The toughening behavior in propylene–ethylene block copolymer filled with carbon black and styrene–ethylene butylene–styrene triblock copolymer

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Abstract

This work examines the toughening behavior of propylene–ethylene block copolymer (Co-PP) filled with carbon black (CB) and styrene–ethylene butylene–styrene triblock copolymer (SEBS). Appropriate amounts of the two components are mixed through melt-blending in a twin-screw extruder. The blended pellets, following preparation in a series of specimens by injection molding, are studied and compared. A scanning electron microscope (SEM) morphology study of the impact-fractured surfaces verifies the changes in fracture mechanisms at various temperatures and SEBS contents. In addition, the flexural modulus, tensile strength, heat distortion temperature (HDT), and dynamic mechanical properties are also studied here. According to those results, the blending of CB in Co-PP not only improves the impact strength, but also enhances the flexural modulus and tensile strength. However, the HDT of the Co-PP/CB blends decreases with a greater filler content. Moreover, SEBS markedly upgrades the impact endurance in the lower temperature range when blended with Co-PP, due to the increased compatibility in the interface between SEBS particles and the Co-PP matrix.   © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Toughening; Co-PP copolymer; Carbon black; SEBS

1. Introduction

Plastics are conventionally used as electric and thermal insulation materials, having desirable features such as ease of molding, light weight, and resistance to corrosion. Modification by blending polymer with filler has already been widely practised and has become the current focus of materials development [1–22]. Carbon black (CB) as a filler in thermoplastic polymers is not limited to use merely as a pigment, but is also used to prolong the life of plastics when used outdoors. This characteristic is attributed to the features that can be found in modified materials, e.g., improved mechanical properties, thermal conductivity, and ultraviolet light absorption, as generally expected in composite materials with a CB filler [1–10]. The filling of CB in polyethylene resin has been extensively investigated [1–6], those investigations including the dynamic mechanical behavior of polymer containing CB by Gandhi and Salovery [7], interaction between polypropylene and CB by Petrovic et al. [8], morphologies and properties of injection-molded specimens

of polypropylene/CB composites [9] and color matching polypropylene (PP) compounds by multi-angle spectrophotometry [10].

In addition, although isotactic polypropylene (i-PP) has been widely studied in elastomer-toughened polypropylene [11–22], propylene–ethylene block copolymer (Co-PP) has seldom been investigated. Therefore, Co-PP has become increasingly important in terms of developing high-impact PP blends, because it possesses the following merits: (1) the polyethylene (PE) component of Co-PP can elevate the interfacial adhesion between Co-PP and styrene–ethylene butylene–styrene triblock copolymer (SEBS); (2) Co-PP yields a better impact strength, particularly a low-temperature impact strength, due to the lower glass transition temperature (T_g) of the ethylene–propylene interface (called T_{g2} in this paper) of Co-PP; (3) Co-PP is a block copolymer, thereby retaining a high crystallinity. Restated, Co-PP can retain adequate stiffness, service temperature, and other characteristics of i-PP. Meanwhile, according to a previous investigation [19], blending of SEBS elastomer with thermoplastic polyolefins gives a better service temperature and solvent resistance than most blends of diene elastomer with thermoplastic

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polyolefin. Gupta and Purwar [22] studied blends of SEBS with PP. Those investigators postulated that the polyolefinic block EB of SEBS offers a satisfactory affinity with i-PP. Therefore, blends of PP–block-PE with SEBS for toughening must be more closely examined.

Scarce attention has been paid to the properties of Co-PP/CB and Co-PP/SEBS composites which go through melt-blending in a twin-screw extruder and then through injection molding. Therefore, in this work, we investigate the respective impact behaviors and other mechanical properties.

2. Experimental

2.1. Materials

Propylene–ethylene block copolymer (Co-PP) TI-4070-G (MFI = 7.6) was supplied by Aristech Chemical Corporation, USA. The filler used is Vulcan-P CB from Cabot Corporation, USA. The major properties are: nitrogen surface area absorption of 143 m^2/g; particle size of 20 nm; volatile content of 1.5%; pH = 9.5; and density = 0.337 g/cm^3. The elastomer used was a styrene–ethylene butylene–styrene triblock copolymer (SEBS), Kraton GX-1675, which was obtained from Shell Chemical Corporation, USA.

2.2. Preparation of blends

The blends were prepared by mixing an appropriate amount of two components through melt-blending using a twin-screw extruder (Welding Engineers HT-0.8″). The temperature profiles for blending were 230, 240, 240, and 230°C. The screw speed was 120 rpm. The Co-PP was also passed through the same extrusion process to provide it with a history identical to that of the blends. The blend pellets were dried in an oven at 80°C for 48 h, followed by injection molding to prepare the specimens. The mold temperature was 60°C, and the temperature profiles for the molding were set at 220, 230, 240, and 230°C.

2.3. Test methods

Notched Izod impact tests were performed for each sample over a wide temperature range from −75 to 23°C. A temperature chamber adapted to an Izod impact testing machine (Amityville TMI No. 43-1) was used to provide a constant chamber temperature. The chamber was equipped with a resistance coil (heat), a liquid-nitrogen coolant, an internal fan, and a digital multi-thermometer. The sample was held in the chamber at the testing temperature for more than 30 min before testing. The flexural modulus was then determined according to ASTM D790, method II, procedure B (four-point loading at 1/4 points) on a universal testing machine (Hung TA-8503); the cross-head speed, span length, and full-scale load were 1.8 mm/min, 25 mm, and 40 kg, respectively. Next, the tensile strength was tested using Hung

Ta-8503 following the ASTM D638-Type I method with a drawing speed of 10 mm/min and a span length of 25 mm. The heat distortion temperature (HDT) was measured on a heat-distortion temperature unit (Ceast 6510). The maximum stress applied on specimens was 455 kPa, and the rate of heating was maintained at 2°C/min. The above HDT testing methods corresponded to the ASTM D256. Dynamic mechanical testing was measured at 6.28 rad/s with a rheometric dynamic spectrometer (RDS, Rheometrics Inc., model RDS-II) over the temperature range from −70 to 200°C, at a heating rate of 3°C/min.

3. Results and discussion

3.1. Notched Izod impact strength

Fig. 1 depicts the notched Izod impact strength of Co-PP versus CB and SEBS content. According to previous literature, increasing the CB concentration gives a decrease in impact strength [8]. However, results in this work show that when the CB content in Co-PP is less than 30 per hundred resin (phr), the notched Izod impact strength of Co-PP markedly increases. Such an increase is approximately three times that of the increase of notched Izod impact strength, which goes up from 12 kg cm/cm of the pure Co-PP to 45 kg cm/cm when the CB content is 30 phr. However, the notched Izod impact strength at a low temperature of Co-PP composite with CB was inadequate. For instance, the impact strength of Co-PP/CB (30 phr) at −30°C was merely 1.3 kg cm/cm, thereby allowing us to infer that adding CB cannot sufficiently enhance the impact strength of carbon-filled Co-PP at lower temperatures.
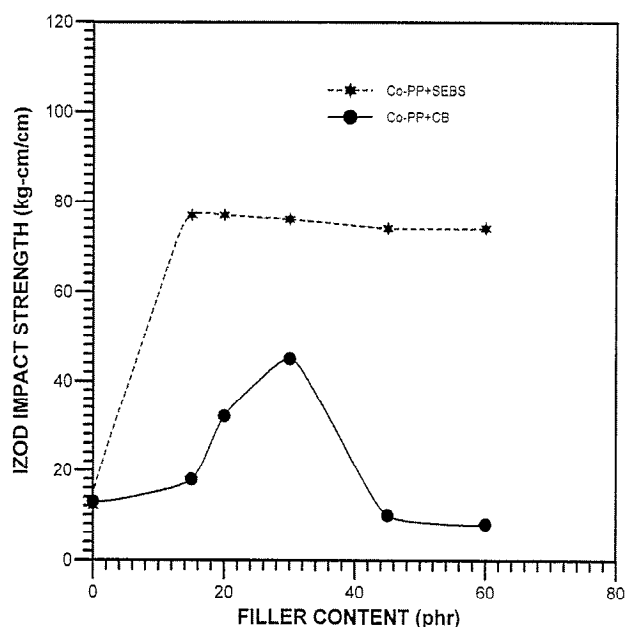

Fig. 1. The notched Izod impact strength as a function of filler loading in reinforced Co-PP (1/8 in thick, notched specimen) at room temperature.

Figs. 1 and 2 depict the above relationships between impact strength and SEBS content or between impact strength and testing temperature. Fig. 2 indicates that below − 15°C, Co-PP is brittle; however, it is more ductile at room temperature. This is because the Co-PP has a lower second glass transition temperatures of − 53°C (Table 1). Actually, Co-PP belongs to those materials in which the brittle–ductile transition in impact tests is related to the glass transition temperature. Its deficiency in low-temperature applications tends toward embrittlement. In fact, temperature also profoundly influences impact behavior in all elastomer-toughened plastics. At extremely low temperatures, the elastomer phase becomes glassy and the elastomer-toughened plastic is brittle as well. At higher temperatures, the shear yielding mechanism becomes dominant, and the impact strength rises. It is understood above that crazing and shear yielding occur simultaneously in most elastomer-toughened plastics. Toughness of a given blend is ascribed to the competition between crazing

and shear yielding. Fig. 2 indicates that, below − 15°C, the impact strength gradually increases with increasing SEBS content up to 20 phr. On the other hand, the blend containing 30 phr SEBS has significantly higher impact strength at − 15°C, while the fractured surface exhibits stress-whitening near the nothced tip. Below − 60°C, the impact strengths of all Co-PP/SEBS are extremely low because the testing temperature is already lower than the T_g of SEBS (− 58°C) and SEBS loses its toughening effect. This indicates that the impact properties of SEBS-toughened Co-PP heavily rely on SEBS content and temperature.

According to Bucknall [23], the elastomer content affects not only the amount of energy absorbed in the impact test, but also the manner in which it is absorbed. At a high elastomer content, the energy absorbed in crack propagation at room temperature is higher than the energy stored elastically in the specimen when the crack initiates. By doing so, additional energy is abstracted from the pendulum during the propagation stage. At a lower elastomer content, the energy abstracted from the crack during propagation is smaller, and the available elastic energy is sufficient to complete the fracture of the specimen.

Fig. 3 displays the relation between the flexural moduli of Co-PP/CB and Co-PP/SEBS blends for different filler contents. Addition of an inorganic filler is able to enhance the flexural modulus and improve the balance of impact strength and stiffness in blends [24–28]. However, according to Fig. 1 and Fig. 3, when the CB content of Co-PP is lower than 30 phr, not only does the flexural modulus increase with a greater CB content, but also the increase in notched Izod impact strength is even more noticeable. Therefore, the addition of the composite of CB in Co-PP improves not only the
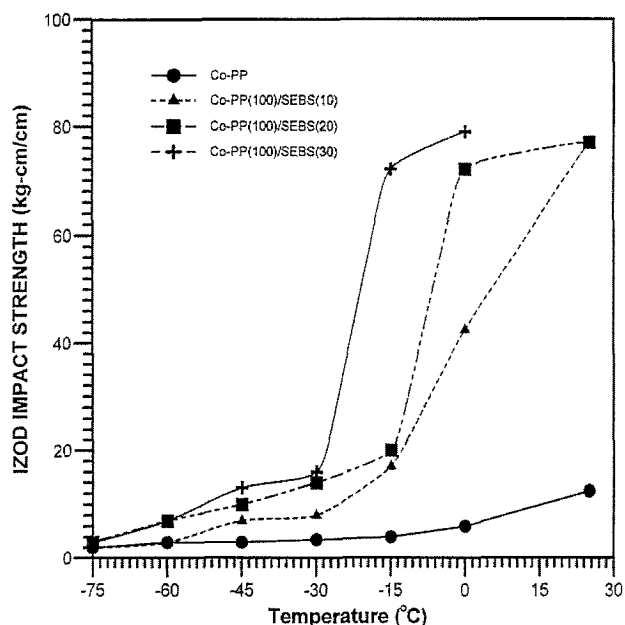

Fig. 2. The notched Izod impact strength of Co-PP and Co-PP/SEBS blends tested at various temperatures.

Table 1
The dynamic properties of Co-PP/CB composites

Co-PP/carbon black	A T_{g2} (°C) [a]	B T_{g1} (°C) [b]	A tanδ	B tanδ
100/0	− 53	7	0.037	0.069
100/15	− 48	7	0.040	0.071
100/30	− 48	7	0.041	0.076
100/45	− 48	7	0.042	0.061
100/60	− 48	7	0.034	0.063

[a] T_{g2} is the glass transition temperature of the EPR (Co-PP).
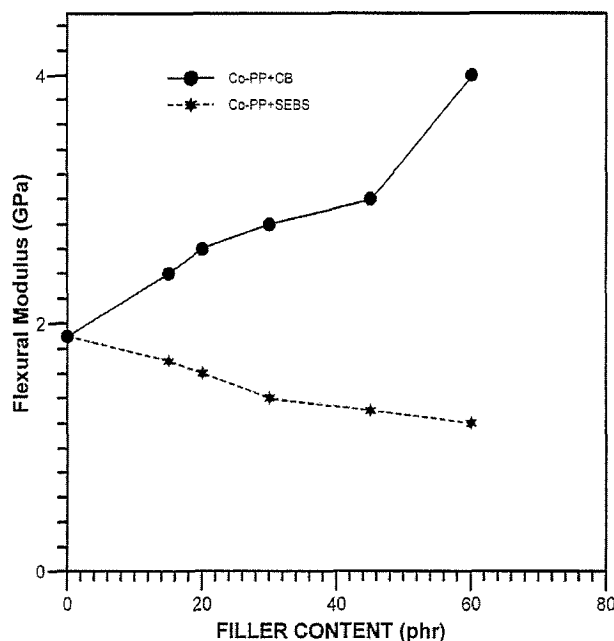[b] T_{g1} is the glass transition temperature of Co-PP.

Fig. 3. Comparison of the flexural moduli of Co-PP/CB and Co-PP/SEBS blends for different filler concentrations at room temperature.

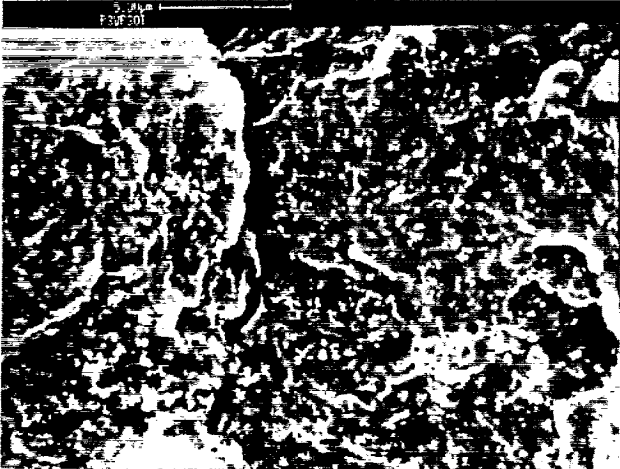Fig. 4. Scanning electron micrograph of impact-fractured surface of Co-PP(100)/CB(30) composite.

● : Carbon Black Aggregate mass

▨ : Aggregate Void (Matrix)

Fig. 5. The toughening mechanism of Co-PP filled with carbon black.

rigidity but also the toughness as well. Moreover, according to Fig. 1 and Fig. 3, Co-PP blended with SEBS, although capable of significantly enhancing the impact strength, causes a decrease in the flexural modulus.

3.2. Morphologies of Co-PP composites

Scanning electron micrographs of the fracture surfaces of the impact-fractured specimens after coating with gold were obtained on a Hitachi S-520 scanning electron microscope (SEM). Some specimens were etched in xylene at room temperature for 2 h to dissolve the SEBS before being examined. Fig. 4 presents the surface fractured by impact testing for Co-PP/CB (30 phr). According to this Figure, the CB remains an aggregate structure, in which cracks propagate through the interface between CB particle/polymer particles. Such CB aggregated structures provide adhesive forces and
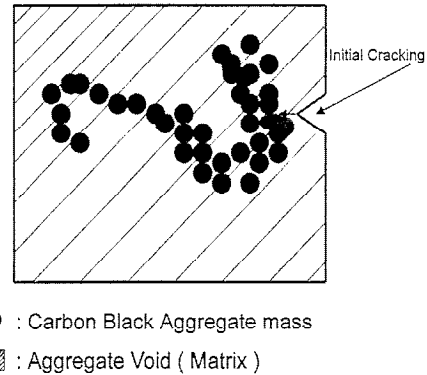
cohesive forces [8] between polypropylene and CB to prevent tearing propagation [29]. This CB aggregated structure may be responsible for the improved impact behavior. The proposed toughening mechanism of matrix filled with CB is shown in Fig. 5.

Furthermore, Fig. 6(a) displays the impact-fractured surface of the Co-PP at low temperature (0°C), which is rather smooth. However, the Co-PP/SEBS(30) blend exhibits extensive shear flow on the surface as shown in Fig. 6(b). In addition, a lateral contraction also occurs in the impact-fractured surface of the specimen. This finding implies some role of SEBS in the energy dissipation mechanism of these blends. In fact, the lateral contraction has been recognized as the result of shear yielding. Fig. 7 shows scanning electron micrographs of the impact-fractured surface of the Co-PP(100)/SEBS(30) blend at −30 and at −15°C, respectively. The impact-fractured surface of Co-PP(100)/SEBS(30) blends at −30°C (Fig. 7(a)) initially reveals that the transverse contraction of the impact-fractured surface of Fig. 6(b) disappears. In addition, the shear flow of Fig. 7(b) appears smaller than that in Fig. 6(b). This difference is due to testing
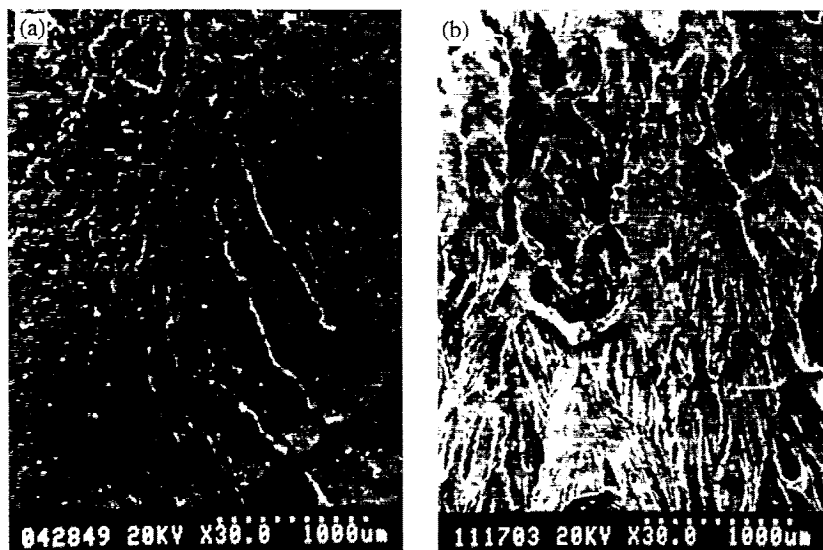

Fig. 6. Scanning electron micrographs of impact-fractured (at 0°C) surfaces of (a) Co-PP and (b) Co-PP(100)/SEBS(30) blend.
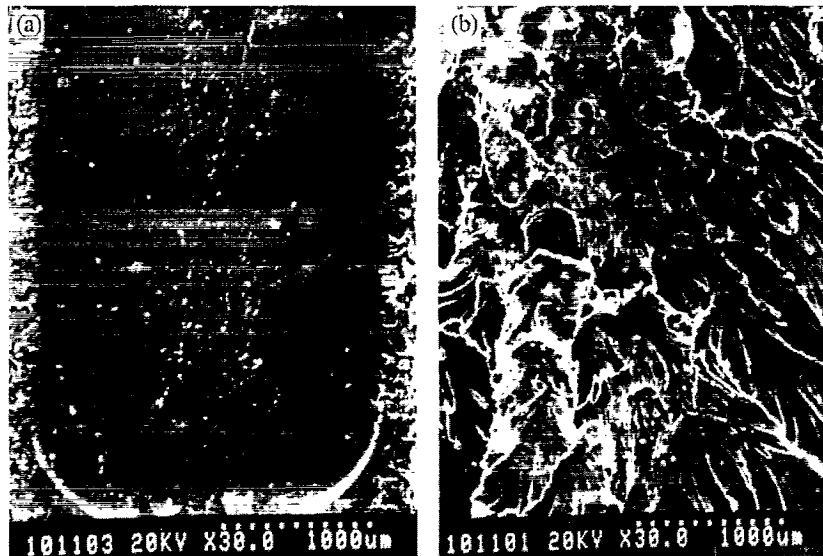
Fig. 7. Scanning electron micrographs of impact-fractured surface of Co-PP(100)/SEBS(30) blend: (a) at −30°C; (b) at −15°C.

at lower temperatures, the SEBS-toughened Co-PP becoming much more brittle. For the Co-PP(100)/SEBS(30) blend, as shown in Fig. 2, the impact strength drops from 78 to 15 kg cm/cm as the test temperature is lowered from 0 to −30°C. In other words, shear yielding becomes less significant in low-temperature fracture behavior. Consequently, the SEM investigation of the deformation behavior of Co-PP/SEBS blends reveals that the main deformation mode is of crazing type at low temperatures.

Fig. 8(b) presents a high-magnification micrograph of the impact-fractured surface of Co-PP(100)/SEBS(30) blend, with the SEBS component leached out by xylene. Fig. 8(a) shows a high-magnification micrograph of the unetched Co-PP(100)/SEBS(30) blend. Comparing Fig. 8(b) with Fig. 8(a) reveals that many small SEBS particles in the Co-PP(100)/SEBS(30) blend were not dissolved out. This observation suggests that there is a better phase dispersion between SEBS and Co-PP, thereby making it more difficult for the xylene to leach out the SEBS. Fig. 8(b) indicates that the SEBS particles are about 0.6 μm or less in diameter in the Co-PP(100)/SEBS(30) blend. In addition, the elastomer's particle size and size distribution significantly influence the impact properties of the elastomer-modified blends. According to previous investigations [30,31], polypropylene blends containing smaller elastomer particles are more ductile and impact resistant than those with larger elastomer particles. However, other investigations [14,32] have noted that the optimum elastomer size for toughened PP is about 0.4–0.6 μm. The optimum elastomer particle size obviously depends on the composition of the elastomer. Furthermore, some authors [33–35] have contended that the stress concentration is lower for phase dispersion with rounded or spherical shapes than for phase dispersion of sharp corners or irregular shapes. Another factor for better mechanical properties is that the PE component of Co-PP can increase
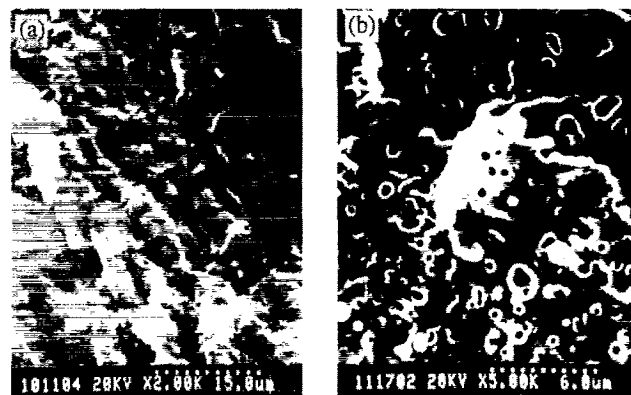

Fig. 8. Scanning electron micrographs of impact-fractured (at 0°C) surface of Co-PP(100)/SEBS(30) blend: (a) unetched; (b) etched with xylene.

the interfacial adhesion between SEBS and Co-PP. A chemical bond exists between the PE and PP components of Co-PP, while only physical bonding exists between PE and PP in i-PP/PE blends. Therefore, the Co-PP/SEBS blends exhibit a greater toughening effect than the i-PP/SEBS/high-density polyethylene (HDPE) ternary blend [36].

3.3. Other mechanical properties

Fig. 9 depicts the changes in tensile yield strength of Co-PP with respect to filler content. The tensile yield strength of the CB-filled propylene–ethylene block copolymer increases with increasing CB content. On the contrary, the tensile yield strength of the Co-PP/SEBS blends decreases with increasing filler content. Fig. 10 illustrates that the heat distortion temperature (HDT) of Co-PP/SEBS and Co-PP/CB blends decreases with increasing filler content. According to Nielsen's prediction regarding the behavior of flexural modulus
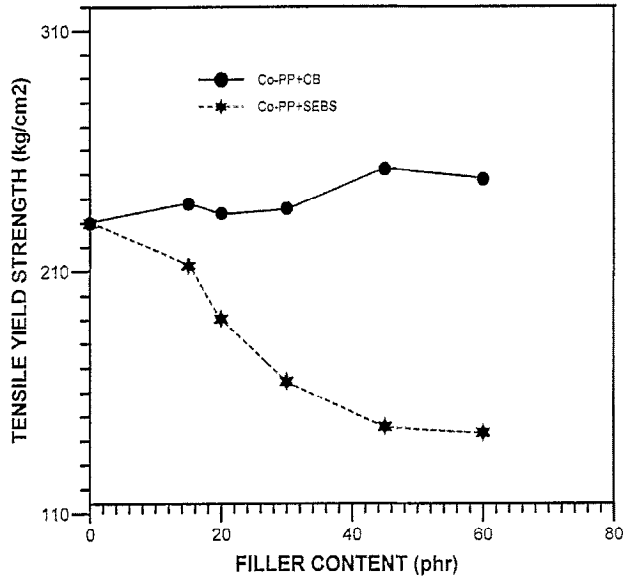
Fig. 9. Comparison of the tensile yield strengths of Co-PP/CB and Co-PP/SEBS blends for different filler concentrations at room temperature.
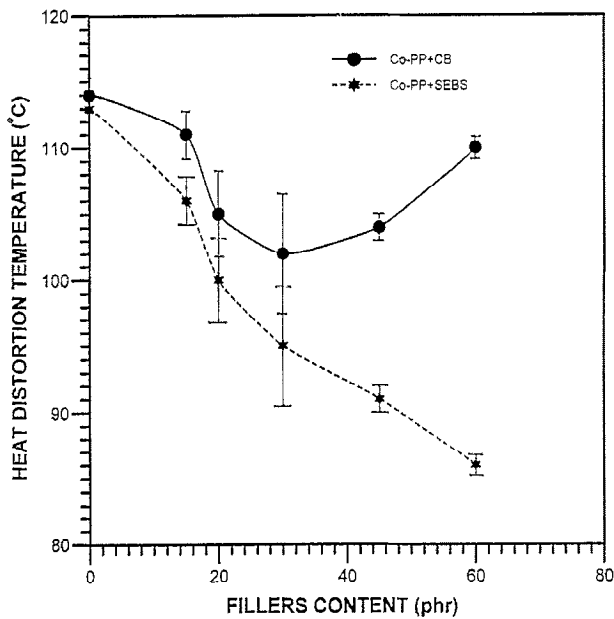

Fig. 10. The heat distortion temperature (HDT) of Co-PP/CB and Co-PP/SEBS blends.

with filler content [37], the increase of the HDT is attributed to a change in flexural modulus. However, compared to Fig. 3, although the flexural modulus of CB-filled Co-PP increases with a greater CB content, yet its HDT markedly decreases. This result contradicts Nielsen's prediction. On the other hand, the behavior of the HDT in the composite material as a result of blending CO-PP and SEBS conforms to Nielsen's prediction. The flexural modulus decreases with greater SEBS content and, likewise, for the HDT.

Dynamic mechanical testing was conducted using a rheometric dynamic spectrometer (RDS). The results of the dynamic mechanical analyses are summarized in Tables 1 and 2. Figs. 11 and 12 demonstrate the changes of loss factors of CB- and SEBS-filled Co-PP with respect to filler content and temperature. These Figures confirm the existence of two secondary loss peaks in pure Co-PP. The first secondary loss peak occurs at 7°C, which is also the first glass transition temperature, T_{g1}. The second secondary loss peak occurs at -53°C, which correspondingly becomes the second glass transition temperature, T_{g2}. However, transmission electron microscopy (TEM) reveals [38] that Co-PP contains an ethylene propylene elastomer (EPR) component in addition to the PP and PE components. The TEM investigation suggested that the first $\tan\delta$ peak (T_{g1}) at 7°C can be attributed to the polypropylene component and that the second $\tan\delta$

Table 2
The dynamic properties of Co-PP/SEBS composites

Sample	A T_{g2} (°C) [a]	B T_{g1} (°C) [b]	A $\tan\delta$	B $\tan\delta$
Co-PP	-53	7	0.037	0.070
Co-PP/SEBS blend				
100/10	-58	7	0.045	0.061
100/20	-58	7	0.065	0.067
100/30	-58	7	0.071	0.068

[a] T_{g2} is the glass transition temperature of the EPR (Co-PP) or SEBS.
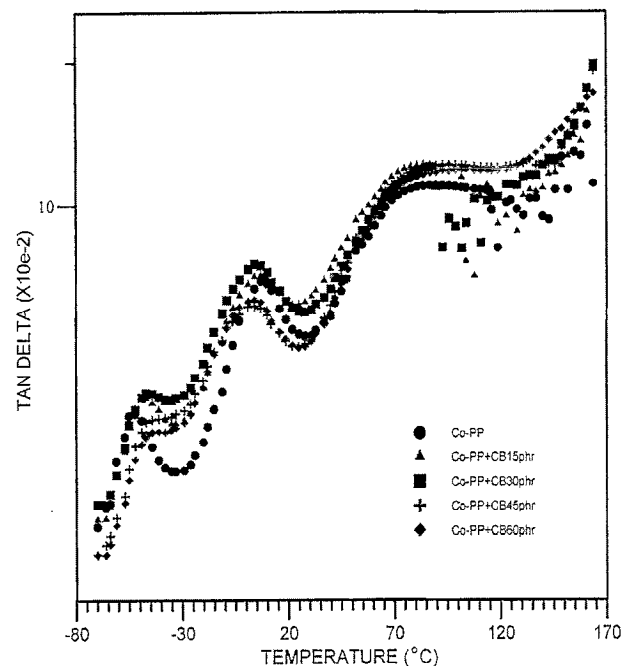[b] T_{g1} is the glass transition temperature of Co-PP.

Fig. 11. Dynamic mechanical curves of Co-PP/CB composites. Change of $\tan\delta$ with temperature and concentration of carbon black.
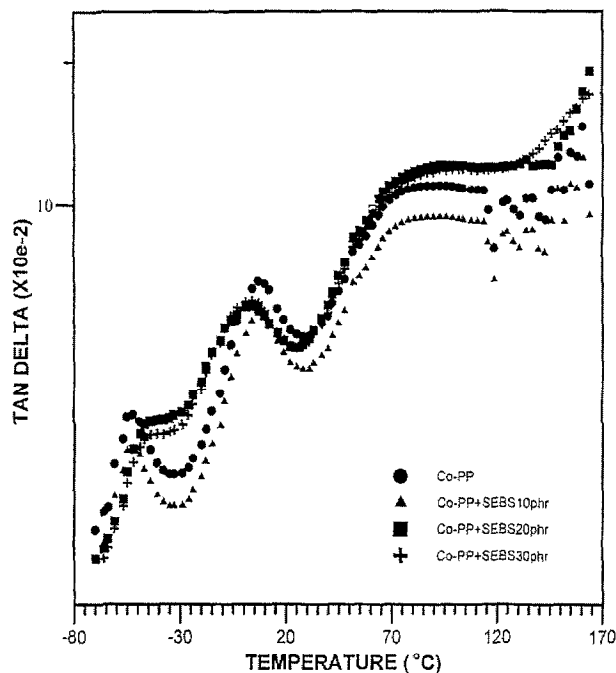
Fig. 12. Dynamic mechanical curves of Co-PP/SEBS composites. Change of tanδ with temperature and concentration of SEBS.

4. Conclusions

This study examined the properties of Co-PP/CB and Co-PP/SEBS composites which go through melt-blending in a twin-screw extruder and, then, through injection molding. Based on the results presented here, we can conclude the following:

(1) For Co-PP/CB composite with CB content below 30 phr, not only does its notched Izod impact strength markedly increase, but its flexural modulus also increases with a greater CB content. Restated, the filling of CB in Co-PP improves not only its rigidity but also its toughness. However, its HDT slightly decreases with a greater CB content. The tensile yield strength also increases correspondingly.

(2) SEBS markedly improves the impact endurance in the lower temperature range when blended with Co-PP, due to the increased compatibility in the interface between SEBS particles and the Co-PP matrix. The studies involving impact behavior indicated that the impact strength and fracture mechanism of Co-PP/SEBS blends depend not only on test temperature, but also on the elastomer content. Meanwhile, variations of HDT versus SEBS content are quite linear over the entire range studied; a higher SEBS content implies a lower value of the HDT. We believe that composition variation of the HDT is related to the modulus of the blends.

peak (T_{g2}) at $-53°C$ is from the EPR component of the Co-PP. Fig. 11 also reveals the existence of two glass transition temperatures in Co-PP/CB. The first one is still 7°C, but the second one changes to $-48°C$. This observation confirms that the interaction of molecules of CB with EPR heavily influences Co-PP/CB. We can also infer that the particles of EPR existing in Co-PP facilitate an efficient association of molecules, which is deemed necessary for the blending of CB and Co-PP. On the other hand, according to Fig. 12, these Co-PP/SEBS blends also have two tanδ peaks at 7 and $-58°C$, respectively. The tanδ peak at $-58°C$ may also be attributed to the T_g of the EPR component. According to the results presented here, Co-PP/SEBS blends cannot have single glass transitions intermediate in temperature between the glass transitions of Co-PP and SEBS. Therefore, their glass transitions are not predictable by the Fox equation [39] or other relevant equations [40,41], used for completely compatible blends. Restated, the Co-PP/SEBS blends are not completely compatible blends. In fact, for toughening, complete compatibility or incompatibility is undesired. A complete compatibility between the elastomer and the plastic does not produce toughening, but merely plasticizes the material. On the other hand, a completely incompatible elastomer does not form a fine dispersion of the type required for good optical, mechanical and rheological properties, nor will it produce a strong mechanical bond at the elastomer–matrix interface. Thus, the ideal elastomer for the purpose of toughening is neither completely compatible nor completely incompatible.

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