Viscosity–Morphology–Compatibility Relationship of Polymer Blends

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SYNOPSIS

To investigate the correlation of viscosity–morphology–compatibility of polymer blends, polystyrene, polybutadiene, and styrene/butadiene triblock copolymer were selected as our materials. A capillary rheometer was used to measure the viscosity. All samples were blended by a two-roll mill, a Brabender, or by the solution casting method. The morphologies of extruded samples from the capillary were observed by SEM. The relation between the viscosity and the composition of the blend changes with shear rate. It was found that the better the compatability between the two phases of the blend the smaller is the disperse phase domain. The viscosity of polyblends is related to the compatability and composition of the two phase in this blend. In the present study, the rheological behavior of polyblends is explained from the viewpoints of morphology and compatability. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Polymer blends are of growing industrial importance. To optimize the commercial operation, the rheology of polyblend systems must be known. The rheological properties of blends may depend heavily on the mutual compatibility and morphology in the molten states of the parent polymers.

Blends of polystyrene (PS) and butadiene (BR) show two distinct glass transition temperatures corresponding to the PS phase and the BR phase, respectively.[1] This indicates that PS and BR are immiscible.[2] However, some miscibility[3] between the PS phase and the BR phase were observed for blends of PS and styrene–butadiene–styrene (SBS). There are chemical bondings between styrene and butadiene blocks existing in SBS, and PS can be well mixed with the styrene block of SBS. Similarly, for the BR/SBS blends, there exists some degree of miscibility between the PS and BR phases. For the miscibility of polyblends, Kim and Burns[4] measured the glass transition temperatures, melt tempera-

tures, crystallization temperatures, and the specific heat increment (ΔCp) of PS/BR blends to study the miscibility of PS and BR. Runt[5] discussed the miscibility of polyblends through the measurements of T_m.

For the morphology of polyblends, Han[6] illustrated that the morphology of the polyblend will affect the rheological behavior of the multiphase system. Aggarwal and Livigni[3] discussed the morphology and mechanical property of the PS/SBS blends. Plochocki[7] stated that the viscosity and elasticity of polyblends would show maximum or minimum at particular rheology compositions (PRC). The particular rheology composition is caused by phase inversion,[8] flow separation,[9] and formation of complex particles.[10] According to the thermodynamic theory by Oene,[11] the phase change will induce the change of melt elasticity. Kulezner[12] discovered that the domain size of the disperse phase approached minimum, as the viscosity ratio of the two phases approached unity. For the two phases of polyblends, the phenomena of droplet deformation and break up were investigated by Wu.[13] It was found that the interfacial tension and viscosity ratio would influence the size of the dispersed domain. Sperling et al.[14] studied the relationships among the phase continuity, viscosity ratio, and volume fraction of two-

phase system. It was pointed out that the cocontinuous phase will form if the viscosity ratio equals the volume ratio of the two phases.

In the present study, the correlation of viscosity, morphology, and compatability for an immiscible system (PS/BR blend), partially miscible system (PS/SBS and BR/SBS), and total miscible system (SBR random copolymer) were investigated.

EXPERIMENT

Materials

The materials used in this study were as follows: (1) polystyrene (PS), $\overline{M_w}$ = 520,000; (2) polybutadiene (BR), $\overline{M_w}$ = 550,000; (3) styrene–butadiene–styrene copolymer (SBS), $\overline{M_w}$ = 300,000, with 30 wt % styrene and 70 wt % butadiene; and (4) styrene–butadiene–rubber (SBR), $\overline{M_w}$ = 530,000, with 23.5 wt % styrene and 76.5 wt % butadiene.

Preparation of the Blends

Compositions of all blends are given in Table I. In each column of Table I, the styrene/butadiene weight ratio in all blends are identical. For example, in the first column, the PS/BR blend with weight ratio 80/20 and the PS/SBS blend with weight ratio 71/29 are of the same weight ratios of styrene (ST) to butadiene (BD) (i.e., 80 wt % styrene and 20 wt % butadiene).

All blends were prepared in a two-roll mill with a surface temperature of 145°C, roller speed of 10 rpm, and mixing time of ca. 20 min. In addition, two blends of the PS/SBS system with 71/29 and 43/57 weight fractions and all blends of the PS/BR system were prepared by a Brabender with an operation condition of 200°C and 20 rpm for about 15 min. The PS/SBS system with a 14/86 weight fraction and all blends of the BR/SBS system were also

Table I   Weight Ratios of the Two Components in the Blends

	ST/BD				
	80/20	60/40	40/60	20/80	23.5/76.5
PS/BR	80/20	60/40	40/60	20/80	23.5/76.5
PS/SBS	71/29	43/57	14/86		
BR/SBS				33/67	22/78

ST: styrene; BD: butadiene.

prepared by the solution-casting method, with toluene as solvent.

Measurement of Viscosity

The viscosities of PS, BR, SBS, and their blends in the shear rate range of 5–1152 s^{-1} at 200 and 220°C were determined by a capillary rheometer. The capillary die with 1 mm inside diameter and an L/D ratio of 30 was used in the measurement.

Morphology

The extrudates from the capillary rheometer at a shear rate of 11.52 s^{-1} were freeze-fractured and their morphologies were observed with a scanning electron microscope. The sample for SEM analysis was etched with a solution that was prepared with 200 mL H_2SO_4, 65 mL H_3PO_4, 63 mL H_2O, and 10 g CrO_3. Etching was performed with samples being soaked in the solution for 3–10 min. The BR on the surface of the sample was extracted by the solution. The samples were then rinsed with H_2O and C_2H_5OH and coated with gold before SEM analysis.

RESULTS AND DISCUSSION

The viscosity curves for blends of PS/BR, PS/SBS, and BR/SBS at 200°C are shown in Figures 1–3, respectively. It can be seen that, for both PS/BR and PS/SBS blends, the viscosity decreases with increasing content of PS. For the BR/SBS blend, the effect of composition on viscosity is quite small. To observe how the viscosity varies with the blending ratio, the viscosity data have been plotted vs. composition at constant shear rate (Figs. 4–6).
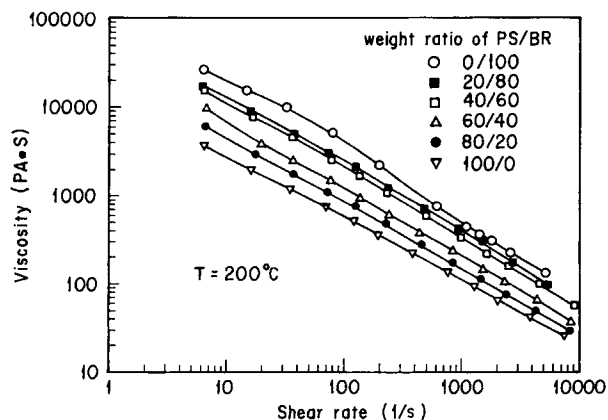
According to Utracki,[15] the viscosity curves of

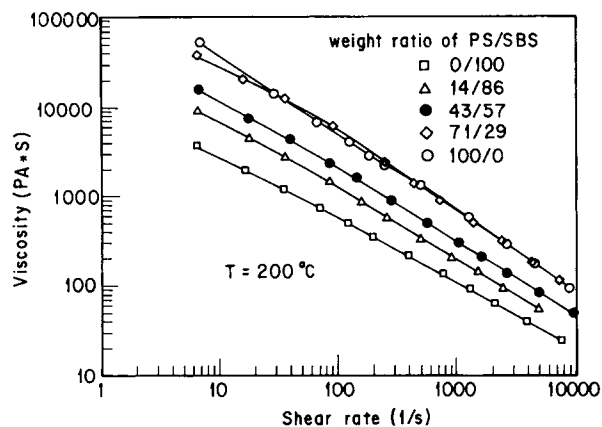**Figure 1**   Viscosity vs. shear rate for PS/BR blends.

Figure 2   Viscosity vs. shear rate for PS/SBS blends.

Figure 4   Melt viscosity vs. blend composition for PS/ BR blends at 200°C at various apparent shear rates (1/s).

polymer blends can be divided into three groups corresponding to the positive, negative, and mixed deviations of viscosity from the log-additivity rule. Since the viscosity variations are quite small in the present study, we plot the viscosity data with a normal scale instead of a log scale. The viscosity curves are compared using the additivity rule instead of the log-additivity rule. It is found from Figure 4 that the viscosity curves of the PS/BR blends exhibit negative deviation from the additivity rule. This may be attributed to the fact that styrene and butadiene are dissimilar in structure; there is little interaction between them. It is well established that negative deviation occurs when the interaction between the two phases of the blend is small, and positive deviation occurs when the interaction is large.

SBS is a triblock copolymer with styrene blocks at two ends and BR in the middle. There are chemical bondings between the PS and BR phases. When PS and SBS are blended, PS will mix with the styrene blocks of SBS. Hence, the interaction between
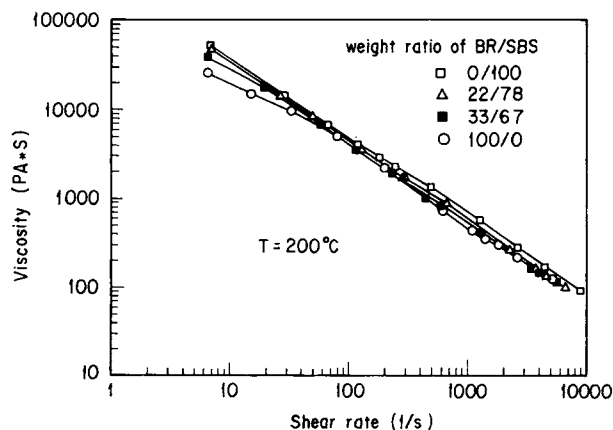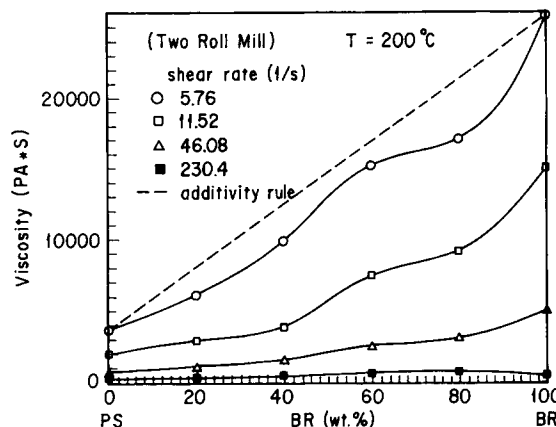
the PS and BR phases in the PS/SBS blend is due mainly to the chemical bondings existing in the SBS. From Figure 5, when the PS/SBS ratio is small, due to the chemical bondings existing in SBS, the interactions between the PS and BR phases are strong. The viscosity curves are, therefore, of positive deviation. When the PS/SBS ratio is large, the interactions between the PS and BR phases become small. The viscosity curve exhibits negative deviation. This is demonstrated in Figure 5 for low shear rates. At high shear rates, the viscosities of both pure PS and pure SBS decrease and the variations in the viscosity become small. Therefore, the viscosity approaches the additivity rule. This is evidenced in Figures 4–6. The positive–negative deviation from the additivity rule for the BR/SBS blends are not so profound as for the PS/SBS blend (Fig.
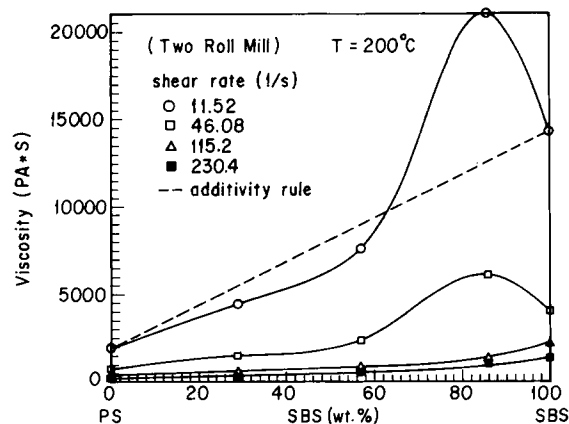

Figure 3   Viscosity vs. shear rate for BR/SBS blends.

Figure 5   Melt viscosity vs. blend composition for PS/ SBS blends at 200°C at various apparent shear rates (1/s).
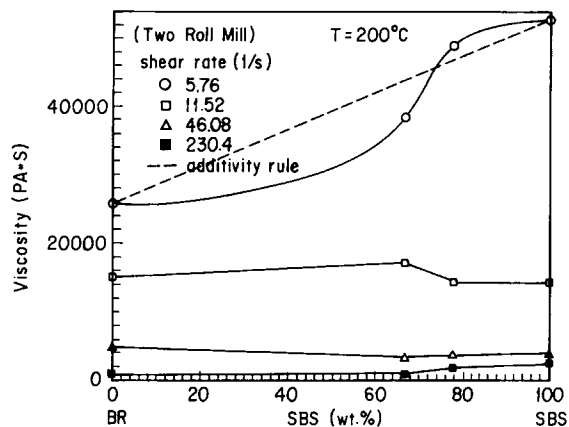
Figure 6 Melt viscosity vs. blend composition for BR/SBS blends at 200°C at various apparent shear rates (1/s).

6). This is due to the fact that the BR is more difficult to be mixed with the BR blocks since the BR blocks are terminated on each end by the domain of rigid PS.

The composition of PS/SBS and BR/SBS polyblends can be expressed in weight ratios of styrene (ST) and butadiene (BD) as shown in Table I. The viscosities of the three polyblends vs. the weight fractions of BD are shown in Figure 7. At low shear rate (e.q. 23.04 s^{-1}), the viscosity values of the PS/BR blends are always smaller than those of the PS/SBS and BR/SBS blends. This is consistent with the previous observation that due to the chemical bondings existing in SBS the interactions between the PS and BR phases are strong for PS/SBS and
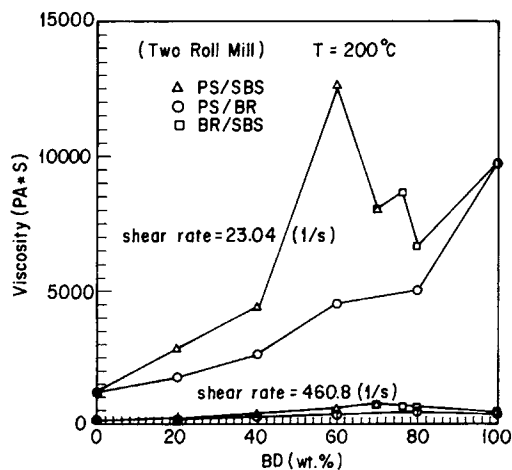
BR/SBS blends and are rather weak for PS/BR blends.

SBR was a random copolymer of styrene and butadiene, with 23.5 wt % styrene and 76.5 wt % butadiene. If we assume that the two components, PS and BR, in the copolymer are completely miscible, then the viscosity of SBR may be predicted by a simple mixing rule as follows:

$$\eta_{SBR} = W_{PS}\eta_{PS} + W_{BR}\eta_{BR} \qquad (1)$$

where η_{SBR} is the predicted viscosity of SBR from mixing rule; W_{PS} and W_{BR}, the weight fractions of PS (23.5 wt %) and BR (76.5 wt %); and η_{PS} and η_{BR}, the measured viscosities of PS and BR.

The viscosity values calculated by eq. (1) at 220°C are plotted in Figure 8, along with the measured ones. It can be seen that the applicability of eq. (1) to the copolymer SBR is quite satisfactory.

Figure 9 gives the SEM micrographs of the extrudates of both the PS/SBS and PS/BR blends (ST/BD = 80/20) obtained from the capillary rheometer. The white areas represent the PS phase and the dark ones represent the BR phase, which had been removed by the etching solution. It is seen in Figure 9 that the morphology of the PS/BR blend is quite different from that of the PS/SBS blend. No discrete droplets are seen in the PS/SBS blend; the PS and BR phases appear to be interlocked. For the PS/BR blend, however, the BR phase is dispersed in the PS phase. According to Han,[6] the interlocked morphology of the PS/SBS blend makes the mixture more resistant to flow because of the relatively strong interactions between the PS and BR phases.
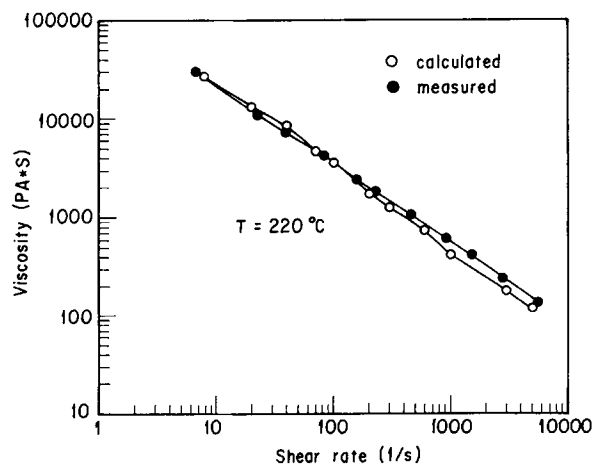

Figure 7 Melt viscosity vs. the weight fraction of BD for PS/BR, PS/SBS, and BR/SBS at 200°C at shear rates of 23.04 and 460.8 (1/s).

Figure 8 Comparison of viscosity values of SBR at 220°C calculated by mixing rule to the measured values.

(a)   (b)

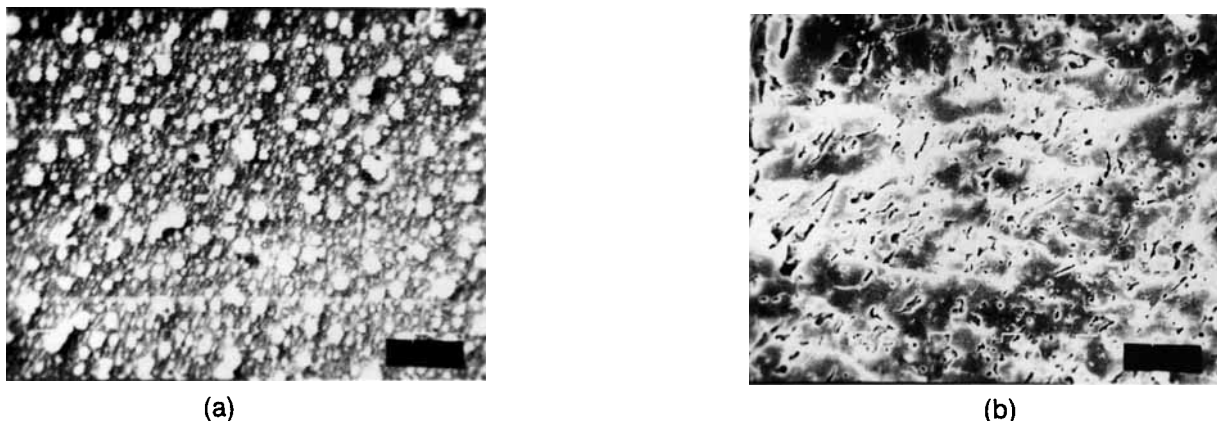**Figure 9**   SEM photomicrographs (×2000) of etched fractured surface for (a) PS/SBS extrudate with weight ratio of PS/SBS = 71/29 and (b) PS/BR extrudate with weight ratio of PS/BR = 80/20 [blended by a two-roll mill, 200°C, and 11.52 (1/s) in a Rheometer].

The morphologies of the extrudates of PS/BR and BR/SBS blends (ST/BD = 20/80) are presented in Figure 10. It is seen that for both blends the styrene component forms the dispersed phase, but the states of dispersions are quite different. The styrene phase of the BR/SBS blend is more uniformly dispersed than that of the PS/BR blend, and the droplet size of the BR/SBS blend is much smaller than that of the PS/BR blend. From the study of Wu,[13] it is known that the stronger the interactions between the two phases are, the smaller the droplet size is.

To study the effect of the blending method on the morphology and the viscosity of the blend, the SEM micrographs and the viscosity data of the PS/

BR and BR/SBS blends, prepared by a two-roll mill, a Brabender, and by the solution-casting method, are examined. The SEM micrographs of the blends are shown in Figures 11 and 12. From Figure 11, it is found that the domain size of the disperse phase of the PS/BR blend prepared by a Brabender is smaller than that prepared by a two-roll mill. This can be attributed to the fact that more efficient blending is achieved in the Brabender due to the high shear stress. However, the difference in morphology is not profound enough to affect the viscosity of the PS/BR blend. From Figure 12, uniform dispersions are observed for the BR/SBS blend, prepared both by a two-roll mill and by the solution-casting method. There is no significant difference
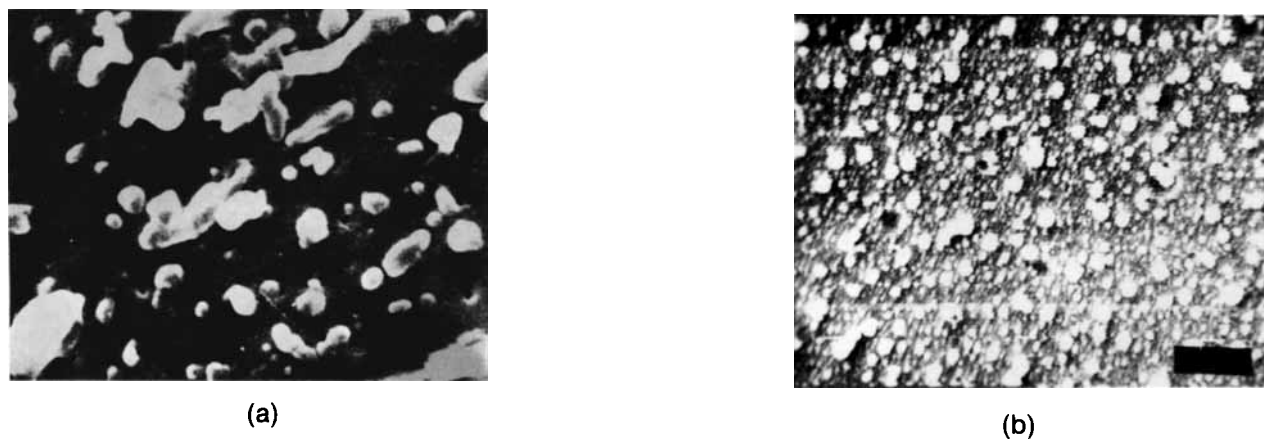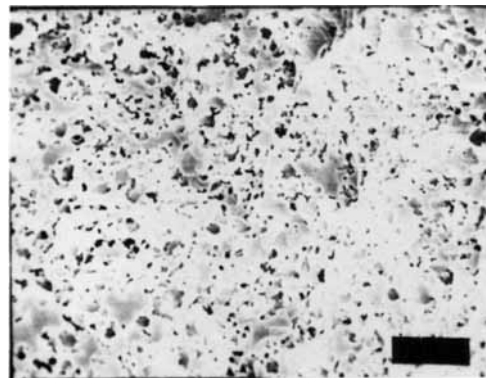

(a)   (b)

Figure 10   SEM photomicrographs (×5000) of etched fractured surface for (a) PS/BR extrudate with weight ratio of PS/BR = 20/80 and (b) BR/SBS extrudate with weight ratio of BR/SBS = 33/67 [blended by a two-roll mill, 200°C, and 11.52 (1/s) in a Rheometer].

Figure 11 SEM photomicrographs (×2000) of etched fractured surface for PS/BR extrudate with weight ratio of 60/40 (a) blended by a two-roll mill and (b) blended by a Brabender [200°C and 11.52 (1/s) in a Rheometer].

in the morphology and the viscosity curves are almost the same for the blends prepared by the two different methods.

CONCLUSION

In this work, the correlation of viscosity–morphology–compatability of polymer blends was investigated. From our observations, the viscosity of a polyblend is influenced by the composition, viscosity ratio between components, interfacial interaction, and morphology.

For the PS/BR blend, the interaction between the PS and BR phases is weak; the viscosity–com-

position curve exhibits negative deviation. For the SEM micrographs, both dispersed and continuous phases are observed. The domain size of dispersion for the PS/BR blend is quite large as compared with that for the PS/SBS and BR/SBS blends. For these two blends, the interactions between the PS and BR phases are due mainly to the chemical bondings existing in the SBS and the viscosity–composition curves are S-shaped. The two phases in the PS/SBS blend appear to be interlocked. In the BR/SBS blend, the domain size of dispersed phase (i.e., the styrene phase) is uniform and small.

Although the blending methods have some effect on the morphology of the blends due to the difference in the extent of mixing, the effect on the viscosity curve is insignificant.
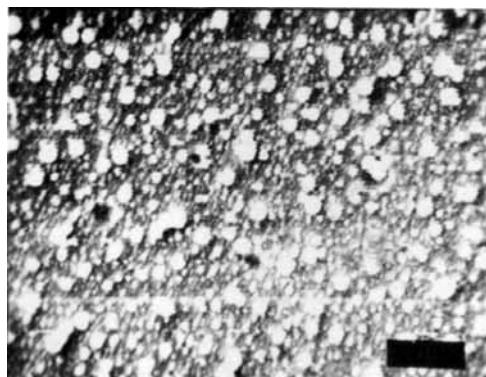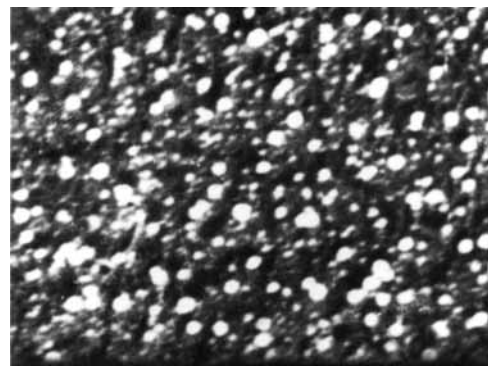
Figure 12 SEM photomicrographs (×2000) of etched fractured surface for BR/SBS extrudate with weight ratio of 33/67 (a) blended by a two-roll mill and (b) blended by solution casting [200°C and 11.52 (1/s) in a Rheometer].

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