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Elaboration and Characterization of an Organic/Inorganic Hybrid Material: Effect of the Interface on the Mechanical and Thermal Behavior of PP/CaCO₃ Composite

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Elaboration and Characterization of an Organic/Inorganic Hybrid Material: Effect of the Interface on the Mechanical and Thermal Behavior of PP/CaCO₃ Composite

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The present work deals with the study of the effect of the interfaces on the thermal and mechanical behavior of a composite based on polypropylene and calcium carbonate that was treated with bifunctional coupling agents. In order to enhance the coupling of the filler and the polymer, a compatibilizer, namely maleic anhydride grafted polypropylene, was used. The synthesis of the compatibilizer was carried out in a brabender mixer at 180°C. The grafting reaction was assessed by two techniques that were titration of the anhydride function and identification by means of Fourier transform infrared spectroscopy. It was found that the resulting structure depends much on the nature of the coupling agent. The use of the treated calcium carbonate had a great effect on the thermal and mechanical properties of the composites. It resulted in an important increase in both the modulus and tensile stress. The extent of reinforcement obtained with the zirconate coupling agent was higher than that of the composite containing the filler treated with the silane coupling agents. The decrease noted in the strain could reflect an important coupling between the filler and the polymer. This coupling was favored by a complex interfacial structure depending on the individual structure of each coupling agent. The thermal analysis showed that the fusion temperature and the crystallization temperature were not affected by the presence of the filler nor the coupling agents. However, the percentage crystallinity varied with both the amount of the filler and the type of the coupling agent.

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INTRODUCTION

Plastic materials are widely used in many applications. Their success is in part due to the fact that some of their drawbacks have been dealt with through reinforcement. The reinforcing agents used vary in their chemical nature and can take many forms, which can be granular or fibrous. Moreover, they differ in their mode of interaction with the polymeric matrix.

Among the large variety of materials presently produced are thermoplastics that are reinforced with inorganic substances. These materials are increasingly used owing to the ease of their processing compared to thermosetting resins that are more difficult and more expensive to process.

The most interesting feature of reinforcement that motivated the development of filled polymers is without any doubt the improvement of the mechanical properties. Many studies [1–4] have been carried out on systems based on micrometric-sized reinforcing particles. It has been established that the mechanical characteristics of the composites containing inorganic reinforcing fillers depend much on composition but also on the nature and extent of interactions between the filler and the polymeric matrix. Different superficial treatments of these fillers were carried out in order to improve the properties of the interfacial zones. Some studies [5–7] have shown the effect of the functionalization of the filler surface on the morphology and on the mechanical properties of the resulting composites through the modification of the interactions between the filler and the matrix.

Importantly, the use of calcium carbonate allows the association of a rigid and resistant material, which does not cost too much, with many polymers including polyolefines.

Polypropylene-based products are widely used and have been continuously developed. Nevertheless, the antagonism between calcium carbonate and polypropylene made it difficult to develop a composite from these two materials with satisfactory properties. In order to overcome this inconvenience and to enhance the filler–polymer interactions, different types of treatments have been carried out. In this context, many studies reported the chemical modification of calcium carbonate by means of organometallic agents that are based on silicon, titanium, or zirconium [8,9].

In fact, it is possible with this type of modifier to obtain new interfaces through the proper choice of the chemical structure of the coupling agent. In the case when the coupling agent is composed of only carbon without any reactive group, it will develop a Van der Waals type of interaction with the polymeric matrix, favoring hence the interdiffusion of the alkyl chain of the coupling agent with the macromolecular chains of the matrix. However, when the coupling agent possesses a functional group the interaction is evidently not possible owing to the apolar nature of the matrix. Due to this incompatibility, the addition of a compatibilizer that is miscible with the matrix would enhance the coupling between the filler particles and the matrix. For polypropylene-based composites, the use of maleic anhydride grafted polypropylene (MAH-g-PP) ensures the continuity between the two phases.

Ko and Ning [10] proved that the degree of grafting as well as the amount of grafted polypropylene are the key parameters in order to achieve a maximum mechanical performance.

The objective of this study is to establish correlations between the mechanical and thermal properties of the composites based on polypropylene/calcium carbonate treated with bifunctional coupling agents and the presence of a compatibilizer that was synthesized by the grafting of the maleic anhydride onto polypropylene matrix.

EXPERIMENTAL

Materials

The matrix used is a polypropylene resin (ISPLEN PP-40) supplied by Repsol Alcludia S.A. in a granular form having a melt flow index of 2 g/10 min (190°C and 5 Kg) and a specific gravity of 0.902 g/cm³.

The filler used is calcium carbonate (Alcal UF-5) supplied by ENG-Algeria with an average particle diameter of 5 μm and a specific surface area of 2.64 m²/g (BET, N₂ at 77 K). X-ray diffraction measurements indicated that the filler was pure calcite [11]. The chemical composition of this calcium carbonate, which is described in a previous article [12], indicated that the degree of purity of the filler was greater than 98%.

The silane coupling agents used in this work were: 3-aminopropyltriethoxysilane (A-1100) obtained from Witco Corp., and N-(2-aminoethyl)-3-aminopropyltrimethoxysilane (Z-6020) obtained from Dow Corning Corp. The zirconate coupling agent is [neopentyl (diallyl) oxy, tri-(N-ethylene diamino) ethyl zirconate] (NZ-44) donated by Kenrich Petrochemicals Inc. The chemical structure of these compounds is given in Table 1. The coupling agents were used as received, without any further treatment.

TABLE 1 The Chemical Structure of the Coupling Agents Used

Abreviation	Chemical structure
A-1100	$\text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{Si}(\text{OC}_2\text{H}_5)_3$
Z-6020	$\text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{NH}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{Si}(\text{OCH}_3)_3$
NZ-44	$\begin{array}{c} \text{H}_2\text{C}=\text{CH}-\text{CH}_2-\text{O}-\text{CH}_2 \\ \\ \text{CH}_3-\text{CH}_2-\text{C}-\text{CH}_2-\text{O}-\text{Zr}[\text{O}-\text{C}_2\text{H}_4-\text{NH}-\text{C}_2\text{H}_4-\text{NH}_2]_3 \\ \\ \text{H}_2\text{C}=\text{CH}-\text{CH}_2-\text{O}-\text{CH}_2 \end{array}$

The compatibilizer used in this study is maleic anhydride grafted polypropylene (MAH-g-PP), which was synthesized in the authors' laboratory. The monomer used for the reaction of grafting was maleic anhydride (MAH) that was supplied by Aldrich Chemical. The peroxide, as the initiator used for the investigation, was a masterbatch of 60% dicumyl peroxide (DCP) in CaCO_3 obtained from Merck. The stabilizer that was incorporated into the reaction media in order to minimize the degradation process occurring simultaneously in the modification reaction in the polypropylene, was triphenyl phosphine (TPP) supplied by Fluka chemical.

Preparation of Maleic Anhydride Grafted Polypropylene

The modification reaction was carried out in the molten state by using a 60 cm³ Brabender plastograph. Polypropylene (PP), 2% (by weight) MAH, 0.75% DCP, and 0.5% stabilizer (TPP) were introduced in the preheated mixer at 180°C and mechanically mixed at 60 rpm for 10 min. Unreacted MAH was then eliminated by washing the reaction product with methanol. The extracted product was then dried at 80°C for 12 h in order to evaporate any remaining free MAH, poly(MAH), and any other volatiles.

The grafting content was determined by titration of the acid groups derived from anhydride functionalities. A 4 g sample of the polymer was heated in a flask for 1 h, 30 min in 200 ml refluxing water and toluene. The hot solution was then treated, without cooling, with 0.1 N KOH-ethanol using phenol-phthalein as an indicator. A blank titration was carried out by the same method.

The extent of grafting was calculated using:

$$\% \text{ grafting} = (V' - V)N \cdot M_{\text{MAH}} / 2W \cdot 100 \quad (1)$$

where V' is the volume (ml) of the KOH-ethanol standard solution used to titrate the sample, V is the volume (ml) of the KOH-ethanol

standard solution used to titrate the blank solution, W is the weight (g) of the sample used, M is the molecular weight (g/mol) of MAH, and N is the normality of the solution.

Surface Treatment of Calcium Carbonate

In a typical experiment the silane coupling agents were prehydrolyzed completely during 24 h in an acetic acid solution having a pH value of 3. The calcium carbonate was then added to the vessel and the suspension was continuously agitated for 1 h at room temperature. The coated particles were filtered on a Büchner filter, dried in air for 24 h, and heated for 12 h at 105°C in order to complete the condensation process.

The modification with the organozirconate coupling agent was performed in isopropyl alcohol solution analogously to the silane process. The volatiles were removed under vacuum at 80°C for 12 h. The treated filler was dried again for the same period of time at the same temperature.

In order to reach an optimum degree of coating of the filler, the Kenrich method of viscosity reduction of a hydrocarbon oil/CaCO₃ mixture was employed [13]. From those results the concentration of the coupling agent to be used was 0.4% (by weight with respect to the total weight of the filler) for the A-1100 agent, 0.6% for both the Z-6020 and the NZ-44. But in order to see the effect of varying the coupling agent concentration, two other concentrations were also investigated.

Preparation of the Composites

All compounds were prepared by mixing, at an appropriate ratio, PP with 6% MAH-g-PP and fillers in a two roll mill at 180°C for 10 min. The resulting slabs were then pelletized and compression molded at 200°C and 200 Kg/cm² for 5 min.

The optimization of calcium carbonate concentration has been carried out using a Brookfield viscometer and following the method described by M/S Kenrich Petrochemicals Inc. [13]. From this experiment, the Curve of Pigment Volume Concentration (CPVC) was obtained. The filler concentration that was used varied from 10 to 40% (by weight) for the untreated CaCO₃ and 10 to 60% for the treated one.

Fourier Transform Infrared Spectroscopy (FTIR)

Fourier transform infrared (FTIR) analysis was performed in order to confirm both the grafting of MAH onto PP and the reaction of different coupling agents with calcium carbonate. The samples of PP and

MAH-g-PP were pressed into films in a press at 200°C and 200 Kg/cm² for about 5 min. Samples were then analyzed by signal averaging 120 scans at a resolution of 4 cm⁻¹.

The KBr plate method was employed to prepare the untreated and treated calcium carbonate samples. About 5 mg of the fillers were mixed with 95 mg of potassium bromide. This mixture was then compacted into thin pellets using a hydraulic press under a force of 5 tons maintained for about 4 min. Samples were analyzed by signal averaging 600 scans at a resolution of 4 cm⁻¹.

Infrared spectra were obtained in transmission mode with a Perkin-Elmer apparatus using a Grams software to analyze the different transmittance bands.

Mechanical Testing

The tensile properties were determined using a Zwick instrument (model 1445) following the ASTM D-638 procedure and using type 1 test specimen dimensions. The crosshead speed was set at 50 mm/min and 5 samples were tested for each composition. Young's modulus, tensile yield stress, tensile strength, and elongation at break were determined from the recorded force versus elongation curve.

Thermal Analysis

The crystallization behavior and melting characteristics of the composites were studied by differential scanning calorimetry (DSC) using a Perkin-Elmer DSC-7 in a nitrogen atmosphere. The heating and cooling rate was set at 20°C/min.

The temperature at which the polymer mass is melted at a maximum velocity is known as fusion temperature (T_f) and corresponds to the maximum peak temperature. Crystallization temperature (T_c) was calculated based on the peak of the exotherm from the thermogram obtained during cooling.

The heats of fusion (ΔH_f) and crystallization (ΔH_m) were determined from the corresponding peak areas in the heating and cooling thermograms.

The percent crystallinity (X_c) of PP in the composites was calculated as follows:

$$X_c = \Delta H_f / \Delta H_f^0 \cdot F \quad (2)$$

where ΔH_f is the apparent enthalpy of fusion per gram of composite, ΔH_f^0 is the heat of fusion of 100% crystalline PP, taken as 49.6 cal/g [14], and F is the weight fraction of PP in the composites.

RESULTS AND DISCUSSION

Fourier Transform Infrared Analysis

First, it is to be noted that the percentage grafting was found to be 0.56%. Figure 1 shows the spectrum of the grafted polypropylene compared to that of pure polypropylene. Two additional bands at 1710 and 1782 cm⁻¹ can be distinguished for the maleic anhydride grafted polypropylene. The first of which is due to the elongation of the carboxyl group that is characteristic of the carboxylic acid. The second peak at 1782 cm⁻¹ is related to the elongation of the carboxyl group of the maleic anhydride. The FTIR spectrum of polypropylene does not show any band in the 2000–1700 cm⁻¹ range.

Figure 2 shows the infrared spectra of the calcium carbonate treated with the A-1100 as well as that of the coupling agent alone and that of the untreated calcium carbonate. The two bands at 1142 and 1030 cm⁻¹, which appear in the spectrum of CaCO₃ treated with the A-1100 agent, are attributed to siloxane bonds and could be due to the formation of dimers, trimers, and tetramers with linear or cyclic structures.

The FTIR spectrum of the calcium carbonate treated with Z-6020, which is shown in Figure 3(c) reveals the appearance of two additional bands at 1120 cm⁻¹ and 1035 cm⁻¹. These two bands are

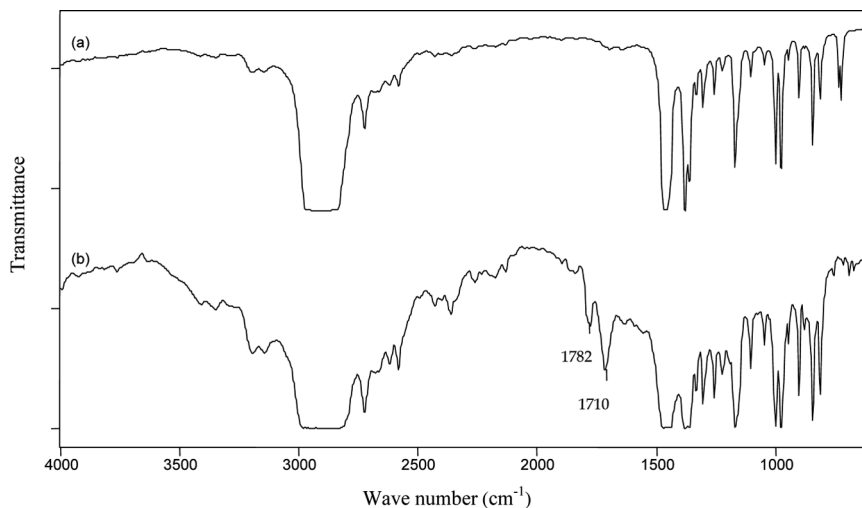


FIGURE 1 FTIR spectrum of (a) polypropylene and (b) maleic anhydride-grafted polypropylene.

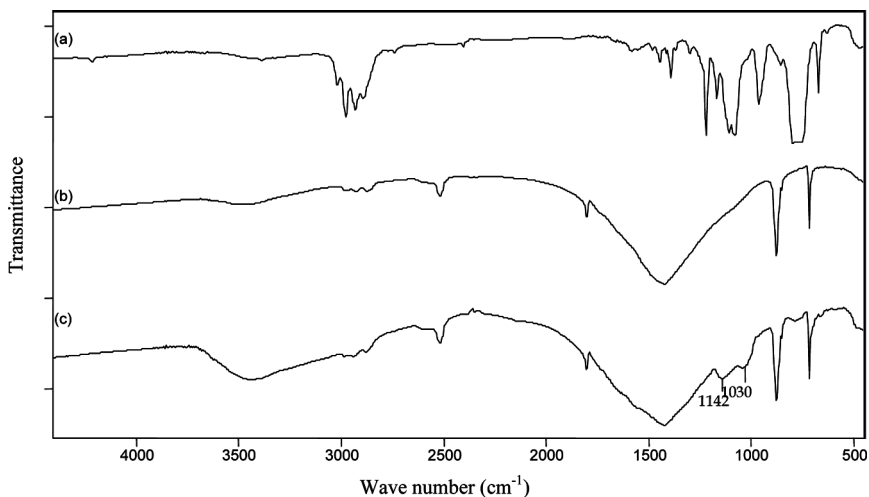


FIGURE 2 FTIR spectrum of (a) A-1100, (b) untreated CaCO₃, (c) CaCO₃ treated with A-1100.

characteristic of the siloxane bonds. The broad band at 3340 cm⁻¹ suggests the presence of NH₃⁺ ion, which means the formation of an amine salt of the H₂N⁺...H...O-Si type. The absorptions at 2932

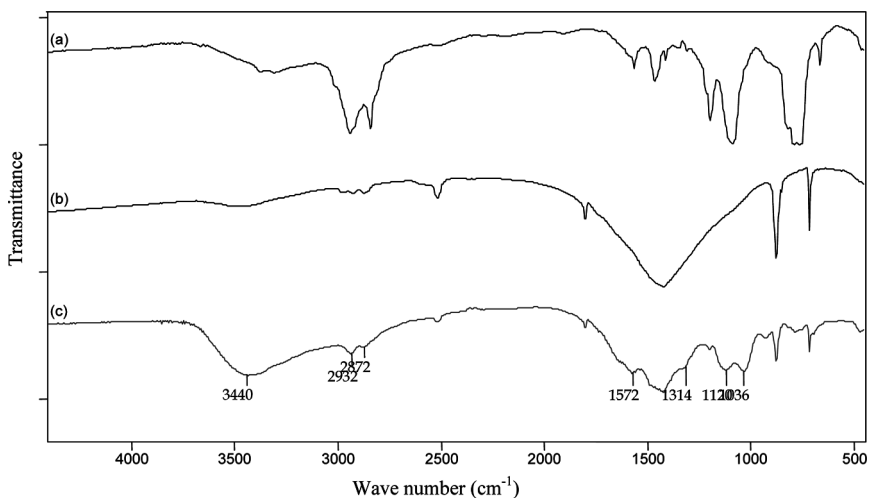


FIGURE 3 FTIR spectrum of (a) Z-6020, (b) untreated CaCO₃, (c) CaCO₃ treated with Z-6020.

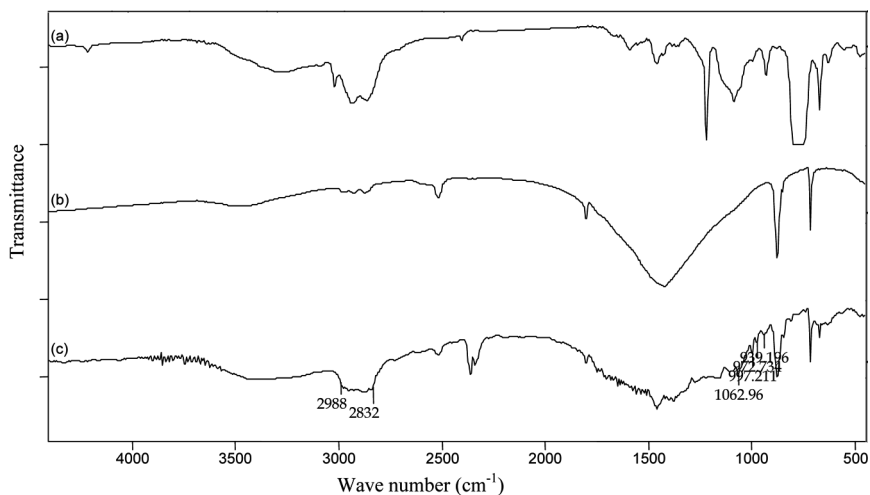


FIGURE 4 FTIR spectrum of (a) NZ-44, (b) untreated CaCO₃, (c) CaCO₃ treated with NZ-44.

and 2872 cm⁻¹ are due to C–H bonds from the aminoethyl or aminopropyl segments of the Z-6020.

Concerning the treatment of CaCO₃ surface with the NZ-44 agent, as shown in Figure 4(c) various bands that are characteristic of the zirconate bonds appear in the 1000–900 cm⁻¹ region. The peaks at 997, 972, 937, and 1062 cm⁻¹ are due to the Zr–O–C and Zr–O–Me (Me : Metal) groups.

The broad band between 2933 and 2862 cm⁻¹ could be attributed to the –CH₂ groups from the organozirconate agent. On the other hand, the set of peaks at the absorption bands of the calcium carbonate seems to be delicate to interpret, for it is composed of progression bands that are equidistant between 1747 and 1374 cm⁻¹ and are produced by the large number of the NZ-44 molecules that are adsorbed on the calcium carbonate.

Mechanical Properties of the Composites

The tensile stress and elongation of the composites have been considered along with the modulus for a better understanding of, on one hand, the effect of the introduction of rigid particles on the mechanical properties of the filled polymer, and on the other hand to check the effect of filler treatment on the interfacial properties of the composites.

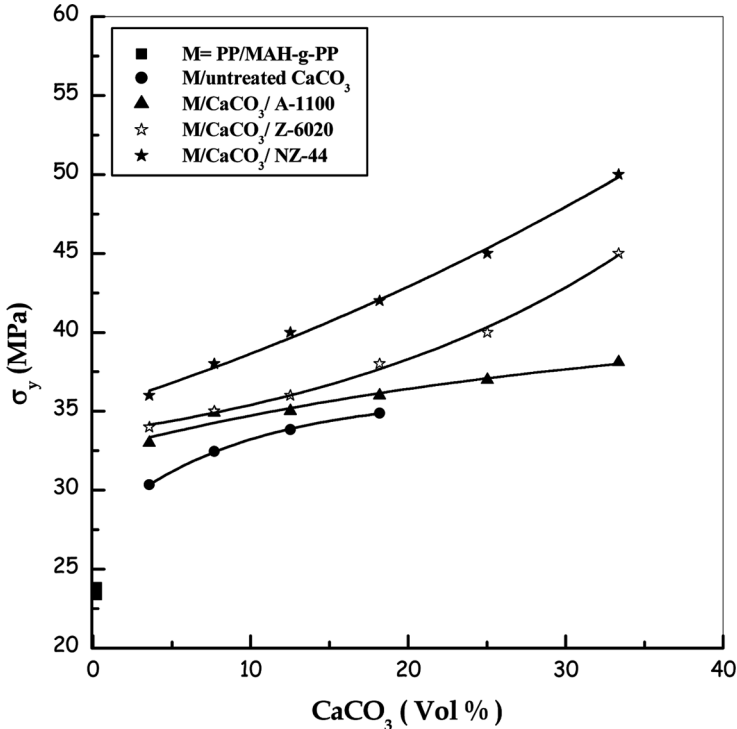


FIGURE 5 Variation of yield stress with CaCO_3 concentration for the composites of PP/ CaCO_3 untreated and treated with different coupling agents.

Pukansky [15] developed an analysis to take into account the variations of yield stress, where a parameter was introduced, B_y , that reflects the state of adhesion between the polymer and the filler. The following semi-empiric equation was proposed:

$$\sigma_{yc} = \sigma_{ym} \cdot \frac{1 - V_f}{1 + 2,5V_f} \cdot \exp(B_y \cdot V_f) \quad (3)$$

where σ_{ym} and σ_{yc} are the yield stresses of the matrix and the composite respectively, V_f the volume fraction of the filler in the composite and B_y is a parameter that characterizes the interaction between the filler and the matrix. The following expression was also proposed in order to assess the interfacial adhesion:

$$B_y = (1 + l \cdot \rho_f \cdot A_f) \ln \frac{\sigma_{yf}}{\sigma_{ym}} \quad (4)$$

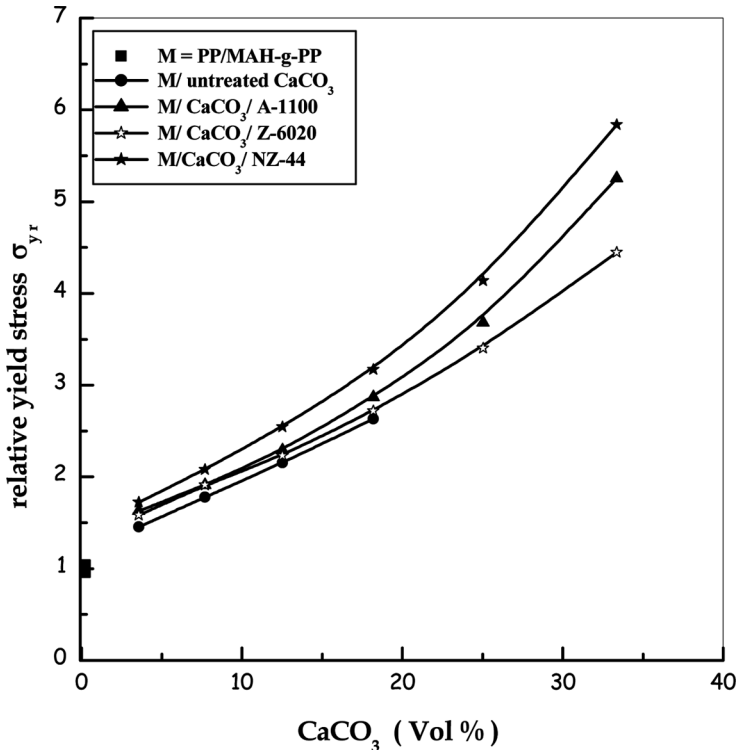


FIGURE 6 Variation of the relative yield stress with CaCO₃ concentration for the composites of PP/CaCO₃ untreated and treated with different coupling agents.

where ρ_f is the specific gravity of the filler, A_f the specific area, l and σ_{yf} are the thickness of the interphase and its relevant property.

Figure 5 shows the variation of yield stress with filler concentration. The addition of the filler, either plain or treated, leads to an increase in yield stress.

In order to compare the behavior of the different composites, the variations of the relative yield stress, which is defined as the ratio of the yield stress of the composite to that of the matrix, have been plotted and are presented in Figure 6. The zirconate coupling agent seems to have a more reinforcing effect than the silane agents. This reinforcing effect reflects a good dispersion of the filler throughout the matrix and a better filler load bearing.

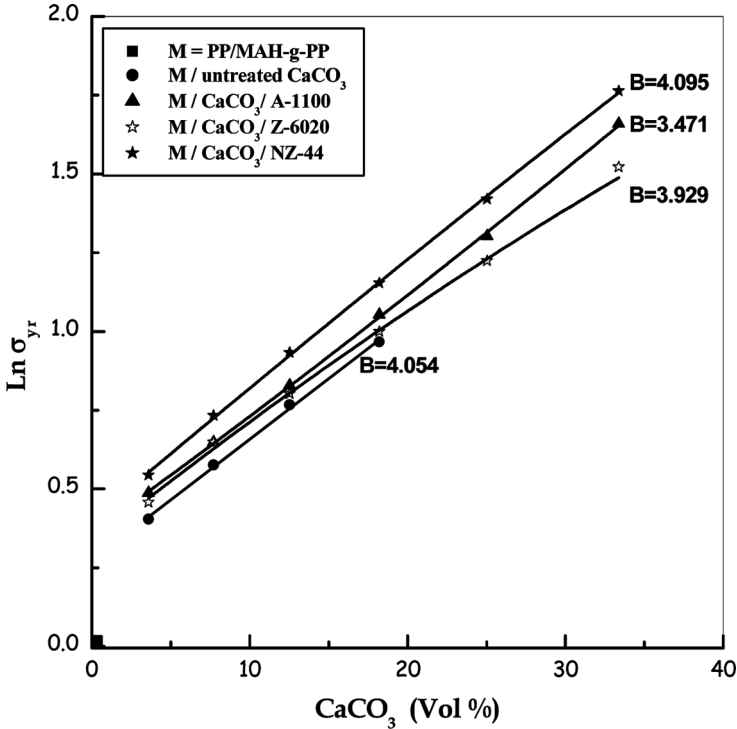


FIGURE 7 Variation of the logarithm of the relative yield stress with CaCO₃ concentration for the composites of PP/CaCO₃ untreated and treated with different coupling agents.

In this study, and for a better analysis of the results, Eq. 3 was linearized as follows:

$$\sigma_{yr} = \frac{\sigma_{yc}}{\sigma_{ym}} \cdot \frac{1 + 2,5V_f}{1 - V_f} = \exp(B \cdot V_f) \quad (5)$$

This method allows the determination of the parameter B from the calculation of the slope of the corresponding line. The values of such a parameter, which are presented in Figure 7, seem to show that the zirconate coupling agent allows a better interfacial adhesion, leading therefore to higher reinforcement than that obtained with the silane agents. The high value obtained with the untreated CaCO₃-based composites could be associated with some adhesion between the compatibilizer and the hydroxides present on the surface of the filler.

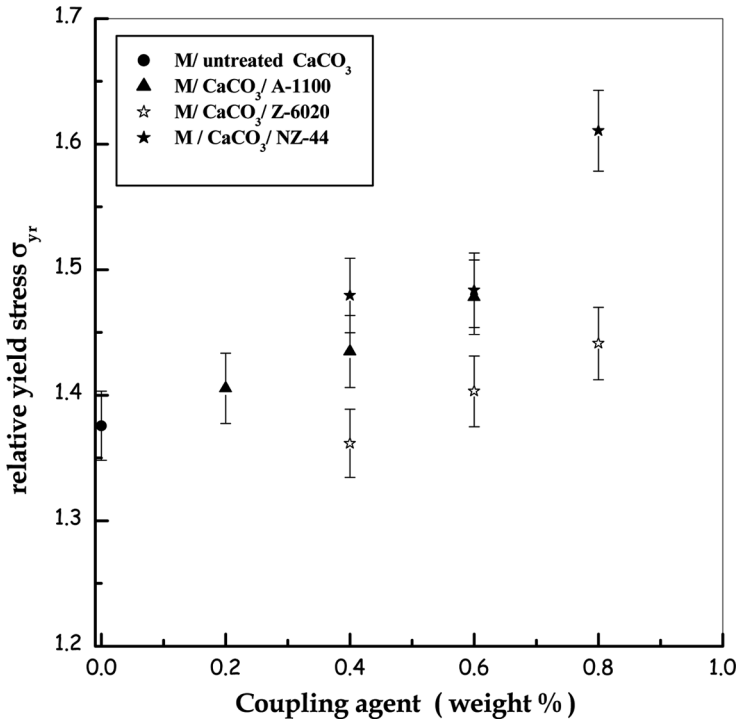


FIGURE 8 Variation of the relative yield stress with the coupling agent concentration for the composites of PP/20% CaCO₃ untreated and treated with different coupling agents.

The study of the effect of the different coupling agents on the relative yield stress has been carried out for composites containing 20% by weight of CaCO₃. In Figure 8 shows that the introduction of the coupling agents at various concentrations leads to an increase in the relative yield stress. This could reflect a higher rigidity of the interface as well as a better load transfer between the filler particles and the matrix.

The effect of the presence of the inorganic particles on the yield stress was studied by comparing the tensile properties of the composites containing 40% CaCO₃ treated with 0.6% of the coupling agents. This is shown in Figure 9. It is clear that the yield point was reached at lower deformations for the composites than for the matrix. Such an evolution could be an indication that the rigid inorganic phase was unable to deform and secondly that an interfacial adhesion between the components of the composite took place.

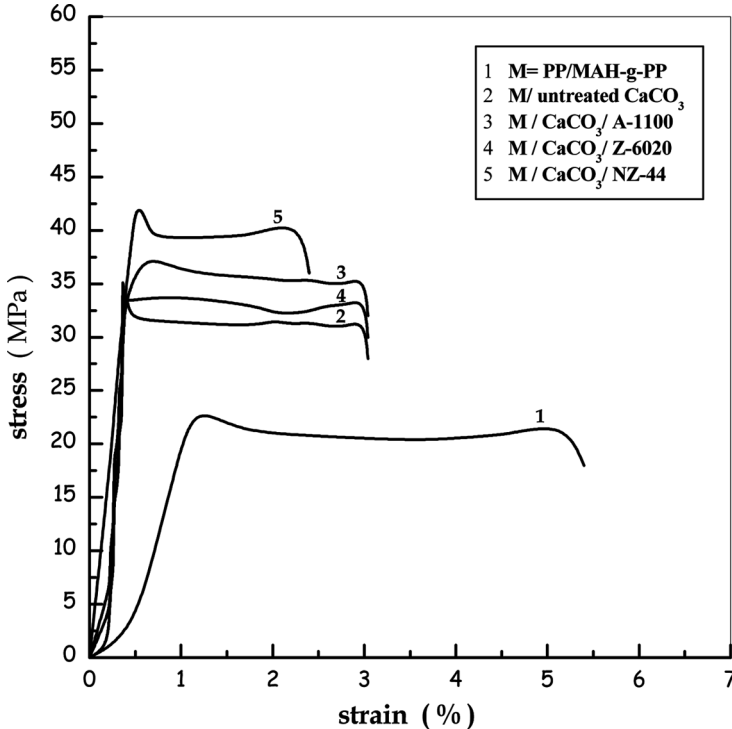


FIGURE 9 Stress/strain curves of the composites of PP/40% CaCO_3 untreated and treated with different coupling agents (0.6%).

The addition of a substantial amount of CaCO_3 , namely 60%, led to a loss of the ductile character of the polymer. A drastic fall of the deformation is observed with the composite containing CaCO_3 treated with NZ-44. Figure 10 shows that the composite ruptures in a brittle manner right after reaching the yield point. Increasing the stresses on the filled polymer leads to a decohesion of the matrix particles prior to any other deformation mechanism. Microcavities will be formed producing macroscopic flaws that lead to an abrupt rupture of the material. Moshev and Evlampieva [16] and Pukanszky et al. [17] suggest that rupture occurs when the cross-section of the polymer composing the structure of the composite undergoes a stress higher than the ultimate stress than the matrix can bear. Rupture takes place when the cavities form a flaw with a critical size.

The study of rupture under tension was carried out using the equations proposed by Nielsen and Landel [18]. The evolution of the tensile

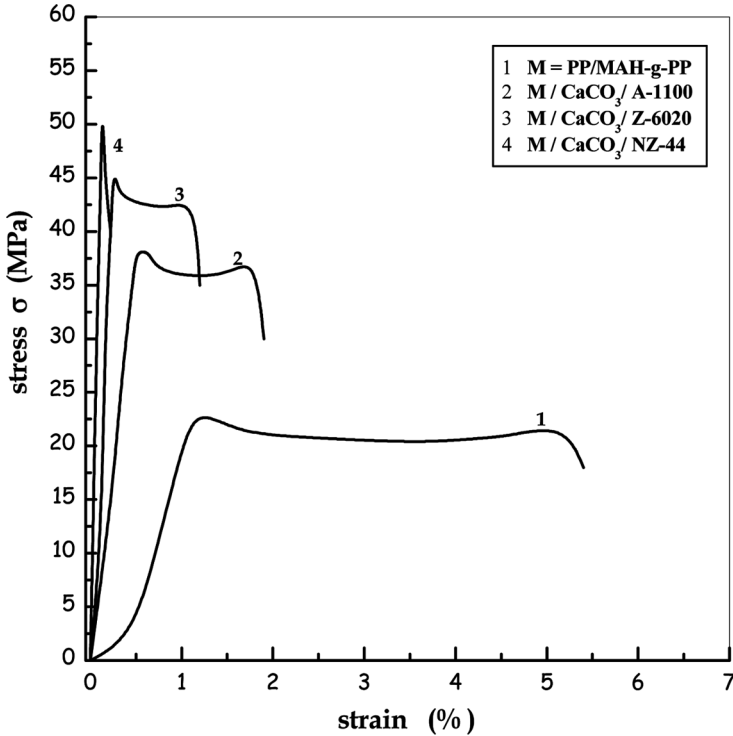


FIGURE 10 Stress/strain curves of the composites of PP/60% CaCO₃ untreated and treated with different coupling agents (0.6%).

stress at break of the composite σ_{rc} with the filler concentration and the tensile stress at break of the matrix σ_{rm} is given by Eq. 6:

$$\sigma_{rc} = \sigma_{rm}(1 - \alpha \cdot V_f^{2/3}) \tag{6}$$

where σ_{rm} and σ_{rc} are, respectively, the stress at break of the matrix and that of the composite and α is a constant. The variation of the strain at break of the composite ϵ_{rc} as a function of the concentration of the filler and the strain at break of the matrix ϵ_{rm} is given by Eq. 7:

$$\epsilon_{rc} = \epsilon_{rm}(1 - 1,101 \cdot V_f^{1/3}) \tag{7}$$

In order to consider reinforcement differences between the different composites, the variations in what has been defined as the relative stress at break and relative strain at break have been plotted as a function of the filler concentration.

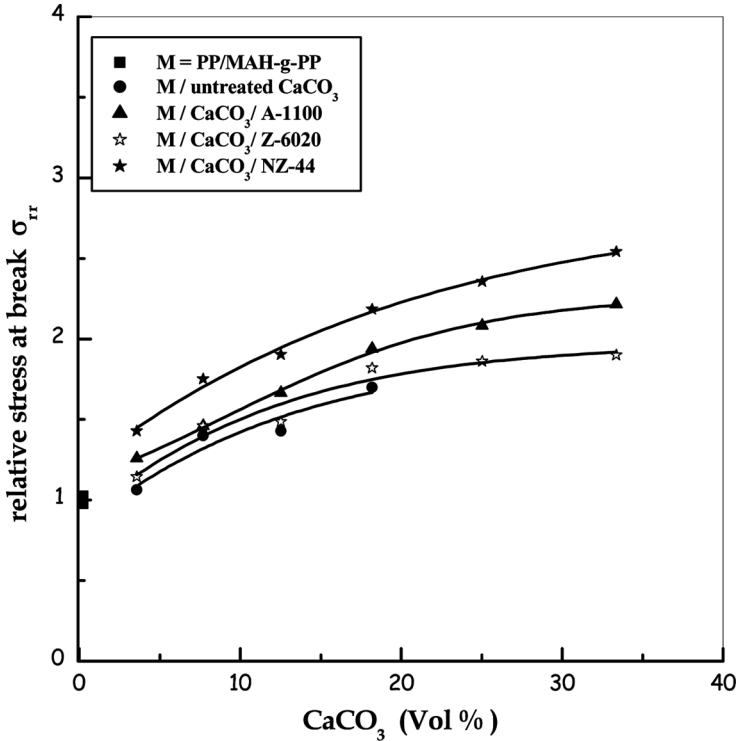


FIGURE 11 Variation of the relative stress at break with CaCO₃ concentration for the composites of PP/CaCO₃ untreated and treated with different coupling agents.

Figure 11 points out the increase of the relative stress at break with increasing filler concentration. In fact, the most important improvements were obtained with NZ-44. This increase confirms the theory according to which when there is a modification in the filler's surface activity owing to the action of a surface agent, the polymer structure might be modified due to chemical reactions between the filler and the polymer.

Figure 12 illustrates the variations of the relative strain at break as a function of the concentration of the filler. The fall of the strain at break of the different composites can only be attributed to changes from ductile to brittle in the behavior of the filled polymer. This decrease is more pronounced with the composites containing the filler treated with NZ-44 agent. It is proposed that this is a property of the

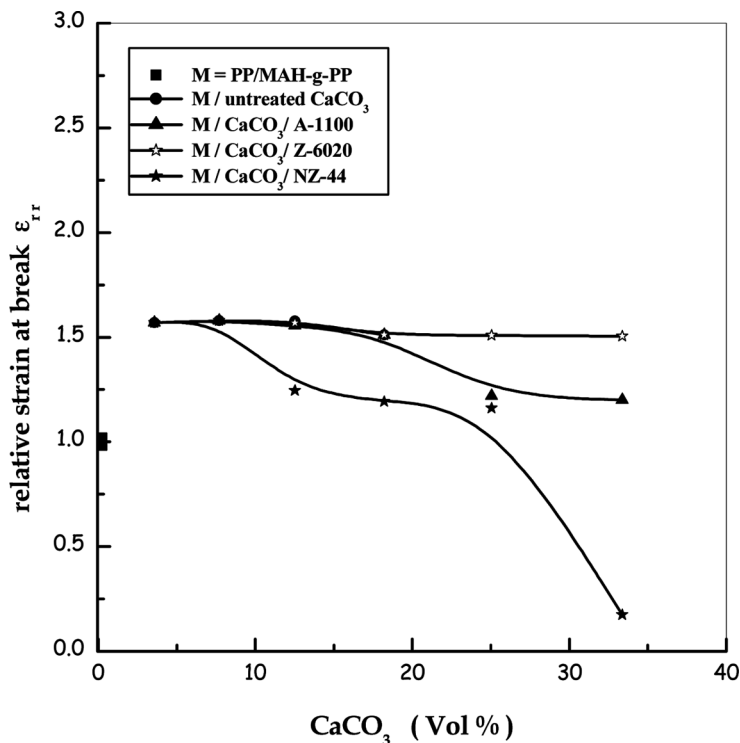


FIGURE 12 Variation of the relative strain at break with CaCO₃ concentration for the composites of PP/CaCO₃ untreated and treated with different coupling agents.

interphase that appears to be a good indicator of the affinity that exists conjointly between the modified filler/compatibilizer and polymer/compatibilizer.

The study of the effect of the concentration of the coupling agents on the relative stress at break and on the relative strain at break was carried out on composites containing 20% CaCO₃ as illustrated in Figures 13 and 14. Within experimental errors, it seems that the use of the coupling agents at different concentrations does not affect much the tensile stress. However, the strain at break decreases rapidly especially with the composites containing the filler treated with NZ-44 agent. This could be due to the stiffening of the interface because a large concentration of the coupling agent can lead to an excessive stiffening of the interfacial zones.

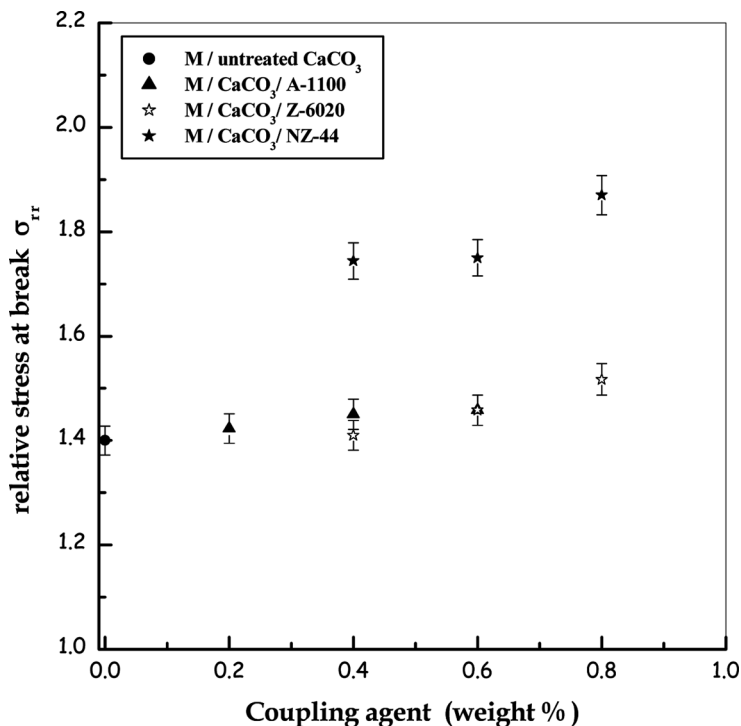


FIGURE 13 Variation of the relative stress at break with the coupling agent concentration for the composites of PP/20% CaCO_3 untreated and treated with different coupling agents.

Thermal Analysis

The results of the thermal analysis that was carried out by means of differential scanning calorimetry (DSC) are presented in Table 2. Overall, there was not a great effect of both the concentration of the filler and its treatment on the fusion temperature (T_f) and the crystallization temperature (T_c). However, a decrease in the energy required for the fusion of the crystalline parts was noted when the concentration of the filler in the composite increased. The heat of fusion (ΔH_f) of the composites containing the CaCO_3 modified with the A-1100 and Z-6020 were higher than those of the composites containing the filler treated with the NZ-44 agent. Yet, the values of the heat of fusion remain lower than that of virgin polypropylene or that of unfilled polypropylene/maleic anhydride grafted polypropylene. It can therefore be noted that the filler alters the crystalline phase of

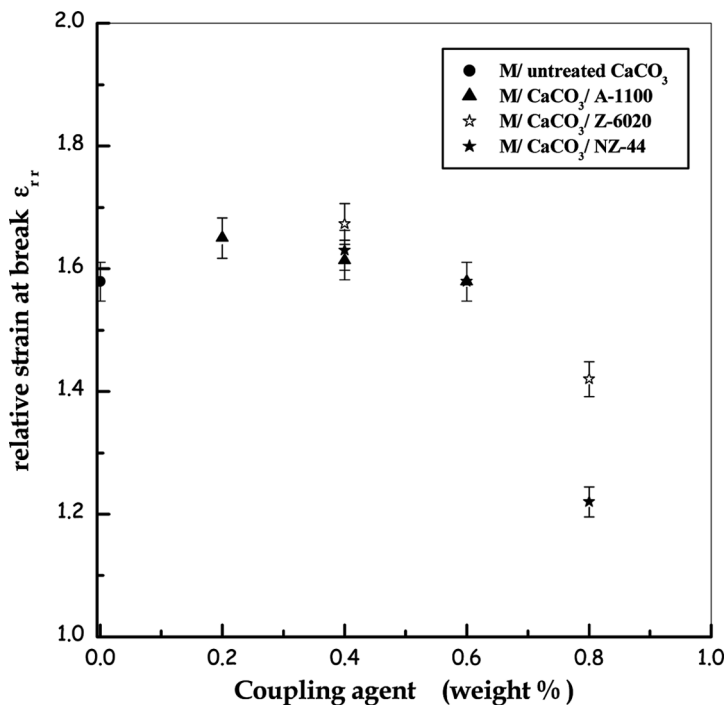


FIGURE 14 Variation of the relative strain at break with the coupling agent concentration for the composites of PP/20% CaCO₃ untreated and treated with different coupling agents.

TABLE 2 Thermal Properties of the Composites

Material	Filler concentration (weight %)	T _f (°C)	T _c (°C)	ΔH _f (j·g ⁻¹)	X _c (%)
PP	—	167.0	112.8	88.10	42.50
M=PP/MAH-g-PP	0	166.0	112.0	72.60	35.00
M/Composite with untreated CaCO ₃	20	165.6	112.7	66.20	31.90
	40	165.0	113.0	65.30	31.50
M/CaCO ₃ /A-1100 Composite	20	166.8	112.6	72.00	34.70
	40	167.0	112.8	70.00	33.70
	60	166.0	113.4	53.00	25.50
M/CaCO ₃ /Z-6020 Composite	20	165.4	112.0	68.70	33.10
	40	166.2	113.0	60.95	29.40
	60	166.0	113.2	63.70	30.70
M/CaCO ₃ /NZ-44 Composite	20	165.0	112.4	58.74	28.30
	40	166.0	113.2	56.80	27.40
	60	166.0	113.0	51.32	24.70

the polymer. The increase in the free volume of the filled systems creates conditions making the development of the crystalline structure becomes more difficult.

CONCLUSIONS

The Fourier transform infrared spectroscopic characterization of the modified filler confirmed the different treatments applied and evidence of the grafting of maleic anhydride on polypropylene in the presence of dicumyle peroxide was obtained through the characteristic C=O bands. Quantitative titration of the grafted maleic anhydride allowed the determination of a degree of grafting that was equal to 0.56%. The measurements of the mechanical properties showed behaviors that are typical of organic–inorganic composites, that is, a sharp decrease of the strain and an increase in Young's modulus and tensile stress. Those properties, which were measured with respect to their relative evolutions, reflected a good quality of the interface, ensuring therefore load transfer between the phases present in the composites. Finally, the thermal analysis has allowed the conclusion that both the fusion and the crystallization temperatures were not sensitive to the presence of the filler particles nor to the coupling agents. The results showed, however, that the filler tends to alter the crystallization structure of the material.

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