Effect of the Characteristic of Matrix on Deformation Mechanism of Polymer Blends

Shiai XU,* Ming JIANG,*† and Jingshu SHEN**

*Department of Macromolecular Science and Laboratory of Molecular Engineering of Polymers,
Fudan University, Shanghai 200433, China

**Polymer Physics Laboratory, Institute of Chemistry, Academia Sinica,
Beijing 100080, China

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ABSTRACT: Polymer blends composed of low-density polyethylene (LDPE) as a dispersed phase, polystyrene (PS) and poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) constituting a matrix phase and a small amount of block copolymer poly(styrene-*block*-ethylene-*co*-butene-*block*-styrene)(SEBS) as a compatilizer were studied for exploring deformation mechanism. The blend specimens prepared *via* solution-melt procedure were observed by transmission electron microscopy (TEM) under *in-situ* stretching. For the blend with PS matrix, crazing initiated by the dispersed LDPE is the deformation mode while micro-shear yielding becomes dominate when a certain amount of PPO is incorporated. In the latter case, the LDPE particles within the deformation zones deform to ellipsoids indicative of the molecular orientation in the microbands. The variation of the deformation mode can be attributed to the change of entanglement density of the matrix with changing composition of PS and PPO.

KEY WORDS Deformation Mechanism / Crazing / Shear Yielding / Cavitation / Morphology / Polymer Blend / Polystyrene / Polyethylene / Poly(2,6-dimethyl-1,4-phenylene oxide) /

Glassy polymers form a large group of industrially important materials for structural applications, but the use is greatly confined by the tendency for these materials to fracture in a macroscopically brittle manner.^{1,2} To improve the brittleness of these polymers has been so one of the main goals of polymer modification for years. Polystyrene (PS) is a typical glassy polymer. Owing to its high strength, high modulus and excellent dimensional stability, attempts to toughen it in order to broaden its application have resulted in a series of industrial products with desirable combination of hardness and toughness such as HIPS, ABS etc.³

The traditional toughening has been to disperse an elastomer into a plastic matrix. The study on toughening mechanism has concentrated on the systems composed of a brittle matrix and an elastomer dispersion.^{4–6} In the last decade, toughening brittle polymers by incorporating a low modulus plastic instead of rubber was studied.^{7,8} Recently we have studied a typical plastic-plastic systems composed of PS and low-density polyethylene (LDPE) with emphasis on deformation mechanism. It was confirmed that incorporation of a compatilizer SEBS, *i.e.*, poly(styrene-*block*-ethylene-*co*-butene-*block*-styrene) into the blends is effective for strengthening the adhesion and decreasing the interfacial energy between the two phases.⁹ In the literature, although the system has been studied with emphasis on the role of block copolymers as a compatilizer and the dependence of the properties of the blends on composition, a little attention had been paid on the morphology and deformation mechanisms of the system because of the difficulties in preparing specimens for transmission electron microscopy (TEM) studies.

By using a solution-melt procedure, we successfully overcame the difficulties and made a series of TEM observations for the PS/LDPE blends.¹⁰ The related results concerning the toughness and deformation mechanisms

of the system have been reported. In the case of LDPE as a minor component, craze deformation of PS matrix is the main mechanism, initiation, and propagation of the crazes are similar with that of rubber-toughened plastics, and termination is probably associated with the yield deformation of the LDPE particles to which the crazes attach. But there is no shear deformation zone observed in the matrix PS of the blend. In contrast, when LDPE is the major component and forms the matrix, localized yield microbands within the matrix become the main deformation mode^{11,12}

The plastic deformation of glassy polymers may advance either by shear yielding or crazing. Crazes are localized planar defects containing a network of interconnected voids and fibrils, whereas shear deformation may be localized or diffuse. According to Kramer *et al.*,^{13–16} the mode by which a glassy polymer deforms plastically depends mainly on $\lambda_{\max}$, namely the maximum value of the extension ratio of the entanglement network of the polymer. The network can be characterized in terms of the chain contour length between entanglements l_e (the length of a molecular chain between entanglements at fully extended state), and the entanglement mesh size d (the length of a straight line between entanglements at undeformed state). If there is no slippage or breakage of entanglement network points, *i.e.*, the entanglement points are treated as permanent crosslinks, and chain scission is neglected, the maximum extension ratio $\lambda_{\max}$ of the network would be gained by the following equation¹⁷:

$$\lambda_{\max} = l_e / d \quad (1)$$

Based on the systematic examination of the deformation process of ten glassy polymers, Kramer concluded that for brittle polymers with high l_e such as polystyrene (PS) crazing is the main plastic deformation mode when these polymers are strained at room temperature. However, tough polymers with low l_e , such as polycarbonate (PC) and poly(2,6-dimethyl-1,4-phenylene oxide) (PPO)

† To whom all correspondences should be addressed.

show a marked tendency of diffuse shear deformation. In addition, the polymers or blends with intermediate l_c may show both crazes and localized deformation zones (DZs).¹⁷

In this paper, in order to investigate the effects of the nature of the matrix on the deformation modes of the plastic-plastic blends, PPO was further incorporated into PS/LDPE/SEBS blends. It is well known that PS and PPO constitute a miscible polymer pair, so the entanglement density of the matrix can be adjusted by changing the relative content of PS and PPO. By *in-situ* stretching of the ultra-thin films of the polymer blends prepared *via* the solution-melt casting procedure,¹⁰ deformation mechanism of the blends was studied by TEM. Here, a great attention is paid on the role of the dispersed particles in the deformation process of the matrix, which of course was not involved in the miscible PS/PPO blends studied by Kramer¹⁷ and Chun.¹⁸ At the mean time, the morphology of the blends and crystalline structure of LDPE are revealed.

EXPERIMENTAL

The details about the characteristic data of homopolymers of PS, LDPE, PPO, and block copolymer SEBS used in this study have been reported.¹²

The thin films of three polymer blends with different matrix compositions, namely PS/LDPE/SEBS 70/20/10, PS/PPO/LDPE/SEBS 50/20/20/10, and PS/PPO/LDPE/SEBS 35/35/20/10 in weight ratio were prepared. In the blends, the amounts of the dispersed component LDPE and the compatilizer SEBS are invariant being 20 wt% and 10 wt%, respectively. The thin films for TEM observations were produced *via* the solution-melt procedure as follows. LDPE, PS, PPO, and SEBS in a desired composition were dissolved sufficiently in xylene at 130°C and the solution was spread on the surface of phosphoric acid at 160°C. After evaporation of the solvent and subsequent cooling of the system, ultra-thin film with thickness about 0.05–0.1 μm formed on the surface. The film was then washed with water and transferred to an annealed TEM grid, which has previously been coated with a film of the same polymer blend. Bonding of the film to the grid was achieved by a short exposure to the vapor of the same solvent (xylene).¹⁹ The details of this procedure have been described previously.¹⁰

The morphology of the films was observed using a HITACHI-800 transmission electron microscope equipped with a micro-stretcher in which the grid was mounted and strained *in situ*. The strain speed is 0.02 mm s^{-1} .

RESULTS AND DISCUSSION

The morphology and deformation mechanisms of the PS/LDPE/SEBS blends without PPO have been discussed in the previous paper.¹² The multi-craze structure of a such kind of blend after being strained is shown as Figure 1. It is observed that all of the crazes are attached to the dispersed LDPE particles, so it implies that these dispersive particles take an important role on initiation and termination of the crazes.

A TEM photograph of the blend film with matrix composed of PS and PPO in weight ratio 50/20 before

Figure 1. Crazes in PS/LDPE/SEBS 70/20/10 blend observed by TEM.

Figure 2. TEM photograph of PS/PPO/LDPE/SEBS 50/20/20/10 blend before being strained.

being loaded is shown in Figure 2. The multiphase morphology of the blend is readily recognized owing to the existence of the crystalline lamellae of LDPE. Although LDPE still constitutes the dispersed phase, the particles of LDPE are no longer spherical and there is not sharp boundary between the two phases. As we have known, PS and PPO form miscible blends as a result of specific interaction between them.²⁰ It is reported that the miscibility of a block copolymer containing PS block with homopolymer PPO is much higher than that between the PS block and homopolymer PS.²¹ These facts

Figure 3. TEM photograph of DZs in PS/PPO/LDPE/SEBS 50/20/20/10 blend after being strained.

are enlightening for understanding the above results: When PPO was added into the PS/LDPE/SEBS system, the PS blocks in SEBS are more readily miscible with the matrix containing PPO, and then the emulsifying effect of the copolymer is strengthened. Generally, the emulsifying effects of the compatilizer are reducing the particle size and broadening the boundary, so sharp boundary between the two phases no longer exists. In addition, we can see that the arrangement of the lamellae is irregular and the dispersed particles do not have clear contours. It means that both phase separation and growth of the lamellae during the film preparation were greatly hindered because the casting temperature was much lower than T_g of PPO and the viscosity of the blend solution dramatically increased as the solvent evaporated very rapidly.

After the film was strained, many deformation zones (DZs) with width less than $1.0\ \mu\text{m}$ came into being as shown in Figure 3. The deformation zones are almost parallel each other, and angled 50° – 60° with the strain direction (the double-arrow in the bottom of the figure denotes the stretching direction, the same below). They are easy to be identified as these bands are thinner than the around area. They are homogenous without inner structure and especially no networks composed of fibrils and voids could be observed. Therefore, these DZs are completely different from the crazes observed in the PS/LDPE/SEBS 70/20/10 blend. These deformation zones are localized thinning regions of drawn but unfibrillated material.²² In other words, they are micro-necks formed in the process of stretching of the blend. These DZs show different characters as follows from those of the crazes in the PS/LDPE blends in which PS is the only component in the matrix. These DZs are several to decade times longer than that of crazes, and can pass through many of the dispersed LDPE particles, whereas, the crazes are stopped by them. These DZs have distinct edge, so they

Figure 4. DZs initiated by voids in PS/PPO/LDPE/SEBS 50/20/20/10 blend.

Figure 5. TEM photograph at high magnification of some area in PS/PPO/LDPE/SEBS 50/20/20/10 blend.

are in nature localized shear bands.¹⁷ In addition, it can be seen that these shear bands are wedge-like in shape with very sharp tips, similar with the crazes in Figure 1. It might be inferred that the propagation of the localized shear deformation is related to the stress concentration at the tips. Besides, we found that voids fortuitously existing in the film are very efficient to initiate shear bands, as shown in Figure 4. This indicates that initiation of the localized shear bands is also associated with the localized stress concentration. Meanwhile, a few deformation zones, at first glance very similar with crazes, are observed at higher magnification. Figure 5

Figure 6. Cavitation phenomenon in the tips of some shear bands in PS/PPO/LDPE/SEBS 50/20/20/10 blend.

Figure 7. TEM morphology of unstrained film of PS/PPO/LDPE/SEBS 35/35/20/10 blend.

shows the typical appearance of one of the DZs. The width is very small, about only $0.1\ \mu\text{m}$. Although there is internal structure in the DZs, a close examination reveals that the details of the internal structure here is in general different from the crazes formed in glassy polymer such as PS.¹³ In the DZ shown in Figure 5, although a “void-fibril” network is formed, the voids do not extend through the entire DZ thickness in some regions. The same phenomenon was observed in ABS by Donald and Kramer.²³ Besides, the voids possess elliptic contour rather than stripes alternatively arranged with microfibrils as seen in ordinary crazes. It is also noted that the lateral direction of these DZs isn't perpendicular to the stress applied. A similar hybrid deformation zone, in which short regions of craze are interspersed with and border on a drawn but unfibrillated DZ, has also been seen in styrene-methyl methacrylate copolymer²² and PS/PPO blend.¹⁸ Therefore, we are inclined to think that

Figure 8. Multi-shear bands of PS/PPO/LDPE/SEBS 35/35/20/10 blend being strained.

Figure 9. Inner structure in the DZs in PS/PPO/LDPE/SEBS 35/35/20/10 blend.

these voids in the DZs are caused by cavitation process rather than crazing. This cavitation phenomena can be clearly observed in the tips of some shear bands as labeled by “A” in Figure 6.

Now, we discuss the results of blend of PS/PPO/LDPE/SEBS 35/35/20/10, here, PS and PPO in equal amount compose the matrix. Figure 7 shows the morphology of the blend before being strained. Comparing to Figure 2, it can be seen that the domains of the dispersed phase become smaller being about $0.2\ \mu\text{m}$ and the interface between the two phases becomes more indistinct also. This is because that the emulsifying and compatilizing roles of the block copolymer SEBS are further strengthened with increasing the content of PPO in the matrix. After the film was loaded, many deformation bands formed (Figure 8), and no crazes were observed any more. The structure of the DZs is similar to that shown in Figure 3 where the matrix has lower PPO content, whereas the area fraction of the DZs is much higher. With increasing strain, the bands are broadened and more shear bands are produced. Figure 9 is a TEM photograph at a high magnification of the deformed film at higher strain. Here, a remarkable fea-

Figure 10. Cavitation in DZs in PS/PPO/LDPE/SEBS 35/35/20/10 blend.

Figure 11. Morphology of DZs prior to film fracture in PS/PPO/LDPE/SEBS 35/35/20/10 blend.

ture is that LDPE domains within the deformation bands can be clearly seen. These LDPE domains within the deformation zones become ellipsoids with the long axis angled closely 45° with the stress applied, while no orientation trend of the LDPE domains outside the deformation zones can be recognized. It is inferred that these particles within the DZs have been experienced the action of shear stress. The concept of molecular orientation in shear deformation zone is widely accepted in the literature,²⁴ but there are not direct experimental evidences. The deformation and orientation of the dispersive particles observed here can obviously be regarded as an indicator of the orientation of the polymer chains within the shear deformation zone. For this blend with matrix of PS/PPO 50/50, at larger strain, cavitation was also observed as shown in Figure 10 as a result of some degree of chain scission and/or slippage. This cavitation develops further as strain increases. A micrograph for an extreme case just prior to breakdown of the film is shown in Figure 11.

From the above discussion as regard to deformation mechanism, we can see that in the blends of PS and

LDPE, there is a mode transition as matrix composition changes, *i.e.*, from predominant DZs in the blends, in which the matrix is composed of PS and PPO to only crazes in the blends, in which the matrix contains of PS only.¹² This result can be rationalized by realizing that the entanglement density of the matrix in the PS/LDPE blends is changed radically after incorporating PPO since PPO has much higher entanglement density and lower l_e than PS. The value of l_e for PPO, which was calculated by Kramer²² according to an equation derived by Prest and Porter,²⁵ is $165 \text{ \AA}$, and l_e of the matrix containing PS and PPO can be obtained from the equation²⁰:

$$l_e(w) = M_e \frac{0.0209 + 0.0175w}{1 + 3.2w} \quad (2)$$

where w is the weight fraction of PPO in the matrix, M_e is the entanglement molecular weight of PS.

Assuming this equation is valid for all values of w , and taking the value of M_e being 19100,²² we get $l_e = 399 \text{ \AA}$ for PS, $258 \text{ \AA}$ for the matrix of the PS/PPO/LDPE/SEBS 50/20/20/10 blend and $218 \text{ \AA}$ for the matrix of the PS/PPO/LDPE/SEBS 35/35/20/10. It is clear that l_e value of the matrix is sharply decreased when PPO is added into the blend, which will lead to a substantial increase of critical stress for initiating crazes. Therefore, the shear yield becomes the main deformation mechanism. Moreover, as mentioned above, the cavitation phenomenon accompanying by shear yielding should not be neglected in the deformation process of the blends containing PPO, especially in the case of high content of PPO. The formation of these cavities will contribute to volume dilation of the blends.

CONCLUSIONS

Incorporating PPO into the PS/LDPE/SEBS blends strengthens the emulsifying and compatilizing effect of copolymer SEBS. With increasing the content of PPO, the domain size of the dispersed LDPE is decreased.

The chain contour length l_e between entanglements of the blend matrix is decreased with increasing the content of PPO, which results in a transition of deformation mode from only crazing in PS matrix to localized shear yielding for the blend matrix composed PPO and PS.

The dispersed LDPE phase can stop crazes in the matrix of PS, while it can not terminate the shear deformation zone in the matrix containing PPO. The deformation zones could pass across the particles.

In the deformed area, the LDPE domains show orientation along the direction perpendicular to the shear bands, which testifies that the polymer chains within the deformation zone are highly oriented. In the deformation process of the PPO-containing blends, cavitation within the DZs is not negligible, causing volume dilation of the blends.

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