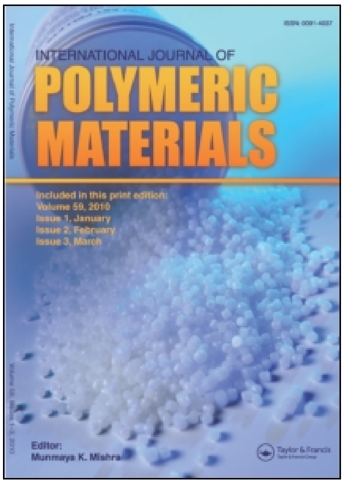

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# The Influence of a Titanate Coupling Agent on the Rheological Properties of PP/$CaCO_3$

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# The Influence of a Titanate Coupling Agent on the Rheological Properties of PP/$CaCO_3$

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*The present work deals with the study of the rheological properties of polypropylene/calcium carbonate composites treated with a titanate coupling agent. The study focused on the examination of the flow behavior of the material under different conditions of shear rate and temperature. A more pronounced pseudoplastic behavior was observed for the filled material than for neat polypropylene. It was also found that the power law index increases slightly with increasing temperature and increased concentration of the coupling agent; but decreases with the amount of filler and shear rate. On the other hand, the viscosity increased with increased amount of the filler, especially at low shear rates, but showed a substantial reduction with increased temperature and concentration of the coupling agent. The activation energy, too, was found to decrease with shear rate and concentration of the titanate agent, confirming, hence, the lubricating action of this coupling agent. Finally, through the shift factor that was calculated for both the viscosity and the shear stress functions, the flow master curves superposed for all the materials that were studied.*

**Keywords:** calcium carbonate, characterization, composite, interfacial effects, polypropylene, rheological properties, titanate coupling agent

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# INTRODUCTION

Research and industrial production of organic matrix-based composites have grown rapidly over the last decades due to the characteristics that can be achieved through this type of materials in comparison to classical ones. In fact, the properties of composite materials are greatly dependent on the interface and/or the interphase. Strong bonding at the interface or through the interphase between the matrix and the reinforcing agent is one of the main requirements for reinforcement of a polymeric matrix by means of particulate fillers. Moreover, the mechanical resistance of composite materials is greatly influenced by the nature of the interface and the interactions that develop in it [1–5]. This is why it is very important to increase the interface and to generate interphases during the processing of composite materials.

Three main factors, namely the structure, the specific area, and the chemical activity of the surface, greatly affect the extent of reinforcement during the incorporation and the dispersion of the filler within the matrix. Even though different types of fillers are used, their choice remains empirical because the interpretation of the mechanisms involved in the process of reinforcement are in part subject to discussion [6–7].

Natural calcium carbonates, which consist of mineral particles, have been used so far in polyolefins, and particularly with polypropylene, in order to modify or enhance certain of their characteristics such as the rigidity and flexural strength.

In many applications the calcium carbonate fillers are simply used to reduce the cost of the final product. But this use is restricted to only small concentrations due to the absence of attraction between them and the polymeric matrix and also to the tendency of these particles to agglomerate. During the processing of the polymeric composites it is important to break up the agglomerates because they can act as defects and initiate fracture, which would considerably reduce the mechanical performance of the materials [8–10].

The processes and equipment used in the transformation of polyolefins rarely allow a direct incorporation of the mineral fillers. This is essentially due to the fact that polypropylene is not polar and because the machinery used is not adaptable to achieve a good dispersion of filler particles. Because of these two reasons the incorporation of $CaCO_3$ in polypropylene is carried out by using masterbatch formulations in order to ensure a complete dispersion of the filler particles throughout the polymeric matrix [11].

Another way of enhancing the dispersion is surface treatment. The treatment is performed either by the physical adsorption of oligomers and fatty acids, by chemical reactions with silanes and titanates, or by grafting with polymers [12–17]. Practice shows [18] that the most spectacular results are obtained with organotitanate coupling agents.

The coupling agents are used to solve problems encountered during the processing of polymeric composites such as the bad dispersion of the particles in the matrix, the absence of interactions between the matrix and the filler and the wetting of the solid particles by the polymer. The surface treatment also enables the addition of large amounts of the filler.

To adapt the processing of these materials to the existing equipment, it is useful to know their flow behavior and particularly to examine the effect of various processing conditions such as temperature, shear stress, and shear rate.

The aim of this work is to study the effect of the surface treatment of calcium carbonate by means of neoalkoxytitanate coupling agents on the rheological properties of PP/CaCO$_3$ composite.

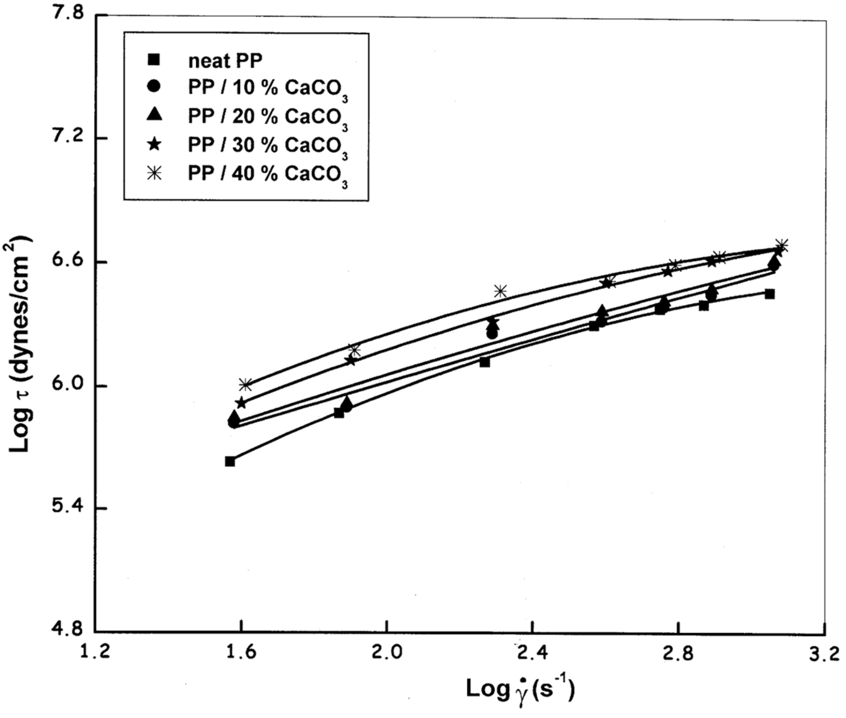

**FIGURE 1** Variation of shear stress with shear rate for neat PP and for the PP/untreated CaCO$_3$ composites at 180°C.

## EXPERIMENTAL

The polypropylene used, trade name Raco GR2, was supplied by Repsol Quimica in a granular form with a melt flow index of 4 g/10 min (measured at 190°C and 5 kg) and a density of 0,905 g/cm$^3$.

The calcium carbonate was supplied by Alcal ENG, Algeria with an average particle diameter of 5 µm. Its chemical composition and physical characteristics are described in a previous publication [4].

The coupling agent used is a liquid organofunctional neopentyl-(diallyl)oxy,tri(dioctyl)phosphatotitanate manufactured under the trade name of Lica 12, and was supplied by Kenrich Petrochemicals, Inc. This coupling agent was used as received without any further purification.

The coating of the coupling agent was carried out by treating the calcium carbonate with a solution of the coupling agent in toluene at room temperature. The coated product was then filtered, dried, and

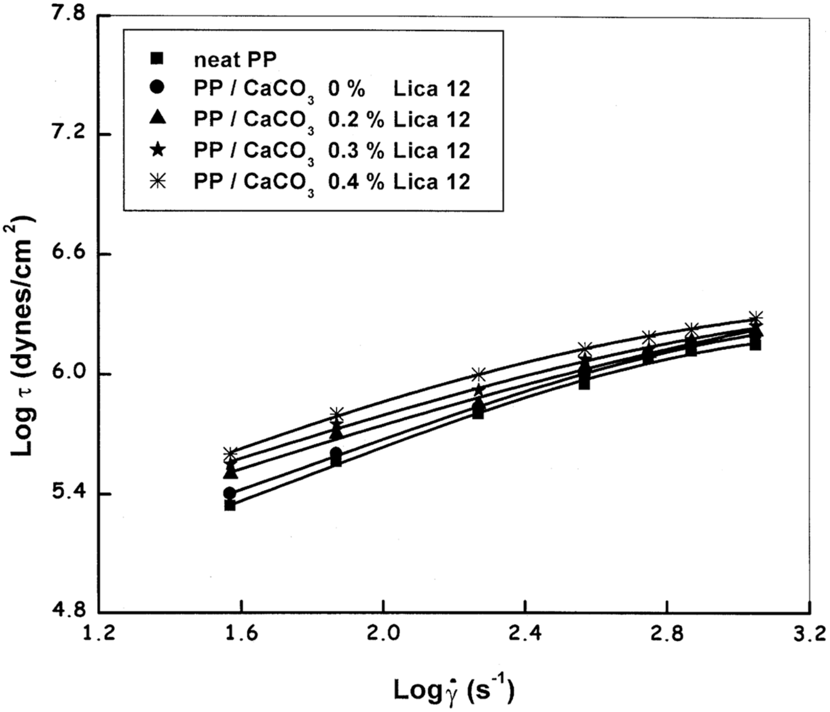

**FIGURE 2** Variation of shear stress with shear rate for neat PP and for the PP/untreated $CaCO_3$ composites at 200°C.

deagglomerated before being used. The level of coating that was determined according to the method described by Monte and coworkers [19] was varied from 0.2 to 0.4 wt%.

The untreated CaCO$_3$ as well as the filler treated with the titanate coupling agent were incorporated into the polypropylene matrix using a two-roll mill at 170°C for 15 min. The slabs obtained were then ground and used for the rheological measurements.

Filler concentrations used varied from 10 to 40 wt% for the untreated CaCO$_3$ and from 10 to 70 wt% for the treated one.

The rheological measurements were carried out at three different temperatures ranging from $T_1 = 180°C$ to $T_3 = 200°C$ using a Controlab capillary rheometer. From these results the flow curves were established using the corrected values of shear stress and shear rate based on Bagley and Rabinowitsch methods [20–21].

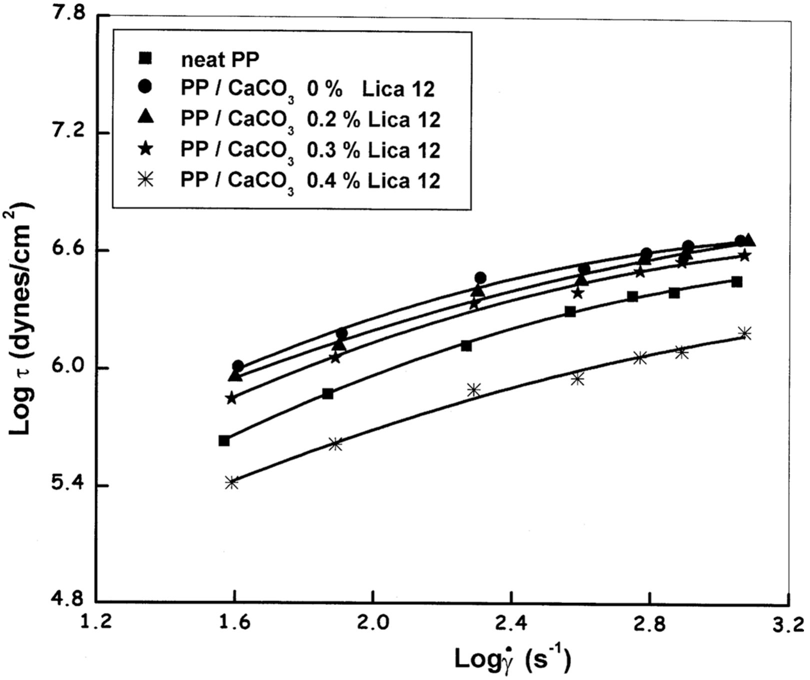

**FIGURE 3** Variation of shear stress with shear rate for neat PP and for the PP/40% CaCO$_3$ composites treated with Lica 12 at different concentrations at 180°C.

## RESULTS AND DISCUSSION

Because of the nonlinearity of the experimental curves in logarithmic scales, the power law index n was calculated using the following expression:

$$\log \tau = a_0 + a_1 \log \dot{\gamma} + a_2 (\log \dot{\gamma})^2 \qquad (1)$$

where $a_0$, $a_1$, and $a_2$ are parameters that were obtained from a polynomial regression using the least square method, $\dot{\gamma}$ is the shear rate, $\tau$ is the shear stress, and n was determined as the slope of the tangent of the corresponding curve.

Because of the similarity of the curves and for the sake of comparison only the flow curves obtained at 180°C and 200°C are presented.

The flow curves in terms of variation of the corrected shear stress $\tau$ with corrected shear rate $\dot{\gamma}$ for neat polypropylene and for the composites based on untreated $CaCO_3$ at different temperatures, which are

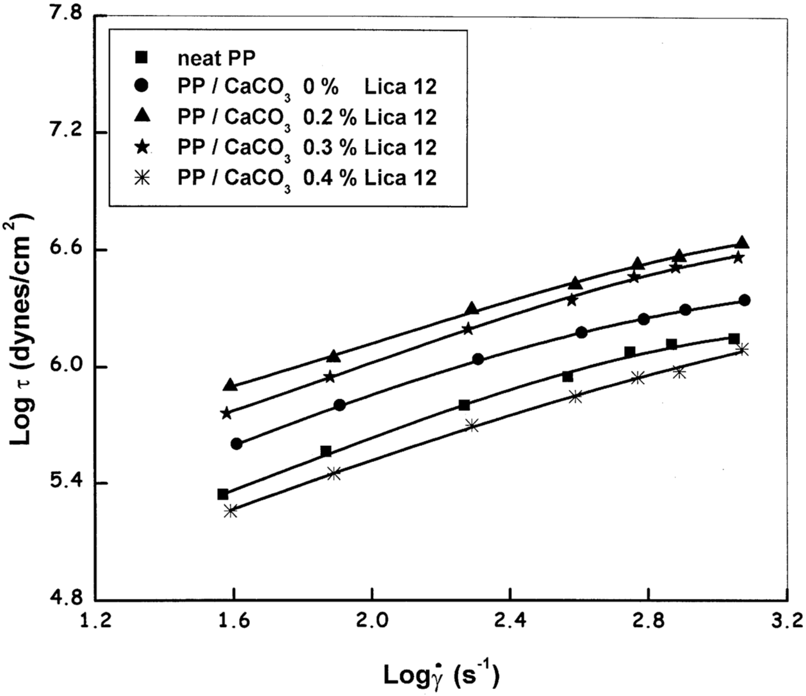

**FIGURE 4** Variation of shear stress with shear rate for neat PP and for the PP/40% $CaCO_3$ composites treated with Lica 12 at different concentrations at 200°C.

presented in Figures 1 and 2, show that the material exhibits a pseudoplastic behavior.

Figures 3 and 4 present the variation of shear stress with shear rate for the composites containing 40% CaCO$_3$ treated with different concentrations of the coupling agent. One can see that the surface modification of the filler did not alter the pseudoplastic behavior of the material. In addition, the values of the power law index remain all less than unity within the whole range of shear rates, but were found to be slightly higher than those obtained with untreated filler-based composites. This suggests that the coupling agent induced a lubricating action on the flow of the composite.

Figures 5 and 6 show the variation of the power law index as a function of shear rate for the neat unfilled matrix and its composites at different concentrations of the untreated filler at 180°C and 200°C.

From these curves one can notice that the power law index decreases with the increase of shear rate. This is attributed to the fact that when increasing shear rate the macromolecules will be more oriented in the flow direction and the brownian motion will not enable their relaxation. So the entanglement density will decrease. This can

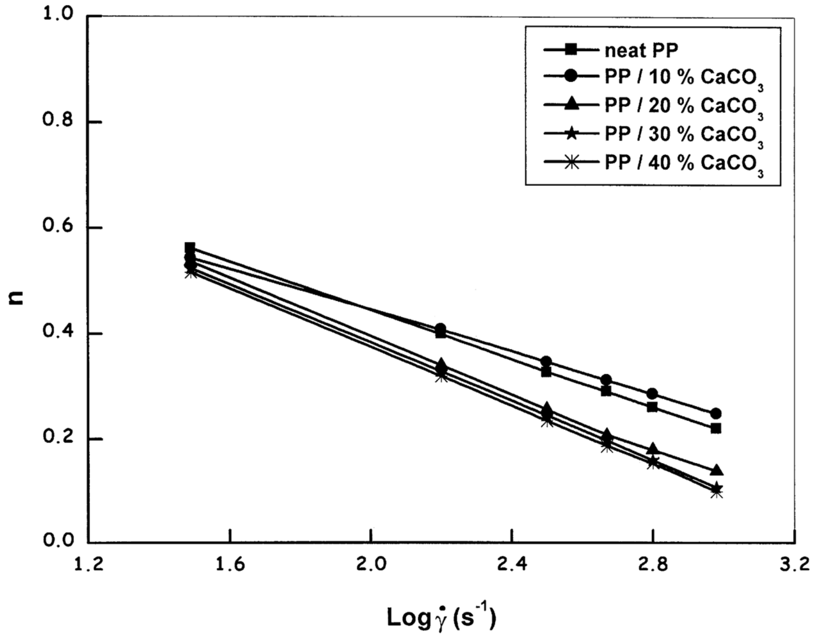

**FIGURE 5** Variation of the Power Law Index with shear rate for neat PP and for the PP/untreated CaCO$_3$ composites at 180°C.

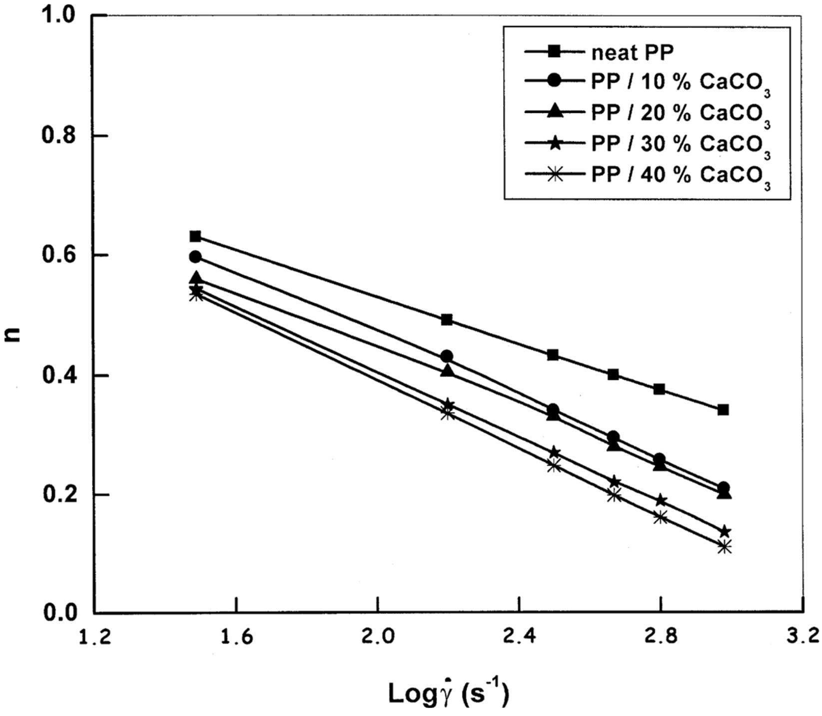

**FIGURE 6** Variation of the Power Law Index with shear rate for neat PP and for the PP/untreated $CaCO_3$ composites at 200°C.

explain the increased pseudoplastic behavior of the materials, as was noticed by many authors [22–24].

It is also observed that as the filler concentration increases the power law index decreases. This is due to the fact that the solid particles of $CaCO_3$ in the thermoplastic matrix suppress the ability of the chains to slide one past another.

The superficial treatment of the filler seems to have conserved the pseudoplastic behavior of the material. As shown in Figures 7 and 8, the general trend of the curves remained unchanged. However, the values of the power law index were slightly higher than those of the composite containing untreated $CaCO_3$.

The flow curves in terms of variation of the apparent viscosity with shear rate for neat PP and for the untreated $CaCO_3$-based composites are presented in Figure 9. It is shown that, as expected, the filler increased the viscosity of the composite owing to an extension effect.

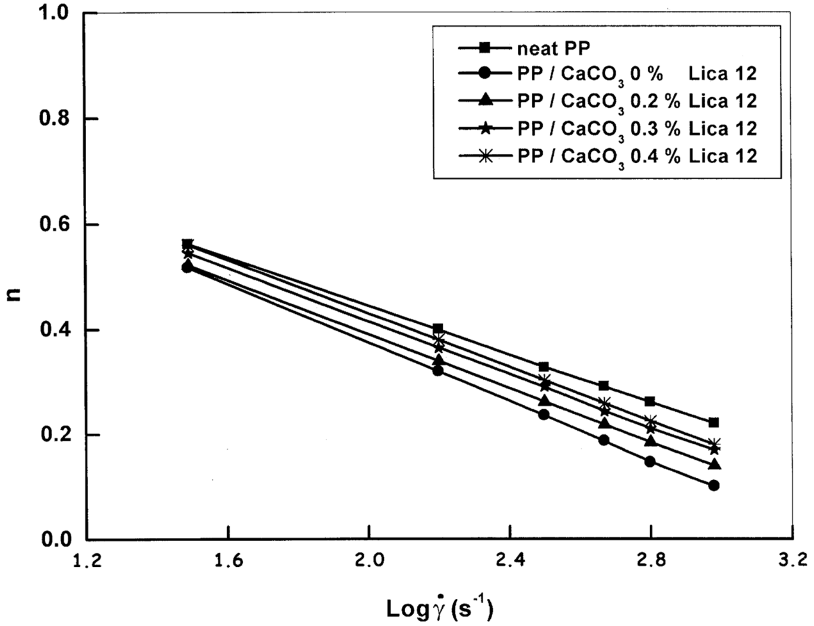

**FIGURE 7** Variation of the Power Law Index with shear rate for neat PP and for the PP/40% CaCO$_3$ composites treated with Lica 12 at different concentrations at 180°C.

These results prove also that despite the absence of functional groups on the surface, some interactions developed between the filler and the coupling agent. These interactions are probably of the ionic type owing to the presence of impurities within the filler composition. These impurities are composed mainly of hydroxides and metallic oxides.

From Figure 9 it is also observed that the viscosity of the composites decreases with increasing shear rate, and at high shear rates the curves converge. It is also noted that for the composites of PP/40% CaCO$_3$ treated with 0.4 wt% Lica 12 the viscosity decreases as the concentration of the coupling agent decreases, and becomes even lower than that of the matrix. This is attributed to the lubricating and plastifying action of the coupling agent.

The flow curves in terms of variation of the viscosity as a function of shear rate for the neat unfilled matrix and for the composites filled with 40 wt% and 70 wt% CaCO$_3$, which is treated with the neoalkoxy-titanate at 180°C are presented in Figures 10 and 11. It is shown that the viscosity of the composites containing treated CaCO$_3$ is lower than that of the untreated one.

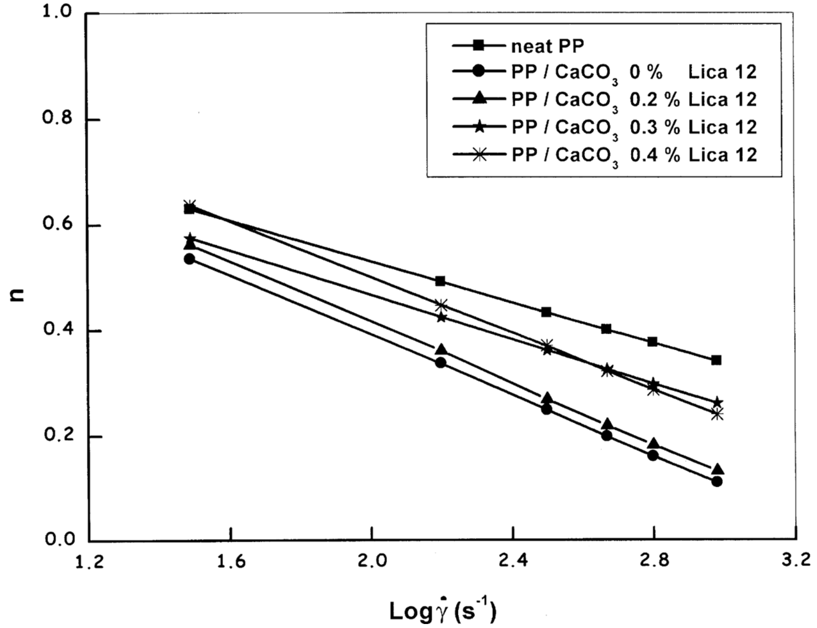

**FIGURE 8** Variation of the Power Law Index with shear rate for neat PP and for the PP/40% $CaCO_3$ composites treated with Lica 12 at different concentrations at 200°C.

This result can be associated exclusively with an interfacial phenomenon: the coupling agent adsorption at the filler surface can generate a greater molecular free motion that facilitates the flow of the composite. The resulting deposition in a monomolecular layer, as is the case with 0.3 wt% of filler, or in multimolecular layer form (case with 0.4 wt% of filler), indicates that the part that constitutes the chemical function is adsorbed at the hydrocarbon chains surface and will induce the compatibility with the polymeric matrix and plays the role of an internal lubricant. The rheological behavior, which is an evidence of the enhancement of the interfacial adhesion between the filler and the matrix as a result of the treatment by the coupling agent, confirms the results reported concerning the effect on the mechanical properties [4].

The logarithmic plots of the variation of the apparent viscosity with shear rate for the composites containing different amounts of the filler that was treated with 0.3 wt% Lica 12 are presented in Figures 12 and 13 at 180°C and 200°C, respectively. The concentration

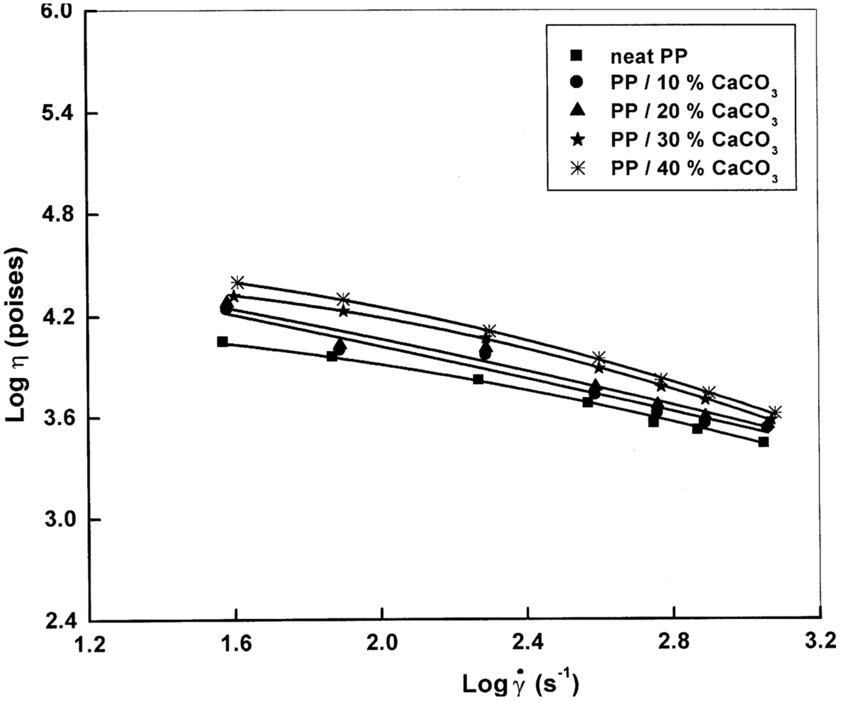

**FIGURE 9** Variation of the viscosity with shear rate for neat PP and for the PP/untreated $CaCO_3$ composites at 180°C.

of the coupling agent here is large enough to ensure the formation of a monolayer.

A comparison of the behavior of the different composites allows one to point out the effect of the coupling agent and its role in improving the processing of this type of materials. In fact, the viscosity of the composite with 20 wt% $CaCO_3$ is almost the same as that of the unfilled matrix within the entire range of shear rates. This shows that the processability of the composite is at least as good as that of neat polypropylene.

## Activation Energy

The flow activation energy was calculated using the Arrhenius equation:

$$\eta_c = A \cdot e^{(\Delta E_\gamma / R \cdot T)} \tag{2}$$

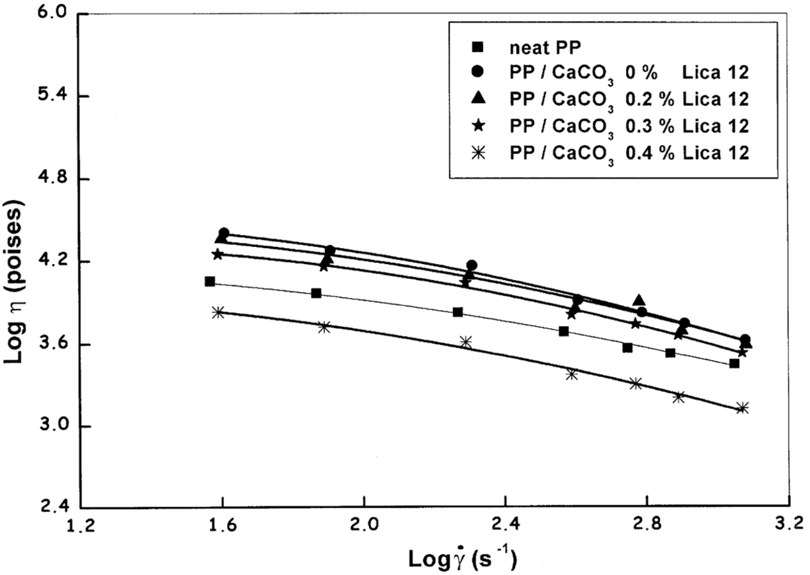

**FIGURE 10** Variation of the viscosity with shear rate for neat PP and for the PP/40% $CaCO_3$ composites treated with Lica 12 at different concentrations at 180℃.

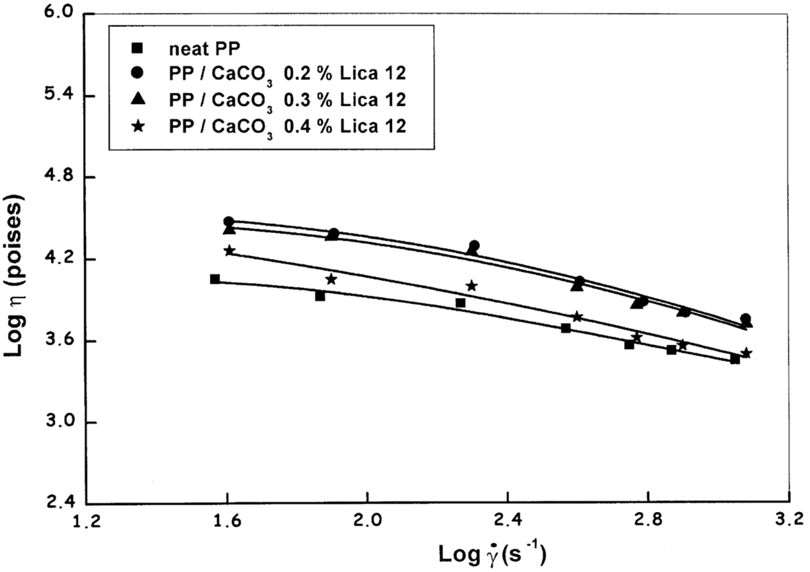

**FIGURE 11** Variation of the viscosity with shear rate for neat PP and for the PP/70% $CaCO_3$ composites treated with Lica 12 at different concentrations at 180℃.

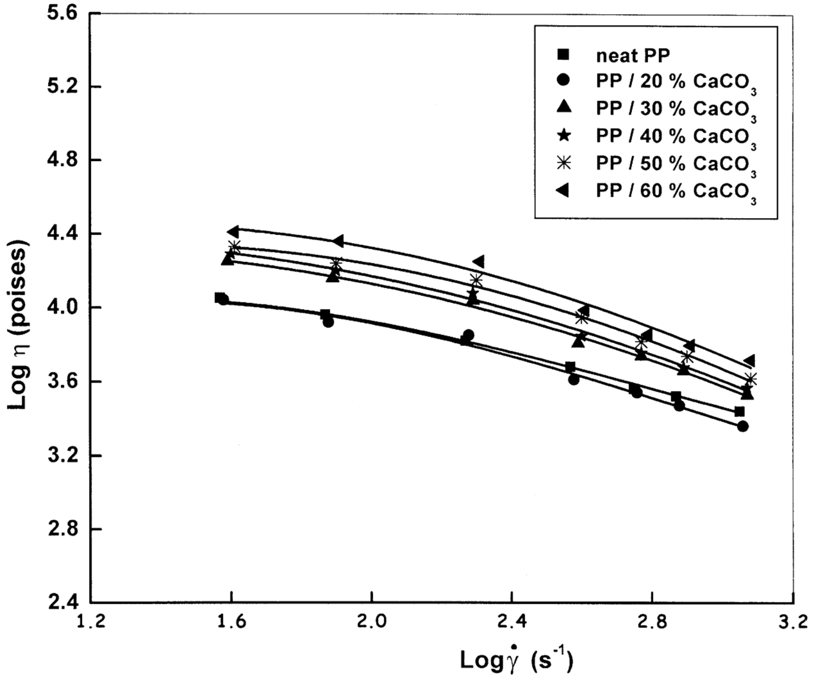

FIGURE 12 Variation of the viscosity with shear rate for neat PP and for the PP/$CaCO_3$ composites treated with 0.3% Lica 12 at 180°C.

where: $\eta_c$ is the corrected viscosity, T the absolute temperature (K), A is a constant, R the universal gas constant, and $\Delta E$ is the activation energy.

The plots of the variation of the activation energy for neat PP and for the composites with untreated filler and those treated with different concentrations of Lica 12 are presented in Figures 14 and 15, respectively. From these curves one can see that the activation energy decreases with increasing amount of filler. This striking result can be attributed to the fact that a fraction of the energy required for the flow is absorbed by the filler rather than the polymeric matrix. Similar results were reported by Guillet et al. [25].

The activation energy decreases also with the increase in the concentration of the coupling agent. This tendency reflects the lubricating effect of the titanate agent. It was also found that the activation energy decreases with increasing the shear rate. This is due to the fact that as the material is sheared the interactions existing between the filler and the matrix diminish.

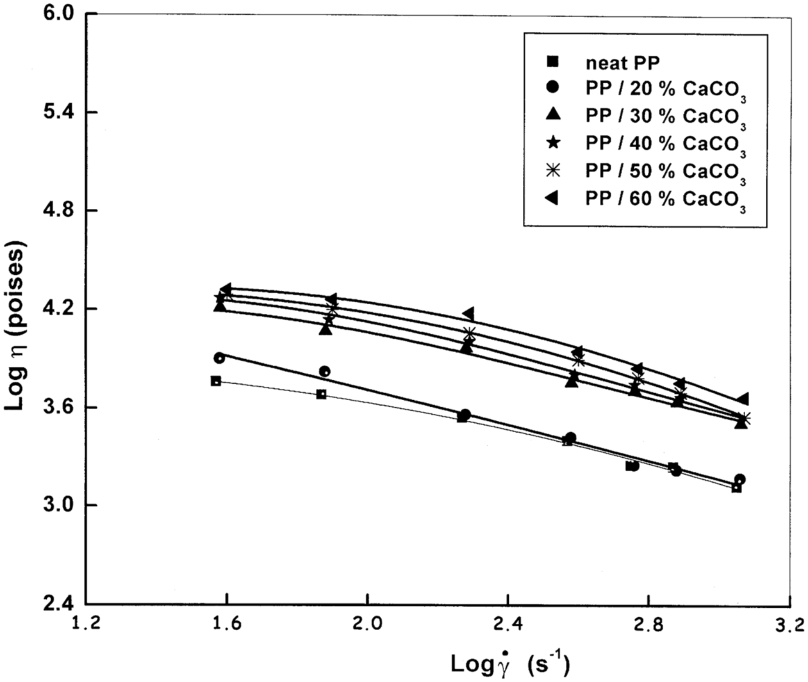

**FIGURE 13** Variation of the viscosity with shear rate for neat PP and for the PP/CaCO$_3$ composites treated with 0.3% Lica 12 at 200°C.

## Reduced Viscosity Function

For a better approach to the analysis of the results and taking into account the interval of temperatures and shear rates that were investigated, the concept of reduced viscosity function was used.

In this context, the shift factor $a_T$ is defined by the following empirical equation as:

$$a_T = \frac{\dot{\gamma}(T_0)}{\dot{\gamma}(T)} \tag{3}$$

where $T_0$ is a reference temperature, $\dot{\gamma}(T_0)$ is the shear rate at $T_0$, and $\dot{\gamma}(T)$ the shear rate at T.

The shift factor can be expressed by an Arrhenius type of equation as:

$$a_T = A\ \exp\left(\frac{E}{R \cdot T}\right) \tag{4}$$

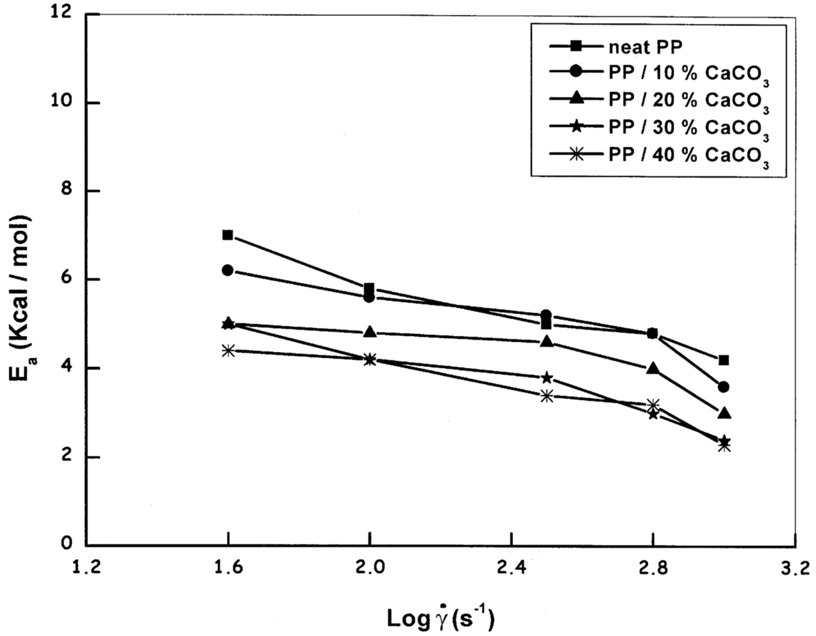

**FIGURE 14** Variation of the activation energy with shear rate for neat PP and for the PP/untreated CaCO$_3$ composites.

By using $T^0$ as the reference temperature one can write:

$$a_T = \exp\left[\frac{E}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right)\right] \tag{5}$$

Then by applying the superposition principle of Mendelson [26–27] and the principle that was developed by Guillet [25] for the viscosity function:

$$\log\frac{\eta}{a_T} = f\lfloor\log(a_T \cdot \dot{\gamma})\rfloor \tag{6}$$

where $\eta$ is the corrected viscosity and $\dot{\gamma}$ is the corrected shear rate, the reduced functions of shear rate and viscosity were obtained.

The aforementioned derivations allowed the establishment of the master curves for the viscosity/shear rate functions that are presented in Figure 16. Through these curves it is possible to make a comparison of the behavior of the different composites over a wide range of

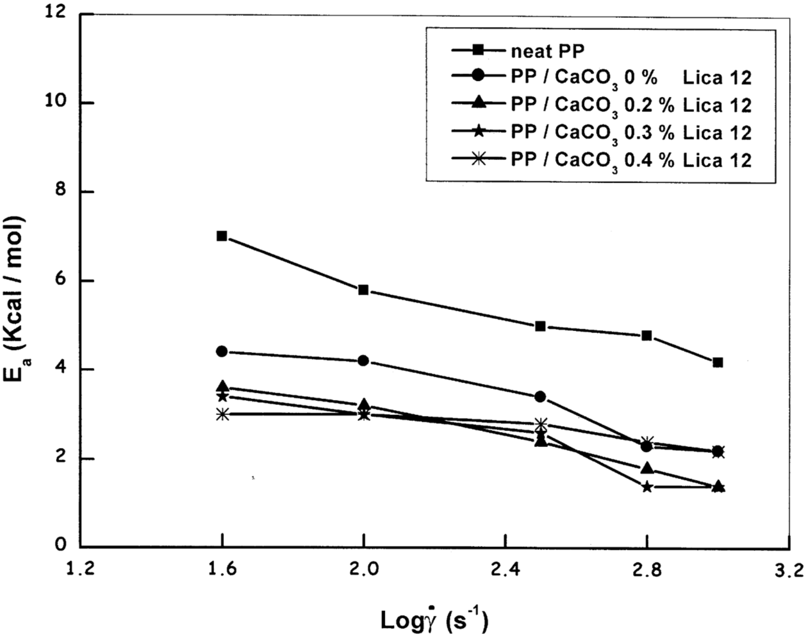

**FIGURE 15** Variation of the activation energy with shear rate for neat PP and for the PP/40% $CaCO_3$ composites treated with Lica 12 at different concentrations.

temperatures and shear rates that would not be possible to measure experimentally.

Similarly, by using the superposition principal proposed by Schoenewald [28], which is expressed as:

$$\log \tau = f\lfloor \log(a_T \cdot \dot{\gamma}) \rfloor \tag{7}$$

and applying it to the shear stress function, this approach allowed the establishment of the master curves for the shear stress/shear rate variables that are presented in Figure 17.

## CONCLUSIONS

This article presents the results concerning the effect of the chemical treatment of calcium carbonate by means of a titanate coupling agent on the rheological properties of the resulting polypropylene/calcium carbonate composite.

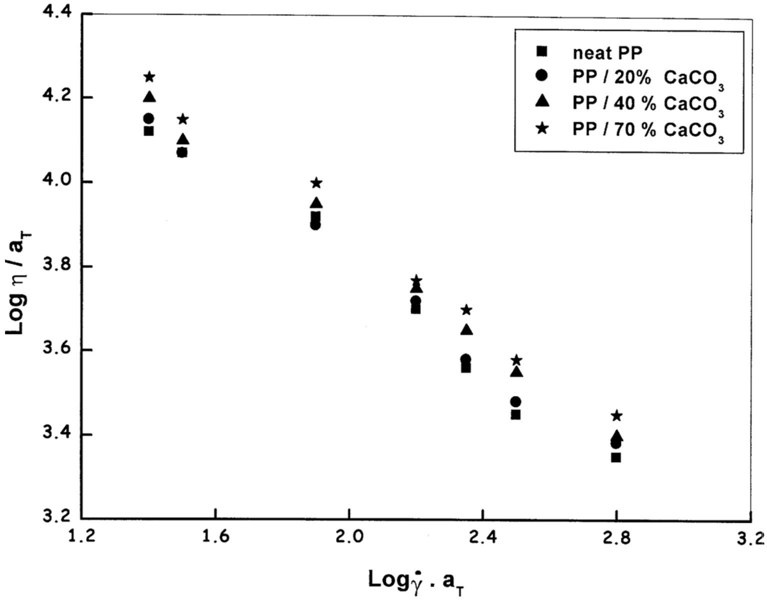

**FIGURE 16** Viscosity/shear rate master curves for neat PP and for the PP/CaCO$_3$ composites treated with 0.3% Lica 12.

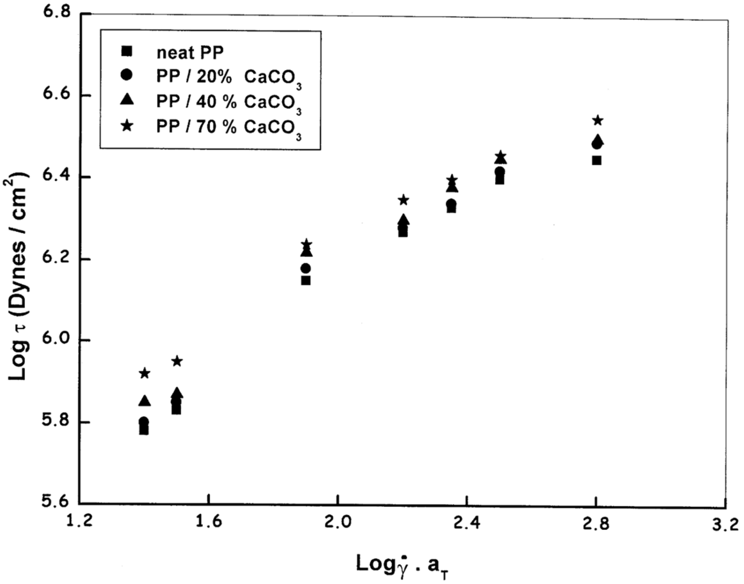

**FIGURE 17** Shear stress/shear rate master curves for neat PP and for the PP/CaCO$_3$ composites treated with 0.3% Lica 12.

The results show that the rheological behavior of such composites can be described by an empirical expression from which the power law index may be determined.

The flow curves show that the material exhibits a pseudoplastic behavior with a power law index that decreases with increasing shear rate but increases with increasing temperature.

The examination of the viscosity flow curves confirms the lubricating effect of the coupling agent. This lubricating effect is evidenced also from activation energy calculations.

Finally, by using the approach of the reduced viscosity function and applying the superposition principle, master curves of the basic rheological parameters are established.

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