Phase Separation and Crystallization Behavior in Extruded Polypropylene/Ethylene-Propylene Rubber Blends Containing Ethylene- α -Olefin Copolymers

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ABSTRACT: Liquid-liquid (L-L) phase separation and its effects on crystallization in polypropylene (PP)/ethylene-propylene rubber (EPR)/ethylene- α -olefin copolymer (ECP) ternary blends obtained by melt extrusion were investigated by time-resolved light scattering (TR-LS) and optical microscopy. L-L phase separation *via* spinodal decomposition (SD) was confirmed by TR-LS data. After L-L phase-separation at 250°C for various durations, the blend sample was subjected to temperature-drop to 130°C for isothermal crystallization and the effects of L-L phase separation on crystallization were investigated. Memory of L-L phase separation *via* SD remained for crystallization. The crystallization rate decreased with increasing L-L phase-separated time at 250°C. Slow crystallization for the long L-L phase-separated time could be ascribed to decrease in chain mobility of PP by decrease in rubbery components in the PP-rich region. The ethylene-octene copolymer exhibited good affinity with PP, leading to a slow growth of a concentration fluctuation during annealing.

KEY WORDS Polypropylene / Ethylene-Propylene Rubber / Ethylene- α -Olefin Copolymer / Phase Separation / Crystallization /

Polypropylene/ethylene-propylene rubber (PP/EPR) blends are injection-moldable thermoplastics with wide applications for automobile parts, appliances and other industrial uses because of good mechanical properties and processability. To further improve properties and expand applications, a new PP/EPR blend containing ethylene- α -olefin copolymers (ECP) has been recently developed.¹

In PP/EPR/ECP ternary blends obtained by melt extrusion, liquid-liquid (L-L) phase separation at high temperatures is very similar to the spinodal decomposition (SD) which should originate from the partially miscible system. When the blend has lower critical solution temperature (LCST) or the upper critical solution temperature (UCST) phase diagram, the formation of crystalline structures should be affected by L-L phase separation.^{2,3} When LCST is located above the melting point of PP, L-L phase separation precedes crystallization and has significant influence on crystallization. For better control of the physical properties of materials, we need more information on phase behavior and effects on crystallization and thus investigated the phase separation and crystallization behavior in extruded PP/EPR/ECP blends.

We first carried out time-resolved light scattering (TR-LS) studies to confirm L-L phase separation *via* SD in PP/EPR/ECP blends and investigated the effects of L-L phase separation on crystallization.

EXPERIMENTAL

Materials

An isotactic PP was supplied by LG Chemical Co. The

density was 0.908 g cm^{-3} and the melt flow rate (MFR) measured by ASTM D1238L was 60. EPR was supplied by SK Co. The EPR contained 54 mol% ethylene and the Mooney viscosity, ML_{1+4} (125°C) measured by ASTM D 1646 was 14. Two commercial ECPs were used. ECP-1 was an ethylene-octene copolymer with density of 0.885 g cm^{-3} and a 1.0 MFR measured by ASTM D1238E (Dow Chemical Co., Engage 8003; octene content = 18%). ECP-2 was an ethylene-butene copolymer with density of 0.880 g cm^{-3} and a 0.8 MFR (Exxon Chemical Co., Exact 4033).

PP/EPR/ECP ternary blends were prepared in a two-stage process. EPR/ECP binary blends made in a Farrel Banbury BR type mixer was subsequently melt-mixed with PP at 250°C on a 30 mm co-rotating twin screw extruder (Werner Pfleiderer) at a speed of 200 RPM. The screw configuration was basic kneading blocks, followed by gear mixer flights, to produce a medium shear and high mixing configuration. In each run, the extrudate was quickly quenched in ice-water to freeze the structure in the melt and then was chopped into granules. The composition of the PP/EPR/ECP blends was 60/30/10 by weight.

TR-LS and OM

A thin film specimen (*ca.* 15 μm thick) was prepared by pressing the blend pellets between two cover glasses at 250°C. Immediately after the melt-pressing, the specimen was quickly transferred onto a hot stage in a light scattering photometer equipped with a CCD (charge-coupled device) camera⁴ and the kinetics of L-L phase separation were investigated.

After the L-L phase-separation at 250°C for a certain

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Figure 1. Changes in light scattering profiles of PP/EPR/ECP blends during L-L phase separation at 250°C : (a) PP/EPR/ECP-1 blend ; (b) PP/EPR/ECP-2 blend.

time (t_s), the sample was rapidly transferred onto a light scattering hot stage set at 130°C for isothermal crystallization and the effects of L-L phase separation on crystallization were investigated. A polarized He-Ne gas laser of 632.8 nm wavelength was applied to the film specimen. V_V geometry, in which the optical axis of the analyzer was set parallel to that of the polarizer, was used.

The final morphology of the crystallized specimen at 130°C was observed under an optical microscope (OM).

DMTA

The pellets were compression-molded between metal plates at 250°C for 3 min. After molding, the specimen was rapidly transferred into an oil bath set at 130°C and was crystallized. This crystallized specimen was used for dynamic mechanical measurements performed with a Polymer Laboratories dynamic mechanical thermal analyzer (DMTA) MK III. DMTA was operated in the dual cantilevers bending mode at a frequency of 1 Hz and at a heating rate of 3°C min⁻¹ in a temperature range of from -120 to 80°C.

RESULTS AND DISCUSSION

L-L Phase Separation Behavior

Figure 1 shows changes of the one-dimensional V_V scattering profiles with L-L phase separation time, t_s in which the scattering vector q is defined by $q = (4\pi/\lambda') \sin(\theta/2)$, where λ' is the wavelength of light in the speci-

Figure 2. log-log plots of (a) $q_m(t) \propto t^{-\alpha}$ and (b) $I_m(t) \propto t^\beta$.

men and θ is the scattering angle. Even at $t_s = 0$, a weak scattering peak appears at large q , suggesting an appreciable development of L-L phase separation in the quenched-and-remelt specimen. The peak intensity I_m increases with t_s , and its position q_m shifts to smaller angles, implying that the L-L phase separation proceeds via SD mechanism.

The phase separation process seen in Figure 1 can be interpreted by the power law relationship. This problem is discussed by Langer based on non-linear statistical consideration.⁵ The theory predicts the power law scheme for the intermediate-to-late stages of SD as

$$q_m(t) \propto t^{-\alpha} \quad (1)$$

$$I_m(t) \propto t^\beta \quad (2)$$

where α and β are the critical exponents. Figures 2a and 2b show the log-log plots of q_m and I_m versus phase separation time, respectively. We see that the β/α ratio is approximately 3, which is in good accord with the dynamics of cluster coalescence, suggested by Binder and Stauffer⁶ for the late stage of SD or by Siggia⁷ for the intermediate stage.

In Figure 3, the periodic length Λ_m obtained by applying the Bragg equation to the peak position of the light scattering profiles is plotted as a function of t_s . Increase of Λ_m with t_s can be clearly seen. Λ_m of the PP/EPR/ECP-1 system is smaller than that of the PP/EPR/ECP-2 system, suggesting the slower growth of SD. The ethylene-octene copolymer (ECP-1) may exhibit better solubility with PP and EPR at high shear fields, leading to a slower L-L demixing in quiescent state.

Dynamic mechanical measurements provide further

Figure 3. Change of Λ_m with t_s .

Figure 4. Temperature dependence of loss tangent ($\tan \delta$) for PP/EPR/ECP blends.

evidence for the slower demixing. The mechanical loss tangent, $\tan \delta$ of the PP/EPR/ECP blends is plotted in Figure 4 as a function of temperature. Both blends show two distinct glass transitions, suggesting phase-separated morphology. The low and high glass transition peaks correspond to the glass transition temperature, T_g of rubber region and T_g of PP-rich region (the T_g s of pure PP, EPR, ECP-1, and ECP-2 were 28.5, -38.6 , -56.4 , and -50.2°C , respectively). The high T_g of the PP/EPR/ECP-1 blend is lower than that of the PP/EPR/ECP-2 blend. This suggests the less segregation of rubber components (EPR and ECP) from PP-rich region in the ECP-1 system than in the ECP-2 system (a relatively larger amount of remaining rubbery components in the PP-rich region).

Supplemental evidence of L-L phase separation was provided through observation of structure formation at 130°C . The apparent mutual diffusion coefficient D_{app} at 130°C was very low.⁸ This implies that the L-L phase separation rate may be negligible at 130°C . The crystallization rate of PP is very high (crystallization completed in about 10 s, as discussed in Figure 9). In such case, the L-L phase separation morphology, *i.e.*, the periodic and interconnected structure, could be preserved during crystallization.² Figures 5 and 6 show optical micrographs of the PP/EPR/ECP blends crystallized at 130°C after the L-L phase separation at 250°C . A dramatic change in the morphology of the blends with annealing at 250°C is observed. At the beginning [Figures 5a and

Figure 5. Optical micrographs of PP/EPR/ECP-1 blend crystallized at 130°C for 10 min after the L-L phase separation at 250°C for (a) $t_s = 0$ min; (b) $t_s = 10$ min; (c) $t_s = 30$ min.

6a], it is not clear which phase is continuous and which is dispersed. At the later stages of L-L phase separation, phase connectivity grows and eventually breaks up into macroscopic spherical texture. These are characteristic to the SD mechanism. The spacing between dark and bright regions in the micrographs was in good agreement with Λ_m obtained from the light scattering profiles.

Based on the above results, a scenario of the melt extrusion to yield near a homogeneous blend may be given as follows: at the high shear rates in the extruder, the spinodal temperature T_s in LCST phase diagram may be elevated, as shown by the arrow in Figure 7 and one-phase region becomes wider.^{9–12} Thus, the system undergoes phase dissolution. The dissolution continues until a new composition is reached in the mixture. The compositions, X_A and X_B , at a static condition move to the compositions, X_A' and X_B' in the shear field. This could be the case for the present PP/EPR/ECP blends. If T_s in the shear field is raised above the barrel temperature T_b , the mixing can be done in one-phase region to obtain a homogeneous mixture. The phase diagram in Figure 7 is just a schematic illustration and does not have any quantitative significance; it indicates that the mixture was thermodynamically unstable. It is conceivable that the blend may not have a LCST phase diagram but rather has an UCST phase diagram. In that case, T_s in the shear fields should be lowered to induce the disso-

Figure 6. Optical micrographs of PP/EPR/ECP-2 blend crystallized at 130°C for 10 min after the L-L phase separation at 250°C for (a) $t_s = 0$ min; (b) $t_s = 10$ min; (c) $t_s = 30$ min.

lution of the components. Once the melt is extruded out from the nozzle, the shear rate turns zero and T_s immediately falls to a static value so that the SD proceeds until the structure is fixed by crystallization.

Effects of L-L Phase Separation on Crystallization

L-L phase-separated specimens at 250°C for various times were allowed to crystallize by rapid temperature drop to 130°C for the isothermal crystallization.

Figure 8 shows typical change in the V_v scattering profiles during crystallization at 130°C. The peak position, indicative of Λ_m caused by SD at 250°C, is kept constant and its intensity (I_m) increases with time. Constant Λ_m suggests that L-L phase separation no longer proceeds during crystallization. The increase of I_m should be caused by crystallization. The crystallization increases the refractive index of PP-rich region, causing larger optical contrast in phase-separated system.

To discuss crystallization, it is convenient to use the light scattering invariant in the V_v mode, Q_{V_v} . The time variation of Q_{V_v} is shown in Figure 9. Q_{V_v} is kept constant for a while, increases rapidly and attains a maximum value. Then, Q_{V_v} decreases slightly and levels off. Finite Q_{V_v} at time zero may be ascribed to the density fluctuation formed by SD at 250°C before crystallization onset. The constant Q_{V_v} at early time is indicative of the incubation period typical of the nucleation process of the crystallization. The rapid increase of Q_{V_v} should be as-

Figure 7. Schematic drawing of changes in phase diagram with shear rate. Arrow indicates spinodal temperature to elevate at high shear rate. T_b is the barrel temperature in an extruder.

Figure 8. Change in light scattering profile of PP/EPR/ECP-1 blend during crystallization at 130°C after $t_s = 10$ min.

cribed to PP crystallization. The slight decrease and leveling-off of Q_{V_v} suggest that the PP in the rubber-rich region may crystallize slowly at the later stages, reducing differences in refractive index between the separated regions.

Neglecting the small contribution from optical anisotropy, Q_{V_v} of crystallized polymer systems can be approximated by¹³

$$Q_{V_v} \propto \phi_c (1 - \phi_c) (\alpha_c - \alpha_0) \quad (3)$$

where ϕ_c is the volume fraction of crystalline aggregate, α_c and α_0 is the polarizability of crystalline aggregate and the melt, respectively. At the early stage of crystallization, eq 3 is further approximated by

$$Q_{V_v} \propto \phi_c (\alpha_c - \alpha_0) \quad (4)$$

Q_{V_v} is assumed to be proportional to ϕ_c so that the linear growth rate of crystallite G is,

$$G \propto d(Q_{V_v})^{1/3} / dt \quad (5)$$

Therefore, one can estimate G from the initial slope of the time variation of $(Q_{V_v})^{1/3}$. G , estimated by eq 5, is shown as a function of t_s in Figure 10. G decreases with

Figure 9. Time variation of the invariant Q_v in PP/EPR/ECP blends crystallized at 130°C after L-L phase separation at 250°C for $t_s = 0, 10$ and 30 min: (a) PP/EPR/ECP-1 blend; (b) PP/EPR/ECP-2 blend.

Figure 10. Change in G with t_s .

t_s ; for G for $t_s = 10$ and 30 min is much smaller than that for $t_s = 0$ min. This may come from differences of amounts of rubbery components (EPR and/or ECP) in PP-rich region. The growth of concentration fluctuation is realized by up-hill diffusion; A molecules diffuse into A-rich region from B-rich region. Thus, in PP/EPR/ECP blends, EPR and ECP molecules are forced to move from PP-rich region to rubber-rich region. As the L-L phase separation proceeds, the amounts of rubbery compo-

nents in PP-rich region should decrease by SD. In PP-rich region, the T_g increases as the amount of the rubbery components decreases. The crystallization rate consists of nucleation and diffusion rates. The higher T_g reduces the diffusion rate so that the crystallization rate may be correspondingly reduced.

Figure 10 shows that the dependence of G on t_s is noticeably influenced by the type of ECP. Stronger influence is observed for the PP/EPR/ECP-2 blend containing ethylene-butene copolymer. This can be explained by differences in the growth rate of the concentration fluctuation; *i.e.*, since concentration fluctuation by SD occurred more rapidly in the PP/EPR/ECP-2 blend, the larger amounts of rubbery components in PP-rich phases decreased with t_s , and the decrease may retard crystallization.

CONCLUSION

L-L phase separation *via* SD was found in extruded PP/EPR/ECP blends. For homogeneity of melt-extruded blends, one may explain that the phase diagram is elevated at high shear rates in the extruder, allowing phase dissolution. The effects of L-L phase separation on the crystalline morphology produced by subsequent crystallization are discussed. Crystallization takes place only in the PP-rich region so that the memory of SD (the periodic structure) is preserved. The amounts of rubbery components in PP-rich region formed by SD were strongly related to the crystallization rate. The amounts of the rubbery components in PP-rich region decreased with increasing the L-L phase separation time and the decrease retarded the crystallization rate. The affinity of ethylene-octene copolymer with PP may be higher than that of ethylene-butene copolymer.

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REFERENCES

1. T. Nomura, T. Nishino, K. Iwanami, K. Yokomizo, K. Kitano, and S. Toki, *J. Appl. Polym. Sci.*, **55**, 1307 (1995).
2. N. Inaba, K. Sato, S. Suzuki, and T. Hashimoto, *Macromolecules*, **19**, 1690 (1986).
3. N. Inaba, T. Yamada, S. Suzuki, and T. Hashimoto, *Macromolecules*, **21**, 407 (1988).
4. C. H. Lee, H. Saito, and T. Inoue, *Macromolecules*, **28**, 8096 (1995).
5. J. S. Langer, M. Baron, and H. S. Miller, *Phys. Rev. (A)*, **11**, 1417 (1975).
6. K. Binder and D. Stauffer, *Phys. Rev. Lett.*, **33**, 1006 (1974).
7. E. D. Siggia, *Phys. Rev. (A)*, **20**, 595 (1979).
8. S. W. Im, K. H. Lee, and C. H. Lee, *Polymer*, **40**, 2837 (1999).
9. I. Hindawi, J. S. Higgins, A. F. Galambos, and R. A. Weiss, *Macromolecules*, **23**, 670 (1990).
10. M. Okamoto and T. Inoue, *Polymer*, **35**, 257 (1994).
11. M. Okamoto, K. Shiomi, and T. Inoue, *Polymer*, **36**, 87 (1995).
12. M. Okamoto and T. Kotaka, *Polymer*, **38**, 1357 (1997).
13. J. T. Koberstein, T. P. Russell, and R. S. Stein, *J. Polym. Sci., Polym. Phys.*, **17**, 1719 (1979).