Structure and Properties of Polypropylene Alloy In Situ Blends

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ABSTRACT: A series of polypropylene (PP) alloys containing different ethylene contents have been prepared by the in situ sequential polymerization technique, using Ziegler–Natta catalyst ($MgCl_2/TiCl_4$/BMF; BMF is 9,9-bis-(methoxymethyl)fluorine, as an internal donor) without any external donor. The structure and properties of PP alloys obtained have been investigated by nuclear magnetic resonance, Fourier transform infrared spectroscopy, dynamic mechanical analysis, differential scanning calorimetry, and scanning electron microscopy (SEM). The results have suggested that PP alloys are the complex mixtures containing PP, the copolymer with long sequence ethylene chain, ethylene-propylene rubber (EPR), and block copolymer etc. In the alloys, PP, EPR, and the copolymer with long sequence ethylene chain are partially compatible. The investigation of the mechanical properties indicates that notched Izod impact strength of PP alloy greatly increases at 16°C/−20°C in comparison with that of pure PP. The noticeable plastic deformation is observed in SEM photograph. The increase in the toughness, the mechanical strength of PP alloy decreases to a certain extent. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 100: 4804–4810, 2006

Key words: polypropylene (PP) alloy; toughness; Ziegler–Natta catalyst; ethylene-propylene copolymer; diether

INTRODUCTION

Polypropylene (PP) as a common plastic is rapidly developed and widely used in a variety of application owing to its low density, the excellent physical and mechanical property, as well as its appropriate price, the ease of processing, and chemical resistance. However, the pendant methyl groups along the chains lower the chain flexibleness of PP and hence the impact strength, especially at low temperature, that strictly limits the uses of PP in the extensive fields such as in automotive and the engineering applications when compared to its potential.[1,2] Several studies were devoted to the increasing toughness of PP.[3] To increase the toughness of a given material, the materials need to possess effective energy absorbing capacity. Several deformation mechanisms of energy absorption have been proposed to explain the toughness of polymers with rubber particles: cavitations around rubber particles, massive crazing, and shear yielding.[4,5] These deformations can consume impact energy and prevent further crack propagation. The shear yielding is more effective than that of another two.

For the production of impact-resistant PP, various rubbers such as ethylene-propylene rubber (EPR),[6] (ethylene-propylene-diene) copolymers,[7] and styrene-ethylene-butylene-styrene copolymers[8] had been investigated as impact modifiers to blend with PP. Because of the poor compatibility between the matrix and the elastomer phases, the compatibilizer must be added to fine the rubbery phase and improve interfacial adhesion between rubber and matrix phases.[9] A more effective way to prepare the impact-resistant PP is to introduce chemical modifications in the polymerization stage. Especially, the more attractive is the in situ sequential polymerization technique, which involves the polymerization of propylene in the first stage, followed by in situ ethylene-propylene copolymerization in the second stage.[10] It is well known that the product obtained by this approach comprises the PP as the matrix, the EP block copolymer as a compatibilizer, while the EPR and part of the EP segmented copolymer as dispersed phases of toughening particle.[11]

Most of the papers[12–14] on preparing PP alloy have been mainly concerned with Ziegler–Natta (Z–N) catalyst, based on $MgCl_2/TiCl_4$ or $MgCl_2/TiCl_4$/DIBP (DIBP is diisobutyl phthalate as an internal donor) catalyst, alkyl aluminum as a cocatalyst, and alkoxysi-

lane as an external donor. Recently, a novel generation Z–N catalyst containing diether compound as an internal donor has high activity and satisfactory stereospecificity without any external donor for propylene polymerization.[15] The novel generation catalyst, however, is used to prepare PP/EPR alloy, which has not been reported yet so far. In this paper, the probability of preparing impact-resistant PP alloy by the in situ sequential polymerization technique with the novel Z–N catalyst ($MgCl_2/TiCl_4$/BMF, BMF is 9,9-bis(methoxymethyl)fluorine as an internal donor) is explored. A series of PP alloys containing different ethylene contents are prepared. The possible composition and sequence distribution of the productions and the compatibility of multiphase system are primarily analyzed using nuclear magnetic resonance (^{13}C NMR), Fourier transform infrared spectroscopy (FTIR), dynamic mechanical analysis (DMA), and differential scanning calorimetry (DSC). The fractography of the impact fracture surfaces is observed through scanning electron microscopy (SEM). The effective toughening and the possible mechanism are discussed.

EXPERIMENTAL

Polymerization

The novel generation Z–N catalyst ($MgCl_2/TiCl_4$/ BMF) was synthesized similarly to a method described in the literature.[15] The polymerization of PP alloy was operated in a two-stage reaction process: the first stage was the liquid bulk polymerization of propylene without any external donor at 70°C for 1 h, in which spherical PP particles were produced, and the second stage was successive gas copolymerization at 60°C. The ethylene-propylene mixture gas of constant composition (molar ratio 1/1) was continuously supplied to the reactor at constant pressure (1.0 MPa). Ethylene content of the in situ blend, which can be adjusted by changing the conditions of copolymerization, gradually increased with the period of time of gas copolymerization in second stage reaction.

Characterization of polymer structure

FTIR were recorded on Perkin–Elmer 2000 spectrometer. Thin film of the sample was prepared by hot-pressing at 190°C. ^{13}C NMR spectrum of polymer was measured on a Bruker DMX300 NMR spectrometer. 1,2-dichlorobenzene-d4 was used as a solvent. The spectrum was recorded at 120°C. Typically 3000 transients were collected.

The melting temperature (T_m) of the polymer was measured by means of DSC, using Perkin–Elmer DSC-7 operating at a heating rate of 10°C/min from 50°C to 200°C. T_m was determined in the second scan.

The glass transition temperature (T_g) was determined by Perkin–Elmer DMA-7, at a heating rate of 10°C/min from −150°C to 100°C and at frequency of 1.0 Hz. The thickness of compression molded plate specimen was 1.5 mm.

The notched Izod impact strength of the polymer sample was measured on an Izod impact strength tester (CSI-137C), according to ASTM D256. Impact rate was 3.35 m/s. The flexural properties of the specimens were measured on an universal testing machine (Instron 3365), according to ASTM D790. Crosshead speed was 2 mm/min. Using a topcon international scientific instruments ISI-SX-40 with secondary electron imaging, impact fracture surfaces of notched Izod specimens (−20°C) coated by gold were studied by SEM.

RESULTS AND DISCUSSIONS

^{13}C NMR analysis results of PP alloys are listed in Table I. The nomenclature assigning the peaks for various carbons of polymer follows the method suggested by Carman and Wilkes.[16] It can be seen that the summation of triad distribution PPP content and EEE content in Sample 1–7 are almost more than 80%, and meanwhile, small amount of triad distribution with center P (PPE and EPE) and center E (EEP and PEP) exist in the products, indicating that the samples contain a lot of long sequences of propylene and ethylene, and still have ethylene-propylene copolymers. So the PP alloy obtained is a complex mixture comprised multiple components with different composition and chain sequence structure.

Kissin[17] has suggested that the highly isospecific Ti-based Z–N catalysts contain two families of active centers. The centers of the first family are capable of polymerizing propylene and copolymerizing both α-olefins and ethylene. These centers are relatively unstable in the kinetic sense. The centers of the second family can efficiently polymerize only ethylene, when exposed to mixtures of ethylene and α-olefins, they incorporate α-olefin molecules into polymer chains very poorly. They are relatively stable in the kinetic sense. In the first stage reaction of PP alloy, only centers of the first family work and form large amounts of long sequences of propylene. Meanwhile, centers of the second family 'sleep'. In the second stage of gas copolymerization, still active centers in the first family produce the ethylene-propylene random copolymer (EPR), block ethylene-propylene copolymer with different length of ethylene and propylene chains. At the same time, the centers of the second family, which awaked from 'sleeping', obtain the ethylene-propylene copolymer containing long sequence ethylene chain inserted by isolated propylene units.

In this work, PP alloy (Sample 7) with 52.4% ethylene by weight (or 62.4% by molar) extracted by boiling

Sample	Ethylene (wt %)	Ethylene (mol %)	PPP	PPE	EPE	PEP	PEE	EEE
PP[a]	0	0	—	—	—	—	—	—
1	6.1	8.9	87.6	2.4	1.1	1.2	2.3	5.4
2	8.0	11.5	83.6	3.6	1.3	1.4	3.8	6.3
3	8.8	12.7	79.8	5.7	1.8	2.4	4.3	6.0
4	13.5	19.0	70.4	7.3	3.2	3.6	6.5	9.2
5	32.4	41.8	50.5	4.3	3.4	1.6	7.1	32.7
6	39.6	49.6	44.4	2.9	3.1	1.4	7.3	40.0
7	52.5	62.4	32.3	3.2	2.1	0.7	5.5	55.5
7-A[c]	53.8	63.6	33.8	0	1.6	0	4.6	59.0
7-B[c]	54.0	63.8	10.7	14.0	11.5	2.8	18.0	43.0
PE[b]	100	100	—	—	—	—	—	—

[a] Polypropylene (PP) is prepared using the method of liquid bulk polymerization. Reaction condition: liquid propylene, 2 L; $MgCl_2/TiCl_4$/BMF catalyst/15 mg; Al-iBu cocatalyst; temperature, 70°C; pressure, 3.4 MPa; hydrogen, 1 L; Time 1 h.

[b] Polyethylene (PE) is prepared in slurry polymerization condition: $MgCl_2/TiCl_4$/BMF catalyst 100 mg; Al-iBu cocatalyst; temperature, 70°C; hexane, 300 mL; pressure, 0.3 MPa; time, 1 h.

[c] Sample 7-A means the insoluble fracture of Sample 7 in boiling heptane; Sample 7-B means the soluble fracture of Sample 7 in boiling heptane.

heptane is divided into two fractions: the soluble and the insoluble. The ^{13}C NMR spectra of two fractions are shown in Figure 1. For the insoluble fraction (Sample 7-A) in Table I, the content of triad sequence PPE is 0, implying that the insoluble fraction has PP with high isospecificity. The contents of triad sequence PEP also is 0 and the EEE is high, thus it is deduced that the insoluble part exists the copolymer containing long sequence ethylene chain inserted by isolated propylene units (EEPEEEPEEPEEEEEE). For the soluble fraction (Sample 7-B) in Table I, sequence distributions

in all triads are relatively homogeneous. The soluble part possibly contains random EPR and block copolymers with different ethylene/propylene sequence length as indicated in literature.[11] In conclusion, under two-stage reaction condition used in this study, PP alloys obtained are the complex mixtures containing PP, the copolymer with long sequence ethylene chain, EPR and block copolymer etc. Obviously, further fractionation analysis is needed to accurately measure the content and structure of each composition in PP alloy.
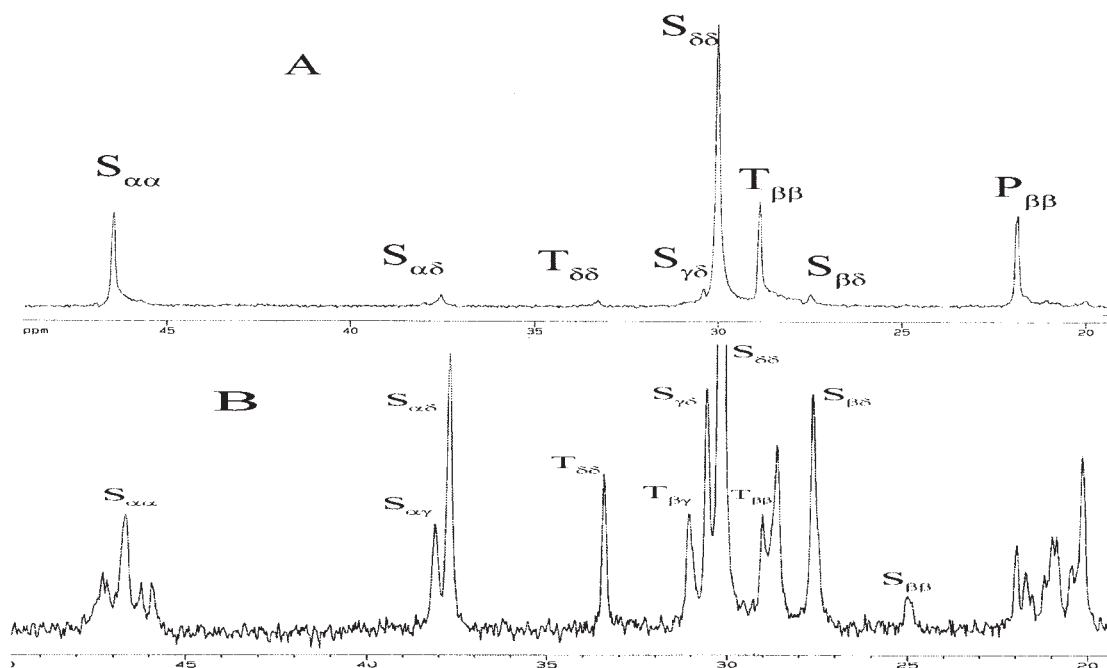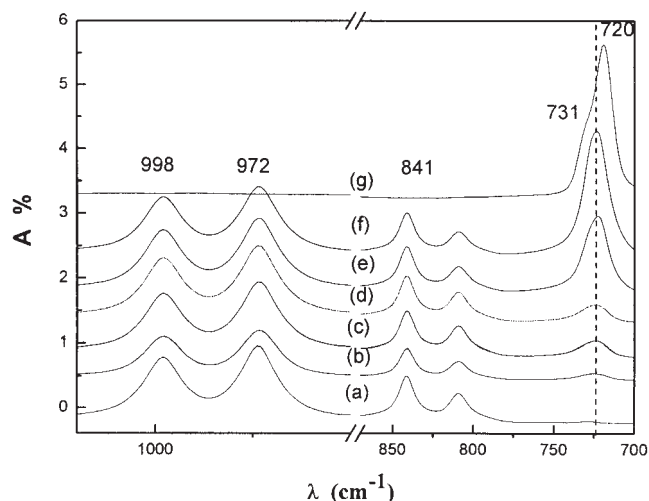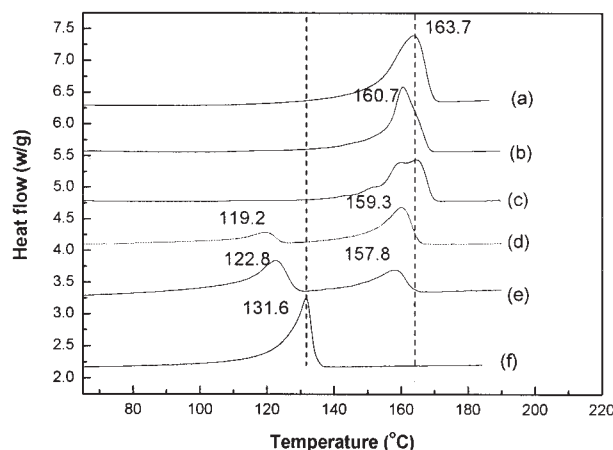

Figure 1 ^{13}C NMR spectra of iPP/EPR alloy(Sample 7). (A) the insoluble fracture in heptane and (B) the soluble fracture in heptane.

Figure 2 FTIR spectra of polymers: (a) PP, (b) Sample 1, (c) Sample 3, (d) Sample 4, (e) Sample 5, (f) Sample 7, and (g) PE.

Figure 3 DSC heating scanning curves of polymers: (a) PP, (b) Sample 1, (c) Sample 4, (d) Sample 5, (e) Sample 7, and (f) PE.

FTIR spectrums of PP alloys are shown in Figure 2. As indicated in earlier literature,[18] the absorption at 998 and 841 cm^{-1} are due to methyl rocking modes and are associated with long helical segments in crystalline lattice of isotactic PP, which are characteristic of the crystalline bands. The band at 972 cm^{-1} is associated with methyl rocking vibrations of relatively short helical segments in amorphous phase of PP. For polyethylene the doublet at 721 cm^{-1} and 730 cm^{-1} is due to the rocking mode of CH_2 group and is characteristic of the crystalline bands, in the meanwhile the amorphous phase also contributes to the band of 721 cm^{-1}. The higher the degree of crystallite and the closer the packing, the bands split more into a sharp doublet. Typical of crystalline polyethylene in the orthorhombic form have two narrow bands at 731 and 720 cm^{-1}. It has been known for many years[18] that the frequency of the band due to the rocking motion of CH_2 groups is sensitive to the number of adjacent CH_2 groups in the polymer chain. When single units, double units, and long sequences of ethylene are present in ethylene-propylene copolymer, two narrow bands of crystalline PE at 731 and 720 cm^{-1} will overlap to a wider band or become a shoulder band in the range of 720–731 cm^{-1}. In Figure 2, evidently, the absorptions of PP crystalline bands are very strong. At the same time, a wider band of PE crystalline bands occurs in these spectra of PP alloys. Such results indicate that sequence distribution of ethylene units in PP alloy is wide and the crystallinity of ethylene chain is low. Examination of the FTIR spectrum of PP alloys is coincident with the result of ^{13}C NMR analysis.

The DSC curves of PP alloys are presented in Figure 3. Thermograms consist of two separate endothermic peaks, indicating the presence of two distinct types of crystallites, one located at about 160°C attributes to the melting point of PP, and the other at about 120°C to that of long sequence ethylene chains. The endothermic peak of crystalline ethylene chain in PP alloy is lower and broader than that of pure polyethylene. However, the change of the melting peak of PP is slight.

For further analysis, the melting temperatures of components as a function of ethylene content are shown in Figure 4. It is apparent from this Figure that the melting temperature of either for PP or for long sequence ethylene chains decreases with the increase of ethylene content. Within the range of ethylene content studied, however, the melting-point depression of crystalline ethylene chain is greater than that of crystalline propylene chain. For instance, in PP alloy (Sample 7) with 52.5% of ethylene the melting-point depression is about 13°C for crystalline ethylene chain and 6°C for crystalline propylene chain. The change in the melting behavior is related with the crystallite size
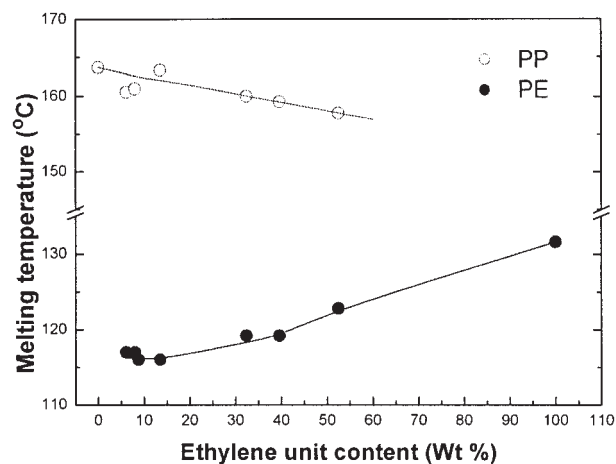
Figure 4 The relationship between ethylene content and melting temperature of polymers.
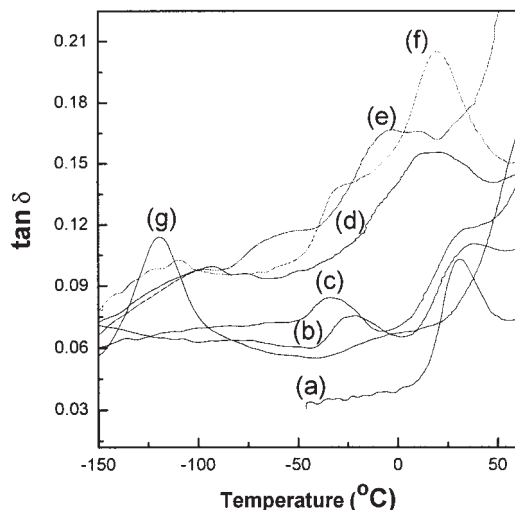
Figure 5 Temperature dependence of the logarithmic decrement of tan δ for PP alloys: (a) PP, (b) Sample 4, (c) Sample 2, (d) Sample 6, (e) Sample 7, (f) Sample 5, and (g) PE.

and its distribution. This is because incorporation of one of the comonomer units will inhibit the other chains folding into growing crystal lamellae to form larger crystals and markedly lowers the melting point of components of copolymer. In the first stage reaction, the large amounts of long sequences of propylene have been formed. While in the second stage, large amounts of ethylene monomers take active part in the copolymerization with propylene to form copolymers with a wider distribution sequence length, and it is believed that a broader distribution of crystallite size in the copolymers will be formed as it solidifies, thus the melting peaks of long sequences ethylene chains become more broader as well as the melting point depresses more than that of PP.

Figure 5 displays the dynamic mechanical properties of PP alloys. The glass transition of pure PP appears at about 30°C and Tg of pure PE appears at about −117°C. It has been reported that the main glass transition of EPR is at about −40°C (it may also comprise transition of EP segmented copolymer).[19] In Figure 5, the peaks between Tg of PP and PE should be the transition of ethylene-propylene copolymer. It can also be seen that transition peaks of PP and ethylene chain in alloy become wider. It just indicates that the alloys, which are multi phases, contain a broad distribution of sequence lengths and are more or less heterogenous with varying segment motion units. It is interesting that the two transition peaks of PP and long sequence ethylene chain in PP alloy are apparently shifted toward each other. The shifting extent increases with the content of ethylene unit in alloy. Furthermore, the relaxation of EPR is closer to Tg of PP, indicating that the PP, EPR, and the copolymer with long sequence ethylene chain in PP alloys are partially compatible, in which the EP block copolymer should act as the compatibilizer. It is very important to modify the toughness of materials for the compatibility, which will be proved by following SEM micrographs.

The most important mechanical property for the application, impact strength, is displayed as a function of ethylene unit content in Figure 6(a). It is found that ethylene content in materials is one of the most important factors that determine the toughness. With increasing the content of ethylene unit, the notched Izod impact strength of alloys greatly increase at 16°C/−20°C. Especially, when ethylene weight percent is 8.8%, the impact strength of material improves 10 times when compared with that of pure PP at 16°C. With the increase of the toughness, flexural strength of materials decreases from 41.6 MPa to 30.1 MPa. The

(a)

(b)
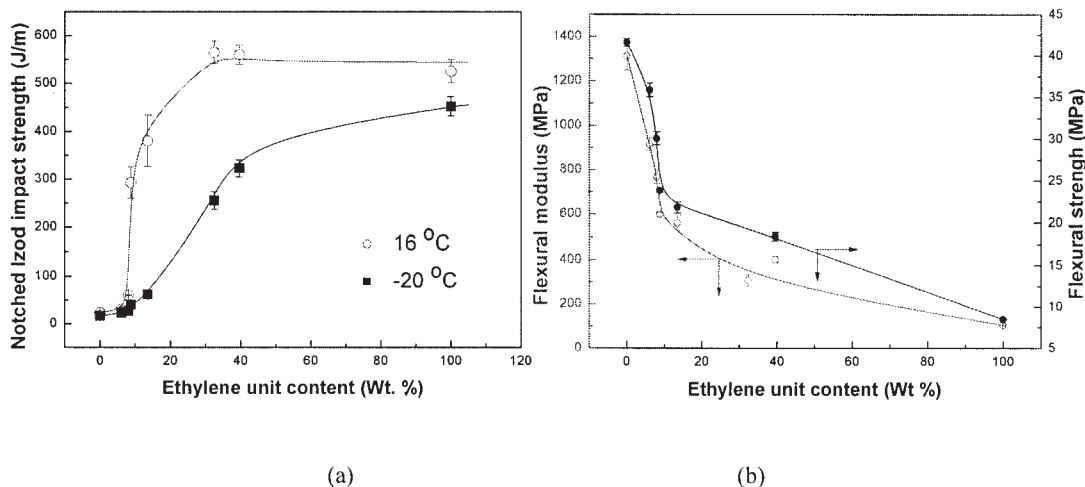
Figure 6 The relationship between mechanical properties and the structure of the impact PP. (a) Notched Izod impact strength at −20°C/16°C and (b) the flexural module and strength.
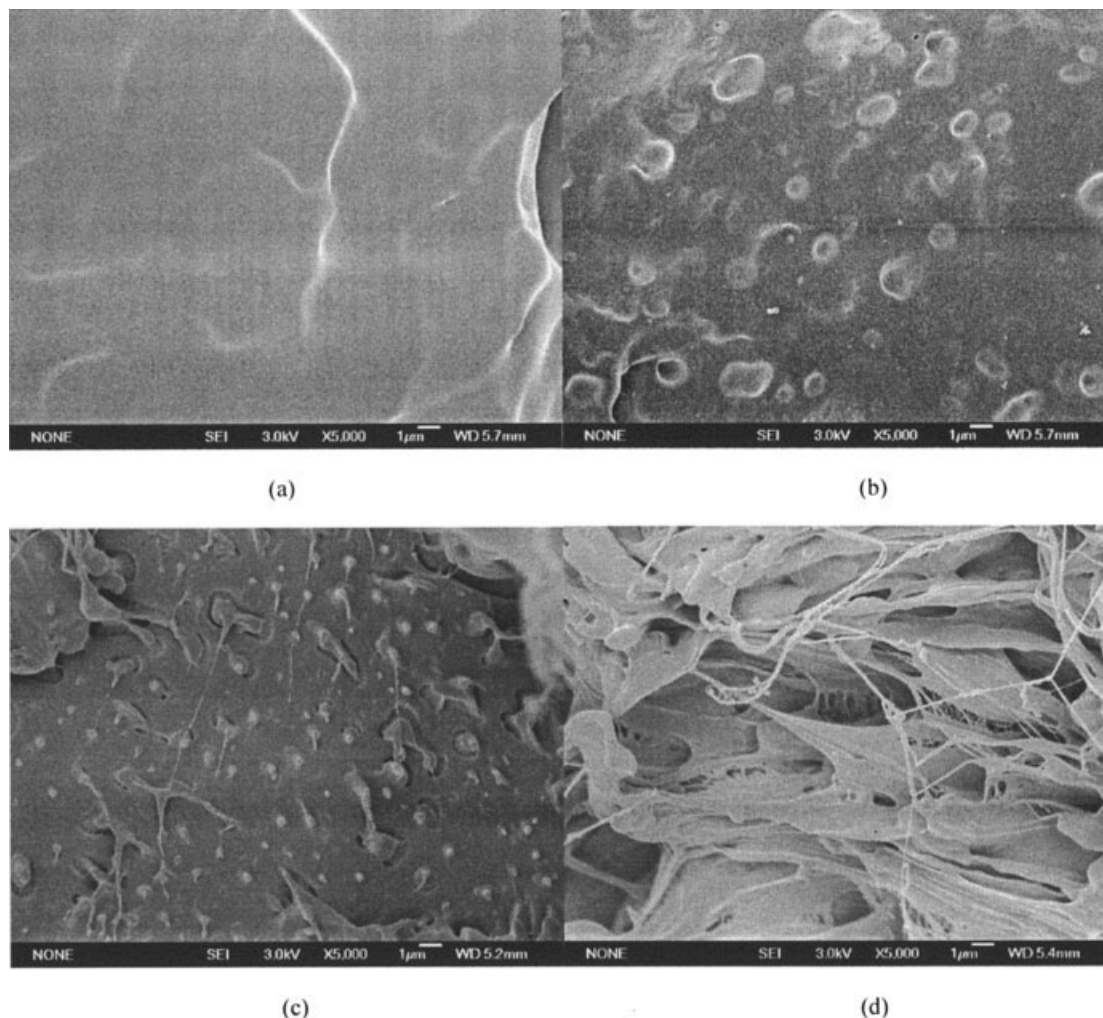
Figure 7 SEM photographs of the impact fracture surface of PP alloy (−20°C) at 5000×magnification—(a) PP, (b) Sample 3, (c) Sample 5, and (d) Sample 6.

flexural modulus and strength as a function of ethylene unit content is shown in Figure 6(b). This is directly resulted by the elastomer with low strength. Controlling a proper proportion of ethylene unit in alloy and definite polymerization condition, the superior product, of which mechanical strength decreases slightly and toughness increases drastically, can be produced.

SEM micrographs of impact fracture surfaces of PP alloys containing various ethylene contents at −20°C are shown in Figure 7. The fracture surface of PP shown in Figure 7(a) is smooth and limited plastic deformation occurs in it, thereby, the material exhibits a brittle fracture during impact process. As the ethylene content increases, the fracture surface becomes coarser. It can be seen from Figure 7(b) that the spherical dispersed phase containing EPR and long sequence ethylene chain copolymer is uniformly distributed in the matrix. The particle size is about 1 μm. Furthermore, the fuzzy interface between the matrix and the dispersed phase demonstrates good interfacial adhesion. It is in agreement with the result of DMA. It

is considered as that the presence of EP block copolymer greatly improves the compatibility in multiphase system. The noticeable plastic deformation is observed in Figure 7(c,d) and that consumes impact energy, hence the toughness of PP alloy enhances.

The granular morphologies of PP alloy revealed by SEM are shown in Figure 8. It is noted that all the particles are free-flowing, spherical in shape, whose diameters are about 1.3 mm, suggesting that the original shape of the homopolymer particle is retained during the copolymerization stage. Most of the copolymer has been formed inside the granules. The shape is suitable to further process.

CONCLUSIONS

PP alloys are prepared by the in situ sequential polymerization technique, using $MgCl_2/TiCl_4/BMF$-$AlEt_3$ as a catalyst system, which contains two families of active centers. The centers of the first family produce PP, EPR, and block copolymer. Those of the second
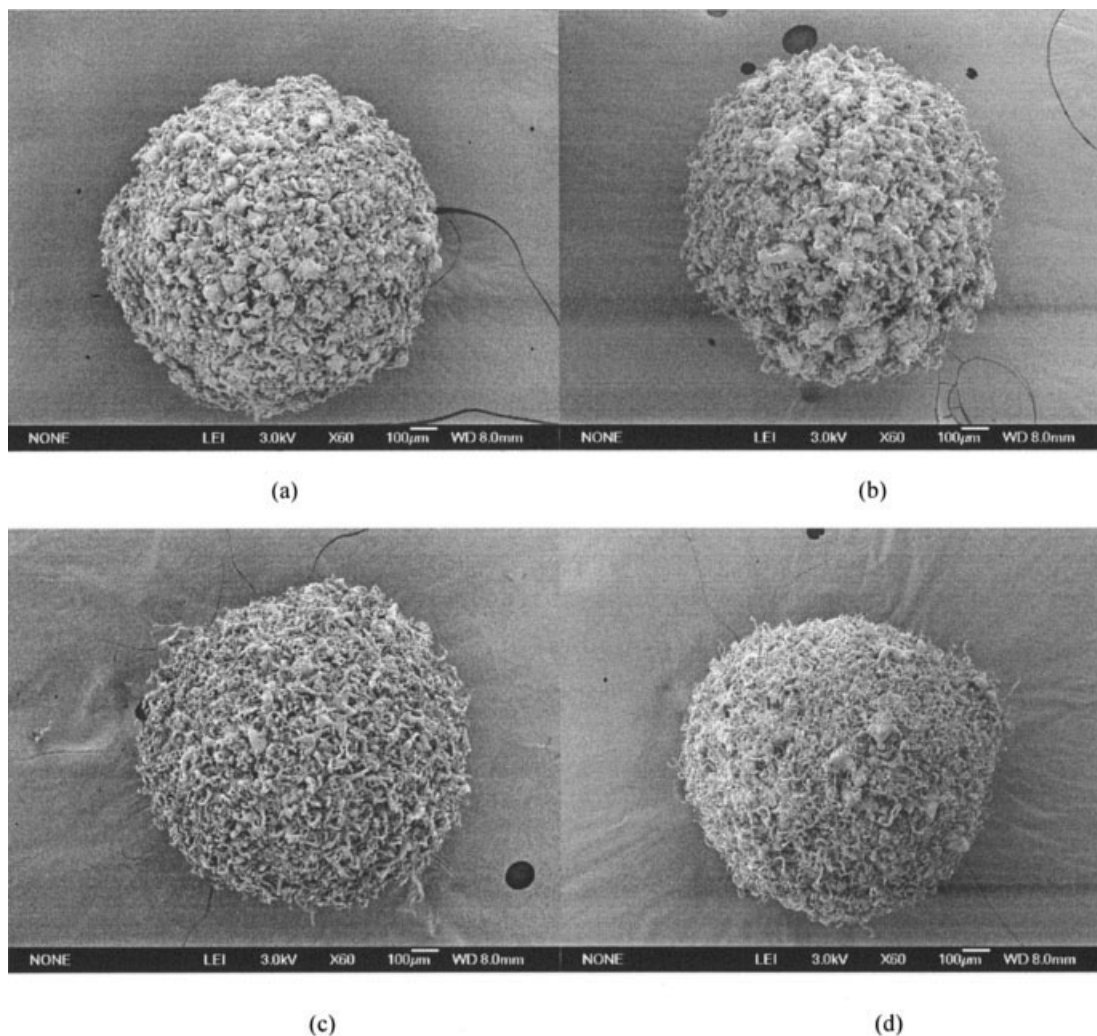
Figure 8 Surface SEM descriptions of impact copolymer at 60× magnification—(a) PP, (b) Sample 5, (c) Sample 6, and (d) Sample 7.

family produce the copolymer with long sequence ethylene chain. The melting-point depression of crystalline ethylene chain is greater than that of crystalline propylene chain. In alloys PP, EPR, and the copolymer with long sequence ethylene chain are partially compatible, in which the EP block copolymer should act as the compatibilizer. In comparison with the notched Izod impact strength of pure PP, that of PP alloy greatly increases at either room temperature or low temperature because of the noticeable plastic deformation occurrence, where the dispersed phase has sheared yielding to form a fibrous matter.

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