The Role of a Novel *p*-phenylen-bis-maleamic Acid Grafted Atactic Polypropylene Interfacial Modifier in Polypropylene/Mica Composites as Evidenced by Tensile Properties

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ABSTRACT: Present work is devoted to the study of the tensile behavior of polypropylene (PP)/mica composites with improved interfacial interactions from the matrix side caused by the presence of a *p*-phenylen-bis-maleamic acid grafted atactic polypropylene (aPP-*p*PBM) as an interfacial agent. Hence, aPP-*p*PBM was previously obtained, in our laboratories, by reactive processing in the melt of a by-product (atactic PP) from industrial polymerization reactors. Present article is two-fold, on one hand it has been planned to evidence the so called interfacial effects caused by this novel interfacial agent (aPP-*p*PBM) yielding better final properties of the heterogeneous system as a whole as revealed by tensile mechanical properties, and on the other to obtain models to forecast the overall behavior of the system. For such purpose, a Box-Wilson experimental design considering the amount of mica particles and of interfacial agent as independent variables was used to obtain polynomials to forecast the behavior of the PP/Mica system in the experimental space scanned. The existence of a critical amount of aPP-*p*PBM to optimize mechanical properties appears to emerge. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 113: 3929–3943, 2009

Key words: PP/mica composites; interfacial activity; aPP-*p*PBM; tensile properties; modeling; FESEM; SEM

INTRODUCTION

To induce any interfacial alterations from the matrix side by means of interfacial agents or interfacial modifiers has been usually used to enhance properties of polymer based composites. When modifications are produced from the matrix side, the interfacial additives appear to be chemically similar to the polymer matrix.[1–6] This implies that the understanding of the interfacial phenomena taking place appears as a very important aspect to be considered in the study of heterogeneous materials based on polymers such as composites[6–15] or polymer blends.[16–18] As the effect of the inter-phase on the properties of a multi-component material depends of its amount and characteristics,[19] the existence of an efficient balance of the interfacial interactions taken place becomes as critical in the concerning to consider the material as useful in terms of final performance.[19,20]

Previous works by authors have revealed that little amounts of interfacial agents replacing part of the polymer matrix in composites are enough as to modify significantly transport phenomena across the inter-phase between components, and so as to enhance the final properties of these kind of polymeric materials.[7–16,21,22] However, the high complexity of polymer systems makes that, nowadays, there is still much to investigate about the macroscopic behavior in terms of its microscopic origin, and much more when interfacial phenomena implies great changes in the overall behavior of the multiphase system.[21,22]

This article deals with the interfacial modifications induced in PP/mica composites by a functionalized atactic PP containing *p*-phenylen-bis-maleamic acid grafted groups (aPP-*p*PBM). This interfacial modifier was obtained in our laboratories from a polymerization reactor by-product such as an atactic PP.[23]

The interfacial modifications of similar composite systems have been already performed in our group by means of other families of interfacial agents such as succinic anhydride and succinil-fluoresceine grafted atactic PP and succinic anhydride isotactic

TABLE I
Properties of iPP (ISPLEN 050) and aPP Raw Material for aPP-pPBM

| Polymer | Molecular weight | | | Melt index 190°C; 5.0 kg (g/10 min) | HDT (°C) | ΔH_m (J/g) | T_m (°C) | ΔH_c (J/g) | T_c (°C) | T_g (°C) | Density (g/cm³) |
	M_w	M_n	HI								
iPP	334,400	59,500	5.62	5.00	5.80	87.5	164	−87.7	117.5	−13.0	0.90
aPP	54,000	2700	12.00	----	----	----	----	----	----	−22.4	0.85

PP. These modifications were ascertained to be proper by way of many analytical techniques such as mechanical (tensile and impact properties), dynamic-mechanical, thermal, infrared and optical microscopy, and so on.[7–16,21–25] Moreover, the preferential location of the interfacial agent in the so called inter-phase rather than in the polymer bulk was suggested from dynamic-mechanical properties for other interfacial agents[21–25] and confirmed by means of synchrotron infrared micro-spectroscopy in the case of a PP/Mica composite system modified with aPP-pPBM.[26] Further, not only the presence and preferential location of aPP-pPBM in the surroundings of mica reinforcement was ascertained by synchrotron FTIR microscopy but also the evidence of coating was found by mapping of appropriate IR reference bands assigned to the interfacial agent and the neat iPP matrix associated to morphological images.[26]

Besides of ascertaining the role of aPP-pPBM as interfacial modifier, the purpose of present study is to find a correlation between each one of the tensile parameters and the composition of the PP/Mica composite with modified inter-phases system studied. Therefore, a Box-Wilson surface response methodology statistical design was used to model the system behavior in all the experimental range scanned. From these a series of remarks concerning the complex character of this kind of systems have been discussed at present work.

EXPERIMENTAL

Materials

An isotactic PP, ISPLEN 050 (Repsol-YPF), and a mica (potassium aluminum silicate platelets, by Alsibronz®), as polymer matrix and reinforcement particles, respectively, were used as starting materials. The reinforcement particles were chosen because of their mean size and because their particle size distribution remains constant before, during and after the processing steps.[13,21,22] Some of the physical properties of PP and mica (as received) are listed in Tables I and II, respectively.

The interfacial agent used was a chemically modified atactic PP with p-phenylen-bis-maleamic acid grafted groups (aPP-pPBM) with 14.8% w/w (4.9 × 10^{-4} mol/g $_{polymer}$). This interfacial agent was obtained in our laboratories from an atactic PP, by-product of industrial reactors to obtain commercial grades of isotactic PP. Main physical properties of the atactic PP as received have been also compiled in Table I. Obtaining and characterization procedures of the aPP-pPBM whose main chemical structure is shown in the Figure 1 were fully described elsewhere.[23]

Processing

Composites were compounded, by incorporating the mica platy mineral reinforcement -between 10 and 40 w/w percent- and the interfacial agent (a-PP-pPBM) –between 10^{-3} and 10 w/w percent- to the molten polymer bulk, in a Rheomix 600 chamber at 190°C, attached to a Rheocord 90 (Haake), following the Box-Wilson worksheet according to Table III. The interfacial agent was incorporated to the system by replacing the same amount of the PP acting as matrix in the composite material. Additional compounds were prepared in the absence of aPP-pPBM in order to serve as contrast samples of the unmodified PP/Mica binary system (Table IV).

Once the components were well mixed (five minutes after the torque values were stabilized), the resulting material was milled to pellets and further
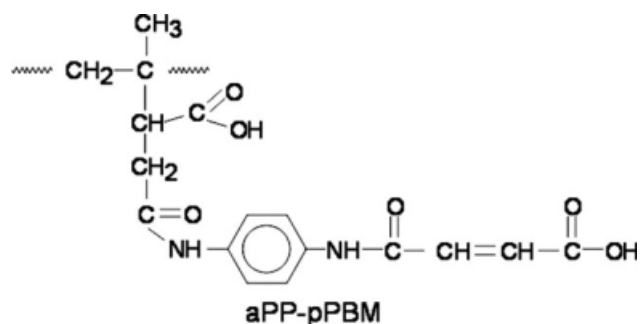
TABLE II
Properties of the Mineral Reinforcement Used

Reinforcement	Density (g/cm³)	specific surface (BET) (m²/g)	Mean particle size (μm)	Supplier
Mica	2.85	1.5	79.8	Alsibronz

Figure 1 Atactic polypropylene with p-PBM grafted groups (aPP-pPBM).

	Controlled factors		Measured parameters				
				Tensile strength (MPa)		Elongation (%)	
Exp.	Mica (%)	aPP-*p*PBM (%)	Modulus (MPa)	At yield	At break	At yield	At break
1	14.4	1.465	1735	33.55	31.75	4.45	8.89
2	35.6	1.465	3685	25.59	34.78	1.36	1.79
3	14.4	8.535	1916	31.10	27.35	4.22	13.03
4	35.6	8.535	3257	35.60	34.56	1.66	2.65
5	10.0	5.000	1649	32.55	30.61	6.88	12.82
6	40.0	5.000	3497	38.15	41.56	1.18	1.78
7	25.0	0.001	2358	34.94	31.81	2.03	5.45
8	25.0	9.999	2448	33.05	28.57	2.49	8.13
9	25.0	5.000	2620	35.23	33.43	1.99	4.64
10	25.0	5.000	2678	35.05	32.44	2.28	5.92
11	25.0	5.000	3043	35.11	33.92	2.11	5.62
12	25.0	5.000	3153	35.70	34.23	1.91	4.26
13	25.0	5.000	2746	34.86	33.61	1.87	5.34

injection molded at 200°C in dog-bone shaped samples by using a Babyplast 6/6 micro-injection machine with a clamping force of 62.5 kN. The dog-bone specimens obtained were the referred as 1BA Type in UNE-EN ISO 527-2 standards for tensile properties.

Characterization procedures

Tensile mechanical properties were measured (for all the specimens resulting from the Box-Wilson worksheet -Table III- plus the additional experiments compiled in Table IV) over the little injection molded dog-bone specimens (1BA type) by following the UNE-EN ISO 527-2 standards. These measurements were conducted in an Instron 4200 dynamometer equipped with a high resolution extensometer (HDR). The universal testing machine was operated at room temperature (23°C) and 50% of humidity. The parameters associated to the specimen were: specimen width (5.0 mm); specimen thickness (2.0 mm); extensometer gage length (20.0 mm); and specimen gage length (50.0 mm). Crosshead speed was established in 1mm/min for modulus calculations,

being programmed the experiment to change to 4mm/min in crosshead rate for the other tensile parameters calculations (tensile strength and elongation determined both at yield and at break point). In all the case the results were averaged with at least ten measurements.

Scanning Electron Microscopy (SEM) micrographs were taken over the tensile fracture surface of selected samples once gold coated by a sputter coater Emitech, K550x model. For such purposes, a Field Emission Electron Scanning Microscope (FESEM), Jeol JSM-6305F model, was used for the morphological observations and a SEM, Jeol JSM-6400 model, with back scattered electron detector for EDX analysis was employed in order to observe mica particles distribution.

RESULTS AND DISCUSSION

Fundamentals

The combination of a polymer with any kind of reinforcing particles implies to consider the existence of interactions between these and the macromolecular

TABLE IV
Tensile Properties of the Neat PP and of the Unmodified Injection Moulded Polypropylene/Mica Composites (Without Interfacial Agent) Obtained Under the Same Conditions Than the PP/Mica Based Composite Materials

Sample PP/mica	Modulus (MPa)	Tensile strength (MPa)		Elongation (%)	
		At yield	At break	At yield	At break
100/0	1000[a]	31.7	30.6	9.3	>500
90/10	1100[a](970)[b]	32.7[a](33.0)[b]	31.8[a](31.2)[b]	4.8[a](6.6)[b]	11.0[a](11.1)[b]
75/25	2500[a](2504)[b]	36.0[a](34.5)[b]	32.0[a](32.0)[b]	2.3[a](2.0)[b]	5.6[a](5.0)[b]
65/35	3400[a](3400)[b]	36.8[a](35.3)[b]	33.3[a](34.8)[b]	1.5[a](1.1)[b]	2.2[a](3.0)[b]

[a] Measured property.
[b] Model forecasts.

chains that form the polymer phase. These interactions must necessarily be taking place trough a dynamical region where transport phenomena (mass, heat and momentum) occurs simultaneously. This region, of finite thickness, is the so called inter-phase, and plays a crucial role in the overall behavior of the material as a whole. Moreover, the effect of the inter-phase and so, the changes produced at this scale, on the properties of a multi-component material strongly depends on its amount and characteristics.[19,21–24]

The assumption that the interfacial region is finite implies that when an interfacial additive is present, it must be necessarily constrained. This support the idea of the existence of a certain amount of interfacial agent considered to be critical in the concerning to enhance the interactions between the phases of the system. Consequently, amounts of interfacial agent close to this critical concentration are expected to cause increasing improvements of the occurring interactions (that it is possible to be ascertained whatever scientific tool the researcher undertakes the study if the problem is well focused) till a limit or threshold value. When this is surpassed no further or even a decay in interactions (and then in properties) is expected to occur, simply by the fact that the interfacial region is now not able to host the interfacial agent excess and then the system may trend to evacuate it to the polymeric phase being caused then the loosing of the thermo dynamical equilibrium in the multiphase system resulting in worse ultimate properties.

An important aspect to be considered would be the fact that the reinforcing particles, which the dispersed phase consist in, could vary either in shape or in size during the processing steps leading the material to the solid state. This simply remark, that can induce the researcher to ascertain seemingly interfacial changes in the composites, is often dismissed in plenty of works in literature. The later would lead to consider as real interfacial changes what are not but mere changes in the flow dynamics of the system. So, choosing the adequate reinforcing particles don't suffering such changes becomes as critical when pretending to isolate the real and only effect of any interfacial treatment, in our case by means of an interfacial agent, causing changes in any composite material.

It is also well established that the amount of interfacial region able to host the active principle (interfacial agent) not only depends of the type of materials present in the hetero-phase system but greatly also of the way it has been shaped (being passed to the solid state). This obvious concept is usually dismissed by seemingly fundamental scientific studies considering this step as trivial and almost unimportant. In these terms composite materials (and also neat polymers)

can be considered as complexes systems since they display a high level of organization without any external organizing principle being applied. A rough definition of a complex system is that consisting in many blocks or "agents" capable of exchanging stimuli with one another and with the environment, resulting in behavior far from the expected from the knowledge of the characteristics or blocks that does not even give a glimpse of the behavior of the system itself. Consequently, complex systems cannot be understood by studying parts in isolation because the essence of the system lies in the interaction between parts and the overall behavior that emerges from those interactions.[27,28] By assuming this principle it is obvious that processing step is one of the main aspects of those for obtaining composite materials and polymers in general, which makes complexity to emerge. Since it is possible to construct a Box-Wilson model from a series of independent terms chosen on the basis that interaction between them must occur, and it must be highly representative of the overall behavior expected for the system, these models appears as agent based model like in order to obtain information. Agents based modeling requires assume that some phenomena can be modeled directly in terms of algorithms rather than in terms of equations.[27,28] In other words, just the contrary than the normal or reductionist approach followed in physics, chemistry, biology and economics, which main consideration is that once the behavior of each block is known the overall behavior of the system can be achieved.[27] Nevertheless, since the Box-Wilson methodology doesn't consider the processing step but only a series of independent terms called characteristics, it results obvious that complexity, if any, must emerge from the interactions occurring between components. The interaction between the polymer and reinforcement if effective it must take place through the inter-phase, a finite region a few angstroms width where transport phenomena take place. However, the region between 1 and 10^3 nm, the realm of self-assembly molecules is poorly understood.[27]

In the system under study, the variables that can influence the ultimate properties of the system are the amount of the components of the composite (polymer, reinforcement and interfacial agent) and those derived from the processing operation such as crystallization rate, shear rate, particle orientation, core shell effects and so on, all of them time dependent. So, our strategy have been based in considering the processing step as the same for all the experimentation in order to have reasonably controlled its effect in final performance and so try to isolate, as far as possible, the neat effect of the interfacial agent in the overall behavior of the system.

It is perhaps noteworthy to mention that the Box-Wilson methodology used at present work is a

TABLE V
Coefficients of the Response Surface Polynomials from the Box-Wilson Experimental Design for Each One of the Characteristic Parameters Considered

		Linear terms			Interaction term	Quadratic terms	
Polynomial Equation: $a_0 + a_1.x_1 + a_2.x_2 + a_3.x_1.x_2 + a_4.x_1^2 + a_5.x_2^2$							
$x_1 = $ [Mica]; $x_2 = $ [aPP-pPBM]							
	$<r^2>$	a_0	a_1	a_2	a_3	a_4	a_5
Elastic modulus	0.933	−276.4	132.5	241.9	−4.063	−0.8512	−14.46
Tensile strength (at yield)	0.955	31.79	0.1321	0.02959	0.01641	−0.000873	−0.06207
Tensile strength (at break)	0.948	32.89	−0.2911	0.5178	0.02789	0.009101	−0.1540
Elongation (at yield)	0.968	11.76	−0.5995	−0.1079	0.003489	0.008405	0.00459
Elongation (at break)	0.982	17.36	−0.7071	0.2961	−0.02184	0.008521	0.05609

central rotary composite design consisting in a series of (2^k+2k+1) experiments plus (2+K) central replicated runs (k; number of independent variables).[29,30] In essence, the model would correspond with a factorial design augmented with a star design plus a series of replicated runs of the central point which coded variable is (0, 0). The interval for the independent variables (mica and aPP-*p*PBM amounts in the composite) compiled in Table III are the resulting of considering the range between 14.4 and 35.6% in the case of Mica and 1.465 and 8.535% in the case of aPP-*p*PBM when constructing the Box-Wilson Experimental worksheet.[29,30]

Polynomial fits and analysis of variance (ANOVA)

The main body of the work developed in this article was performed by following a Box-Wilson experimental design with the purpose of obtaining models capable to explain the behavior of the system in terms of the mechanical response. So, Table IV compiles all the results obtained by following the experimental worksheet that considers two independent variables (also named controlled factors) and each one of the tensile mechanical parameters considered in this investigation. Such as mentioned in the experimental section, the two controlled factors, or independent variables chosen here were the amount of mica and interfacial agent (aPP-*p*PBM) to be present in the composite while as the dependent variables at this first approach, the characteristic parameters of the three main regions at the stress/strain curves : elastic initial zone (elastic modulus) and the yield and break points (strength and strain) were considered.

Data sets of each one of the mechanical parameters measured were fitted to quadratic models by following the surface response methodology.[30] From here, five different polynomials which describe the evolution of each one of the parameters considered (modulus, strength at yield and at break, and elongation at yield and at break) were obtained. Both the terms as well as the values for the coefficient of

determination $<r^2>$ for each one of the polynomials obtained are compiled in Table V. Moreover, also the parameters for the ANOVA (included $<r^2>$ as listed in Table VI). As shown, the values for $<r^2>$ for whatever polynomial we consider, higher than 0.9 in all cases, appear as excellent (values higher than 0.75 are considered as very good for quadratic models[29–31]). The term "lack of fit", meaning the percentage of the pure error that explain the lack of fit of a polynomial due to the foreign factors to the model but significant in the response evolution, results as very good, being the corresponding to the modulus and elongation at break higher. These looks to indicate that they are the parameters in which pure error is easier to cumulate that is indeed in agree with the fact that both must be the most sensitive parameters to the stress transmission across the matrix/particle inter-phase as the respectively, starting and end points of the mechanical test. Likewise, the very high value for the "confidence factor" (close to 100% in all cases) indicates that all the factors considered to build the model play a prime role in the behavior of the system. Even more, the latter also would be indicating the right of the assumption made when considered the processing step as the same for obtaining of all the samples in order to try to isolate the effect of the interfacial agent in the overall behavior of the system. Consequently, and based on the above mentioned, we can assume that the behavior of the system can be properly discussed on the basis of the models forecasts.

TABLE VI
Statistical Parameters of the Analysis of Variance (ANOVA)

	$<r^2>$	Lack of fit (%)	Confidence factor (%)
Elastic modulus	0.933	56.0	99.6
tensile strength (at yield)	0.955	11.3	99.8
Tensile strength (at break)	0.948	12.0	99.7
Elongation (at yield)	0.968	4.0	99.8
Elongation (at break)	0.982	58.8	99.9

Influence of composite composition in mechanical properties

As mentioned in previous sections of this article, it results obvious the existence of a critical concentration of both interfacial agent and reinforcement particles that maximize the interactions between components. Therefore, and previously to undertake the discussion of the model predictions, it would be well worth to make a few considerations about the latter on the experimental data compiled in Table III and Table IV. Let observe, for example, the measured values for the modulus of samples with 25% of reinforcement and with 0% (in Table IV), 0.001%, 5% and 9.999% of aPP-pPBM (in Table III). Meanwhile the one with none interfacial agent throw a value of 2500 MPa, that in which only a tiny amount of aPP-pPBM (0.001%), this plays an important role as to change notably the value for this parameter (in this case to down). And what is more important, if compared the samples incorporating 0.001%, 5% and 9.999% we realize that the one with higher measured properties for this parameter is that with the intermediate amount of interfacial agent (Table III). This latter would indicate that the behavior of the system is strongly dependent of the amount of interfacial agent, and what is more important, of the existence of critical values for the concentration of components in a heterogeneous material that can even be ascertained from experimental data if they are properly chosen. A way to avoid the possibility of missing this kind of data due to a bad election of the experiments would be the use of experimental designs. A similar discussion may be developed for the other parameters in Tables III and IV.

Otherwise, it may deserve to notice that the great accuracy of model predictions that can be ascertained from the differences between the values predicted by the different polynomials and the measured values compiled in Table III. Even more, the above mentioned applies even in the case that one of the characteristics of the system is just at the limits of the established model conditions such is the case of the composite material in absence of interfacial agent. In this way, in Table IV we have listed either the measured values for the indicated properties as well as the models forecast for each one of them, being very close each other even at the model limit conditions. It must be noted that Table IV doesn't include predictions for the neat PP due to the fact that in this case the characteristic named as Mica used to build up the model is in the 10 up to 40% range, and consequently the neat PP behavior is out from these models purposes.

In next sections, the mechanical parameters considered are fully discussed on the basis of the model forecasts.
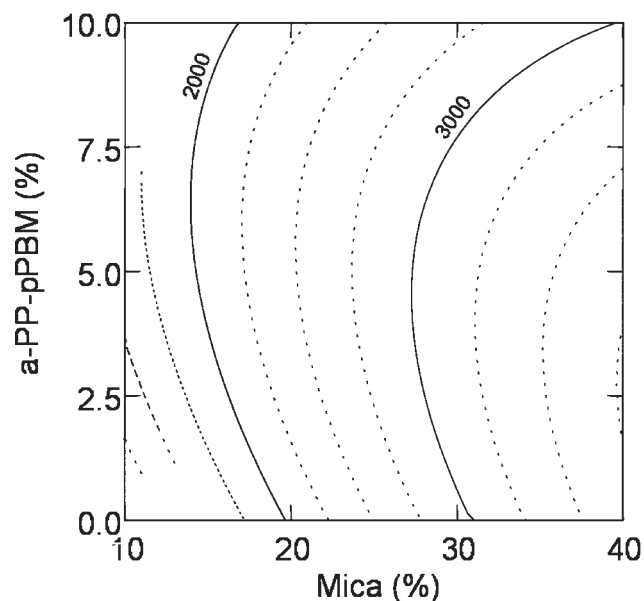

Figure 2 Isoline map showing tensile modulus as a function of mica and the interfacial agent contents.

Influence in tensile modulus evolution

Figure 2 shows the isoline map for tensile modulus as a function of the amount of mineral reinforcement (mica) and of interfacial agent (aPP-pPBM). From this the existence of a critical value for the interfacial agent (and/or the mica amount) is clearly observed. Meanwhile, at low levels of reinforcement the critical amount of aPP-pPBM to maximize modulus is quite high (7%), when mineral fraction increases it becomes lower. This phenomenon is twofold. On one hand, the lower is the mineral fraction the higher is the amorphous phase able to host the interfacial agent, and on the other once the interfacial optimum has been surpassed the property of the system decrease. In other words, aPP-pPBM works properly to enhance this parameter till a certain limit, after what it effect results just the contrary.

Figure 3 shows a series of curves from the model forecasts that represent the modulus evolution with the amount the mineral reinforcement at the different quantities of interfacial agent displayed.

A first approach looks to indicate that the higher is the mica content the higher is modulus, and so the rigidity of the system. However, the presence of the interfacial agent let us make a series of remarks about the latter. At a glance, a critical point clearly showing a change in the tendency of the behavior can be observed nearby 25% in mica. Since below this point while interfacial agent increases the modulus values do and above it occurs just the contrary, the latter can be clearly assumed. When studied this figure more accurately it can be concluded that the above mentioned is only strictly true for the composite with the lower amount of mica (10%). The
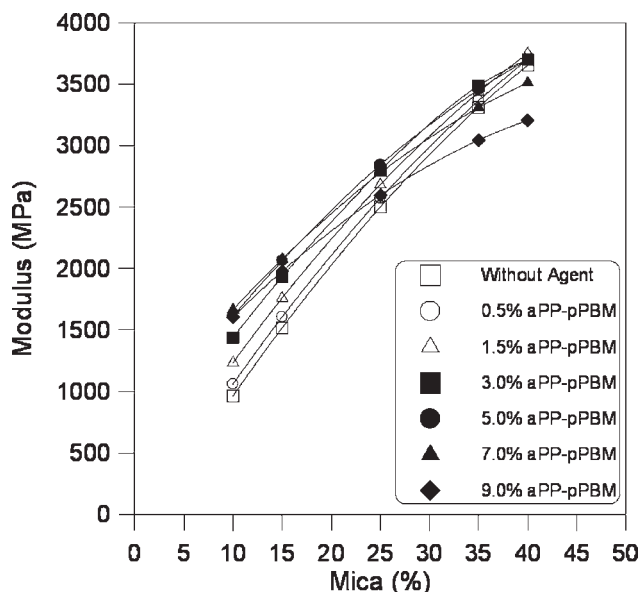
Figure 3 Evolution of tensile modulus versus mica content at different amounts of interfacial agent.

presence of a mere 5% of additional mica makes that the maximum value for this property is reached for 5% of aPP-*p*PBM and not for 7–9% of it as occurred previously. A content of 25% in mica leads the system to improve the behavior when 3-5% of interfacial agent is present, and what is more important : the highest level of aPP-*p*PBM throws values similar to those with only 0.5 or 1.5% of agent, clearly indicating that such an amount has saturated the interfacial area available and then the capability of proper interfacial interactions. Higher levels of mica (35–40%) lead the system the need of lower amounts of interfacial agents (1.5-3%) to throw the highest performance, which naturally, becomes worse with increasing levels of interfacial agents.

As a partial conclusion, it can be supported that the level of interfacial agent present (and the kind of it too) strongly depends at least of the amount of rigid phase in the composite and, consequently, of the amorphous phase and the interfacial area generated too.[32,33]

In the same sense the model predictions for modulus as a function of the interfacial agent and for the concentration of mica indicated have been represented in Figure 4. So, a series of curves representing he latter are displayed (and naturally the higher is mica the higher is the rigidity of each system and the modulus). The first remark to be done is the fact that all of them exhibit a maximum reached with lower amount of interfacial agent while mica increases. So, the more mica the lesser amount of interfacial agent is necessary to lead the composite system to a critical point in terms of composition and desired property. This latter can be assumed to be due by the fact that mica must be necessarily em-

bedded in the amorphous phase and consequently the more mica is present in the system the more constrained the amorphous phase is, and so a lower amount of this amorphous phase is accessible to host the interfacial agent. This effect was already observed by authors for other polymer composite systems.[21–25] An interesting remark can be extracted by the observation of the separation between curves one another. The more separate one another are them the response of the system is governed mainly by the polymer matrix response and little amounts of mineral greatly affect the matrix behavior. On the contrary, the closer are them then it is the mineral phase which governs the system and increasing levels of it affect poorly the matrix. To conclude only to say that, at least under our experimental conditions, the amount of interfacial agent that maximizes the behavior of the system in terms of tensile modulus is different, decreasing with an increase in mineral content. Otherwise, the very important influence of aPP-*p*PBM as interfacial agent to improve modulus in this family of composites is clearly established. In other words, this parameter appears as very sensitive to the presence of interfacial agent in the system.

Influence in tensile strength evolution

Figure 5 shows the contour plot of the evolution of the tensile strength at yield [Fig. 5(A)] and at break [Fig. 5(B)] as a function of mica and aPP-*p*PBM. This parameter follows the typical rising ridge evolution [Fig. 5(A)], indicating that a critical point is also determined in such a way that the best conditions to maximize tensile strength at yield would be those of
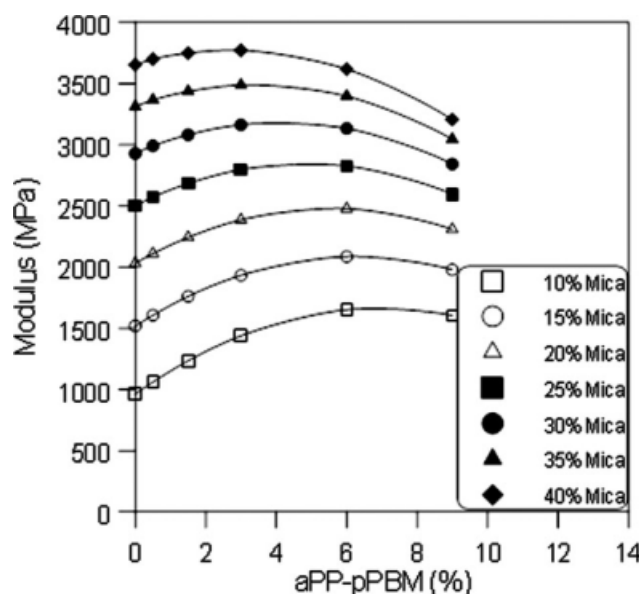

Figure 4 Evolution of tensile modulus versus interfacial agent at different amounts of mica in the composite.
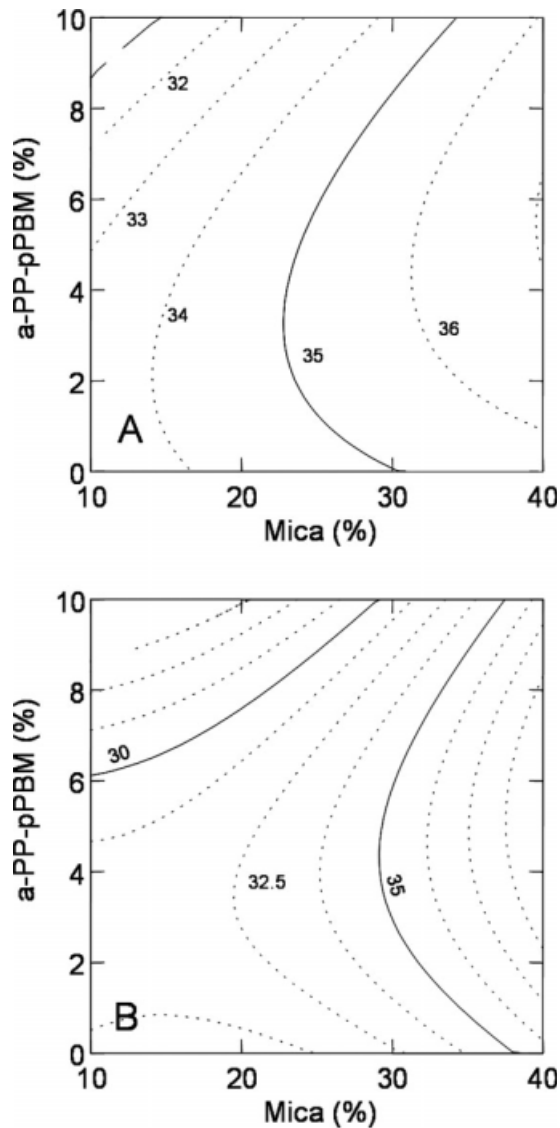
Figure 5 Isoline maps showing tensile strength at yield (A) and at break (B) as a function of mica and the interfacial agent content.

a composite with 30% of mineral and somewhat close to 4% of interfacial agent. The existence of a critical concentration for both mineral and interfacial agent appears to emerge once again.

When studying Figure 5(B) we observe that the behavior of tensile strength at break shows that also at 4% of aPP-*p*PBM a critical point is observed. Obviously, better properties for this parameter would be possible by incorporating higher amounts of interfacial agent till values close to 6%, but in this case Modulus (Fig. 4) would decay.

Figure 6 shows the evolution of tensile strength versus mica for the level of interfacial agent displayed in the plot legend such as predicted by the model either when determined at the yield point [Fig. 6(A)] or at the break point [Fig. 6(B)].

When discussed on Figure 6(A), besides to the fact that strength increases with mica content, we observe that at the lowest contents of mica considered (10–15%) the presence of interfacial agent not only doesn't improve the performance of the system but even go to worse with amounts of interfacial agent surpassing 5%. This is probably because at such reinforcing particles amount there is too much amorphous phase available to host the interfacial agent. Consequently, interfacial agent presence below 3% is diluted enough in the amorphous phase as to play any efficient role as interfacial agent in such conditions. On the contrary, when the level of
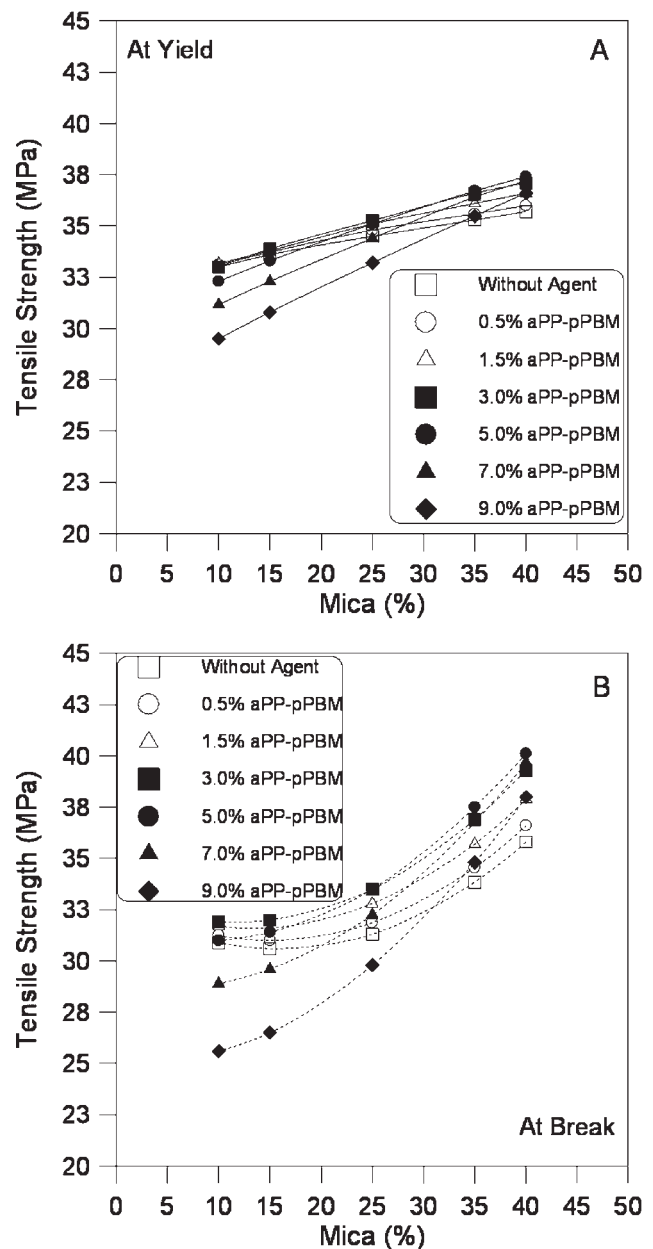

Figure 6 Evolution of tensile strength versus mica content at different amounts of interfacial agent. A: at yield; B: at break.

interfacial agent surpasses 5% (and increasing as close to 9%) this results as too much for the system and so the behavior of the system resembles more a three component system rather than a real two component heterogeneous material.

Increasing amounts of mineral particles aid to change the tendencies. This can be explained by the fact that the increase of mineral particles makes the amorphous phase in the composite (where they are located) to be more constrained, obliging the interfacial agent to be also in a highly constrained scenario. Since this point of view, up to a certain value for mica (25%) the system exhibits just the opposite behavior than the former. Note that at 25% of mica values for tensile strength are similar whatever is the level of interfacial agent excepting those with 9% of aPP-*p*PBM. The former indicates that till this value any incorporation of interfacial agent to the composite is no sense if looking for maximizing this property. This is especially important because properties at yield are the traditionally considered as criteria of design for parts made of these kind of materials. From this figure it can be also evaluated that above 25% of mica in the composite amounts between 1.5 and 3% of aPP-*p*PBM are not only sufficient but optimal in maximizing properties. Even more, both higher and lower amounts of interfacial agent would mean decay in the properties. All the latter is based in the above mentioned criteria of the free amorphous phase able to host the interfacial agent, and then in the self motion possibilities of the agent towards interacting with the mineral reinforcement.

By observing Figure 6(B) we can appreciate two different families of curves: One which exhibits dispersion in tensile strength values, and other shows just the opposite mode with increasing amounts of mica. The former corresponds to composites till 5% of aPP-*p*PBM and the latter to that with higher amounts. Taking in mind that at the break point it is the amorphous phase the final responsible of the ultimate property determined, and that after the so called dragging mechanism occurring after the yield point is surpassed is when the interconnecting chains in the amorphous phase are mainly aligned in the parallel to the load applied, a series of remarks can be exposed in what follows.

The first family of curves in Figure 6(B) above mentioned shows that at low levels of mica the best of aPP-*p*PBM is 3% meanwhile 5% of it is too much and so property appears to suffer an inversion that is more noticeable if we observe the second family of curves. A little more amount of mica appears to change this tendency and now 5% of agent improves the system up to close 3%, fact that is even closer at 25% of mica. Further this amount of mica 5% of agent looks to provide better properties. This fact strongly depends of the capability of the interfacial agent to be diluted and to interact in the body of the interconnecting molecules. Equally as it was observed in Figure 6(A), at low mica contents an excessive amount of interfacial agent results in a counter producing effect in the ultimate performance, but at increasing quantities of reinforcement this situation appears to change, being produced this in the surroundings of 25% of mica. Nevertheless, the highest values are the corresponding to intermediate levels of interfacial agent, being confirmed the existence of an optimum in terms of interfacial agent in order to maximize the property. It is well worth to mention that, although the design criteria lies on properties at yield, the highest resistance is obtained at the break point. And this occurs at the same levels of agent than at yield. The latter appears to be important because if the system is rigid enough and additional criteria for designing final parts would be governed by criteria at break. Meanwhile, at yield the best behavior is obtained around 37 MPa, at break increases beyond 40 MPa for interfacial agents in the 3–5% range.

A complementary way to see this is by the observation of the evolution of curves in Figure 7 where tensile strength versus interfacial agent has been plotted for a series of PP/mica composites as indicated.

In both cases, either at yield or at break, it can be clearly noticed that the higher is mica content the higher is the value for this property. Also, whatever case, the curves exhibit a maximum that increases with mica content. This maximum is the related to the optimal content of aPP-*p*PBM able to maximize this property. It is also well worth to remember that meanwhile the variation of tensile strength with mica is lower than when determined at yield, where the system has evolved by disentanglement molecules. This can be appreciated [Fig. 7(A)] by mentioning that al low mica contents (0–10%) tensile strength looks like stable till 4% of agent after what suffer a sudden decay. Meanwhile for an higher mica ratio the tendency is to grow up to a limit placed at the 3-5% agent interval and dependent of an increasing mica content. The observed in Figure 7(B) is similar but a clearly maximum in the same interval of interfacial agent above mentioned but that grows with the mineral content. So the existence of a noticeable optimum is concluded once again.

Influence in elongation evolution

Figure 8(A,B) exhibit the contour plots for the elongation behavior at yield and at break, respectively, as a function of the controlled factors. At the early stages of the strain processes under normal stress conditions, the polymer chains trend to be reoriented in order to flow parallel to the load applied. Such mechanisms makes possible always a significant
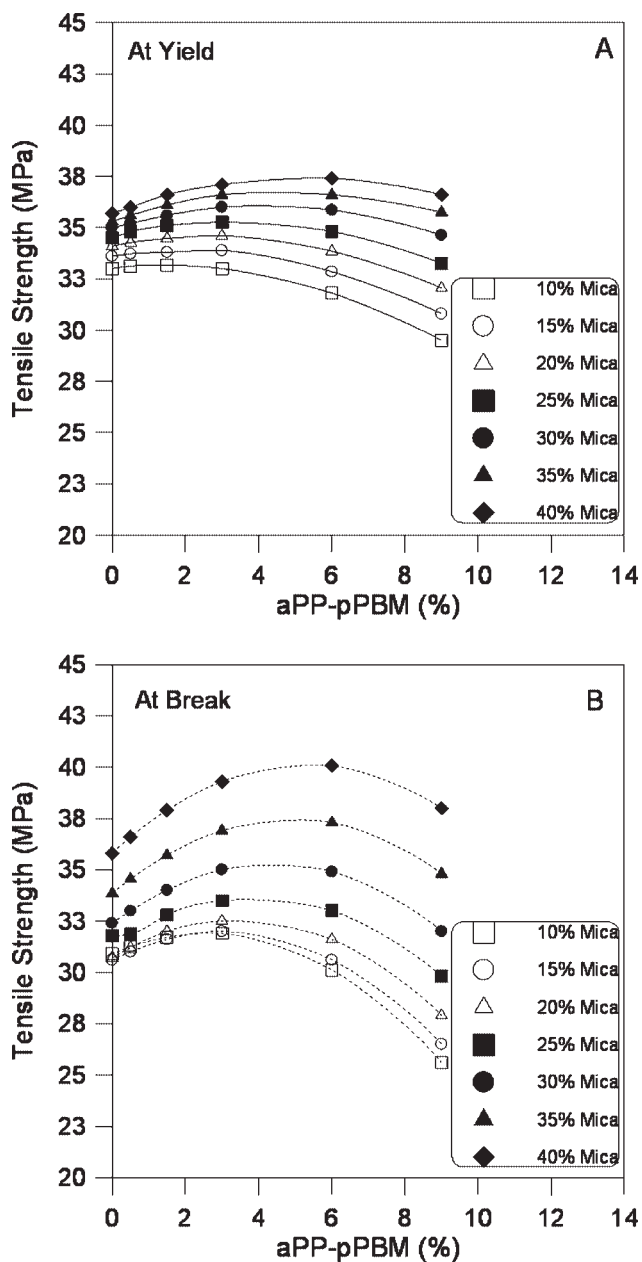
interfacial agent is clearly shown by the elongation at yield contour plot. From Figure 8(A) we can appreciate that the most rigid system, the one that is hardly able to flow under a normal applied force, is that with 35% of mica in absence of interfacial agent and the presence of increasing amounts of interfacial agent leads the system to a slight improvement in the yielding capability of the composites. From both Figures it can also be ascertained that the higher is mica the lower is the elongation in both cases. The difference lies in the fact that meanwhile at yield the parameter is not sensitive to the interfacial agent until at least 25% of mica, as mentioned before, after the yield point once the deformation mechanism progresses by dragging the solid particles close to the break point, all the stresses in the system are supported by those highly stressed so called tie molecules in the amorphous phase, and then the influence
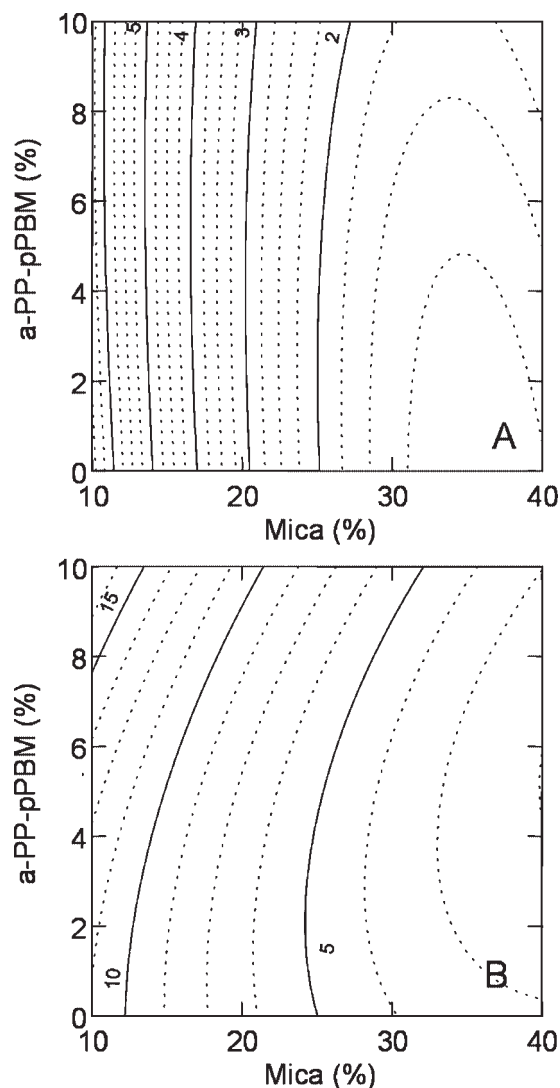
Figure 7 Evolution of tensile strength versus interfacial agent content at different amounts of mica in the composite. A: at yield; B: at break.

number of interconnecting or tie chains in the amorphous phase to be able to reach the yield point through the slippage between their different segments. It means that the polymer matrix is the main responsible of the strain material related to the start of the cold-drawing mechanism. Then the presence of the mica particles in the bulk of the amorphous phase just means a sharp decrease in the composite yield strain values as in Figure 8(A) can be appreciated. Indeed below the 20% of mica content the yield strain isolines appear as straight lines non sensitive to the interfacial agent amount in the composite. Nevertheless, beyond the 25% in mica, the presence of the

Figure 8 Isoline maps showing the elongation at yield (A) and at break (B) as a function of mica and the interfacial agent content.
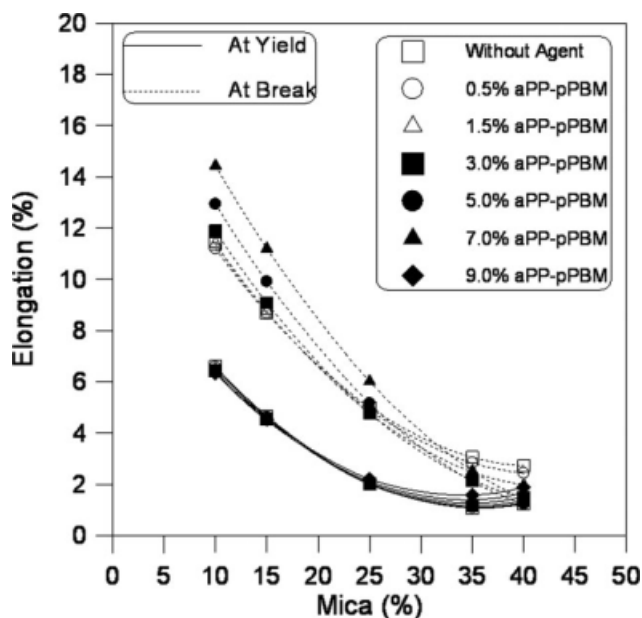
Figure 9 Evolution of elongation (both at yield and at break) versus mica content at different amounts of interfacial agent.

of the interfacial agent in the concerting to avoid the progress of any craze increases notably, mainly in the fore front and in the rear of the dragged mica particles.[33] The latter would be an evidence of the activity of aPP-*p*PBM as interfacial modifier.

Figure 9 shows the evolution of elongation, at yield and at break, as a function of mica for the different content of aPP-*p*PBM displayed.

At a glance we observe that at yield the system performance is rigid enough as to show the same values for the deformation parameter till values for mica close to 25% whatever the concentration of aPP-*p*PBM, being observed afterwards an almost constant elongation with yield evolution with increasing levels of the additive. The former confers a great robustness to discussion over Figures 7 and 8. The real interaction effect can be ascertained from curves at break, where it is observed that even at the first stages (10% of mica) the higher elongation is not produced just at the limits of the interfacial agents' concentration range but at 7%. Attending to the hypothetical final performance of a part built up from this kind of material, very important properties such as permeability or dimensional stability, which are strongly related to the rigidity of the system, and then on the elongation capability, it would be desirable a little deformation either at yield (mainly) or at break. In this way it can be observed that the presence of about 3-5% of aPP-*p*PBM appears as sufficient for this purpose.

From Figure 10 it can be observed the distinct evolution at yield as well as the different ranges strain

values at yield and at break. Although there is an almost constant evolution with the amount of aPP-*p*PBM whatever the mica content, the existence of a critical value, seemly optimal value, near to 3-5% of aPP-*p*PBM is clearly observed for all the composites, and much more noticeable in those highly reinforced (those in the range of 25 up to 40% of mica). By considering that the differences between the values at yield and at break are greatly noticeable, it can be ascertained that for composites (for whatever amount or not of interfacial agent) with contents of mica below 25% the property measures at break is around twice than at yield. This tendency remains even above 25% of mica in the composite but only in the case that the aPP-*p*PBM content is 3% or below. For aPP-*p*PBM contents higher than 3%, in the case of highly reinforced composites, elongation at break trend to similar values to those measured at yield. According with contour plots as displayed on Figure 8 there is not lost of the yielding and cold drawing mechanisms but a shortening in the end elastic zone of the composite due of the presence of the highest levels of the interfacial modifier once over-passed its optimal amount.

To support all the previously discussed for the PP/Mica tensile behavior, a series of SEM micrographs obtained from the fracture surface of the 75/25 w/w PP/mica composites are shown in Figures 11–13. This composition was chosen due to be the corresponding to the central point of the Box-Wilson worksheet as well as to be that what exhibits the critical amount of mica above which the mineral
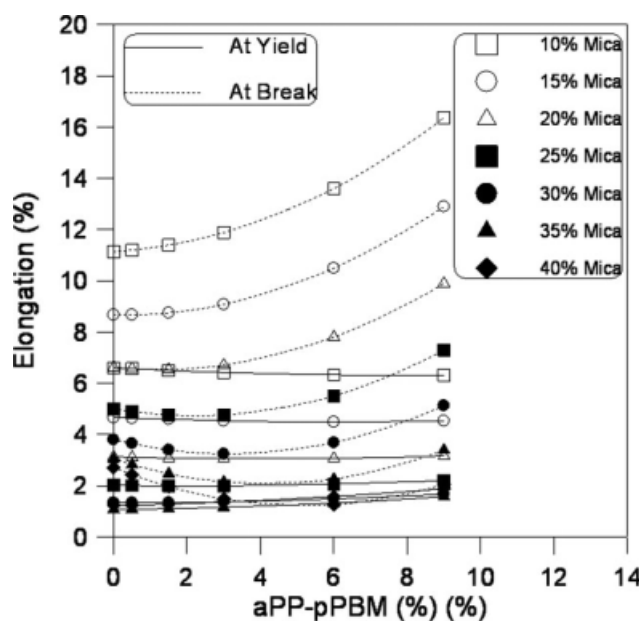

Figure 10 Evolution of elongation (both at yield and at break) versus interfacial agent content at different amounts of mica in the composite.
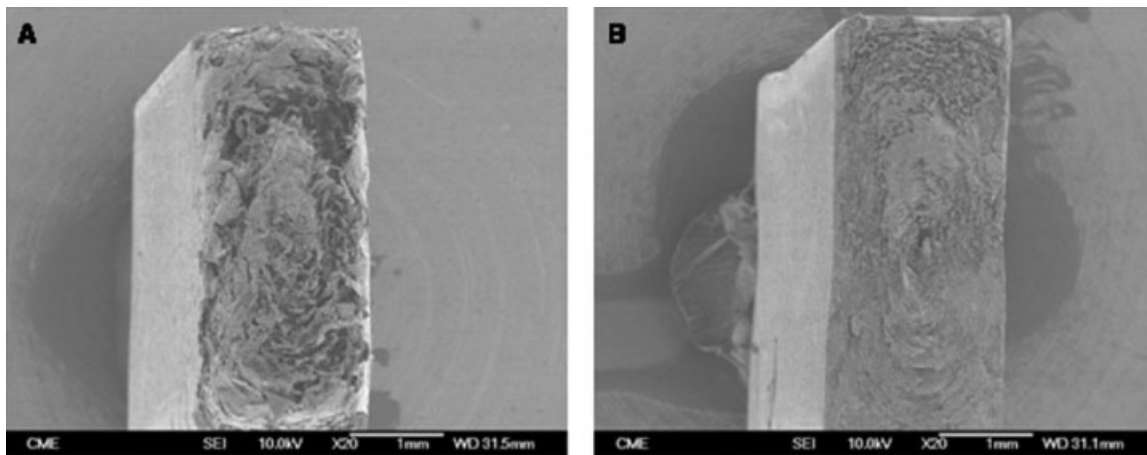
Figure 11 FESEM micrographs of PP/Mica 75/25 tensile fracture surfaces (magnification ×20). Unmodified PP/Mica (A); PP/Mica/aPP-*p*PBM (B).

particles are able to participate in the overall stress transmission mechanism in an efficient manner.

Hence, the micrographs in Figure 11 (20× magnification) are showing almost the whole tensile fracture surface of the 75/25 w/w PP/Mica composites with (B) and without (A) modified inter-phases by the presence of 5% aPP-*p*PBM. It is noteworthy to mention that, as it is well known, the mica particles dispersed in the PP bulk may be considered as stress concentrators. Moreover, the classical ductile fatigue cracks of the PP matrix are clearly distinguished in the unmodified PP/Mica composite (A) at this magnification level. Meanwhile, the tensile fracture surface corresponding to the PP/Mica/aPP-pPBM composite exhibits a much

more homogeneous and smoother tensile fracture surface what evidence the effect of aPP-pPBM as interfacial agent in the composite.

Even such a low magnification level let identify (further the observation of the fracture surface as a whole) the so-called core-shell morphology typical to injection molded specimens as well as to visualize the three classical flow regions, i.e., shear and elongation flows close to the shell region, and the fountain flow around the core all of them symmetrically arranged trough all the section of the observed sample.

Images in Figure 12 are a composition obtained by overlapping, in every case, two different micrographs
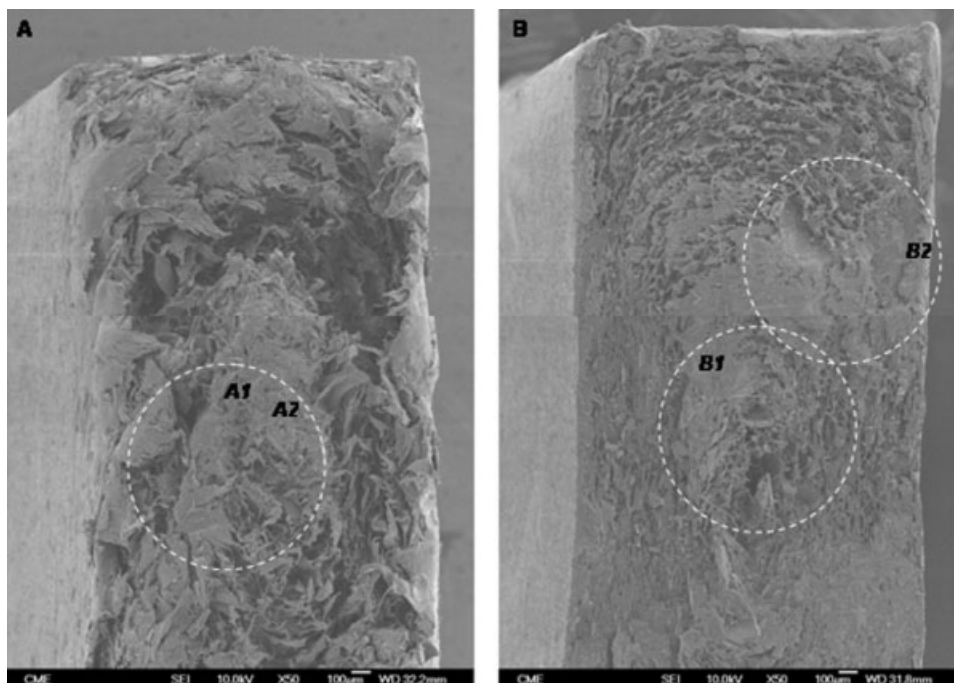

Figure 12 Composition of FESEM micrographs of PP/Mica 75/25 tensile fracture surfaces (magnification ×50). Unmodified PP/Mica (A); PP/Mica/aPP-*p*PBM (B).
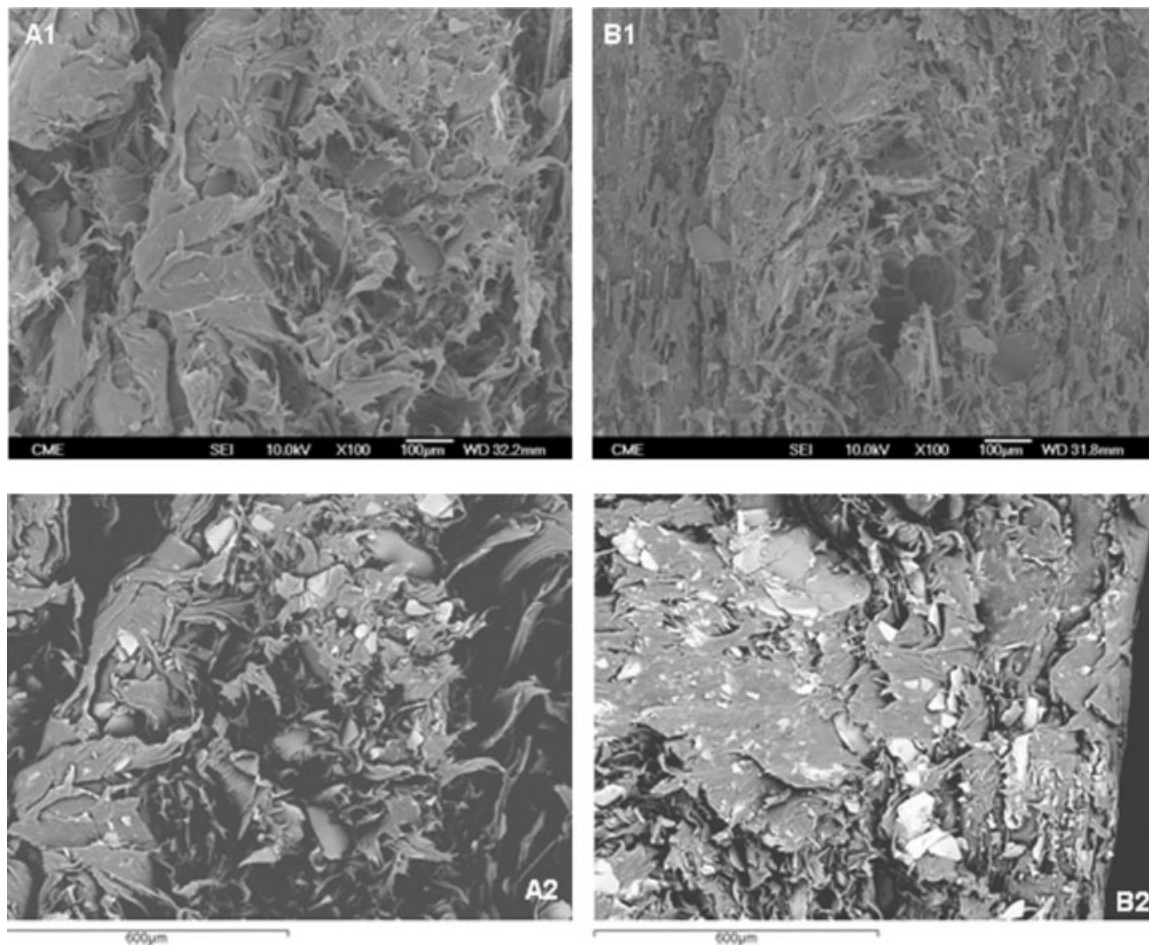
Figure 13 FESEM (top) and SEM-EDX (bottom) micrographs of PP/Mica 75/25 tensile fracture surfaces (magnification ×100). Unmodified PP/Mica (left); PP/Mica/aPP-*p*PBM (right).

under the same observation field than in Figure 11 but at higher magnification (50×). These images let observe the detail of the ductile fatigue cracks in both composites. It can be assumed that, according to the tensile test fundamentals concerning morphology, the fracture initiates after a localized plastic deformation all along the cross section of whatever specimen, as so, leads to the nucleation of the microscopic cracks around the stress concentration sites. So, the increase in the interaction level between mica particles and PP matrix caused by aPP-*p*PBM can be clearly concluded from the much lower size of the cracks in the modified composite (B) respecting the unmodified one (A) besides of a cleaner surface fracture in the former (B). Moreover, the shell in the unmodified PP/Mica composite (A) exhibits a much higher deformation compared with the other zones of the fracture surface. Also, striations that spread out from the fracture initiation sites (in the case of the unmodified composite) are larger than those corresponding to the modified one.

On the other hand, the PP/Mica/aPP-*p*PBM composite image (B) shows a higher nucleation of the microscopic cracks caused by the increase in the interaction between PP and mica. In this sense, higher magnification (100×) images taken from the marked zones (dotted circles in Fig. 12) collected by FESEM, top images (A1 and B1) in Figure 13, let clearly observe the detail of the clean inner wall of the holes left by mica particles when pulled out from the PP bulk in the case of the unmodified PP/Mica composite (A1). The latter is in a sharp contrast with the images (B1) for the PP/Mica/aPP-*p*PBM composite whose inner walls are showing little filaments coming from the deformation of the PP matrix around each one of the mica particles that had been pulled out during the failure process.

Bottom images in Figure 13 have been obtained for the same samples (the marked as dotted lines identified in Fig. 12) but under the back scattered detector for EDX analysis in order to a preferential visualization of the mica particles embedded in the polymer bulk. Further of confirming the homogeneous distribution of the particles such as expected from the processing steps described previously, these images let observe that flaws and holes appear

as dark features while mica particles (as identified by EDX analysis) and they results as much clear and more coated by the PP matrix in the case of the modified composite (B2) than in the case of the unmodified PP/Mica composite. While the bottom-left image (A2) is focused almost in the center of the fracture surface, the bottom-right photo (B2), what corresponds to PP/Mica/aPP-*p*PBM composite, is displaying a field that includes the outer regions of the fracture surface to confirm the cleanness of the shell regions during the whole deformation process up to failure.

From all the above observations and according the well known three factors that have to be necessarily balanced (opening, shearing, and tearing) to let the material being able to relieve any applied stress, it can be concluded that the tearing factor has been lowered by the presence of this interfacial modifier such as evidenced by the mechanical parameters studied and in view of the close to 30% and 20% decrease observed for elongation at yield and at break, respectively, for the modified composite (PP/Mica/aPP-*p*PBM) respecting the unmodified PP/Mica system (Fig. 10).

Finally, there is a very interesting to remark (to be further studied in a forthcoming work)the correlation between the amount of interfacial agent (aPP-*p*PBM) appearing to optimize the system (3–5%) and those findings on previous works by authors,[8–10] carried out also over mechanical properties on injection molded PP/talc composites where the modifier was a succinic anhydride grafted PP. Those results showed that just a 1.5% of such modifier was enough as to obtain the best performance in PP/talc composites.[8–10] By considering the ratio between the molecular weight of both grafted species (aprox. 3/1) and the amount of interfacial agent necessary to optimize the system in both cases (also in a similar ratio), the suggestion to explore more accurately this aspect in future works appears to emerge.

CONCLUSIONS

The effective role as an interfacial modifier played by a novel atactic PP containing *p*-phenylen-bis-maleamic grafted molecules in PP/mica composites is demonstrated in this work. Furthermore, the possibility to model the performance of the composite by means of a quadratic model considering the different variables affecting the overall behavior of the system is also concluded. From this the complex character of the phenomena associated to the interactions between the rigid and the mobile phases appears to emerge. In such situation, the Box-Wilson experimental methodology has proved to be a powerful tool when attempting to model the tensile behavior

of this kind of systems as well as in order to discuss the experimental results.

From all the above mentioned the real interfacial interactions improvement caused by the presence of the interfacial agent used in has been properly proved by studying the tensile test parameters, and supported by FESEM and SEM observations. Also, and as a consequence of the complex character of the system, the existence of critical points in terms of the amount of each one of the components of the composite, and especially of the interfacial agent able to lead the system to very different properties has been demonstrated.

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