

Melt Rheology and Morphology of PP/SEBS/PC Ternary Blend

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SYNOPSIS

Melt rheological properties of the ternary blend of isotactic polypropylene (PP), styrene-ethylene-butylene-styrene terpolymer (SEBS), and polycarbonate (PC), PP/SEBS/PC, are studied in a wide range of composition, such that PP is the matrix and SEBS and PC are the minor components, with the proportion of one varying from 0 to 30% at various fixed compositions of the other. The respective binary blends, PP/SEBS and PP/PC, studied as the reference systems for interpretation of results on the ternary blends yielded interesting new information about the morphology development and its correlation with melt rheological properties of these binary blends. The studies include the measurement of melt rheological properties on a capillary rheometer in the shear rate range 10^1 – 10^4 s⁻¹ at a fixed temperature of 240°C. The data presented as conventional flow curves are analyzed for the effect of blend composition and shear rate on pseudoplasticity, melt viscosity, and melt elasticity, and role of each individual component is identified. Morphology of dispersed phases of these blends is studied through scanning electron microscopy of the cryogenically fractured and suitably etched surfaces. Variations of morphology with blend composition and shear rate showed interesting correlation with melt rheological properties, which are discussed in detail. An important finding of the morphological studies is that in the PP/SEBS/PC ternary blend the SEBS phase forms two types of morphologies depending on the blend composition and shear rate: (i) simple droplets and (ii) boundary layer at the surface of the PC droplets. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Blending of isotactic polypropylene (PP) with various elastomers has generated a great deal of interest for many years for the improvement of impact properties and processing.^{1–6} The tensile and flexural properties, however, decrease on addition of elastomer to PP.⁷ This calls for the incorporation of a third component to such blends to improve the tensile properties and stiffness. Some studies in this direction have already been reported in recent years on systems such as addition of rigid fillers like CaCO₃,⁸ glass fibers (GF)^{9,10} and rigid polymers like polystyrene.¹¹ Our work on incorporation of GF to the PP/HDPE blend⁹ and PP/EPDM blend^{12,13} has provided interesting results regarding the improvement of tensile properties. The present work is de-

voted to another similar system, where the blend of PP with elastomer styrene-ethylene-butylene-styrene (SEBS) terpolymer is reinforced by a rigid polymer bisphenol-A-based polycarbonate (PC).

This paper presents a study of melt rheological properties and its correlation with the morphology of PP/SEBS/PC ternary and their corresponding binary blends. Binary blends in themselves are quite interesting and, hence, their behavior was studied in the full range of composition, viz., up to 30 wt % inclusions. In case of ternary blends, the compositions selected were such that the third component was added in appropriate proportion to the binary blend of the other two at fixed blending ratios. The samples, being too varied and large in number, are described in Table I, which should serve as a ready source for the terminology used in the subsequent discussion.

These studies were conducted with PP as the matrix and SEBS and PC as the dispersed phases. The amount of SEBS added was varied from 0 to 20%

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Table I Nomenclature and Composition of Blends Studied

Serial No.	PP/SEBS/PC Sample Code	Wt %			Sample No.
		PP	SEBS	PC	
1	PP	100	0	0	1
2	PP/SEBS binary blend at 5% SEBS	95	5	0	2
3	10% SEBS	90	10	0	3
4	15% SEBS	85	15	0	4
5	20% SEBS	80	20	0	5
6	PP/PC binary blend at 5% PC	95	0	5	6
7	10% PC	90	0	10	7
8	15% PC	85	0	15	8
9	20% PC	80	0	20	9
10	30% PC	70	0	30	10
11	PP/SEBS/PC ternary blend at constant SEBS (i.e., 10%) content ^a at 10% PC	81	9	10	11
12	20% PC	72	8	20	12
13	30% PC	63	7	30	13
14	PP/SEBS/PC ternary blend at constant SEBS (i.e., 20%) content ^b at 10% PC	72	18	10	14
15	20% PC	64	16	20	15
16	30% PC	56	14	30	16
17	PP/SEBS/PC ternary blend at constant PC (i.e., 10%) content ^c at 10% SEBS	81	9	10	11
18	20% SEBS	72	18	10	14
19	PP/SEBS/PC ternary blend at constant PC (i.e., 20%) content ^d at 10% SEBS	72	8	20	12
20	20% SEBS	64	16	20	15
21	PP/SEBS/PC ternary blend at constant PC (i.e., 30%) content ^e at 10% SEBS	63	7	30	13
22	20% SEBS	56	14	30	16

^a This corresponds to the PP/SEBS blending ratio 90/10.

^b This corresponds to the PP/SEBS blending ratio 80/20.

^c This implies that PC was 10% and the rest 90% was the blend of PP/SEBS at varying SEBS content.

^d This implies that PC was 20% and the rest 80% was the blend of PP/SEBS at varying SEBS content.

^e This implies that PC was 30% and the rest 70% was the blend of PP/SEBS at varying SEBS content.

at constant PC content of the blend and the amount of PC added was varied from 0 to 30% at a constant SEBS content of the blend. The melt rheological properties were also studied for PP/SEBS and PP/PC binary blends, to be used as reference systems for analyzing the results of ternary blends. The data for melt viscosity and melt elasticity are presented and discussed as a function of blend composition. This analysis has produced interesting results regarding the effects of the third component (SEBS in the case of the PP/PC blend and PC in the case of the PP/SEBS blend) on the melt flow properties of the PP/SEBS/PC ternary blend.

Scanning electron micrographs of the extrudates reveal a peculiar, composition-dependent dispersion

pattern for SEBS in the ternary PP/SEBS/PC blend. SEBS seems to decrease the PC droplet size in the ternary blends. All these observations regarding morphology are found to be consistent with the melt rheological properties for the blends studied.

EXPERIMENTAL

Materials

The isotactic polypropylene (PP) used was Koylene M-0030 (MFI = 10), a product of Indian Petrochemicals Corp. Styrene-ethylene-butylene-styrene block copolymer (SEBS) used was Kraton G-1652

of the Shell Chemical Co. and polycarbonate (PC) was the injection-molding grade from Baeyer.

Preparation of Blends

Both the binary (PP/SEBS and PP/PC) and ternary (PP/SEBS/PC) blends were prepared by melt-mixing the component polymers, in the requisite ratios, in a single-screw extruder (Windsor SX-30) at a screw speed of 30 rpm and temperature range of 230–240°C from first zone to the die. The strands obtained from the extruder were cut into small granules in a granulator and used for rheological measurements.

Measurements

Melt-rheological measurements were carried out on a piston-type capillary rheometer (Goettfert Werkstoff Pruefmaschinen-Rheograph 2001). The apparent shear stress and shear rate obtained from the rheometer using the conventional expressions were corrected using Bagley and Rabinowitsch corrections as per the procedures described elsewhere.^{4,14} The extrudates from the rheometer at various shear rates were quenched and collected. The extrudate swell, used in the calculation of melt elasticity parameters by Tanner's equation,¹⁵ were determined from the measurement of extrudate diameters after solidification using a Projectina microscope.

Morphology of the extrudate cross sections were studied on a scanning electron microscope (StereoScan S360) of Cambridge Instruments. For this the extrudate, strands were broken by flexing under cryogenic temperature. To study the morphology of the binary blends PP/SEBS and PP/PC, the dispersed component was etched out using chloroform, as it dissolves both PC and SEBS, whereas for the case of ternary blend PP/SEBS/PC, SEBS was selectively etched out using cyclohexane, which is a solvent for SEBS and not for PC.

RESULTS AND DISCUSSION

Flow Curves

Flow curves as the variation of shear stress with shear rate for the binary PP/SEBS and PP/PC and ternary PP/SEBS/PC blends are given in Figures 1–4. The flow curves are linear for all the blends in the studied shear-rate range. Thus, the general behavior of the systems can be explained well with the Ostwald de Waele power law,¹⁶ which can be stated as

$$\tau_w = K\dot{\gamma}^n$$

where τ_w and $\dot{\gamma}$ are the shear stress and shear rate, respectively, and n is the exponent describing the characteristics of the fluid and K is the constant of proportionality.

The power law exponent, n , for these blends varies, as shown in Table II. There is a systematic variation in the n values showing its decrease with increasing SEBS content, both in the presence and absence of PC. The value of n is in the range 0.34–0.41 for the various compositions of the blend. In spite of this small range of variation of n , specific trends are discernible in the variation of n with the blend composition. PC has a general tendency to increase the value of n , and this increase becomes less prominent at higher levels of SEBS. This is consistent with the role of SEBS on the value of n at constant PC content, viz., that the SEBS tends to decrease the value of n . This behavior may be explained on the basis that the increased compatibility or interfacial interaction increases the pseudoplasticity of the melt (or decreases the value of n). n can be visualized as the rate dependence of the melt viscosity.¹⁷ For a given composition of the binary blend, the shear dependence of melt viscosity decreases with increasing interfacial interaction between the two components, because the better the continuity of apparent shear stress across the interface between the two components of the blend, the greater is the homogeneity of the melt. Thus, from these results, it may be stated that the interface interaction is better for the PP/SEBS blend compared to the PP/PC blend. The comparison of the value of n for the binary blend also confirms this role of the interface in pseudoplasticity, since PP/SEBS has a greater pseudoplasticity than does the PP/PC blend.

Effect of SEBS

In the absence of PC (i.e., the PP/SEBS binary blend), in the lower shear rate region (below $3 \times 10^2 \text{ s}^{-1}$), flow curves at the compositions studied lie above that for PP, with an exception of the 5% SEBS blend. With increasing shear rate, the flow curves for all the compositions of the blend tend to converge. Thus, the SEBS phase seems to have greater influence on the melt flow of the PP/SEBS blend at the lower shear rate than at the higher ones. This behavior will be explained on the basis of morphology.

In the presence of PC, the flow behavior of the PP/SEBS blend changes such that at constant PC

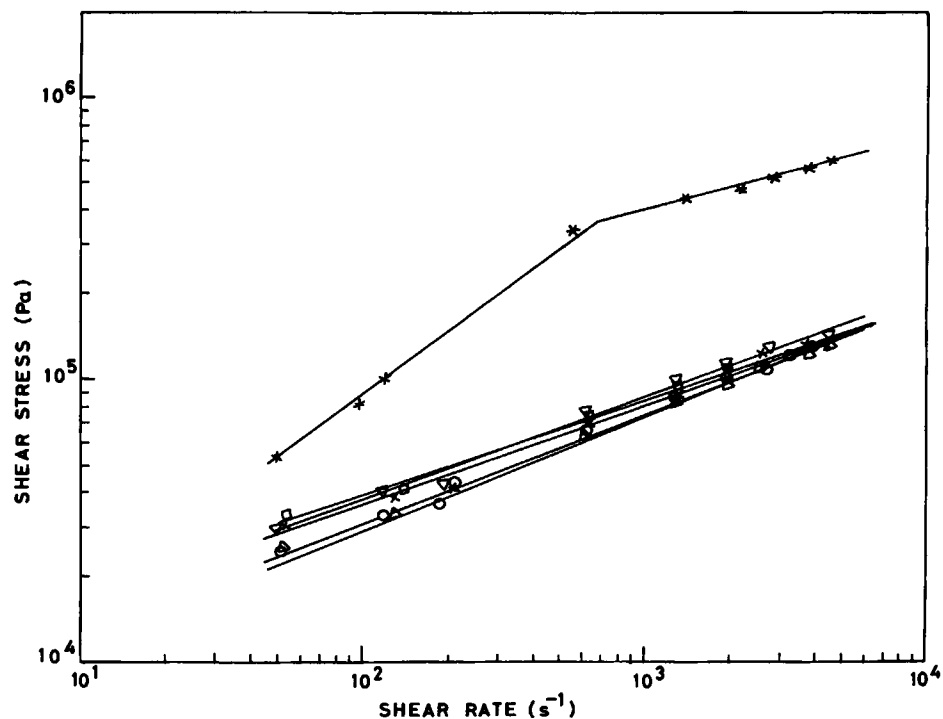


Figure 1 Flow curves for PP/SEBS binary blend at 240°C at various compositions of the blend (wt % SEBS content): (○) 0; (△) 5; (+) 10; (□) 15; (▽) 20; (*) 100.

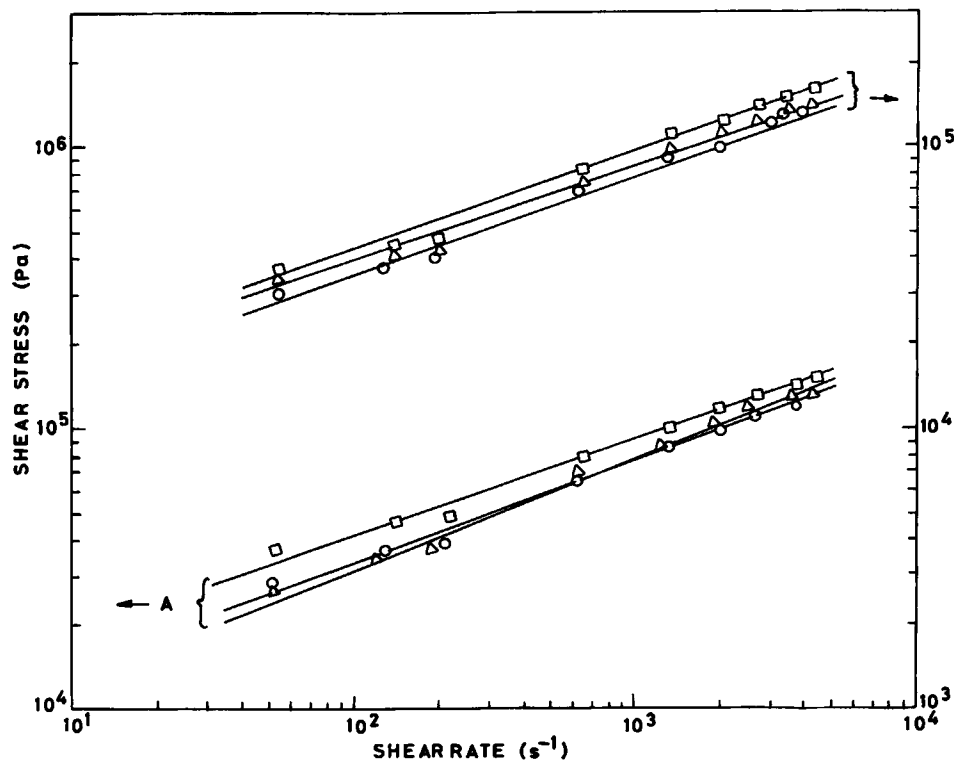


Figure 2 Flow curves for PP/SEBS/PC ternary blend at 240°C at (A) 10% and (B) 20% PC content at varying SEBS content (wt %): (○) 0; (△) 10; (□) 20.

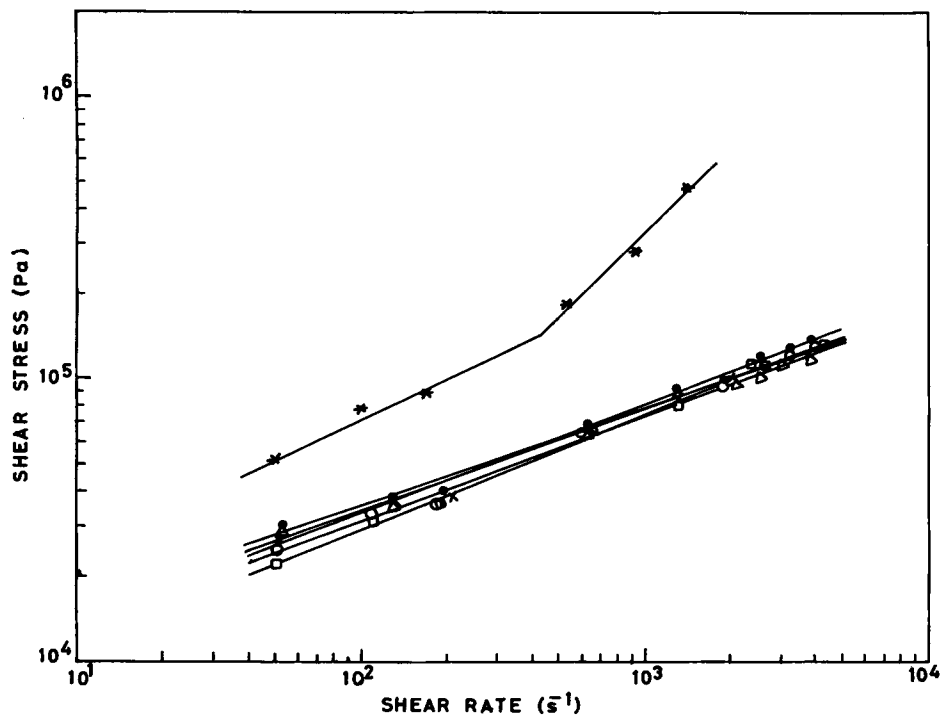


Figure 3 Flow curves for PP/PC binary blend at 240°C at various compositions of the blend (wt % PC content): (○) 0; (△) 5; (+) 10; (●) 20; (□) 30; (*) 100.

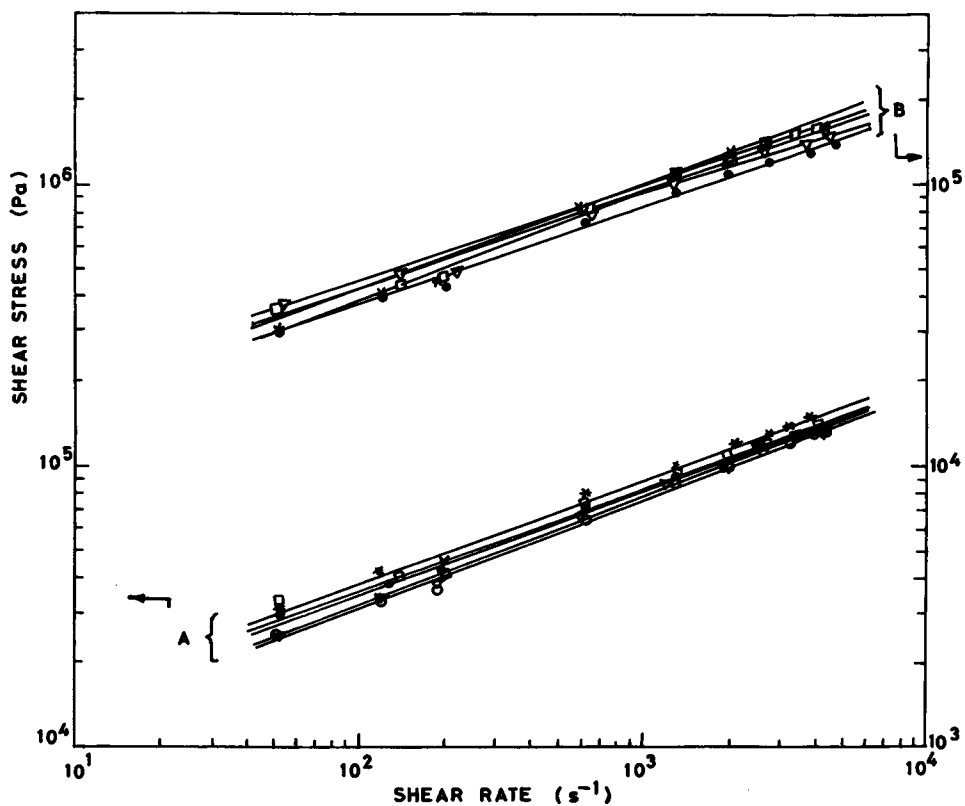


Figure 4 Flow curves for PP/SEBS/PC ternary blend at 240°C at (A) 10% and (B) 20% SEBS content at varying PC content (wt %): (○) 0; (▽) 10; (□) 20; (*) 30.

Table II Pseudoplasticity Index (n) of the Blends

Sample No.	(n)
1	0.39
2	0.38
3	0.35
4	0.34
5	0.36
6	0.36
7	0.38
8	0.38
9	0.38
10	0.41
11	0.39
12	0.36
13	0.37
14	0.35
15	0.36
16	0.39

content the increase of SEBS content shifts the flow curves above that for the corresponding PP/PC binary blend in the whole range of the shear rate studied (Fig. 2), implying an increase of melt viscosity on addition of SEBS. Unlike the case of the curves for the PP/SEBS blend (Fig. 1), the separation of the curves for the PP/SEBS/PC ternary blend at various SEBS contents is uniform over the entire range of blend compositions. This might be due to the effect of PC domains that share the energy of the applied shear stress.

Effect of PC

In the absence of SEBS, i.e., the case of the PP/PC binary blend, the flow curves are well separated in the low shear rate region, but converge in the higher shear rate region (Fig. 3). This is similar to the behavior of the PP/SEBS binary blends. At low

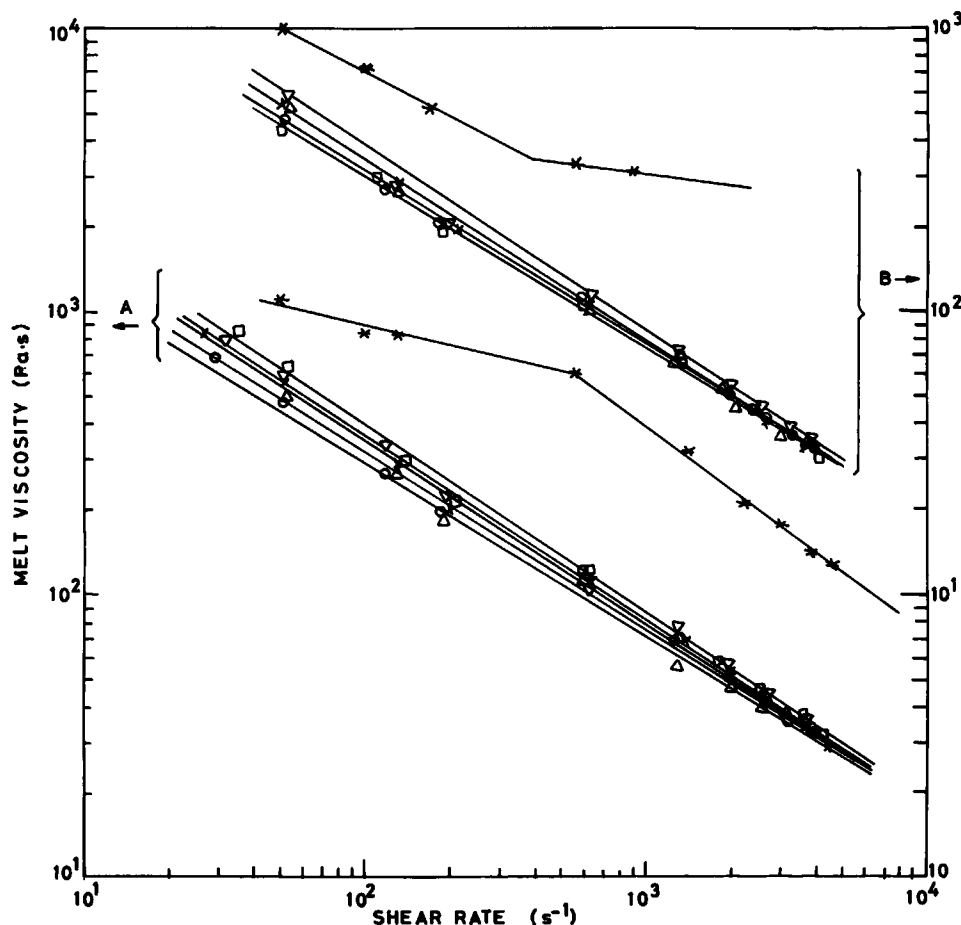


Figure 5 Melt viscosity as a function of shear rate for (A) PP/SEBS and (B) PP/PC binary blends at various compositions (wt % SEBS or PC, respectively): (○) 0; (△) 5; (+) 10; (□) 15; (▽) 20; (*) 100 for PP/SEBS blend; (○) 0; (△) 5; (+) 10; (□) 20; (▽) 30; (*) 100 for PP/PC blend.

shear rates, the dissipation of shear stress energy is less than that at the higher shear rates because the dissipation may be due to deformation of droplets, which is possible only at higher shear rates.

In the presence of SEBS, the flow curves with varying PC content are merged together in the low shear rate region compared to high shear rate region (Fig. 4). This effect increases with increasing SEBS content. The explanation for this is given in relation to the morphology in a subsequent section.

Melt Viscosity

Melt viscosity of these binary and ternary blends decreases with increasing shear rate quite linearly, as shown in Figs. 5 and 6. The effects of SEBS and PC components on melt viscosity will be discussed below. The individual components, SEBS and PC,

on the other hand, show a change of slope in their melt viscosity vs. shear rate curve at a critical shear rate, which is, incidentally, the same, $\dot{\gamma} = 5 \times 10^2 \text{ s}^{-1}$, for both cases. But on the melt viscosity vs. shear stress plots (which are not shown), the slope change for SEBS and PC occur at shear stress values 3.7×10^5 and $1.4 \times 10^5 \text{ Pa}$, respectively. This change of slope is presumably due to shear-induced change in their molecular conformation. The difference in shear energy needed for the change in molecular conformation for SEBS and PC is obvious from the difference in molecular rigidity of these two molecules.

Furthermore, the melt viscosity at any given shear rate of SEBS and PC is higher than that of PP, implying greater rigidity of both dispersed phases than of the medium. Thus, these blends may be visualized as the rigid viscoelastic inclusions dispersed in a viscoelastic fluid.

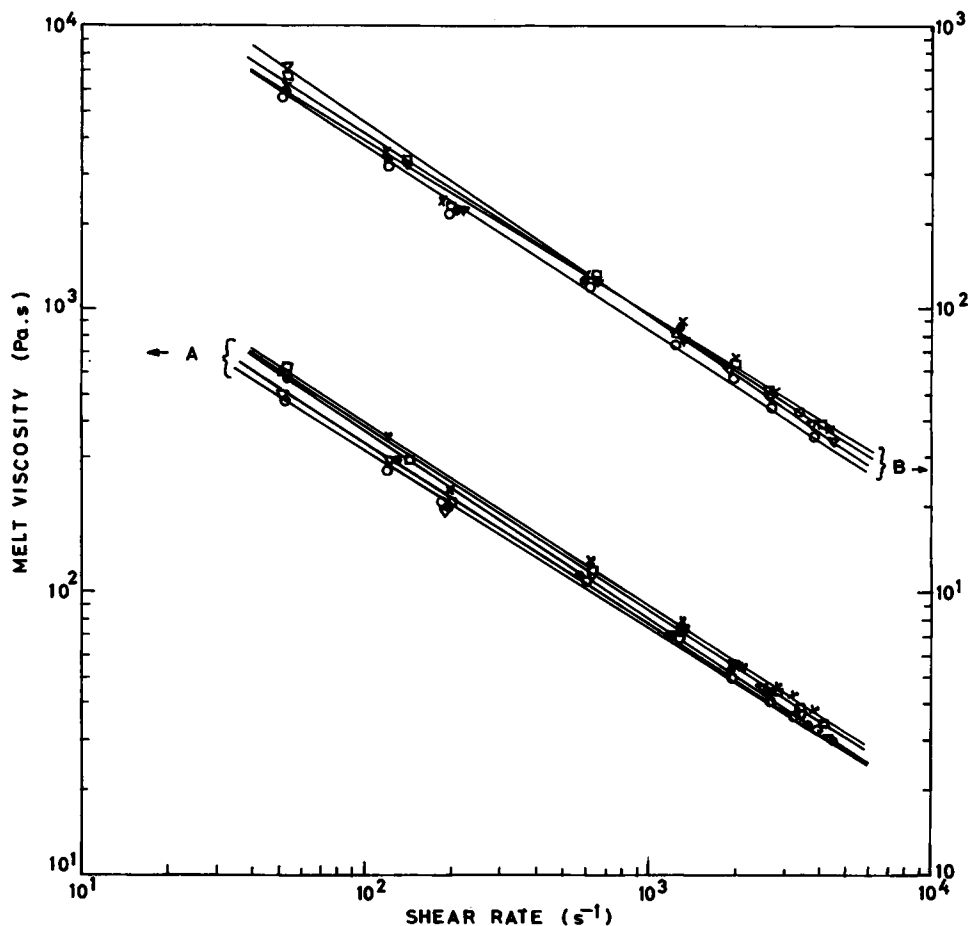


Figure 6 Melt viscosity as a function of shear rate for PP/SEBS/PC ternary blend at (A) 10% and (B) 20% SEBS content at varying PC contents (wt%): (O) PP; (●) 0; (▽) 10; (□) 20; (+) 30.

Effect of SEBS

Melt viscosity as a function of SEBS content, at constant shear rates, in the absence and presence of PC varies as shown in Figure 7 (a) and (b), respectively. In the absence of PC, the melt viscosity at a shear rate $1 \times 10^2 \text{ s}^{-1}$ shows a minimum at 5% SEBS content followed by a rise up to a maximum at 15% SEBS and then a fall. The values of melt viscosity, when viewed in comparison to PP, indicate a lubricating effect of SEBS on PP at low SEBS content (i.e., 5% SEBS) and an obstruction to flow at the higher SEBS content. A lubricating effect is recognized for various binary blends in the literature.¹⁸ The profile of melt viscosity vs. SEBS content changes with shear rate [Fig. 7(a)] such that the features of maxima and minima gradually decrease with increasing shear rate and, finally, the curve becomes quite flat at the highest shear rate ($\dot{\gamma} = 3 \times 10^3 \text{ s}^{-1}$).

The effect of SEBS in the presence of PC shown in Figure 7(b) for the case of a constant 10% PC content is apparently a continuous increase of melt viscosity up to the highest studied range, i.e., 20% SEBS content.

Effect of PC

Melt viscosity as a function of PC content, at constant shear rates, in the presence and absence of SEBS is shown in Figure 8 (a) and (b). In the absence of SEBS, melt viscosity increases with increasing PC content up to 20% and then decreases at higher PC content. On the other hand, in the presence of SEBS (at a constant 10% SEBS level), the melt viscosity of the blend increases continuously with increasing PC content after a slight dip in the curve at 10% PC content [Fig. 8(b)]. The sharpness of increase and decrease diminishes with increasing shear rate, implying that the role of dis-

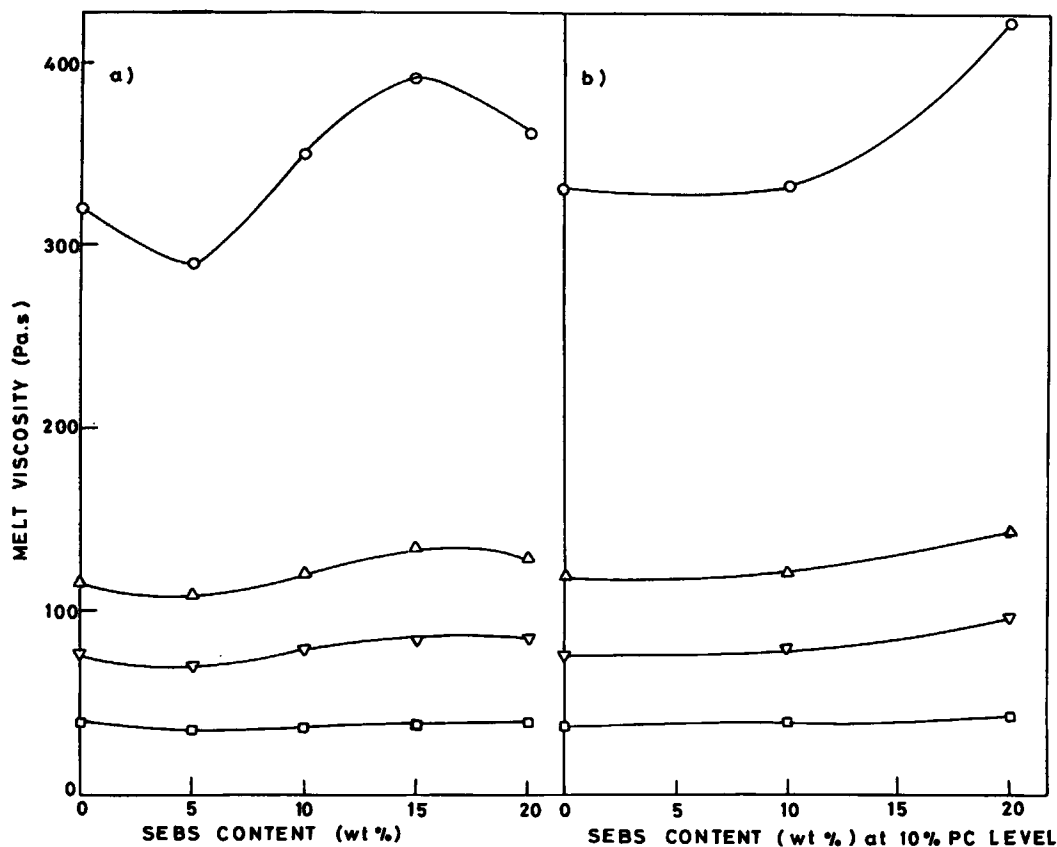


Figure 7 Melt viscosity as a function of SEBS content for PP/SEBS/PC ternary blend (a) in the absence of PC and at (b) 10% PC content with shear rate (s^{-1}) as the parameter: (O) 1×10^2 ; (Δ) 5×10^2 ; (∇) 1×10^3 ; (\square) 3×10^3 .

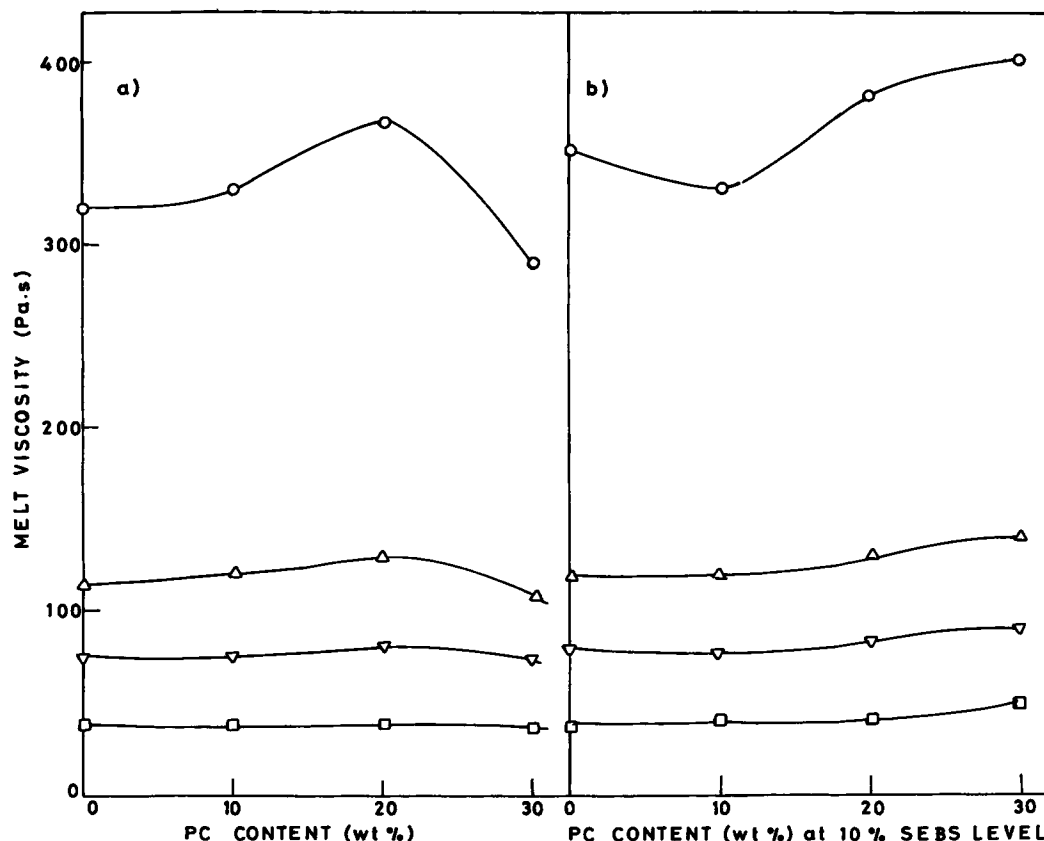


Figure 8 Melt viscosity as a function of PC content for PP/SEBS/PC ternary blend (a) in the absence of SEBS and (b) at 10% SEBS content with shear rate (s^{-1}) as the parameter: (○) 1×10^2 ; (△) 5×10^2 ; (▽) 1×10^3 ; (□) 3×10^3 .

persed SEBS and PC domains in the melt flow behavior is more prominent when they are under low shear stress.

Thus, the contribution of SEBS in the melt viscosity behavior of the PP/PC blend is mainly through the improvement of compatibility of PC with PP, which will be shown due to the presence of SEBS at the PP-PC interface.

Melt Elasticity

Recoverable shear strain (S_r), calculated from the extrudate swell using Tanner's equation,¹⁵ is taken as a parameter to represent the melt elasticity. The variations of S_r with shear rate for the various samples shown in Figures 9–11 reveal, in general, that (i) S_r increases sharply with increasing shear rate, and (ii) at low shear rates, all these blends have a higher melt elasticity than that of PP, whereas at high shear rates, the melt elasticity of the blends is generally smaller than that of PP.

It may be worthwhile to know the melt elastic behavior of the individual components in bulk that form dispersed droplets in the blend. Both SEBS and PC have a higher melt elasticity than that of PP at shear rates below $3 \times 10^2 s^{-1}$ and a much lower melt elasticity than that of PP above this critical shear rate (Figs. 9 and 10). This critical shear rate corresponds to a single shear stress value of $3.5 \times 10^4 Pa$. This difference of the elastic recovery behavior may arise due to irreversible shear-induced changes in molecular conformations of these polymers.

Effect of SEBS

For the PP/SEBS binary blend, S_r varies nonlinearly depending on the shear rate, as shown in Figure 12(a). At low shear rate, S_r increases sharply at 5% SEBS followed by a decrease up to 20% SEBS. As we will see, the droplets of SEBS are much larger at this former composition of the blend than at the

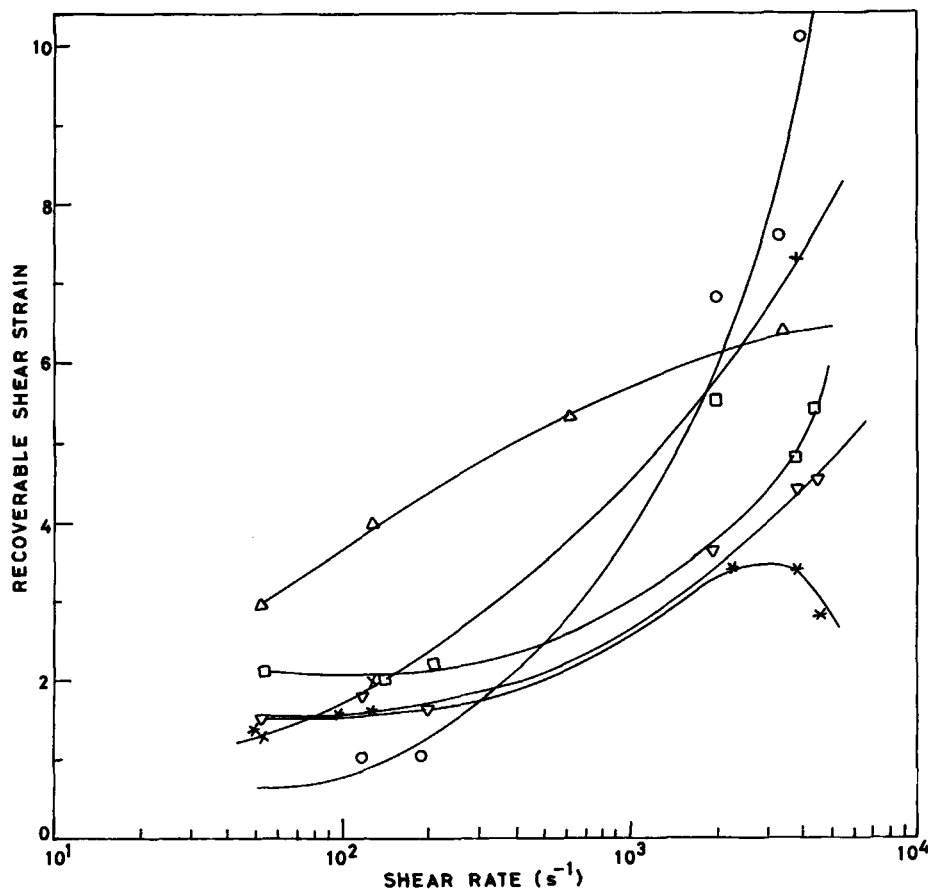


Figure 9 Recoverable shear strain as a function of shear rate for PP/SEBS binary blend at various compositions (% SEBS content): (○) 0; (△) 5; (+) 10; (□) 15; (▽) 20; (*) 100.

higher SEBS contents, hence, the shear dependence of elastic recovery of the melt will be influenced by the dispersed droplets. The sharpness of increase at 5% SEBS content decreases with increasing shear rate, and at the highest shear rate, plotted S_r decreases continuously.

On the other hand, in presence of PC, the effect of SEBS on the melt elasticity is a continuous decrease of S_r with SEBS content, as shown in Figure 12(b) at a constant PC loading. This decrease of melt elasticity is accompanied by changes in the morphology of dispersion and will be discussed later.

Effect of PC

In the absence of SEBS, the melt elasticity of the PP/PC binary blend as a function of PC content varies nonlinearly, showing a maximum around 10% PC content, followed by a decrease of melt elasticity at higher PC content [Fig. 13(a)]. This decrease of

melt elasticity with PC content is accompanied by the increase in PC droplet diameter, as will be shown and discussed in subsequent sections. Furthermore, at the lowest PC content (i.e., 10%), melt elasticity of the blend is greater than that of PP, and the difference decreases with increasing shear rate. These results will be discussed further in a subsequent section.

In the presence of SEBS, the melt elasticity as a function of PC content shows a maximum around 20% PC content for the ternary blend at a constant 10% SEBS level [Fig. 13(b)]. The effect of initial addition of PC (i.e., 10% PC as compared to 0% PC in this case) is an increase of melt elasticity that becomes less prominent with increasing shear rate, which is similar to the effect in the absence of SEBS [see Fig. 13(a)].

Furthermore, the relative magnitude of the S_r of the blend (both binary and ternary) at the highest PC content (i.e., 30% PC) and the unblended PP is

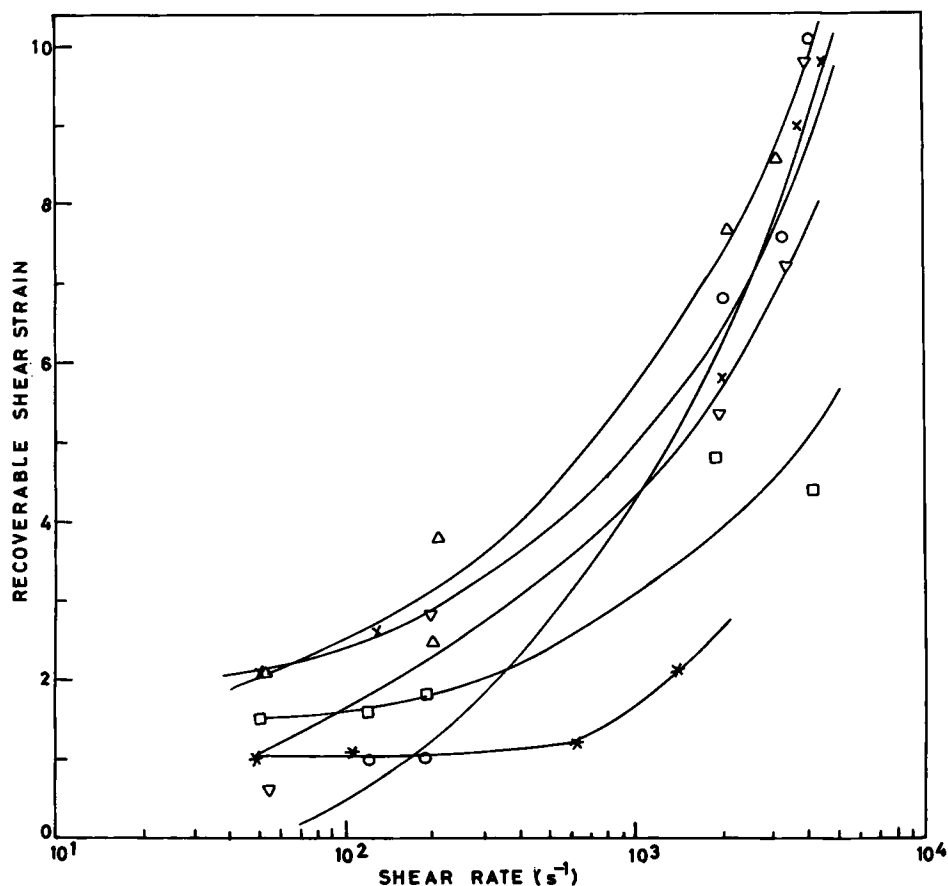


Figure 10 Recoverable shear strain as a function of shear rate for PP/PC binary blend at various compositions (% PC content): (○) 0; (△) 5; (+) 10; (▽) 20; (□) 30; (*) 100.

shear-dependent, such that at the low shear rates (i.e., below the aforementioned critical shear rate $3 \times 10^2 \text{ s}^{-1}$), the blend has a higher melt elasticity than that of PP, whereas at higher shear rates, the situation is reverse. This seems to be due to the reduction of droplet size at higher shear rates.

Morphology

Effect of Blend Composition on Morphology

Scanning electron micrographs (SEM) of the cryogenically fractured surfaces of etched extrudates are shown in Figures 14–19. The number-average diameter, $\langle d \rangle$, of the droplet was calculated after measuring the diameter of at least 200 droplets for each blend sample studied, using the following relation:

$$\langle d \rangle = \frac{\sum N_i d_i}{\sum N_i}$$

where N_i is the number of droplets having diameter d_i . The number-density of droplets has been defined to be the number of droplets present in a given constant area of the sample surface.

Figure 14 shows the SEM of etched extrudates of the PP/SEBS binary blend with varying SEBS content. The dispersion of SEBS is quite homogeneous and fine with sufficiently round-shaped domains of mean diameter ranging from 0.2 to 0.6 μm depending on the SEBS content. The droplets at 5% SEBS content are distinctly larger and more spherical than at the higher two SEBS contents.

The micrographs of the PP/PC binary blend at 10 and 30% PC content are shown in Figure 15. It is seen that PC forms discrete spherical droplets dispersed in the PP matrix. The mean diameter of these droplets increases with increasing PC content of the blend (being 0.22 μm at 10% and 0.4 μm at 30% PC content). The number-density of the droplets is significantly larger at 30% than at 10% PC

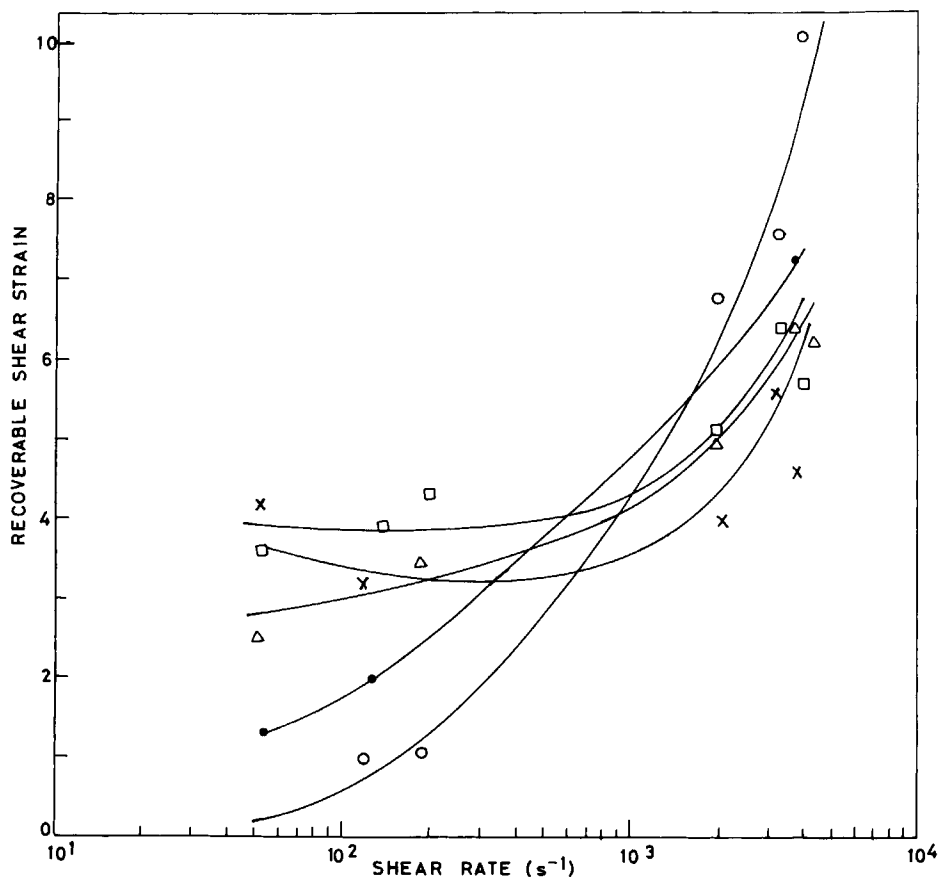


Figure 11 Recoverable shear strain as a function of shear rate for PP/SEBS/PC ternary blend at 10% SEBS content at varying PC content (%): (○) PP; (●) 0; (▽) 10; (□) 20; (+) 30.

content. Furthermore, the spherical shape of the droplets is maintained even at the highest PC content studied, unlike the case of SEBS droplets in the PP/SEBS blend.

Micrographs grouped in Figure 16 represent the effect of PC content in the PP/SEBS/PC ternary blend at constant SEBS content. The SEBS component has been dissolved out by selective etching. Thus, the empty spaces correspond to the regions where the SEBS component was sitting. It is seen from these micrographs that SEBS in this ternary blend disperses in two ways: (i) as separate droplets, and (ii) as the boundary phase surrounding the PC droplets (note that the PC droplets are not etched out; hence, they appear as solid spheres). Type (i) morphology is apparently predominant at the lower PC content, whereas type (ii) morphology is more widespread at the higher PC content, as Figure 16(b) shows that a larger number of PC droplets are surrounded by the boundary phase than those

in Figure 16(a). Moreover, the mean diameter of PC droplets in these ternary blends are larger than that in the PP/PC binary blend, the mean diameter being $0.3 \mu\text{m}$ at 10% and $0.9 \mu\text{m}$ at 30% PC content. This confirms that the occurrence of SEBS surrounding the PC domains would reduce the tendency of droplet breakup. Furthermore, the role of SEBS as a compatibilizer in the PP/PC blend has also been reported by other authors.¹⁹

The effect of increasing SEBS content at constant PC content is represented by the micrographs shown in Figure 17 (sample nos. 11 and 12) for the PP/SEBS/PC ternary blend, at constant PC content, and at 10 and 20% SEBS contents. At the lower SEBS content [Fig. 17(a)], more SEBS goes into the boundary phase than in the case of higher SEBS content [Fig. 17(b)]. This is evident from the fact that there is a larger number of droplets of SEBS in the latter case and the size of PC droplets is larger in the former case owing to the above-stated role of

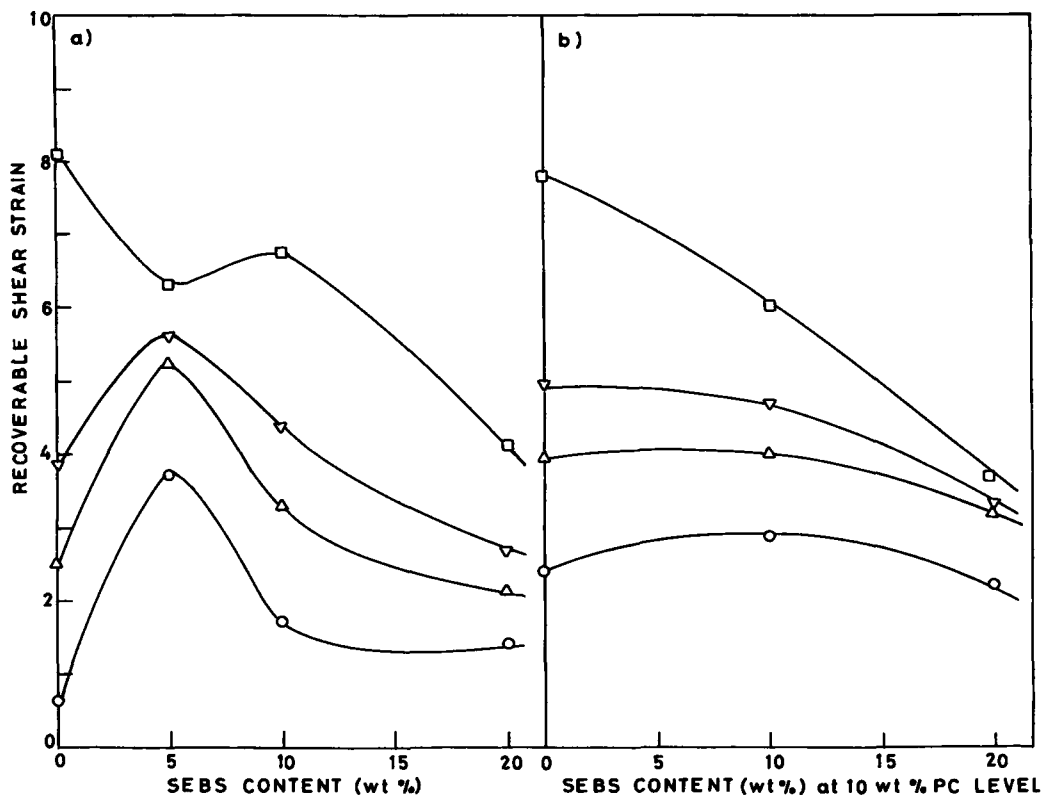


Figure 12 Recoverable shear strain as a function of SEBS content for PP/SEBS/PC ternary blend (a) in the absence of PC and (b) at 10% PC content with shear rate (s^{-1}) as the parameter: (○) 1×10^2 ; (△) 5×10^2 ; (▽) 1×10^3 ; (□) 3×10^3 .

the SEBS boundary phase in the droplet breakup. Thus, depending on the PC content, SEBS has a tendency to first go into the boundary phase and thereafter to form individual droplets. Furthermore, increasing SEBS content at constant PC content decreases the average diameter of the PC droplets or, in other words, the SEBS phase facilitates dispersion of PC in the PP matrix only after exceeding a certain proportion.

Effect of Shear on Morphology

The effect of shear rate in the case of the PP/SEBS binary blend at a constant SEBS content (5%, sample no. 2) can be seen in the micrographs of Figures 18 and 14(a), which represent the three shear rates. At the lowest shear rate ($1.2 \times 10^2 s^{-1}$), the SEBS droplets are large [mean diameter $0.6 \mu m$; Fig. 14(a)]. At the next highest shear rate ($6 \times 10^2 s^{-1}$), the mean diameter is $0.2 \mu m$ [Fig. 18(a)], whereas at the highest shear rate ($4 \times 10^3 s^{-1}$), the mean diameter again increases to $0.3 \mu m$; the size distribution is wider in the latter case.

The effect of shear rate on the morphology of PP/SEBS/PC at a fixed composition (sample no. 11) can be seen by looking at the micrographs of Figure 17(a) for the shear rate $1.2 \times 10^2 s^{-1}$, Figure 19(a) for the shear rate $2 \times 10^3 s^{-1}$, and Figure 16(a) for the shear rate $4 \times 10^3 s^{-1}$. The mean diameter of the PC droplets, which is $0.6 \mu m$ at the lowest shear rate [Fig. 17(a)], goes to a high value $1.2 \mu m$ at the middle shear rate [Fig. 16(a)]. With increasing shear rate, coalescence of PC droplets occurs, which gives rise to a larger diameter of these droplets at the middle shear rate compared to the lower one. A careful look at the micrograph also reveals the sticking of smaller droplets onto the larger ones, indicating the beginning of the coalescence. A further increase of shear rate leads to the breakup of the PC droplets into smaller ones.

The tendency of coalescence of SEBS droplets observed for the PP/SEBS binary blend at the same shear rate [Fig. 18(b)] results in the formation of a large number of separate droplets of SEBS in the ternary blend [Fig. 16(a)]. Furthermore, on increasing the shear rate, the morphology of dispersion

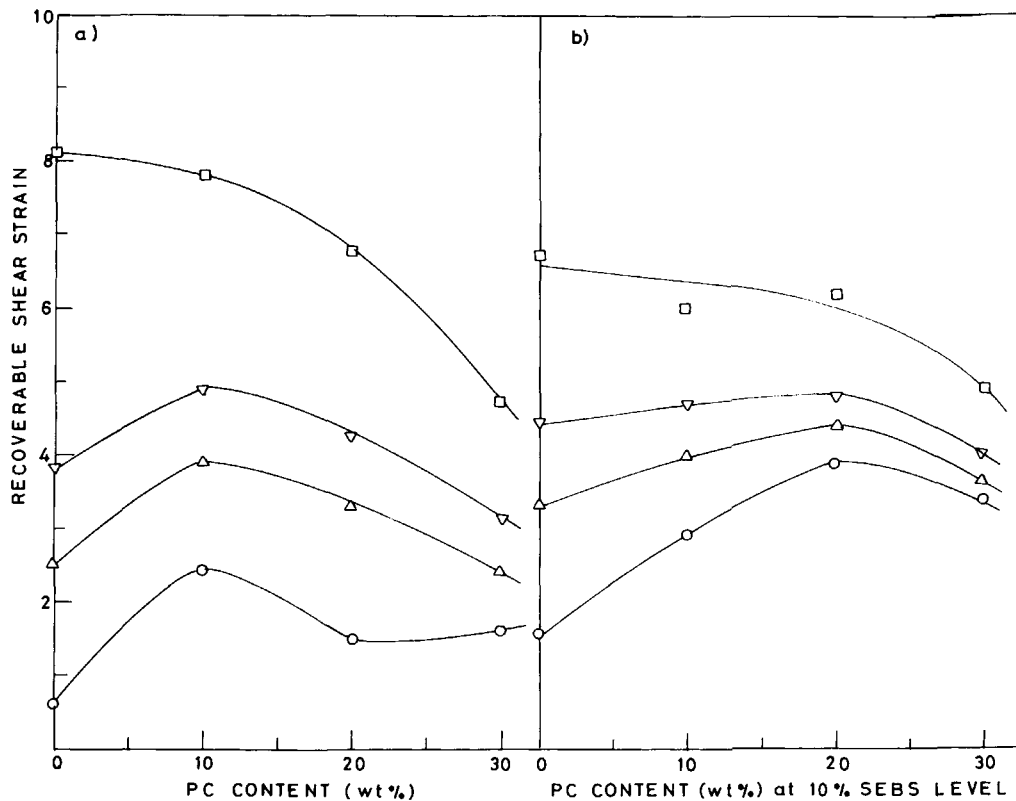


Figure 13 Recoverable shear strain as a function of PC content for PP/SEBS/PC ternary blend (a) in the absence of SEBS and (b) at 10% SEBS content with shear rate (s^{-1}) as the parameter: (O) 1×10^2 ; (Δ) 5×10^2 ; (∇) 1×10^3 ; (\square) 3×10^3 .

of SEBS changes from type (ii) (i.e., boundary phase) to type (i) (i.e., separate droplets).

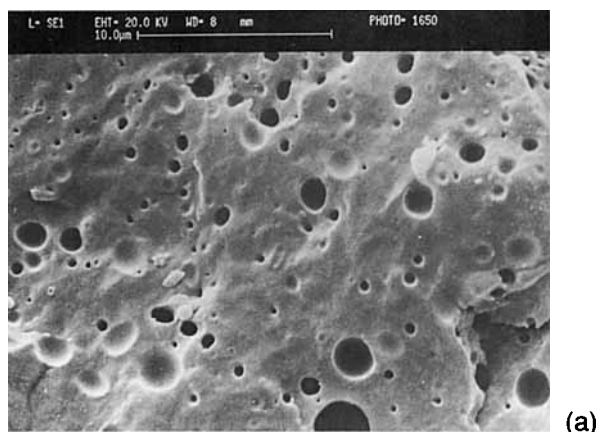
Correlation of Morphology and Melt Rheology

As shown in the micrographs, SEBS forms spherical droplets in the PP matrix. At lower shear rate, some energy is spent to deform these droplets and, hence, the shear stress for a given shear rate will increase, which increases the melt viscosity of the PP/SEBS binary blends with increasing SEBS content. With increasing shear rate, the droplets deform, break into smaller ones, and are oriented in the flow direction, thus producing less obstruction to flow. This explains the diminishing role of the dispersed phase droplets with increasing shear rate on the melt flow of the blend. Thus, the effect of the blend composition on melt viscosity becomes less prominent at higher shear rate.

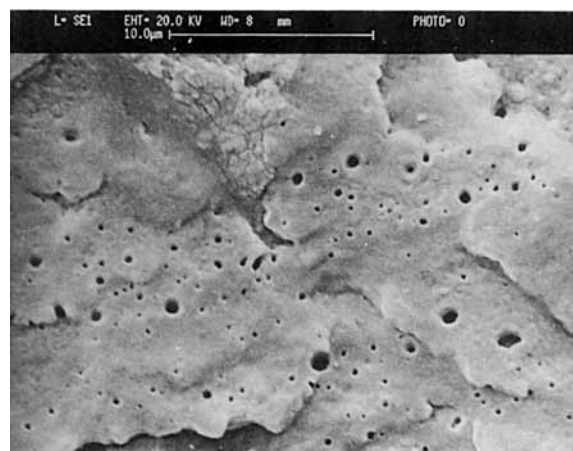
In the PP/PC binary blend, PC forms uniformly dispersed spherical droplets that increase in size and number-density with increasing PC content. So, at

low shear rate, the melt viscosity increases with PC content and this effect decreases with increasing shear rate due to the orientation of PC droplets in the flow direction at high shear rate.

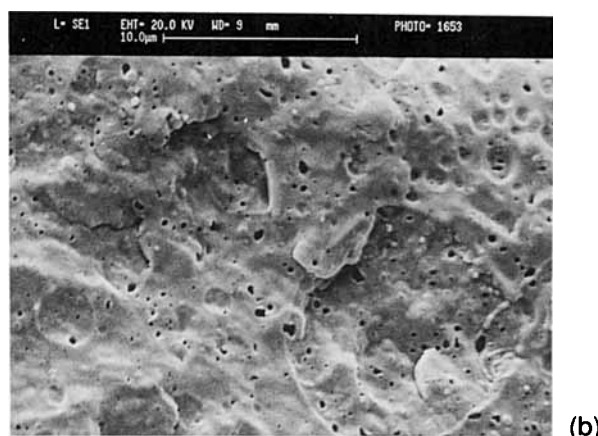
The contribution of SEBS towards the melt elasticity of the PP/SEBS binary blend is significantly larger than that of PC in the case of PP/PC binary blends. This is due to the following reasons: (i) The more deformable SEBS droplets in the PP/SEBS blend contribute more towards the melt elasticity compared to the less deformable PC droplets in the PP/PC blend, and (ii) the SEBS droplets in the PP/SEBS blend have more interfacial interaction with PP compared to the PC droplets in the PP/PC blend. At 5% SEBS content, the dispersed SEBS droplets have much larger diameters than at higher SEBS content in this blend. These SEBS droplets contribute to the elastic recovery behavior of the melt, such that the bigger the droplet size, the larger the melt elasticity. Furthermore, with increasing SEBS content, at constant shear rate, the droplet size decreases, which explains the decrease of melt



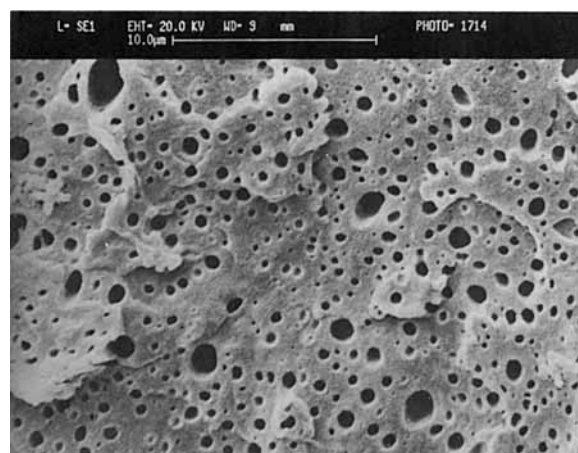
(a)



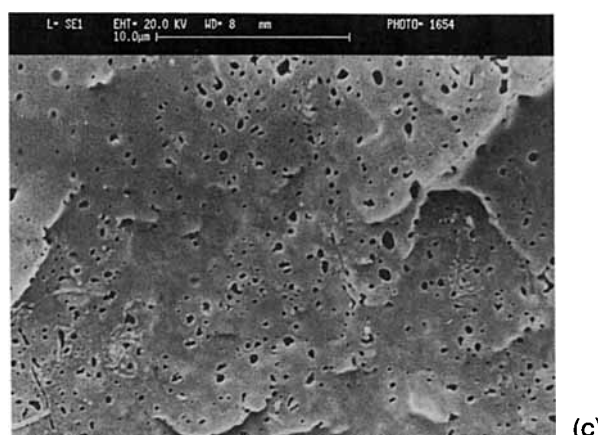
(a)



(b)



(b)



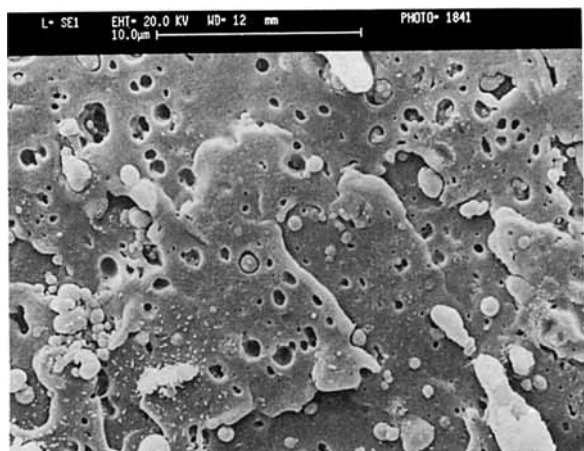
(c)

Figure 14 Scanning electron micrographs of extrudates of PP/SEBS binary blend at constant shear rate ($1.2 \times 10^2 \text{ s}^{-1}$) and at various SEBS contents (%): (a) 5; (b) 10; (c) 20.

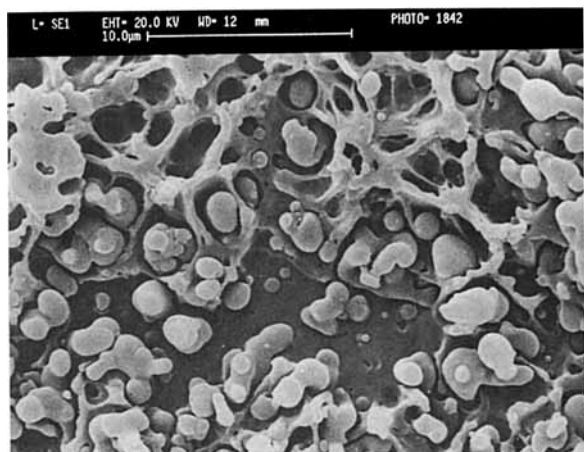
Figure 15 Scanning electron micrographs of extrudates of PP/PC binary blend at constant shear rate ($3.3 \times 10^3 \text{ s}^{-1}$) and at various PC contents (%): (a) 10; (b) 30.

elasticity with increasing SEBS content. At high shear rate (higher than the above-stated critical value of $3 \times 10^2 \text{ s}^{-1}$), the PP/SEBS 95/5 blend has smaller SEBS droplets, which do not contribute enough toward melt elasticity of the blend. Thus, at high shear rate, there is a continuous decrease of melt elasticity with increasing SEBS content due to decrease of droplet size.

Because of the small interfacial interaction of PC with PP, the PC droplets in PP/PC binary blend act presumably as voids and, hence, the melt elasticity decreases with increasing PC content. But at



(a)



(b)

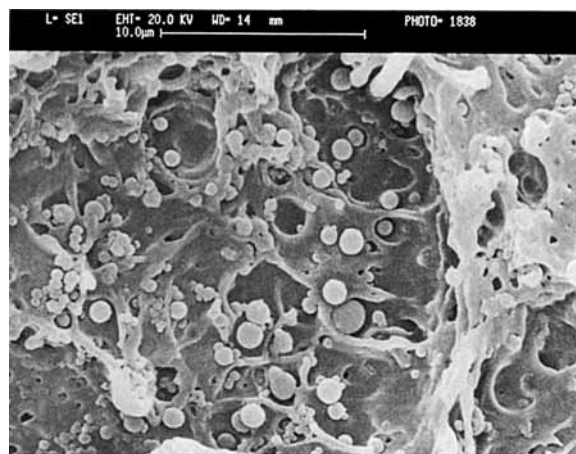
Figure 16 Scanning electron micrographs of extrudates of PP/SEBS/PC ternary blend (with only SEBS component etched out) at constant shear rate ($4 \times 10^3 \text{ s}^{-1}$) and at various PC contents (%): (a) 10; (b) 20.

10% PC content, the melt elasticity of the blend is higher than that for PP, probably due to the increased interfacial interaction because of the smaller size of the PC droplets. At high shear rates, melt elasticity will be due mainly to PP and, hence, it decreases with increasing shear rate.

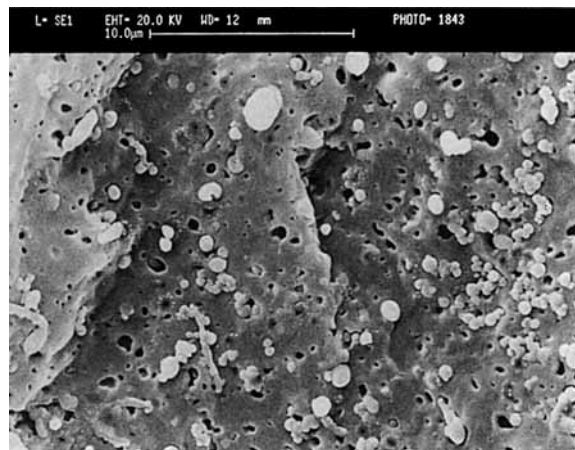
Thus, it can be concluded that the effect of droplet size is mutually opposite for SEBS and PC droplets: Bigger droplets of SEBS increase the melt elasticity of the PP/SEBS binary blend, whereas smaller droplets of PC increase the melt elasticity of PP/PC binary blend.

In the presence of PC, the increasing PP/SEBS blending ratio increases the number-density of

smaller SEBS droplets [of type (i) morphology]. This change in morphology increases the melt viscosity of the blend at low shear rates. At high shear rates, because of the high shearing forces, all these droplets deform and orient in the flow direction, thus decreasing the melt viscosity of the ternary blend. Furthermore, at high shear rates, plastic deformation of PP sets in, which decreases the melt elasticity. Thus, it can be concluded that the presence of a third phase (SEBS or PC) in the respective blends causes greater dissipation of shear forces and thus minimizes the effect of blend composition on the

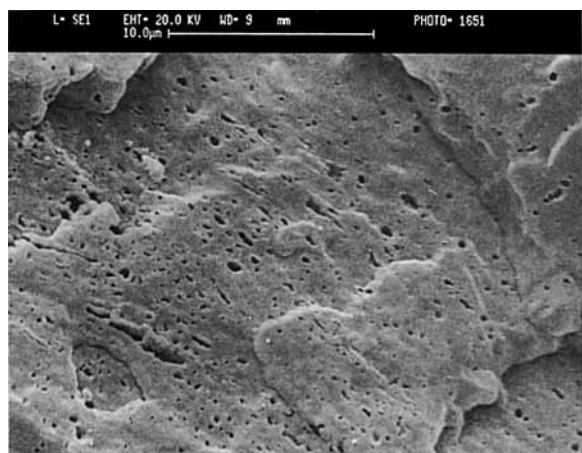


(a)

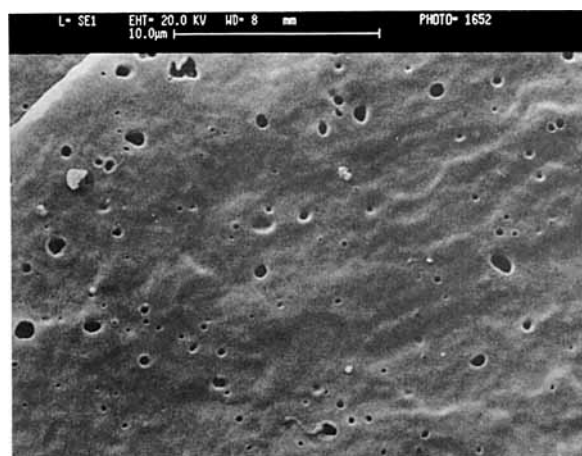


(b)

Figure 17 Scanning electron micrographs of extrudates of PP/SEBS/PC ternary blend at 10% PC loading (with only SEBS etched out) at constant shear rate ($1.2 \times 10^2 \text{ s}^{-1}$) and at various SEBS contents (%): (a) 10; (b) 20.



(a)



(b)

Figure 18 Scanning electron micrographs of extrudates of PP/SEBS binary blend at constant SEBS content (5%) and at varying shear rate (s^{-1}): (a) 6.1×10^2 ; (b) 4×10^3 .

melt flow at high shear rates. In the presence of SEBS, an increase of PC content increases the number-density and size of PC droplets. Furthermore, with increasing PC content, SEBS tends to form a continuous phase. These effects increase the melt viscosity with increasing PC content. At low PC contents, SEBS forms separate droplets [type (i) morphology] that, along with the small PC droplets, increase the melt elasticity of the blend. But at higher PC contents, SEBS is located mostly in the boundary-phase layer with the bigger PC

droplets inside the boundary layer. Thus, the melt elasticity of the system decreases. At high shear rates, SEBS forms type (i) morphology with smaller droplets. Thus, with increasing shear rate, the contribution of SEBS towards the melt elasticity of the blend becomes insignificant and, hence, the melt elasticity of the blend decreases with increasing shear rate, as it is mainly due to PP only.

CONCLUSIONS

The present work shows that both SEBS and PC in their respective binary blends with PP form sufficiently spherical discrete droplets in the PP matrix by mixing in a single-screw extruder. The SEBS droplets are large at 5% SEBS content and decrease in size with increasing SEBS content, whereas the PC droplets increase in size with increasing PC content of the blend. In the ternary blend, SEBS forms two types of morphologies: (i) discrete droplets, and (ii) the boundary phase surrounding the PC droplets depending on the relative proportions of the two dispersed components. SEBS goes first in the boundary phase and the surplus forms the discrete droplets. The SEBS in the boundary phase reduces the tendency of droplet breakup, thus resulting in the large diameter of PC droplets. Thus, by altering the relative proportion of PC and SEBS and the shear rate, the morphology can be controlled.

Flow curves are quite linear for all the compositions of these blends, showing some regularity in the composition dependence of pseudoplasticity of



Figure 19 Scanning electron micrographs of extrudates of PP/SEBS/PC ternary blend at a fixed composition 90/10/10 and shear rate (s^{-1}): 2×10^3 .

the melt, which, in general, increases on addition of SEBS and decreases on addition of PC.

In PP/SEBS binary blend, droplet size is the key factor controlling the melt viscosity, whereas in PP/PC binary blend, not only the size but also the number-density of the droplets influence the melt viscosity. The significantly larger contribution of SEBS towards melt elasticity compared to that of PC in their respective binary blends is attributed to the greater deformability and interfacial interaction of SEBS with PP than that of PC with PP. Furthermore, it is found that, in their respective binary blends, bigger SEBS droplets increase the melt elasticity, whereas bigger PC droplets decrease the melt elasticity.

In the case of ternary blends, increasing the SEBS content at constant PC content increases the number-density of smaller SEBS droplets, thereby increasing both the melt viscosity and melt elasticity. But increasing the PC content at constant SEBS content increases the number-density as well as the size of the PC droplets. This change in morphology increases the melt viscosity but decreases the melt elasticity.

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