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Orientation of crystalline lamellae in the vicinity of interface of immiscible polyethylene/poly(methyl methacrylate) blends containing polyethylene-*block*-poly(methyl methacrylate)

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Abstract

Morphologies in the vicinity of interfaces of immiscible linear-low-density polyethylene/poly(methyl methacrylate) (LLDPE/PMMA) = 80/20 (w/w) blends containing polyethylene-*block*-poly(methyl methacrylate) (PE-*b*-PMMA) were investigated by transmission electron microscopy (TEM). It was found that crystalline lamellae of polyethylene was oriented vertically to the interface between LLDPE and PMMA phases in LLDPE/PMMA blends containing PE-*b*-PMMA. In addition, length of lamellae oriented vertically to the interface became longer with increasing content of PE-*b*-PMMA in the blends. © 2002 Published by Elsevier Science Ltd.

Keywords: Polymer blend; Compatibilizer; Transmission electron microscopy

1. Introduction

One of the conventional ways to improve compatibility of immiscible polymer blends is addition of compatibilizers [1,2]. In many studies, block or graft copolymers, the segments of which are chemically identical or miscible to the blend components, have been used as compatibilizers [3–15]. When this type of block copolymer is added to an immiscible polymer blend, the block copolymer assembles at interface of the phase separated phases and behaves as a surfactant [2].

When one segment of the block copolymer and a component that is identical with the segment in the blend are crystalline polymers, such as polyethylene, it is expected that crystalline morphology of the component of the blend is affected by crystalline growth of the block copolymer. Especially, the effect of crystallization of the block copolymer should appear remarkably on the crystallization of the blend component in the vicinity of interface. Since crystallization of the block copolymer is strongly affected by the spatial constraint [16], orientation of crystalline lamellae of a blend component in the vicinity of the interface should be strongly affected by population of block copolymer and curvature of the interface. In the present study, we investigate the change in the orientation of crystalline lamellae in the vicinity of interface of immiscible polymer blends with varying the population of block copolymer at the interface using linear-low density polyethylene/poly(methyl methacrylate) (LLDPE/PMMA) blends with polyethylene-*block*-poly(methyl methacrylate) (PE-*b*-PMMA).

2. Experimental

LLDPE was obtained from Mitsui Chemical Co. Ltd (LLDPE 220E). PMMA was supplied from Mitsubishi Rayon Co. Ltd with molecular weight $\bar{M}_n = 8.7 \times 10^3$ and $\bar{M}_w = 1.7 \times 10^4$. PE-*b*-PMMA was supplied from and Maruzen Peterochemical Co. Ltd with molecular weight $\bar{M}_v = 2.0 \times 10^5$ and MMA content = 16 wt%, respectively.

LLDPE/PMMA = 80/20 (w/w) blends containing 0, 5,

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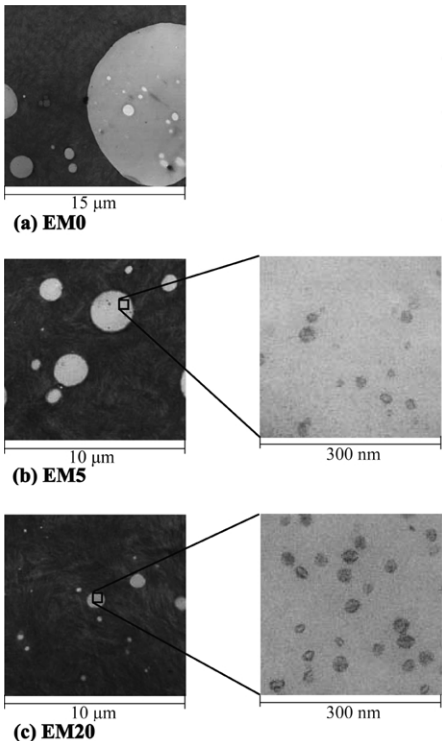

Fig. 1. TEM micrographs of (a) EM0, (b) EM5, and (c) EM20. The photos appended to (b) and (c) are TEM micrographs for inside of droplets of EM5 and EM20, respectively. In these photos, bright (white) area is corresponding to PMMA-rich phase and dark (gray) area is LLDPE-rich phase.

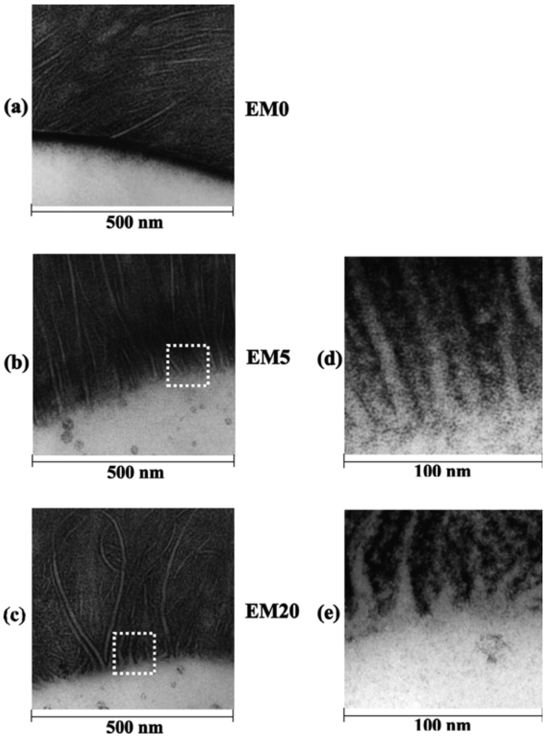

Fig. 2. TEM micrographs near interface between LLDPE-rich and PMMA-rich phases for (a) EM0, (b) EM5, and (c) EM20. Photos (d) and (e) are the magnified images in dotted square in photos (b) and (c), respectively.

and 20 phr of PE-*b*-PMMA were prepared by melt-kneading at 180 °C for 3 min using a laboratory-made single screw kneader. The resulting blend samples were annealed at 180 °C for 2 h to remove any internal strains. The LLDPE/PMMA = 80/20 (w/w) blends containing 0, 5 and 20 phr of PE-*b*-PMMA are denoted as EM0, EM5 and EM20, respectively.

The blend samples were stained by RuO_4. The stained samples were cut into ca. 100 nm thickness by a Reichert ULTRACUT-N ultramicrotome. TEM observations were performed using a JEOL JEM 100CX at an acceleration voltage of 100 kV.

3. Results and discussion

Fig. 1 shows TEM micrographs of macroscopic views of EM0, EM5 and EM20. The photos appended to EM5 and EM20 are TEM micrographs for inside of the dispersed droplets of EM5 and EM20, respectively. In these photos, dispersed droplets (white phases) are PMMA-rich phases and matrix (dark phase) is LLDPE-rich phase. In EM0, large droplet of ca. 13 μm diameter exists and distribution of size of dispersed droplets is broad. On the contrary, in EM5, sizes of dispersed droplets are less than 3 μm in diameter. This result indicates that PE-*b*-PMMA behaves as a compatibilizer for LLDPE/PMMA blends. Therefore, PE-*b*-PMMA assembles at the interfaces between LLDPE-rich and PMMA-rich phases. In addition, average diameter of dispersed droplets of EM20 becomes half the size that of EM5. However, as shown in TEM photos for inside of dispersed droplets for EM5 and EM20, many micelles of the PE-*b*-PMMA in the droplets in both EM5 and EM20 were observed. This suggests that the interfaces of both EM5 and EM20 are saturated by PE-*b*-PMMA and excess block copolymers exist in the droplets. Therefore, it is expected that population of PE-*b*-PMMA in unit area of the interface in EM5 is equivalent to that in EM20, while size of the dispersed droplet, i.e. curvature of the interface, of EM5 is different from that of EM20.

Fig. 2 shows TEM micrographs of EM0, EM5 and EM20 in the vicinity of the interface between LLDPE- and PMMA-rich phases. In EM0, direction of crystalline lamellae is independent of interface. Since the narrow interface between LLDPE-rich and PMMA-rich phases is clearly observed as deeply black layer in EM0, there is little contact between LLDPE and PMMA through the interface. Therefore, crystallization of LLDPE occurs independently of the interface or existence of another phase. On the other hand, in EM5 and EM20, LLDPE-rich and PMMA-rich phases are sufficiently adhered. This result is an evidence that PE-*b*-PMMA assembles at the interface in both EM5 and EM20. In EM5, the crystalline lamellae are oriented vertically to the interface to ca. 400 nm from the interface. Fig. 2(d) shows magnified image in the area surrounded with the dotted line in Fig. 2(b), which is just around the interface of EM5. Although the microphase separation is not recognized obviously at the interface, the lamellae exist more closely just at the interface. In addition, the lamellae grow continuously from the PMMA-rich phase and the direction of the lamellae at the interface is almost vertical to the interface. Since PE chains assemble closely at the interface, direction of growth of the crystalline lamellae is limited vertically to the interface due to existence of neighboring crystalline lamellae. The curvature of the interface in EM5 is relatively level. Therefore, it is considered that the spatial constraint of growth direction of crystalline lamellae by neighboring lamellae is effective in long range in EM5. This would cause the spontaneous orientation of crystalline lamellae in long range. On the other hand, in EM20, although the crystalline lamellae in the region within 50 nm from the interface tend to orient perpendicular to the interface as shown in Fig. 2(c) which shows the magnified image just around the interface in Fig. 2(c), the orientation of the crystalline lamellae becomes irregular with increasing distance from the interface in the region beyond 50 nm from the interface. As same as the case of EM5, since PE chains assemble closely at the interface, direction of growth of the crystalline lamellae is limited vertically to the interface by neighboring PE chains in the vicinity of the interface. However, the curvature of the interface of EM20 is relatively sharp compared with that of EM5 as shown in Fig. 1. Because the constraint of the growth direction of crystalline lamellae is released with increasing distance from the interface due to curvature of the dispersed droplets, it is considered that the orientation of the crystalline lamellae is distorted.

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