Sugarcane Bagasse Reinforced Phenolic and Lignophenolic Composites

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ABSTRACT: Lignin, extracted from sugarcane bagasse by the organosolv process, was used as a partial substitute of phenol (40 w/w) in resole phenolic matrices. Short sugarcane fibers were used as reinforcement in these polymeric matrices to obtain fiber-reinforced composites. Thermoset polymers (phenolic and lignophenolic) and related composites were obtained by compression molding and characterized by mechanical tests such as impact, differential mechanical thermoanalysis (DMTA), and hardness tests. The impact test showed an improvement in the impact strength when sugarcane bagasse was used. The inner part of the fractured samples was analyzed by scanning electron microscopy (SEM), and the results indicated adhesion between fibers and matrix, because the fibers are not set free, suggesting they suffered a break during the impact test. The modification of fiber surface (mercerization and esterification) did not lead to an improvement in impact strength. The results as a whole showed that it is feasible to replace part of phenol by lignin in phenolic matrices without loss of properties. © 2002 John Wiley & Sons, Inc. J Appl Polym Sci 83: 880–888, 2002

Key words: lignin; sugarcane bagasse; composites; vegetal fibers; phenolic matrix; mechanical properties

INTRODUCTION

The most common matrix materials for composites are polymeric. The processing of polymer matrix composites (PMCs) does not necessarily involve high pressures and does not require high temperatures. Therefore, problems associated with the degradation of the reinforcement during manufacture are less significant for PMCs than for composites with other matrices. For these reasons, polymer matrix composites were developed rapidly and soon became accepted for structural applications.¹

Phenolic resins are frequently used in the plastic and automotive industries because of their versatile properties, and their application in the aerospace industry is growing. The resole phenolic resin presents excellent properties as an adhesive on metal surfaces and it can develop a relatively strong chemical bond due to the complex formation between units of *o*-methyl hydroxyl phenol and the hydrated metal oxide surface.²

The fire resistance of phenolic resins is directly related to the structure and thermal degradation mechanisms of these polymers. The thermal degradation of the phenolic resins leads to the production of a crosslinking structural chain, which results in low flame spread rates. The fire resistance of phenolic resins can still be improved by the addition of flame retardant elements, such as phosphorous or bromine. The phosphorous addition at the monomeric stage increases both the thermal stability and the limiting oxygen index of

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the resin when compared with resins obtained by the addition of phosphorous at the polymeric stage.³ Phenolic resins have a high critical oxygen index (45–70%) and therefore are difficult to ignite and keep burning. Phenolic resins are among the lowest known smoke-producing plastics and they produce less toxic smoke than most flameretardant plastics. A typical phenolic resin produces four times less carbon monoxide, six times less hydrogen chloride, and a lower level of hydrogen bromide than a flame-retardant polyester resin.³

Phenolic resins also present excellent dimensional stability, thermal stability, chemical resistance, and load-bearing capability at elevated temperatures. Usually, engineers designate the phenolic resins for precision moldings in aggressive environments. The thermomechanical properties of the phenolic resins are directly related to the high crosslinking density that results from the cure (polymerization) of these resins. However, the high crosslinking density results in low impact strength, making the phenolic resins fragile compared with many other plastics, which for some application corresponds to a limitation.³

Because of the low impact strength limitation, increasing this property in phenolic resins has become the objective of several studies in an effort to develop materials with better properties. These studies have led to the current development of phenolic matrix based-composites.³

Industrialized countries highlight the importance of research related to the conversion of agricultural byproducts and surpluses of the crops into new, profitable products. Aiming to develop technology allied with environmental preservation, research centers have been studying the viability of using natural fibers as reinforcement agents in polymeric matrices in composites. Over the past several years, natural fibers have begun to be used as reinforcement, seeking the production of low-cost composites. Fibers based on cellulose are strong, light in weight, low cost, broadly available, and obtained from a renewable source.⁴

The raw materials used in the production of phenolic resins (usually phenol and formaldehyde) are derived from petrochemicals. More and more, the substitution of synthetic products for its natural equivalent has been studied because of both economic and environmental reasons. Lignin, a natural macromolecule that is usually discarded by the paper industry, can be used to substitute part of phenol in phenolic resins because aromatic rings of the phenolic type⁵ are present in its complex structure. Using lignin leads to the formation of an integrated network of phenol and lignin-based units without loss of the properties of the resin.⁶

With the intent of adding more value to sugarcane bagasse, a natural raw material that is readily available in Brazil, studies have been developed in our laboratory to determine the usefulness of bagasse, as well as the lignin and cellulose extracted from sugarcane.^{5,7–14} In our search for the use of vegetable materials, as well as the components of the vegetables, cellulose and lignin, research on composites reinforced with natural fibers has also been undertaken. In this paper, thermoset phenolic and lignophenolic matrices reinforced with sugarcane bagasse are discussed.¹⁵

EXPERIMENTAL

Pre-Polymer Syntheses

Formaldehyde (37%) was added to a phenol/KOH solution (1.38:1.0:0.06, w/w) and mixed by mechanical stirring. After 90 min under reflux (70 °C), the solution was cooled to room temperature and HCl was added until the solution was neutralized. Water was eliminated under reduced pressure.

In the synthesis in which phenol was partially substituted by lignin (40%, w/w), the first step was to add formaldehyde to a KOH solution of lignin (pH 9), keeping the solution under reflux (70 °C) for 60 min. In that way, the methylol group (-CH₂OH) was introduced in the phenolic rings of lignin. Next, phenol and formaldehyde were added to the "methylolated" lignin following a procedure similar to the one just described.

Cure Reaction

The phenolic pre-polymer was mixed with resorcinol (10%, w/w) by mechanical stirring at 50 °C for 30 min. The cure reaction was carried out in a mold (220.0 × 99.5 × 5.0 mm) under pressure (50 kgf/cm²) at two different temperatures (85 and 125 °C). Non-modified sugarcane bagasse fibers (length: 1.5 cm; 47.9% cellulose; crystallinity index, $I_c = 0.50$)¹⁶ were added to the pre-polymer (40, 50, 60, and 70%, v/v) and the mixture was mechanically stirred (30 min, 50 °C), before the cure process. The composites were prepared with randomly oriented fibers. The pre-polymer lignophenolic was mixed with resorcinol as already described for the phenolic pre-polymer; then it was added to *p*-phenolsulfonic acid (0.5%, w/w), a cure accelerator. The lignophenolic composites were prepared as already described.

Phenolic and lignophenolic composites were also prepared using modified sugarcane bagasse fibers according to the following procedure. In step 1, the fibers were suspended in NaOH solution (10%) for 1 h at 0 °C, under mechanical stirring. Then, the fibers were washed until all alkali was eliminated and dried in an air-circulating stove. In step 2, the fibers obtained in step 1 were exposed to a saturated solution of succinic anhydride in xylene, under reflux, with mechanical stirring for 24 h. The fibers were then extensively washed with water and dried in an aircirculating stove.

Analyses

Impact Strength

Two type of tests were performed. In one, 10 unnotched samples were cut from each plate and shaped according to DIN 53453 (Deutscher Industrie Normen: $50.0 \times 4.0 \times 6.0$ mm). Impact behavior was assessed with a Charpy impact tester (model PSd 50/15, built by Heckert). Impact tests were carried out at room temperature with an impact speed of 4 m/s and incident energy of 15 J. In the second type of test, 10 unnotched samples were cut from each plate and shaped accordingly to ASTM D256 (63.5 \times 12.7 \times 4.0 mm). Impact strength was assessed with an Izod impact tester (CEAST Resil 25). Impact tests were carried out at room temperature with an impact speed of 3.46 m/s and incident energy of 5.5 J. From these results, a mean value was calculated (see Figure 1 and Table III) for each composite.

Shrinkage Test

The shrinkage test was performed according to DIN 53464. To calculate the shrinkage, the lengths of the mold and of the composites after compression molding were considered.

Shore Hardness Test

The Shore hardness test was carried out at room temperature according to ABNT NBR7456 (Brazilian Association Technical Standard). A Shore D durometer (5 Kg load) was used, and five measurements were carried out for each sample. A mean value was calculated from those measurements.

Water Absorption

The water absorption test was performed according to ASTM D570 (American Society for Testing and Materials), which describes several types of tests. The selected test considers water absorption both during 24 h and until saturation.

Thermal Analysis

Differential scanning calorimetry (DSC) measurements were performed with Netzsch equipment (model DSC 200) at a heating rate of 10 °C/min, an atmosphere of synthetic air (20 mL/min), and a temperature rangeof -25 to 300 °C. Differential mechanical thermoanalysis (DMTA) was performed with Du Pont equipment (model 983). Samples of the thermosets and composites were cut (\sim 40 \times 10 \times 3 mm) and carried out under the following conditions: fequency, 1 Hz; temperature range, 20–250 °C; heating rate, 10 °C/min; bending, mechanical.

Microscopy

Scanning electron microscopy (SEM) was carried out in a Zeiss-Leica apparatus (model 440), with electron acceleration of 20 kV. The analyzed fractured samples were covered with a thin layer of gold in a "Coat System" Bal-Tec.

RESULTS AND DISCUSSION

The results of the Charpy impact tests are shown in Figure 1. The impact strength presented by the thermoset phenolic is within the range mentioned in the literature $(3.5-6.0 \text{ kJ/m}^2)$.^{17–19} The impact resistance of a composite is determined by the total energy dissipated in the material before final failure occurs. The total energy absorbed by the material is the sum of the shock or dynamic wave energy dispersed and the energy consumed during plastic deformation, plus the energy needed for creating new surfaces. The microfailure mechanisms possibly operating during impact loading include matrix cracking, fiber-matrix debonding, fiber breakage, and fiber pull-out. At the moment of impactor-material contact, the dynamic energy is partly dispersed in the material.²⁰ The data indicate that the total fracture



Figure 1 Unnotched Charpy impact strength of thermoset phenolic and composites as a function of the fraction of fiber (v/v).

energy of the composites increased with the quantity of fibers. The results reveal that when the volume of fibers increases, the energy-absorbing capability of the composites also increases, indicating that during fracturing, the contribution from sugarcane bagasse short fibers is significant.²¹

Comparing the results of the phenolic samples cured at 85 °C and those cured at 125 °C,¹² it is observed that the thermosetting cured at 125 °C has lower impact strength. Probably, at 125 °C the crosslinking reaction was more extensive and the material became harder and brittle. On the other hand, for the composites, when the cure occurs at 125 instead of 85 °C, a small increase in impact strength is observed. Cellulosic fibers such as bagasse act as useful crack growth inhibitors (crack stoppers).²²

In Figure 2, the behavior of phenolic and lignophenolic thermosets, as well as the behavior of the related composites, can be compared. It can be inferred that the introduction of lignin as a component of the phenolic matrix practically does not alter the impact strength of the composites.

The results of the shrinkage test (Table I) show that the presence of lignin does not affect the shrinkage. The incorporation of fibers into the polymeric matrix promoted a slight increase in the shrinkage of the molded piece, probably due to the interaction between fibers and matrix that happens during the cure process. These results are in agreement with those found in the literature, which reports the shrinkage of composites of phenolic matrix is in the range of 0.2 to 0.5%.¹⁸

The hardness test is a reference that can inform about the tenacity characteristics of the ma-



Figure 2 Unnotched Charpy impact strencth of phenolic and lignophenolic thermosets and related composites, cured at 85 °C as a function of fiber fraction (v/v).

terial. The Shore hardness test is applied to polymeric samples and it measures the resistance to the durometer penetration in cone form, being the measure done by the spring contraction. Therefore, the durometer works as a static method. It is important to note that in that test, the material surface hardness is evaluated and not the hardness of the inner part of materials. The results (Figure 3) show that the hardness decreases as the fiber percentage increases. These results indicate that the presence of fibers decreases the mechanical resistance to the penetration of another body because of the difference of elastic modulus between matrix and fiber. However, the result could also be a consequence of the fiber hygroscopicity, because the water molecules could act as a plasticizer on the surface. Because the test is made on the sample surface, the larger the fiber fraction, the larger the humidity absorption, and the smaller the degree of hardness. The same behavior is observed when lignin is present in the

Table IShrinkage Percentage of Thermosetsand Bagasse Fiber Composites

Material	Shrinkage (%)	
Thermoset phenolic	0.40	
Composite phenolic/40% fiber	0.54	
Composite phenolic/50% fiber	0.54	
Composite phenolic/70% fiber	0.54	
Thermoset lignophenolic	0.45	
Comp. lignophenolic/40% fiber	0.50	
Comp. lignophenolic/50% fiber	0.50	
Comp. lignophenolic/70% fiber	0.50	



Figure 3 Hardness (Shore D) as a function of fiber volume fraction for phenolic and lignophenolic thermosets and related composites.

matrix. Comparing the hardness of the samples with and without lignin, it is observed that the presence of lignin in the matrix leads to a slight decrease in the hardness. Probably, this difference is a consequence of a larger absorption of water in the surface due to the presence of several polar functional groups in lignin.

In Table II, the results of water absorption tests are shown for thermosets and related composites. These cumulative results indicate that the composites containing a larger fiber proportion present better performance in relation to the impact strength. On the other hand, a larger proportion of fibers increased the water absorption of the composites because of the fiber hygroscopicity.

The results of DMTA analysis are shown in Figure 4. It should be noted that this analysis was



Figure 4 *E'* as a function of temperature for lignophenolic composites.

made under dynamic conditions, whereas the other mechanical properties were evaluated under static conditions. Therefore, there is not necessarily a direct correlation between the results using those different techniques. Above 150 °C, the modulus increases as a consequence of a second curing step (that turns the material more rigid). This result is confirmed by thermogravimetric (TG) results (mass loss in this temperature range)²³) and DSC, which shows an endothermic peak (due to the water vaporization that is liberated in the cure condensation reaction) also in that temperature range that disappeared following heating samples to 150 °C for 90 min (Figure 5).

From the macroscopic point of view, to use the whole potential of the reinforcement material during the application, good adhesion at the fiber-matrix interface is necessary.²⁴ A reinforce-

Material	Weight Percent				
	24 Hours	1^{st} Week	3 rd Week	$5^{\rm th}$ Week	$7^{\rm th}$ Week
Phenolic	0.03	0.32	0.45	0.61	1.12
40% Fiber	1.30	4.41	6.22	7.30	7.80
50% Fiber	1.50	4.04	6.70	7.41	7.60
70% Fiber	2.12	6.97	10.85	11.42	12.17
Lignophenolic	0.47	1.01	1.97	2.52	2.94
40% Fiber	1.48	4.46	7.09	7.80	8.16
50% Fiber	2.04	5.09	8.12	8.73	9.57
70% Fiber	3.06	5.60	9.06	10.07	10.72

Table IIAccumulative Results of Water Absorption Test of Thermosets andRelated Composites (cured at 85°C)



Figure 5 DSC curves of composite-reinforced 70% bagasse fiber: (1) cured at 85 °C; (2) post-cured at 150 °C for 90 min.

ment can increase the impact strength and decrease the matrix elastic modulus. However, the ideal situation would be a synergic implication between those two properties.²⁵

The composite storage modulus depends on the fraction of fiber and also on the matrix type. Because the fiber module is usually higher than that of the matrix, it would increase with the fiber fraction. However, other factors need to be considered: (a) fiber length (very short fibers have few contact points with the matrix, which can lead to the pull-out mechanism; very long fibers turn more difficult an homogeneous distribution); and (b) adhesion intensity at the matrix–fiber interface.^{26,27}

The DMTA composite behavior, considering lignophenolic matrices, is shown in Figure 4. Similar curves were obtained for phenolic composites. It can be inferred that the composites have smaller module than the matrix, considering the whole temperature range, with the exception of the composite containing 70% fiber. In the evaluation of that property, the following factors must be highlighted because they can explain why the incorporation of fiber reduced the matrix storage modulus: (a) Because of the consolidation or the processing, the surfaces of most composites have an excess of polymer, and the properties of surface can be emphasized at the expense of the interior. As a consequence, the experimental modulus can be lower than the expected one because normally the modulus of the polymer is lower than that of the reinforcing fiber. This is the socalled skin effect.²⁸ (b) Because of the differences between the coefficients of thermal expansion of the filler and of the polymer, tensile stress in the matrix can appear. This stress can be significant enough to place the polymer in the nonlinear portion of its stress–strain curve. As a consequence, the modulus becomes lower than the value obtained in the absence of stresses.²⁸

To analyze the influence of the first-mentioned effect, the composites were polished, to eliminate the excess of polymer on sample surface. However, the DMTA curves obtained using those samples were similar to those shown in Figure 4. It is not easy to check the second effect and, to date, there are no data indicating that factor (b) is the acting factor.

The addition of 70% fiber improves the modulus values compared with the matrix modulus, particularly above 50 °C. As the amount of sugarcane bagasse increases, the amount of matrix decreases. Probably, in this case, most of the polymeric material surrounds the fiber, which renders matrix molecular motion more difficult. As a consequence, the modulus increases. Pothan observed a similar effect with banana fiber-reinforced polyester composites.²⁹

In the second step of the present work, after finding the suitable reaction and molding conditions to prepare the composites, the fiber surface was modified by treatment with alkaline solution and also by chemical reaction to verify the influence of those treatments on the composite properties, especially the impact strength.

The treatment with cold caustic soda (mercerization process) leads to fiber bundle fibrillation; that is, it breaks down the fiber bundle into smaller fibers, which increases the effective surface area available for contact with the wet matrix.³⁰ However, the NaOH treatment can also lead to changes in mechanical properties of fibers because of the rupture of alkali-sensitive bonds present in the lignocellulosic fibers. Gassan³¹ found that jute hemicellulose is much more sensitive to the action of NaOH (room temperature) than lignin or α -cellulose. The fiber mechanical properties can be changed due to reorientation of crystalline and noncrystalline parts of cellulose.

The mercerized lignocellulosic material was also submitted to chemical modifications by reaction with succinic anhydride. The infrared (IR) spectrum of the fiber clearly showed the absorption corresponding to the carbonyl group (1730 cm⁻¹, spectrum not shown).¹⁶

	Material	Impact Strength (J/m)
P-0	Phenolic thermoset	12.8
P/B1	Composite phenolic/bagasse	20.2
P/B2	Composite phenolic/mercerized bagasse	22.0
P/B3	Composite phenolic/mercerized and esterified bagasse	21.2
PL-0	Lignophenolic thermoset	13.3
PL/B1	Composite lignophenolic/bagasse	21.5
PL/B2	Composite lignophenolic/mercerized bagasse	24.9
PL/B3	Composite lignophenolic/mercerized and esterified bagasse	19.2

To prepare the composites using those modified fibers, a 70% volume fraction of bagasse was chosen because the presence of such a volume fraction of fiber leads to the higher values of impact strength and storage modulus, for both phenolic and lignophenolic composites (see Figs. 1, 2, and 4). The impact test was changed to Izod because the Izod method makes it possible to directly compare the results obtained with bagasse as the reinforcer with those of phenolic and lignophenolic composites reinforced with other vegetable fibers (for examples, jute and sisal, which are also being studied by our research group)¹⁶ Nonetheless, it must be emphasized that the most common interpretation of the impact tests is qualitative, so the change from the Charpy to the Izod test does not alter the interpretation of the result.

The Izod impact strength results (Table III) show that the phenolic and lignophenolic thermoset (P-0 and PL-0, respectively) present close values (as was observed when the Charpy test was used); that is, it is feasible to partially replace phenol by lignin without decreasing the impact strength. The presence of sugarcane bagasse improved the impact strength (see P-0 and P/B1; PL-0 and PL/B1, Table III); that is, the necessary energy to break the samples was higher for the composites than for the thermoset. This result confirms, therefore, that that lignocellulosic material acts as a reinforcement on phenolic and lignophenolic matrices. Considering that some oligomeric fractions of lignin can be extracted during the alkaline treatment, the content of lignin was determined (Klason lignin) before and after mercerization. The total lignin content changed from 19.5 to 14.3% with that treatment, showing that even at low temperature $(0 \ ^{\circ}C)$ the lignin bonds were alkali sensitive. That partial delignification can change the fiber properties,

which can explain why the impact strength did not increase in a significant way when mercerized fiber was used. At first, the interactions between pendant carboxylic groups at the fiber surface with the polar groups of the matrix could improve the fiber-matrix interactions and then lead to an increase in the impact strength. However, the results obtained point out a tendency to decrease the impact strength when the mercerized fiber, which suffered chemical modification with succinic anhydride (compare P/B3 and PL/B3, with P/B2 and PL/B2, Table III), was used. Probably, that decrease in property was caused by the previous partial delignification on mercerization. Also, the esterification reaction probably did not occur in a significant extension.

The SEM results for fractured composites (phenolic matrix, 70% bagasse fiber), obtained after the impact test are shown in Figures 6 and 7. The SEM investigation (Fig. 6) showed that the bagasse-reinforced composite demonstrates adhesion



Figure 6 SEM photomicrograph of P/B1 composite phenolic/bagasse fractured $(200 \times)$.

in some extension between fibers and matrix because the fibers are not set free, suggesting that they suffered a break during the impact test. The bagasse-reinforced lignophenolic composite has fibers that were broken during the impact test and fibers (located at the superior left side) and that demonstrate some deformation (Fig. 7). Adhesion between fiber and matrix and the occurrence of fracture propagation around the fibers (located at the center of the photomicrograph) are observed. It is known that the cellulosic fibers have a cell arrangement, which can divert the crack path by blunting it. Thus the crack does not have a straight path because it surrounds the fiber cells and finally stops.³²

Voids were observed in all the SEM images obtained (thermoset and composites). It is important to note that usually the smaller the amount of microvoids, the better the mechanical properties of the materials. Microvoids appear because, during the cure step when the molar weight increases, both the residual water already present in the resin and that which can be produced during the cure reaction become insoluble and separate from the cured resin, resulting in the vaporization and formation of domains denominated by microvoids in the cured matrix.³³ The voids act as stress concentrators, reducing the load-carrying and energy-absorbing capabilities of the composites.³⁴

The presence of resin among the fibers is noted in Figure 8. This result shows that after mercerization, the resin can more easily penetrate the bundles of fibers, which could indicate better adhesion. It must be emphasized that better adhesion does not always lead to an improvement in impact strength.



Figure 7 SEM photomicrograph of PL/B1 composite lignophenolic/bagasse fractured $(200 \times)$.



Figure 8 SEM photomicrograph of PL/B1 composite lignophenolic/mercerized bagasse fractured (1000×).

CONCLUSIONS

The impact results reveal that during fracturing, the contribution of bagasse (short fibers) is significant and, when the volume of fibers increases, the energy-absorbing capability of the composites also increases. These preliminary results are promising and indicate the modifications that must be introduced to improve properties (e.g., impact strength) of composites to reach values compatible with industrial applications of those materials. Considering mainly the impact strength results, the following features must be considered in the next steps of the research:

- It is necessary to optimize the mercerization process (NaOH concentration, temperature, treatment time);
- It is necessary to look for other coupling agents and optimize the esterification reaction conditions because, for the considered reaction conditions and with the esterification degree reached, succinic anhydride was not a good coupling agent for the fibers used in the present work. Ideally, the vegetable fiber should be modified by an agent in such a way that the absorption of water decreases, the temperature resistance increases, and the adhesion at the interface fiber-matrix as well as the mechanical properties are improved. In fact, it is difficult to gather all those properties through a single chemical modification of the fiber;
- To establish what the possible applications are, more data on properties of those natural fiber-reinforced composites are needed (e.g., data on tensile strength).

Our research group is presently looking for properties other than impact strength and considering all the characteristics just mentioned.

The results as a whole indicate that it is feasible to partially replace phenol by lignin in phenolic-type matrices without loss of properties. The ideal situation for natural fiber-reinforced composites would be a combination of properties to obtain resistant composites and to have reproducibility of data during the mechanical tests. Many parameters should be investigated further and properties improved. However, it can be foreseen that the use of this kind of material will increase progressively in the future because of the intrinsic properties of composites and environmental requirements.

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