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Flexural behavior of PP/Mica composites interfacial modified by a *p*-phenylen-bis-maleamic acid grafted atactic polypropylene modifier obtained from industrial wastes

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ABSTRACT: The study of the flexural behavior of the polypropylene/mica system with modified interface by the presence of an interfacial agent obtained from an industrial polymerization by-product is one of the purposes of present work. The interfacial agent used was a *p*-phenylen-bis-maleamic grafted atactic polypropylene, aPP-*p*PBMA, obtained in authors' laboratories. Jointly to the study of the effect of the interfacial modification in the composite system, this paper has tried to underline a mathematical model to make predictions of the ultimate properties of the composite. So, a statistical two independent variables Box-Wilson experimental design have been used to model the behavior of the composite system. The two independent variables considered were the amount of mica particles and of interfacial agent. The fact that the flexural test consist in a combination of compressive and tensile stresses emerges from the analysis of both the data and the statistic parameters of the model. Additionally, a lower sensitivity to changes in the amount of the interfacial agent is found if compared to the obtained for tensile properties. Furthermore, an excellent correlation emerges between the flexural modulus forecasts and those obtained under tensile conditions. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 42437.

KEYWORDS: compatibilization; composites; grafting; theory and modeling

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INTRODUCTION

The 1970s energy crisis empowered among others those research activities dealing with the development of new materials with improved properties specially for those sectors related to the best energy proficiency. In the 1990s, both the growing scarcity of natural resources and the environmental requirements acted as concurrent driving forces claiming for advanced materials matching the largest performance requirements.[1–4] At the beginning of the third millennium, the new advances materials must combine the best available mechanical and chemical recycling routes.[5–11] Indeed, from several decades ago the lightweight parts design (key factor on transport sectors) needs of advanced composites based on thermoplastic matrices with improved interfaces to maximize the stiffness to weight ratio.[12–15] Also, it is necessary in order to minimize the fabrication costs extended to the Life Cycle Assessment principles.[16–20]

One of the best ways to improve the interaction level between the components of the heterogeneous materials based on polymers, composites, and polyblends is by means of additives chemically resembling to the polymer matrix but showing certain affinity with the dispersed phase (reinforcement and/or polymer) in the heterogeneous material through the so-called interphase between components.[21–32] So, polymer composites and/or polymer blends and alloys are good examples.[21,23,25,27,30–33] It must be mentioned here that the silicate particles which constitutes mica are aggregates of smaller primary platelets consisting of thin lamellae of ultra thin dimensions (a few nanometres) just in the scale wherein the interfacial phenomena occurs.[21,25] The use of new interfacial agents appears as a promising way to understand and to control the performance of such advanced materials and more when these are obtained from industrial by-products. Further, the better the interfacial agent (in terms of type and critical amount) the better ultimate properties of the composite material can be reached.[31,32] Most works in literature concerning the use of interfacial agents in polypropylene-based materials are mainly referred to isotactic polypropylene-grafted polymers containing maleic anhydride moieties.[31] However, this paper is devoted to the interfacial modifications caused by a novel interfacial agent synthesized in our laboratories from polymerization wastes[33] on heterogeneous materials with a rigid interphase such as the case

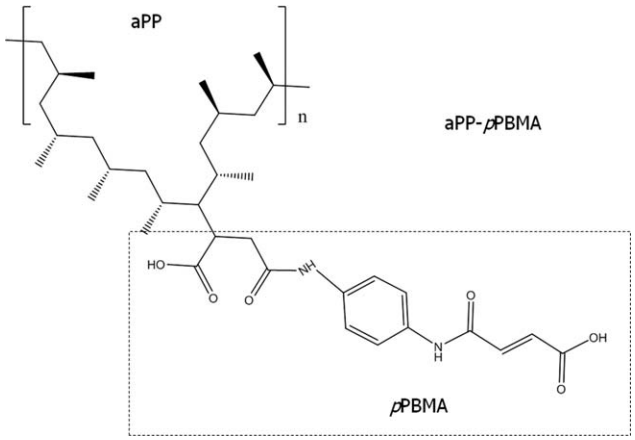

Figure 1. Atactic polypropylene with *p*-PBMA-grafted groups (aPP-*p*PBM).

study a PP/mica system. Flexural testing is frequently used in the mechanical characterization of composite materials because it saves time and usually demands smaller material amounts besides of showing simplest specimen geometry. In this work, a three-point bending flexural test is used to ascertain the interfacial modifications caused in the PP/mica system by means of a functionalized atactic polypropylene with *p*-phenylen-bis-maleamic acid groups, aPP-*p*PBMA. This new interfacial agent (aPP-pPBMA) interfacial agent was obtained in our laboratories by chemical modification of an industrial polymerization by-product, overcoming the drawbacks of the maleic anhydride handling during the chemical modification processes.[33] First published results evidencing the efficiency of this newly appointed interfacial agent in the PP/mica system dealt with the tensile[26] and the dynamic mechanical properties.[27] From dynamic mechanical data, authors ascertained the expected preferential location of whatever the interfacial agents in the surroundings of the reinforcement particles that means at the particle/matrix interphase rather than in the polymer bulk.[34–38] Further, synchrotron FTIR microscopy studies evidenced this fact.[39] The present study evaluates the effect of the interfacial modifications performed in the injection molded PP/Mica system, by the presence of the aPP-*p*PBMA as revealed by flexural properties. The Box-Wilson surface response methodology used to model the composite flexural behavior allows correlation of each one of the parameters associated to the flexural test with the composition of the composite. Further, the comparison between both the flexural and the tensile parameters models shows that a correlation between them must emerge.

EXPERIMENTAL

Materials

As respectively, polymer matrix and reinforcement particles, an isotactic polypropylene, ISPLEN 050 by Repsol-YPF ($\rho = 0.90$ g/cm^3; $M_w = 334{,}400$; $M_n = 59{,}500$; $T_g = -13$°C) and mica platelets (potassium aluminum silicate) supplied by Alsibronz® ($\rho = 2.85$ g/cm^3; specific surface, BET = 1.5 m^2/g; mean particle size = 78.9 μ) were used. The mineral particles did not suffer any significant changes in their mean size and size distribution during processing.[26] The interfacial agent used was obtained in our laboratories from an atactic polypropylene supplied by Repsol-YPF ($\rho = 0.85$ g/cm^3; $M_w = 54{,}000$; $M_n = 2700$; $T_g = -24.4$°C), by-product of industrial reactors, through a chemical modification process in the melt to yield an atactic polypropylene with *p*-phenylen-bis-maleamic acid grafted groups (aPP-*p*PBMA) with 14.8% w/w (4.9×10^{-4} mol/g $_{\text{polymer}}$). Obtaining and characterization procedures of the aPP-*p*PBMA used here were fully described elsewhere.[33] Figure 1 shows the chemical structure or the interfacial agent employed.

Processing

The Box-Wilson methodology used in the present work is a 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).[40,41] 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*PBMA amounts in the composite) compiled in Table I 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*PBMA due to the factorial component coded as (−1, 1) when calculating the Box-Wilson Experimental worksheet that considers $\alpha = \sqrt{2}$ as the coded variable for the star points of the model.[40,41] This has been also included in Table I. So, by fitting any measured property (the mean value) under the Box-Wilson experimental worksheet in Table I a polynomial predicting (if adequate correlation is obtained) the measured property in all the experimental range scanned is established.[40,41] The different amounts of mica according to the Box-Wilson worksheet listed in Table I were added into the molten polypropylene in a Rheomex 600 chamber, set up 190°C and attached to a Rheocord 90, both from Haake, while those of the interfacial agent, aPP-*p*PBMA were incorporated as dry blend to the polypropylene matrix. The interfacial agent amount just replaced the same amount of the polypropylene matrix in the composite material. The latter is done in order to keep constant the PP/mica ratio for a further comparison with the unmodified PP/mica composites, Table II. Mixing time was setup on 5 min after the stabilization of the torque values, once the components went into the mixing chamber. Once the mixing time elapsed, the compounds were recovered and immediately cooled by immersion into an ice water bath, air dried and finally pelletized. Pellets were injection molded at 200°C, as dog-bone-shaped specimens by using a Babyplast 6/6 microinjection machine with a clamping force of 62.5 kN. Prismatic specimens (40 × 5 × 2 mm) for the flexural testing according the UNE-EN ISO178 standards were obtained by machining the dog–bone specimens obtained by injection molding. Prior to test, the specimens were conditioned for 48 h at 23°C and 50% of relative humidity.

Characterization

Thermogravimetric analysis (TGA) on a TAQ50 thermogravimetric analyzer equipped with automatic sample feeding, and scanning electronic microscopy (SEM) observations by using a Philips XL30 ESEM SEM to check respectively, the correct dosing of mica particles in the composites and their homogeneous distribution in the polymer matrix.

Table I. Experimental Design and Results for Flexural Parameters (Factors) According to the Box-Wilson Experimental Worksheet

	Controlled factors[a]		Coded factors		Measured factors		
Exp	x_1 (%)	x_2 (%)	x_1	x_2	Modulus (MPa)	Strength [max load] (MPa)	Strain [max load] (mm/mm)
F1	14.4	1.465	−1	−1	2700 ± *90*	56.20 ± *0.60*	0.057 ± *0.001*
F2	35.6	1.465	1	−1	5500 ± *146*	68.90 ± *1.70*	0.027 ± *0.002*
F3	14.4	8.535	−1	1	2630 ± *110*	50.20 ± *0.85*	0.057 ± *0.002*
F4	35.6	8.535	1	1	5660 ± *119*	65.30 ± *1.05*	0.031 ± *0.001*
F5	10.0	5.000	$-\sqrt{2}$	0	2300 ± *90*	50.40 ± *0.53*	0.062 ± *0.001*
F6	40.0	5.000	$\sqrt{2}$	0	6500 ± *59*	69.40 ± *1.81*	0.025 ± *0.001*
F7	25.0	0.001	0	$-\sqrt{2}$	3950 ± *53*	58.50 ± *1.46*	0.045 ± *0.002*
F8	25.0	9.999	0	$\sqrt{2}$	3700 ± *72*	55.50 ± *1.22*	0.046 ± *0.002*
F9	25.0	5.000	0	0	3770 ± *87*	59.40 ± *0.29*	0.045 ± *0.002*
F10	25.0	5.000	0	0	3900 ± *114*	59.10 ± *0.18*	0.046 ± *0.001*
F11	25.0	5.000	0	0	3850 ± *42*	59.20 ± *0.45*	0.045 ± *0.000*
F12	25.0	5.000	0	0	3790 ± *55*	59.30 ± *0.23*	0.046 ± *0.001*
F13	25.0	5.000	0	0	3840 ± *90*	59.20 ± *0.27*	0.046 ± *0.001*

[a] x_1 = [Mica]; *x_2 = [aPP-*p*PBMA].

For TGA, about 20 mg of selected samples were placed on a crucible and analyzed under nitrogen atmosphere by heating from 30 up to 750°C at a heating rate of 10°C/min. Table III lists the results obtained.

The fractured surfaces of the frozen specimens after 30 min immersed in liquid nitrogen were gold coated using a Thermo VG Scientific SC7640 sputter coater and then observed. Figure 2 compiles these images.

Flexural tests under the three points bending mode and support span, 32 mm, were performed by an Instron dynamometer, 4200 model by following UNE-EN ISO 178:1993 standards at room temperature, 23°C and 50% of relative humidity. According to the specimen thickness, crosshead speed was 1 mm/min. On each run, five specimens were tested and the mechanical parameters measured were the flexural modulus; and both the flexural strength and strain levels at the maximum load conditions.

RESULTS AND DISCUSSION

Background

The so-called interphase plays a key role in the ultimate properties of the heterogeneous materials based on polymers. The modifications carried out at this regions have a great influence in the material performance, more or less significant depending on one hand of the nature and intensity of such changes[26,31,34–39] and, on the other one, of the relationship between them and testing mode. Since the interfacial region is finite, the presence of an interfacial additive implies it must be necessarily constrained. This supports the idea of the existence of a certain amount of interfacial agent considered to be critical in order to enhance the interactions between the phases of the system. Consequently, if the amount of the interfacial agent is close to this critical concentration, the effect is to improve of the occurring interactions between both phases till a limit or threshold value. Growing amounts of the interfacial agent above the optimal would unable to improve the interaction level between the components (besides the unnecessary increase in cost), but even worse the overall performance because of the active sites hindering.[26,35]

A second very important question when undertaking early studies on new advanced composites deals with the effect that the changes in shape and size of the reinforcing particles during processing operations affect the ultimate behavior of the material. Frequently, these changes in the overall interfacial area available (between the matrix and the particle) are wrongly

Table II. Measured Properties and Flexural Model Forecasts for the Indicated Samples

SAMPLE: PP/Mica	Modulus (MPa)	Strength at max load (MPa)	Strain at max load (mm/mm)
100/0	1530[a]	45.60[a]	0.068[a]
90/10	2500[a] (2485)[b]	54.00[a] (53.30)[b]	0.060[a] (0.062)[b]
75/25	4080[a] (3900)[b]	62.30[a] (60.30)[b]	0.042[a] (0.043)[b]
65/35	5667[a] (5500)[b]	64.28[a] (66.61)[b]	0.027[a] (0.028)[b]

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

Table III. Thermo-Gravimetric Results Obtained Under N_2 Atmosphere

PP/Mica/aPP-*p*PBMA	Residue (%)
100/0/0	0
90/10/0	9.8±0.2
75/25/0	24.8±0.3
65/35/0	34.7±0.2
75/25/5	24.9±0.1
75/25/10	25.0±0.1

assigned to changes in the interfacial interaction level across the particle/matrix interphase. Therefore, when undertaking early studies to check the effect of any interfacial treatment, the variables influencing ultimate properties of the thermoplastic composites are the matrix/reinforcement ratio and the interfacial agent amount, it is convenient to remain constant or well controlled, both the mean particle size and the particle size distribution of the discrete reinforcement.

Finally, the third fundamental is the key role played by the emergent morphology imposed by the processing steps.[12–16,38] Premixing and molding procedures would determine (among others) the amorphous/crystal ratio; the particle orientation grade; or the mean size and distribution of the matrix crystalline aggregates, all of them playing a key role in the material responses. Indeed, since composite materials (and any other organic polymer-based material) display a high level of organization without being applied any external organizing principle; they act as complex systems and so the prediction of their mechanical behavior becomes very difficult. The latter usually lead to further overdesigning of plastic parts.

A rough definition of a complex system is that consisting in many blocks, or items, capable of exchanging stimuli, both between them and with the environment. It gives rise to behavior far from those expected from just the knowledge of the individual characteristics of the blocks that does not even give a glimpse of the behavior of the system itself. Consequently, complex systems imply the existence of interaction effects between the parts that just overflow those expected by just studying parts in isolation[42,43] and which significantly affect the overall performance of the complex system as a whole.

Because there are insufficiently developed processing/properties simulation models to take the control of the emerging morphologies,[44] the Box-Wilson response surface methodology is advantageous as it considers a series of interaction terms helping to detect additional effects on the materials responses, more than those assigned to the well-controlled independent variables do. It becomes an advantage at the level of formulation developments in order to discriminate between efficient and noneffi-cient treatments or components and to find optimal compositional coordinates.

In the light of these fundamentals, under the following sections, the flexural parameters of the aPP-*p*PBMA-modified PP/mica system are used to ascertain the interfacial modifier action. Pure elastic materials under the three-point-loading flexural testing conditions undergo a combination of tensile and compression stresses at the same time that converge at the neutral or axial fiber of the specimen. Nevertheless, for a thermoplastic polymer-based material, the specimen undergoes both the tensile and compression loads but now combined with a cross-sectional shear component caused by the viscoelastic nature of the polymeric material.[29,44–46] The Figure 3 shows the load/displacement flexural curves for both the pristine PP/mica composites (A) and those from the Box-Wilson worksheet (B, C). While Figure 3(A) shows the maximum load data point criteria and displays the flexural curve type for the PP, Figure 3(B,C) shows the curves for the Box-Wilson design. Figure 3(C) shows the almost overlapping between the load/displacement curves for the central point at the 75/25 PP/mica ratio and the four additional replicas, required by the Box-Wilson experimental design (Table II). On each plot in Figure 3, it can be appreciated that there are different families of plots depending on the increasing reinforcement content leading to an increase in both the modulus and the maximum load levels obtained with decreasing values in displacement. Figure 4 shows a scheme of the forces acting in a flexural test for the PP/mica system *ab initio* (A), as well as the main alignment of the mica particles in the injection-molded specimen in the elongational flow regions (B), together their seemingly concentric distribution in some areas of the cross section because of the flow fountain effect[26] (C).

Polynomial Fits and Analysis of Variance

Table I compiles all the results obtained for each one of the flexural parameters considered at present work according to the Box-Wilson two independent variables (or controlled factors) experimental worksheet. As mentioned before, the controlled factors were the w/w amounts of both the mica, between 10 and 40%, and the interfacial agent, aPP-*p*PBMA, between 10^{-3} and 10%. Data for each one of the flexural parameters measured were fitted to quadratic models by following the surface response methodology[40] giving rise to three different polynomials describing the evolution of each one of the parameters considered: flexural modulus, flexural strength, and strain at maximum load. Table IV compiles the terms and the values for the $<r^2>$ coefficient for each one of the polynomials obtained the parameters for the corresponding analysis of variance (ANOVA). The $<r^2>$ values for the three flexural test polynomials: 0.9979 (modulus); 0.9771 (strength); and 0.9945 (strain), are well above 0.75 which is considered as very good for quadratic models.[40,41] The Table IV also shows the corresponding "lack of fit" values associated to the percentage of the pure error. The latter is related with possible foreign factors ignored by the model, but significant in the response evolution. The Table IV shows low values for all the three parameters evaluated when considering the correlation obtained. Likewise, the very high values for the confidence factor, close to 100% in all cases, indicate the full significance of the independent variables chosen to model the flexural behavior of the PP/mica system with modified interfaces from the matrix side all over the experimental range checked. Hence, it validates the thereinafter discussion of the mechanical flexural parameters considered in this work over the model forecasts. Nevertheless, for the aim of present

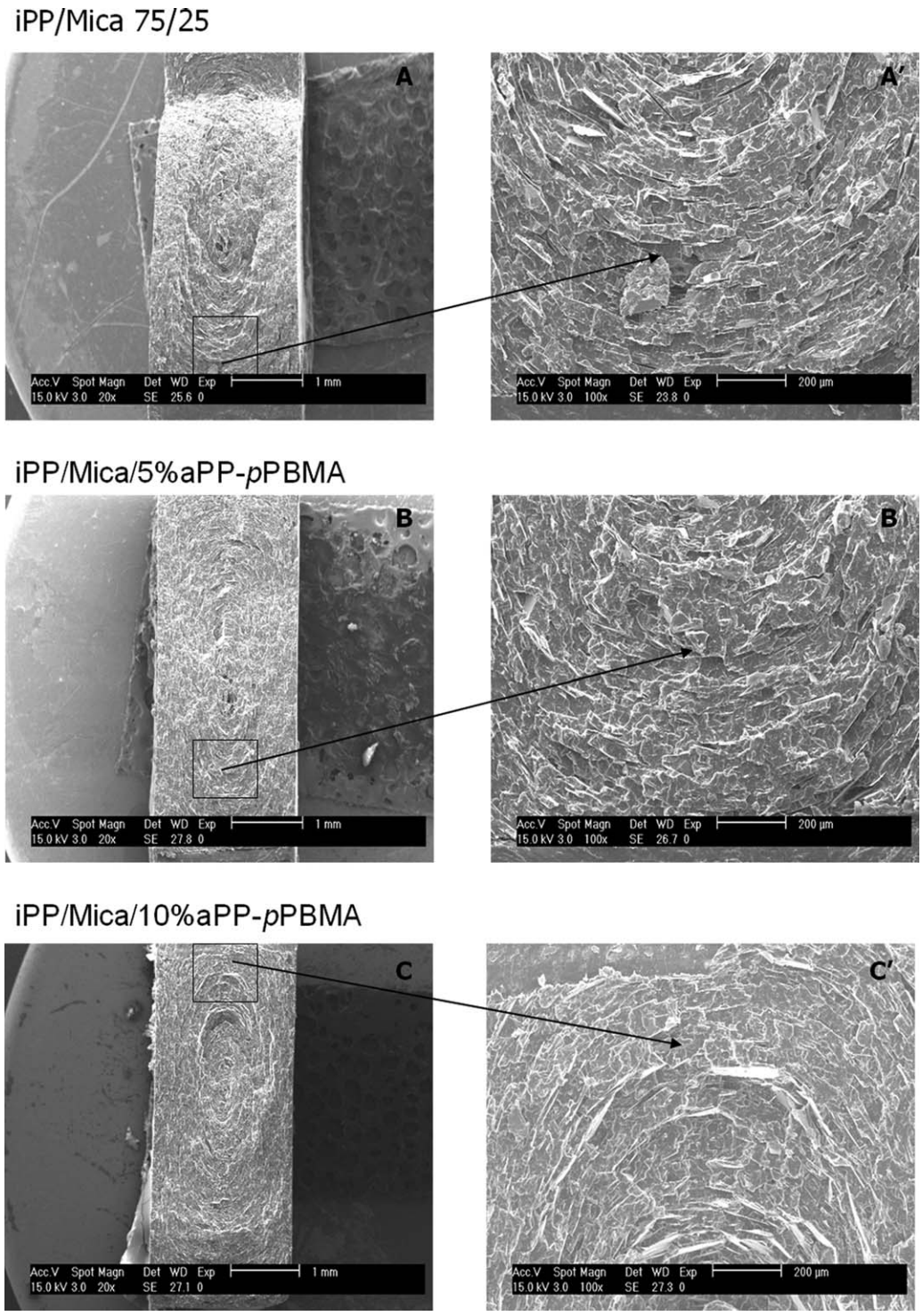

Figure 2. ESEM micrographs of PP/Mica 75/25 cryogenic fracture surfaces.Unmodified PP/Mica (A, A′), PP/Mica/ 5% aPP-*p*PBMA (B, B′) and PP/ Mica/ 10% aPP-*p*PBMA (C, C′).

work and before proceeding to that discussion, a comparison between the statistic *t*-values of the different terms of the polynomial coefficients for flexural parameters and those obtained for the tensile ones fully discussed elsewhere is interesting.[26] Table V compiles them respectively, jointly with their associated confidence coefficients.

By observing the largest significance levels, that means *t*-values equal or higher than |2|, for the models obtained from flexural properties, Table V, one finds that the quadratic terms in mica content, for both the modulus and the flexural strain, are always statistically significant, while the flexural strength do not account with any t-student value equal or higher than |2|. In

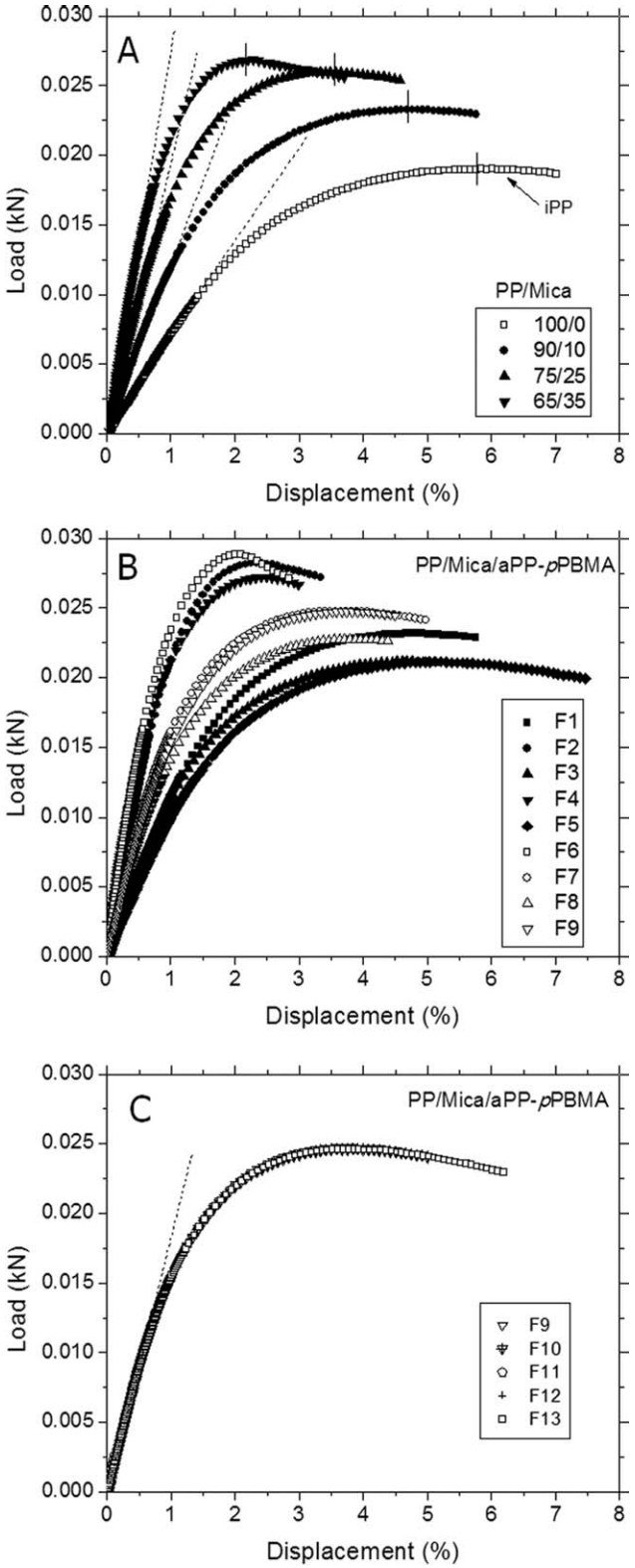

Figure 3. Flexural load vs displacement curves for the indicated samples. PP/mica without aPP-*p*PBMA (A); and for the different (B) and the central point experiments (C) of the Box-Wilson experimental design used.

addition, the flexural strain also shows an always statistically significant linear term in the mica amount. In contrast, all the four tensile parameters, Table V, show several statistically significant *t*-values, all of them in the quadratic ones, which are similar to the observed for the flexural polynomials and agree well with the interfacial nature of the modifications proposed. Furthermore, while the statistically significant tensile modulus and tensile strength *t*-values correspond to the quadratic terms in the interfacial agent amount, the tensile strength at yield point shows its statistically significant *t*-value in the quadratic term of the mica amount, just like the flexural strain one that nevertheless was less sensitive to the interfacial agent amount. It agrees well with the different mechanisms checked by each of the testing modes (flexural and tensile modes) and the different parameters measured in each case. Likewise, at the break point under tensile conditions, it can be observed that (besides the quadratic terms in mica and interfacial agent) both the interaction terms on these two variables are always highly significant. This agrees with the fundamentals previously discussed about the different mechanism of tensile and flexural (combination of tensile and compression forces) tests.

The t-values for the linear terms in the mica amount for the tensile modulus and both the tensile at yield and at break strains are always significant, while only that of the flexural strain was. It evidences the higher sensitivity of the tensile than the flexural modulus to changes in the interfacial activity in the composites. The high orientation level of the mica particles on injection molded specimens compensates the interfacial modification effects on the flexural tests parameters, while those of the tensile tests remain sensitive to those changes. Moreover, the tensile modulus also shows a highly significant *t*-value for the linear term in the interfacial agent amount. From the whole perspective of both the different parameters set of flexural and tensile models, it is appreciated that the flexural parameters models are in general, less sensitive to the influence of the interfacial agent aPP-*p*PBMA, than the models for the tensile properties. It agrees with the fact than under the flexural mode each specimen is supporting a combination of tensile and compressive forces (which in despite the modulation effect of the cross shear stress component) are almost the same in strength but

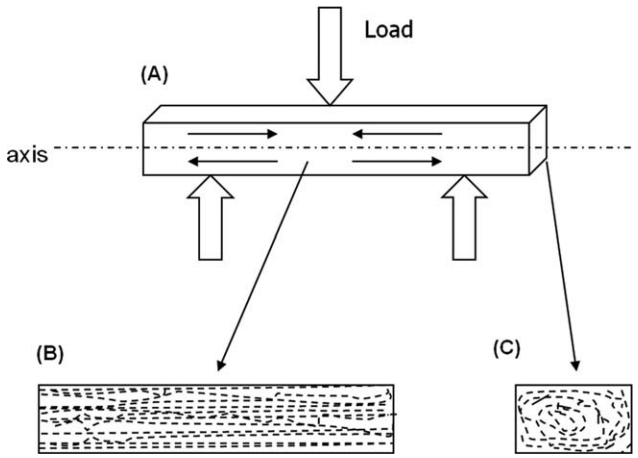

Figure 4. Scheme representation of the forces implied in a flexural test (A), the particle distribution along the preferential dimension of the sample (B), and concentrically distribution of them in the transversal section of it (C).

Table IV. Statistical Parameters of the Analysis of Variance (ANOVA) and Coefficients of the Polynomials from the Box-Wilson Experimental Design for the Flexural Test Parameters

				Polynomial equation: $a_0+a_1{\cdot}x_1+a_2{\cdot}x_2+a_3{\cdot}x_1{\cdot}x_2+a_4{\cdot}x_1^2+a_5{\cdot}x_2^2$					
				x_1 = [Mica]; x_2 = [aPP-*p*PBMA]					
				linear terms			Interaction term	Quadratic terms	
	$<r^2>$ (%)	Lack of fit (%)	Confidence factor (%)	a_0	a_1	a_2	a_3	a_4	a_5
Modulus	99.79	15.1	99.9	2197.8	3.183	−47.78	1.535	2.559	$-1.09{\cdot}10^{-4}$
Flexural strength (max load)	97.71	0.7	99.9	50.38	0.2287	−0.3336	$1.6{\cdot}10^{-2}$	$6.72{\cdot}10^{-3}$	$-5.56{\cdot}10^{-2}$
Flexural strain (max load)	99.45	5.6	99.9	$7.11{\cdot}10^{-2}$	$-7.77{\cdot}10^{-4}$	$1.36{\cdot}10^{-4}$	$-2.7{\cdot}10^{-5}$	$-1.3{\cdot}10^{-5}$	$-3.4{\cdot}10^{-5}$

opposite, mainly at the first stages of the test [Figure 4(A)]. The more orientation of the reinforcement (parallel to the flow lines) the more significant is this aspect.

Influence of Composite Composition in the Flexural Properties

Before discussing on the flexural properties it is necessary to determine the real particle content, distribution and orientation in the composite. TGA studied over chosen samples were performed in order to check the proper dossing of reinforcement particles during the processing operations. The results listed in Table III confirm the dosing of these in the composites. Otherwise, if predictions in the previous section are confirmed (once the interfacial efficiency of a interfacial agent has been demonstrated by other means),[26,27] the absence of noticeable changes in flexural properties (mainly for properties measured at the first stages of the test such as the flexural modulus) would be explained by the concentrically distributed platelets aligned parallel to the flow lines. In fact, as it is well known, injection molding greatly affects the morphology of the system in this way. Figure 2 displays representative micrographs of the overall cryogenic fracture surfaces (20×) and some detail (100×) of the pristine PP/mica, 75/25 composite (A, A′) and once modified by 5% (B, B′), or 10% of aPP-*p*PBMA (C, C′). They exhibit a very homogeneous distribution concentric pattern that suggests that they are mainly aligned all along the polymer flow profile, acting as tracers of the injection molding flow lines, almost all showing its lowest dimension to the observer. Figure 4 tries to schematically represent the forces present in a flexural test (A) as well as the alignment (B) and concentric distribution (C) of mica particles in the specimen to be tested. Not being the purpose of present work to the study of the morphology of the composite but to confirm the flow pattern of the concentric distribution of mica particles in the composite (Figure 4), the reader is submitted to a previous a study by the authors concerning the morphology and the mica distribution as evidenced by back scattered electron field emission scanning electron microscopy (FESEM).[26]

To undertake the discussion of the model predictions, some considerations about the experimental data compiled in Tables I and II must be done. For example, the measured values for the flexural modulus (obtained at very little strain) of samples with 25% of reinforcement and with 0% (in Table II), 0.001%, 5%,

Table V. Confidence Coefficient (%) and *t*-Values for the Different Terms of the Box-Wilson Model Obtained for Flexural and Tensile[26] Properties

Polynomial equation: $a_0+a_1{\cdot}x_1+a_2{\cdot}x_2+a_3{\cdot}x_1{\cdot}x_2+a_4{\cdot}x_1^2+a_5{\cdot}x_2^2$					
x_1 = [Mica]; x_2 = [aPP-*p*PBMA]					
	Linear parameters		Interaction parameter	Quadratic parameters	
	x_1	x_2	$x_1{\cdot}x_2$	x_1^2	x_2^2
Flexural modulus	0.2 (25%)	1.4 (79.5%)	1.6 (84.0%)	10.4 (99.9%)	0.0 (15.9%)
Flexural strength (max load)	1.0 (66.1%)	0.6 (44.0%)	1.0 (64.6%)	1.7 (86.7%)	1.6 (83.7%)
Flexural strain (max load)	3.9 (99.2%)	0.3 (26.5%)	1.8 (89.3%)	3.4 (98.8%)	1.0 (64.9%)
Tensile modulus	3.2 (98.5%)	2.4 (95.3%)	1.4 (78.4%)	1.1 (69.8%)	2.1 (93.5%)
Tensile strength at yield	1.5 (81.0%)	0.1 (20.6%)	2.5 (96.2%)	0.5 (39.4%)	4.2 (99.4%)
Tensile strain at yield	8.7 (99.9%)	0.6 (44.3%)	0.7 (48.2%)	6.6 (99.8%)	0.4 (64.9%)
Tensile strength at break	1.5 (82.7%)	1.1 (67.4%)	2.0 (92.0%)	2.6 (96.7%)	4.9 (99.6%)
Tensile strain at break	5.9 (99.8%)	1.0 (62.8%)	2.5 (96.2%)	3.9 (99.2%)	2.8 (97.5%)

and 9.999% of aPP-*p*PBMA (in Table I) though almost the same value, showing the very little influence of aPP-*p*PBMA due to the fully compensated forces in the specimen [Figure 4(A)] at the early stages of the test. However, those for the flexural strength at yield exhibit different values showing that when strain increased the resulting forces from the test are not compensated and the effect of the interfacial agent can be properly interpreted. In fact the one with 25% mica and none of interfacial agent produces a value of 62.3 MPa, the one with only a tiny amount of aPP-*p*PBMA (0.001%), indicates that the interfacial agent (even at such amount) plays an important role as to change notably the value for this parameter down to 58.50 MPa. If compared the samples incorporating 0.001%, 5%, and 9.999%, the one with higher measured properties for this parameter is that with the intermediate amount of interfacial agent (5% of aPP-*p*PBMA) giving a value of 59.4 MPa (Table I). This indicates that the behavior of the system depends on the amount of interfacial agent, and what is more important, is the existence of critical values for the concentration of components in a heterogeneous material as it has been concluded in other works by authors with this same[26] and with other interfacial agents.[33–39] A way to avoid the possibility of missing this kind of data due to a bad selection of the experiments is the use of experimental designs. A similar discussion may be developed for the other parameters in Tables I and II. 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 II. Predictions for the neat PP are not included as they fall outside the experimental space scanned (10 up to 40% for mica content) making the neat PP behavior purposes to be not within the purpose of the model. Figure 5 shows the contour maps of all the flexural parameters as a function of the mica and the interfacial agent contents.

Flexural Modulus Evolution

Figure 5(A) shows a quasi-stationary ridge pattern corresponding to the contour plot for the modified PP/mica system flexural modulus as a function of the mica and of the aPP-*p*PBMA amounts. Therefore, the isoline values grow as the mica content increases and exhibit an almost parallel evolution above the 30% in mica indicating an almost full compensation of the influence of the interfacial agent in the flexural modulus evolution once the maximum packing level in the composites is reached.[29,45,46] The risk to only characterize a complex material by just a single test method is evidenced here. Indeed, forgetting the physical sense of the flexural test and in the absence of a previous work on tensile modulus,[26] the noninfluence of the aPP-*p*PBMA in the PP/mica system would be an acceptable conclusion. Nevertheless, above the 25% on mica particles, it is clearly observed the smooth slope to higher flexural modulus values with increasing amounts of the aPP-*p*PBMA. It agrees with the fact that the 25% on discrete reinforcement particles corresponds to the threshold value to reach the minimum interparticle distance able to significantly co-participate in the overall mechanical load absorption process conducting to the improvement of the mechanical performance of the composite.[26,30,44,47–50] The Figure 6 plots visualize the former

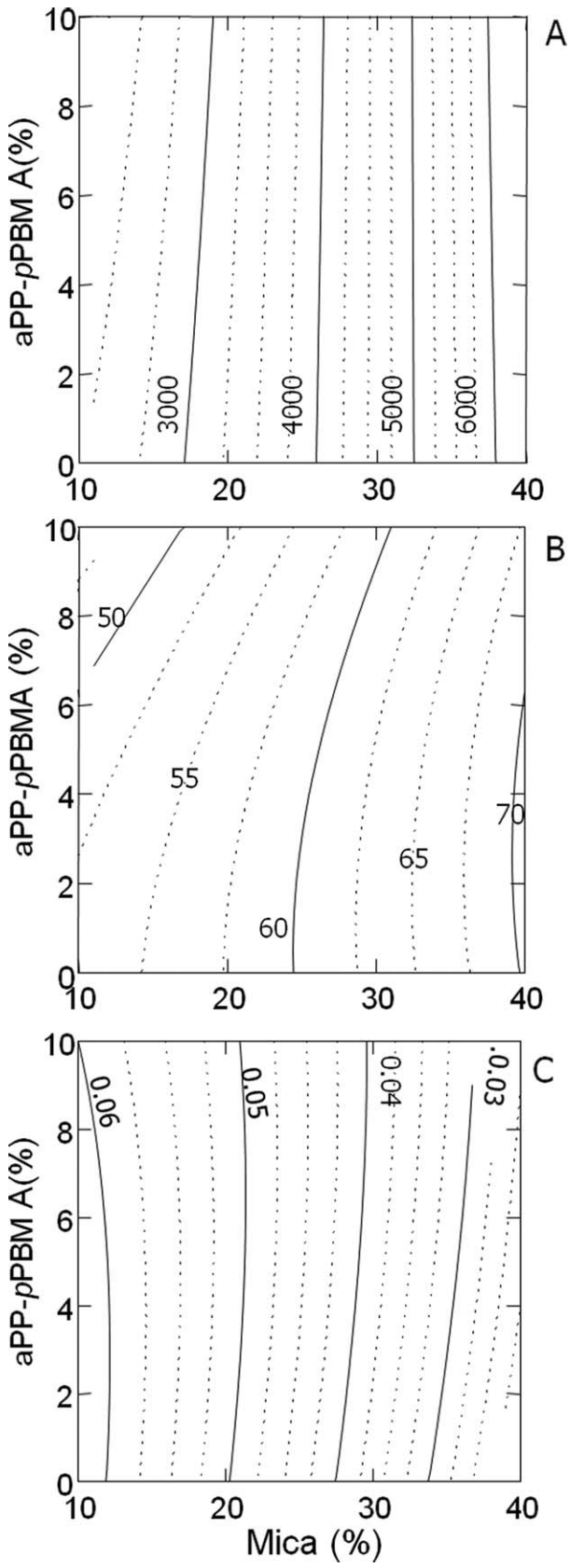

Figure 5. Contour map showing flexural modulus (A); strength (B); and strain (C); as a function of the mica and interfacial agent contents.

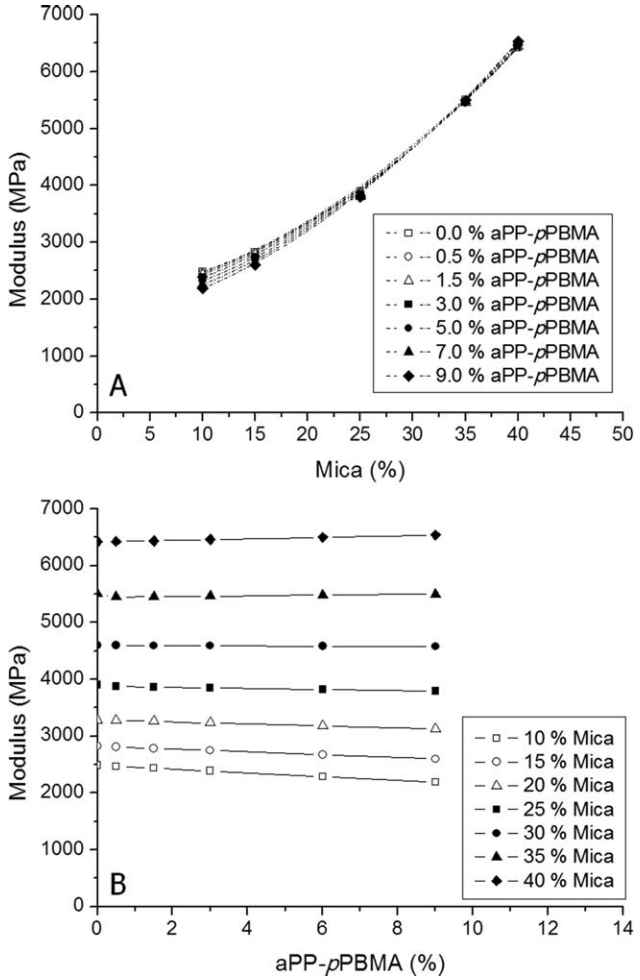

Figure 6. Evolution of flexural modulus with mica: At different amount of interfacial agent (A) and at different amount of mica (B) in the composite.

observations by showing both the flexural modulus evolution for the modified PP/mica system at constant levels of the aPP-*p*PBMA interfacial modifier [Figure 6(A)] and at constant levels of mica as a function of the interfacial modifier amount [Figure 6(B)]. The almost overlapping of the flexural modulus values above the 25% on mica content is clear, as well as how the curves split below these values, giving rise at the highest aPP-*p*PBMA content to an almost straight line evolution of the flexural modulus of the modified composites as the mica content grows [Figure 6(A)]. Hence, the plots in the Figure 6(B) shows the full significance of the mica content to increase the flexural modulus of the modified composites, showing upward shifted straight lines with almost zero slopes as the mica content increases. For the two lowest mica content plots, it is possible to detect the hindering effect of the interfacial modifier excess by the slightly negative slope of these curves. Despite the low sensitivity of the model to the interfacial agent content, this can be explained by the abovementioned fact[34,35,38] that the interfacial agent is preferentially allocated in the interphase between the polypropylene matrix and at the two lowest mica contents the particle/matrix interfacial area available is the lowest too.

Flexural Stress Evolution

Figure 5(B) shows a typical rising ridge evolution for the compositional contour map for the flexural strength evolution of the modified PP/mica system. The rising ridge evolution usually informs about the existence of optimal coordinates in the experimental space scanned. Because of the high PP ductility, the flexural strength of the composites does not correspond to a break end property but to a mechanical yield point, after that the specimen strain follows at a constant stress level but without elastic behavior. However, when the maximum load is reached, the interaction level between the matrix and the particles is significant, as the isolines in the Figure 5(B) show. This is confirmed by plots in the Figure 7. Plots for flexural strength evolution on both the Figures 5(B) and 7 looks like an unfolded version of those, respectively displayed, in the Figures 5(A) and 6 for the flexural modulus showing how indeed a critical concentration of interfacial modifier appears close to the 3%, Figure 7(B). Above this value, the stress threshold to maximum load decays so much significantly as lower the mica content

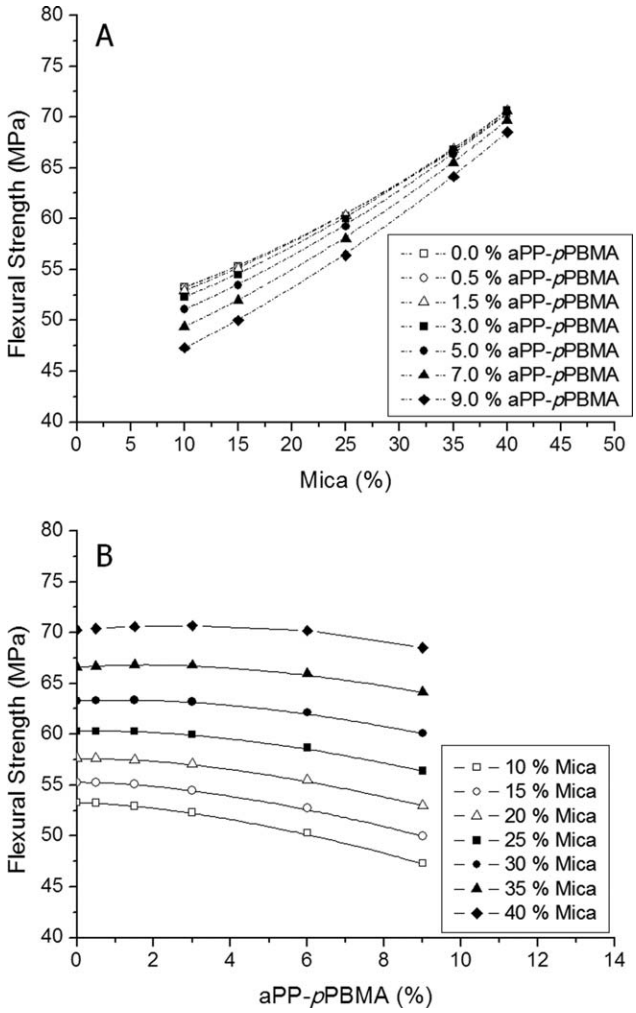

Figure 7. Evolution of flexural strength versus interfacial agent content: At different amounts of interfacial agent (A) and of mica (B) in the composite.

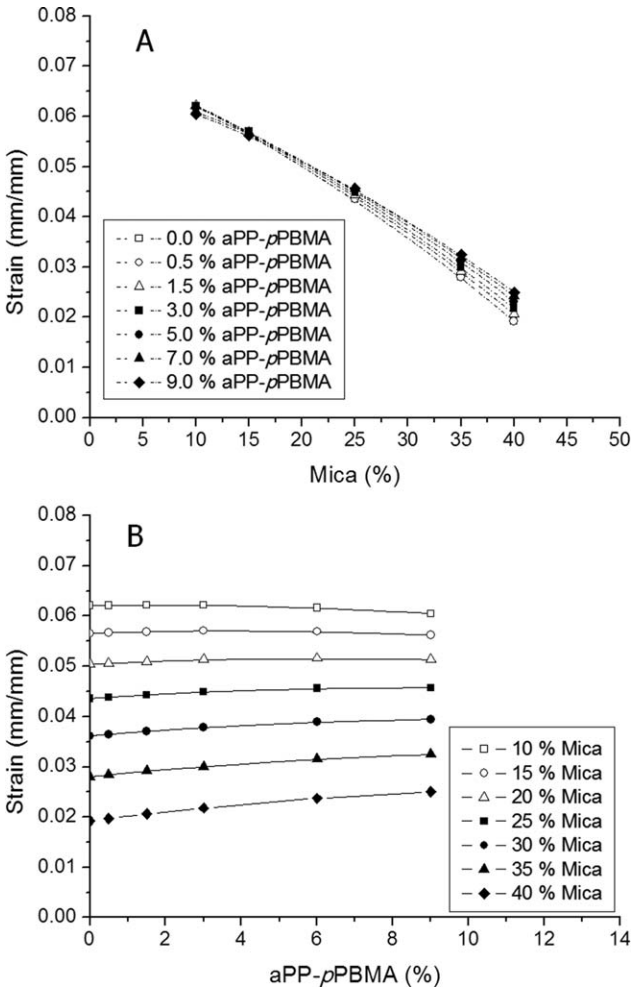

Figure 8. Evolution of flexural strain versus interfacial agent content: At different amounts of interfacial agent (A) and of mica (B) in the composite.

does, because of the abovementioned decrease in the available particle/matrix interfacial area.

Strain Evolution

Figure 5(C) shows the compositional contour map for the flexural strain at the maximum load conditions of the modified PP/mica system evolving as a rising ridge in a similar way that both the flexural modulus and strength but just in an opposite manner with respect to the interfacial agent effect. The polymer chains tend to reorient by themselves from the early stages of a strain processes under normal stress conditions, allows to the possibility to oppose the minimum resistance by flowing parallel to the external applied loads. Such a mechanism is always possible if a significant number of interconnecting or tie chains in the amorphous phase assure the material integrity. Hence, the polymer matrix is mainly responsible for the strain behavior and consequently, increasing presence of the mica particles in the bulk of the amorphous phase means a sharp decrease in its flexural strain capability because of the increasing fraction of polymer chains that must incorporate the foreign component, otherwise polar faced to the nonpolar polypropylene matrix. According to this perspective, increasing values of the flexural strain in the modified composites should mean a decrease in the effect of the reinforcement particles in the polymer matrix bulk, but always restricted to the finite dimensions of the interface. The compositional plots displayed in the Figure 8 show, how the flexural strain values for the composites above the 25% on mica amount change their almost overlapping below such value as an upwards shift as the aPP-*p*PBMA content increases, Figure 8(A). The detail of these evolutions at different constant mica amounts, Figure 8(B), visualizes how the flexural strain plots of the modified composites below the 25% in mica and above the 3% in the aPP-*p*PBMA content, show almost constant values for further increasing contents of the aPP-*p*PBMA, evolving likewise the pristine composite. On the contrary, the modified composites containing a 25% of mica and upward, with an increasing amount of particle/matrix interfacial area available and closing to the maximum packing fraction clearly show the lowest flexural strain values at the lowest interfacial modifier contents up to the 3%. From here, it can be concluded the sensitivity of the flexural parameters to the presence of the aPP-*p*PBMA as interfacial modifiers in the PP/mica system and the coherence between the Box-Wilson models describing their respective evolutions.

Flexural Versus Tensile Modulus

Figure 9 displays the correlation plot between the flexural and the tensile modulus forecasts for the different PP/mica composites, the pristine one, and those modified with the different interfacial agent amounts as displayed on legends. The flexural modulus values are always higher than of the tensile ones, both parameters increasing as the mica content does. The effect of the interfacial agent is clearly more significant in the tensile modulus increase of the modified composites.

Two different areas appear in this Figure 9 when observing the data point's disposal. On one hand, the PP/mica composites below the 25% in mica show almost constant flexural modulus values from the pristine to the aPP-*p*PBMA-modified composites, while the tensile ones significantly increases as the aPP-*p*PBMA does up to the 3%. Double amount of aPP-*p*PBMA makes decrease the flexural modulus while thrice the amount in the interfacial agent reduces both the flexural and the tensile modulus values. Furthermore, for all these composites well

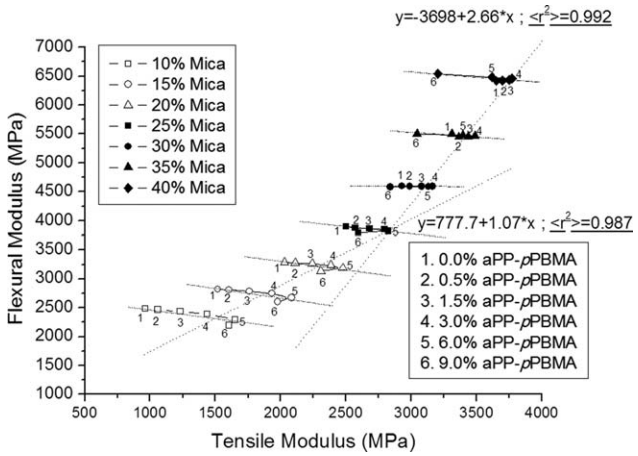

Figure 9. Flexural versus tensile modulus correlation.

below the compositional threshold on reinforcement particles, to assure the critical interparticle distance to mica has influence in the overall mechanical energy absorption process, the tensile modulus values of each compositional ratio distribute along an average range of about 700 MPa, and even wider the lower the mica content is.

On the other hand, the tensile modulus values of the modified 75/25 PP/mica composites and above in mica content appears distributed in a shorter range of around 250 MPa. While the flexural ones stay virtually the same with the interfacial agent amount remaining constant in the pristine composite value. Moreover, the saturation level at the interface when the aPP-*p*PBMA amounts are twice or thrice that of the optimal value of the 3% results and it is clearly observable in this region of Figure 9, just as it was in the previous discussed region. Indeed, such modified composites always show tensile modulus values lower than of the optimal aPP-*p*PBMA level of the 3%. In this sense, it is interesting to observe linear evolution of all the composites with 3% aPP-*p*PBMA whatever the PP/mica ratio correlating the flexural modulus values with those of the tensile ones. In fact, it can be clearly observed that the composites with the optimum amount of aPP-*p*PBMA (3%) follow two different linear evolution, (above and below 25% in mica content) with a pretty correlation degree. This very interesting result previously advanced on the tensile parameters study[26] agrees with other findings by authors on the study of the mechanical behavior on injection molded PP/talc composites with modified interface by the presence of a commercial isotactic succinic anhydride-grafted polypropylene.[30,45,47–50] Those results showed that just a 1.5% of such modifier was enough as to obtain the best performance of the PP/talc composites. By considering the ratio between the molecular weight of both grafted species, *p*PBMA and SA (ca. 2.8/1) as fully discussed elsewhere,[33] the respective optimal amounts of each one of both interfacial modifiers results similar. It otherwise agrees on one hand, with the finite dimensions of the polymer/particle interface, the same whatever the interfacial polypropylene based agent, and on the other with the fact, that is the isotactic polypropylene matrix, whatever the lamellar reinforcement particles, talc, or mica, which imposes the matrix/particle interfacial area available to the interfacial modifiers. Finally, for mica below 25% the slope is almost one, indicating that, in such conditions, the measurement under tensile or flexural conditions is equivalent. However, above this amount the latter is not true.

CONCLUSIONS

The effect of a novel interfacial modifier obtained from polymer residues has been used here to modify the properties of a PP/mica composite as evidenced by flexural properties**.** It is concluded that the interfacial agent effect 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. In other words, this parameter appears as very sensitive to the processing steps (mainly injection molding in our case) followed to obtain the specimen. 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 able to lead the system to very different properties has been demonstrated. The process has been demonstrated to be modeled by using a Box-Wilson experimental design. So, 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 emerges. Moreover, since the flexural text is a combination of tensile and compression forces, this model has been even proved useful to conclude about the real influence of the interfacial agent and the reinforcement. The well-known fact that the flexural text consists in a combination of compressive and tensile stresses emerges from the analysis of both the data and the statistic parameters of the model, becoming more evident when compared these to the obtained for a model for pure tensile properties In such scenario, the Box-Wilson experimental methodology has proved to be a powerful tool when attempting to model the flexural behavior of this kind of systems as well as in order to discuss the experimental results. Additionally, the correlation of tensile and flexural modulus indicating the existence of critical points in every case has been demonstrated.

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