

## Use of Polymeric Compatibilizers in Polypropylene/Calcium Carbonate Composites

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**Abstract**—The effects of compatibilizing agents on the mechanical properties, viscoelastic properties, and morphology of polypropylene filled with calcium carbonate composites are investigated. It is found that the use of PP-g-MA and PP-g-AA significantly increases the tensile strength and improves particle dispersion and interfacial adhesion. The higher effect of compatibilization is obtained by using PP-g-MA as a compatibilizer. The results on the dynamic thermomechanical properties, viscoelastic properties, and SEM pictures also support the improved interfacial characteristics. It is also found that there exists a limiting amount of PP-g-MA at about 5% beyond which a further increase in the tensile strength is not obtained. The use of untreated calcium carbonate or SEBS-g-MA does not allow films to be drawn for the purpose of testing.

Key words: PP-g-MA, Polymer Compatibilizer, Polypropylene Composite, Thermomechanical Properties, Calcium Carbonate

### INTRODUCTION

Although polypropylene (PP) is widely used due to its excellent processing characteristics, good mechanical properties and low cost, much time and effort has gone into improving these properties through the addition of other polymers or fillers. Inorganic fillers such as talc, glass fibers or calcium carbonate are often added to polymer resins either to reinforce the material or to reduce material costs. Since the addition of filler into a polymer matrix interferes with the macromolecular structure of the polymer, mechanical properties are often sacrificed. Most often surface modification of the filler is used to improve this interface. Stearic acid and coupling agents such as silane [Demjen, 1998], as well as plasma modification [Akovali, 1994] have been used to modify the surface of calcium carbonate. However, in the case of polypropylene, poor adhesion between matrix polymer and filler is present due to the absence of functionalities that could interact with the filler [Wang, 1996; Xanthos et al., 1995]. Compatibilizing agents are most often used to improve the interfacial adhesion between blended polymers. This same approach can be made for composite systems rather than the conventional treatments that focus on filler surface treatments [Pukansky et al., 1989]. By adding compatibilizers with reactive functional groups, it is expected that improved adhesion at the polymer/filler interface will result in more efficient stress transfer and better dispersion.

Previous studies on the mechanical properties of polypropylene filled with calcium carbonate ( $\text{CaCO}_3$ ) have shown an increase in flexural modulus with increasing concentrations of filler and a decrease in tensile strength and elongational properties [Maiti et al., 1991; Demjen et al., 1998]. In an attempt to improve compromised properties, three compatibilizers, PP-g-MA, PP-g-AA and

SEBS-g-MA are incorporated into the PP/ $\text{CaCO}_3$  composites. Since PP-g-MA and PP-g-AA are essentially polypropylene in nature, these compatibilizers are miscible with PP, especially in small amounts. SEBS-g-MA is not thermodynamically miscible with PP, although some dispersion does occur upon mechanical mixing. The functional groups associated with these compatibilizers are expected to interact with the  $\text{CaCO}_3$  filler providing increased adhesion between the filler and matrix, ultimately resulting in enhanced mechanical properties.

### EXPERIMENTAL

#### 1. Materials

The polypropylene used for sample preparation is Escorene® 3155 (Exxon Chemical) with a melt index of 34 g/10 min at 230 °C. Polybond® 3150 (Uniroyal Chemical) is a maleated polypropylene (PP-g-MA) with 0.7 wt% graft level and a melt index of 50 g/10 min at 230 °C. Polybond® 1001 (Uniroyal Chemical) is a polypropylene grafted with 6% of acrylic acid (PP-g-AA) with a melt index of 40 g/10 min at 230 °C. The SEBS-g-MA used is Kraton® FG-1901X (Shell Chemical) with a melt index of 22 g/10 min at 230 °C and a graft level of 1.84%. Microground calcium carbonate, UFI® (Omya, Switzerland) is used with an average particle size of 0.7  $\mu\text{m}$  and a specific surface area of 12  $\text{m}^2/\text{g}$ . Calcium carbonate powder is used either as an untreated form or as a treated form coated by stearic acid.

#### 2. Equipment

A Brabender D6/2 twin screw extruder with 42-mm intermeshing screws and an L/D ratio of 7 : 1 is used to blend the PP and  $\text{CaCO}_3$ . The speed of the extruder is controlled by a Haake Rheocord Torque Rheometer model number EU3V. The materials are fed to the extruder by a Horizontal Metering Screw Feed Hopper with variable speed control. A Sheet Extrusion Take-off model-SE unit equipped with a water bath is used to collect film samples from a 4" Horizontal Flex-Lip Ribbon Die. Tensile properties are tested by using an Instron model 4204 tensile tester on 20 mm

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samples at an elongation rate of 0.2 mm/s. Thermomechanical properties are tested with a Rheometric Scientific DMTA IV at a frequency of 1 Hz and a ramp rate of 2.5 °C/min in single-cantilever bending mode. Viscoelastic properties are measured by a Rheometrics RMS 800 at a strain of 5% and temperature range of 170–200 °C in dynamic oscillatory mode. An Amray 1600 scanning electron microscope is used at a beam voltage of 20 kV to examine cryogenically fractured composite samples.

### 3. Procedures

To avoid any absorption of moisture from the atmosphere, the compatibilizers are dried in a vacuum oven for 8 hours prior to mixing, and immediately mixed upon removal from the oven. The mixtures are fed to a Brabender twin screw extruder operating at 200 °C and 80 RPM by a metering feed hopper. Immediate quenching in a room temperature water bath follows melt blending. The amount of calcium carbonate in all samples is 40% and a 10% compatibilized blend consists of a 50/40/10 blend of PP/CaCO<sub>3</sub>/compatibilizer. In the initial phase of experimentation (experiment 1), 10% compatibilizer is used. In the follow-up study with PP-g-MA (experiment 2), the amount of PP-g-MA ranges from 0% to 10% by increments of 2.5%.

## RESULTS AND DISCUSSION

### 1. Mechanical Properties

The composites prepared by using the untreated CaCO<sub>3</sub> could not be collected through available film drawing methods. These composites showed poor processability as a result of poor dispersion and melt strength. The poor processing characteristics created by the use of untreated calcium carbonate are due primarily to caking that results from the absence of surface treatments such as stearic acid. Similar results were obtained from the composite containing treated CaCO<sub>3</sub> and Kraton<sup>®</sup> FG-1901X (SEBS-g-MA). This could be due to the immiscibility of SEBS-g-MA with both polypropylene and CaCO<sub>3</sub>, resulting in weak bonding of the SEBS-g-MA and CaCO<sub>3</sub> with the PP matrix. The immiscibility of SEBS with PP is too disruptive to the melt strength to allow drawing.

The mechanical properties measured on all test samples are presented in Tables 1 and 2. The results of the initial study (experi-

ment 1, Table 1), aimed at identifying which compatibilizer provides the best properties, show that significant differences exist at the 95% confidence level for tensile strength. An increase of 33% is possible using 10% PP-g-MA and 16% using 10% PP-g-AA versus the uncompatibilized case, indicating that compatibilization is present. A 10% PP-g-MA compatibilized composite also shows increases of 20% in bending modulus and 30% in elongation at break. Since the compatibilizing effect of PP-g-MA turns out to be superior to PP-g-AA, follow-up work (experiment 2, Table 2) is carried out by using PP-g-MA to determine the optimal amount of PP-g-MA required. It shows that an asymptotic increase in tensile strength is seen with increasing amounts of PP-g-MA. A maximum of approximately 15 MPa is observed using as little as 5% PP-g-MA. The incorporation of additional compatibilizer beyond 5% does not have a significant effect on the strength. About 10% difference is observed in tensile strength of 10% PP-g-MA samples between experiments 1 and 2. But, this difference is generally acceptable in the mechanical tests of composites.

### 2. Viscoelastic Properties

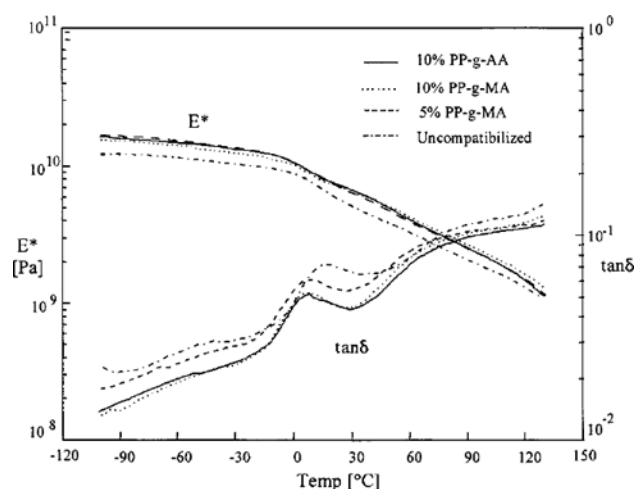
Plots of dynamic thermomechanical test results obtained by using DMTA are given in Fig. 1. The effect of compatibilization reveals a stiffening effect as the three samples listed consisting of 5% PP-g-MA, 10% PP-g-MA and 10% PP-g-AA all show a similar positive effect on modulus. The presence of a compatibilizer serves to provide a stronger interface that better reflects the maximum levels of modulus possible for perfect adhesion. In effect, the inherently high modulus of the calcium carbonate is better utilized when compatibilized properly due to improved interfacial adhesion. The effect of compatibilization on energy dissipation is observed in the  $\tan\delta$  curves, also given in Fig. 1. The observed decrease in  $\tan\delta$  is an indication that properly compatibilized composites provide enhanced toughness or impact strength due to improved interfacial adhesion. Improved stress transfer as seen in the compatibilized blends is the result of better adhesion at the CaCO<sub>3</sub> surface. Poor interfaces prevent efficient stress transfer leading to stress concentration and the formation of microcrazes at the polymer-filler interface that weaken the composites and lead to fracture.

**Table 1. Mechanical properties of composites obtained in experiment 1**

	Tensile strength (MPa)	Bending modulus (Gpa)	Elongation at break (%)
Uncompatibilized	12.28	6.20	6.70
10% PP-g-MA	16.33	7.46	8.69
10% PP-g-AA	14.26	7.67	6.64

**Table 2. Tensile strength of composites obtained in experiment 2**

	Tensile strength (MPa)
2.5% PP-g-MA	14.17
5% PP-g-MA	14.91
7.5% PP-g-MA	15.01
10% PP-g-MA	14.88



**Fig. 1. Effect of compatibilization on dynamic mechanical properties of PP/CaCO<sub>3</sub> composites.**

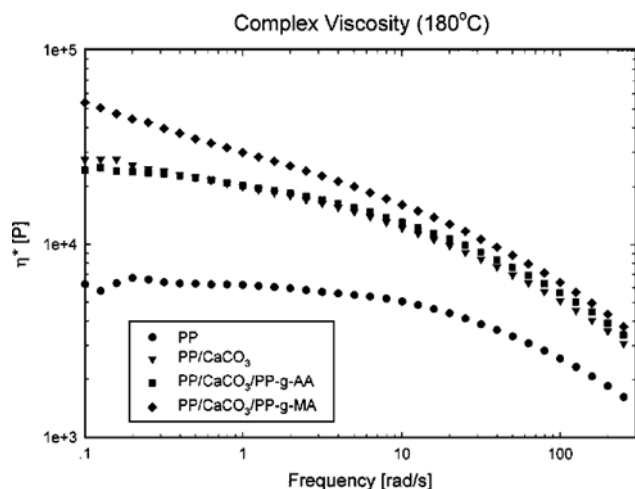


Fig. 2. Complex viscosities of PP, PP/CaCO<sub>3</sub>, and the compatibilized composites at 180 °C.

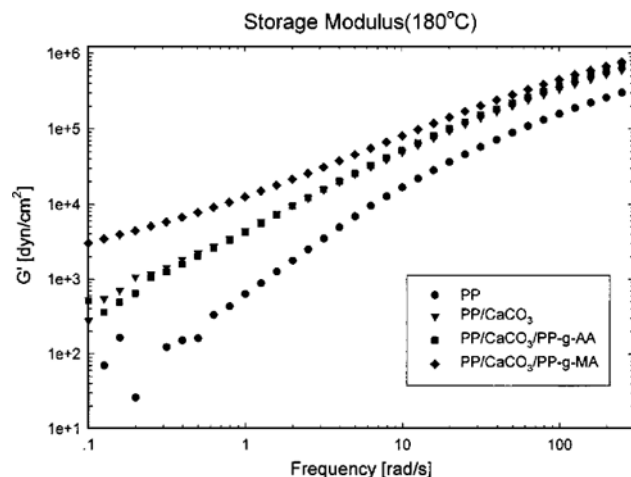
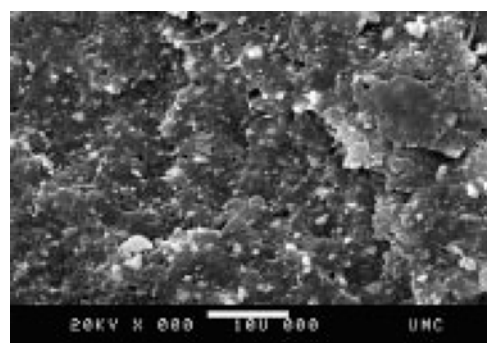


Fig. 3. Storage moduli of PP, PP/CaCO<sub>3</sub>, and the compatibilized composites at 180 °C.

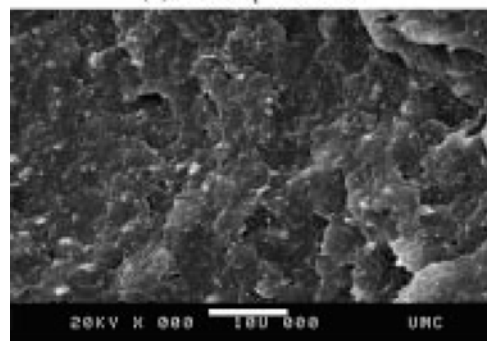
Viscoelastic properties of PP, PP/CaCO<sub>3</sub>, and the compatibilized composites measured at 180 °C by using RMS 800 are given in Figs. 2 and 3, respectively. The complex viscosity and storage modulus of 10% PP-g-MA compatibilized composite show higher values than those of 10% PP-g-AA compatibilized composite, especially at low frequencies, which further supports the better interfacial adhesion in the case of PP-g-MA compatibilized composite. The scattering data shown in Fig. 3 on the storage modulus of pure PP at low frequencies are primarily due to the limit of the transducer used in the measurements.

### 3. Morphology

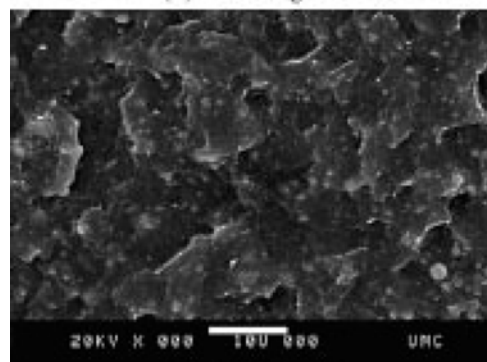
The morphology of each of the composites obtained in the primary study is presented in Figs. 4 and 5, taken at 2,000X and 10,000X magnifications, respectively. The uncompatibilized composite shows poor dispersion and particle agglomeration within the fracture surface as shown in Fig. 4(a). However, the composites prepared by using compatibilizers show better dispersion characteristics with PP-g-MA showing the best dispersion as shown in Figs. 4(c). Fig. 5 shows the interaction between matrix and filler at 10,000X magnification. The compatibilized composites show



(a) Uncompatibilized



(b) 10% PP-g-AA



(c) 10% PP-g-MA

Fig. 4. SEM photographs of fracture surface at 2,000X magnification. (a) Uncompatibilized composite. (b) 10% PP-g-AA compatibilized composite. (c) 10% PP-g-MA compatibilized composite.

much-improved adhesion at the CaCO<sub>3</sub> surface with PP-g-MA showing the greatest interaction as shown in Fig. 5(c) while the uncompatibilized composite shows a lack of adhesion at the CaCO<sub>3</sub> surface. Although not shown here, SEM pictures show that increasing percentages of PP-g-MA improves dispersion and adhesion. As is the case for tensile strength, the effect of adding compatibilizer beyond some threshold value in the 5% range is not significant. This is due to the presence of excess PP-g-MA, which is not capable of reacting or interacting with CaCO<sub>3</sub> since all available CaCO<sub>3</sub> surface sites are occupied.

### CONCLUSIONS

The positive effect of compatibilization in PP/CaCO<sub>3</sub> composites is the result of improved interfacial adhesion at the interface between the filler and the polymer matrix as shown through exam-

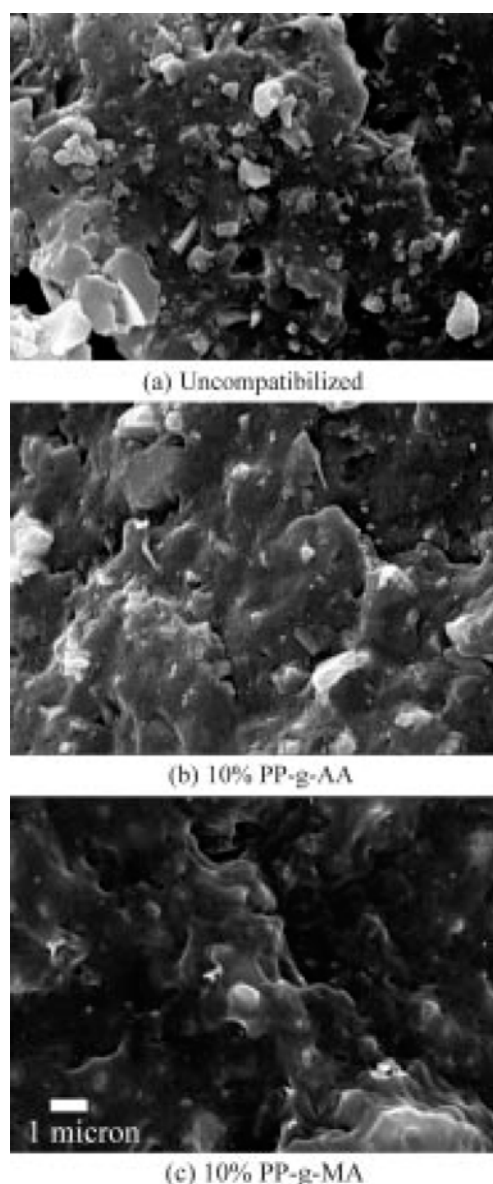


Fig. 5. SEM photographs of fracture surface at 10,000X magnification. (a) Uncompatibilized composite. (b) 10% PP-g-AA compatibilized composite. (c) 10% PP-g-MA compatibilized composite.

ination of the fracture surface with SEM and from dynamic mechanical analysis. The use of PP-g-MA provides enhanced adhesion at the  $\text{CaCO}_3$  surface due to the higher reactivity of PP-g-MA compared PP-g-AA. The effect on tensile strength also supports

this finding. The tensile strength of composites treated with compatibilizers shows significant increases in strength of 33% with 10% PP-g-MA and 16% with 10% PP-g-AA. A PP-g-MA compatibilized composite also shows increases of 20% in bending modulus and 30% in elongation at break due to improved adhesion. In addition, there exists a threshold value of 5% in the addition level of PP-g-MA beyond which no tangible benefits are obtained in terms of its tensile strength.

The use of either SEBS-g-MA or untreated calcium carbonate does not provide films with sufficient melt strength to be drawn in the form of a film. The immiscibility of SEBS with PP is too disruptive to the melt strength to allow drawing. The poor processing characteristics created by the use of untreated calcium carbonate are due primarily to caking that results from the absence of surface treatments such as stearic acid. This study reveals the potential use of compatibilizers for improving the properties of not only calcium carbonate filled polypropylene but possibly other polymers and fillers as well.

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