MORPHOLOGICAL DEVELOPMENT IN COPOLYMER BLENDS OF POLY(ETHYLENE-CO-HEXENE) AND POLY(ETHYLENE-CO-BUTENE)

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Introduction

The phase behavior of the copolymer blends of poly(ethylene-co-hexene) and poly(ethylene-co-butene) (abbreviated as PEH and PEB, respectively) is the focus of this study.[1-3] Recently, the liquid-liquid phase boundary and equilibrium melting temperature in this blend has been measured by the techniques of light scattering and differential scanning calorimetry.[2] A upper critical solution temperature of 146 °C at the composition $\phi = 0.44$ and a systematic PEH composition dependence of the equilibrium melting temperatures have been obtained. Due to the micro-structural similarity between PEH and PEB, it is difficult to distinguish the two co-existent phases during the phase separation, however it is scientifically important to measure the liquid-liquid phase separation. In this paper, we will report the results of the morphological development in copolymer blends of PEH and PEB by using transmitted optical microscopy.

Experimental•

The statistical copolymers of PEH and PEB were synthesized by the metallocene-catalysts.* The sample information can be found in a previous publication.[2] The blends of PEH and PEB, which have the PEH mass fraction of 100 % (PEH), 90 % (H90), 50 % (H50) and 40 % (H40) were prepared by the co-precipitation method. The blends were first dissolved in a xylene solution at 120 °C, then the solution was cooled to 100 °C and kept for 24 h. The solution was poured into the cold methanol at 0 °C to precipitate the blends. The blends obtained were dried in the air for 24 h and further dried for 72 h in vacuum oven. Samples were pressed between cover glasses to the thickness of approximately 20 μm.

The morphological development was observed by using a Nikon optical microscope (OPTIPHOT-2) with a Kodak CCD camera (MEGAPLUS).* A hot-stage was used to control the sample temperature. The obtained optical micrographs were analyzed by using the software Scion Image (Scion Corporation).

Two kinds of temperature control procedure were employed. The first one is normal quench measurement from 160 °C to different isothermal crystallization temperatures. The second one is a double quench measurement. In this measurement, the sample was cooled down from 160 °C to 130 °C, which is above the equilibrium melting temperature, and kept for 5 h to promote the liquid-liquid phase separation and then cooled down to different isothermal crystallization temperatures.

Results and Discussion

Figures 1 and 2 show the selected optical micrographs of the PEH and H50 isothermally crystallized at 117 °C, respectively. At 117 °C, the spherulites of PEH are spread in the whole image with passing time and finally they touch each other. However in case of H50, the number of spherulites is less than that in PEH and the spherulites cease to grow after certain time. **Figure 3** shows the spherulitic growth rates in PEH, H90 and H50 as a function of the isothermal temperatures. At the low isothermal temperature region, it is difficult to discriminate the difference of the growth rates between the samples. With the increasing isothermal temperature, the difference becomes obvious and the growth rates at each isothermal temperature decrease with the increase of PEB composition.

According to the phase diagram of PEH/PEB blends, PEH and H90 do not undergo the phase separation and H50 phase separates in the experimental condition of this study. However in the normal quench measurement, the rate of liquid-liquid phase separation is too slow to be observed. In order to observe the liquid-liquid phase separation, the double quench measurement was carried out using the H40, which is close to the critical composition of $\phi = 0.44$.

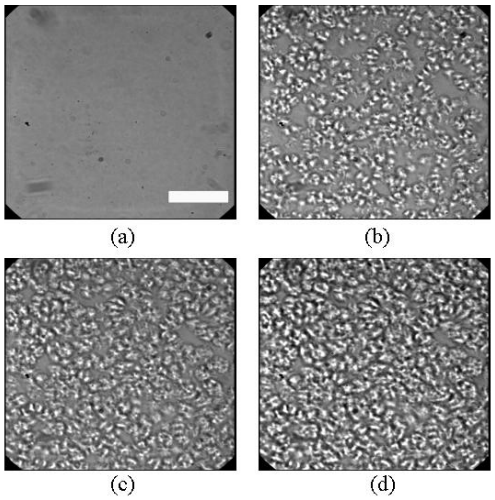

Figure 1. Optical micrographs of PEH isothermally crystallized at 117 °C. (a) 0 min, (b) 48 min, (c) 79 min, (d) 119 min. Scale bar represents 40 μm.

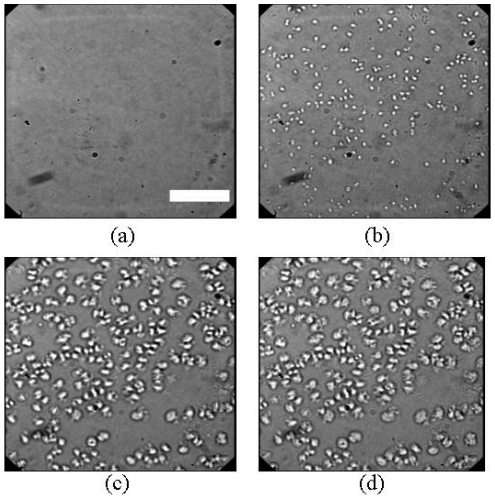

Figure 2. Optical micrographs of H50 isothermally crystallized at 117 °C. (a) 0 min, (b) 30 min, (c) 150 min, (d) 249 min. Scale bar in (a) represents 40 μm.

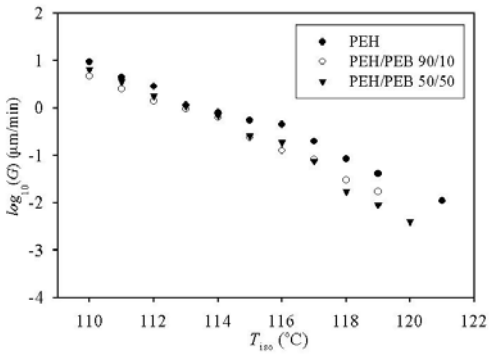

Figure 3. Spherulitic growth rates in PEH, H90 and H50 blends as a function of the isothermal temperatures.

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

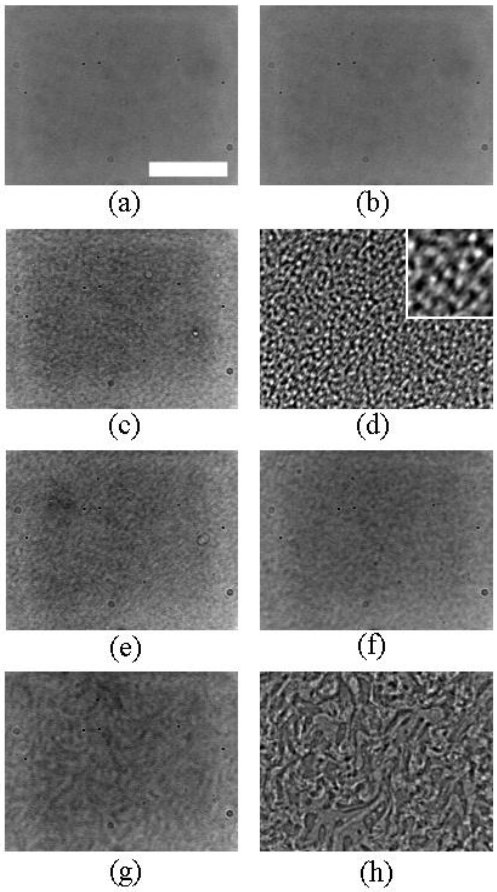

Figure 4. Optical micrographs with the double quench measurement of H40. (a) 160 °C, (b) 130 °C, (c) 130 °C for 300 min, (d) room temperature from (c), (e) 130 °C from (d), (f) 219 min from (e), (g) 938 min from (e), (h) room temperature from (g). Scale bar in (a) represents 40 μm.

Figure 4 shows the optical micrographs with the double quench measurement. The sample was heated up from room temperature to 160 °C (a), and then quenched to 130 °C (b). After waiting for 300 min at 130 °C (c), the interconnected bicontinuous structure is clearly seen. When the above sample was cooled to room temperature (d), both the interconnected bicontinuous structure and spherulites appear. The spherulites disappear after reheating the sample to 130 °C and the interconnected bicontinuous structure still remain (e). The size of the interconnected bicontinuous tubes grows with time (see, (f) and (g)). When the sample was cooled down to room temperature again, both the interconnected bicontinuous structure and spherulites are seen (h). However the number of the spherulite is less than that in the previous image (d) and the size of the interconnected bicontinuous tube is bigger than that in the image (d).

During the time from (e) to (g), the sample was cooled to different isothermal crystallization temperatures to observe the crystallization behavior under the phase separation condition. **Figure 5** shows the optical micrographs with this double quench measurement. The phase-separated sample H40 was cooled to 116 °C ((a) and (b)). The spherulite is found to grow from the dark part (see the enclosed part in (b) and (c)) and its size increases with time (enclosed part in (d)). This result indicates that the dark part on the phase-separated blend corresponds to the PEH-rich phase.

Conclusions

In order to understand the liquid-liquid phase separation and crystallization in copolymer blends of PEH and PEB, the transmitted optical microscopy was employed to observe the morphological development with the normal quench and double quench measurements. In the normal quench measurement, the spherulites were observed and the spherulitic growth rates in PEH, H90 and H50 were obtained. However the liquid-liquid phase separation could not be observed in this measurement. These results suggest that the blends are ease to crystallize at the isothermal crystallization temperature and it is difficult to observe the liquid-liquid phase separation due to the similarity of the refractive indices between PEH and PEB components. In the double quench measurement, both the interconnected bicontinuous structure and spherulites can be observed. The size of the interconnected bicontinuous tubes was increased with time. The results show that the liquid-liquid phase separation can be observed in the nearly isorefractive PEH/PEB blends and the morphology in the blends can be controlled by adjusting the sample temperatures.

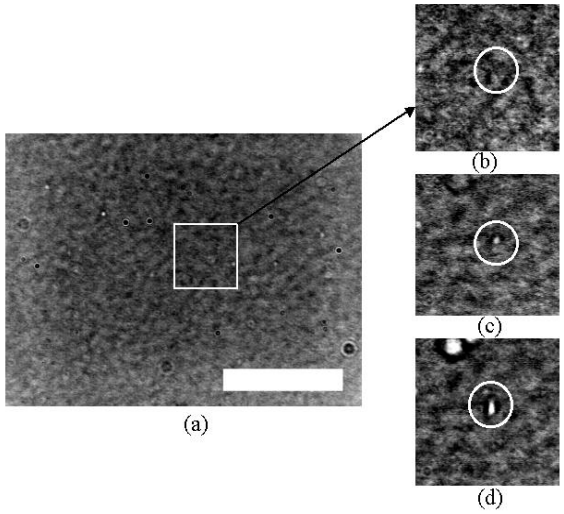

Figure 5. Optical micrographs with the double quench measurement of H40, phase separated at 130 °C for 10h first and then isothermally crystallized at 116 °C. (a) 0 min, (b) magnified enclosed part in (a) 0 min, (c) 3 min, (d) 6 min. Scale bar in (a) represents 40 μm.

References

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(2) Wang, H.; Shimizu, K; Hobbie, E.K.; Wang, Z.G.; Meredith, J.C.; Karim, A.; Amis, E.J.; Hsiao, B.S.; Hsieh, E.T.; Han, C.C. *Macromolecules,* in press.

(3) Wang, H.; Shimizu, K; Kim, H.; Hobbie, E.K.; Wang, Z.G.; Han, C.C. *J. Chem. Phys.,* in press.