

Effects of Vinyltrimethoxy Silane on Thermal Properties and Dynamic Mechanical Properties of Polypropylene–Wood Flour Composites

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ABSTRACT: The viability of vinyltrimethoxy silane was investigated as a coupling agent for the manufacture of wood–plastic composites (WPC). The effect of silane pretreatment of the wood flour on the thermal and the dynamic mechanical properties and thermal degradation properties of the composites were studied. Moreover, the effect of organosilane on the properties of composites was compared with the effect of maleated polypropylene (MAPP). DSC studies indicated that the wood flour acts as a PP-nucleating agent, increasing the PP crystallization rate. In general, pretreatment with small amounts of silane improved this behavior in all the WPCs studied. Thermal degradation studies of the WPCs indicated that the presence of wood flour delayed degradation of the PP. Silane pretreatment of the wood flour

augmented this effect, though without significantly affecting cellulose degradation. Studies of dynamic mechanical properties revealed that the wood flour (at up to 30 wt %) increased storage modulus values with respect to those of pure PP; in WPCs with a higher wood flour amount, there was no additional increase in storage modulus. Pretreatment of the wood flour with silane basically had no effect on the dynamic mechanical properties of the WPC. These results show that with small amounts of vinyltrimethoxy silane similar properties to the MAPP are reached. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 1197–1204, 2008

Key words: wood flour; coupling agent; polypropylene; DMA; morphology; crystallization

INTRODUCTION

In recent years, agrowastes and agroforest materials have attracted great interest in the reinforced plastics market.^{1,2} Fillers of this type are very cheap and readily available. The use of woody materials as reinforcement in thermoplastics offers numerous advantages, including low cost, low density, and relatively high strength and stiffness.^{3–6} However, the poor compatibility between hydrophilic natural fillers and the hydrophobic polymers used as matrix may have adverse effects on the final properties of the composite: the polarity of the filler affects its dispersion in the nonpolar matrix,^{7,8} and poor adhesion may lead to composites with rather poor durability and toughness.^{9,10} The use of a coupling agent or “compatibilizer” may improve adhesion between the filler and the matrix, and thus enhance the mechanical properties of the composite. The most commonly

used coupling agents are the maleated polyolefins,^{9,11,12} isocyanates,^{13,14} and various organosilanes.^{15,16} There have been several studies^{17,18} about the use of organosilanes as coupling agents in wood flour (WF) composites, but the effectiveness of a given organosilane depends strongly on its organic group, so that the influence of each organosilane on composite properties needs to be characterized individually. In this study, a vinyltrimethoxy silane was evaluated as coupling agent for polypropylene (PP)–WF composites.

The silane crosslinking reaction takes place in the presence of water. This reaction proceeds over two steps. In the first step, the methoxyl groups are hydrolyzed to hydroxyl groups with production of methanol. The crosslinking takes place in the second step, in which the hydroxyl group is recombined through condensation.¹⁹ The reaction between the silanol groups (Si–OH) and hydroxyl groups of the wood creates covalent bonds, so that the vinyl group may be either chemically bonded to the PP matrix (covalent C–C) or may interact with it through van der Waals forces.

The aim of this study was to evaluate and explain the influence of vinyltrimethoxy silane on the thermal and dynamic mechanical properties of PP–WF

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composites. The effects of the organosilane were compared with those of a classic coupling agent, maleated polypropylene (MAPP).

EXPERIMENTAL

Materials

The raw material used to prepare the wood flour (WF) composites was an isotactic polypropylene (PP) (ISPLEN[®] PP 070 G2M), provided by RepsolYPF, with a density of 0.902 g/cm³ and a melt flow index (230°C; 2.16 kg) of 10 g/10 min. A WF from red pine, provided by Maderas del Noroeste S.A., Spain, was used as filler. It is known that the particle size of a WF can affect the mechanical properties of resulting composites; thus the WF was first passed through a 400- μ m-mesh sieve, discarding larger particles. The coupling agent used was Geniosil XL 10, a vinyltrimethoxy silane, provided by Wacker. The MAPP used was Fusabond[®] PMD511D, provided by Dupont, with a melt flow index (190°C; 1.0 kg) of 49 g/10 min. Finally, an alkene bis fatty amide (Glycolube WP2200), provided by Lonza Group, was added to the formulation as a processing aid, at a proportion of 3% with respect to the blend mass.

Sample preparation

Prior to the extrusion process, the WF was dried for 24 h at 100°C to 0.5–1% moisture content to prevent steaming in the extruder. It is important to dry WFs before processing, because moisture acts as a separating agent in the filler–matrix interphase.¹ Thermogravimetric tests showed that WF did not suffer thermal degradation during the drying process. A twin-screw extruder (DSE 20 Brabender) was used for the preparation of the composites. The temperatures of the barrel and the die were maintained at 190°C during extrusion, and the screw rate was 45 rpm. The extrudate was cooled and pelletized at the die exit, then dried and injection-molded into standard specimens using a Battenfeld Plus 350 apparatus, with an injection pressure of 1400 bar, a barrel temperature of 180°C, and an injection rate of 56 cm³/s.

WF–polypropylene composites (WPC) were prepared with different amounts of WF (0–50% by weight). Previously, the WF was treated with different quantities of vinyltrimethoxy silane (0–1% by weight with respect to WF weight). The silane was added to water using a standard mixing method (high-speed stirrer); the solution was then mixed into WF, which was then dried at 100°C for 24 h before composite preparation.

The nomenclature used for the different WF/polymer composites was (a) polypropylene with

untreated WF, designated A, B, C, D, and E with 10, 20, 30, 40, and 50% of WF mass, respectively; and (b) polypropylene with silane-treated WF, with percentage silane weight indicated next, e.g., A1 corresponds to the WPC with 10 wt % WF treated with 1 wt % silane.

Finally, the E_{MAPP} sample was extruded with 50 wt % WF, 40 wt % PP, and 10 wt % MAPP. The amount of MAPP was chosen taking into account manufacturer's guidelines and previous reports.^{20–22}

Thermal analysis

DSC analyses were carried out using a TA Instruments DSC 2010 differential scanning calorimeter. All the composite samples studied (around 10 mg) were heated from 30 to 200°C at a rate of 10°C/min under nitrogen atmosphere, to study melting behavior. To study the thermal behavior of the composites in depth, selected samples were subjected to nonisothermal crystallization: specifically, the B and E samples and the pure PP were maintained at 200°C for 5 min to erase their thermal history, then cooled to 30°C at different cooling rates (1, 2, 5, 10, and 12°C/min), and finally heated again to 200°C at 10°C/min to analyze nonisothermal crystallization and subsequent melting.

Thermogravimetric analysis

Thermogravimetric analysis of individual components and the WF–PP composites was performed using a Perkin–Elmer TGA-7 instrument with a platinum sample pan. All tests were performed in an argon atmosphere. Approximately 3–5 mg of sample was heated at 10°C/min from 50 to 700°C. The TG curves and their first derivative (DTG curve) were recorded in each test.

Dynamic mechanical analysis

The dynamic mechanical behavior of the samples was studied using a Perkin–Elmer DMA 7 analyser. The samples were parallelepipeds of 20 mm \times 4 mm \times 2 mm, analyzed in the three-point bending mode, from –50 to 150°C at 2°C/min under helium, with a frequency of 1 Hz. The storage modulus (E') and damping ratio ($\tan \delta$) were recorded as a function of the temperature.

RESULTS AND DISCUSSION

Before studying WPC properties, we characterized the WF, specifically its particle size distribution and its degradation behavior in TGA. This information proved very useful for explaining some of the experimental data (see later).

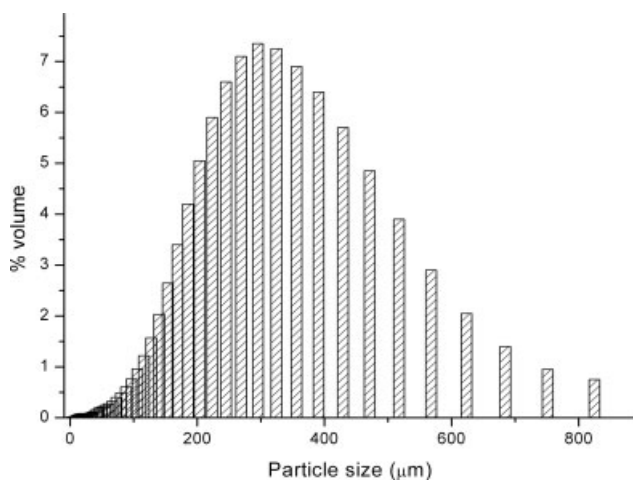


Figure 1 Particle size distribution of the wood flour.

Characterization of the WF

The average size of the WF particles was determined by a laser granulometric technique using a Coulter LS 200 apparatus. The high resolution of this instrument allows measurement of particles size between 0.4 and 2000 μm .

Figure 1 summarizes the size distribution of the WF particles, a wide distribution with a maximum at 300 μm . The WF was obtained using a sieve with 400- μm mesh, but some larger particles are present, indicating that some large elongated (nonspherical) particles were able to pass through the sieve.

The WF thermogram obtained by TGA (Fig. 2) shows two degradation steps. Degradation begins at 200°C with the degradation of lignin and hemicelluloses.²³ There is a larger shoulder region before the cellulose degradation, because of the degradation of the hemicelluloses.²⁴ The principal peak is that corresponding to the degradation of the cellulose (334.6°C), the main component of wood. The second peak (478.7°C) corresponds to the degradation of the

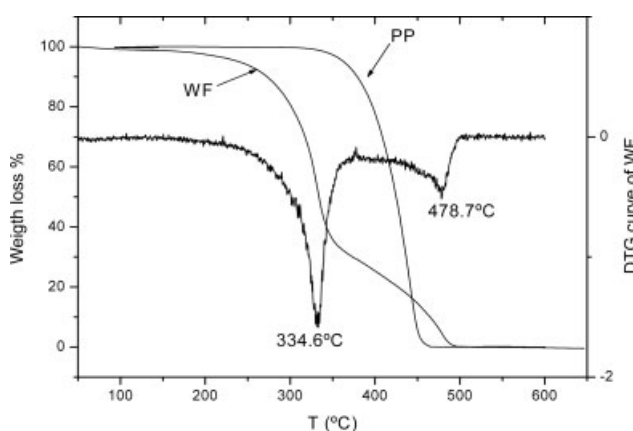


Figure 2 TGA and DTG curves for the wood flour and TGA curve for the PP.

lignin fraction.²⁵ The thermogram shows general agreement with other reports on the thermal degradation of wood and cellulose.^{26,27} As reported previously, the lignin degradation continues over a wide temperature range up to 800°C.²⁸

Thermal analysis

To obtain more information about the influence of WF on the melting and crystallization behavior of polypropylene, DSC analyses were performed. Table I shows the melting parameters for the PP and the WPCs, obtained at a heating rate of 10°C/min. The melting temperature (T_m) of the PP was 166.1°C, while the T_m of the WPCs was somewhat lower. In the WPCs with silane, the drop in T_m was lower than in the WPCs without silane. These drops in T_m could be related to a reduction in crystallite size in the presence of the WF.²⁹ Crystallinity values (X) were calculated using eq. (1), with $\Delta H_m^* = 190$ J/g for the melting enthalpy of 100% crystalline PP³⁰:

$$X = \frac{\Delta H_m}{\Delta H_m^*} \quad (1)$$

The values obtained (Table I) confirm that crystallinity undergoes slight variations with increasing WF amount. Only with 50 wt % of filler (sample E) is a marked increase in crystallinity seen with respect to the pure PP. In general, addition of silane gave somewhat higher crystallinity values with respect to the corresponding no-silane WPC. In the WPCs with small amounts of filler (samples A and B), the increase was proportional to the silane content; however, in the other composites (C–E), large amounts of silane did not further increase crystallinity. This is perhaps because the crystallinity increase due to the

TABLE I
Melting Parameters of the PP and the WPCs

Sample code	T_m (°C)	ΔH_m (J/g)	X
PP	166.1	94.4	0.50
A	163.2	82.8	0.48
A05	165.9	79.0	0.46
A1	164.8	86.7	0.51
B	163.5	68.5	0.45
B05	164.9	76.5	0.50
B1	164.7	80.2	0.53
C	163.8	59.5	0.45
C05	164.0	87.9	0.66
C1	164.9	85.6	0.64
D	165.4	56.4	0.49
D05	164.5	72.5	0.64
D1	165.3	68.8	0.60
E	163.9	62.2	0.66
E05	163.8	72.5	0.76
E1	164.1	67.8	0.71
E _{MAPP}	168.3	68.9	0.73

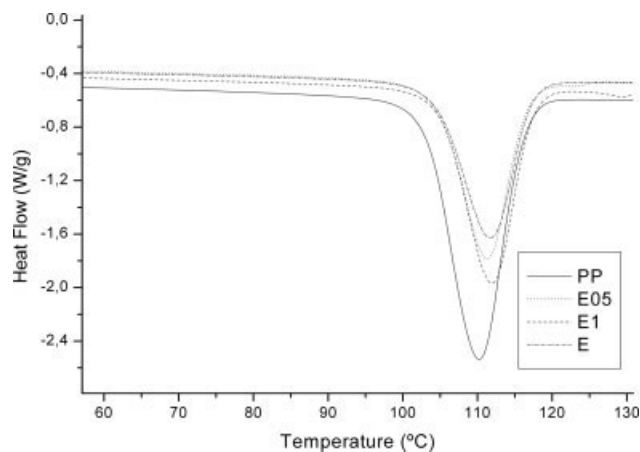


Figure 3 Normalized nonisothermal crystallization thermograms for the PP and the PP-WF composites with 50 wt % of wood flour.

better dispersion of the filler into the PP is counteracted by an increasing number of chemical bonds, hindering crystallization.

To study the crystallization behavior of the WPC in greater depth, nonisothermal crystallization tests were carried out with two selected samples, samples B (20 wt % WF) and E (50 wt % WF). Figure 3 shows an example of the cooling scans of the WPCs, with only one exothermic peak in each case, but with different peak shape and temperature. Some useful parameters obtained from the normalized DSC curves are listed in Table II.³¹ To simplify the results and discussion, only the data obtained at the cooling rate of 10°C/min was presented. The temperature of the crystallization peak (T_p) slightly shifted with the incorporation of WF. T_c is the temperature at the intercept of the tangents at the baseline and the high-temperature side of the exotherm, and ΔW is the width at half-height of the exothermic peak. The presence of WF in the polymer matrix increased the crystallization temperature and narrowed the exothermic peaks. These results indicate that the filler enhanced the crystallization rate, acting as a nucleating agent due to the heterogeneous nucleation of the

PP.^{22,29,32,33} In sample E, however, the crystallization rate did not increase as expected, probably because of the formation of agglomerates. In the WPCs made with silane-treated WF, the crystallization rate improved, although the silane effect was clearer in the $T_c - T_p$ values. These data corresponding to the temperature interval within which the crystallization rate is highest show that this interval was reduced in the WPCs with silane. Only the E1 sample showed slight deviation from this behavior. The ΔW data, determined after normalization of the exotherm peaks, indicate that the crystallite size distribution is narrower in the WPCs than in the pure PP.

Starting from the cooling scans, we tried to study the nonisothermal crystallization kinetics of the materials, calculating the crystalline conversion as $\frac{\Delta H_m(T)}{\Delta H_m^*}$, where $\Delta H_m^* = 190$ J/g is the melting enthalpy of 100% crystalline PP. The Figure 4 shows the crystalline conversion curves versus temperature obtained for the E and E1 samples. The other samples have a similar behavior. As can be expected, the conversion curves are displaced to lower temperatures as the cooling rate increases. It can be observed that the shape of the curves, with a much accelerated primary, does not allow the application of the Ozawa method (or similar) for the analysis of nonisothermal crystallization kinetics. And although alternative analyses were tested (as the calculus of the temperature at which 10% of the crystalline transformation is achieved (T_{10})), any new conclusions were obtained.

The second heating scan, after dynamic crystallization, demonstrated that T_m was maintained constant in all the samples, with a value similar to the pure PP (Fig. 5). The silane treatment improved the effectiveness of the WF as a PP nucleating agent, crystallinity increasing with increasing silane amount. The exception was again the E1 sample, the higher silane content of which did not increase crystallinity with respect to the E05 sample.

Comparing the E and E_{MAPP} samples, we see that the composite with MAPP had a higher T_m associated with the formation of larger crystallites. Both

TABLE II
Melting and Cooling Parameters of the PP and the WPC with 20 wt % and 50 wt % of Wood Flour

Sample code	Cooling scan			Second heating scan		
	T_p (°C)	$T_c - T_p$ (°C)	ΔW	T_m (°C)	ΔH_m (J/g)	X
PP	110.2	5.9	9.6	165.7	102.3	0.54
B	112.1	5.8	9.9	165.0	78.4	0.52
B05	111.1	5.3	9.2	164.6	92.3	0.61
B1	111.0	5.1	9.0	165.2	93.9	0.62
E	111.3	5.3	9.1	164.7	71.1	0.75
E05	111.8	5.1	9.1	164.9	83.2	0.88
E1	111.9	5.5	9.4	164.4	80.5	0.85
E_{MAPP}	111.8	6.3	11.1	165.8	74.9	0.79

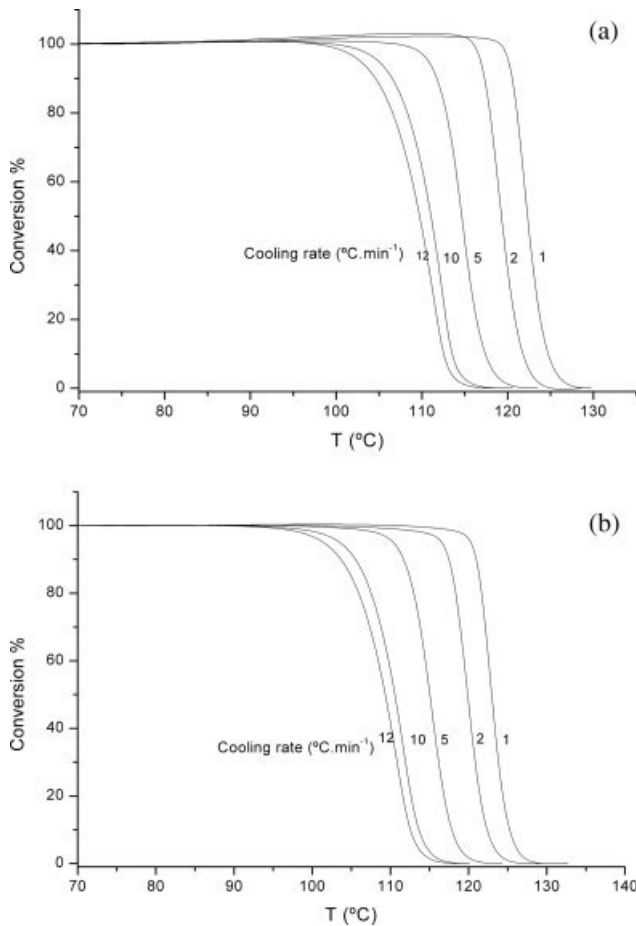


Figure 4 Crystalline conversion curves at the different cooling rates: (a) E sample (b) E1 sample.

the temperature range over which the crystallization occurs, and the crystallization peak, are wider. That is, the WF is not as effective as a nucleating agent when MAPP is used as coupling agent instead of the organosilane. In line with this, the crystallization value obtained for the E_{MAPP} sample was slightly

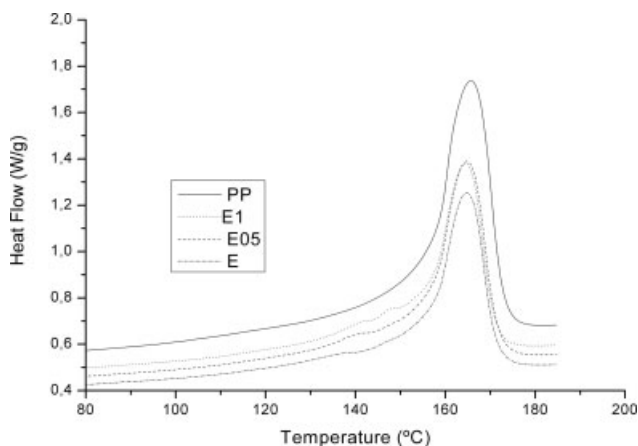


Figure 5 DSC heating scans of the PP and the PP-WF composites with 50 wt % of wood flour.

lower than that of the E05 sample (0.5 wt % of silane).

Thermogravimetric analysis

The thermal degradation data for the WF and the PP revealed that most of the degradation events occur between 300 and 500°C (Fig. 2). The WF is degraded at a lower temperature than the PP, but the slow charring reaction of wood still continues into the temperature range of PP degradation. The WPC samples showed two degradation steps, corresponding to degradation of the PP (at around 470°C) and of cellulose (at around 390°C). These thermal events can be correlated with the two peaks seen in the DTG curves. Plots of peak temperatures against WF amount in the composite are shown in Figure 6. These data indicate that the PP degradation peak migrated to higher temperatures as the WF content increased, but the temperature of the cellulose degradation peak remained constant. These results confirm that increasing WF amount influenced the thermal degradation of the PP in the WPC: the increasing thermal energy necessary for the PP degradation may be due to entry of the PP into wood capillaries.

The silane treatment slightly modified the thermal stability of the cellulose, and led to a small increase in the temperature of the PP degradation peak. However, no clear trend was observed with increasing silane amount.

Dynamic mechanical properties

The values of the storage modulus (E') in the glassy zone (-30°C) and the rubbery zone (30°C) are summarized for the different samples in Table III. These data show that adding WF to the PP increased the E' modulus in the glassy zone. This increase was constant up to 30 wt % WF, as expected, when a rigid filler is added to the PP. Composites with more than 30 wt % WF showed a reduction in E' modulus in

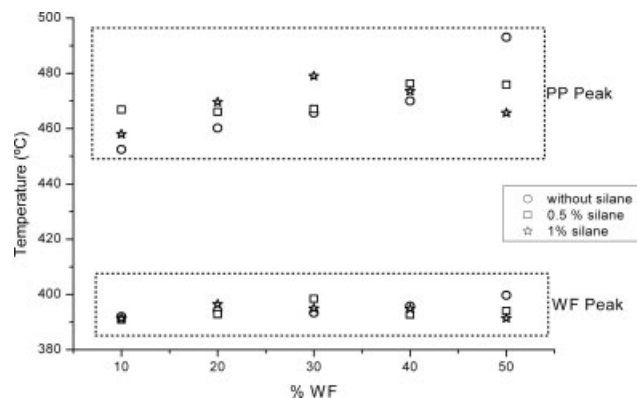


Figure 6 Peak temperature of the DTG curves as a function of WF content.

TABLE III
Storage Moduli and Glass Transition Temperatures of the PP and the WPCs, as Measured by DMA

Sample code	E' (10^9 Pa)		T_g ($^{\circ}$ C)
	$T = -30^{\circ}$ C	$T = 30^{\circ}$ C	
PP	4.63	2.34	9.4
A	5.53	3.78	11.2
A05	4.55	2.63	10.9
A1	4.51	2.54	9.7
B	5.49	3.60	11.5
B05	4.25	2.82	9.6
B1	6.22	3.57	9.9
C	5.87	3.84	10.0
C05	3.42	1.64	10.3
C1	7.08	3.94	10.6
D	4.84	2.95	12.6
D05	4.49	3.98	10.6
D1	6.47	4.11	9.6
E	4.29	2.66	13.7
E05	2.38	1.23	10.6
E1	4.69	2.90	9.9
E_{MAPP}	4.54	3.09	–

the glassy zone, and indeed with 50 wt % WF, the value obtained was lower than that for the pure PP. This decline in glassy-zone E' modulus at more than 30 wt % WF may be attributable to aggregation of the filler particles.³⁴

The WF also had a marked effect on rubbery-zone E' modulus, attributable principally to the fact that the ratio between the modulus of the filler and that of the PP is higher in the rubbery zone than in the glassy zone. Again, rubbery-zone E' values increased with WF amount up to 30 wt %, but all formulations showed better dynamic mechanical behavior than the pure PP in the rubbery zone.

Figure 7 shows plots of the damping factor ($\tan \delta$) versus temperature for the different WPCs. The $\tan \delta$ curve for the PP shows two maxima at around 10° C and 75° C, corresponding to the two transitions of this material. The lowest temperature (the β transition) is often assigned to the glass transition, and is related to molecular relaxations of the amorphous phase of the PP. The highest temperature (the α transition) is associated with the bound amorphous phase surrounding the crystals.³⁵ No clear trend was seen in the behavior of concentrated samples at temperatures above T_g , which could be attributed to problems of particle agglomeration due to the high proportions of WF used. The WF particles introduced a high degree of restraint, reducing the mobility and deformability of the matrix.³⁶ The values shown in Table III indicate that the $\tan \delta$ peaks of the WPCs appear at approximately the same temperatures. The small variations seen are possibly attributable to different residual moisture contents, which are possible in the dried samples because of the different WF proportions.

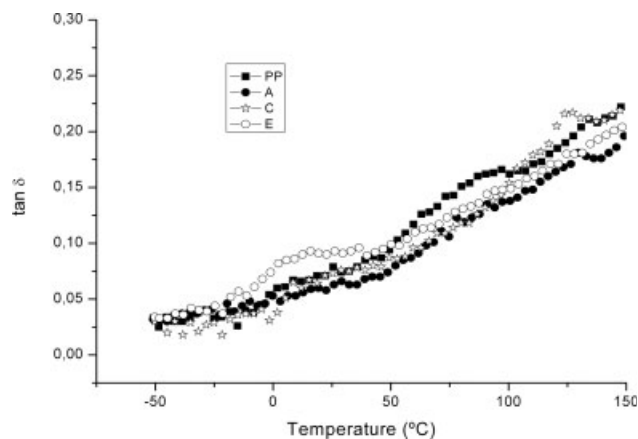


Figure 7 Plots of damping factor ($\tan \delta$) versus temperature for the different WPCs.

Increasing WF amount led to a broadening of the peak of the β transition, as well as a slight displacement to higher temperatures, resulting in higher T_g than the pure PP (see Fig. 7). This indicates that the filler particles increased the temperature interval over which glassy relaxations occurred, and reduced the mobility of the amorphous segments, perhaps due to inclusion of PP into the capillaries of the wood. The micrograph of the Figure 8 shows clearly as the wood cells stuff of PP. This behavior indicates a certain degree of miscibility between the WF and the PP, which could produce cooperative chain movements in the amorphous phase of the composites. When WF amount was increased, the second transition of the PP became flatter (indeed in some formulations the peak is scarcely appreciable), and is shifted to a slightly higher temperature.

The plots of storage modulus and $\tan \delta$ against the temperature obtained for the WPCs with silane were similar to those for the composites made with

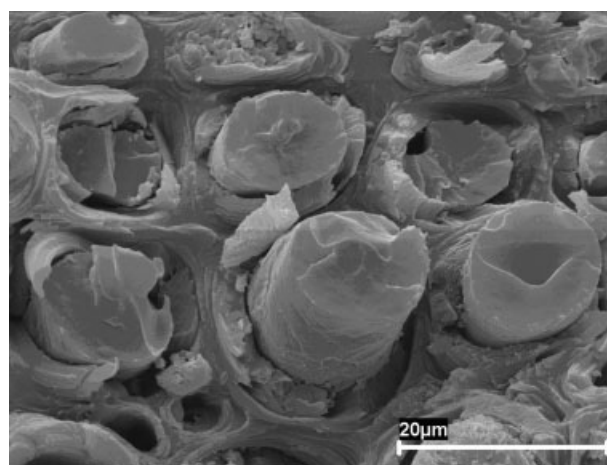


Figure 8 SEM micrograph of a PP/WF composite with 20% of untreated wood flour.

untreated WF. Table III summarizes the E' data and the glass transition temperatures for the composites. These data show that pretreatment of the WF with 0.5% silane did not improve the storage modulus, either in the glassy zone (-30°C) or in the rubbery zone (30°C). However, pretreatment with 1% silane led to a slight increase in E' in all formulations, except those with 10 wt % WF. This increase in E' obtained by silane pretreatment can be attributed to improvement of matrix/filler adhesion and filler dispersion. Nevertheless, the tests showed that silane addition did not prevent the decline in E' with higher WF amount. By contrast, the $\tan \delta$ curves show that silane pretreatment reduced the glass transition temperature and maintained it constant (around 10°C) even in the composites with higher WF content. A possible explanation for this behavior is that the silane treatment modified the filler surface; this might improve filler particle dispersion into the PP matrix, but could block PP inclusion into the wood capillaries, thus increasing the mobility of the amorphous PP phase.

When the E_{MAPP} sample is compared with the composites made with 50 wt % of silane-pretreated WF, it can be seen that the storage modulus values are of the same magnitude. The glass transition was not measurable from the $\tan \delta$ curve for the E_{MAPP} composite, since the curve is very flat in the temperature range of the transition.

CONCLUSIONS

WPCs were prepared with different WF contents (0–50 wt %) using a twin-screw extruder. A new organosilane was tested in different proportions as coupling agent. Both thermal and dynamic mechanical properties were studied and compared with the pure PP, and with composites prepared with WF not pretreated with the organosilane. Our conclusions are as follows:

- The thermal analyses indicate that the WF modified the crystalline structure of the PP: the WF particles acted as nucleating agent, increasing crystallization rate. However, the crystalline structure obtained was less perfect, showing smaller crystallites and, consequently, slightly lower melting-peak temperatures than the pure PP.
- Pretreatment of the WF with 0.5 wt % of the silane increased the crystallinity of the WPC, pretreatment with 1 wt % silane did not have any additional effect on crystallinity, perhaps because it increased adhesion between filler and matrix, hindering the mobility of the PP molecules.
- Nonisothermal crystallization analyses of the WPCs made with 20 or 50 wt % of WF helped

clarify the behavior of the WF as a PP nucleating agent. These analyses demonstrated that the presence of WF in the polymer matrix enhanced the crystallization rate. In general, the silane pretreatment enhanced the effectiveness of WF as PP nucleating agent, crystallinity increasing with increasing silane amount.

- Thermal degradation studies of the WPCs showed that degradation of the WF and the PP occurs simultaneously, within the same range of temperatures. However, the derivative of the thermal degradation curve of the WPC showed two different peaks, corresponding to degradation of the PP and of cellulose (the major component of the WF). Analysis of the temperature of these peaks indicated that degradation of the PP was affected by the amount of WF in the composite: the PP peak was shifted to higher temperatures with increasing WF amount. This could be explained by entry of the PP into the capillaries of the wood, requiring more thermal energy for the same degradation. In contrast, the cellulose peak was maintained at the same temperature. The silane pretreatment of the WF slightly modified the temperatures of the PP and cellulose peaks, but there was no clear relationship between amount of silane and direction or magnitude of effect.
- The dynamic mechanical experiments indicated that storage modulus in the glassy zone increased with WF amount up to a maximum value in the C sample (30% WF). Storage modulus in the rubbery zone showed a more marked increase with WF amount; again, the maximum value was obtained for the C sample. Thus WF amounts above 30% do not have favorable effects on dynamic mechanical properties.
- The damping factor curves for the WPC indicated that the PP glass transition temperature (T_g) increased proportionally with WF amount. This rise in T_g could be due to a reduction in the mobility of the amorphous segments of the PP when it is located within the capillaries of the wood.
- Pretreatment of the WF with the organosilane did not induce major variations in the storage modulus of the resulting WPCs. However, the glass transition temperature was reduced in all of the WPCs made with silane-pretreated WF, by comparison with WPCs made with untreated WF. The silane treatment probably modified the filler surface, improving its dispersion into the matrix but hindering the inclusion of the PP into the wood, and thus increasing PP chain mobility.
- Comparing the effects on WPC properties of WF pretreatment with MAPP and the organosilane,

we see that in the composites with MAPP-pretreated WF crystallization was slower than in the composites made with silane-pretreated WF. However, the dynamic mechanical behavior of the two types of composite was similar.

- These findings indicate that MAPP can be replaced with small quantities of organosilane, obtaining materials with similar properties.

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