

Simultaneous SAXS and WAXS Study of the Isothermal Crystallization in Polyolefin Blends

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INTRODUCTION

Polyolefins are widely used partly because their semi-crystalline characteristic meets both property and engineering needs for practical applications. The crystalline structure and phase morphology in polyolefins have direct impact on their final properties. Recently, the effect of blending on structure formation and morphology development in model and commercial polyolefins has attracted much of the interest, particularly on systems where liquid-liquid phase separation takes place.^{1,2} The dynamics of simultaneous crystallization and liquid/liquid phase separation can lead to novel morphology development. In this study, simultaneous small and wide angle X-ray scattering (SAXS and WAXS) technique has been used to investigate the morphological parameters during the dual phase ordering.

EXPERIMENTAL

The statistical copolymers of ethylene/hexene (PEH) and ethylene/butene (PEB) were obtained from ExxonMobil Inc.³, and were both metallocene-catalyst synthesized. The characteristics of the two polymers, including weight averaged molecular mass (M_w), mass density (ρ_m), branching density (ρ_b , in unit of per 1000 backbone carbon atoms (kC)) as well as melting (T_m) and crystallization temperatures (T_c), are listed in Table 1. T_m and T_c were measured using a Perkin-Elmer differential scanning calorimeter (DSC7), and were determined as the temperature of maximum melting rate for heating a rapidly cooled sample at a rate of 10 °C/min, and the temperature of the maximum crystallization rate at a cooling rate of -1 °C/min from the melt, respectively.

Table 1. Characteristics of PEH and PEB

	M_w (kg/mol)	ρ_m (g/cm ³)	ρ_b (kC ⁻¹)	T_m (°C)	T_c (°C)
PEH	110	0.922	9	127	118
PEB	70	0.875	77	61	--

Simultaneous SAXS/WAXS measurements were carried out at the X27C beamline of the National Synchrotron Light Source, Brookhaven National Laboratory. Two linear position sensitive detectors (European Molecular Biology Laboratory) were configured for data acquisition at small and wide angles. A dual-chamber temperature control unit was used to realize the temperature jump for isothermal crystallization. The samples used were pure PEH polymer and a blend with PEH/PEB=50/50 by weight, denoted as H50. The samples were held at a temperature of 160 ± 1 °C for 10 min to be an equilibrium homogeneous melt and were rapidly transferred to isothermal temperatures (temperature-jump) for isothermal crystallization measurements. The fluctuation of the isothermal temperature T_{iso} was controlled to be ± 0.2 °C.

RESULTS AND DISCUSSION

Figure 1 shows selected Lorentz-corrected SAXS (a) and WAXS (b) profiles during isothermal crystallization at 118°C for H50. SAXS profiles show that peak intensity increases with time indicating the development of the lamella stacking structure in the blend. WAXS

profiles show a prominent amorphous halo and increase in the intensity of the <110> reflection with time. At the later times, the <200> reflection also starts to develop.

From the time-resolved SAXS profiles, the correlation and interference distribution functions were used to obtain scattering invariant (Q), long spacing (L), and the crystal (I_c) and amorphous (I_a) thicknesses in the lamellar stack. From the WAXD profiles, the position and dispersion of the amorphous halo and crystal diffraction peaks, and integrated intensities for all crystal reflections and the amorphous background can be evaluated. The apparent mass crystallinity (X_c) was calculated as the ratio of the diffraction peak intensity to the overall WAXS intensity. Here in, we will discuss only quantities Q , L and X_c .

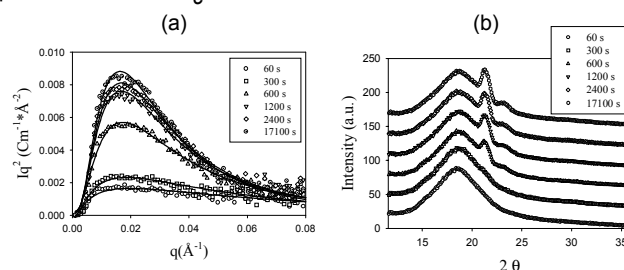


Figure 1. Selected SAXS (a) and WAXS (b) profiles for H50 isothermal at 118 °C.

Figure 2 shows time evolution of the invariant Q at various isothermal temperatures for H50. Q increases with time after an initial induction period, and levels off at later times. With higher T_{iso} , or smaller degree of undercooling, induction period becomes longer and the plateau Q is suppressed, which have been observed in many semicrystalline polymers.⁴

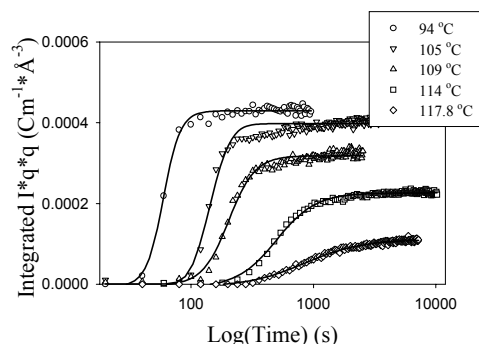


Figure 2. Time evolution of SAXS invariant Q for H50 at several isothermal temperatures.

Figure 3 shows the evolution of long period L for H50 (a) and PEH (b) at several T_{iso} . At low T_{iso} , L is small and decreases with time, whereas at high T_{iso} , L is large and increases with time. Both H50 and PEH exhibit the same behavior. Decrease of long period with time is known as a result of isothermal thickening and secondary crystallization. Increase of L can be understood considering the competition between the segregation of the highly branched polymer from the lamella growth and inclusion of the amorphous component within the amorphous phase between the lamellae. At low T_{iso} , crystallization kinetics is fast, primary crystal growth fills the volume quickly and lamellar thickening or secondary crystal growth dominates. At high temperatures, slow kinetics of the crystal growth and increase in diffusion coefficient (though small) allow the amorphous phase to diffuse away from the crystal therefore the crystal grows in a medium ever rich in amorphous phase. As this process continues, diffusion is retarded and more amorphous phase can be included within the lamellar stacks contributing to the increase in long period. This

transition occurs at much lower temperature in H50 than in PEH, because more non-crystallizable chains present in the blend, and corresponds to a morphological transition of the lamella habits.⁵

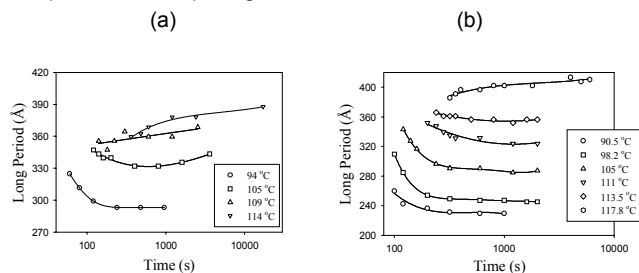


Figure 3. Time evolution of the long period L for H50 (a) and PEH (b) at several isothermal temperatures.

Figure 4 compares the final long period at various T_{iso} for H50 and PEH. Over the entire temperature range, L of PEH is larger than that of H50 indicating segregation of the amorphous PEB rich phase away from the lamellar stacking. Whether this segregation is due to liquid-liquid phase separation or liquid-solid separation is not clear. However, closeness of L at higher T_{iso} suggests that slow crystallization allow liquid-liquid phase separation to occur and crystals essentially grow from similar medium resulting in close long period.

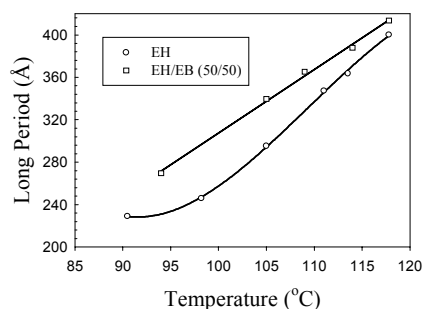


Figure 4. The final long period as a function of isothermal crystallization temperature for H50 and PEH.

Figure 5 shows the evolution of the WAXS crystallinity for H50 at various isothermal temperatures. Both crystallization kinetics and the final plateau crystallinity decrease sharply with T_{iso} . Figure 6 compares the plateau crystallinity at various T_{iso} for H50 and PEH after normalized by the amount of pure PEH. It is interesting that the normalized crystallinity is similar at high temperatures, whereas that of the H5 is significantly larger at lower T_{iso} . This effect is understood as the interplay between the cocrystallization and liquid-liquid phase separation. At high T_{iso} , slow crystallization kinetics allows liquid-liquid phase separation to proceed so crystallization takes place mainly in the PEH-rich phase leading to similar crystallinity as in pure PEH. At lower T_{iso} , crystallization is fast so crystal growth can accommodate the long chain segment from PEB, leading to a much higher crystallinity than that predicted by the level rule.

CONCLUSION

We have used simultaneous SAXS and WAXS with synchrotron radiation to study crystallization in a statistic ethylene/hexene (PEH) copolymer and its blend with another copolymer of ethylene/butene (PEB). Scattering invariant, long period, L , and crystallinity, X_c , are quantified from the measurements. It is seen that L decreases or increases with time at low or high isothermal temperatures, respectively. A comparison of the final L and X_c between pure PEH

and a blend with PEB suggests that liquid-liquid phase separation play a role in morphology development.

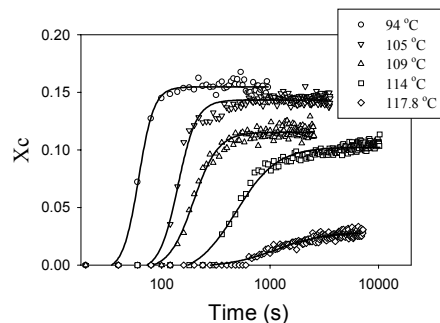


Figure 5. Time evolution of the WAXS crystallinity for H50 at various isothermal temperatures.

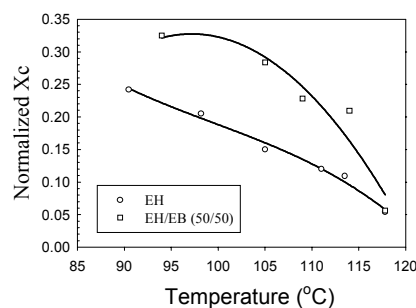


Figure 6. Normalized final crystallinity at various T_{iso} for H50 and PEH.

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3. The references to commercial equipment or materials do not imply recommendation or endorsement by the National Institute of Standards and Technology.
4. See, for example, Wang, Z.G.; Hsiao, B.S.; Sirota, E.B.; Agarwal P.; Srinivas, S. *Macromolecules* **2000**, 33, 978
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