

Regularly phase-separated structure in an injection-molded blend of isotactic polypropylene and high density polyethylene

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High-density polyethylene (HDPE) is known to be immiscible with isotactic polypropylene (PP) in the quiescent state. In an injection-molded blend of PP/HDPE (= 60/40 wt. ratio), a regularly phase separated structure with periodic distance of about 0.15 μm was found. The regular structure could not be formed by a simple melt mixing of immiscible polymer pair but only by the spinodal decomposition (under zero shear rate in mold) from a single-phase mixture attained (by UCST depression or LCST elevation) in high shear fields in an injection machine. The shear-dependent mixing and demixing mechanism was supported by transmission electron microscopy: the volume ratio of PP-rich region and HDPE-rich region being different from the charge ratio and the HDPE crystal lamellae developed in the PP-rich region. The mechanism was also supported by microscopic observation of the structure development (characteristic to the late stage of spinodal decomposition) during isothermal annealing above the melting point of PP; i.e. bicontinuous structure with nice regularity developed and grew up self-similarly. © 1998 Elsevier Science Ltd. All rights reserved.

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Most pairs of high molar mass polymer are immiscible. This is so because the combinatorial entropy of mixing of two polymers is dramatically less than that for two low-mass compounds. However, several combinations of dissimilar polymers have been found to follow phase diagram; i.e. the polymers are miscible in limited temperature and composition ranges but are immiscible outside of these ranges. Such phase behaviour is called LCST (lower critical solution temperature)-type and UCST (upper critical solution temperature)-type¹. The phase behaviour is in the quiescent state.

Shear fields affect the phase behaviour. Shear induces phase separation at low shear rates and depresses LCST. At a higher shear rate, phase dissolution is induced by shear flow and LCST is elevated². LCST depression and elevation have been observed in several systems^{3–6}. The effect of shear fields on phase behaviour is theoretically interpreted in terms of the enhancement of concentration fluctuations^{7,8} and the elastic contribution to the free energy of mixing⁹.

The shear effect should be taken into account in understanding the structure development in polymer blends during melt processing, such as extrusion and injection molding. A bicontinuous two-phase structure, with unique periodicity in the μm range, in an extruded 50/50 blend of polycarbonate (PC) and poly(butylene terephthalate), was shown to develop by a dissolution caused by LCST elevation under high shear rate in an extruder, and then spinodal decomposition under zero shear rate after the melt was extruded from a nozzle¹⁰. Similar structure development was observed for injection molding of a 50/50 PC/poly(styrene-co-acrylonitrile) blend¹¹. In this paper, we describe such a result in a blend of isotactic polypropylene (PP) and high-density polyethylene

(HDPE), which is believed to be a highly immiscible system and have very high UCST or very low LCST locating outside of the processable window, between the thermal decomposition temperature and the melting point.

Both PP and HDPE in this study were commercial polymers from Mitsubishi Chemical Co.: PP, $M_w = 33 \times 10^3$, MFR = 9.0; and HDPE, $M_w = 85 \times 10^3$, MFR = 5.0. A 60/40 PP/HDPE blend was made by melt extrusion, using a co-rotating twin-screw extruder (Model PCM30, Ikegai Machinery Co.; $\phi = 30$ mm, $L/D = 25$, 150 rpm) set at a barrel temperature of 240°C. Average residence time was 40 s. The maximum shear rate was estimated to be 377 s^{-1} . The extruded melt was quenched in water and then chopped into pellets. The pellets were injection molded into a sheet of 2 mm thickness, using an injection molder (Arburg Co.) set at 240°C and 1000 kg cm^{-2} . The maximum shear rate was 21.2 $\times 10^3$ s^{-1} . To observe the morphology in the injection-molded blend under a transmission electron microscope (TEM), the specimen was stained by RuO_4 vapour at 40°C for 1 h, and then an ultrathin section, 70 nm in thickness, was prepared by an ultramicrotome (Ultracut L, Leica Co.). The section was cut parallel to the sheet surface at a depth of ca. 1 μm from the surface. TEM observation was carried out under a Jeol TEM, JEM-100CX, at an accelerating voltage of 100 kV. For light scattering analysis and optical microscopic observation, a rather thick (20 μm) section was also cut parallel to the sheet surface.

TEM micrographs are shown in Figure 1. In Figure 1a, one can see a stripe pattern with periodicity of about 0.15 μm . The dark region is assigned to the HDPE-rich region, in which thick lamellar crystals (ca. 10 nm thick) characteristic to PE¹² are visualised at a higher magnification, as shown in Figure 1b. In the bright region, one can see

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^a RuO_4 stains only the amorphous region of PE and PP by oxidation to yield a carboxylic acid group, a carboxylate (COORu) group and RuO_2 .

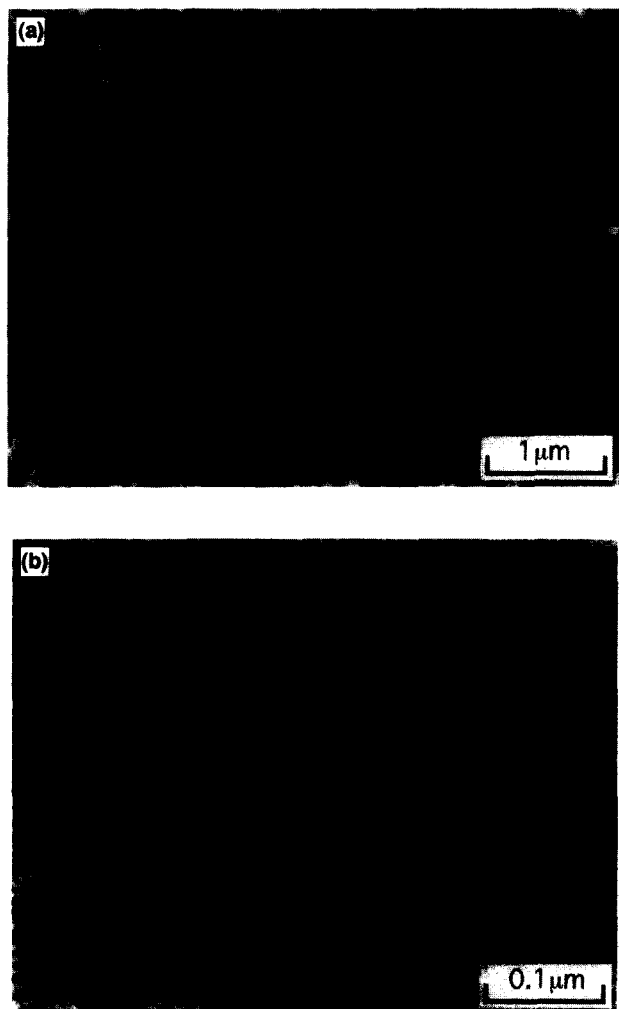


Figure 1 TEM micrographs of the skin part of an injection-molded sheet of the 60/40 PP/HDPE blend. (a) Low and (b) high magnifications. The arrow indicates flow direction.

the cross-hatched lamellar structure which is very characteristic to the PP crystal (*Figure 1b*). That is, the PP- and PE-rich regions are oriented in flow direction (see arrow) and arranged alternately and regularly. Such regularity could not be attained by a simple mixing of immiscible systems. It may be attained only by the spinodal decomposition from a single-phase mixture prepared under a high shear rate in the injection molder. That is, a relatively early stage of spinodal decomposition (liquid–liquid phase transition) may be arrested by the crystallization (liquid–solid phase transition) to yield the regularly phase-separated structure in *Figure 1*.

It is interesting that the area of dark region is rather wider than that of the bright region for the 60/40 PP/HDPE blend. This suggests that the PE-rich region should contain a significant amount of PP. The PP may reside in an amorphous region between PE lamellae. Furthermore, one can see thick PE lamellae in the bright region. The development of PE lamellae in the PP-rich region strongly suggests that PE chains had existed in the PP-rich melt even after the spinodal decomposition, and that they then segregated in the PP-rich region. The results imply that the periodic structure is fixed by the crystallization at a relatively early stage of spinodal decomposition.

If this is the case, one could observe a later stage of spinodal decomposition by annealing the blend above the melting point of PP. We tried to follow the late stages by light scattering using a highly sensitive CCD camera¹³, using

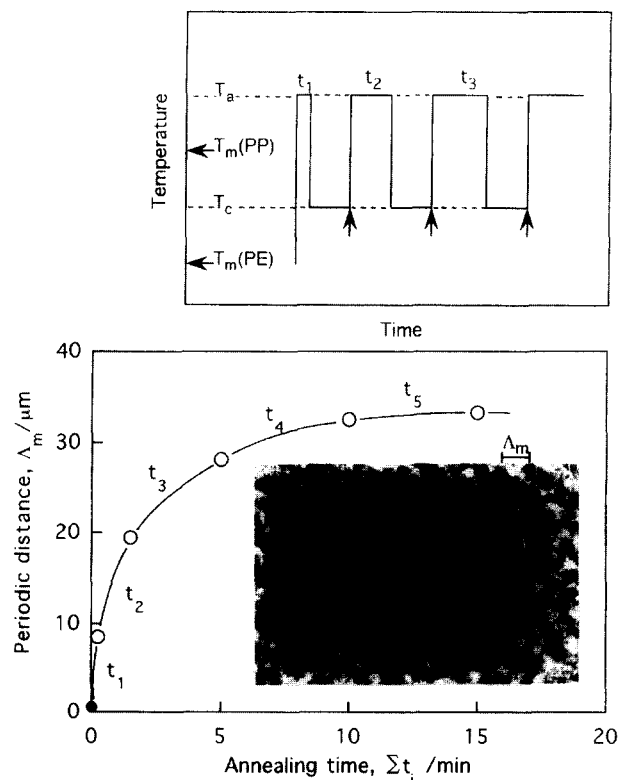


Figure 2 Upper: annealing–crystallization program; annealing for phase separation at $T_a = 170^\circ\text{C}$ and crystallization at $T_c = 145^\circ\text{C}$ (for visualization). Lower: polarizing optical micrograph, after annealing for 5 min ($= t_1 + t_2 + t_3$) and time variation of periodic distance in the micrograph. (●) by TEM.

the thick-sectioned specimen. However, the evolution of a scattering peak characteristic of spinodal decomposition could not be detected. This may be due to a small difference in refractive index n ($n = 1.469$ for PP and $n = 1.453$ for HDPE at 170°C by ellipsometry). Phase contrast microscopy also failed to follow the late stage; possibly for the same reason.

The phase contrast is expected to be enhanced by the crystallization of one component; i.e. if the melt undergoes a temperature drop to a crystallization temperature T_c between T_m of PP (167°C) and T_m of HDPE (140°C) after annealing at T_a above T_m of PP for a while, PP will crystallize mostly in the PP-rich region so that the PP-rich region will become bright under a polarizing optical microscope. We then set up an annealing-and-crystallisation program, as shown in the upper part of *Figure 2*, and investigated the late stage of spinodal decomposition by polarizing microscopy. When the melt annealed at $T_a = 170^\circ\text{C}$ for 15 s ($= t_1$) underwent a temperature drop to $T_c = 145^\circ\text{C}$, we saw nothing for a while and, after waiting for 30 min, observed a clear image. A picture was taken at that point (indicated by the arrow). Then, a temperature jump to T_a and isothermal annealing for t_2 were conducted. Such a temperature jump–drop process was repeated. The periodic distance Δm between bright regions in the polarizing micrograph is shown as a function of net annealing time ($t_1 + t_2 + \dots$) in *Figure 2*.

The structure grows up to be visualized under a microscope, as demonstrated by a typical micrograph and the time variation of Δm in *Figure 2*. The micrograph clearly shows the bicontinuous structure with nice periodicity which is characteristic to the spinodal decomposition. Note that the orientation in *Figure 1* has been lost and the structure in *Figure 2* is isotropic. It is interesting that the periodically bicontinuous character is maintained even at

late stages of $\Delta m \approx 30 \mu\text{m}$, suggesting the self-similar growth in a range of two orders of magnitude in periodicity, from sub- μm to $10 \mu\text{m}$.

References

1. Olabishi, O. Robeson, L. M., Shaw, M. T., *Polymer-Polymer Miscibility*. Academic Press, New York, 1979.
2. Hindawi, I. A., Higgins, J. S. and Weiss, R. A., *Polymer*, 1992, **33**, 2522.
3. Katsaros, J. D., Malone, M. F. and Winter, H. H., *Polym. Eng. Sci.*, 1989, **29**, 1434.
4. Rectpr, L. P., Mazich, K. A. and Carr, S. H., *J. Macromol. Sci. Phys.*, 1988, **B27**, 421.
5. Lyngaae-Jorgensen, J. and Sondergaard, K., *Polym. Eng. Sci.*, 1987, **27**, 344–351.
6. Cheikh Larbe, F. B., Malone, M. F., Winter, H. H., Halary, J. L., Leviet, M. H. and Monnerie, L., *Macromolecules*, 1988, **21**, 3532.
7. Helfand, E. and Fredrickson, G. H., *Phys. Rev. Lett.*, 1989, **62**, 2468.
8. Onuki, A., in *Taniguchi Conf. on Polymer Research by Neutron Scattering*, Kyoto, Japan, Nov. 1989.
9. Horst, R. and Wolf, B. A., *Macromolecules*, 1993, **26**, 5676.
10. Okamoto, M. and Inoue, T., *Polymer*, 1994, **35**, 257.
11. Okamoto, M., Shiomi, K. and Inoue, T., *Polymer*, 1995, **36**, 87.
12. Sano, H., Usami, T. and Nakagama, H., *Polymer*, 1987, **27**, 1497.
13. Lee, C.-H., Saito, H. and Inoue, T., *Macromolecules*, 1995, **28**, 8096.