Effect of Composition and Component Structure on Thermal Behavior and Miscibility of Polypropylene Catalloys

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ABSTRACT: The thermal behavior and the miscibility of an *in-situ* polypropylene blend named polypropylene catalloys (PP-cats) were investigated by using modulated differential scanning calorimeter (MDSC). It is found that all PP-cats samples present two glass transitions, one of which is ascribed to the ethylene-propylene random copolymer (EPR), and the other, to isotactic polypropylene (PP). However, no glass transition of ethylene-propylene block copolymer (E-*b*-P) responsible for a third component in PP-cats could be found. With the increase of EPR, the glass transition temperatures responding to PP and EPR components, $T_{g, PP}$ and $T_{g, EPR}$, shift to low temperature, because of the enhancement of the interaction between PP and EPR component and the increase of ethylene content in EPR, respectively. Furthermore, the difference between $T_{g, PP}$ and $T_{g, EPR}$ remarkably decreases with the increase of the total ethylene content in PP-cats, which indicates that the miscibility of PP-cats is strongly dependent on the composition. Comparing the $T_{g, PP}$ and $T_{g, EPR}$ with T_g of fractionated PP and EPR, we ascribe the T_g change of PP fraction to the increase of EPR content; while that of EPR, to the increase of ethylene content in EPR. These experimental results suggest that the existence of E-*b*-P plays an important role in improving the miscibility between propylene homopolymer and EPR in PP-cats. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 106: 448–454, 2007

Key words: polypropylene catalloys; thermal behavior; miscibility; glass transition

INTRODUCTION

Over the last decades, blending and copolymerization have been realized as effective approaches to improve physical and mechanical properties of polymeric materials. The polymer blends usually present not only excellent performances, but also complex composition, structure, and morphology. To understand the dominant factors affecting and controlling ultimate properties/performances, investigations concerning the relationship between the composition, structure and properties for polymer blends have attracted increasing attention. It is widely accepted that the poor low-temperature impact property is one of the main shortages of isotactic polypropylene (*i*PP).

By blending PP with elastomer such as ethylene-propylene random copolymer (EPR), ethylene–propylene–diene monomer (EPDM) etc, the impact properties of blends could be improved to some extent. The miscibility for these blends has been studied experimentally and theoretically.[1–8] In recent years, a novel *in-situ* polypropylene blend named polypropylene catalloys (PP-cats) has drawn great interest because they can provide better mechanical properties and considerably cheaper production costs than polypropylenes modified generally by mechanical blending with thermoplastic elastomer.[9–12] The reason is that these preferred polypropylene blends can be prepared by in-reactor blending technology with a spherical TiCl$_4$/MgCl$_2$ catalyst. As is reported previously, PP-cats consist mainly of three compositions, i.e., *i*PP, EPR, and ethylene-propylene block copolymer (E-*b*-P) with different PE and PP segmental length.[10,11]

Similar to most semicrystalline/amorphous blends, the properties of PP-cats are strongly related to the crystallization behavior of PP. In our previous studies,[13,14] we have reported the isothermal crystallization kinetics of PP-cats, i.e., PP-cats present faster crystallization rate and slower spherulite growth rate

compared with those of pure PP. Also, we have investigated the crystalline structure, morphology and the melting behaviors of the PP-cats crystallized under nonisothermal and isothermal conditions.[15,16] The corresponding results suggest that the miscibility of PP-cats is different from the general PP/EPR and PP/EPDM blends. Though E-b-P can reach a high degree of dispersion in PP-cats and they exhibit better low-temperature impact properties than those polypropylene blends prepared by mechanical blending,[10,11] few reports concerning the miscibility of PP-cats and its impact factors have been published to date.

On the basis of various characterizations such as small-angle neutron scattering (SANS), small-angle light scattering (SALS), nuclear magnetic resonance spectra (NMR), dynamic mechanical analysis (DMA), differential scanning calorimeter (DSC), and morphology analysis, some studies on the miscibility of ethylene-propylene (EP) copolymer,[17] PP/EPR,[1–8] have been conducted. The results show that the composition and chain structure has a great effect on the miscibility, and some miscible blends with special composition could be obtained.[6,10] In general, it is understood that the glass transition behavior is an important indication of the miscibility of the blends and the thermal behavior is easily examined by using DSC. However, to our knowledge, the detection of T_g sometimes seems to be difficult and invalid since glass transition usually overlaps with relaxation behavior, or several T_gs are close to one another. Putting the modulated differential scanning calorimeter (MDSC) into application facilitates improving or solving the aforementioned situation/problem to a certain extent. In this technique, a sinusoidal modulated heating ramp yields a profile in which the increased instantaneous heating rate results in an increase in resolution and sensitivity, leading to attainment of more effective and satisfactory glass transition data of polymer blends. In the present article, we try to investigate the thermal behavior of PP-cats and focus on the effects of composition and polymer chain structure of PP-cats on the thermal behavior. The miscibility between PP and EPR in PP-cats tested by means of MDSC will be discussed.

EXPERIMENTAL

Materials

The PP-cats used were supplied by the Institute of Polymer Science of Zhejiang University of China. The synthesis details of PP-cats were reported by Zhang et al.,[18] involving three steps, i.e., prepolymerization of propylene, bulk polymerization of propylene, and gas-phase copolymerization of ethylene and propylene. Here the PP-cats are designated as PEP20, PEP40, and PEP60, respectively, in which capital E

TABLE I
Characteristic Parameters of PP and PP-cats

Sample	Content of ethylene (mol %)	Content of ethylene-propylene copolymer (wt %)	MFI (g/10 min)
PEP20	2.87	27.6	1.54
PEP40	11.80	31.4	1.27
PEP60	27.10	42.3	0.56

stands for ethylene component and the numbers stand for its percentage used in the gas-phase copolymerization in the third stage. The content of ethylene and ethylene-propylene copolymer (EP) in the catalloys and the melt flow indices (MFI) of these specimens are listed in Table I.

Separation of random copolymer and block copolymer from the *in-situ* blends

To separate the random copolymer from PP-cats, a modified Kumagawa extractor was used to conduct a temperature-gradient extraction fractionation of PP-cats.[19] Firstly, about 10 g of blend sample was dissolved at 50°C in *n*-Octane and stirred violently for 2 h. To avoid the oxidation of EPR, the sample was doped with 0.1 wt % of the antioxidant. The filtrate was obtained and was then precipitated and washed by acetone, dried in vacuum. The weight percentage of the fraction was used to characterize the content of random copolymer in the blends.[20] Secondly, the insoluble remaining samples was extracted at 105°C in a Kumagawa extractor by boiling *n*-Octane for 24 h, and the extract solution was concentrated and precipitated by ethanol, then washed and consequently dried in vacuum. The weight percentage of the fraction was used as a criterion of the content of block copolymer in the blends. The insoluble part was washed with *n*-octane and dried in vacuum. The weight percentage of soluble part was applied to the analysis of the propylene homopolymer in the blend. Here, the random copolymers, block copolymers and homopolymers separated from PEP20 are referred to as EPR20, E-b-P20, and PP20, respectively. Figure 1(a) gives the fractionation data of PP-cats through temperature rising elution fractionation.

FTIR measurements

An empirical equation proposed by Fan et al. was used for the evaluation of the ethylene content in copolymer and homopolymer based on the infrared spectrum:[11]

$$\ln A_{1150}/A_{720} = 2.98 - 0.060 \times C_2$$

in which C_2 is the molar percentage of ethylene in the polymer. The Fourier-transfer infrared spectra of the
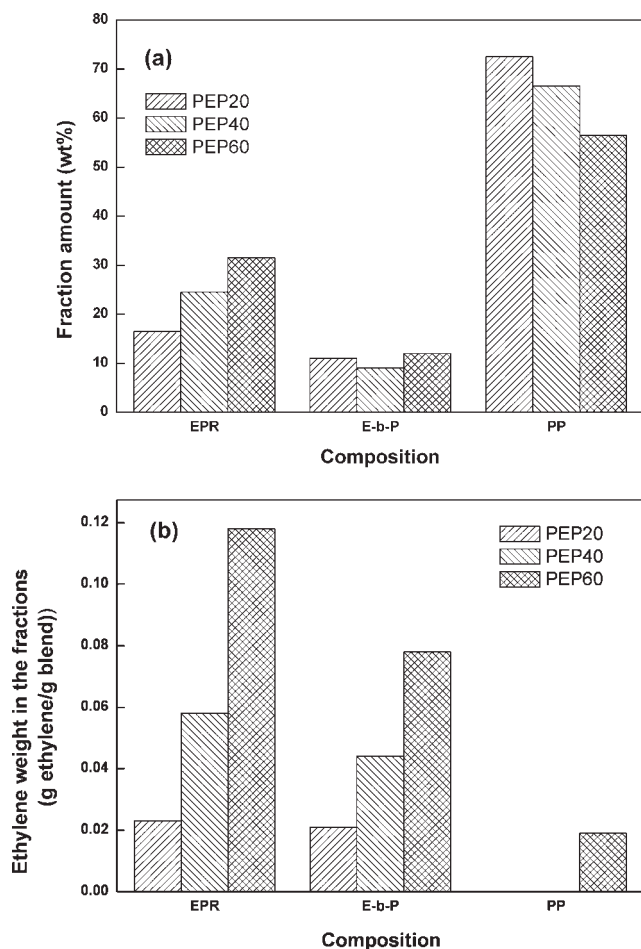
Figure 1 (a) The fractions distribution of PP-cats samples and (b) ethylene weights in the fractions.

thin hot-pressing sample films for these fractions were recorded on a Nicolet 5DX FTIR spectrometer. Figure 1(b) presents the calculated ethylene content of fractions.

The isotacticity of fractionated PP was also calculated from FTIR data using the equation

$$IIP = K \times A_{975}/A_{1460}$$

in which K is a constant relevant to apparatus. A_{975} and A_{1460} are the absorb peak area for isotactic helical segment and methyl, respectively.

GPC measurements

Weight-average molecular weight ($\overline{Mw}$) and polydispersity of molar mass for fractionated EPRs and PP were determined by gel permeation chromatography (GPC) at 150°C. The GPC system used is a PL-GPC220 equipped with three PLgel 10 mm MIXED-B columns using polystyrene as standards and 1,2,4-trichlorobenzene (1.0 mL min^{-1}) as the eluent. Table I lists the molecular weight and polydispersity data of EPRs and PP extracted from PP-cats.

Thermal analysis

The lower temperature thermal behavior was examined by using Q100 MDSC, with nitrogen as purge gas. Pure indium and zincum were used as reference materials to calibrate both the temperature scale and the melting enthalpy before the samples were tested. Before recording DSC thermograms, the PP-cats samples were heated to 200°C and held at this temperature for 3 min, and then quenched to −20°C. Samples were subsequently heated from −120°C to 200°C at 3°C/min and a modulation amplitude of (1°C with a period of 60 s). The midpoint of the slope change of the heat capacity plot was taken as the glass transition temperature (T_g). For the EPR fractions extracted from PP-cats, the experiments were conducted upon heating from −120 to 100°C at 5°C/min. For the PP fractions, the samples were heated to 200°C and held for 3 min and then quenched to −20°C. Subsequently, the samples were heated again from −120 to 200°C at 5°C/min to record the thermal behavior.

RESULTS AND DISCUSSION

Figure 1(a) presents the composition data of PP-cats obtained through fractionation. It is clear that in PP-cats both the content of propylene homopolymer and random copolymer is higher than block copolymer. It is noted that the block copolymer contents in three PP-cats samples are basically equal, but the random copolymer increases and propylene homopolymer decreases while the total ethylene content in PP-cats increases. These results imply that the PP-cats composition varies regularly in three different PP-cats. Since the block copolymer content is much lower than that of the random copolymer or propylene homopolymer, PP-cats can be regarded as a binary blend to some extent. Figure 1(b) gives the ethylene content of each component calculated from FTIR data. It can be found that the ethylene content in EPR rapidly increases from PEP20 to PEP60. Undoubtedly, these results mean that the more ethylene segments or longer ethylene segments exist in the EPR chain with the same weight. As a result, it is believed that there are obvious structure differences among the three EPR fractions. For the EP block copolymer, it is found that the ethylene content increases from PEP20 to PEP60. Similarly, there are more or longer ethylene segment in polymer chain in the copolymer with the same weight. In addition, it is interesting that there exist some ethylene segments in PP fraction extracted from PEP60. Hence, we suggest that some extra E-*b*-P could hardly be extracted at 105°C.

The molecular weight, polydispersity, and isotacicy of fractionated EPRs and PPs are listed in Table II. It can be found that the polydispersity of EPR in the three PP-cats is close and the molecular weight

	$\overline{M}_w(\times 10^{-4})$	$\overline{M}_w/\overline{M}_n$	Isotacticity (%)
PP20	7.93	2.31	96.0
PP40	8.35	1.83	95.8
PP60	9.32	1.64	96.0
EPR20	5.73	2.0	–
EPR40	6.23	2.1	–
EPR60	6.97	2.1	–

slightly increases from EPR20 to EPR60, indicating that the microstructures differences among EPRs can be ascribed to the molecular weight. On the other hand, the isotacticiy data of PP fractions is the same, with only some differences existing in the molecular weight and polydispersity of propylene homopolymer, meaning that the PP fractions have almost the same microstructure.

It is widely accepted that the presence of a single glass-transition temperature (T_g) intermediates between those of the compositions is usually an indication of full miscibility on a dimensional scale between 10 and 30 nm.[21,22] Figure 2 presents the typical DSC thermograms of PP-cats with different compositions. Two T_gs for PP-cats could be observed in Figure 2(a). Obviously, the higher T_g should be attributed to the propylene homopolymer and the other is EPR, in accordance with previous reports.[10,23] All PP-cats samples presenting two T_g show that it is difficult to observe glass-transition behavior of E-*b*-P, although the block copolymer has been confirmed as a third component in PP-cats. Taking the microstructure of E-*b*-P into account, it is believed that the difference of ethylene segment length in block copolymer fraction is a more important factor when the block copolymer content in PP-cats is low.

Figure 2(b) gives the melting trace of PP-cats. It can be found that a single melting peak exists in the vicinity of 160°C for PEP20 and PEP40 samples. However, For PEP60, two melting peaks can be found, one of which is at about 160°C, and the other, about 120°C. Certainly, the melting peak at about 160°C is attributable to propylene homopolymer, and the melting peak at about 120°C, to the melting of the polyethylene crystal. These results suggest that there probably exist some ethylene segment with enough length in PP-cats, which could crystallize independently. In the above analysis on polymer chain structure, we conclude that there exist some E-*b*-P with extra longer ethylene segments in PP fraction extracted from PEP60 sample, and as a result, the melting peak at 120°C for PP fraction should be attributed to the melting of PE crystal.

For PP/EPR blends, although all of them have been proved to be immiscible at molten state and most of them are also immiscible below the crystallization

temperature of PP, some miscible blends with special composition can be obtained through some methods at room temperature.[6,24] Moreover, the dispersion degree of dispersed phase in PP/EPR blends depends directly on the preparation methods of mixing samples.[1,2,24,25] Furthermore, it is suggested that the addition of a third polymer component such as diblock copolymer of propylene and PP-*b*-EPR could be in favor of improving the phase morphology and properties of PP/EPR blends, and the diblock copolymer act actually as the compatibilizer of binary blend.[4,10,26]

For immiscible and partially miscible blends, the change of T_g of each component could indicate certain interaction or partial miscibility to some degree between components.[3,4] The value of $\Delta T_g = T_{g2} - T_{g1}$ has usually been used as an indirect proof of evaluating the miscibility of blends. For PP-cats, the ΔT_g was defined as the T_g difference between EPR and PP. Figure 3 shows the dependence of ΔT_g on the composition of PP-cats. The value of ΔT_g decreases with the increase of EPR content in PP-cats, indicating that the
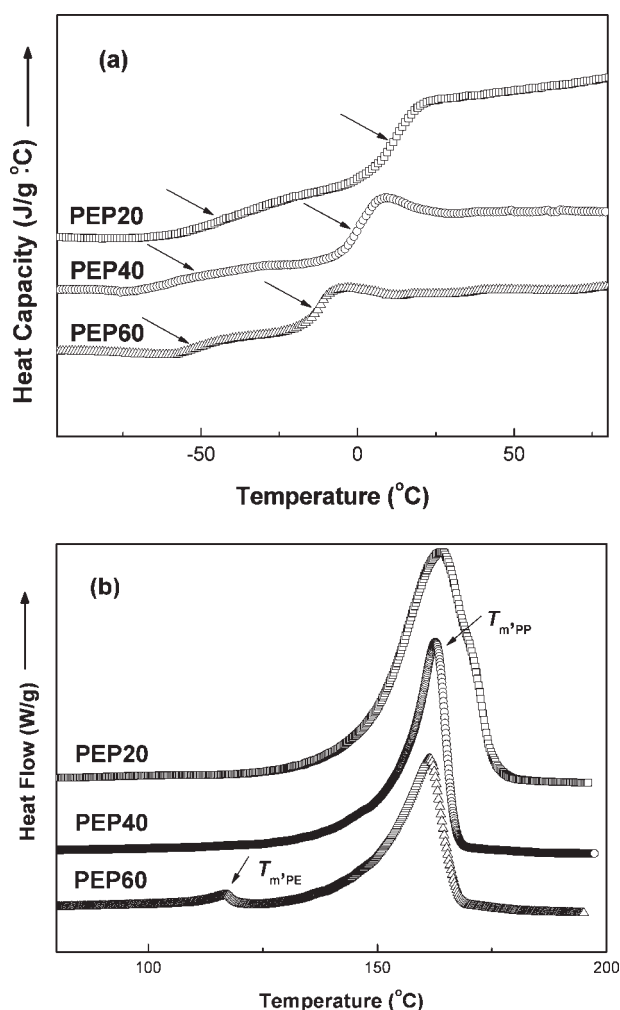

Figure 2 DSC traces of PP and PP-cats samples within the temperature ranges (a) −100 to 80°C, and (b) 80–200°C.
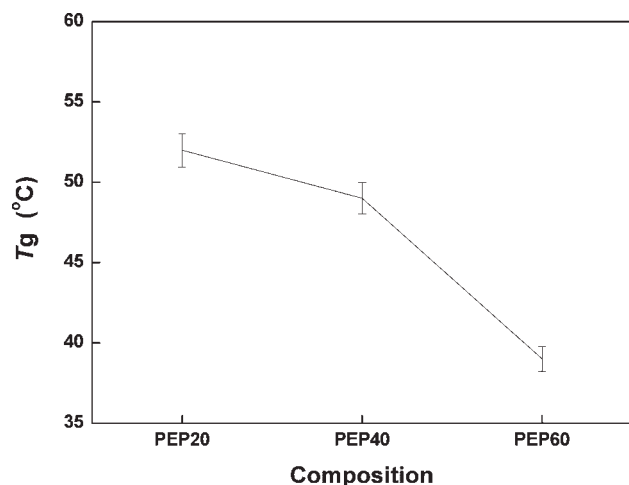
Figure 3 The effect of PP-cats composition on the ΔT_g.

Figure 4 The glass transition behavior of propylene homopolymer extracted from PP-cats.

propylene homopolymer and EPR may be immiscible or partially miscible in amorphous phase and the sample presents more miscible from PEP20 to PEP60.

It is well-known that the interaction between PP and EPR is considerably weak, and as a result, the variation of composition hardly affects the miscibility.[27,28] To explain these thermal behaviors of PP-cats, it is necessary to take their compositions into account. It can be seen from Figure 1 that, although the total weight fraction of E-*b*-P is near among three different PP-cats samples, the ethylene mol fraction is greatly different from one another. From PEP20, PEP40 to PEP60, the ethylene content of E-*b*-P markedly increases. According to reports by Lohse et al.[4] and by Nitta et al.,[24] the compatibility effects of the diblock copolymer were dependent on the chain structure and the molecular composition. Thus, we suggest that, as compared with the amount of E-*b*-P, its structure plays a more important role in affecting the miscibility of PP-cats. In other words, the miscibility of PP-cats samples is not only involved in the content of propylene homopolymer and EPR in PP-cats samples, the dominate factor seems the compatibilizing effect of the block copolymer in PP-cats.

It needs to be pointed out that both the differences of T_g and ΔT_g might result from the EPR chain structure, because in theory component structure can lead to the shifting of T_g and the decrease of ΔT_g. Moreover, it can also be seen from Figure 1 that the EPR fractions in the three PP-cats samples contain different ethylene content. To explain the exact reason for the different T_g and ΔT_g of PP-cats, Figures 4 and 5 gave the lower temperature DSC curves of propylene homopolymer and EPR, respectively. The extracted PP fractions present almost the same T_g, which is in accordance with the structure analysis of PP extracted from PP-cats. Table II lists the $\overline{M}_w$ and $\overline{M}_w/\overline{M}_n$ value of PP samples. For these PP fractions, both the differences of $\overline{M}_w$ and $\overline{M}_w/\overline{M}_n$ are little, implying that the
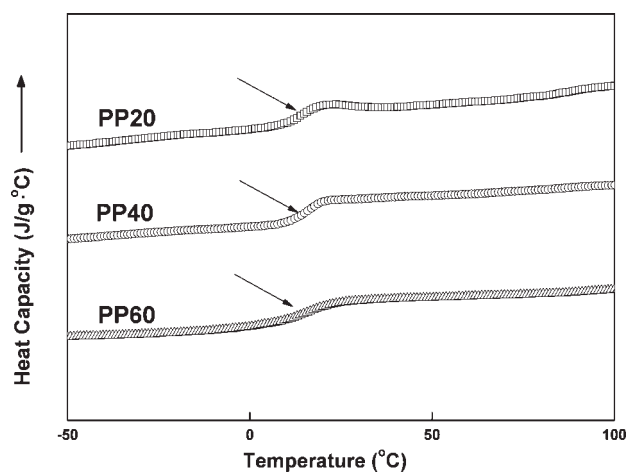
PP fraction of PP-cats have the same structure and the same glass transition behavior. Besides, as can be seen from Figure 5, the T_g of EPRs decreases with the increase of ethylene content in the fraction. Because of the better flexibility of ethylene segment than that of propylene segment, more and longer ethylene segments make EPR chain more flexible and easier to move. Considering the ethylene content difference in EPR chain, it could be understood that the EPR60 sample containing more ethylene unit presents lower T_g temperature. Meanwhile, these results support the above view that the T_g difference of EPR in Figure 5 results from the chain structure of EPRs.

Figure 6 gives a comparison of the T_gs between PP-cats with those of the corresponding compound extracted from PP-cats, and Table III lists the value of T_g and ΔT_g of fractions as well as those of PP-cats. Obviously, all T_gs of PP fraction are higher than the corresponding $T_{g, PP}$ in PP-cat. The more the ethylene
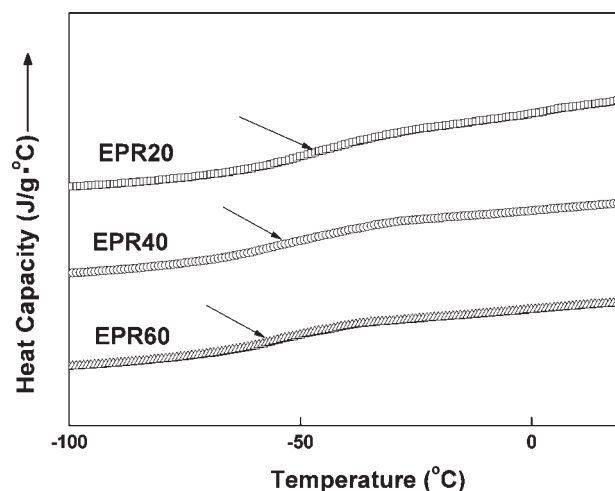

Figure 5 The glass transition behavior of ethylene-propylene random copolymer extracted from PP-cats.

content of PP-cats is, the greater the difference between $T_{g,\ PP}$ and PP fraction. Because the T_g of PP fraction is almost the same, the lower $T_{g,\ PP}$ in PP-cats is independent of the structure of PP fraction, but related to composition difference of the PP-cats. On the other hand, the T_g of EPR fractions is lower than the corresponding $T_{g,\ ERP}$ in PP-cats. These results
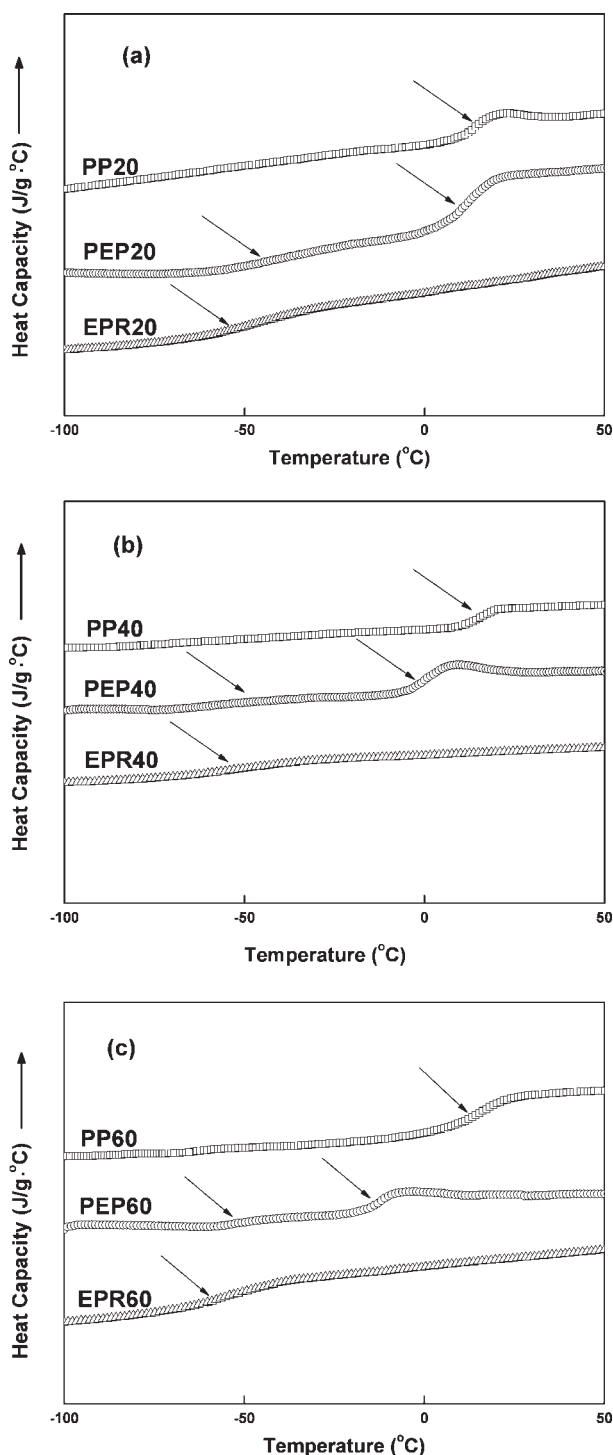
TABLE III
Thermal data for PP and PP-cats

Sample	T_g (°C)	T_g (°C)	ΔT_g (°C)	Crystallinity (%)
PEP20	−42	10	52	33
PP20	–	15	–	41
EPR20	−48	–	63[a]	–
PEP40	−48	1	49	29
PP40	–	13	–	42
EPR40	−52	–	65[a]	–
PEP60	−51	−13	38	26
PP60	–	12	–	41
EPR60	−57	–	69[a]	–

[a] The ΔT_g is the difference between T_g of EPR and PP extracted from the same PP-cats sample.

mean that the PP-cats composition affects the $T_{g,\ EPR}$. It is emphasized that the interaction between PP and EPR in PP/EPR binary blend is rather weak and the composition change could hardly affect the T_g. Hence, the change of $T_{g,\ EPR}$ should be attributed to the enhancement of the interaction between EPR and PP. The stronger interaction results in the existence of PP chain with less flexibility and affects the flexibility of EPR, leading to the increase of $T_{g,\ EPR}$ in PP-cats. Through composition analysis of PP-cats, we conclude that the block copolymer plays an important role in enhancing the interaction between EPR and PP, based on which the change of ΔT_g and miscibility of PP-cats can also be explained. According to free volume theory, as a kind of α-polyolefin, the flexibility of PP chain is lower than that of EPR, and PP has smaller free volume fraction and higher T_g. The increase of EPR content in PP-cats will increase the free volume fraction of the PP component in amorphous phase and result in the T_g depression of PP. On the other hand, as is seen from Figure 1, both the EPR content of PP-cats and the ethylene content of EPR obviously increase from PEP20 to PEP60. The increase of the ethylene content in EPR indicates that the increase of the ratio of ethylene segment may make the EPR chain more flexible and present lower T_g. In addition, the increase of the EPR content in PP-cats is in favor of the decrease of its T_g, and the unusual T_gs of PP-cats result from the structure of EPR and the compatibilizing effect of E-b-P.

Figure 6 Comparison of T_g between EPR fractions, PP fractions, and PP-cats, (a) PEP20, (b) PEP40 and (c) PEP60.

CONCLUSIONS

The thermal behavior and the miscibility of PP-cats have been investigated. All PP-cats samples present two glass transitions; one is ascribed to the EP random copolymer, and the other to propylene homopolymer. However, no glass transition of EP block copolymer which a third component in PP-cats is could be found. It is believed that, as compared with the low block copolymer content, different ethylene seg-

ment lengths in block copolymer fraction are the more important factor.

It has been found that the T_gs of PP-cats are dependent on the composition, and the $T_{g, PP}$ and $T_{g, EPR}$ shift to low temperature with the increase of ethylene content in PP-cats. Because the interaction between PP and EPR is rather weak in ordinary PP/EPR binary blends and the variation of composition could hardly result in the remarkable change of component's T_g, the existence of the E-*b*-P plays a more important role in enhancing the interaction between PP and EPR. Furthermore, the difference between $T_{g, PP}$ and $T_{g, EPR}$, ΔT_g decreases with the increase of total ethylene content in PP-cats. These results indicate that the miscibility of PP-cats is dependent on the composition.

Comparing the $T_{g, PP}$ and $T_{g, EPR}$ with T_g of fractionated PPs and EPRs, the T_g change of PP can be attributed to the increase of EPR content, and one of EPR is due to the increase of ethylene content in EPR. The experimental results have confirmed that the unusual T_gs of PP-cats result from the structure of EPR and the compatibilizing effect of the block copolymer. Moreover, the existence of EP block copolymer affects the miscibility between propylene homopolymer and the random copolymer.

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