

Preparation and Characterization of Anionically Polymerized Butadiene-Isoprene Copolymer/Clay Nanocomposites

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ABSTRACT: Butadiene-isoprene copolymer/montmorillonite (BIR/MMT) nanocomposites were synthesized successfully via *in situ* anionic polymerization. The results of transmission electron microscopy and X-ray diffractometer showed that the clay layers were exfoliated and high reaction temperature benefited the exfoliation of layers in BIR/MMT. The polymerization still exhibited "living" characteristics with the addition of organophilic montmorillonite (OMMT). However, the contents of 1,2-polybutadiene and 3,4-polyisoprene of the copolymer decreased with the addition of OMMT, because of its absorption effect on

N,N,N',N'-tetramethylethanediamine as revealed by ¹H NMR. Moreover, it was observed that the glass-transition temperature of the BIR/MMT nanocomposites also decreased when compared with the BIR copolymers. The thermal stability of the nanocomposites was improved, because of the barrier property of exfoliated clay layers. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 1167–1172, 2006

Key words: nanocomposites; butadiene-isoprene copolymer; montmorillonite; anionic polymerization

INTRODUCTION

When compared with the conventional materials, nanoclay-filled polymeric systems offer many new and greatly improved properties. The properties of the polymer/clay nanocomposites strongly depend on the extent of dispersion of the clay. Exfoliated polymer/clay nanocomposites are regarded as high performance composites because exfoliated clays have high aspect ratio and thereby offering large surface areas to polymers.¹ Usually, polymer/clay nanocomposites can be prepared by three methods: melt blending, solution blending, and *in situ* polymerization. *In situ* polymerization offers the ability to impart the significant control over both the polymer architecture and the final structure of the composite,² and various polymerization methods have been used in the fabrication of polymer/clay nanocomposites.^{3–14} Although many polymer/clay nanocomposites have been prepared via various polymerization techniques, there is a lack of report on rubber/clay nanocomposites produced by *in situ* polymerization. This is because conventional rubbers are generally synthesized by anionic polymerization, a polymerization method that exhibits "living" charac-

teristics, which requires high reaction condition,¹⁵ such as isolation of water and oxygen.

Recently, we have reported the synthesis of polystyrene,¹⁶ styrene-butadiene random¹⁷ and block copolymers,¹⁸ and styrene-butadiene-isoprene rubber (BIR)/clay¹⁹ nanocomposites via *in situ* anionic polymerization. Results reported from the above have provided a new method to prepare nanocomposites with dispersion of MMT layers in SBS elastomer matrix. In this article, we studied the synthesis of BIR/clay nanocomposites by *in situ* anionic polymerization, and characterized the structure and properties of the nanocomposites.

EXPERIMENTAL

Materials

Organophilic montmorillonite (OMMT, NANNOLIN DK4) was supplied by Fenghong Clay Chemical Corp. in China. The clay was exchanged by a quaternary long quaternary organic ammonium salt with cation exchange capacity of 110 meq/100 g to obtain an average particle size of 25 × 1000 nm in the dry state. All materials were purified before use. Styrene and isoprene were of polymerization grade, and were obtained from Yanshan Petrochem. Co., China. They were treated with activated alumina to remove the inhibitor and deoxygenated before use. Butadiene (polymerization grade, Yanshan Petrochem. Co., China)

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was treated with minor *N*-butyllithium (*n*-BuLi) to remove moisture and inhibitor. Cyclohexane (chemical grade, Jinxi Chemical Plant, China) was dried with 5-Å molecular sieves and deoxygenated. *N*-BuLi was prepared in laboratory, and its concentration was calibrated by Gilman double titration method.²⁰ Lithium bromide (LiBr, Sinopharm Chemical Reagent Co., Ltd, China) was of chemical grade. *N,N,N',N'*-tetramethylethylenediamine (TMEDA) was kindly provided by Ji Zeng.

Purification of OMMT

OMMT was dried under vacuum for 48 h at 60°C, then BuLi was added to remove the impurities, and the excessive BuLi was washed with cyclohexane. After vacuum drying for 2 h at 50°C, toluene was added to obtain OMMT toluene solution (10 wt %).

Synthesis of BIR/MMT nanocomposites

A given amount of butadiene, isoprene [butadiene/isoprene = 1/1 (by weight)], TMEDA (TMEDA: *n*-BuLi = 0.2), OMMT toluene solution, and toluene were introduced into a 250 mL polymerization flask filled with purified N₂. After stirring for 3 h, a little *n*-BuLi was added to remove impurities in the system, and then a stoichiometric amount (according to a designed molecular weight of 1.2×10^5) of *n*-BuLi as an initiator was added into the bottle. The polymerization was carried out at 50°C for 6 h to obtain butadiene-isoprene copolymer/montmorillonite (BIR/MMT), and absolute ethyl alcohol was used as terminating agent. The product was vacuum-dried at 40°C up to a constant weight. BIR/MMT nanocomposites containing 0, 1, 2, 3, 4, and 5 wt % OMMT were prepared, and coded as BIR, BIR-M1, BIR-M2, BIR-M3, BIR-M4, and BIR-M5, respectively. To study the effect of the content of TMEDA on the microstructure of the copolymer, a given amount of styrene (30 wt %), isoprene (30 wt %), butadiene (40 wt %), TMEDA (TMEDA: *n*-BuLi = 1), OMMT, and toluene were introduced into a 250 mL polymerization bottle filled with purified N₂. By using the same procedure, the products of styrene-butadiene-isoprene copolymer (SIBR)/MMT nanocomposites containing 0, 1, 2, 3, 4, and 5 wt % were obtained, and coded as SIBR, SIBR-M1, SIBR-M2, SIBR-M3, SIBR-M4, and SIBR-M5, respectively.

Characterization

The molecular weights and molecular weight distributions were measured with a gel permeation chromatography (GPC, SHIMADZU 10A, Japan) equipped with three columns of TSK-GEL multipore HXL-M (7.8 mm × 300 cm) at room temperature. The eluent used was tetrahydrofuran (THF). Before the test, the polymer

chains were cleaved from the silicate layers by refluxing in THF solution containing LiBr. The samples were dissolved in THF for overnight to prepare transparent solution of 1.0 mg/mL. The THF and polymer solution were purified by a 0.2 μm filter, and then degassed before use. The injection volume was 100 μL for each sample solution, and the flow rate was 1.0 mL/min. The calibration curves for GPC were obtained by using TSK standard samples of polystyrene (TSK, Japan). Class-LC10 software was used for data acquisition and analysis.

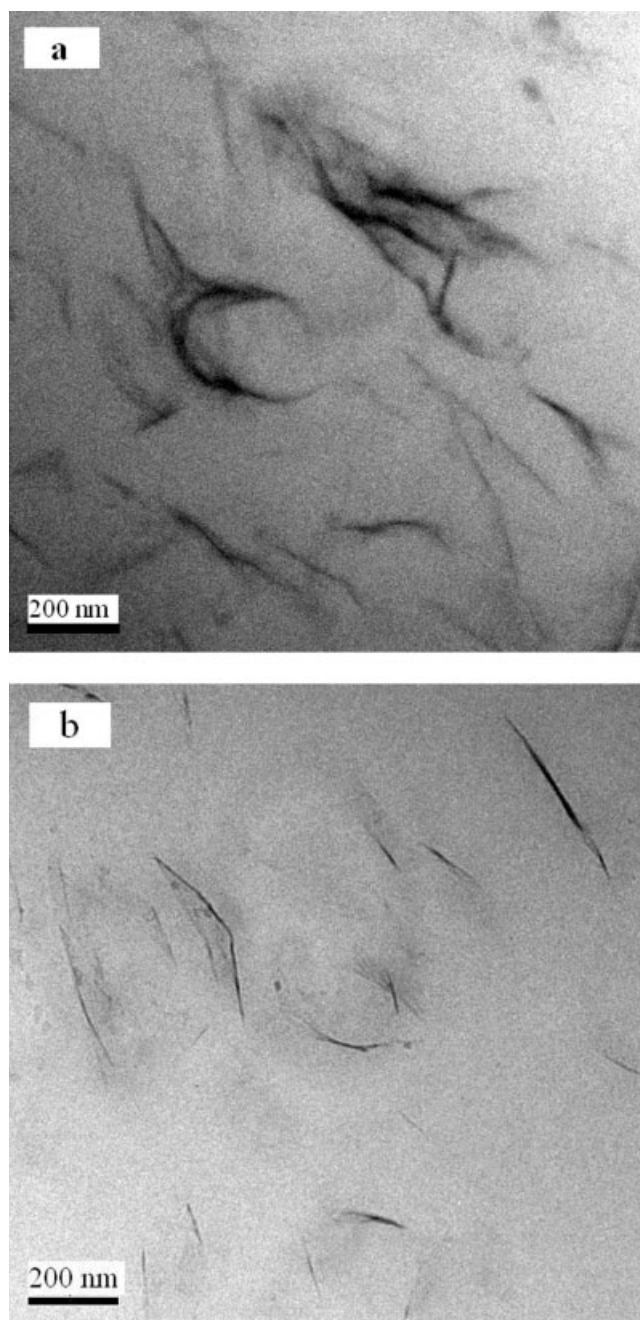


Figure 1 TEM images of the BIR/MMT nanocomposites synthesized at different polymerization temperatures: (a) 30°C; (b) 60°C.

The X-ray diffraction measurement of the samples was carried out on an X-ray diffractometer (XRD, Rigaku D/max-II, Japan) using Cu K α target at 40 kV and 100 mA ($\lambda = 0.154$ nm) with 2θ scan range from 1 to 15°. Transmission electron microscopy (TEM) analysis was carried out on a TECNAI G²20 transmission electron microscope (FEI Company, USA) at an acceleration voltage of 200 kV. Ultrathin sections of the samples were prepared using a Ultracut UCT (Leica, Holand) with EMFCS cryo-attachment at -120°C . The cross sections with the thickness of 50 nm were obtained by using a diamond knife. ¹H NMR spectrum was recorded on a DRX 400 NMR spectrometer (Bruker, Switzerland) with 400 MHz at 25°C . The spinning speed, pulse delay, and total numbers of scans were 20 Hz, 15 s, and 128, respectively. The sample was dissolved in deuterated chloroform (CDCl₃) to prepare the polymer solution with concentration of 150 mg/mL. Differential scanning calorimetry (DSC) was performed on a DSC model 2910 (DSC, TA, USA) at a heating rate of $10^\circ\text{C}/\text{min}$ from -130°C to 30°C under nitrogen atmosphere. Thermogravimetric analysis (TGA) and derivative thermogravimetric (DTG) measurement was performed with a TGA 2050 thermogravimetric analyzer (TA, USA). Samples were heated to 600°C at a heating rate of $20^\circ\text{C}/\text{min}$ under nitrogen atmosphere.

RESULTS AND DISCUSSION

Effect of reaction temperature on the exfoliation of MMT layers

The TEM images of the BIR/MMT nanocomposites synthesized at different polymerization temperature are shown in Figure 1. The OMMT content was 3 wt % in the nanocomposites. Figure 1(a) shows the TEM image of nanocomposite synthesized at 30°C . Although the MMT layers are exfoliated, some platelets thicknesses are above 10 nm, indicating that the MMT layers are not completely exfoliated. However, for the nanocomposites synthesized at 60°C , the clay layers are found to be not only exfoliated but also disorderly dispersed at the monolayer level [Fig. 1(b)]. This indicates that the MMT layers are completely exfoliated in the nanocomposites synthesized at higher temperature.

TABLE I
Values of \overline{M}_n , \overline{M}_w , and $\overline{M}_w/\overline{M}_n$ of the BIR and BIR/MMT Nanocomposites

Sample	$\overline{M}_n \times 10^{-5}$	$\overline{M}_w \times 10^{-5}$	$\overline{M}_w/\overline{M}_n$
BIR	1.25	1.32	1.06
BIR-M1	1.21	1.33	1.10
BIR-M2	1.33	1.53	1.15
BIR-M3	1.28	1.64	1.28
BIR-M4	1.45	1.96	1.35
BIR-M5	1.41	2.06	1.46

TABLE II
The Microstructure of the Samples

Sample	1,2-PB (wt %)	1,4-PB (wt %)	3,4-PI (wt %)	1,4-PI (wt %)
BIR	10.6	39.5	8.5	41.5
BIR-M1	9.7	41.6	6.4	42.3
BIR-M2	8.1	42.2	5.6	44.1
BIR-M3	8.4	42.6	5.8	42.7
BIR-M4	8.4	43.0	6.0	42.6
BIR-M5	8.2	42.9	5.9	43.0
SIBR	33.2	21.4	21.6	0
SIBR-M1	32.9	23.1	18.7	0
SIBR-M2	28.1	24.6	17.1	6.4
SIBR-M3	27.8	27.1	15.2	7.7
SIBR-M5	26.0	35.0	12.5	9.2

Obviously, this observation shows that a relatively high polymerization temperature benefits the exfoliation of MMT layer. This is so because more polymerization heat is released in unit time at higher reaction temperature, which benefits the exfoliation of MMT layers. However, high reaction temperature can change the microstructure of copolymer, thus the polymerization temperature of 50°C has been selected for the following studies.

Effect of OMMT content on the copolymerization

The number-average molecular weight (\overline{M}_n), weight-average molecular weight (\overline{M}_w), and polydispersity index ($\overline{M}_w/\overline{M}_n$) determined by GPC are summarized in Table I. In view of the results, the \overline{M}_n values of all samples are basically consistent with the designed value (1.2×10^5), and the polydispersity index is less than 1.5, indicating a "living" anionic polymerization mechanism.²¹ The contents of 1,2-polybutadiene (1,2-PB), 1,4-polybutadiene (1,4-PB), 3,4-polyisoprene (3,4-PI), and 1,4-polyisoprene (1,4-PI) by ¹H NMR have been analyzed according to the literature,²² and the data are listed in Table II. With an increase of OMMT, the 1,2-PB and 3,4-PI contents of the copolymer decrease, while the 1,4-PB and 1,4-PI contents increased compared with those of BIR. For the BIR-M5 sample, the 1,2-PB and 3,4-PI contents decreased by 23 and 31%, respectively, compared to those of BIR. The 1,2-PB and 3,4-PI contents of the dienes polymer are strongly depended on the concentration of polar additives (including tetrahydrofuran, TMEDA, etc.) in the reaction system.²³ So the concentration of TMEDA may be decreased with the introduction of OMMT into the polymerization system. However, in our previous reports the addition of OMMT hardly changed the microstructure of diene polymers.¹⁷⁻¹⁹ Because the intercalation agent of the OMMT is quaternary ammonium salt and TMEDA has nitrogen atoms, OMMT has some adsorption effect on TMEDA, leading to the decrease of its content in the polymerization system. However, THF rather than

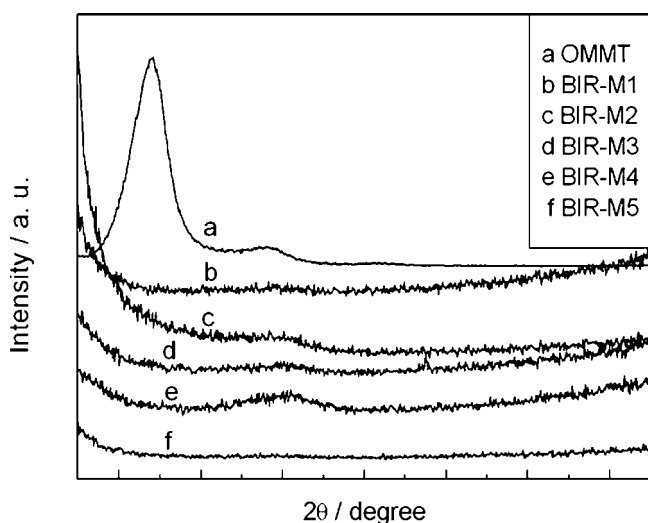


Figure 2 X-Ray diffraction patterns of the OMMT and BIR/MMT nanocomposites with different OMMT contents.

TMEDA was used in our previous work. To further investigate the adsorption effect of OMMT, the concentration of TMEDA increased five times in the reaction system, and the microstructure data of the copolymer with different OMMT content are listed in Table II. With the introduction of OMMT, the contents of 1,2-PB and 3,4-PI obviously decrease, and their corresponding contents of 1,4-PB and 1,4-PI increase. Therefore, OMMT has a great effect on the microstructure of copolymer as a result of absorption of TMEDA in the polymerization system.

Structure and properties of BIR/MMT nanocomposites

The XRD patterns of the OMMT and BIR/MMT nanocomposites with different OMMT contents are shown in Figure 2. The diffraction peak of OMMT lies at 2.46° , and the corresponding distance between the adjacent layers is 3.59 nm. However, the BIR/MMT nanocomposites show no peak in the range from 1° to 15° , indicating the fact that the clay layers are fully intercalated (at least 8.9 nm of layer distance) or even exfoliated. TEM images of the BIR-M1 and BIR-M3 are shown in Figure 3. Both images show exfoliated structure rather than micron-sized clay tactoids. The MMT layers in the nanocomposites disperse disorderly as monolayers or 2–5 layer stacks in the copolymer matrix. This result further confirms that exfoliated BIR/MMT nanocomposites were successfully prepared by anionic polymerization with toluene as solvent.

The DSC curves of BIR and BIR/MMT nanocomposites are shown in Figure 4. The glass-transition temperature (T_g) of BIR is -69.1°C , and all BIR/MMT nanocomposites show lower T_g than BIR. With an

increase in the amount of OMMT, the T_g of BIR/MMT nanocomposites decreases slightly. The T_g values of diene polymers greatly depend on the contents of 1,2-PB and 3,4-PI.²⁴ The result from $^1\text{H NMR}$ indicates that the contents of 1,2-PB and 3,4-PI of copolymer decrease with the addition of OMMT, and the corresponding T_g values of nanocomposites decrease. The interaction between copolymer chains and MMT layers may prevent the segmental motion of the macromolecules, leading to the increase of T_g as mentioned in our earlier reports.^{17–19} However, the structure of the main chain

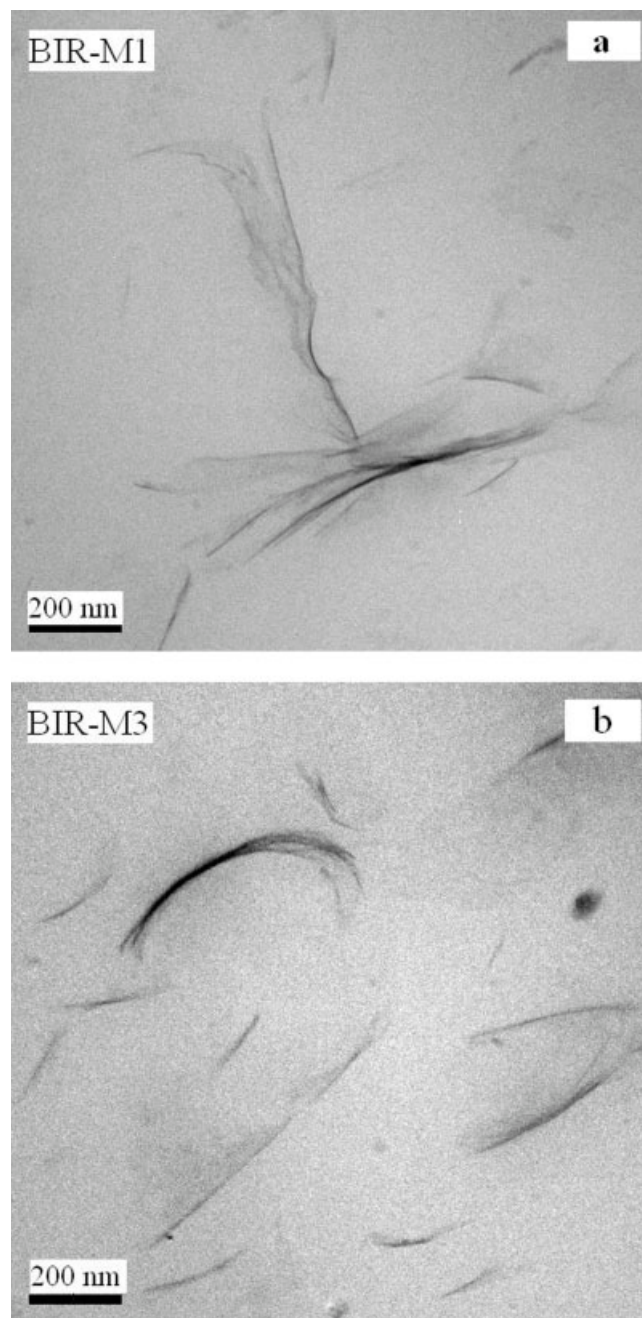


Figure 3 TEM images of the BIR-M1 and BIR-M3 nanocomposites.

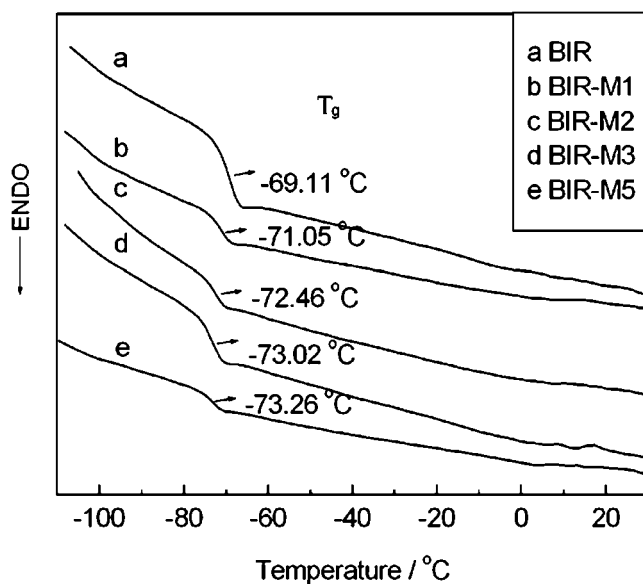


Figure 4 DSC curves of the BIR and BIR/MMT nanocomposites with different OMMT contents.

has larger effect on T_g than that of the interaction between copolymer and MMT layers.

The DTG curves of BIR and BIR/MMT nanocomposites are shown in Figure 5. There are two thermal decomposition peaks (T_{d1} and T_{d2}), which correspond to the PI and PB, respectively. The isoprene molecule has a methyl group and since methyl is relatively alive, so decomposition temperature of PI is lower than that of PB. The values of T_{d1} and T_{d2} are listed in Table III. The T_{d1} and T_{d2} values of BIR are 370.6°C and 436.4°C, respectively. Obviously, the introduction of OMMT caused the values of T_{d1} and T_{d2} to increase. When the OMMT content is 2 and 3 wt %,

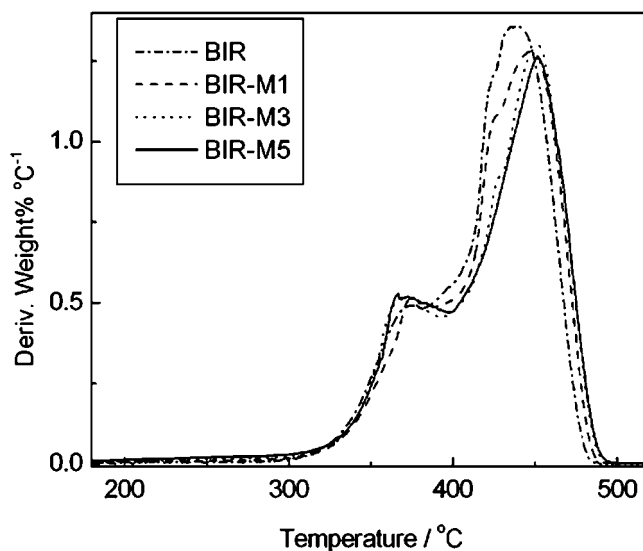


Figure 5 DTG curves of the BIR and BIR/MMT nanocomposites with different OMMT contents.

TABLE III
Values of T_{d1} and T_{d2} of the BIR and BIR/MMT Nanocomposites

Sample (°C)	BIR	BIR-M1	BIR-M2	BIR-M3	BIR-M4	BIR-M5
T_{d1}	370.6	372.6	381.2	371.6	371.6	365.7
T_{d2}	436.4	448.5	448.6	451.4	449.5	448.4

the values of T_{d1} and T_{d2} reach maximum values and increased by 10°C and 15°C, respectively, compared with those of BIR. Moreover, the values of T_{d1} decreased while T_{d2} were maintained invariably with further addition of OMMT. The result indicates that the BIR/MMT nanocomposites have higher thermal stability than BIR. This can be explained by the strong interaction between the copolymer chains and the OMMT layers in the nanocomposite, hence preventing the decomposition. In view of the results, the PB has higher interaction with clay layers than the PI, which manifested in an increase in its thermal decomposition temperature. With further addition of OMMT the T_{d2} maintained invariable while T_{d1} decreases because of the microphase separation between the PI and MMT layer.

CONCLUSIONS

Exfoliated BIR/MMT nanocomposites were successfully synthesized by anionic polymerization. High polymerization temperature benefited the exfoliation and dispersion of MMT layers. The addition of OMMT hardly changed the "living" anionic polymerization. However, OMMT absorbed TMEDA, and the 1,2-PB and 3,4-PI contents of the copolymer in the nanocomposites decreased and the glass-transition temperatures of the nanocomposites were lower than that of the BIR. There was the existence a strong interaction between the copolymer chains and the OMMT layers in the nanocomposites, leading to a relatively higher thermal stability.

References

- Choi, Y. S.; Choi, M. H.; Wang, K. H.; Kim, S. O.; Kim, Y. K.; Chung, I. J. *Macromolecules* 2001, 34, 8978.
- Zhao, H.; Shipp, D. A. *Chem Mater* 2003, 15, 2693.
- Usuki, A.; Kojima, Y.; Kawasumi, M.; Okada, A.; Fukushima, Y.; Kurauchi, T.; Kamigaito, O. *J Mater Res* 1993, 8, 1179.
- Usuki, A.; Kawasumi, M.; Kojima, Y.; Okada, A.; Krauchi, T.; Kamigaito, O. *J Mater Res* 1993, 8, 1174.
- Changa, J.; Ana, Y.; Kima, S.; Im, S. *Polymer* 2003, 44, 5655.
- Changa, J.; Kima, S.; Joob, Y.; Im, S. *Polymer* 2004, 45, 919.
- Davis, C. H.; Mathias, L. J.; Gilman, J. W.; Schiraldi, D. A.; Shields, J. R.; Trulove, P.; Sutto, T. E.; Delong, H. C. *J Polym Sci Part B: Polym Phys* 2002, 40, 2661.
- Liang, Z.; Yin, J.; Xu, H. *Polymer* 2003, 44, 1391.
- Okamoto, M.; Moritaa, S.; Taguchi, H.; Kim, Y. H.; Kotaka, T.; Tateyama, H. *Polymer* 2000, 41, 3887.

10. Yeh, J.; Liou, S.; Lai, M.; Chang, Y.; Huang, C.; Chen, C.; Jaw, J.; Tsai, T.; Yu, Y. *J Appl Polym Sci* 2004, 94, 1936.
11. Pan, M.; Shi, X.; Li, X.; Hu, H.; Zhang, L. *J Appl Polym Sci* 2004, 94, 277.
12. Yeh, J.; Liou, S.; Lai, C.; Wu, P. *Chem Mater* 2001, 13, 1131.
13. He, A.; Hu, H.; Huang, Y.; Dong, J.; Han, C. C. *Macromol Rapid Commun* 2004, 25, 2008.
14. Zhang, W.; Shen, X.; Liu, M.; Fang, Y. *J Appl Polym Sci* 2003, 90, 1692.
15. Liao, M.; Shan, W.; Zhu, J.; Li, Y.; Xu, H. *J Polym Sci Part B: Polym Phys* 2005, 43, 1344.
16. Zhang, Z.; Zhang, L.; Li, Y.; Xu, H. *J Appl Polym Sci*, to appear.
17. Zhang, Z.; Zhang, L.; Li, Y.; Xu, H. *Polymer* 2005, 46, 129.
18. Zhang, Z.; Zhang, L.; Li, Y.; Xu, H. *J Appl Polym Sci* 2006, 99, 2273.
19. Zhang, Z.; Zhang, L.; Li, Y. *Macromol Mater Eng* 2005, 290, 430.
20. Gilman, H.; Haubein, A. H. *J Am Chem Soc* 1944, 66, 1515.
21. Szwarc, M. *Nature* 1956, 178, 1168.
22. Sardelist, K.; Michels, H. J.; Allen, G. *Polymer* 1984, 25, 1011.
23. Zhao, B.; Liu, H.; Gu, M.; Li, Y. *China Elastomerics* 2001, 11, 44.
24. Wang, Y.; Yang, Y.; Li, G. *J Shenyang Inst Chem Technol* 1996, 10, 26.