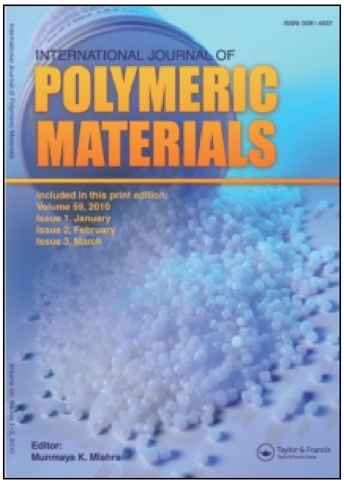

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Effects of Coupling Agents on the Tensile Properties of Calcium Carbonate Filled LDPE Compatibilized with Maleic Anhydride-g-LDPE (Part I)

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Effects of Coupling Agents on the Tensile Properties of Calcium Carbonate Filled LDPE Compatibilized with Maleic Anhydride-g-LDPE (Part I)

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In this study many composites based on low density polyethylene (LDPE) with calcium carbonate ($CaCO_3$) and maleic anhydride-grafted polyethylene (MAH-g-LDPE) as a compatibilizer have been investigated in order to study their behavior and the reinforcing mechanisms involved.

Different types of chemical modifications of the filler surface were carried out in an attempt to enhance the interactions with the polymeric matrix by using silane and zirconate coupling agents.

The compatibilizer was created using a single screw extruder by impregnating LDPE granulates with a solution obtained by dissolving in acetone the dicumyl peroxide used as the initiator for the grafting reaction, maleic anhydride as the grafting monomer, and triphenyl phosphine (TPP) as the stabilizer. Titration measurements indicated that the extent of grafting achieved was 0.21% by weight.

The composites containing different concentrations of untreated $CaCO_3$ and those treated with 2% of the compatibilizer were prepared by melt mixing using a two roll mill.

It was found that the mechanical properties, which depended greatly on the state of the dispersion of the filler as well as the nature of the interface, were relatively better than the composites prepared by the humid method. Higher reinforcement

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was obtained with the composites treated with the zirconate coupling agent than those modified with the silane coupling agent.

Keywords: calcium carbonate, characterization, composite, interfacial effects, low density polyethylene, silane and zirconate coupling agents, tensile properties

INTRODUCTION

Since over twenty years ago, synthetic composite materials have been widely replacing conventional materials which do not meet the requirements of modern technology. Composites are complex materials whose creation, properties and use may raise many problems. Different types have been used depending on their particular field of application. For example, organic matrix-based composites have been developed in order to face the increasingly more severe conditions to which they are subjected in various fields such as automotive, households, sports and transportation uses [1].

Among composites being developed, polyolefines reinforced with inorganic particles have been qualified as lower limit materials in terms of mechanical reinforcement. However, the commercial success of certain products made researchers appreciate differently this type of composite [2]. In fact polyolefines possess many characteristics among the fact that they are ready for use, can be recycled, and often exhibit a good resistance to impact [3]. Even though their performance is satisfactory at service temperatures, the properties of pure polyolefines fall with increasing temperature. This is why it was thought to extend their field of application by linking their advantages to those of an organic phase through an adequate choice of the components as well as the preparation method. The resulting materials would present excellent properties such as hardness, stiffness, improved temperature resistance, impact resistance, lower shrinkage and better thermal stability.

The particulate fillers most used with polyolefines are silica, mica, talc, calcium carbonate, and alumin a hydrates [4]. The three main characteristics which control the effectiveness and the dispersion of the filler within the matrix are the structure, the surface area, and the chemical activity. Therefore it is important to use high shear mixers in order to break up agglomerates and insure a good wetting and dispersion of the filler throughout the polymeric matrix [5].

The mechanical behavior of composites depends greatly on the interactions that develop between the particles and the matrix. The nature of these interactions or the interface depends on many parameters such as the physico-chemical characteristics of both components, concentration, and the method of preparation.

In the case of LDPE/$CaCO_3$, the filler does not embed easily in the matrix and tends to agglomerate. The chemical treatment of the filler surface allows it to modify its chemical activity and therefore enhance the interactions between the filler and the matrix. This treatment can be carried out by varying its extent as well as the chemical functionality. Hence the surface treatment can be monofunctional that is, grafting on the filler, or bifunctional capable of forming covalent bonding with the matrix.

The low extent of interactions of polyethylene with polar substances, which is due to its crystallinity and its apolarity, limits sometimes the use of bifunctional coupling agents. The addition of a low proportion of grafted polyolefines is one of the most efficient ways to improve the adhesion properties [6,7]. The functionalization of the nonpolar chains by cyclical maleic anhydride is carried out mainly by FREE radical means. Moreover, grafting is a complex operation and requires a good understanding of the phenomena involved and strict control of the experimental conditions.

The objective of this work is to develop composites based on low density polyethylene and calcium carbonate treated at the surface with bifunctional coupling agents. In order to improve the compatibility between the two phases, maleic anhydride grafted polyethylene (MAH-g-LDPE) was used. The interface was assessed through measurement of the mechanical properties.

EXPERIMENTAL

Materials

Commercially available low density polyethylene (LDPE) grade B-24 was supplied by ENIP (Algeria). The specific properties of the polymer are presented in Table 1. The filler calcium carbonate ($CaCO_3$) was

TABLE 1 Characteristics of Low Density Polyethylene

Properties	Values
Density (g/cm^3)	0.962
Melt Flow Index MFI (g/10 min)	12.00
Melting temperature, T_m (°C)	118.00
Molecular weight, Mw	45000

TABLE 2 Characteristics of Calcium Carbonate

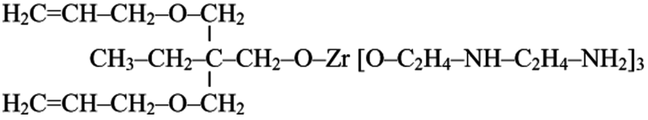
Properties	Values
Density (g/cm^3)	2.7
Size, d_{50} (μm)	5.0
Specific surface area (m^2/g)	2.64
pH	9.0
Purity (%)	98.5
Whiteness	95.0

obtained from ENG (Algeria). It is denoted as Alcal UF-5 and its characteristics are given in Table 2.

Four coupling agents were used in this work: 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) oxy tri-(N-ethylene diamino)ethyl zirconate (Ken-React NZ-44) donated by Kenrich Petrochemicals Incorp. The coupling agents were used as received without any further purification. The respective chemical formulas and designation are presented in Table 3.

The compatibilizer used in this study is maleic anhydride grafted low density polyethylene (MAH-g-LDPE) which was synthesized in our laboratory. The monomer used for the reaction of grafting was maleic anhydride (MAH) that was supplied by Aldrich Chemical. The peroxide as the free radical generator used was a masterbatch of a 60 wt% dicumyl peroxide (DCP) in $CaCO_3$ obtained from Merck.

TABLE 3 Coupling Agents used in this Study and Their Respective Abbreviations

Coupling agents	Abbreviations
$H_2N{-}CH_2{-}CH_2{-}CH_2{-}Si\,(OC_2H_5)_3$	Silquest A-1100
$C_2H_3O\,{-}CH_2{-}O{-}CH_2{-}CH_2{-}CH_2{-}Si\,(OCH_3)_3$	Silquest A-187
$H_2N{-}CH_2{-}CH_2{-}NH{-}CH_2{-}CH_2{-}CH_2{-}Si\,(OCH_3)_3$	Dow Corning Z-6020
 $\begin{array}{l} H_2C{=}CH{-}CH_2{-}O{-}CH_2 \\ \qquad\qquad CH_3{-}CH_2{-}C{-}CH_2{-}O{-}Zr\,[O{-}C_2H_4{-}NH{-}C_2H_4{-}NH_2]_3 \\ H_2C{=}CH{-}CH_2{-}O{-}CH_2 \end{array}$	Ken-React NZ-44

The stabilizer, which was incorporated in the reaction media to minimize the degradation and crosslinking processes occurring simultaneously in the modification reaction, was triphenyl phosphine (TPP) supplied by Fluka Chemica. All other reagents and solvents were high purity commercial products.

Calcium Carbonate Surface Modification Procedure

The surface modification of calcium carbonate was performed by two different methods: adsorption from solution and dry blending. In the first method the silane coupling agents were hydrolyzed for about 24 h in a bi-distilled water whose pH had been adjusted to a value of 3 by adding acetic acid. Calcium carbonate was added to the solution of the silane agent, and the suspension was vigorously stirred for about 1 at room temperature. The calcium carbonate particles were removed from each solution in a bûchner 1 h filter and subsequently washed with THF to remove the loosely bonded physisorbed compounds attached to the particles. The surface treatment of calcium carbonate with the silane coupling agents was completed after drying the slurry in a vacuum oven at 105°C for 12 h.

The modification with the organozirconate coupling agent was performed in isopropyl alcohol solution similar to the silane process. The treated filler was washed with CCl_4 and dried again as above.

For the second method of treatment, the calcium carbonate was dry-blended with the four coupling agents. The powder was placed in a high intensity solid mixer and the pure silane coupling agents were slowly sprayed for 30 min. The treated sample was then washed with THF and dried at 105°C to complete the surface reaction. Contrary to the silanes, the zirconate coupling agent was dissolved in isopropanol to reduce its viscosity. Then this solution was pumped and sprayed onto the filler powder while agitating. Following the spraying, the calcium carbonate powders were washed with pure CCl_4 and dried in an oven under controlled conditions of temperature and pressure.

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 four coupling agents [8,9].

Preparation of the Compatibilizer: Grafting Procedure

Polyethylene pellets were mixed with a previously prepared acetone solution of maleic anhydride, dicumyl peroxide and triphenyl phosphine. Acetone in the uniform slurry was removed by evaporating the slurry in an oven at 60°C for 20 min.

The grafting reaction of maleic anhydride onto polyethylene was performed in a single screw extruder ($d = 25\,mm$, $L/D = 20$).

The temperatures of the three zones in the extruder were: 140, 140 and 160°C. The screw rotation was fixed at 30 rpm. The extrudate was cooled in water at room temperature to stop further reactions, pelletized and then dried overnight at 60°C in a vented oven. 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 remove remnant MAH, poly (MAH) and other volatiles.

Determination of the Grafting Yield

The grafting level was determined through end point titration analysis of the acid groups derived from the anhydride functions. Approximately 4 g of LDPE modified samples were dissolved in toluene at boiling temperature. Then water was added to hydrolyze the anhydride functions into carboxylic acid functions.

The boiling temperature was maintained for 1 h, 30 min.

Titration was performed at room temperature using potassium hydroxide in ethanol. The indicator used was a solution of 1% phenolphtaleine in methanol.

A blank titration was carried out by the same method.

The extent of grafting was calculated using the following equation:

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

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.

Determination of Insoluble Fraction

Since the grafting of maleic anhydride on LDPE is accompanied by a competing crosslinking reaction and in order to optimize the concentrations of the grafting monomer, the initiator and the stabilizer, the following procedure was followed. First, the grafted polymer was dissolved in cyclohexane during 60 hours at room temperature. Then the insoluble fraction was separated from the solution by filtration and the soluble part was treated by acetone which precipitates the uncrosslinked polymer. After decantation and filtration, the product was dried under vacuum in an oven at 60°C. The composition of each fraction was determined by titration.

Preparation of Composites

All compounds were prepared by mixing, at an appropriate ratio, LDPE with 2 wt% MAH-g-LDPE, the untreated and surface-treated calcium carbonate in a two roll mill at 170°C. Total mixing time was typically 10 min. The resulting composites were then pelletized before being compression molded at 180°C and 200 Kg/cm^2 for 7 min. In order to ensure consistency of our data, the LDPE/MAH-g-LDPE blend was also subjected to this treatment. A series of composites was studied with composition varying from 10 to 40 wt% for the untreated $CaCO_3$ and from 10 to 60 wt% for the treated one.

Fourier Transform Infrared Spectroscopy (FTIR)

Fourier transform infrared spectroscopy (FTIR) was performed to check the formation of MAH-g-LDPE. The samples of LDPE and MAH-g-LDPE films were prepared by thermal press molding between two Teflon sheets on a compression machine at 180°C under a pressure of 200 Kg/cm^2 for about 5 min. Samples were then analyzed by signal averaging 120 scans at a resolution of 4 cm^{-1}. Infrared spectra were obtained in transmission mode with a Perkin-Elmer spectrometer.

Tensile Properties

The tensile properties of the composites were obtained according to ASTM D-638-86 using a Zwick machine model 1445 with a 50 Kgf load cell and a gauge length of 50 mm. Tensile tests were performed at room temperature and aimed to determine the young's modulus (E), tensile yield stress (σ_y), the ultimate tensile strength (σ_r) and the strain at break (ε_r). The cross-head speed was 20 mm/min and the reported values are based on the average of five determinations.

RESULTS AND DISCUSSION

Grafting of Maleic Anhydride on Polyethylene

Even though the mechanism of the grafting of maleic anhydride on polyethylene has been largely described by many studies [10–14], it seems that no single proposed mechanism was accepted unanimously. The main points of discord arise from the possibility of homopolymerization of the grafted chains. The initiation of the grafting reactions causes the formation of free radicals that result from the thermal decomposition of the peroxide. The decomposition rate which is governed by the peroxide half-life time is greatly dependent on temperature. The radicals react mainly with the secondary and tertiary carbons or on the double bonds of the macromolecules. The resulting chains react with maleic anhydride. Along with the main grafting reaction, two other secondary reactions may take place. These are side-branching leading to crosslinking, and maleic anhydride homopolymerization. The extent of the first secondary reaction depends on the nature and the stability of the intermediate macroradicals that are formed during the grafting reaction.

The addition of certain additives may minimize the extent of the secondary reactions and improve that of grafting [15–18]. In this context triphenyl phosphine was added as a stabilizer for MAH-g-LDPE at different concentrations of the monomer and the peroxide. The results of the extraction with cyclohexane showed that the losses are situated between 1 and 5%.

Table 4 indicates that the fraction of the insolubles increases with increasing the amount of peroxide at a given concentration of maleic anhydride, reflecting therefore the extension of the polyethylene chain. This test also showed that grafting maleic anhydride on low density polyethylene can take place as well as a crosslinking reaction. However, the presence of triphenyl phosphine reduced considerably the amount of the insolubles, which means that the competing crosslinking reaction was less important. The two types of reactions can therefore take place, but grafting occurs preferably if the concentration of the peroxide is low.

The extent of the grafting, which was determined by classical chemical titration of MAH-g-LDPE stabilized with 0.5% triphenyl phosphine using 1.2% maleic anhydride and 0.15% dicumyl peroxide, was found to be 0.21% by weight.

The infrared spectroscopy analysis has also made it possible to characterize the grafted polymer. Figure 1 presents the infrared spectra of the grafted polyethylene in comparison to that of the matrix. Two

TABLE 4 Variation of the Insoluble Fraction with the Concentrations of Maleic Anhydride, Dicumyl Peroxide, and Triphenyl Phosphine

			Extraction with cyclohexane	
MAH (%)	DCP (%)	TPP (%)	Soluble (%)	Insoluble (%)
0	0	–	100	0
0	0.15	–	84	12
0	1.5	–	73	25
1.2	0.15	–	58	40
1.2	1.5	–	45	54
2.1	0.15	–	71	27
2.1	1.50	–	52	43
1.2	0.15	0.5	76	23
1.2	1.5	0.5	64	34

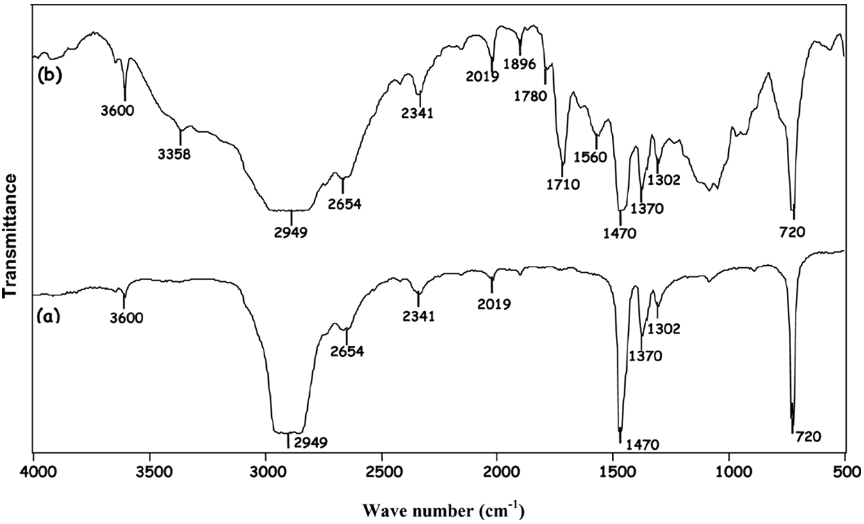


FIGURE 1 FTIR spectrum of (a) Low density polyethylene (LDPE) and (b) Maleic anhydride grafted low density polyethylene (MAH-g-LDPE).

additional bands at 1780 and 1710 cm^{-1} can be distinguished in spectrum (b) of the grafted polyethylene. The reference spectrum (a) does not show any band in this region. The peak at 1710 cm^{-1} is related to the elongational vibrations of the carbonyl group which is characteristic of the carboxylic acid. The peak at 1780 cm^{-1} is related to the elongational vibrations of the carbonyl group of the maleic anhydride.

Mechanical Properties

The effect of inorganic reinforcing agents on the mechanical properties is the main reason for the development of filled polymers. The mechanical characteristics of composite systems are essentially governed by the nature of the interactions that develop at the particle-polymer interface.

The yield is confined in a field delimited by two ideal modals: one boundary defined by a perfect interface adhesion, and another one with a total absence of the adhesion between the matrix and the reinforcing agent. In the case where there is no adhesion, the deformation will be supported by the efficient section of the matrix which is available in the filled polymer. The following relation between the stress at yield of the composite (σ_{yc}) and that of the matrix (σ_{ym}) has been proposed:

$$\sigma_{\mathrm{yc}} = (1 - 1.21\ \mathrm{V_f}^{2/3})\sigma_{ym} \tag{2}$$

where $\mathrm{V_f}$ is the filler volume fraction.

Pukanszky [19,20] defined another parameter, B_y, which reflects the state of adhesion between the polymer and the filler. He has therefore used the following semi empirical equation:

$$\sigma_{yc} = \sigma_{ym} \cdot \frac{1 - V_f}{1 + 2.5\ V_f} \cdot \exp(B_y \cdot V_f) \tag{3}$$

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

where l is the interphase thickness, ρ_{f} is the filler density of the filler, $\mathrm{A_f}$ the filler specific area, and σ_{yi} the stress at yield of the interphase.

The ultimate properties of filled polymers have been developed by Nielsen and Landel [21]. They established relations for the reduction of the efficient section. In the case of poor adhesion, they proposed the following equation:

$$\sigma_{\mathrm{rc}} = (1 - \alpha\ V_f^{2/3})\sigma_{\mathrm{rm}} \tag{5}$$

where σ_{rm} and σ_{rc} are the stress at break of the matrix and that of the composite respectively, α is a geometrical constant which is dependent on the packing of the particles. In the case where there is no adhesion between the matrix and the filler particles, the value of α is estimated to be 1.21.

Similarly, in the case of no adhesion, Nicolais and Narkis [22] and Smith et al. [23] proposed the following relation, by taking into account the variation of the deformation at break of the composite (ξ_{rc}) as a function of the concentration of the reinforcing filler and the deformation at break of the matrix (ξ_{rm}):

$$\xi_{\mathrm{rc}} = (1 - \beta\ \mathrm{V}_f^{1/3})\xi_{\mathrm{rm}} \tag{6}$$

The value of the parameter β is evaluated to be 1.101.

In order to assess the effect of both the introduction of rigid particles and the modification of the filler surface on the mechanical properties, in terms of stress and elongation at yield and at break as well as Young's modulus, are reported.

Figure 2 presents the behavior of the neat matrix compared to those of the composites containing 40% of untreated and $CaCO_3$ treated in the humid method by different coupling agents. It is noted that for

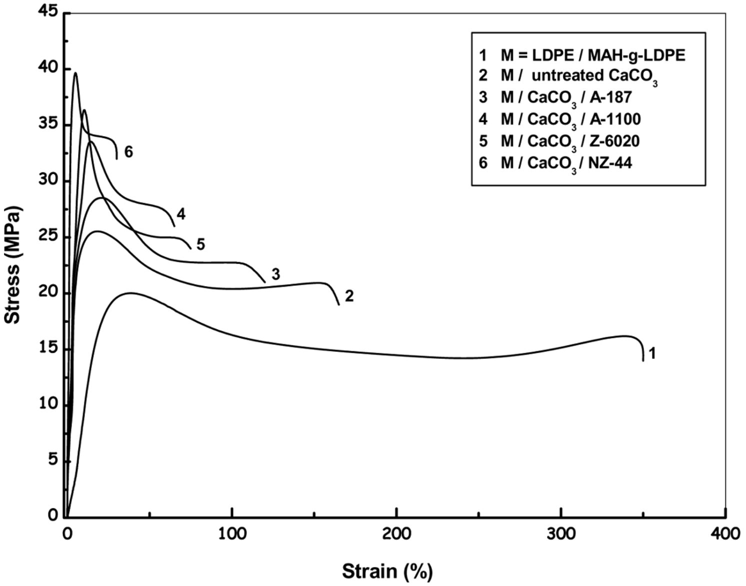


FIGURE 2 Stress/strain curves of the composites of LDPE/MAH-g-LDPE/ 40% $CaCO_3$ untreated and treated with different coupling agents by the humid method.

the composites yielding is reached at deformations lower than those for the matrix. This may appear to be the consequence of the introduction of rigid particles in the matrix leading to the restriction of the fraction of the polymer which withstands the load. Along with this an increase of the stress at yield is noted with the incorporation of the filler particles. This reinforcing effect reflects a distribution of the applied stresses between the rigid particles and the polymer. Such an evolution of the stress at yield could also reflect a certain adhesion between the different components of the composites.

In order to point out this reinforcing effect we define the relative stress at yield (σ_{yr}) which is the ratio of the stress reached by the filled polymer (σ_{yc}) to that of the matrix (σ_{ym}). Figure 3 shows the variations of the relative stress at yield for the composites with untreated filler and those treated with different coupling agents. The stress at yield increases linearly with the amount of the inorganic filler. The increase is relatively more pronounced with the composites containing the treated filler. The resulting reinforcement is a function of the quality of the dispersion of the particles within the matrix, but depends also on the potential of the interaction of the coupling agents with

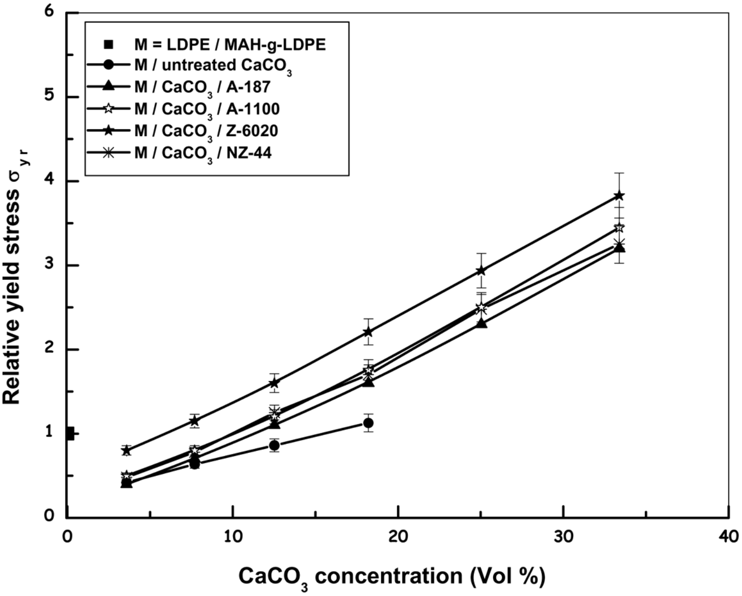


FIGURE 3 Variation of the relative yield stress with $CaCO_3$ concentration for the composites of LDPE/MAH-g-LDPE/$CaCO_3$ untreated and treated with different coupling agents by the humid method.

the polymer. Strong interactions at the interface between the filler particles and the macromolecular chains of the polymeric matrix through the coupling agents and the compatibilizer will lead to deep changes at the interfacial zone. Contrarily, weak interactions at the interface, as is the case with untreated filler-based composites, will limit the load transfer and might even cause the damage of the material as a result of the decohesion of the particles and the formation of voids around the filler.

Farris [24] observed this damage through volume expansion measurements and interpreted the shape of the stress-strain curve by considering the decohesion and void formation. The stress required to overcome wetting depends on the state of the interface, that is, on the extent of the interaction between the filler and the matrix as well as the properties of the polymeric matrix. By improving the adhesion of the matrix on the surface of the filler through the use of an organosilane, the decohesion is limited.

Figure 4 shows a clear difference in the tensile behavior of the composite systems. Compared to the composites with the filler treated by the humid method, the point of yielding reached by the composites

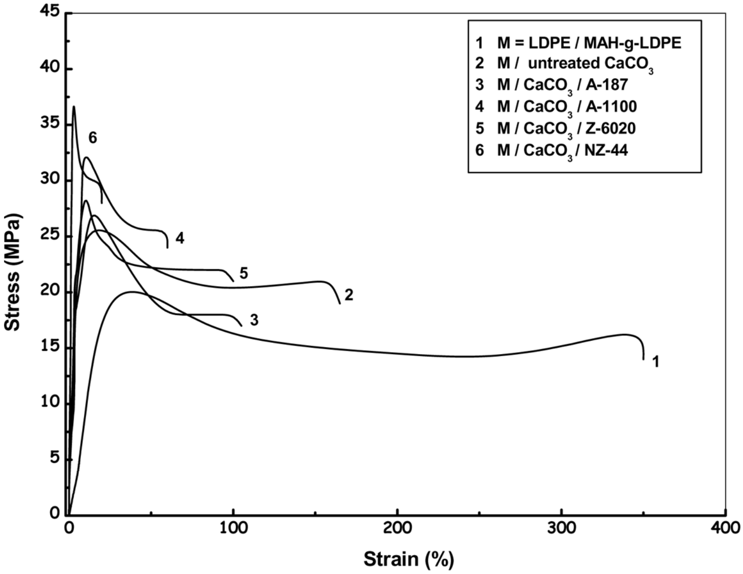


FIGURE 4 Stress/strain curves of the composites of LDPE/MAH-g-LDPE/ 40% $CaCO_3$ untreated and treated with different coupling agents by the dry method.

containing the filler treated by the dry method is lower. This could therefore be attributed to the efficiency of the treatment mode. In fact, the major inconvenience with the treatment by the dry method is the difficulty in achieving a uniform dispersion of the coupling agent throughout the entire mass. The brittle behavior observed with the composites with the filler treated by the dry method reflects an agglomeration of $CaCO_3$ particles. Such a structure within the material provides fewer surfaces for an eventual load transfer.

In order to quantify the resulting reinforcement, the variations of the relative stress at yield as a function of the filler content for the composites with the filler treated by the dry method are shown in Figure 5 and compared to those of the untreated $CaCO_3$ and that of the neat matrix. As was mentioned earlier, the rigid phase causes an increase of the stress at yield especially for the composites containing a treated filler.

A comparison between the behavior of the different composites is shown in Figure 6. The effect of the treatment mode can clearly be shown through those bar graphs. It is noted that the increase in the relative stress at yield is more important in the case where the filler is treated by the humid mode. The medium values obtained with the

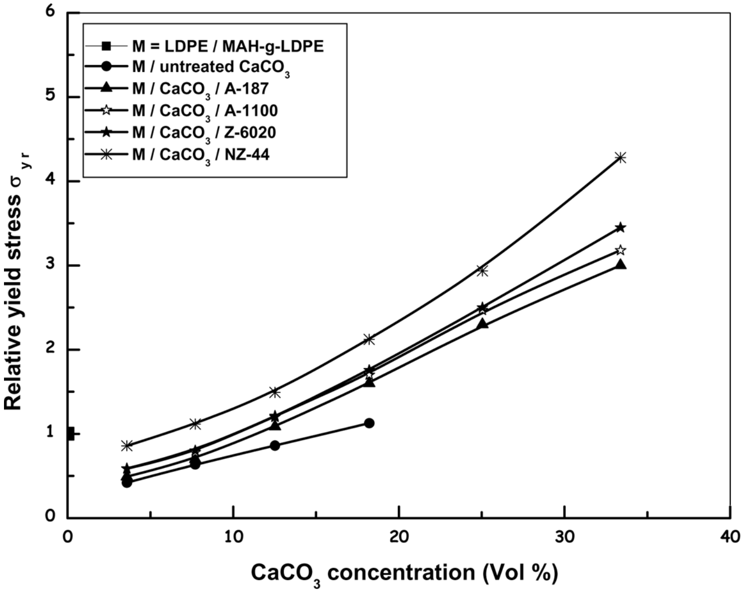


FIGURE 5 Variation of the relative yield stress with $CaCO_3$ concentration for the composites of LDPE/MAH-g-LDPE/$CaCO_3$ untreated and treated with different coupling agents by the dry method.

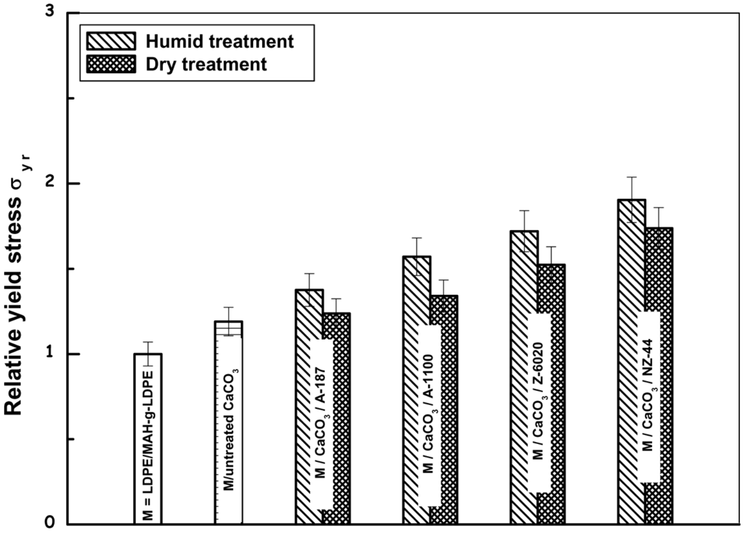


FIGURE 6 Effect of the method of treatment on the relative yield stress of the composites of LDPE/MAH-g-LDPE/40% $CaCO_3$.

composites containing $CaCO_3$ treated by the dry method could be an indication of the nonhomogeneity in the distribution of the stresses among the different components of the composite. This nonhomogeneous distribution of the stress throughout the polymer is certainly due to the agglomeration of the filler particles. It seems that the absence of a solvent during the process of the treatment of the filler does not ensure a good wetting of the coupling agent on the whole filler surface. We can also, through these results, compare the effect of different types of coupling agents. The NZ-44 caused higher reinforcement than the organosilanes. The effect could be an indication of stronger interactions between the filler and the matrix. It could also be due to a uniform distribution of $CaCO_3$ particles within the polymer. The use of the other three coupling agents lead to a lower extent of reinforcement which could be attributed to a less uniform dispersion.

To assess the extent of adhesion between the polymer and the filler, Pukanszky [19,20] defined the interaction parameter B. The plots of the variation of the relative stress at yield with the filler volume fraction according to Eq. 4 are presented in Figures 7 and 8 for the composites with $CaCO_3$ treated by the humid and dry method

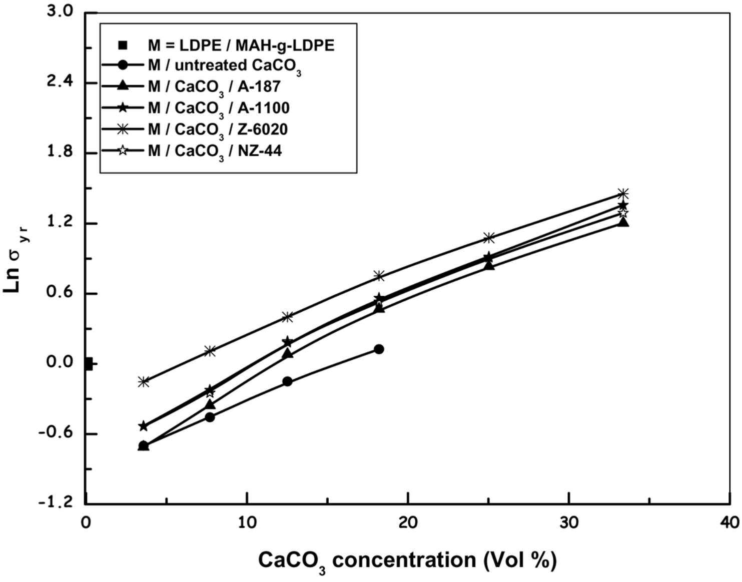


FIGURE 7 Variation of the logarithm of the relative yield stress with $CaCO_3$ concentration for the composites of LDPE/MAH-g-LDPE/$CaCO_3$ untreated and treated with different coupling agents by the humid method.

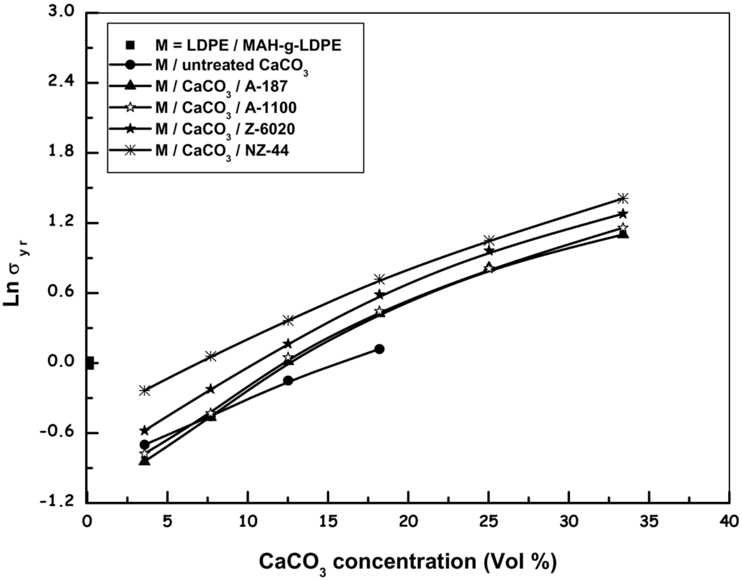


FIGURE 8 Variation of the logarithm of the relative yield stress with $CaCO_3$ concentration for the composites of LDPE/MAH-g-LDPE/$CaCO_3$ untreated and treated with different coupling agents by the dry method.

respectively. The values of the parameter B, which were determined from the slope of those plots, are presented in Table 5. It was found that the highest values of the slopes were obtained with the composites where the filler was treated with the NZ-44 agent no matter what the mode of treatment. Knowing that a higher value of the parameter B means a higher extent of reinforcement, we can therefore deduce that the composites based on $CaCO_3$ treated with the NZ-44 showed better adhesion and dispersion.

TABLE 5 Effect of Filler Treatment on the Value of Parameter B

Coupling agent	B values Humid treatment	 Dry treatment
No coupling agent	5.46	
Silquest A-187	5.75	5.36
Silquest A-1100	6.08	5.48
Dow corning Z-6020	6.41	5.40
Ken-React NZ-44	6.54	5.52

Figures 9 and 10 present the variations of the relative Young's modulus which is defined as the ratio of the Young's modulus of the filled polymer to that of the matrix. It is noticed that the greater the amount of the filler the higher the modulus. This trend is more pronounced with the treated filler-based composites. In accordance with the previous results, the composites created from $CaCO_3$ treated with the zirconate coupling agent exhibited a higher modulus. This increased stiffness is attributed to the interfacial adhesion resulting from the strong interactions that developed conjointly between the filler and the coupling agent and between the polymer and the coupling agent.

Figure 11 presents a comparison between the modulus of the composites containing 40% untreated $CaCO_3$ and those where the filler was treated by means of the two modes. The relative Young's modulus increases considerably for the treated composites and high values are obtained with the systems based on $CaCO_3$ treated by the humid mode. The excellent results found with the NZ-44 reflect once again a better affinity between the different components of the composite. Figures 12 and 13 show the effects of the filler concentrations as well

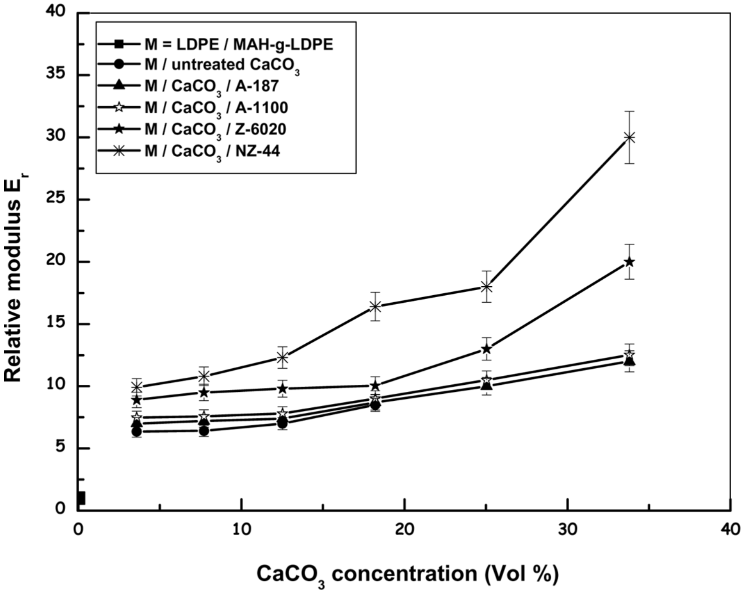


FIGURE 9 Variation of the relative modulus with $CaCO_3$ concentration for the composites of LDPE/MAH-g-LDPE/$CaCO_3$ untreated and treated with different coupling agents by the humid method.

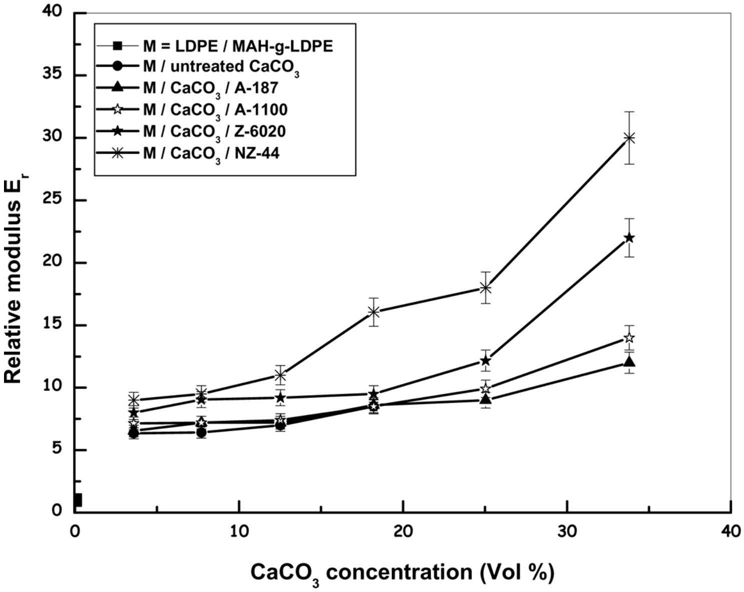


FIGURE 10 Variation of the relative modulus with $CaCO_3$ concentration for the composites of LDPE/MAH-g-LDPE/$CaCO_3$ untreated and treated with different coupling agents by the dry method.

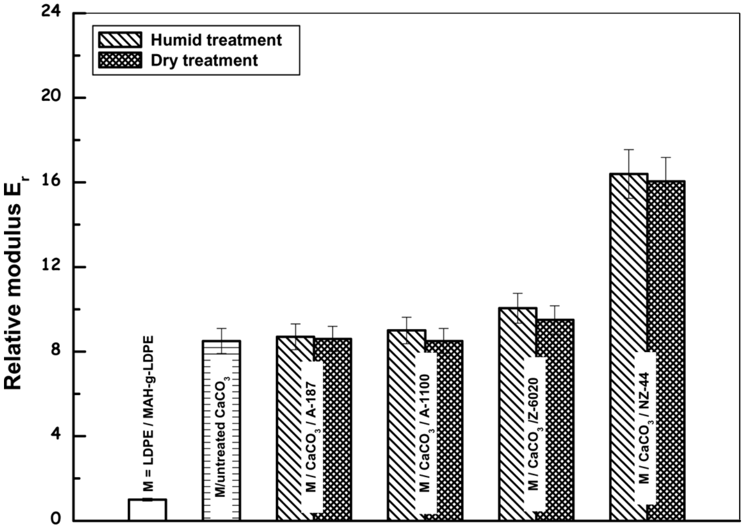


FIGURE 11 Effect of the method of treatment on the relative modulus of the composites of LDPE/MAH-g-LDPE/40% $CaCO_3$.

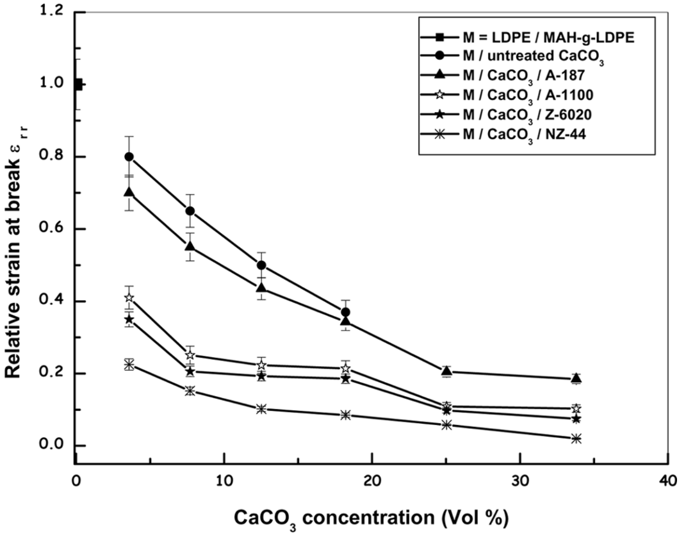


FIGURE 12 Variation of the relative strain at break with $CaCO_3$ concentration for the composites of LDPE/MAH-g-LDPE/$CaCO_3$ untreated and treated with different coupling agents by the humid method.

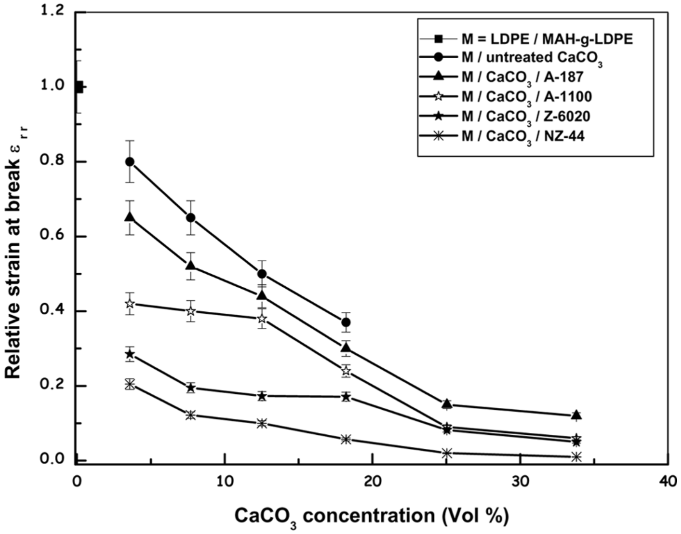


FIGURE 13 Variation of the relative strain at break with $CaCO_3$ concentration for the composites of LDPE/MAH-g-LDPE/$CaCO_3$ untreated and treated with different coupling agents by the dry method.

as its treatment on the relative strain at break, which is defined as the ratio of the deformation at break of the composite to that of the matrix. It appears that at low filler fractions, there is a moderate reduction of the deformation. This reduction becomes more pronounced with the increase of the filler concentration. This is associated with a transition from ductile to brittle in the behavior of the filled polymer. Li et al. [25], who examined the broken surface of filled polymer specimens, found that the samples corresponding to a ductile rupture showed very tormented surface accompanied by a whitening of the sample which was not observed in the neat matrix. They noted also the presence of cavities around the particles. Those voids could coalesce laterally or longitudinally until a flaw of a critical size may be formed. Concerning the samples that broke in a brittle fracture mode, their surface which was nonuniform was characterized by a more or less flat zone and another smooth zone where no decohesion could be observed.

Beshenov and coworkers [26], who studied PETG/$CaCO_3$ composites, have established a certain critical volume fraction above which the rupture mode changes. According to them, the main parameter of this transition is the consolidation capacity of the matrix that results from the progresssive orientation of the macromolecular chains with the main direction of the deformation.

The introduction of inorganic filler particles can affect the conditions of the appearance of a flaw because they lead to a heterogeneous distribution of the stress within the composite material. They can also add to the decohesion mechanism at the particle/polymer interface followed by a possible cavitation originating from the broken interface.

Figure 14 illustrates the effect of the type of coupling agent and the mode of treatment on the deformation at break for the different composites which contain 40% $CaCO_3$. These results show that the deformation at break depends much on the interface that is, the extent of interaction between the matrix and the filler. The most important drop in the deformation at break was obtained with the treated $CaCO_3$-based composites with both modes of treatment. The consequent decrease of the relative deformation at break for the composites prepared from $CaCO_3$ treated with NZ-44 is attributed to a strong rigidification of the interfacial zone, reflecting a strong interfacial adhesion.

Figures 15 and 16 present the variations of the relative stress at break, which is defined as the ratio of the stress of the composite to that of the matrix. The results show clearly that the stress at break is strongly dependent on the filler volume fraction, the nature of the interface and on the treatment mode. It is noted that the addition of

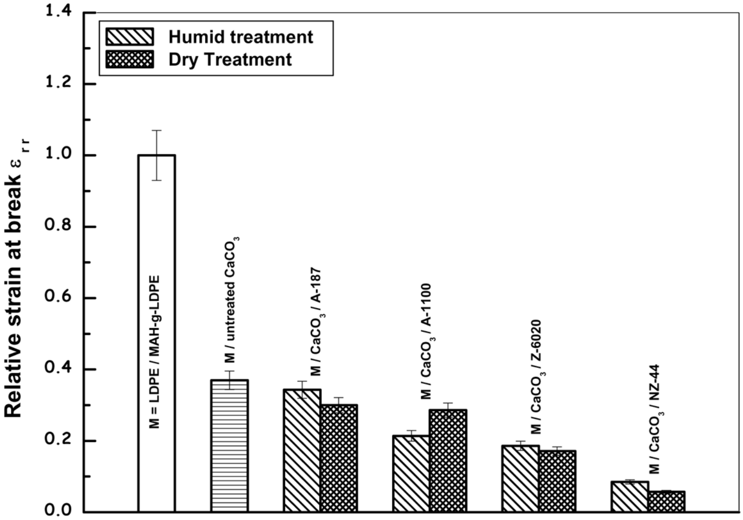


FIGURE 14 Effect of the method of treatment on the relative strain at break of the composites of LDPE/MAH-g-LDPE/40% $CaCO_3$.

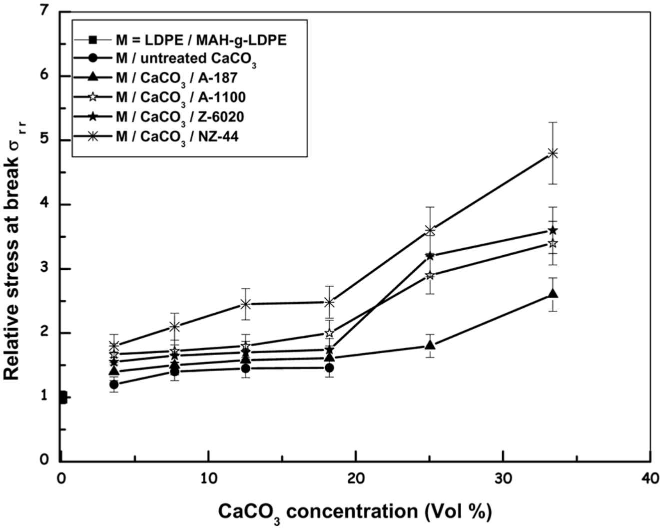


FIGURE 15 Variation of the relative stress at break with $CaCO_3$ concentration for the composites of LDPE/MAH-g-LDPE/$CaCO_3$ untreated and treated with different coupling agents by the humid method.

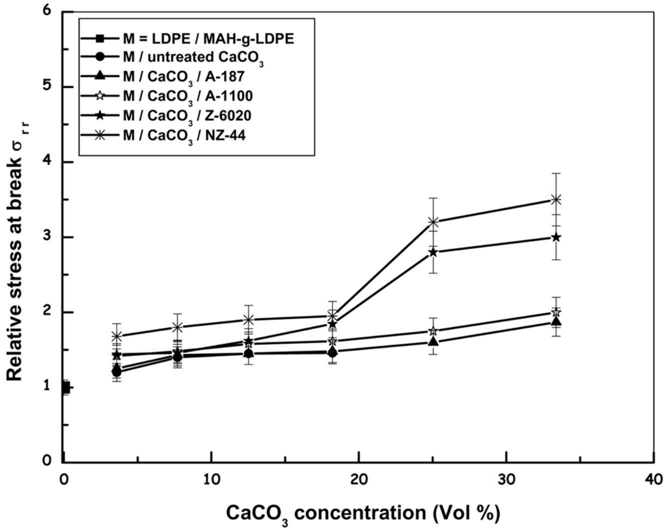


FIGURE 16 Variation of the relative stress at break with $CaCO_3$ concentration for the composites of LDPE/MAH-g-LDPE/$CaCO_3$ untreated and treated with different coupling agents by the dry method.

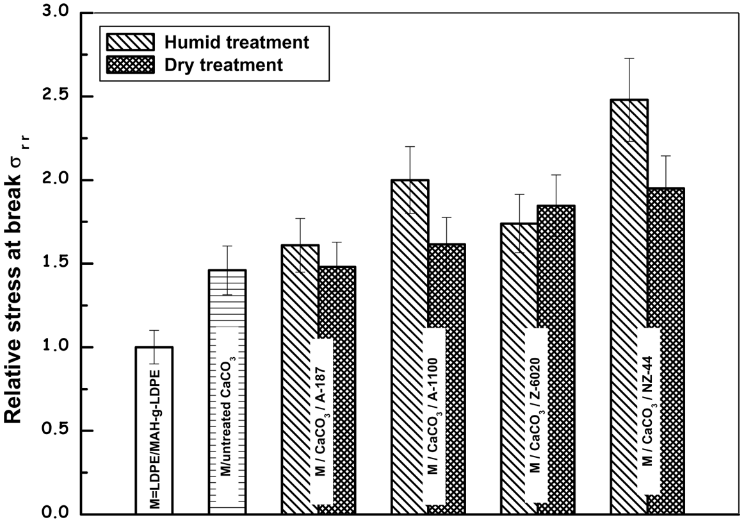


FIGURE 17 Effect of the treatment method on the relative stress at break of the composites of LDPE/MAH-g-LDPE/40% $CaCO_3$.

the rigid filler particles to the polymeric matrix causes an increase of the relative stress at break. This reinforcing effect gets more pronounced as the interfacial adhesion and the dispersion of the filler are improved. In fact, as a result of the treatment, the filler surface free energy decreases, leading to a reduction of the tendency towards aggregation. These last two parameters lead to a better load transfer between the matrix and the filler.

As shown in Figure 17, from a comparison between the behavior of the different created composites, it appears that there is a difference in the evolution of the relative stress at break depending on the structure of the interface and the degree of the dispersion of the filler within the matrix. On the other hand, the composites containing 40% $CaCO_3$ treated by means of the humid mode exhibited a better behavior compared to that of the composites with the filler treated by the dry mode.

CONCLUSION

This study dealt with the preparation and the use of maleic anhydride-grafted low density polyethylene as a compatibilizer for a LDPE/ $CaCO_3$ composite. Using triphenyl phosphine was found to be necessary to reduce the extent of the side crosslinking reaction that takes place during the grafting reaction. Titration measurements showed that 0.21% by weight grafting was achieved. The surface modification of $CaCO_3$ by means of silane and zirconate coupling agents lead to significant improvements in the mechanical properties. The tensile properties, in terms of stress at break and modulus, were much higher for the composites based on the treated filler as a result of a change in the structure of the polymer/filler interface. The resulting reinforcement effects were found to be much dependent on the state of the dispersion of the filler particles within the matrix, but also on the potential interactions of the coupling agents with the compatibilizer. The assessed mechanical properties, expressed in terms of their relative magnitudes, showed a higher extent of reinforcement for the zirconate-based composites than those treated with the silane coupling agents.

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