

# Flour Rice Husk as Filler in Block Copolymer Polypropylene: Effect of Different Coupling Agents

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**ABSTRACT:** Flour rice husk (FRH) was employed as a filler in block copolymer polypropylene (PPB) in order to prepare polymer-based reinforced composites. Four coupling agents were selected to modify the surface of the rice husk in the composite materials, including two types of functionalized polymers [PP homopolymer grafted with maleic anhydride (MA-PP) and an elastomer styrene–ethylene–butadiene–styrene triblock copolymer grafted with MA (MA-SEBS)] and two bifunctional organometallic coupling agents (silane and titanate with linear low-density polyethylene as a carrier). The influence of each type of coupling agent on the interfacial bonding strength was studied by dynamic mechanical analysis, scanning electronic microscopy, and rheological tests. The results showed that strong

interactions were formed between the coupling agents and the filler surface. The addition of a coupling agent with an elastomeric carrier (MA-SEBS) increased the loss tangent and reduced the storage modulus of the composite. A similar but less intense effect was observed for the titanate coupling agent. However, an antagonistic performance was obtained when MA-PP and silane were employed as coupling agents. In addition, when the percentage of MA-SEBS was increased, the impact properties of FRH/PPB blends were improved and the strength was reduced. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 1823–1831, 2006

**Key words:** natural fiber composites; compatibilization; flour rice husk; polypropylene; viscoelastic properties

## INTRODUCTION

Recent investigations of polymer-based composite materials have opened new routes for polymer formulations and have allowed the manufacture of new products with optimal properties for special applications.<sup>1,2</sup> In most cases, these composites improve the product design and reduce the material and energy consumption. A special interest has grown in composites based on thermoplastic matrixes reinforced with raw lignocellulosic materials such as wood fillers,<sup>3</sup> wheat straw, almond husk, or ash rice husk.<sup>4,5</sup> These fillers introduce some advantages compared to traditional inorganic fillers, including their renewable nature, low density, nonabrasive properties, reasonable strength, and stiffness.<sup>6,7</sup> In addition, the processing of these composite materials is flexible, economical, and ecological and it is possible to use the same machinery employed with other traditional fillers. Because of

their high crystalline structure and high molecular weight, organic fillers are solid at the processing temperature of thermoplastic materials, but their degradation temperature is low because of the weakness of their chemical bonds.<sup>1</sup>

The raw lignocellulosic materials are mainly made up of a complex network of three polymers: cellulose, hemicellulose, and lignin.<sup>7</sup> Table I shows the percentage of each polymer in different organic fillers<sup>8</sup> and the percentage of natural moisture. The percentage of silica in the rice husk is included. Cellulose is a lineal polysaccharide-type polymer with high molecular weight. It is the responsible for the strength of the plant because of its high elastic modulus (40–130 GPa), depending on the separation method.<sup>9</sup> In contrast, hemicellulose is a branching polysaccharide composed mainly of pentosanes and hexosanes, which contain a large number of hydroxyl groups. Because of its branching formation and complex chemical structure, its contribution to the polar behavior of the filler is higher than cellulose. Finally, lignin is an aromatic polymer with a high content of branched molecules, which are polar hydroxyl groups that are responsible for the hydrophilic nature of the lignocellulosic materials and nonpolar hydrocarbon and benzene rings. For this reason, lignin is the least polar polymer of the three. Because of its low polarity, it can be used as a coupling agent.<sup>10</sup> However, its degradation tempera-

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TABLE I  
Dry Chemical Composition of Different Organic Fillers and Fibers

Organic filler	Cellulose (%)	Hemicellulose (%)	Lignin (%)	Silica (%)	Natural moisture (%)
Pine (softwood)	44.0	27.0	28.0	—	25
Yellow birch (hardwood)	47.0	31.0	21.0	—	25
Jute	73.2	13.6	13.4	—	10
Wheat straw	48.8	35.4	17.1	—	18
Rice husk	45.0	19.0	19.5	15.0	14

ture and mechanical properties are distinctly lower than the other natural filler components.<sup>11</sup>

As shown in Table I, flour rice husk (FRH) is a special lignocellulosic material. Although it contains the typical components of a standard lignocellulosic material, its lignin and hemicellulosic contents are lower than wood flour, whereas the cellulose content is similar. For this reason, the rice husk filler can be processed at higher temperatures than wood, which has thermal stability problems at temperatures above 200°C,<sup>12</sup> whereas FRH is stable until 250°C. Moreover, compared to wood, FRH contains 15% (w/w) silica. With this percentage of inorganic filler, it would be possible to obtain composites with better mechanical and thermal properties than with conventional flour woods, but possibly with lower impact properties because this filler is less flexible. In addition, the inorganic filler and low lignin content could improve the fire resistance of the composite in comparison with other organic fillers.

The performance and processing of block copolymer polypropylene (PPB)/FRH composites have some problems compared with composites made with wood. The lower lignin content causes worse compatibilization and higher density, whereas the high silica content produces moderate abrasion in the cylinder and screw of the machine. To improve the performance of these blends, compatibilization is needed<sup>13</sup> in order to reduce the interfacial tension facilitating dispersion, stabilize the morphology against high stress and strain processing, and enhance the adhesion between the matrix and the filler in the solid state, thus improving the mechanical properties of the composite.<sup>14</sup>

Two different commercial procedures are being developed to improve the wettability of the organic filler surface by the polymeric matrix and the adhesion in the solid state. These procedures include either the superficial chemical modification of the filler to change its surface tension or the use of polymers bearing active functions capable of coupling between the filler and matrix. In the first group the most used systems are acetylation,<sup>15</sup> which reduces the equilibrium moisture content, and alkali treatment,<sup>6</sup> which improves the nonpolar properties of the organic filler by removing hemicellulose and small quantities of lignin. In the second group it is possible to find a large

number of products. Because the surface energies of organic fillers are closely related to their hydrophilicity, they are commonly modified with fatty acids in order to drastically decrease the surface tension of the filler. Other organic compounds can be used to enhance the interfacial adhesion between the filler and matrix, such as silane,<sup>16,17</sup> zirconate, dicarboxylic anhydride, titanates,<sup>18</sup> and phosphate ester.

The most important commercial systems are formed by silanes and titanates. According to the interphase coupling theories,<sup>19</sup> the behavior of these reactive coupling agents is different. The hydrophilic group of the silane molecule reacts chemically with the functional groups of the organic filler surface, whereas the hydrophobic group reacts with the carbonyl groups formed by oxidation of the PP at high temperatures. In contrast, the hydrophilic part of the titanate molecule reacts with the proton of the organic substrate and the hydrophobic part provides polymer compatibility and van der Waals entanglement via aliphatic long carbon chains.<sup>20</sup>

Finally, other systems that can be used in the commercial modification of wood/polymer composites are copolymer formations (block or graft type) in which the nonpolar polymer is functionalized with compatible elements with the filler, such as maleic anhydride (MAH)<sup>21</sup> or acrylic acid, and substances with isocyanate functional groups.<sup>6</sup> Other articles cite the use of elastomeric materials, which could have been functionalized or not in order to improve the impact properties.<sup>3,22</sup>

The aim of this article is to test different commercial coupling agents in order to improve the low compatibility of the FRH with apolar polymers. The different types of coupling agents we chose (functionalized polymers with MAH, titanate, and silane) were added to the composite PPB/FRH. The results of dynamic mechanical analysis (DMA), scanning electron microscopy (SEM), and rheological analysis were used to select the best compatibilizer according to the desired ultimate properties of the composite material.

## EXPERIMENTAL

### Materials

The matrix employed in the preparation of the composite samples was commercial PPB (Reliance B0220

TABLE II  
Percent Weight of Each Component in Blends

Material or additive	BL	A3	B1	B3	B5	B7	C1	D3
PPB	62.5	59.5	61.5	59.5	57.5	55.5	61.5	59.5
FRH	37.0	37.0	37.0	37.0	37.0	37.0	37.0	37.0
Antioxidant	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
MA-PP	—	3.0	—	—	—	—	—	—
MA-SEBS	—	—	1.0	3.0	5.0	7.0	—	—
Si	—	—	—	—	—	—	1.0	—
Ti-LLDPE	—	—	—	—	—	—	—	3.0

MN) provided by Reliance Industries Ltd. (melt flow index = 22 g/10 min, density = 0.91 g/cm<sup>3</sup>). The FRH used as a filler (moisture content = 5%, medium particle size = 400  $\mu$ m) was supplied by MIDSUF S.L.

Four different commercial coupling agents were included in the formulation of the composites in order to improve the compatibility between the filler and the matrix. Grafted MAH PP homopolymer (MA-PP, commercial grade EXXELOR PO 1020, MAH content = 0.71%, melt flow index = 430 g/10 min) was provided by Exxon Mobil. Maleated styrene–ethylene–butadiene–styrene triblock copolymer (MA-SEBS, commercial grade Kraton FG1901X, functionality = 1.7% by weight with MA, melt flow index = 22 g/10 min) was supplied by Shell. The silane coupling agent was 3-aminopropyltriethoxysilane (commercial grade Dynasylan Ameo-T) was procured from Degussa-Hüls. The titanate coupling agent [titanate with linear low-density polyethylene (Ti-LLDPE)] was a pellet system (Ken-React CAPS L12/L) provided by Kenrich Petrochemicals, Inc. (melt flow index = 20 g/10 min) containing 20% (w/w) titanium(IV), 2-bis-2-propenoate-methylbutanoate, tris(dioctyl)pyrophosphate, 11% (w/w) hydrated amorphous silica, and 69% (w/w) LLDPE. All the melt flow indexes were measured under the same conditions (230°C and 2.16 kg).

To prevent thermomechanical degradation during the extrusion and injection processes, all composites were prepared with the addition of 0.5% (w/w) antioxidant (IRGANOX 1010, CIBA Specialty Chemicals).

### Sample preparation

The mixing of the filler and matrix was carried out with a Collin single-screw extruder. A standard polyolefin screw (compression ratio = 2) with a 30-mm diameter and a 30:1 length/diameter ratio was employed. One forcing venting system (water vacuum pump) was mounted over the extruder to remove the rice moisture and other gases formed during the extrusion process. The melt extrusion temperature was 190°C and the screw speed was 60 rpm.

The coupling agents with masterbatch presentation were mixed and added directly to the extruder hopper. The bifunctional organosilane was premixed with the flour rice and a solution of water with ethanol in a

10-L Valtorta turbomixer at 2800 rpm for 20 min. Afterward, the rice–silane blend was dried at 50°C for 2 h to reduce the moisture content of the rice until it reached 5%. The extruded strands were cooled in a water slide system, pelletized, and dried for 4 h at 70°C.

The compositions and denoted names of the prepared blends are presented in Table II. All samples have the same filler volume fraction of 0.41 (v/v), which was calculated with FRH and PPB densities of 1300 and 910 kg/m<sup>3</sup>, respectively.

The compounded pellets were injection molded in a standard 130Tn injection molding machine (METEOR 480/130, Mateu & Solé) into ISO impact mechanical test specimens (100 × 10 × 4 mm) under identical conditions (injection speed = 80 mm/s, injection temperature = 220°C, molding temperature = 45°C).

### DMA measurements

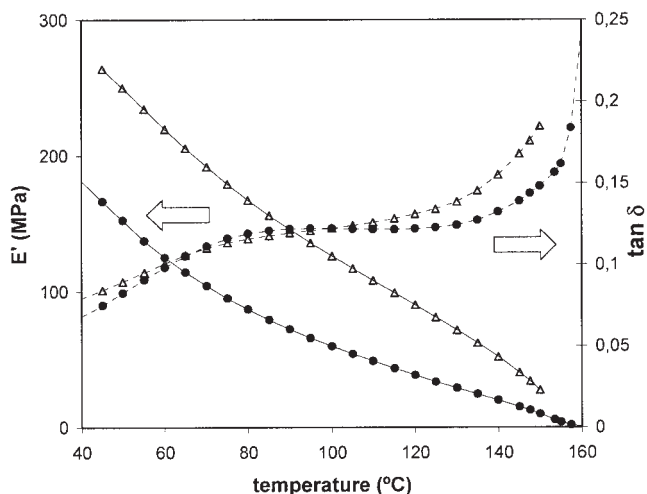
Four composite specimens from each blend (50 × 10 × 4 mm) were cut from injected ISO impact test bars and subjected to DMA in a TA Instruments DMA 2100 (New Castle, DE) using three-point bending geometry with a support length of 48 mm. The measurements were carried out at a frequency of 1 Hz, a heating rate of 3 K min<sup>-1</sup>, and temperatures between 40 and 160°C.

### Rheological analysis

The rheological properties of the composite were measured using a Physica VS200 Rheometer (Anton Paar GmbH) with a plate–plate configuration at a temperature of 190°C. The diameter of the plate was 25 mm and the dynamic oscillatory mode was adopted. The complex viscosity was measured as a function of the shear rate at a constant strain of 5%.

### SEM

The fracture surface of the composites at room temperature was examined employing a JEOL JSM 6300 scanning electron microscope (Peabody) at an acceleration voltage of 20 kV. A thin layer of gold was coated on the fractured surfaces for good conduction before SEM examination.



**Figure 1** The dependence of the viscoelastic properties on the temperature for (●) PPB and (△) nontreated FRH composite (BL): (—) storage modulus ( $E'$ ) and (---) loss tangent ( $\tan \delta$ ).

## RESULTS AND DISCUSSION

### DMA study

The viscoelastic behavior of the different composite samples was studied by DMA in order to discuss the influence of the coupling agents on the mechanical properties of the PPB/FRH composites. From these results it would be possible to analyze the compatibilizer effect of each coupling agent and to identify the suitable one, depending on the desired ultimate properties of the composite material.

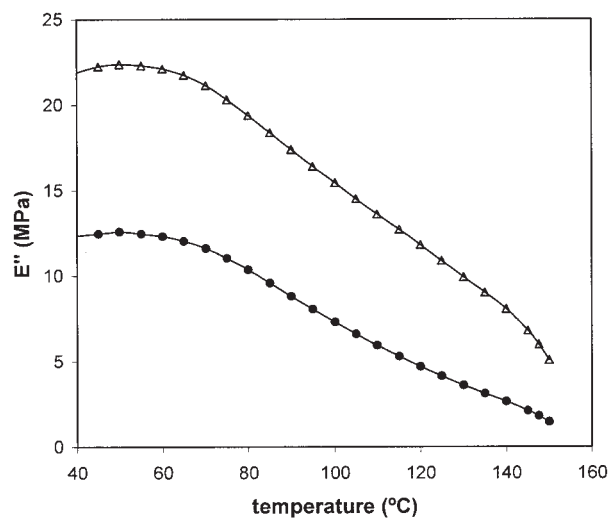
In the first part of the viscoelastic analysis of the PPB/FRH composite materials the influence of rice husk addition into the PP matrix are discussed from the results of Figures 1 and 2, which show the evolution of the storage modulus ( $E'$ ), loss tangent ( $\tan \delta$ ), and loss modulus with the temperature for the unfilled PP sample (PPB) and the untreated PP/FRH composite (BL). It is widely recognized that the incorporation of disperse fillers into polymers induces substantial changes in their mechanical and thermal properties. These changes are due to several factors, such as variations in the mobility of the macromolecules in the boundary layers, the orientating influence of the filler surface, or the different types of filler-polymer interactions.<sup>23</sup> As observed in Figure 1, the first effect of the filler addition on the polymer is the rigidity increase that occurs mainly at low and medium temperatures. However, at higher temperatures the large difference between the storage modulus of the filled and unfilled PP is reduced, because of the increasing mobility of the polymer molecules, which is responsible for the diminution of the low interfacial interactions between the two components of the composite material. Moreover, Figure 2 shows that the loss modulus of the DMA tests increases when the PP is filled.

This phenomenon may be produced by a mobility restriction of the polymer molecules that is due to the presence of the filler, decreasing the possibility of energy storage and the impact properties of the filled polymer.<sup>24</sup>

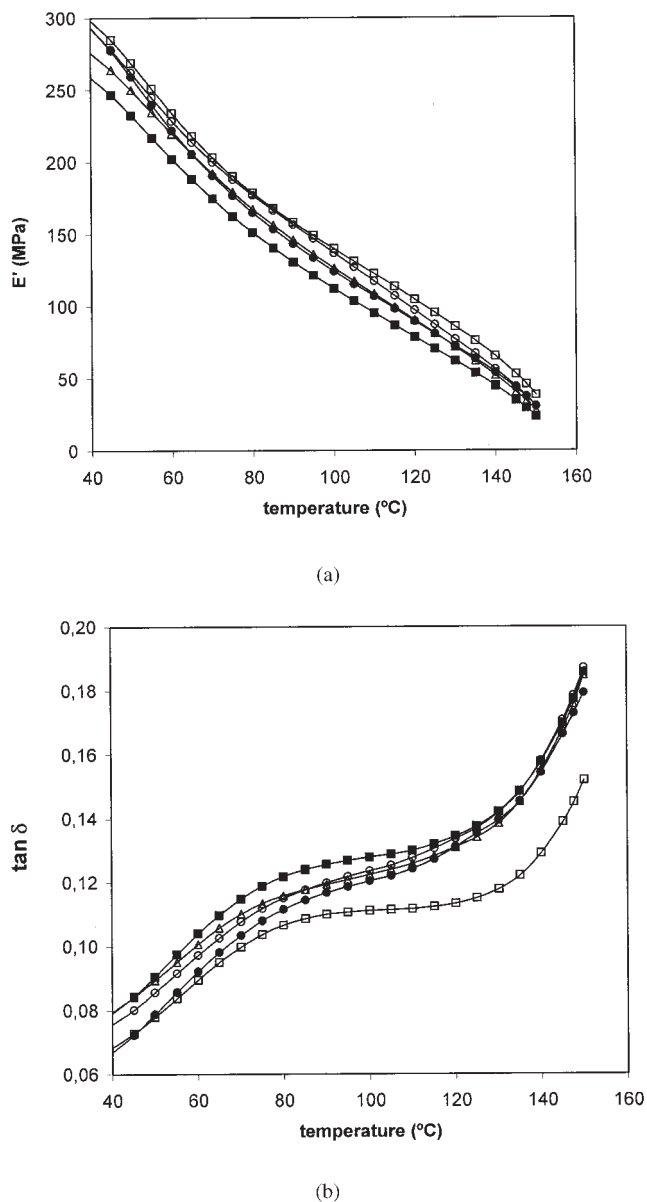
Different coupling agents were tested to improve the interfacial adhesion and the mechanical properties of the rice husk filled PP composite material. Figure 3 shows the variation of the viscoelastic properties (storage modulus and  $\tan \delta$ ) with different coupling agent types as a function of temperature in comparison with the untreated sample. Moreover, Table III shows the values of the storage modulus and the loss tangent of the composite FHR/PPB materials compatibilized with different coupling agents for some selected temperatures (40, 100, and 140°C). From these results, it is possible to show how each coupling agent causes a different compatibilizer effect between the PP matrix and the FRH filler.

In other works where similar materials were employed,<sup>25</sup> the addition of different coupling agents was responsible for an increase of the  $E'$  and the reduction of the peak of the  $\tan \delta$ . However, in our study, two antagonist behaviors occurred, as shown in the curves of Figure 3. On the one hand, MA-PP and the organosilane coupling agents (samples A3 and C1, respectively) acted in accordance with the cited studies, because the values of  $E'$  increase and the  $\tan \delta$  decreases. On the other hand, the addition of MA-SEBS as a compatibilizer in sample B3 reduces the modulus and increases the loss tangent of the PP composite.

Considering that it is possible to relate the values of the storage modulus to the stiffness of the material and the loss tangent with its damping and impact properties,<sup>23</sup> the effect of the different coupling agents



**Figure 2** The loss modulus ( $E''$ ) as a function of the temperature for (●) PPB and (△) nontreated FRH composite (BL).



**Figure 3** The viscoelastic properties as a function of the temperature for treated and untreated composite samples: (a) storage modulus ( $E'$ ) and (b) loss tangent ( $\tan \delta$ ) for (□) A3, (■) B3, (○) C1, (●) D3, and (△) BL.

on the mechanical properties of the materials is discussed in relation to the results of Figure 3 and Table III. The composite treated with MA-PP (sample A3) shows the highest storage modulus and the lowest loss tangent values for all ranges of temperatures. This mechanical behavior of sample A3 can be explained by the bad impact properties of the PP homopolymer with a high melt flow index used as carrier and by the strong bond between the MAH and the rice husk, which could be responsible for the fact that the matrix tends to fail in a rather brittle mode, as claimed by some sources.<sup>26</sup> In contrast, the composite compatibilized with organosilane (sample C1) has high modulus values and good impact properties at high tempera-

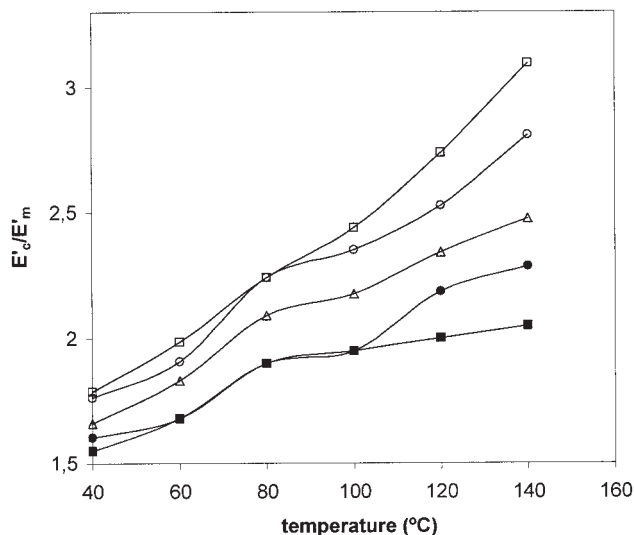
tures, proving the good performance of the organosilane as coupling agent for the FRH/PPB composites. Sample D3 with Ti-LLDPE as the coupling agent possesses a lower storage modulus and loss tangent than the untreated composite material, which could be attributed to the low compatibility between the LLDPE present in the coupling agent and the PP matrix. Finally, the MA-SEBS coupling agent reduces the strength of the composite material, but it is responsible for the excellent impact properties of sample B3, mainly at low temperatures. However, at 140°C, the low temperature resistance of the elastomeric carrier present in sample B3 produces a drop of its mechanical properties. As reported by some authors,<sup>17</sup> the major benefit of adding MA-SEBS as a coupling agent in natural fiber polymeric composites is the substantial improvement of the impact strength, which is attributable to the ductile SEBS interface layer formed between the fibers and the polymeric matrix.

Similar results about the effect of the analyzed coupling agents on the stiffness of the composite materials are obtained when the relative storage modulus ( $E'_c/E'_m$ ) is plotted as a function of the temperature. The  $E'_c/E'_m$  is defined as the relationship between the storage modulus of the composite ( $E'_c$ ) related to the modulus of the matrix ( $E'_m$ ). As can be observed in Figure 4, the addition of MA-PP and silane as coupling agents enhances the modulus values of the composites compared to the untreated sample, especially at high temperatures. Conversely, the addition of MA-SEBS and Ti-LLDPE as coupling agents worsens the stiffness of the composite material, which is evidenced by the reduction of their relative modulus in comparison with the untreated sample.

For variable temperature applications of fibers and reinforced composite materials, it is a common practice to evaluate the modulus retention term in the temperature range in use, in order to obtain better knowledge about the stability of the viscoelastic properties with temperature. Considering the range of temperatures between 40 and 100°C, the modulus retention term of a composite material was defined by Khanna et al.<sup>27</sup> from the expression  $E'_{100^\circ\text{C}}/E'_{40^\circ\text{C}} \cdot 100$ . The modulus retention terms of the different composites are provided in Table IV.

**TABLE III**  
Storage Modulus ( $E'$ ) and Loss Tangent ( $\tan \delta$ ) at Various Temperatures of FHR/PPB Composites

Sample	$E'$ (MPa)			$\tan \delta$		
	40°C	100°C	140°C	40°C	100°C	140°C
A3	298.5	139.7	65.3	0.0684	0.1111	0.1290
C1	293.1	136.8	56.1	0.0757	0.1236	0.1580
D3	288.5	124.0	52.6	0.0683	0.1204	0.1543
BL	275.9	126.2	52.0	0.0764	0.1224	0.1550
B3	258.8	112.1	44.7	0.0791	0.1278	0.1576

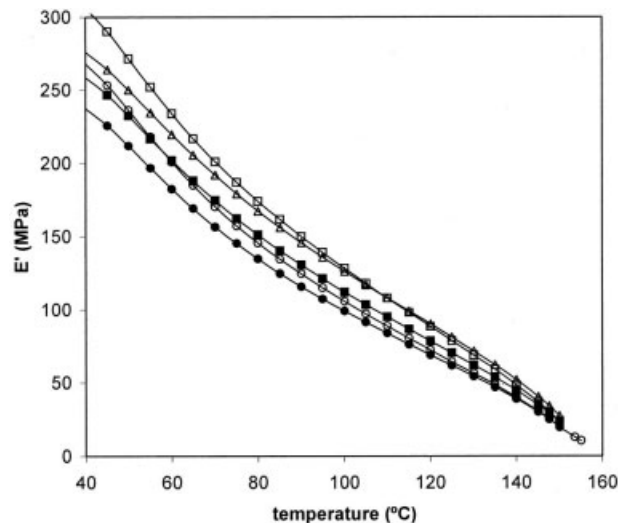


**Figure 4** The variation of the relative storage modulus (composite/matrix,  $E'_c/E'_m$ ) as a function of the temperature for treated and untreated composite samples: (□) A3, (■) B3, (○) C1, (●) D3, and (△) BL.

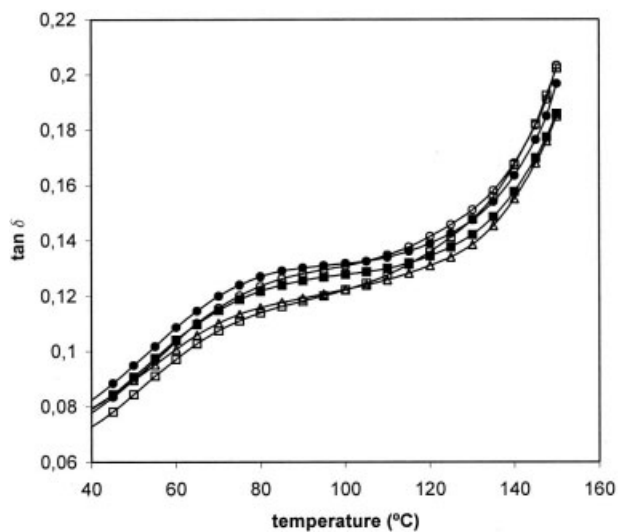
The modulus retention term is a very sensitive indicator of the changes of the storage modulus with the temperature. The value of this term is inversely proportional to the slope of the curve of the storage modulus versus the temperature. Therefore, an increase in the modulus retention term produces composites with more stable mechanical properties with the temperature. Among the different composite blends prepared in this study, the one with MA-PP as the coupling agent (sample A3) possesses the best mechanical performance within the studied temperature range, probably motivated by the strong interaction between MAH and the organic filler. In addition, the high melt flow index of the PP homopolymer as a carrier agent of the MA-PP coupling agent seems to have a low effect on the thermal properties of the final composite. By contrast, the storage moduli of the composites with MA-SEBS and Ti-LLDPE as compatibilizers (samples B3 and D3, respectively) are rather sensitive to the increase of temperature compared to the untreated sample (BL). In the case of the B3 sample, the presence of an elastomeric material (SEBS) with low deformation temperature could be responsible for this behavior. The low temperature stability of composite D3 could be motivated by the weak interaction of the organotitanate with the rice husk and by the low temperature resistance of the LLDPE carrier.

**TABLE IV**  
Variation of Modulus Retention Term of Different Samples

	A3	B3	C1	D3	BL	PPB
$E'_{100^\circ\text{C}}/E'_{40^\circ\text{C}} \times 100$	47.4	43.7	46.4	42.2	45.6	34.8



(a)

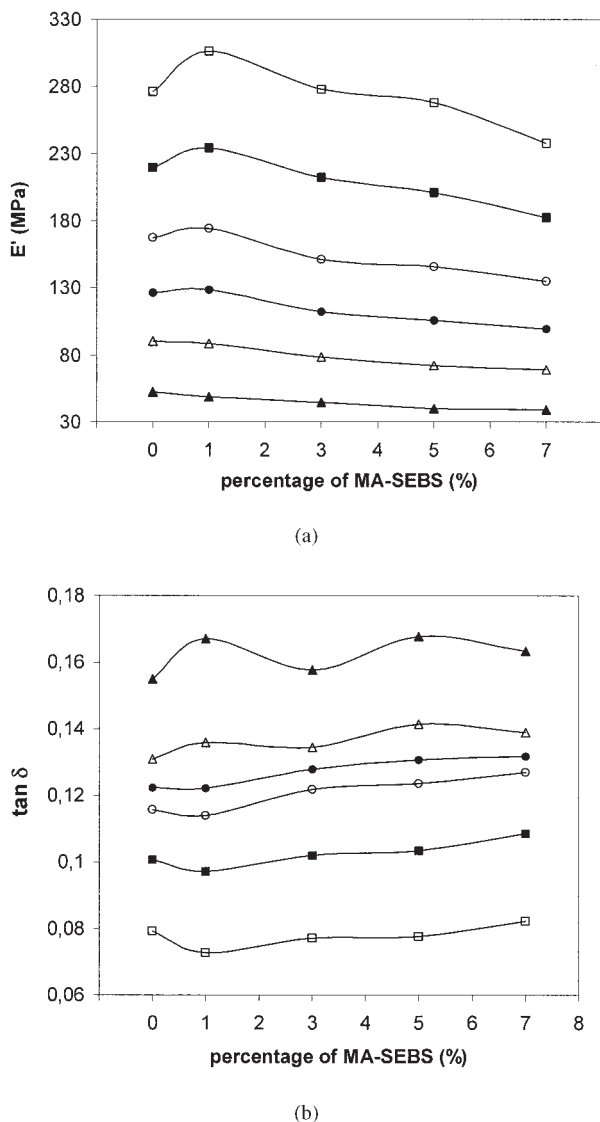


(b)

**Figure 5** The viscoelastic properties as a function of the temperature for MA-SEBS treated and untreated composite samples: (a) storage modulus ( $E'$ ) and (b) loss tangent ( $\tan \delta$ ) for (□) B1, (■) B3, (○) B5, (●) B7, and (△) BL.

One of the most important handicaps for the employment of polymer/organic filler composite materials is their impact behavior. Therefore, to improve the industrial possibilities for FRH as a filler of PP, tests with different concentrations of MA-SEBS coupling agent were performed. Figure 5 shows the storage modulus and the loss tangent as a function of the temperature for the treated composites with 1, 3, 5, and 7% (w/w) of MA-SEBS (samples B1, B3, B5, and B7) compared with the untreated sample (BL).

As can be observed, the tensile properties of sample B1 coupled with a small amount of MA-SEBS (1%) improve until the temperature is near the deformation temperature of the SEBS, when the modulus begins to decrease in comparison with the BL sample. However,



**Figure 6** The viscoelastic properties as a function of the amount of MA-SEBS at temperatures of (□) 40, (■) 60, (○) 80, (●) 100, (△) 120, and (▲) 140°C; (a) storage modulus ( $E'$ ) and (b) loss tangent ( $\tan \delta$ ).

with increasing coupling agent content, the elastomeric nature of the SEBS slightly reduces the stiffness of the composite material; but this effect is compensated with the enhancement of the impact properties, as evidenced by the higher loss tangent values. Chiang et al.<sup>28</sup> studies the interphase of PP/mica composites and demonstrated that with increasing coupling agent content the thickness of the interphase increases and the stress transfer improves significantly. These effects result in a slight decrease of the modulus and in an increase of the loss tangent, the same as in our study.

Figure 6 shows the variation of the viscoelastic properties as a function of the amount of coupling agent for different temperatures. Note that, with increasing temperature, the difference between two consecutive series of storage moduli decreases. This effect may be explained by the fact that the diminution of

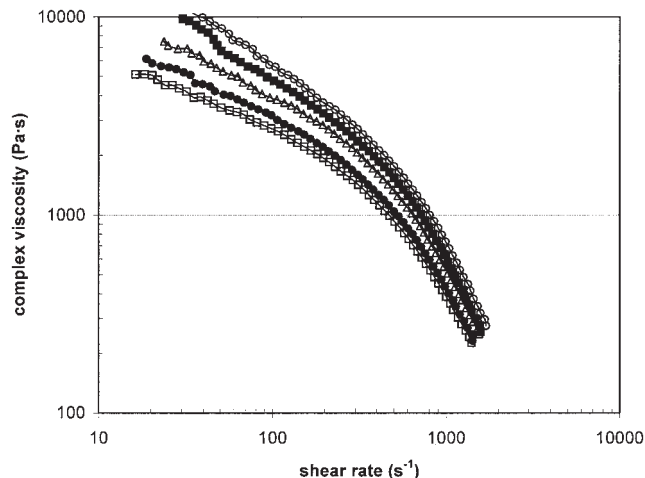
the modulus by the inclusion of an elastomeric material is compensated by the increase of the adhesion between the polymeric matrix and the filler. However, at higher temperatures, the presence of the elastomeric material and the low compatibility between PP and rice could be responsible for the unstable behavior.

### Rheological analysis

The effect of the proposed coupling agents on the rheological behavior of the PPB/FRH composites was analyzed by monitoring the complex viscosity of the samples with different shear rates. It is well known that the complex viscosity represents the viscoelastic resistance of the material during flow.<sup>29</sup> When different fillers are added to a polymeric matrix, the rheological behavior of the composite material is substantially modified. The fillers tend to align in the direction in which the shear force is applied, so the friction caused by the movement of the filler during its alignment is responsible for the viscosity variation. If the filler is not treated, its rough surface reduces the movement and the viscosity increases. Moreover, the different chemical surfaces of the matrix and the filler causes the formation of filler agglomerates, which hinder the flowing of the blend and consequently increases the viscosity.<sup>17</sup>

The effect of a coupling agent on the rheological behavior of a composite material depends on several factors, such as the flowing properties of the coupling agent indicated by their melt flow index or their bonding capability with the filler and the matrix. Some authors have reported that a high viscosity implies a strong interaction between the fibers and matrix motivated by the addition of a suitable coupling agent. Conversely, if the compatibilizer effect of the coupling agent is weak, the coupling agent may act as lubricant, reducing the friction between the fiber and matrix and leading to lower viscosity values compared to the untreated sample.<sup>17,29</sup>

Figure 7 shows the complex viscosity curves as a function of the shear rate at a constant strain of 5% for the untreated and treated composite samples. Observe that the coupling agents show different behaviors in regard to the relative increase or decrease of the composite viscosity in comparison with the untreated sample. Therefore, the high complex viscosity of the C1 composite suggests that the silane coupling agent provides strong interfacial bonding between the rice husk and the PP matrix, as was reported from the DMA studies. In contrast, the high melt flow index of the MA-PP coupling agent could explain the reduction of the viscosity of sample A3, following the mixture rule of viscosity,<sup>30</sup> because the DMA tests suggested a high interaction between the MAH and the filler. The strong interaction between each component of the blend provided by the MA-SEBS coupling agent is responsible for the viscosity increase of the sample



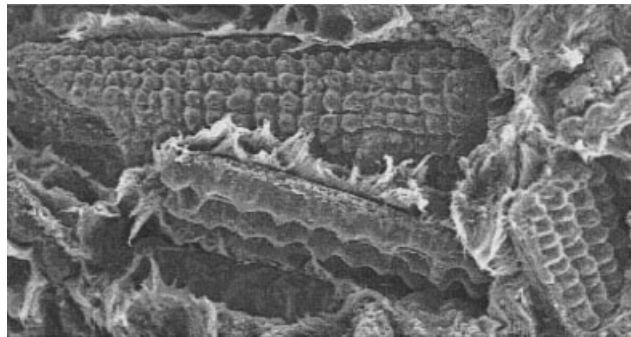
**Figure 7** The complex viscosity at 180°C as a function of the shear rate for treated and untreated composite samples: (□) A3, (■) B3, (○) C1, (●) D3, and (△) BL.

compared to sample BL, because the melt flow indexes of the coupling agent and the PP base material are rather similar. Conversely, the D3 sample has lower viscosity than the BL sample. This behavior can be explained by the weak interaction between the titanate coating and the rice filler, as the DMA tests demonstrated. The most probable hypothesis for this decrease of the viscosity may be the fact that the titanate can act as a lubricant, reducing the friction between the matrix and filler.

Considering the range of high shear rate values, the differences in the complex viscosities among the composites are reduced. This behavior can be attributed to the improved alignment of the PP chains caused by the high shear and to the formation of a thin “dead layer” of PP on the surface of the rice husk. This dead layer may act as a lubricant and reduce the friction and the viscosity of all the samples, as it has been pointed by different sources.<sup>31</sup>

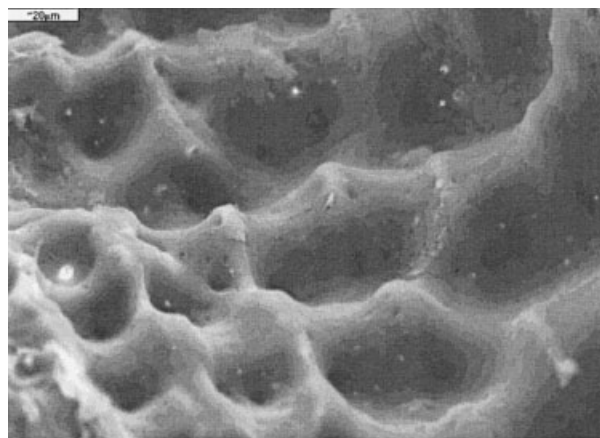
### SEM analysis

Several SEM micrographs of the rice husk filler and the fracture surfaces of some composite materials were performed at room temperature in order to analyze their morphology. Figure 8 shows the morphology of the surface of the rice husk filler, which possesses a structure similar to an ear of maize. In contrast, the SEM micrographs of the fracture surfaces from untreated and treated PPB/FRH composite samples are shown in Figure 9. Considering the filler–polymer interface, several differences in the fracture can be found between the untreated (BL sample) and treated composites (A3 sample). The fracture of the BL composite is clean, but the fracture of the A3 composite exhibits some irregularities in the holes where the filler was situated before the fracture (the negative of

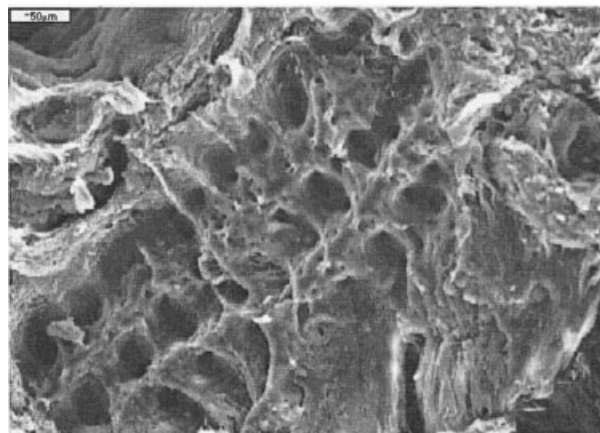


**Figure 8** An SEM micrograph of the fractured surface of an untreated PPB/FRH composite.

an ear of maize) due to the effects of the pull-out phenomenon. These irregularities can be explained by the enhanced compatibility between the filler and the



(a)



(b)

**Figure 9** SEM micrographs of an interphase filler–matrix from (a) an untreated PPB/FRH composite and (b) a treated PPB/FRH composite (A3); scale bars = (a) 20 and (b) 50  $\mu\text{m}$ .



matrix provided by the MA-PP coupling agent, as was reported from the DMA and rheological tests.

### CONCLUSIONS

The performance of four different coupling agents as compatibilizers in PP reinforced with FRH composites was analyzed by means of DMA, rheological tests, and SEM. From this study it was possible to select a suitable coupling agent for the PPB/FRH composite material, according to the desired mechanical and rheological properties.

The analyzed coupling agents showed different effects on the viscoelastic properties of the PPB/FRH composites. Both MA-PP and the organosilane coupling agents were responsible for an increase of the storage modulus and the reduction of the loss tangent, which was related to the enhancement of the stiffness of the composite and the reduction of its impact properties. Conversely, the employment of a coupling agent with an elastomeric carrier (MA-SEBS) caused a substantial improvement of the impact strength and a reduction of the storage modulus of the composite. Finally, the employment of the Ti-LLDPE coupling agent showed the worst compatibilizer effect, because the storage modulus and the loss tangent decreased in comparison with the untreated composite material. From the analysis of the storage modulus retention term it was concluded that the MA-PP coupling agent exhibited the best performance at high temperatures as a compatibilizer for PPB/FRH blends, enhancing the adhesion between the filler surface and the matrix. Moreover, the SEM micrographs evidenced the excellent compatibilizer effect of the MA-PP coupling agent.

We observed that the addition of coupling agents substantially modified the rheological behavior of the composite samples. The high melt flow index of the MA-PP coupling agent was responsible for the reduction of the viscosity of the composite. In contrast, the high complex viscosity of the composites with silane and MA-SEBS as coupling agents suggested that both coupling agents provided strong interfacial bonding between the rice husk and the PP matrix.

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