Study on Morphological, Rheological, and Mechanical Properties of PP/SEBS-MA/SGF Hybrid Composites

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Received 29 January 2006; accepted 9 October 2006
DOI 10.1002/app.25700

ABSTRACT: Hybrid composite samples composed of polypropylene as matrix, 20% short glass fibers (SGF) as reinforcement and varying amount of maleic anhydride (MA) grafted SEBS as compatibilizer and impact modifier were prepared by melt mixing in a modular twin screw extruder. The SEM examination performed on cryogenically fractured surfaces of hybrid samples showed a three-phase type morphology in which SGF and rubber phase finely distributed in the PP matrix. SEM results also revealed that in the hybrid samples containing SEBS-MA, the surface of the SGF are coated with a thin layer of SEBS-MA, indicating a strong adhesion between SGF and matrix materials. The results of rheological studies showed nearly equal viscosity for compatible and incompatible hybrid samples. Tensile yield strength enhanced with increasing rubber content up to 10% above which it decreased and highest impact strength enhancement was obtained for sample containing 20% rubber. The impact strength of composites was found to be increased with increasing the SGF content. In final, it was shown that a good balance between stiffness and toughness could be achieved by adjusting the SGF and rubber content in this ternary system. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 104: 2704–2710, 2007

Key words: polypropylene; fibers; hybrid composites; compatibility; impact behavior

INTRODUCTION

Polypropylene (PP) has been widely used in domestic and industrial applications because of its good properties, excellent processability, and low cost. However, PP often fails in a brittle mode when subjected to impact loading at temperature below its T_g. To overcome this drawback, PP is usually blended with elastomeric materials, this, however, results in reduction of its yield strength and stiffness. Reinforcement by inorganic fillers such as calcium carbonate or short glass fibers (SGF) can lead to desired yield strength and stiffness, but incorporation of these rigid reinforcers leads to a decrease in tensile ductility and impact toughness. Therefore by addition of both elastomeric phase and reinforcement in the PP matrix, a good balance of stiffness to toughness could be achieved in hybrid composite. The structure and mechanical properties of mineral filler-reinforced PP/elastomer blends are well documented in the literature,[1–7] but little information is available in the literature concerning the properties of short glass fiber(SGF) reinforced PP composites containing an elastomeric phase.

Jancar et al.[8] studied the effect of elastomer content on the yielding and impact behavior of maleated PP/EPR/SGF hybrids. They showed that the Charpy notched impact strength of composites at −20°C increases with increasing volume fraction of EPR. Large plastic deformation in the fiber–matrix interface and fiber pull out are the primary energy dissipative processes during yielding and impact fracture. Tam et al.[9] also showed that fiber debonding and pull out are the main energy absorption mechanisms for PP/EPR/SGF hybrids.

Micro structural parameters such as matrix type, size, and percentage of rubber particles, volume fraction, and length of fibers and matrix/fiber interface have strong effect on the mechanical performance of hybrid composites. Furthermore, the addition of appropriate compatibilizers during melt processing of composites is known to improve their mechanical performance, as a result of increasing interfacial adhesion between the fibers and matrices of composites. Tjong et al.[10,11] studied the effect of interface strength of matrix/fiber on the mechanical properties of PP/SEBS/SGF hybrid and showed that by using MA-grafted-SEBS as compatibilizer, creates a strong interface between fiber and rubber as well as fiber/matrix and causes an increase in tensile and impact strengths of the composites. Also their studies revealed that it is inefficient to improve the impact strength of the blend via grafting of both PP and SEBS with MA, since there is an optimum amount for interfacial strength. Kelnar[12] studied

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Contract grant sponsor: Petrochemical Technology and Research Company.

Journal of Applied Polymer Science, Vol. 104, 2704–2710 (2007)

properties of PP/EPR/SGF hybrid composite while PP and EPR were grafted by acrylic acid and showed that very strong interfacial bonding between SGF and PP matrix can impair the toughness of the composites. Morphology of rubber particles size is another important factor, which affects mechanical properties of these composites. Wu[13] studied toughening of nylon 6.6 by different active and nonactive rubbers. His studies indicated that at constant rubber content, there is a sharp brittle-tough failure at a critical size of rubber particles. The same results have been reported by Oshinski[14] in toughening of nylon 6.6 by SEBS and SEBS-MA. Regarding the effect of rubber particle size on the toughening phenomena, Wu have introduced a term ligament length, Γ (distance between two rubber particles) and showed that brittle-tough transition occurs at a critical thickness (Γ_C).[13] However, little work is done on the effect of rubber particle size and morphological studies on the properties of hybrid composites. To study this effect and explore mechanical properties and morphology of PP/SEBS-MA/SGF hybrid composites, the present work was carried out.

EXPERIMENTAL

Materials

Polypropylene (PP) (PI0800) with density and MFI 0.9 g/cm^3, 10.5 g/10 min, respectively, was supplied from Bandar Imam Petrochemical Company. SEBS (kraton G1652) and SEBS-MA (kraton FG1901x) copolymers were obtained from shell company. The copolymers had PS block and central ethylene-butylene (EB) block molecular weights of 7500 and 37,500, respectively, and a PS weight fraction of 28.6%. The MA (maleic anhydride) content in kraton FG1901x was 1.84 (wt %). Short glass fibers (SGF) (ECS 305) with diameter of 13 μm manufactured in Korea was used as reinforcement.

Blending

The composition of the hybrid composites samples prepared are listed in Table I. All materials were dried separately in ovens for more than 24 h under vacuum at 90°C. To prepare the hybrid composite samples, PP and SEBS-MA (or SEBS) granules were first blended by using a modular twin screw extruder (ZSK 25), then prepared blends after drying were mixed with SGF using the same extruder with an operating temperature profile of 150, 160, 170, 175, 180, 185°C and mixing speed of 200 rpm. The extrudate strands were granulized and then dried at 90°C under vacuum for 24 h. Dried granules were in injection molded to produce samples for mechanical tests. For injection molding process, temperature profile of 190, 210, 210°C were used.

TABLE I
Composition (wt %) of the Hybrid Samples Studied

Samples	PP	SEBS-MA	SEBS	SGF	Irganox (Phr)
C_0	78.5	12.5	–	–	0.5
C_1	75	5	–	20	0.5
C_2	70	10	–	20	0.5
C_3	65	15	–	20	0.5
C_4	60	20	–	20	0.5
C_5	75	15	–	10	0.5
C_6	55	15	–	30	0.5
C_7	65	–	15	20	0.5
C_8	90	–	–	10	0.5
C_9	80	–	–	20	0.5

Morphology observation

Samples ~ 10 mm long were cut from midsections of tensile bars and subsequently were fractured in liquid nitrogen along the injection molding direction. The cryo fractured samples were etched in a tetrahydrofuran (THF) for 6 h such that the elastomeric particles from the matrix would be dissolved. They were then washed with fresh THF and dried in an oven operated at 30°C. Finally, the surfaces were coated with a thin layer of gold before examination with a scanning electron microscope (XL-30). Image analysis was used to determine rubber particles size.

Rheological measurements

The melt-state linear viscoelastic properties of samples were studied using a rheometric mechanical spectrometer, RMS (Paar Physica USD200) equipped with parallel plate geometry. All measurements were performed in a solution mode with strain 1% and temperature of 190°C.

Mechanical measurements

The static tensile behavior of the hybrid samples were determined at 23°C using an universal tensile machine (Zwick model) with a crosshead speed of 50 mm/min. Test specimens were prepared by injection molding and tested according to ASTM D638. Five specimens of each composition were tested, and the average value was reported. Notched samples for Izod impact tests (ASTM D256) were cut from the injection molded plaques. The impact tests were carried out with an impact tester (Ueshima U-F model) at 23°C. The fracture surfaces of hybrid composites were also examined with scanning electron microscopy (SEM).

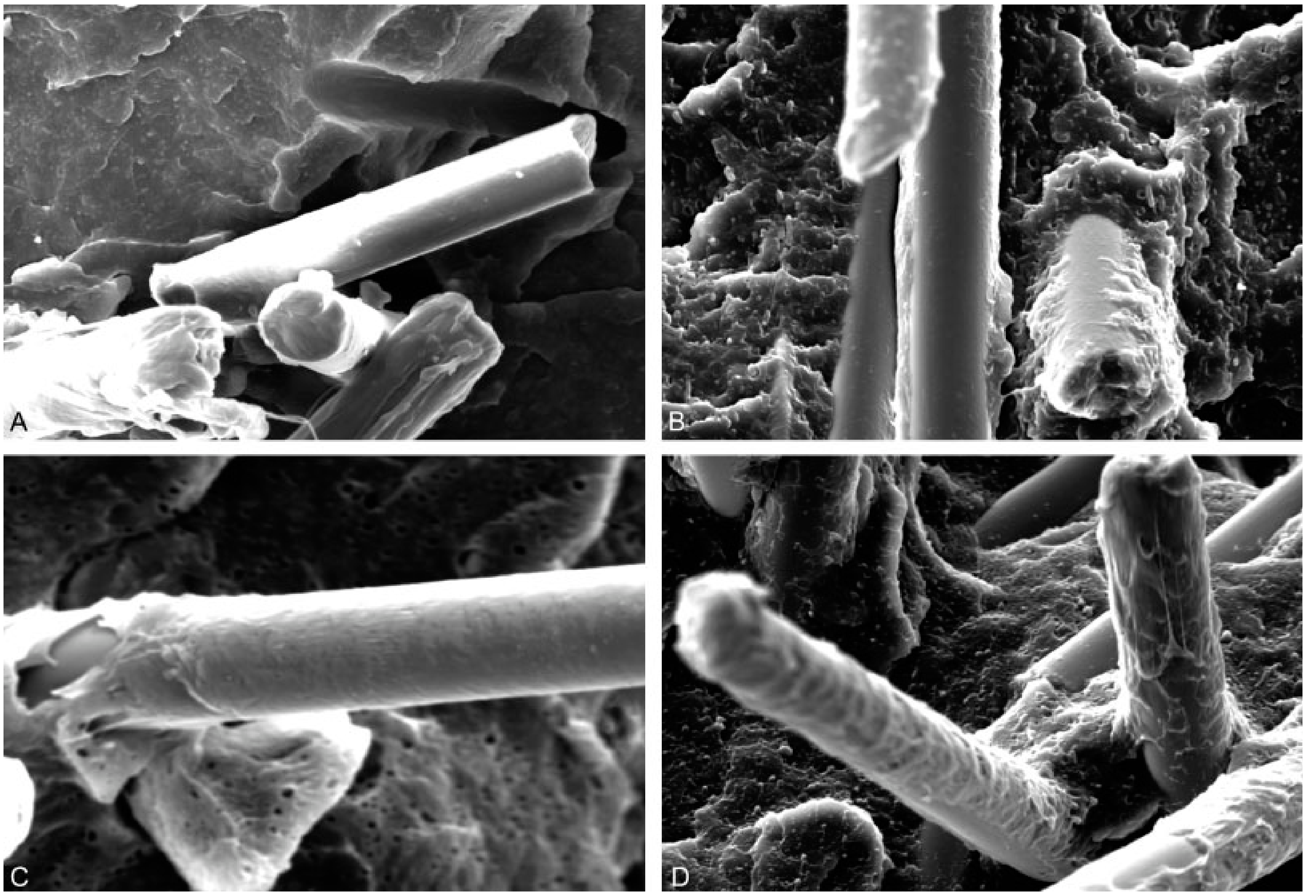

Figure 1 SEM micrographs showing fracture surfaces of (a) PP/SEBS/SGF hybrid, (b–d) PP/SEBS-MA/SGF hybrid.

RESULTS AND DISCUSSION

Morphology study

Figure 1 shows SEM micrographs of PP/SEBS/SGF and PP/SEBS-MA/SGF hybrids. As it can be seen in Figure 1(a), the extent of fiber pull out and debonding of SGF from the matrix is much greater when compared with other three samples containing compatibilizer in Figure 1(b–d). The fiber surfaces of PP/SEBS/SGF hybrid sample are almost free of rubber, indicating that the bonding between the glass fiber and matrix is approximately weak. In this hybrid sample, the interface between PP and SEBS is fairly strong due to the compatibility of PP and SEBS phases because SEBS could diffuse into the PP phase under the formation of micelles[15] (mid block structure of SEBS is close to that of PP). However, the interaction between SGF and PP is limited because SGF has a polar surface and PP is a non polar polyolefin. In contrast, the fiber surfaces of PP/SEBS-MA/SGF composite were coated with matrix material in Figure 1(b–d). This photograph indicated that a strong bonding developed between SGF and SEBS. This bonding was due to the fact that the MA functional groups grafted to the ethylene butylenes (EB) mid block of SEBS could react with hydroxyl groups on the SGF surfaces during compounding. The reaction between SEBS-MA and SGF can be depicted as follows:

Thus adding SEBS-MA copolymer into PP/SGF composite can introduce a ductile interface between SGF and PP matrix. This rubbery SEBS sheathed layer can prevent the fiber and PP matrix from brittle fracture at the early stages of impact. From SEM observations, it appears that a stronger interface promotes fiber assisted localized plasticity, whereas a weaker interface favors fiber pull out. Figure 2(a–c) presents cross-sectional SEM micrographs for samples C_2, C_3, and C_4 in which rubber concentration

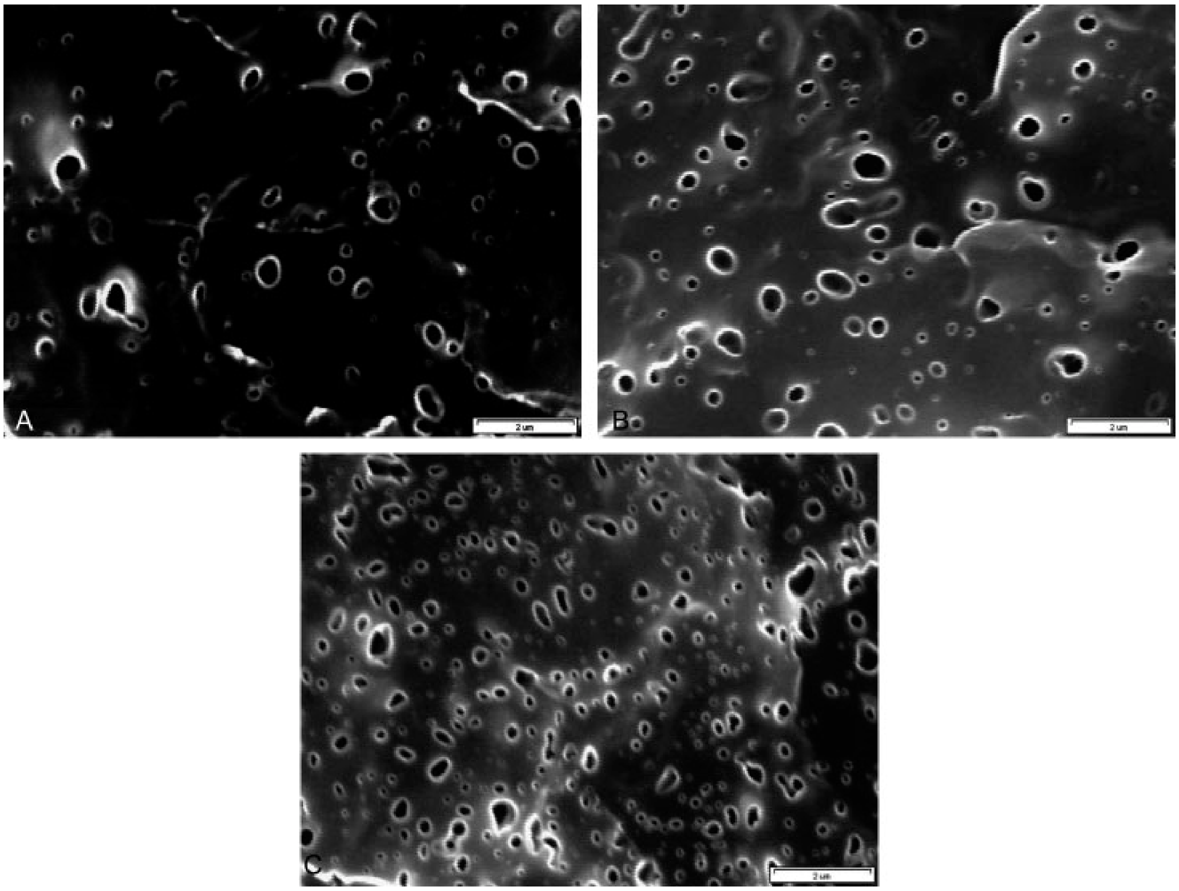

Figure 2 SEM micrographs showing the dispersion of SEBS-MA particles in the matrices of PP/SEBS-MA/SGF hybrids with different rubber concentration: (a) 10%, (b) 15%, (c) 20%.

increase from 10 to 20%, respectively, and SGF content of these hybrids was fixed at 20 % wt. By comparing these results, one may notice that with increasing rubber content, rubber particles size become smaller and dispersion of particles were improved. Decrease in rubber particles size could be due to the stronger interfacial adhesion between SEBS-MA and SGF phases. Because of the presence of third phase (glass fibers) in the hybrid and the affinity of this phase to react and absorb functionalized elastomeric phase(SEBS-MA), increasing rubber content to the hybrid enhances interface layer on the glass fibers and this leads to decrease in the amount of rubber, which is dispersed in the matrix. Since the surface area of fibers is much greater than the surface area of individual rubber particles, collision of rubber particles and fiber surfaces are favored and coalescence of rubber particles are prevented. During mixing process, applying shear also leads to smaller particles.

Rheological behavior

Figure 3(a) shows dynamic viscosity (η') and storage modulus (G') as a function of angular frequency (ω) for samples C_3, C_7 (with 15% rubber and 20% short glass fiber) and pure PP. Similar results obtained for PP, SEBS and SEBS-MA granules are also shown in Figure 3(b). As the concentration of the short fibers is lower than that reported for φ_m of short fibers (0.3), the increase in viscosity and elasticity of the hybrid samples compared with PP at low shear rate range can be attributed to the increase of the interfacial adhesion between SGF and the matrix caused by the SEBS compatibilizer and partly due to higher viscosity of rubber phase compared with PP matrix as shown in Figure 3(b). Having accepted this explanation, the viscosity as well as the storage modulus of sample C_3 are expected to be greater than those of sample C_7 because of its stronger interfacial interaction as revealed by SEM results in Figure 1. However, as it can be seen in Figure 3(a), viscosity and storage modulus of these two samples are very close. The reason behind is that in sample C_7 due to lower absorption of rubber particles on the fibers (lower interfacial interaction) greater amount of SEBS-MA rubber phase will be remain in the matrix as a dispersed phase, which can itself lead to increasing viscosity and elasticity of sample C_7 as a separate parameter.

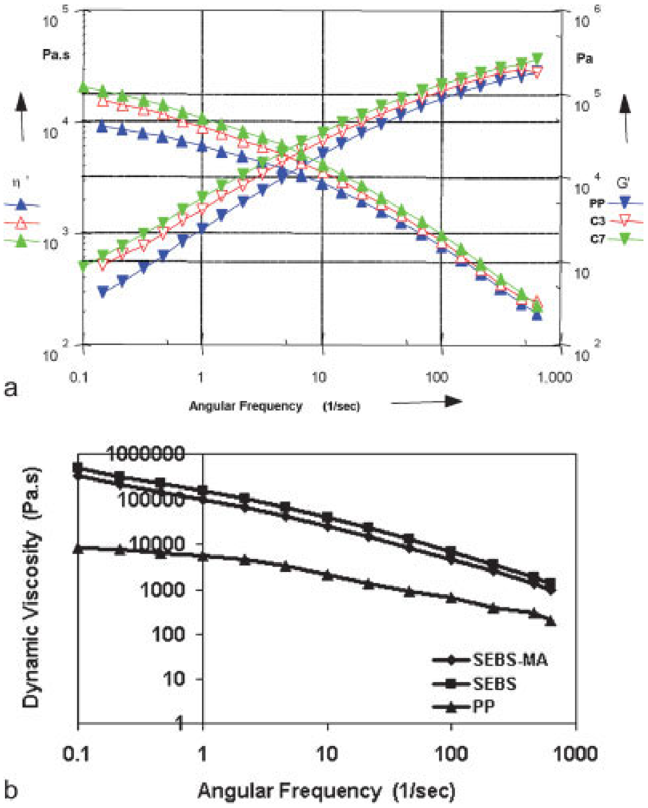

Figure 3 Dynamic viscosity and storage modulus of (a) compatible (C_3) and incompatible (C_7) hybrid composites, (b) pure PP, SEBS, and SEBS-MA granules. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Tensile studies

Figure 4(a) shows the tensile yield strength as a function of SEBS-MA content for the hybrid samples C_1–C_4 with rubber content 5–20%, respectively, and fiber content 20%. The stress–strain curves obtain for above hybrid samples are shown in Figure 4(b). It is interesting to note that the yield strength of the samples increase with the rubber content up to some concentration (10%) above which it declines. From these results, one may suggest two distinct roles for the elastomeric phase, at low concentration, the rubber phase act as interfacial interaction resulting in lowering the PP crystallinity as well as lowering the PP chain mobility in the amorphous region both increasing the yield strength of the samples. However, by further increase in the rubber content, effect of the rubber particles as the third phase becomes dominate and leading to yield strength decrease.

Izod impact properties

Figure 5 shows the results of Notched Izod impact strength of samples C_1–C_4 at room temperature. As it can be seen, the rate of increasing impact strength of the hybrid composite samples increase when the rubber content exceeds by 10%. It is generally known that impact strength of polymeric materials can directly be related to the fracture toughness G_c defined by relation: $G_c = G_0 + \Psi$, where G_0 is intrinsic fracture toughness associated with the strain linear elastic energy and Ψ is loss parameter. The impact strength of hybrid samples containing less than 10% of SEBS-MA is mainly controlled by the G_0 whose value is determined by the interfacial adhesion between PP matrix and SGF, while, for the samples containing more than 10% of SEBS-MA, the impact strength is determined by value of Ψ. By further addition of rubber content (up to 20%), rubber particle size decreases as shown in Figure 2 and in the same time particle–particle distance (matrix ligament, Γ) also decreases. According to Wu,[13] there is a critical value for matrix ligament (Γ_C), below which, rubber particles can enhance toughening of ductile matrices, since the cavitation mechanisms contributes to higher energy dissipation during fail-

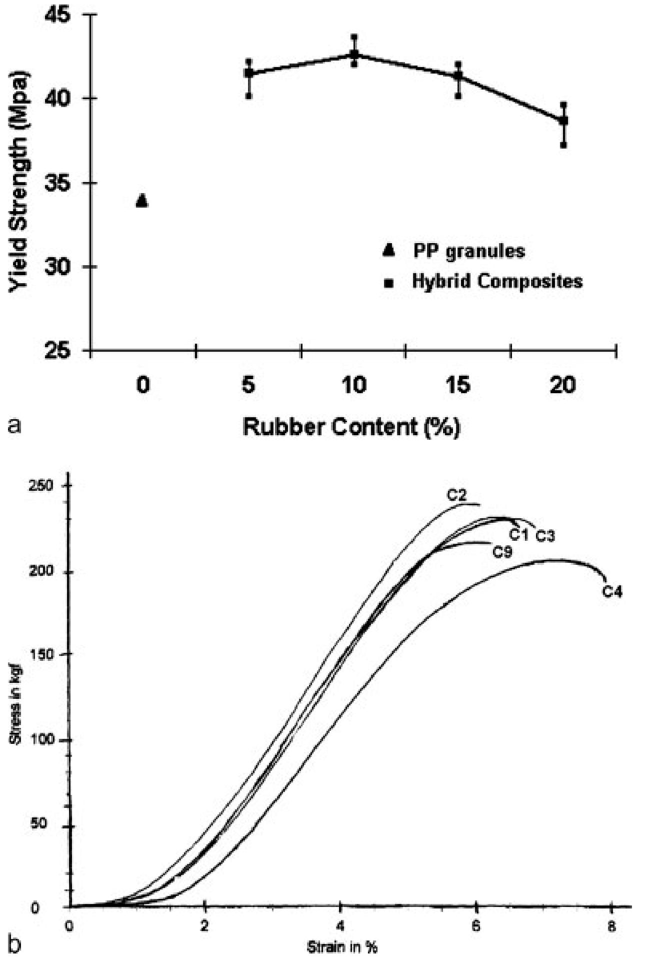

Figure 4 Tensile behavior of hybrid samples (a) yield strength versus rubber content (b) stress–strain curves for PP/SEBS-MA/SGF hybrid composites containing 20% short glass fiber.

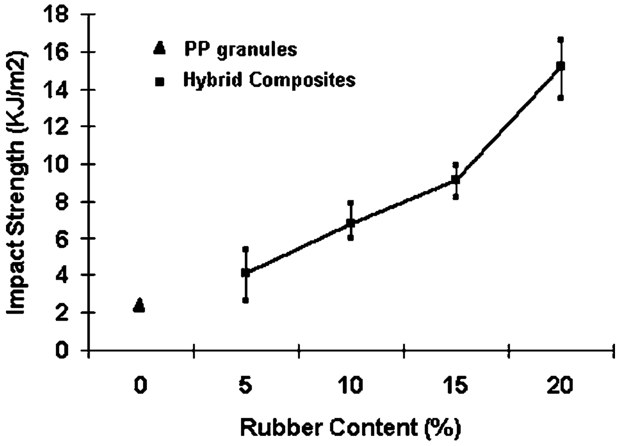

Figure 5 Variation of Notched Izod impact strength with rubber content for compatibilized hybrid composites containing 20% short glass fiber.

ure. Therefore, in the range of 10–20% rubber content, term Ψ is a dominating factor in increase of fracture toughness. Figure 6 presents impact strength versus glass fiber content for hybrids containing 10–30% fiber and 15% rubber content. According to this figure, increasing of impact strength with increasing fiber content is believed to be due to enhance in the G_0 of the composite and so increasing of G_c is achieved.

Relationship between impact and yield strength

It is generally known that incorporation of glass fiber into PP increases the yield stress, stiffness, and dimensional stability of glass fiber reinforced composites. On the other hand, addition of rubber to PP increases impact strength through reducing the yield strength of PP matrix. A good balance between stiffness to toughness for these composite samples could be achieved by use of optimum amount of glass fibers and elastomer into PP matrix. Figure 7 shows relationship between yield and impact strength of PP/SEBS-MA/SGF hybrid at different rubber content. As it can be seen from Figure 7, the yield stress of hybrid samples, in contrast to toughened samples whose yield strength decreases linearly with increasing rubber content, enhance with increasing of rubber concentration up to 10%, above which it declines linearly. This can be attributed to the dominating effect of G_0 resulting from SGF on enhancing of yield and impact strength of the hybrid samples and distinct roles for the elastomeric phase as compatibilizer on increasing of interfacial adhesion in which the rubber concentration is below 10%. This is evidenced by the result shown in Figures 4, 5, and 6.

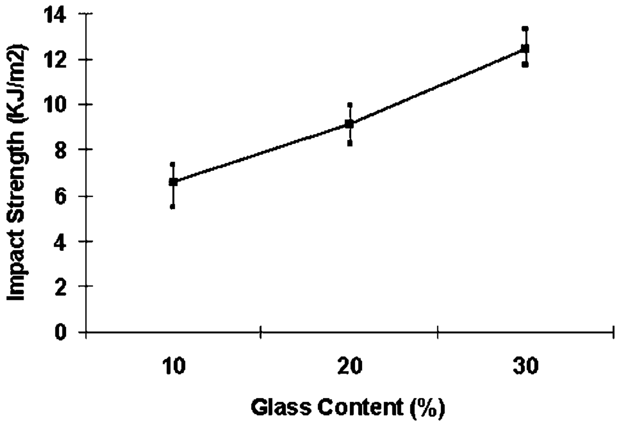

Figure 6 Impact strength versus glass fibers content for PP/SEBS-MA/SGF hybrid composites containing 15% SEBS-MA.

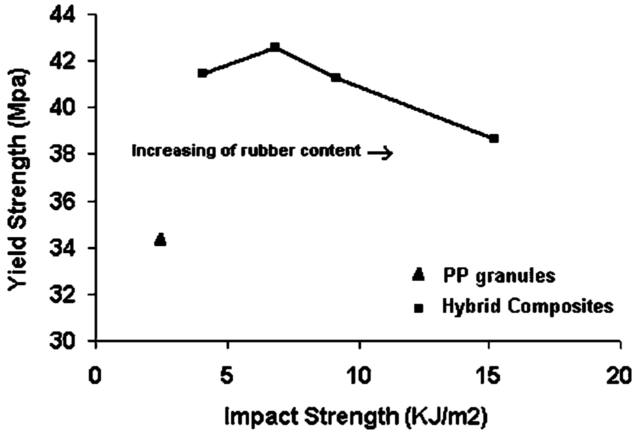

Figure 7 Variation of yield strength versus impact strength of hybrid composites at different rubber content.

For purpose of comparison, yield and impact strengths of pure PP have been shown in Figure 7. For example, impact and tensile strength of pure PP, by addition of 20% SGF and 15% rubber have increased 195 and 65%, respectively. By use of Figure 7, different combination of rubber and short glass fiber could be chosen for different industrial applications.

CONCLUSIONS

PP/SEBS-MA/SGF and PP/SEBS/SGF hybrid composites were prepared by melt mixing in a modular twin screw extruder. Morphological, rheological, and mechanical properties of the hybrid samples were investigated. Morphological observations revealed that a strong interface between fiber and matrix was formed in PP/SEBS-MA/SGF hybrids. By increasing rubber content in the hybrid samples, rubber particle size decreased. This was believed to be due to the stronger adhesion between SEBS-MA and SGF phases and increase in the collision of rubber particle and short glass fiber leading to decrease of coalescence of rubber particles. The results of melt rheological measurments showed that viscosity of compatibilized (C_3) and uncompatibilized (C_7) hybrid composites were nearly the same because of mutual action between the interfacial interaction in maleated hybrid sample and high amount of rubber particles dispersed in the matrix in uncompatibilized hybrid. Mechanical measurements indicated that increasing of rubber content up to 10% led to an increase in the yield strength. This could be attributed to lowering the PP crystallinity as well as lowering the PP chain mobility in the amorphous region caused by elastomeric phase. The rate of increasing impact strength of the hybrid samples with increasing the rubber content was found to be different. The impact strength of hybrid samples containing less than 10% SEBS-MA was mainly controlled by the G_0 whose value was determined by the interfacial adhesion between matrix–glass fibers. In the range of 10–20% rubber content, the loss parameter (Ψ) was dominating factor in increasing of fracture toughness. Increasing glass fiber content up to 30%, led to an increase in impact strengths. Increment in the impact strength of the hybrid sample containing 30% glass fiber was due to increment in the G_0 factor of the system, which led to an increase in the G_c of the composite. There was a nonlinearly relationship between yield and impact strength of the PP/SEBS-MA/SGF hybrid, in contrast to toughened samples, whose yield strength decreased linearly with increasing rubber content. This could be attributed to the dominating effect of G_0 resulting from addition of SGF and distinct roles of the elastomeric phase as compatibilizer. Addition of 20% short glass fiber and 15% rubber to pure PP led to an increase in the impact and yield strength of 195 and 65%, respectively.

Authors thank Dr. A. Taeb and Dr. M. Ebrahimi for their useful supports.

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