



MORPHOLOGY EVOLUTION OF PBT/PC BLENDS:

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ABSTRACT

Morphology evolution of melt mixing of Polycarbonate/Poly(buthylene terephthalate) (PC/PBT) have been investigated. PC and PBT were mixing in a twin screw extruder prior to injection moulding. Compositions of PC/PBT blends were prepared vis. 10/90, 30/70, 50/50, 70/30 and 90/10 wt/wt. SEM was applied to observe the change of morphology before and after injection moulding. There is dispersed particle size increase at composition of PBT-rich as well as PC-rich. Co-continuous morphology was provided by PBT/PC 50/50 blend. The change of morphology indicates that phase separation takes place during injection process. As comparison, it was also investigated PC/PBT blends prepared by directly melt mixing in injection moulding.

Keywords: Poly(buthylene terephthalate), Polycarbonate, blend, morphology, phase separation.

INTRODUCTION

Melt mixing of PBT/PC has been studied many researchers for different manners [1-13]. During melt mixing of PBT and PC exchange reaction can take place. The exchange reaction, well known as transesterification, being dependent on the reaction time and temperature, induces copolyester formation influencing the compatibility of PBT and PC [1-6]. Thermal study using DSC is the most popular way to investigate compatibility of polymer blends. Even miscibility PC/PBT blend is still controversially, partial miscibility has been generally found in the melt blends [2 4, 6 12].

In molten state PC/PBT blends was miscible, but phase separation and crystallization of PBT-component was taking place on cooling [7,8]. PBT being well recognized having high rate crystallization can influence phase structure of the blends. For example, PBT/PC 50/50 having lower critical solution temperature (LCST) with the spinodal temperature of 198°C can initiate forming homogeneous phase mixture during cooling, but higher rate crystallization of PBT inhibit the

homogeneous phase and despite some retardation due to the presence of phase-mixed PC. Because of those, many researchers interested to investigate crystallization of the blends using such as thermal analysis, infrared, and/or X-ray [6-13].

When melt blending two immiscible homopolymers or random copolymers in mixing equipment, one encounters many types of blend morphology, such as co-continuous morphology and dispersed morphology. These morphologies can be seen as droplets, fibrils, strands, blades and lamellae. Since the morphology of polymer blends can affect many of physical and mechanical properties, it is of great importance to know how these complicated morphologies are formed in situ and can be controlled during compounding. However, work on morphology development during the mixing process has been reported by very few authors and the evolution of morphologies during compounding process has not been fully explained. The nature of co-continuity, phase inversion and morphology evolution after melt blending or after re-melt

blending in twin-screw extruders is quite limited. The effect of polymer/polymer blending in injection moulding machines on morphology development is also unknown. This study carried out an experimental investigation on the evolution of blend morphology, using SEM, during melt blending of PC/PBT in a twin-screw extruder and in an injection moulding machine. For the investigation, five compositions of PC/PBT were selected.

Moreover, miscibility and morphology of PC/PBT blends strongly depend on preparation method, mixing time and temperature [11]. Then, authors performed blending PC and PBT over two different preparation methods. Regular procedure of melt mixing polymers, then mentioned as method-1, involves sequentially two processes i.e. extruding and injection moulding. Second process involves reheating the blends in injection moulding machine at certain temperature. Reheating process in injection moulding can be considered as annealing. Most publications deal with investigating the polymer blends only after injection moulding. No work to author's knowledge has been investigated phase structure and morphology of PC/PBT blend at intermediate product (after extrusion) and compared to the final product, after injection moulding. Hence, this paper discusses the change of morphology. As comparison, morphology of PBT/PC blends prepared by directly melt mixed in injection moulding (method-2) is investigated as well.

EXPERIMENTAL

Materials

Materials used to study are Polycarbonate (PC) under trade name Kotex grade K-30 obtained from Kotec Japan and Poly(buthylene therephthalate), PBT, under trade name Lupox grade GP-1000 obtained from LG Chemical Korea. The densities are 1.1977 and 1.2991 gr/cc for PC and PBT respectively, measured under ultrapycnometer 1000 version 2.2 (Quantachrome corp.). The glass transition temperature values are 50°C and 146°C for PBT and PC respectively.

Process

Compositions of PBT/PC blends were 10/90, 30/70, 50/50, 70/30 and 90/10 of weight%. Injection moulding type 50M-Boy was employed. There was no addition of transesterification inhibitor

and/or catalyst during melt processing. The polymers were dried at air circulating oven at 100°C at least 24 hours prior to melt mix. Two different preparation method of melt mixing polymers were performed. Method-1, melt mixing was conducted in twin screw extruder (Haake Rheocord 9000) with barrel temperature at 235–250°C and a screw speed at 50 rpm. The strand extrudates were immediately quenched in water then granulated. After dried the granulated plastics were injection moulded at 240–250°C for all compositions except 10/90 (at 250–270°C) due to high melt flow index of PC. Method-2, PBT and PC were melt mixing directly in injection molding at an elevated temperatures. Barrel temperatures are 270–280°C for all composition except for 10/90 (245–255°C) in order to avoid thermal degradation of PBT component due to excessive transesterification.

Scanning Electron Microscopy

Morphology of PC/PBT blends was investigated using SEM (Philips XL-40). Samples were fractured after immersing in liquid nitrogen over night, and then stained using DETA (Diethylene triamine, purity 99%, obtained from Aldrich) for 5 minutes to remove PC component. Washing in water was immediately conducted to release DETA and followed by drying in air circulating oven at 40°C for 5 hours. The samples, then, were sputter coated using gold for 170 seconds.

Result and discussion

Morphologies of strand extrudates of PBT/PC blends are shown in figure 1(a) to figure 1(e). Meanwhile, morphologies of the blends after injection moulding are exhibited in figure 1(f) to figure 1(j). The PBT/PC 10/90 blend shows a dispersed PBT phase structure (figure 1(a)). It is similar with early reported by Bennekorn et al. [1997]. They measured diameter of the dispersed particles of about 0.1–0.2 μm using TEM. There is no clear boundary between the dispersed PBT particles and the PC phase matrix. It indicates that the blend is having good adhesion. Figure 1(f) exhibits that after injection moulding, particles size of the dispersed PBT increases. It indicates that phase separation takes place. PBT particles were dispersed in form of flakes rather than spherical particles. It is probably due to high melt viscosity of PC causing difficulty of PBT-minor movement.

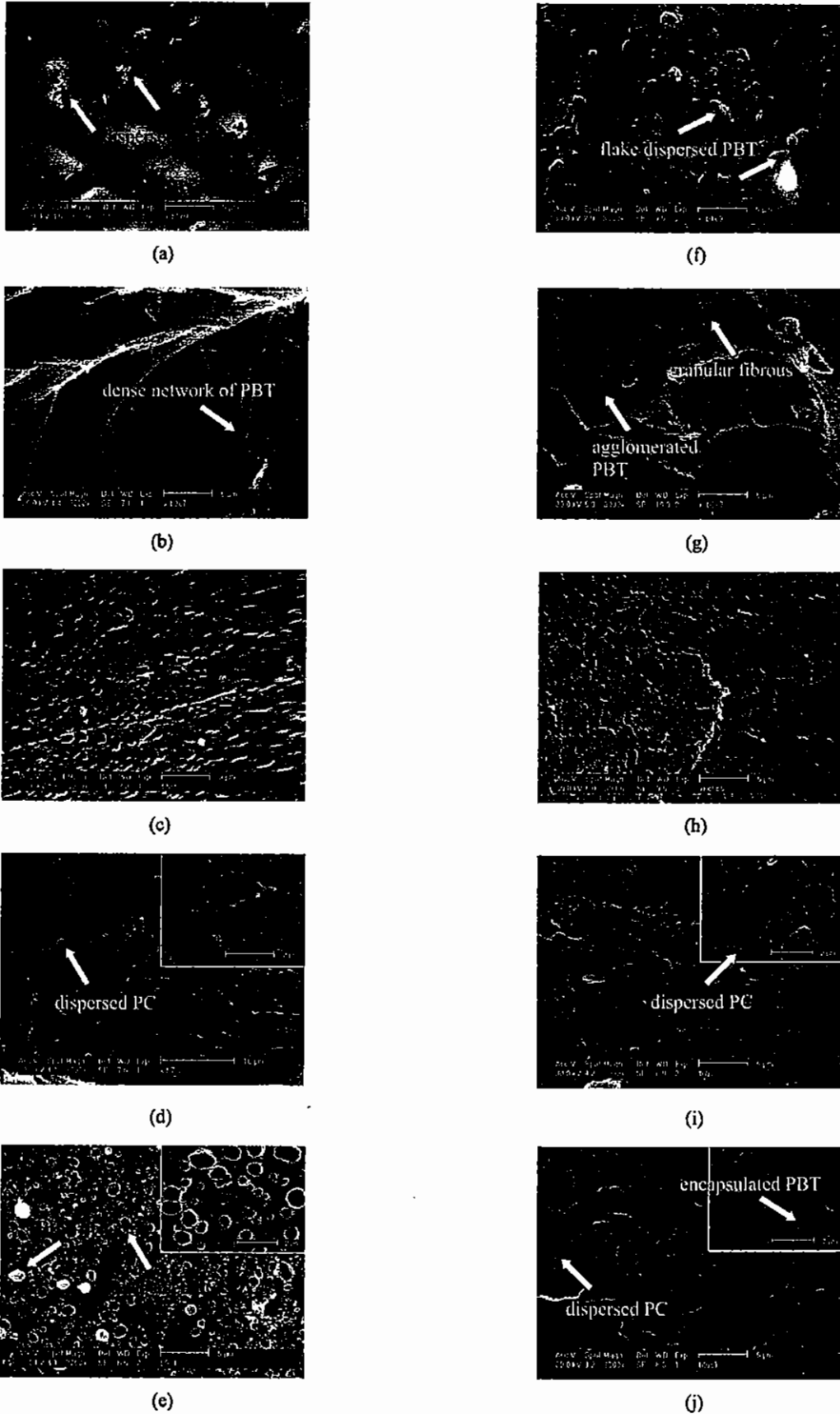


Figure 1. SEM photographic of the PBT/PC blends as quenched into water after extruding (left) and after injection moulding (right). Compositions of PBT/PC are (a) (f) 10/90, (b) (g) 30/70, (c) (h) 50/50, (d) (i) 70/30 and (e) (j) 90/10.

Shearing deformation applied from the screw leads to formation of long dispersed PBT. Since it release the deformation, the dispersed PBT reforms to be flake.

Addition of 30wt% PBT into PC-matrix produced a blend that has phase structure of PBT-rich in the form of a dense network, figure 1(b). This morphology conforms to Delimoy et al. [1995]. According to Bennekorn [1997] the average particle size of the dense network was about 0.1–0.3 μm . Injection moulding changed the fine dense network phase structure of PBT-rich phase to be agglomerated, as shown in figure 1(g). The agglomeration indicates that phase separation takes place induced by crystallisation of PBT-rich.

Co-continuous morphology is clearly shown by the PBT/PC (50/50) blend after injection moulding as shown in figure 1(h). Prior to injection moulding, phase structure of the blend show network formation as shown in figure 1(c). The co-continuous phase structure should be reached at this composition as reported by many researchers. The network formation is due to uncompleted phase separation during melt mixing in the extruder and fast quenching in water. Injection moulding followed by cooling process in the mould facilitates phase separation. As a result, co-continuous morphology is developed. The co-continuous morphology was well described by previous researchers such as Bennekorn et al. [1997] and Delimoy et al. [1995]. Morphologies of the PBT/PC 70/30 and 90/10 blend are displayed in figure 1(d) and figure 1(e) respectively. PC particles are finely dispersed in PBT-phase with a broad size distribution. Spherical dispersed particles are clearly shown by the blend at low PC content rather than of low PBT content. This is due to that solubility of PC in PBT is higher than of PBT in PC [Bennekorn et al., 1997 and Delimoy et al., 1995]. After injection moulding, there is no change of morphology of the blends. However, the dispersed particles size significantly increases, especially at 70/30 composition as shown in figure 1(i).

From the changes of the phase structure as well as of the increase of dispersed particles size, injection moulding is postulated to facilitate phase separation of the PBT/PC blends especially when melt mixing of PBT and PC is performed without any catalyst and/or transesterification inhibitor. It is well known that addition of any catalyst into PBT/PC blend is aimed to enhance transesterification in order to get copolymer phases.

As a result, miscibility of the PBT/PC blend is increased. In contrast, addition of any transesterification inhibitor is aimed to hinder excessive transesterification, due to presence of any residual catalyst. Then, the residual catalyst will lead to degradation of PBT [Montaudou et al. 1993]. Whether PBT/PC blend is performed either with or without any catalyst/inhibitor, injection moulding should change phase structure of the blends. It is due to injection moulding remixing and reheating the blend. In the best of our knowledge, most researchers did not take intention toward this change of morphology.

Figure 2 displays SEM photographic of PBT/PC blends performed by directly melt mixing in injection moulding (method-2). At low PBT content (10wt %), the blend appears inhomogeneous as shown in figure 2(a). The ravines formation show PC-neat phases, while the walls formation shows presence of phase-mixed PBT. In the phase-mixed, it can be seen that PBT particles are dispersed in the PC-rich system. Addition of 30wt% PBT content into PC phase system produced the blend with fibrous network, figure 2(b). This indicates crystallized PBT content. The fibrous network is a result of uncompleted mixing process, because of insufficient time and difficulty of PBT to dissolve in PC matrix as well as crystallisation of PBT content. Increasing PBT content further will lead to increase fibres size.

It is not similar to the PBT/PC 50/50 blend prepared by method-1; the blend performed directly by melt mixing in injection moulding can not form the co-continuous morphology. Figure 2(c) displays network formation rather than co-continuous morphology of PBT. The developed morphology is probably due to limited time for mixing in the single plasticizing screw during injection moulding and inhomogeneous distribution of its constituents. Difficulty of PBT to dissolve in PC is perhaps to be the most acceptable reason. Look at the PBT/PC blend with low PC content. The blend performed directly by melt mixing in injection moulding results the PC particles dispersed finely into PBT matrix (figure 2(e)). The disperse morphology with a broad size distribution is due to melt mixing condition in injection moulding. Agglomeration as shown in the inserted picture for high magnification indicates the crystallized PBT content. Figure 2(d) exhibits that particles size of the dispersed PC in the PBT/PC 70/30 blend is large due to mixing at low rpm.

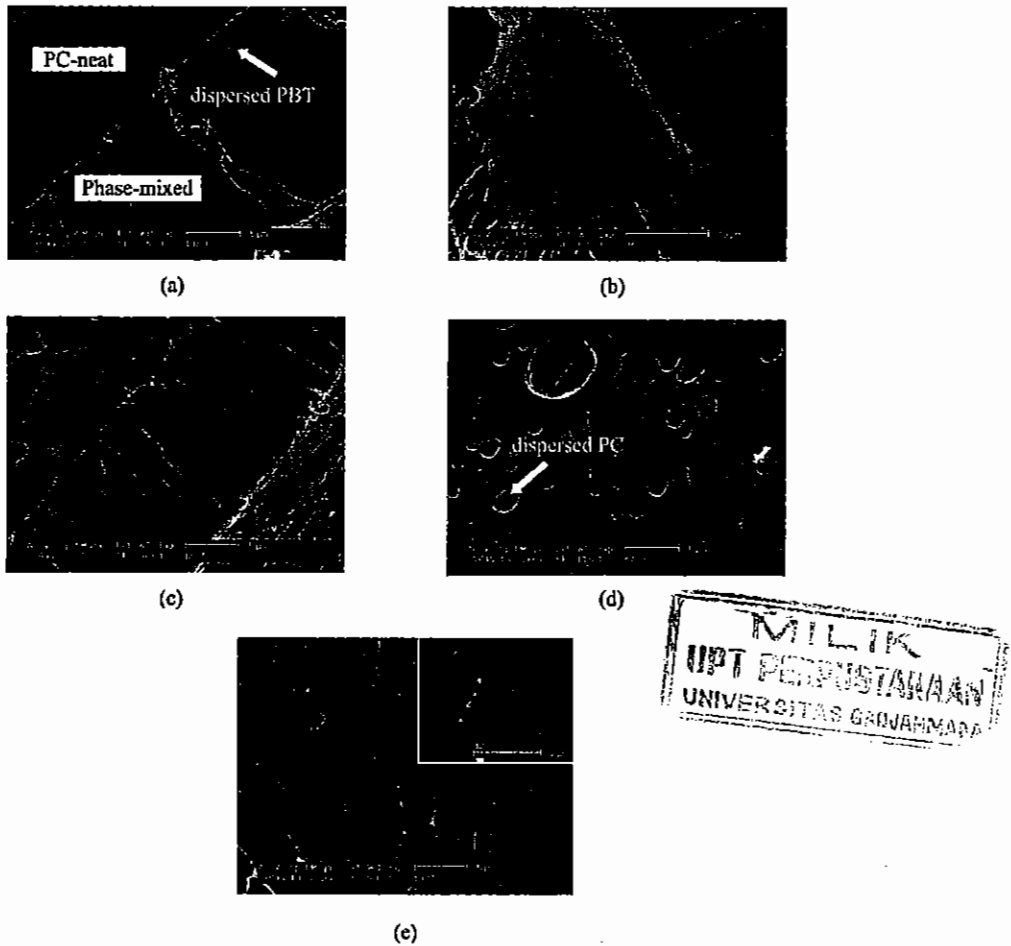


Figure 2. SEM photographic of PBT/PC blends performed by directly melt mixing in injection moulding (method-2). Compositions of PBT/PC are (a) 10/90, (b) 30/70, (c) 50/50, (d) 70/30 and (e) 90/10.

CONCLUSION

SEM was applied to observe the change of morphology before and after injection moulding. As comparison, it was also investigated PC/PBT blends prepared by directly melt mixing in injection moulding. There is dispersed particle size increase of the PBT/PC blends at PBT-rich as well as PC-rich compositions after injection moulding. Meanwhile, co-continuous morphology was developed by PBT/PC 50/50 blend. From the changes of phase structure as well as dispersed particles size increase, injection moulding is postulated to facilitate phase separation of the PBT/PC blends especially when melt mixing of PBT and PC is performed without any catalyst and/or transesterification inhibitor.

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