Changes in Morphology and Properties by Grafting Reaction in PP/EOR/CaCO₃ Ternary Composites

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ABSTRACT: The phase morphology and mechanical properties of polypropylene (PP) composites containing ethylene–octene elastomer (EOR) and calcium carbonate (CaCO₃) filler were investigated by comparing the toughening effect of unmodified EOR with EOR grafted with maleic anhydride (EOR–MA). EORs of various MA contents were prepared by free-radical grafting of MA onto the EOR backbone using a reactive extrusion process. The composite morphology was directly explored by scanning electron microscopy technique and indirectly explored by differential scanning calorimetry and dynamic mechanical analysis. Separate dispersion of the elastomer and filler particles was achieved by using unmodified EOR. Modification of EOR by maleic anhydride grafting resulted in encapsulation of the filler particles. The mechanical properties of the composites were found to depend mainly on composite morphology and composition and, to a lesser degree, on maleic anhydride concentration. The results of this study showed that when composites contained an equal or higher amount of elastomer relative to filler, a composite with a separate dispersion structure was preferred. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 89: 3557–3562, 2003

Key words: polypropylene; ethylene–octene elastomer; composite; morphology; mechanical properties; maleic anhydride grafting

INTRODUCTION

Polypropylene (PP) composites with mineral fillers are of great practical importance because it is possible to modify the physical properties of PP using low-cost fillers. The addition of rigid filler into PP increases the composite modulus but generally results in increasing brittleness. To compensate for this effect, a rubbery component is incorporated into the system, producing a ternary-phase polymer composite. Earlier studies of ternary PP/elastomer/filler composites showed that morphology, not just composite formulation, also plays an important role in the mechanical behavior of a polymer system.[1–10] In ternary-phase composites there may be two types of phase structure: separate dispersion, in which the elastomer and filler particles are dispersed separately in the polymer matrix[1–4]; and encapsulation (core–shell), in which the elastomer encapsulates filler particles,[5–8] resulting in a low-modulus interlayer between matrix and filler. Although encapsulation is the thermodynamically favored process, it is believed that the final structure has been determined by the adhesion between phases and the stability of the encapsulated units against shear forces in the melt during the mixing process.[9] In our previous work it was found that the composite phase structure was determined mainly by the chemical character of the components and, to a lesser degree, by the mixing sequence of each component.[7–8]

Analysis of composite structure and mechanical property relationships revealed that composites containing an encapsulated filler have higher impact strength but lower modulus than those with a separation structure because the effect of the incorporated elastomer is extended by the filler.[11] However, contradictory results have also been reported.[7,10,12] In a PP/EVA/CaCO₃ composite in which encapsulation structure was observed, the composite exhibited lower impact strength than that with a separation structure. It was believed that poor interfacial adhesion between the core–shell inclusions and the polymer matrix was a possible reason for this result. During impact fracture cracks propagated along those interfaces, resulting in poor impact strength in the composites.[7] An effective way of enhancing the interfacial adhesion between phases and of being able to control composite morphology is to introduce functionalized polar groups such as carboxyl groups onto polymer backbone chains via grafting.
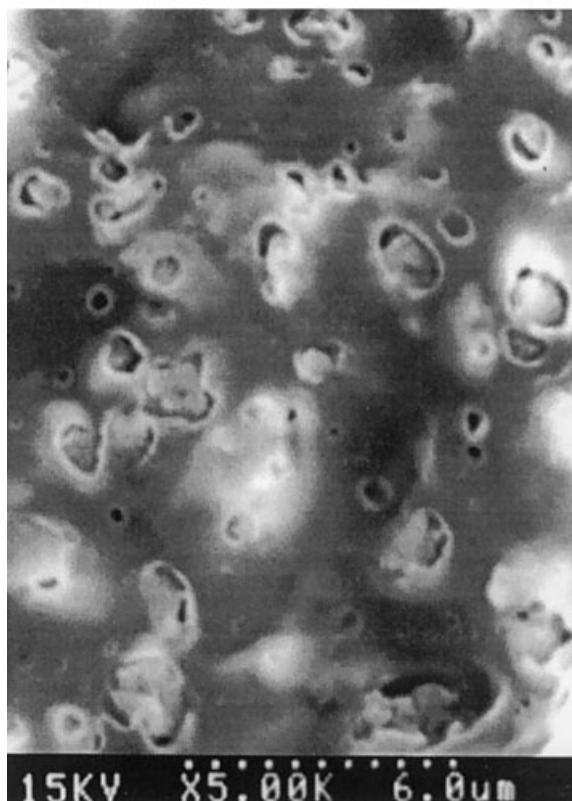
In this work ternary PP composites containing calcium carbonate (CaCO₃) filler together with either an unmodified ethylene–octene elastomer (EOR) or functionalized EOR (EOR–MA) were investigated. The PP/EOR/CaCO₃ composites represented the composites with separation structure, whereas the PP/EOR–
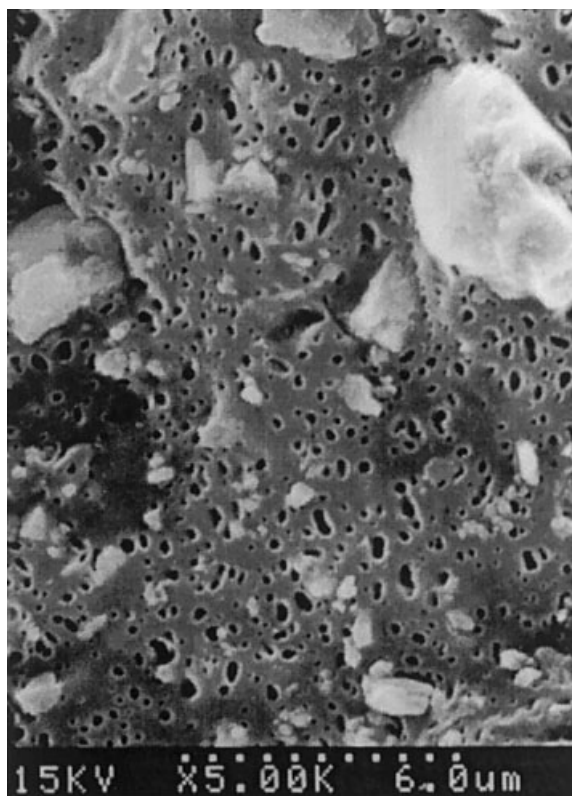
(a)

(b)

MA/CaCO$_3$ composites are representative of encapsulation structure composites with good adhesion between phases. Functionalized EORs with various contents of maleic anhydride (MA) were prepared by free-radical grafting of MA onto the EOR backbone, using a reactive extrusion process, under the conditions that produced EOR–MAs with a certain amount of reactive functionality without the expense of their elastomeric characteristics. Phase structure of the PP composites was investigated using scanning electron microscopy (SEM), differential scanning calorimetry (DSC), and dynamic mechanical analysis (DMA). The effects of filler and elastomer concentrations as well as the MA content of EOR–MA on the phase structure and mechanical properties of the PP composites were also studied.

EXPERIMENTAL

Materials

Polypropylene homopolymer (PP) grade P400S with an MFI of 4 g/10 min (Thai Polyethylene Co., Ltd., Bangkok, Thailand) was used as a matrix polymer. The calcium carbonate (CaCO$_3$) filler used was supplied by Lime Quality Co., Bangkok, Thailand, in an uncoated form (Microcal). Average particle size and surface area were 5.3 μm and 1.8 m^2/g, respectively. The two elastomers used were an unmodified ethylene–octene elastomer (EOR; Engage 8150, DuPont Dow Elastomer Co.) containing 25 wt % octene comonomer with a melt flow rate of 0.5 g/10 min; and EOR functionalized with maleic anhydride (EOR–MA). Functionalized EORs with various contents of MA were prepared by free-radical grafting of MA onto the EOR backbone, using dicumyl peroxide (DCP) as the initiator. The grafting reactions were carried out in a Prism TSE 16 intermeshing corotating twin-screw extruder, operating at 100 rpm with a temperature range of 100°C–190°C. During grafting homopolymerization of MA and/or the crosslinking reaction of EOR may occur. Dimethyl formamide (DMF) was used here to inhibit those reactions. The DCP initiator was introduced into the extruder as a solution in DMF. The reaction products were cooled in a water bath and pelletized. Details of the grafting procedure were reported in a previous article.[13] The amount of grafted MA in the reaction products (% MA) was determined by titrating the acid groups after complete hydrolysis of the anhydride groups with 0.05N potassium hydroxide, using 1–2 drops of thymol blue (1%) in DMF as the indicator.

Figure 1 Cryogenic fractured and etched surfaces of ternary PP composites: (a) PP/EOR/CaCO$_3$ and (b) PP/EOR-MA/CaCO$_3$.

TABLE I
Melting (T_m) Onset of Crystallization ($T_{c\ onset}$)
and crystallization (T_c) Temperatures
of Various PP Composites

Sample	MA content (% wt)	T_m (°C)	$T_{c\ onset}$ (°C)	T_c
Pure PP	—	163	115	110
PP/EOR	—	164	114	110
PP/EOR–MA	—	165	115	110
PP/CaCO₃	—	164	137	132
PP/EOR–MA/CaCO₃	0	164	136	131
	0.5	164	119	114
	1.0	166	119	113
	1.5	165	119	114

Compounding and sample preparation

The ternary PP composites were prepared by melt-mixing in a corotating twin-screw extruder. The barrel temperature profile was set between 160°C and 200°C (from feed zone to die). The screw speed used was 200 rpm, giving a throughput rate of 3 kg/h. All composites contained the same amount of PP at 60 vol %. The elastomer and filler contents were varied. Test specimens for tensile and impact tests were prepared by injection molding (Dr Boy 22S).

Mechanical testing and morphological study

Tensile properties were measured in accordance with ASTM Standard D 638-89, using an Instron Model 4301 tensile testing machine with a crosshead speed of 50 mm/min. Notched Izod impact strength was investigated using a pneumatic impact tester (Radmana ITR-2000). An impact velocity of 3.4 m/s was used. Fifteen specimens were analyzed for each composite. All mechanical testing was undertaken at 23°C.

The dynamic mechanical properties of selected composites were determined using a Polymer Laboratories dynamic mechanical thermal analyzer (Mk II). Testing was carried out in bending mode using a single cantilever, over a temperature range from −100°C to 120°C at a frequency of 6.28 rad/s (1 Hz).

The phase morphology of the composites was examined by scanning electron microscopy (SEM). Specimens were cryogenic-fractured and etched with hot heptane vapor for 20 s to remove the elastomer particles from the polypropylene matrix. The surfaces prepared in this way were platinum/palladium sputter-coated and examined in a Hitachi S2500 scanning electron microscope.

The thermal behavior of the composites was studied using a Perkin–Elmer DSC-7 differential scanning calorimeter over a temperature range from 50°C to 230°C and at a scan rate of 10°C/min.

RESULTS AND DISCUSSION

Morphological study

Figure 1(a,b) shows the differences in phase morphology between the composites containing unmodified EOR elastomer and those containing EOR grafted with 0.5 wt % of MA (containing <2% gel). The tiny holes that can be observed on the micrographs are imprints of the elastomer phase that were removed from the PP matrix by chemical etching. The brighter irregular-shaped particles are CaCO₃ filler. In the composites using an unmodified EOR, the particles of EOR and CaCO₃ filler were found to be dispersed separately in the PP matrix. The contrasting morphology is shown in Figure 1(b), where encapsulation of filler particles by EOR–MA was observed. In this study we found that 0.5 wt % of MA in the EOR phase was sufficient to produce a composite with an encapsulation structure. The formation of an encapsulation structure was found also to be dependent on the molecular mobility of the elastomer phase.[14] During grafting of EOR, some crosslinking (gel) may occur. This would lead to an increase in elastomer viscosity, in other words, a reduction in elastomer mobility. It was found that a full encapsulation structure could not be obtained by the use of EOR–MA with a high viscosity (high crosslinking content).[14] The rheological properties of elastomer therefore are also important factors, apart from the polarity, that need to be considered in the preparation of ternary composites of the required phase structure.

In addition to SEM, another method that has been used successfully in the investigation of phase morphology in multiphase composites is DSC technique.[3,8] Changes in the melting (T_m) and crystallization (T_c) temperatures of PP because of the elastomer and filler additions were investigated. Table I shows the T_m, $T_{c\ onset}$, and T_c of various PP composites. Both elastomers and CaCO₃ filler were observed to have little effect on the melting temperatures of PP. Therefore, the melting temperatures observed in their corresponding ternary composites were similar. Contrary to the melting temperatures, the effect of elastomers and CaCO₃ filler on the crystallization of PP was significantly different. The addition of either EOR or EOR–MA to PP scarcely changed the $T_{c\ onset}$ and T_c values of PP, whereas adding the same amount of

TABLE II
Calculated Relaxation Strength (S_l) of Ternary PP
Composites with Various MA Contents

MA content (% wt)	Relaxation strength (S_l)
0	0.27
0.5	0.96
1.0	0.85
1.5	0.86

TABLE III
Effect of MA Content on Modulus, Yield Strength (S_y), Elongation at Yield (E_y),
and Elongation at Break (E_b) of Various PP Composites

PP/EOR–MA/CaCO$_3$ (% vol)	MA (% wt)	Modulus (GPa)	S_y (MPa)	E_y (%)	E_b (%)
100:0:0	—	1.69	34.76	7.65	442.03
60:20:20	0	1.81	16.97	3.85	280.18
60:20:20	0.5	1.18	20.37	10.10	45.52
60:20:20	1.0	1.17	21.31	13.63	39.74
60:20:20	1.5	1.22	21.73	16.12	39.86
60:10:30	0	2.73	17.21	1.52	43.64
60:10:30	0.5	1.78	21.14	7.19	21.05
60:10:30	1.0	1.74	22.84	9.83	18.89
60:10:30	1.5	1.72	24.23	12.04	19.22

CaCO$_3$ led to a notable increase in both values. This indicates that the CaCO$_3$ filler had much more influence on the crystallization of PP than did elastomer. It acted as a nucleating agent, promoting crystallization of PP at its surface. Therefore, in ternary composites in which both elastomer and filler are involved, changes in the $T_{c\,onset}$ and T_c values can be used as a tool for determining the phase structure in the composites. For instance, if the elastomer and filler particles are dispersed separately in the PP matrix (separation structure), the effect of CaCO$_3$ on the crystallization of PP should be pronounced because of the direct contact between CaCO$_3$ and PP. On the other hand, if the filler particles are wetted out by the elastomer phase (encapsulation structure), the effect of CaCO$_3$ should be diminished or should disappear, depending on the extent of encapsulation. Table I shows the strong effect of CaCO$_3$ in the ternary composite with an unmodified EOR (0% MA). High $T_{c\,onset}$ and T_c values, of 136°C and 131°C, respectively, were observed, revealing direct contact of CaCO$_3$ and PP in the system. In contrast, the use of EOR–MA instead of pure EOR caused a marked reduction in the $T_{c\,onset}$ and T_c values of the composites, to 119°C and 114°C, respectively. Therefore, this result confirmed the previous SEM observations, which showed that an encapsulation of CaCO$_3$ particles by EOR–MA was obtained in such composites. The extent of encapsulation by the use of different concentrations of MA in the composites cannot be verified by this technique, however.

Dynamic mechanical analysis (DMA) was used here for quantitative estimation of the extent of encapsulation. The extent of molecular motion over a temperature interval of glass transition can be characterized by calculating the relaxation strength (S_I) of the materials using the following equation.[15]

$$
\begin{aligned}
S_I &= (E_u - E_r)/E_r \\
&= E'(-50°C)/E'(10\ °C) - 1
\end{aligned}
\tag{1}
$$

where E_u and E_r are unrelaxed and relaxed moduli, respectively. They can be approximated at tempera-

tures well below and above the glass-transition temperature (T_g) of the elastomers used.[1,10] In this study EOR–MA showed a T_g peak at −27°C; therefore, moduli at −50°C and 10°C were used in the calculation. The calculated S_I values are shown in Table II. The ternary composite with separated elastomer and filler (PP/EOR/CaCO$_3$) was characterized by a theoretical S_I value of 0.27, which is much lower than that of composites with an encapsulation structure (PP/EOR–MA/CaCO$_3$). A comparison of the S_I values of various encapsulation composites showed no significant differences among them. Variation in the MA content, which ranged from 0.5 to 1.5 wt %, did not have a considerable effect on the extent of encapsulation.

Mechanical properties

Effect of MA content at constant elastomer and filler concentrations

The effects of MA content in the elastomer phase on composite properties are shown in Table III. The modulus of ternary composites containing EOR–MA was found to be much lower than that of composites using unmodified EOR in both series. A drastic reduction in the reinforcing efficiency of the filler in the former composites could be a result of their core–shell encapsulation structure. Increasing the MA content of the composites from 0.5% to 1.5 % produced no significant change in composite modulus. The tensile yield stress (S_y) of the ternary composites of both compositions was much lower than that of pure PP. The addition of elastomer and filler into PP led to a decrease in tensile stress of PP of about 50%. This property was found to increase slightly with increasing MA content. The same trend was also observed for the elongation at yield. Contrary to the elongation at yield results, the values of elongation at break were found to decrease drastically after the introduction of EOR–MA. However, no significant effect of MA content was observed.

Table IV shows the effect of MA content on the notched Izod impact properties. The ternary compos-

TABLE IV
Effect of MA Content on Impact Initiation, Propagation, and Failure Energies

PP/EOR–MA/CaCO₃ (% vol)	MA (% wt)	Initiation energy (J/m)	Propagation energy (J/m)	Failure energy (J/m)
100:0:0	—	16.2	15.0	31.3
60:20:20	0	104.9	157.8	262.8
60:20:20	0.5	77.1	30.3	107.4
60:20:20	1.0	106.5	33.3	139.8
60:20:20	1.5	127.5	39.9	167.4
60:10:30	0	30.8	23.2	54.0
60:10:30	0.5	31.9	19.0	50.8
60:10:30	1.0	36.5	22.7	59.1
60:10:30	1.5	41.0	27.6	68.7

ites of both composition series, although they had higher impact energies than the PP matrix, had different toughening mechanisms. In the composite of the 60:20:20 series, the highest impact energy was observed in the composite of the separate dispersion structure (0% MA). The use of EOR grafted with 1.0% and 1.5% MA, although exhibiting an increase in composite initiation energy because of better adhesion between filler and elastomer phase, showed a total failure energy of these encapsulation composites that was still lower than that of the separation-type composite. The relationships between impact strength and blend morphology have been reported by Wu.[16] He observed that at a constant elastomer volume fraction the interparticle distance between elastomer droplets in polymer–rubber blends was thinner when the elastomer particles were smaller. During the fracture process the thin ligaments may yield, whereas the thick ones may not. Because of yielding, a tough behavior was obtained.[16] In an encapsulation composite the size of elastomers is a combination of filler core and elastomer shell; therefore, the elastomer particles in the encapsulation structure are relatively larger than those in the separate dispersion structure of the same composition. This may be the reason why the 60:20:20 composite with a separate structure was tougher than that with an encapsulation structure.

Tough behavior was not achieved in the separation composite of the 60:10:30 series, however. One possible reason for this is an insufficient amount of elas-tomer for conveying and propagating the impact energy throughout the entire sample. As a consequence, the composite of this series failed in a brittle manner. A slight improvement in the impact energy of this composite was obtained by the use of grafted EOR to enhance the adhesion between the elastomer and filler particles. Similar findings have been reported,[7] in which a small concentration of elastomers did not have any beneficial influence on the impact properties, regardless of whether elastomer and filler were dispersed separately or whether elastomer encapsulated the filler particles. At a higher elastomer volume fraction (>10%), a separate dispersion structure was apparently more effective in improving the impact strength of the composites than was an encapsulation structure of the same composition.

Effect of elastomer concentration with constant concentration of filler and 0.6 wt% concentration of MA

The effects of EOR–MA concentration on composite properties are shown in Table V. The incorporation of CaCO₃ to PP yielded a significant increase in composite modulus. In contrast, the addition of EOR–MA led to a sharp drop in this property. As the amount of EOR–MA in the composites increased, the modulus decreased systematically. Contrary to the effect on composite modulus, the elongation at yield and break of the composites increased as the EOR–MA loadings

TABLE V
Effect of EOR–MA Loadings on Modulus, Yield Strength (S_y), Elongation at Yield (E_y), and Elongation at Break (E_b) of Various PP Composites (PP/CaCO₃ = 60:20)

EOR–MA loadings (by vol)	Modulus (GPa)	S_y (MPa)	E_y (%)	E_b (%)
Pure PP	1.69	34.76	7.65	442.03
0	3.31	21.04	1.64	27.95
5	2.02	24.92	4.70	13.37
10	1.63	24.11	7.02	27.11
20	1.26	22.10	10.87	38.69
30	0.97	19.50	15.05	81.93

TABLE VI
Effect of EOR–MA Loadings on Impact Initiation, Propagation, and Failure Energies (PP/CaCO$_3$ = 60:20)

EOR–MA loadings (by vol)	Initiation energy (J/m)	Propagation energy (J/m)	Failure energy (J/m)
Pure PP	16.12	15.07	31.28
0	18.77	11.67	30.42
5	20.19	14.22	34.41
10	36.37	23.35	59.73
20	72.58	38.42	111.00
30	159.26	60.66	219.92

increased. The addition of CaCO$_3$ filler to PP also resulted in a sharp drop in tensile yield stress. However, this property could be improved by adding a small amount of EOR–MA (~5–10 vol %) to the system. This result is in accordance with that of Jancar and Dibenedetto, in whose study the yield strength was found to increase with the addition of the functionalized elastomer (EPR–MA) for the PP/EPR/Mg(OH)$_2$ system.[17] Enhancement of the failure impact energy of the composites also was found as the EOR–MA was incorporated (Table VI). As the amount of EOR–MA increased, the impact energies increased accordingly. The improvement in impact energies in all composites was governed more by an increasing crack initiation energy. A sudden jump in impact energy was observed when 20 vol % of EOR–MA was incorporated.

CONCLUSIONS

The effects of functionalized ethylene–octene elastomer (EOR–MA) on the morphology and mechanical properties of PP composites containing CaCO$_3$ filler were investigated. SEM revealed a separate dispersion of elastomer and filler in the PP–EOR–CaCO$_3$ composites. The use of EOR–MA, on the other hand, led to encapsulation of the filler particles. The variation in MA content, which ranged from 0.5 to 1.5 wt %, showed no significant effect on the extent of encapsulation. The composites of the separation structure exhibited a higher modulus and elongation at break, whereas those of the encapsulation structure showed higher tensile strength because of good adhesion between filler and elastomer. All composites prepared showed a much higher impact strength than did the pure PP. The composites with the encapsulation structure did not always exhibit a higher impact strength than those with the separation structure. Impact strength also was found to depend mainly on blend composition and, to a lesser degree, on MA concentration. In the composites containing an equal or higher amount of elastomer relative to filler, separately dispersed elastomer and filler produced a noticeably greater toughening effect than did the encapsulated structures.

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