Phase Behavior in Polyolefin Blend

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INTRODUCTION

The phase behavior in copolymer blends of poly(ethylene-co-hexene) (PEH) and poly(ethylene-co-butene) (PEB) is the focus of our present study. We have reported the phase diagram of PEH/PEB blends, including the liquid-liquid phase boundary and equilibrium melting temperature in a recent paper.[1] The phase diagram of this PEH/PEB system has an upper critical solution temperature of 146 ^{o}C at the composition ϕ = 0.44 and a systematic composition dependence of the equilibrium melting temperature. The phase behavior in PEH(40)/PEB(60) was first reported by using a bright-field optical microscopy with cyclic quench.[2] In the phase separated melt, an interconnected bicontinuous structure was observed which typifies a spinodal decomposition mechanism. The coarsening of this interconnected structure can be accelerated through cyclic quench between melt and crystalline states. Due to the chemical micro-structural similarity between PEH and PEB, the difference in the refractive indices between these two components is very small, however, the phase contrast optical microscopy can provide enough contrast to study the liquid-liquid phase separated structure as well as the crystalline structure. In this paper, we will report the phase behavior in melt by using the phase contrast optical microscopy for different thermal history.

EXPERIMENTAL*

Materials. The Exxon Mobil Chemical Company supplied PEH and PEB copolymers. Details of the material properties can be found in a previous paper.[1] The PEH/PEB blend was prepared by co-precipitating method. The PEH and PEB copolymers were first dissolved in *p*-xylene solvent with mass fraction of 3 % at 120 ^{o}C. After dissolving, the solution was cooled to 100 ^{o}C and kept for 24 h for completely mixing of the two components. The solution was then poured into methanol (room temperature) and filtered. The blend polymer obtained was dried in the vacuum oven for 24 h at room temperature and further dried for 48 h at 100 ^{o}C. In this paper, the blend polymer of PEH x % mass fraction is symbolized as Hx. The blend polymer was pressed between two cover glasses on a hot-stage at 160 ^{o}C and film samples were obtained. The sample thickness was approximately 50 μm.

Optical Microscopy. The transmission optical microscopy was carried out using Leitz optical microscope with Sony CCD video camera module (XC-77). A hot-stage was used for controlling the sample temperature within a stability of 0.3 ^{o}C. The cooling rate of the hot-stage was 60 ^{o}C/min. Two kinds of thermal history were employed (single quench and cyclic quench). The thermal history of the single quench and the cyclic quench are shown in Figure 1. In the single quench measurement, the sample was melted at 160 ^{o}C for 5 min to remove previous thermal history and quenched to 130 ^{o}C for 1440 min and then quenched to room temperature. In cyclic quench measurement, the sample was melted at 160 ^{o}C for 5 min to remove previous thermal history and quenched to 130 ^{o}C for 240 min. Following that, the cooling and heating of the sample was repeated between 130 ^{o}C and 110 ^{o}C for four times and then the sample was quenched to room temperature.

RESULTS AND DISCUSSION

Figure 2 shows the phase contrast optical micrographs of PEH(60)/PEH(40) blend with single quench. After 240 min, the interconnected bicontinuous structure was observed. The interconnected bicontinuous tubes coarsen with time. In order to quantitatively understand the liquid-liquid phase separation observed, FFT analysis was carried out with the single quench results. The optical micrographs were analyzed by using the Scion Image (Scion Corporation) software. The FFT analysis results are displayed in Figure 3. The characteristic length due to the liquid-liquid phase separation appeared at 200 min. The value of the characteristic wave number, q_{max} , (inverse of the characteristic length) decreases and the intensity of the peak increases with time. The peak position was estimated from the FFT profiles. Figure 4 shows the time dependence of the characteristic wave number, q_{max}. The time dependence of the characteristic length can be represented by a power-law with an exponent of –0.46. The estimated characteristic length from Figures 2(b) and 2(d) are 1.5 μm^{-1} and 0.7 μm^{-1}, respectively. The optical micrographs of H60 with cyclic quench are shown in Figure 5. The liquid domain was enhanced by cyclic quench between molten and crystalline states. Figure 6 shows the final stage of the cyclically quenched sample. At 110 ^{o}C, the spherulite can be observed with cross polarizer (F) and the spherulite corresponds to the lighter matrix in (E). The contrast of the domains is reversed in crystalline and molten states. Consequently, the lighter matrix in (E) or the darker one in (G) corresponds to PEH-rich phase. It is clear that a large secondary structure was formed through the repeated crystallization processes with little or no change of the original phase separated domain (smaller structure) size. The large structure is accented by the crystalizable PE rich region.

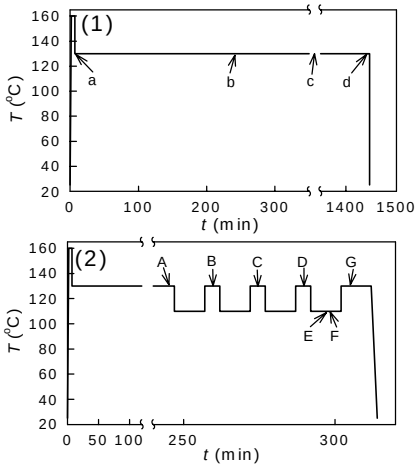

Figure 1. Thermal history. (1) Single quench, (b) Cyclic quench.

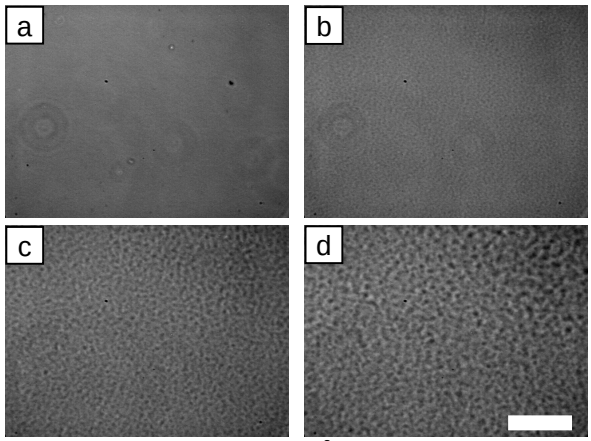

Figure 2. Optical micrographs (130 ^{o}C) of H60 with single quench. (a) 0 min, (b) 244 min, (c) 724 min, (d) 1450 min. Scale bar represents 50 μm. The alphabet in figure corresponds to that in **Figure 1(1)**.

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

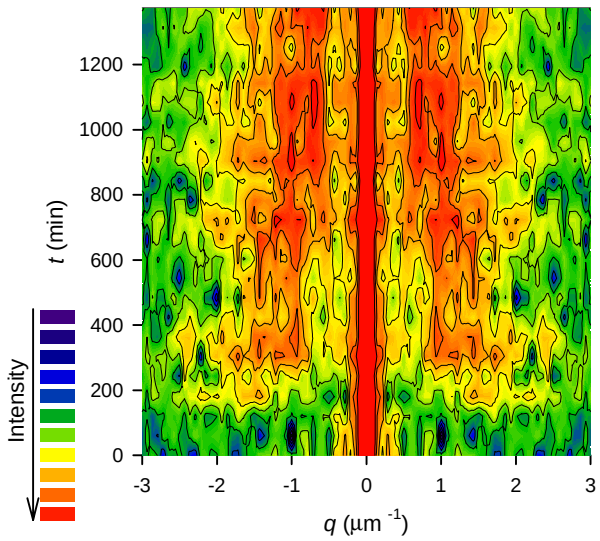

Figure 3. A composite plot of the FFT results as a function of time

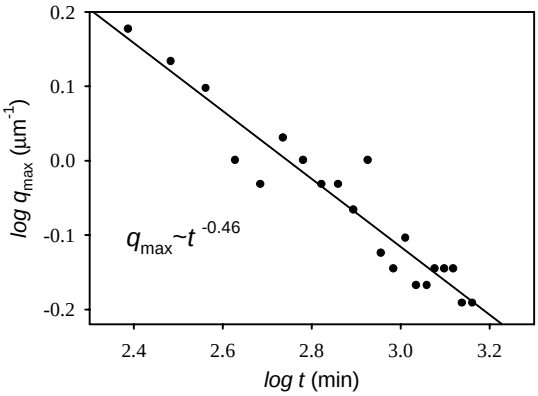

Figure 4. Characteristic length as a function of time.

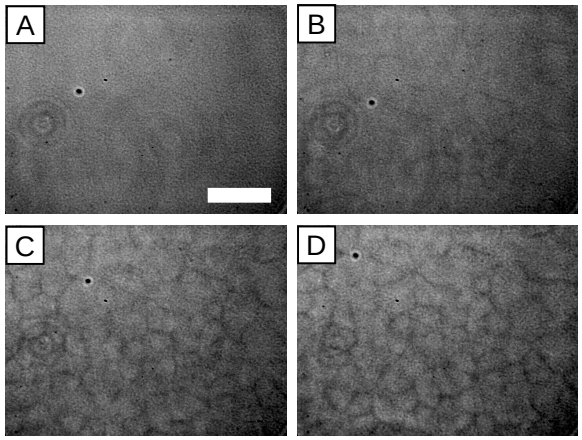

Figure 5. Optical micrographs (130 °C) of H60 with cyclic quench. Scale bar represents 50 μm. The alphabet in figure corresponds to that in **Figure 1(2)**.

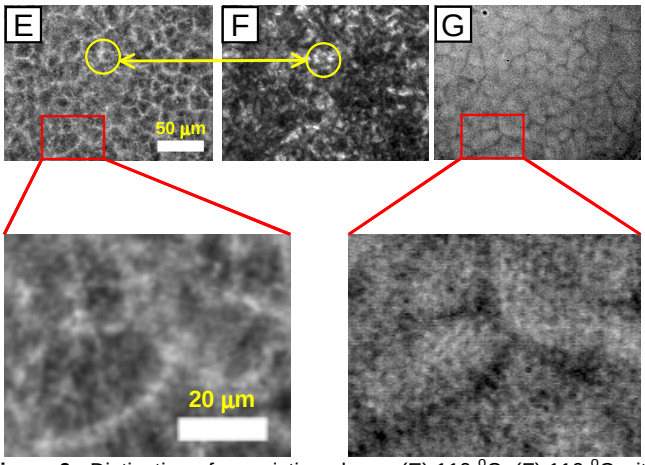

Figure 6. Distinction of co-existing phase. (E) 110 °C, (F) 110 °C with cross polarizer, (G) 130 °C. The alphabet in figure corresponds to that in **Figure 1(2)**.

CONCLUSION

The phase behavior in copolymer blend of PEH(60)/PEB(40) blend has been studied by phase contrast optical microscopy within the two phase region. In single quench, the interconnected bicontinuous structure was observed in molten state. The interconnected bicontinuous tubes coarsen with time. The FFT analysis with single quench results shows that the phase separation behavior observed can be explained by power-low and is the late-stage of the spinodal decomposition. On the other hand in cyclic quench, the liquid domains were enhanced by cyclic quench between molten and crystalline state. In molten state, the darker and lighter matrix corresponds to PEH and PEB-rich phase, respectively. A large secondary structure was formed through this repeated crystallization processes, which was accented by the PE rich region.

REFERENCES

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2. Shimizu, K; Wang, H.; Wang, Z. G.; Kim, H.; Han, C. C. submitted to *Abstr. Pap. Am. Chem. S.*