Characterization of High Melt Strength Propylene/1-Butene Copolymer Synthesized by *In Situ* Heat Induction Melt Reaction

Yanjie An,[1,2] Haiping Xing,[2] Yanhui Wang,[2] Tao Tang[2]

[1]*Daqing Petrochemical Research Center, Petrochemical Research Institute, Daqing 163714, People's Republic of China*
[2]*State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, People's Republic of China*

ABSTRACT: Propylene/1-butene copolymer powders were produced through bulk copolymerization of propylene with 1-butene in a 12 m^3 polymerization reactor. High melt strength polypropylene (HMSPP) was synthesized by *in situ* heat induction melt reaction, in which pure propylene/1-butene copolymer powders without any additives were used as a basic resin and trimethylolpropane triacrylate (TMPTA) as a crosslinking agent. The structure and properties of the resultant HMSPP were characterized by means of various measurements. The content of TMPTA strongly influenced the melt strength and melt flow rate (MFR) of HMSPP. With increasing the content of TMPTA, the melt strength of HMSPP increased, and the MFR reduced. In addition, owing to the existence of crosslinking structure, thermal stability and tensile strength of HMSPP were improved compared with pristine propylene/1-butene copolymer. © 2012 Wiley Periodicals, Inc. J Appl Polym Sci 125: 2724–2731, 2012

Key words: crosslinking; melt strength; reactive processing; polypropylene

INTRODUCTION

Polypropylene (PP) is one of the leading and fast growing thermoplastic polymers in the world due to its high tensile strength, stiffness, and chemical resistance.[1] However, there are some weaknesses in the performance of PP, such as low melt strength, which is ascribed to the linear structure of PP chain. The melt strength of polymers is a measure of the melt resistance to extensional deformation, which influences the thermoforming behavior of polymers, especially the tendency of polymer sheets to sagging. Recently, high melt strength PP (HMSPP) has been developed to improve the processing performance in thermoforming.[2–4] In general, there are long branching chains on the backbones or chain entanglement in the microstructure of HMSPP.[5–8] Under normal circumstances, it is not easy to synthesize long branching chains of PP directly using copolymerization method.

Compared with homopolymerization of propylene, ethylene, and ethylene/α-olefin copolymerization, there are few studies in the open literatures about the synthesis of propylene/1-butene copolymers. In the reports that have been published, most of them investigated polymerizations in suspensions of heptane, hexane, or toluene,[9–14] although some few studies were related to polymerizations performed in bulk[15,16] and in gas-phase.[17] Furthermore, there were rare studies about HMSPP prepared by using propylene/1-butene copolymers as a basic resin.[18–32]

To make PP with high mechanical properties and high melt strength, researchers have explored many methods to prepare HMSPP, such as blending, radiation crosslinking, peroxide crosslinking,[18–32] etc. Compared with radiation and peroxide crosslinked PP, crosslinking propylene/1-butene copolymers through *in situ* heat induction reaction shows various advantages, such as easy processing, low cost, and capital investment, and favorable properties in the processed materials.

In this work, using trimethylolpropane triacrylate (TMPTA) as a crosslinking agent, we reported a novel method to prepare HMSPP from propylene/1-butene copolymers via melt reaction initiated by *in situ* heat induction, in which propylene/1-butene copolymers were synthesized by bulk copolymerization of propylene and 1-butene. As we know, compared with the other crosslinking agents, TMPTA has three double bonds with high reactivity, which can capture free radicals easily and form crosslinking structure. This method can avoid severe degradation and crosslinking of PP comparing with the

previous methods using peroxide as initiator for preparing HMSPP. In addition, random copolymers of propylene and 1-butene contain an amount of short-chain branching, which might be good to improve melt strength of the basic resin after modification.

EXPERIMENTAL

Materials

Propylene (purity $\geq$ 99.5%), 1-butene (99.2% of purity), hydrogen (purity $\geq$ 95.0%), and the catalyst with the content of 3.43 wt % titanium were used in propylene polymerization plant of Daqing Huake Company Limited, China. The triethylaluminum (TEA) as cocatalyst was obtained from Liao Yang, China. Cyclohexylmethyldimethoxymonosilane (CHMMS) was used as external electron donor. Trimethylolpropane triacrylate (TMPTA) was standard laboratory reagents used as received.

Preparation of propylene/1-butene copolymer

Copolymerization of propylene with 1-butene was carried out in a 12 m^3 polymerization reactor. Propylene and 1-butene were prepolymerized under 20°C for 10 min, in which the 1-butene content was kept to 2.86 wt %, while the molar ratios of CHMMS/Ti and TEA/Ti were kept to 40 and 100, respectively, and then polymerized under isothermal conditions (at 70°C for 4.5 h). The polymerization catalyst was commercial $MgCl_2$ supported $TiCl_4$ with the content of 3.43 wt % titanium.

Preparation of high melt strength polypropylene (HMSPP)

Propylene/1-butene copolymer powder was tumble-premixed with TMPTA. The crosslinking processes were carried out in TSSL-25 corotating twin-screw extruder with a length/diameter ratio of 36/1 and a diameter of 25 mm. The screw configuration was designed to provide good dispersive and distributive mixing. The barrel temperatures from the feed zone to the die zone were set as follows: 190°C, 210°C, 225°C, 230°C, 230°C, 230°C, 230°C, 215°C, and 195°C. The screw rate and feed rate were kept constant at 65 rpm and 21 rpm, respectively. After the reaction, the crosslinking products were shaped into 1-mm thick compression-molded sheets as follows: the polymers were preheated at 210°C for 5 min and then pressed for 5 min under 15 MPa of pressure. After cooling, a sheet was cut into tensile bars. The specimens were stored under dried conditions before testing. As a control, pure propylene/1-butene copolymer powder was also treated under the same conditions.

Characterizations

The ^{13}C NMR spectra of propylene/1-butene copolymers were recorded on a Bruker 400 MHz spectrometer (Germany) at 120°C. Samples were dissolved in deuterated *o*-dichlorobenzene. Wide-angle X-ray diffraction (WAXD) measurements were performed at room temperature by a D/max-2500/PC X-ray diffractometer (Rigaku, Japan) using CuKα radiation operated at 35 kV and 50 mA. The data were collected from 6° to 50° at a scanning rate of 3°/min. Before testing, all specimens were treated uniformly. FTIR spectra were recorded with a FTIR spectrometer (GX-2000) in the range of 600–4000 cm^{-1} with a resolution of 4 cm^{-1}. The products from the extruders were first purified using a dissolution-precipitation method in order to remove unreacted TMPTA. Samples for FTIR measurements were prepared by making films of the HMSPP in a hot press. Films (30 μm thick) were prepared by hot pressing at 210°C.

Melt flow index (MFR) was determined using CEAST 6542 Modular Flow Index. The condition of experiment is at 230°C under a load of 2.16 kg. The melt strength was measured by using Rheotens method with die $L/D = 20/2$ and melt temperature of 230°C. Here, a melt strand was extruded through a capillary die and pulled down with increasing velocity (at constant acceleration 27 mm/s^2) by using a pair of wheels, and the force was measured till the rupture of the melt strand occurred. The average force was defined as melt strength, and the drawdown velocity at break was a measure of melt extensibility.

The melting and crystallization behavior of the samples were studied with a Perkin-Elmer DSC1 differential scanning calorimeter (USA) under nitrogen atmosphere. The samples were first heated from 50 to 200°C at a scanning rate of 10°C/min and then maintained at 200°C for 5 min before cooling to 50°C at the same rate. After that, the samples were reheated from 50 to 200°C at a scanning rate of 10°C/min. The crystallinity of samples was calculated from the heat of fusion (a heat of fusion for 100% crystalline PP (H_0) was 207 J/g).[33] Thermogravimetric analysis (TGA) was performed using Perkin-Elmer Pyris 1 under nitrogen atmosphere at a heating rate of 10°C /min. The tensile strength and the tensile modulus were measured with a WD-20D Electronic Universal Testing Machine at the crosshead speed of 50 mm/min.

RESULTS AND DISCUSSION

Composition and microstructure of propylene/1-butene copolymer

The composition of the resultant propylene/1-butene random copolymer was measured by means of FTIR after the products were purified using a precipitation method. FTIR spectra of the pure PP and
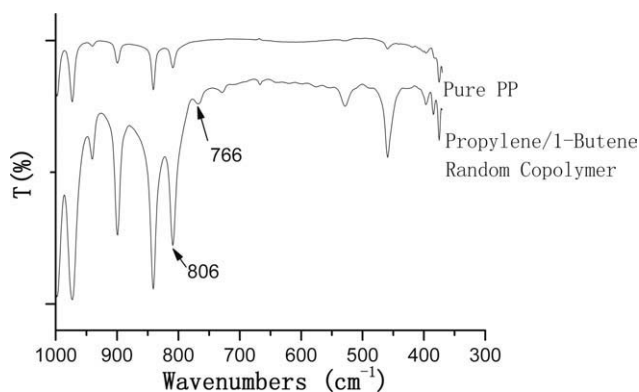
Figure 1 FTIR spectra of pure PP and propylene/1-butene random copolymer.

copolymer are shown in Figure 1. In the case of the pure PP, there were no any new absorption bands near 766 cm^{-1}. However, a new absorption band at 766 cm^{-1} was observed in the FTIR spectra of copolymer, which can be assigned to the absorption of 1-butene unit. This confirms that the 1-butene has inserted into PP backbone, which can also be confirmed by NMR spectra later.

PP is a crystalline polymer in three polymorphic forms, i.e., α (monoclinic), β (pseudohexagonal), and γ (triclinic), depending on the composition of PP and the crystallization conditions. Figure 2 shows the WAXD profiles of pure PP and propylene/1-butene random copolymer. The diffraction peaks of pure PP are located at 14.0°, 16.8°, 18.5° 21.0°, and 21.8° in the range of 10°–25°, which correspond to the α (110), α (040), α (130), α (111), and α (131) planes, respectively.[34,35] It is clearly shown that there is a strong diffraction peak at 2θ = 16.8° for the copolymer, which is much higher than that of pure PP. Furthermore, the intensity of diffraction peak at 2θ = 14.0° for the copolymer is smaller than that of pure PP. In addition, a small diffraction peak at 2θ = 20.1°, which results from γ (117) reflection in the γ form,[36] becomes obvious in the copolymer. It indicates that the copolymer presents slight change of crystallization growth and crystalline form.
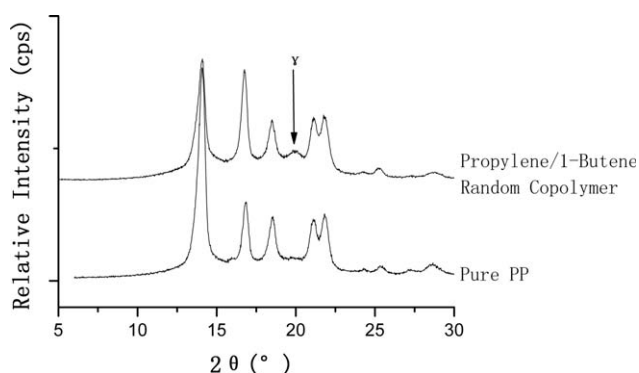

Figure 2 WAXD profile of pure PP and propylene/1-butene random copolymer.
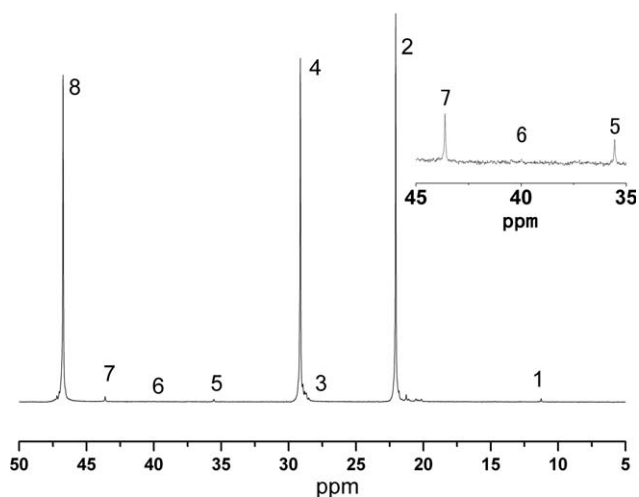
Figure 3 ^{13}C NMR spectra of propylene/1-butene random copolymer.

Figure 3 shows characteristic NMR spectra of the propylene/1-butene copolymer, which were used for the microstructure characterization and computation of copolymer composition.[37] The copolymer composition was obtained through quantitative analysis of the characteristic peaks of the group CH$_2$ based on the dyads PP, BP, and BB, which are located at 46.00–46.95, 43.02–43.51, and 40.11 ppm, respectively, as shown in Figure 3 and Table I, where P denotes propylene and B denotes 1-butene monomer units.

The 1-butene content of the copolymer ($\xi_{C4}^=$ was obtained with the following equations.[37]

$$B = [BB] + 0.5[BP] \tag{1}$$

$$P = [PP] + 0.5[BP] \tag{2}$$

$$\xi_{C4}^= = \frac{B}{P} = \frac{[BB] + 0.5[BP]}{[BB] + [PP] + [BP]} \tag{3}$$

Number average sequence lengths can also be determined from the dyad distributions and used to

TABLE I
Peak Assignment of ^{13}C NMR Spectra of the Copolymers

Signal	Carbon type	Detection range
	$\begin{pmatrix} \text{⑧} & \text{④} & \text{⑥} & \text{⑤} \\ \text{—CH}_2\text{—CH—CH}_2\text{—CH—} \\ \text{⑦} \\ \text{②CH}_3 \quad \text{③ CH}_2 \\ \text{①CH}_3 \end{pmatrix}_n$	
		ppm
8	CH$_2$	46.00–46.95
7	CH$_2$^{BP}	43.02–43.51
6	CH$_2$^{BB}	40.11
5	CH	35.05–35.10
4+3	CH + CH$_2$	28.00–28.90
2	CH$_3$	20.96–21.93
1	CH$_3$	10.96–11.18

Average Sequence Lengths and Sequence Distribution of Propylene/1-Butene Copolymer

			Sequence composition (%)								Average sequence lengths	
B	P	PP	PB	BB	PPP	PPB	BPB	PBP	BBP	BBB	$\overline{n_B}$	$\overline{n_P}$
2.36	97.64	97.04	2.96	0	81.97	16.55	0	1.48	0	0	1	65

characterize the chain structure of copolymers through the following relationships.[37]

$$\overline{n}_B = \frac{[BB] + 0.5[BP]}{0.5[BP]} \quad (4)$$

$$\overline{n}_P = \frac{[PP] + 0.5[BP]}{0.5[BP]} \quad (5)$$

According to the above formulas, the average sequence lengths and sequence distribution of propylene /1-butene copolymer can be calculated. From Table II, the content of BB sequence is zero, confirming that there is no BB sequence in the whole molecular chains of copolymer and monomer 1-butane is inserted into copolymer backbone in a single molecular mode.

Structural characterization of the HMSPP

The preparation process of HMSPP via melt reaction initiated by *in situ* heat induction involves two main stages. In the first stage, copolymer chains break to form macromolecular radicals under shear field at high temperature. In the second stage, TMPTA, which has three active double bonds, can react with macromolecular radicals, thus crosslinking and/or branching structure can be formed. The whole reaction process is shown in Scheme 1.

After the products were purified using a precipitation method, the composition of the modified copolymers with different content TMPTA were measured by means of FTIR, which is shown in Figure 4. In the case of the HMSPP, a new absorption band at 1740 cm^{-1} is observed, which can be
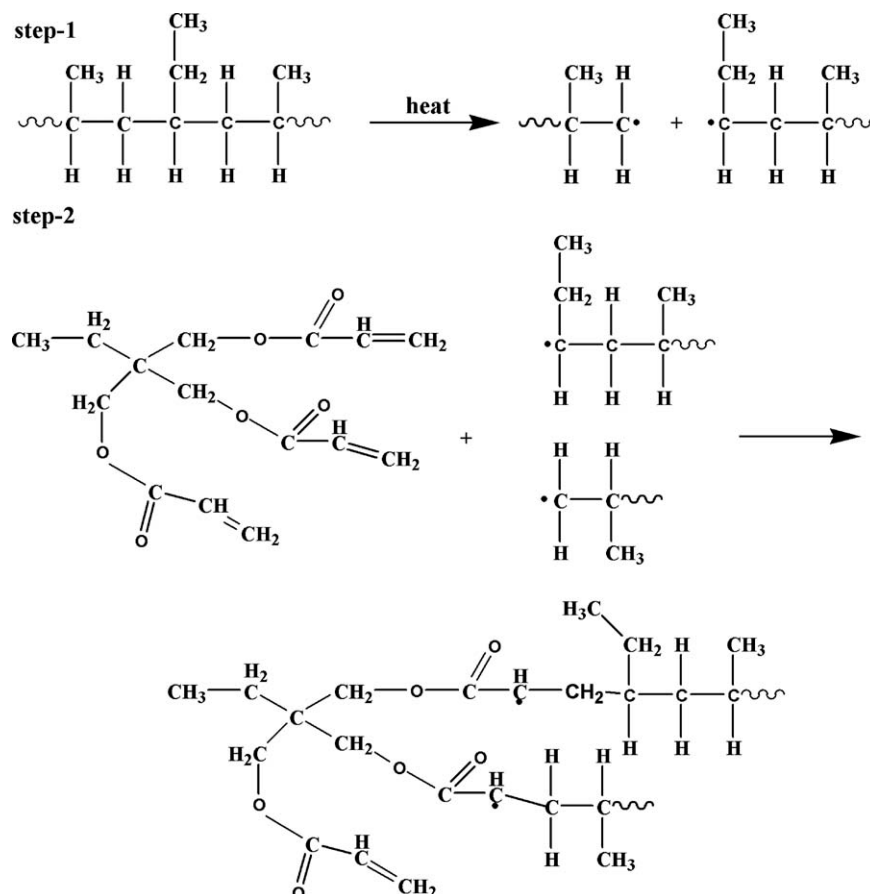
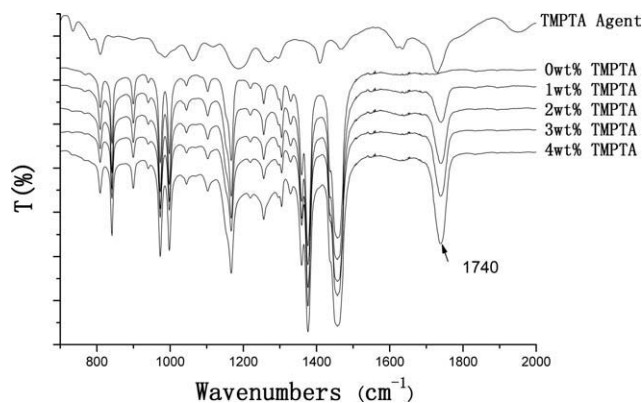Scheme 1 Schematic diagram of reaction mechanism for preparation of HMSPP.

Figure 4 FTIR spectra of HMSPP.

assigned to the absorption peak of C=O. Meanwhile, no absorption peak of carbon–carbon double bond is observed in the FTIR spectra of HMSPP (1500–1700 cm^{-1}), indicating no residue of free TMPTA in the purified products. Furthermore, with the increasing content of TMPTA, the absorption peak at 1740 cm^{-1} is increased correspondingly.

The gel content is generally used to evaluate the crosslinking degree of polymers. Figure 5 presents the effect of TMPTA concentration on the gel content of the HMSPP. The gel content of the HMSPP increases gradually with the TMPTA concentration. This means that the crosslinking structure was formed in the HMSPP. When the TMPTA concentration was 4 wt %, the gel content of the HMSPP was 45.4 wt %.

Melt properties of the HMSPP

The influence of TMPTA concentration on melt flow rate (MFR) of HMSPP is shown in Figure 6. The MFR of HMSPP decreases with increasing concentration of the TMPTA. The reduction of MFR values
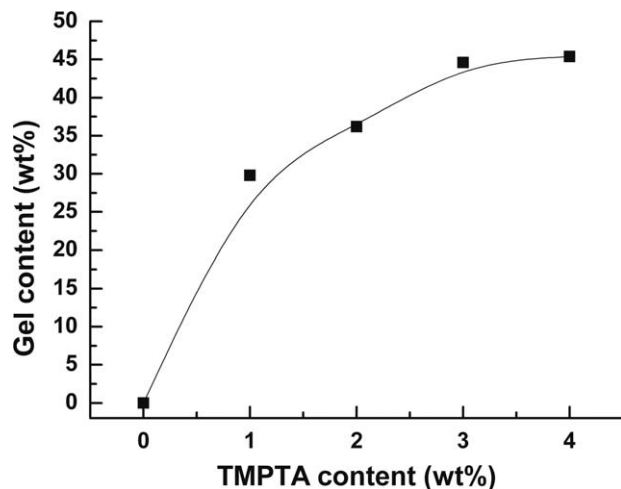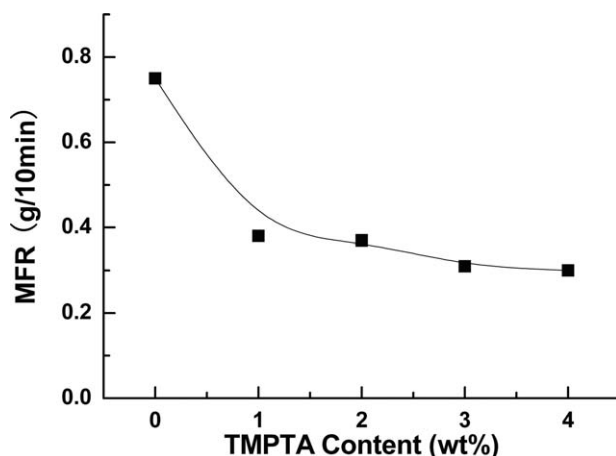

Figure 6 Effect of TMPTA content on MFR of HMSPP.

implies the decrease of the chain mobility due to the fact that some crosslinking occurs, which makes the molecular chains extended each other.

The melt strength of HMSPP was measured by Rheometer-7D instruments. Here, the diameter of capillary die is 2 mm. Figure 7 presents the effect of TMPTA concentration on expansion ratio and diameter of extrude bar of the HMSPP. The diameter and expansion ratio of the extrude bar increased gradually with increasing of the TMPTA concentration. The concentration of TMPTA strongly influences the melt strength of HMSPP (Fig. 8). It can be seen that the average melt strength of the HMSPP increases with the TMPTA concentration. The melt strength of the HMSPP is 18 cN when the TMPTA concentration is 4 wt %. In contrast, the melt strength of pure copolymer is 6 cN. It further indicates that the chain structure of a part of PP copolymers changes from linear structure to crosslinking structure after modification, which results in the increase of the melt strength of HMSPP.
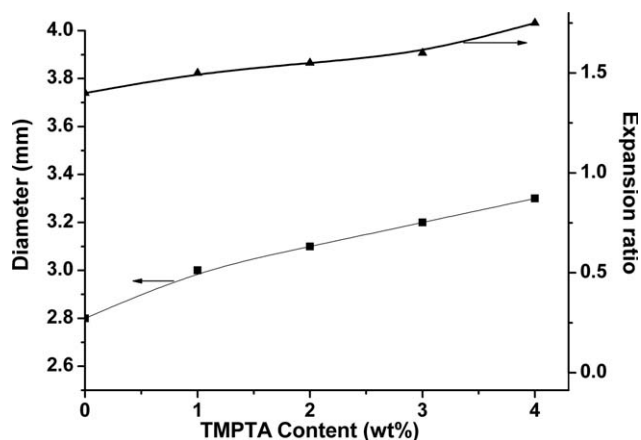

Figure 5 Effect of TMPTA content on gel content of HMSPP.

Figure 7 Effect of TMPTA content on expansion and diameter of HMSPP extrude bars.
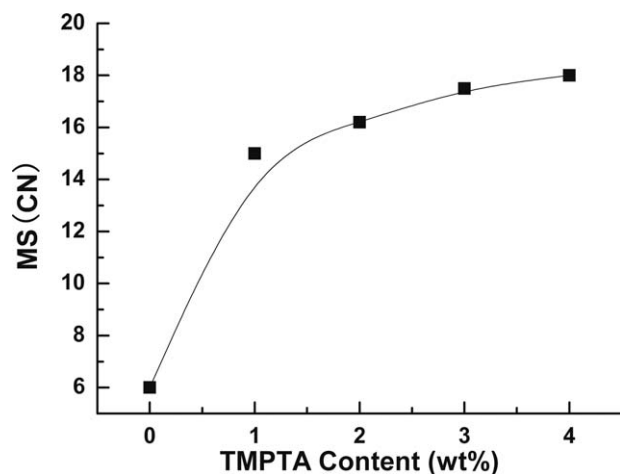
Figure 8 Effect of TMPTA content on melt strength of HMSPP.

Melting and crystallization behavior of HMSPP

Figures 9 and 10 present the heating and cooling thermograms of the copolymer and HMSPP. From Figure 9, it can be seen that T_m (160°C) of the HMSPP is higher than that (158°C) of the parent copolymer. In comparison with the parent copolymer, the HMSPP shows evidently the higher onset temperature of crystallization and higher peak value of crystallization (T_c) (Fig. 10). This means that the crystallization of the HMSPP starts earlier than that of the parent copolymer. The crosslinking unit considerably increases the nucleation density of HMSPP, which accelerates the crystallization and increases the crystallinity of HMSPP (Fig. 11). An important application of HMSPP is to make foam materials. In the process of foaming, when the mixture of PP and gas is extruded out, the pressure decreases sharply after leaving the die. Consequently, PP and gas will expand instantaneously, especially the gas. At this time, if the crystallization temperature of PP is higher, the crystallization of PP
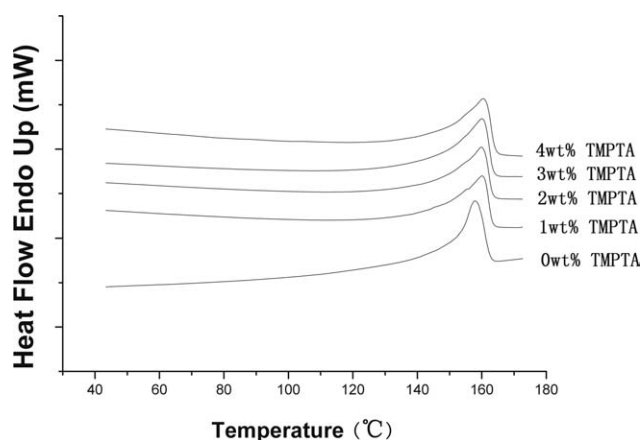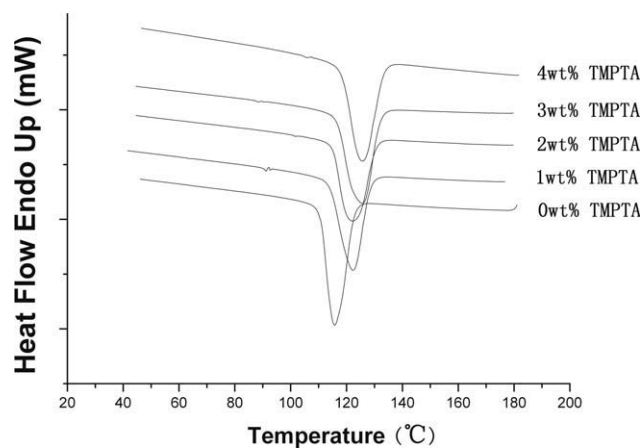

Figure 10 The crystallization curves of HMSPP.

will grow rapidly, which benefits the stability of foaming. The results also imply that the HMSPP could induce the rapid case hardening of the foams. Therefore, the high crystalline temperature of the resin is propitious to the foam in the twin-screw extruder.

Thermal stability of the HMSPP

TGA curves of the HMSPP are illustrated in Figure 12. The results show that the HMSPP has the higher decomposition temperature comparing with that of the parent copolymer. For example, when the TMPTA concentration is 4 wt %, the temperature (446.5°C) at 10% weight loss for HMSPP is much higher than that of the parent copolymer (428.5°C). It indicates that the HMSPP becomes more thermal stable after crosslinking reaction and raised its upper temperature limit of application. The improved thermal stability also ensures the applications of the crosslinking PP in many applications.
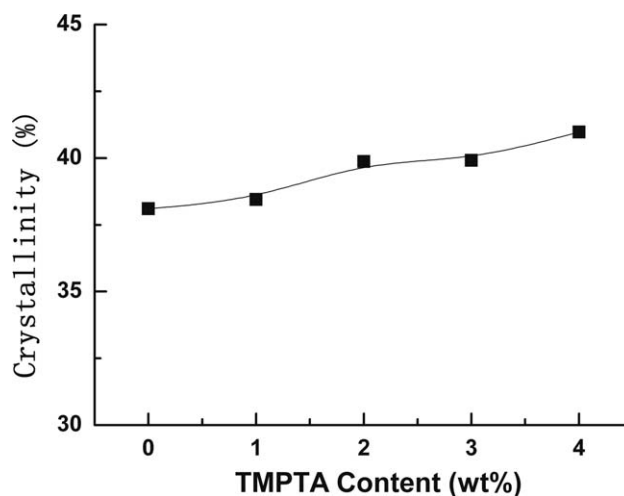

Figure 9 The melting curves of HMSPP.

Figure 11 Effect of TMPTA content on crystallinity of HMSPP.

Figure 12 TGA curves of HMSPP.
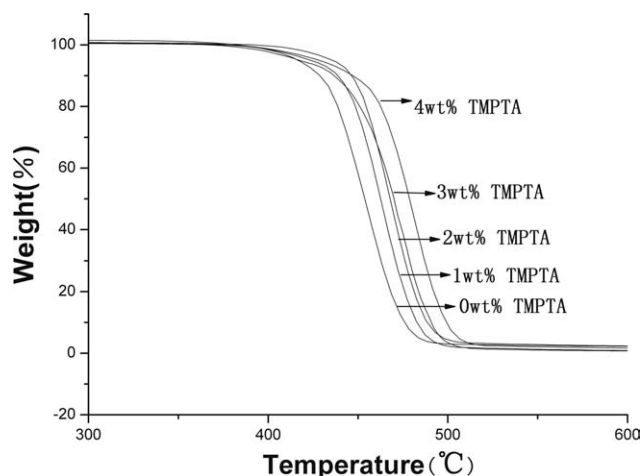

Figure 14 Effect of TMPTA content on tensile modulus of HMSPP.

Mechanical properties of HMSPP

Effect of TMPTA concentration on mechanical properties is shown in Figures 13 and 14. It can be seen that, with increasing of TMPTA concentration, the tensile strength and tensile modulus of the HMSPP increases. Therefore, the crosslinking reactions enhance the mechanical properties. After the crosslinking reaction, some linear molecules of copolymer have been changed into three-dimensional network ones, leading to the increase in the tensile strength and tensile modulus.

CONCLUSIONS

The HMSPP was successfully synthesized via melt crosslinking reaction initiated by *in situ* heat induction, in which pure propylene/1-butene copolymer powders without any additives and TMPTA were used as a basic resin and a crosslinking agent, respectively. The results indicated that the properties
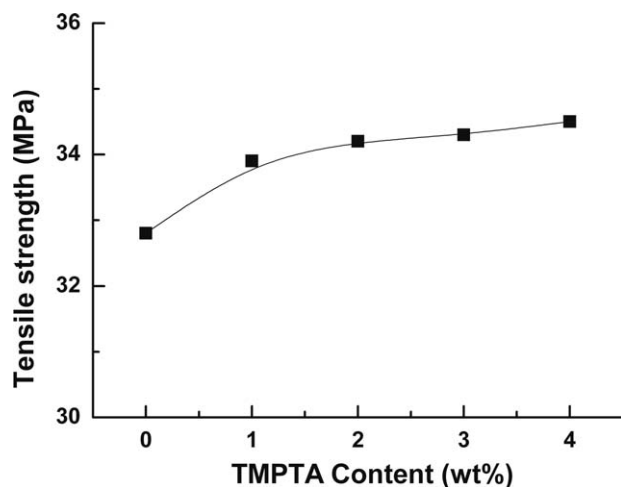
of HMSPP were greatly affected by the content of crosslinking agent. The melt strength of HMSPP was dramatically improved due to crosslinking of the propylene/1-butene copolymer. The HMSPP showed a better thermal stability and higher tensile strength than pure propylene/1-butene copolymer.

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Figure 13 Effect of TMPTA content on tensile strength of HMSPP.

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