Polypropylene/Mica Composites Modified by Succinic Anhydride–Grafted Atactic Polypropylene: A Thermal and Mechanical Study Under Dynamic Conditions

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ABSTRACT: In this study the thermal and mechanical behaviors of PP/mica composites, under dynamic conditions, are discussed on the basis of the changes induced by the presence of the interfacial modifier succinic anhydride–grafted atactic polypropylene, with different degrees of grafting, prepared in our laboratories by chemical modification of a by-product from industrial polymerization reactor. Changes in the interfacial activity, induced by the substitution of a very small amount of polymer matrix by the interfacial agent with different grafting levels, were conclusively obtained. The results obtained from either the thermal or the dynamic mechanical behavior led to the same conclusions, and agree with data obtained from macroscopic mechanical properties. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 81: 625–636, 2001

Key words: PP/mica composites; interfacial activity; interfacial modifier; a-PP-SA; DSC; DMA

INTRODUCTION

One way to improve the final performance of polypropylene/mineral composites is by means of interfacial modifiers acting from the matrix side.[1–3] In general these interfacial modifications have generated great interest in heterogeneous materials based on polymers as polymer composites[4–12] or polyblends,[13–17] because these agents are able to enhance the interaction level between the material components. Such interactions take place through the interphase, a dynamic region where momentum, mass, and energy transfer occur. The main purpose of interfacial modifications is to improve such transport phenomena by incorporating additives into the heterogeneous system, in such amounts that they are not considered as an additional component in the system but, rather, considered as an efficient transducer of the phenomena that may occur.[9]

In spite of their very low levels, the changes that interfacial agents can induce in the transport phenomena, through the interphase existing between components, are important enough to sharply affect the macroscopic behavior of the polymeric material. This can be concluded from a study of the classical parameters obtained from tensile tests under the linear elastic theory conditions on those materials when well processed.[4–10] Otherwise, the effects of time and temperature in the responses of polymeric materials have sufficient influence so as to be considered when testing because of deviation from the

Table I   Properties of ISPLEN 050 Polypropylene Before Mold Processing

| Molecular Weight | | | Melt Index | | | | DSC | | | | |
| | | | Conditions | | | | | | | | |
M_w	M_n	HI (M_w/M_n)	T (°C)	P (kg)	(g/10 min)	HDT (°C)	ΔH_m (J/g)	T_m (°C)	ΔH_c (J/g)	T_c (°C)	Density (g/cm³)
334,400	59,500	5.62	190	5.00	5.80	58.5	87.5	164.0	−87.7	117.5	0.90

principles of linear elastic theory,[14,15] developed for isotropic materials. Thus, the study of the thermal and dynamic mechanical responses of composites is a way to observe the extent of the interfacial modifications.

Moreover, and because of the importance of the interfacial agents acting from the matrix side, much work has been directed toward their mechanistic processes: chemical reaction engineering, process conditions, and characterization of the products.[18,19] As a consequence, first isotactic polypropylene[17,20–22] and, more recently, an atactic polypropylene from a polymerization reactor by-product[16,17,23] have been considered by the authors as raw materials for such interfacial agents.

This investigation deals with the study of the interfacial modification induced in polypropylene/mica composites by a functionalized atactic polypropylene containing succinic anhydride–grafted (a-PP-SA) groups, which has proved to be efficient as an interfacial agent in PP/mineral reinforcement materials, as evidenced by tensile mechanical properties.[9,10] This study was undertaken by means of thermal and dynamic mechanical analysis of PP/mica composites incorporating interfacial agents with different grafting levels.

EXPERIMENTAL

Materials

Isotactic polypropylene (i-PP) ISPLEN 050 (Repsol Química, Madrid, Spain) and a micronized mica, with an aspect ratio higher than 100 (Alsibronz), as polymer matrix and reinforcement particles, respectively, were used as starting materials. The reinforcing mineral particles were chosen because their size and particle size distribution remain constant after, during, and before the processing steps.[8–10] Characteristics of polypropylene and mineral reinforcement (as received) are presented in Tables I and II, respectively.
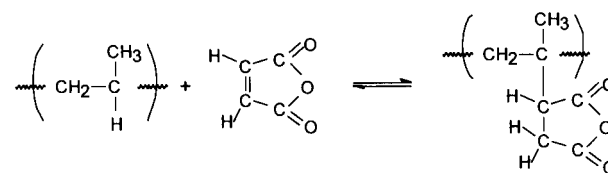
The interfacial agents considered in the present study were modified atactic polypropylenes with succinic anhydride (a-PP-SA)–grafted groups containing different grafting levels (1.0, 2.0, 3.0, and 4.0%), prepared in our laboratories by a batch process in the melt under the reaction conditions compiled and discussed elsewhere.[16,17] Figure 1 shows a reaction scheme for the preparation of a-PP-SA.

Processing

Compounding was performed in an internal mixer Rheomix 600, working at 190°C and attached to a Rheocord 90 (Haake, Schott Iberica, Barcelona, Spain). Composite materials were prepared by incorporating 30% w/w of mica to the molten polymer bulk. A small amount (1.5%) of polymer matrix (PP) was replaced by the interfacial modifier a-PP-SA. In this way a series of composites, with and without interfacial agent with different grafting levels (1.0, 2.0, 3.0, and 4.0%), were obtained. After the compounding step, 3-mm-thick plies were prepared by compression molding at 200°C and then cooled under con-

Table II   Properties of the Mineral Reinforcement

Reinforcement	Density (g/cm³)	Specific Surface (BET) (m²/g)	Mean Particle Size (μm)	Supplier
Lamellar mica	2.85	1.5	79.8	Alsibronz

Figure 1   Reaction scheme for the preparation of the interfacial agent used in the present study.

trolled conditions in a Collin press (Semsa, Barcelona, Spain. Samples were cut from these plies for thermal and dynamic mechanical measurements, and as standarized specimens for mechanical properties.

Characterization Procedures

Thermal measurements were performed in a Perkin–Elmer DSC-7 calorimeter (Perkin–Elmer, Hispania, Madrid, Spain), previously calibrated with indium standards, as usual. Runs were performed under nitrogen atmosphere at heating/cooling rates of 10°C/min from 40 to 200°C. After 5 min at 200°C in the molten state (softening state), a cooling scan was performed to 40°C, followed by a second heating scan from 40 to 200°C. Peak temperature was considered as the transition temperature. The enthalpic calculations were performed by the DSC-7 software. Crystalline contents, which are values corrected by the real amount of organic polymer in each composite (70% as average), were calculated by using 209 J/g for a 100% crystalline polypropylene.[24] In all cases three pots containing about 10 mg of each sample were tested, thus confirming reproducibility of results.

Dynamic mechanical properties, in torsional mode, were conducted on prismatically shaped specimens ($30 \times 12 \times 3$ mm) obtained from the compression plies. Runs were performed in a TA-983 dynamic spectrometer (TA Instruments, Dupont, Madrid, Spain). Thermal scanning was performed from -30 to 150°C, working at a constant frequency (1 Hz) and 0.2 mm of oscillation amplitude.

Mechanical properties were obtained following UNE-EN-ISO 527 standards, working at room temperature (23°C). Standardized specimens were tested in an Instron (Semsa, Barcelona, Spain) dynamometer 4200 series, equipped with a high-resolution extensometer (HDR). The crosshead speed was 1.0 mm/min for modulus calculations, the results of which were averaged from at least 10 measurements.

RESULTS AND DISCUSSION

Fundamentals

There are numerous studies in literature concerning the performance of polymer-based composite materials, mainly on their mechanical properties,[4–10,15,25–27] but also on thermal and dynamic mechanical studies.[11–13,28] From these studies a series of conclusions have been derived. Factors influencing the properties of the system are the polymer matrix nature, the particle size distribution, and their homogeneous distribution in the polymeric composite material, as well as the preferential orientations of these mineral particles. Then, for a material in which the reinforcing particles are embedded in the polymer bulk, interactions between these and the macromolecular chains through a dynamic interphase must occur. Hence, to enhance the interactions through this interphase would be an objective in designing this kind of material. From previous studies it was demonstrated that replacing a small amount of the polymer matrix by an interfacial modifier results in the enhancement of these interactions[1–13]; thus, there must be an optimum value for the amount of interfacial agent, which is also related to the processing history of the material.[1,3,9,15,29] In these terms, good reproducibility of properties (i.e., tensile parameters) would indicate that the material was well processed,[9,10,30] and then the changes in properties can be attributed to modifications induced by interfacial agents.[5–8]

Likewise, when trying to evaluate any given interfacial modification of a heterogeneous system one must consider reinforcing particles without any size variation during the processing, premixing, and molding steps.[10,12,31] Otherwise, any effect merely resulting from changes in the flow dynamics of the system caused by particle size distribution variations might be wrongly assigned to changes in interfacial activity. Lamellar mica, because of its well-defined geometry, thus appears to be a good option to act as a true reinforcement particle and not merely as a filler.[1,2,28,29,32–34] With respect to the processing operations, when a composite material that incorporates interfacial agents is processed, it must be taken into account that if this operation implies the preferential orientation of reinforcement particles, then an additional improvement, besides that caused by the interfacial agent, would be expected.[28] Hence, initial studies attempting to isolate only the effect of interfacial agents in the behavior of the finished heterogeneous material should minimize the preferential orientation of the particles.[9] Thus, compression-molded samples would be useful for these purposes.

Furthermore, the nucleating effect, which results in higher degrees of crystallinity in the semicrystalline polymer that is produced by the
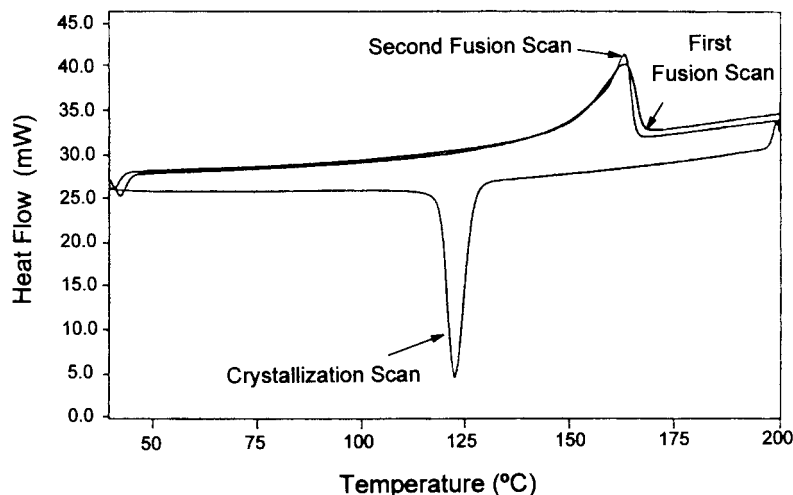
Figure 2 Typical DSC thermogram of a PP/mica composite.

reinforcing particles, is also well established. However, the amorphous character of the polymer segments defining the interface from the matrix side, closer to the mica particle surface, must also be considered. Assuming that the higher the conformational freedom of the regions involved (chain segments close to the reinforcing particles), the higher the interfacial activity, then the amorphous regions would be more easily involved than would ordered regions in the interfacial interchanges.

Indeed, when the interfacial modifiers from the matrix side (grafted polymers) are incorporated into composite materials, two main effects may be considered for evaluating the efficiency of the interfacial modification produced: (1) the changes in the transport phenomena throughputs across the interphase caused by replacing different amounts of the polymer matrix by the interfacial agent, and (2) the changes in the driving forces responsible at those throughputs, which occur when the number of polar groups in the interfacial agent (grafted groups) varies. The second aspect was considered in this present investigation.[10]

Thermal Behavior

When the crystallinity values of any given polymeric material, calculated from either the cooling or the second heating scan, are similar it can be assumed that the material has suffered a processing history that makes it exhibit a well-balanced crystal/amorphous interaction level, which remains even after the melting/crystallization processes. If the shear, elongational, and thermal histories have been well balanced during the processing operations, a thermal analysis would provide the researcher information not only about crystallinity but also about the amorphous-phase fraction present in the system, including the chain segments of the so-called tie-molecules that confer continuous character to the material.[35]

In fact, the amorphous phase contains the chain ends, the shortest chains, and the interconnecting chain segments.[12] Then, the reinforcement particles and other foreign substances (such as the interfacial agents) in the system would preferably be located in this zone.[9–13,28] Because of the close relationship between the amorphous and the crystalline polymer phases, it can be expected that changes in the thermal-response parameters of the material may be used to detect interfacial changes related to the presence of the interfacial modifier in a way that would disturb the flow across the phases involved.[11,39] Figure 2 shows a typical DSC thermogram of a PP/mica-based composite, in which the first and second fusion scans appear to be almost identical.

Peak Temperatures

As mentioned earlier, the interfacial modifiers must be preferentially located in the amorphous phase because they disrupt the polymer matrix. Furthermore, the amorphous character of the a-PP-SA interfacial agents is another reason to be excluded from the crystalline phase.[16,23] Then, if the a-PP-SA agent changes, there must be no variations in peak temperatures associated with the crystalline regions of the polymer matrix. The
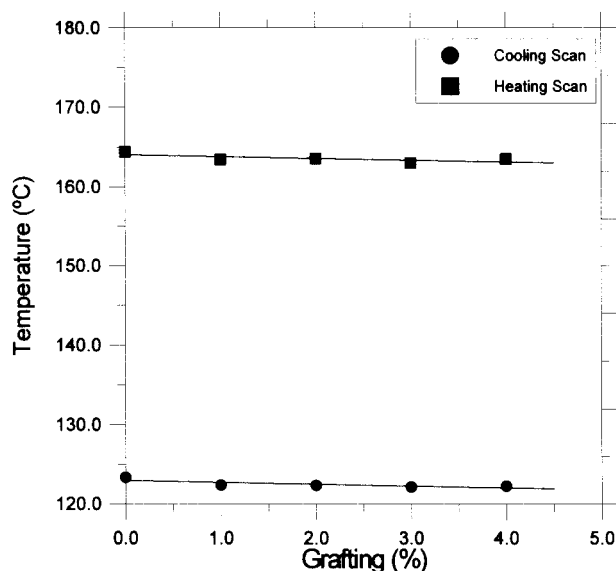
Figure 3 Evolution of melting and crystallization temperatures with grafting level in the interfacial agent a-PP-SA. (a-PP-SA = atactic polypropylene with succinic anhydride–grafted groups.)
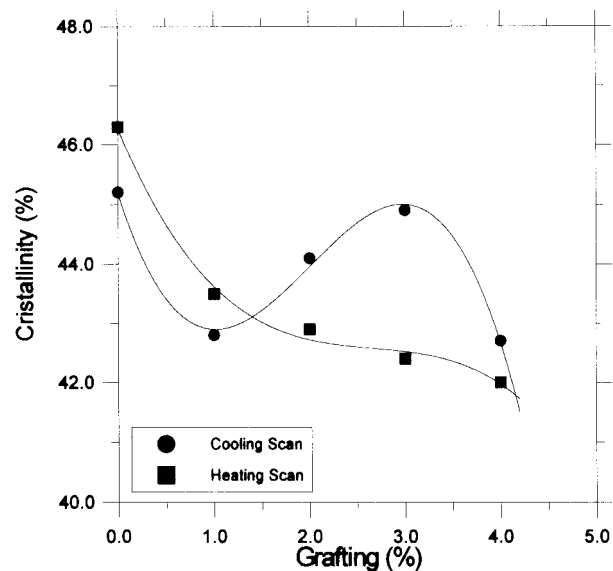

Figure 4 Evolution of crystalline content (obtained from the cooling and the second heating scan) with the grafting level in the interfacial agent a-PP-SA.

latter is clearly evident in Figure 3, where the peak temperatures, corresponding to either the fusion or the crystallization scans, have been plotted as a function of the grafting level of the interfacial agent in the composite material.

Crystalline Fraction Content

A mineral reinforcement changes the degree of crystallinity of a semicrystalline polymer matrix, the so-called nucleation effect. Table III lists some thermal properties for a compression-molded PP and a PP/mica composite without interfacial agent, both processed at the same conditions. From these data the nucleating effect exerted by mica on PP is clearly evident. In these terms the substitution of a certain amount of matrix by an

Table III Thermal Properties of the Molded Neat PP and PP/Mica Composite in the Absence of Interfacial Agents

Sample	T_m (°C)	λ_m (%)	T_c (°C)	λ_c (%)	$\Delta\lambda$[a] (%)
i-PP	164.7	27.0	123.0	24.8	8.87
i-PP/mica	164.4	46.3	123.3	45.2	2.40

[a] $\Delta\lambda = [(\lambda_m - \lambda_c)/\lambda_c] \times 100$, where λ_m and λ_c are the crystallinities obtained from the melting and the crystallization curves, respectively.

accommodating substance (interfacial agent) with the foreign component (reinforcement particle) should result, *a priori,* in a lower level of crystallinity. The evolution of polymer matrix crystallinity with the grafting level in the interfacial agent is shown in Figure 4, where it can be observed that the inclusion of the interfacial agent a-PP-SA induces a decrease in crystallinity that follows a linear evolution with the increase in the grafting level of a-PP-SA from 1.0 to 4.0%, when the crystalline level is determined from the fusion peaks. This evolution is similar to that found for other PP/mica composites but incorporating succinyl fluoresceine–grafted atactic polypropylene (a-PP-SF),[28] and contrary to that found for the PP/talc system with a-PP-SA.[12] This effect is primarily assigned to the difference of surface area (and then the interfacial capability) between mica and talc particles in a 1 : 4 (mica : talc) ratio as well as the differences in their mean particle size in a 10 : 1 (mica : talc) ratio.[11] All the above-mentioned results indicate the very complex character of the interfacial interactions in polymer-based composites.

On the other hand, the evolution of crystallinity, when obtained from the cooling scans, is such that after a decrease in crystalline content once the interfacial agent a-PP-SA(1.0%) is present in the system, a linear increase in the matrix crystalline content is obtained with an increase in the grafting level of the additive, similar to that found

for other PP/mica systems.[12] This continues until the point corresponding to a-PP-SA(3.0%), then the crystallinity of the matrix drops again to the same level as that when the grafting level was 1%. The interpretation of such a response requires some considerations about the crystalline behavior of the polypropylene matrix under dynamic conditions.

In fact, in the cooling step, after maintaining the sample for 5 min in the softened state, the motion possibilities of the polymer would become so sharply restricted that a fraction of the polymer has to pass suddenly to tridimensional order. When some semicrystalline polymers such as polyethylene undergo this process, *a priori,* all the material cannot be ordered and incorporated into the crystal. On the contrary, when other semicrystalline polymers such as polypropylene undergo the same dynamic crystallization process, they can trap some mesomer units into the sharply constrained crystalline regions that, during the following dynamic heating step, would travel to the amorphous phase through the dynamic amorphous/crystal interface.[9,28,36,39] The preceding results show that the complex nature and the competitive effects taking place at the interfacial level make it very difficult to study interfacial modifications, besides being strongly related to the history of the material.[35] These reorganization possibilities of the chain segments on the polymer matrix across the dynamic amorphous/crystal interphase must be related to the differences in crystallinity found between the cooling and subsequent heating processes. We can thus define a parameter ($\Delta\lambda$) related to the polymer melting in the heating scan compared to that previously ordered in the cooling scan,[11,12,28] expressed as follows:

$$\Delta\lambda = \frac{\lambda_m - \lambda_c}{\lambda_c} \times 100 \qquad (1)$$

where λ_m and λ_c are the crystallinities obtained from the second heating scan and the cooling scan, respectively.

The physical sense of $\Delta\lambda$ can be easily understood, keeping in mind the phenomena occurring for classical fully crystalline materials (such as metals or ionic solids), in which all the material (e.g., structural units) pass to the tridimensional order (crystallizes) at the same time, without the coexistence of an amorphous phase; then, the value of $\Delta\lambda$ in eq. (1) would always be zero. Hence, values for $\Delta\lambda$ different
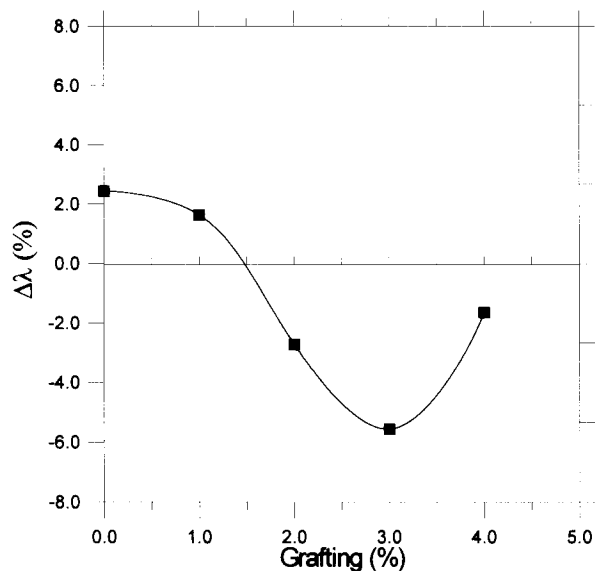

Figure 5   Evolution of ($\Delta\lambda$) with grafting in the interfacial agent a-PP-SA. ($\Delta\lambda = [(\lambda_m - \lambda_c)/\lambda_c] \times 100$, where λ_m and λ_c are the crystallinities obtained from the melting and the crystallization curves, respectively.)

from zero would indicate that there is no equilibrium in the system because of the material reorganization possibilities through the crystal/amorphous interphase. Variations in this parameter can be associated with changes in interfacial activity induced by the presence of interfacial agents[11,12,26] or any other strange substance from the polymer bulk.[36] Then, values of $\Delta\lambda$ higher than zero would indicate a dynamic flow from the amorphous to the crystalline phase, and values lower than zero would indicate the travel of some chain segments from the crystal to the amorphous phase, that is, the classical response given by the isotactic polypropylene grades. On the other hand, $\Delta\lambda = 0$ would indicate some kind of dynamic equilibrium, in the sense that the fraction of ordered material obtained from either the fusion or the cooling cycle is the same.

The evolution of the $\Delta\lambda$ parameter with grafting level is shown in Figure 5, where it can be observed that the presence of a-PP-SA with different grafting levels means sharp qualitative changes in the response of the polypropylene matrix of the composites. The evolution is such that $\Delta\lambda$ values are positive for the unmodified PP/mica system (as for the neat PP), as well as for when a-PP-SA(1%) is incorporated, although this value is closer to zero. The latter confirms that the addition of this interfacial agent means a displacement of the system toward a certain dynamic equilibrium. The increase in the number of

polar groups placed at the polymer/mica interface [a-PP-SA(2%) and a-PP-SA(3%)] exhibits negative $\Delta\lambda$ values, which would indicate the travel of chain segments from the crystal to the amorphous phase. Furthermore, the evolution follows a quadratic curve. Meanwhile, a-PP-SA(2%) and a-PP-SA(3%) show decreasing values for $\Delta\lambda$. The presence of a-PP-SA(4%) yields values of $\Delta\lambda$ that are higher than those of the former systems, and are closer to zero. This is a typical evolution of the interfacial phenomena where throughputs across the interface are limited by the feasible interfacial area, indicating the existence of optimum values of interfacial interaction levels as the key to designing these kinds of materials. This same effect was also found for other heterogeneous systems based on polymers.[4–12,28]

Dynamic Mechanical Behavior

The study of elastic and viscoelastic materials under cyclic stress or strain conditions is called dynamic mechanical analysis (DMA). To describe the stress caused by a modulated stress one can define a complex modulus (stress/strain ratio), G^*. To evaluate G^*, the measured stress is separated into two components, one in-phase with the strain (G') and one out-of-phase (G''), called storage modulus and loss modulus, respectively. The tangent of the phase difference is the loss factor, where $\tan\delta = G''/G'$. It is well known that the mechanical behavior of polymer materials is governed by viscoelastic processes and plastic deformation mechanisms that, when a critical stress is reached, lead to a failure in the material at a macroscopic scale. Both plastic and viscoelastic contributions are inherent to the mechanical behavior of polymer materials because of their complex and dynamic character. However, the difficulty of this technique lies in understanding the macroscopic measurement in terms of the microscopic origin. Hence, it is well known that transitions from brittle to ductile behavior, responsible for the yielding before failure, are mainly governed by microscopic parameters such as the entanglement density and the chain stiffness,[15,37,38] which are responsible for the necessary stress levels to induce crazing and yielding, respectively. Such parameters become critical in the case of a composite material consisting of a polymer matrix that incorporates reinforcement particles, and even more so when the interactions between the particles and the macromolecular chains, through the interface, increase by the action of the so-called interfacial agents.
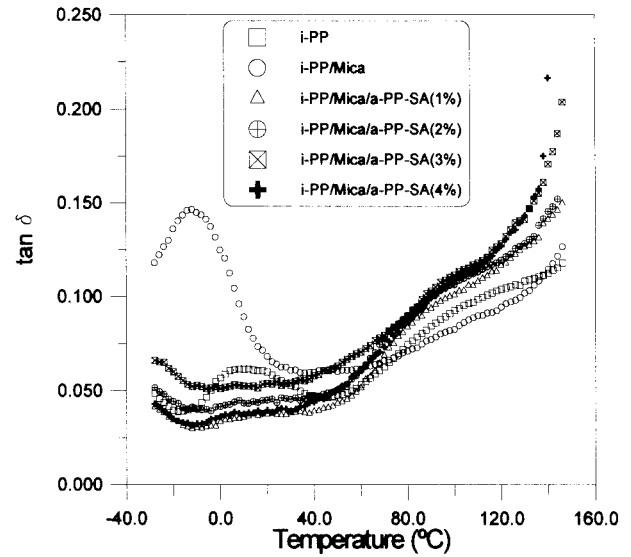

Figure 6 Loss factor ($\tan\delta$) versus temperature when varying the grafting level in the interfacial agent a-PP-SA($x\%$). [a-PP-SA($x\%$) = atactic polypropylene with $x\%$ of succinic anhydride–grafted groups.]

A first step to study the modifications associated with changes in interfacial activity would be to determine the glass-transition temperature for the composites studied. It is well known that the glass transition can be assigned to the dissipation possibilities taking place in the free amorphous regions. They are assumed to be caused by the rotation of free chain segments when a certain energetic level (associated with any given temperature) is reached.[35] As a consequence, the fact that such phenomena begin at lower temperatures would mean more mobility of the amorphous phase.

Loss factor values versus temperature, for different composite materials, are plotted in Figure 6. Comparison of the curves corresponding to the neat PP and the PP/mica composite shows a great difference in the area under the curves. This aspect is related to the previously discussed fact that the reinforcement particles act to disrupt the polymer bulk, forcing a fraction of the macromolecular segments to be ordered. Thus, the amorphous regions trapped at the polymer/reinforcement interface, which necessarily must coat the mineral particles, would be sharply constrained; consequently, only a very small fraction of the amorphous phase in the system would remain free and ready to become mobile.[9,11,39] This would explain the 20°C drop in the glass-transition temperature (T_g) of the PP/mica system ($T_g = -13$°C)

Table IV   Glass-Transition Temperatures and Dynamic Mechanical Parameters for PP and PP/Mica Molded Composites Determined at Their T_g

Sample	T_g (°C)	tan δ ($\times 10^2$)	G' (GPa)	G'' (MPa)
i-PP	7.0	6.18	0.85	52.34
i-PP/mica	−13.0	14.67	1.14	167.70
i-PP/mica/a-PP-SA(1%)	−7.0	3.05	1.36	40.50
i-PP/mica/a-PP-SA(2%)	−11.0	3.89	1.70	66.30
i-PP/mica/a-PP-SA(3%)	−3.0	5.08	1.08	53.90
i-PP/mica/a-PP-SA(4%)	−7.0	3.21	1.49	47.20

compared to that of the neat PP ($T_g = 7$°C) (Table IV). In Figure 6, the PP/mica composites with 1.5% of the interfacial agent (a-PP-SA) at the different grafting levels (1, 2, 3, and 4%) show a noticeably lower area under the curves. The glass transitions displayed are not very clear but yield T_g values higher than that of the unmodified PP/mica system. This clearly indicates that replacing only 1.5% of the polymer matrix by the interfacial agent changes the responses associated with the amorphous phase, where such an agent ought to be preferentially placed. Table IV shows very similar values for tan δ corresponding to the different PP/mica/a-PP-SA systems at their glass-transition temperatures, except that with 3% of grafts.

In Figure 6, it is also interesting to note a similar evolution shown by composites with a-PP-SA(1%) and a-PP-SA(4%) all along the temperature axis up to 80°C, showing the lowest values for tan δ of all the composites and even of the neat PP. In contrast, the composites with a-PP-SA(2%) and a-PP-SA(3%) show, in this temperature range, successively higher values for the loss factor of all the modified composites. These results seem to be in excellent agreement with results previously discussed on thermal properties from dynamic cooling/heating steps.

Plots of storage (G') and loss (G'') components of the complex modulus (G^*) versus temperature, for all the systems studied, are shown in Figures 7 and 8, respectively. By comparing both figures, one observes that the increase in the elastic component of the PP/mica composite, compared to that of the neat PP, results from the presence of the mica particles in the composite. However, the 30% increase in this elastic component ($G' = 1.14$ GPa for PP/mica versus $G' = 0.85$ GPa for PP; Table IV) means an almost threefold increase of the loss component of the modulus for PP/mica
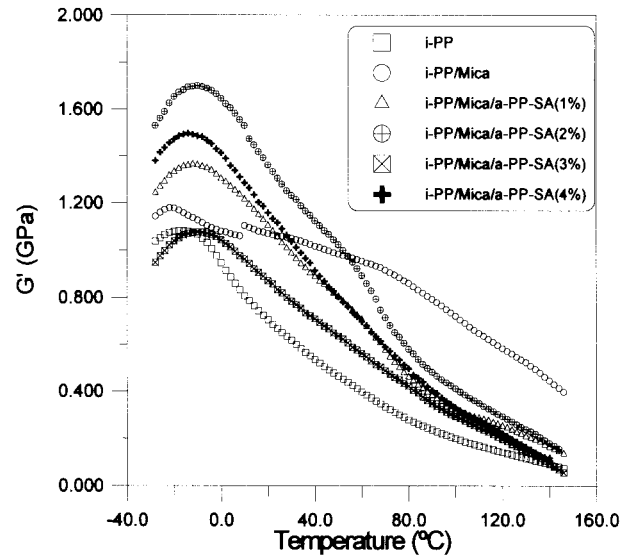

Figure 7 Storage modulus G' versus temperature when varying the grafting level in the interfacial agent a-PP-SA(x%).

compared to that of PP ($G'' = 167.7$ MPa versus $G'' = 52.3$ MPa; Table IV). Such a sharp increase in the G'' value for the PP/mica system confirms the role of an important fraction of the amorphous phase of the polypropylene in assimilating the mica particles and acting as a transducer (between the polymer and the reinforcement) of the energy received by the material as a whole. Obviously, this transmission must take place across
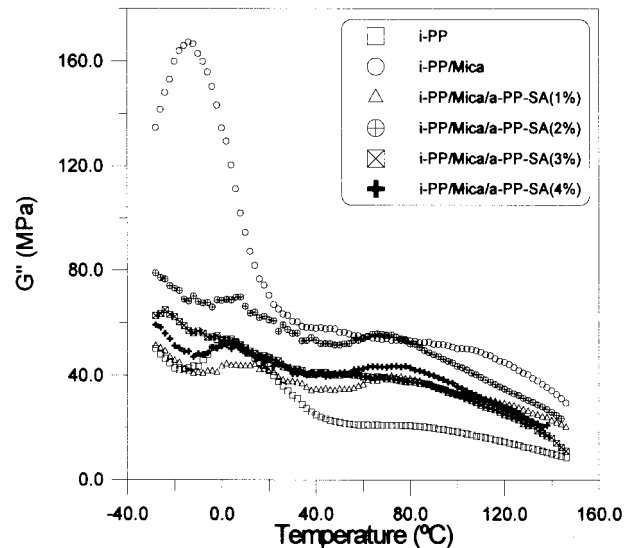

Figure 8 Loss modulus G'' versus temperature when varying the grafting level in the interfacial agent a-PP-SA(x%).

the polymer/mica particle interface, and then the modifications induced at such a level by the presence of interfacial agents must change the overall composite behavior.

In fact, the substitution of 1.5% of the polymer matrix by a-PP-SA(1%), containing only a few grafted groups able to interact with the polar surface of the mica particles, means an increase of the elastic response of the composite. Below room temperature (23°C) the G' values of the composites exceed those of the neat PP and the unmodified PP/mica system. Meanwhile, the loss component G'' also exhibits a great decrease in the case of the modified composites compared to that of the original PP/mica system, even overlapping with that of the neat PP at very low temperatures. Moreover, a very sharp decrease in the peak area assigned to their own T_g is found for all the modified composite systems, that is, in the fraction of the free amorphous phase able to participate in the cooperative motion that glass transition means.

It was demonstrated that the effect of the number of groups grafted in the interfacial modifier a-PP-SA(2%) increases the elastic response of the system, yielding the highest value for G' of all the modified composite systems. However, the loss component G'' of the composite with a-PP-SA(2%) increases only to twice the value of G'', compared to that of the neat PP, and not to the more than three times that occurred in the original unmodified PP/mica system. In any case, it is still far away from an optimal stress/strain transmission across the polymer/particle interface.

The presence of a-PP-SA(3%) as interfacial agent in the composite shows the sharpest decrease both in the G' values of all the modified composites and in the G'' values, with respect not only to the uppermost values obtained for the PP/mica composite but even values below those obtained for the PP/mica/a-PP-SA(2%) system.

Finally, when a-PP-SA(4%) is added to the PP/mica system, the elastic component of the complex modulus (G', Fig. 7) exhibits intermediate values between the uppermost values of the modified composites [represented by the PP/mica/a-PP-SA(2%) composite] and the corresponding neat PP. Meanwhile, the loss component G'' shows lower values than those found for the composites with a-PP-SA(2%) and a-PP-SA(3%), and even overlaps, in the neighborhood of their T_g, with the curve corresponding to the original PP. The fact that composite with a-PP-SA(4%) as interfacial agent shows the highest peak area (corresponding
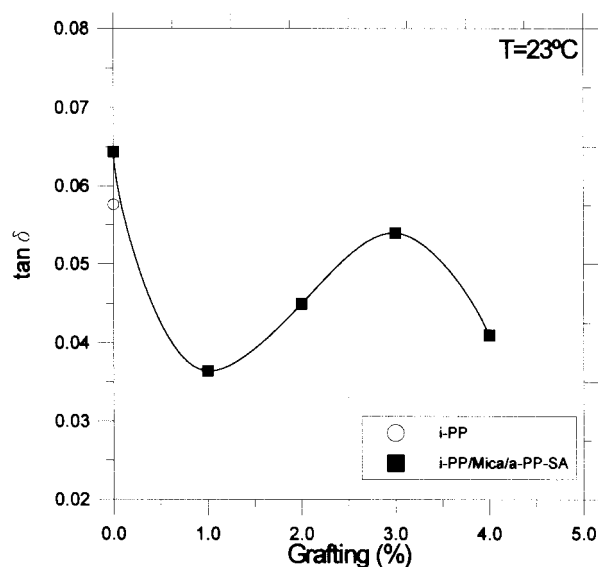

Figure 9 Loss factor tan δ determined at room temperature versus grafting level in the interfacial agent a-PP-SA.

to the T_g transition) confirms that this agent has the highest fraction of free amorphous phase able to cooperate in the glass-transition motion.

In a second zone (Fig. 7), corresponding to temperatures above room temperature (23°C) up to 50°C, it can be noticed that all the modified composites, except that with a-PP-SA(2%), show G' values that range between that corresponding to the unmodified PP/mica system and that of the neat PP. Above 50°C the original PP/mica system exhibits the highest G' values; meanwhile, all the modified composites trend to the values displayed by the original PP, even more so when the temperature is higher. Once the overall response of the systems with respect to the components of the complex modulus has been discussed, the effect of the different grafting levels present in the interfacial agents may be reviewed.

Loss factor values (tan δ) at room temperature versus the interfacial agent grafting level are plotted in Figure 9. The same min–max evolution is observed that was observed for crystallinities obtained from the dynamic cooling scan. The incorporation of the interfacial agent decreases the values of the loss factor to values below those of the PP/mica and the neat PP, then increases with increased grafting level of interfacial agent up to 3%. Afterward, a higher degree of grafting causes a decrease of this parameter, which would indicate, as mentioned earlier, that 3% of grafting in the interfacial agent maximizes the nonequilib-
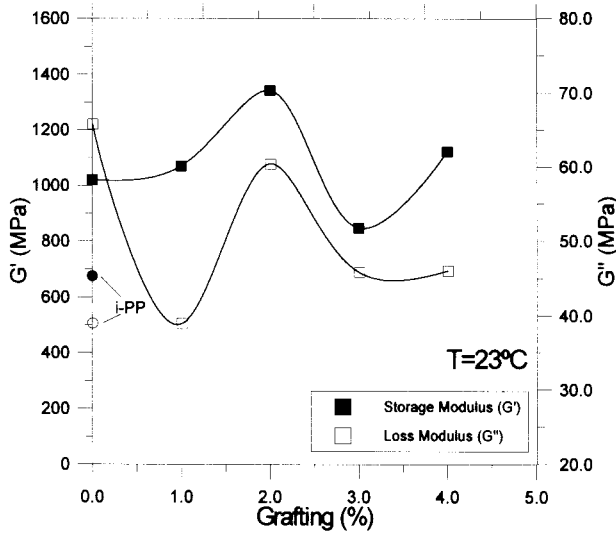
Figure 10 Storage modulus G' and loss modulus G'' determined at room temperature versus grafting level in the interfacial agent a-PP-SA.

rium between the elastic and the viscous response of the composite; meanwhile, 4% of grafting in the interfacial agent seems to minimize such nonequilibrium features between the modulus components.

Likewise, Figure 10 shows the evolution with grafting of both storage modulus G' and loss modulus G'', measured at room temperature (23°C). Once again, they follow a quadratic evolution similar to that found before and provide further evidence of the dynamic interfacial effect as discussed that, because of the flow interchange through a defined and finite area (interface), ought to yield a quadratic evolution. Plotting the loss factor (tan δ), storage modulus (G'), and loss modulus (G'') versus grafting, at room temperature, one can establish the evolution of this parameter for further correlation with macroscopic mechanical properties. Figure 11 displays the evolution of tensile modulus for the different composites, measured at room temperature (23°C), versus the interfacial agent grafting level. The quadratic evolution found seems to show a compromise situation between the elastic and the viscous response of the material whose microscopic yielding was previously discussed. In fact, the presence of a-PP-SA(1%) in the composites means a decrease in the elastic modulus at a macroscopic scale, exactly in the same way that was previously detected for the complex modulus, as a combination of the responses obtained for the composites displayed in Figure 10. Because the elastic

modulus is determined under normal stress conditions at the early stages of the strain, the presence of 1% of polar groups grafted in a-PP-SA(1%) induces a flexibilization with respect to the original PP/mica system. An increase of twice [a-PP-SA(2%)] and three times [a-PP-SA(3%)] in the number of polar groups grafted in the interfacial modifier results in an increase of the matrix/particle interaction level through their interface, also inducing an increase of the elastic modulus (E), higher than that of the original composite system. The presence of either a-PP-SA(2%) or a-PP-SA(3%) as interfacial agent results in values far from equilibrium, as determined from either the thermal (discussed for Fig. 5) or the dynamic mechanical analysis (Fig. 10).

In Figure 10 it can be noticed that the presence of a-PP-SA(2%) as interfacial agent increases the elastic component G' as well as the loss component G'' of the complex modulus, both of them being the highest of all the composites studied. On the contrary, the presence of a-PP-SA(3%) results in a decrease of both G' and G'' to values even below that of the original PP/mica composite. However, from a macroscopic point of view, the evolution of the elastic modulus E with the grafting level in the interfacial agent, as shown in Figure 11, confirms that the system with a-PP-SA(3%) generated the highest values.

Finally, as shown in Figure 10, an increase of the G' and G'' values for PP/mica/a-PP-SA(4%) over those of the composite with a-PP-SA(3%) can
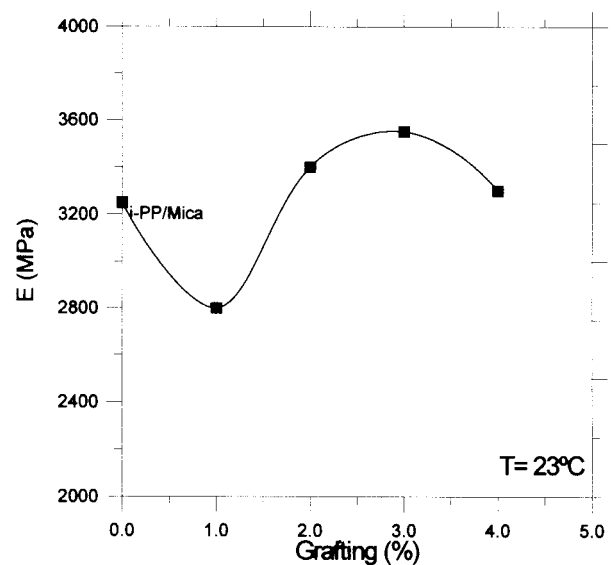

Figure 11 Tensile modulus E at room temperature versus grafting level in the interfacial agent a-PP-SA.

be observed. Meanwhile, at the macroscopic scale (E values in Fig. 11) the PP/mica/a-PP-SA(4%) system showed a decrease to values similar to those of the original PP/mica composite. These seemingly contradictory results suggest some considerations about the physical sense of the elastic modulus E. As is well known, on one hand, this parameter (E) is mainly related to the amorphous/crystal ratio in the case of a semicrystalline polymer such as PP. This is the reason that E must be obtained at the first stages of the strain during the tensile test, in that the number and size of the crystals and their aggregates are strongly related to this parameter. On the other hand, when a component (the mica particles) is dispersed in the polymer bulk, the obvious effect would be an increase in the elastic modulus, too, and thus in the stiffness of the system. As a consequence, when the composite material is based on a semicrystalline polymer, and because of the nucleant effect of the reinforcement particles, the two above-mentioned effects are necessarily combined.

As discussed earlier, in Figure 5 the $\Delta\lambda$ parameter was plotted as representative of any potential crystal/amorphous equilibrium in the polymer matrix, which could be reached by the presence of any interfacial modifiers in an optimized composite. Zero values for this parameter would identify this target.[11,12,28] From Figure 5 it may be observed that such a value ought to be reached either by interpolation [conducting to a hypothetical a-PP-SA(1.5%) interfacial agent] or by extrapolation of the curve [a-PP-SA(4.5%)]. Both inter- and extrapolated values would yield the same elastic modulus according to data displayed in Figure 11, and then that equilibrium state also would have been found from the macroscopic response of the composites.

The foregoing results and remarks seem to provide a way to configure tailor-made composite materials based on thermoplastics polymers. Investigations are in progress now that seek further correlation with other macroscopic parameters such as strain and strength levels under normal load conditions.

CONCLUSIONS

By replacing only of a small amount of the polymer matrix by an interfacial agent (a-PP-SA) interfacial modifications are induced in the PP/mica system. The induced interfacial changes can be studied from either a macroscopic or a microscopic point of view; however, if these interfacial changes can be measured by means of the macroscopic parameters of the system, they must be detected by measuring the microscopic parameters, but not the reverse.

Otherwise, the well-known nucleating effect induced by mica on PP is confirmed from the crystalline variations detected into the polymer bulk as well as by those attributed to the presence of interfacial modifier agents acting from the matrix side. The fact that those changes follow a quadratic evolution also agrees with the proposed interfacial nature of the phenomena. Furthermore, there seems to be a critical level of grafting on the interfacial agent, which maximizes the polar interaction level between PP and mineral particles across the interface of the heterogeneous systems.

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