# CORRELATIONS BETWEEN THE MECHANICAL AND THERMAL PROPERTIES OF POLYPROPYLENE/ HIGH DENSITY POLYETHYLENE/CaCO₃ COMPOSITES WITH THE PRESENCE OF COUPLING AGENTS

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Blends of polypropylene and high density polyethylene (PP/HDPE) were prepared in the presence of particulate nano-filler calcium carbonate (CaCO₃) treated on the surface with two coupling agents, namely: (organosilane Silquest A-172 and organozirconate Ken-React NZ-12). The structure and properties of the modified blends were investigated by means of differential scanning calorimetry (DSC), wide-angle X-ray scattering (WAXS), and macro- and micro-mechanical measurements. The crystallinity of the modified samples (PP, HDPE and their blends) does not seem to be so much affected by the presence of the filler.  The study of thermal properties by differential calorimetric analysis (DSC) indicates that the melting temperature varies slightly with the filler content. The presence of coupling agents promotes the development of spherulites by causing a slight increase in crystallinity levels. The addition of the treated or untreated filler to the mixtures increases impact strength and Young's modulus. The micromechanical results show that the microhardness of the PP/HDPE blends notably increases with the PP content. The micromechanical properties of the modified blends only improve slightly as a consequence of the addition of the treated filler with the coupling agents.
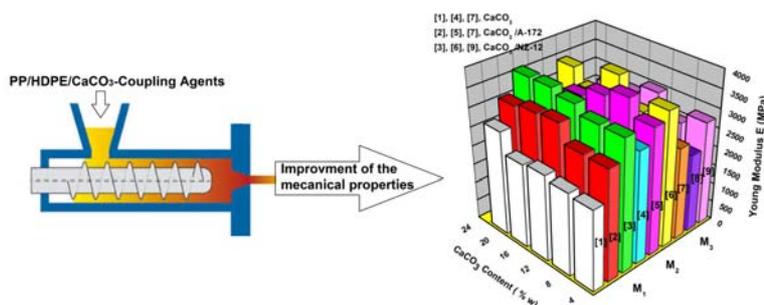
## INTRODUCTION

Nanocomposites are an attractive and innovative class of materials with new performance benefits. Due to some of their excellent properties even with a small filling amount, they are increasingly adopted by industry while replacing the use of traditional filling materials.

Among the wide variety of nanoscale fillers, both laminated silicates and nanoparticles, are capable of enhancing the mechanical and thermal properties of nanocomposites, such as strength, impact and resistance to heat.[1,2] CaCO₃ is one of the most widely used fillers in thermoplastics, particularly polyolefins. It is inexpensive and can be used at high loads.[3,4] However, inorganic nano-particles very easily agglomerate because of their large specific surface area and high surface energy and they show poor dispersability in nonpolar polymers like polyolefins, resulting in poor mechanical properties. Most fillers have a polar surface and are chemically inert to the polymer.

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Therefore, in order to ensure contact between the filler and the polymer and also to facilitate the dispersion of the particles within the matrix, the surface of the filler has to be treated with coupling agents. This treatment can increase the adhesive energy between the filler and the polymer so that the interface becomes as resistant as the polymer itself. In this case the composite has improved properties.

In relation to the chemical nature of the components, different coupling agents were used to stabilize the interface, with dominance for silanes and titanates whose role is to bond the filler to the polymeric matrix by covalent bonds[5]. In the case of PP/HDPE, the filler is difficult to incorporate and tends to agglomerate in the incompatible mixture due to their different chemical nature. Indeed, the surface chemistry of inorganic fillers allows, by means of different surface treatments, to modify their chemical behaviour and thus to control the interactions between the filler and the polymer mixture.

Polypropylene and polyethylene, despite having very similar chemical structures, are immiscible and incompatible in the majority of cases. Their mixtures have often uninteresting and unpredictable mechanical properties, due to the influence of many parameters such as their morphology and crystallinity.[6] Many studies have focused on improving the compatibility between these two phases by using coupling agents. In order to reach a better performance, an application of the coupling agent in organic materials or inorganic filler processing had to be used. This enhances the covalent bond or molecular chain of materials, thus improving the performance of composites.[7–9] Albano *et al.*[10] studied the morphological and mechanical behaviour of polyolefin mixtures in the presence of 30% CaCO$_3$. According to their results, a slight increase in Young's modulus is obtained with PP/PEHD and PP/rPEHD mixtures compared to the value of the modulus of PP alone. In another study ARROYO RAMOS *et al.*[11] investigated the optimization of the mechanical properties of composites based on Polyolefin and talc which is modified on the surface with an organotitanate (KR-11). The authors showed that when PP is the continuous phase (greater than 50%) a reinforcing effect is observed. Ichazo *et al.*[12] analyzed the effect of CaCO$_3$ on blends of PP/HDPE and found that the addition of this blend at 30 wt. % does not improve the mechanical properties of the composite regarding the equivalent blend prepared with PP.

Gonzalez *et al.*[13] studied the mechanical properties of the PP/PEHD mixture with two different CaCO$_3$ particle sizes, treated with different concentrations of Lica 12. The mixtures show that Young's modulus, elongation at break and impact strength are higher when the particle size of CaCO$_3$ is smaller. One of the simplest ways to measure the micromechanical properties of a material is by the use of the indentation test.[14] This technique is very sensitive to the changes that take place in the morphology and microstructure of polymers and has been successfully applied to many different systems. Thus, in preceding investigations we have examined the influence of a compatibilizer on the morphology and microhardness of iPP/PET /Mmt[15] and iPP/HDPE/compatibilizers and clay.[16] Therefore, our contribution aims to improve the compatibility of hybrid composite materials consisting of a mixture of two initially incompatible polyolefin (PP/HDPE) and particulate nano-filler (CaCO$_3$) treated on the  surface with two coupling agents, namely: (organosilane sold under the name Silquest A-172 and organozirconate marketed under the reference Ken-React NZ-12). The aim is to study the relationships between morphology and the mechanical and thermal properties of composites by means of microhardness indentation in combination with DSC and WAXS.

## RESULTS AND DISCUSSION

### Differential scanning calorimetry

The results of the differential scanning calorimetry analysis are summarized in Tables 1 and 2. Fig. 1 and Fig. 2 provide the graphic representation of the blends of M1 / 8% CaCO$_3$ and M2 / 8% CaCO$_3$ treated with coupling agents. The data of the melting enthalpies of the different compounds were determined from the areas corresponding to the melting of the samples and are expressed in J.g$^{-1}$. The measurement of $\Delta Hm$ should allow us to quantify the percentage of crystallinity knowing the heat of fusion of polypropylene and perfectly crystalline polyethylene. Within the limits of the experimental sensitivity, there is no overall influence of the filler amount or its treatment on the melting and crystallization temperatures. The HDPE endothermic melting peak is at 125°C, while PP melts around 139°C. The PP/HDPE and the PP/HDPE/CaCO$_3$-A172 and PP/HDPE/CaCO$_3$-ZN-12 blends show two peaks corresponding to the melting points of the two polymers.
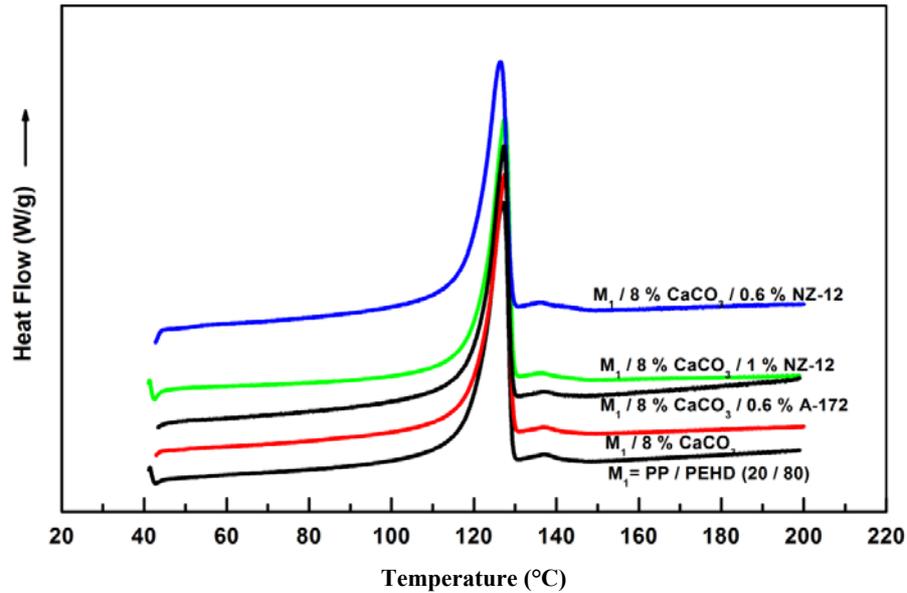
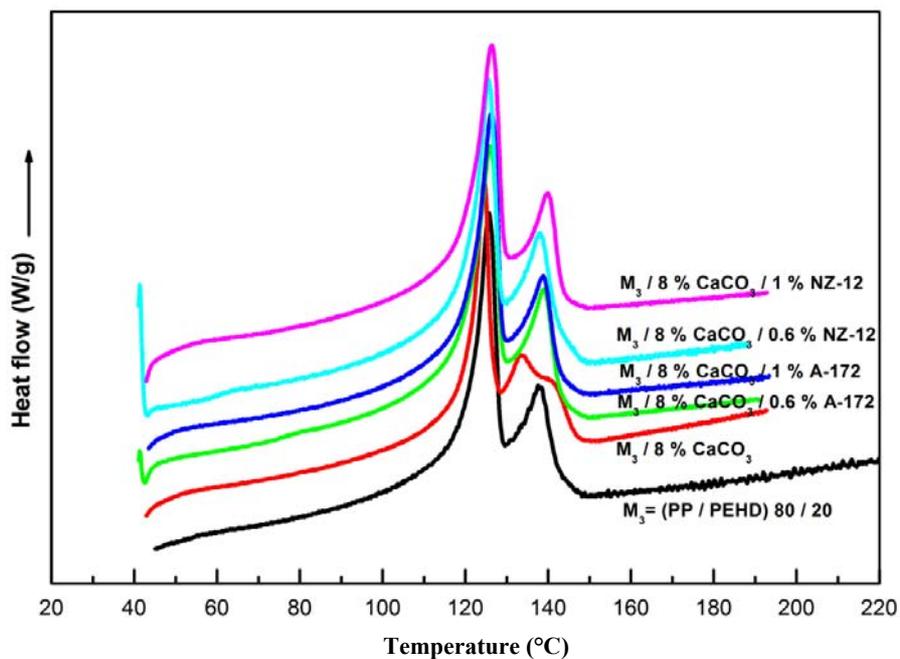Fig. 1 – DSC thermograms of the blends of M1 / 8% CaCO₃ / coupling agents.



Fig. 2 – DSC thermograms of the blends of M3/ 8% CaCO₃ / coupling agents.

The constant position of the peaks suggests that the crystal thickness of these two compounds is almost constant. Similarly, considering the experimental sensitivity, there is practically no significant influence of the filler content on the crystallinity level of the components. The untreated filler therefore does not act as a heterogeneous nucleating agent for polymers. Melting temperatures of HDPE and PP are collected in Table 1 and 2 as example. From these tables, it is clear that both components melt at practically constant temperatures in all compositions (including the blends of PP/HDPE, 50/50 which are not presented here). This indicates that the crystal thickness $l_c$ of the components, derived from the Thomson-Gibbs equation [eq. (1)] was not affected by the blending process, or by the addition of untreated and treated filler:

$$T_m = T_m^0 \left[ 1 - \left( \frac{2\sigma_e}{\Delta H_m^\infty} l_c \right) \right] \qquad (1)$$

In this equation, $\sigma_e$ is the surface free energy, $T_m^0$ is the equilibrium melting point of each component, and $\Delta H_m^\infty$, as it was above defined, is the melting enthalpy for an infinitely thick crystal. In what follows, we will take, for PP, $(T_m^0)^{17}=$ 460.7 ºK and $\sigma_e^{18}=$ 100 erg/cm$^2$; for HDPE, we will take:$(T_m^0)^{19}=$ 414.6 ºK and $\sigma_e^{18}=$ 79 erg/cm$^2$.

The $l_c$ values obtained from eq. (3) for both components in all the blends are about: $l_c =$ 17-18 nm for the PP, and $l_c =$ 19-21 nm for the HDPE.

## Wide-angle X-ray diffraction

X-ray diffraction analysis is used to confirm the results of the differential thermal analysis. The crystallinity values of the different composites are calculated from the intensity profile analysis by combining a holomorph and a crystalline peak. The main peak constitutes most of the crystalline phase diffraction.

Fig. 3 and Fig. 4 show the diffraction profiles of the main peaks of the composites studied. Tables 3 and 4 group together the values of the recorded crystallinity values for the two sets of blends M1 and M3.

As the characteristic X-ray peaks for neat HDPE were observed at the scattering angles of 21.9, 24.3, 30.4, and 36.6, which correspond to the reflections from the (110), (200), (210), and (020) planes, respectively.

It must be said that the two methods do not involve exactly the same phenomena that is why the values differ slightly. But in any case, the examination of the results shows a variation in the crystallinity values with the incorporation of the filler and coupling agents. A slight decrease in crystallinity is recorded with the increase in the proportion of raw $CaCO_3$ in the mixtures. It is estimated that one of the important factors in the decrease in crystallinity is the filler hindrance to form the nuclei responsible for the crystallization of the polymers.

*Table 1*

Results of the differential scanning calorimetry (DSC) study of the blends of M1/ CaCO3 / coupling agents

| Composition | HDPE T$_m$ (°C) | PP T$_m$(°C) | ΔH$_f$ HDPE (J.g$^{-1}$) | ΔH$_f$ PP (J.g$^{-1}$) |
|---|---|---|---|---|
| M$_1$ = PP / HDPE (20/80) | 126 | 137 | 144.4 | 1.5 |
| M$_1$ / CaCO$_3$ (8 %) | 127 | 137 | 147.3 | 2.3 |
| M$_1$ / CaCO$_3$ (16 %) | 127 | 136 | 135.6 | 1.4 |
| M$_1$ / CaCO$_3$ (8 %)/ 0.6 % A-172 | 127 | 136 | 160.9 | 2.5 |
| M$_1$ / CaCO$_3$ (8 %)/ 1 % A-172 | 126 | 136 | 154.3 | 2.4 |
| M$_1$ / CaCO$_3$ (16 %)/ 0.6 % A-172 | 127 | 136 | 138.9 | 2.3 |
| M$_1$/ CaCO$_3$ (16 %)/ 1 % A-172 | 127 | 136 | 139.3 | 2.0 |
| M$_1$ / CaCO$_3$ (8 %)/ 0.6 % NZ-12 | 127 | 136 | 146.9 | 1.1 |
| M$_1$ / CaCO$_3$ (8 %)/ 1 % NZ-12 | 126 | 136 | 136.4 | 2.9 |
| M$_1$ / CaCO$_3$ (16 %) / 0.6 % NZ-12 | 125 | 136 | 130.9 | 2.8 |
| M$_1$ / CaCO$_3$ (16 %) / 1 % NZ-12 | 125 | 136 | 29.9 | 11.5 |

*Table 2*

Results of the differential scanning calorimetry (DSC) study of the blends of M3/ CaCO3 / coupling agents

| Composition | HDPE T$_m$ (°C) | PP T$_m$(°C) | ΔH$_f$ HDPE (J.g$^{-1}$) | ΔH$_f$ PP (J.g$^{-1}$) |
|---|---|---|---|---|
| M$_3$ = PP / HDPE (80/20) | 125 | 138 | 35.7 | 12.4 |
| M$_3$ / CaCO$_3$ (8 %) | 124 | 134 | 29.7 | 16.8 |
| M$_3$ / CaCO$_3$ (16 %) | 125 | 138 | 30.4 | 11.7 |
| M$_3$ / CaCO$_3$(8 %) / 0.6 % A-172 | 125 | 138 | 31.4 | 13.2 |
| M$_3$ / CaCO$_3$ (8 %)/ 1% A-172 | 126 | 138 | 33.5 | 12.5 |
| M$_3$ / CaCO$_3$ (16 %) / 0.6 % A-72 | 126 | 139 | 33.7 | 11.8 |
| M$_3$ / CaCO$_3$ (16 %) / 1% A-172 | 126 | 139 | 32.6 | 11.5 |
| M$_3$ / CaCO$_3$ (8%) / 0.6% NZ-12 | 125 | 137 | 31.7 | 13.9 |
| M$_3$ / CaCO$_3$ (8%) /1 % NZ-12 | 126 | 139 | 35.9 | 12.5 |
| M$_3$ / CaCO$_3$ (16 %) / 0.6% NZ-12 | 124 | 135 | 25.9 | 12.3 |
| M$_3$ / CaCO$_3$ (16 %) / 1 % NZ-12 | 126 | 139 | 35.3 | 11.1 |
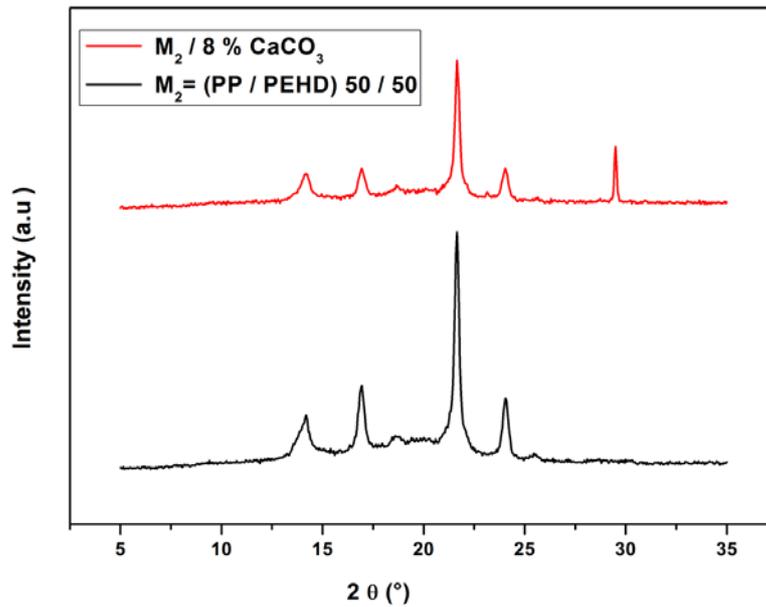
Fig. 3 – WAXS diffractograms of the blends of M2 with and without CaCO₃.
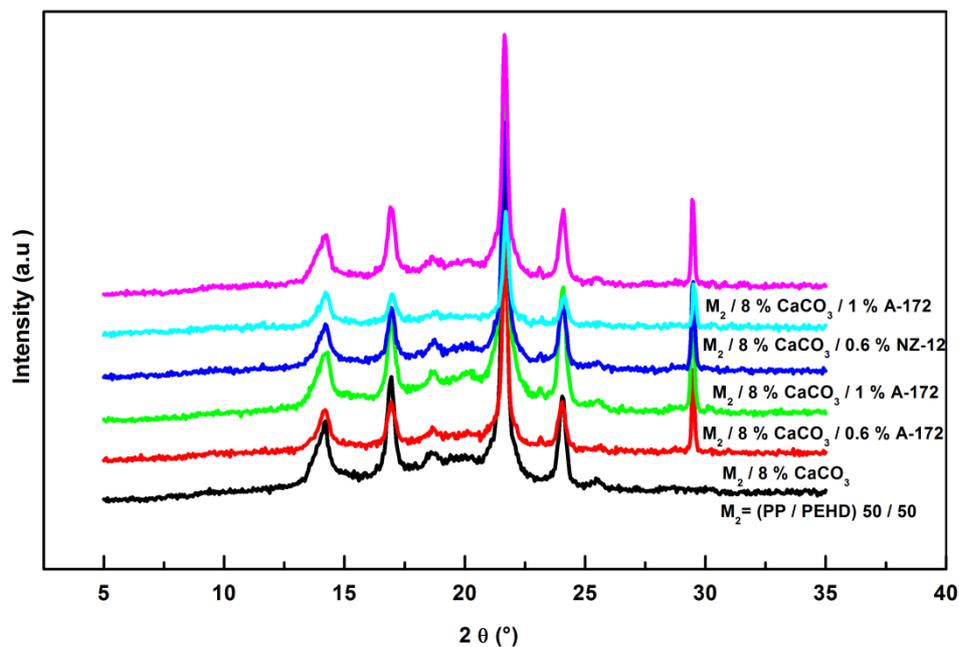


Fig. 4 – WAXS diffractograms of the blends of M2 with 8% CaCO3 treated with 0.6% and 1% coupling agents.

*Table 3*

Crystallinity value of composites M1/CaCO₃ /Coupling agent determined by WAXS

| Composites | $X_c$ HDPE (%) | $X_c$ PP (%) |
|---|---|---|
| $M_1$ = (PP / PEHD) 20/80 | 48 | 15 |
| $M_1$ / CaCO₃ (8 %) | 48 | 13 |
| $M_1$ / CaCO₃ (16 %) | 43 | 12 |
| $M_1$ / CaCO₃ (8 % )/ 0.6 % A-172 | 43 | 12 |
| $M_1$ / CaCO₃ (8 %) / 1 % A-172 | 50 | 13 |
| $M_1$ / CaCO₃ (16 %) / 0.6 % A-172 | 47 | 15 |
| $M_1$/ CaCO₃ (16 %) / 1 % A-172 | 46 | 12 |
| $M_1$ / CaCO₃ (8 %) / 0.6 % NZ-12 | 48 | 10 |
| $M_1$ / CaCO₃ (8 %) / 1 % NZ-12 | 43 | 14 |
| $M_1$ / CaCO₃ (16 %) / 0.6 % NZ-12 | 40 | 13 |
| $M_1$ / CaCO₃ (16 %) / 1 % NZ-12 | 41 | 13 |

*Table 4*

Crystallinity value of composites M3/CaCO$_3$ /Coupling agent determined by WAXS

| Composites | X$_c$ HDPE (%) | X$_c$ PP (%) |
|---|---|---|
| M$_3$ = (PP / PEHD) 80/20 | 11 | 4 |
| M$_3$ / CaCO$_3$ (8 %) | 10 | 6 |
| M$_3$ / CaCO$_3$ (16 %) | 9 | 4 |
| M$_3$ / CaCO$_3$ (8 %) / 0.6 % A-172 | 9 | 4 |
| M$_3$ / CaCO$_3$ (8 %) / 1 % A-172 | 10 | 3 |
| M$_3$ / CaCO$_3$ (16 %) / 0.6 % A-172 | 10 | 4 |
| M$_3$ / CaCO$_3$ (16 %) / 1 % A-172 | 10 | 4 |
| M$_3$ / CaCO$_3$ (8 %) / 0.6 % NZ-12 | 8 | 5 |
| M$_3$ / CaCO$_3$ (8 %) / 1% NZ-12 | 10 | 4 |
| M$_3$ / CaCO$_3$ (16 %) / 0.6 % NZ-12 | 7 | 5 |
| M$_3$ / CaCO$_3$ (16 %) / 1% NZ-12 | 11 | 4 |

The modification of CaCO$_3$ by Silquest A-172 and Ken-React NZ-12, results in some variation in crystallinity levels. A slight increase is observed with the lowest coupling agent amounts. The improvements observed are due only to a better dispersion of the filler within the matrix. An excess of coupling agents can create unfavourable conditions for the development of a crystal lattice.

It is seen that in all cases the diffraction angles of the various diffraction peaks remain the same but that their relative intensities change considerably with an increasing concentration of the filler. The reflections observed in the region of 12-24° correspond to diffraction from polymers crystallites and none are observed that can be attributed to the CaCO$_3$, which exhibits diffraction peaks only at values greater than 30°. Further analysis of these various peaks reveals that they correspond to the crystal structure of PP and HDPE.

## Macromechanical and micromechanical properties

The microhardness of the different blends as a function of PP content is plotted in Fig. 5. A straight line shows the additivity behavior of the hardness. From the plot, it is clear that neither the unmodified nor the modified blends with CaCO$_3$ treated with Silquest A-172 and Ken-React NZ-12 obey the additivity law of a binary blend as a function of composition:[14]

$$H = H_1\phi_1 + H_2(1 - \phi_2) \qquad (2)$$

In this equation, H$_1$, H$_2$, $\phi_1$, and $\phi_2$ are the hardness values of the blend components and their molar fractions, respectively. The results obtained for the blends without filler show a hardness increase with increasing PP content. This is due to

an increase in the crystal size and crystal surface perfection with increasing the PP content.
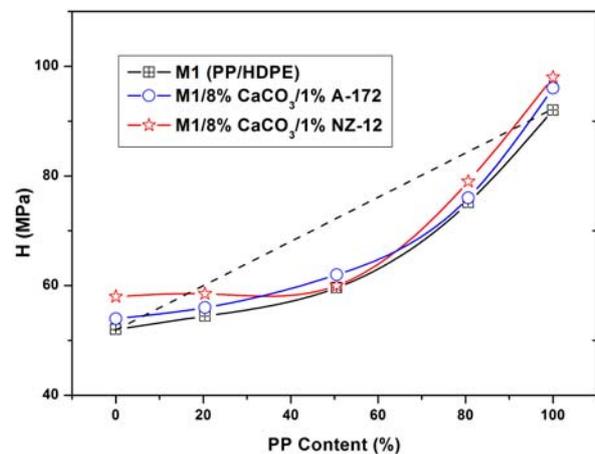


Fig. 5 – Dependence of the hardness on the PP content of M1 blends (pure and with different amounts of filler contents treated with 1% coupling agent.

The same trend was obtained with the addition of the treated and untreated filler, *i.e.* the ternary blends PP/HDPE/ CaCO$_3$/A-172 and PP/HDPE/ CaCO$_3$ –NZ-12. On the other hand, according to the two phase model, the hardness of a semicrystalline polymer can be described by the expression[14]

$$H = H_c\alpha + H_a(1 - \alpha) \qquad (3)$$

where H$_c$ and H$_a$ are the intrinsic hardness values for the crystalline and amorphous phase, respectively, and α is the volume fraction of the crystalline material

By combining the equations (3) and (4), we obtain:[14]

$$H = H^{PP}\phi_1 + [H_c^{PP}\alpha^{PP} + H_\alpha^{PP}(1 - \alpha)](1 - \phi_1) \quad (4)$$

This expression takes into account the crystalline $H_c$ and amorphous $H_a$ hardness of every

component, their degree of crystallinity α , and the compositions of the blends. Here, again, the blends with filler show *H* values that are notably lower than the ones derived by writing the additivity law according to equation (4).

From the foregoing, it is clear that the two main effects to be considered when adding the compatibilizer to these blends are the decrease in the crystallinity, and the simultaneous increase in the hardness of them. Both effects can be associated to the presence of the treated filler. On one hand, one may think that the filler contributes to a decrease of the PP and HDPE chains flexibility, so that they cannot crystallize more easily. On the other hand, the hardness increase in the filled samples could be explained by the increase in the crystalline hardness of the PP and HDPE component. The relationship between the microhardness of the lamellae crystallites $H_c$ and the average lamellar thickness $l_c$[14] is:

$$H_c = H_c^{\infty} / \left(1 + \frac{b}{l_c}\right) \qquad (5)$$

where $H_c^{\infty}$ is the hardness for an infinitely thick crystal, and the *b*-parameter is defined as $b = 2\sigma_e/\Delta h$. In this expression $\Delta h$ is the energy required to plastically deform the crystalline lamellar stacks.

As the crystal thickness $l_c$ for both components remains practically constant in all compositions, the variation in the $H_c$ value for the blends could be explained by an increase of the *b*-parameter (equation 7) through the surface free energy $\sigma_e$, which is known to be related with the degree of order at the crystal surface[14]. Thus, the *b*-parameter increase might be originated by the blending process of the samples, by the disorder created in the crystals surface due to the presence of the filler.

The tensile properties (stress and elongation) were measured at the same time as the modulus to approximate as well as possible the simple effect of incorporating the filler and consequently of restricting organic matter on the mechanical properties of the filled polymer, and on the other hand, to determine the influence of the chemical modification of the filler with coupling agents on the properties of the interfacial regions.

The addition of an inorganic phase to the polymer may lead to an additional mechanism: decohesion at the polymer-particle interface, followed by a possible cavitation from the breakdowns in the polymer-particle interface. The effect of the addition of filler particles on the flow threshold was analyzed by comparing the behaviour of blends filled with raw and modified CaCO₃ with Silquest A-172 and Ken-React NZ-12 and the blend without filler. The introduction of coupling agents with a concentration of 1% leads to a decrease in the ductility of the polymer. The increase in stresses of the filled blend results locally in decohésion of the matrix particles, before any other deformation mechanism, micro-cavities appear and accumulate, forming macroscopic defects leading to the failure of the material. To discuss the strength differences, the variations in relative stress at break defined as the stress ratio of the filled polymer to that of the matrix plotted as a function of the coupling agent content (see Fig. 6). The increase in the filler incorporation content leads to a decrease in the relative stress at break. Indeed, the most spectacular property failures are observed with the untreated CaCO₃. Materials prepared from treated CaCO₃ exhibit quite remarkable performance, although there is some reduction in tensile strength for 20/80 composition blends. For composites formulated from the 80/20 composition with treated CaCO₃, a significant increase in relative stress at break is observed. The proposed explanation is that there is a certain synergism between the filler, the matrix and the coupling agents. At the same time, the stress at break increases with the level of incorporation of the coupling agent. This may reflect a greater rigidity of the interfacial area. The very particular behaviour of the composite made up of the 80/20 blends and calcium carbonate treated with 1% Ken-React NZ-12 is however attributed to the formation of a more rigid interface whose content is proportional to the interactions developed between the treated particles and the polypropylene that forms the continuous phase.

The effect of the presence of the filler and its treatment on the elongation at break of the composites is illustrated in Fig. 7.

The decrease in elongation at break is associated with a ductile-fragile change in the behaviour of the filled blend, but it should be noted that there is some improvement for composites formulated from the 80/20 blend and treated CaCO₃ compared to the pure matrix.

Fig. 8 shows the influence of composition on the relative modulus. The comparative examination of the histograms reveals the differences previously reported, particularly between the filler materials treated with organozirconate. The excellent results obtained with the Ken-React NZ-12 confirm that there is a high affinity between the filler/coupling agent and polymer/coupling agent.
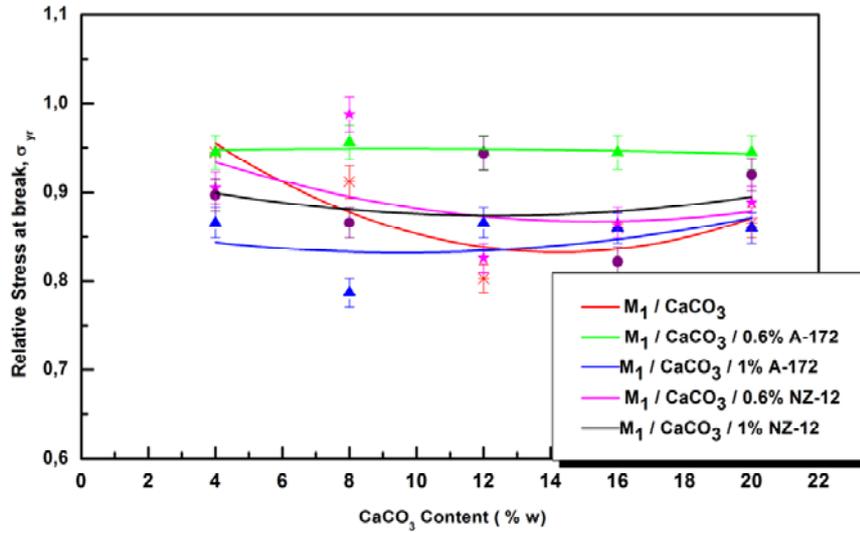
Fig. 6 – Variation of the relative stress at break of composites M1 (20/80) as a function
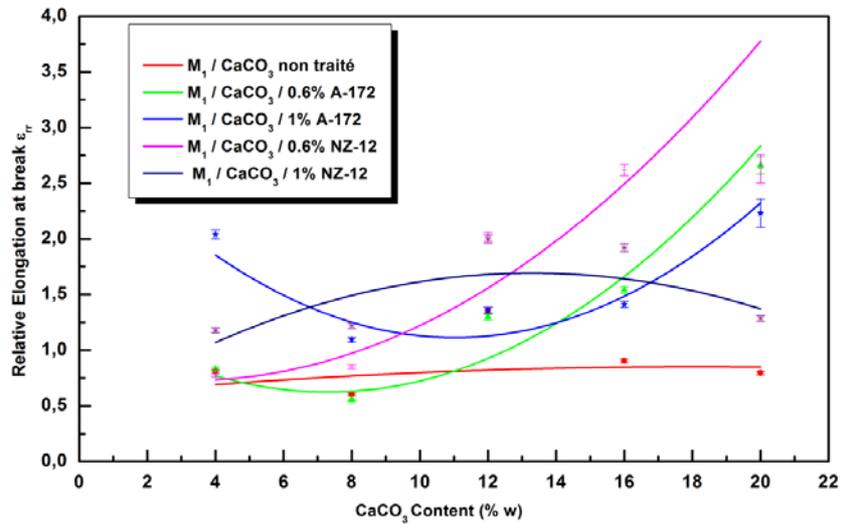of CaCO₃ contents and treated with coupling agents.



Fig. 7 – Variation in relative elongation at break of composites M1 (20/80) as a function
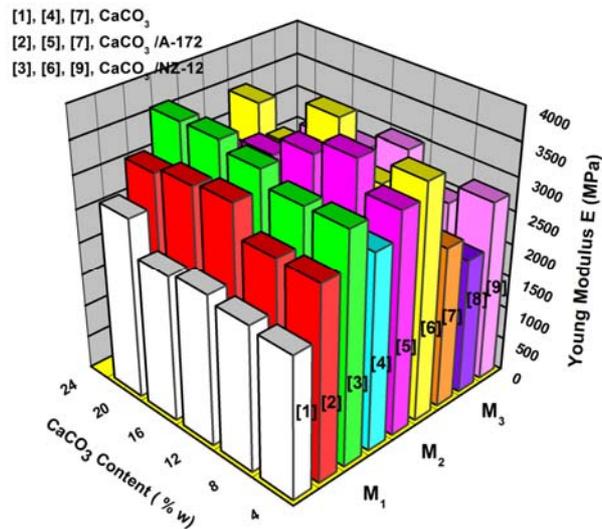of  CaCO₃ contents and treated with coupling agents.



Fig. 8 – Young Modulus variation of the different composites
as a function of the amount of  untreated  CaCO₃ and treated with 1% coupling agents.

## EXPERIMENTAL

### Material

The resins used are high density polyethylene (HDPE), B-22 supplied by ENIP Skikda (Algeria) and isotactic polypropylene (iPP), Basell Moplen RP24 provided by ALCUDIA, a clarified random copolymer for extrusion applications. The filler used is calcium carbonate ($CaCO_3$), Alcal UF.5 furnished by ENG El Khroub (Algeria). The coupling agents are Organosilane, Silquest A-172 (WITCO Corporation) and Organozirconate, Ken-React NZ-12 (Kenrich Petrochemical).

### Impregnation of calcium carbonate with Silquest A-172

The Silquest A-172 was deposited on calcium carbonate from a solution obtained by dissolving the coupling agent in distilled water. Before subjecting the surface of the filler to this chemical modification, Silquest A-172 was first hydrolyzed in acid medium (pH = 3). The pH is adjusted to the desired value using acetic acid. Two aqueous impregnation baths were prepared with concentrations by weight equal to 0.6 and 1% by weight with respect to the total weight of the filler. The suspensions are stirred for 3 hours in order to disaggregate and homogenize the mixture. After stirring, most of the solvent is removed by filtration. Finally, the collected mass will be dried in an oven at a temperature of 105°C in order to obtain condensation of the silanol groups on the surface and to remove water and/or traces of methanol or ethanol.

### Impregnation of calcium carbonate with Ken-React NZ-12

Zirconate as well as organosilane is applied to the mineral surface according to the same experimental protocol, but from a solution resulting from the dissolution of Ken-React NZ-12 in dry toluene. The mixture is stirred for 3 hours in order to homogenize the mixture, which will then be filtered and dried at 80°C.

### Blend preparation

The composites were obtained by dispersing the filler in the resins previously melted on a two roll mill type "SCHWABENTHAN". The various mixtures were mixed and homogenized at 190°C for 10 minutes. Finally, grinding is necessary for mechanical, thermal or spectroscopic measurements of the processed materials. The filler content incorporated in the various blends varies from 4 to 20% by weight in steps of 4; while the PP/HDPE blends selected are respectively 20/80, 50/50 and 80/20 by weight. To simplify the writing, the PP/PEHD blend will be noted by the letter M, the various blends will then be designated by the nomenclature M1, M2 and M3 for the three compositions indicated in the order given above. The composites will be noted M/CaCO₃/Coupling agent.

From the preceding blends, samples for characterization were prepared by compression molding in a Zwick machine model 7102 (Ulm, Germany), working at a pressure of 150 kg/cm². The compression was performed at 210°C during 6 min (4 min for preheating and 2 min for compression). Then, the mold was quickly transferred to a thermostatic bath maintained at 25°C.

### Techniques

All samples, as well as their blends, were characterized by using the following techniques: Wide-angle X-ray scattering (WAXS), differential scanning calorimetry (DSC), and measurement of the macro- and micromechanical properties, *i.e.*, Impact strength, Young's modulus $E$, and microhardness $H$, respectively. For the WAXS experiments, a Seifert (Ahrensburg, Germany) diffractometer (reflection mode) was used. The following conditions were employed: 40 kV; 35 mA; angular range: 5°–35° (2θ); scan rate: 0.05°/s. The degree of crystallinity $\alpha_{WAXS}$ of all samples was derived from the ratio of the area corresponding to the crystalline peaks to the total area of the diffractogram. The thermal analysis was performed in a Perkin-Elmer differential scanning calorimeter DSC-7 (Norwalk, CT, USA), working in an inert $N_2$ atmosphere. The temperature range studied was 40–200°C, and the heating rate 10°C/min. The sample weight was about 1 mg. Pure indium was used to calibrate the instrument. The crystallinity of every component, HDPE and iPP, measured by calorimetry, αDSC, was derived from the enthalpy corresponding to each melting peak using the expression:

$$\alpha_{DSC} = \Delta H_m / \Delta H_m^\infty \qquad (6)$$

here, $\Delta H_m$ and $\Delta H_m^\infty$ are the experimental melting enthalpy and the melting enthalpy for an infinitely thick crystal, respectively.

For HDPE, $\Delta H_m^\infty$ used is 293.86 J/g[19] and for PP, $\Delta H_m^\infty$ used is 207.33 J/g.[20] We calculated the total crystallinity of every sample by adding the contribution of both HDPE and iPP components. The Young's modulus $E$ of every material was obtained from the tensile experiments (stress-strain measurements) performed in a Zwick/Roell (D89079ULM) apparatus, according to the ASTM D-638 norm. Crosshead speed: 20 mm/min. The microhardness $H$ was measured at room temperature using a Leica VMHT Mot 320 DFC tester, adapted with a square-based diamond indenter. The $H$ value was derived from the residual projected area of indentation according to the formula:[20]

$$H = kP / d^2 \qquad (7)$$

where $d$ is the length of the impression diagonal in meters, $P$ is the contact load applied in N, and $k$ is a geometrical factor equal to 1.854. Loads of 0.5 N were used. The loading cycle was 0.1 min. The $H$ value was derived from the average of 8–10 indentations performed on the surface of every sample. The tensile test was performed using specimens obtained according to the specifications of ASTM D-638. The traction machine used is the "MTS/50 LP" type.

## CONCLUSION

The incorporation of untreated and treated calcium carbonate into the polyolefin mixture is apparent in all the mechanical and thermal properties of the composites studied.

The study of thermal properties by differential calorimetric analysis (DSC) indicates that the melting temperature varies slightly with the filler content. The crystal thickness values of these two compounds (PP and HDPE) are almost constant. The presence of coupling agents promotes the development of spherulites by causing a slight

increase in crystallinity levels. All these results are confirmed by X-ray diffraction. The microhardness of untreated and treated calcium carbonate composites increases with increasing the proportion of PP in the blends. The reason is that the crystalline hardness of PP and HDPE components increases, which is originated by the blending process of the samples. The addition of the treated or untreated filler to the mixtures increases impact strength Young's modulus, reflecting good particle dispersion within the matrix and better interfacial adhesion.

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