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Compatibilizing effects of poly(ethylene-*block*-methyl methacrylate) on blends of polyethylene and poly(4-vinylphenol)

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Abstract

Compatibilizing effects of polyethylene–poly(methyl methacrylate) diblock copolymer (P(E-*b*-MMA)) on immiscible blends of polyethylene (PE) and poly-4-vinylphenol (PVPh) have been investigated by scanning electron microscopy (SEM) and optical microscopy (OM). In OM observation, it was found that there was coalescence of the PVPh particles in the PE/PVPh blends without P(E-*b*-MMA) at 180°C. On the contrary, the coalescence of the PVPh particles was not observed in the PE/PVPh blends added with P(E-*b*-MMA) at 180°C. In addition in the SEM observation, when small amount of P(E-*b*-MMA) are added to the PE/PVPh blends, the size of PVPh particles decreased drastically and their size distribution become narrower with increasing P(E-*b*-MMA) content. Therefore it has been concluded that P(E-*b*-MMA) acts as the compatibilizer in the PE/PVPh blends. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Polymer blends; Compatibilizer; Block copolymer

1. Introduction

Since most polymer pairs are mutually immiscible due to their high degree of polymerization, polymer blends show various morphologies [1]. It is well known that the phase structures have significant effects on performances of polymer alloys [1]. Hence, it is considered that the compatibilization of polymer blends is of great importance to control the performance of polymer alloys. Especially, it is considered that establishment of compatibilizing techniques for blends of polar and non-polar polymers is needed in practical aspects, such as surface modification. However, compatibilization for these polymer blends is difficult because the component polymers are strongly segregated.

One way to improve the compatibilization and interfacial adhesion in immiscible polymer mixtures is addition of a block copolymer having same or miscible blocks with components of the polymer blends [2–8]. Since these types of the block copolymers added to blends of immiscible polymer pairs locate at the interface between separated two phases, interfacial tension is reduced and compatibilization in the blends are enhanced due to the reduction of interaction parameter [9–11]. Further, it has been reported that an exothermic interaction between a block of copolymer and component polymers enhances the compatibility in the polymer blends [11]. Therefore, it might be expected that a block copolymer constructed by polar and non-polar blocks acts as a compatibilizing agent for the blends of polar and non-polar polymers. Then, we focus on poly(ethylene-*block*-methyl methacrylate) (P(E-*b*-MMA)) as a compatibilizer for blends of polyethylene (PE) and poly(4-vinylphenol) (PVPh).

It is well known that PVPh is immiscible with PE and forms miscible mixtures with PMMA due to exothermic interactions [12]. Therefore, P(E-*b*-MMA) has the ability as a compatibilizer for PE/PVPh blends. Then, we investigate the compatibilizing effects of P(E-*b*-MMA) on immiscible PE/PVPh blends by mainly morphological observations.

2. Experimental

2.1. Materials

Polymers used in this study were PE of linear low density type, PVPh, and (P(E-*b*-MMA)). PE was supplied from Mitsui Chemical Co., Ltd. (Mitsui LLDPE 220E). PVPh ($\overline{M}_n = 1200$, $\overline{M}_w = 2100$,) and P(E-*b*-MMA) ($\overline{M}_v = 2.0 \times 10^4$, MMA:16 wt%) were supplied from Maruzen Petrochemical Co., Ltd.

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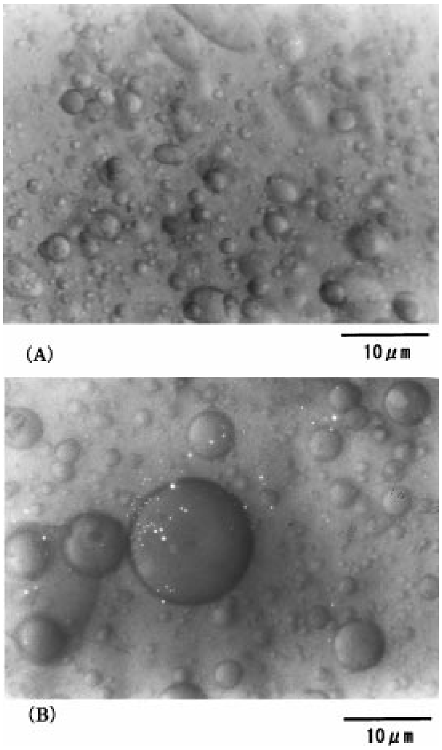

Fig. 1. Optical micrographs for PE/PVPh = 80/20 (w/w) blend: (A) as-blended; (B) annealed at 180°C for 2 h.

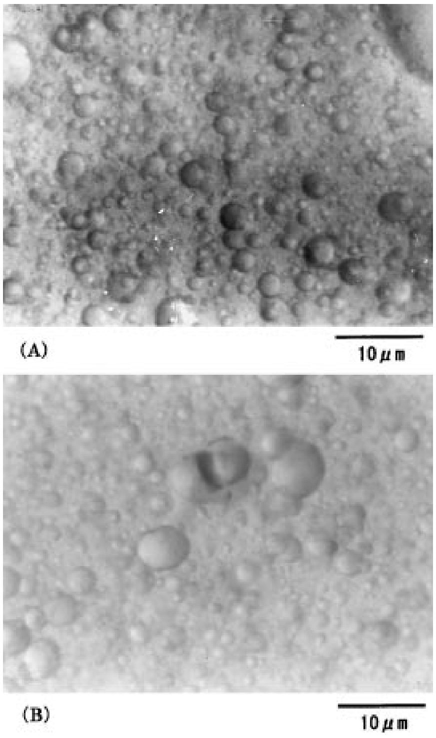

Fig. 2. Optical micrographs for PE/PVPh/P(E-*b*-MMA) = 80/20/1.0 (w/w/w) blend: (A) as-blended; (B) annealed at 180°C for 2 h.

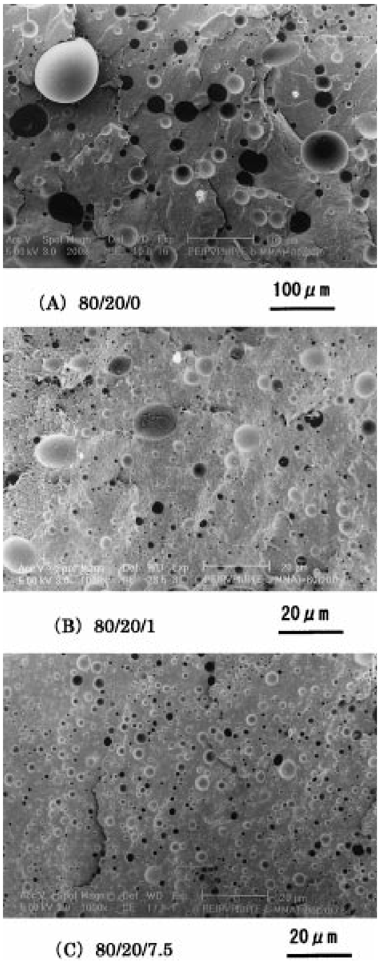

Fig. 3. SEM micrographs of PE/PVPh = 80/20 (w/w) blends added P(E-*b*-MMA): (A) 0; (B) 1.0; (C) 7.5 phr.

2.2. Blend preparation

Firstly, polymer blends were prepared by solution mixing. PE and P(E-*b*-MMA) were weighted to the desired composition and dissolved in toluene at 5 wt% polymer concentration at 110°C. Then, the desired amount of PVPh was poured into the solution and dispersed Toluene was evaporated on glass plates at room temperature for 24 h and dried in vacuum at 80°C for 1 week and further dried at 180°C for 2 h. Resulting blend samples were further mixed mechanically in molten state at the constant rotation rate.

2.3. Transmission optical microscopy

Transmission optical microscopy for PE/PVPh/P(E-*b*-MMA) blends were performed using a Nikon S-Ke optical microscope equipped with a heating stage. All the optical micrographs were taken at 180°C on the heating stage.

2.4. Scanning electron microscopy

Scanning electron microscopy (SEM) for the PE/PVPh/

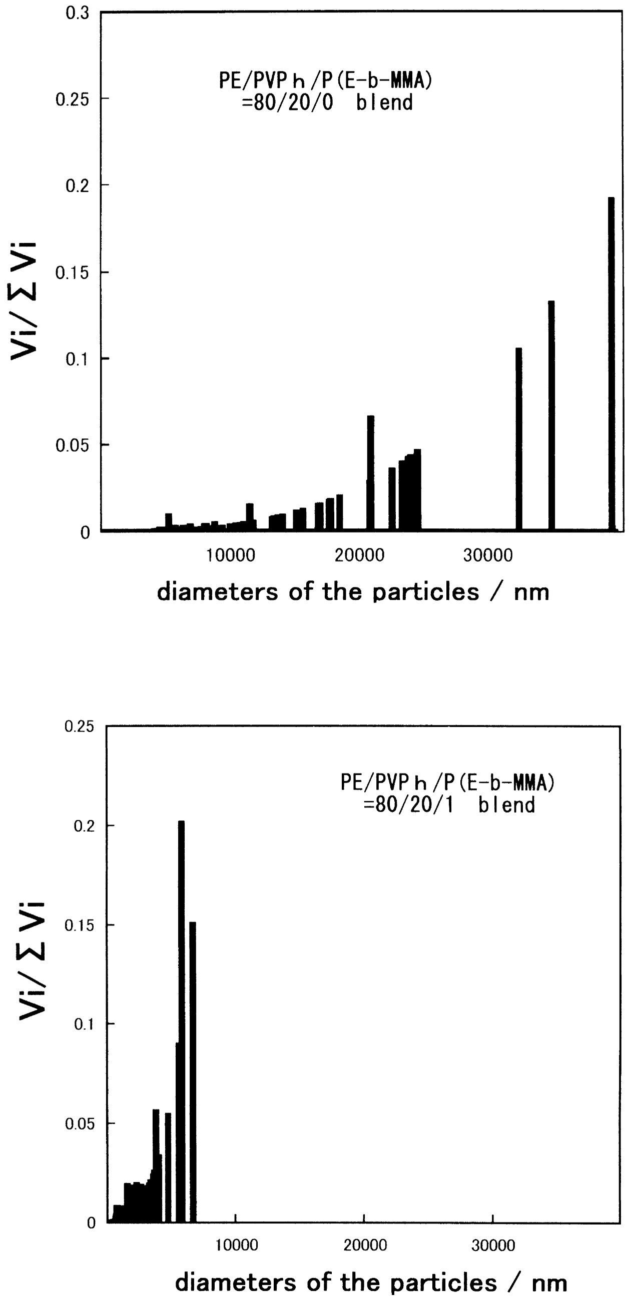

Fig. 4. Results of image analysis for SEM micrographs in Fig. 3.

P(E-*b*-MMA) blends were performed using a PHILIPS XL30 scanning electron microscope at an accelerating voltage of 5 kV. The blend samples were annealed at 180°C for 2 h and then were quenched and fractured in liquid N_2. The resulting fracture surfaces were etched by tetrahydrofuran (THF) to remove PVPh-rich phases and coated by Au.

3. Results and discussion

Fig. 1 shows optical micrographs for PE/PVPh = 80/20 (w/w) blends without P(E-*b*-MMA) annealed at 180°C for 0 and 2 h. When the PE/PVPh blends are not annealed, it seems that the dispersed particles are relatively small and the size of the particles is homogeneous as shown in Fig. 1A. On the contrary, when the PE/PVPh blends are annealed above the melting temperature of PE and glass transition temperature of PVPh, it is clearly recognized that the PVPh particles are roughened and enlarged as shown in Fig. 1B. Therefore, it has been pointed out that the interfaces between matrix and dispersed particles in PE/PVPh blends are unstable in the case of absence of P(E-*b*-MMA) in the blends. On the contrary, for PE/PVPh blends added P(E-*b*-MMA) show different developments of phase morphology with annealing at 180°C. Fig. 2 shows optical micrographs for PE/PVPh = 80/20 (w/w) blend added 1.0 phr of P(E-*b*-MMA) annealed at 180°C for 0 and 2 h. For the PE/PVPh/P(E-*b*-MMA) blends, coalescence of dispersed particles is not observed even for the blend samples annealed for 2 h at 180°C. Therefore, it is pointed out that the interfaces between matrix and dispersed particles in PE/PVPh blends are stabilized by adding P(E-*b*-MMA). It is considered that the stabilization of the interfaces between separated two phases is caused because P(E-*b*-MMA) added to the PE/PVPh blends present at the interface between the matrix and dispersed particles and act as surfactants. Since the stability of the interfaces in PE/PVPh blends is driven by adding P(E-*b*-MMA), it is considered that P(E-*b*-MMA) has an ability to become a effective compatibilizer for PE/PVPh blends. Then, morphological changes of PE/PVPh blends by adding P(E-*b*-MMA) are investigated.

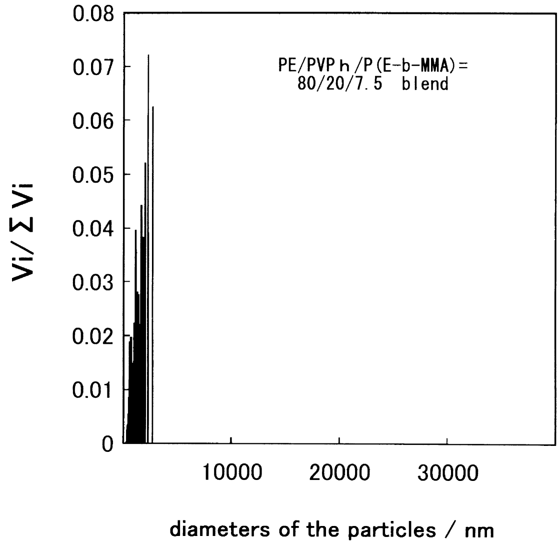

Fig. 4. (*continued*)

Fig. 3 indicates SEM micrographs for PE/PVPh = 80/20 (w/w) blends with 0, 1.0 and 7.5 phr of P(E-*b*-MMA) annealed at 180°C for 2 h. The dispersed particles in the SEM micrographs are attributed to PVPh-rich phases because the fractured surfaces of the PE/PVPh/P(E-*b*-MMA) blends were treated by THF as a good solvent for PVPh and a poor solvent for PE. Rough and large dispersed particles of PVPh-rich phases corresponding to Fig. 1B are observed for the PE/PVPh = 80/20 (w/w) blends without P(E-*b*-MMA) as shown in Fig. 3A. On the contrary, by adding 1.0 phr of P(E-*b*-MMA) to PE/PVPh = 80/20 (w/w) blends, the sizes of dispersed particles are drastically diminished as shown in Fig. 3B. Therefore, P(E-*b*-MMA) demonstrates remarkably the compatibilizing effects on PE/PVPh blends when a small amount of P(E-*b*-MMA) is added to PE/PVPh blends. Further, it can be seen that the sizes of the dispersed particles composed of PVPh-rich phases are decreasing with increasing P(E-*b*-MMA) contents as shown in Fig. 3B and C. Hence the compatibilizing effects of P(E-*b*-MMA) of PE/PVPh blends are maintained with increasing P(E-*b*-MMA) contents. To discuss the change in the morphology of PE/PVPh blends by adding P(E-*b*-MMA) more quantitatively, image analysis for the SEM micrographs is performed.

Fig. 4 represents the histograms of the diameter of the dispersed domains for PE/PVPh = 80/20 (w/w) blends with 0, 1.0, and 7.5 phr of P(E-*b*-MMA). As can be seen in Fig. 4a, the diameters of the dispersed particles of PE/PVPh = 80/20 (w/w) blend with 0 phr of P(E-*b*-MMA) have large value. In addition, the distribution of the size of the diameters of dispersed particles are relatively wider in the PE/PVPh/P(E-*b*-MMA) = 80/20/0 (w/w/w) blend. On the contrary, when 1.0 phr of P(E-*b*-MMA) is added to PE/PVPh = 80/20 (w/w) blends, the distribution of the diameter of dispersed particles constructed by PVPh-rich phases are drastically sharpened and the diameter which gives a peak of the distribution is shifted to a smaller diameter of the dispersed particles comparing with the PE/PVPh = 80/20 (w/w) blend without P(E-*b*-MMA). Therefore, morphology of the PE/PVPh blend is homogenized by adding a small amount of P(E-*b*-MMA). Further, in the PE/PVPh = 80/20 (w/w) blend with 7.5 phr of P(E-*b*-MMA), the distribution of the dispersed particles further become narrower and peak of the distribution is smaller than those of the PE/PVPh = 80/20 (w/w) blend with 1.0 phr of P(E-*b*-MMA). Therefore, the compatibilizing effects of P(E-*b*-MMA) on PE/PVPh blends appear in decreasing the diameter of dispersed domains and sharpening the distribution of diameter of dispersed particles. However, when the P(E-*b*-MMA) content in PE/PVPh blends is much larger than 7.5 phr, different effects of P(E-*b*-MMA) on the morphological change of PE/PVPh blends appear.

Figs. 5 and 6 show SEM micrographs and results of image analysis for the SEM micrographs for PE/PVPh = 80/20 (w/w) blends added 15 phr of P(E-*b*-MMA), respectively. As can be seen in these figures, the morphology of phase separated structures in the PE/PVPh = 80/20 (w/w) blend with 15 phr of P(E-*b*-MMA) is more rough and larger than that of the PE/PVPh = 80/20 (w/w) blend with 7.5 phr of P(E-*b*-MMA). In addition, as shown in Fig. 6 there are two ranges of the distribution of the particle. One is the range of 0–7500 nm and the another is 7500–10,000 nm. This type of distribution of dispersed particles has not been found in the other blends. Hence the distribution of the dispersed particles of PE/PVPh = 80/20 (w/w) blends changes from mono- to bi-modal distribution with increasing P(E-*b*-MMA) contents at over 7.5 phr of P(E-*b*-MMA). Therefore, when the content of P(E-*b*-MMA) in PE/PVPh blends is over 7.5 phr, the compatibilizing effects of P(E-*b*-MMA) on PE/PVPh blends are losing with increasing P(E-*b*-MMA) content. Although the mechanism of the change in the morphology in PE/PVPh blends with over 7.5 phr of P(E-*b*-MMA) is indistinct, there is a minimal content of P(E-*b*-MMA) acting as a compatibilizer for PE/PVPh blends.

Fig. 7 indicates that change in volume average diameter of dispersed particles in PE/PVPh = 80/20 (w/w) blends with P(E-*b*-MMA) contents. The diameter of the dispersed particles is drastically decreased by adding small amounts of P(E-*b*-MMA). Further, dispersed particles of PVPh-rich phases becomes smaller with increasing P(E-*b*-MMA)

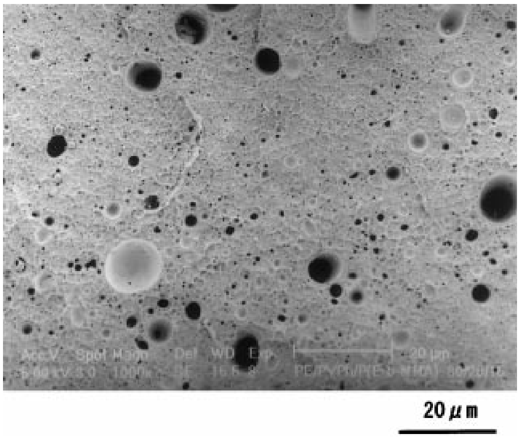

Fig. 5. SEM micrograph of PE/PVPh = 80/20 (w/w) blend added 15 phr of P(E-*b*-MMA).

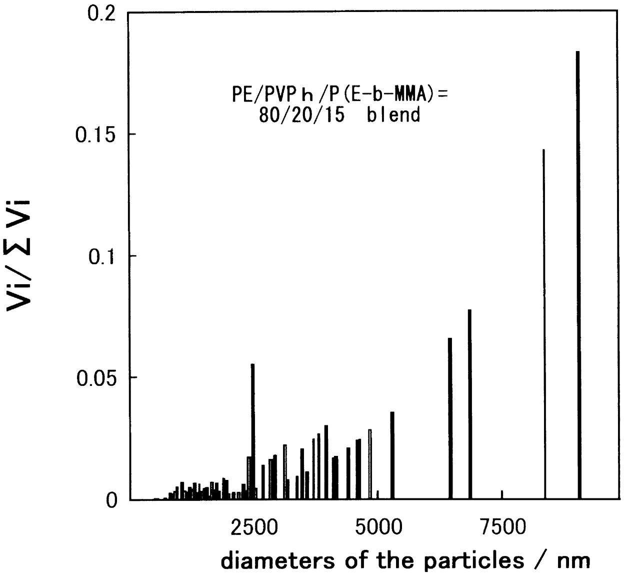

Fig. 6. Results of image analysis for SEM micrographs in Fig. 5.

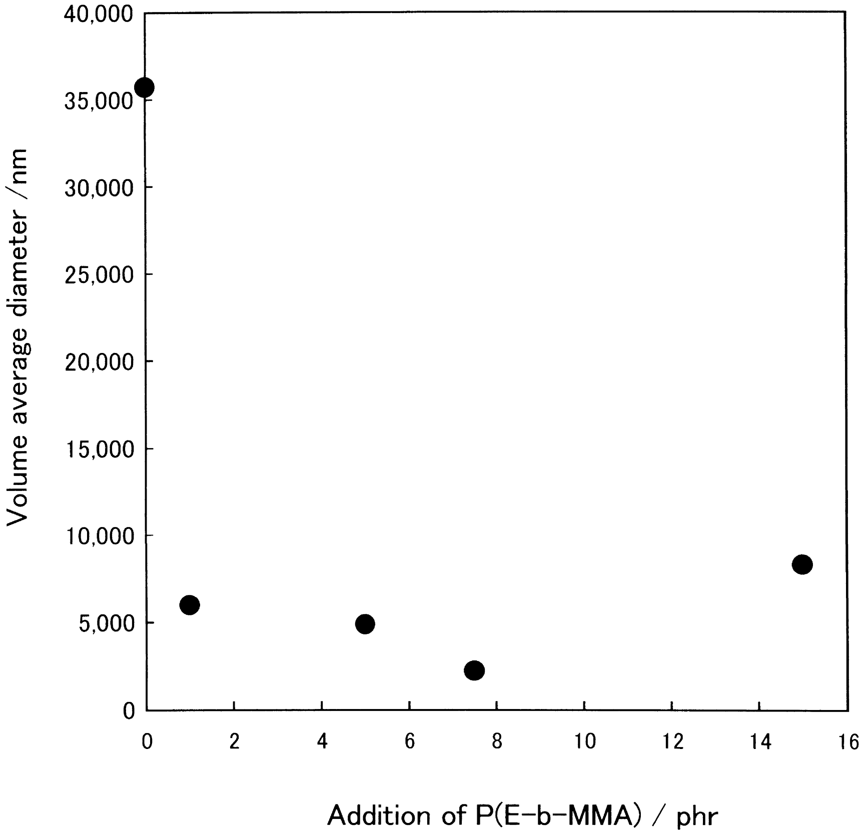

Fig. 7. Change in volume average diameter of dispersed particle in PE/PVPh = 80/20 (w/w) blends with P(E-*b*-MMA) contents.

contents up to 7.5 phr. However, at over 7.5 phr of P(E-*b*-MMA), the average diameter of the dispersed particles is increasing with increasing P(E-*b*-MMA) contents. In case of the blends of homopolymer A and B with the A-*b*-B block copolymer, it is expected that the diameter of the dispersed particles is decreasing and shows saturation with increasing A-*b*-B contents and block copolymers form micelle themselves in the matrix of the A/B blends over a certain content of block copolymers. However, in this study, different behavior from the prediction is observed. Although the detailed mechanism of the morphological change in PE/PVPh blends by adding P(E-*b*-MMA) is not clear, it is expected that this phenomenon is a characteristic feature in polymer blends by adding a compatibilizing agent which compatibilizes through the exothermic interactions. Further studies concerned with this phenomena will be carried out in our future works.

4. Concluding remarks

It was revealed that poly(ethylene-*b*-methyl methacrylate) is an effective comaptibilizer for the blend of PE and PVPh. Addition of the block copolymer into the blend makes the size of the dispersed PVPh particles decrease and the size distribution gets narrow with the addition of 7.5 phr of P(E-*b*-MMA). Further, by adding more amounts of P(E-*b*-MMA), the bimodal structure is observed. For studying this structure better, we should explore further.

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