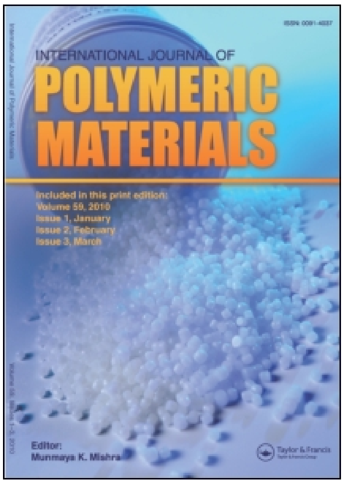

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EFFECT OF TITANATE COUPLING AGENT ON THE MECHANICAL PROPERTIES OF CALCIUM CARBONATE FILLED POLYPROPYLENE

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Composites of polypropylene filled with untreated and treated calcium carbonate ($CaCO_3$) have been prepared. The surface modification of calcium carbonate was done by using titanate coupling agent. The effect of this treatment on the interfacial adhesion and the dispersion of filler particles in the polymeric matrix was evaluated by performing mechanical, thermal and optical analysis.

The results obtained indicate that the incorporation of non-treated $CaCO_3$ decreases in general the mechanical properties (except the modulus) of the composites. However, the use of treated calcium carbonate increases the amount of filler that can be incorporated in the polymeric matrix. Mechanical properties such as tensile and flexural stresses, elongation at break, modulus and impact strength are also improved. Differential thermal analyses indicate the existence of an interface between the polymeric matrix and the treated filler particles. Micrographic analyses confirm the efficiency of surface treatment of the filler on its dispersion.

Keywords: Reinforcement of polypropylene, $CaCO_3$, titanate coupling agents, surface treatments, interfacial interaction

INTRODUCTION

In recent years, there has been a spectacular growth in the use of mineral fillers in the plastics industry in order to improve specific properties or to reduce cost.

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Polypropylene is one of the most important polymers used in technical applications and it can be filled with a wide range of fillers [1–5]. Its main advantages are low density, good heat stability, chemical resistance and ease of processing. Among the fillers used, calcium carbonate is the most common, due to its low cost, good dispersion of the particles in the polymeric matrix and ability to improve the rigidity of the system [6].

It is well known that polypropylene filled with calcium carbonate is a simple, two-component system with dispersed rigid particles in a continuous matrix phase [7]. The final properties of composite materials do not depend only on the intrinsic properties of each component (filler and matrix), but also on the existence of an interface between them, which is often the weakest point of the system.

To improve the compatibility between filler particles and the matrix, the surface of $CaCO_3$ is generally treated with coating agents. The role of these agents is to improve the dispersion of filler in the matrix and increase the adherence between them [8].

The importance of interfacial interactions is established by the numerous attempts to modify them [9–11]. In the case of polypropylene/$CaCO_3$ composites, two techniques are mainly used, nonreactive and reactive treatments:

- Non reactive treatment: in this method, the surface of calcium carbonate is covered by a surfactant. Typical modification consists of depositing on the surface of the filler long chain fatty acids, in order to reduce interparticle frictions, to minimize aggregations and to improve the dispersion of the particles in the polymer matrix [12–16]. However, the interfacial bonds of PP/$CaCO_3$ are either intrinsically weak or deteriorated when the composite is exposed to humid environments [8].
- Reactive treatment: the surface of particulate calcium carbonate is precoated with a so-called "coupling agent." The most widely used coupling agents are the neoalkoxy titanates, whose chemical composition allows them to react with both the surface of the filler and that of the polymer matrix [17–27].

Titanate may react with fillers according to the following alcoholysis chemical mechanism:

$$\mathrm{MOH} + \mathrm{R'O\text{-}Ti(O\text{-}X\text{-}R\text{-}Y)_3} \longrightarrow \mathrm{MO\text{-}Ti(O\text{-}X\text{-}R\text{-}Y)_3} + \mathrm{R'OH}$$

where M is the substrate, H is the surface proton, R′O is the Monohydrolysable group, and R, Y are respectively the thermoplastic and thermoset functional groups.

The neoalkoxy coupling agents react with substrate surface protons at the inorganic interface. However, the calcium carbonate does not have active side groups on its surface that could react with titanates [8, 27, 28]. Nevertheless, some success has been reported in improving the mechanical properties of $CaCO_3$–filled polypropylene using coupling agents [1, 19, 29].

The aim of this study is to investigate the effect of $CaCO_3$ surface modification by the use of a titanate coupling agent in order to increase its chemical affinity towards polypropylene. Mechanical, morphological and thermal analyses were carried out in order to determine the reinforcing effect of the treated filler on the properties of polypropylene/$CaCO_3$ composites.

EXPERIMENTAL

The matrix used is a polypropylene resin (Raco GR2/1k24EAC1) supplied by Repsol Quimica S.A. in a granular form having a nominal melt flow index of 4 (g/10 min. at 190 °C and 5 Kg) and a density of 0.905 g/cm^3.

The reinforcing filler used was calcium carbonate ($CaCO_3$), having an average particle size of 5 μm, was supplied by Alcal –E.N.G Algeria. Its chemical composition and physical properties are shown, respectively, in Tables 1 and 2.

The coupling agent used is liquid organo-functional titanate neopentyl (diallyl)oxy,tri(dioctyl)phosphatotitanate, supplied by Kenrich Petrochemicals Inc., commercialized under the name of "Lica 12" with a degree of purity greater than 99% as obtained by GPC analysis.

The optimization of coupling agent concentration has been carried out using a Brookfield viscosimeter, according to the method described by J.M. Salvatore [27]. The obtained results are given in Figure 1.

The results obtained indicate that the best coupling agent content to be used is 0.3% by total weight of filler. Upper and lower concentrations were also investigated.

TABLE 1 Chemical Composition of Calcium Carbonate (%)

$CaCO_3$	: 98.50
$MgCO_3$	: 0.41
Al_2O_3	: 0.08
Fe_2O_3	: 0.04
SiO_2	: 0.30

TABLE 2 Physical Properties of Calcium Carbonate

Density (g/cm^3)	: 2.7
Apparent density (g/cm^3)	: 1.7
Specific surface area using "blaine method" (m^2/g)	: 0.6
Weight loss (24 hr at 130 °C) (DIN ISO 787/2) (%)	: <0.2
Refractive index	: 1.57
Mean particles diameter (µm)	: 5
pH of aqueous dispersion (DIN ISO 787/9)	: 9.45
Weight loss at 1000 °C(%)	: 43.4

Calcium carbonate was coated by the titanate dissolved in dry toluene and stirred for 30 minutes; the reaction was carried out at room temperature. Then the suspension was filtered and dried at 80 °C until the remaining solvent was completely removed.

The optimization of calcium carbonate concentration has been carried out using a Brookfield viscosimeter. From this experiment, we can obtain the curve of pigment volume concentration (CPVC). The CPVC curve may be defined as that point in calcium carbonate filled polypropylene at which just as sufficient polymer is present to fill the air voids completely to provide the densest degree of calcium carbonate packing commensurate with the degree of dispersion of the matrix [27,30].

Figure 2 shows the PVC curve for calcium carbonate filled with mineral oil. This curve can be viewed as a model for calcium carbonate filled polypropylene. We notice that the curve of the untreated filler under a maximum mechanical dispersion begins to break sharply at a concentration between 30 and 40%. However, the filler treatment shifts the PVC curve to the right and the CPVC is now between 60 and 70 (% by weight).

Formulations were prepared using a two roll mills "Polymix 80T" at 170 °C. The obtained composites were ground and then compression molded.

Filler concentrations used vary from 10 to 40 (% by weight) for the untreated $CaCO_3$ and from 10 to 70 (% by weight) for the treated one.

Tensile and flexural tests were carried out on samples prepared according to ASTM-D638 and ASTM-D790 respectively, using an Adamel-Lhomargy–type mechanical testing universal machine coupled to a microcomputer. Impact "charpy" test was performed using a "65HG model CEAT apparatus" according to ISO-R-180. Melting behavior of composites were studied using a Setaram Differential thermal analyser "DTA" with a heating rate of 10 °C/min.

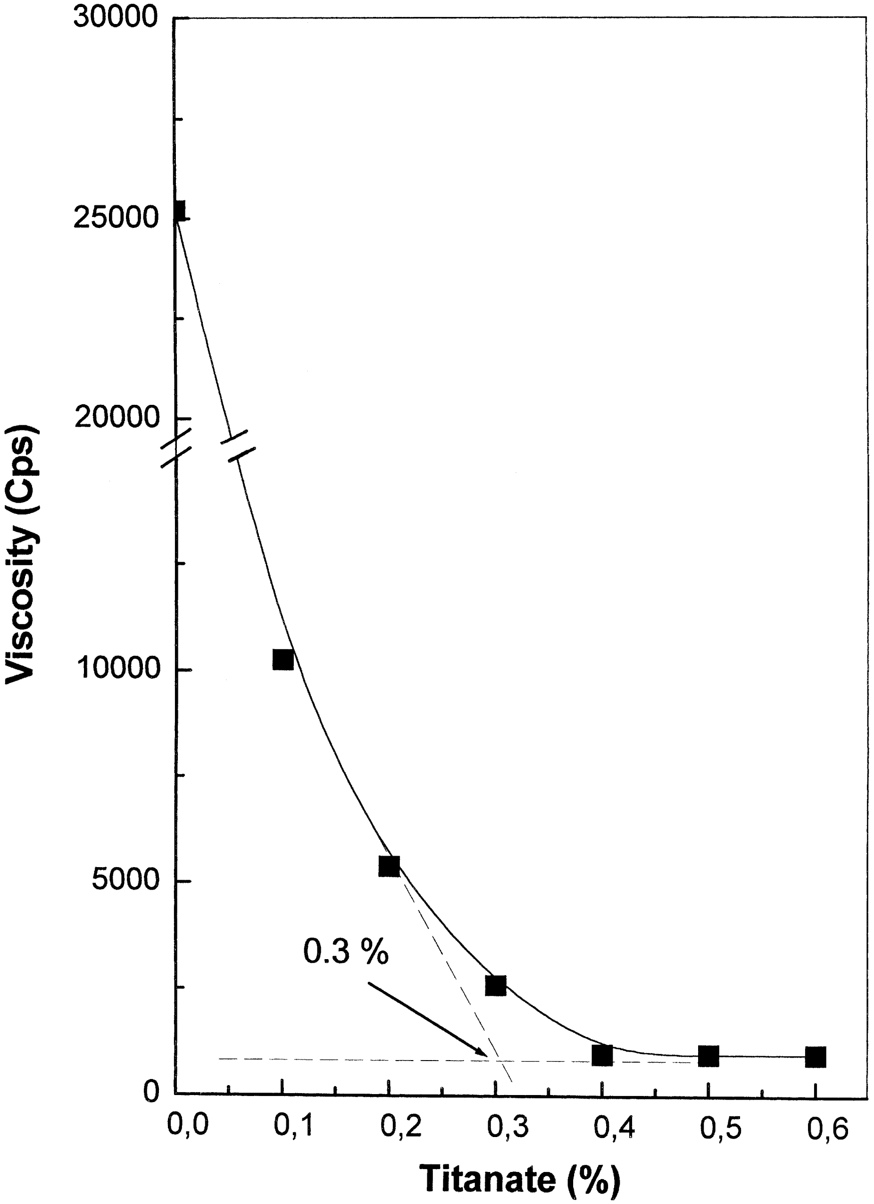


FIGURE 1 Effect of titanate content on the variation of Brookfield viscosity of $CaCO_3$/mineral oil.

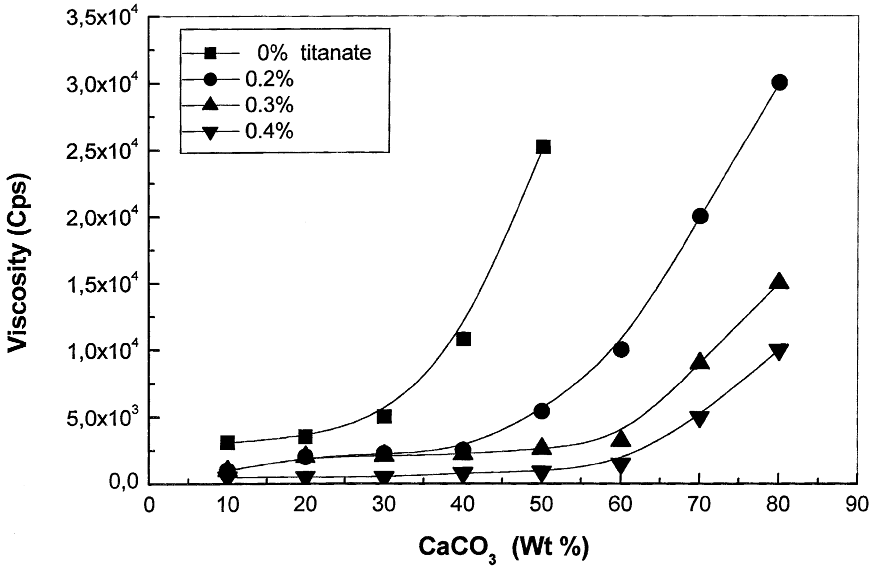


FIGURE 2 PVC curves of non treated and treated $CaCO_3$/mineral oil systems.

Microphotographic analysis has been made with a Neophot-21 optical microscope.

RESULTS AND DISCUSSION

Before approaching the mechanical properties, an observation of the behavior of the mixtures during their preparation revealed that the composite behavior is not only a function of filler content, but also of the coupling agent concentration.

a. Case of composites with untreated filler:

- The mixtures stick to the metallic surface of the two roll mills.
- The incorporation of filler particles in the matrix is very difficult due to the agglomeration of filler particles, instead of being dispersed in the matrix.
- Specimen extraction from the molds is very difficult.

b. Case of treated filler:

- Dispersion of filler particles in the polymeric matrix is easier.
- Coupling agent acts as lubricant, so the mixtures don't stick to the two roll mills walls.
- Specimen demolding is faster.

To obtain a full range of information about of the behavior of the different composites prepared the mechanical, thermal and morphological properties were studied.

Mechanical Properties

Figures 3 and 4 show, respectively, the variation of the tensile and flexural stresses at break of PP filled with calcium carbonate. These figures reveal that both stresses at break decrease with increasing filler content. Furthermore, the stress at break of specimens prepared with untreated $CaCO_3$ is lower than that of those prepared with treated one, especially for the composites with a high content of filler. This decrease in stress with the increase of filler content can be attributed to the poor adhesion between filler and matrix and to the bad dispersion of the untreated $CaCO_3$ into the non-polar polypropylene matrix. Filler particles may also form aggregates, which have poor adhesion to the matrix [31–33].

Also, the decrease in stress of particulate–filled thermoplastics is attributed to the inability of filler to support stress transfer from the polymeric matrix as reported by D.M. Bigg [34].

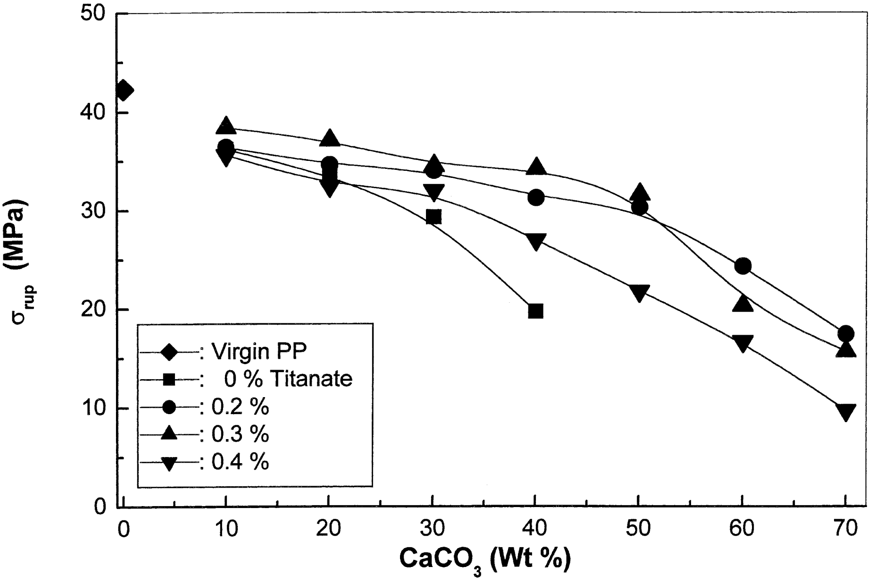


FIGURE 3 Effect of filler content on the tensile stress at break of PP/$CaCO_3$ with different concentrations of titanate.

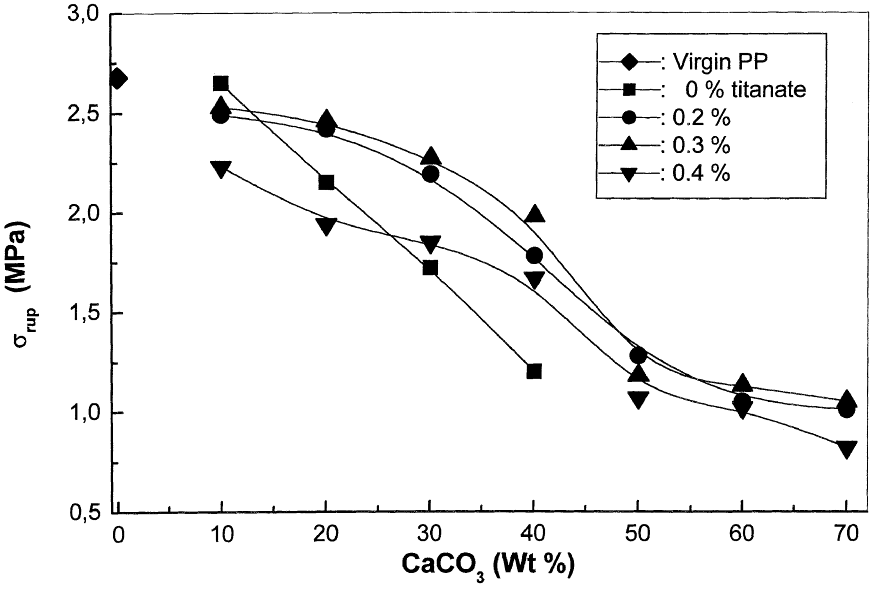


FIGURE 4 Effect of filler content on the flexural stress at break of PP/$CaCO_3$ with different concentrations of titanate.

Surface treatment of $CaCO_3$ particles by titanate gives them a better dispersion in the matrix and produces strong interactions between filler and matrix, leading to the development of an interface with properties different from those of the filler and the matrix. Also, it is well known that the treatment of $CaCO_3$ lowers its surface energy, which leads to a reduction of the wetting angle in polypropylene [35]. Thus, the titanate coupling agent appears to modify the mechanisms of the stress distribution inside the composites. The stress transferred from the polymer matrix to the filler phase is better than that from filler to filler particles.

The decrease of the tensile stress at 0.4% concentration of coupling agent is probably due to an excess of coupling agent concentration.

Figures 5 and 6 show the variation of the tensile and flexural elongation at break with calcium carbonate content. They indicate that the elongation at break increases with increasing filler content, especially in the case of treated filler. In general, when there is an interaction between the polymer and the filler, the elongation at break tends to decrease. In our case, the increase in this property is probably due to the presence of a long hydrocarbon chain inside the structure of titanate coupling agent, which acts as an internal lubricant. This

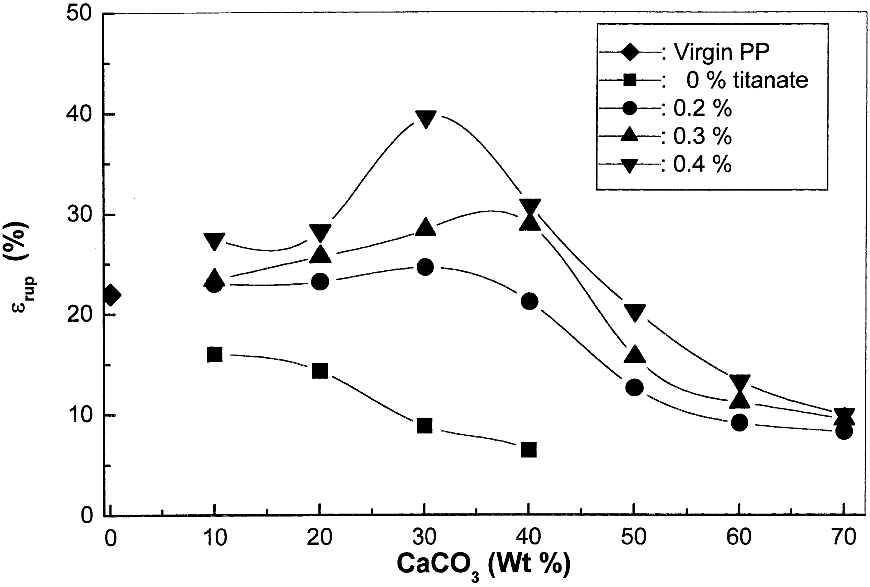


FIGURE 5 Effect of filler content on the tensile elongation at break of PP/$CaCO_3$ with different concentrations of titanate.

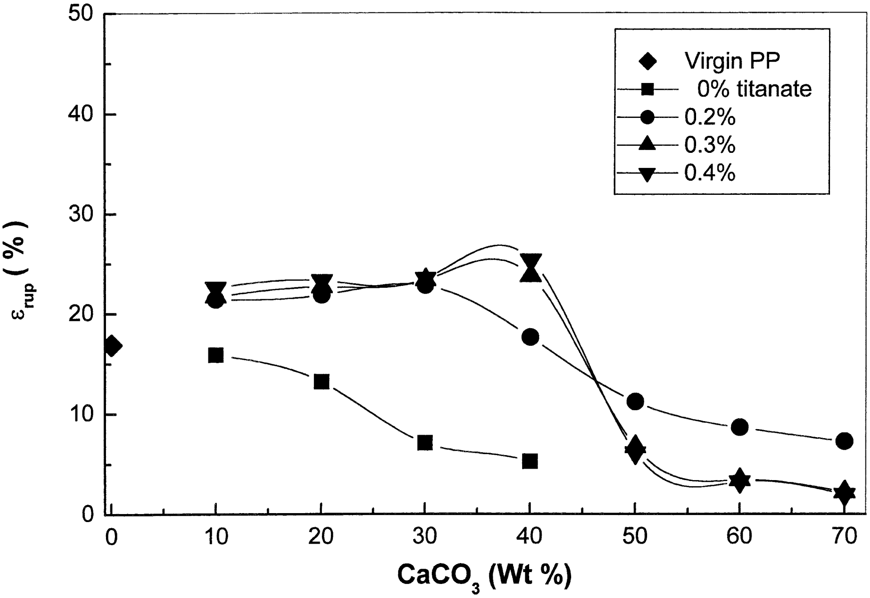


FIGURE 6 Effect of filler content on the flexural elongation at break of PP/$CaCO_3$ with different concentrations of titanate.

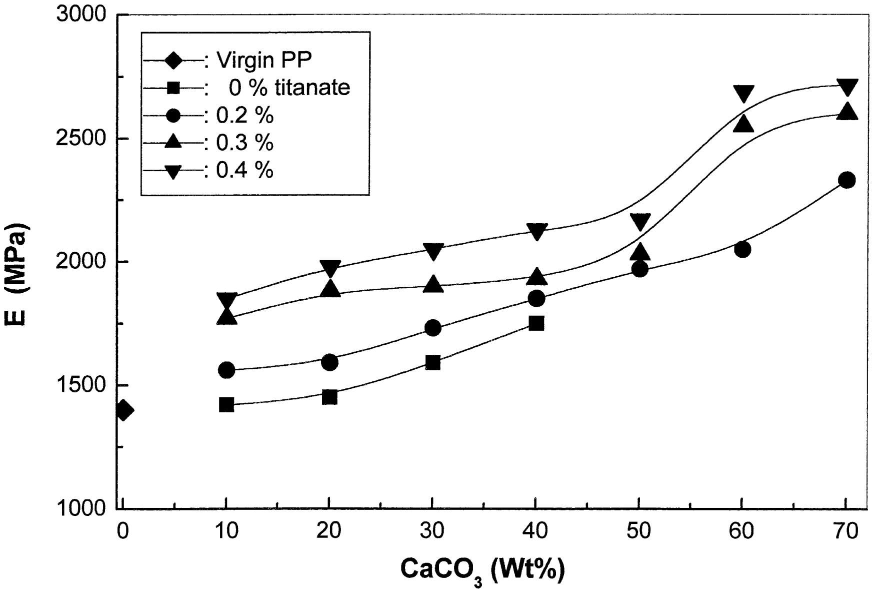


FIGURE 7 Effect of filler content on the tensile modulus of PP/$CaCO_3$ with different concentrations of titanate.

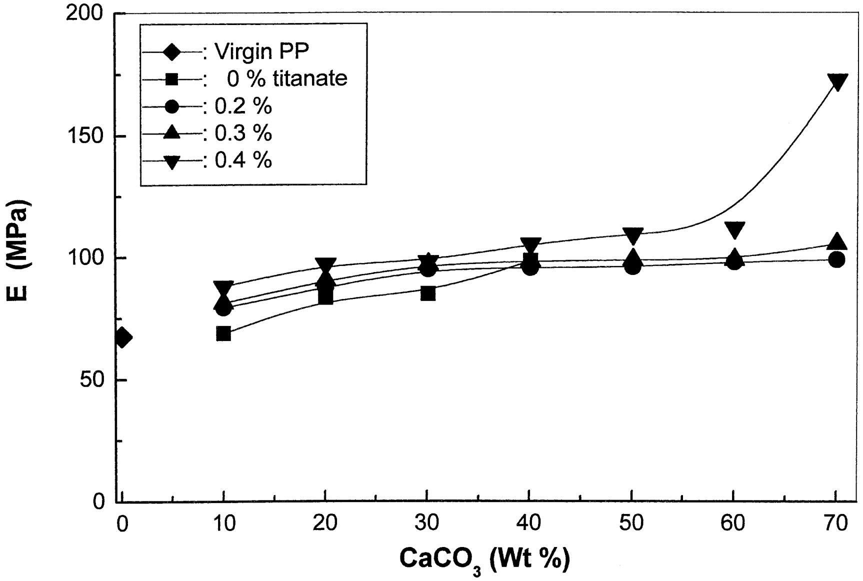


FIGURE 8 Effect of filler content on the flexural modulus of PP/$CaCO_3$ with different concentrations of titanate.

observation is only true for composites with treated filler content under 30% (by weight). Also, it is observed that there is a direct correlation between the improvement of the elongation and the viscosity of the composites (Figure 1) for various levels of titanate. If we accept that the value of 0.3% corresponds to a monolayer coverage, then that of 0.4% will indicate the adsorption of multilayers. This excess frequently provides lubrication and plasticizer effects.

In the case of virgin $CaCO_3$, the elongation at break decreases with increasing filler content. It could be due to poor adhesion between virgin calcium carbonate and PP, leading to the formation of two distinct phases. The filler phase will decrease the possibility of elongation of the polymeric chains.

Figures 7 and 8 show the variation of tensile and flexural modulus of the composites with $CaCO_3$ content. These figures reveal that the tensile and flexural modulus increase with increasing filler content. It is generally known that the addition of any rigid filler to a polymer matrix increases its modulus. Furthermore, for the same content of $CaCO_3$, the modulus of composite increases with the amount of coupling agent used in the surface treatment. This is due to the formation of good interfacial adhesion between matrix and filler.

According to Goujon et al. [36], $CaCO_3$ contains a small amount of $Ca(OH)_2$ or other oxide and hydroxide impurities, which may react with the organofunctional groups of the coupling agent. Thus, the increased modulus may be attributed to the adhesion of titanate to the surface of $CaCO_3$, via the reaction with the reactive impurities present at the surface of the filler.

Fracture impact strength of PP filled with virgin or treated $CaCO_3$ as a function of filler content is reported in Figure 9. This figure indicates that the incorporation of virgin $CaCO_3$ with the polymer matrix decreases the fracture impact strength of the composites. However, the addition of treated filler increases the impact strength of composites. In the case of virgin $CaCO_3$ and during the impact test, cracks tend to propagate through the polymer matrix as well as the weaker interfacial regions (existence of two distinct phases) and thus the impact strength is reduced. But, in the case of treated $CaCO_3$, there is a certain affinity between filler and matrix, which increases the interfacial adhesion. So the resistance of the interfacial regions to crack propagation is higher.

From the mechanical properties, we can say that an adequate chemical modification of the mineral filler improves the mechanical properties of the composites due to the good dispersion of $CaCO_3$ particles in the polymeric matrix and a formation of strong interfacial regions.

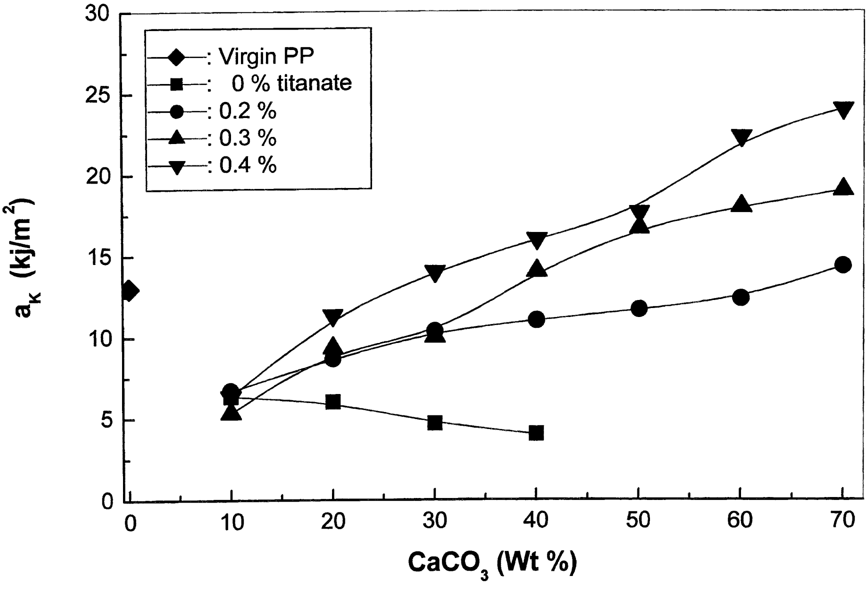


FIGURE 9 Effect of filler content on the impact strength of PP/CaCO$_3$ with different concentration of titanate.

THERMAL ANALYSIS

A melting test was made using a differential thermal analyzer “DTA” and the obtained results are summarized in Table 3.

The melting point at the peak summit corresponds to the total or quasi-total melting of the mixture. Its area represents the sample melting enthalpy ΔH_f (cal/g).

To determine crystallinity percentage, the melting enthalpy of specimens was measured. This method is based on the hypothesis that this parameter is proportional to the crystallinity level relative to the value of melting enthalpy corresponding to 100% crystallinity of the sample “ΔH_{fx}.”

- The incorporation of treated or virgin CaCO$_3$ influences significantly the thermal behavior of composites.
- The melting point of formulations increases with increasing filler content, except for those filled with treated filler (0.2% Lica12) and virgin one. Their melting point decreases with increasing filler content. The positive difference between melting temperature of the composites prepared and virgin polypropylene is related

TABLE 3 DTA Values of PP/$CaCO_3$

Formulations	$CaCO_3$ (%)	T_f (°C)	ΔHapp (cal/g)	Crystallinity (%)
PP	0	145.70	14.00	42.50
PP/($CaCO_3$ virgin)	30	148.00	20.80	63.00
	40	145.00	20.13	61.00
PP/($CaCO_3$ treated with 0.2% Lica 12)	30	156.40	20.56	62.00
	40	155.00	22.30	67.50
	70	140.00	20.90	63.00
PP/($CaCO_3$ treated with 0.3% Lica 12)	30	160.00	21.10	64.00
	40	162.00	21.60	65.50
	70	169.50	23.00	70.00
PP/($CaCO_3$ treated with 0.4% Lica 12)	30	160.50	21.50	65.00
	40	164.50	22.90	69.50
	70	171.90	23.60	71.00

according to some authors [37,38] to the existence of strong matrix/filler interactions due to the formation of true chemical bonding.

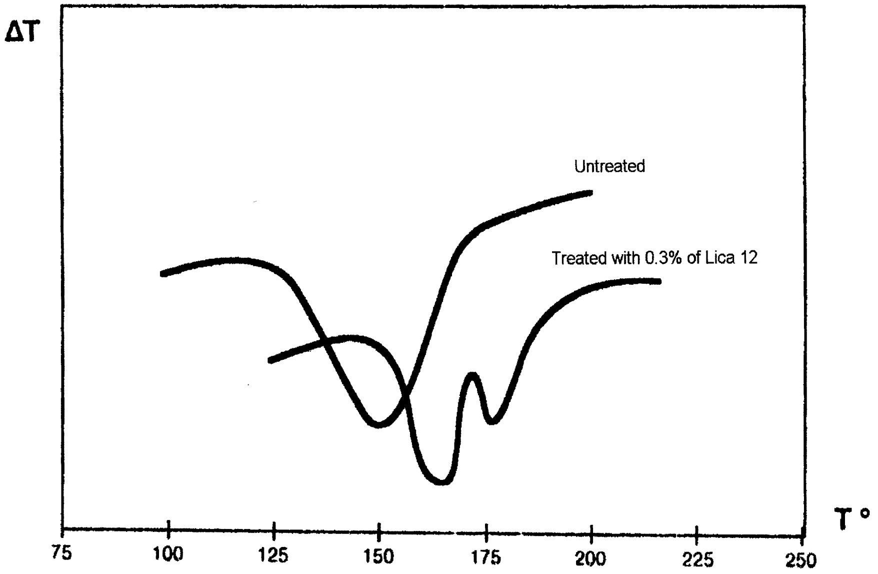


FIGURE 10 Thermogram of fusion of untreated and treated PP/$CaCO_3$ (60/40).

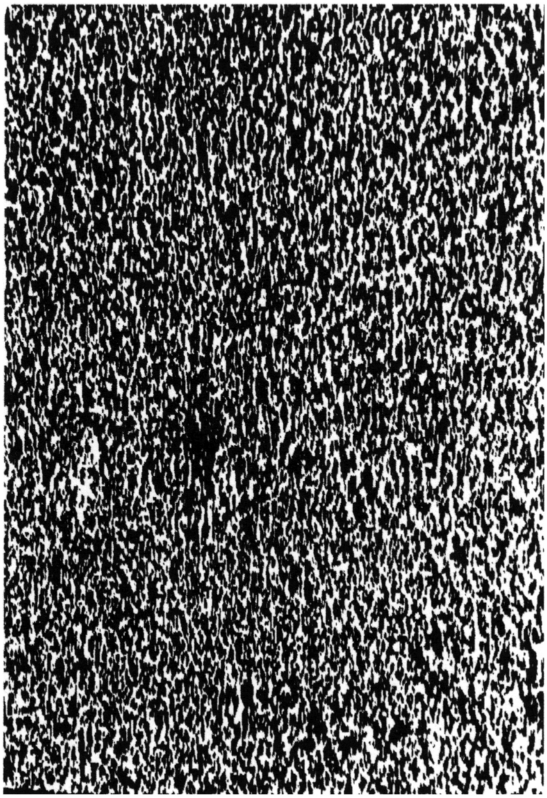

(a)

FIGURE 11 a: Microphotograph of PP. b: Microphotograph of PP/$CaCO_3$ untreated (60/40). c: Microphotograph PP/$CaCO_3$ treated with 0.3% Lica12 (60/40). (*Continued*).

- The crystallinity of the composites generally increases with both filler contents and Lica 12 concentration. An exception however, is observed with Lica 12(0.2%) and 70(%wt) of $CaCO_3$
- The treated filler exhibits a high surface activity, which affect the structure of the matrix. This observation can explain the existence of two peaks of fusion in the thermogram of treated PP/$CaCO_3$ (Figure 10).

The molecular chains of polypropylene cannot assume all the conformational positions that are generally possible. Furthermore, in

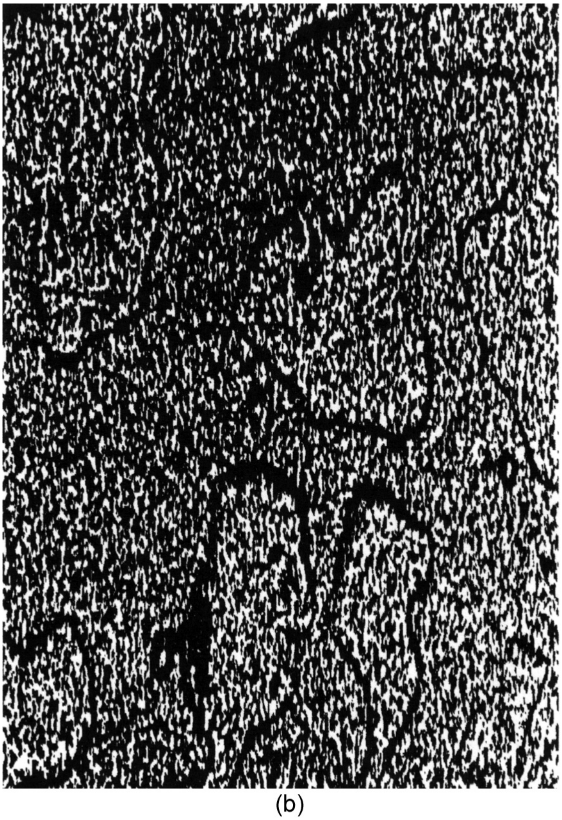
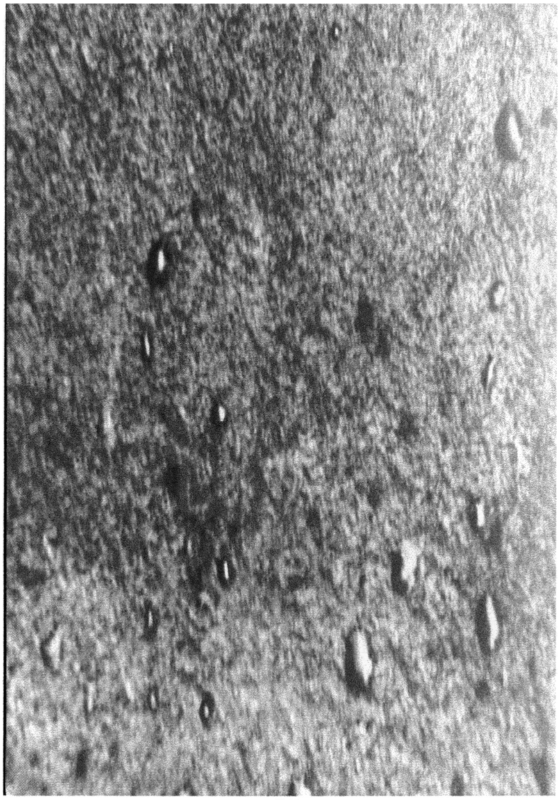


FIGURE 11 (Continued).

the regions around the filler particles, the polymeric phase differs in structure and properties from those of the bulk matrix. The polymer segments linked to filler surfaces by primary or secondary valence bonds. A certain immobilization of the adjacent segments enables the orientation of the polymeric matrix [28].

Figure 10 shows the existence of two peaks. The first peak corresponds to the fusion temperature of the system and the second one to the interface formed by the interaction between the coupling agent and filler. $CaCO_3$ is known as an inert filler (no reactive sites), so the interactions are probably due to the presence of metal oxides in the $CaCO_3$ base formulation. However, Béla Pukànszky relates the presence of the first peak to the crystallization temperature of the matrix [39].



(c)

FIGURE 11 (Continued).

OPTICAL MICROGRAPH OBSERVATION

The microphotographs in Figure 11 show that the treated particles present a better dispersion in the matrix; an improvement in interfacial bonding is then possible. As a result, the PP composite materials exhibit higher impact strength. In the case of untreated $CaCO_3$, the optical observation (Figure 11b) shows agglomerated inorganic particles having deleterious water of hydration and air voids mixed into the organic matrix.

CONCLUSIONS

The study suggests that the best coupling agent composition needed to cover completely the surface of calcium carbonate used is that of 0.3% of the total weight of filler.

The maximum filler content that can be incorporated in the polymeric matrix is greatly increased by the filler surface treatment, without affecting the mechanical and thermal properties.

Filler surface modification led to significant consequences relative to the base polymer. This is expressed by an increase in the modulus, and particularly in the impact strength.

The DTA data confirms that a good adhesion exists at the polymer/filler interface and confirms the presence of two morphological structures.

The suitable effect of this surface modification is more clearly seen in the microphotographic analysis. Surface treatment of the filler reveals its effectiveness in improving the dispersion and confirms its potential to modify efficiently these polymers; moreover, the impact strength improvement is due to a better dispersion of the filler within the polymer.

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