Phase separation mechanism and structure development in poly(butylene terephthalate)/polycarbonate blends

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(Received 31 May 1993)

The phase separation mechanism in poly(butylene terephthalate) (PBT)/polycarbonate (PC) and PBT/PC-copolymer (cPC) blends was investigated by time-resolved light scattering. The early stage of phase separation followed the linearized theory of spinodal decomposition. The temperature dependence of the apparent diffusion coefficient showed lower critical solution temperature (*LCST*) type phase behaviour (*LCST*= 198°C for PBT/PC and 228°C for PBT/cPC). Scaling rules were applied for the late stages to show serious deviations from theoretical expectations. Time variation of the scattering invariant showed that the deviations were caused by an ester exchange reaction. A plausible scenario is presented for the development of a bicontinuous two-phase structure in the melt-extruded blends.

(Keywords: phase separation; structure development; blends)

INTRODUCTION

There are many experimental studies on the two-phase morphology[1-3], dynamic mechanical properties[4] and ester exchange reaction[5] of the poly(butylene terephthalate) (PBT)/bisphenol A polycarbonate (PC) blend. Some authors claimed that the ester exchange reaction was important for morphology development. Hobbs *et al.* reported that a highly interconnected two-phase structure developed in melt-mixed blends[2]. This suggested to us the possibility of structure formation via spinodal decomposition. In this paper, after reproducing their results by transmission electron microscopy (TEM), we undertake a kinetics analysis of the phase separation by time-resolved light scattering to justify the spinodal decomposition mechanism. On the basis of kinetics results, we try to determine the critical point for the polymer–polymer miscibility. Then we extend the discussion to the effect of the ester exchange reaction on the separation kinetics.

EXPERIMENTAL

The blends used in this study were prepared from commercial grades of PBT ($M_n = 4.7 \times 10^4$; Toyobo Plastic Division), PC ($M_n = 2.4 \times 10^4$, $T_g = 145°C$; S-2000, Mitsubishi Gas Chemicals) and PC-copolymer (cPC) ($M_n = 2.4 \times 10^4$, $T_g = 192°C$; APEC HT KU I-9360). Blends (50/50 w/w) were prepared of both PBT/PC and PBT/cPC. The blends were made by melt extrusion, using a co-rotating twin screw extruder (IKEGAI Machinery Corp.; $\phi = 30$ mm, $L/D = 16$, barrel temperature = 290°C).

The extruded melt was quickly quenched in ice-water to freeze the two-phase structure in the melt. The quenched blend was stained with ruthenium tetroxide and microtomed into ultrathin sections (~ 0.1 μm thick). The frozen morphology was observed by TEM (Hitachi H-600, 100 kV).

The quenched blend was placed between two cover glasses and melt-pressed to a thin film (~ 20 μm thick) at 245°C (>melting point of PBT) for 1 min on a hot stage. Immediately after melt-pressing, the specimen which had remelted was quickly transferred into a hot chamber on light scattering apparatus and time-resolved light scattering measurements were carried out. *Figure 1* shows the light scattering photometer. The photometer is equipped with a 46 photodiode array which facilitates the time-resolved measurement of the scattering profile, the angular dependence of the scattered light intensity, with a time slice of 1/30 s (ref. 6). A He–Ne laser (wavelength 632.8 nm) was applied vertically to the film specimen and the scattering profile was observed under parallel polarized (V_v) optical alignment. Thus the change of the V_v light scattering profile with time after the specimen was placed in the hot chamber was observed.

RESULTS AND DISCUSSION

Figure 2 is a TEM photograph of a PBT/cPC blend quenched from the extruded melt. *Figure 2* shows a high level of connectivity between both phases and regular

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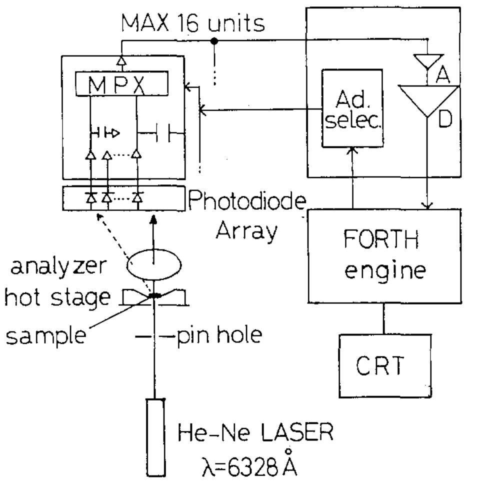

Figure 1 Light scattering photometer equipped with a 46 photodiode array for time-resolved measurement of the angular dependence of the scattered light intensity

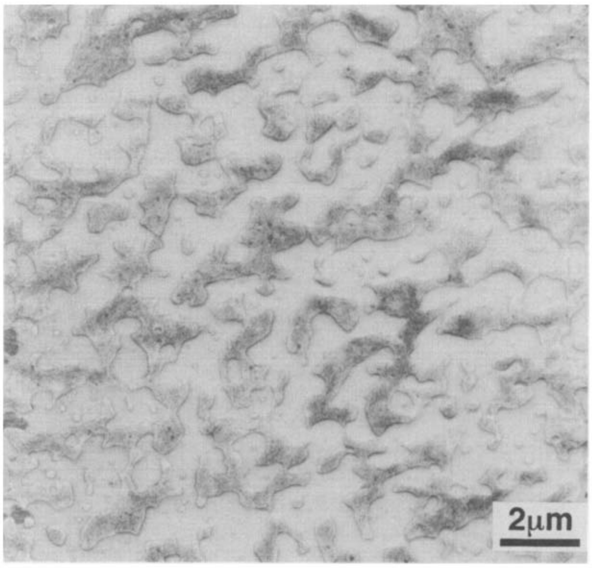

Figure 2 Transmission electron micrograph (RuO_4) of a melt compounded and quenched PBT/cPC (50/50 w/w) blend

spacing of the phases. That is, the results by Hobbs *et al.*[2] are nicely reproduced here. The two-phase structure with unique periodicity and phase connectivity is one of the hallmarks of spinodal decomposition. (Note that crystal lamellae appear in the dark PBT phase).

Figure 3 shows the change in the scattering profile with demixing time t in the PBT/cPC blend at 270°C. Here, the scattered light intensity I is shown as a function of the magnitude of the scattering vector q $[=(4\pi/\lambda')\sin(\theta/2)$, where λ' is the wavelength of light in the specimen and θ is the scattering angle$]$. Note that, at $t=0$, the scattering intensity is very weak and it has no q-dependence, suggesting that the blend just after remelting at 245°C is a nearly homogeneous mixture. This implies that phase dissolution* had taken place before measuring at 270°C. The homogeneous mixture starts to phase separate by annealing at 270°C, as shown by the increase in the scattering intensity. The appearance of a scattering peak suggests that separation is by the spinodal decomposition mechanism. To confirm this, we analysed the early stage on the basis of the linearized Cahn–Hilliard theory[8].

In the early stage of spinodal decomposition, the scattering intensity is expected to increase exponentially with time:

$$I(q,t)=I(q,t=0)\exp[2R(q)t] \qquad (1)$$

The amplification factor $R(q)$ is given by:

$$R(q)=-Mq^2(\partial^2 f/\partial c^2+2kq^2) \qquad (2)$$

where f is the local free energy of mixing, c is the concentration, k is the concentration-gradient energy coefficient and M is the mobility. According to equation (1), a plot of $\ln I$ *versus* t at a fixed q should yield a straight line of slope $2R(q)$. A linear regime is seen in the initial stage, as shown in *Figure 4*, indicating that the initial stage can be described by the linearized theory. Linear results were also obtained for various q values.

Figure 5 shows a plot of $R(q)/q^2$ *versus* q^2. As expected from equation (2), the plot yields a straight line for large q values, indicating again that the initial stage can be described within the framework of the linearized theory.

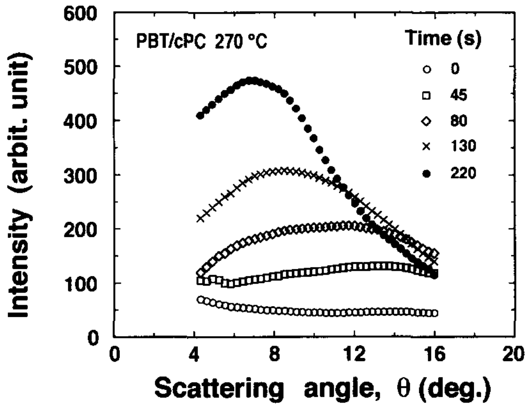

Figure 3 Time evolution of the light scattering profile during isothermal phase separation of a PBT/cPC (50/50 w/w) blend at 270°C

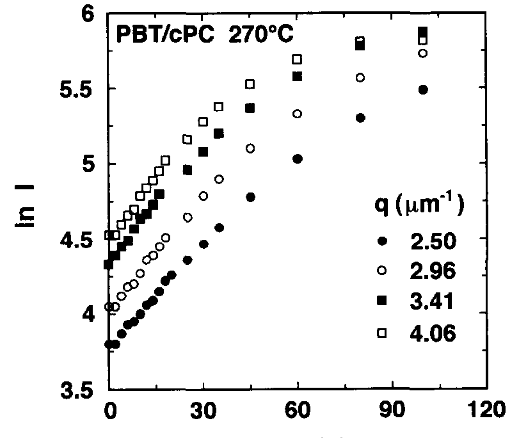

Figure 4 Change in scattered light intensity for various scattering vector q values with time at 270°C

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* As will be discussed later, this system has a lower critical solution temperature (*LCST*) at 228°C. The remelting process at 245°C corresponds to a temperature drop from 290°C (extruding temperature) to a lower temperature at about the *LCST*. The apparent phase dissolution is caused by the temperature drop inside the two-phase region of the phase diagram[7]

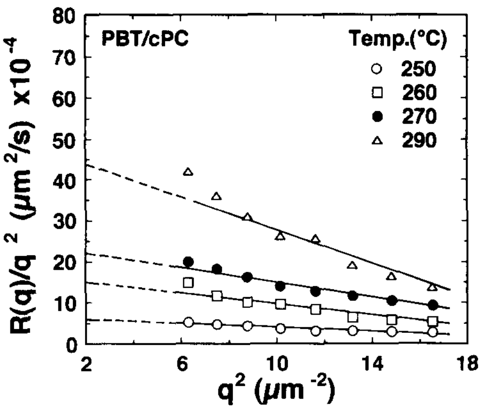

Figure 5 Plot of $R(q)/q^2$ *versus* q^2 at various temperatures

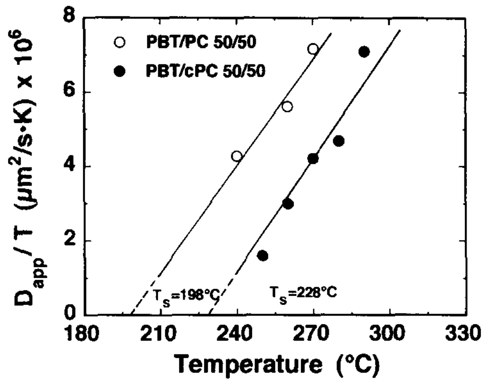

Figure 6 Temperature dependence of D_{app}

From the plot one can estimate a series of characteristic parameters: q_c, q_m and D_{app}. These parameters describe the dynamics of phase separation; q_c is the critical wavenumber of fluctuations that can grow, q_m is the most probable wavenumber of fluctuations having the highest rate of growth and D_{app} is the apparent mutual diffusion coefficient. According to equation (2), q_c is given by the intercept on the q^2 axis, q_m is calculated from the relation $2q_m^2=q_c^2$ and D_{app} is obtained from the intercept on the vertical axis. D_{app} is defined by:

$$D_{\mathrm{app}} = -M(\partial^2 f/\partial c^2) \qquad (3)$$

and given by:

$$D_{\mathrm{app}} \propto D_c(|\chi-\chi_s|/\chi_s) \qquad (4)$$

where D_c is the self-diffusion coefficient for translational diffusion, χ is the interaction parameter and χ_s is the interaction parameter at the spinodal. Employing the relationship $D_c \propto T$ from the Stokes–Einstein equation and $(|\chi-\chi_s|/\chi_s) \propto |T-T_s|$ (where T_s is the spinodal temperature), equation (4) leads to:

$$D_{\mathrm{app}} \propto T|T-T_s| \qquad (5)$$

Figure 6 shows the temperature dependence of D_{app}. From the intercept of the T axis at $D_{\mathrm{app}}/T=0$, one can estimate the T_s at which D_{app} is zero. The T_s values thus obtained were 198°C (PBT/PC) and 228°C (PBT/cPC), respectively. The results imply that both the systems have a *LCST* type phase diagram.

Based on the above results, a scenario of the melt extrusion to yield a bicontinuous two-phase structure may be given as follows. Cold pellets of both polymers are fed into the extruder and are then gradually heated up. After the polymer temperature exceeds both the T_g of PC (145°C) and the T_m of PBT (225°C), phase dissolution will start. Even after attaining the T_s (= 198°C for PBT/PC), dissolution will be continued, since T_s can be elevated under shear[9]. Under the high shear rate in the extruder, T_s might be elevated over the barrel temperature. Thus, mixing could be done in a wide temperature window for dissolution to obtain a homogeneous mixture. However, once the melt is extruded from the nozzle, the shear rate turns to zero and T_s will immediately fall to a constant value (= 198°C) so that the spinodal decomposition will proceed until the system is cooled down to the constant T_s.

From the kinetics results of the early stage, it is interesting to estimate the polymer–polymer interaction range l. Since the interaction range l is described as a function of q_m and T_s:

$$2\pi/q_m = \Lambda_m = 2\pi l(3|T-T_s|/T_s)^{-1/2} \qquad (6)$$

the value of l can be estimated from the slope of the Λ_m *versus* $(3|T-T_s|/T_s)^{-1/2}$ plot, as shown in *Figure 7*. The estimated values were 574 Å for PBT/PC and 278 Å for PBT/cPC. The l value of the PBT/PC system is larger than that of the PBT/cPC system, suggesting a comonomer effect of cPC on the interaction.

In the late stage, Binder and Stauffer[10] proposed scaling rules, assuming that clusters aggregate by a diffusion process and coalesce into larger clusters, and described the self-similar growth of the structure by:

$$q_m(t) \propto t^{-\alpha} \qquad (7)$$

$$I_m(t) \propto t^{-\beta} \qquad (8)$$

where I_m is the scattered light intensity at q_m. *Figure 8* shows typical examples of log–log plots for time variations of q_m and I_m. One can find a t regime at which both α and β are constant. However, the β/α ratio is 1.24, which is very much lower than the theoretical value (= 3.0) predicted by Furukawa[11]. Furthermore, in the very late stage, both I_m and q_m start to deviate from straight lines. These points will be discussed later.

Figure 9 shows the universal curve in terms of the dimensionless variables Q_m and τ defined by:

$$Q_m = q/q_m(t=0) \qquad (9)$$

$$\tau = D_{\mathrm{app}} q_m^2 t \qquad (10)$$

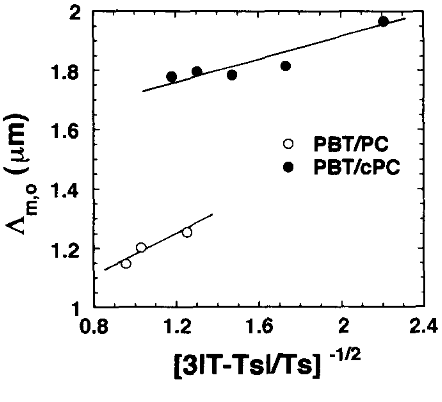

Figure 7 Temperature dependence of $\Lambda_{m,o}$

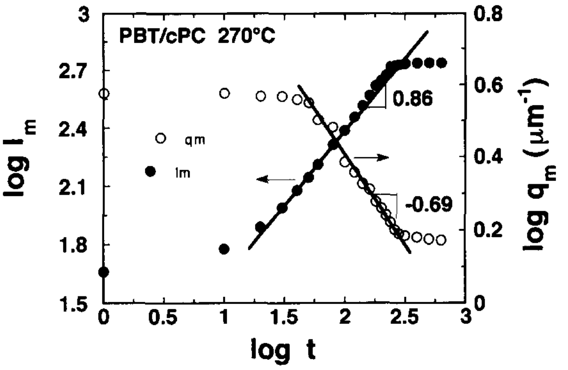

Figure 8 Log–log plots of q_m and I_m *versus* annealing time

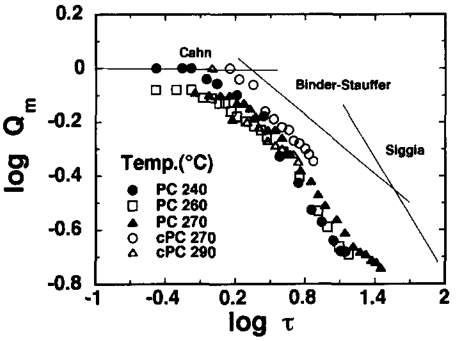

Figure 9 Universal plots of dimensionless variables; Q_m *versus* τ

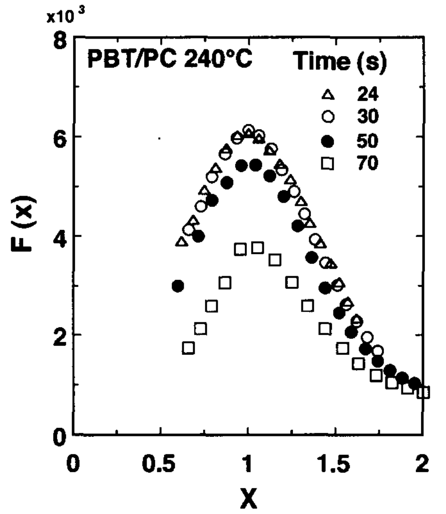

Figure 10 Scaled structure function, showing a serious deviation in the very late stage

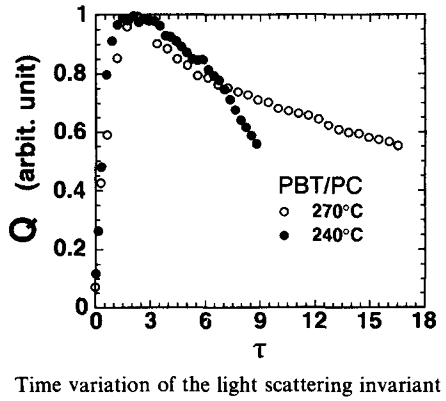

Figure 11 Time variation of the light scattering invariant

One can see that the superposition is not so good and the τ dependence deviates from the theoretical one[12], especially in the very late stage. We also examined the separation kinetics in terms of the scaled structure factor[11] $F(x)$. Since $F(x)$ is a Fourier transform of the space correlation function of the composition, it is related to the scattered intensity $I(q, t)$ at a given time t:

$$I(q,t) \sim \langle \eta^2 \rangle \xi(t)^3 F(x) \tag{11}$$

with

$$x = q\xi(t) \tag{12}$$

$$\xi(t) = 1/q_m(t) \tag{13}$$

where $\langle \eta^2 \rangle$ is the mean-square fluctuations of the refractive index. Then the structure factor $F(x)$ is described as:

$$F(x) \sim I(q,t) q_m^3(t) \tag{14}$$

Figure 10 shows typical results for $F(x)$. Curves are nicely superimposed for $\tau < 2$ ($t < 40$ s), while a serious deviation is seen for $\tau > 2$. The deviation is due to the decrease in F values. The F decrease may be caused by the decrease of $\langle \eta^2(t) \rangle$ during phase separation. To justify the change of $\langle \eta^2(t) \rangle$, we calculated the light scattering invariant Q:

$$Q \propto \int q^2 I(q)\,\mathrm{d}q \propto \langle \eta^2(t) \rangle = \phi_1 \phi_2 (\alpha_1 - \alpha_2)^2 \tag{15}$$

where ϕ_i and α_i are the volume fraction and polarizability of phase i, respectively[13]. In the late stage of spinodal decomposition, one can expect both ϕ_1, ϕ_2 and $(\alpha_1 - \alpha_2)^2$ to be constant so that Q will remain constant. The results shown in *Figure 11* clearly exhibit the decrease in Q for $\tau > 2$. The decrease may be due to the decrease in $(\alpha_1 - \alpha_2)^2$, which could be caused by the ester exchange reaction. The ester exchange reaction in the late stage may also render the deviation from the theoretical expectations in *Figures 8* and *9*.

CONCLUSIONS

Both PBT/PC and PBT/cPC systems were shown to exhibit *LCST* phase behaviour. A plausible scenario is presented for the development of a bicontinuous structure in the melt-extruded blends in terms of the spinodal decomposition. The spinodal decomposition in the late stage seems to be disturbed by the ester exchange reaction.

ACKNOWLEDGEMENTS

We express our appreciation to Dr Heinz-J. Fuellmann, Bayer Japan Ltd, for fruitful discussions and we are also indebted to Mr Nobumasa Ishiai, Bayer Japan Ltd, for supplying the co-polycarbonate, APEC HT series.

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