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Compatibilization of PP/elastomer/microsilica composites with functionalized polyolefins: Effect on microstructure and mechanical properties

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Abstract

The morphology and mechanical properties of polypropylene/elastomer/silica composites were investigated with the aim of improving stiffness and impact resistance. Two different types of silica were tested: Precipitated silica and polymer grade microsilica (silica fume). The composites were compatibilized with commercial polypropylene and polyethylene containing maleic anhydride functionality as a means of controlling their microstructure and ultimately their mechanical properties. Comparisons were made with surface coated silica and hydroxyl-functionalized copolymers prepared with metallocene catalysts. The effect of adding the polymeric compatibilizers was assessed by morphology studies, thermal analysis and mechanical testing. Significant improvements in impact strength were obtained by tailoring the microstructure of polypropylene/elastomer/microsilica composites. With introduction of PP-*g*-MAH as compatibilizer, stiffness was enhanced simultaneously with impact strength. DSC curves of crystallization provided evidence to support the formation of different microstructures.

Keywords: Compatibilization; Functionalized polyolefins; Microsilica

1. Introduction

The insufficient low-temperature impact strength of polypropylene (PP) significantly limits its wider application as an engineering plastic. Compounding PP with a dispersed elastomeric phase, such as an ethylene–propylene rubber (EPR) copolymer, has been of wide interest because it has been shown to increase the overall toughness of the polypropylene. An unfortunate consequence is a reduction in stiffness and strength. Any efforts made to overcome this shortcoming must ensure that easy processability is not compromised [1,2].

Multi-component PP composites are of interest to researchers in both industry and academia, as they make possible simultaneous improvements in stiffness and toughness. Most often, these composites contain an elastomer to improve the impact resistance and a filler to increase stiffness. Numerous studies with different elastomers and fillers have been carried out in recent years [3–8]. Two extremes in the phase structure have been observed in these composites: Separate dispersion of the filler in the polymer matrix and encapsulation of the filler by the elastomer. The extent to which one of these structures develops depends on many factors, including the surface energies of the components, processing conditions and the geometry of the rigid filler particles. Particle size is another important factor. Fillers generally have wide particle distributions and, as a result, composites often contain small particles that are encapsulated by the elastomer and larger ones that are not [1].

Particulate fillers commonly have highly polar hydrophilic surfaces, whereas the polymers (e.g. polypropylene) into which they are introduced are often non-polar and hydrophobic. Poor adhesion between the filler surface and the matrix is observed. In addition, achieving uniform dispersion of the fillers tends to be difficult. Modification of

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the filler surface through coating alters the properties of the surface, and the degree of interfacial adhesion may thereby be improved. Common coating agents for fillers containing hydroxyl groups are fatty acids and their salts (e.g. stearic acid). Filler coatings improve filler dispersion, which results in enhanced mechanical properties and easier processability. Short chains, such as those in stearic acid, are too short to entangle with the matrix, but are still capable of reducing interfacial tension [9,10]. An alternative method of improving the adhesion between filler particles and matrix in polyolefin composites is modification of the matrix itself.

Hydrophobic polyolefins can be made more hydrophilic by copolymerization or grafting with polar monomers. The polar groups are then able to interact with functional groups on the inorganic filler, while the long hydrocarbon tails are able to anchor to the polymer matrix through physical entanglements and van der Waals interactions. A bridge between the filler and the matrix is thereby established [11].

This paper describes studies on PP/elastomer/silica composites. Two different types of silica were tested: Precipitated silica and polymer grade microsilica (PG-MS). Elkem ASA and Mondo Minerals (now Omya group) possess a patent on the use of polymer grade microsilica as impact modifier in thermoplastics [12]. The morphology of the PP composites was investigated to gain insight into the types of microstructures formed when different polymeric compatibilizers are added. The effectiveness of several commercially available polymeric compatibilizers was assessed and comparison was made with hydroxyl-functionalized copolymers prepared in our laboratory. The study also aimed to explain, in terms of microstructure, the achieved improvements in stiffness and toughness.

2. Experimental

2.1. Materials

The impact-modified polypropylene was SB 35 11 J supplied by Borealis polymers. This is a block copolymer with a melt flow index of 3.5 g/10 min (230 °C/2.16 kg). SEM micrographs showed the size of the ethylene–propylene rubber (EPR) inclusions to be around 1 μm. Two different types of silica were tested: Precipitated silica (FK 310) and polymer grade microsilica (PG-MS). Details of these materials are given in Table 1.

The polymeric compatibilizers are listed in Tables 2 and 3. In addition to commercial grades (Table 2), two polymeric compatibilizers prepared in our laboratory with commercial metallocene catalysts were used. One of them was a copolymer of propylene and 10-undecenol and the other a copolymer of ethylene and 10-undecenol. Both were prepared by a reported polymerization procedure [13]. Table 3 shows the polymerization conditions and properties of these copolymers.

Table 1
Silica grades used in PP/EPR composites

Grade	Type of silica	Manufacturer	Surface treatment	Average primary particle size (μm)
Ultrasil (FK 310)	Precipitated	Degussa AG	No	5.5
Sipernat (D17)	Precipitated	Degussa AG	Yes (silane)	7
PG-MS (MS 983)	Silica fume	Elkem materials	No	0.15

2.2. Compounding

The composites contained 80-wt% PP/EPR and 20-wt% silica. When polymeric compatibilizer (10 wt%) was added to a composite, the PP/EPR phase was reduced by the amount of the compatibilizer. All commercial compatibilizers were dried overnight at 60 °C before blending.

The compounding was done in a co-rotating twin-screw midi-extruder (DSM, capacity 16 cm^3, screw length 150 mm) with a screw speed of 65 rpm. The extrusion temperature was 200 °C. After a 3-min mixing step, tensile and impact test specimens were injection-moulded using a mini-injection moulding machine (DSM). The barrel temperature was 200 °C, while the mould temperature was 100–105 °C for tensile test specimens and 50 °C for impact test specimens.

2.3. Characterization

Before testing, all specimens were conditioned at 23 °C and 50% relative humidity for 3–5 days. Tensile properties were characterized using an Instron 4204 universal testing machine with a test speed of 2 mm/min. The tests were conducted according to standard ISO 527-1993(E) using specimen type 1BA. Charpy impact strength tests of notched specimens with dimensions $4\times6\times50$ mm^3 were carried out according to standard ISO 179-1993(E) using a Zwick 5102 pendulum-type testing machine.

The phase structure of the composites was examined with a JEOL JSM-6330F field emission scanning electron microscope (FESEM). SEM images were taken from

Table 2
Commercial compatibilizers tested in PP/EPR/silica composites

Type	Functionality	Content of functionality (wt%)	Grade	Manufacturer
E/BA	Butyl acrylate	7.0	LE 6471	Borealis polymers
E/BA/MAH	Maleic anhydride	0.5	ME 0420	Borealis polymers
	Butyl acrylate	5.3		
PP-*g*-MAH	Maleic anhydride	0.5 (BA ~ 1)	BB 125 E	Borealis polymers

Table 3
Polymerizations performed with metallocene catalyst and properties of copolymers

Copolymer	Catalyst	$n_{com.}$ (mmol)	n_{cat} (μmol)	Al/Zr	$n_{Al}/n_{com.}$	T_p (°C)	P (bar)	t_p (min)	A (kg/(mol Zr*h))	M_w (g/mol)	M_w/M_n	T_m (°C)	ΔH (J/g)	Content of functionality (mol%)	Content of functionality (wt%)
PP-*co*-OH	$Me_2Si(2\text{-}Me\text{-}4\text{-}Ph\text{-}1\text{-}Ind)_2ZrCl_2$	9.0	1.5	2000	5.0	70	2.0	30	14,700	104,000	2.0	139	92	1.0	4.1
PE-*co*-OH	$Et(Ind)_2ZrCl_2$/MAO	10.0	5.0	8000	4.0	70	1.5	60	2900	94,000	2.8	127	153	1.0	5.9

cryogenically fractured surfaces of tensile test specimens. The fracture surfaces were etched with xylene to selectively dissolve the elastomeric phase, leaving the PP and silica in original form. The etching procedure was carried out in a thermostated ultrasonic bath at 20 °C for 20 min. All fracture surfaces were sputter-coated with gold. The electron micrographs were obtained with an acceleration voltage of 5.0 kV.

A Mettler Toledo Star DSC821^e was used to study the thermal behaviour and microstructure. Measurements were made on samples of approximately the same mass. Crystallization temperatures (T_c) and melting temperatures (T_m) were determined by cooling and then reheating the samples at 10 °C/min. The temperature ranged between 25 and 200 °C.

3. Results and discussion

3.1. Morphology

Morphologies of the uncompatibilized and some of the compatibilized blends of PP/EPR with polymer grade microsilica are presented in Fig. 1. The dark voids seen in Fig. 1(a) are the areas from which the elastomer has been selectively dissolved. The SEM micrographs show the PP/EPR blends to exhibit a distinct phase separation. PP is the continuous matrix in which the elastomer inclusions are dispersed. The dispersion of PG-MS particles in the PP/EPR/PG-MS composite is more or less uniform. In compatibilized PP/EPR/PG-MS composites, the location of the filler is the key factor defining the morphology.

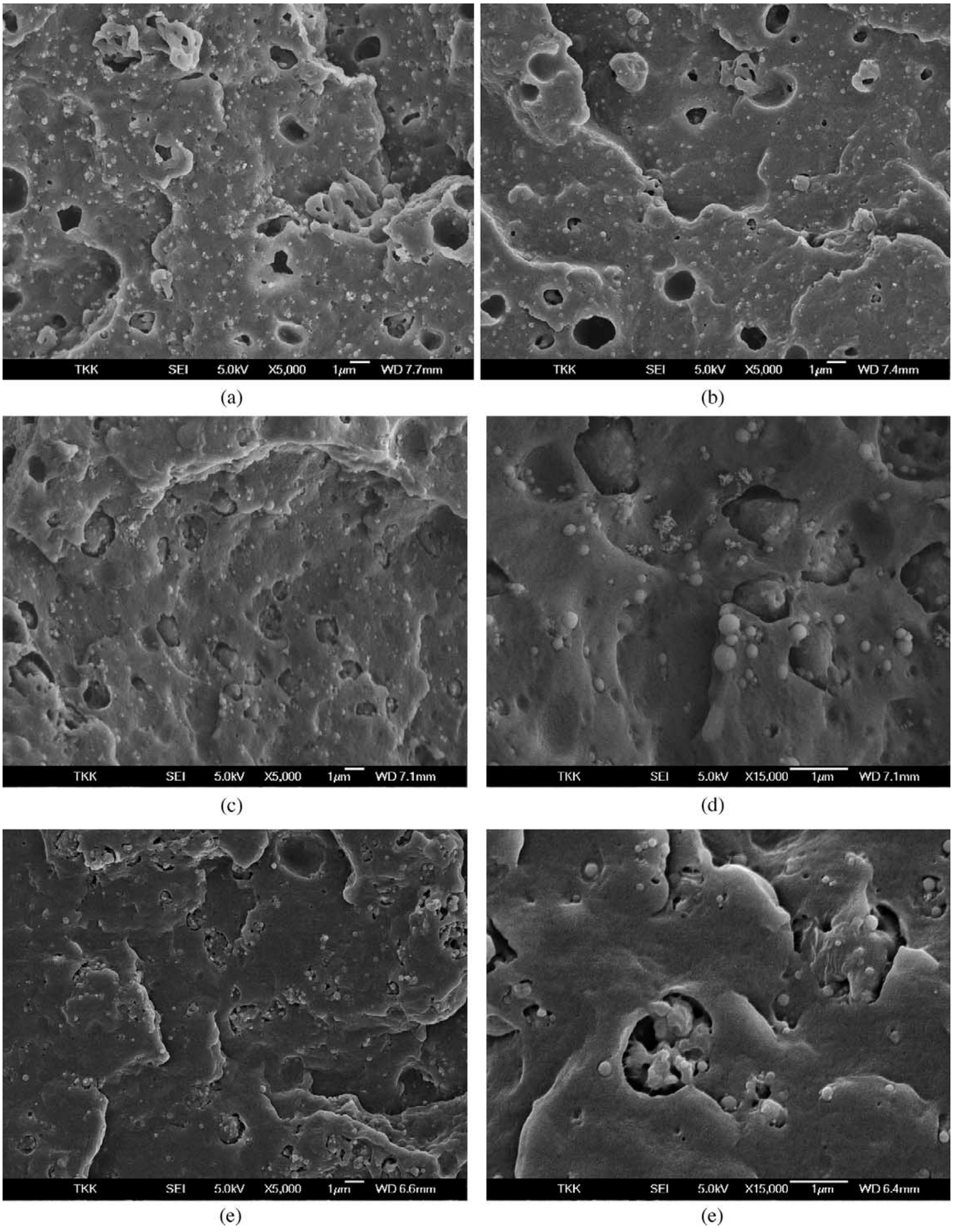
Introduction of different polymeric compatibilizers affected the location of the filler particles, which ultimately changed the microstructure. When E/BA was used as compatibilizer, the E/BA gravitated towards the EPR phase (Fig. 1(c) and (d)). This was concluded from the absence of large dark areas in the matrix. Smaller voids around the E/BA phase indicated that the EPR phase had been removed from these locations. The filler particles remained uniformly dispersed in the matrix. Gravitation towards the EPR phase also occurred with E/BA/MAH as compatibilizer (Fig. 1(e) and (f)). Evidently almost none of the E/BA/MAH phase was left dispersed in the PP matrix. Large amounts of the PG-MS also precipitated towards the EPR phase. It is highly probable that the maleic anhydride group (MAH) interacted with the OH functionality on the surface of the PG-MS, dragging the filler particle along with it towards the EPR phase. This resulted in the formation of a morphology closely resembling a core-shell microstructure. A further indication of this occurring was the increase in the total surface area of the rubber inclusions, which can be seen by inspecting Fig. 1(d) and (f). It has earlier been proposed [14–16] that when filler particles are encapsulated within the elastomer phase they increase the total surface area of the elastomer. The distance between the rubber particles is decreased as a result, and the compatibilized composite is more effective in preventing the propagation of microcracks, ultimately leading to improved toughness.

Fig. 1(b) shows how, with PP-*g*-MAH as compatibilizer, the microsilica particles were dispersed throughout the PP matrix, forming predominately a phase-separated microstructure. It is proposed that PP-*g*-MAH substantially improves the interfacial adhesion between the PG-MS and the PP matrix. The improved coating of the PG-MS particles, as compared with the particles in other composites, is an indication of this. In addition, some of the PG-MS particles gravitated towards the EPR phase, causing a slight degree of encapsulation. This is explained by the small amount of butyl acrylate (BA) that is present in this compatibilizer.

Fig. 2 shows the morphologies of compatibilized and uncompatibilized PP/EPR/FK 310 composites. As can be seen, the precipitated silica particles are much larger in size than the microsilica particles. The addition of E/BA/MAH as compatibilizer led to encapsulation of some of the filler particles by the elastomer. The degree of encapsulation, however, remained low owing to the numerous precipitated silica particles that were too large to become embedded in the rubber phase.

3.2. Thermal properties

DSC results for the PP/EPR binary blend and compatibilized and uncompatibilized PP/EPR/silica composites are summarized in Tables 4 and 5. Melting temperatures showed no significant trends, and the slight deviations in temperature fell within margins of error. Fig. 3 shows DSC curves for the crystallization behaviour of compatibilized and uncompatibilized PP/EPR/PG-MS composites. As has



(a) (b)

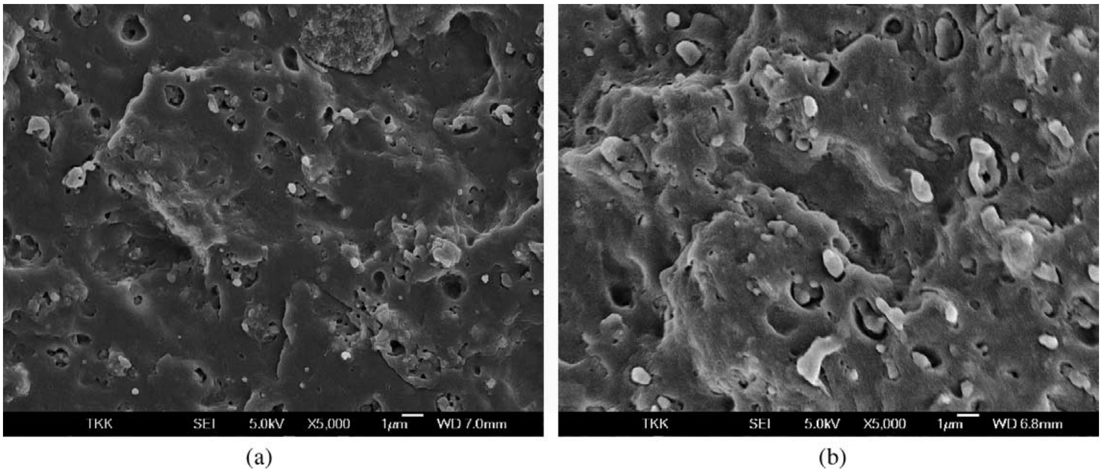
(c) (d)

(e) (e)

Fig. 1. SEM micrographs of PP/EPR/PG-MS composites. (a) PP/EPR/PG-MS (80/20) (×5000), (b) PP/EPR/PG-MS/PP-*g*-MAH (70/20/10) (×5000), (c) PP/EPR/PG-MS/(E/BA) (70/20/10) (×5000), (d) PP/EPR/PG-MS/(E/BA) (70/20/10) (×15,000), (e) PP/EPR/PG-MS/(E/BA/MAH) (70/20/10) (×5000), (f) PP/EPR/PG-MS/(E/BA/MAH) (70/20/10) (×15,000).

been shown [1,9,17], some filler surfaces can act as nucleating centres. The shift of the whole crystallization exotherm to higher temperature is an indication of a strong nucleation effect. As can be seen from Table 4, introducing PG-MS into the PP/EPR binary system increased the crystallization temperature (T_c) of PP, but had no noticeable effect on the T_c of the EPR phase. From this it was inferred that most of the filler particles remained in contact with the PP phase and did not become encapsulated by the EPR phase. Changes in the crystallization temperature data when different compatibilizers were introduced into the PP/EPR/PG-MS system confirm the formation of different microstructures.

Addition of E/BA/MAH to the PP/EPR/PG-MS



(a) (b)

Fig. 2. SEM micrographs of PP/EPR/FK 310 composites (×5000). (a) PP/EPR/FK 310 (80/20), (b) PP/EPR/FK 310/(E/BA/MAH) (70/20/10).

composite resulted in a marked change in the crystallization temperature of the EPR phase: The T_c of EPR increased from 102.1 to 108.4 °C. This indicates that part of the filler particles were embedded in the EPR phase, where they acted as nucleating agents. The slightly lower crystallization temperature of the PP phase upon compatibilization is attributed to the loss of nucleating efficiency of the mainly encapsulated PG-MS. As a result, fewer filler particles remain in direct contact with the PP surface. Similar results have been reported for other PP/elastomer/filler systems [18]. The above observation supports the SEM micrograph findings, which suggested the formation of a core-shell microstructure.

When PP-*g*-MAH was used as compatibilizer, the crystallization temperature of the PP phase increased noticeably while that of EPR was increased only slightly. This strongly suggests the formation of a phase-separated microstructure, in which most of the PG-MS particles remain attached to the PP component of the blend. The increase in T_c of the PP phase is thought to be due to increased interaction between the PG-MS and the PP matrix, which leads to improved contact between the two phases [19]. The slight increase in the T_c of the EPR phase is attributed to the low degree of encapsulation resulting from the small amount of BA present in the compatibilizer. Once again, the results support the conclusions from SEM findings.

The application of PP-*co*-OH as compatibilizer improved the nucleating activity of the PG-MS even further and promoted crystallization during the cooling process. An explanation for this is that there are strong interactions between the OH groups on the surface of the PG-MS and the OH groups of the hydroxyl-functionalized copolymers. Hence, the filler particles, which otherwise tend to form aggregates, are more likely to be uniformly dispersed within the matrix, providing more centres from which the nucleation may begin [10]. The T_c of the EPR phase is unchanged.

Precipitated silica was more active as a nucleating agent than PG-MS (Table 4). Differences in surface chemistry have been shown to influence the crystallization behaviour [9]. Precipitated silica has a higher concentration of

Table 4
Crystallization temperatures of PP/EPR/FK 310 and PP/EPR/PG-MS composites with compatibilizer addition of 10 wt%

Composite	Temperature of crystallization of PP phase (°C)	Temperature of crystallization of EPR phase (°C)
PP/EPR	114.9	102.1
+FK310	122.2	103.1
+D17	116.2	102.4
+FK310+E/BA/MAH	118.1	115.0
+FK310+PP-*g*-MAH	121.1	103.7
+FK310+PE-*co*-OH	118.7	113.9
+PG-MS	116.9	102.1
+PG-MS+E/BA	120.1	102.1
+PG-MS+E/BA/MAH	116.3	108.4
+PG-MS+PP-*g*-MAH	119.1	104.1
+PG-MS+PP-*co*-OH	128.2	101.7

Table 5
Melting temperatures of PP/EPR/FK310 and PP/EPR/PG-MS composites with compatibilizer addition of 10 wt%

Composite	Melting temperature of PP phase (°C)	Melting temperature of EPR phase (°C)
PP/EPR	160.2	118.2
+FK310	164.1	118.5
+D17	160.5	117.8
+FK310+E/BA/MAH	163.7	125.6
+FK310+PP-*g*-MAH	164.9	119.4
+FK310+PE-*co*-OH	163.9	122.0
+PG-MS	162.3	118.0
+PG-MS+E/BA	162.0	–
+PG-MS+E/BA/MAH	164.3	121.9
+PG-MS+PP-*g*-MAH	163.1	118.4
+PG-MS+PP-*co*-OH	163.1	117.8

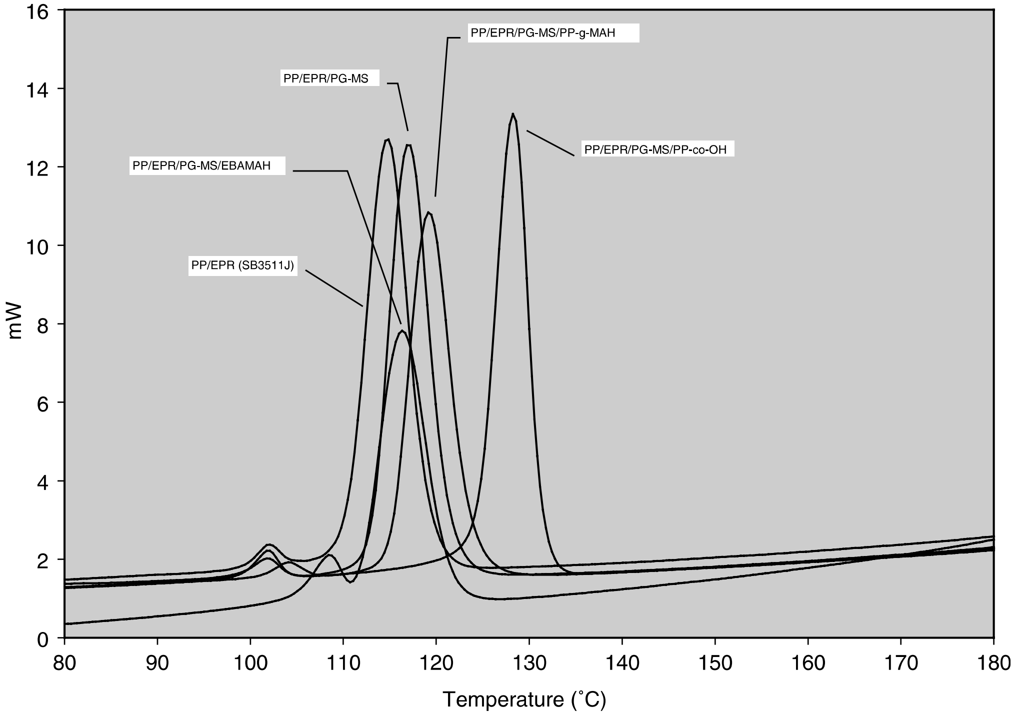


Fig. 3. Cooling thermograms of PP/EPR, uncompatibilized and some compatibilized PP/EPR/PG-MS composites.

hydroxyl groups on its surface and high interfacial tension between the non-polar PP matrix and the extremely polar hydroxyl groups may be the root cause of the effectiveness of the silica as a nucleating agent.

3.3. Mechanical properties

Table 6 shows the results of tensile and impact tests on the series of PP/EPR blends modified with precipitated silica (FK 310) and polymer grade microsilica (PG-MS). Fig. 4 shows schematically the tensile modulus and impact strength of the tested materials. The addition of 20 wt% of FK 310 or PG-MS clearly increased the tensile modulus of PP/EPR. At the same time the samples became much more brittle, as can be seen in the lower values of impact strength and elongation at break. Impact strength was decreased less by the introduction of PG-MS than the introduction of FK 310, probably because of the smaller particle size of the PG-MS. When elastomer and filler particles are phase-separated in the PP matrix, the filler particles tend to produce a range of microcracks in response to an applied impact. This occurs especially at low temperatures. Elastomer particles hinder crack propagation, but are not fully effective. Long and Shanks [14] have suggested that if the rigid filler particles are covered by elastomer and a core-shell structure is formed, microcracks will not be initiated by the filler particles and a yielded zone will form around the elastomer particle. Unlike the particles of precipitated silica, polymer grade microsilica particles are small enough to be encapsulated by the elastomer; so cracking is deterred

Table 6
Tensile modulus (E), tensile strength (σ), elongation at break (ε_b), and charpy impact strength of notched specimens of PP/EPR/FK 310 and PP/EPR/PG-MS composites with compatibilizer addition of 10 wt%

Composite	E (MPa)	(SD)	σ (MPa)	(SD)	ε_b (%)	(SD)	Charpy impact strength (notched) (kJ/m^2)	(SD)
PP/EPR	595	36	24.0	1.0	293	130	13.2 (C)	1.0
+FK310	763	14	23.0	0.4	24	4	6.5 (C)	0.7
+D17	736	31	22.0	0.6	76	35	10.7 (C)	0.5
+FK310+E/BA/MAH	647	19	22.5	0.8	28	5	9.7 (C/H)	0.6
+FK310+PP-*g*-MAH	671	34	22.5	0.6	24	7	8.8 (C/H)	0.3
+FK310+PE-*co*-OH	695	13	21.5	0.9	28	6	9.5 (H)	0.5
+PG-MS	757	47	24.3	0.3	92	30	10.2 (C)	1.0
+PG-MS+E/BA	699	19	19.5	0.4	89	28	12.3 (C)	2.4
+PG-MS+E/BA/MAH	531	15	22.5	0.7	99	10	30.7 (H)	4.0
+PG-MS+PP-*g*-MAH	868	13	23.1	0.3	109	12	22.3 (C)	4.9
+PG-MS+PP-*co*-OH	838	12	24.1	0.6	24	20	7.2 (C)	0.7

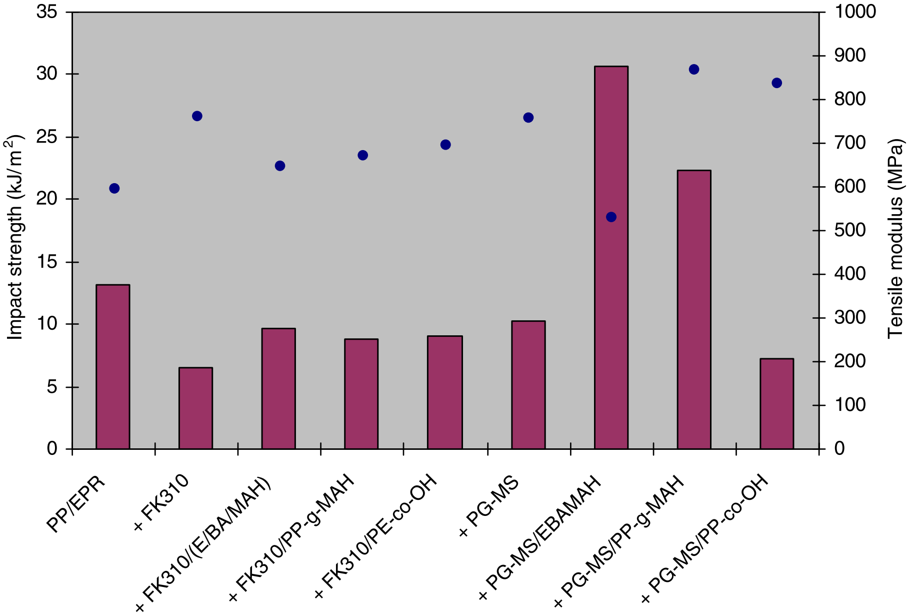


Fig. 4. Charpy impact strength (columns) and tensile modulus (points) of notched specimens of PP/EPR/FK310 and PP/EPR/PG-MS composites with compatibilizer addition of 10 wt%.

and impact strength is higher [20]. Since, the usual method in industry to minimize the loss of toughness is to use coating agents, we also prepared blends of PP/EPR with silane-treated precipitated silica (D17). As expected, the toughness was slightly improved in the case of the surface-treated precipitated silica.

Addition of commercially available functionalized polyolefins to PP/EPR/PG-MS composites resulted in considerable improvement in impact strength. The addition of E/BA/MAH was most effective, resulting in a 300% increase in notched impact strength. This occurred at the expense of decreased stiffness. The cause of these changes is related to the formation of a distinct microstructure. The morphology studies discussed above showed the PP/EPR/PG-MS/(E/BA/MAH) system to consist largely of a core-shell microstructure and numerous studies have shown that a core-shell morphology enhances impact strength dramatically. Decreased stiffness can be explained by the fewer filler particles in the PP matrix. The addition of PP-*g*-MAH as compatibilizer more than doubled the impact strength, and stiffness was enhanced as well. Once again, the morphology studies offer an explanation. Since the microstructure was predominately phase-separated, enough PG-MS remained in the PP matrix phase to effectively stiffen it. Both the small amounts of filler particles that gravitated towards the elastomer phase and the improved adhesion between the PG-MS and the PP matrix contributed to the improvement in toughness. The copolymer prepared with metallocene catalyst was unsuccessful in improving toughness, perhaps because of its lower molar mass. Alternatively, the nature of the functional groups of the copolymer may have hindered its miscibility with the PP matrix.

The addition of compatibilizers to precipitated silica composites did not lead to dramatic improvements in toughness. Moderate improvements in impact strength were achieved, but all other mechanical properties remained at the same level or were deteriorated. As a result of its larger average particle size, only small amounts of the precipitated silica particles were encapsulated by the EPR phase.

4. Conclusions

This work has shown that the microstructure of PP/EPR/PG-MS composites can be controlled through the selection of suitable compatibilizers. Controlling microstructure is the most straightforward route to the improvement in stiffness and toughness. Selection of a suitable filler particle size also plays a crucial role. Precipitated silica, which was of larger particle size than polymer grade microsilica, was not encapsulated by the EPR phase to any large extent and the microstructure was not predominately core–shell. As well, a slight difference in the surface chemistries of the precipitated silica and polymer grade microsilica is believed to have contributed to their differing effects on the PP/EPR blend. Two clearly different microstructures were achieved using various functionalized polyolefins as compatibilizers: Separate dispersion of the filler in the polymer matrix and encapsulation of the filler by the elastomer. The present research also gave us an understanding of the relationship between microstructure and mechanical properties in such systems. The addition of PP-*g*-MAH as compatibilizer enhanced both the stiffness and toughness of PP/EPR/PG-MS composites. Impact strength significantly exceeded that of the PP/EPR system.

Mechanical properties and differences observed in the DSC curves of crystallization supported the formation of different microstructures as indicated by the SEM micrographs.

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