Influence of Grafting Formulations and Extrusion Conditions on Properties of Silane-Grafted Polypropylenes

H. HUANG, H. H. LU, N. C. LIU

School of Chemistry and Chemical Engineering, Shanghai Jiao Tong University, Shanghai 200240,
People's Republic of China

Received 3 September 1998; accepted 23 March 2000

ABSTRACT: The melt grafting of unsaturated silanes onto powdered polypropylene (PP) in a Haake TW100 twin-screw extruder and curing in hot water were studied. The influence of grafting formulations and extrusion conditions on the melt flow rates of grafted PP and the gel percentages of crosslinked PP was investigated. The gel percentages of methacryloylpropyltrimethoxysilane (VMMS)-grafted PP were markedly higher than those of vinyltriethoxysilane (VTES)- and vinyltrimethoxysilane (VTMS)-grafted PP, while significantly less degradation of PP during grafting was observed for VMMS-grafted PP. When benzoyl peroxide (BPO) was used as an initiator, no degradation of PP during grafting was observed, and the melt flow rates of grafted PP decreased with increasing BPO concentration. In contrast, use of dicumyl peroxide (DCP) as an initiator resulted in severe degradation of PP, and the melt flow rates of grafted PP increased gradually with increasing DCP concentration. BPO resulted in higher gel percentages than those of DCP at a fixed initiator concentration. Introduction of styrene into the grafting system greatly improved the gel percentage of crosslinked PP and reduced the degradation of PP during grafting. The optimum molar ratio of styrene to monomer is at about 1.5:1. Relatively low processing temperatures and high screw speeds are favorable. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 78: 1233–1238, 2000

Key words: polypropylene; crosslinking; silane; grafting; reactive extrusion

INTRODUCTION

Polyolefins are the largest volume family of commercially important high-tonnage thermoplastic polymers. Crosslinking of polyolefins may improve their high-temperature properties and extend their applications. Peroxide crosslinking, radiation crosslinking, and silane crosslinking are the three main ways of crosslinking employed industrially.[1] Both radiation and peroxide crosslinking techniques suffered some disadvantages such as high investment cost and thickness limitation in radiation crosslinking, the risk of precuring, and high production cost in peroxide crosslinking.

In the silane crosslinking technique, unsaturated hydrolyzable alkoxysilanes are first grafted onto or copolymerized into polyolefins; grafted (or copolymerized) products are then processed and shaped using conventional thermoplastic processing equipment, followed by catalyzed crosslinking of the shaped products in the presence of trace amounts of water. The silane crosslinking technique offers technological advantages and improvements in many useful properties of silane-crosslinked polyolefins in comparison with radiation and peroxide-crosslinked polyolefins. Munteanu[2,3] and Brown[4]

Correspondence to: N. C. Liu.

Contract grant sponsor: Science and Technology Commission of Shanghai, China.

Journal of Applied Polymer Science, Vol. 78, 1233–1238 (2000)

reviewed the state of the art of moisture crosslinkable silane-modified polyolefins. Although silane-modified polyolefins have been used in an industrial method employed in practice, the literature concerning polyolefin crosslinking by silane grafting consists mainly of patents.[2–4] Little data have been published on the dependence of silane-grafting reactions and the properties of crosslinked polyolefins on reaction parameters.[5–11]

Crosslinking of polyolefins may be applied to all polyolefin types; however, the vast majority of the publications were concerned with polyethylenes. Few studies concerning the crosslinking of polypropylene (PP) have been reported.[12,13] Crosslinking of PP has gained no practical importance. This is most likely a consequence of the nature of the PP chain structure. Chain scission (β-scission) is the dominant reaction in PP when subjected to free radicals at elevated temperatures during processing. Crosslinking of PP by peroxide may only be performed with unusual high peroxide concentrations at low temperatures or in the presence of multifunctional crosslinking coagents.[14–19]

Crosslinking of PP via silane grafting and moisture curing has rarely been reported. Cartasegna[11] reported that a sample of PP, subjected to the same silane grafting and subsequent curing procedure as used for crosslinking other polyolefins, gave a complete absence of insoluble gel. In other studies,[20–24] silane-crosslinked PP has only been obtained under severe processing conditions and strict grafting formulation requirements such as extremely high silane and initiator concentrations.

The purpose of this article was to study the crosslinking of PP with unsaturated silanes. The influence of grafting formulations and extrusion conditions on the melt flow rate of grafted PP and the gel percentage of crosslinked PP were investigated.

EXPERIMENTAL

Materials

The starting material was a powdered isotactic PP supplied by the Shanghai Petrochemical Complex (Shanghai, China). It had a melt flow rate of 6.7 dg/min (ASTM D1238, 230°C, and 2.16 kg). The silane monomers, methacryloylpropyltrimethoxysilane (VMMS), vinyltrimethoxysilane (VTMS), and vinyltriethoxysilane (VTES), were provided by Osi Specialties Asia Ltd. (Hong Kong, China). The initiators dicumyl peroxide (DCP) and benzoyl peroxide (BPO), the catalyst dibutyltindilaurate, and additive styrene were analytical grade and used as received.

Grafting Procedure

The grafting reaction was carried out in a laboratory-scale Haake TW100 twin-screw extruder with a ratio of length over diameter of 20:1. Powered PP was first dry-blended with the desired amounts of monomers, initiators, and additives and then fed into the extruder, which already had been adjusted to the required conditions. Unless otherwise specified, the processing temperature for the first heating zone was kept low while the temperatures of other zones were controlled at 190°C; the screw speed was maintained at 30 rpm. The feed rate was manually controlled in the range of 12–15 g/min.

Analysis of Grafted PP

The reaction products from extruders were purified using a precipitation method. Samples were first dissolved into refluxing xylene and then precipitated into six times the volume of methanol, followed by drying at 90°C under a vacuum for 48 h. Samples were purified twice using the precipitation procedure before characterization. No significant change in the intensity of IR absorbance was observed after further purification, indicating that the purification procedure was effective. Dried samples were compression-molded into thin films with a thickness of about 80 μm. Fourier transformed infrared spectroscopy was performed for both pure PP and VMMS-grafted samples. The melt flow rates of the grafted products were measured at 230°C with a load of 2.16 kg according to ASTM D1238, using an RL-11A-type melt indexer produced by Shanghai Sierda Scientific Instruments.

Crosslinking of Grafted PP

Before moisture crosslinking, 100 parts of grafted PP was dry-mixed with 5 parts of the catalyst concentrate and extruded at 190°C and 30 rpm for the uniform distribution of the catalyst. The catalyst concentrate was prepared by extruding 4 parts of dibutyltindilaurate with 100 parts of PP at 190°C and 30 rpm. The catalyst concentrate was extruded twice in order to obtain a uniform distribution of the catalyst.

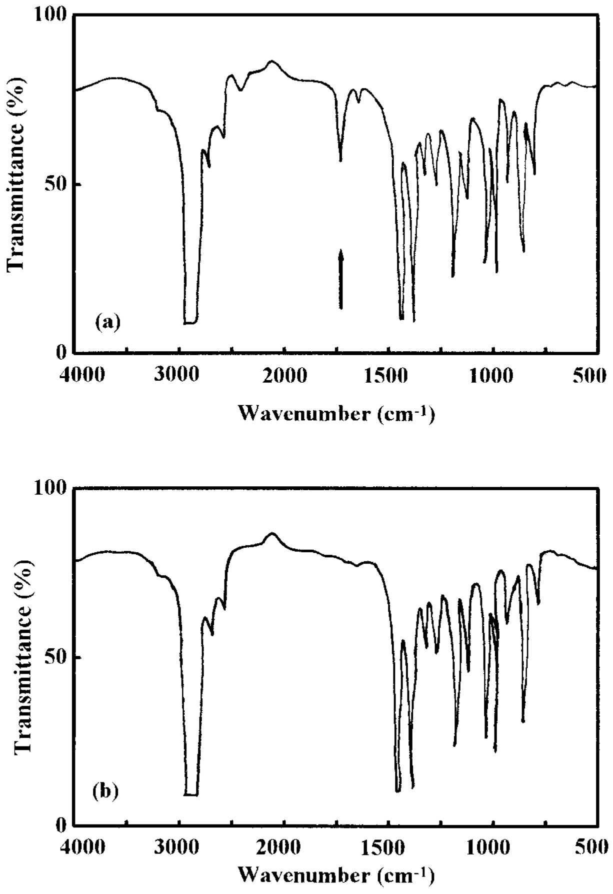

Figure 1 FTIR spectra of (a) VMMS-grafted PP and (b) pure PP.

The mixture of grafted PP with the hydrolysis catalyst was compression-molded into thin sheets of 1 mm thick. The sample sheets were then immersed in boiling water for 6 h, allowing for the hydrolyzation of alkoxy groups and the formation of three-dimensional networks. The hydrolyzed samples were dried and cut into small pieces of sizes of about 1 mm for the determination of the gel percentage.

Determination of Gel Percentages

The crosslinking ability was compared by measuring the percentages of insoluble gel after extraction in refluxing xylene. The sample, 0.2–0.3 g, was packaged in a copper cloth of 120 mesh and extracted with refluxing xylene for 12 h using a Soxhlet extractor. Samples were dried in a vacuum oven at 120°C for 24 h. The gel percentage of crosslinked PP was calculated as the percentage of the weight remaining with respect to the initial weight. At least three extractions were performed for each sample and the average gel percentages were calculated and used for discussion.

RESULTS AND DISCUSSION

Characterization of VMMS-grafted PP

Figure 1 shows the Fourier transform infrared spectra of pure PP and VMMS-grafted PP. The spectrum of VMMS-grafted PP shows clearly a new absorbance band at about 1730 cm^{-1}, which is characteristic of carbonyl groups. This confirms the grafting of VMMS onto PP.

Influences of Monomer Type and Concentration

Figure 2 shows the influences of monomer type and concentration on the gel percentages of crosslinked PP. With increasing monomer concentration, the gel percentages of VMMS-crosslinked PP increased rapidly from 0 to about 22 wt % at low monomer concentrations, and the gel percentage increased slowly at high monomer concentrations. In the case of VTMS and VTES as monomers, no gel was obtained at low monomer concentrations; at monomer concentrations higher than 2 wt %, slow increases in the gel percentages were observed with increasing monomer concentration. These indicate a much greater grafting and crosslinking efficiency of VMMS than of VTMS and VTES, which is probably the result of large steric hindrance in the case of VTMS and VTES since the reactive sites are close to the

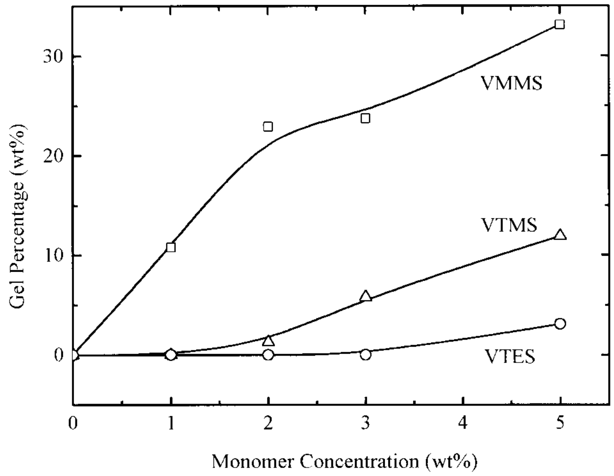

Figure 2 Influence of the type and amount of monomers on the gel percentage of crosslinked PP (DCP: 0.18 wt %; molar ratio of styrene to VMMS: 1.5:1).

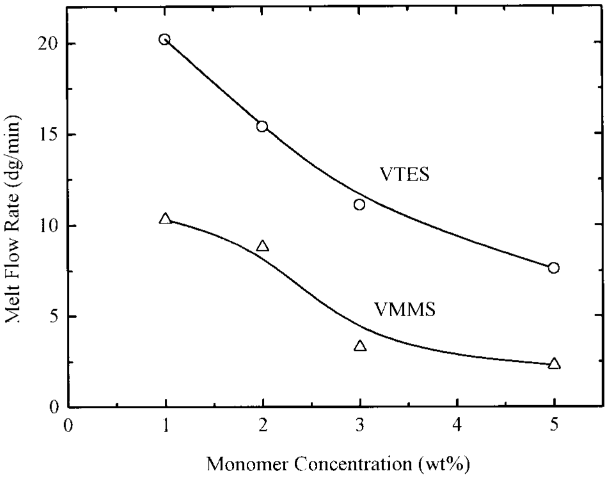

Figure 3 Influence of the type and amount of monomers on the melt flow rate of grafted PP (DCP: 0.18 wt %; molar ratio of styrene to VMMS: 1.5:1).

bulky alkoxysilane groups. Furthermore, the conjugated structure in VMMS could improve grafting efficiency by stabilizing the macroradicals of VMMS-grafted PP.

The influence of monomer type and concentration on the melt flow rates of grafted PP is shown in Figure 3. With increasing monomer concentration, similar trends of decreasing melt flow rates were observed for both VMMS- and VTES-grafted PP. However, the melt flow rates of VMMS-grafted PP were at much lower levels than those of VTES-grafted PP, indicating that more degradation of PP occurred during grafting with VTES. This again could be a result of large steric hindrance in VTES-grafted PP macroradicals, which inhibits the termination of macroradicals by combination. In addition, stabilization of VMMS-grafted PP macroradicals by conjugation could increase the possibility of termination by combination. At monomer concentrations higher than 2 wt %, the melt flow rates of VMMS-grafted PP were even smaller than that of pure PP (6.7 dg/min), indicating that some crosslinking of PP occurred during grafting. This may be due to the increased amount of termination by combination at high monomer concentrations.

Effects of Additive

Sun et al.[25] studied the free-radical grafting of glycidyl methacrylate onto PP in a twin-screw extruder and reported that the presence of styrene not only increased grafting yields but also reduced PP chain degradation. The effects of styrene on the gel percentages of silane-crosslinked PP and the melt flow rates of silane-grafted PP were studied and the results are shown in Figure 4. The gel percentages increased rapidly with increasing amounts of styrene at low molar ratios of styrene to monomer and reached a constant value of about 23 wt % at a molar ratio of about 1.5. One possible reason for the improvement could be that the high reactivity of styrene to PP macroradicals reduces the probability of radical termination and the resulting macroradicals react easily with the silane monomer, thus improving grafting and crosslinking efficiency. Another reason would be that the introduction of styrene into the grafting system improves the solubility of the silane monomer in the PP melt since styrene is a good solvent for both PP and the silane monomer.

The melt flow rates of grafted PP decreased gradually with an increasing amount of styrene additive, indicating a reduced amount of PP degradation during grafting. With the introduction of a large amount of styrene into the grafting system, the melt flow rate of grafted PP was reduced to a very low level of about 0.7 dg/min, which is much smaller than is the melt flow rate of pure PP. Considering both the gel percentage of crosslinked PP and the melt flow rate of grafted PP, the optimum molar ratio of styrene to monomer should be about 1.5:1.

Influences of Initiator Type and Concentration

Figure 5 shows the influence of the DCP concentration on the gel percentages of crosslinked PP

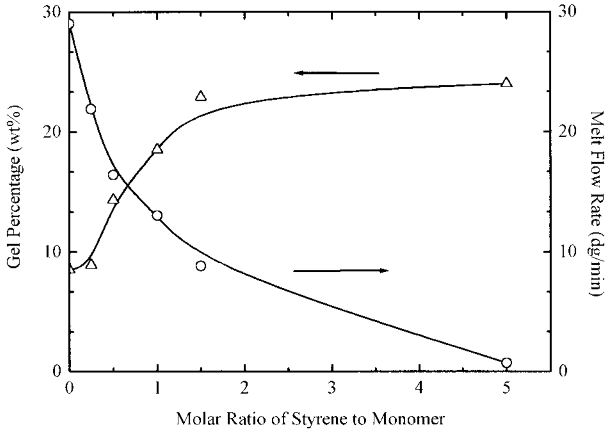

Figure 4 Influence of the amount of styrene additive on the gel percentage of crosslinked PP and the melt flow rate of grafted PP (DCP: 0.18 wt %; VMMS: 2.0 wt %).

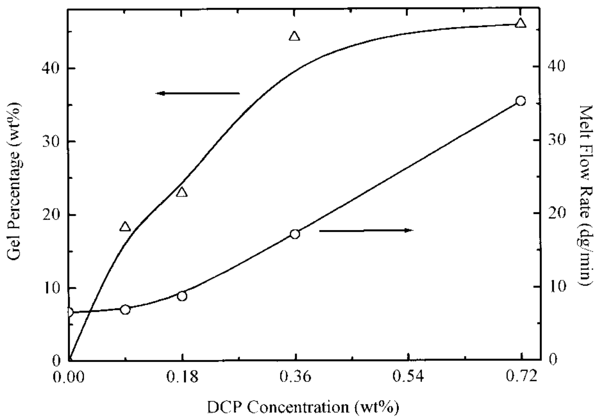

Figure 5 Influence of DCP concentration on the gel percentage of crosslinked PP and the melt flow rate of grafted PP (VMMS: 2.0 wt %; styrene: 1.3 wt %).

and melt flow rates of grafted PP. With increasing DCP concentration, the gel percentage increased rapidly to a high level of about 45 wt % and leveled off at high DCP concentrations. The melt flow rates of grafted PP increased gradually with increasing DCP concentration, indicating increased degradation of PP during grafting at high DCP concentrations.

Figure 6 shows the influence of BPO on the gel percentages of crosslinked PP and the melt flow rates of grafted PP. The gel percentage of crosslinked PP with BPO as an initiator showed the same increasing trend as that with DCP. Nevertheless, BPO resulted in slightly higher gel percentages than those of DCP at a fixed initiator concentration. In contrast to the case of DCP, the melt flow rate of grafted PP decreased with increasing BPO concentration, indicating that degradation of PP did not occur during the grafting process. This should be because that combination instead of disproportionation becomes the dominant termination reaction in the case of BPO as an initiator, which is in agreement with the literature.[12,13]

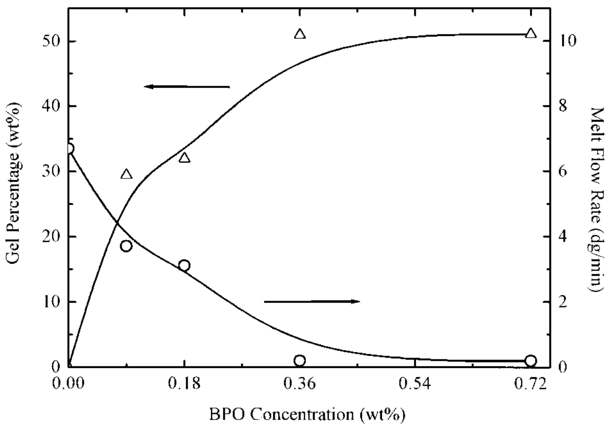

Figure 6 Influence of BPO concentration on the gel percentage of crosslinked PP and the melt flow rate of grafted PP (VMMS: 2.0 wt %; styrene: 1.3 wt %).

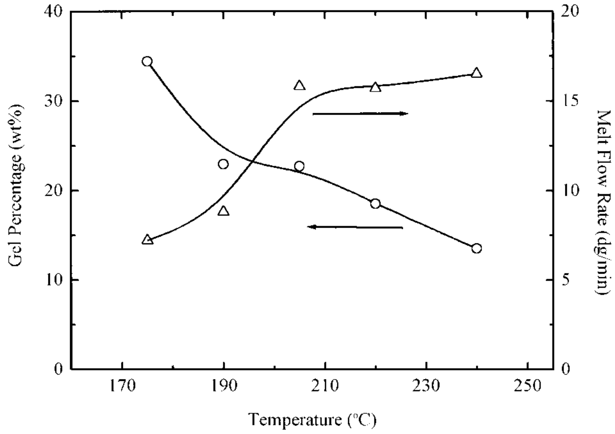

Figure 7 Influence of processing temperature on the gel percentage of crosslinked PP and the melt flow rate of grafted PP (DCP: 0.18 wt %; VMMS: 2.0 wt %; styrene: 1.3 wt %).

Effects of Processing Conditions

The effects of processing temperature on the gel percentages of crosslinked PP and the melt flow rates of grafted PP are shown in Figure 7. As indicated by the melt flow rates of grafted PP, higher processing temperatures clearly caused more degradation of PP during grafting, which is consistent with the literature.[19] In the ranges studied, the gel percentages of crosslinked PP decreased with increasing processing temperature. Considering the processability of PP, extrusion temperatures between 180 and 190°C would be optimum choices.

Figure 8 shows the effects of screw speed on the gel percentages of crosslinked PP and the melt flow rates of grafted PP. The gel percentages of crosslinked PP increased significantly with increasing screw speed at a relatively low screw speed and became stable at a high screw speed. This may be explained by the balanced effects of improved mixing efficiency and reduced residence time at high screw speeds. The average residence time was decreased from more than 200 s at 15 rpm to about 30 s at 90 rpm, which is not long enough for the complete decomposition of the ini-

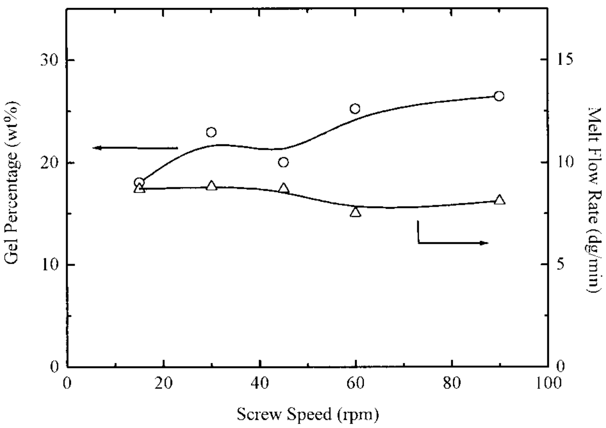

Figure 8 Influence of screw speed on the gel percentage of crosslinked PP and the melt flow rate of grafted PP (DCP: 0.18 wt %; VMMS: 2.0 wt %; styrene: 1.3 wt %).

tiator. The melt flow rates of grafted PP were almost constant in the ranges of the screw speed studied.

CONCLUSIONS

Fourier transformed infrared spectroscopy confirms the grafting of unsaturated silane onto PP. Influence of the type and amount of the monomer on the gel percentage of crosslinked PP and the melt flow rate of grafted PP were remarkable. The gel percentages of VMMS-grafted PP were markedly higher than those of VTES- and VTMS-grafted PP; at the same time, much less degradation of PP during grafting was observed for VMMS-grafted PP.

DCP and BPO showed different behavior. When BPO was used as an initiator, no degradation of PP during grafting was observed, and the melt flow rates of grafted PP decreased with increasing BPO concentration. In contrast to the case of BPO, use of DCP as an initiator resulted in severe degradation of PP, and the melt flow rates of grafted PP increased gradually with increasing DCP concentration. BPO resulted in higher gel percentages than those of DCP at a fixed initiator concentration.

Introduction of styrene into the grafting system greatly improved the gel percentage of crosslinked PP and reduced the degradation of PP during grafting. The optimum molar ratio of styrene to monomer is about 1.5:1.

In the range studied, higher processing temperatures clearly caused more degradation of PP during processing. Processing temperatures between 180 and 190°C would be optimum choices considering the gel percentage of crosslinked PP, melt flow rates of grafted PP, and processability of PP. Higher screw speed resulted in higher gel percentages of crosslinked PP due to improvement in the mixing efficiency.

The authors acknowledge the financial support of this project by the Science and Technology Commission of Shanghai, China.

REFERENCES

1. Sultan, B. A; Palmlof, M. Plast Rubb Comp Process Appl 1994, 21, 65.
2. Munteanu, D. Reactive Modifiers for Polymers; Blackie: London, 1997; pp 197–265.
3. Munteanu, D. Metal-containing Polymeric Systems; Plenum: New York, 1985; pp 479–509.
4. Brown, S. B. Reactive Extrusion Principles and Practice; Hanser: New York, 1992; pp 102–109.
5. Wong, W. K.; Varrall, D. C. Polymer 1994, 35, 5447.
6. Sen, A. K.; Mukherjee, B.; Bhattacharyya, A.S. J Appl Polym Sci 1992, 44, 1153.
7. Anderlik, R.; Fritz, H. G. Int Polym Process 1992, 7, 212.
8. Ultsch, S.; Fritz, H. G. Plast Rubb Process Appl 1990, 13, 81.
9. Narkis, M.; Tzur, A.; Vaxman, A. Polym Eng Sci 1985, 25, 857.
10. Chodok, I. Prog Polym Sci 1995, 20, 1165.
11. Cartasegna, S. Rubb Chem Tech 1986, 59, 722.
12. Hogt, A. H.; Meijer, J.; Jelenic, J. Reactive Modifiers for Polymers; Blackie: London, 1997; pp 84–132.
13. Shu, W. Suliao 1992, 21, 29.
14. Tang, P.; Zeng, B.L.; Tang, J.; Li, G.Y. Suliao Gongye 1995, 23, 14.
15. Kim, B. K.; Kim, K. J. Adv Polym Technol 1993, 12, 263.
16. Borsig, E.; Malcherova, E.; Lazar, M. Polym Int 1993, 30, 367.
17. Endstra, W. C. Kunststoffe 1990, 43, 790.
18. Chodaok, I.; Lazar, M. Agnew Makromol Chem 1982, 106, 153.
19. Borsig, E.; Fiedlerova, A.; Lazar, M. J Macromol Sci Chem A 1981, 16, 513.
20. Shen, J. Z.; Liu, S. L. Gaofenzi Tongbao 1992, 3, 170.
21. Deguchi, J.; Inoue, T. In ANTEC'97, Conference Proceedings, Society of Plastics Engineers, 1997; p 786.
22. Sano, M.; Mikamo, H.; Kitamura, K. Jpn Patent 330 497, 1994.
23. Daijo, K.; Ito, K. Jpn Patent 02 160 852, 1990.
24. Ohta, S.; Yamada, M. Jpn Patent 52 040 555, 1977.
25. Sun, Y. J.; Hu, G. H.; Lambla, M. J Appl Polym Sci 1995, 57, 1043.