

# Correlation Between Phase Separation and Crystallization in Poly(ethylene-co-hexene) and Poly(ethylene-co-octene)

Go Matsuba, Katsumi Shimizu, Howard Wang, Zhigang Wang and Charles C. Han

Polymers Division, National Institute of Standards and Technology,  
100 Bureau Drive MS 8543, Gaithersburg, MD 20899-8543

## INTRODUCTION

It is very important from both scientific and industrial points of view to elucidate the interaction between liquid-liquid phase separation (LLPS) and crystallization in polyolefin blends. Our group has paid much attention to poly(ethylene-co-hexene) (PEH)/poly(ethylene-co-butene) (PEB)<sup>1,2</sup> and PEH/poly(ethylene-co-octene) (PEOC) blends<sup>3</sup>. In PEH/PEOC blend, liquid-liquid phase separation (LLPS) can happen above the melting temperature and then miscible region can be found at even higher temperature, with an upper critical solution temperature of 171 °C. In this paper, we report the study of the kinetics of phase separation and crystallization of PEH/PEOC blend with differential scanning calorimetry (DSC), simultaneous small and wide angle X-ray scattering (SAXS/WAXD) and optical microscopy (OM).

## EXPERIMENTAL\*

**Samples and Preparation.** The statistical copolymers of PEH and PEOC were synthesized by the metallocene-catalysis. The PEH was supplied by ExxonMobil, and PEOC by Dow Chemical. The side chain density of PEH and PEOC is 1.8 and 7.6 per 100 backbone Carbon, respectively. The melting temperature of PEH and PEOC were 120 °C and 50 °C, respectively, measured by a Perkin-Elmer DSC7 System. The blends of PEH and PEOC, which have the PEH mass fraction 100 % (PEH), 70 % (H-70), 50 % (H-50) and 30 % (H-30) were prepared by the co-precipitation method. The blends were first dissolved in a xylene solution at 120 °C, and then the solution was cooled to 100 °C and kept for 1 d. The solution was then poured into methanol to precipitate the blends. The obtained blends were washed with methanol and dried in a vacuum oven for 3 d before use.

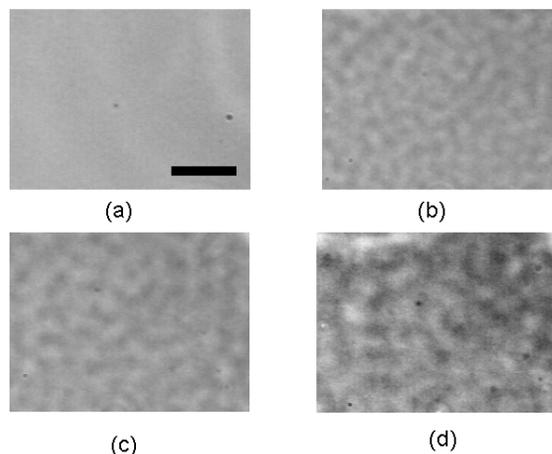
**Apparatus.** The OM measurements were carried out using a Leitz Wetzlar optical microscope system with a Sony CCD camera (XC-77). A hot stage was used to control the sample temperature. Time-resolved simultaneous SAXS/WAXD measurements were performed at Advanced Polymers Beamline (X27C) in National Synchrotron Light Source (NSLS), Brookhaven National Laboratory (BNL). The storage ring was operated at an energy level of 2.8 GeV with a ring current 250 mA. The detailed experimental setup and temperature controlling apparatus has been described by Wang *et al.*<sup>4,5</sup>. The sample was melted at 200 °C, 160 °C and 140 °C and quenched to some temperatures and time-resolved SAXS/WAXD measurement was performed during the process with a data acquisition time of 30 s/scan.

## RESULTS AND DISCUSSION

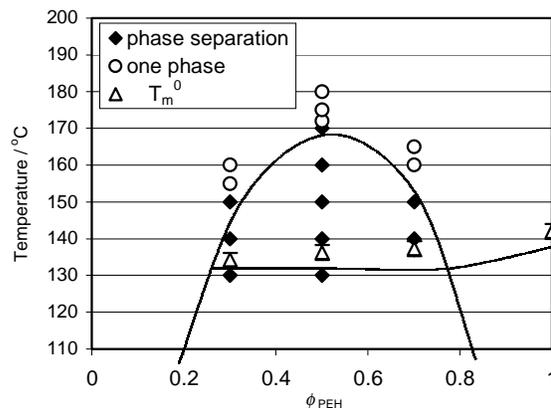
Some selected phase contrast optical micrographs of the H-50 sample melted at 200 °C for 10 min and isothermally annealed at 150 °C are displayed in Figure 1. The bicontinuous structure grows and characteristic length increases with annealing time. This bicontinuous structure signifies the typical spinodal decomposition of LLPS.

The LLPS diagram of the PEH/PEOC blend obtained from the phase contrast microscopy technique is shown in Figure 2. The critical temperature is about (171±0.2) °C. Also shown in Figure 2 are the equilibrium melting temperatures ( $T_m^0$ ) of PEH and the three blends obtained from the Hoffman-Weeks Plots. In the two-phase region,  $T_m^0$  is almost constant and at higher PEH concentration  $T_m^0$  decreases with the PEOC concentration. The standard uncertainty of  $T_m^0$  is about 2 °C.

\*The references to commercial equipment or materials do not imply recommendation or endorsement by the National Institute of Standards and Technology.



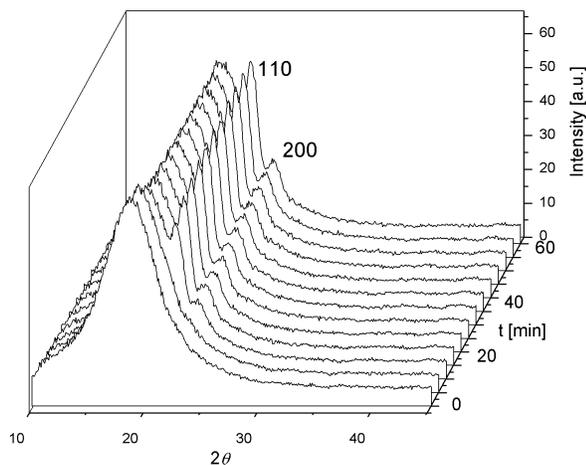
**Figure 1.** Phase contrast micrographs of H-50 blend isothermally annealed at 150 °C after melting 200 °C for 10 min. (a) 0 min, (b) 253 min, (c) 353 min, (d) 753 min. Scale bar represents 40 μm.



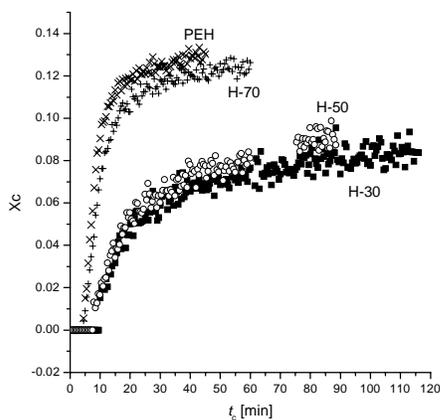
**Figure 2.** Phase diagram of the PEH/PEOC blend. The open circle and solid diamond indicate sample stayed miscible and phase separated after annealing for 1 d, respectively. The triangles are the equilibrium melting temperatures obtained from the Hoffman-Weeks plots.

Figure 3 shows WAXD profiles during crystallization of the H-70 sample melted at 160 °C (one phase) and then quenched to (113.8±0.2) °C. From WAXD profiles, relative crystallinity ( $X_c$ ), amorphous  $d$ -space are obtained, which are displayed in Figures 4 and 5, respectively. The  $X_c$ 's are about 13 % for the PEH, 12 % for the H-70, 9 % for the H-50 and 8 % for the H-30. This can be explained by the fact that the samples are all quenched from 160 °C to 113.8 °C, crystallization kinetics is much faster than the LLPS kinetics at this temperature. The PEOC chains which are not crystallizable alone at 113.8 °C, are still mixed together with the PEH chains, which prevents the crystalline structure to grow to the same degree as the PEH/PEOC at the co-existence composition at the LLPS equilibrium. Also, it is very natural that the amorphous  $d$ -space decreases with the increase of PEH concentration. However, if we normalize the crystallinity by the volume fraction of PEH in each sample, then the order of crystallinity is reversed which may be caused by the co-crystallization of PEOC chains into the PE crystals. Figure 6 displays the subtracted intensity profiles of melt-quenched sample (at 0 min) from those annealed samples during annealing at (143±1.0) °C (two-phase region). The sample used is a H-50 which was melted at 200 °C for 10 min first before quenched to 143 °C. The profiles in the low- $q$

region increase very rapidly, due to some large scale structure growth. We believe the blending and LLPS may play an important role. The standard uncertainly amount of WAXD/SAXS measurements is about 5 %.



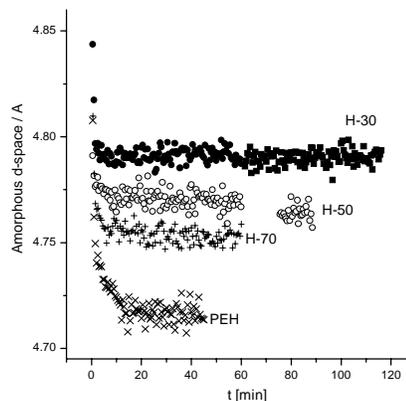
**Figure 3.** WAXD profiles during crystallization process at 113.8 °C of H-70 sample.



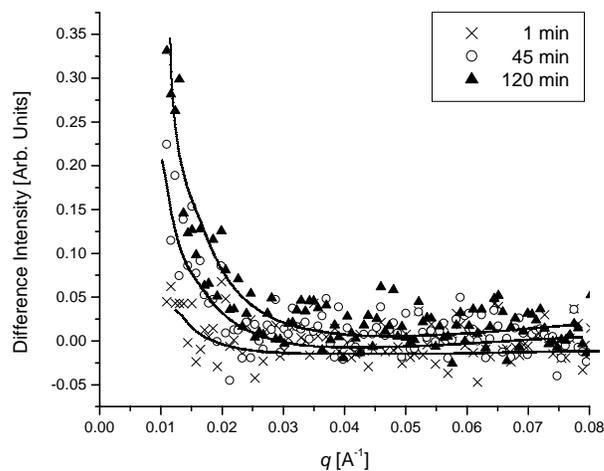
**Figure 4.** Time dependence of crystallinity of each sample crystallized at 113.8 °C. (Relative standard deviation of  $X_c$  is 1 %.)

### CONCLUSIONS

In order to understand the interaction between LLPS and crystallization in copolymer blends of PEH and PEOC, the phase contrast microscopy and simultaneous SAXS/WAXD measurements were employed to observe the morphological developments. The LLPS can be observed with the phase contrast microscopy technique even with a very small refractive indices difference between PE and PEOC. Phase contrast microscopy is a very sensitive measurement tool for such polyolefin blends system. We can find the LLPS and study the late stage spinodal decomposition kinetics with this technique. From the simultaneous SAXS/ WAXD measurements, we can find the crystallinity dependence of PEH concentration. This suggests that the presence of PEOC component decreases the crystallinity of PE, however, it can co-crystallize with the PE and increase the relative crystallinity of the system. In SAXS measurement, we can find the low- $q$  side increasing because of the LLPS.



**Figure 5.** Time dependence of amorphous d-space of each sample crystallized at 113.8 °C.



**Figure 6.** Difference scattering intensity profiles of PEH/PEOC blends annealed at 143 °C after melting at 200 °C for 10 min. The difference intensity represents the intensity profile of the sample after indicated annealing time, by the profile of melt-quenched sample (just after quenching).

### REFERENCES

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