

Influence of Grafted Polypropylene on the Mechanical Properties of Mineral-Filled Polypropylene Composites

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ABSTRACT: The purpose of this work was to study how mineral fillers would behave in a polypropylene (PP) matrix when PP modified with maleic anhydride (MA) and/or itaconic acid (IA) was used as a coupling agent in the preparation of mineral-filled PP composites. The composites were characterized with tensile mechanical measurements and morphological analysis. The optimum amount of the coupling agent to be used to obtain composites with improved mechanical properties was established. The results indicated that these coupling agents enhanced the tensile strength of the composites significantly, and the extent of the coupling effect depended on the nature of the interface that formed. The incorporation of coupling agents enhanced the

resistance to deformation of the composite. The behavior of IA-modified PP as a coupling agent was similar to that of a commercial MA-modified PP for the filled PP composites. Evidence of improved interfacial bonding was revealed by scanning electron microscopy studies, which examined the surfaces of fractured tensile test specimens; their microstructures confirmed the mechanical results with respect to the observed homogeneous or optimized dispersion of the mineral-filler phase in these composites.

Key words: compatibilization; composites; fillers; graft copolymers; mechanical properties

INTRODUCTION

In recent years, organic–inorganic composites have attracted great interest from researchers because they frequently exhibit unexpected hybrid properties derived from the two different components.¹ The effects of a filler on the mechanical and other properties of composites depend strongly on the filler shape, particle size, aggregate size, surface characteristics, and degree of dispersion. Polypropylene (PP) is one of the most widely used polyolefins in plastic composites. The most commonly used mineral fillers for PP are calcium carbonate, talc, mica, and clays.^{2–9} Because PP does not contain any polar groups in its backbone, a homogeneous dispersion of these fillers in PP is not possible on account of the poor adhesion at the PP/filler interface.

Therefore, one of the challenges in creating composites with a filler and PP is finding a way to improve the bonding between the nonpolar PP matrix and the polar filler. Usually, the mineral fillers used for manufacturing PP composite have poor compatibility with

the hydrophobic thermoplastic, and this in turn leads to poor mechanical properties. Furthermore, the applications of composites are diversifying into various fields as they can meet the requirements of respective applications by changes in the matrix, filler resources, and processing ingredients. The structure and properties of the polymer interface with the filler play crucial roles in determining the performance and properties of the composites. An optimum degree of adhesion between the filler and the polymer matrix is required for efficient stress transfer from the matrix to the filler.¹⁰ To promote the adhesion between a polar filler and PP, coupling agents or compatibilizers are generally used to modify the filler–matrix interface and thereby enhance the filler–matrix adhesion.

Modified PPs with polar functional groups are normally used as coupling agents in mineral-filled PP composites.^{11–18} The modification of PP via grafting with monomers that contain polar functional groups, such as maleic anhydride (MA), itaconic acid (IA), and their derivatives, has been reported.^{19–22}

Maleic anhydride grafted polypropylene (MAPP) has been studied extensively as a coupling agent in bonding between PP and different fillers.^{11–16} MAPP is formed by the reaction of MA with PP in the presence of an initiator to produce PP chains with pendant MA groups. The PP portion of MAPP can entangle and cocrystallize with unmodified PP, whereas the MA groups can bond to the hydroxyl (–OH) or polar groups on the filler surface.

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TABLE I
Polymer Characterization

| Code | T_g (°C) | T_c (°C) | T_m (°C) | Crystallinity (%) | MFI (g/10 min) | $M_w \times 10^3$ ^a |
|-------|------------|------------|------------|-------------------|----------------|--------------------------------|
| PP 03 | -2.0 | 108.6 | 166.8 | 31.0 | 3.1 | 340 |
| PP 06 | -0.8 | 114.9 | 164.2 | 38.6 | 4.5 | 300 |
| PP 13 | -3.1 | 113.4 | 164.7 | 42.9 | 12.5 | 250 |
| PP 26 | -19.5 | 118.3 | 166.9 | 45.1 | 24.5 | 170 |

^a Weight-average molecular weight.

In another study,¹⁷ four different coupling agents based on ethylene/acrylic ester/maleic anhydride terpolymers and ethylene/acrylic ester/glycidyl methacrylate terpolymers were used to enhance the performance properties of high-density polyethylene composites filled with rice husks. Coupling agents such as PP functionalized with monomethyl itaconate and/or vinyltriethoxysilane improved the mechanical properties of PP/silica and PP/rice-husk composites.¹⁸

Furthermore, it is possible to apply a coupling agent in addition to the grafted polymer usually used for the enhancement of the performance of polymer-filler composites. A similar enhancement of the properties of composites can be observed when fillers are chemically modified by coupling agents; for example, for bamboo-husk-reinforced poly(butylene succinate) composites, commercial silane coupling agents have been used for a fiber surface treatment.²³ The effects of stearic acid coated talc, calcium carbonate, and mixed talc and calcium carbonate were evaluated for PP composites containing these fillers.²⁴

In this work, a comparison of two grafted PP polymers, a commercial PP grafted with MA (PP-g-MA) and a PP modified in our laboratory via grafting with IA (PP-g-IA), were used as coupling agents for manufacturing PP composites filled with talc or calcium carbonate. The effects of the filler size and shape on the mechanical and morphological properties of the PP composites were studied, and an optimum filler size corresponding to the best mechanical properties was established.

EXPERIMENTAL

Polymers

Commercial PP homopolymer samples with different molecular weights were kindly donated by Petroquim S.A. (Concepción, Chile) and were characterized (see Table I).

Polymer characterization

The thermal analysis of the PP samples was carried out under nonisothermal conditions under a nitrogen atmosphere with a model 2920 differential scanning

calorimeter from TA Instruments (New Castle, DE). The instrument was calibrated with an indium standard. Samples of about 8 mg were first heated at a rate of 20°C/min from -50 to 190°C and kept at this temperature for 5 min to eliminate any previous thermal history in the material. Then, they were cooled to -50°C at 20°C/min to determine the crystallization temperature (T_c). The sample was heated again to 190°C at 20°C/min to obtain the glass-transition temperature (T_g), melting temperature (T_m), and heat of fusion. Differential scanning calorimetry measurements were performed by Dr. Daniel Serafini of the Physics Department at the Universidad de Santiago (Santiago, Chile).

The molecular weights of the PP samples were determined by high-temperature gel permeation chromatography with a Waters Alliance 2000 system equipped with a differential refractometer detector. Three gel permeation chromatography columns (HT6E, HT5 and HT3), previously calibrated with polystyrene standards of narrow molecular weight distributions, were used. 1,2,4-Trichlorobenzene was used as a solvent, and the flow rate for analysis was 1 mL/min at 135°C.

The melt flow index (MFI) of the PP samples was determined with a Ray-Ran melt flow indexer according to ASTM D 1238-90b (2.16 kg at 230°C for 10 min).

Coupling agent

PP grafted with MA with an MFI value of 115 g/10 min (2.16 kg at 230°C) and a T_m value of 135°C was purchased from Aldrich (Milwaukee, WI).

Functionalized PP with IA was obtained by a free-radical melt grafting process with a Brabender plastimeter (Duisburg, Germany) at 190°C and with Lupersol 101 as the initiator. The final product had 1.3 wt % IA grafted, as determined by Fourier transform infrared spectroscopy (Bruker FTIR model IFS-28, Germany). Details of the synthesis and characterization of modified PP with IA and its derivatives have already been reported in our previous work.²¹

Fillers

Commercial talc samples with different grain sizes were characterized, and the results are shown in Table II and Figure 1. These commercial talc samples were designated as follows: TA1 from Rocco Industry

TABLE II
Properties of the Mineral Fillers

| Filler type | Nomenclature | Particle size (μm) | | | BET area (m^2/g) | Pore diameter (\AA) |
|-------------------|--------------|---------------------------------|----------|----------|------------------------------------|--------------------------------|
| | | X_{10} | X_{50} | X_{90} | | |
| Calcium carbonate | CC1 | 2.7 | 17.1 | 42.6 | 2.2 | 68 |
| | CC2 | 0.4 | 2.0 | 10.2 | 3.2 | 104 |
| | CC3 | 0.3 | 0.7 | 1.7 | 9.1 | 124 |
| Talc | TA1 | 3.0 | 10.7 | 29.5 | 4.6 | 90 |
| | TA2 | 0.7 | 2.4 | 6.5 | 6.3 | 110 |
| | TA3 | 0.4 | 0.5 | 2.8 | 11.9 | 110 |

(Santiago, Chile) and TA2 and TA3 from Imifabi LLC Industry (West Virginia). Commercial calcium carbonate samples with different grain sizes were characterized, and the results are shown in Table II and Figure 1. These commercial calcium carbonate samples were designated as follows: CC1 from Trucco Industry (Santiago, Chile) and CC2 and CC3 from Reverte Industry (Bellvei, Germany).

Filler characterization

A Mastersizer from Malvern Instruments, Ltd. (Malvern, UK), was used for the particle size characterization of the fillers. The particle sizes of the fillers were examined on a water dispersion of these particles with a Malvern Mastersizer model MSX1 refractive particle device. The characterization of the particle size was determined from the volume percentage at i (X_i ; $i = 10, 50, \text{ or } 90$); X_{50} is the mean particle size.

The Brunauer–Emmett–Teller (BET) specific surface areas and pore size distribution of different fillers were determined from nitrogen adsorption isotherms with a Micrometrics ASAP 2010 apparatus. Before the adsorption measurements, all fillers were degassed *in vacuo* at 200°C .

Composite preparation

PP–filler composites were prepared by the melt mixing of PP with a filler and with Irganox 1010/Irgafos 168 mixtures in a 2 : 1 ratio as an antioxidant at 190°C with a Brabender plasticorder under a nitrogen stream for 10 min at 75 rpm. The commercial fillers were dried for 12 h at 90°C before being mixed with PP.

Modified composites with PP grafted either with IA or MA as a coupling agent were prepared in a similar manner. The weight percentage of the coupling agent was calculated with respect to the weight of the filler used, and the weight of the added coupling agent was taken from the weight of PP to keep constant the total weight of the polymer in the composite. After melt mixing, the composite was cut into small pieces and then pressed at 190°C at 50 psi to obtain laminates, from which test specimens were cut for the tensile testing according to ASTM D 638.

Tensile measurements

The mechanical properties of the composites were determined by means of tensile testing according to ASTM D 638-95 with a HPD500 dynamometer (HP Industry, Buenos Aires, Argentina) at 23°C and 35% relative humidity. The crosshead speed was 50 mm/min, and the results were reported as averages of at least five measurements.

Scanning electron microscopy (SEM)

The fractured surfaces of the composites after electro-spraying with gold were analyzed with a Tesla model BS343 scanning electron microscope (Berno, Czech Republic). SEM analysis was performed by Professor J. L. Arias of the Bioceramics Laboratory, Facultad de Ciencias Veterinarias, Universidad de Chile.

RESULTS AND DISCUSSION

Material characterization

The T_g , T_c , and T_m values as well as the crystallinity percentages, MFIs, and molecular weights of PP samples are shown in Table I. The values obtained for different properties of the PP samples are near those reported in the corresponding technical data sheet for each polymer provided by Petroquim.

Fillers were characterized for the particle size, specific surface area, pore size, and microstructure. The results are shown in Table II and Figure 1.

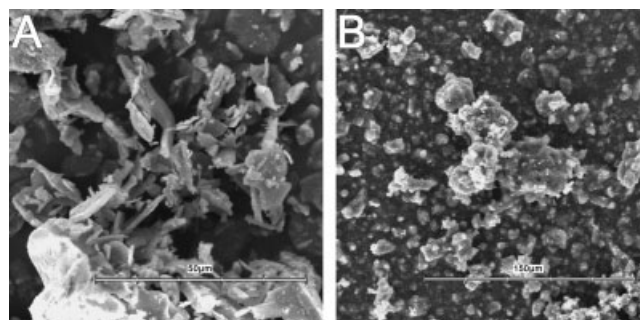


Figure 1 SEM micrographs of fillers (A) TA2 and (B) CC2 (magnification = $1700\times$).

In general, for both filler types, talc and calcium carbonate, with finer particles or smaller X_{50} values, higher values of the specific surface area were found. In the case of CC2 and TA2, the twice higher specific surface area of TA2 could be related to the smaller difference between X_{50} and X_{10} or X_{90} values in comparison with CC2, for which the difference between the X_{50} values and X_{10} or X_{90} values was large. The narrower particle size distribution determined for TA2, compared with that determined for CC2, could explain the values of $6.3 \text{ m}^2/\text{g}$ for the specific surface area of TA2 and $3.2 \text{ m}^2/\text{g}$ for CC2. A higher aspect ratio (surface/volume) could be estimated for TA2 from the morphological study of the TA2 and CC2 fillers, as shown in Figure 1. This finding could explain the higher value of the specific surface area of TA2 compared with that of CC2.

Mechanical properties

Unmodified PP composites with mineral fillers of different mean particle sizes were first studied to determine the most appropriate filler size and percentage to be used for reinforcement in PP composites modified with coupling agents. This selection was based on the values obtained for the Young's modulus (E), tensile resistance (δ), and elongation at break (ϵ).

Composites of PP with talc or calcium carbonate without a coupling agent

In general, higher E and lower δ and ϵ values were obtained as the proportion of the filler increased from 20 to 40 wt % for PP/talc and PP/calcium carbonate composites.

The E values obtained for PP/talc and PP/calcium carbonate composites for different proportions and

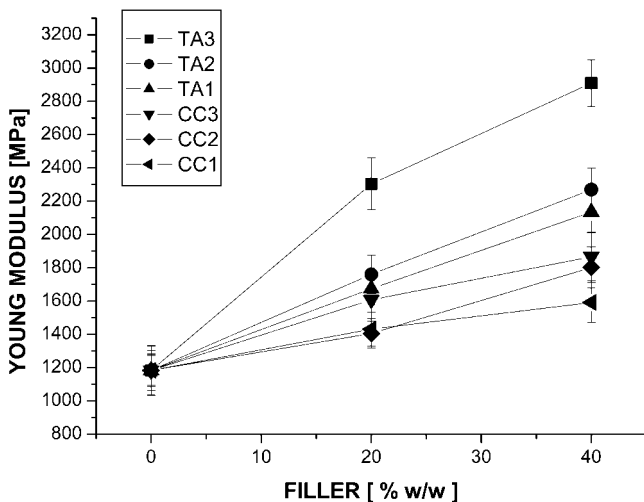


Figure 2 E of the PP composites without a coupling agent.

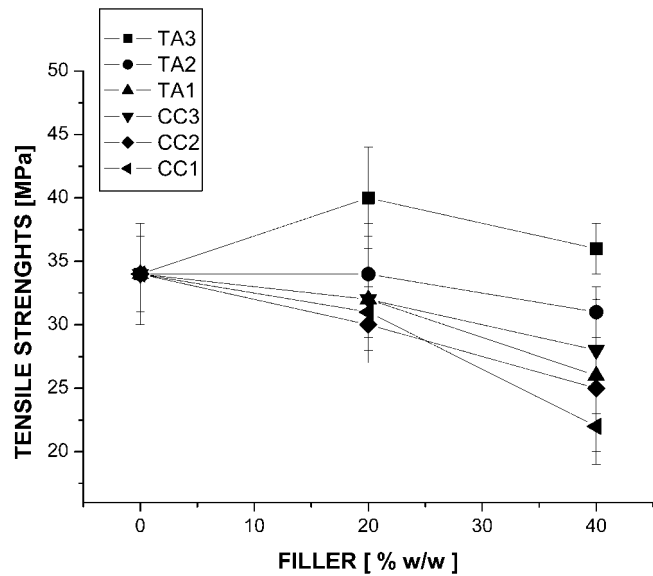


Figure 3 Maximal tensile strengths of the PP composites without a coupling agent.

particle sizes (X_{50}) of the fillers are compared in Figure 2. Generally, E increased with an increasing amount of the filler for both types of composites. The increase in E could be due to both the incorporation of a rigid, inorganic filler in the PP matrix and the movement restriction of the polymer chains.

Figure 3 shows that δ of the composite decreased with an increasing amount of the filler from 20 to 40%. This could be attributed to the fact that stress caused by the application of an external force was transferred to the filler through the polymer matrix. When the amount of the filler was increased, the interfacial area of the noncompatible components (polymer and filler) was increased. Therefore, δ decreased as a result of the low transfer yield at the interface.

Moreover, it was determined that the decrease in δ as the result of the addition of the filler was more significant for the PP/calcium carbonate composites than for the PP/talc composites. Bulky calcium carbonate particles caused greater discontinuity of the applied stress to the matrix, producing more stress concentration and hence less resistance. On the contrary, in the PP/talc composites, less discontinuity of the matrix was produced because of the laminar shape and size of the talc, which allowed less free space in the polymer–filler interface. On the other hand, δ was higher when X_{50} of the filler decreased for the composites containing 20 or 40% reinforcement. This higher δ value was more noticeable for composites containing 40 wt % filler than those with 20 wt %. This could be attributed to a better distribution of the filler with smaller particles in the polymer matrix. Moreover, X_{50} of the filler had a greater influ-

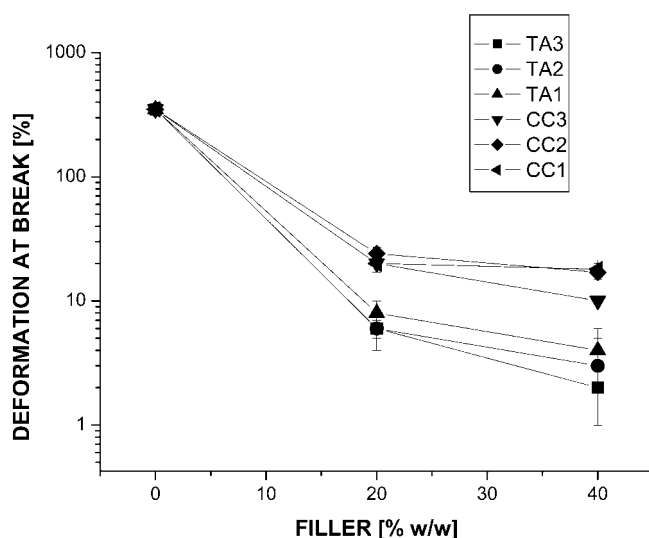


Figure 4 ϵ of the PP composites without a coupling agent.

ence on the δ values in the PP/talc composites than in the PP/calcium carbonate composites. As can be appreciated in Figure 3, the value of δ for PP/TA3 with 20 wt % TA3 talc was higher than δ for PP. This could be due to the existence of a better interaction between PP and TA3 talc. Therefore, the TA3 particles were more homogeneously distributed in the PP matrix because of its particular particle size and morphology.

The dependence of ϵ of the PP composites as function of the type and proportion of fillers is shown in Figure 4. The incorporation of the filler resulted in a decrease in ϵ in all cases with respect to ϵ of PP. This indicated that the incorporation of the filler as a reinforcement changed the fracture behavior of PP from ductile to fragile. This reduction in the deformability of PP could be attributed to a heterogeneous and

insufficient dispersion of the filler in the PP matrix as well as the rigidity of the reinforcement particles.

There was a greater decrease in the ϵ values of the PP/talc composite in comparison with the PP/calcium carbonate composite containing 20–40 wt % talc or calcium carbonate. However, this behavior was independent of the mean grain size of the filler and could be attributed to less interaction between PP and calcium carbonate. The lack of sufficient interaction between PP and calcium carbonate could be due to the granular morphology of this filler.

Composites of PP and talc or calcium carbonate containing a coupling agent

The study carried out with PP composites without added coupling agent and containing 40 wt % filler showed a 50% increase in E and moderate changes in the strengths and deformation at break in comparison with those of the neat polymer. The aforementioned composition was selected to prepare PP/talc and PP/calcium carbonate composites containing different types and amounts of coupling agents. Moreover, this selection was based on the effect of the size and morphology of the fillers. Therefore, PP composites containing 40 wt % TA2 or CC2 were prepared, and the influence of different types and amounts of coupling agents on their mechanical properties was studied.

In general, an increase in E and δ values was observed as the proportion of the coupling agent in the PP composite increased. This confirmed the existence of a better interaction between the PP matrix and the mineral reinforcement in the presence of a coupling agent, indicating its role in promoting specific interactions, most likely through hydrogen bonding (Table III).

Table III shows that for all proportions of the added coupling agent, the PP/TA2 composites had higher E

TABLE III
Mechanical Properties of the Modified PP Composites Containing PP-g-MA or PP-g-IA as the Coupling Agent

| Coupling agent | | PP composite with 40% TA2 | | | PP composite with 40% CC2 | | |
|----------------|------|---------------------------|----------------|----------------|---------------------------|----------------|----------------|
| Type | wt % | E (MPa) | δ (MPa) | ϵ (%) | E (MPa) | δ (MPa) | ϵ (%) |
| MA | 0 | 2270 ± 160 | 31 ± 1 | 3 | 1800 ± 40 | 25 ± 1 | 17 |
| | 1 | 2580 ± 300 | 35 ± 3 | 3 | 2010 ± 150 | 29 ± 2 | 3 |
| | 5 | 2615 ± 140 | 34 ± 2 | 3 | 2070 ± 100 | 35 ± 3 | 4 |
| | 9 | 2720 ± 130 | 35 ± 3 | 3 | 2066 ± 95 | 40 ± 3 | 5 |
| | 13 | 2780 ± 110 | 35 ± 3 | 3 | 2125 ± 80 | 40 ± 3 | 5 |
| | 17 | 2811 ± 280 | 35 ± 2 | 3 | 2149 ± 190 | 40 ± 3 | 5 |
| | 25 | 3070 ± 370 | 45 ± 5 | 3 | 2210 ± 210 | 43 ± 4 | 6 |
| IA | 0 | 2270 ± 160 | 31 ± 1 | 3 | 1800 ± 40 | 25 ± 1 | 17 |
| | 1 | 2450 ± 150 | 30 ± 1 | 2 | 1910 ± 80 | 27 ± 2 | 4 |
| | 5 | 2495 ± 120 | 33 ± 2 | 3 | 1917 ± 60 | 31 ± 2 | 3 |
| | 9 | 2575 ± 100 | 35 ± 3 | 3 | 1985 ± 70 | 35 ± 3 | 4 |
| | 13 | 2600 ± 110 | 36 ± 2 | 3 | 2010 ± 65 | 35 ± 3 | 4 |
| | 17 | 2651 ± 200 | 39 ± 3 | 3 | 1820 ± 250 | 35 ± 2 | 4 |
| | 25 | 2760 ± 240 | 44 ± 2 | 3 | 2350 ± 180 | 42 ± 2 | 4 |

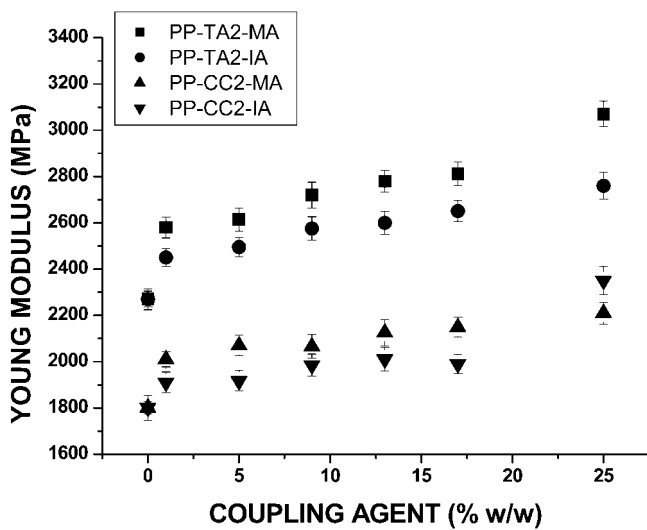


Figure 5 E of the PP composites containing 40 wt % mineral filler with either PP-g-MA or PP-g-IA added as a coupling agent.

values than the PP/CC2 composites. The difference in the rigidity between different types of composites was maintained because of the difference in the filler type and contact area of PP with the filler produced by a particular coupling agent. The difference in the E values of these composites reflected the influence of the coupling agent as well as the surface area of the filler; TA2 had twice the surface area of CC2 (Table II). Moreover, the laminar morphology of TA2 allowed a preferential orientation of this filler in the PP matrix because of the pressure applied during melt mixing. In contrast, the granular morphology of calcium carbonate did not allow the aforementioned orientation of this filler in the polymer matrix, resulting in a less rigid material.

With respect to the δ values, a difference was observed for noncompatibilized composites: values of 25 and 31 MPa were found for PP/CC2 and PP/TA2, respectively. This difference in the δ values decreased slightly for composites containing coupling agents because of the better adhesion of the filler to the PP matrix.

In this way, as the proportion of PP-g-MA and/or PP-g-IA increased, the difference in the δ value was lowered, reaching zero when the amount of the coupling agent reached 25 wt % of the composite. This behavior was due to the fact that the coupling agent improved the interaction between PP and the inorganic reinforcement in both composites types independently of the shape, type, and size of the filler.

No significant variation of ε values was observed for composites containing a coupling agent. Composites containing 40 wt % filler had a consolidated microstructure independent of the type of coupling agent, PP-g-IA or PP-g-MA, up to 25 wt %. The rein-

forcement filler, which provided rigidity to the polymeric matrix, did not allow the coupling agent to improve the tenacity of these composites.

Another relevant aspect of the effect of PP-g-MA and PP-g-IA as coupling agents in PP composites reinforced with mineral fillers is the improvement of the mechanical properties, with the E and δ values of these materials increasing. This is the change in the E and/or δ values with the unit weight of the coupling agent. Therefore, the increase in E and δ depended directly on the proportion of PP-g-MA and/or PP-g-IA. The greater change corresponded to 1% PP-g-MA and/or PP-g-IA (Table III and Figs. 5 and 6).

This reflected the effectiveness of the coupling agent in improving phase cocontinuity between PP and the filler. As shown in Figure 6, differences in the morphology and surface area of the fillers did not affect their performance, as can be appreciated from the δ values. These values were similar for a 25% loading of the coupling agent, being independent of the type of filler.

Morphology

SEM was used to study the morphology of fillers and PP composites filled with either talc or calcium carbonate particles, and the results are shown in Figures 1 and 7, respectively. The laminar morphology of talc can be seen clearly in Figures 1(A) and 7(A).

The different morphologies of the talc and calcium carbonate particles in the PP matrix are shown in Figure 7. The talc particles were more embedded in the PP matrix than the calcium carbonate particles because of their laminar morphology. This was most likely due to the higher surface/volume relation for

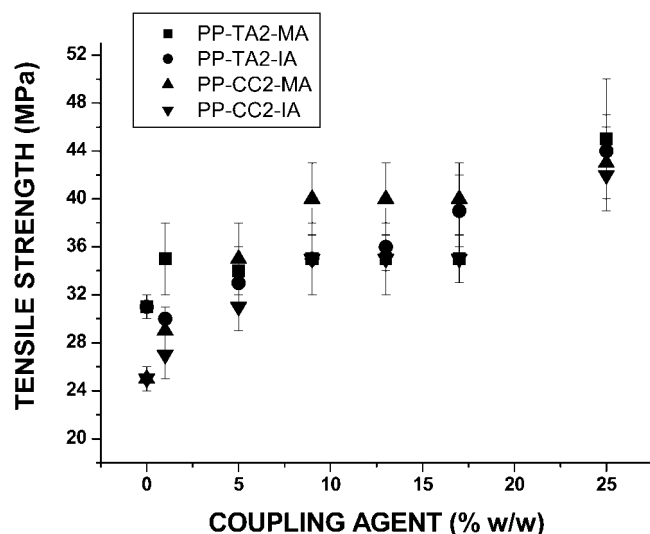


Figure 6 Maximal tensile strength of the PP composites filled with 40 wt % mineral filler with either PP-g-MA or PP-g-IA added as a coupling agent.

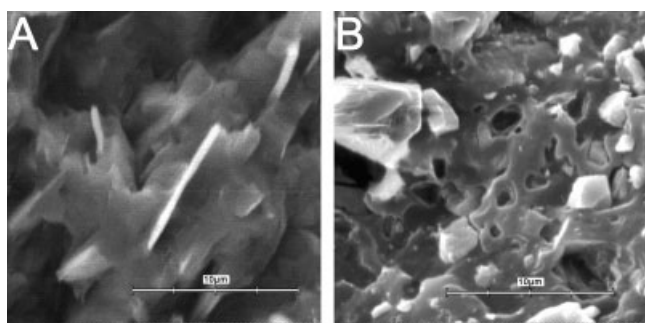


Figure 7 SEM micrographs of the PP composites with 40 wt % (A) TA2 and (B) CC2 without a coupling agent (magnification = 6700 \times).

this filler than that for calcium carbonate. Figure 8 clearly shows that PP-g-IA was very efficient as a coupling agent: both the talc and calcium carbonate fillers were well coated by the polymer. Better adhesion between the talc particles and PP was observed in comparison with calcium carbonate when 25 wt % PP-g-IA was added as a coupling agent.

The coupling effect of PP-g-MA in the PP filled with CC2 as a reinforcement is shown in Figure 9: the addition of 1 wt % of this coupling agent resulted in better adhesion of the calcium carbonate particles to the PP matrix. Moreover, the filler particles were well coated by the polymer matrix in this composite. When the concentration of the added PP-g-MA coupling agent reached 25 wt %, SEM micrographs revealed a more homogeneous distribution of the reinforcing filler, indicating improved adhesion between PP and the filler interface. We concluded that the improvement in the mechanical properties of the composites with coupling agent PP-g-MA or PP-g-IA could be attributed to the existence of better interfacial adhesion between the filler and PP matrix.

CONCLUSIONS

The use of either talc or calcium carbonate as a filler in PP, for three different sizes, increased the stiffness

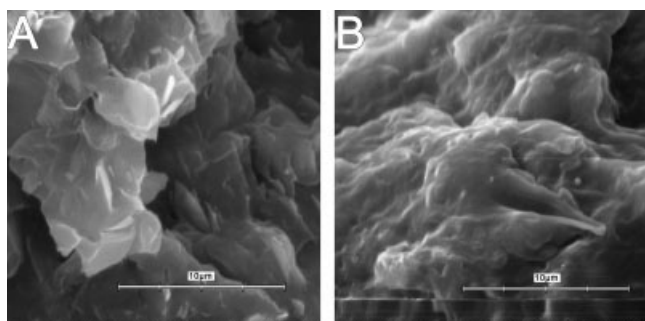


Figure 8 SEM micrographs of the PP composites with 40 wt % (A) TA2 and (B) CC2 with 25 wt % PP-g-IA as a coupling agent (magnification = 6700 \times).

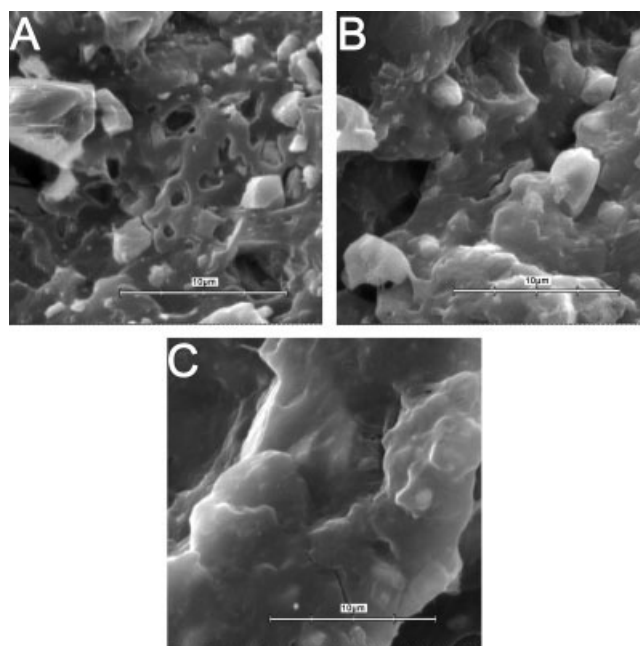


Figure 9 SEM micrographs of PP composites containing 40 wt % CC2 with (A) 0, (B) 1, or (C) 25 wt % PP-g-MA as a coupling agent (magnification = 6700 \times).

and reduced the deformation at breakage of PP composites as the content of the filler increased and as the particle sizes decreased.

The size and distribution of the mineral reinforcements were decisive factors in achieving better adhesion of the polymer to the talc and calcium carbonate in PP/talc and PP/calcium carbonate composites either with or without PP-g-MA or PP-g-IA as a coupling agent. The improvements in the mechanical properties were attributed to the filler/matrix interface improvement by the addition of coupling agents, as determined from SEM analyses.

It was demonstrated that the addition of 1.0 wt % PP-g-IA to a PP composite filled with a mineral improved the strength and modulus of the composite, and this suggested that PP-g-IA could replace commercially available PP-g-MA as a coupling agent.

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