

This article was downloaded by:

On: 18 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



International Journal of Polymeric Materials

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713647664>

Effect of Coupling Agents on the Performance of PP/MAH-g-PP/CaCO₃ Ternary Composites

R. Doufnoune^a; N. Haddaoui^a; F. Riahi^b

^a Département de Génie des procédés, Laboratoire de Physico-Chimie des Hauts Polymères (LPCHP), Faculté des sciences de l'ingénieur, Université Ferhat Abbas, Sétif, Algeria ^b Département de Génie des procédés, Laboratoire des Matériaux polymériques Multiphasiques (LMPMP), Faculté des sciences de l'ingénieur, Université Ferhat Abbas, Sétif, Algeria

To cite this Article Doufnoune, R. , Haddaoui, N. and Riahi, F.(2006) 'Effect of Coupling Agents on the Performance of PP/MAH-g-PP/CaCO₃ Ternary Composites', International Journal of Polymeric Materials, 55: 11, 989 – 1007

To link to this Article: DOI: 10.1080/00914030600583845

URL: <http://dx.doi.org/10.1080/00914030600583845>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Effect of Coupling Agents on the Performance of PP/MAH-g-PP/CaCO₃ Ternary Composites

R. Doufnoune

N. Haddaoui

Département de Génie des procédés, Laboratoire de Physico-Chimie des Hauts Polymères (LPCHP), Faculté des sciences de l'ingénieur, Université Ferhat Abbas, Sétif, Algeria

F. Riahi

Département de Génie des procédés, Laboratoire des Matériaux polymériques Multiphasiques (LMPMP), Faculté des sciences de l'ingénieur, Université Ferhat Abbas, Sétif, Algeria

This study deals with the creation and characterization of a polypropylene/calcium carbonate composite in the presence of maleic anhydride-grafted polypropylene used as a compatibilizer. In order to improve the properties of the interfacial zones, the reinforcing filler was treated with two different coupling agents, which were a silane named Dow Corning Z-6020 and a zirconate coupling agent named Ken-React NZ-44. The performance of the interface within the composites was assessed through the measurement of the mechanical and thermal properties. The results revealed an important enhancement of the impact strength and the heat deflection temperature as a result of surface treatment. The analysis of the relative evolution of those properties showed that a more pronounced reinforcing effect was obtained with the NZ-44 coupling agent. The improvement in the properties seemed to depend particularly on the state of the dispersion of the filler throughout the matrix and on the nature of the interface. The thermogravimetric analysis allowed the conclusion that the filler improved the thermal stability of the material but the coupling agent did not seem to have any influence on this property.

Keywords: calcium carbonate, compatibilizer, composite materials, coupling agents, interfacial effects, interphase, polypropylene

Received 30 December 2005; in final form 9 January 2006.

Address correspondence to F. Riahi, Département de Génie des procédés, Laboratoire des Matériaux polymériques Multiphasiques, Faculté des sciences de l'ingénieur, Université Ferhat Abbas, Sétif 19000, Algeria. E-mail: faridriahi@yahoo.com

INTRODUCTION

During the last fifty years polypropylene has gained a great importance and is now present in daily life in general purpose applications as well as for technical use. In fact, polypropylene possesses many attractive properties such as low density, ease of processing, recyclability, low cost, and exhibits a good resistance to impact. However, its use is limited, especially in applications where thermomechanical properties along with high stiffness are required. To compensate for these drawbacks, and extend the field of its application, it has been mixed with an inorganic phase, thus coupling its own advantages with those of the filler, giving rise to a composite material with improved properties.

The most common agents used for reinforcement are inorganic fillers such as talc [1] or calcium carbonate [2–3]. Some other manufactured reinforcing agents, such as glass fibers, have also been used [4]. This list is not exhaustive and other materials have been used [5–6].

The gain in stiffness brought up through a rigid second phase is counterbalanced by stress concentration at the interface, which causes reduction of the resistance to crack propagation of the material. In order to fully take advantage of the reinforcing effect of high modulus fillers, it is therefore convenient to enhance the interactions between the reinforcing agent and the matrix. In this context, the surface treatment of the inorganic filler appears to be an appropriate way to favor the interfacial adhesion.

This work deals with the study of the effect of surface treatment of calcium carbonate on the mechanical and thermal performance of a ternary blend of polypropylene (PP)/Maleic Anhydride grafted polypropylene (MAH-g-PP)/calcium carbonate (CaCO_3).

EXPERIMENTAL

Materials

Isotactic polypropylene (ISPLEN PP-40) supplied by Repsol Alcludia S.A. was used as the matrix. It has a melt flow index (MFI) of 2 g/10 min. 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 m^2/g . The coupling agents selected for the investigation were: N-(2-aminoethyl)-3-aminopropyltrimethoxysilane (Z-6020) obtained from Dow Corning Corp. and neopentyl diallyl oxytri-(N-ethylene) diamino ethyl zirconate (NZ-44) donated by Kenrich

Petrochemicals Inc. The maleic anhydride (MAH) used for grafting was supplied by Aldrich Chemical and has a melting point of 51–56°C. Dicumyl peroxide used as the initiator for the grafting reaction was 60% active with a half life time of 2 h at 130°C [7] and was supplied by Merck Company. The thermal stabilizer that was used to avoid the degradation of PP was triphenyl phosphine (TPP) and was supplied by Fluka Chemica.

All the concentrations of all additives in this study are expressed in % by weight.

Optimization of the Coupling Agents Concentration

The optimum amount of coupling agents required was determined following the method described by Kenrich Petrochemicals Inc. [8]. It is based on first plotting the decrease in the Brookfield viscosity of a mixture of a hydrocarbon oil and calcium carbonate with the increase of coupling agents' concentrations. Then a ratio of 50:50 of the inorganic filler to the hydrocarbon oil was maintained constant while varying the concentration of the coupling agent from 0.2 to 1.2%. The intersection of the two tangent lines resulting from this curve gives the optimum concentration to be used.

Surface Treatment of Calcium Carbonate with Coupling Agents

The surface modification of calcium carbonate with the silane coupling agent (Z-6020) was performed as follows. First the required amount of the coupling agent was dissolved in a deionized water solution with a pH of 3; that was adjusted to this value by adding acetic acid. To ensure a total dissolution, the solution was stirred continuously for 24 h at room temperature. Calcium carbonate was then added and the mixture was agitated for 1 h at room temperature. The CaCO₃ particles from these solutions were dried in air for one day and the silane layers were cured for 12 h at 105°C. Treatment with the zirconate coupling agent (NZ-44) was carried out in an isopropanol solution analogously to the silane process. The particles were then filtered and dried at 80°C under vacuum until the solvent was completely evaporated.

Optimization of Calcium Carbonate Concentration

The optimization of calcium carbonate has been determined according to the method described in the reference manual from Kenrich Petrochemicals Inc. [8]. The method allows the determination of the Critical

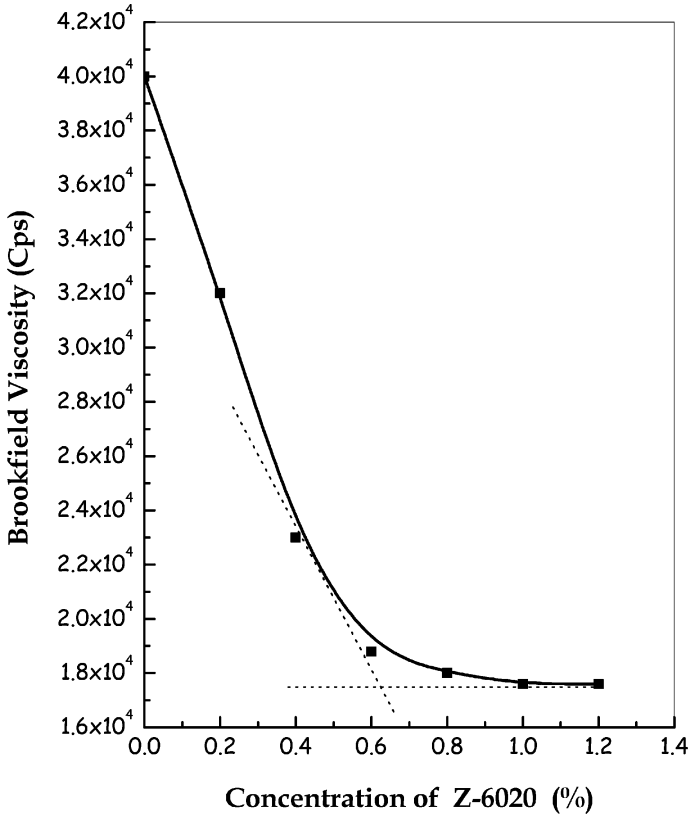


FIGURE 1 Variation of the Brookfield viscosity of the mixture CaCO_3 /hydrocarbon oil with the silane coupling agent (Z-6020) concentration.

Pigment Volume Concentration (CPVC). The CPVC may be defined as that point in an inorganic/organic system at which just sufficient organic matter is present to fill completely the voids left between the inorganic particles incorporated in the organic matrix. It represents the optimum degree of packing of the inorganic particles commensurate with the degree of dispersion of the system and provides a theoretical point of optimum filler loading to obtain the best balance of mechanical properties. The procedure consisted of measuring the Brookfield viscosity of mixtures of hydrocarbon oil with calcium carbonate at different ratios. The concentration of the filler varied from 10 to 80%. The upward sweep of the curve of Brookfield viscosity as a function of filler concentration corresponds to the optimum amount to be used.

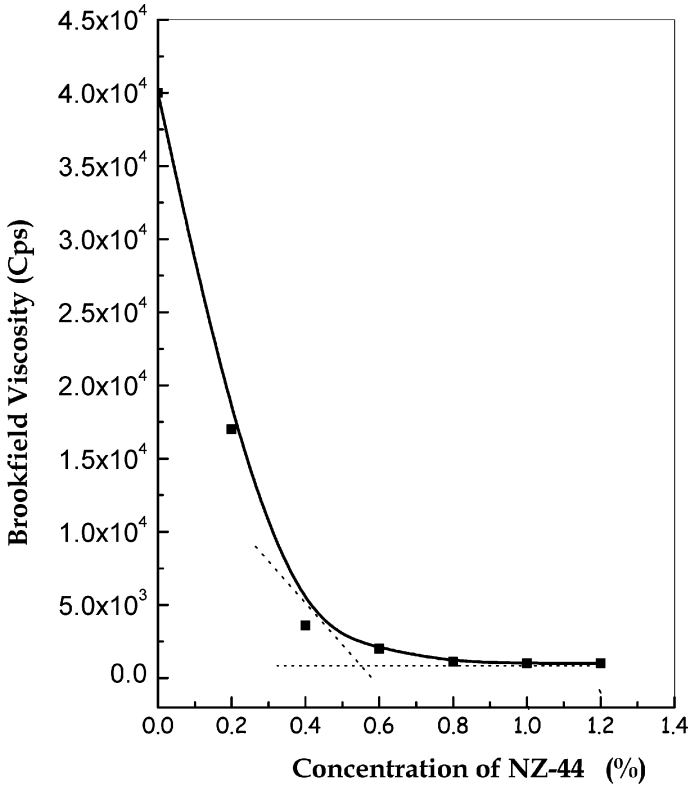


FIGURE 2 Variation of the Brookfield viscosity of the mixture CaCO_3 /hydrocarbon oil with the zirconate coupling agent (NZ-44) concentration.

Preparation of the Compatibilizer: Grafting of Maleic Anhydride onto PP

The MAH-g-PP has been synthesized in the molten state by using a Brabender plastograph. Polypropylene, maleic anhydride (2%), dicumyl peroxide (0.75%), and triphenyl phosphine (0.5%) were introduced in the preheated batch mixer at 180°C, and mixed at 60 rpm for 10 min. The grafting degree was determined following a previously described procedure and it was found to be equal to 0.56% [9].

Preparation of Composites

The different composites were prepared in the molten state by using a two-roll mixer at 180°C for 10 min. The resulting compounds were then

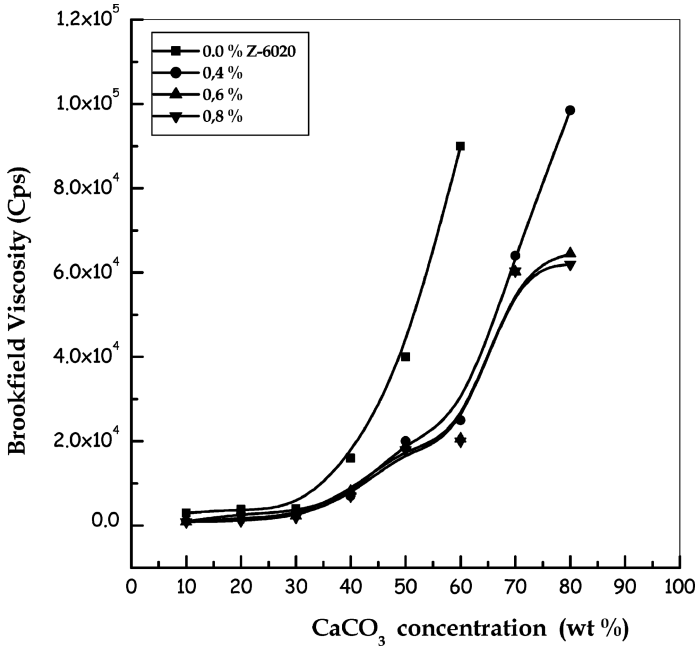


FIGURE 3 CPVC curves of the hydrocarbon oil/ CaCO_3 untreated and treated with different concentrations of the silane coupling agent (Z-6020).

pelletized. Test specimens were prepared using an electrically heated compression molding machine, with a clamping pressure of 200 Kg/cm^2 , heated to a temperature of 200°C for about 5 min.

Optimization of the Concentration of the Compatibilizer

In order to optimize the concentration of the compatibilizer, different amounts of MAH-g-PP ranging from 0 to 12% were added to PP and then mixed in the roll-mill at 180°C for 10 min. Sheets of these blends were then ground and their Melt Flow Index (MFI) was measured according to ASTM D 1238-82 procedure at 190°C under a load of 2160 g.

Impact Strength

The notched Izod-impact strength test was performed using a Ceat (model 65HG) pendulum tester at an impact energy of 7.5 KJ and following ASTM D 256-73 procedure. All tests were carried out in an

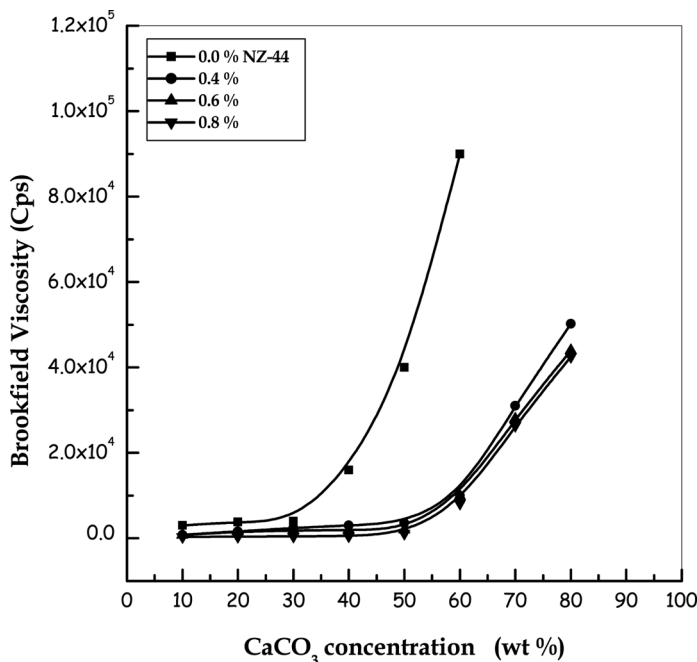


FIGURE 4 CPVC curves of the hydrocarbon oil/ CaCO_3 untreated and treated with different concentrations of the zirconate coupling agent (NZ-44).

air conditioned room (25°C). A minimum of five specimens were tested and the average energy was calculated for each point reported.

Heat Deflection Temperature

The Heat Deflection Temperature (HDT) of the samples was tested according to ASTM D 292-52 method A using a Davenport apparatus. The heat deflection temperature test measures the temperature at which deformation occurs when the specimen having dimensions 127 mm in length, 13 mm in thickness, and 3 mm in width is placed in an oil bath under a load of 1.82 MPa while the temperature is raised continuously at a rate of 2°C per min.

Thermal Gravimetric Analysis

The Thermal Gravimetric Analysis (TGA) was performed using a TG-DTA 92 thermal analyzer. The weight loss was measured over a range of temperatures varying from room temperature up to 250°C , at a rate of 10°C per min, under a nitrogen purge flow of 30 ml/min.

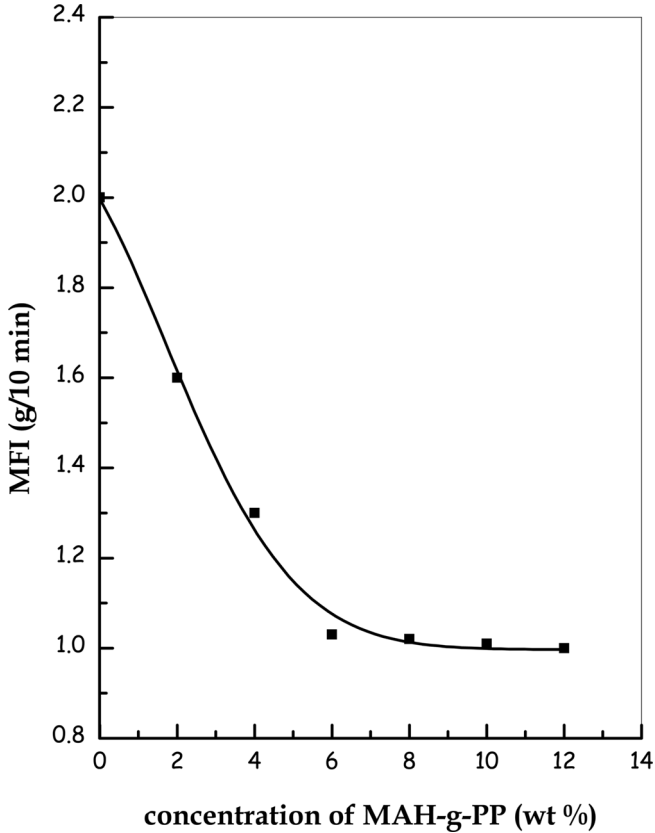


FIGURE 5 Variation of the Melt Flow Index of PP/MAH-g-PP with the compatibilizer concentration.

RESULTS AND DISCUSSION

Determination of the Optimum Concentration of Coupling Agents

It is most critical to use the right amount of coupling agent. The level of silane and zirconate coupling agents to be used in composites to form a monolayer is based on the reaction of silane hydroxy groups and zirconate alkoxy groups, with available surface protons provided by the inorganics and organics in the polymer matrix systems. Figures 1 and 2 show the effect of coupling agents' concentration on the viscosity of a mixture of hydrocarbon oil and calcium carbonate. More specifically, they show that a concentration of 0.4% of both coupling

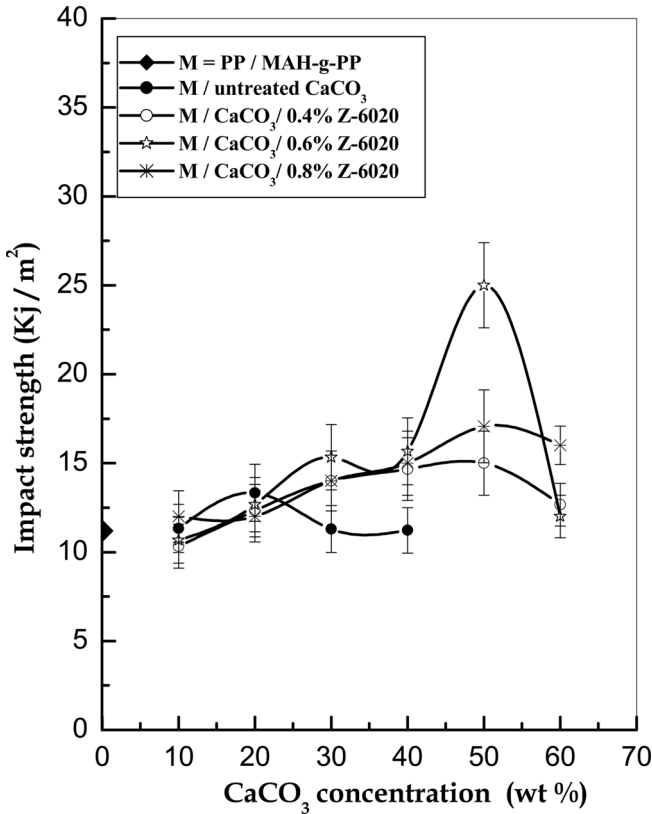


FIGURE 6 Effect of CaCO_3 concentration on the impact strength of PP/MAH-g-PP/ CaCO_3 untreated and treated with different concentrations of the silane coupling agent (Z-6020).

agents studied provides the most optimum viscosity reduction. Yet, a concentration of 0.6% with respect to the total weight of the filler, which corresponds to the intersection of the two tangent lines, presented as dotted lines in Figures 1 and 2, was chosen based on the method proposed by Kenrich Petrochemicals Inc. [8]. In order to confirm this result, the effect of another concentration that is 0.8% was also investigated.

Determination of the Optimum Concentration of Calcium Carbonate

Figures 3 and 4 show the CPVC curves for calcium carbonate filled hydrocarbon oil. It is noted that the curve for the nonchemically

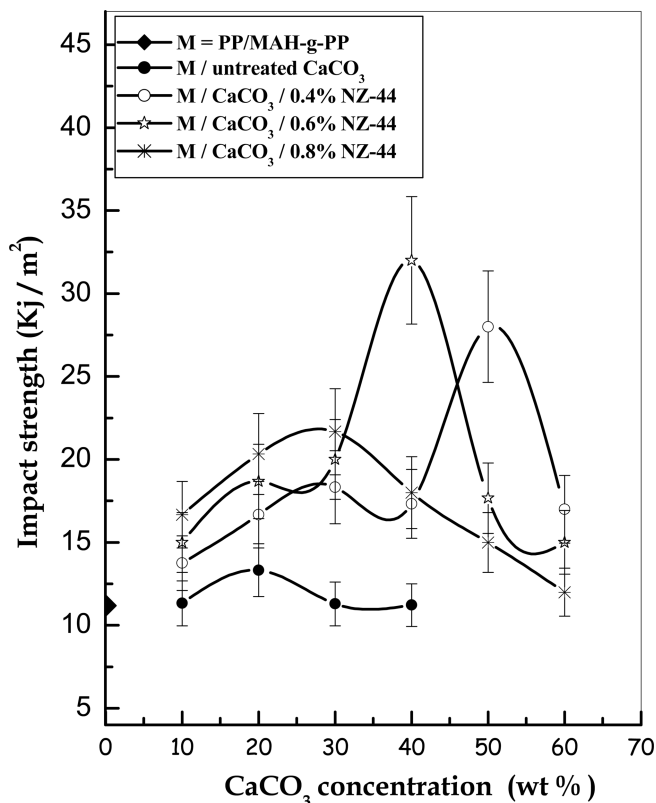


FIGURE 7 Effect of CaCO_3 concentration on the impact strength of PP/MAH-g-PP/ CaCO_3 untreated and treated with different concentrations of the zirconate coupling agent (NZ-44).

treated calcium carbonate begins to break sharply at a concentration between 30 and 40%. This is one reason why uncoupled filled thermoplastics are not usually filled above this concentration. The chemical treatment shifts these curves to the right and the CPVC reaches a value between 50 and 60%. This predicts that the equivalent rheology level for the filled polymer will be between 50 and 60%.

Determination of the Optimum Concentration of the Compatibilizer

The variation of Melt Flow Index (MFI) as a function of the compatibilizer content is shown in Figure 5. The MFI of the blend decreases

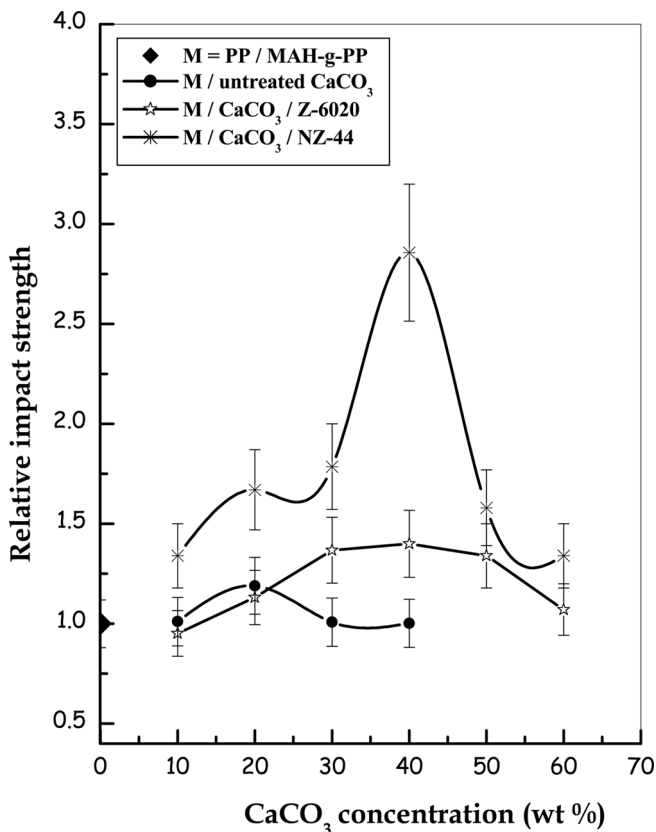


FIGURE 8 Effect of CaCO₃ concentration on the relative impact strength of PP/MAH-g-PP/CaCO₃ untreated and treated with 0.6% of the silane coupling agent (Z-6020) and the zirconate coupling agent (NZ-44).

as the MAH-g-PP content increases before leveling off at a concentration of 6%. The reduction of the MFI, which means an increase in viscosity, can be attributed to the enhanced interactions between PP and MAH-g-PP. Consequently, the optimum content of MAH-g-PP in PP was fixed at 6% with respect to the total weight of the matrix.

Impact Strength

Figures 6 and 7 present the variations of the impact strength as a function of filler and coupling agents' concentration. These results show a clear increase of this property up to a concentration of 20%

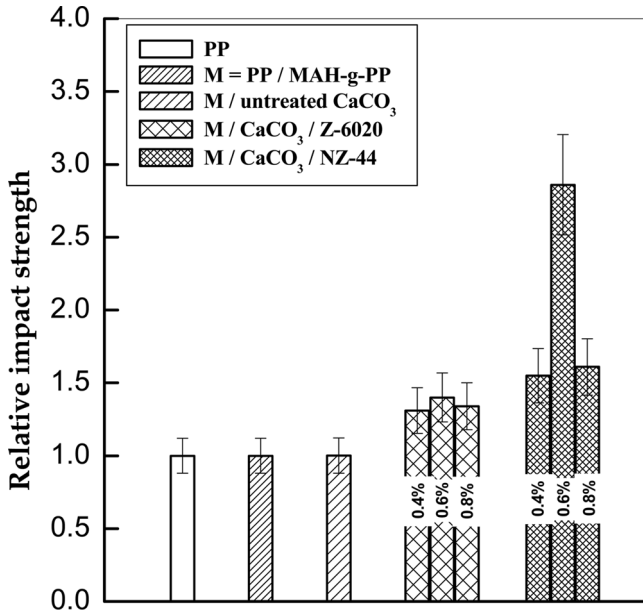


FIGURE 9 Variation of the relative impact strength for the composites of PP/MAH-g-PP/40% CaCO₃ untreated and treated with different concentrations of the coupling agents.

for the composites with untreated filler. Then a small decrease is observed for the composites containing 30% and 40%. This is explained by the tendency of the untreated filler to agglomerate due to its high surface tension, which would favor the formation of structures with low contact area available for any eventual load transfer mechanism and would favor also the formation of weak interfacial areas.

The modification of the surface activity of the filler seems to contribute to an important improvement of the impact strength of all the composites that were studied. The evolutions observed appear to depend greatly on both the concentration and the nature of the coupling agent. In fact, the curves show an abrupt fall in reinforcement for a concentration of 50% of the CaCO₃ treated with the silane coupling agent. However, for the zirconate-based composites, the maximums observed vary up to between 30 and 50% depending on the concentration of the coupling agent. This increase is a result of the increased chemical interactions between the polymer and the filler as well as a uniform distribution of the CaCO₃ particles within the matrix. Moreover, as

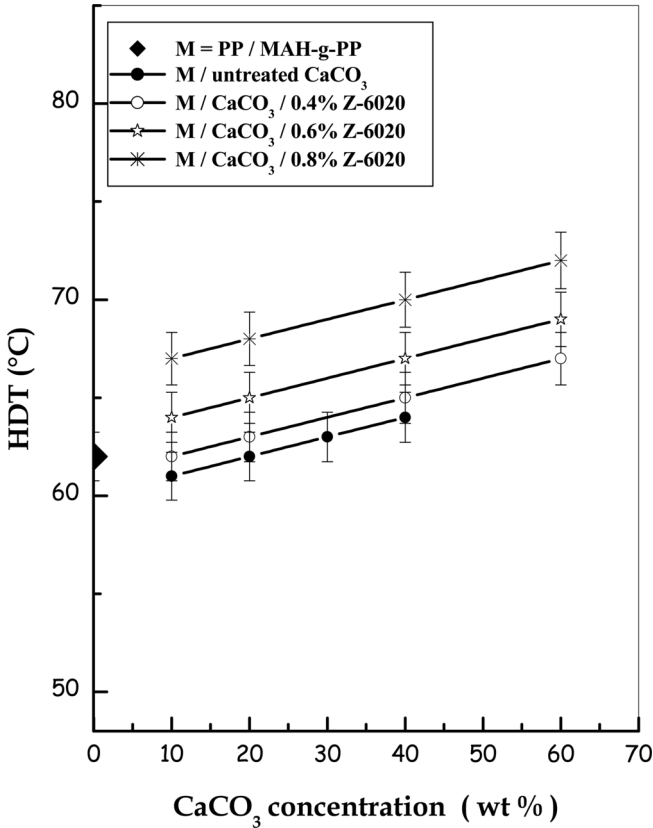


FIGURE 10 Effect of CaCO_3 concentration on the Heat Deflection Temperature of PP/MAH-g-PP/ CaCO_3 untreated and treated with different concentrations of the silane coupling agent (Z-6020).

both the filler and the matrix share the input energy, reinforcement results as long as the CaCO_3 particle distribution throughout the matrix is homogeneous.

The increase in the solids' concentration reduces the interparticulate distance; that is the tendency for the filler particles to agglomerate. Consequently, the applied impact energy will be absorbed by the particulate-rich zones of the material, creating the phenomenon of localized stress concentration, leading therefore to a nonhomogeneous material.

For a more precise estimation of the observed variations between the different composites, the analysis of the results was carried out

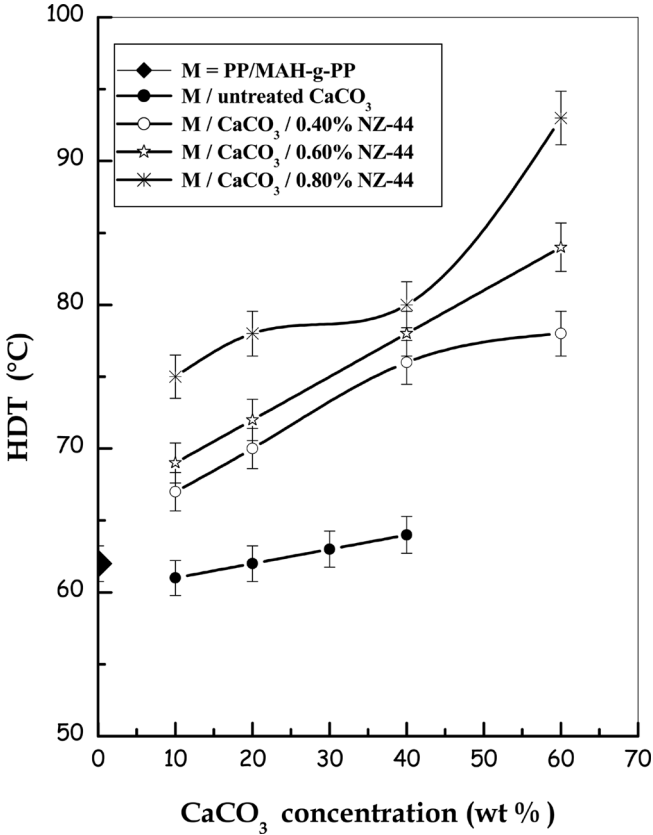


FIGURE 11 Effect of CaCO_3 concentration on the Heat Deflection Temperature of PP/MAH-g-PP/ CaCO_3 untreated and treated with different concentrations of the zirconate coupling agent (NZ-44).

using the approach of relative entities. Figure 8 illustrates the variations of the Relative impact strength, for the composites with untreated filler and those modified with 0.6% of the coupling agents. It is shown that the composites based on CaCO_3 treated with NZ-44 exhibited a higher extent of reinforcement. This is attributed to a pseudo-interphase that was formed as a result of strong physico-chemical interactions between the filler and the organic matrix owing to the compatibilizer and the coupling agent.

The comparison of the bar graphs, presented in Figure 9, showing the variation of the Relative impact strength with the coupling agent concentration for the composites containing 40% CaCO_3 , confirms the

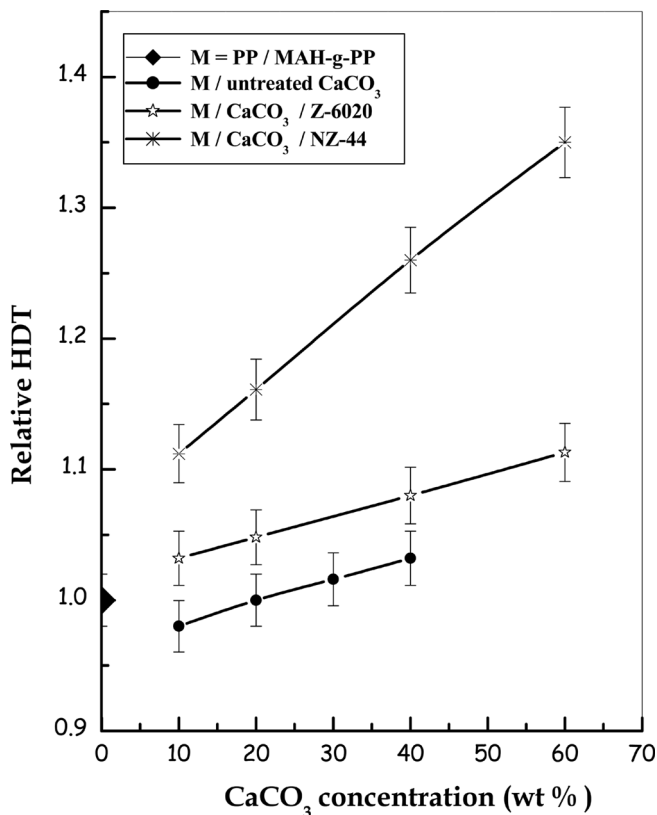


FIGURE 12 Effect of CaCO_3 concentration on the Relative Heat Deflection Temperature of PP/MAH-g-PP/ CaCO_3 untreated and treated with 0.6% of the silane coupling agent (Z-6020) and the zirconate coupling agent (NZ-44).

differences that had already been observed. That is the excellent results obtained with NZ-44 prove once more that the quality of the polymer-filler interfacial adhesion is strongly dependent on the chemical nature of the surface treatment.

Heat Deflection Temperature

The Heat Deflection Temperature (HDT) is a property that measures the deformability of a sample subject to a continuous heating while being stressed under tension. Preliminary studies [10] have indicated that it is possible to obtain from such measurements valuable information such as the morphology of the material, the orientation of

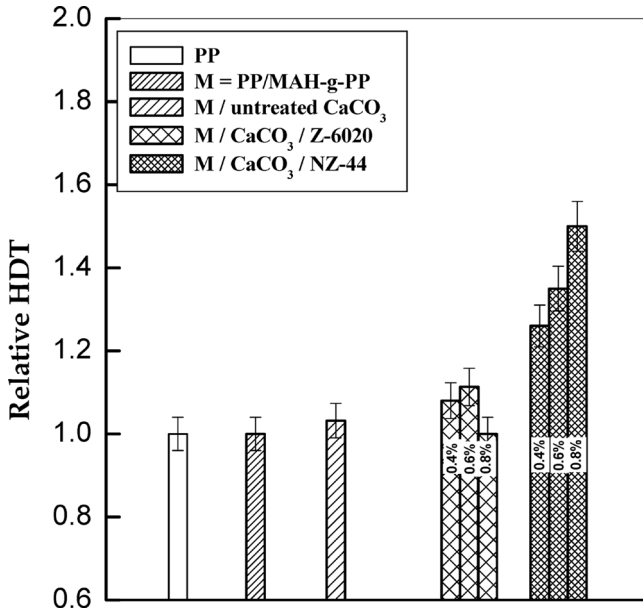


FIGURE 13 Variation of the Relative Heat Deflection Temperature for the composites of PP/MAH-g-PP/40% CaCO₃ untreated and treated with different concentrations of the coupling agents.

the macromolecules, and the dispersion of the filler throughout the polymer. The results presented in Figures 10 and 11 show that the filler either plain or treated affects the Heat Deflection Temperature. The increase that is noted can be associated with the formation of an interphase or rather a pseudo-interphase where strong physico-chemical interactions between the filler and the polymer take place owing to their mutual affinities.

The presence of coupling agents can play a two-fold role as far as the behavior under deflection of the composites is concerned: on one hand coupling agents contribute to the change of the filler's surface properties by reducing the surface free energy of the mineral particles. This leads to an improvement in the dispersion of the filler, giving rise therefore to a better distribution of the stress through the material. On the other hand they help the formation of the interphase through the interactions that develop between the different phases of the composites.

The comparison between the different composites is also made with respect to relative variations. Figure 12 presents the variation of the

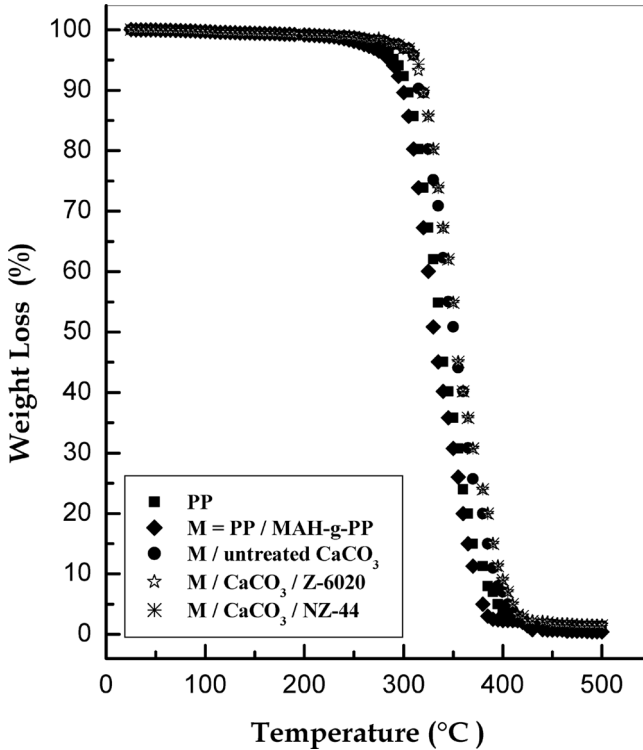


FIGURE 14 TGA thermograms of PP, PP/MAH-g-PP blend and the composites of PP/MAH-g-PP/40% CaCO₃ untreated and treated with 0.6% of the silane coupling agent (Z-6020) and the zirconate coupling agent (NZ-44).

Relative Heat Deflection Temperature as a function of filler concentration for untreated-based composites as well as those treated with 0.6% coupling agents. These variations are in conformity with the previous trends observed for the impact strength. It is proposed to attribute the differences to the properties of the interphase, which is a good indicator about the affinity that exists conjointly between the filler and the coupling agent as well as between the polymer and the coupling agent.

The Relative Heat Deflection Temperature plotted as a function of coupling agent concentration for the composites containing 40% CaCO₃, as shown in Figure 13, confirms the importance of surface treatment. The increase observed is a consequence of the excessive rigidity of the interfacial zones due to the development of a rather more complex interphase. The nature of this interphase is dependent

on the mutual influence between the coupling agent and the compatibilizer and varies as a function of the type of the surface activity of the filler with the polymeric matrix.

Thermal Gravimetric Analysis (TGA)

Figure 14 presents the thermograms in terms of variation of weight loss as a function of temperature for PP alone, PP/MAH-g-PP blend, and the composites with 40% untreated CaCO_3 and those treated with 0.6% coupling agents. The introduction of the compatibilizer does not induce any significant modification of the thermal stability in comparison to the initial polymer. This observation is well illustrated with the two temperatures characterizing these thermograms. The first of which is the temperature of the onset of the decomposition that takes place between 215 and 220°C. The second temperature is the one that marks the constant weight reached that corresponds to the end of the reaction around 400°C signifying the total decomposition or degradation of the samples.

However, the addition of calcium carbonate did improve slightly the thermal stability of the composite. The observed trends concerning the effect of the chemical nature of the coupling agents on the thermal stability of the composites remain identical for the coupling agents that were considered in this study. Aside from these observations, no effect of the treatment on the temperature of the onset of the decomposition was noted for all the materials.

CONCLUSIONS

The present work explored the possibilities of correlating the properties of the ternary composites based on PP/MAH-g-PP/ CaCO_3 with the surface treatment of the mineral particles by means of coupling agents.

The results confirmed the importance of the surface treatment, which determines the right equilibrium between the ease of the dispersion of this powder during mixing and the resulting mechanical and thermal properties of the composite.

The optimum extent of reinforcement was found to be strongly dependent on weight fraction of the filler, and on the chemical nature as well as the concentration of the coupling agents. The resulting reinforcement was attributed to a homogeneous dispersion of the filler throughout the matrix, and secondly on the development of an interphase whose quality was a function of the structure of the coupling agent.

The variation of the Heat Deflection Temperature allowed to confirm the efficacy of reinforcement. The advantage of the addition of the inorganic reinforcing filler was clearly shown through the improvement of the thermal stability of the composite.

REFERENCES

- [1] Parmeland, G. "Journée d'étude sur les hauts polymères, charges, renforts et compatibilisants: facettes des principales charges utilisées dans les TP, évolution du marché des produits chargés; exemple du polypropylène," a seminar organized by La Société Française des Ingénieurs Plasticiens (SFIP), Paris (France), November (1986).
- [2] Doufnoune, R., Chebira, F., and Haddaoui, N., *Inter. J. Polym. Materials* **52**, 967 (2003).
- [3] Pukanszky, B., *New Polymeric Mater.* **3**, 205 (1992).
- [4] Nishitani, Y., Sekiguchi, I., Nakamura, K., Nagatsuka, Y., and Kitano, T., *Seikeikakou* **10**, 139 (1998).
- [5] Xiaohui, L. and Qiuju, W., *Polymer* **42**, 10013 (2001).
- [6] Acosta, J. L., Linares, A., and Ojeda, M. C., *Eur. Polym. J.* **21**, 821 (1985).
- [7] Xanthos, M. (1980). *Reactive Extrusion, Principles and Practices*, First Edition, Hanser, New York.
- [8] Monte, S. J. (1994). *Titanate, Zirconate and Aluminate Coupling Agents*, Ken-React reference manual, USA.
- [9] Doufnoune, R., Haddaoui, N., and Riahi, F., *Inter. J. Polym. Materials*, in press.
- [10] De Armitt, C. and Breesed, K. D. (2001). *Plastics Additives and Compounding Filled Polypropylene: A Cost Performance Comparison of Common Fillers*, Mark Holms, U.K., pp. 28–33.