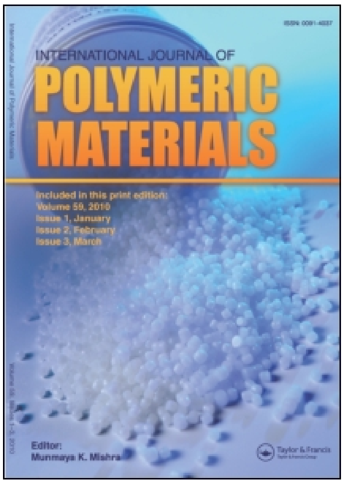

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The Effects of Coupling Agents on the Mechanical, Rheological and Thermal Properties of Calcium Carbonate-Filled LDPE Compatibilized with Maleic Anhydride-g-LDPE (Part II)

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The Effects of Coupling Agents on the Mechanical, Rheological and Thermal Properties of Calcium Carbonate-Filled LDPE Compatibilized with Maleic Anhydride-g-LDPE (Part II)

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This study deals with the chemical modification of calcium carbonate ($CaCO_3$) by means of coupling agents and its effect on the mechanical, rheological, and thermal properties of the ternary composite of low density polyethylene (LDPE), calcium carbonate ($CaCO_3$), and maleic anhydride-grafted low density polyethylene (MAH-g-LDPE).

The variations in the properties were dependent on the treatment method and on the nature and extent of the interactions developed between the filler particles, the matrix and the compatibilizer.

The impact resistance results revealed a transition in the behavior of the composite from ductile to brittle. This embrittlement becomes more pronounced as the concentration of $CaCO_3$ and that of the coupling agents are increased.

The rheological characterization showed that the interactions developed at the interface greatly affected the flow of the material.

The differential scanning calorimetry results showed that even though the fusion temperature and the crystallization temperature were not influenced by the filler or by its treatment, crystallization was altered.

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Finally, the thermogravimetric analysis showed that the dispersion and the adhesion of the filler with the matrix significantly affect the thermal stability.

Keywords: calcium carbonate, characterization, composite, interfacial effects, low density polyethylene, maleic anhydride-g-LDPE, silane and zirconate coupling agents

INTRODUCTION

The properties of a composite strongly depend on the physicochemical characteristics of its components, the matrix and the reinforcing agent. But the behavior resulting from the composite cannot be represented as the simple combination of the properties of each constituent. Other factors, as important as the choice of the constituents, affect the composite performance: the method of the preparation of the composite and the properties of the interface between the matrix and the reinforcing agent.

In fact it has been established that the mechanical behavior of composites with a thermoplastic matrix and a particulate filler depend greatly on the interactions that develop between the filler and the matrix [1–4]. For filled polymers, the theory of adsorption is widely considered to characterize the filler-matrix interactions.

In the presence of a filler and during the solidification, some organic molecules get adsorbed on the surface of the filler particles and mass transport gradients are created near the interface due to a local fluctuation of the temperature. Consequently, the submolecular structure and the chains mobility are affected, leading to the formation of a layer with different properties than those of the matrix.

The presence of the filler induces also different heterogeneities within the system [5]. An interface, which is a zone of molecular dimensions around the filler, will appear and in which interactions take place between the macromolecules and the solid surface. We can also distinguish an intermediate zone where the macromolecules are situated in a different environment. This transition zone is referred to as the interphase.

The addition of the filler can also cause a modification in the transmission or the distribution of the stresses within the polymeric phase, or may impose particular characteristics onto the interface and the interphase [6]. It is therefore possible to modify the properties of this zone by treating the filler particles as a surface. The choice of the type of the treatment substance, such as a surfactant or a coupling agent, and its concentration should be optimized because they affect not only the interfacial interactions between the polymer and the inorganic filler, but also modify the state of the dispersion of the particles [1–3,7].

Many studies dealt with composite systems based on a thermoplastic matrix and a reinforcing filler. Overall, it has been reported that the mechanical characteristics of these systems are governed mainly by the composition of the composite and by the volume fraction of the reinforcing filler as well as its distribution throughout the matrix. This type of composite, particularly those composed of polypropylene/calcium carbonate and polyethylene/calcium carbonate, are widely used in many applications such as in sports goods or in the automotive product sector. It has also been reported that it is very difficult to obtain a uniform dispersion of the filler throughout the matrix, especially at high loadings since the mineral particles, which are not miscible with the polymeric matrix, tend to agglomerate. These agglomerates may not easily be broken up even at high temperatures [8].

It appears therefore necessary to modify the surface of the fillers in order to limit their tendency to agglomerate. Moreover, owing to the progress made in the field of polymer blending, a large variety of materials in terms of chemical structure is now accessible. In this context, maleic anhydride-grafted polyolefines have been used in composites as coupling agents [9–12]. A maximum adhesion is achieved reflecting the level of grafting and the microstructure and polarity of the particular polymer used.

This study focuses on the compatibilization of a composite of low density polyethylene (LDPE) and calcium carbonate ($CaCO_3$) by using maleic anhydride-grafted low density polyethylene (MAH-g-LDPE). Coupling agents were chosen so that better adhesion between the different phases will be promoted. In order to assess the role of the coupling agents and the compatibilizer, the resulting composites were characterized through measurements of the mechanical, rheological and thermal properties.

EXPERIMENTAL

Materials

The low density polyethylene (LDPE) used was supplied by ENIP (Algeria). It has a standard Melt Flow Index of 12 g/10 min. The calcium carbonate filler, trade name Alcal UF-5 was delivered by ENG (Algeria). It has an average particle size of 5 μm and a surface area of 2.64 m^2/g.

The four coupling agents used for the surface modification of calcium carbonate were: 3-aminopropyltriethoxysilane (Silquest A-1100) and 3-glycidoxypropyltrimethoxysilane (Silquest A-187) obtained from Witco Corp., N-(2-aminoethyl)-3-aminopropyltrimethoxysilane (Dow Corning Z-6020) obtained from Dow Corning Corp., and the neopentyl-(diallyl)oxytri-(N-ethylene diamino)ethyl zirconate (Ken-React NZ-44) donated by Kenrich Petrochemicals Incorp. All coupling agents were used without further purification.

The surface treatment of the filler was performed by two different methods. In the first method, which will be referred to as the humid method, the calcium carbonate particles were added to an aqueous solution of the silane coupling agent. The slurry was stirred for 1 h at 25°C. The treated sample was extracted with tetrahydrofuran in order to remove the excess coupling agent adsorbed. The extracted filler was then dried in a vacuum oven at 105°C for 12 h. The modification with zirconate coupling agent was conducted in isopropanol solution for 1 h. After washing with carbon tetrachloride the treated particles were dried again for the same time at the same temperature.

In the second method, which will be referred to as the dry method, surface modification of calcium carbonate particles with silane coupling agents was carried out in dry conditions. The filler was dry-blended with coupling agents for 30 min at 60 rpm in a high intensity solid mixer. The treated sample was then extracted with tetrahydrofuran and then dried at 105°C.

The surface treatment by means of the zirconate coupling agent was carried out as follows: the required amount of the coupling agent (0.4 wt%) was diluted with a small amount of isopropanol in order to reduce its viscosity. Then, the concentrated solution was thoroughly sprayed on the filler. The calcium carbonate powder was then washed with carbon tetrachloride and dried in an oven under controlled conditions of temperature and pressure.

The compatibilizer used in this study is maleic-anhydride-grafted-low-density polyethylene (MAH-g-LDPE) which was prepared according to the procedure described in Part I [4] using a solution of 1.2 wt% of maleic anhydride, 0.15 wt% of dicumyl peroxide and 0.5 wt% of triphenylphosphine. LDPE pellets were first impregnated with the resulting solution. Next, the solvent was removed by evaporating in an oven at 60°C for 20 min. The grafting reaction of MAH onto LDPE was performed in the melt state in a single-screw extruder having a length-to-diameter ratio of 20. The temperature settings of the barrel three zones were 140, 150 and 160°C, respectively. The extent of grafting which was determined by titration was found to be 0.21 wt%.

The ternary composites of LDPE/MAH-g-LDPE/$CaCO_3$ systems, with 2 wt% of the compatibilizer and calcium carbonate composition varying from 10 to 40 wt% for the untreated $CaCO_3$ and from 10 to 60 wt% for the treated one, were prepared using a two-roll mill at 170°C for 10 min. Samples for testing were taken from slabs which were pelletized and pressed in a laboratory press at a plate temperature of 180°C, a pressure of 200 Kg/cm^2, and a pressing time of 7 min followed by cooling to room temperature.

Testing

Impact tests were carried out according to method I procedure A of ASTM D-256 standard. Conventional notched and unnotched Izod impact specimen were tested at a temperature of -10°C using a CEAT testing machine. The notch was made with an angle of 45° and a depth of 1 mm.

Melt Flow Index measurements were carried out according to ASTM D-1238-82 specifications. The test was performed at a temperature of 190°C and a load of 2160 g using a Davenport Melt Indexer.

Differential scanning calorimetry analysis was carried out on a Perkin-Elmer DSC-7 differential scanning calorimeter thermal analyzer. Samples were heated at a rate of 20°C/min from 25 to 150°C for 10 min to eliminate the influence of thermal history. Then they were cooled at a rate of -20°C/min to 25°C. On the second heating run, the samples were heated from 25 to 150°C at a rate of 20°C/min. The peak minimum from the melting thermogram was considered as the fusion point (T_f). Crystallization temperature (T_c) was calculated based on the peak of the exotherm from the thermogram obtained during cooling. The heat of fusion (ΔH_f) and that of crystallization (ΔH_c) were determined from the corresponding peak areas in the heating and cooling thermograms. The weight percentage crystallinity was calculated based on a heat fusion of 293 j/g for the perfect polyethylene crystal [13]. The percent crystallinity (χ_c) of LDPE in the composites was calculated as follows:

$$\chi_c = \Delta H_f / \Delta H_f^0 \cdot \Phi \cdot 100$$

where ΔH_f is the apparent enthalpy of fusion per gram of composite, $\Delta H_f{}^0$ is the extrapolated value of the enthalpy corresponding to the melting of 100% crystalline pure PE, and Φ is the weight fraction of LDPE in the composite.

To investigate the thermal stability of the composites, thermogravimetric analysis was performed on a TG-DTA 92 instrument.

The experiments were carried out from 25 to 300°C at a heating rate of 10°C/min, under a nitrogen purge flow of 30 ml/min.

RESULTS AND DISCUSSION

Impact Properties

The unnotched Izod impact resistance results shown in Figure 1 and Figure 2 show clearly the influence of the filler concentration and its treatment as well as the method of treatment on the impact properties of the composites. It was found that the impact resistance shows a significant decrease with the increase of the filler concentration. This decrease is attributed to a transition from ductile to brittle in the behavior of the material. However, a slight improvement of the impact resistance was observed with the composites containing the compatibilizer. This improvement reflects the development of interactions between the two phases composing the material. It seems also adequate to attribute the increase in the impact resistance of the LDPE/LDPE-g-MAH/$CaCO_3$ composite to an increase in the

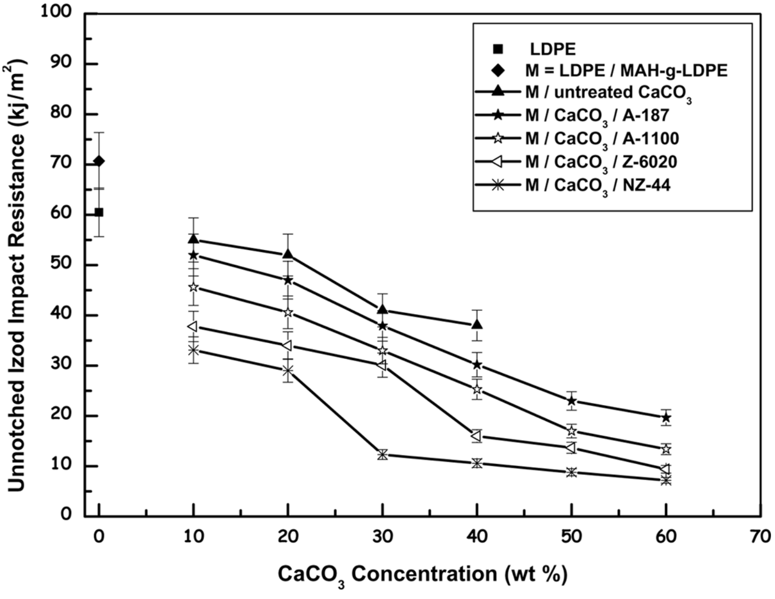

FIGURE 1 Variation of the Unnotched Izod Impact Resistance with $CaCO_3$ concentration for the composites of LDPE/MAH-g-LDPE/$CaCO_3$ untreated and treated with different coupling agents by the humid method.

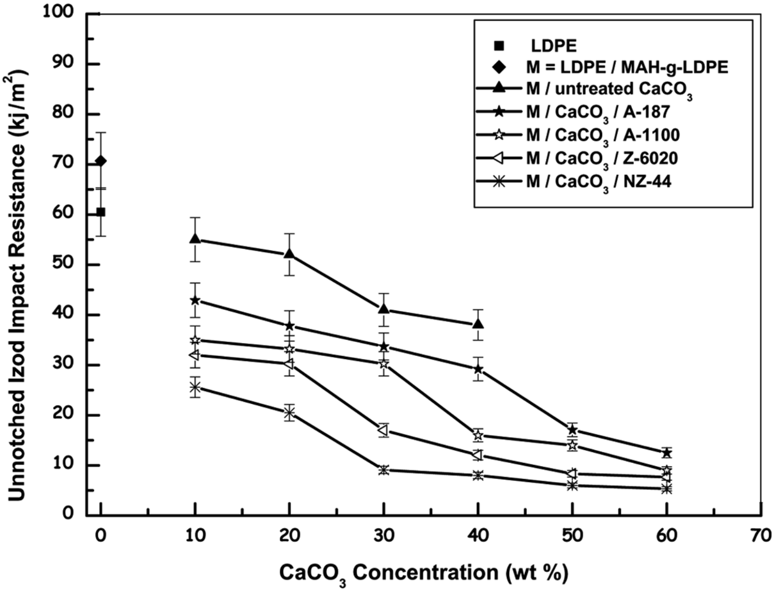

FIGURE 2 Variation of the Unnotched Izod Impact Resistance with $CaCO_3$ concentration for the composites of LDPE/MAH-g-LDPE/$CaCO_3$ untreated and treated with different coupling agents by the dry method.

amorphous phase, which is characterized by a capacity to absorb the impact shock. At the molecular scale, the pendant maleic anhydride groupings sterically hinder the chains, hence decreasing the intermolecular interactions as a result of an increased free volume.

The filler surface modification reduces the impact resistance of composite materials. This diminution becomes more pronounced as the filler concentration is increased. As for the deformation, the impact resistance greatly depends on the states of adhesion and dispersion of the inorganic particles within the matrix [4].

The severe embrittlement of the composites made from $CaCO_3$ treated with the Ken-React NZ-44 is attributed to a rigidification of the interfacial zone.

Figure 3 allows a comparison or the behavior of the different composites with 40 wt% $CaCO_3$. These bar graphs reflect the effect of the treatment mode as well as the type and structure of the coupling agent used. The most important drop in the impact resistance is observed with the composites made from $CaCO_3$ treated by the dry method. As was noted in part I of this publication [4], the dispersion of $CaCO_3$ particles becomes difficult with this method owing to its conditions.

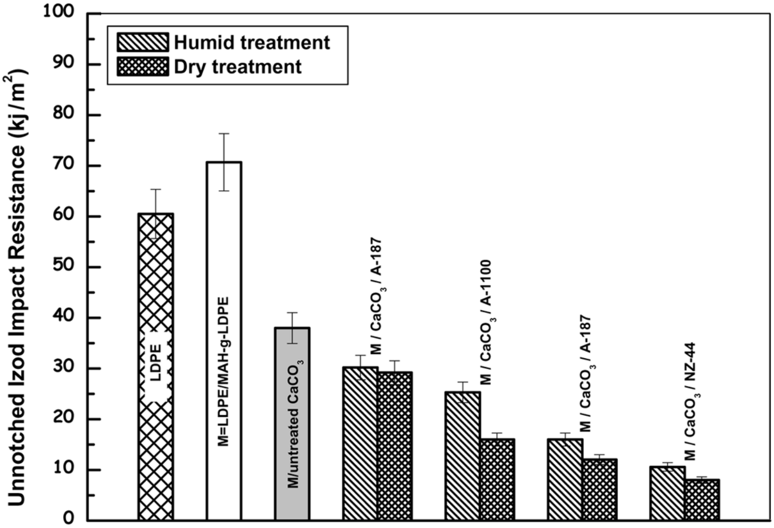

FIGURE 3 Effect of the method of treatment on the Unnotched Izod Impact Resistance of the composites of LDPE/MAH-g-LDPE/40% CaCO$_3$.

The absence of a solvent leads to a poor dispersion of the coupling agent over the surface area of the filler. This gives rise to weak interfacial interactions, and an agglomeration of the particles causing stress concentration at the interface which resulted in a decrease of the impact resistance. The agglomeration of the filler particles can also modify the crack propagation mechanism. This may lead to an effective volume of the filler higher than that of the inorganic phase because part of the matrix gets trapped within the agglomerates which are formed.

Figures 4 and 5 show the results of the notched Izod specimens. It can be seen that the addition of the compatibilizer affected very little the impact properties. In fact, for filler loadings lower than 30 wt% a significant drop in the resistance to impact is observed. With respect to these results, the presence of the filler weakened the material. Godfroy et al. [14], who studied the performance of polypropylene/talc/polyethylene-octene composites, reported that the impact properties depended on the composition of the system, since their results confirmed the negative effect of talc. However an important improvement in the resistance to impact was noted with composites having higher concentrations of ethylene-octene. With the notched specimen, the authors reported that the total energy required for

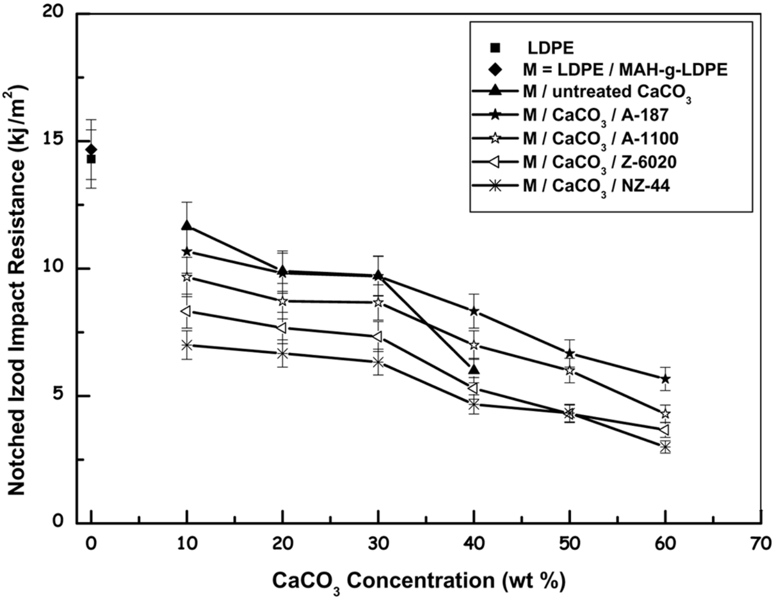

FIGURE 4 Variation of the Notched Izod Impact Resistance with $CaCO_3$ concentration for the composites of LDPE/MAH-g-LDPE/$CaCO_3$ untreated and treated with different coupling agents by the humid method.

rupture is composed of two parts. The first part is the energy required to initiate the crack whereas the second part is the energy required for its propagation. With brittle materials the initiation energy is dominating and is reduced when the notched specimen are being tested. So the presence of the notch would be desired if the material is ductile but would be inconvenient if the material is brittle or if dispersion of the filler is to be measured.

Figure 6 affords a comparison between the different composites in terms of the effect of the treated filler creation process. These bar graphs show that, as with the unnotched Izod tests, an important diminution of the impact resistance is observed with the composites prepared from $CaCO_3$ treated by means of the dry method. This could be an indication of reduced adhesion and dispersion. The significant drop of the impact resistance of the composites made from $CaCO_3$ treated with the Dow Corning Z-6020 and the Ken-React NZ-44 is attributed to an important coupling between the filler and the polymeric matrix. It is noted that the improvement in the interface gave rise to a material which is harder but less crack-resistant.

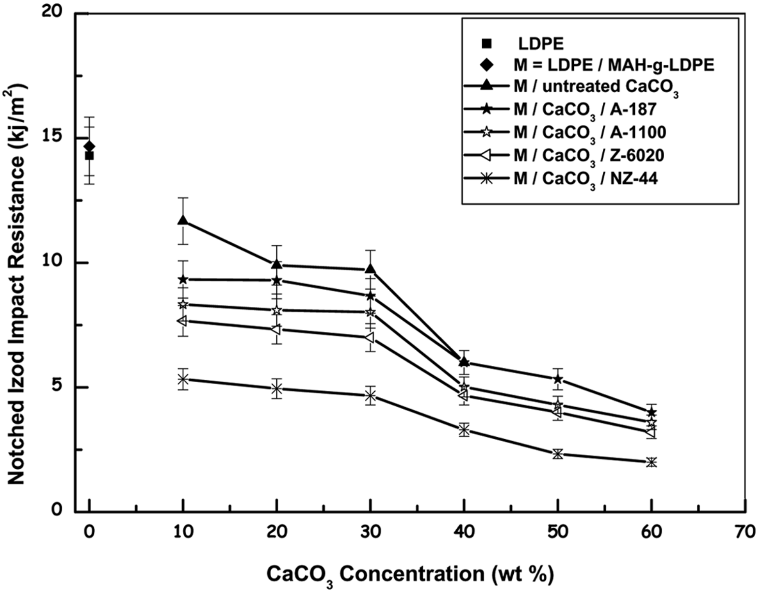

FIGURE 5 Variation of the Notched Izod Impact Resistance with $CaCO_3$ concentration for the composites of LDPE/MAH-g-LDPE/$CaCO_3$ untreated and treated with different coupling agents by the dry method.

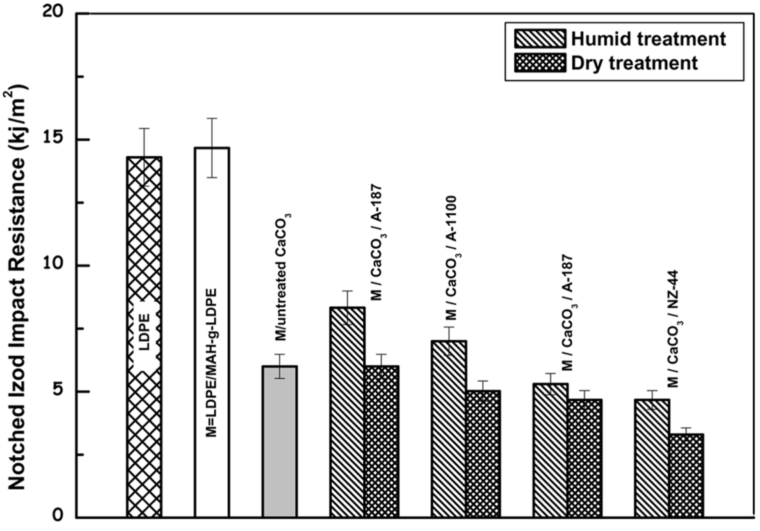

FIGURE 6 Effect of the method of treatment on the Notched Izod Impact Resistance of the composites of LDPE/MAH-g-LDPE/40% $CaCO_3$.

Melt Flow Index (MFI)

Figures 7 and 8 show the variation of the melt flow index with concentration of the filler that was treated with the different coupling agents. It is noted that the melt flow index shows a slight decrease for the composites containing 10 and 20 wt% of $CaCO_3$. But above this concentration the drop in the MFI becomes important, owing probably to the dispersion which gets worse as the quantity of the filler embedded in the matrix is increased. At low filler loadings the wetting of the particles by the matrix is ensured, but beyond a certain fraction the interparticle-interactions become more pronounced, increasing therefore the tendency towards agglomeration. This agglomeration constitutes hence a hindrance against the free flow of the polymer melt.

The chemical modification of the filler by means of the coupling agents causes an increase in the viscosity which leads to a decrease in the melt flow index. This decrease is a result of the interactions that developed between the filler and the compatibilizer through

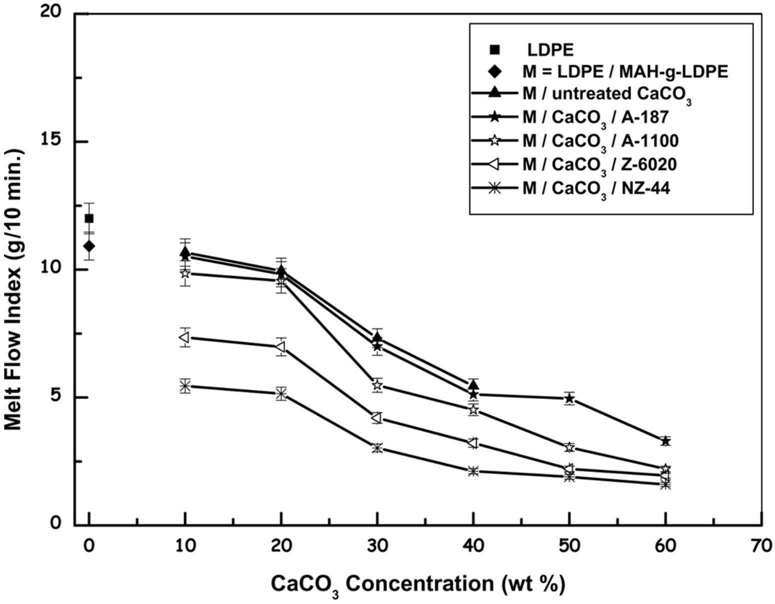

FIGURE 7 Variation of the Melt Flow Index with $CaCO_3$ concentration for the composites of LDPE/MAH-g-LDPE/$CaCO_3$ untreated and treated with different coupling agents by the humid method.

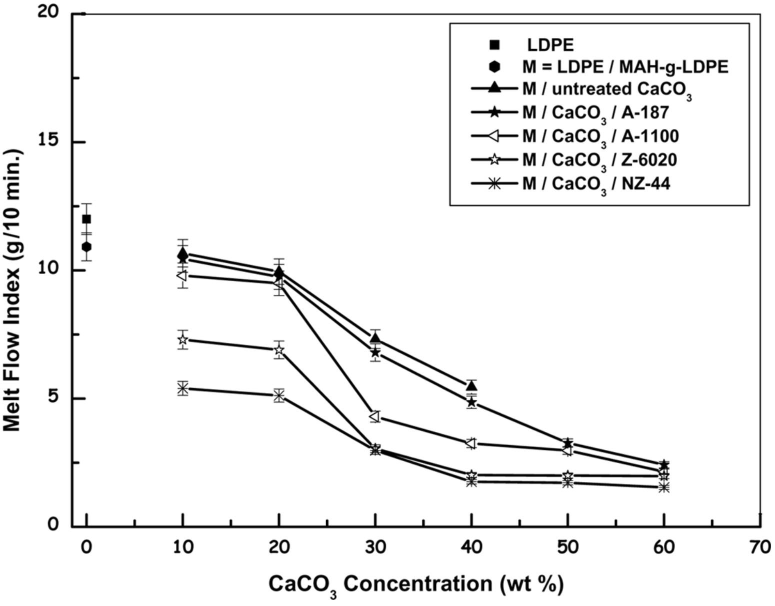

FIGURE 8 Variation of the Melt Flow Index with $CaCO_3$ concentration for the composites of LDPE/MAH-g-LDPE/$CaCO_3$ untreated and treated with different coupling agents by the dry method.

the coupling agents, reducing therefore the chains mobility around the filler.

In fact, the variations of the observed melt flow index appear to be strongly dependent on the type of the treated filler production process. In general, only slight variations are observed at low filler concentrations. But at high loadings a more pronounced decrease in the melt flow index is observed for the composites made from $CaCO_3$ treated by the dry method. This is attributed to the inefficiency of the process used for the surface modification of the filler. In other words, as was mentioned in part I of this publication [4], the main drawback of the dry method is that it does not enable a uniform dispersion of the coupling agents throughout the entire material resulting in the agglomeration of the filler particles. This agglomeration hinders the free flow of the macromolecular chains.

Figure 9 presents the variations of the melt flow index for the composites with 40 wt% $CaCO_3$ modified with the different coupling agents by means of the two methods. These plots point out, again, the efficiency of the treatment by means of the humid method *versus* the dry one. The results reflect a better state of dispersion which leads

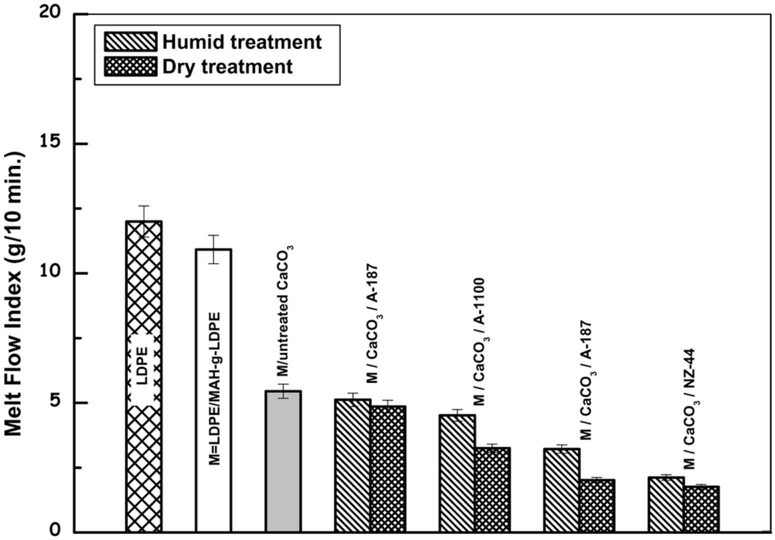

FIGURE 9 Effect of the method of treatment on the Melt Flow Index of the composites of LDPE/MAH-g-LDPE/40% $CaCO_3$.

to an improvement in the rheological behavior of the investigated composites.

Differential Scanning Calorimetry (DSC)

The differential scanning calorimetry results presented in Table 1 show that neither the addition of the filler nor its treatment affected the fusion temperature or the crystallization temperature. However, the energy required for the fusion of the crystalline part of the material seems to be particularly affected by the filler surface treatment and by its concentration. The reduction of the heat of fusion with increasing filler concentration could therefore be attributed to $CaCO_3$ particles which hindered the crystallization of the polymer.

On the other hand, no clear trend could be observed concerning the variations of the crystallization level as a function of the nature of the interface or the treatment method.

An increase in the heat of crystallization was noted with all the composites studied. Based on the literature [14], the development of an interface leads to an increase in the number of spherulites and a decrease of their diameter. Concerning the method of treatment,

TABLE 1 DSC Data for LDPE, MAH-g-LDPE and Composites of LDPE/MAH-g-LDPE/$CaCO_3$ Treated by Humid and Dry Method

Composite	$CaCO_3$ (wt%)	T_c (°C)		ΔH_c ($J \cdot g^{-1}$)		T_m (°C)		ΔH_m ($J \cdot g^{-1}$)		χ(%)	
		Humid	Dry	Humid	Dry	Humid	Dry	Humid	Dry	Humid	Dry
LDPE	–	97.0		– 80.4		117.0		137.7		47.0	
M = LDPE/MAH-g-LDPE	–	98.2		– 78.0		117.4		135.1		46.1	
M/untreated $CaCO_3$	20	98.5		– 80.9		117.2		135.2		46.1	
	40	98.7		– 85.6		117.5		134.6		45.9	
M/$CaCO_3$/A-187	20	98.7	98.7	– 86.8	– 86.5	117.0	117.0	129.4	125.4	44.1	42.7
	40	98.1	98.8	– 85.4	– 87.0	116.0	116.5	123.7	120.2	42.2	41.0
	60	98.7	98.3	– 101.3	– 102.0	117.3	116.3	120.3	119.8	41.0	40.9
M/$CaCO_3$/A-1100	20	98.8	98.4	– 102.4	– 98.8	117.3	116.8	137.8	134.6	47.0	45.9
	40	98.6	98.2	– 102.9	– 101.3	117.0	116.3	137.2	134.0	46.8	45.7
	60	99.0	99.2	– 109.3	– 102.6	118.2	116.8	129.7	130.0	44.2	44.3
M/$CaCO_3$/Z-6020	20	98.8	98.8	– 92.9	– 89.3	117.1	118.1	124.0	123.3	42.3	42.0
	40	98.6	98.1	– 95.4	– 96.1	117.6	117.9	119.2	117.0	40.7	39.9
	60	99.9	98.0	– 101.6	– 101.3	116.8	123.3	111.4	110.0	38.0	37.5
M/$CaCO_3$/NZ-44	20	98.4	98.0	– 80.2	– 82.3	118.4	119.6	109.0	109.8	37.2	37.4
	40	98.4	98.2	– 97.8	– 97.0	118.4	120.4	103.0	102.4	35.1	34.9
	60	98.1	98.0	– 112.3	– 112.0	117.8	117.4	98.7	98.6	34.0	34.0

it seems from the variations observed in the heat of crystallization of the composites, that it had no significant effect.

Thermogravimetric Analysis (TGA)

Thermogravimetric measurements were carried out in order to study the effect of the surface chemical treatment on the thermal stability of the material. The variations of the weight loss of the 40 wt% $CaCO_3$ composites as a function of temperature are shown in Figures 10 and 11. Two phenomena can clearly be distinguished: the main weight loss occurs between 340 and 430°C, which corresponds to the decomposition of the organic matrix, and another slight weight loss is observed between 50 and 100°C. Different works [10,15] have shown that this kind of weight loss would be the result of the evaporation of water physically adsorbed on the mineral filler surface. Overall, it is noted that the addition of LDPE-g-MAH compatibilizer to the matrix did not cause any significant change in the thermal stability of the composite.

The same trends were also observed concerning the effect of the filler surface treatment on the thermal stability of the composites.

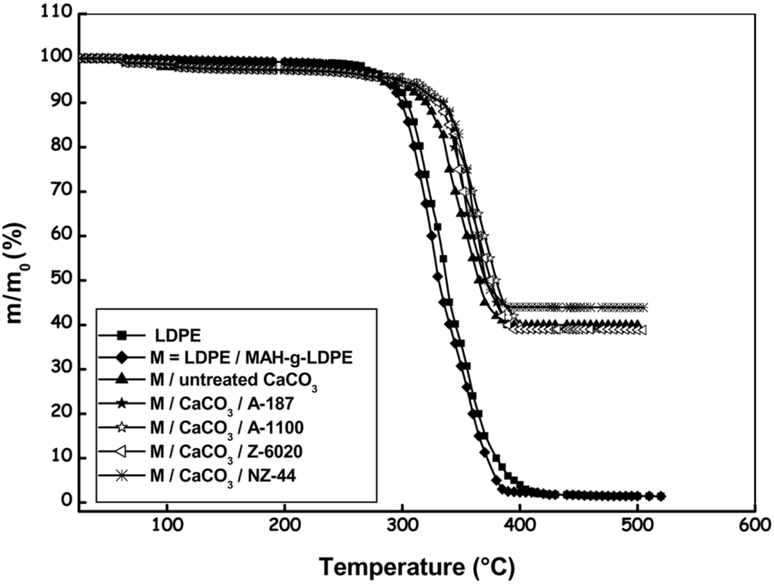

FIGURE 10 Variation of the relative weight loss with temperature of the composites of LDPE/MAH-g-LDPE/40%$CaCO_3$ untreated and treated with different coupling agents by the humid method.

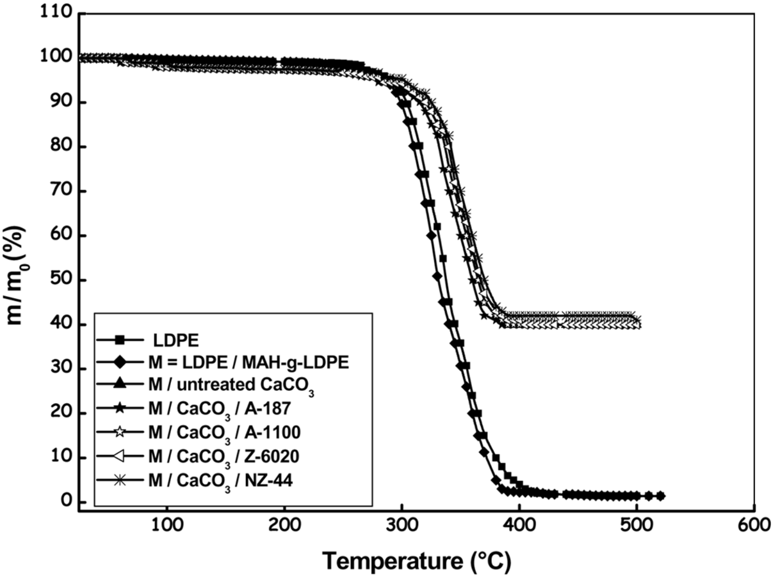

FIGURE 11 Variation of the relative weight loss with temperature of the composites of LDPE/MAH-g-LDPE/40%$CaCO_3$ untreated and treated with different coupling agents by the dry method.

The relative variations of weight loss as a function of temperature for the composites based on $CaCO_3$ treated with the Silquest A-1100 by means of the dry and humid method are presented in Figures 12 and 13. A slight weight loss can be observed between 50 and 100°C. This loss is proportional to the concentration of $CaCO_3$ present in the sample. In fact, for concentrations less than 40 wt% the thermal stability is not affected. But for higher loadings the decomposition of the composites is greatly shifted towards higher temperatures.

Figure 14 illustrates the effect of the chemical modification as well as the treatment method on the decomposition temperature of the composites. In this context, the thermal stability is better when the filler is modified. This may be attributed to a uniform distribution of the particles throughout the matrix. This state of dispersion acts as a barrier against the release of volatilization gases during thermal degradation. It may also be attributed to an adsorption effect of these gases at the filler surface which slowed down the polymer decomposition. This effect is amplified as the filler concentration increases. Importantly, the method of treatment seems to have no effect on the thermal stability of the composites.

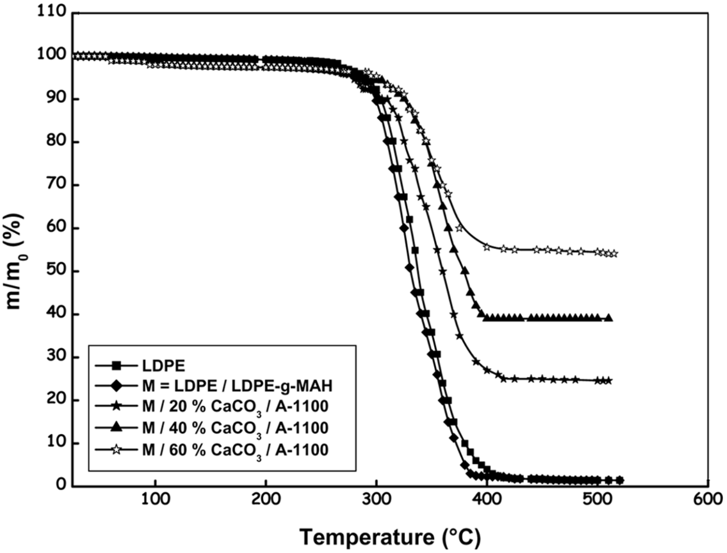

FIGURE 12 Variation of the relative weight loss with temperature of the composites of LDPE/MAH-g-LDPE/$CaCO_3$ untreated and treated with Silquest A-1100 coupling agent by the humid method.

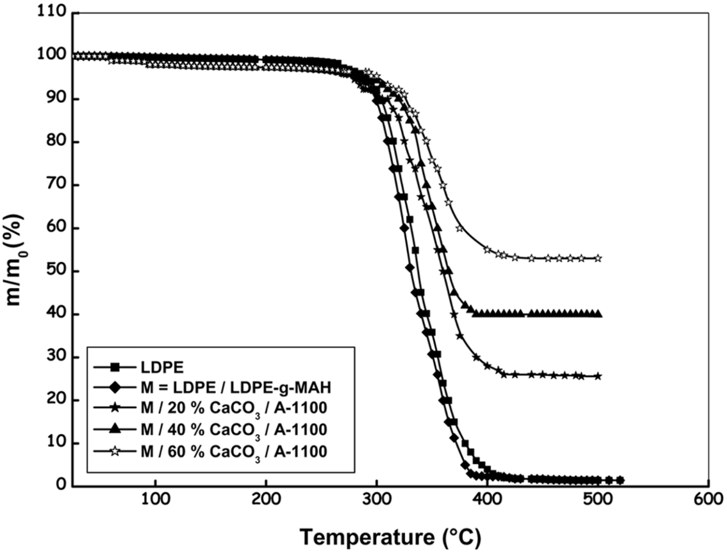

FIGURE 13 Variation of the relative weight loss with temperature of the composites of LDPE/MAH-g-LDPE/$CaCO_3$ untreated and treated with Silquest A-1100 coupling agent by the dry method.

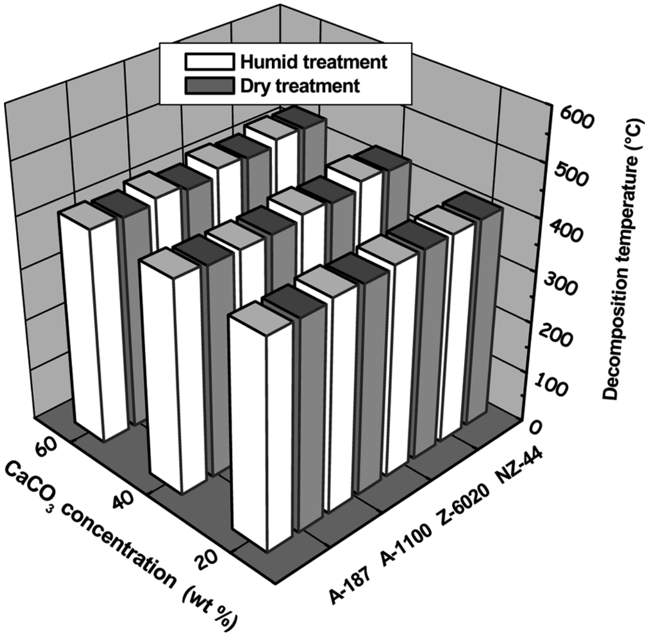

FIGURE 14 Effect of the chemical modification and the treatment method on the decomposition temperature of the composites of LDPE/MAH-g-LDPE/$CaCO_3$.

CONCLUSIONS

In this study many composites made from LDPE as a thermoplastic matrix, $CaCO_3$ as a mineral filler and MAH-g-LDPE as a compatibilizer were characterized. In order to enhance the interactions between the matrix and the filler, chemical treatments by means of different coupling agents were carried out. Emphasis was made with respect to the effect of the filler surface treatment method and the type and extent of the interaction developed at the interface on the mechanical, rheological, and thermal properties of the composites.

Overall, the results showed that the properties were greatly dependent on the state of the dispersion of the filler particles throughout the polymeric matrix and on the interaction potential of the coupling agents and the compatibilizer. According to the impact resistance results, the change in the structure at the interfacial zone led to an embrittlement of the composites, especially those treated with the Ken React NZ-44 agent.

The study revealed that both the state of the dispersion and that of adhesion at the interface affected the rheological behavior. The decrease of the melt flow index was a result of an interface less mobile than the neat matrix.

The DSC results showed that the degree of crystallinity depended much on the amount of the filler. However, no significant trend could be observed concerning the variation of the degree of the crystallinity with the nature of the interface or the filler treatment method. It was also found that, based on the thermal gravimetric analysis, the chemical modification of $CaCO_3$ improved the thermal stability of the material.

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