

Agrofillers in Polypropylene Composites: A Relationship Between the Density and the Mechanical Properties

Mauro Moresco, Simone Maria Leal Rosa, Evelise Fonseca Santos, Sônia Marlí Bohrz Nachtigall

Chemistry Institute, Federal University of Rio Grande do Sul, 9500 Bento Gonçalves Avenue, Porto Alegre, Rio Grande do Sul, Brazil 91501-590

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ABSTRACT: One of the most interesting properties of agrofilled polymer composites is their light weight. Polypropylene composites containing six different agrofillers were prepared in a mixer, and their properties were examined in terms of the density of the fillers and composites. The densities of the composites increased with the level of filler but did not show a direct relationship with the density of the fillers used. This probably happened because of the different degrees of filler densification during processing. The composites showed decreased tensile strength

and increased elastic modulus with filler loads, and the specific mechanical properties showed similar trends. However, the addition of maleated polypropylene improved the tensile strength and decreased the density; this improved the specific properties of the composites filled with cane, wood, and bamboo. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 117: 400–408, 2010

Key words: composites; density; fibers; mechanical properties; renewable resources

INTRODUCTION

Polymer composites containing agrofillers have attracted technological and academic interest in recent decades, mainly because of their economical and ecological advantages. In comparison to traditional synthetic fillers, such as carbon and glass fibers, most vegetable fillers are very inexpensive.¹ In addition, they do not need high energy consumption for preparation and present reduced abrasiveness.² Other advantages over traditional reinforcing fillers include renewability, biodegradability, and environmentally friendly characteristics. Also, the hollow nature of vegetable fibers may impart acoustic insulation or damping properties to certain types of matrices.³ Natural fiber polymer composites have been chosen for many applications, mainly in automotive components,⁴ building materials, and household articles.⁵

One of the most interesting properties of lignocellulosic materials is their low density. It allows the preparation of polymer composites with good specific properties. In many applications, such as in the shoe industry, weight is a very important point

(lightweight shoes are comfortable, and their transportation is easier). In the automotive industry, weight reduction improves fuel consumption, which addresses environmental issues. However, despite its importance, few studies have focused on the relationship between the density of natural fillers and the overall properties of their polymer composites.^{1,6}

Agrofillers can exhibit some variation in chemical composition according to their kind, their origin, and the part of the plant from which they are obtained. However, most are essentially composed of cellulose, hemicellulose, and lignin. These natural polymers constitute the cell wall of plants and are responsible for their high specific strength.⁷ Lignin not only holds together the other components but also acts as a stiffening agent for the cellulose molecules within the cell walls. Therefore, the lignin and cellulose content of fillers influences the strength of composites.⁸ Table I shows the chemical composition of the agrofillers used in this study, as described in the literature. With the exception of cork, one can observe from these data that the main constituent of most fillers is cellulose. Cork is the bark of *Quercus suber L.*, and it shows another important feature: a high content of suberin (ca. 30 wt %). Suberin is an aromatic–aliphatic crosslinked polyester that acts as a protective barrier between the plant and the surrounding environment.⁹ The different compositions of cork in comparison to the other fillers are expected to produce significant differences in the properties of polymer composites prepared with it, mainly in the density and mechanical properties.

Correspondence to: S. B. Nachtigall (nachtiga@iq.ufrgs.br).
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TABLE I
Chemical Constituents of Selected Agrofillers (wt %)

Filler	Cellulose	Hemicellulose	Lignin	Suberin	Extractives	Ash	Reference
Bamboo	42–49	24–28	24–26	–	–	1–2	9
Coir	43	21	31	–	4	–	10
Sisal	74–75	10–14	8	–	2–6	1	11
Cane	54–55	17–30	25	–	1–3	1	11
Wood	40–50	21–36	22–34	–	3	–	9
Cork	11	12	33	29–33	9	–	12

Two different forms are usually used to describe the density of lignocellulosic materials. One is the absolute density, which is hard to measure and is related only to the solid part of the material, that is, the cell walls, and disregards any voids present in the structure. The other is the apparent (or bulk) density, which considers the solid parts plus the voids present. Although the cell wall of typical lignocellulosic materials show very close absolute densities (according to Aziz and Ansell,⁶ it varies from 1.4 to 1.5 g/cm³), the apparent densities can be quite different from one filler to another.^{10,11} However, the densification of the filler can occur during composite processing resulting from compression of its porous cellular structure.¹ It can be expected that different degrees of densification can be accomplished by different fillers during similar processing conditions according to their specific structure or apparent density.

Additionally, a new kind of porosity can be developed during composite preparation, that is, a porosity in the otherwise continuous polymer matrix.¹² This new porosity has been attributed to low compatibility among the phases because lignocellulosic materials are polar and polymer matrices can sometimes be very apolar. Such porosity can be identified by air-filled cavities at the fiber/matrix interface regions or by air-filled cavities in the interior of filler subassemblies due to poor matrix impregnation. Heterogeneous forms and dimensions of plant fibers can help to restrict matrix impregnation, to increase void content and reduce density.

The polymer matrix must transfer the stress to the filler through the interface when it is submitted to mechanical forces. So, good adhesion among the fillers and the polymer matrix is important for achieving composites with good properties.¹³ The addition of coupling agents has been a common way to improve this adhesion. Coupling agents based on small molecules (silanes, titanates, etc.) or on functionalized polymers [polypropylene modified with maleic anhydride (MAPP), organosilane, etc.] have been described.^{3,13,14} The presence of a coupling agent is also expected to affect the composite density.

In summary, all of the mentioned features have a noteworthy contribution on the overall composite density. Henceforth, it was our objective in this study

to establish a relationship between the density of various lignocellulosic materials and the density and overall properties of polypropylene (PP) composites prepared with these materials and to obtain materials with good properties for the shoe industry. Bamboo, sisal, coir, wood, and sugarcane were used as fillers. For comparison, cork particles were also used in the preparation of the composites because cork shows a very low density and could lead to composites with high specific properties. The effect of the addition of a commercial MAPP was also investigated.

EXPERIMENTAL

Materials

Sisal, sugarcane, and bamboo (in the form of fibers); wood and coir (in the form of powder); and cork (in the form of particles) were supplied by Arteccla SA (Campo Bom, Brazil). The fillers were oven-dried to a constant weight before the preparation of the composites at 60°C and at reduced pressure. Isotactic PP (melt flow index = 3.5) from BRASKEM SA (Trinunfo, Brazil) was used as the matrix. MAPP (CHEMS MP 300PP, Chemko, Seoul, Korea) was used as the coupling agent.

Characterization of the fillers

We measured the fiber lengths from expanded photographs with the software ImageJ v1.4, developed at the National Institute of Mental Health (Bethesda, MD) and considering 200 units. Around 8 mg of filler was submitted to thermogravimetric analysis (TGA) in a TGA Q50 analyzer from TA Instruments (New Castle, DE). Samples were heated from ambient temperature to 800°C at 20°C/min under nitrogen.

We determined the apparent density of the fillers by introducing an adequate volume of the material in a glass funnel of standard dimensions (ASTM D 1895, for plastic materials) and allowing the filler to flow freely into a cup of 100 cm³ capacity mounted 3.8 cm below the funnel. After all of the material passed, the excess was scraped off. The filler was weighed, and the density was calculated. A helium



Figure 1 Photographs of the fillers. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

pycnometer Multipycnometer MVP-1 acquired from Quantachrome Instruments (Boynton Beach, FL) was used to measure the absolute density of the fillers (duplicated samples).

Compounding

PP pellets were introduced in a Haake Rheometer 600p internal mixer (Karlsruhe, Germany) at 170°C and 50 rpm. After 2 min of processing, with two contrarotatory rotors, the filler was added, and the system was maintained to process for 3 min more. Compositions with 10, 20, and 30 wt % filler were prepared. In some formulations, 1% of the coupling agent was added. MAPP was dry-mixed with the filler, and they were introduced together.

Characterization of the composites

Hot-pressed samples were prepared at 190°C for 2 min at 2.500 Lbf. Before compression was started, the samples were premelted for 5 min. At the end, they were cooled to 90°C under controlled conditions, that is, at a rate of -2°C/min.

The bulk density of the composites (ρ_c) was determined according to ASTM D 792-91; the sample was weighed in air (W_a) and immersed in pure ethanol (W_e), with a known density of ethanol ($\rho_e = 0.91 \text{ g/cm}^3$), ρ_c was calculated with eq. (1):

$$\rho_c = \rho_e W_a / (W_a - W_e) \quad (1)$$

Tensile tests were done with samples obtained by hot compression. Tests of at least five specimens of

each sample were performed with a universal testing machine (Emic DL 10000, São José dos Pinhais, Brazil) equipped with a 5-kN load cell at a cross-head speed of 5 mm/min and at room temperature (ASTM 638-90). Before the tests, the specimens were dried at 60°C for 4 h.

RESULTS AND DISCUSSION

Characterization of the fillers

Visual observation showed that the morphology of the fillers was quite different. Although coir and wood were in the form of powder, cork was in the form of particles of irregular shapes, and bamboo, sugarcane, and sisal were in the form of short fibers. The photographs of the materials are shown in Figure 1. The fiber lengths determined from expanded photographs of bamboo, sugarcane, and sisal indicated that bamboo fibers had shorter sizes, whereas sugarcane and sisal presented similar distributions of fiber lengths (Fig. 2).

Before the preparation of the composites, the thermal stability of the fillers was studied by TGA because the allowed processing temperature depended on its thermal resistance. TGA also provided the level of water absorption of each material and the residual mass after degradation. Figure 3 shows the derivative curves of weight loss of the fillers as a function of the temperature under nitrogen.

The thermal degradation profile of the fillers reflected the differences in their structures, showing some steps relative to the various components of the materials. According to the literature, the

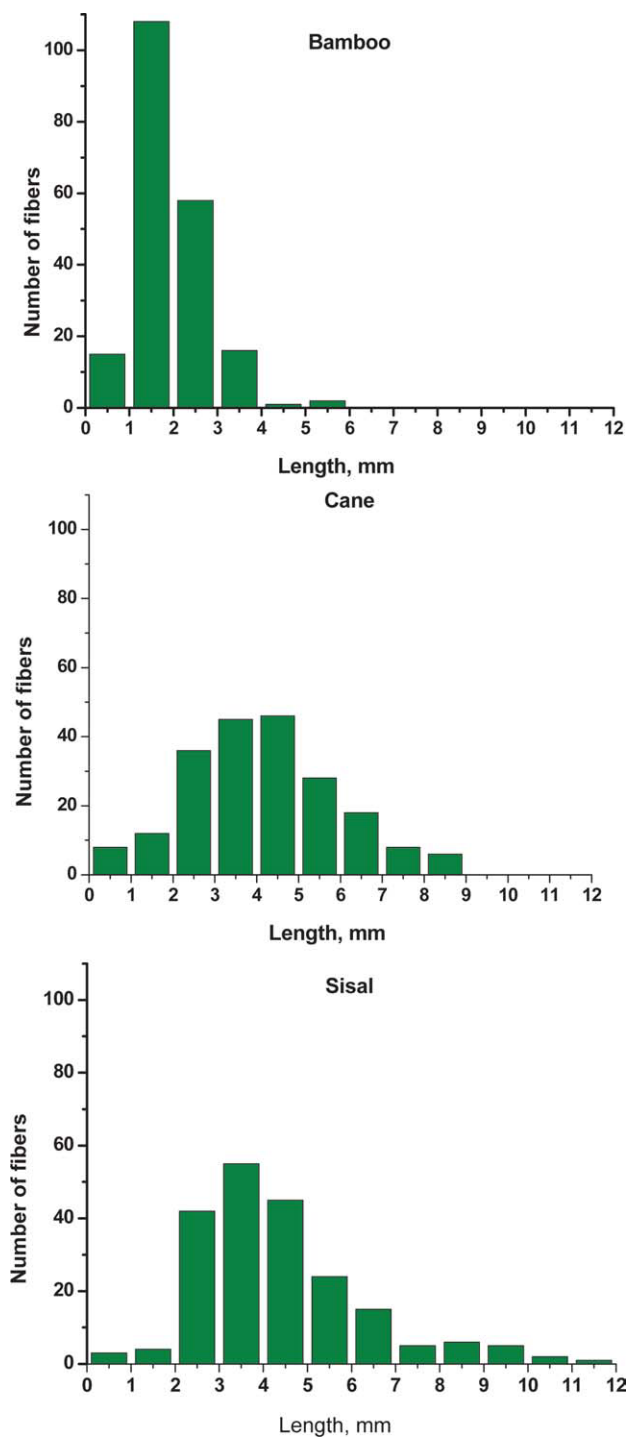


Figure 2 Length distributions of the bamboo, cane, and sisal fibers. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

decomposition temperature of hemicellulose is around 225–325°C, that of cellulose is 325–375°C, and that of lignin is 250–500°C.¹⁵ In our study, all of the fibers started thermal degradation near 200°C and showed minimal mass loss at the usual processing temperature of PP in the mixer, that is, around 180–190°C. The filler that showed the earliest degra-

degradation was coir. Its derivative thermogravimetry (DTG) curve displayed two intense peaks centered at relatively low temperatures (~ 280 and 340°C); these corresponded to the decomposition of superposed hemicellulose, lignin decomposition (first peak), and cellulose decomposition (second peak). We already saw this behavior in a previous study using coir flour from another source.¹⁶ These thermogravimetric patterns showed a relatively high lignin content of native Brazilian coir samples, as already described.¹⁷ On the other hand, we observed that the maximum temperature of decomposition of cork was substantially higher than that of the other fillers. This was probably related to the presence of suberin, which shows a higher thermal resistance than cellulose.¹⁸ The other four lignocellulosic materials showed quite similar degradation patterns, with the peak corresponding to the degradation of hemicellulose seen as a shoulder at the left of the main peak coming from cellulose and lignin.

From the plotted curve, the materials showed a thermal event below 100°C corresponding to the loss of absorbed water. The mass losses in this step and the residual mass obtained at 800°C are shown in Table II.

Cork showed the lowest degree of water absorption. This was probably because of its lower content of cellulose and hemicellulose; these are very hydrophilic substances. Lignocellulosic fillers in the form of fibers (bamboo, cane, and sisal) showed intermediate degrees of water absorption, whereas the highest degree of water absorption was found for fillers in the form of flour, probably because of the highest surface area of its particles, which facilitated contact with humidity.

A high level of residue was found at 800°C in all fillers; this showed that thermal degradation was not complete at that temperature.

Table III shows the values of the fillers' densities determined with the helium pycnometer (absolute density) and through the Archimedes' principle (apparent density). The absolute density of the cork could not be determined experimentally. The results obtained with the helium pycnometer showed that cane short fibers were the more dense material (1.62 g/cm^3). The other lignocellulosic materials showed similar absolute densities, varying from 1.40 to 1.44 g/cm^3 . However, all of the densities were higher than that of PP and other common polyolefins; this indicated that the lignocellulosic composites prepared with such polyolefins showed a tendency to present densities higher than that of the matrices.

The filler density determined by gravimetry showed different features of the fillers. The apparent density can give ideas about the presence of pores in fillers and about the effect of the particle geometry on its own flow and arrangement. We cannot forget

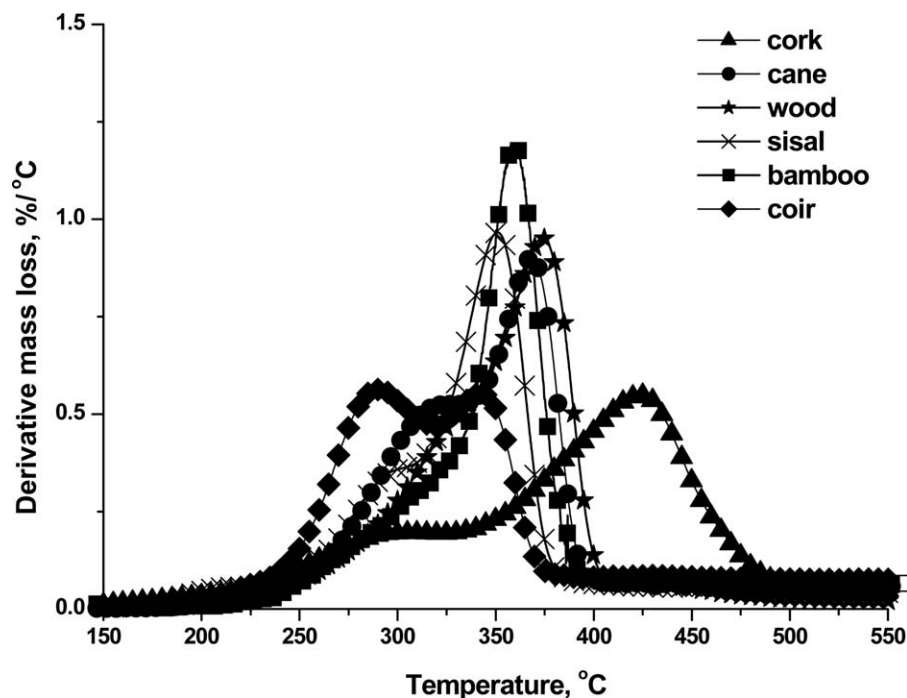


Figure 3 DTG curves of the fillers.

that the fillers showed distinct morphologies, and this certainly affected the results. Considering this, we had the following growing apparent densities: Cork < Sugarcane < Wood < Sisal < Bamboo < Coir. We observed later that this sequence was followed in some of the analyzed parameters, which thus validated these results.

Characterization of the composites

Torque

First, PP composites with six different fillers were prepared with an internal mixer. The filler content varied from 10 to 30 wt %. Ongoing torque measurements indicated the incorporation of fillers into the matrix and showed stability after some minutes. Table IV presents the final torque values of the compositions. An increasing torque was observed with filler loading; this indicated an increase in the viscosity of the systems. The viscosity rose with filler because the mobility of the polymer chains was re-

stricted by the added particles. At the same time, an increase in filler loading was accompanied by a decrease in the polymer loading, and this helped to increase the viscosity.

A straight relation was found among the final torque and the apparent density of the fillers. With exception of the wood flour composites, the other composites showed a tendency of decreasing final torque with increasing apparent density of the filler. This behavior is well represented graphically in Figure 4. Deviations were probably related to the different morphologies of the particles (fibrous, rounded, or irregular) that affected the flow of polymer chains and dispersed particles during the experiments and to the wettability of the fillers with the polymer during compounding.

Density

The bulk densities of the composites were determined by immersion in ethanol with the Archimedes' principle. This method precludes the use of

TABLE II
Moisture Content and Residual Mass Determined by TGA

Filler	Moisture content (wt %)	Residual mass (wt %)
Bamboo	7.1	12.1
Coir	7.4	9.6
Sisal	6.3	16.7
Cane	6.6	7.9
Wood	7.8	14.5
Cork	4.0	13.1

TABLE III
Densities of the Fillers

Filler	Absolute density (g/cm ³)	Apparent density (g/cm ³)
Bamboo	1.40	0.328
Coir	1.41	0.510
Sisal	1.42	0.224
Cane	1.62	0.106
Wood	1.44	0.210
Cork	–	0.094

TABLE IV
Final Torque of the Composites (N m)

Filler ^a	Filler load		
	10%	20%	30%
Cork	7.9	9.8	11.4
Cane	7.1	7.8	8.3
Wood	6.6	7.2	8.1
Sisal	7.1	7.8	8.9
Bamboo	6.5	7.1	7.5
Coir	6.5	6.9	7.1

^a The fillers are arranged by increasing apparent density.

a liquid that is less dense than the samples to be tested. Unfortunately, the composites prepared with cork did not meet this requirement, and its densities could not be determined. Less dense solvents (toluene and hexano) were also used, but they were not effective at all. As the mechanical properties of the cork composites were later found to be very low, no more efforts were made for its density determination. The bulk densities determined for the other composites are shown in Figure 5. Most compositions presented densities higher than the polymer matrix, and the density increased with filler loading. These results are in good accordance with those of previous studies in the literature.¹²

Because most fillers had similar absolute densities and their weights in the composites were equal, variations in the composite densities revealed that other factors affected this property. These factors were related to the geometry of the fillers, the size of the holes and voids that made polymer penetration difficult, and also some differences in the chemical composition that could impart different wettabilities by the matrix. In summary, all of these factors affected

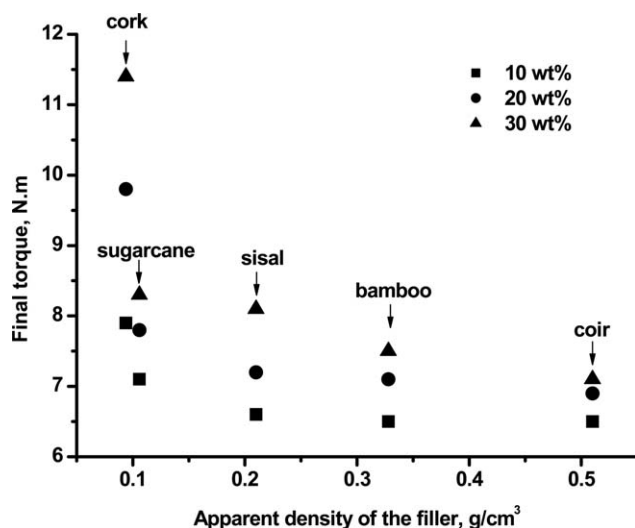


Figure 4 Final torque of the composites with respect to the apparent density of the fillers.

the degree of densification suffered by the fillers during processing. The highest density was achieved by the composite containing 30 wt % bamboo fibers (0.97 g/cm^3); this was quite apart from the absolute density of the filler (1.40 g/cm^3) and was closer to the density of the polymer matrix (0.905 g/cm^3). This result indicates that a large percentage of voids was still present in this material.

Tensile properties

The bulk use of lignocellulosic fillers in plastic composites today is based on chips or flour, which have adverse implications on the mechanical properties of the materials. It is known that unlike fibers with a uniform cross section and a relatively high aspect ratio, the capability of irregularly shaped fillers to support stress transmitted from a thermoplastic matrix is rather poor.¹⁹ This behavior has been attributed to the weak bonding between the hydrophilic filler and the hydrophobic polymer matrix, which obstructs the stress propagation allied to the possibility of filler agglomeration.²⁰ For short fiber composites, it has been proposed that failure occurs either by fiber breakage or by fiber pullout combined with matrix fracture.²¹ PP showed a tensile strength of $31.8 \pm 0.4 \text{ N/m}^2$. All composites had decreased tensile strength as compared to the matrix (Fig. 6). This decrease was bigger at higher filler loadings. The cork composites showed the poorest properties and made these materials almost inadequate for most applications. Because cork contains a low level of cellulose, which was an important structural component of the other fillers, this behavior was expected. On the other hand, as the absolute density of cork was supposed to be very low, its volume fraction in the composites was high; this contributed to the lower tensile properties. Among the other fillers, the results were quite

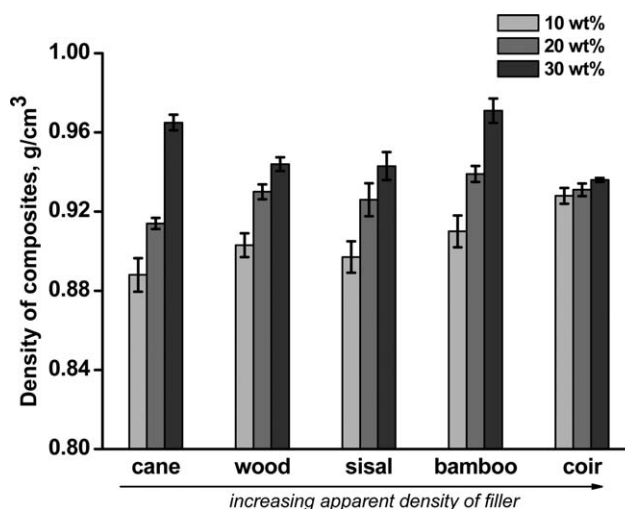


Figure 5 Density of the composites (density of PP = 0.905 g/cm^3).

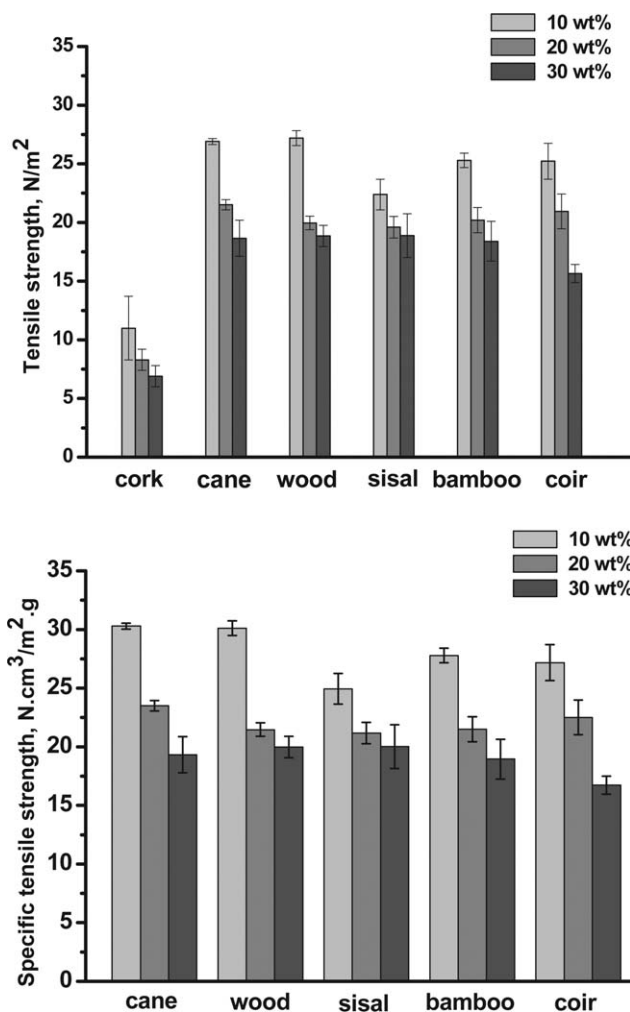


Figure 6 Tensile strength and specific tensile strength.

similar, but the sugarcane (fiber) and wood (flour) composites presented slightly better tensile strengths. The lowest tensile strength was achieved by the composite containing 30 wt % coir fibers; this matched well with our previous observations from TGA, which indicated a low level of the structural component cellulose for the coir fibers.

The specific tensile strength was calculated from the ratio of tensile strength to density, and it is also shown in Figure 6. The same tendency of decreasing properties with filler loading was observed. Even when we considered that bamboo, cane, and sisal were in the form of short fibers, their properties were not significantly different from the other fillers. This indicated that low adhesion to the matrix, chemical composition, and other parameters, regardless of the size of the units (within this range), showed bigger contributions to the specific tensile strength. With regard to the specific tensile strength, the composites containing 30 wt % coir presented the lowest performance.

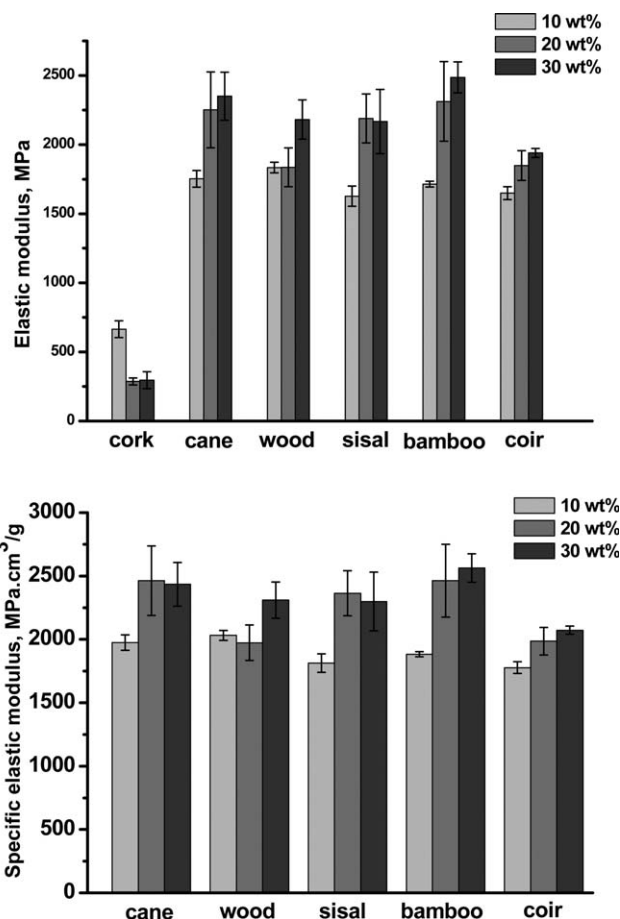


Figure 7 Elastic modulus and specific elastic modulus.

The results from the elastic modulus and specific elastic modulus testing are shown in Figure 7. Composites containing cork again showed low properties, even lower than those of the polymer matrix. For the other fillers, we verified a tendency of both properties to increase with filler loading; this

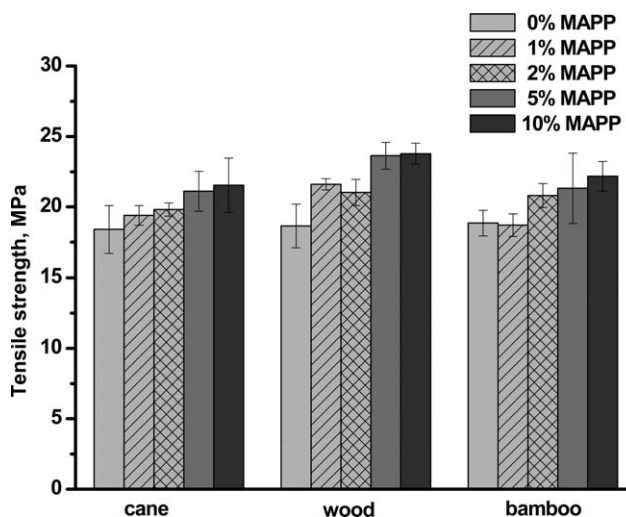


Figure 8 Tensile strength of the composites containing 30 wt % filler and various MAPP concentrations.

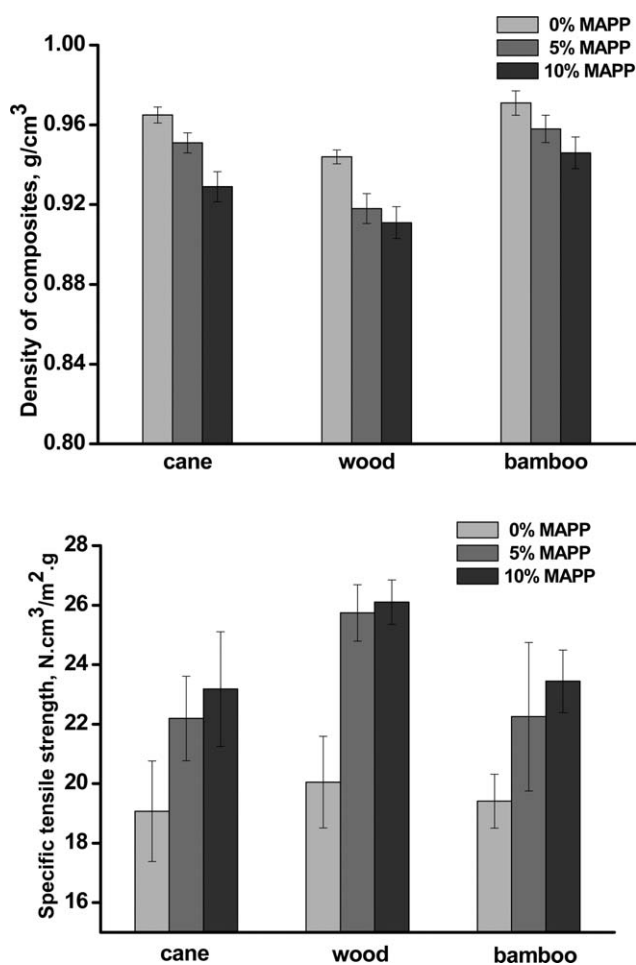


Figure 9 Density and specific tensile strength of the composites containing MAPP (filler content = 30 wt %).

indicated that the lignocellulosic fillers used were more rigid than the PP used as the matrix. Bamboo composites with 30 wt % filler showed the highest elastic modulus and the highest specific elastic modulus.

Coupled composites

To improve the interfacial bonding strength between the fillers and the matrix polymer, maleated PP was used as a compatibilizing agent in selected compositions. Samples containing 30 wt % sugarcane, wood flour, and bamboo and 1, 2, 5, and 10% MAPP were prepared. The tensile tests indicate that the coupling agent improved the mechanical properties of the composites, as shown in Figure 8. A comparison among the three different fillers used indicated that the beneficial effect was more pronounced in the wood flour composites, in which the maximum tensile strength increased by more than 27% with the addition of 10 wt % MAPP.

Surprisingly, the density determinations of the coupled composites reported a new behavior, that is,

a slight decrease in the density with MAPP addition, as shown in Figure 9. The determined densities of the coupled composites were somehow unexpected because, usually, the presence of coupling agents decreases the spaces between fillers and the matrix, turning the matrix more homogeneous.¹³ This could lead to higher densities. Instead of this, a decrease in the density was observed. The explanation we propose for these results is that the coupling agent probably formed a layer on the surface of the fillers, preventing the penetration of the polymer matrix into the particles. In this way, the holes and voids present in each filler particle were not filled with the matrix and pushed down the densities of the composites. Despite small differences among them (<4%), the densities affected the results of the specific tensile strengths of the coupled composites. In conclusion, addition of MAPP improved both the tensile strength and the density of the materials and led to better specific tensile strengths (Fig. 9). A better balance among the tensile strength and low weight was achieved for composites prepared with 30 wt % wood flour containing 5 and 10 wt % MAPP.

CONCLUSIONS

PP composites containing 10–30 wt % of six different vegetable fillers were prepared to obtain materials with good properties for the shoe industry. The fillers were cane, wood, sisal, bamboo, coir, and cork. TGA showed that coir was the less thermal stable filler, whereas cork was the more thermal stable filler. However, the results indicate that no appreciable degradation occurred at the processing temperature used in this study.

The absolute densities of the fillers determined with the helium pycnometer showed values from 1.40 to 1.62 g/cm³ for all but one filler: the absolute density of cork was not possible to determine. The values of its apparent densities varied in a wider range, from about 0.1 to 0.5 g/cm³; these denoted different morphologies and void contents in the fillers.

We verified that the viscosity and the densities of the composites increased with filler load. The viscosity was seen to be dependent on the filler apparent density and on its geometry. However, the density of the composites could not be strictly related to the density of the fillers, but it showed some variations, probably related to different degrees of filler densification during processing. The highest density was achieved for the 30 wt % bamboo fiber composite (0.97 g/cm³).

The composites showed decreased tensile strengths and increased elastic moduli in comparison to the polymer matrix in all cases. The specific properties showed similar trends. The composites

prepared with cork showed very low mechanical properties. Among the other composites, that with 30 wt % coir showed the lowest properties.

The addition of maleated PP improved the tensile strength and decreased the density of the composites containing 30 wt % cane, wood, and bamboo. In this way, the specific properties of these composites were greatly improved, mainly in the case of the wood composites.

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