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Enhanced Crystallization of Blended Poly(ethylene terephthalate) and Poly(butylene terephthalate)

By Katsuya ITO,[1,*] Yuki HARAGUCHI,[1] Shota HAYAKAWA,[1] and Akihiko TODA[2]

We have studied the crystallization of blended poly(ethylene terephthalate) (PET) and poly(butylene terephthalate) (PBT). The effect of transesterification in the blend on crystallization has been examined by thermal analysis and optical microscopy. At higher temperatures above 200 °C, the crystallization of one of the component (PBT) was enhanced by the existence of the crystals of another component (PET) for the intermediate degree of transesterification. The results indicate the importance of the details of the transesterification at molecular scale.

KEY WORDS: Poly(ethylene terephthalate) / Poly(butylene terephthalate) / Differential Scanning Calorimetry / Crystallization / Transesterification /

Poly(ethylene terephthalate) (PET) is a synthetic polymer widely used for fibers, films, bottles, injection-molded parts and other products. PET blending with other polyesters is of great scientific and industrial interest for obtaining new desirable property combinations without having to synthesize novel structures. Poly(ethylene-2,6-naphthalate),[1–5] polycarbonate[6] and ethylene-acrylic acid copolymer[7] have been examined as blending polymers to improve the mechanical properties or gas permeability of PET. Poly(butylene terephthalate) (PBT) has also been studied as a blend polymer because of its softer mechanical property and faster crystallization than PET.[8,9] PET and PBT are miscible with each other and reactive by transesterification between the components.[10–12] The process of transesterification has been examined by Fakirov et al.[10] Backson et al.[11] and Matsuda et al.[12] also studied the reaction by using NMR.

The aim of this study is to analyze the crystallization process of the blend of PET/PBT by thermal analysis and by optical microscopy. It is known that PET and PBT crystallize separately in the miscible blend of PET/PBT.[13] It has also been reported that the crystallization of PET component is enhanced in the blend.[13,14] We examine the enhancement of crystallization behaviors of PET and PBT in the blend under the influence of different degrees of the reactive transesterification.

EXPERIMENTAL

Sample Preparation

PET and PBT used for extruded films have intrinsic viscosities of 0.62 and 1.20 dl/g. PET was melted by a single screw extruder (60 mmφ screw diameter) at 285 °C. PBT and two kinds of PET/PBT blended film (1/1 weight ratio) were prepared by the extruder at temperatures of 260 °C (PBT), 260 and 295 °C (EB260, EB295), respectively, at the residence time

of 4 min. The melted polymer was molded into sheets on metal drum at 30 °C. The thickness are 100–150 μm.

Blended film was also made by solution casting (EBsol). Solutions of PET and PBT were prepared in phenol/tetra-chloroethane of 6/4 (w/w), such that the total concentration of polymer was 5% (w/v) at room temperature. EBsol film of approximately 80 μm in thickness was obtained after the evaporation of solution at 23 °C.

Measurement

Thermal behavior was examined by differential scanning calorimetry (TA Instrument, DSC Q100). Measurements were done by constant cooling and under isothermal conditions. The cooling rate was 5, 20 and 40 °C/min after holding 1 min at 280 °C. The isothermal condition was achieved by the cooling rate of 60 °C/min after holding 1 min at 280 °C. The crystallization process was also observed on a hot stage (LINKAM; model TH-600PH) at a cooling rate of 10 °C/min by optical microscopy.

RESULTS AND DISCUSSION

Figure 1 shows the DSC thermograms at the cooling rates of 20 °C/min. It is seen that the exothermic peaks of crystallization appear at higher temperatures in the order of EB260 (192 °C), EBsol (178 °C), and EB295 (153 °C). It means that the crystallization rate of EB260 was the fastest and that of EB295 was the slowest. It is well known that PET and PBT crystallized separately from the miscible blend.[13] Therefore, the exothermic peaks must be composed of independent peaks of crystallization of PET and PBT.

In EB260 and EBsol, the degree of copolymerization by transesterification will be much smaller than that of EB295, and that of EBsol will be at the smallest due to lower mixing temperature in solution. Therefore, the difference between

[1] Toyobo Co., Ltd. Research Center, 2-1-1 Katata, Otsu 520-0292, Japan
[2] Graduate School of Integrated Arts and Sciences, Hiroshima University, Higashi-Hiroshima 739-8521, Japan
*To whom correspondence should be addressed (Tel: +81-77-571-0061, Fax: +81-77-571-0065, E-mail: katsuya_ito@toyobo.jp).
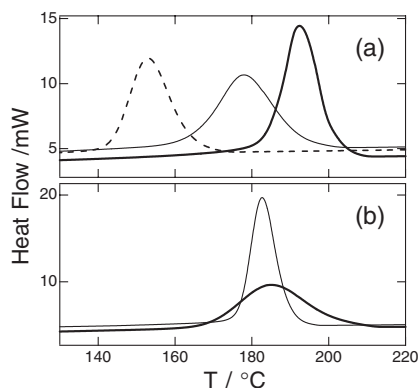
Figure 1. DSC thermograms of exothermic heat flow on crystallization by constant cooling at the rate of 20 °C/min.

Figure 2. Plots of the apparent crystallinity against temperature. Cooling rates are (a) 5 °C/min, (b) 20 °C/min and (c) 40 °C/min. Symbols represent pure PET (●), pure PBT (▲), EB260 (○), EBsol (□), and EB295 (■).

EBsol and EB295 in the crystallization behavior can be reasonably attributed to the effects of copolymerization by transesterification. The exothermic peak temperature of EBsol is lower than those of pure PET (185 °C) and PBT (183 °C), as seen in the comparison of Figure 1. This lowering of the crystallization for EBsol will be simply explained by the dilution effect of mixing, so that the crystallization of each component needs molecular segregation from the mixture.[13] On the other hand, the total crystallization rate of EB260 was faster in comparison with pure PET and PBT. The fastest growth of EB260 needs some special mechanism of acceleration by copolymerization of transesterification.

Figure 2 shows the apparent crystallinity representing the integrated heat flow plotted against temperature at the cooling rate of 5, 20 and 40 °C/min. In this plot again, we can confirm faster crystallization of EB260 in comparison with pure PET and PBT especially for faster heating. The crystallization of EBsol, on the other hand, is slower, indicating the dilution effect.

For the examined samples of pure PET and PBT, as seen in Figures 1 and 2, the nucleation of pure PET crystals begins at higher temperature than that of pure PBT probably because of the higher melting point of pure PET, inducing larger supercooling for PET. On the other hand, the growth rate of pure PET crystals becomes slower than that of pure PBT, as typically indicated by the longer completion time of pure PET than pure PBT by fast heating at lower temperatures in Figure 2c.

For the miscible blend of PET/PBT, there have been two different suggestions of the acceleration mechanism of the slower PET crystallization in the blend. Firstly, Escala and Stein[13] have reported that the crystallization of PET becomes faster and that of PBT becomes slower at lower temperature near the glass transition due to the change in the glass transition temperature, T_g, in the miscible blend; T_g of PBT is at 30 °C and that of PET is at 69 °C and the blend has T_g in between the T_g of PET and PBT. Due to the monotonous shift of T_g between 30 and 69 °C, the medium becomes softer for PET molecules and harder for PBT. Near the glass transition at lower temperatures, it is known that the crystallization kinetics is dominated
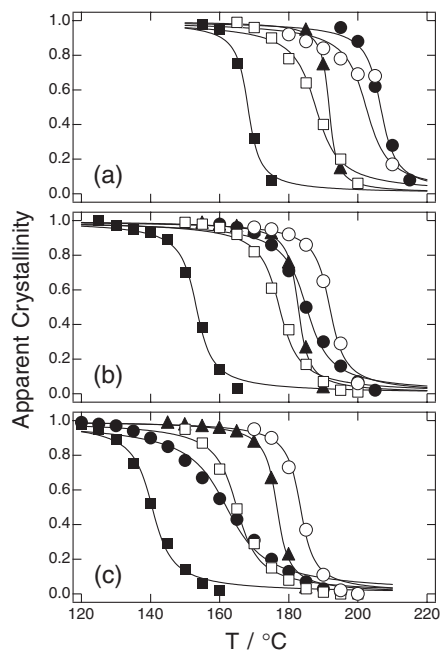
by the mobility of chains, and hence PET can crystallize faster and PBT slower in the blend due to the shift of T_g.

On the other hand, Misra and Carg[14] suggested a mechanism of built-in nucleation sites for the crystallization of PET by the preexisting crystals of PBT at the crystallization temperature of 95 °C which is also near T_g. They have confirmed the effect of enhanced crystallization for the block copolymer of PET/PBT, while the effect disappeared for the random copolymer of them, indicating the important role of the crystal block of PBT not being the simple mixture of PET and PBT molecules.

In the present experiments, the blend of EB260 with slight copolymerization by transesterification has faster crystallization rate in comparison with pure PET and PBT. The faster growth was confirmed for faster cooling, and hence at lower temperatures, so that the results will be in agreement with the prediction of those suggestions of the acceleration of PET crystallization by PBT crystals. However, the crystallization of EB260 was even faster than that of PBT, indicating the enhancement of PBT crystallization in EB260. At higher temperatures, it is clearly seen that the nucleation of PET takes place at higher temperature than that of PBT, so that the inverse acceleration of PBT crystallization by PET crystals may also be possible at higher temperatures. In order to examine the possibility, we have conducted the isothermal crystallization measurements at higher crystallization temperatures in the following.

Figure 3 shows the typical examples of the exothermic heat flow on isothermal crystallization of EB260, EBsol, and EB295 blends. In Figure 3a for EB260, two crystallization peaks are recognized. Though only single peak is observed for EBsol in
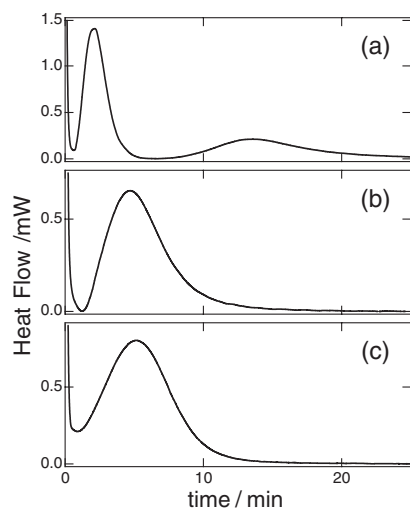
Figure 3. DSC thermograms of the exothermic heat flow on isothermal crystallization of (a) EB260, (b) EBsol, and (c) EB295 at 215, 215 and 180 °C, respectively.
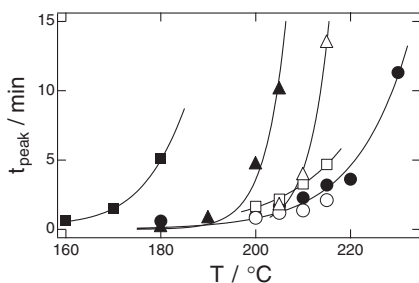

Figure 4. Plots of the peak time of exothermic heat flow on isothermal crystallization against crystallization temperature. Symbols represent pure PET (●), pure PBT (▲), 1st EB260 (○), 2nd EB260 (△), EBsol (□), and EB295 (■).

Figure 5. 80 × 130 μm² optical micrographs of the crystallization processes of (a) and (b) EB260, (c) and (d) EBsol, and (e) and (f) EB295 by constant cooling at 10 °C/min.

Figure 3b within the examined time interval, there was one more exothermic peak by a subsequent cooling. For EB295, only single peak was observed at much slower crystallization rate only at much lower temperatures. Figure 4 shows the peak times of crystallization for EB260, EBsol, and EB295 blends in comparison with those of pure PET and PBT. By the comparison, it will be clearly seen that the first peak in EB260 corresponds to the crystallization of PET and the second one will be that of PBT. The peak time in EBsol will also be of the crystallization of PET. The difference between the peak time of pure PET, and the 1st peak of EB260 may be within the experimental error due to the uncertainty of the starting time of isothermal crystallization by DSC of heat flux type. The peak time of EBsol is slightly delayed probably due to the dilution effect. In terms of the crystallization peak of PBT in EB260, the acceleration of crystallization is evidently seen in comparison with pure PBT in Figure 4 at such high temperatures above 200 °C. On the other hand, the crystallization of PBT in EBsol is delayed by the dilution effect in the blend and could not be observed by the isothermal runs. For well-reacted blend of EB295, there was only single exothermic peak, indicating
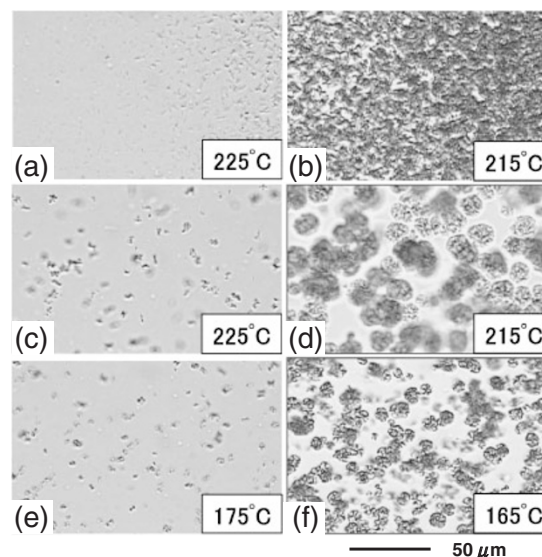
co-crystallization due to more random copolymerization of PET and PBT by the mixing at higher temperature (295 °C).

Figure 5 shows the optical micrographs of the cooling process of blended polyesters at the rate of 10 °C/min. On cooling, small crystallites began to appear at 225 °C with EB260 and EBsol, and at 175 °C with EB295. Large number of small nuclei of PET is formed in EB260, and seems to assist the crystallization of PBT. The formation of nuclei of PET became less and slow in EBsol, and the difference in the total crystallinity between EB260 and EBsol will be clearly seen as the difference in the number and the size of the spherulites at 215 °C. On the other hand, the nucleation and growth in EB295 was extremely retarded.

Those behaviors at higher temperatures strongly suggest the acceleration of PBT crystallization by the existence of PET crystals for the intermediate degree of copolymerization by transesterification of EB260. For the smallest copolymerization of EBsol, such enhancement of crystallization has not been observed, and the result is in accordance with the reported dilution effect by the mixing.[13] The crystallization of EB295 was severely delayed by the largest copolymerization. In terms of the acceleration of crystallization in EB260, the role of PBT and PET in our results is reversed, when compared with the previous reports[13,14] which were mainly on the crystallization at lower temperatures. Even though the reversed relationship, the results also suggest the important role of transesterification in the miscible blend for the acceleration mechanism of crystallization in comparison with the simple mixing in EBsol. The transesterification initially promotes the copolymerization in blocks, and further reaction results in the randomization of the copolymer.[12] We suppose that certain length of blocks will be required for the crystallization of each block, so that this reaction process may be the reason for the existence of the maximum enhancement of crystallization in the reactive blend

at a certain degree of copolymerization. For the better understanding of the effects of transesterification on crystallization, it will be important to determine the degree of transesterification and the average length of the sequence estimated by blockness. The quantitative analysis of the transesterification will be the subject of our future work.

CONCLUSION

We have examined the crystallization behaviors of miscible blends of PET/PBT with different degree of copolymerization by transesterification. Thermal analysis of cooling experiments has shown that the crystallization is enhanced by the copolymerization of the intermediate degree. Under isothermal condition at higher temperatures (>200 °C), it is confirmed that PET crystallizes first and then the crystallization rate of PBT is enhanced by the existence of PET crystals in the blend of the intermediate degree of copolymerization. We have suggested the role of transesterification in blocks for the enhanced crystallization of one of the components with the existence of the crystals of another component. The optical microscopic observation confirmed the results of thermal analysis.

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