

Toughening of Polypropylene with Styrene/Ethylene-Butylene/Styrene Tri-Block Copolymer: Effects of Mixing Condition and Elastomer Content

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ABSTRACT: The effect of processing conditions and elastomer content on the toughening of Polypropylene (PP) by melt blending with styrene/ethylene-butylene/styrene tri-block copolymer (SEBS) in a twin-screw extruder has been investigated. The parameters analyzed were: temperature profile, screw speed, and feed rate of the blend components. Their effect was evaluated through the mechanical properties (tensile strength and Izod impact resistance at room temperature) as well as the morphology of the dispersed phase by means of scanning electron microscopy (SEM). The results showed that the impact resistance increases with increasing rotor speed and feed rate and decreases when the temperature profile is increased. The parameter with the greatest effect on the mechanical properties was the variation in rotor speed. Despite the fact that impact resistance as high as 25 times that of neat PP has been achieved with blends containing 20 wt % SEBS, no significant modification in phase morphology has been observed. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 2185–2193, 2001

Key words: polypropylene; SEBS; toughening; processing; blends

INTRODUCTION

Polypropylene (PP) is a semicrystalline polymer with very interesting mechanical and thermal properties. For application as an engineering plastic, however, its toughness and, in particular, its notched toughness, is not sufficient for many applications. Its low impact resistance at subambient temperatures may also impair its performance. As with several polymers, the notched impact toughness of the PP matrix can be considerably improved by the presence of a dispersed rubber phase. Rubber-modified polypropylene can be obtained in a reactor process or by blending

with elastomeric materials.¹ In this way “super ductile” materials are obtained.

The deformation and impact behavior of polypropylene–rubber blends has been studied extensively.^{2–6,8–19} Extensive research has been published on blends of polypropylene with ethylene–propylene rubber (PP/EPR), polypropylene with ethylene–propylene–diene monomer (PP/EPDM),^{2–6,10,12} and polypropylene with styrene/ethylene–butylene/styrene tri-block copolymers (PP/SEBS).^{13–19} Ethylene–propylene copolymers are commonly employed as impact modifiers for polypropylene and the morphology of the polypropylene matrix is affected by the dispersed rubber phase.³ The notched fracture behavior of rubber-toughened polypropylene depends on test conditions such as temperature and test speed.^{3,4} With increasing temperature and decreasing test speed⁴ the fracture type changes from brittle to ductile.

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The fracture behavior of rubber-toughened polypropylene also depends strongly on the blend morphology: size, shape, and distribution of the components, and rubber content.⁵⁻⁷ As most polymers are immiscible, blending usually leads to heterogeneous morphologies. The type and dimensions of the morphology will determine the properties of the blend. The type of morphology, which is formed during processing, depends on the nature of the polymers (interfacial tension, viscosity, and viscosity ratio), their volume fractions, and the processing conditions.^{7,8} At low test speed, the brittle-ductile temperature decreases slightly with increasing particle size, whereas at high test speed (impact conditions) the brittle-ductile temperature increases strongly with increasing particle size.⁵

In rubber-toughened polypropylene, the effect of the particle size on the toughening process has been studied under impact conditions. According to Jang et al.,^{9,10} smaller particles are more effective in this respect than larger particles. The authors reported that under impact conditions particles with size below 0.5 μm will favor yielding in the matrix, while particles with size above 0.5 μm will favor formation of crazes in the matrix. Thus, the effect of the particle size of polypropylene seems to depend on the dominant deformation mechanism. If crazing is the mechanism, then the impact strength increases with increasing particle size. If shear banding is the dominant mechanism, then the impact strength decreases with increasing particle size. Van der Wal et al.⁶ studied the deformation mechanism of rubber-toughened polypropylene for various test conditions and blend morphologies, and no evidence of crazing was found in their blends, either for large particle sizes ($\geq 0.5 \mu\text{m}$), or at low temperatures (about -50°C).

The effect of particle size and the effect of rubber concentration for the notched Izod data of PA-EPDM blends have been combined to a single parameter, the interparticle distance.¹¹ It is more advantageous to have a large amount of small particles rather than a small amount of large particles.

A method of altering the particle size is to vary the molecular weight of the rubber. Some studies have demonstrated that the effect of the molecular weight of the rubber phase on the impact strength of polypropylene rubber blends is very small.¹² Another method is to change the processing conditions. During blend processing the final size and shape of the dispersed phase are deter-

mined by several factors. When blending is performed in an extruder, for example, the processing parameters that may affect blend morphology include temperature profile, screw design and speed, as well as feed rate of the blend components. These are important in generating appropriate morphologies for enhanced mechanical properties.

Styrene/ethylene-butylene/styrene tri-block copolymers are frequently used as compatibilizers in fragile polymers.¹³⁻²³ Many previous investigations have shown that the impact resistance of PP is satisfactorily increased in blends with SEBS, and that the yield modulus and stress decrease with increasing SEBS content.¹³⁻¹⁶ In PP/Nylon blends a combination of SEBS and SEBS-*g*-MA through reactive extrusion resulted in a decrease in particle size and improvement in impact resistance.²⁰⁻²³ Investigations of several properties of PP/SEBS blends have shown many advantages in employing SEBS to toughen polypropylene,¹³⁻¹⁷ arousing much interest in exploring the behavior of this blend. As is discussed in the literature,¹³⁻¹⁹ more insight is required into the morphological behavior of PP/SEBS blends; therefore, it is of great interest to study the relationship between the processing conditions, mechanical properties and morphology of these blends.

The scope of this work was to investigate the effect of processing conditions: temperature profile (T), screw speed (rpm), and feed rate of the blend components (Q) on a PP/SEBS blend system in a corotating twin-screw extruder.

EXPERIMENTAL

Materials

The polypropylene homopolymer used in this work was Prolen KM 6100, in pellets, supplied by Polibrasil S.A.

As an elastomer was used a styrene/ethylene-butylene/styrene block copolymer (SEBS)—Kraton G 1652, in flakes, supplied by Shell Chemical.

Characteristic properties of the PP and SEBS used in this study are listed in Table I.

Blend Preparation

A Werner & Pfleiderer ZSK-30 intermeshing corotating twin-screw extruder was used (screw diameter $D = 30 \text{ mm}$; length-to-diameter ratio $L/D = 35$) to prepare the blends. As the SEBS was in

Table I Characteristic Properties of the PP and SEBS Used in This Study

Materials	Trade Name	Supplied	MFI	M_n	M_w	Other Characteristics
Polypropylene	Prolen KM 6100	Polibrasil	3.5 dg/min ^a	—	—	$T_m = 165^\circ\text{C}$
SEBS	Kraton G 1652	Shell	—	50,000	52,000	Styrene/EB \approx 29/71 wt %

^a ASTM 1238 @ 2160 g and 230°C.

the form of flakes, separate feeding was used for each material. The elastomer contents used were 10, 15, and 20 wt %. The materials and the blends were dried at 80°C at least 4 h in a vacuum oven prior to compounding.

Processing Conditions

Two temperature profiles were used: T1 (190, 200, 210, 210, 210, 200°C) from the feed zone to the die and T2 (200, 230, 240, 240, 240, 230°C). For comparison sake, profile T1 was used based on previous works^{13,14} and profile T2 with higher temperatures, because PP degrades easily. The screw speeds were 100 and 250 rpm and the feed rates 5 and 10 kg/h. For the sake of comparison the neat PP was submitted to the same processing conditions as the blends.

Morphological and Mechanical Characterization

The effect of the processing parameters was evaluated through the mechanical properties (yield

stress, strain at break, elasticity modulus, and impact resistance) and morphology.

Specimens for impact resistance and tensile tests were prepared by injection moulding (Arburg Allrounder 270 V). The temperature range for injection molding was 190–215°C, and the temperature of the mold 50°C. Prior to molding the pelletized resins were dried at 80°C for 4 h.

Tensile tests were performed in an Instron tensile machine with dumbbell-shaped specimens according to ASTM-D 638 at a stretching speed of 50 mm/min. At least five specimens were tested for each blend.

The Izod impact resistance tests were performed according to ASTM D256 in notched samples at room temperature. Ten specimens were tested for each blend.

Prior to the mechanical tests all samples were kept at room temperature for at least 48 h.

The blend morphology was characterized by means of a scanning electron microscope (SEM). Notched specimens equal to those used in the

Table II Izod Impact Strength of the PP/SEBS Blend at Varying SEBS Content and Processing Conditions

Composition % wt SEBS	Izod Impact Strength (J/m)			
	Temperature Profile (T1)			
	Condition 1	Condition 2	Condition 3	Condition 4
10	42 ± 2	43 ± 2	47 ± 4	45 ± 6
15	112 ± 5	121 ± 11	128 ± 11	125 ± 9
20	407 ± 10	517 ± 14	561 ± 13	489 ± 11
Composition % wt SEBS	Temperature Profile (T2)			
	Condition 5	Condition 6	Condition 7	Condition 8
	10	45 ± 3	47 ± 8	46 ± 5
15	104 ± 5	103 ± 7	105 ± 5	101 ± 5
20	406 ± 11	504 ± 14	525 ± 11	481 ± 11

Condition 1: T1, 100 rpm, 5 Kg/h; Condition 2: T1, 250 rpm, 5 Kg/h; Condition 3: T1, 250 rpm, 10 Kg/h; Condition 4: T1, 100 rpm, 10 Kg/h; Condition 5: T2, 100 rpm, 5 Kg/h; Condition 6: T2, 250 rpm, 5 Kg/h; Condition 7: T2, 250 rpm, 10 Kg/h; Condition 8: T2, 100 rpm, 10 Kg/h.

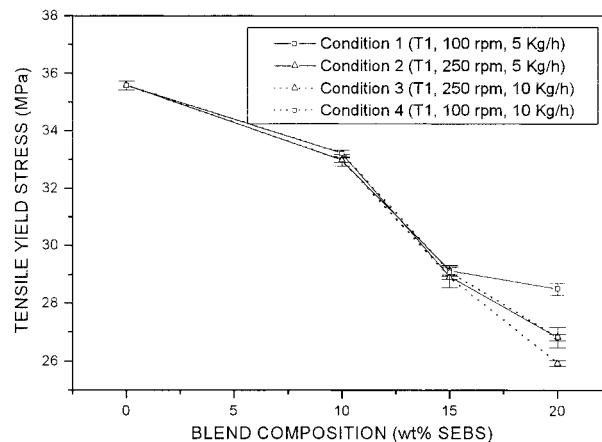
impact resistance tests were kept in liquid nitrogen for 30 min and then cryogenically fractured. The elastomeric particles (SEBS phase) were selectively extracted from the blends by xylene at room temperature for 30 min. All samples were washed in an ultrasonic bath and sputter coated with gold in a Balzers-SCD 050 Sputter Coater. SEM examination was performed with a Leica/Cambridge S440 microscope. A Leica Quantimet image analyzer was used for analyzing the micrographs.

RESULTS AND DISCUSSION

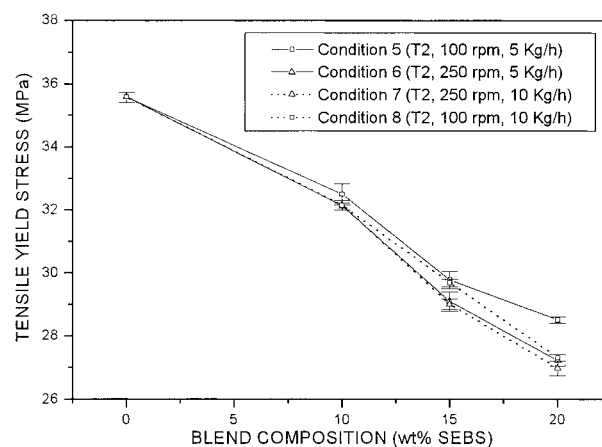
The variation in impact resistance of the blends with the amount of elastomer is shown in Table II, where the impact strength is seen to increase with increasing SEBS content. At a 20 wt % SEBS content the increase in impact strength showed to be very significant, i.e., 25 times that of neat PP. At lower SEBS contents (10 and 15%) the increase in impact resistance was not very remarkable, compared to the blend containing 20 wt % SEBS. However, the impact resistance showed some improvement in relation to the work of Gupta,¹³ who obtained an impact resistance of 80 J/m for a blend containing 15 wt % SEBS.

The outstanding increase in impact resistance of the 20 wt % SEBS blend is likely due to the large increase in the amount of stress concentration regions within the polymer matrix, increasing the energy absorbing capacity of the system. The lower increase in impact resistance for the blends with 10–15 wt % of SEBS might be attributable to the low energy dissipation during the break, which is due to the small amount of elastomer. The rubber content affects not only the amount of energy absorbed in the impact test, but also the manner in which it is absorbed. At high rubber contents, the energy absorbed in crack propagation at room temperature is higher than the energy stored elastically in the specimen when the crack initiated, so that additional energy is abstracted from the pendulum during the propagation stage. At lower rubber contents, the energy abstracted from the crack during propagation is smaller, and the available elastic energy is sufficient to complete the fracture of the specimen.

The yield stress, strain at break, and tensile modulus as a function of rubber content and processing parameters are shown in Figures 1, 2, and 3. SEBS addition is seen to reduce both



(a)



(b)

Figure 1 Tensile yield stress of the PP/SEBS blend at varying SEBS content and processing conditions: (a) Conditions 1, 2, 3, and 4, (b) Conditions 5, 6, 7, and 8.

the yield stress and the tensile modulus and increase the strain at break. The modulus and yield stress decrease almost linearly with increasing rubber content, which can be seen in Figures 1 and 3. This is expected when adding a phase with elastomeric characteristics. The modulus did not present significant drop, the decrease is approximately 25% for the blend with 20 wt % SEBS compared to pure polypropylene for the processing condition with 250 rpm, 10 kg/h, and T1. The decrease in the yield stress is approximately 27% for the blend with the same conditions.

The mechanical properties of pure polypropylene are listed in Table III. No significant variations were observed when processed at the different processing conditions investigated.

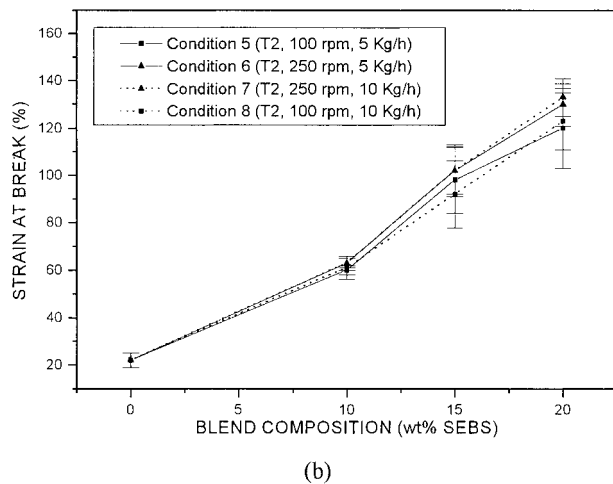
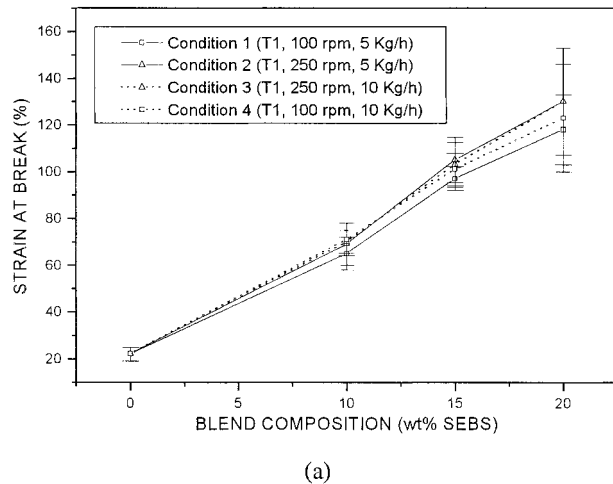


Figure 2 Strain at break of the PP/SEBS blend at varying SEBS content and processing conditions: (a) Conditions 1, 2, 3, and 4, (b) Condition 5, 6, 7, and 8.

Morphology of the Blends

The morphology of the blends was studied with SEM, in surfaces perpendicular to the flow direction during injection moulding. All PP/SEBS blend compositions showed a finely well-dispersed rubber phase. The rubber particles are fairly randomly distributed, and no elongation of particles was observed. The particle sizes of the blends are listed in Table IV.

The dispersed SEBS phase presented a smaller average particle size than that already observed in the literature for this system,^{13–17} which might be related to a better adhesion obtained for our system at the processing conditions investigated. When adhesion between the phases is optimum stress transfer across the interface is continuous

and in the absence of adhesion, there is a discontinuity in stress transfer or stress concentration. We may, therefore, state that the current system presents good adhesion between the phases, and that the SEBS particles might be acting as efficient initiators as well as terminators of the toughening mechanisms, because the impact resistance properties showed significant improvement.

The phase morphology is seen to vary more with the SEBS concentration than with the variation in the processing conditions, despite the fact that these variations are very small. For all the processing conditions used, the equivalent average diameter is smaller for the composition of 20 wt % SEBS. Although the average size and the shape of the dispersed SEBS particles were not

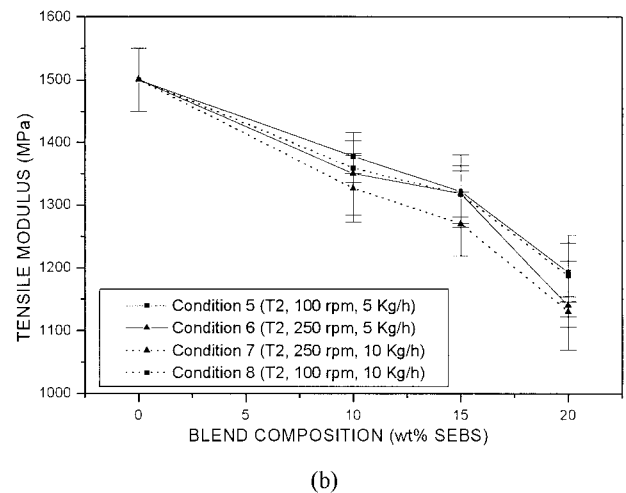
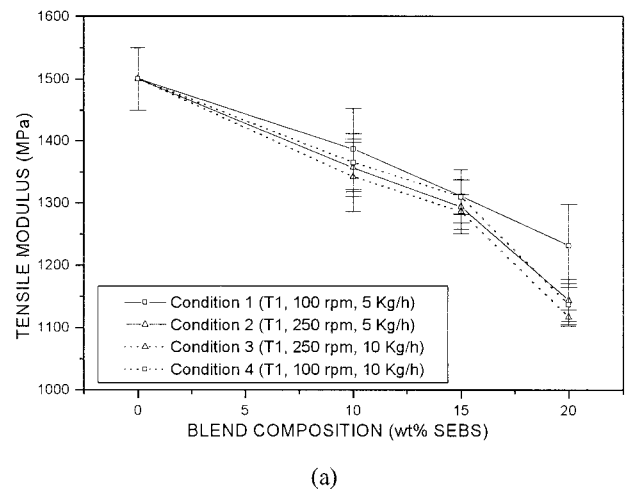


Figure 3 Tensile modulus of the PP/SEBS blend at varying SEBS content and processing conditions: (a) Conditions 1, 2, 3, and 4, (b) Condition 5, 6, 7, and 8.

Table III Mechanical Properties of Neat PP Used in This Study

Material	Izod Impact Strength (J/m)	Tensile Modulus (MPa)	Tensile Yield Stress (MPa)	Strain at Break (%)
Pure PP	22 ± 1.4	1500 ± 50	35 ± 0.2	22 ± 3

significantly altered by the variations in screw speed, temperature profile and feed rate, as seen in Table IV and Figure 4, the mechanical impact properties presented some variation with the different processing conditions as will be shown later (Figs. 5, 6, and 7).

Effect of Temperature Profile

The Izod impact resistance tests show that the modification of the temperature profile did not cause significant changes in the blend behavior (Table II). The three compositions investigated presented very close values of impact resistance on changing the temperature profile T1 (190, 200, 210, 210, 210, 200°C) to T2 (200, 230, 240, 240, 240, 230°C), even when rotor speed and feed rate were varied.

From Figure 5 it may be seen that maintaining the feed rate of the components constant (5 kg/h) and varying the temperature profile from T1 to T2 the impact resistance values remain almost unal-

tered; the changes observed are with the variation in rotor speed.

These results indicate that improved mixing between the elastomer (SEBS) and a thermoplastic cannot be accomplished merely through temperature change, because the viscosity of the elastomer may be little changed by temperature modification.

Effect of Rotor Speed

Analysis of the effect of the rotor speed on the impact resistance during blend preparation showed that for low SEBS contents this variable does not significantly affect the impact resistance of the system. However, at a 20 wt % content of SEBS a remarkable effect was observed, as illustrated in Figures 5 and 6. Maintaining feed rate (5 kg/h) and temperature profile constant (T1), which is shown in Figure 5, an increase in rotor speed from 100 to 250 rpm resulted in impact resistance increase of about 27%, and maintain-

Table IV Equivalent Average Diameter of Dispersed Elastomer of the PP/SEBS Blend with Varying Composition and Processing Conditions

Composition % wt SEBS	Equivalent Average Diameter (μm)			
	Temperature Profile (T1)			
	Condition 1	Condition 2	Condition 3	Condition 4
10	0.21 ± 0.12	0.20 ± 0.12	0.19 ± 0.11	0.22 ± 0.13
15	0.21 ± 0.10	0.19 ± 0.10	0.20 ± 0.09	0.19 ± 0.10
20	0.15 ± 0.07	0.16 ± 0.08	0.15 ± 0.08	0.17 ± 0.09
	Temperature Profile (T2)			
	Condition 5	Condition 6	Condition 7	Condition 8
	10	0.22 ± 0.16	0.19 ± 0.11	0.22 ± 0.11
15	0.21 ± 0.12	0.22 ± 0.12	0.19 ± 0.11	0.19 ± 0.10
20	0.18 ± 0.08	0.15 ± 0.06	0.16 ± 0.07	0.16 ± 0.09

Condition 1: T1, 100 rpm, 5 Kg/h; Condition 2: T1, 250 rpm, 5 Kg/h; Condition 3: T1, 250 rpm, 10 Kg/h; Condition 4: T1, 100 rpm, 10 Kg/h; Condition 5: T2, 100 rpm, 5 Kg/h; Condition 6: T2, 250 rpm, 5 Kg/h; Condition 7: T2, 250 rpm, 10 Kg/h; Condition 8: T2, 100 rpm, 10 Kg/h.

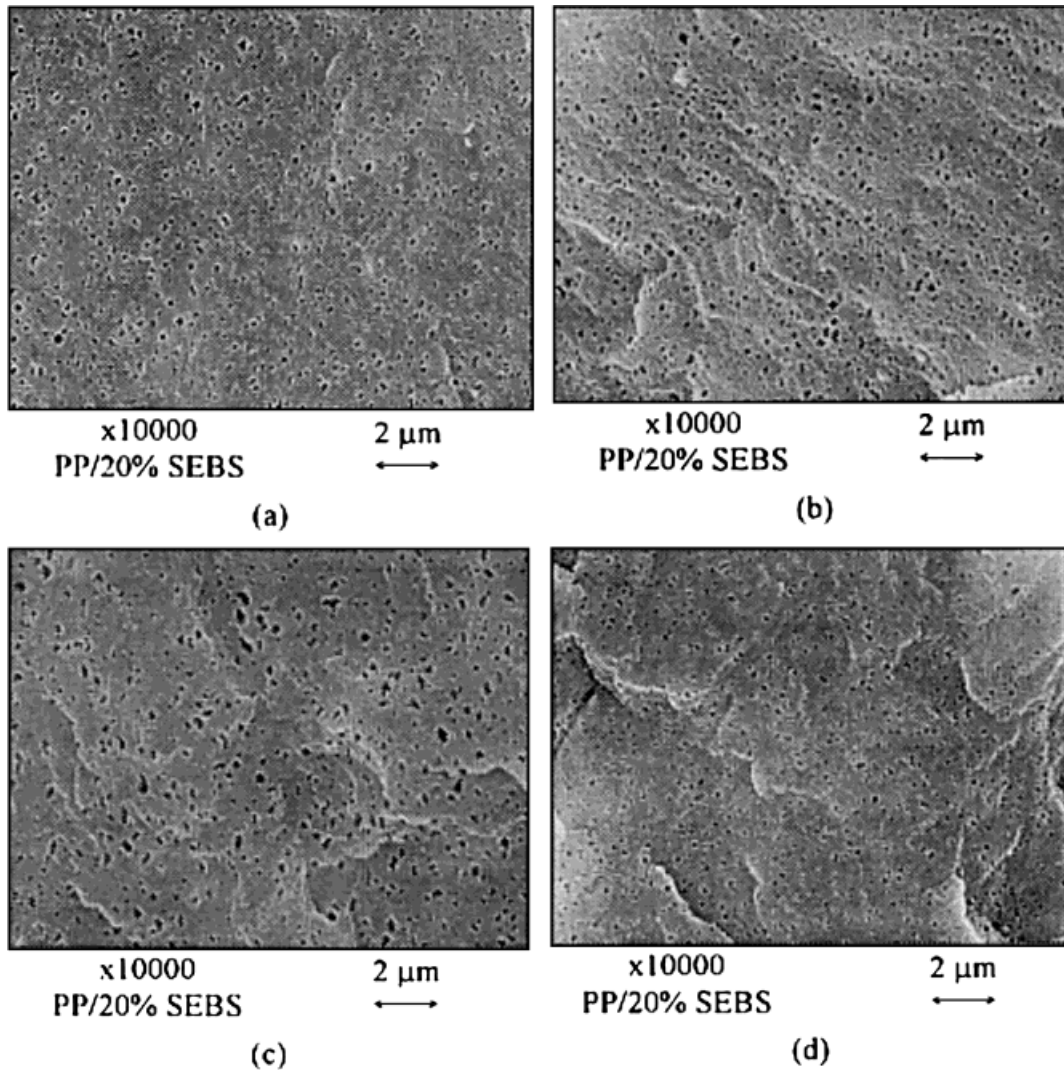


Figure 4 Micrographs of the PP/SEBS blend containing 20 wt % SEBS. (a) Condition 4 (T1, 100 rpm, 10 kg/h); (b) condition 3 (T1, 250 rpm, 10 kg/h); (c) condition 7 (T2, 250 rpm, 10 kg/h); and (d) condition 6 (T2, 250 rpm, 5 kg/h).

ing the same feed rate and temperature profile constant (T2) an increase in rotor speed from 100 to 250 rpm resulted in impact resistance increase of about 24%.

The most significant increase in impact resistance can be seen in Figure 6. For temperature profile T1, feed rate of 10 kg/h and rotor speed of 250 rpm the impact resistance equaled 560 J/m, i.e., an increase of 25 times in relation to pure polypropylene.

In general, an increase in rotor speed leads to an increased shearing in the extruder. This increased shearing promotes a better dispersive mixing of the blend components, with a consequent reduction in particle size of the dispersed

phase. This reduction in size of the dispersed particles with increased rotor speed was not observed for the PP/SEBS system, as the equivalent mean diameter remained unaltered at approximately $0.15 \mu\text{m}$, which can be seen in the micrographs presented in Figure 4, despite the remarkable increase in impact resistance. This increase in impact resistance might be attributable to a better distributive mixing of the blend components, which correlates with a lower interparticles average distance, when the rotor speed was increased. When the interparticles distance is optimized, a higher capacity of the matrix in absorbing energy might be obtained, leading to an increase of the impact strength of the system.

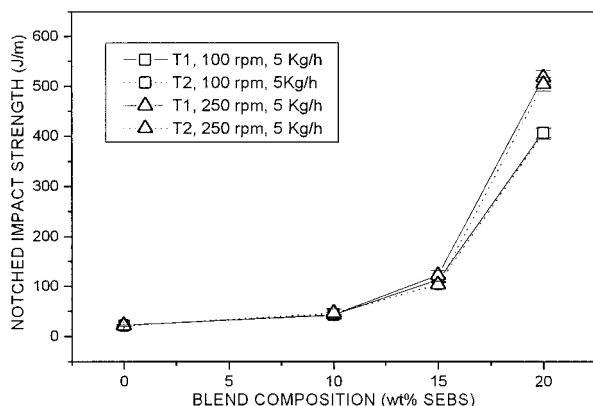


Figure 5 Izod impact strength of the PP/SEBS blend at varying SEBS content and processing conditions, maintaining a constant feed rate of 5 kg/h and varying both the rotor speed (□) 100 rpm and (Δ) 250 rpm, and temperature profile (—) T1 and (---) T2.

According to Jang,^{9,10} of major importance is the number of particles capable of initiating the deformation mechanism under impact conditions, being that smaller particles are more effective than larger ones. The particles with a size below 0.5 μm initiate yielding, while particles with a size above 0.5 μm initiate crazes.

As the twin-screw extruder has different regions of mixing and shearing, the morphology will go through several stages before the final morphology is attained. Hu²⁴ observed that the morphology of mechanical blends is not completely stable and prone to changes along the course

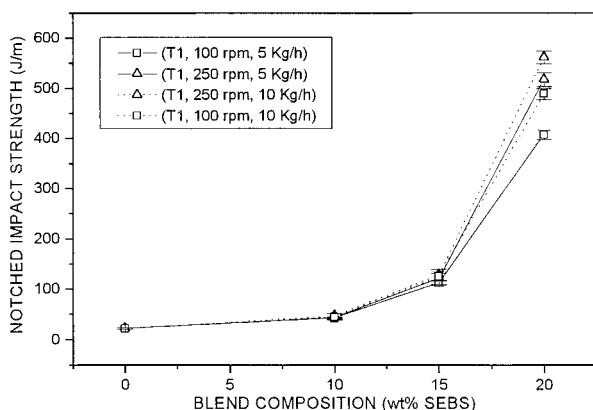


Figure 6 Izod impact strength of the PP/SEBS blend at varying SEBS content and processing conditions, maintaining a constant temperature profile T1 (190, 200, 210, 210, 200°C) and varying both the rotor speed (□) 100 rpm and (Δ) 250 rpm, and feed rate (—) 5 kg/h and (---) 10 kg/h.

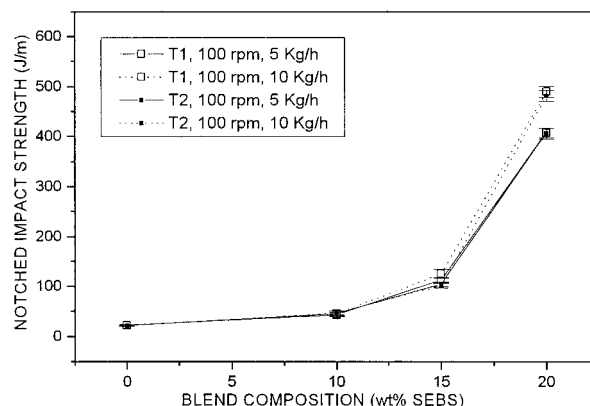


Figure 7 Izod impact strength of the PP/SEBS blend at varying SEBS content and processing conditions, maintaining a constant rotor speed of 100 rpm and varying both the feed rate (—) 5 kg/h and (---) 10 kg/h, and temperature profile (□) T1 and (+) T2.

within the extruder. During this course the morphology evolves slowly, and will only be defined at the die outlet, unlike reactive blends where morphology is defined right after fusion of the phases and stabilizes in virtue of chemical reactions, without experiencing further changes. The screw design used in the current investigation allows high shearing, and the final morphology is expected to consist of small size particles, which was as observed. The difference between the two rotor speeds employed might have been too little, making further breaking up of the disperse particles difficult, and no significant alteration would be observed in the morphology when going from one rotor speed to the other.

Effect of Feed Rate

The effect of feed rate on impact resistance presented the same trend as that observed for the rotor speed, where the most significant changes were obtained for the highest SEBS content, i.e., 20 wt % SEBS. When the temperature profile and rotor speed are constant higher impact resistance values are obtained at the higher feed rate (10 kg/h), as illustrated in Figure 7. An increase in feed rate might also improve mixing, as this process condition showed to have a similar effect as the variation in rotor speed.

CONCLUSIONS

In this work the effect of the processing parameters (rotor speed, feed rate, and temperature pro-

file) on the mechanical properties and morphology of PP/SEBS blends was studied. The results showed that the SEBS copolymer performs excellently as a toughening agent of PP. The processing conditions were seen to have a strong effect on the mechanical properties of the PP/SEBS blend. The processing condition with the lower temperature profile, the higher rotor speed, and the higher feed rate resulted in the best impact resistance properties, where the 20 wt % SEBS blend achieved an impact resistance of 560 J/m, i.e., an increase of 25 times in relation to pure PP. This blend also showed to be the most affected by processing conditions. The screw speed showed to be the parameter that exerted the strongest influence on the impact strength, although no alterations in average particle size of the disperse elastomer phase were observed. This might be attributable to the small difference between the two rotor speeds studied, which makes further breaking up of the disperse particles difficult, and no significant alteration would be observed in the morphology when increasing rotor speed. An increase in rotor speed leads to an increased shearing in the extruder, which promotes a better distributive mixing of the blend components without reduction in particle size of the disperse phase.

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