

Morphology of the Transparent IPN-like System PE: (BMA-co-S)

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ABSTRACT: In the study of interpenetrating polymer networks (IPN)-like systems consisting of polyethylene (PE) and butyl methacrylate (BMA)–styrene (S) copolymer PE/(BMA-co-S), the effect of the crosslinker on the morphology of IPN by using electron microscopy and atomic force microscopy (AFM) was investigated. The IPN-like system PE/(BMA-co-S) represents a two-phase system with finely dispersed domains of crosslinked PE matrix. The interphase between dispersed domains and PE matrix is inhomogeneous and is considered the most interpenetrated part of this IPN-like system. The size of the domains decreases with the content of crosslinker used. The AFM micrographs allowed the observation of PE lamellae with lengths of about 25 nm. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 2615–2620, 2001

Key words: IPN-systems; morphology of IPN; butyl methacrylate–styrene copolymer; polyethylene matrix

INTRODUCTION

The method used for the preparation of interpenetrating polymer networks is described in detail in our previous papers.^{1–9} The interpenetrating polymer network (IPN)-like method used makes it possible to mix up two types of immiscible polymers such as polyethylene–vinyl polymer (styrene, methacrylate copolymers) and offers the possibility of obtaining heterogeneous polymer systems with interesting mechanical and optical properties^{10–12} and also cation-exchange membranes.^{13–14}

The IPN-like preparation leads to a system consisting of polyethylene (PE) and butyl methacrylate (BMA)–styrene (S) copolymer (BMA-co-S), which is transparent when of particular composition at room temperature and becomes opaque at higher temperatures. However, this process is reversible. On the other hand, this IPN-like system represents a two-phase system with finely dispersed domains of crosslinked butyl methacrylate–styrene copolymer in a crosslinked PE matrix, both partly interpenetrated with the partner polymer component.⁶

The main reason for the transparency of IPN obtained is ascribed to matching refractive indices (RI) of PE and BMA-co-S copolymer.⁴ The loss of transparency with the increasing temperature can be assigned to unequal changes in RI of the components of the IPN system.^{4,9}

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Previous work⁴ has shown that the amount of the crosslinking agent of BMA-co-S copolymer affects not only mechanical but also optical properties of this IPN system. From a deeper study of the morphology of this system, where attention was directed toward the effect of the crosslinking agent primarily on the morphology of IPN by using electron microscopy as well as atomic force microscopy (AFM), new valuable information was expected, which would shed light on the properties observed.

Two IPN samples of highest transparency were studied, consisting of PE and BMA-co-S, the molar ratio of both components being always 1 : 1. The difference between both components consisted of a different ratio between BMA and S. In one IPN sample, the ratio was BMA : S = 70 : 30 [i.e., PE/(70B : 30S)] and in the second one 80 : 20 [i.e., PE/(80B : 20S)].

EXPERIMENTAL

Synthesis of IPN-like Samples

PE—low-density polyethylene (LDPE; type Bralen RA 2–19, Slovnaft, Bratislava, Slovak Republic) with a melt-flow index of 1.7–2.3 g/10 min was dissolved in a mixture of monomers [S and BMA (Merck, Darmstadt, Germany)]. 2,5-Dimethyl-2,5-di(tert butylperoxy)hexane [Luperox-101 (Peroxid-Chemie, Pullach, Germany)], as crosslinker of PE phase, and 1,4-butanediol dimethacrylate [BDDM (Merck, Darmstadt, Germany); 0.5, 1.5, and 3.0 mol %], as crosslinker of methacrylic copolymer phase, were added to the mixture.

The polymerization of the poly(BMA-co-S) copolymers, their crosslinking by BDDM as well as the final PE crosslinking, proceeded in glass forms at 120°C for 5 h; then the temperature was raised to 160°C and reaction took place for another 1 h.

The copolymer/PE molar ratio in all samples was kept equal to 1. The copolymer molar ratio BMA/S was varied. One assumes that the polymerization of vinyl monomers and their crosslinking occurred first; this may be accompanied by grafting of vinyl monomers onto PE and the incorporation of PE chains into a vinyl network. In the last stages of reaction, a PE network was formed as a result of the presence of peroxide (and absence of a monomer).^{1–3}

Transmission Electron Microscopy

The transmission electron microscopy (TEM) measurements on blends were carried out with a

LEO CEM 912 transmission electron microscope applying an acceleration voltage of 120 keV. The specimens were prepared by using an ultramicrotome (Ultracut E, Reichert and Jung) equipped with a cryochamber. Thin sections of about 50 nm were cut with a Diatome diamond knife at –120°C. The vinyl portions of the samples were stained with RuO₄.

Atomic Force Microscopy

Atomic force microscopy (AFM) experiments were performed with a Nanoscope III scanning probe microscope. Height and phase images were obtained simultaneously, while operating the instrument in the tapping mode under ambient conditions. Images were taken at the fundamental resonance frequency of the Si cantilevers, which was typically around 300 kHz. Typical scan speeds during recording were 0.3–1 line/s using scan heads with a maximum range of 16 × 16 μm. The phase images represent the variations of relative phase shifts (i.e., the phase angle of the interacting cantilever relative to the phase angle of the freely oscillating cantilever at the resonance frequency). The flat surfaces which were examined were obtained by cutting the sample with a Diatome diamond knife at ≈ –120°C using an ultramicrotome (Ultracut E, Reichert and Jung) equipped with a cryochamber.

RESULTS AND DISCUSSION

TEM Micrographs of IPN Samples

The Effect of the Composition of the Sample on the Morphology of IPN

TEM micrographs of the sample PE/(70B : 30S) (Fig. 1) point to the formation of the domains of BMA-co-S, with the average up to about 1 μm dispersed in PE matrix. The domains, with the average around 1 μm, prevailed. The shape of the majority of domains is irregular because of the fact that the amount of the second phase (i.e., of the polyethylene phase) in IPN is small (about 15 mass %) and the neighboring domains are deformed. The situation of the two-phase system is seen on the TEM micrograph [Fig. 1(b)], which shows that, in some cases of the mutual deformation of domains, a complete fusion of the domains does not proceed, although they are deformed on the longer section of its circumference and are placed close one to another. In most cases, the

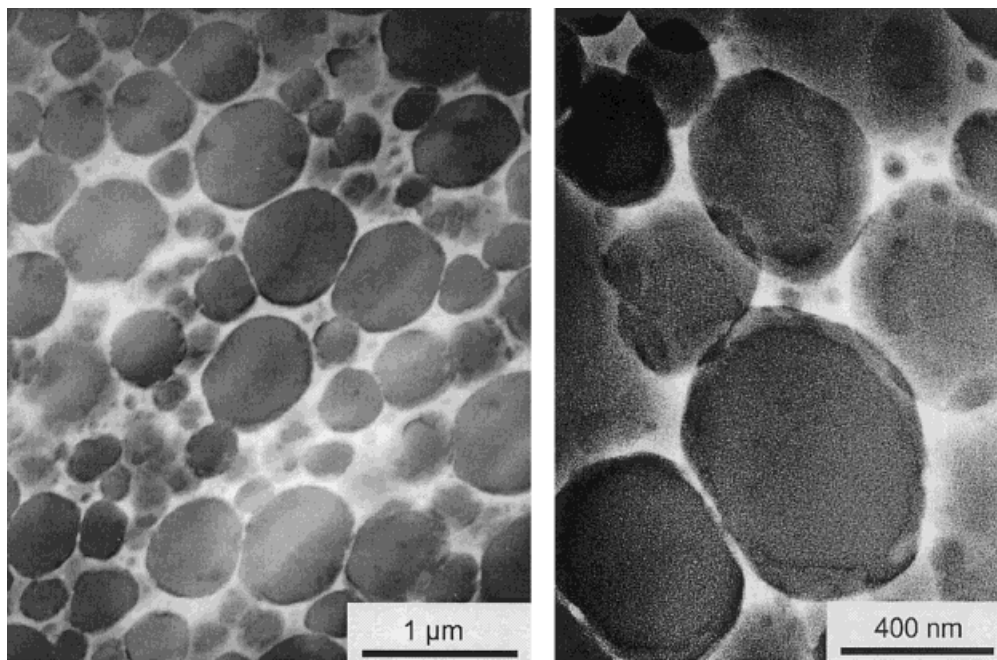


Figure 1 TEM micrographs (a) and (b) of IPN sample PE/(70B : 30S), crosslinker = 1.5 mol % with different enlargements.

domains are separated by a thin layer of the PE phase, but there are also some hints of partial mutual interconnection of the domains.

In the case of the second IPN sample in PE/(80B : 20S), the TEM micrographs of the domain of BMA-co-S are smaller than 1 μm . Domains

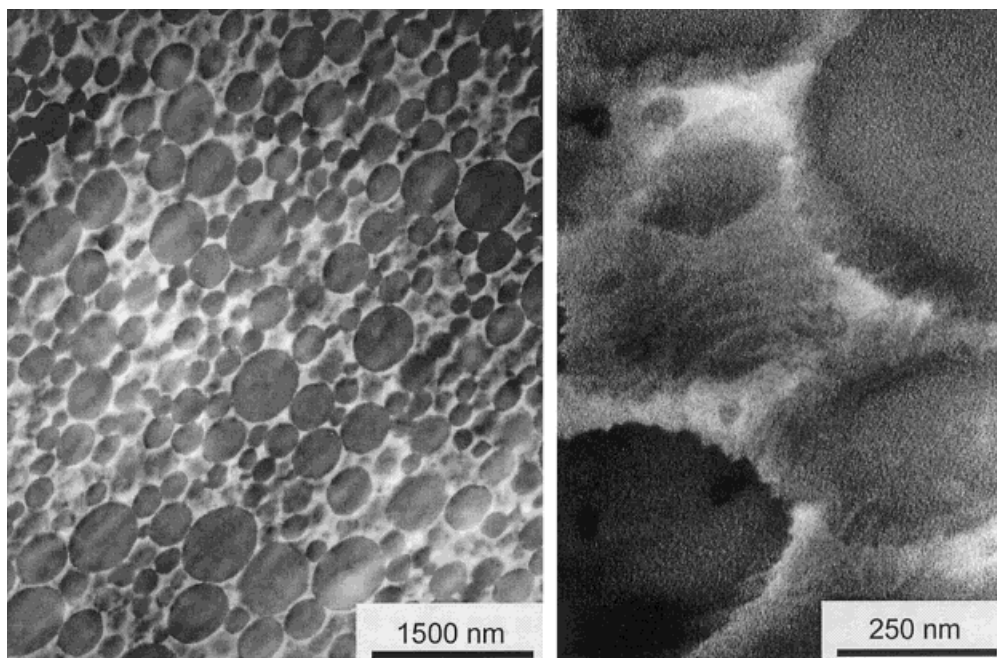


Figure 2 TEM micrographs (a) and (b) of IPN sample PE/(80B : 20S), crosslinker = 1.5 mol % with different enlargements.

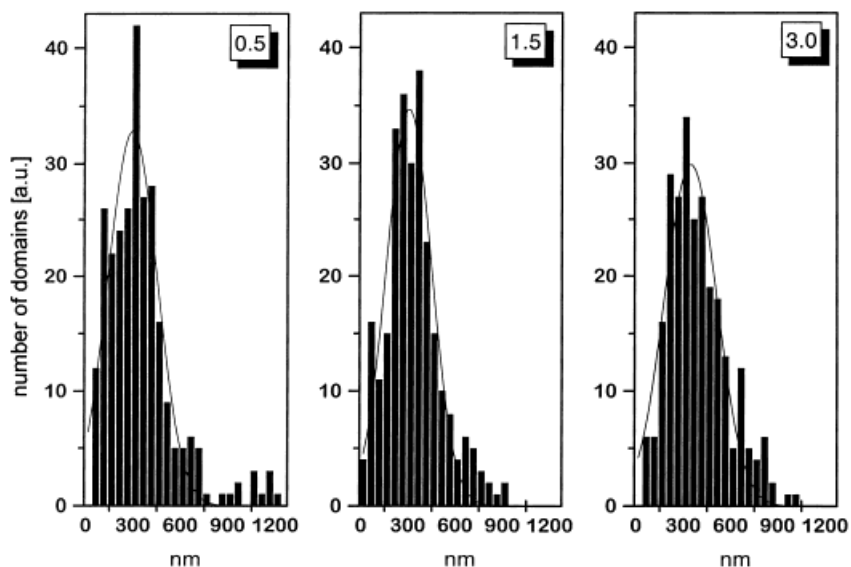


Figure 3 The effect of the crosslinker 1,4-butanediol dimethacrylate (BDDM) 0.5, 1.5, and 3.0 mol % BDDM on the domain size distribution in IPN sample PE/(70B : 30S).

with the average smaller than $0.5 \mu\text{m}$ [Fig. 2(a)] prevail. Smaller diameters of the domains in this IPN sample are probably due to the more rapid course of copolymerization with respect to a higher portion of BMA in the reaction mixture as well as changes in the solubility of the BMA-co-S formed [the lower content of butyl methacrylate component with respect the previous sample IPN, PE/(70B : 30S)]. The domains of the copolymer start to separate from the PE phase after a certain degree of the conversion of the copolymerization and a decrease in the monomer concentration, which results not only in the separation of copolymer domains but also of PE, which forms a matrix of the two-phase system.

Figure 2(b) shows the situation at the interphase between the PE phase and the domains of BMA-co-S in the sample PE/(80B : 20S). At this magnification, the PE lamellae became clearly visible. In contrast to Figure 1(b), it is seen here that the boundary between the BMA-co-S domains and the PE matrix is not so sharp as in Figure 2(a), but it is wrinkly at the edge of the domains as well as in the PE matrix. Such a structure of the two-phase IPN system appears as a joint penetration of the BMA copolymer phase into the PE phase and vice versa.

The Effect of the Crosslinking Agent on the Morphology of IPN

The effect of the amount of the crosslinking agent (BDDM) was followed in the IPN system at the ratio

of the components in the sample PE/(70B : 30S). Figure 3 depicts the distribution of domain sizes as determined from TEM images. It shows that, with the increasing content of the crosslinking agent (0.5, 1.5, and 3.0 mol % BDDM), the size of the domains of the dispersed phase which represent, as follows from the foregoing conception, the parts enriched with BMA-co-S changes. As follows from the distributions of the size of domains, it can be seen that, by using 0.5 mol % of the crosslinking agent, the maximum number of domains has an average of 450 nm with a relatively wide distribution (domains with an average above 1200 nm are also present). As the content of the crosslinking agent BDDM increases during the preparation of these samples to 1.5 and 3.0 mol %, the distribution curve is narrowed. These samples [Fig. 3(b) and 3(c)] do not contain domains with an average above 1200 nm anymore, and, on the other hand, the content of the domains with averages smaller than 150 nm decreases. The narrow minimum of domains with averages around 450 nm gradually decreases but, at the same time, this maximum is extended by the domains on an average of between 150 and 450 and 450 and 600 nm.

AFM Micrographs of IPN—The Effect of the Crosslinking Agent on the Morphology of IPN

AFM micrographs of IPN samples of PE/(70B : 30S), crosslinked in the presence of 1.5 mol % of crosslinker [Fig. 4(a)], show that the PE matrix is partly crystalline; lamellae are well recognizable.

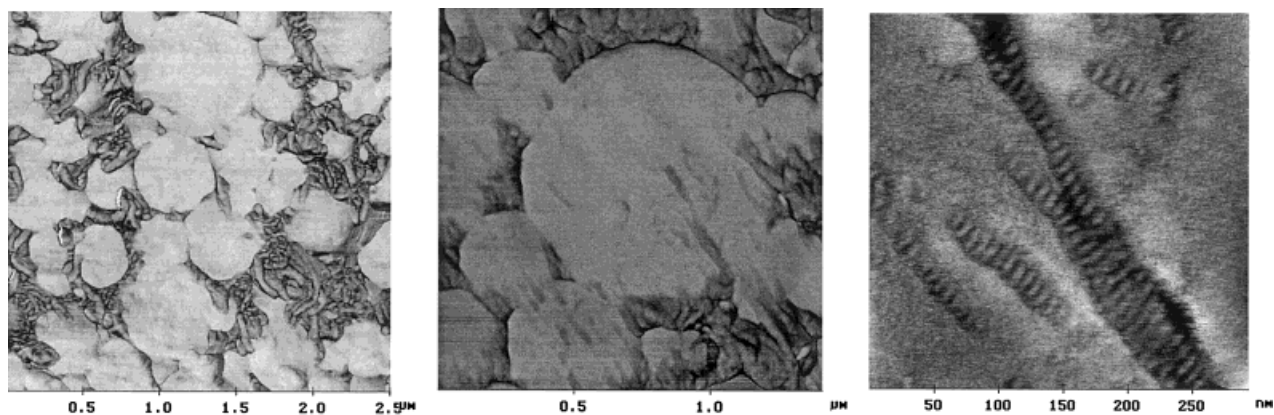


Figure 4 AFM micrographs of IPN sample PE/(70B : 30S), crosslinker = 1.5 mol % with different enlargements (a), (b), and (c).

The presence of the crystalline portion of PE in this IPN was also found and determined by the WAXS methods.⁴ The crystallization of the PE happened at the end of the synthesis, when the samples were cooled from the annealing temperature of 160°C, which is above the melting point of PE, to room temperature. Figure 4(b) depicts an enlarged image of the morphology. At this magnification, elongated morphologies embedded in the BMA-co-S domains are visible. Figure 4(c) shows one of these elongated morphologies enlarged. It is clear that these elongated structures are formed also by PE crystallized in the form of well-defined lamellae. It is actually that part of PE which, during the formation of the IPN system

by the interpenetration of the *in situ* method, did not take part in crosslinking and is therefore able to crystallize. On the other hand, looking at the domains of the copolymer in Figure 4(a), some irregularities in the shape are already recognizable compared to TEM micrographs. These irregularities can be caused by the joint spatial influence of the domains with respect to the tightness of the PE matrix, because a relatively small amount of PE that forms the matrix of the IPN system is present. At higher BMA content in IPN [i.e., PE/(80B : 20S), a similar AFM micrograph was obtained [Fig. 5(a) and (b)]. Similar to Figure 4(a) and 4(b), the PE forms well-defined lamellae. Figure 5(b) shows a region with edge-on standing

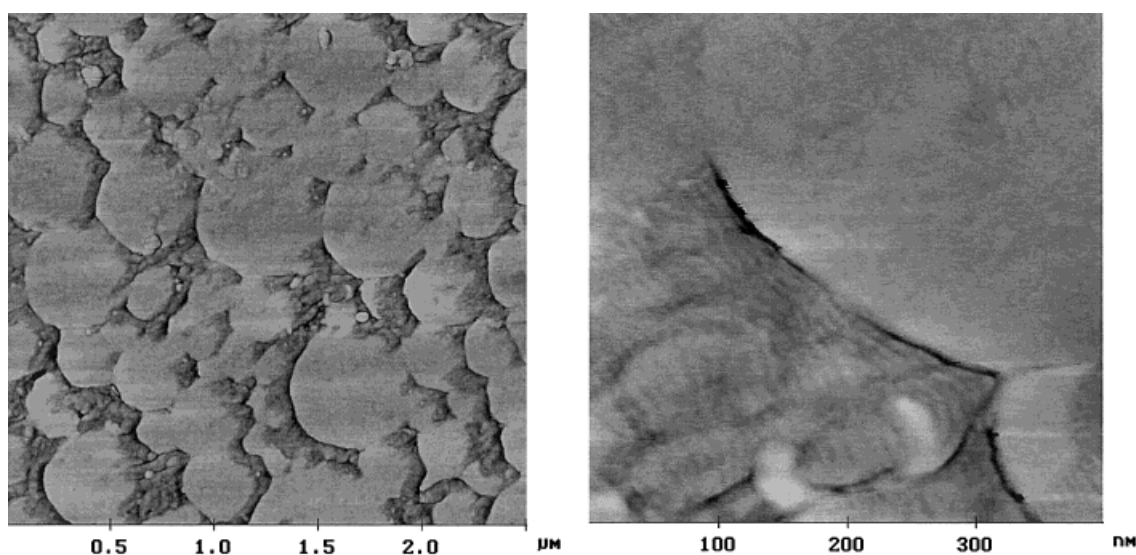


Figure 5 AFM micrographs of IPN sample PE/(80B : 20S), crosslinker = 1.5 mol % with different enlargements (a) and (b).

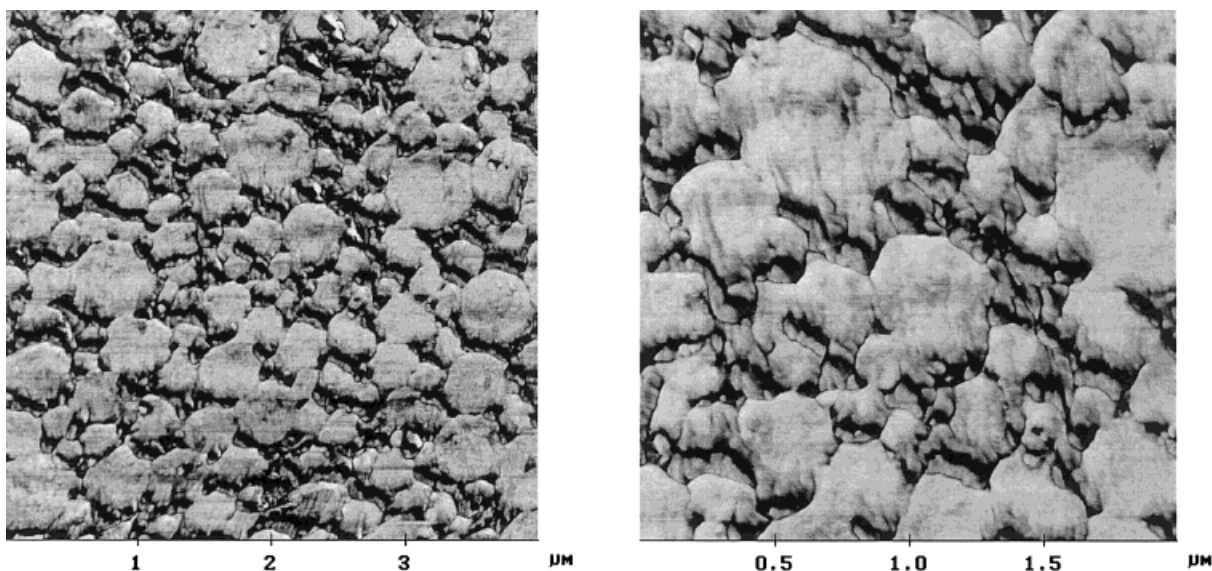


Figure 6 AFM micrographs of IPN sample PE/(70B : 30S) with higher amount of crosslinker = 3 mol %.

lamellae. The long period (the lamella distance) is about 25 nm.

The effect of the higher content of the crosslinking agent is seen in an AFM micrograph of the IPN sample PE/(70B : 30S) with 3 mol % of the crosslinking agent (Fig. 6). Here one can observe significant changes in the morphology of IPN, in comparison with Figure 5 showing an AFM micrograph prepared with the same ratio of monomers but with a lower content of the crosslinking agent (BDDM = 1 mol %). The shape of BMA-S domains is more irregular and wrinkly and the crystalline regions are less ordered. Such a significant change in morphology, due to the effect of the crosslinking agent, can be explained by the fact that, with the increasing concentration of the crosslinking agent, structures are frozen in the early stages of the synthesis when irregularly formed PE crystallites present at that temperature have a significant influence on the morphology. In the final stage of synthesis, the samples were heated up to 160°C, above the melting point of the PE. It seems that in samples with a low content of crosslinking agent the BMA domains are able to relax to perfect spheres at that temperature, but not the samples with a high degree of crosslinking agent.

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