Mechanical Properties and Morphology of PP/SEBS/PC Blends

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SYNOPSIS

Rubber toughening of thermoplastic polymers always decreases the tensile and flexural properties. In this article, an attempt is made to improve the tensile and flexural properties of a rubber-toughened polymer system viz., polypropylene (PP)/styrene-ethylene-butylene-styrene tri-block copolymer (SEBS) binary blend by blending a rigid polymer viz., polycarbonate (PC) with this binary system. The PP/SEBS blend with a blending ratio fixed at three levels, namely 95/5, 90/10, and 80/20, was melt mixed with 0–30 wt % PC to generate the various blend compositions studied. This choice of compositions enabled us to show how the mechanical properties varied as a function of (1) PP/SEBS ratio at a constant PC content and (2) PC content at a constant PP/SEBS ratio of the blend. Data on the corresponding binary blends, namely PP/SEBS and PP/PC, are also presented and discussed as reference systems. The data are discussed in detail for the effect of each component of the blend. As regards the morphology, some distinct changes were seen in the middle of composition ranges of the additives, i.e., around 10 to 20% PC level, and 95/5 and 90/10 PP/SEBS ratios. Variation of mechanical properties in the respective composition ranges are found consistent with the variations of blend morphology. Hence, a correlation of morphology and the properties is discussed. Furthermore, the results suggest stronger interfacial interaction between SEBS and PP than that between PC and PP. Scanning electron microscopic studies of appropriately etched impact fractured samples reveal the existence of composite droplets of SEBS and PC embedded in PP matrix, with SEBS forming the outer envelope around PC.

INTRODUCTION

Polypropylene (PP) is a commodity plastic and is one of the largest consumed polyolefins in the plastic industry. The main disadvantage of PP is its low impact strength, particularly at low temperatures. Blending a polymer with rubber has always been one of the useful methods to improve the impact strength of the polymer.[1] Our earlier studies have shown that the impact strength of PP is improved satisfactorily by blending PP with styrene-ethylene-butylene-styrene copolymer (SEBS).[2] But this method has a disadvantage; namely, deterioration of tensile properties of PP.

Improving the tensile properties of rubber-toughened PP has been the subject of research for many years. Incorporation of a rigid filler is one of the practical solutions suggested by many authors.[3–5] Calcium carbonate,[6] talc,[3,4,7] and glass fiber (GF)[5,8] are some of the fillers used by various authors for this purpose. Even though the addition of calcium carbonate or talc is cheaper, dispersing these fillers uniformly in PP matrix in the presence of an elastomer is difficult. Furthermore, the resulting final morphology is unpredictable. Hence, tailoring such a composite to get a desired combination of properties is not always easy, due to the strong dependence of final properties on the morphology of the composite. So, the addition of a suitable third polymer may be a better way of improving the tensile properties to get a ternary blend with good combination of properties.

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Improvement in tensile properties of PP by blending it with polycarbonate (PC) is already known.[9,10] Thus, in this work, PC is blended with the blend of PP and SEBS to improve the stiffness and strength of PP/SEBS blend.

In this article, tensile and flexural properties of PP/SEBS/PC ternary blend are studied as a function of: (a) PC content at constant PP/SEBS blending ratio and (b) PP/SEBS blending ratio at constant PC content of the blend. Data collected for binary PP/PC and PP/SEBS blends are also presented to serve as reference systems for the role of individual component of the blends.

EXPERIMENTAL

Materials

PP used in this work was Koylene M 0030 (MFI 10) of Indian Petrochemicals Corporation Ltd. SEBS (Kraton-G-1652) was a product of Shell Development Company and was a triblock copolymer with its middle block being hydrogenated polybutadiene and two side blocks of polystyrene. Approximate weight average molecular weight of SEBS used was 60×10^3 and the (E/B) ratio of this copolymer was 0.52. Polycarbonate used in this work was an injection molding grade polymer from Baeyer with MFI 3.2.

Sample Preparation

PP/SEBS, PP/PC, and PP/SEBS/PC blends were prepared by melt mixing the appropriate quantities of all the respective individual components in one step using a single screw extruder (Windsor SX-30) at a screw speed of 20 rpm with a temperature of 200–230°C of various zones. For the case of PP/SEBS/PC ternary blends, the PP/SEBS ratio was fixed at three levels, viz., 95/5, 90/10, and 80/20, and the PC content in each case was varied from 0–30 wt %.

Test specimens for tensile and flexural tests were prepared by injection molding on Injection Moulding Machine Windsor SP-1 with a temperature range of 210–240°C. Dumbbell-shaped specimens conforming to ASTM-D-638 were used for tensile, and rectangular bar shapes conforming to ASTM-D-790-81 were used for flexural tests.

Measurements

Tensile measurements were made on dumbbell-shaped specimens with thickness of 3 mm and a width of 12 mm at the center, using an Instron Universal Tester (model 1121) at a strain rate of 2 cm/min and an initial gauge length of 6 cm. Flexural tests were carried out on the same machine using a three-point bending method with center loading on a simply supported beam. The distance between the spans was 7 cm and the strain rate used was 2 cm/min.

More than five samples were tested for each composition, and average values are reported. The deviation was less than 5% in all cases.

Scanning electron micrographs of impact fractured surfaces were recorded on Stereoscan S4-10, of Cambridge Scientific Instruments Ltd. For the case of PP/SEBS binary blend and PP/SEBS/PC ternary blend, as the SEBS phase was not distinguishable from the matrix, it was selectively etched out by cyclohexane. Thus, the holes visible in the scanning electron micrographs of these blends are the sites where the SEBS phase was present. The average size of the dispersed phase droplet (d) was determined by measuring the diameter of around 200 droplets and calculating the number average diameter.

RESULTS AND DISCUSSIONS

The stress–strain curves for PP/SEBS and PP/PC binary and PP/SEBS/PC ternary blends are shown in Figure 1. The effect of SEBS is such that, both in the absence and presence of PC, with increasing SEBS content the yield peak broadens while the yield stress decreases and the breaking strain increases. Whereas the effect of PC is such that, both in the absence and presence of SEBS, with increasing PC content, the modulus increases, the yield peak narrows down (or disappears), and the breaking strain reduces. Thus, the addition of SEBS to PP has an opposite effect as compared to addition of PC to PP, and it is likely that by adjusting the proportion of SEBS and PC to be added to PP, a desirable combination of tensile properties might be achieved. This will be examined in detail below for the respective binary and ternary blends.

PP/SEBS Binary Blend

Values of the various tensile and flexural properties at varying SEBS content for the PP/SEBS binary blend are given in Table I. Tensile modulus remains constant from 0 to 5% SEBS content, followed by a sharp decrease at 10% SEBS content and then shows no significant change in the composition

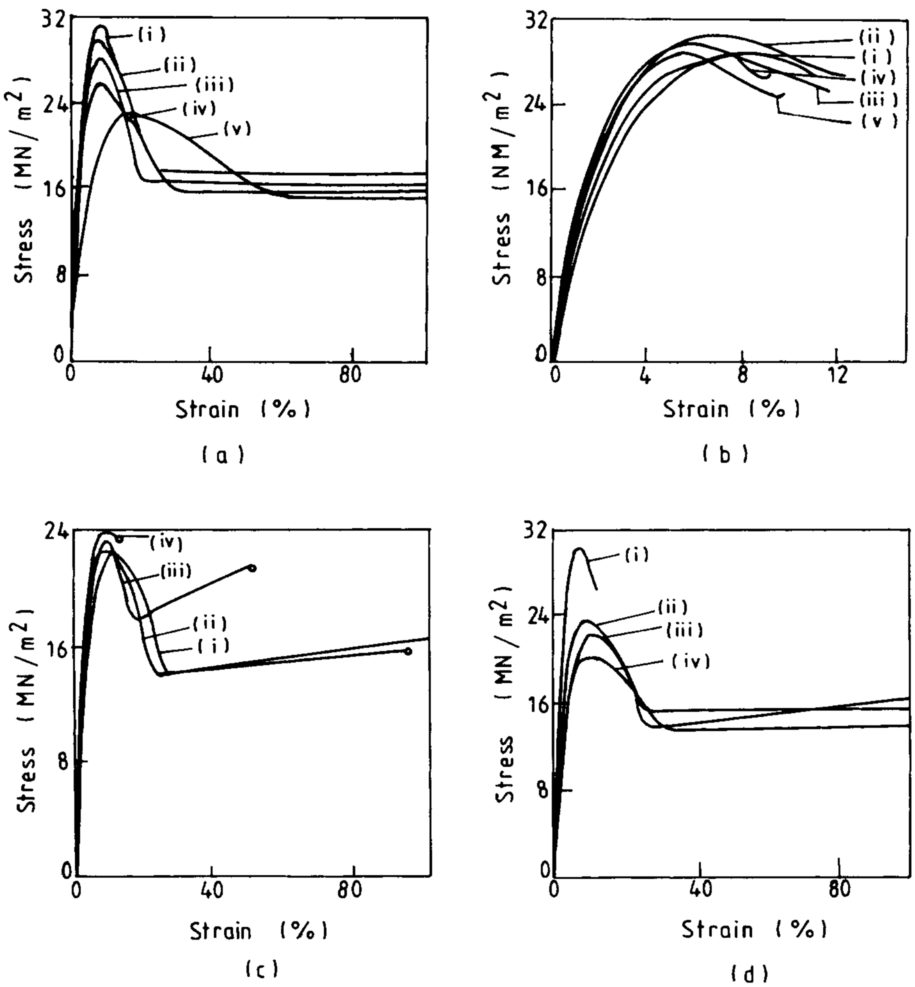


Figure 1 Tensile stress–strain curves for various binary and ternary blends studied. (a) PP/SEBS binary blends at varying SEBS contents (wt %): (i) 0; (ii) 5; (iii) 10; (iv) 15; and (v) 20. (b) PP/PC binary blends at varying PC contents (wt %): (i) 0; (ii) 5; (iii) 10; (iv) 20; and (v) 30. (c) PP/SEBS/PC blends at constant PP/SEBS ratio (90/10) and varying PC contents (wt %): (i) 0; (ii) 5; (iii) 10; and (iv) 20. (d) PP/SEBS/PC ternary blends at constant PC content (5 wt %) and varying PP/SEBS ratio: (i) 100/0; (ii) 95/5; (iii) 90/10; and (iv) 80/20.

range of 10 to 20% SEBS content. The yield stress changes insignificantly from 0 to 5% SEBS content, and decreases almost linearly in the range of 5 to 20% SEBS content. The yield strain and breaking strain seem to depend only on the total elastomer content, as these properties increase continuously with increasing SEBS content. Breaking stress decreases sharply on addition of 5% SEBS and thereafter remains almost constant up to 20% SEBS content. Flexural modulus and flexural strength of PP/SEBS binary blend decrease continuously with increasing SEBS content of the blend.

Thus, the addition of SEBS to PP improves the elongation/flexibility of the blend but decreases the stiffness and strength.

PP/PC Binary Blend

Various tensile and flexural properties of PP/PC binary blend at varying PC content are shown in Table II. Elastic modulus increases with increasing PC content up to 10%, followed by a decrease up to 30% PC content. Yield stress remains constant up to 20% PC content and then decreases at 30% PC content. Yield strain and breaking strain show a general decrease with increasing PC content of the blend.

Flexural modulus increases with increasing PC content. Flexural strength increases on addition of 5 wt % PC, followed by a linear decrease with increasing PC content. Thus, unlike the effect of

Table I Mechanical Properties of PP/SEBS Binary Blend

		Yield		Break			
Wt % Minor Component	Tensile Modulus	Stress (MN/m^2)	Strain (%)	Stress (MN/m^2)	Strain (%)	Flexural Modulus (MN/m^2)	Flexural Strength (MN/m^2)
0	884.60	28.81	7.73	26.61	11.20	997.06	45.22
5	879.85	28.21	7.78	16.22	154.55	874.62	40.27
10	742.69	25.89	7.88	14.84	250.61	847.48	36.57
15	737.83	23.86	8.12	14.85	389.39	786.99	36.06
20	746.51	21.29	8.41	14.26	620.76	728.71	33.51

SEBS, the addition of a small amount of PC to PP improves the strength and stiffness of the blend.

PP/SEBS/PC Ternary Blend

Variation of tensile properties of the PP/SEBS/PC ternary blends are presented in the following two ways: (1) as a function of PP/SEBS ratio at a constant PC content, and (2) as a function of PC content at a constant PP/SEBS ratio.

At Constant PC Content and Varying PP/SEBS Ratio

The role of SEBS in the properties of the PP/SEBS/PC ternary blend is represented by the variations of the properties as a function of PP/SEBS ratio at various constant PC levels in Figures 2–6 [part (a) of each figure]. With increasing SEBS level of the blend, tensile modulus, yield stress, and breaking stress decrease while yield strain and breaking strain increase. At the PP/SEBS ratio of 90/10, both modulus (Fig. 2a) and yield stress (Fig. 3a) show maxima at almost all PC contents. These maxima may be attributed to the possibility of stronger interfacial adhesion at the specified composition of the blend. Yield strain shows a maximum at a 95/5 PP/SEBS ratio, where both yield stress and modulus show minima (Fig. 4a).

Flexural modulus and flexural strength vary with SEBS content, as shown in Figures 7a and 8a, such that in the presence of PC, maxima in both the properties occur at a 95/5 PP/SEBS ratio. These maxima, incidentally, coincide with maxima in tensile yield strain. These results suggest a significant role of PC in the flexural properties of the ternary blend at a 95/5 PP/SEBS ratio. At higher SEBS contents, the flexural strength and modulus decrease with increasing SEBS content.

Thus, from the above results it may be stated that the recommendable composition of PP/SEBS/PC ternary blend could be a 95/5 or 90/10 PP/SEBS ratio, depending upon whether the end use requirement is flexural or tensile, respectively, or, any composition within this range for optimum tensile and flexural properties.

At Constant PP/SEBS Ratio and Varying PC Content

The role of PC in PP/SEBS/PC ternary blend is represented by the variation of tensile properties with PC content, at various fixed PP/SEBS ratios,

Table II Mechanical Properties of PP/PC Binary Blend

		Yield		Break			
Wt % Minor Component	Tensile Modulus (MN/m^2)	Stress (MN/m^2)	Strain (%)	Stress (MN/m^2)	Strain (%)	Flexural Modulus (MN/m^2)	Flexural Strength (MN/m^2)
0	884.60	28.81	7.73	26.61	11.20	997.06	45.22
5	1070.60	29.81	6.67	26.76	12.12	1033.05	46.24
10	1194.14	28.98	6.06	24.91	11.37	1050.00	45.60
20	1065.09	29.08	6.61	26.60	9.09	1060.37	44.44
30	1055.73	22.46	3.99	22.46	4.36	1199.99	39.27

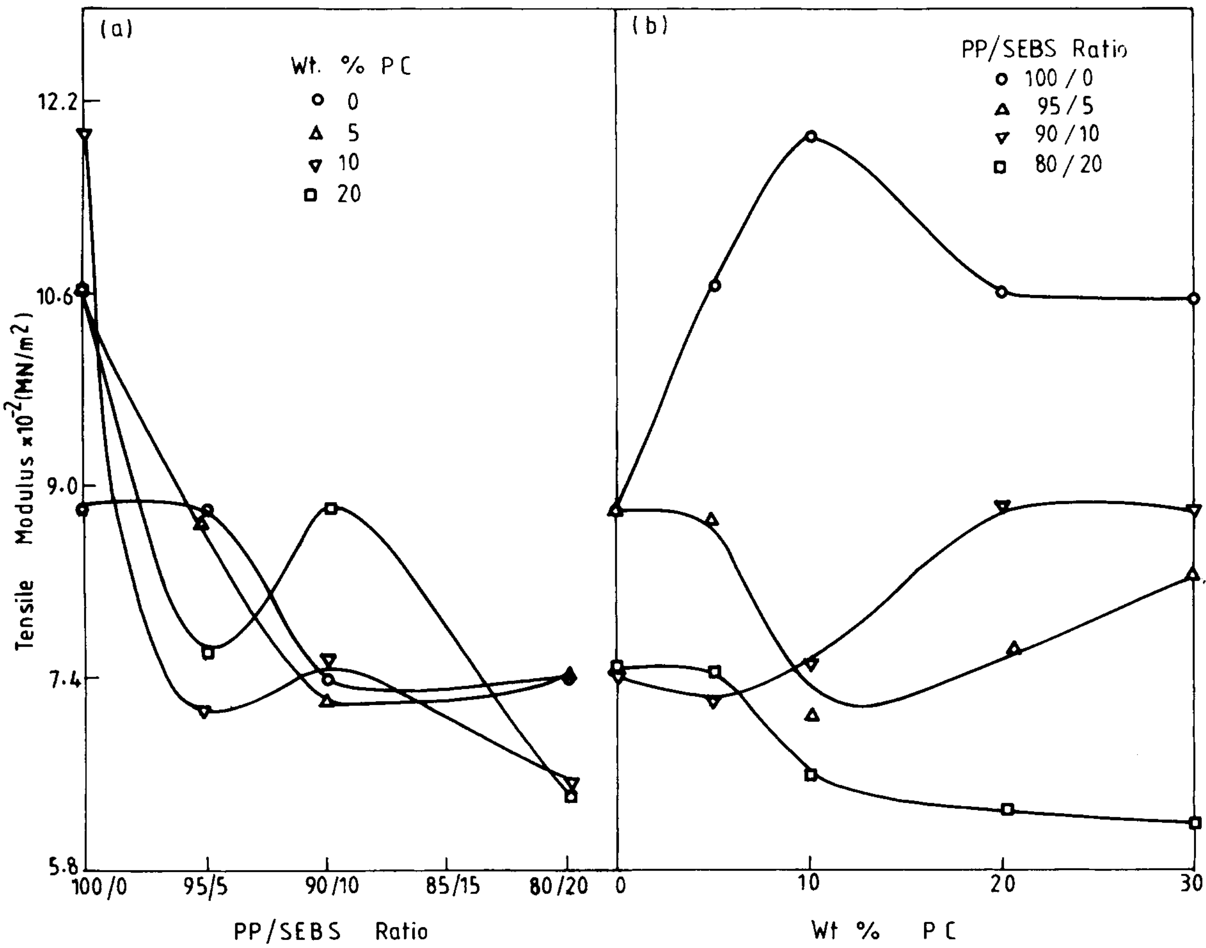


Figure 2 Variation of tensile modulus of various PP/SEBS/PC ternary blends studied. (a) as a function of PP/SEBS ratio at constant PC content: (○) 0; (△) 5; (▽) 10; and (□) 20. (b) as a function of PC content at constant PP/SEBS ratio: (○) 100/0; (△) 95/5; (▽) 90/10; and (□) 80/20.

as shown in Figures 2–6 (part b of each figure) as a function of PP/SEBS ratio.

The low deformation properties, viz., modulus (Fig. 2b) and yield stress (Fig. 3b) are quite sensitive to the SEBS level of the blend. On the other hand, it is seen that the effect of the SEBS level on the role of PC in this ternary blend is quite insignificant on the large deformation properties, viz., the breaking stress (Fig. 5b) and breaking strain (Fig. 6b). Addition of PC to the PP/SEBS blend produces a small deterioration of modulus and yield stress initially up to 10% PC content for most of the blends studied, and then the properties improve with increasing PC content, at all the SEBS levels studied. However, the effect of PC on yield strain depends on the SEBS level, also (Fig. 4b). At the PP/SEBS ratio 95/5, yield strain increases on addition of PC up to 10% PC content and then decreases, while at PP/SEBS ratios 90/10 and 80/20, it continuously increases with increasing PC content. The overall improvement of modulus and yield stress on addition of PC is smaller when the SEBS level of the blend is higher.

Variation of flexural properties with increasing PC content of the blend at fixed PP/SEBS ratios is given in Figures 7b and 8b. Both the properties vary similarly with increasing PC content of the blend. At the PP/SEBS ratio of 95/5, the properties show a maxima at 5% PC content. Furthermore, at this blending ratio, the values are higher than the corresponding PP/PC binary blends. At all other PP/SEBS ratios studied, the properties decrease up to 10% PC content and then increase up to 30% PC content.

Thus, the message to technologists from these results is that, in order to develop PP/SEBS/PC

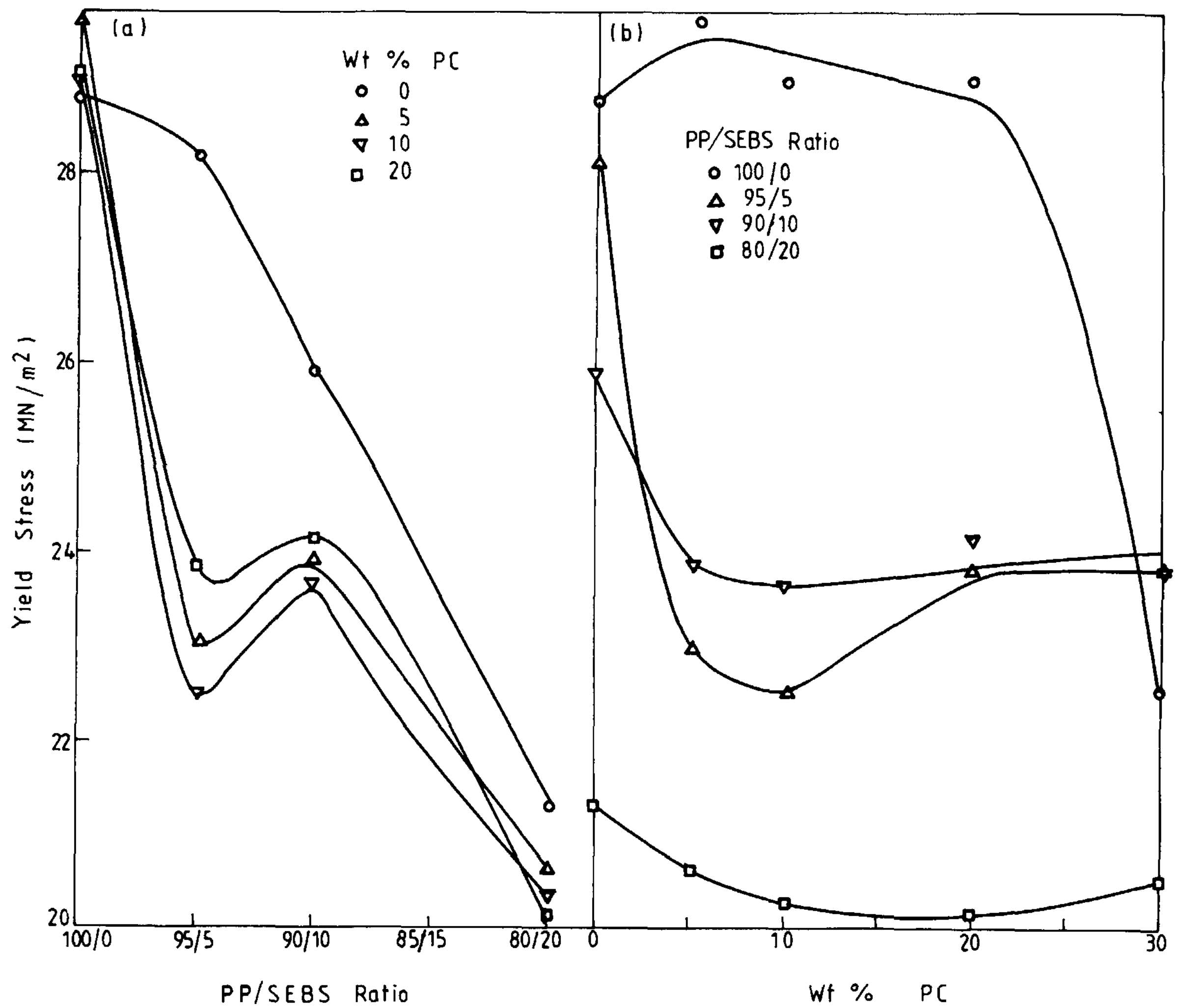


Figure 3 Variation of tensile yield stress of various PP/SEBS/PC ternary blends studied. (a) as a function of PP/SEBS ratio at constant PC content: (○) 0; (△) 5; (▽) 10; and (□) 20. (b) as a function of PC content at constant PP/SEBS ratio: (○) 100/0; (△) 95/5; (▽) 90/10; and (□) 80/20.

ternary blend for optimum tensile and flexural properties, one must keep in mind that PC content should be above a critical level and SEBS level should not be very high.

MORPHOLOGY

PP/SEBS and PP/PC Binary Blends

Both SEBS and PC form spherical droplets in PP matrix in their respective binary blend (Figs. 9 and 10). In the case of the PP/PC binary blend, with increasing PC content, both the average size [(*d*) of PC increases from 0.62 to 1.32 μm)] and the number density of droplets (defined as the number of droplets/unit area) increases. The presence of empty holes even in the unetched samples indicate poor interfacial interaction between PC and PP compared to that of SEBS and PP.

Increasing the SEBS content increases the number density of droplets but decreases the average size of droplets [(*d*) of SEBS decreases from 0.37 to 0.26 μm]. Unlike the perfectly spherical droplets of PC in the PP/PC binary blend, SEBS droplets in the PP/SEBS blend are only near spherical. The droplet size distribution is more uniform in the PP/PC blend.

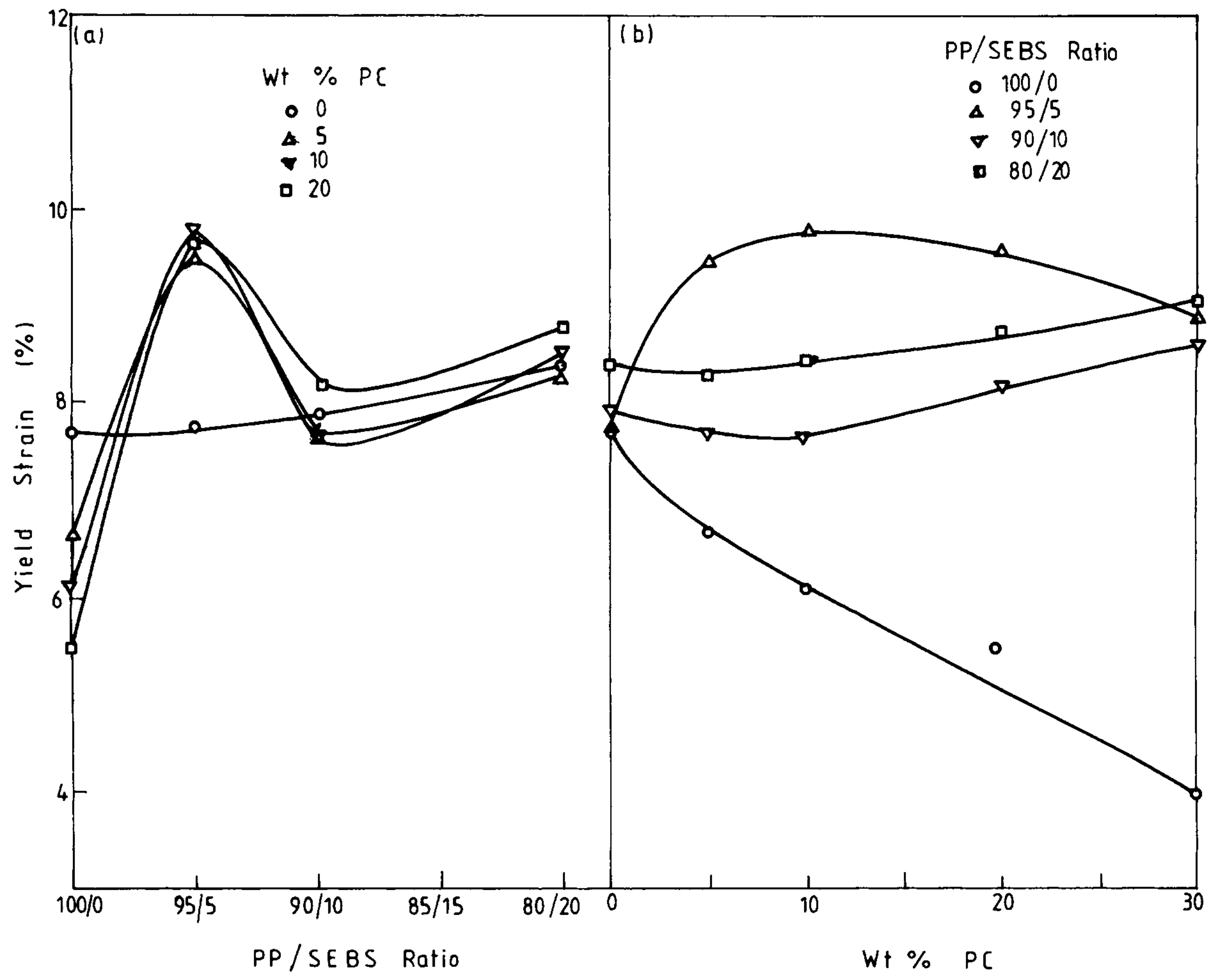


Figure 4 Variation of tensile yield strain of various PP/SEBS/PC ternary blends studied. (a) as a function of PP/SEBS ratio at constant PC content: (○) 0; (△) 5; (▽) 10; and (□) 20. (b) as a function of PC content at constant PP/SEBS ratio: (○) 100/0; (△) 95/5; (▽) 90/10; and (□) 80/20.

PP/SEBS/PC Ternary Blend

The etched out SEBS phase leaves two kinds of traces in the PP/SEBS/PC ternary blend, viz., (1) holes that may be due to pure SEBS phase or PC/SEBS composite droplets with fully developed SEBS layer, and (2) PC droplets surrounded by holes (note that the PC droplets are present as solid spheres) due to the SEBS phase forming a partially developed outer layer of PC/SEBS composite droplets. The effect of increasing PC content at a constant PP/SEBS ratio can be seen from Figure 11. It is already shown that SEBS has more interfacial interaction with PP than that of PC with PP. Thus, PC droplets in PP/SEBS/PC ternary blend stick to PP matrix more firmly than those in the PP/PC binary blend because of the SEBS layer surrounding PC droplets. A comparison of SEM photographs of the PP/PC binary blend and PP/SEBS/PC ternary blend samples with constant (i.e., 10 wt %) PC content show this effect. Increasing the amount of PC increases the average PC droplet size. These bigger droplets of PC may or may not be entirely covered by an SEBS envelope, depending upon the ratio of amount of SEBS to PC present in the blend. Hence, it is the ratio of SEBS to PC that governs the morphology of the PP/SEBS/PC ternary blend.

The effect of increasing PP/SEBS ratio at constant PC content can be seen by comparing Figures 12a, 11b, and 12b. Average PC droplet size decreases on increasing the SEBS level of the blend. This can be seen by comparing SEMs of samples with con-

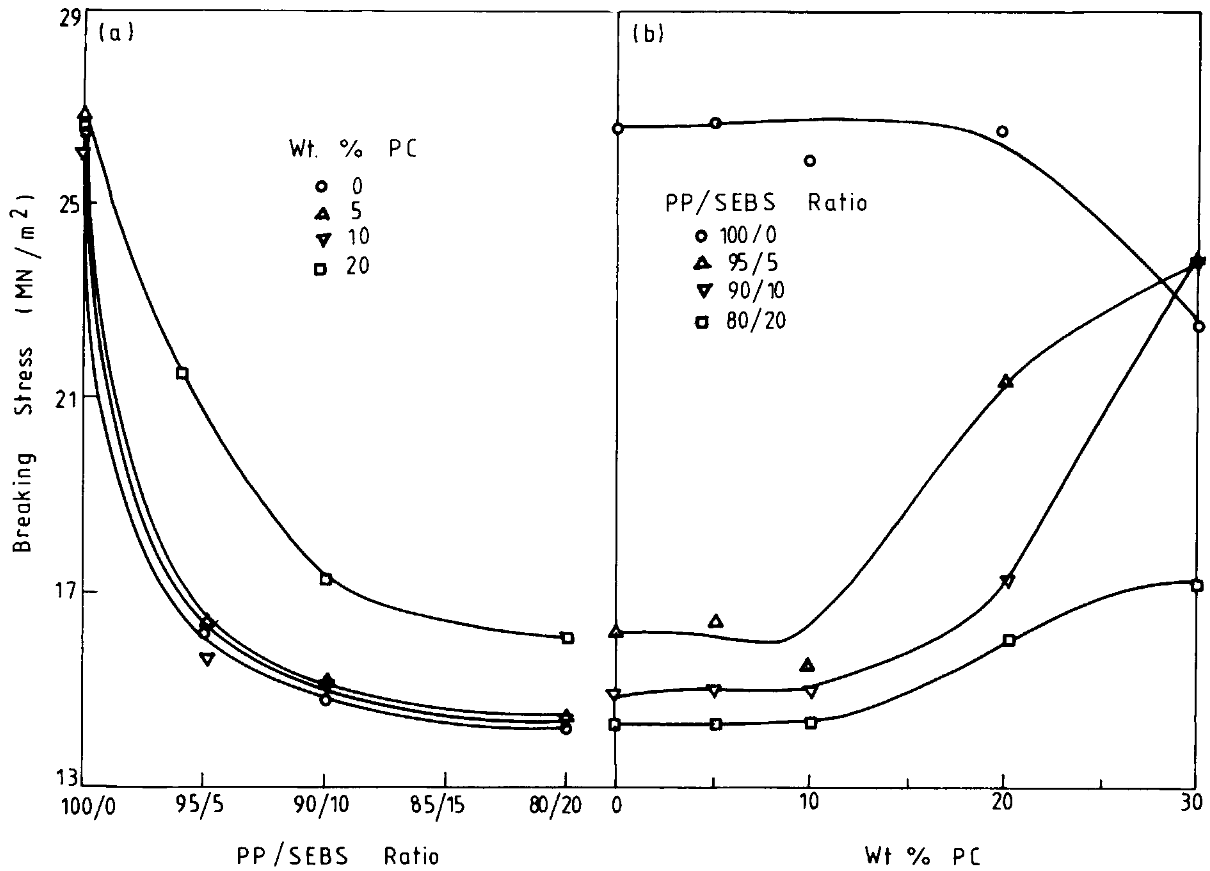


Figure 5 Variation of tensile breaking stress of various PP/SEBS/PC ternary blends studied. (a) as a function of PP/SEBS ratio at constant PC content: (○) 0; (△) 5; (▽) 10; and (□) 20. (b) as a function of PC content at constant PP/SEBS ratio: (○) 100/0; (△) 95/5; (▽) 90/10; and (□) 80/20.

stant (5 wt %) PC content and different PP/SEBS ratios (90/10 and 80/20). Thus, the effect of the SEBS content, at a constant PC content of the ternary blend, is apparent in compatibilizing PC with PP.

EFFECT OF MORPHOLOGY ON YIELD STRESS AND MODULUS

PP/SEBS and PP/PC Binary Blends

In the case of the PP/SEBS binary blend, modulus and yield stress depend more upon the morphology than does any other tensile property. The number of SEBS droplets increase with increasing SEBS content. Each droplet is a stress concentration site. Thus, the number of stress concentration sites and the load transferred to the SEBS phase increase with increasing SEBS content. This leads to a decrease in yield stress and modulus of the blend.

For the case of the PP/PC binary blend, Fisa et al.[9] have attributed the increase of modulus to the differential thermal contraction of PP and PC. PP contracts more compared to PC when cooled from the melt. Hence, the system behaves as if there is interfacial adhesion (physical bonding) between PP and PC. This explains the observed variation of modulus and yield stress at low PC contents. But the large deformation property, namely breaking stress, decreases in the composition range of 0–10% PC content. This is because, under large deformations, the physical bonding becomes poor; hence, the stress transfer becomes less effective. When PC droplet size exceeds a particular value, this mechanism might become ineffective because when the matrix tries to envelope a bigger size droplet, minor

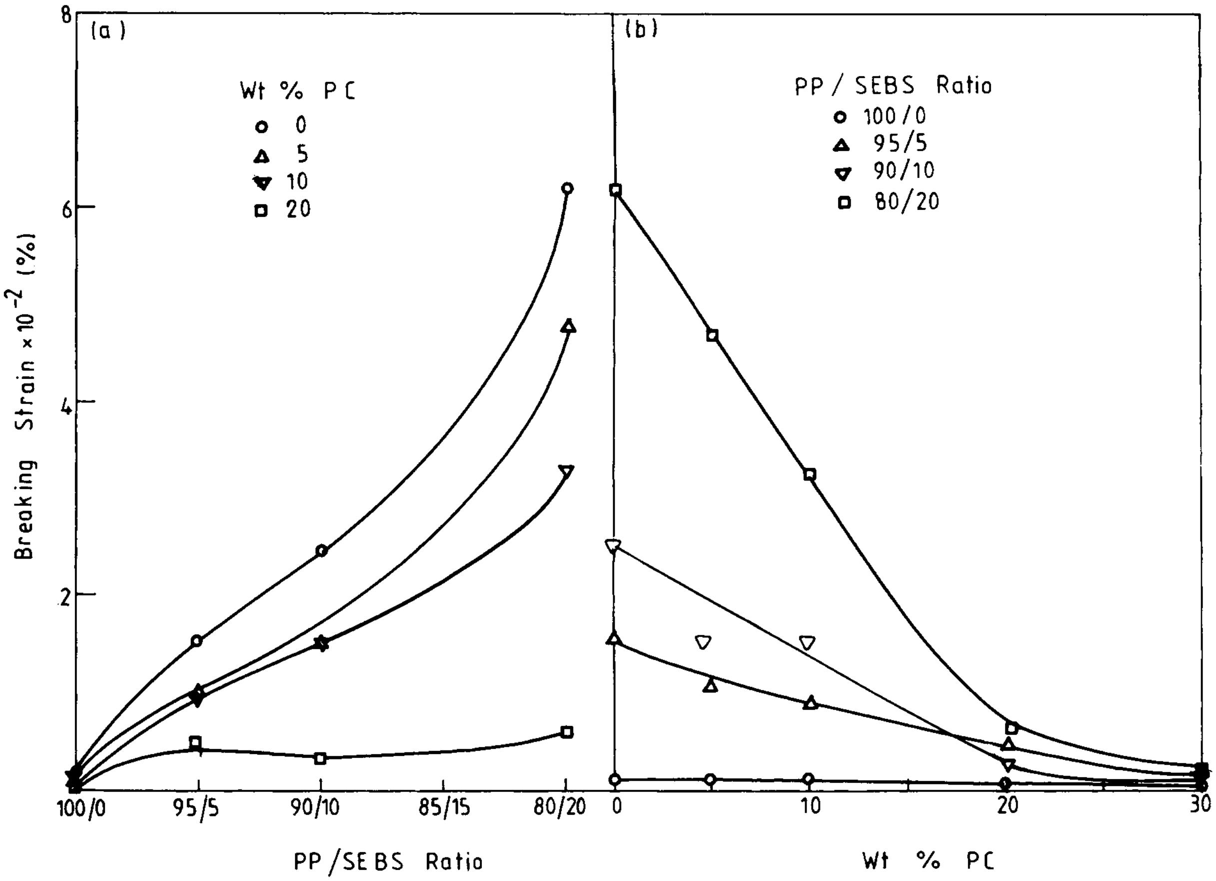


Figure 6 Variation of tensile breaking strain of various PP/SEBS/PC ternary blends studied. (a) as a function of PP/SEBS ratio at constant PC content: (○) 0; (△) 5; (▽) 10; and (□) 20. (b) as a function of PC content at constant PP/SEBS ratio: (○) 100/0; (△) 95/5; (▽) 90/10; and (□) 80/20.

cracks might develop at the interface. This may be the reason for the observed decrease of modulus at higher PC contents.

PP/SEBS/PC Ternary Blend

At Constant PC Content and Varying PP/SEBS Ratio

With an increasing SEBS level of the blend at any constant PC content, PC droplet size decreases. At the 95/5 PP/SEBS ratio, the amount of SEBS is not enough to form a fully developed SEBS envelope around all the PC droplets. This might lead to nonuniform stress concentration around the PC droplets, leading to a decrease in yield stress and modulus with increasing PC content. But the occurrence of maxima in yield stress and modulus at a 90/10 PP/SEBS ratio for all PC contents of the blend, suggest that at this PP/SEBS blending ratio, PC is compatibilized well with PP, and PC droplets attain an optimum size required for reinforcement. Further increase in SEBS level reduces the modulus and yield stress values due to the following reasons: (a) PC droplets become too small to produce reinforcement and (b) there occurs a greater abundance of pure SEBS droplets or PC/SEBS composite droplets.

At Constant PP/SEBS Ratio and Varying PC Content

At the PP/SEBS ratio of 95/5, yield stress and modulus decrease up to 10 wt % PC. This is due to the stress concentration resulting from the partially developed SEBS envelope of the PC/SEBS composite droplets. At high PC contents, the effect of PC compensates that of SEBS, leading to improve-

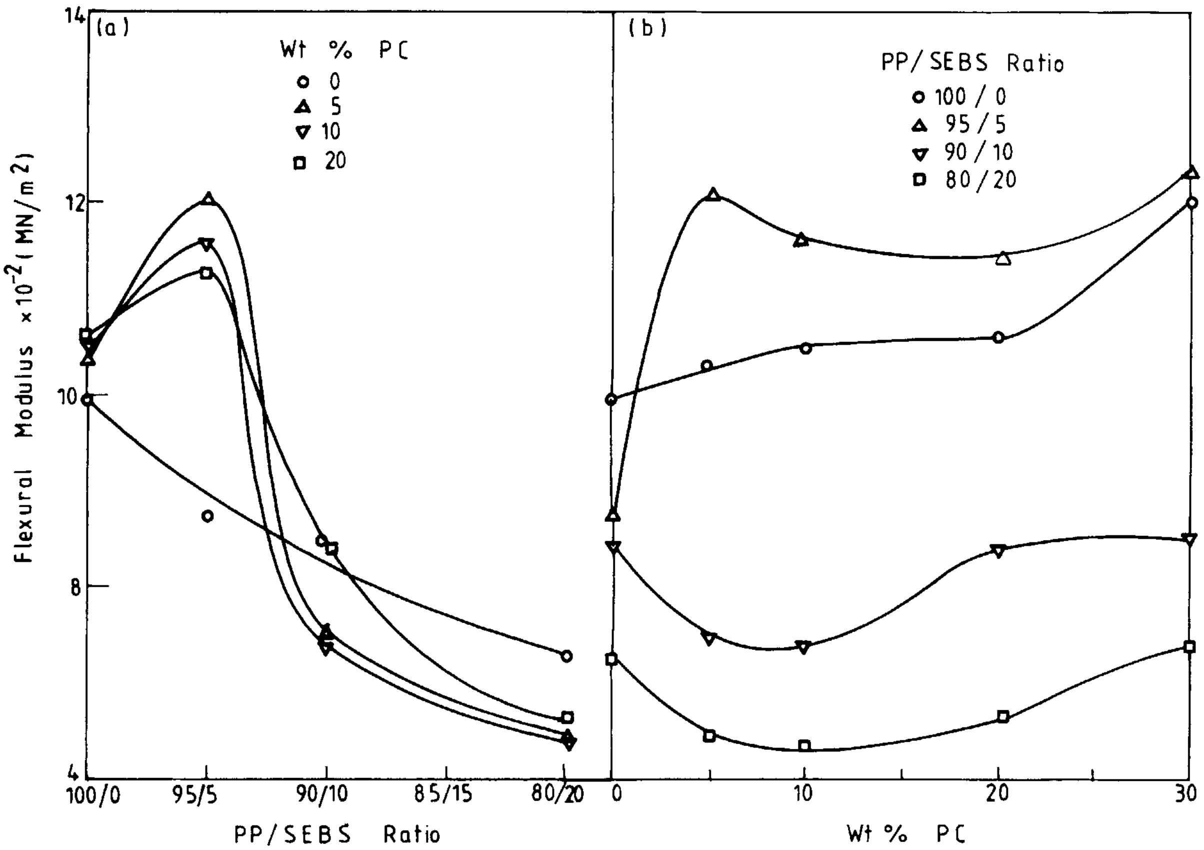


Figure 7 Variation of flexural modulus of various PP/SEBS/PC ternary blends studied. (a) as a function of PP/SEBS ratio at constant PC content: (○) 0; (△) 5; (▽) 10; and (□) 20. (b) as a function of PC content at constant PP/SEBS ratio: (○) 100/0; (△) 95/5; (▽) 90/10; and (□) 80/20.

ment in properties. At the PP/SEBS ratio of 90/10, the better compatibilization of PC leads to high values of yield stress and modulus. But at high SEBS contents, viz., PP/SEBS ratio 80/20, the role of SEBS dominates.

Thus, it can be stated that the ternary blends containing a 90/10 PP/SEBS ratio and PC contents in the range of 10–30% show improvement of yield stress and modulus due to compatibilization of PC with PP.

ANALYSIS OF YIELD STRESS DATA

Analysis of tensile properties as a function of the blending ratio leads to an estimation of discontinuities in stress transfer at the interface of the dispersed phase and the matrix. The higher the stress concentration, the smaller will be the stress transfer across the interface. Thus, the interfacial characteristics play an important role in tensile properties of multiphase blends. When there is perfect adhesion between the phases, the stress transfer across the interface is continuous and, in the absence of any adhesion, the blend will behave as if the matrix is embedded with holes, causing complete discontinuity in stress transfer or stress concentration at the interface. In practice, most of the blend systems were seen to behave in between these two limits. The shape of the dispersed phase domains alter the stress concentration pattern such that the smoother the surface of the dispersed phase domains, the lesser will be the stress concentration.

Many theories have been put forward for the variation of tensile properties with blend composition, some of which are summarized below, with yield stress as the tensile property. One of the earlier theories is Leidner's "first power law"[11] given as

$$\mathrm{RYS} = 1 - V \qquad (1)$$

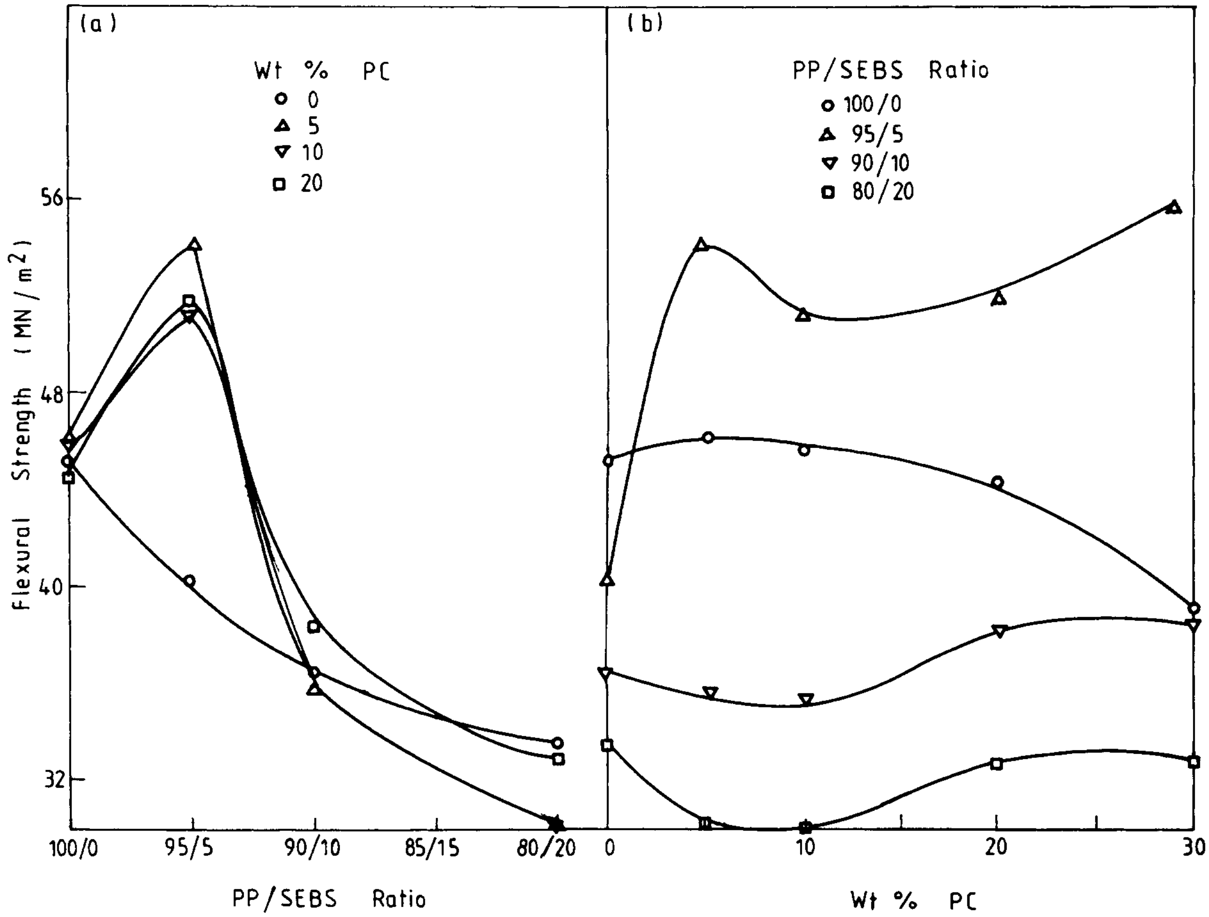


Figure 8 Variation of flexural strength of various PP/SEBS/PC ternary blends studied. (a) as a function of PP/SEBS ratio at constant PC content: (○) 0; (△) 5; (▽) 10; and (□) 20. (b) as a function of PC content at constant PP/SEBS ratio: (○) 100/0; (△) 95/5; (▽) 90/10; and (□) 80/20.

where V is the volume fraction of the minor component and RYS is the "relative yield stress," defined as the ratio of yield stress of the blend to that of the matrix.

Nielsen,[12] on the other hand, suggested the "two-thirds power law" given as

$$RYS = 1 - V^{2/3} \quad (2)$$

This law assumed spherical inclusions embedded in the matrix.

Nicolais and Narkis[13] equation (Eq. 3) is a slight modification of Nielsen's equation such that the $V^{2/3}$ term is further accentuated by a factor greater than unity, i.e., 1.21. Or, in other words, this model assumes poorer adhesion between the phases.

$$RYS = 1 - 1.21\,V^{2/3} \quad (3)$$

PP/PC Binary Blend

The variation of RYS with a volume fraction of PC (V_{PC}) in the PP/PC binary blend is shown in Figure 13(i) along with the theoretical variations, according to the equations described above. All these three equations predict lower values of RYS than the observed values for PP/PC blend in the whole composition range studied, and the difference between experimental and theoretically predicted values increases with increasing PC content. Hence, it may be stated that the above three equations are not adequate to represent the behavior of the PP/PC blend. PC has a reinforcing effect, which is apparently not incorporated in the above three equations.

Thus, the three equations discussed above may be applicable to reinforcing blends after appropriate modification. It is clear that the two power laws (Eqs. 1 and 2) underestimate the contribution of

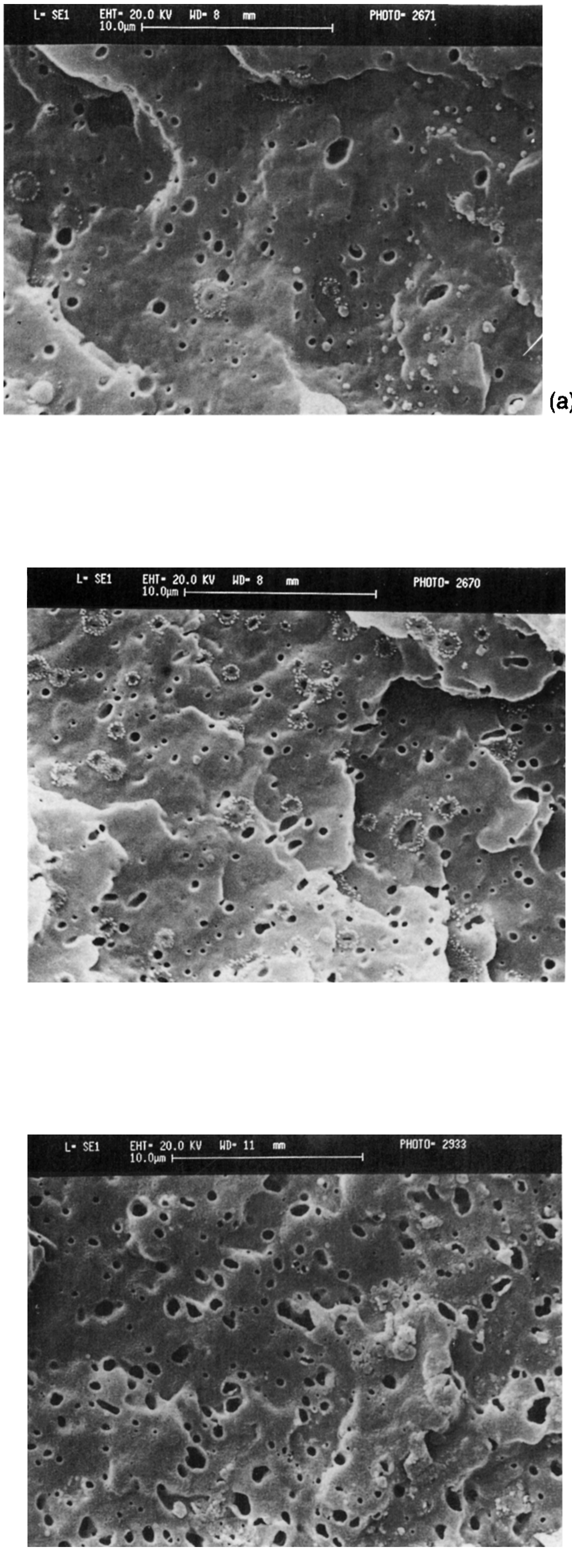


Figure 9 Scanning electron micrographs of binary PP/SEBS binary blend with varying PP/SEBS ratio: (a) 95/5; (b) 90/10; (c) 80/20.

the minor component PC in the yield stress of the PP/PC blend. It is the second term of these equations that takes care of the effect of minor component. Thus, the introduction of a new parameter as a multiplicative factor in the second term may improve the applicability of the equations. The modified equations for the "first" and "two-thirds" power laws can be given as,

$$\text{RYS} = 1 - a_1 V \tag{4}$$

$$\text{RYS} = 1 - a_2 V^{2/3} \tag{5}$$

The values of a_1, a_2 fitting the experimental data on the PP/PC blend are shown in Table III. These values are very much less than unity, thus reducing the negative contribution of the second term to RYS of the blend.

Very low positive values for a_1 and a_2 show that the inclusion of PC in the PP matrix has very little effect on the yield stress of the blend, and the effect increases more slowly with increasing PC content.

The modified "two-thirds power law" can also be visualized as a modified form of Nicolais and Narkis equation, with a_2 replacing 1.21. The reduction of this value from 1.21 to 0.04 implies insignificant stress concentration effect in the PP/PC blend.

The single parameter modification of the power laws discussed above assumes that the yield stress of the matrix in the blend is the same as that in its bulk state. This need not be true because, depending upon the nature of the minor component and the interfacial characteristics, the stress concentration effects can strengthen or weaken the matrix.

Thus, two parameter modification of these power laws were carried out as follows.

$$\text{RYS} = b_1 - a_3 V \tag{6}$$

$$\text{RYS} = b_2 - a_4 V^{2/3} \tag{7}$$

where b_1 and b_2 are the parameters used with the first terms and a_3 and a_4 are the multiplying factors used in the second terms of the "first" and "two-thirds" power laws, respectively.

Values of a_3 and a_4 for the PP/PC binary blend, as shown in Table III, are higher than those of the corresponding parameters a_1 and a_2 of Eqs. 4 and 5, and the values of b_1 and b_2 are higher than unity. Thus, these models suggest that even though there is a negative contribution of PC towards the yield stress of the blend, the inclusion of PC in the PP matrix slightly increases the overall yield stress of

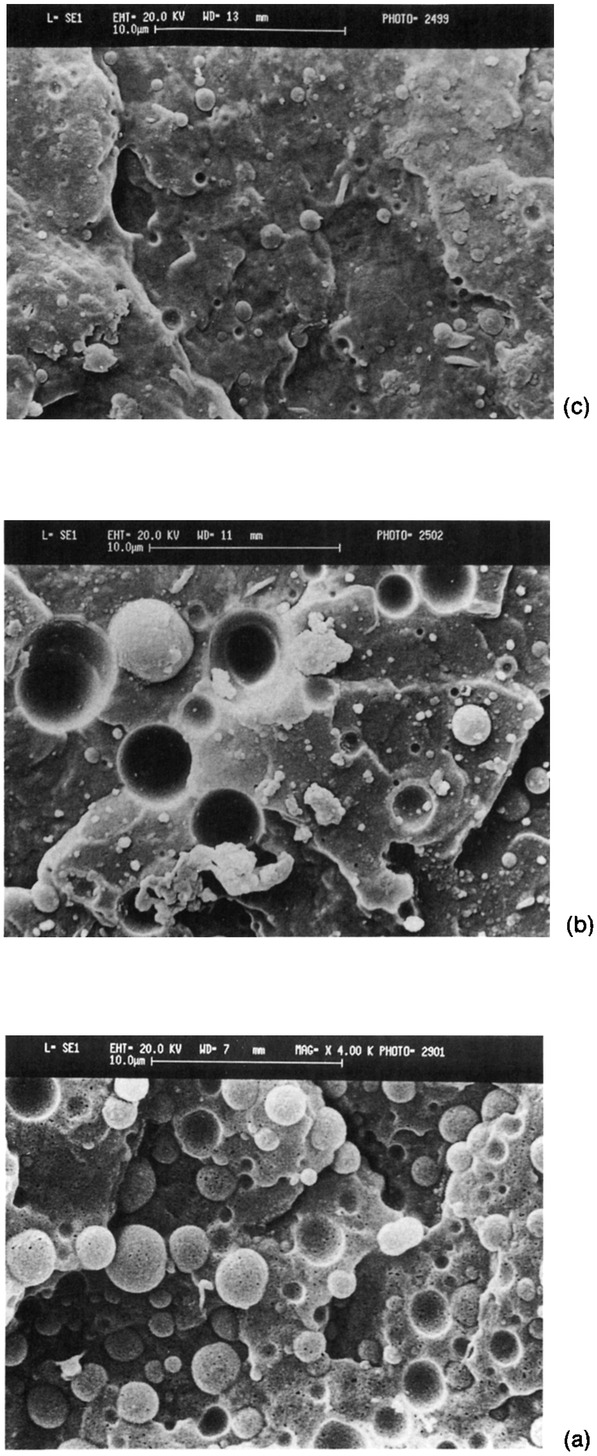


Figure 10 Scanning electron micrographs of binary PP/PC binary blend with varying PC content (wt %): (a) 5; (b) 10; (c) 30.

the matrix. Hence, at low PC contents there is a chance of improvement of yield stress of the blend. But at higher PC contents, the role of the second term in Eqs. (6) and (7) dominates, thereby decreasing the yield stress of the blend.

After proper modification, both "first" and "two-thirds" power laws fit the experimental data on the PP/PC blend equally well.

PP/SEBS Binary Blend

Variation of RYS for the PP/SEBS binary blend with SEBS content is shown in Figure 13(i) along with the theoretical variations corresponding to Eqs. 1 to 7. The first power law fits the experimental data well at low SEBS contents, i.e., for volume fraction of SEBS, $V_s < 0.08$. The two-thirds power law and the Nicolais and Narkis equation predictions differ considerably from the experimental data. Modified first power law equation (Eq. 4) with $a_1 = 1.225$ fit the data more closely compared to modified two-thirds power law (Eq. 5) with its best fitting value of $a_2 = 0.645$. A higher positive value of a_1 indicates the detrimental effect of SEBS. A value of a_1 for the PP/SEBS blend is 10 times greater than that for PP/PC blend, implying considerable difference in the effects of PC and SEBS on the tensile properties of the PP matrix. Thus, the parameter a_1 can be used for comparing the efficiency of the minor component in improving or decreasing the yield stress of the matrix.

The variation of RYS is almost linear with SEBS content for the PP/SEBS blend. A modified first power law (Eq. 4) predicts RYS values reasonably close to the observed values. This suggests proportional contribution from both PP and SEBS to yield stress of the blend, which may imply the presence of some interfacial interaction, presumably between the ethylene-butylene block of SEBS with the PP matrix.

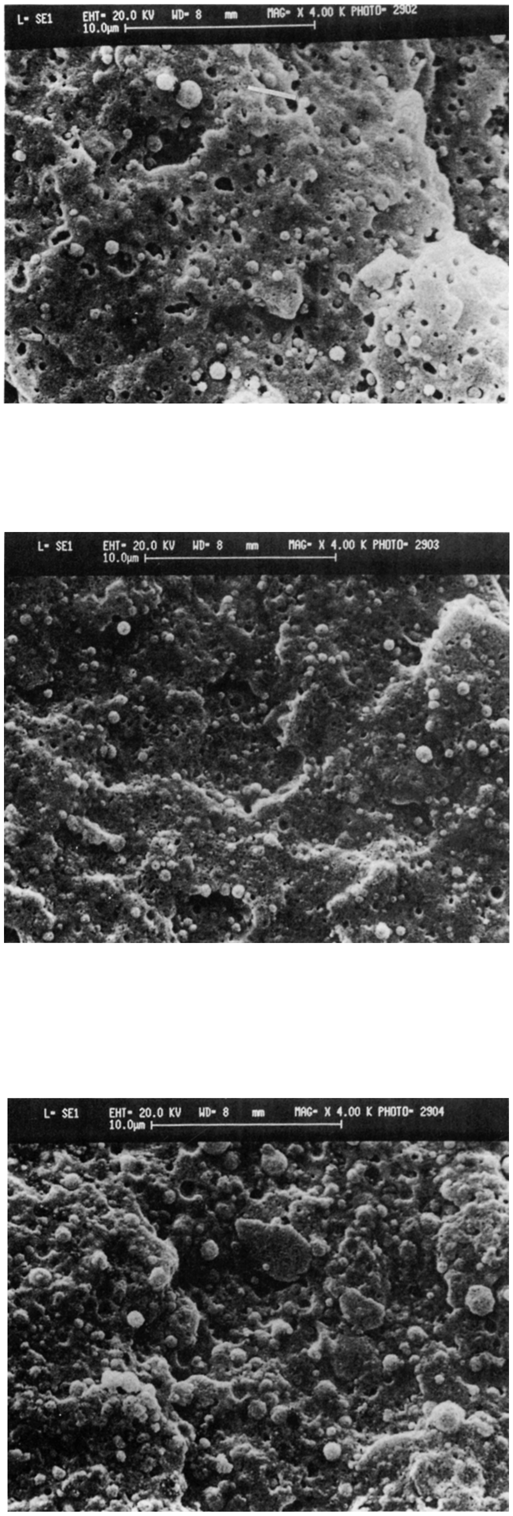
Fitted values of various parameters for the two-parameter modified power laws (Eqs. 6 and 7) corresponding to the PP/SEBS blend are given in Table III. The values of a_1, a_2, a_3, and a_4 for the PP/SEBS blend is higher than the corresponding values for the PP/PC blend, suggesting greater discontinuity in stress transfer due to the incorporation of SEBS than that of PC, in the PP matrix. The values of b_1 and b_2 for both PP/SEBS and PP/PC blends are nearly equal, indicating that the effect of both SEBS and PC on the PP matrix is almost equal.

As for the case of the PP/PC binary blend, the a_3 and a_4 values are greater than those of a_1 and a_2, respectively and b_1 and b_2 are greater than unity. Hence, it can be seen that higher levels of SEBS is detrimental to the tensile strength of the blend. The value of b_1 indicates a slight improvement in the overall yielding of the matrix, which may be due to the interfacial adhesion of PP with SEBS.

PP/SEBS/PC Ternary Blends

In the case of ternary blends, PP/SEBS is considered as the matrix and PC is treated as the inclusion, to enable their analysis in terms of the above equations for the binary systems.

Variation of RYS vs. volume fraction of PC (V_{PC}) for the ternary blend, with 95/5 PP/SEBS as the matrix, is shown in Figure 13(ii). The experimental

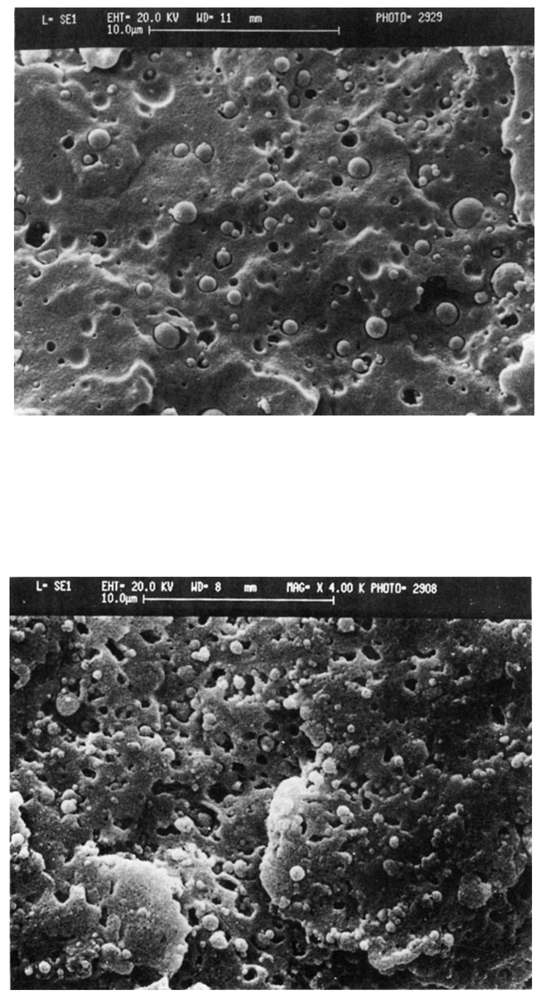


(a)

(b)

(c)

Figure 11 Scanning electron micrographs of ternary PP/SEBS/PC blends with varying PC content and at constant PP/SEBS ratio (90/10): (a) 5; (b) 10; (c) 20.



(a)

(b)

Figure 12 Scanning electron micrographs of ternary PP/SEBS/PC blends with varying PP/SEBS ratio and at constant PC content (10 wt %): (a) 95/5; and (b) 80/20.

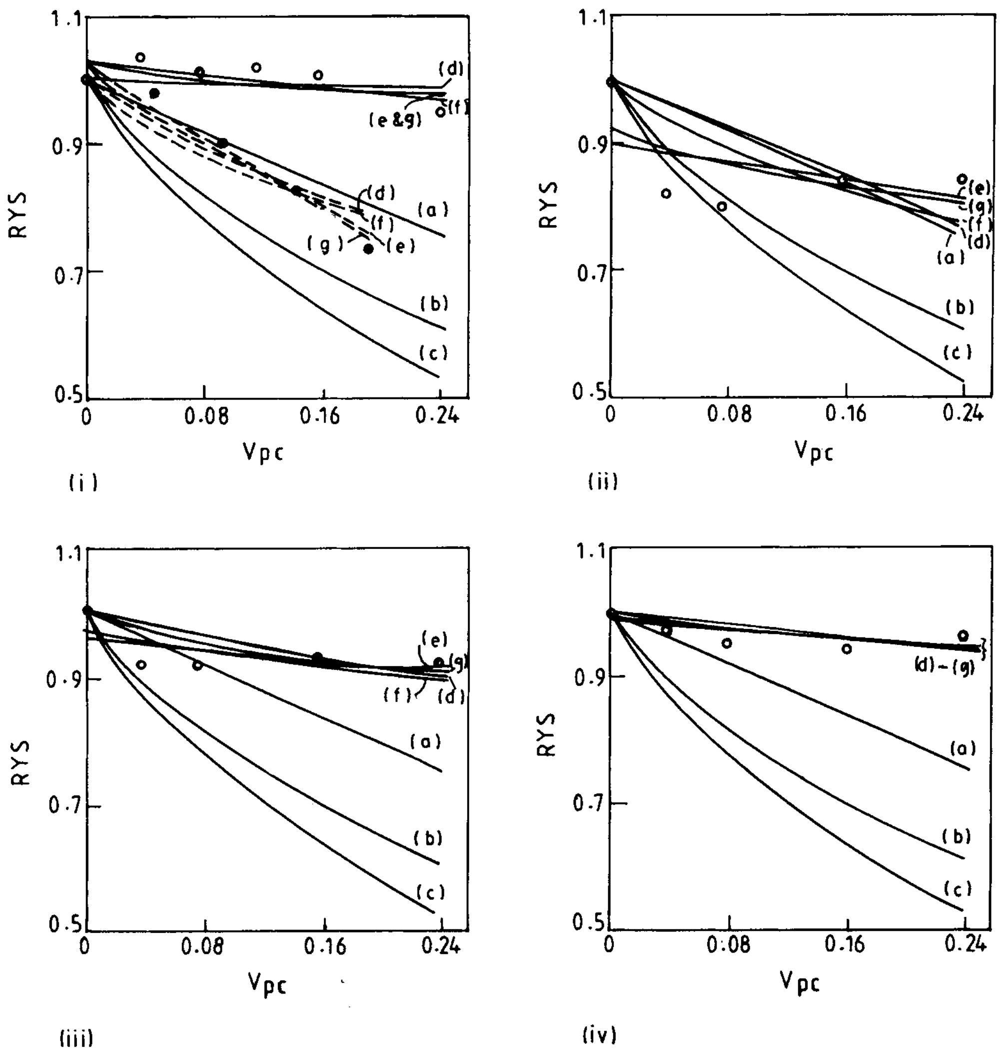


Figure 13 Variation of experimental tensile yield stress and the theoretical predictions based on equations (a) Eq. 1, (b) Eq. 2, (c) Eq. 3, (d) Eq. 4, (e) Eq. 5, (f) Eq. 6, and (g) Eq. 7: (i) (●) PP/SEBS binary blends at varying SEBS contents. (○) PP/PC binary blends at varying PC contents. (ii) (○) PP/SEBS/PC ternary blends at constant PP/SEBS ratio (95/5) and varying PC contents. (iii) (○) PP/SEBS/PC ternary blends at constant PP/SEBS ratio (90/10) and varying PC contents. (iv) (○) PP/SEBS/PC ternary blends at constant PP/SEBS ratio (80/20) and varying PC contents.

data in the region $V_{PC} = 0$ to 0.08 suddenly decreases to a very low value compared to the PP/PC binary blend. The linear first power law, which gave better fit compared to "two-thirds power law" for the PP/SEBS and PP/PC binary blends, shows a poor fit for this case of the ternary blend in the V_{PC} range 0 to 0.08. Equations 2 and 3 show a better fit with the experimental data compared to the first power law equation (Eq. 1) in this range of PC content. This suggests high stress concentration at low PC contents, which was discussed in an earlier section. Furthermore, the Nicolais and Narkis model (Eq. 3) fits the experimental data better than the Nielsen's model (Eq. 2), suggesting greater stress concentration in this ternary blend due to PC inclusion.

Two parameter modifications of both power laws (Eqs. 6 and 7) show a distinct difference in the behavior of the ternary blend as compared to the binary blends. The values of b_1 and b_2 decrease from unity in case of all the ternary blends studied (see data

Table III Evaluated Parameters of Various Models

S. No.	Matrix	Inclusion	a_1	a_2	a_3	a_4	b_1	b_2
1.	PP	SEBS	1.23	0.65	1.41	0.71	1.02	1.02
2.	PP	PC	0.09	0.04	0.27	0.15	1.03	1.03
3.	PP/SEBS 95/5	PC	0.93	0.58	0.34	0.30	0.90	0.92
4.	PP/SEBS 90/10	PC	0.44	0.27	0.92	0.16	0.96	0.97
5.	PP/SEBS 80/20	PC	0.25	0.15	0.13	0.10	0.98	0.99

in Table III), unlike the case for both the binary blends, where these values are greater than unity. This indicates the decrease in yield stress of the matrix (PP/SEBS) on addition of PC.

Variation of RYS for ternary blends with a PP/SEBS ratio of 90/10 [Fig. 13(iii)] show that neither of the first three equations (Eqs. 1, 2, and 3) fit the experimental data in the whole range. When $V_{PC} = 0$ to 0.08, the experimental data lie in between the lines corresponding to the first power law equation and two-thirds power law equation, suggesting a modification in the exponent of the volume fraction term. The experimental data fall above the curve corresponding to the Nicolais and Narkis equation in this range, whereas the data in this range of PC contents for the ternary blend with 95/5 PP/SEBS ratio fit the Nicolais and Narkis equation. This indicates that the stress concentration of the system in this range is low.

Single parameter modification of the "first power law" and "two-thirds power law" (Eqs. 4 and 5) fit the data when $V_{PC} > 0.08$. The values of a_1 and a_2 are lower than that for blends with a 95/5 PP/SEBS matrix. This shows the improvement in the efficiency of PC in maintaining the yield stress of the blend at high PC contents compared to the previous set of blends. This improvement may be a result of the compatibilization of PC with PP by the addition of SEBS, leading to smaller PC droplets. The two-parameter modification seems to explain the variation of RYS better than all the other equations discussed. The values of a_3 and b_1 are higher than that for blends with a 95/5 PP/SEBS ratio, indicating that the improvement in yield stress of these blends are mainly due to the facilitated overall yielding of the matrix, which is possible only when the interfacial interaction in this blend is better than that in the previous set of blends. The better interfacial interaction is due to the fully formed SEBS layer over the PC droplets and the reduction in PC droplet size.

The trend regarding the b value is the same for the two-parameter modification of the two-thirds power law also. But a_4 value is lower than that for the previous set of blends, suggesting less stress concentration due to PC. Thus, a modified two-thirds power law explains the variation of yield stress better than the other equations.

Variation of RYS for ternary blend with a PP/SEBS ratio of 80/20 is given in Figure 13(iv). In the range $V_{PC} = 0$ to 0.08, the line corresponding to "first power" law falls closer to the experimental data while the "two-thirds" power law and the Nicolais and Narkis equation curves predict lower values of yield stress.

A careful look at the Figure 13 shows that the experimental data in this region of PC content lie: (a) in between the Nicolais and Narkis and two-thirds power law curves for blends with a 95/5 PP/SEBS ratio, (b) in between the two-thirds power law and first power law for blends with a 90/10 PP/SEBS ratio, and (c) above the first power law line for blends with a 80/20 PP/SEBS ratio.

This shows that the stress concentration effect due to the inclusion of PC decreases with increasing SEBS content of the matrix. At high PC contents, the role of PC dominates and, hence, there is not much change in the displacement of experimental data with respect to the theoretical predictions.

Single-parameter modification gives smaller a_1 and a_2 values than those for the previous sets of ternary blends, indicating lesser stress concentration. The two-parameter modification indicates that with increasing SEBS content of the matrix, the stress concentration due to PC decreases and the overall yielding of the matrix increases.

CONCLUSIONS

Both SEBS and PC form spherical droplets in their respective binary blends with PP, with the number density and size of dispersed droplets depending upon the blending ratio. In the case of the PP/SEBS binary blend, a peculiar observation is that with increasing SEBS content, the size of SEBS droplets decreases and the number of droplets/unit area of fracture surface increases. The droplets are more spherical at 5% SEBS than at higher SEBS content of the blend. In the case of the PP/PC blend, a specific feature of the blend morphology was poorer interfacial adhesion than that in the PP/SEBS blend.

Addition of SEBS to PP improves the large deformation properties, e.g., breaking stress, but decreases the small deformation properties, e.g., yield stress and modulus. On the other hand, addition of PC to PP improves only modulus and yield stress among the tensile properties and that, too, only up to 10 to 20 wt % PC content, and produces a small change or slight decrease of flexural properties.

When SEBS is added to PP in the presence of PC, it has a tendency to go in to the interface between PP and PC and form an envelope around the PC droplets. Depending upon the ratio of SEBS to PC present in the blend, this envelope is fully formed or partially formed. A partially formed envelope leads to stress concentrations.

The results show that the PP/SEBS/PC ternary blends containing not too low PC contents (PC content greater than 5%) and not too high SEBS contents (a PP/SEBS ratio of 95/5 or 90/10) have the most appropriate combination of properties. The recommendable composition of a PP/SEBS/PC ternary blend is that with a 95/5 or 90/10 PP/SEBS ratio and PC content about 10 wt %, for applications demanding a good combination of flexural and tensile properties. The amount of PC to be added depends upon the PP/SEBS ratio of the blend.

Analysis of the yield stress data shows that the addition of SEBS to the PP/PC blend decreases the stress concentration effect and increases the overall yielding of the matrix. Variation of yield stress of the blend could be represented by various modified forms of the power law expressions, differing at low and high PC contents.

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