Polymer Bulletin 43, 285–289 (1999)

Polymer Bulletin

Crystallization in blends of isotactic polypropylene with polyethylene-*b*-poly(ethylene-*co*-butylene)-*b*-polyethylene block copolymer

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Received: 19 May 1999/Revised version: 15 July 1999/Accepted: 19 July 1999

Abstract

In this study, isothermal crystallization in blends of isotactic polypropylene (i-PP) with polyethylene-*b*-poly(ethylene-*co*-butylene)-*b*-polyethylene block copolymer (CEBC) was investigated using a polarized photometer, polarized microscope and differential scanning calorimeter. Half time of crystallizaiton ($\tau_{1/2}$) is increasing with increasing CEBC content in i-PP/CEBC blends. Avrami index and rate constant of crystal growth decrease with increasing CEBC content in i-PP/CEBC blends. On the contrary, heat of fusion of i-PP crystal in the blends is almost constant against the variation of CEBC content in i-PP/CEBC blends. Hence, it is pointed out that blending i-PP with CEBC caused only retardation of rate of crystalline growth and change in mechanism of crystalline growth from three dimensional to two dimensional growth.

Introduction

In general, isotactic polypropyrene (i-PP) shows brittle fracture on impact stress due to relatively high glass transition temperature (1). Hence, modification of impact resistance for i-PP has been examined extensively (1, 2). Especially, blending i-PP with elastomer is one of the effective methods for impact modification.

Block copolymers containing rubbery segments have been mixed extensively with plastics to toughen the plastics (3-5). In general, phase morphology of polymer blends plays important role on mechanical properties in the system (3). Hence, it is thought that controlling the phase morphology has significant value to prepare the polymer blends having synergistic properties between each component. Especially, in polymer blends including crystalline component, it is considered that controlling the crystalline morphology, such as spherulite structure, of the blend is of great importance. Hence, studies on crystalline structure in blends of i-PP with rubbery polymers have been focused (1, 2, 6-8). Then, in this study, we investigate growth and morphological observation of spherulite in blends of i-PP and polyethylene-*b*-poly(ethylene-*co*-butene)-*b*-polyethylene block copolymer. (CEBC)

Experimental

Polymers used in this study were iso-polypropylene (i-PP, Toso Co., Ltd.) and polyethylene-b-poly(ethylene-co-butene)-b-polyethylene block copolymer (CEBC, ethylene content=40 wt%). Here, CEBC is trial products of JSR Co., Ltd. Weight averaged molecular weights of i-PP and CEBC were 2.5×10^5 and 3.0×10^5, respectively. Blends of i-PP and CEBC were prepared using a twin-screw type extruder. Blend samples were molten at 220°C and then quenched to constant crystallization temperature (T_c= 140°C). Isothermal crystallization processes of i-PP spherulite in i-PP/CEBC blends were measured using a polarized photometer (Kotaki Co., Ltd.). Figure 1 shows a result of measurement of

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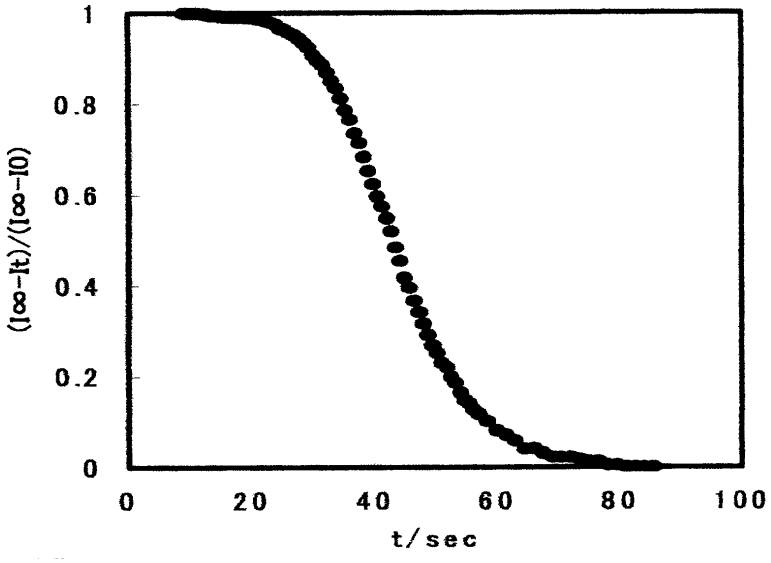

Figure 1 Measurements of isothermal crystallization for i-PP at 140℃ using a polarized photometer.

isothermal crystallization for i-PP using a polarized photometer. In Figure 1, I0, I∞, and It represent initial light intensity, saturated light intensity, and light intensity at time t in polarized photometer, respectively (9). For isothermally crystallized samples, morphological observations and thermal analysis were carried using a polarized optical microscope of a Nikon S-Ke optical microscope and differential scanning calorimeter (DSC) of a Du Pont 910 DSC, respectively.

Results and Discussion

Figure 2 shows Avrami plots for isothermally crystallization process of i-PP in i-PP/CEBC blends isothermally crystallized at 140°C. Since linear line is shifted to right hand side in the Figure 2 with increasing CEBC contents in i-PP/CEBC blends, rate of crystalline

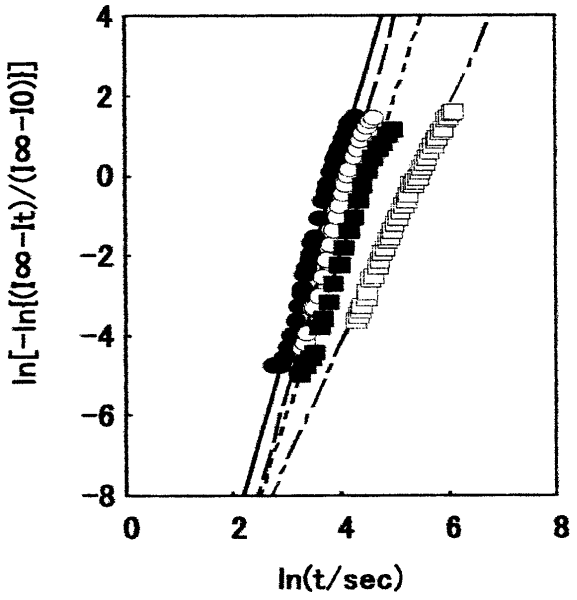

Figure 2 Avrami plots for i-PP/CEBC blends; ●: 100/0, ○: 90/10, ■: 80/20, □: 50/50 (wt/wt).

growth in i-PP/CEBC blends is decreasing with increasing CEBC contents in the blends. Further, slopes of linear line of the plots seem to be decreasing with increasing CEBC contents in i-PP/CEBC blends. Therefore, it is considered that mechanism of crystalline growth of i-PP is affected by existence of CEBC as a miscible impurity.

Avrami parameters are summarized in Table 1. Avrami index and rate constant of crystal growth tend to decrease with increasing CEBC content in i-PP/CEBC blends. Hence, it is

considered that mechanism of growth of spherulite of i-PP is affected by adding CEBC to i-PP. When Avrami index, n, =4, the system shows sporadic nucleation and three dimensional (spherical) growth (10). Further, when n=3 in the case of sporadic nucleation, crystalline structure grow two dimensional (circle) (10). Hence, in i-PP/CEBC blends, it is considered that mechanism of crystalline growth of i-PP is changed from three dimensional to two dimensional by increment of CEBC contents in the blends. In addition, half time of crystallization ($\tau_{1/2}$) is increasing with increasing CEBC content in i-PP/CEBC blends. It is considered that these results show blending i-PP with CEBC caused reduction of frequency of nucleation of i-PP crystalline.

Table 1 Avrami parameters of i-PP/CEBC blends crystallized at 140℃. n, k, and $\tau_{1/2}$ represent Avrami index, rate constant and half time of crystallization.

PP/CEBC(wt/wt)	n	k/sec^{-n}	$\tau_{1/2}$/sec
100/0	4.6	1.5×10^{-8}	430
90/10	4.6	3.1×10^{-9}	624
80/20	3.9	8.1×10^{-9}	856
50/50	2.9	3.3×10^{-9}	2160

Figure 3 shows plots of half time of crystallization ($\tau_{1/2}$) of i-PP/CEBC blends against blend composition. $\tau_{1/2}$ of i-PP/CEBC blends is monotonously increasing with increasing CEBC contents in the i-PP/CEBC blends. In general, it has been well known that the existence of miscible impurity causes retardation in rate of crystalline growth in a polymer blend. Therefore, it is considered that poly(ethylene-*co*-butene) block in CEBC is miscible or partial miscible with i-PP in molten state. Miscibility of blends of i-PP and poly(ethylene-*co*-butene) was investigated by Bates et. al. (11). According their results, miscibility between i-PP and poly(ethylene-*co*-butene) is enhanced with increasing butene contents in

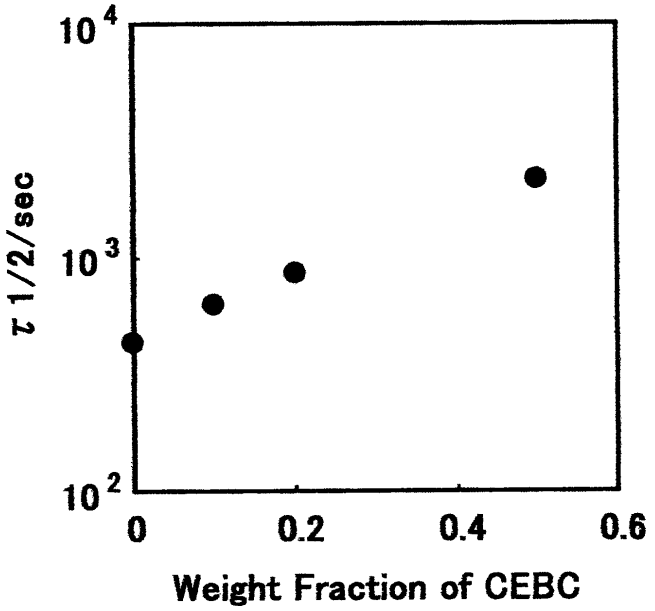

Figure 3 Compositional dependence of $\tau_{1/2}$ of i-PP in i-PP/CEBC blends isothermally crystallized at 140℃.

poly(ethylene-co-butene) and the blends are miscible in 80mol% of butene contents in

poly(ethylene-*co*-butene). Hence, it is reasonable that i-PP and poly(ethylene-*co*-butene) blocks of CEBC are partially miscible each other. Therefore, it is considered that a part of poly(ethylene-*co*-butene) blocks of CEBC play miscible impurity and cause retardation of spherulite growth of i-PP in i-PP/CEBC blends.

Figure 4 shows plots of heat of fusion (ΔH_f) of i-PP crystal in i-PP/CEBC blends crystallized at 140°C. The ΔH_fs were estimated from DSC thermograms. Each ΔH_f was calculated for unit weight of i-PP. The ΔH_f of i-PP crystal of i-PP/CEBC blends is almost constant against the variation of CEBC contents in the blends. ΔH_fs were the values per unit i-PP weight. Hence, it is considered that degree of crystallization of i-PP in i-PP/CEBC blends is almost constant against variation of blend composition. Thus existence of CEBC in i-PP/CEBC blends has no effects on degree of crystallization of i-PP. Therefore, it is considered that existence of CEBC in i-PP have significant effects on mechanism of growth of spherulite and have little effect on degree of crystallinity.

Figure 5 shows polarized optical micrographs for i-PP/CEBC blends isothermally crystallized at 140°C. The size of spherulite of the i-PP/CEBC blend is increasing with increasing CEBC contents in the blends. As shown in Table 1, it is considered that mechanism of nucleation of i-PP in the blends are invariant by blending with CEBC. Therefore, the number of nuclear of the i-PP crystals are decreasing with increasing CEBC contents since frequency of nucleation in i-PP is constant in both pure i-PP and i-PP/CEBC blends. Then, it is considered that growth of spherulites of i-PP is prevented by another crystal growth of i-PP since there are a lot of nuclear in pure i-PP. On the contrary, in i-PP/CEBC blends, growth of spherulites of i-PP is not prevented since the distance between nuclear is longer to growth large spherulite in i-PP/.CEBC blends than pure i-PP.

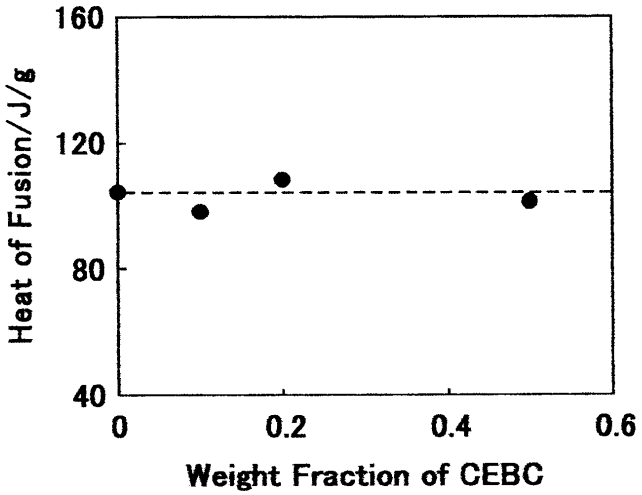

Figure 4 Compositional dependence of heat of fusion of i-PP crystal in i-PP/CEBC blends isothermally crystallized at 140℃.

Conclusion

Crystallization of i-PP in i-PP/CEBC blends is investigated. Degree of crystallinity is almost constant with variation of blend composition. However, rate of growth of spherulites of i-PP is retarded and manner of crystallization are changed from three dimensional to two dimensional due to existence of CEBC. Therefore, it is considered that existence of miscible impurity causes retardation of crystalline growth and linear growth of spherulite.

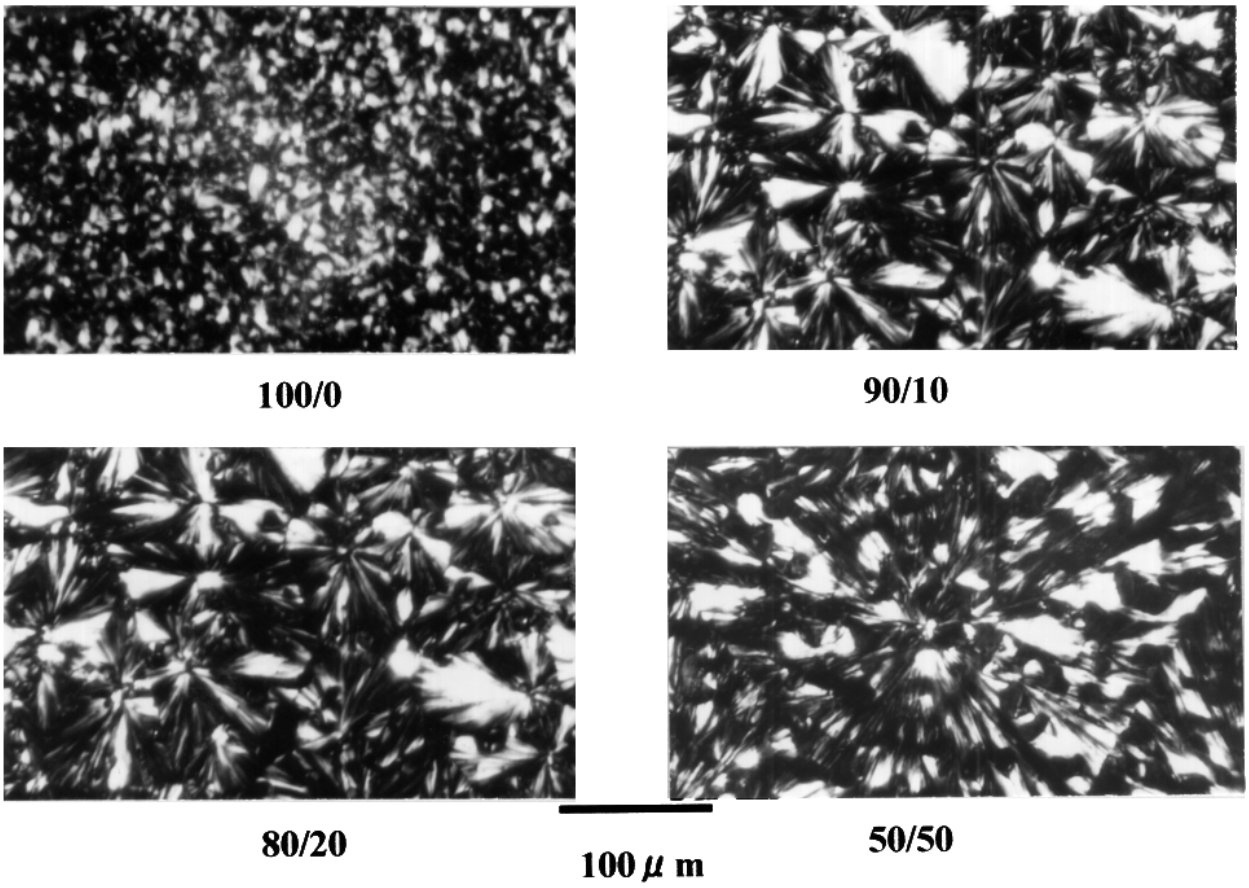

Figure 5 Polarized optical micrographs for i-PP/CEBC blends isothermally crystallized at 140℃.

Acknowledgement

The authors wish to thank to Dr. S. Kawahara and Dr. S. Izawa for their helpful discussions. The authors also thank to Mr. K. Ishikawa of JSR Co., Ltd. for providing CEBC samples. We got the financial support on this work from JSR Co., Ltd.

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