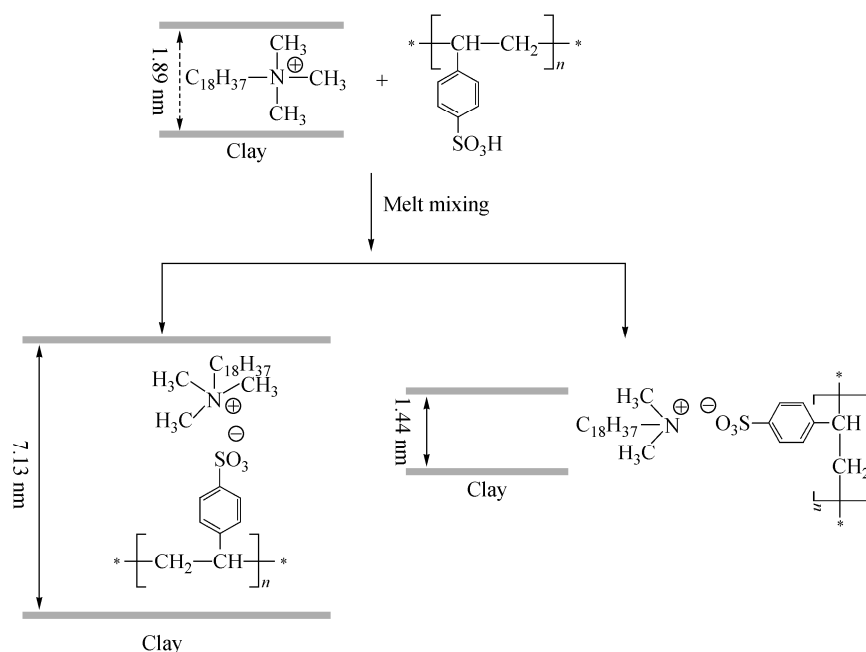


Fig. 1 The X-ray diffraction profiles for all samples: (a0) original clay, (a) organoclay, (b) PP/PS/clay, (c) PP/sPS/clay, (d) PP/PPMA/PS/clay and (e) PP/PPMA/sPS/clay. The clay content was 4 phr for all of the composites.

In the XRD curve of PP/sPS/clay system, two broad peaks were found at $2\theta = 1.3^\circ$ and 6.2° , corresponding to the interlayer spacing of 7.13 nm and 1.44 nm, respectively. The intercalation of clay in polymer nanocomposites was strongly dependent on the polarity of polymer matrixes^[24, 25]. In comparison with the clay in the PP/PS/Clay composite, the remarkably increased d-spacing indicated that the sulfonation of PS resin improved the polarity of the PS phase. The secondary peak at $2\theta = 6.2^\circ$ suggested that partial unsteady intercalating agent was possibly removed from the interlayer of clay for the strong reaction between sulfonic group of sPS and amidogen of the intercalating agent. The possible mechanism is described as Scheme 1.



Scheme 1 The possible mechanism of variation of d-spacing of clay layers

As for PP/PPMA/PS/clay system, the curve still demonstrated two peaks appearing at $2\theta = 2.5^\circ$ and 5.0° , corresponding to the interlayer spacing of 3.72 nm and 1.82 nm, respectively. Compared to PP/PS/clay system, the d-spacing of PP/PPMA/PS/clay system was a little smaller which indicated that the possible different intercalating reaction existed between clay and the matrix polymers in two systems. The contrast between curves of PP/PPMA/sPS/clay and PP/sPS/clay samples showed the former did not exhibit visible clay diffraction peaks in the small angle region. The variation suggested that partial clay platelets were exfoliated in the composites, in agreement with the previous work^[26]. When PP and PS both were modified, the improvement of the polarity resulted in the disappearance of characteristic peak in the small angle region. However, the characteristic peak $2\theta = 6.0^\circ$ still exist, for the same reason as PP/sPS/clay system.

Water contact angle measurements are the most convenient way to assess the hydrophilicity and wetting characteristics of polymers, which may respond the polarity of polymers. When water is applied to the surface, the outermost surface layers interact with the water. A hydrophobic surface with low free energy gives a high contact angle with water, whereas a wet high-energy surface allows the drop to spread, *i.e.* gives a low contact angle. Figure 2 shows a series pictures of the initial static water contact angle on the pure and modified polymers. Before modified with polar group, the contact angles of PP and PS are 101.4° and 92.7° , respectively. After introducing polar groups, the contact angle of modified PP (PP/PPMA) is reduced to 80.7° , and that of modified PS (sPS) is reduced to 65.1° . The variation of contact angle is consistent with the variation of polarity of the polymer matrices and also can be used as an effective evidence to explain the phenomena in XRD.

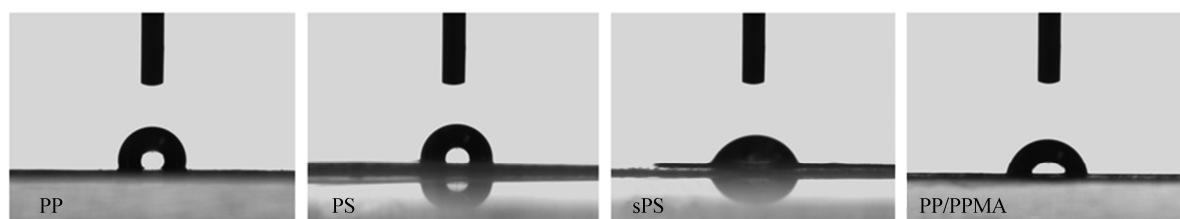


Fig. 2 Initial static water contact angle on the pure and modified polymers

Clay Dispersions

However, it is difficult for XRD to draw definitive conclusions about the visualized dispersion of clay in nanocomposites, especially for the clay dispersion in binary polymer blends. Thus, TEM techniques are necessary to provide an actual image of the clay layers to permit the identification of the morphology of the nanocomposites. Figure 3 shows TEM images for the different clay filled systems. Spherical domains with different diameters correspond to the dispersed PS or sPS phase, and the rest was the continuous PP or PP/PPMA phase. Since clay has much higher electron density than neat polymers, it appears as dark lines or tactoids in TEM images.

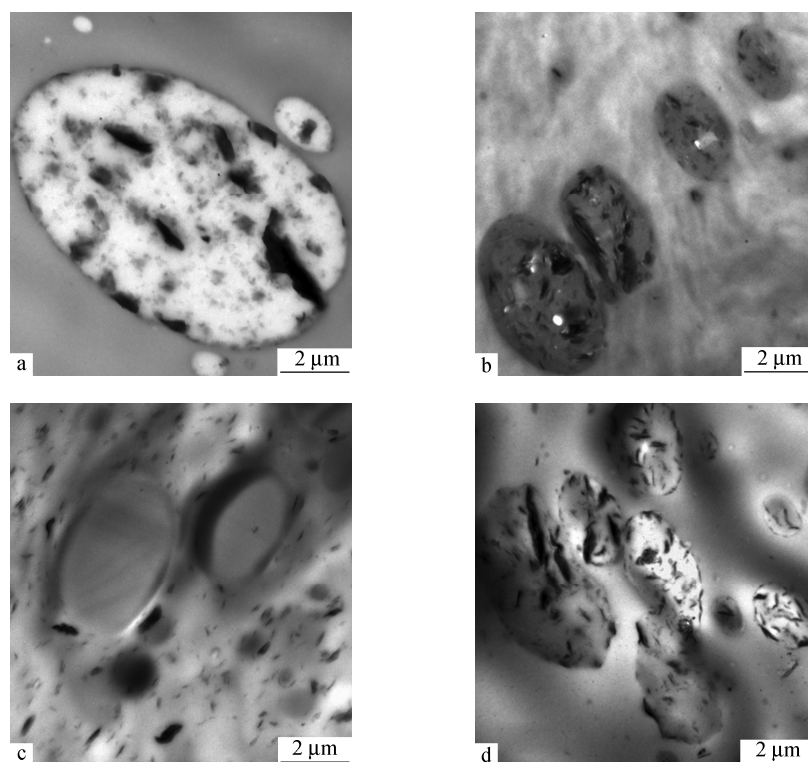


Fig. 3 TEM images for (a) PP/PS/clay, (b) PP/sPS/clay, (c) PP/PPMA/PS/clay and (d) PP/PPMA/sPS/clay systems

TEM image of the PP/PS/Clay composite is shown in Fig. 3(a). A stacked structure of clay layers only preferentially located in the PS phase, indicating the higher polarity of PS than PP resin, and PS phase had a stronger affinity to clay surfaces than PP component. Besides, some clay platelets dispersed in the PS phase displayed as intercalated structure. However, there was still plenty of clay aggregated together, in agreement with the two characteristic peaks observed in the XRD pattern (Fig. 1b). It was worth to emphasize that no any discernible clay platelets could be found in the continuous PP phase and the interface region. The distinct TEM

micrographs confirm that the preferential intercalation of clay did occur in binary polymer blends with various polarities.

In the PP/sPS/clay composite (Fig. 3b), we could find clay layers still selectively located in the dispersed sPS phase. Besides, the clay dispersion was greatly improved, and the degree of clay aggregation was much reduced. The better dispersion of clay could be attributed to the improved polarity of PS phase after sulfonating modification and reflected by the enlargement of *d*-spacing of clay in the XRD pattern.

In the PP/PPMA/PS/clay composite (Fig. 3c), it is interesting to notice that all clay migrated from the PS phase to the modified PP phase, and no single clay platelet can be seen in the dispersed PS phase and interface region. The above results confirmed that the polarity of polymers had a significant impact on the intercalating action of clay. The migration of clay from PS to PP phase was also confirmed by the shift of the (001) characteristic peaks in XRD profiles. The different *d*-spacing demonstrated by (d) and (b) curves indicated that PP and PS had different intercalating ability to clay.

In TEM image of PP/PPMA/sPS/clay composite (Fig. 3d), when PP and PS are both modified, the state of clay dispersion is again greatly changed. Majority of clay platelets rearranged and migrated from the modified PP phase to the sPS phase again. Some enriched in the interface region, some still stayed in the modified PP phase in the highly exfoliated states. This indicates that the interaction between sPS and clay was stronger than that of PPMA modified PP. The discussion above indicated the preferential intercalation behavior of clay was significantly dependent on the polarity of polymers. All the TEM results are consistent with the XRD data shown in Fig. 1.

Thermal Degradation

The thermal degradation of the different systems was analyzed, and the TGA and DTG curves under air and nitrogen are presented in Fig. 4 and Fig. 5, respectively. The summary of the TGA and DTG results for the various composites in air and nitrogen are presented in Table 2. Only a one-step decomposition was found for PP/PS blend because of the similar degradation behavior of pure PP and PS. Moreover the organoclay-added samples also showed the same thermal degradation behavior under both nitrogen and air atmosphere. However, the degradation of all samples in air was much earlier than that in N₂. This indicated that the participation of oxygen accelerated the formation of free radicals in PP and PS chains during thermal decomposition at lower temperatures.

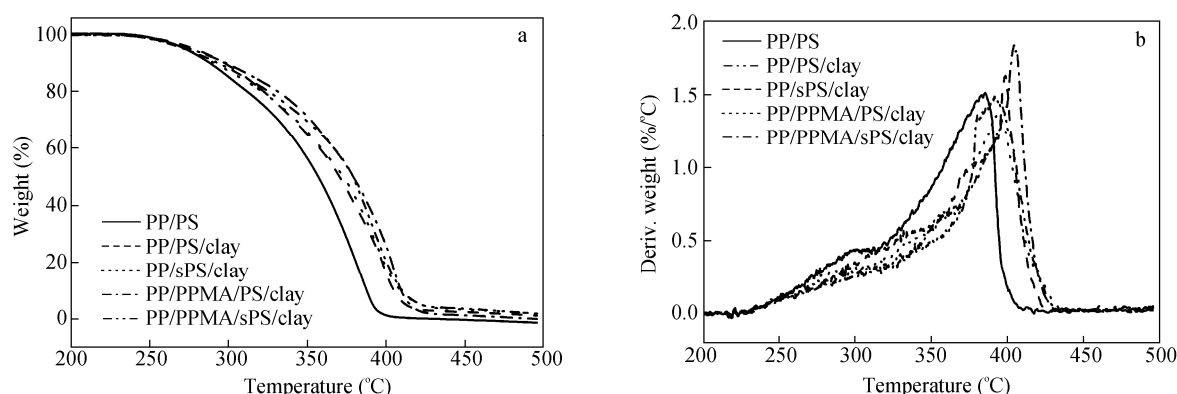


Fig. 4 TGA (a) and DTG (b) curves of PP/PS/clay, PP/sPS/clay, PP/PPMA/PS/clay and PP/PPMA/sPS/clay systems under air

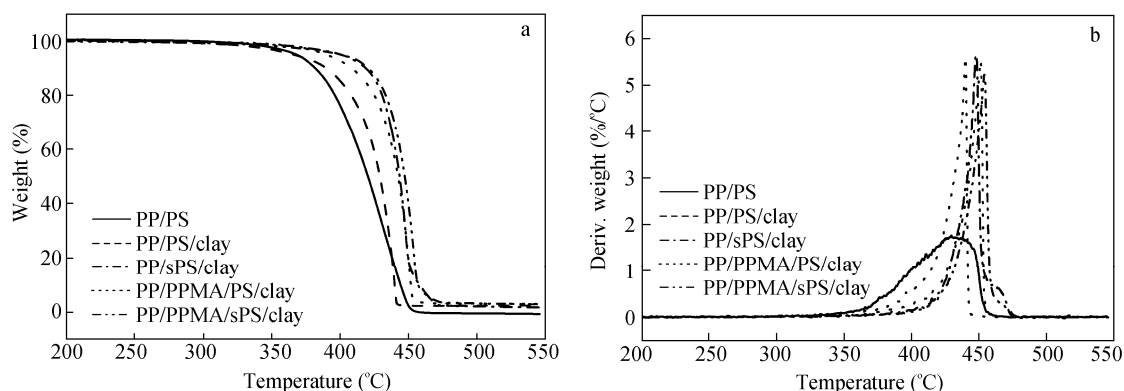


Fig. 5 TGA (a) and DTG (b) curves of PP/PS/clay, PP/sPS/clay, PP/PPMA/PS/clay and PP/PPMA/sPS/clay systems under nitrogen

Table 2. Results of TGA analysis of all samples under different atmosphere environment

Samples	in air			in N ₂		
	T_{onset} (°C)	T_{max} (°C)	Residue at 500°C (%)	T_{onset} (°C)	T_{max} (°C)	Residue at 500°C (%)
PP/PS	272	385	0	367	429	0
PP/PS/clay	277	391	2.5	364	440	2.4
PP/sPS/clay	272	398	3.3	388	448	3.2
PP/PPMA/PS/clay	274	394	1.3	398	451	2.2
PP/PPMA/sPS/Clay	271	405	3.2	399	454	3.3

Under air conditions, for a closer analysis, there were no obvious alternations for the initial degradation temperature (T_{onset}), maybe, because the organoclay used in this study had the almost same T_{onset} . It was worth noting that the T_{onset} of PP/PS/clay system was the highest among all samples, maybe, because the modification of PP and PS caused the reduction of the molecular weight and then the thermal stability. At higher temperatures, the addition of organoclay could enhance the thermal stability of all systems. For PP/PS/clay and PP/sPS/clay systems, although the clay platelets were located in the dispersed PS phases in both cases, the T_{max} of the latter was 7 K higher than that of the former. This indicated that the clay preferentially located in the dispersed PS phase could still enhance the thermal stability of the blends. Moreover, the better dispersion of clay in the dispersed phase could execute a better protection of the matrix. T_{max} of PP/PPMA/PS/clay sample was 3 K higher than that of PP/PS/clay with the same clay intercalation, indicating the location of clay in continuous phase could more efficiently improve the thermal stability than that in dispersed phases in the blends. The PP/PPMA/sPS/clay system with the best clay dispersion had the highest T_{max} , providing a positive proof that the dispersion of clay in both phases could give the best protection for the immiscible PP/PS blends. For residues, all samples gave eligible chars, indicating all PP and PS are almost entirely decomposed.

Compared to the degradation under air, the thermal degradation of the composites in nitrogen demonstrated some differences. Firstly, the initial degradation of all samples was significantly retarded, indicating the different decomposing mechanism with the presence or absence of oxygen. Secondly, differing from the degradation in air, the T_{onset} in N₂ of all samples were greatly improved except PP/PS/clay sample. Due to the absence of oxygen, the decomposition of the intercalated agent was prohibited, and the clay could better execute its barrier effect. Comparing with PP/PS, the T_{onset} of PP/PS/clay was basically unchanged due to the relatively poor dispersion of clay in the dispersed PS phase, and this was confirmed by the higher T_{onset} of PP/sPS/clay sample in which the clay was also located in PS phase but with a better dispersion. A 10 K higher T_{onset} was found in

PP/PPMA/PS/clay sample than that of PP/sPS/clay sample, indicating that the location of clay in the continuous PP phase could enhance the initial thermal stability of the blends more effectively than in the dispersed PS phase. The highest T_{onset} was found in PP/PPMA/sPS/clay system, indicating the intercalation of clay in both PP and PS phase could give the best protection of the blends. As for the T_{max} and residues, all samples in N_2 show the same trend as that in air.

All the results above indicated that both the dispersing state and the location of clay had significant influence on the thermal degradation behavior of immiscible PP/PS blends. The better the clay dispersed, the higher thermal stability could be achieved due to the better barrier effect of exfoliated clay platelets than intercalated ones. On the other hand, the preferential location of clay in the continuous phase had better protective effect than that in the dispersed phase. It was easy to understand that the majority of the polymer blends (PP phase) could be protected by clay platelets since the clay located in it.

Dynamic Mechanical Properties

The dynamic mechanical properties for all samples were analyzed, and the storage modulus (E') and loss tangent ($\tan\delta$) are shown in Fig. 6 and Fig. 7 as a function of temperature. For the clay added systems, there was a significant enhancement of the modulus over the temperature range investigated, as compared with that of neat PP/PS blend because of the strengthening effects of organoclay with a large aspect ratio. For a closer analysis, although the clay platelets located in the dispersed PS phase, the PP/sPS/clay sample with better clay dispersion had much higher E' than that of PP/PS/clay sample, indicating the better dispersed clay not only can enhance the thermal stability but also improve the storage modulus of the blends. The highest E' was found in PP/PPMA/PS/clay sample in which the clay platelets were located in the continuous PP phase. It indicated that the better strengthening effect could be achieved under such situation. It was worth noting that PP/PPMA/sPS/clay sample with the best clay dispersion did not exhibit the highest stiffness. It is, maybe, because the modulus of whole polymer blend materials is chiefly determined by the modulus of their continuous phase, while less depended on the modulus of the dispersed domain. For PP/PPMA/PS/clay system, the best strengthening effect of clay can be obtained when all the clay was located in the continuous PP/PPMA phase. However the strengthening effect of clay on the continuous phase was weakened in PP/PPMA/sPS/clay system because a part of clay platelets migrated from the continuous PP/PPMA phase to the dispersed sPS phase.

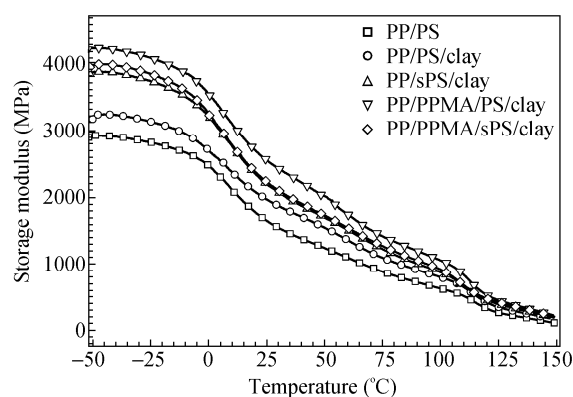


Fig. 6 Temperature dependence of the storage modulus (E') for PP/PS/clay, PP/sPS/clay, PP/PPMA/PS/clay and PP/PPMA/sPS/clay systems

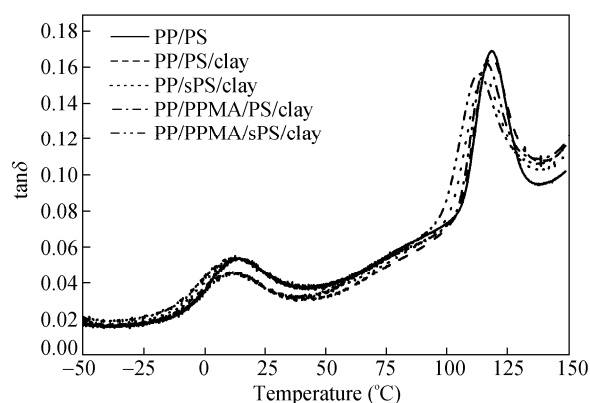


Fig. 7 Temperature dependence of $\tan\delta$ for PP/PS/clay, PP/sPS/clay, PP/PPMA/PS/clay and PP/PPMA/sPS/clay systems

The glass transition temperature (T_g) can be obtained from the peak temperature of $\tan\delta$. In the curve of $\tan\delta$ versus temperature, two peaks at about 10°C and 120°C represent the T_g of PP and PS, respectively. Very interesting results were found after the overall investigation of all samples. The T_g of PS basically did not have any change when PS was not modified, while a 3–6 K decrease was found after PS was sulfonated. Two entirely

opposite factors of clay influencing the T_g of polymer/clay nanocomposites were usually considered. The addition of clay could hinder the movement of molecular chains and then cause the increase of T_g . On the other hand, a plasticizing function of the chains of alkyl ammonium used as the surfactant of organically modified clay has been proposed^[23]. Such plasticizing function could be responsible for the promoted mobility of polymer chains and caused the reduction of T_g . In this study, the basically unchanged T_g was, maybe, caused by the balance between the two opposite effects of clay. However, due to the modification of PS, the average molecular weight of PS was reduced, and the mobility of PS chains was improved which generated the decrease of T_g of the according composites. However, the T_g of PP had eligible variations in all samples, because the amount of added modified PP (PPMA) was too small to significantly change the molecular chain mobility.

CONCLUSIONS

In immiscible PP/PS blends, the clay dispersion and location are significantly influenced by the polarity of PP and PS. The clay location can be controlled by the alternation of the polarity of PP and PS by chemical modification. The clay is initially located in PS phase and can migrate to PP phase when the polarity of PP is improved. However, the clay may migrate back to the dispersed PS phase when the PS is sulfonated. The dispersion and location of clay have profound influence on the thermal and dynamic mechanical behavior of PP/PS blends. The better the clay disperses, the higher the thermal stability of the samples could be achieved due to the better barrier effect of exfoliated clay platelets than intercalated ones. Moreover, the sample, in which the clay preferentially locates in the continuous phase, has better thermal stability than that with clay in the dispersed phase. The intercalation of clay in both PP and PS phases could give rise to the best thermal stability of the blends. The modulus of all the systems are increased by introduction of clay platelets, and the location of clay in the continuous phase can give the best strengthening effect.

REFERENCES

- 1 Gelfer, M.Y., Song, H.H., Liu, L.Z., Hsiao, B.S., Chu, B., Rafailovich, M., Si, M.Y. and Zaitsev, V., *J. Polym. Sci., Part B: Polym. Phys.*, 2003, 41(1): 44
- 2 Yurekli, K., Karim, A., Amis, E.J. and Krishnamoorti, R., *Macromolecules*, 2003, 36(19): 7256
- 3 Xu, Y.J., Brittain, W.J., Vaia, R.A. and Price, G., *Polymer*, 2006, 47(13): 4564
- 4 Artzi, N., Khatua, B.B., Narkis, M. and Siegmann, A., *Polym. Compos.*, 2006, 27(1): 15
- 5 Chow, W.S., Ishak, Z.A.M., Karger-Kocsis, J., Apostolov, A.A. and Ishiaku, U.S., *Polymer*, 2003, 44(24): 7427
- 6 You, C.J., Xu, Y.J., Xi, S., Duan, X.X., Shen, J. and Jia, D.M., *Chinese J. Polym. Sci.*, 2005, 23(5): 471
- 7 Wu, Q., Du, M., Peng, M., Zuo, M. and Zheng, Q., *Acta Polymerica Sinica*(in Chinese), 2007, (3): 223
- 8 Xu, B., Song, Y.H., ShangGuan, Y.G. and Zheng, Q., *Chinese J. Polym. Sci.*, 2006, 24(3): 299
- 9 Lai, S.M., Liao, Y.C. and Chen, T.W., *J. Appl. Polym. Sci.*, 2006, 100(2): 1364
- 10 Gonzalez, I., Eguiazabal, J.I. and Nazabal, J., *Compos. Sci. Technol.*, 2006, 66(11-12): 1833
- 11 Hong, J.S., Namkung, H., Ahn, K.H., Lee, S.J. and Kim, C., *Polymer*, 2006, 47(11): 3967
- 12 Khatua, B.B., Lee, D.J., Kim, H.Y. and Kim, J.K., *Macromolecules*, 2004, 37(7): 2454
- 13 Ray, S.S. and Bousmina, M., *Macromol. Rapid Commun.*, 2005, 26(20): 1639
- 14 Si, M., Araki, T., Ade, H., Kilcoyne, A.L.D., Fisher, R., Sokolov, J.C. and Rafailovich, M.H., *Macromolecules*, 2006, 39(14): 4793
- 15 Wang, Y., Zhang, Q. and Fu, Q., *Macromol. Rapid Commun.*, 2003, 24(3): 231
- 16 Lim, S.K., Kim, J.W., Chin, I., Kwon, Y.K. and Choi, H.J., *Chem. Mater.*, 2002, 14(5): 1989
- 17 Chow, W.S., Ishak, Z.A.M. and Karger-Kocsis, J., *Macromol. Mater. & Eng.*, 2005, 290(2): 122
- 18 Li, Y.J. and Shimizu, H., *Macromol. Rapid Commun.*, 2005, 26(9): 710
- 19 Su, Q.S., Feng, M., Zhang, S.M., Jiang, J.M. and Yang, M.S., *Polym. Int.*, 2007, 56(1): 50

- 20 Chow, W.S., Ishak, Z.A.M., Ishiaku, U.S., Karger-Kocsis, J. and Apostolov, A.A., *J. Appl. Polym. Sci.*, 2004, 91(1): 175
- 21 Li, C.Q., Zhang, Y. and Zhang, Y.X., *Polymer Testing*, 2003, 22(2): 191
- 22 Makowski, H.S., Lundberg, R.D. and Singhal, G.H., 1975, U.S. Pat., 3,870,841
- 23 Ma, H.Y., Xu, Z.B., Tong, L.F., Gu, A.G. and Fang, Z.P., *Polym. Degrad. Stab.*, 2006, 91(12): 2951
- 24 Ma, H.Y., Fang, Z.P. and Tong, L.F., *Polym. Degrad. Stab.*, 2006, 91(9): 1972
- 25 Usuki, A., Kawasumi, M., Kojima, Y., Fukushima, Y., Okada, A., Kurauchi, T. and Kamigaito, O., *J. Mater. Res.*, 1993, 8: 1179
- 26 Wang, K., Liang, S., Deng, J.N., Yang, H., Zhang, Q., Fu, Q., Dong, X., Wang, D.J. and Han, C.C., *Polymer*, 2006, 47(20): 7131