

Dynamic Mechanical Analysis of the Interfacial Changes in Polypropylene/Talc Composites Induced by Different Interfacial Modifications from the Reinforcement Side

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ABSTRACT: This article is intended to establish a comprehensive interpretation of the noticeable differences in the dynamic mechanical behaviors of polypropylene/talc composites with and without modified interphases. The latter are discussed on the basis of different surface treatments applied to the reinforcement particles. To this end, a series of 75/25 (w/w) polypropylene/talc composites with and without interfacial modifications from the reinforcement side were evaluated by dynamic mechanical analysis. The proven capability of this technique analysis to follow the transitions and structural and morphological changes in organic polymers, which are largely influenced by the degree of compatibility between the components of heterogeneous materials based on polymers, was used in this study to check and discuss the kinds and efficiencies

of different physisorption- and chemisorption-based processes carried out on the surface of talc particles. We tackled this study by embracing the different relaxation phenomena taking place in the polymer matrix. To this end, five different temperature intervals were distinguished according to the relaxation phenomena taking place. Finally, a correlation between the parameters on the microscopic scale and others on the macroscopic scale appeared to emerge. Thus, the interfacial effects caused by the modified reinforcements could be determined by observations on either scale. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 551–561, 2009

Key words: composites; interfaces; modification; poly(propylene) (PP); viscoelastic properties

INTRODUCTION

The main reasons justifying the great amount of effort spent to enhance interfacial interactions between components in composites and nanocomposites (so-called advanced materials), with an emphasis on the matrix/particle interphase, are well known.¹

The fundamentals of the experimental strategy, mainly concerning the mixing and molding operations used to pass the material into the solid state and looking to minimize the effects caused by the distribution and orientation degree of the solid particles present in the polymer bulk and the uncontrolled changes in the reinforcement particle size and distribution or even the possible heterogeneous distribution of the particles in the polymer bulk during the processing steps, have already been discussed elsewhere.^{2–5}

This study involved the so-called top-down approach framework,⁶ which has also been followed in previous studies concerning the macroscopic response under normal stresses with controlled loads (tensile^{7–9} and flexural⁸) and instantaneous testing rates of applied loads (impact⁹) and others.¹⁰ From this, it has been concluded that the substitution of just a small amount (e.g., 1.4% w/w) of the polypropylene (PP) matrix by a commercial isotactic polypropylene (iPP) grafted with succinic anhydride groups is enough to maximize the interaction level between the PP matrix and the talc particles. Also, in these studies, the efficiency of the surface treatments on talc particles has been ascertained on the macroscopic scale. Treatments of mineral particles have been performed, on the one hand, by the removal of the hydroxyl groups present on the particle surface by a chemisorption process¹¹ and, on the other hand, by treatments based on physisorption processes,¹² with the aim of finding a mere coating of hydroxyl groups by moieties able to enhance the PP/talc affinity. Whatever treatment was used, in all cases, the final goal was the modification of the interaction level between the talc particles (the dispersed phase) and the PP matrix. Nevertheless, the chemisorption processes, consisting of the shifting of

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TABLE I
Physical Properties of PP As Received

M_w	M_n	HI	Density (kg/m ³)	Melt index (g/10 min) ^a	HDT (°C)	T_m (°C)	T_c (°C)	λ_m (%)	λ_c (%)
334,400	59,500	5.62	901	5.80	58.5	164.0	117.5	41.8	41.9

HDT = heat distortion temperature; λ_c = crystallinity obtained from the crystallization curve; λ_m = crystallinity obtained from the melting curve; M_n = number-average molecular weight; M_w = weight-average molecular weight; T_c = crystallization temperature; T_m = melting temperature.

^a At 190°C and 5.0 kg.

the hydroxyl group forming silanol groups at the surface of talc particles by chlorine atoms and then (in a second step) by amine groups coming from a gas source, were shown to be the most effective in improving the properties of composites of a wide spectrum.

This article deals with a dynamic thermomechanical study of a 75/25 (w/w) PP/talc composite system with a modified interphase from the reinforcement side. The PP/talc ratio was chosen on the basis of previous studies that identified this ratio as critical for ascertaining any interfacial change, no matter what kind of interfacial modification was performed (from the matrix side or the reinforcement side).⁷⁻⁹ Consequently, forthcoming works will deal with the role of interfacial agents forming the matrix side in systems previously modified from the reinforcement side, looking for synergistic effects and also considering the influence of the molding step in the dynamic mechanical behavior of the PP/talc system. The final objective of the latter will be to correlate different parameters at the macro-, micro-, meso-, and nanoscales, the last being where interfacial phenomena occur.

EXPERIMENTAL

PP (Isplen 050) and laminar talc (20M00S) were supplied by Repsol Química (Madrid, Spain) and Luzenac (Luzenac, France), respectively. Tables I and II compile some of their physical properties.

We prepared the modified talc particles.^{11,12} The experimentation and characterization procedures have been fully described and discussed elsewhere.^{11,12} For the purpose of this work, some important information related to these processes is compiled in Tables III and IV. Likewise, the main results concerning the characterization of surface-

modified talc are summarized in Table V. The reader is kindly referred to refs. 11 and 12 for further information. In essence, the surface modification of talc particles was undertaken in two different ways. On the one hand, a series of solid/gas chemisorption processes yielded chlorinated or aminated talc (depending on the reactants used); on the other hand, two different solid/liquid physisorption processes were performed to obtain either silane-coated talc or *n*-butyl amine (*n*-BuNH₂)-coated talc (with evidence of an absence of chemical bonds between these and the talc surface phase determined by Fourier transform infrared, as discussed elsewhere^{11,12} and compiled in Table V). All the composites studied in this work were compounded in a 75/25 (w/w) PP/talc ratio because this ratio had been proven to be critical for ascertaining interfacial modifications in this system.⁷⁻⁹ Compounding was performed through premixing of the components in a Collin ZK-50 (Barcelona, Spain) counter-rotating twin-screw extruder. The cokneader screw design ensured the uniform mixing of the solid particles by direct feeding from the barrel vacuum section into the molten PP matrix. The four temperature zones from the hopper to the die were set at 200, 210, 210, and 220°C, whereas the die temperature was controlled at 230°C. The screw speed and throughput were 85 rpm and 10 kg/h, respectively. After being dried at 80°C overnight in a convection oven, the pelletized compounds were ready for the molding step, once the compound quality was verified by ash content determination and optical microscopy analysis, as described elsewhere.⁷

Compression sheets (120 × 120 × 4 mm³) were molded in a Dr. Collin press (Barcelona, Spain). The hot-plate temperature was set at 180°C, and the maximum operation pressure available was 3.3 MPa. Pressure was applied in two steps for 2 and 3 min, respectively. The first step ensured the heating and softening of the material, and the second ensured the material packing once the mold was fully closed. Once the molding time elapsed, the mold was cooled to room temperature with a water-cooled cartridge, and the molding pressure was maintained until the set temperature was reached. Thereafter, the molded plies were extracted, and we verified them by checking for the absence of any kinds of

TABLE II
Physical Properties of the Talc Mineral As Received

Density (kg/m ³)	Specific surface (m ² /g) ^a	Mean particle size (μm)
2750	5.3	10.1

^a Brunauer–Emmett–Teller.

TABLE III
Chemisorption Solid/Gas Processes

Treatment	Process feature				
	Temperature (°C)	Reaction time (min)	Reactor	Reactant ^a	Supplier (grade)
Chlorination	420	30	Moving bed	Carbon tetrachloride	Ercros (synthesis)
Amination (from the vapor phase)				Ammonia hydroxide	Panreac (25% NH ₃)
Amination (from the gas phase)				Ammonia gas	Argon (99.999%)

^a Nitrogen (N₄₈-grade), supplied by SEO, was always used as the gas stream carrier.

molding defects such as inner bubbles, holes, or warpage. After a conditioning period of at least 48 h at room temperature and 50% humidity, the plies were ready to be cut and shaped according to the specification dimensions imposed by each test mode.

Dynamic mechanical tests under a reverse loading mode were performed in a TA-983 dynamic spectrometer (TA Instruments, Madrid, Spain). The specimen dimensions were 21.2 × 10.4 × 4 mm³. The test frequency and oscillation amplitude were fixed at 1 Hz and 0.2 mm, respectively, with a clamping distance of 14.5 mm. Thermal scanning was performed from -30 up to 150°C at a heating rate of 2°C/min. We undertook this study by distinguishing five different zones or intervals in the dynamic mechanical spectra. These zones, dependent on the kinds of relaxation phenomena taking place, can be clearly identified when any dynamic mechanical parameters versus the temperature are plotted. Therefore, Figure 1 shows the evolution of the storage modulus (G'), loss modulus (G''), and loss factor ($\tan \delta$) with the temperature for the neat PP (iPP) and an unmodified iPP/talc composite. Here, the five aforementioned intervals can be appreciated. In the first interval, which is located between -20 and -10°C, the dissipation capability is lowest; this is due to mere atomic vibration motions. Consequently, in this zone, the variations of G' , G'' , and $\tan \delta$ for each of the measured samples must be very slight. The second zone is placed between -10 and 40°C. This is distinguished by the occurrence of the so-called

β -relaxation peak or glass-transition zone, in which (besides the former motions described) short-range diffusion motions at a chain-segment level occur. A third zone is located between 40 and 80°C. This one is characterized by the presence of a rubber-elastic plateau transition; this indicates the existence of rapid short-range diffusion motions sharply dependent on the molecular mass and the chain entanglement density. A fourth interval is placed between 80 and 140°C; here the polymer macromolecules are greatly improved with respect to their ability to flow and thus to participate in dissipative phenomena through long-range configurational changes. Finally, the fifth zone is above 140°C, and it is characterized as the zone in which the material passes from the softening state to the liquid state; consequently, the tendency of the curves is to converge upon one another.

To correlate the dynamic mechanical behavior and the macroscopic mechanical properties, a series of tensile mechanical tests were conducted according to UNE-EN ISO 527-1/2 standards at room temperature (23°C) with an Instron 4200 dynamometer (Barcelona, Spain) equipped with a high-resolution extensometer (high dynamic range). The crosshead speed for modulus calculations was 1.0 mm/min, at least five measurements being recorded for each specimen. The obtained modulus values agreed with those measured elsewhere.¹²

Additionally, thermal analyses under dynamic conditions were performed on the neat iPP and on iPP/talc composites with a DSC-7 differential

TABLE IV
Physisorption Solid/Liquid Phase Processes (1/27 w/w Ratio)

Treatment	Process feature				
	Temperature (°C)	Reaction time (min)	Reactor	Coating system	Supplier (grade)
Silanization	20	30	Glass	Silane mixture (3%)/ isopropyl alcohol	Union Carbide (3/1 Ucarsil A/Ucarsil B) ^a
<i>n</i> -BuNH ₂				<i>n</i> -BuNH ₂	Merck (pure)

^a Peroxide index (as active oxygen) for Ucarsil A = 9 ppm; peroxide index (as active oxygen) for Ucarsil B = 43 ppm.

TABLE V
Characterization of the Treated Talc

Treated talc	Technique	Results
Talc-Cl (chlorinated)	Titration (Mohr's method)	<ul style="list-style-type: none"> • The mean chlorine concentration is 2.0×10^{-3} mol/g. • The characteristic sharp band at 3000 cm^{-1} for the isolated —OH groups Si-bonded onto the talc surface disappears.
	IR	<ul style="list-style-type: none"> • The intensity of the 3750-cm^{-1} sharp band, which is assigned to isolated silanol groups on the siliceous network, is increased 3-fold.
Talc-NH _{2(g)} (gas-phase-aminated after chlorination)	IR	<ul style="list-style-type: none"> • The characteristic sharp band at 3000 cm^{-1} for the isolated —OH groups Si-bonded onto the talc surface disappears. • The intensity of the 3750-cm^{-1} sharp band, which is assigned to isolated silanol groups on the siliceous network, is increased 3-fold. • Characteristic —NH₂ deformation bands between 3100 and 3300 cm^{-1}, as well as a sharp band at 1400 cm^{-1}, appear.
	IR	<ul style="list-style-type: none"> • The characteristic sharp band at 3000 cm^{-1} for the isolated —OH groups Si-bonded onto the talc surface disappears. • The intensity of the 3750-cm^{-1} sharp band, which is assigned to isolated silanol groups on the siliceous network, is increased 3-fold. • Characteristic —NH₂ deformation bands between 3100 and 3300 cm^{-1}, as well as a sharp band at 1400 cm^{-1}, appear.
Talc-NH _{2(v)} (vapor-phase-aminated after chlorination)	IR	<ul style="list-style-type: none"> • The characteristic sharp band at 3000 cm^{-1} for the isolated —OH groups Si-bonded onto the talc surface disappears. • The intensity of the 3750-cm^{-1} sharp band, which is assigned to isolated silanol groups on the siliceous network, is increased 3-fold. • Characteristic —NH₂ deformation bands between 3100 and 3300 cm^{-1}, as well as a sharp band at 1400 cm^{-1}, appear.
Talc- <i>n</i> -BuNH ₂ (<i>n</i> -BuNH ₂)	IR	<ul style="list-style-type: none"> • The characteristic sharp band at 3000 cm^{-1} for the isolated —OH groups Si-bonded onto the talc surface disappears. • The intensity of the 3750 cm^{-1} sharp band, which is assigned to isolated silanol groups on the siliceous network, is increased 3-fold. • Characteristic —NH₂ bands are not appreciable.
Talc-silane (silanized)	TGA	<ul style="list-style-type: none"> • The mean loss weight for coated talc up to 400°C is 2.0%.
	IR	<ul style="list-style-type: none"> • The IR spectrum is similar to that of the untreated (original) talc.

TGA = thermogravimetric analysis.

scanning calorimeter (PerkinElmer, Madrid, Spain) previously calibrated with indium standards. Tests were performed in a nitrogen atmosphere at heating/cooling rates of $10^\circ\text{C}/\text{min}$ from 40 to 200°C . After the first heating step, each sample was left in the molten state (softening state) for 5 min. The cooling scan was then begun, and this was followed by the second heating step. Enthalpy calculations were performed with DSC-7 software. The crystalline content of the organic matrix in the composite was calculated with 209 J/g used as the standard for 100% crystalline PP.¹³ Corrections were then made for the real amount of the polymer in the composite. In all cases, approximately 10 mg of each sample was tested three times in calorimetric cells, and the reproducibility of the results was concluded. Table VI compiles some thermal properties of these samples.

RESULTS AND DISCUSSION

Dynamic mechanical analysis (DMA) of the PP/talc composites

It is well known that the study of polymer-based materials under cyclic stress and strain conditions (DMA) offers many possibilities for separately determining both their plastic and viscoelastic behaviors. However, the difficulty lies in the understanding of macroscopic measurements in terms of their microscopic origin.

At a glance, Figure 1 indicates that the presence of 25% talc in the PP bulk introduces a sharp change in the magnitude of the dynamic mechanical response in comparison with that of the neat PP. In this figure, the dynamic parameters G' , G'' , and $\tan \delta$ versus the temperature for the neat PP and the original PP/

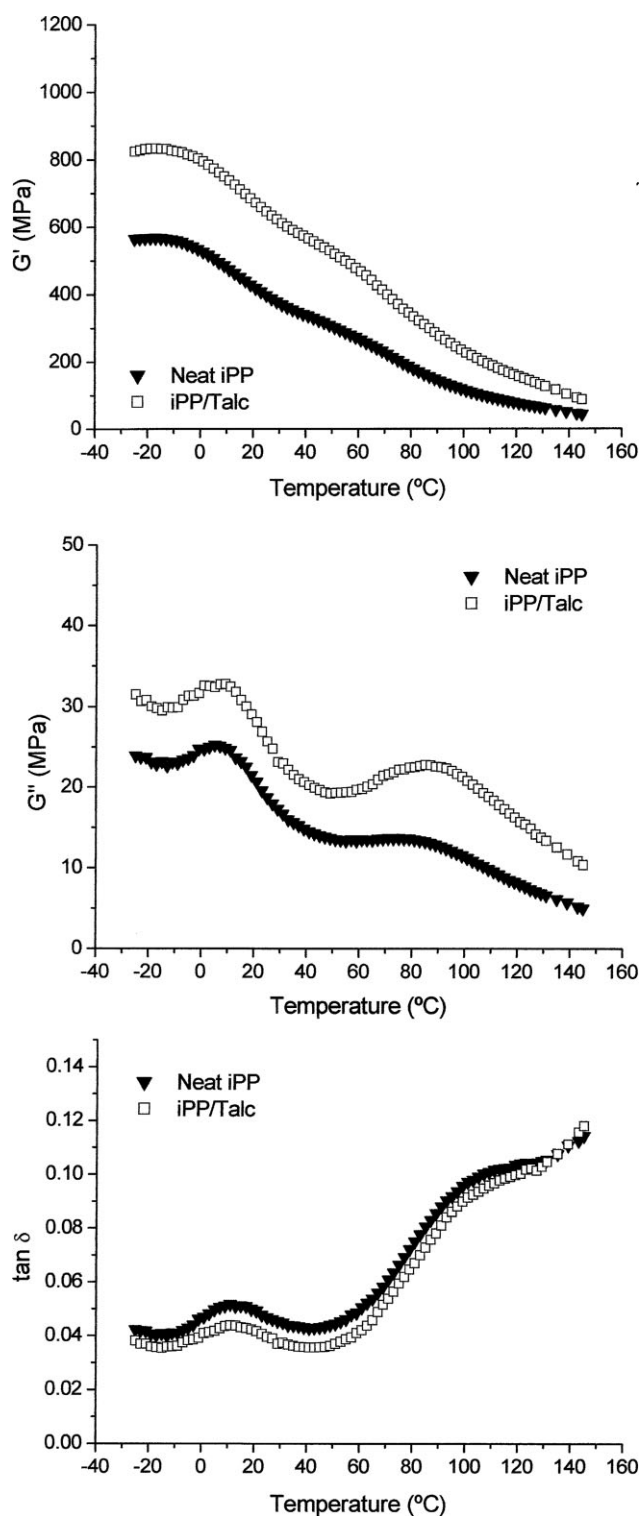


Figure 1 Evolution of G' , G'' , and $\tan \delta$ with the temperature for the neat PP (iPP) and the original (unmodified) iPP/talc composite.

talc composite are plotted. The increases in the G' and G'' curves obtained for the composite with respect to the neat matrix are clearly observable and agree, as a first approach, with the highest crystal-

line content for the PP matrix in the composite according to the thermal parameters displayed in Table VI. The five well-defined response zones, typical for a semicrystalline polymer, are clearly observable in each of the curves in Figure 1.

Furthermore, Figure 2 displays semilogarithmic plots of the elastic (G') and loss (G'') components of the complex shear modulus and the $\tan \delta$ values along the temperature axis for the six different composites considered in this work. The G' , G'' , and $\tan \delta$ plots for the neat PP matrix are also included in this figure.

In general, it can be affirmed that the presence of a foreign component (e.g., mineral reinforcement particles) in a thermoplastic organic matrix implies a decrease in its viscous response.¹⁴ Therefore, an overall increase in G' and G'' for both the original 75/25 PP/talc composite and all the other composites with modified interphases (from the reinforcement side) can be clearly observed in comparison with the neat PP. In agreement, for temperatures higher than room temperature (23°C), $\tan \delta$ values for all the composites are below those for iPP. This means a decrease in the phase-out between both modulus components (G' and G'') for both the unmodified and modified composites. It must be noted that such a decrease in the phase-out remains with a much more elastic response than that found for the neat PP matrix.

From these results, the complexity shown by DMA either to obtain valuable information on adhesion or to ascertain the interaction level at the matrix/particle interphase is once more confirmed.¹⁵

Therefore, once the efficiency of the different surface treatments of talc particles at the interfacial regions has been clearly concluded by means of plot clusters almost overlapping just after the glass-rubber transition zone, for better and easier visualization, further discussion of the different changes in the composite behavior correlated with the different natures and types of the surface treatments experienced by the talc particles will be carried out

TABLE VI
Thermal Properties of the Neat PP and the Unmodified 75/25 PP/Talc Compression-Molded Composite

Sample	T_m (°C)	T_c (°C)	λ_m (%)	λ_c (%)	$\Delta\lambda$ (%) ^a
Neat iPP	164.0	123.0	27.0	24.8	8.87
iPP/talc	164.0	125.2	42.2	43.8	0.90

λ_c = crystallinity obtained from the crystallization curve; λ_m = crystallinity obtained from the melting curve; T_c = crystallization temperature; T_m = melting temperature.

^a $\Delta\lambda = [(\lambda_m - \lambda_c)/\lambda_c] \times 100$.

with the dynamic mechanical parameters separately plotted by the type of treatment on the talc reinforcements. The five previously identified response zones will be used to distinguish the effects of the different kinds of treatments used to modify the dissipation capabilities of the PP matrix.

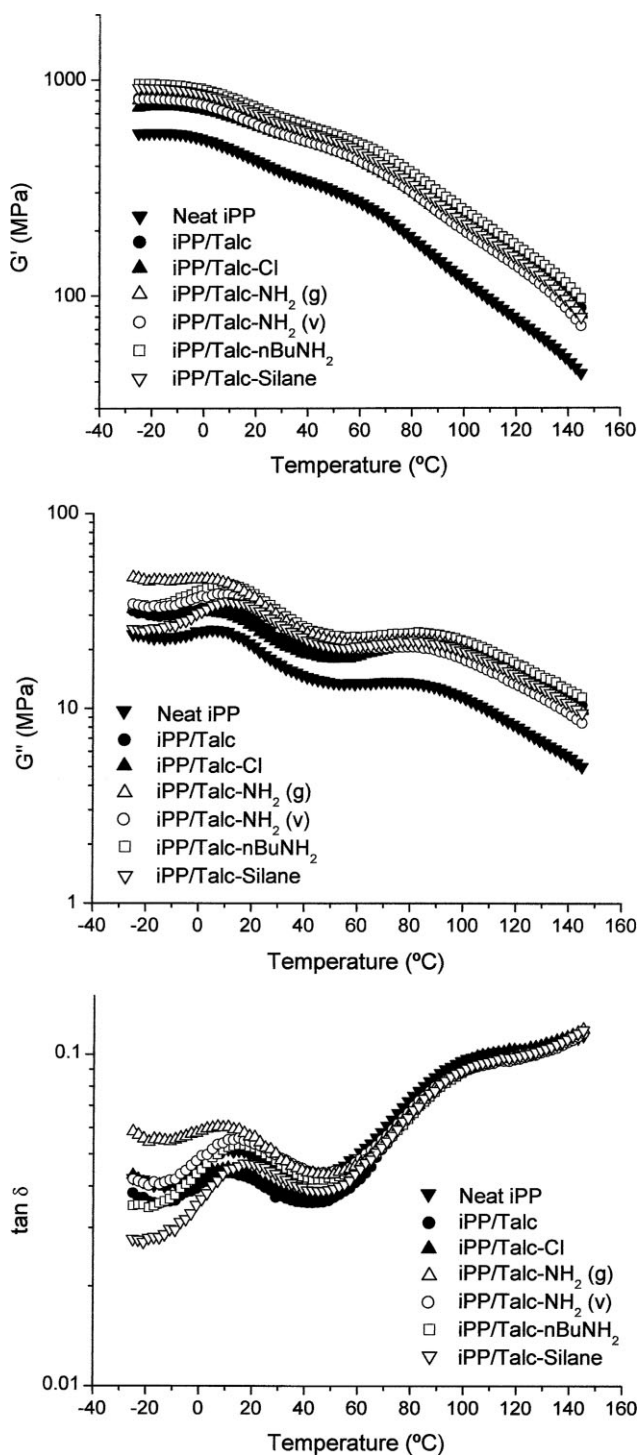


Figure 2 Semilogarithmic plots of G' , G'' , and $\tan \delta$ versus the temperature for the indicated samples.

DMA of the PP/talc composites: Talc particles modified by chemisorption processes

As discussed elsewhere,¹¹ by means of chemisorption treatments, almost all the silanol groups initially attached to the talc particle surface were shifted by chlorine, and this led (after incorporation into iPP) to the iPP/chlorinated talc composites (iPP/talc-Cl).

Moreover, the chlorine atoms bonded to the talc particle surfaces were shifted by amine groups in a second reaction step. Two different sources of amine groups were chosen to carry out this second step: ammonium hydroxide as a vapor phase and direct ammonia gas, the latter being more effective in providing better ultimate properties.¹¹ The composites compounded with these modified reinforcements are called iPP/talc-NH_{2(v)} and iPP/talc-NH_{2(g)}, respectively.

Figure 3 shows the dynamic mechanical behavior of the talc-based composites either unmodified or modified by means of chemisorption processes. A glance at Figure 3 shows a clear inflexion point near 60°C that can be clearly identified by a change in the slope of the G'' curve. This inflexion point is due to overlapping between α - and β -transition peaks. At a temperature below this point, the behavior of these materials appears very different, indicating the differences in the interfacial interactions occurring in each composite system. It is noticeable that in the case of iPP/talc-Cl, the evolution of $\tan \delta$ appears similar to that of iPP/talc from this point until at least around 100°C.

Although G'' for iPP/talc-Cl is the same as that for PP/talc in Figure 2, as for the α -transition peak, both aminated talc composites (iPP/talc-NH_{2(v)} and iPP/talc-NH_{2(g)}) display a rubbery plateau in the same way that neat iPP does in Figure 2 but without any α -transition peak.

The higher G'' values for iPP/talc-NH_{2(v)} and iPP/talc-NH_{2(g)} versus the iPP/talc composite all along the rubbery plateau as well as the near disappearance of the α -relaxation peak in the G'' plot of the latter are clearly observable. Meanwhile, the $\tan \delta$ values for the three aforementioned composites show overlapping that indicates an increase in the dissipation capabilities through the matrix/particle interphase. The latter is caused by an improvement in the affinity between iPP and talc caused by the substitution of the hydroxyl groups at the talc surface by chemically bonded amine groups.

The fact that G'' plots in the case of iPP/talc-Cl appear merely displaced in comparison with the unmodified iPP/talc system (both even exhibiting the so-called α -relaxation peak) agrees with the former observations. Furthermore, this agrees (because it approaches the G'' values of the neat PP) with the differences in electronegativity between the chlorine atoms and the hydroxyl groups and then their

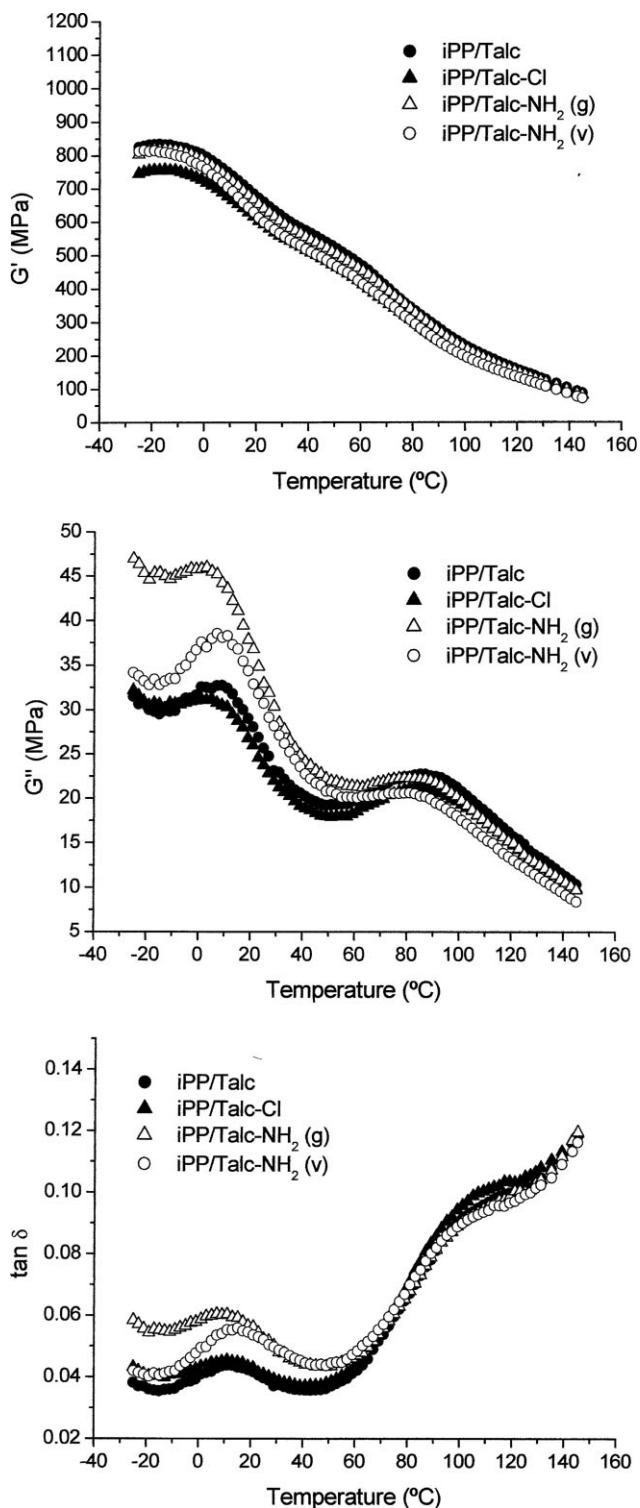


Figure 3 Evolution of G' , G'' , and $\tan \delta$ with the temperature for the unmodified (original) iPP/talc composite and the composites with modified interphases by means of chemisorption talc treatments.

respective affinity to the PP matrix. In all the observed cases, such behavior is indicative of a similar dissipation mechanism available for the modified and unmodified composites in the third dynamic

thermomechanical response zone, in which the rapid short-range diffusion motions together with some contribution across the amorphous–crystalline interphase become mainly responsible for the retarded long-range segmental motions.

In contrast, for both the fourth and second dynamic mechanical response zones, noticeable differences exhibited by both iPP/talc-NH_{2(v)} and iPP/talc-NH_{2(g)} and by iPP/talc-Cl are displayed.

Therefore, in the fourth response region between 100 and 140°C, in which, as mentioned previously, the polymer molecules show an increasing ability to flow because they may participate as a whole in the dissipative phenomena across the long-range configurational changes, the increase in the $\tan \delta$ values exhibited by iPP/talc-Cl is noteworthy and in any case is in excellent agreement with the decrease in the interatomic distance, which can be expected at the PP/chlorinated talc interphase because of the larger size of the chlorine atom with respect to the hydroxyl group in the unmodified talc, as shown in the scheme in Figure 4. In this figure, it can be appreciated that although hydroxyl and amine groups are both isoelectronic and have comparable sizes (ionic radius = 1.18 Å), the chloride group is 40% larger (ionic radius = 1.67 Å)

Furthermore, in this same dynamic mechanical response zone, in the case of iPP/talc-NH_{2(v)} and iPP/talc-NH_{2(g)}, a slight decrease in the $\tan \delta$ values with respect to those of the composite based on the unmodified talc is noticeable. Such a decrease, which starts above 80°C, could be correlated with the lower electronegativity of the nitrogen of the amine groups bonded to the particle surface of the modified talc with respect to the oxygen in the hydroxyl groups

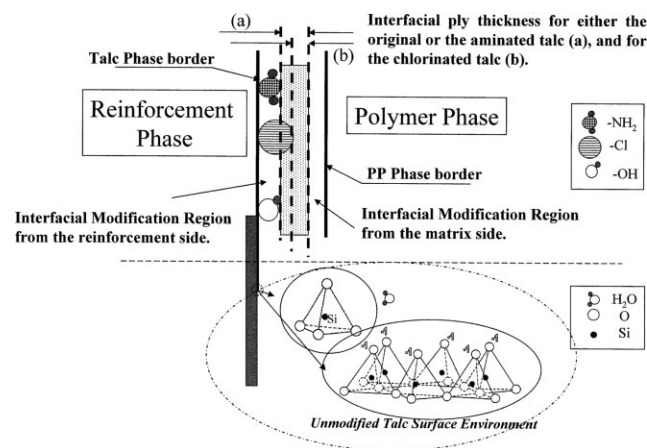


Figure 4 Conceptual scheme showing both the changes in the interfacial ply thickness at the PP/talc interface caused by the different functionalities bonded to the mineral surface for the original and chemisorption-modified talcs (top) and the environment of the unmodified talc surface (bottom).

bonded as silanol groups on the original (unmodified) talc surface. In this figure, it can be observed that iPP/talc exhibits an inflexion close to 60°C. Therefore, with this temperature taken as a reference, the study of the evolution of $\tan \delta$ from 60°C to values close to 40°C (close to the second response zone) shows that the decreasing evolution of iPP/talc-Cl almost overlaps that of unmodified iPP/talc. However, the evolution of $\tan \delta$ for iPP/talc-NH_{2(v)} and iPP/talc-NH_{2(g)} does not diminish with decreasing temperature in this interval but shows an almost constant value close to that exhibited at 60°C all along the interval. Thus, in this temperature range, the rapid short-range diffusion motions become mainly responsible for the retarded long-range segmental motions characteristic of this third response zone. Thus, the higher $\tan \delta$ values observed here for both iPP/talc-NH_{2(v)} and iPP/talc-NH_{2(g)} agree with the increase in the interaction level across the PP/talc interphase because of the higher affinity between the aminated groups bonded at the talc surface and the PP matrix versus that between the hydroxyl groups present at the talc unmodified surface.

Furthermore, in the second dynamic mechanical response zone (-10 to 40°C), in which those rapid short-range diffusion motions at the PP matrix appear frozen-like, all the dissipation capabilities of the composites are restricted to the short-range diffusion motions at the chain-segment level all along the glass-transition region of the matrix. Because the maximum exhibited by $\tan \delta$ in Figure 3 is a function of the dissipation mechanism constraints affecting the amount of the amorphous polymer present in the matrix, the area under the curve indicates the amount of the free amorphous phase able to participate in the cooperative segmental motion mechanism, which the glass transition indicates. In the plots of Figure 3, it can be observed that the β -transition peak does not change in the case of the chemisorption-modified talc-based composites; however, in the case of the unmodified iPP/talc, it appears at 10°C, just where the glass transition of the PP matrix is placed.

Below the glass-transition temperature, at 10°C, all the modified composites show the sharpest differences in the dynamic mechanical responses in comparison with those of the unmodified talc-based composite. Therefore, $\tan \delta$ and G'' for iPP/talc-NH_{2(g)} do not fall below the glass-transition temperature of the matrix but remain almost constant with decreasing temperature, being linked to the first response zone below -20°C, in which the dissipation mechanisms remain restricted to the atomic vibration field.

From here and according to the interface ply model, as described elsewhere,¹ the increase in ei-

ther $\tan \delta$ or G'' values for iPP/talc-NH_{2(g)} with respect to those for iPP/talc could be correlated with the recovery of the interfacial thickness of the dynamic PP/talc interfacial ply after the chlorination step (see the scheme in Fig. 4). The latter should mean higher interfacial transport throughputs between the composite components because of the lower electronegativity of nitrogen with respect to oxygen. Otherwise, iPP/talc-NH_{2(v)} shows a sharp reduction in $\tan \delta$ and G'' values, and this means a noteworthy increase in the peak area under the glass-transition maximum in comparison with either the iPP/talc-Cl composite or the unmodified iPP/talc. Such an increase in the peak area for the former once more would indicate a larger amount of the free amorphous phase present in iPP/talc-NH_{2(v)} than in iPP/talc-Cl or iPP/talc. This is in excellent agreement with the higher level of interaction between the PP matrix and the aminated talc and even the chlorinated talc with respect to the unmodified talc.

This increase in the interaction level between the modified talc particles and the PP matrix (in the interval in which the lowest short-range dissipation mechanism just based on the atomic vibrations begins to be the only one available) can be clearly concluded from the dynamic mechanical response shown by the composites and is in excellent agreement with the improvement in their macroscopic mechanical behavior, as fully discussed elsewhere.¹⁴ The former observations are confirmed by the study of the evolution of G' with temperature for all the composites. Besides, it is also remarkable that, by the way in which the elastic component of the modulus decreases with increasing temperature (as is usual), the nonexistence of changes in the energy elasticity by the entropy elasticity as the driving force of the relaxation mechanisms all along the experimental range scanned can be concluded.

DMA of the PP/talc composites: Talc particles modified by physisorption processes

It is well worth indicating here that the coating of talc surfaces has been fully described in previous works.^{11,12} It was early established in the literature¹⁶⁻¹⁸ that, because of the mild experimental conditions used to perform the process (Table IV), the silanes (and equally *n*-BuNH₂) are adsorbed physically through hydrogen bonding with the talc surface silanol groups.¹⁶⁻¹⁸ In fact, the absence of any chemical bond was deduced by Fourier transform infrared spectroscopy^{11,12} (Table V). Consequently, the presence of bonded and chemisorbed silanes (or *n*-BuNH₂) layers was discarded. If we had been looking for any hypothetical siloxane links with the talc surface, much more strenuous reaction

conditions would have been necessary.^{16,17} Nevertheless, the latter lies beyond the scope of this work.

Otherwise, Figure 5 shows the dynamic mechanical behavior of the talc-based composites either unmodified (iPP/talc) or modified by means of physisorption processes (iPP/talc-*n*-BuNH₂ and iPP/talc-silane).

In this figure, the $\tan \delta$ values for both iPP/talc-*n*-BuNH₂ and iPP/talc-silane show behavior almost identical to that of iPP/talc at temperatures higher than 60°C, at which the inflexion point in the minimum–maximum evolution for the G'' plot of iPP/talc was previously identified (Fig. 2). This means that both physisorption treatments are not enough efficient at significantly influencing the transport throughput enhancement across the interface in the zone in which the retarded long-range segmental motions of the polymer matrix become available because of the rapid short-range diffusion motions together with some contribution across the amorphous–crystalline interphase at the matrix α transition. In this respect, we find noteworthy the near disappearance of the α -relaxation peak in the G'' plots for both iPP/talc-*n*-BuNH₂ and iPP/talc-silane composites, which show a real rubbery plateau; this stands in contrast to the unmodified iPP/talc and is similar to the response of the neat iPP in Figure 2. It agrees with the enhancement of the dissipation capabilities across the particle/matrix interphase in the surface-treated talc composites.

However, at decreasing temperatures below 60°C (and more when the temperature is close to the glass-transition temperature of iPP), both *n*-BuNH₂ and silane-treated talc appear to be very effective in participating in the dissipation mechanisms of the PP matrix, as can be deduced from the increases in the G'' and $\tan \delta$ values of both iPP/talc-*n*-BuNH₂ and iPP/talc-silane. Nevertheless, the proper efficiency is obtained for iPP/talc-*n*-BuNH₂, which exhibits a higher increase in G'' and $\tan \delta$ values.

The efficiency of both physisorption treatments at temperatures below 60° can also be concluded from the shifting observed in the maximum G'' and $\tan \delta$ values (which identify the glass transition of the polymer). These values appear 5°C above the glass-transition temperature of both the neat iPP and iPP/talc (and of the other composites based on chemisorption-modified talc; Fig. 3).

Otherwise, the increase in the matrix glass-transition peak area for both iPP/talc-*n*-BuNH₂ and iPP/talc-silane composites, in comparison with iPP/talc, indicates an increase in the amount of the free amorphous phase of the matrix able to participate in the dissipation mechanisms based on the cooperative segmental motions at the so-called β transition. This means a decrease in the incompatibility degree

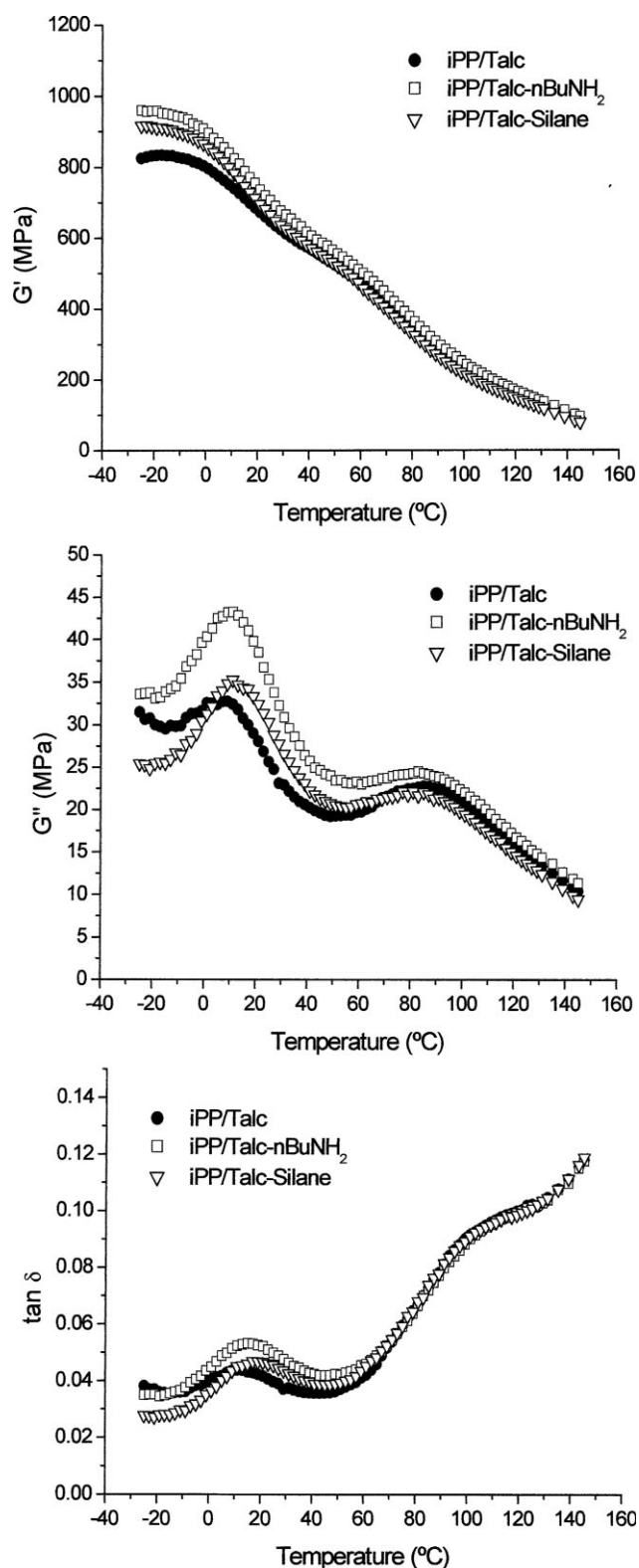


Figure 5 Evolution of G' , G'' , and $\tan \delta$ with the temperature for the unmodified (original) iPP/talc composite and the composites with modified interphases by means of physisorption talc treatments.

between the treated talc and the PP matrix. The higher efficiency of the *n*-BuNH₂ treatment, in comparison with the classical treatment based on a

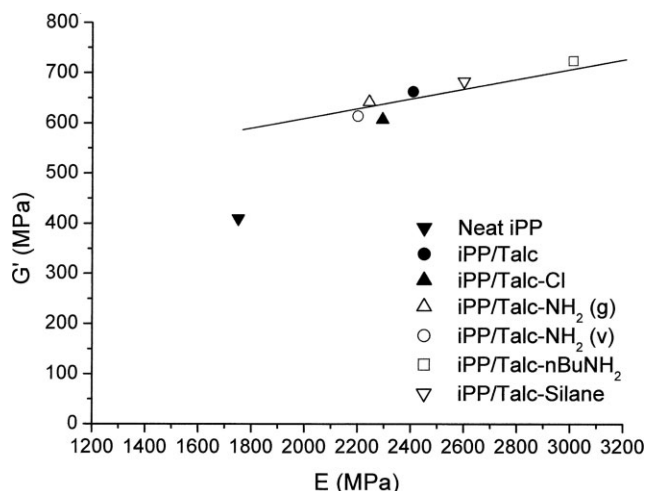


Figure 6 G' versus E for the indicated samples measured under room conditions.

silane mixture, can be further concluded because the G'' and $\tan \delta$ values for iPP/talc-silane fall below those for iPP/talc-*n*-BuNH₂ and even iPP/talc at temperatures below the glass-transition temperature of the matrix.

Correlation between macroscale and microscale properties

It is clear that if an interfacial phenomenon is detected by parameters on the macroscopic scale, it must necessarily be measurable in terms of parameters on the microscopic scale. However, the reverse is not always true.^{2,19–22} Then, if the interpretation based on microscopic parameters is correct, it necessarily has to be correlated with the macroscopic mechanical scale. Therefore, when the parameters related to the elastic behavior are measured with both scales [G' and the tensile elastic modulus (E)], the expected correlation can be seen. Figure 6 plots the values of G' versus E measured at room temperature. A clear linear correlation can be appreciated for all the composites. However, this appears different, depending on the kind of surface treatment of the reinforcement particles. In fact, those coming from a chemisorption process (iPP/talc-NH_{2(v)}, iPP/talc-NH_{2(g)}, and iPP/talc-Cl) appear very close to one another, probably because of the very similar nucleation effect induced (quite similar sizes of the bonded groups; see the scheme in Fig. 4). However, the other composites (iPP/talc-*n*-BuNH₂ and iPP/talc-silane) exhibit very different behavior because of the more heterogeneous character of the coating of the reinforcement particles, as expected from a physisorption process. It is well worth noting that the compression-molded iPP is not included in the linear correlation. This is attributed to the difference

in the crystallinity observed for the molded iPP with respect to the iPP/talc composite (Table VI) caused by the aforementioned nucleation effect of talc particles producing an increase in the elastic response of the material (E and G'), as already discussed for G' (Fig. 1). The latter is related to the fact that all of them were molded under the same processing conditions as we looked for better performance of the composites rather than the neat iPP. In fact, if we compare the values for the crystallinity of iPP processed to maximize its behavior (iPP in Table I) and neat iPP compression-molded under the same processing conditions to maximize composite behavior (Table VI), we can see that the value of the crystalline content of the former is very similar to that of the composite. Therefore, as discussed elsewhere,^{2,19–22} values for $\Delta\lambda$ (as defined in Table VI) close to zero (Table VI) would mean a well-balanced processing step. Hence, it can be concluded that the obtained composite is almost optimally well processed ($\Delta\lambda = 0.9$) in comparison with the neat iPP ($\Delta\lambda = 8.87$) in terms of thermal and unshared reorganization possibilities through the amorphous-crystalline interface^{2,19–22} (Table VI). This agrees with the very important influence of the processing steps on the structural development and thus final properties of a polymer-based material. This obvious remark^{2,19–22} is often discarded in seemingly basic studies claiming to monitor and isolate real interfacial interactions.

CONCLUSIONS

Dynamic mechanical spectroscopy has been used to detect and evaluate interfacial changes induced in PP/talc composites by means of modifications performed on the mineral reinforcements. Also, this technique has proven to be very useful in the understanding of the macroscopic responses and measurements of PP/talc composites in terms of their microscopic, mesoscopic, and nanoscopic origins, ascertaining the degree of incompatibility between the inorganic talc particles and the organic iPP matrix in PP/talc composites by different surface treatments of the talc particles.

The higher efficiency (in terms of the combination of both the plastic and viscoelastic behaviors of the composites) shown by the aminated reinforcements with respect to those based on physisorption processes has been established. Therefore, although both families of modified composites, in comparison with the unmodified composite, show a release of free amorphous PP at the particle/matrix interphase able to participate in the cooperative segmental motions near the glass-transition temperature, those based on physisorption-modified talc exhibit a higher temperature (5°C) for the β -transition peak of the PP matrix, and this means an upward shift in the energy

threshold to permit the aforementioned motions. Therefore, if we assume that the temperature at which the damping peak is located is not coincident with that at which the real change in the thermodynamic properties occurs, this increment in temperature for the β transition can be assigned to an increase in the elapsed time necessary to reach a new equilibrium. This would mean an increase in the natural relaxation time with the temperature of the chain segments involved in the glass transition. The latter agrees with the increase in the interfacial thickness of the physisorption-modified talc-based composites, as can be expected from the greater molecular size of both the physisorbed silane and *n*-BuNH₂ moieties with respect to the chemisorbed amine and chlorine groups. Also, this depends on the kind of interaction (secondary forces versus covalent bonds) existing between the talc particles and the sorbed (physisorbed versus chemisorbed) groups in every case.

By very similar dynamic mechanical responses found for the composite based on the unmodified talc and for the composite based on the chemisorption chlorinated talc, no loss of the properties of the last is also confirmed. Even more so, by the slightly higher $\tan \delta$ values (vs those for the unmodified talc-based composite) that are exhibited by the chlorinated talc-based composite, just below the β PP matrix transition and just above the α PP matrix transition, the improvement in the PP/talc interphase obtained by the shift of the hydroxyl groups from the silanol groups by the chlorine atoms can be clearly concluded. Nevertheless, the higher efficiency of the aminated talc, especially in the iPP/talc-NH_{2(g)} composite, is evidenced.

Finally, it can be affirmed that if the interfacial changes can be measured by macroscopic means,

they must be necessarily be detectable with microscopic parameters but not vice versa.

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