Physical and Mechanical Properties of Al(OH)₃/Polypropylene Composites Modified by In Situ-Functionalized Polypropylene

KANCHENG MAI,[1,2] ZHENGJUN LI,[1] YUXIN QIU,[1] HANMIN ZENG[2]

[1] Materials Science Institute, School of Chemistry and Chemical Engineering, Zhongshan University, Guangzhou, 510275, People's Republic of China

[2] Key Laboratory of Polymeric Composites and Functional Materials, The Ministry of Education, Zhongshan University, Guangzhou, 510275, People's Republic of China

ABSTRACT: Al(OH)₃/polypropylene (PP) composites modified by *in situ*-functionalized polypropylene (FPP) were prepared by a one-step melt-extrusion process. The effect of *in situ* FPP on the crystallization and melting behavior, melt-flow index, limiting oxygen index, thermal degradation, mechanical properties, and fracture morphology of Al(OH)₃/PP composites was studied. Formation of *in situ* FPP resulted in a decreased crystallization temperature and melting point of PP in the composites, an increased melt-flow index, and improved tensile and flexural strengths of Al(OH)₃/PP composites, whereas the thermal degradation behavior and limiting oxygen index was not been influenced. The impact strength of the Al(OH)₃/PP composites modified by *in situ* FPP depended upon the content of the initiator, dicumyl peroxide, and the monomer, acrylic acid. © 2002 John Wiley & Sons, Inc. J Appl Polym Sci 83: 2850–2857, 2002; DOI 10.1002/app.10269

Key words: functionalized poly(propylene); Al(OH)₃; physical and mechanical properties

INTRODUCTION

Aluminum hydroxide, Al(OH)₃, has all the characteristics required for use as a flame-retardant filler, offering high levels of flame retardancy, without the smoke and corrosive fumes associated with some other types of flame retardants. However, effective flame retardation of polypropylene (PP) requires Al(OH)₃ levels in excess of 60 wt %. Generally, there is a lack of adhesion between PP and Al(OH)₃ due to large surface energy differences. One of the shortcomings of PP filled with high levels of Al(OH)₃ is the steep reduction of the impact strength compared to that of neat PP. Although the effect of the filler treated by coupling agents with a low molecular weight on the physical and mechanical properties of Al(OH)₃/PP composites were investigated,[1–5] few studies on the surface treatment of Al(OH)₃ by a macromolecular coupling agent, a functionalized polymer, have been reported on Al(OH)₃/PP composites. In PP composites filled with magnesium hydroxide, Mg(OH)₂, or other flame-retardant additives, improvements in the flame retardance and mechan-

ical properties of PP composites was observed by addition of a functionalized polymer.[6–11] Studies have shown that the addition of a functionalized polymer is an effective method for the modification of the compatibility of immiscible polymer blends and interfacial adhesion in polymeric composites.[8–31] In our laboratory,[32–34] PP functionalized with acrylic acid (AA) was prepared by the melt-extrusion process and the effect of PP-*g*-AA (FPP) on the structure and physical and mechanical properties of Al(OH)$_3$/PP composites was investigated. The experimental results indicated that the addition of FPP led to an increase in the melt-flow index, flame retardance, and mechanical properties. In this article, Al(OH)$_3$/PP composites modified by *in situ*-functionalized PP grafted with AA (*in situ* FPP) were prepared by a one-step melt-extrusion process. The effect of *in situ* FPP on the crystallization and melting behavior, melt-flow index, limiting oxygen index, thermal degradation behavior, mechanical properties, and fracture morphology of Al(OH)$_3$/PP composites was studied.

EXPERIMENTAL

Materials

PP, powdered F401, was a commercial product of the Guangzhou Petrochemical Co. (Ghangzhou, China). Pelletized PP, 1600, was obtained from the Beijing Yanshan Petrochemical Co. (Beijing, China). Chemical-grade AA was purchased from the Fushan Chemical Factory (Guangdong, China) and used without further purification. Chemical-grade dicumyl peroxide (DCP), used as an initiator for the AA grafting reaction, was a commercial product of the Shanghai Chemical Reagent Factory (Shanghai, China). Al(OH)$_3$ was obtained from the Shandong Aluminum Co. (Shangdong, China). The solvent, acetone, was obtained from the Guangzhou Chemical Reagent Factory (Ghangzhou, China).

Preparation of Samples

DCP and AA were dissolved in acetone and totally blended with powdered PP and Al(OH)$_3$ in a GH-10 high-speed mixing machine. After the solvent, acetone, had completely evaporated, the mixture of AA and DCP was coated onto the surface of the powdered PP and Al(OH)$_3$ and was then extruded by an SHJ-53 twin-screw extruder at a temperature of 185–190°C, with the screw speed set at 60 rpm. The extruded products, Al(OH)$_3$/FPP/PP composites, were frozen in-line in a water bath, dried, and granulated to less than 3 mm.

Preparation of Test Specimens

The pelletized Al(OH)$_3$/PP and Al(OH)$_3$/PP composites modified by *in situ* FPP were dried at a temperature of 90°C for 4 h before injection molding and were then injection-molded into test specimens using a CJ150 ME-NC injection-molding machine, set with a barrel temperature profile ranging from 190 to 210°C. The shape and size of the test specimens were described elsewhere.[35]

Characterization of Structure and Properties

The melting and crystallization of the samples were studied by differential scanning calorimetry (DSC) using a Perkin–Elmer DSC-7 in a nitrogen atmosphere with 10°C/min heating and cooling. The samples were heated from 30 to 220°C and held at that temperature for 3 min. The nonisothermal crystallization process was recorded from 210 to 50°C, followed by heating from 50 to 210°C for the second heating run. The crystallization and melting parameters were obtained from the cooling and reheating scans. The transition temperature and heat of crystallization and fusion were calibrated using an indium standard.

Melt-flow index (MFI) measurements were conducted according to ASTM D1238 using a XVR-400 melt indexer (Changchun Second Tester Factory, China). The limiting oxygen index (LOI) was measured in accordance with ASTM D 2683-70. The sample, consisting of a bar 6 mm wide, 3 mm thick, and 150 mm in length, was placed vertically at the center of a glass chimney 75 mm in diameter with a height of 450 mm. A mixture of oxygen and nitrogen of a known composition was passed through the chimney at a rate of about 10 L/min.

The mechanical properties were determined in both tension and flexure and under impact loading. Tensile properties were measured on a WD-5A electronic universal testing machine (Guangzhou Test Machine Factory, China) at a crosshead speed of 10 mm/min, in accordance with GB/T1040-92. The flexural properties were measured on an LWK-5 electronic tension testing machine (Guangzhou Test Machine Factory, China) following GB1040-92, using a crosshead
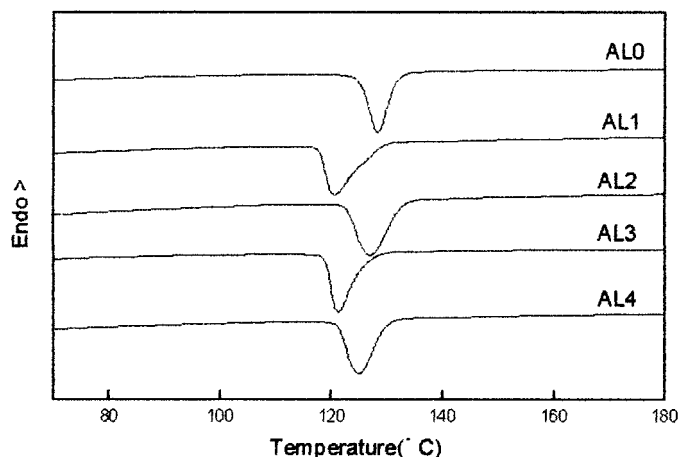
Figure 1   DSC cooling curves of Al(OH)$_3$/PP and modified Al(OH)$_3$/PP composites.

speed of 10 mm/min and a specimen span length of 50 mm. The Izod impact strength was performed on an XJJ-5 impact testing machine (Chengde Test Machine Factory, Hebei Province, China) on notched specimens, using procedures given in GB/T1043-93. The reported values were the average of five measurements for each sample at room temperature.

Thermal degradation of the samples was investigated with a Shimazu TGA-50 thermogravimetric analyzer. Thermogravimetric analysis (TGA) was performed at a heating rate of 20°C/min and a nitrogen flow rate of 33 mL/min. Through the above analyses, the pyrolysis peak temperature (T_{pm}), the temperature of 5 wt % weight loss ($T_{5\%}$), and the weight loss at different temperatures were obtained.

The fracture morphology of specimens for the Al(OH)$_3$/PP and modified Al(OH)$_3$/PP composites were obtained by scanning electron microscopy (SEM) using a Hitachi S-520 electron microscope operated at 25 kV. The fracture surface of the specimens were broken during the impact tests and a thin layer of gold was deposited prior to observation.

RESULTS AND DISCUSSION

Crystallization and Melting Behavior

Crystallization and melting curves of DSC for Al(OH)$_3$/PP and Al(OH)$_3$/PP composites modified by *in situ* FPP prepared by one-step melt-extrusion are shown in Figures 1 and 2. Crystallization and melting parameters are given in Table I. Compared to neat powdered PP, the addition of Al(OH)$_3$ resulted in an increase in the crystalli-
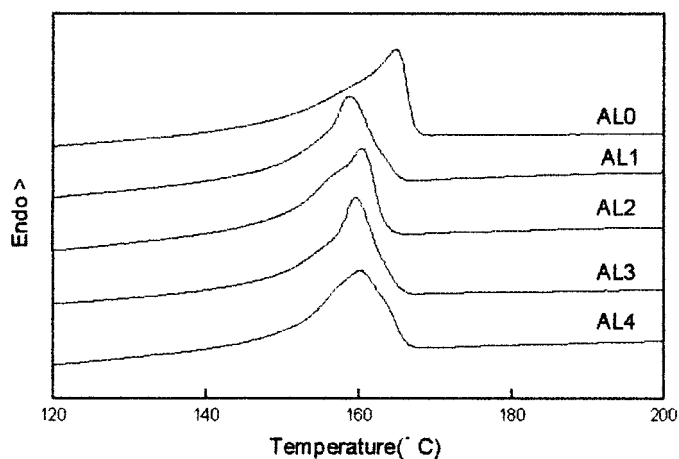
Figure 2   DSC heating curves of Al(OH)$_3$/PP and modified Al(OH)$_3$/PP composites.

Table I   DSC Data of Al(OH)$_3$/PP and Al(OH)$_3$/PP Composites Modified by *in situ* FPP

Samples	PP (wt %)	Al(OH)$_3$ (wt %)	DCP (phr)	AA (phr)	T_c (°C)	T_{co} (°C)	T_m (°C)	T_{mo} (°C)	X_c (%)
PP	100	—	—	—	119.1	122.3	162.2	155.3	38.9
AL0	40	60	—	—	128.2	131.5	164.8	156.0	45.6
AL1	40	60	0.4	2	120.6	127.3	158.7	153.8	44.6
AL2	40	60	0.4	1	126.9	132.5	160.4	152.4	44.5
AL3	40	60	0.2	2	121.2	125.8	159.6	154.8	45.1
AL4	40	60	0.2	1	124.9	129.7	158.1	148.2	45.9

ΔH_f = 207.15 J/g.[38]

zation temperature (T_c), melting temperature (T_m), and degree of crystallization (X_c) of powdered PP. The onset temperature of crystallization (T_{co}) for the Al(OH)$_3$/PP composite was higher than that of PP, indicating a higher nucleating ability. This increased nucleation (and crystallization) rate significantly increased the degree of crystallization above that of the unfilled composite. Even the T_c and T_m of powdered PP filled with Al(OH)$_3$ are higher than those of pelletized PP filled with Al(OH)$_3$. It is well known that many fillers are heterogeneous nucleating agents for PP, influencing not only its temperature and degree of crystallization, but also the nature of the micromorphology in the crystalline phase.[36,37] It is suggested that Al(OH)$_3$/PP composites prepared by powdered PP more significantly improved the filler dispersion in the matrix. An increase of the interfacial area between PP and Al(OH)$_3$ due to the improved filler dispersion resulted in an increase in the heterogeneous nucleation sites of Al(OH)$_3$, crystallization of the normally noncrystallizing PP chain, and an improvement in the crystalline perfection.

For the modified Al(OH)$_3$/PP composites prepared by the one-step extrusion process, addition of AA and DCP led to a decrease in the T_c and T_m of PP in the Al(OH)$_3$/PP composites. However, the change of the DCP content did not influence the crystallization and melting behavior of PP. The T_c and T_m of PP in the composites decreased with an increasing AA content. It is suggested that increase in the AA content resulted in the forma-

tion of FPP with a higher grafting rate and an AA homopolymer (PAA). The increase in the number of grafting sites and the length of the grafting chain restricted the nucleation and crystallization of PP. The PAA formed during the grafting reaction reacted with the surface of Al(OH)$_3$ and decreased the effect of the heterogeneous nucleation of Al(OH)$_3$ on PP. The surface treatment of Al(OH)$_3$ by fatty acid was found to lead to a decrease in the heterogeneous nucleation of Al(OH)$_3$ in the Al(OH)$_3$/PP composites.[39]

The shape of the melting peak of the Al(OH)$_3$/PP composites was affected by the DCP and AA content. For the Al(OH)$_3$/PP composites (AL0), the low-temperature region of the melting peak was wider. The addition of AA shifted the temperature of the melting peak of PP to a lower temperature and the high-temperature region of the melting peak became wider with increasing AA content. These experimental results indicated that the increase in the AA content not only led to the formation of a large amount of *in situ* FPP, but also to the formation of PP with different distributions of crystalline perfection in the Al(OH)$_3$/PP composites.

MFI

The MFI of the Al(OH)$_3$/PP and modified Al(OH)$_3$/PP composites prepared by the one-step extrusion process is shown in Table II. It was observed that the type of PP (powdered and pelletized) had no influence on the MFI. The addition of AA and

Table II   MFI of Al(OH)$_3$/PP and Al(OH)$_3$/PP Composites Modified by *in situ* FPP

Samples	Al(OH)$_3$/PP (Pelletized)	AL0	AL1	AL2	AL3	AL4
MFI	0.10	0.07	74.4	86.3	32.5	19.8

Table III   TGA Data of Al(OH)$_3$/PP and Al(OH)$_3$/PP Composites Modified by *in situ* FPP

Samples	$T_{5\%}$ (°C)	T_{pm1} (°C)	T_{pm2} (°C)	Weight Loss (wt %)			
				350°C	400°C	500°C	600°C
AL0	305.7	334.0	488.9	16.2	18.4	54.7	58.8
AL1	305.4	329.9	484.1	16.9	18.9	58.4	61.3
AL2	303.1	327.4	483.4	17.5	19.4	57.0	59.4
AL3	302.9	327.2	483.5	17.1	19.1	58.5	61.0
AL4	310.3	330.9	488.4	16.1	17.7	55.6	59.0
Powdered PP	390.1		470.3		7.1	99.6	
Two-step extrusion	302.5	328.6	488.4	15.6	17.1	58.1	61.9

DCP caused a significant increase in the MFI of the Al(OH)$_3$/PP composites. These experimental results indicated that the flow property and processability of the Al(OH)$_3$/PP composites was improved. The increase in the MFI was more significant with an increasing DCP content due to the degradation of PP. For a low DCP content (0.2 phr), an increase in the MFI of the composite was observed, whereas for a high DCP content (0.4 phr), the opposite tread was found with an increasing AA content, suggesting that a large amount of PAA with a low molecular weight was formed for the lower DCP content. It is believed that at a low DCP content the PAA formed during the grating reaction acted as a lubricant, both externally causing wall slip and/or internally between adjoining particles. Therefore, the flow property and processability of the Al(OH)$_3$/PP composites were improved. When the DCP content was increased, more radicals were formed. A large amount of *in situ* FPP with a higher grafting rate was produced with an increasing AA content. In this case, the increase in the amount of FPP resulted in an increase in the effect of the interfacial interaction between FPP and Al(OH)$_3$. Upon increasing the interfacial interaction, the molecular mobility in the interlayer was more hindered, which led to an increase in the melt viscosity and a decrease in the MFI.

Thermal Stability

TGA data in a nitrogen atmosphere is shown in Table III. The addition of Al(OH)$_3$ resulted in an increase in the pyrolysis peak temperature (T_{pm2}) and a decrease in the temperature of 5% weight loss ($T_{5\%}$) due to the effect of Al(OH)$_3$. The method of preparation by one-step and two-step extrusion had no influence on the thermal stability of the composites. For the modified Al(OH)$_3$/PP composites prepared by one-step extrusion, the addition of AA and DCP and the change of their content had little effect on the thermal degradation of the Al(OH)$_3$/PP composites.

Mechanical Properties

The mechanical properties of the Al(OH)$_3$/PP and modified Al(OH)$_3$/PP composites containing the filler content of 60% by weight are presented in Table IV. For the DCP content of 0.2 phr, the impact strength (IS), flexural strength (FS), tension strength (TS), and elongation at break (EB)

Table IV   Mechanical Properties of Al(OH)$_3$/PP and Al(OH)$_3$/PP Composites Modified by *in situ* FPP

Samples	IS (kJ/m^2)	FS (MPa)	FM (GPa)	TS (MPa)	TM (MPa)	EB (%)
AL0	1.25	37.7	4.2	19.9	3.4	1.1
AL1	1.15	53.7	4.2	30.7	3.7	1.8
AL2	0.99	51.2	3.0	29.4	3.5	1.6
AL3	1.47	49.9	4.0	31.7	3.4	2.7
AL4	1.42	52.4	4.3	29.6	3.4	2.1

Table V　LOI of Al(OH)$_3$/PP and Al(OH)$_3$/PP Composites Modified by *in situ* FPP

Samples	AL0	AL1	AL2	AL3	AL4
LOI	27.3	27.8	27.0	27.6	27.6

of the Al(OH)$_3$/PP composites modified by *in situ* FPP are higher than those of the unmodified Al(OH)$_3$/PP composite (AL0). Although the impact strength of the modified Al(OH)$_3$/PP composites decreased with increasing DCP content, the content of DCP had no influence on the tension and flexural properties of the modified Al(OH)$_3$/PP composites. Compared to the unmodified Al(OH)$_3$/PP composite (AL0), the formation of *in situ* FPP led to a significant increase in the tension and flexural strength of the Al(OH)$_3$/PP composites. The tension and flexural strengths of the modified Al(OH)$_3$/PP composites prepared by one-step extrusion are higher, 37 and 52%, respectively, than those of unmodified Al(OH)$_3$/PP composites. The tension modulus (TM) and flexural modulus (FM) were little influenced. These results indicated that the formation of *in situ* FPP improved the interfacial interaction and adhesion of the two components. Therefore, the mechanical properties of the Al(OH)$_3$/PP composites was significantly improved. Comparing the tension and flexural strengths of the Al(OH)$_3$/PP composites modified by the addition of FPP[34] with that of the Al(OH)$_3$/PP composites modified by *in situ* FPP, it was found that the Al(OH)$_3$/PP composites modified by *in situ* FPP exhibited higher tension and flexural strengths.
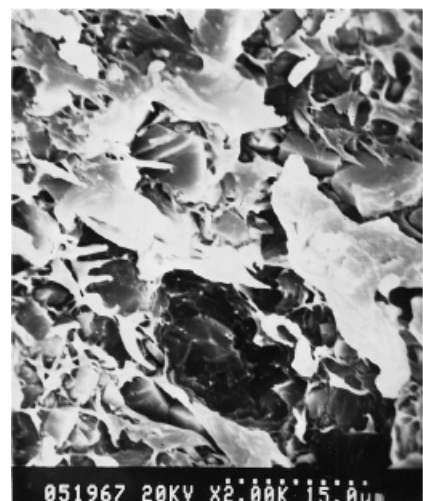
Flame Retardance

The LOI of the Al(OH)$_3$/PP and modified Al(OH)$_3$/PP composites are given in Table V. The addition of AA and DCP had little influence on the LOI of the Al(OH)$_3$/PP composite, which may be due to the better dispersion of the filler in the Al(OH)$_3$/PP composites prepared by powdered PP. The LOI of the Al(OH)$_3$/PP composites modified by *in situ* FPP was also found to be higher than that of the composites modified by the addition of FPP.[33] The interfacial interaction and the filler dispersion appeared to be more significantly im-
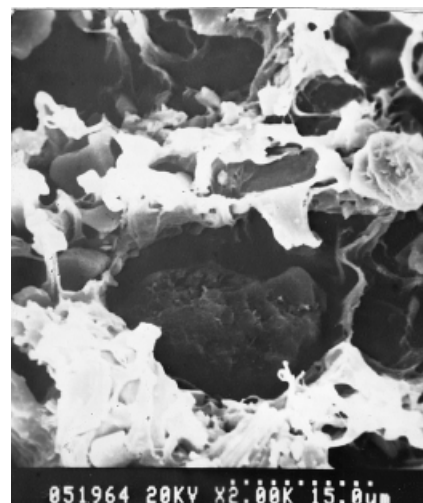
Figure 3 Fracture morphology of Al(OH)$_3$/PP and modified Al(OH)$_3$/PP composites.

proved in composites modified by *in situ* FPP than by the addition of FPP, resulting in enhanced mechanical properties and flame retardance of the Al(OH)$_3$/PP composites.

Fracture Morphology

SEM photographs of the fracture surface of impact specimens of unmodified Al(OH)$_3$/PP and Al(OH)$_3$/PP composites modified by *in situ* FPP are shown in Figure 3. The filler distribution in the modified Al(OH)$_3$/PP composites was better than that of the unmodified Al(OH)$_3$/PP composites, which was attributed to the improvement of the flow property due to the lubrication of FPP with a low molecular weight. On the other hand, the interfacial adhesion between Al(OH)$_3$ and PP was improved due to the interfacial interaction of FPP in the composites. As a result, the physical and mechanical properties of the Al(OH)$_3$/PP composites were improved.

CONCLUSIONS

Al(OH)$_3$/PP composites modified by *in situ* FPP were prepared by a one-step melt-extrusion process. The addition of Al(OH)$_3$ resulted in an increase in the crystallization temperature (T_c), melting temperature (T_m), and degree of crystallization (X_c) of PP. The T_c and T_m of powdered PP filled with Al(OH)$_3$ are higher than those of pelletized PP filled with Al(OH)$_3$. The addition of AA and DCP led to a decrease in the T_c and T_m of PP in the composites. The T_c and T_m of PP in the composites decreased with increasing AA content. The addition of AA and DCP caused a significant increase in the MFI in the composites and had little effect on the thermal stability of the composites. The mechanical properties of the composites modified by *in situ* FPP are higher than those of the unmodified composite. The formation of *in situ* FPP appears to have improved the interfacial interaction, the filler dispersion, and the adhesion between two components. However, the formation of *in situ* FPP had little influence on the LOI of the composites.

REFERENCES

1. Liauw, C. M.; Lees, G. C.; Hurst, S. J.; Rothon, R. N.; Dobson, D. C. Plast Rubb Compos Proc Appl 1995, 24, 249.
2. Liauw, C. M.; Lees, G. C.; Hurst, S. J.; Rothon, R. N.; Dohson, D. C. Angew Makromol Chem 1996, 235, 193.
3. Ren, D.; Wang, J.; Wu, W. Gaofenzi Cailiao Kexue Gongcheng 1993, (1), 101.
4. Xu, W.; Liu, P.; Luo, L. Gaofenzi Cailiao Kexue Gongcheng 1997, (1), 103.
5. Fang, Z.; Xu, C.; Bai, X. Zhongguo Suliao 1998, (3), 49.
6. Jancar, J.; Dibenedetto, A. T. J Mater Sci 1995, 30, 1601.
7. Jancar, J. J Mater Sci 1989, 24, 4268.
8. Wang, J.; Tung, J. F.; Fuad, M. Y.; Hornsby, P. R. J Appl Polym Sci 1996, 60, 1425.
9. Hornsby, P. R.; Watson, C. L. J Mater Sci 1995, 30, 5347.
10. Jancar, J.; Kacera, J. Polym Eng Sci 1990, 30(12), 714.
11. Chiang, W. Y.; Hu, C. Eur Polym J 1996, 32, 385.
12. Mai, K.; Xu, J. Handbook of Thermoplastics; Olabisi, O., Ed.; Marcel Dekker: New York, 1997; Chapter 22.
13. Chang, F. Handbook of Thermoplastics; Olabisi, O., Ed.; Marcel Dekker: New York, 1997. Chapter 21.
14. Li, J.; Mai, K. Gongcheng Suliao Yingyong 1998, (7), 32.
15. Qiu, W.; Mai, K.; Zeng, H. J Appl Polym Sci 1999, 71, 847.
16. Marco, C.; Ellis, G.; Gomez, M. A.; Fatou, J. G.; Arribas, J. M.; Campoy, I.; Fontecha, A. J Appl Polym Sci 1997, 65, 2665.
17. Sun, Y.; Hu, G.; Lambla, M. Polymer 1996, 37, 4119.
18. Jancar, J.; Dibendetto, A. T. J Mater Sci 1995, 30, 2438.
19. Khunova, V.; Sain, M.; Sinick, I. Polym Plast Technol Eng 1993, 32, 311.
20. Kokarik, J.; Jancar, J. Polymer 1992, 33, 4961.
21. Hanamann, K.; Flaris, V. Polym Compos 1997, 5, 113.
22. Brannock, G. R.; Barlow, J. W.; Paul, D. R. J Polym Sci Part B Polym Phys 1991, 29, 413.
23. Bratawidjaja, A. S.; Gitopadmoy, I.; Watanabe, Y.; Hatakeyama, T. J Appl Polym Sci 1989, 37, 1141.
24. Gaylord, N. G.; Mehta, R.; Kumar, V.; Tazi, M. J Appl Polym Sci 1989, 38, 359.
25. Datta, R. K.; Polk, M. B.; Kumar, S. Polym Plast Technol Eng 1995, 34, 551.

26. Duval, J.; Sellitti, C.; Myers, C.; Hiltner, A.; Baer, E. J Appl Polym Sci 1994, 52, 591.
27. Subramanian, N.; Nelson, T. J Polym Plast Technol Eng 1993, 32, 635.
28. Duvall, J.; Sellitti, C.; Topolkaraev, V.; Hiltner, A.; Baer, E. Polymer 1994, 35, 3948.
29. Chiang, W. Y.; Yang, W. D.; Pukanszky, B. Polym Eng Sci 1994, 34, 488.
30. Chun, I.; Woodhans, R. T. Polym Compos 1994, 15, 250.
31. Khunova, V.; Zamorsky, Z. Polym Plast Technol Eng 1993, 32, 289.
32. Mai, K.; Li, Z.; Zeng, H. J Appl Polym Sci 2001, 80, 2609.
33. Mai, K.; Li, Z.; Qiu, Y.; Zeng, H. J Appl Polym Sci 2001, 81, 2679.
34. Mai, K.; Li, Z.; Qiu, Y.; Zeng, H. J Appl Polym Sci 2001, 80, 2617.
35. Qiu, W.; Mai, K.; Zeng, H. J Appl Polym Sci 1999, 71, 1537.
36. Alonso, A.; Gonzalez, A.; de Sada, J. A.; Requejo, A. Plast Rubb Comp Proc Appl 1993, 20, 165.
37. Khunova, V.; Smatko, V.; Hudec, I.; Beniska, J. Prog Coll Polym Sci 1988, 78, 188.
38. Wunderlich, B. Thermal Analysis; Academic: Boston, 1990.
39. Rybnikar, F. J Appl Polym Sci 1991, 42, 2727.