

Morphology and Deformation Mechanisms of Polystyrene/Low Density Polyethylene Blends Studied by TEM

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ABSTRACT: The present investigation deals with morphology and deformation mechanisms of the plastic-toughened plastic system composed of a crystalline (low density polyethylene, LDPE) and an amorphous (polystyrene, PS) component. By proper use of a solution-melt procedure of specimen preparation for transmission electron microscope (TEM), not only the multiphase structure of the PS/LDPE blends, but also details of the crystalline morphology of LDPE in the blends have been successfully revealed. Based on the TEM morphological observations of the blends under *in-situ* stretching process, the toughness and deformation mechanisms of the blends are explored. It is found that multiple-craze is the main mechanism of deformation and toughening when LDPE constitutes the dispersed phase, whereas shear-yielding becomes major deformation mode when LDPE forms the continuous phase.

KEY WORDS Polyethylene / Polystyrene / Polymer Blends / Electron Microscopy / Deformation Mechanism / Craze / Shear Yield /

In the broad research field of polymer blends, rubber-toughened plastics have attracted much interests due to their important industrial value.^{1,2} Based on a great number of investigations of deformation mechanisms using transmission electron microscopy (TEM), relatively deep understanding of the toughening mechanisms of the systems has been achieved—mainly depending on the inherent cohesion and chain entanglement density of the matrix, toughening of the plastics may be caused by crazing or shear yielding of the matrix.^{3,4} However, addition of low modulus rubber often brings about remarkable decrease of the modulus, heat resistance and processing property of the toughened polymer.^{5,6} During the last decade, great interests arose for realizing toughening of brittle plastics by incorporating another plastic instead of an

elastomer.⁷⁻⁹ Polystyrene (PS)/low density polyethylene (LDPE) is one of the successful examples of such plastics-plastics combinations.¹⁰⁻¹³ Incorporation of a compatilizer of a block or graft copolymer has been proved necessary for strengthening interfacial adhesion for the system.^{10,11} Although the related studies have succeeded in realizing beneficial combination of the stiffness of PS and toughness of LDPE reaching the level of high impact polystyrene (HIPS) in terms of main mechanical properties, a little attention has been paid on the morphology of the blends, especially, there have been almost no reports on the mechanisms of deformation and toughening for the system in the literature. This lack of the interesting information is probably associated with the technical difficulties in preparing specimens of the blends for TEM

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observations.

Fayt *et al.*^{14,15} investigated the morphology of PS/LDPE system by optical microscopy using a special staining technique, but the limitation of the method in providing morphological information at a scale less than micrometers is evident due to the low resolution power. Scanning electron microscopy (SEM) has been used to the system providing structural feature of the fracture surface.¹¹ However, the fracture topology explored by SEM does not necessarily reflect the phase structure of the examined blend. Although selective extraction of one component by solvent can usually make the morphology distinct, false appearance may be created when the continuous phase is extracted. Generally, TEM is a forceful technique to study morphology of blend systems. Besides detailed information on a nanometer scale, the deformation mechanisms can be investigated by *in-situ* observation of the blend specimens under microstretching. However, for the PS/PE blends, it is difficult to prepare ultra-thin film used for TEM observations because ultramicrotomy of the bulk specimen often destroys true structure and the great difference in solubility between PE and PS makes solvent-casting procedure difficult. This might be the main reason for a lack of systematic investigations on the morphology and deformation mechanisms of PS/PE blends by TEM reported in the literature.

In this paper we report the result of TEM observations of PS/LDPE blends. The success of the work is based on a proper use of a solution-melt procedure for specimen preparation similar with that employed in the morphology study on polyethylene¹⁶ and polyethylene/polypropylene blends.¹⁷ In this procedure, homogeneous dilute solution containing PS, LDPE, and SEBS in xylene is prepared at 130°C followed by casting it on the liquid surface of heat phosphoric acid. Then thin blend film, which can directly be used for TEM observations, can be obtained by cooling the system according to a desired program.

Based on the TEM morphological studies, it is possible to explore the deformation mechanisms of the blends. The related results for two typical blends, in which the tough component LDPE is minor and major constituents respectively, will be discussed.

EXPERIMENTAL

Materials

The characteristic data of the polymers used in this study are the following. LDPE (2F2B, Jinshan Chemical Co.): melt index 1.8 g/10 min; PS (666D, Yanshan Chemical Co.): $\bar{M}_w = 230000$, $\bar{M}_n = 97000$, $\bar{M}_w/\bar{M}_n = 2.4$, melt index 6.9 g/10 min. Hydrogenated poly(styrene-*b*-butadiene-*b*-styrene) tri-block copolymer (SEBS G1652) was kindly supplied by Shell Company with respective molecular weights of PS block and central EB block being 7500 and 37500, and the PS weight fraction being 28.6%.

Solution-Melt Procedure for Sample Preparation

Given amounts of PS, LDPE and SEBS were mixed with xylene and heated at 130°C to make a solution with total concentration of 0.1%—0.5 g ml⁻¹. The hot solution was dripped on the surface of phosphoric acid at 160°C. Xylene then volatilized very quickly, and the blend layer in molten state formed on the surface of phosphoric acid. The system was kept at 160°C for three minutes, followed by gradually cooling to room temperature. The blend film formed was then washed with distilled water and transferred to a copper grid and stored in a desicator. The thickness of the ultra-thin film prepared was about 0.55—0.10 μm, estimated by the volume of the solution dripped on the surface and the area of the film formed.

TEM Observation

The dried film was observed using a HITACHI-800 transmission electron microscopy equipped with a micro-stretcher, operating at 100 kV.

RESULTS AND DISCUSSION

In this paper, we discuss the morphologies and deformation mechanisms of two blends, in which LDPE is the minor (PS/LDPE 80/20, weight ratio, the same below) and major (PS/LDPE 20/80) component respectively. Both of the blends contain 10% SEBS (related to the total weight of the blend) acting as a compatilizer.

The TEM photograph of the blend PS/LDPE 80/20 (10% SEBS) shows enough contrast due to the big difference in crystallizability between the two phases although the sample hasn't been stained (Figure 1a). The structural detail within the dispersed particles can be seen in Figure 1b observed at higher magnification for a rarely big particle. The particle is composed of aggregates of black needles which can be assigned as stacks of the LDPE lamellar crystals. Image analysis of Figure 1a provides size distribution of the dispersed particles of LDPE shown in Figure 2. The diameters of the most particles lie in the range from 0.1 μm to 1 μm with the number average value about 0.5 μm . For a blend with the composition of PS/LDPE 80/20, containing 9% hydrogenated poly(styrene-*b*-butadiene) diblock copolymer, based on SEM observations for the specimen extracted by tetrahydrofuran, Fayt *et al.*¹⁴ concluded that the blend exhibited bi-continuous morphology although the weight fraction of PS is four times more than that of LDPE. This is completely different from our TEM result for the blend of similar composition just mentioned. This discrepancy, in our opinion, probably reflects the limitation of SEM for the blend specimen in which the continuous phase is extracted. During extraction, aggregation and accumulation of the insoluble dispersed particles may not be avoidable completely, leading to a false appearance of the continuity of the remaining particles.

It is clear that the solution-melt procedure is practical for preparing specimens of PS/

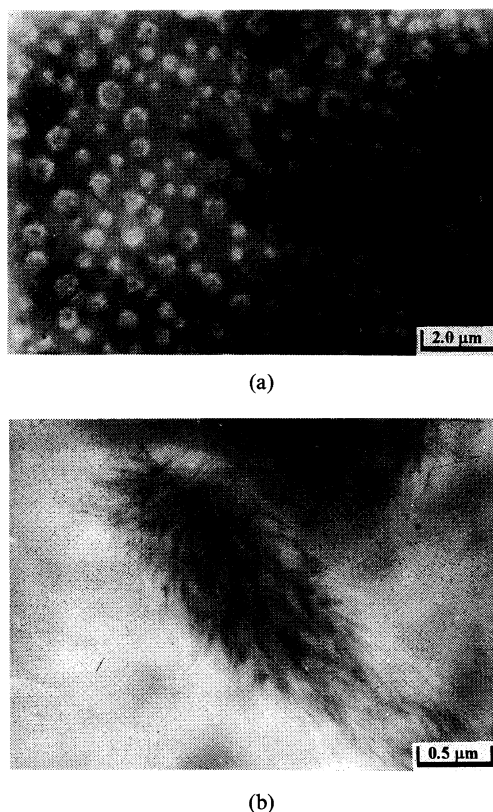


Figure 1. TEM photographs of PS/LDPE 80/20 blend containing 10% SEBS. (1(b): at higher magnification showing internal structure of a rarely seen large dispersed particle.)

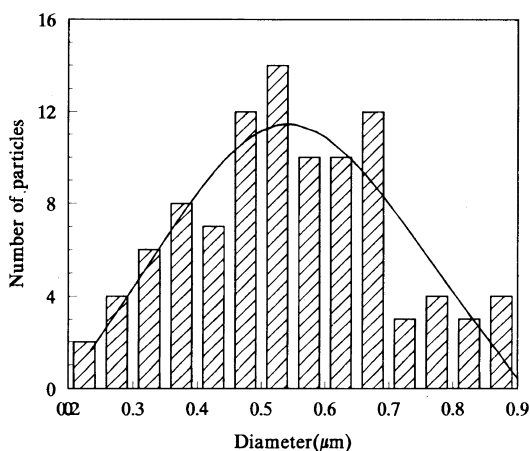
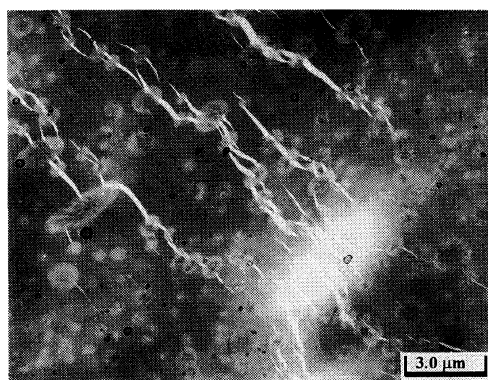
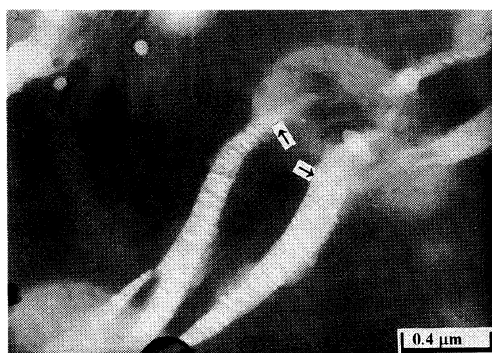


Figure 2. Particle diameter distribution of PS/LDPE 80/20 blend containing 10% SEBS.



(a)



(b)

Figure 3. TEM photographs of PS/LDPE 80/20 blend containing 10% SEBS showing multicraze structure. (3(b): at a higher magnification showing internal structure of crazes.)

LDPE blends for TEM observations without staining. The procedure is potential for other blends, particularly those composing one crystalline and one amorphous component.

Figure 3a clearly shows multi-craze morphology of PS/LDPE 80/20. It is seen that all the crazes in the matrix are almost parallel each other. For the most crazes, the two ends of each craze are attached to the dispersed LDPE particles. However, the two ends are usually not equivalent, *i.e.*, one is broader than the other. Therefore, the crazes are actually in the form of a wedge. The thickness of most of the crazes is in the range of 0.2–0.5 μm , apparently smaller than that observed in HIPS.^{1,2} Besides,

there are some crazes which have not been sufficiently developed with thickness of about 0.1 μm . For these thin crazes, one end is at the phase interface while the other is blunted in the matrix. Just as rubber particles in rubber-toughened plastics, the LDPE particles here being a tough component with modulus, which is two orders of magnitude less than that of the matrix, play the role of stress concentrator to initiate crazes. The wedge shape of the crazes enables their tips to have high concentrated stress for craze propagating. In addition, it is also seen from Figure 3a that the efficiency of initiating craze greatly depends on the particle size, *i.e.*, the larger the particle is, the higher the efficiency is. A lot of small particles with diameters less than 0.5 μm do not show any ability to initiate crazes. Besides, it is interesting to find that all the particles to which crazes attach undergo deformation, *i.e.*, original spheres become ellipsoids with long axis perpendicular to the crazes while the particles without crazes attached remain spherical. Figure 3b obtained at a higher magnification shows the peculiar internal structure of crazes composed of fibrils and voids. Although the crazes seem to have penetrated to inside of the particle, there is not the characteristic fibril-void network structure of crazes in the white bands within the particles. Considering the results of deformation for the blends with LDPE as the major component, which will be discussed below, we are inclined to think that the crazes are not actually able to extend to inside of LDPE particles, but the stress concentration at the interface may cause yield deformation within the particles leading to white bands. It is worth to note that, the sample showing crazes in Figure 3 is the blend film without being stretched using the micro-stretcher. We believe that the tensile stress caused by film contraction during the process of film drying on the TEM grid is responsible for crazing.

Figure 4 shows the morphology of the blend with LDPE as a major component revealed by

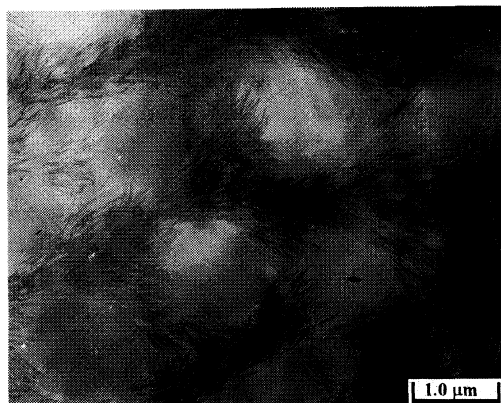


Figure 4. TEM photograph of PS/LDPE 20/80 blend containing 10% SEBS.

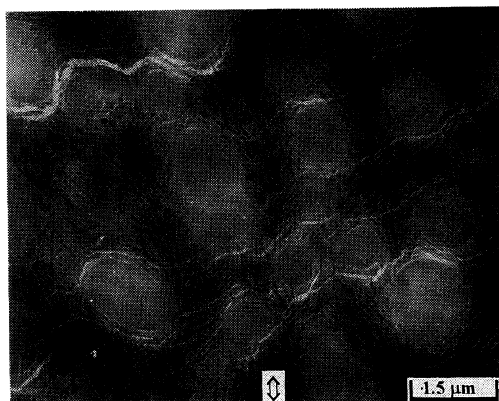


Figure 5. TEM photograph of PS/LDPE 20/80 blend (10% SEBS) after being stretched with a double-arrow denoting the stretching direction.

TEM. Thanks to the crystalline ability of LDPE component, the blend film provides natural contrast showing clear two-phase structure. The spherical dispersed phase without any internal structure and the matrix constituted by irregular crystalline lamellae can obviously be assigned to PS and LDPE phases respectively. The size of the dispersed PS particles is generally in the range of 0.5–2 μm , which indicates the role of SEBS as an effective compatilizer. In comparison with the results of optical microscopy for PS/LDPE blends with similar compositions reported by Fayt *et al.*,¹⁴ it is clear that this TEM result provides more abundant information on the detailed structure in the crystalline matrix. The crystalline lamellae exist in bundles. Although the lamellae are randomly oriented, they are close to be parallel on a small scale ($\sim 0.1 \mu\text{m}$). According to crystalline kinetics in multi-phase systems,^{18,19} the dispersed particles often play a role of crystalline nuclei and the lamellae grow preferentially along the surface of the particles to minimize the interfacial energy. The orientation of the lamellae shown in Figure 4 generally supports this argument.

A quite different deformation mechanism from crazing is shown for the blend with LDPE as a major component. Figure 5 presents the morphology of the blend after being stretched

at the TEM specimen stage with a micro-stretcher. In comparison with that before stretching, remarkable variation takes place showing the appearance of the white bands. These bands are generally parallel and angled with the stress applied. A close examination of the deformation bands shows that there aren't fibrils and voids existing in the bands but the crystalline lamellae overpassing the bands can be observed. Based on these facts we may think that these bands actually are caused by local yield deformation. This means that, the deformation mode transition from crazing to shear takes place when the content of LDPE increases. The contrast between the deformation bands and matrix is believed to be caused by local thinning in the bands. The bands are actually localized micro-necking area. Recently, Chun *et al.*²⁰ reported the deformation mode transition from crazing to shear for miscible blends PS/poly(2,6-dimethyl-1,4-phenyl oxide) and PS/poly(vinyl methyl ether) caused by changing the blend composition. This conclusion was made based on a series of TEM observations. In comparison with Figure 4, apparent orientation of the crystalline lamellae in the stretched film along the direction close to stretching can be clearly observed (Figure 5). In addition, the bands are

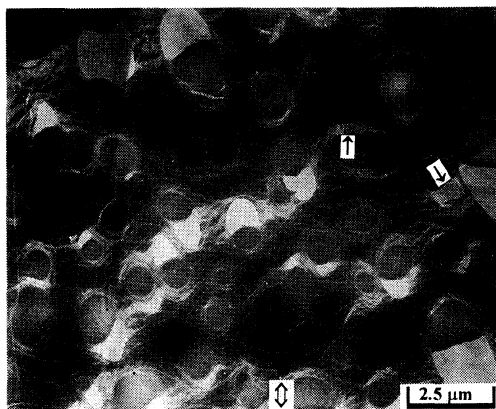


Figure 6. TEM photograph of PS/LDPE 20/80 blend (10%SEBS) undergoing larger elongation prior to break.

located around the particle-matrix interface, this means that the interfacial area is still the weak part of the film to applied stress, although effective compatibilization of SEBS has greatly improved the adhesion between the phases. Figure 6 is a micrograph of the blend film undergoing larger stretching deformation just prior to fracture. Besides a large number of deformation bands pervading the whole area examined, many holes with the shape of semi-ellipse appear. Being the prelude of catastrophic break of the film, these voids exclusively grow at the interface between PS particles and LDPE matrix. In some voids, as those labeled with the arrows, there are sparse fibrils tying the dispersed particle and matrix, which might be the result of fibrillation of rubbery SEBS being stretched at the interface.

CONCLUSIONS

The results of PS/LDPE blends clearly demonstrate that the solution—melt procedure is a proper way for preparing specimens for TEM observations without staining and the procedure is potential for other blends, particularly those composed of one crystalline and one amorphous component. TEM observations for the blends with tough component LDPE as minor and major components re-

spectively present clear indication of deformation modes of the blends. For the case of LDPE being minor (20%) component, craze deformation of PS matrix is the main mechanism. Termination is probably associated with the yield deformation within the LDPE particles to which the crazes attach. For the case of LDPE being major (80%) component constructing matrix, localized yield producing microbands within the matrix becomes the main deformation mechanism.

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Deformation Mechanisms of LDPE/PS Blends

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