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# The effect of compatibility on toughness of PPS/SEBS polymer alloy

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## Abstract

The effect of compatibility on the improvement of the toughness of polyphenylenesulfide (PPS) blended with styrene–ethylene–butylene–styrene block copolymers (SEBS) has been studied. In PPS/SEBS polymer alloy having SEBS, which was highly modified by maleic anhydride, it was confirmed that the elastomers were dispersed finely because of high compatibility with the PPS matrix, and the toughness was improved efficiently by the release of constraint of the strain due to void formation in the elastomer particles. On the contrary, in the PPS/SEBS polymer alloy having the conventional SEBS or SEBS, which was lightly modified by maleic anhydride, the diameter of dispersed elastomer particles was larger, and the particles were deformed into a rod-like shape, and oriented along to the direction of injection flow, particularly in high content of elastomer. These oriented particles were fractured easily, and many cracks, which were distributed along to the direction of flow were formed. These cracks would result in suppression of improvement or decrease in toughness of the polymer alloy.

*Key words*: Polyphenylenesulfide/styrene–ethylene–butylene–styrene polymer alloy; Toughness; Compatibility

## 1. Introduction

PPS is one of the plastics that is excellent in thermal and chemical resistance, but its toughness is not enough because of its rigid structure.

The technique of forming a polymer alloy, in which a modifier such as an elastomer is dispersed in a matrix polymer, is generally attempted in order to improve the toughness of polymers [1–3]. It is pointed out that the efficiency of improvement in the toughness of a polymer alloy is affected by many factors such as the molecular weight of the matrix polymer, the mechanical property of the elastomer and the states of distribution of the elastomer. Several explanations have been proposed to account for the toughening mechanism of polymer alloys [1]. It was pointed out and certified experimentally by one of the authors that the relaxation of stress concentration due to the release of constraint of the strain was the basic mechanism of improvement in toughness of polymer alloys [4,5]. This release of constraint of the strain was brought about by the formation of many voids in the elastomer particles with low cohesive force. If the above-mentioned mechanism is valid, the efficiency of improvement of toughness depends on both strength of craze and the degree of relaxation of stress concentration. It is known that the strength of craze of the polymer increases with an increase of molecular weight of the polymer. As a result, its toughness would be improved [6]. On the contrary, the states of dispersion of the elastomer are considerably affected by the compatibility and the difference of viscosity between the matrix polymer and the elastomer [7,8]. It is expected that the finely and uniformly dispersed particles of the elastomer are effective on the release of the constraint of the strain in the polymer alloy. But, the effect of the states of the dispersed particles on the release of constraint of the strain and the fracture mechanism of polymer alloy is not well known.

The purpose of this study is to examine the effect of compatibility between polyphenylenesulfide (PPS) as a matrix polymer and styrene–ethylene–butylene–styrene block copolymers (SEBS) as elastomers on the improvement of toughness of the PPS/SEBS polymer alloy.

## 2. Experimental

### 2.1. Materials

The materials used in this study were a linear type of PPS as the matrix polymer, and conventional SEBS (H-SEBS) and two kinds of maleic anhydride modified SEBS

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Table 1
Properties of SEBS (S: Stylene, EB: Ethylene–Butylene, MFR: Melt flow rate (503 K, 21.3 N))

| SEBS | Ratio S/EB (%/%) | MFR (g/min) | Maleic anhydride (wt.%) | Strength (MPa) |
|---|---|---|---|---|
| H-SEBS | 30/70 | 5.0 | 0 | 21.6 |
| M-SEBS(L) | 30/70 | 5.0 | 0.5 | 21.6 |
| M-SEBS(H) | 30/70 | 5.0 | 1.8 | 21.6 |

(M-SEBS) as the elastomers. The weight average molecular weight of PPS was $8.5 \times 10^4$, and its viscosity (MFR) was 4.6 g/10 min (503 K, 21.3 N). Table 1 shows the characteristics of the SEBS used. The viscosities of these elastomers were all equivalent. The amounts of the grafted maleic anhydride of the lightly modified SEBS (M-SEBS(L)) and the highly modified SEBS (M-SEBS(H)) were 0.5 and 1.8 wt.%, respectively. PPS was blended with SEBS at weight ratios of 2, 5 and 10 wt.%.

### *2.2. Preparation of specimens*

PPS and SEBS were blended by a single-screw extruder (slip and shear type, KCK 70-22VEX(6)), at a barrel temperature of 578 K. The dumbbell-shaped test pieces for the uniaxial tensile test and the rectangular bars for the three-point bending test were molded by an injection molding machine (Nihon Seikosyo JSWJ30E) at 568 K. The temperature of the mold was 413 K.

### *2.3. Observation of the dispersed structure of the elastomer*

The states of dispersion of the elastomer were observed by scanning electron microscopy (SEM) (Nihon Denshi JSM5310). The samples were immersed in a liquid nitrogen bath and then were broken parallel to the direction of the injection flow. After surface etching of the samples in xylene solvent for 10 min, dispersion of voids at the center of the specimens were observed.

### *2.4. Evaluation of mechanical properties*

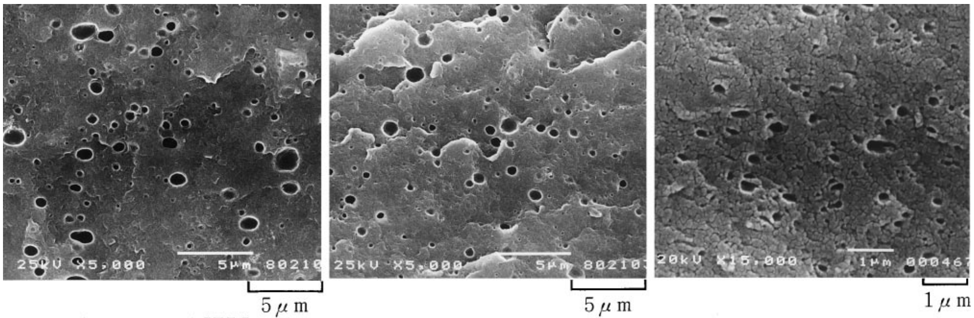
The uniaxial tensile test and the three-point bending test were done by an Instron-type testing machine (Shimadzu AG-500E). The tensile specimen was prepared with dimensions of a thickness of 1.5 mm, a width of 6 mm and a span length of 40 mm, and was loaded at a strain rate of 0.25/min at 296 K. The yield strength and the elongation at rupture were calculated from the stress–strain curve. The bending specimen was prepared with dimensions of a thickness of 4 mm, and a width of 10 mm. A round notch with dimensions of a radius of 0.5 mm and a depth of 1 mm was shaped by machining with the convex milling cutter. The specimen was loaded at a bending rate of 100 mm/min with a span length of 40 mm. Toughness was estimated by the three-point bending test. The storage modulus and tan $\delta$ were measured by a dynamic viscoelasticity equipment (Rheometric RSA-11) using the bending mode at the frequency of 10 Hz. The temperature was increased at the rate of 2 K/min from 173 to 630 K. The injected specimen had a width of 10 mm, a thickness of 4 mm and a length of 50 mm.

### *2.5. Morphological analysis of the deformation process*

The morphology of crazes and plastic deformation zone was observed by an optical microscope (OM). The microstructure of crazes was observed by a SEM. The preparation of these specimens was as follows. The deformation by the three-point bending test was fixed by casting in epoxy resin which consisted of 100 phr of Epon 828 and 50 phr of Ankamide 506, because the strain recovery on unloading significantly influences the morphology of the deformation zone [9]. For OM observation, thin sections of about 10 μm were cut perpendicular to the plane of the initial notch by using a conventional microtome. For SEM observation, the specimen was first immersed in a liquid nitrogen bath for 5 min, and broken normal to the plane of the notch immediately after removal.

## 3. Results

The morphology of the PPS/SEBS polymer alloy was changed during the injection molding process due to the high shear rate. The state of dispersion of the elastomers



Conventional SEBS Modified M-SEBS(L) Modified M-SEBS(H)

Fig. 1. Variation of the morphology of dispersed particles of SEBS elastomer in the PPS matrix polymer with the degree of modification by maleic anhydride at the center of the width of the specimen. The content of SEBS is 2 wt.%.

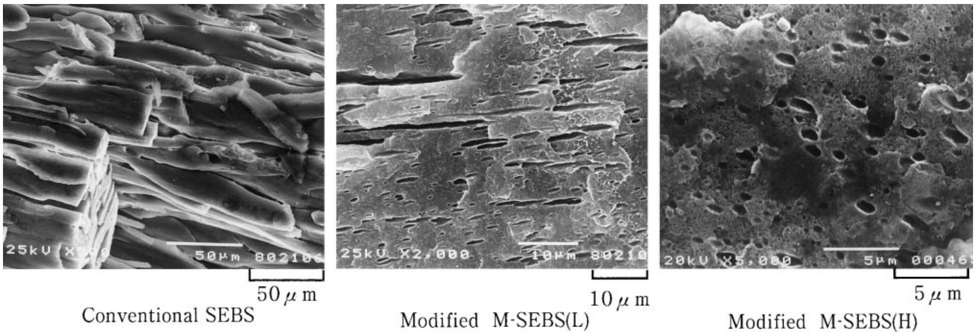


Fig. 2. Variation of the morphology of dispersed particles of SEBS elastomer in the PPS matrix polymer with the degree of modification by maleic anhydride at the center of the width of the specimen. The content of SEBS is 10 wt.%.

might be influenced by both the degree of modification by maleic anhydride and the content of the elastomer. Fig. 1 shows that the shape of SEBS particles was almost spherical and the particles were uniformly dispersed at a SEBS content of 2 wt.%. For PPS/H-SEBS, the particles varied from 0.1 to 1.0 μm in diameter. In the case of PPS/M-SEBS, the particles varied from 0.1 to 0.7 μm in diameter for M-SEBS(L), and they were lower than 0.3 μm in diameter for M-SEBS(H). Fig. 2 shows the morphology of the polymer alloy in a SEBS content of 10 wt.% at the center of the width of specimen. As the content of SEBS increased, the diameter of the dispersed particles became large and not uniform in distribution, and it was observed that the particles were oriented along to the direction of injection flow in the polymer alloy having H-SEBS or M-SEBS(L). The rod-like shape orientation was remarkable for H-SEBS. On the contrary, the orientation was almost not observed for M-SEBS(H). Fig. 3 shows the morphology of the PPS/M-SEBS polymer alloy with a content of 10 wt.% at the surface of the specimen. It is evident that the effect of high shear rate at the surface leads to a strong orientation even in highly modified SEBS.

Fig. 4 shows the effect of maleic anhydride modification on the dynamic viscoelasticity of the PPS/SEBS polymer alloy. The effect of the degree of modification on storage modulus was not observed with a low content of SEBS (a). In the case of 10 wt.% SEBS content (b), all the storage modulus was decreased at over 220 K, which was the transition temperature of SEBS. Particularly in the case of the polymer alloy having H-SEBS, the decrease in storage modulus was remarkable. The dynamic bending load introduced the shear stress parallel to the direction of injection flow. Therefore, it was considered that the orientation of the elastomer phase affects the decrease in the rigidity of the polymer alloy.

Fig. 5 shows the stress–strain curve of the polymer alloy composed of H-SEBS (a) and that of M-SEBS(L) (b). Though the yield stress of the PPS/M-SEBS polymer alloy decreased by the addition of SEBS, the elongation at rupture tended to increase. At a content of 2 wt.%, the elongation at rupture of the polymer alloy having H-SEBS was larger than that of PPS, but it decreased at a content of SEBS more than 5 wt.%. The elastic modulus also decreased at a H-SEBS content of 10 wt.%. The same tendency was also observed in the dynamic bending test. It was considered that the change of phase based on the increase in content of SEBS affected the decrease in the elastic modulus.

Fig. 6 shows the variation of yield stress as a function of the content of SEBS. The broken line in this figure shows the yield stress calculated from Eq. (1). In the calculation, it was assumed that SEBS did not bear the load of yield at all, and that the shape of the SEBS particle was spherical [10].

$$\sigma_{\mathrm{Blend}} = \sigma_{\mathrm{Y}}\left\{1 - \left(\frac{3\phi\pi^{1/2}}{4}\right)^{2/3}\right\} \tag{1}$$

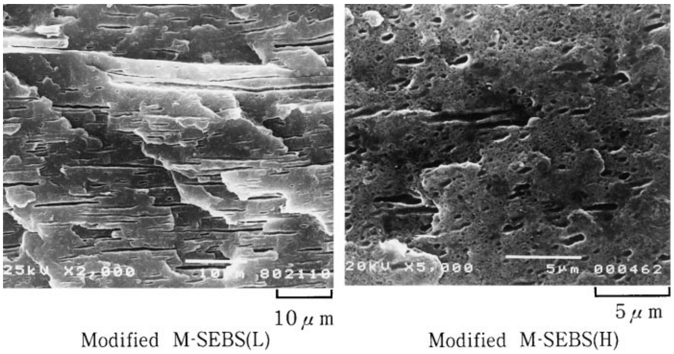
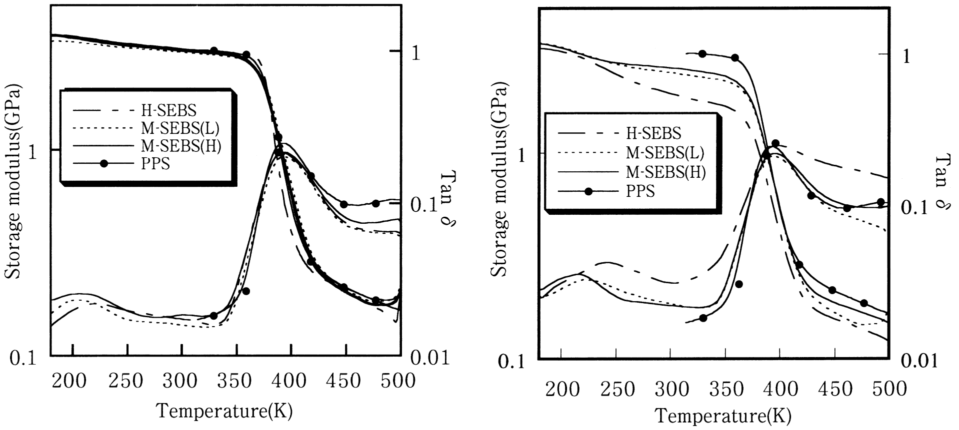


Fig. 3. Variation of the morphology of dispersed particles of SEBS elastomer in the PPS matrix polymer with the degree of modification by maleic anhydride at the surface of the specimen. The content of SEBS is 10 wt.%.



98/2=PPS/SEBS
(a)

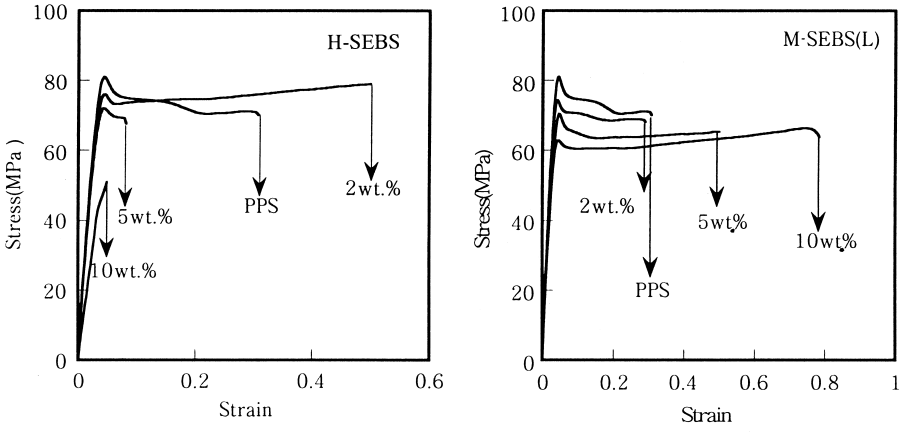
90/10=PPS/SEBS
(b)

Fig. 4. Effect of modification of maleic anhydride on the dynamic viscoelasticity of the PPS/SEBS polymer alloy.

where $\phi$ is the content of SEBS, and $\sigma_Y$ is the yield stress of uniaxial tensile test. The yield stress of the polymer alloy having M-SEBS was a little larger than the calculated value. The result indicates that the SEBS phase bears a part of the yield stress.

Fig. 7 shows the variation of the bending moment–displacement curves of the PPS/SEBS polymer alloys having H-SEBS (a) and M-SEBS (b) as a function of the SEBS content. In addition to 2 wt.% of H-SEBS, both bending moment and displacement at rupture of the polymer alloy increased. Then, the toughness of the polymer alloy increased. But, the toughness decreased at SEBS content more than 5 wt.%. On the contrary, as the content of the M-SEBS increases, the maximum bending moment decreased gradually, and above a content of 10 wt.%, the fracture by unstable propagation of crack after general yielding could not be observed in these experimental conditions. Therefore, in the case of blending M-SEBS, the toughness of the polymer alloy was improved greatly.

Fig. 8 shows optical micrographs of the cross-sections of the PPS/SEBS polymer alloy having M-SEBS(H). These specimens were obtained from unbroken samples in which deformation was fixed just before fracture for brittle samples and at the maximum bending moment for ductile samples. When the load was applied to the U-notched PPS, a uniform and stable plastic deformation zone was formed at first, and when it reached a certain size, the craze which was unstable local plastic deformation was formed at the tip of this local plastic zone. These behaviors were also reported for polyamide [11] or poly ether ether ketone (PEEK) [12] which had a glass transition temperature above room temperature. In the case of amorphous polymer, these crazes grow to cracks, but in the crystalline polymer including PPS, it is observed that numerous crazes are formed and become large. The brittle fracture is initiated from the craze. When the elastomer is added to such a crystalline polymer, the size of the plastic zone is extended until the crack is nucleated as shown in the polymer alloy at a



(a)

(b)

Fig. 5. Effect of modification of maleic anhydride on the stress–strain curve of the PPS/SEBS polymer alloy.

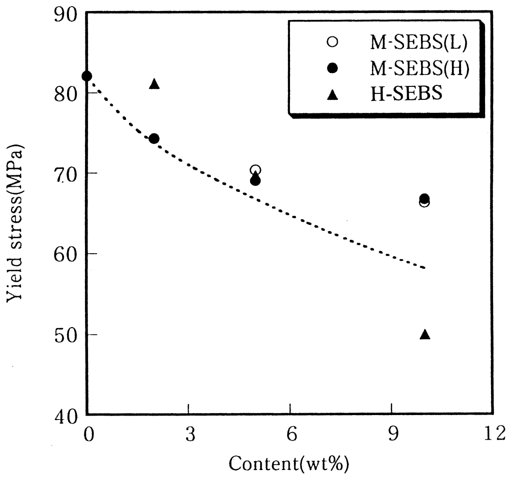


Fig. 6. Variation of yield stress as a function of content of SEBS. The broken line in this figure is the calculated yield stress with Eq. (1) on the assumption that SEBS does not bear the load of yield at all, and that the shape of SEBS particles is spherical.

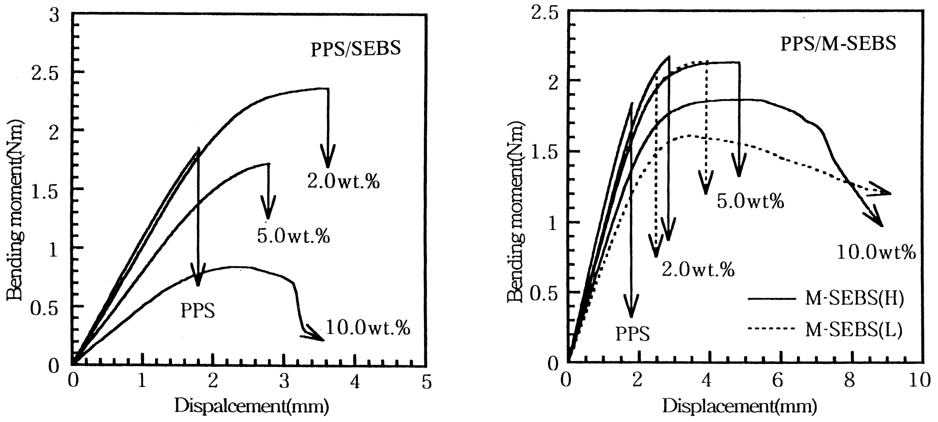
M-SEBS(H) content of 5 wt.%. That is to say, the addition of 5–10 wt.% of M-SEBS(H) were required for the general yielding in which brittle fracture was suppressed. In spite of addition over 10 wt.%, the morphology of the plastic deformation zone slightly changed. In the polymer alloy at a M-SEBS(H) content of 10 wt.%, the oriented cracks which are generated by the fracture of SEBS were scarcely observed. Fig. 9 shows the microstructure of the plastic deformation zone with a M-SEBS(H) content of 10 wt.%. Many voids were observed in the stable plastic zone. It was noticed that the voids had a large deformation and were oriented along to the direction of maximum principal stress. These voids were also observed in the polymer alloy with a content of M-SEBS(H) at 2 and 5 wt.%. Fig. 10 shows the plastic deformation zone of the polymer alloy having M-SEBS(L). With low content of the elastomer, the degree of modification of SEBS did not influence the morphology of the polymer alloy. But, it was recognized in the polymer alloy having M-SEBS(L) at a content of 10 wt.% that there were many cracks which were formed by the fracture of SEBS normal to the direction of injection flow at the tip of the U-notch. This tendency was more remarkable in the case of H-SEBS addition as shown in Fig. 11, and the fracture of the SEBS phase was observed even at a content of 5 wt.%.

## 4. Discussion

In general, the stress, which suppresses Poisson's shrinking of material, takes place normal to the direction of maximum principal stress in U-notched bars, and consequently the constraint of the strain occurs at the tip of the notch. Therefore, the stress concentration due to the constraint of plastic deformation occurs even in ductile material, and the maximum stress is generated at the tip of the plastic deformation zone [4]. Brittle fracture occurs when the stress ahead of the plastic zone reaches the strength of craze.

In the polymer alloy, if many voids are generated uniformly at the elastomer phase which has lower strength than that of the matrix, Poisson's shrinking would occur between the voids, and the relaxation of stress concentration due to the release of constraint of the strain can be accomplished at the tip of the notch. The mechanism of toughening of the polymer alloy has already been pointed out as the method of the release of constraint of the strain by one of the authors [4,5].

In the PPS/SEBS polymer alloy, with the increase in the content of SEBS, the plastic deformation zone of PPS/M-SEBS spread widely until unstable crazes were generated, and the general yielding occurred at a SEBS content of 5–10 wt.%. As it was apparent from the observation of the cross-section of the polymer alloy, the constraint of the strain was released by the voids which were generated at the SEBS phase, and consequently the relaxation of the stress concentration led to the stabilization of crazes and



(a) (b)

Fig. 7. Variation of the bending moment–displacement curves of the PPS/SEBS polymer alloy with H-SEBS (a) and M-SEBS (b) as a function of SEBS content.

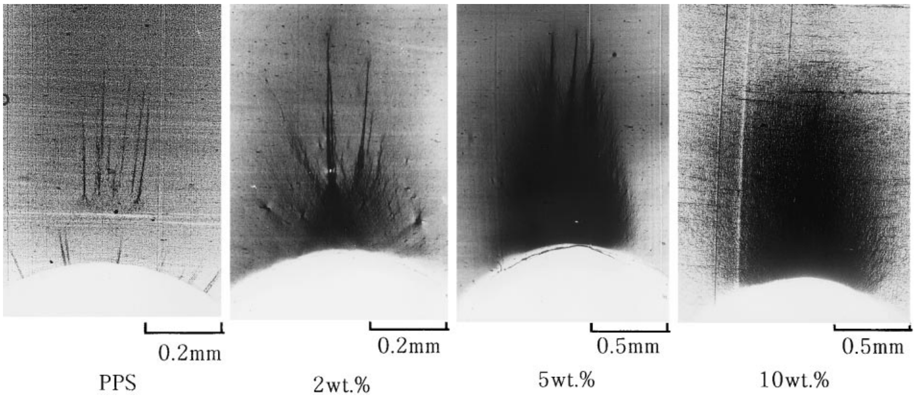


Fig. 8. Variation of plastic zone developed from the tip of the U-notch of the PPS/SEBS polymer alloy with M-SEBS(H) as a function of SEBS content.

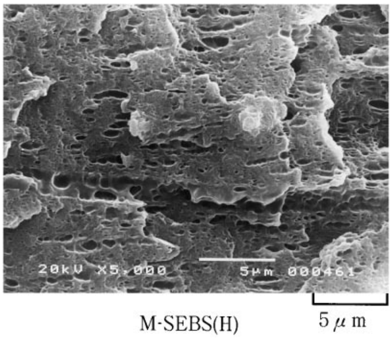


Fig. 9. Microstructure of the plastic deformation zone in the polymer alloy composed of highly modified M-SEBS(H) with a content of 10 wt.%.

the general yielding. This mechanism of toughening is the same as that of the SEBS/PPE/Nylon-6 polymer alloy [13].

It is well known that the states of dispersion of the elastomer depend highly on its viscosity. For example, when the viscosity of the elastomer is close to that of the matrix polymer, the elastomer is strongly orientated along to the direction of injection flow, and when the difference in both viscosities is large, the shape of the particles becomes spherical [14]. Whereas our study shows that though the elastomer and the matrix are equal in viscosity, the states of dispersion are affected by both compatibility and content of the elastomer. The diameter of the dispersed particle of SEBS increases with the decrease in compatibility of the PPS/SEBS polymer alloy, and as the increase in the content of the elastomer, it is difficult to divide rod-like SEBS into spherical particles, and consequently SEBS easily forms the state of orientation. This orientation does not give much effect in the mechanical property of uniaxial tensile test, but it leads to the considerable decrease in toughness of the polymer alloy. It is pointed out that the tensile stress component normal to the direction of SEBS orientation decreases considerably because the matrix polymer occupies a small part of sectional area in that direction. Therefore, the orientation of the elastomer easily leads to the fracture of the elastomer phase by the tensile stress component normal to the direction of maximum stress as shown in Fig. 10 at a M-SEBS(L) content of 10 wt.% and in Fig. 11 at a H-SEBS content of 5 wt.%. This fracture leads to the fibrillation of the plastic deformation zone, and in the case of M-SEBS(L), it decreases the capacity to bear outer load. Further, in the case of H-SEBS, the deflection at rupture also decreases because of its low uniaxial tensile strain of fracture. Therefore, these orientated phases of the elastomer result in the decrease in toughness of this polymer alloy. The remarkable decrease in fracture elongation and elastic modulus at a high content of H-SEBS can be explained with an assumption that change of phase between the matrix polymer and the modifier happens, and the elastomer

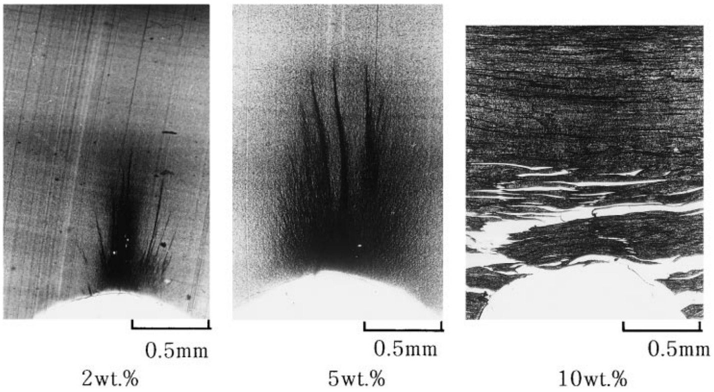


Fig. 10. Variation of the plastic zone developed from the tip of the U-notch of the PPS/SEBS polymer alloy with M-SEBS(L) as a function of SEBS content.

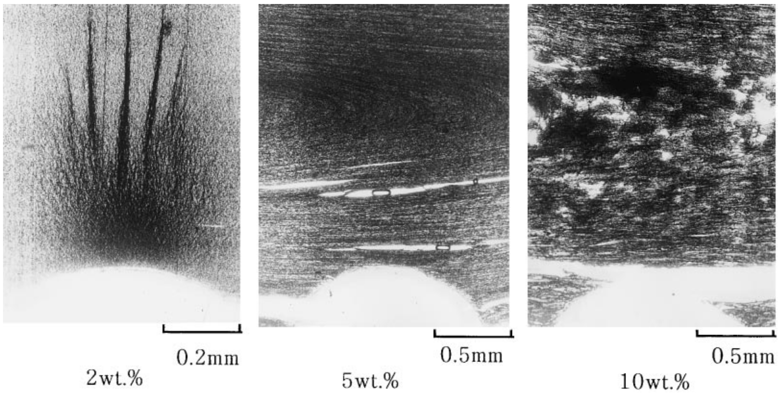


Fig. 11. Variation of the plastic zone developed from the tip of the U-notch of the PPS/SEBS polymer alloy with H-SEBS as a function of SEBS content.

occupies a continuous matrix. More study is required on this point in the future.

## 5. Conclusions

In the PPS/SEBS polymer alloy having SEBS, which was highly modified by maleic anhydride, it was confirmed that elastomers were dispersed finely because of high compatibility, and toughness was improved effectively by the release of constraint of the strain due to void formation in the elastomer phase. On the contrary, in the polymer alloy having conventional SEBS or SEBS which was lightly modified by maleic anhydride, the diameter of the dispersed elastomer particles was large, and the particles were orientated along the direction of injection flow, particularly with high content of the elastomer. The easy fracture of these orientated elastomer phases resulted in the suppression of improvement or the decrease in toughness of the polymer alloy.

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