LYOCELL AND COTTON FIBERS AS REINFORCEMENTS FOR A THERMOSET POLYMER

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Cellulose fibers obtained from the textile industry (lyocell) were investigated as a potential reinforcement for thermoset phenolic matrices, to improve their mechanical properties. Textile cotton fibers were also considered. The fibers were characterized in terms of their chemical composition and analyzed using TGA, SEM, and X-ray. The thermoset (non-reinforced) and composites (phenolic matrices reinforced with randomly dispersed fibers) were characterized using TG, DSC, SEM, DMTA, the Izod impact strength test, and water absorption capacity analysis. The composites that were reinforced with lyocell fibers exhibited impact strengths of nearly 240 Jm^{-1}, whereas those reinforced with cotton fibers exhibited impact strengths of up to 773 Jm^{-1}. In addition to the aspect ratio, the higher crystallinity of cotton fibers compared to lyocell likely plays a role in the impact strength of the composite reinforced by the fibers. The SEM images showed that the porosity of the textile fibers allowed good bulk diffusion of the phenolic resin, which, in turn, led to both good adhesion of fiber to matrix and fewer microvoids at the interface.

Keywords: Lyocell fiber; Cotton fiber; Phenolic matrix composite; Textile cellulosic fibers

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INTRODUCTION

Phenolic polymers exhibit dimensional stability, thermal stability, and chemical resistance at high temperatures. The thermomechanical properties of the phenolic resins are directly related to the high crosslinking density resulting from the curing (polymerizetion) of these resins. However, the high crosslinking density results in a low impact strength, which makes the phenolic resins more fragile than many other plastics, and this presents a limitation for some applications (Zhong et al. 2010; Jang et al. 2009; Ramires et al. 2009; Carrillo et al. 2010; Johnson et al. 2008; Silva et al. 2006).

From the earliest decades of the twentieth century, with the pioneering work by L.H. Baekeland on phenolic polymers (Baekland 1909), phenolic resin has been combined with a wood flour filler and used in radios, telephones, and other products. The molding of fibers and fabrics pre-impregnated with phenolic resins has produced phenolic matrices fiber-reinforced composites, which were used initially (in the 1930s) in aircraft and automotive applications (Lewark 2007). The properties of phenolic-type matrices and their favorable cost/performance characteristics guarantee to these materials an outstanding position in the area of thermoset-matrices composites (Frollini and Castellan 2011).

Composites of polymers and natural fibers have regained importance in recent years because of both a need for products that reduce global environmental pollution (Kim et al. 2006; Suñol et al. 2007) and the intrinsic properties of these materials (Silva et al. 2006; Silva and Frollini 2007; Gu et al. 2010; Barbosa et al. 2010; Guimarães et al. 2009; Hubbe et al. 2008; Ramires et al. 2010; Bodîrlau et al. 2009).

The impact strength of a phenolic thermoset matrix can be improved if it is reinforced with fibers. In previous studies, sisal (Ramires et al. 2009, 2010; Megiatto et al. 2008), coir (Barbosa et al. 2010), and curaua (Trindade et al. 2008) fibers have been used to reinforce phenolic-type matrices. Research in this field is ongoing. Following the approach of using various fibers obtained from renewable resources to reinforce phenolic-type matrices, the aim of this study was to prepare polymeric materials with a high content of raw materials obtained from renewable sources using cellulosic textile fibers (cotton and lyocell, Fig. 1) to improve the mechanical properties of these materials.

These fibers are produced at a massive scale for the textile industry and are available as a continuous supply of material with reproducible properties because of the high demand and strict requirements of the textile sector. These aspects favor the large-scale use of these fibers as a reinforcing agent for polymeric matrices.

Cotton is a plant of the genus *Gossypium*, of which the stalks correspond to lignocellulosic materials (Silvertein et al. 2007; Kargarfard and Jahan-Latibari 2011). The cellulosic textile fibers are obtained from fibers that grow in a ball, around the seeds. To obtain yarns, the fibers are initially separated from the seeds (ginning), followed by spinning (Fig. 1). Cotton is one of the most widely produced textile fibers for commercial use worldwide.

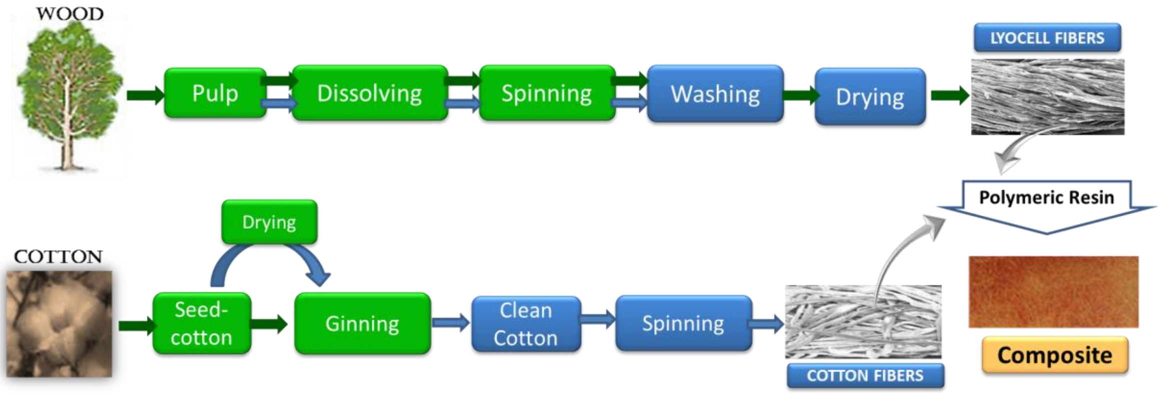


Fig. 1. Schematic representation of lyocell and cotton fiber processes and their use in composite production (based on Rosenau 2001; Ganster and Fink 2006)

Lyocell fibers are prepared from cellulose obtained from wood pulp. Such pulp can be regarded as sustainable, because it can, in principle, be prepared in a continuously renewable manner by utilizing the growth and replanting of forests dedicated to cellulose production (Fink et al. 2001; Gindl et al. 2006). The lyocell process (Fig. 1) is carried out using special solvents and production techniques (solvent spinning), which enables these solvents to be recycled (Seavey and Glasser 2001; Ganster and Fink 2006).

In the lyocell process, wood pulp is dissolved by action of the N-methylmorpholine-N-oxidemonohydrate (NMMO-MH) at elevated temperatures (Biganska and

Navard 2009; Adorjan et al. 2005; Rosenau et al. 2001; Tatárová et al. 2010). The filtered solution is forced through fine holes in multiple dies (spinnerets) into an air gap, and the fine threads are pulled through a bath of dilute NMMO. The spun fibers are regenerated by exposure to water, and then further submitted to washing, drying and, in some cases, post-treatment. NMMO is non-toxic, and around 99% can be recovered by the evaporation of water. The water is condensed and reused for washing (Fink et al. 2001; Rosenau et al. 2001; Tatárová et al. 2010). Lyocell fibers are produced on a large industrial scale and show good mechanical properties (Ganster and Fink 2006; Seavey and Glasser 2001; Öztürk et al. 2006).

The use of lyocell as a reinforcement for thermoplastics has been reported in many studies. Bio-based composites have been prepared from cellulose esters (such as cellulose acetate propionate and cellulose acetate butyrates) and lyocell (Franko et al. 2001; Seavey et al. 2001). Among the results obtained for these bio-based composites, it can be highlighted that the composites reinforced by lyocell were stronger and stiffer than the corresponding rayon-based materials (Franko et al. 2001). Spun cellulose fibers from lyocell, in addition to other fibers, have been used to reinforce thermoplastics such as polypropylene, polyethylene, and poly(lactic acid). A strong reinforcing effect was observed for lyocell as well as for the other materials. According to work by Ganster and Fink (2006), lyocell improves the stiffness of polypropylene composites. Polypropylene-lyocell composites have been fabricated from random wet-lay and compression molding processes. In general, the properties were comparable to melt-processed, rayon-reinforced PP composites (Johnson et al. 2008). Lyocell has been modified, for example, with silver nanoparticles (Smiechowicz et al. 2011), which leads to other possibilities regarding its application in composites.

In this paper, the capacity of lyocell as a strengthening agent of a phenolic thermoset matrix is evaluated. The results are compared with those of the corresponding textile cotton reinforced matrices. Particular attention was paid to the possibility of increasing the impact strength of phenolic-type thermosets.

EXPERIMENTAL

Synthesis of Pre-Polymer

The synthesis was based on earlier studies (Megiatto et al. 2009; Paiva and Frollini 2002). Formaldehyde (Synth, 37%) was added to a phenol (Synth)/KOH solution (Synth) at a ratio of 1.0:1.38:0.06 wt%, respectively, under mechanical stirring. The solution was heated to 70 °C and refluxed at this temperature for 1 h and then neutralized with HCl (Synth, 37%) after cooling to room temperature. Before molding, the water was eliminated by evaporation under reduced pressure. Resins with relative average molar weight of approximately 500 g mol^{-1} are obtained following this procedure (Frollini et al. 2004).

Thermosets

The phenolic pre-polymer was heated to 50 °C, 10 wt% resorcinol was added as a cure accelerator, and the mixture was stirred for 30 min. At 50 °C, the viscosity of the pre-polymer is lower than at room temperature, making it easier to mix it with resorcinol. In addition, when a composite is prepared, as described next, the lower viscosity at this temperature increases the impregnation of the fiber by the pre-polymer. The cure reaction was performed in a mold (300 x 140 x 5 mm). The cure cycle (65 °C/25 min, 75 °C/65 min, 85 °C/95 min, 95 °C/35 min/28.6 kgf cm^{-2}, 105 °C/35 min/28.6 kgf cm^{-2}, 115 °C/65 min/28.6 kgf cm^{-2}, 125 °C/90 min/28.6 kgf cm^{-2}) was determined by DSC measurements in a previous study (Paiva and Frollini 2002).

Composites

The composites were reinforced with textile fibers, namely, cotton (supplied by Rossignolo Ltda, São Carlos, São Paulo, Brazil), tenacity: 13 cN/tex, and lyocell (supplied by Pegaso Têxtil Ltda, Jacareí, São Paulo, Brazil), tenacity (from literature): 37 cN/tex (Eichinger et al. 1995). Composites reinforced with lyocell and cotton fibers were obtained by impregnating the fibers with the pre-polymers plus resorcinol (50 °C). Layers of fibers and pre-polymers were placed alternately in the mold, and the impregnation of the fibers occurred during the first steps of the cure cycle under temperature and temperature/pressure. The pre-polymers were mixed with 10 mm lyocell or 50 mm cotton fibers with variable fiber content from 30 to 70 wt%. In addition, the fiber length of lyocell and cotton fibers on the composites with 30 wt% fiber introduced was also investigated (from 10 to 50 mm).

The composites were prepared with randomly oriented fibers in a mold, as described for thermoset, but cured at a higher pressure (38.1 kgf cm^{-2}).

Fiber Characterization

Fiber analyses generally followed the same procedures reported elsewhere (Megiatto et al. 2008; Ramires et al. 2010). Some details were as follows.

The fiber moisture content was determined by the method described by ABNT (Brazilian Association for Technical Standards) NBR9656, which consists of determining the percentage difference between the initial weight of the sample (1.0 g) and that after 4 h drying at 105 °C. The ash content was determined by considering the difference between the initial weight of dried fibers and that after calcination for 4 h at 800 °C.

The Klason lignin content was determined as specified in the TAPPI standard T13m-54. This method is based on the isolation of lignin after polysaccharide hydrolysis and the dissolution with concentrated sulfuric acid (Synth, 72%). The holocellulose content was determined, as described in TAPPI T19m-54, by the selective degradation of the lignin polymer by sodium hypochlorite at 70 °C. The cellulose content was determined by the removal of hemicellulose from the holocellulose with NaOH, as specified in TAPPI T19m-54. The hemicellulose content was then calculated by subtracting the cellulose content from the holocellulose content. The analyses were performed in triplicate.

Crystallinity index (Diller and Zeronian, 1992)

The cellulose crystallinity index I_c was determined by X-ray diffraction with a RIGAKU Rotaflex model RU-200B diffractometer, operating at 40 kV, 20 mA and λ (CuK_{α}) = 1.5406 Å. The crystallinity index was calculated with the Buschle-Diller and Zeronian equation (Diller and Zeronian 1992), as follows,

$$I_c = 1 - I_1/I_2 \tag{1}$$

where I_1 is the intensity at the minimum (2θ between 18° and 19°) and I_2 is the intensity at the maximum of the peak (2θ between 22° and 23°) in the cellulose powder diffraction pattern.

Tests of Fiber, Thermoset, and Composites

Thermal analysis

Thermogravimetric analyses (TGA) of the fiber, neat thermoset, and composites were performed (Shimadzu model TGA-50TA, samples of approximately 7.5 mg) from room temperature to 800 ºC (10 ºC min^{-1}) under air atmosphere (20 mL min^{-1}).

Runs of differential scanning calorimetry (DSC) were performed (Shimadzu DSC-50, samples of approximately 6.5 mg) from room temperature to 500 ºC (10 ºC min^{-1}) under air atmosphere (20 mL min^{-1}).

Dynamic mechanical thermal analysis (DMTA) was performed in a DMA model 2980 device from TA Instruments. The neat thermoset and composites were tested in the 3-point-bending mode (flexural mode). The dimensions of the specimens for this analysis were 35.0 mm x 12.0 mm x 3.2 mm. The following experimental conditions were set: an oscillation amplitude of 1 μm, a frequency of 1 Hz, a heating rate of 2°C min^{-1}, and a temperature range of 25 to 230°C.

Scanning electron microscopy (SEM)

A sample stub with the composites was surface-metalized by a sputter coating (MED 020, BAL-TEC) with evaporated gold (in 10 nm thickness) and microscopy performed by SEM (Zeiss-Leica 440) at an acceleration voltage of 20 kV.

Izod impact test

Ten specimens (63.5 x 12.7 x 4.0 mm) were extracted from the neat thermoset and the composites sheets, respectively. The tests were conducted with an Izod impact tester (CEAST Resil 25) according to ASTM D256 at room temperature (impact speed: 4.0 m s^{-1} incident energy: 5.5 J).

Water absorption

The water absorption was tested according to ASTM D570-98. The dimensions of the specimens for this analysis were 76.2 x 25.4 x 3.2 mm, and the measurements were made in triplicate. Each sample was immersed in distilled water at room temperature for 24 h. After specific intervals (every hour, during the first 10 h, and then at t=24 h), the samples were removed from water, placed in a piece of dry cloth (only to remove the excess water), and then weighed and immersed again in water. The water absorption was calculated by the weight change. The analysis of the diffusion mechanism is based on Fick’s law. The experimental values were fit well with Eq. 2. After certain intervals, they were removed from water, and put in a piece of dry cloth (only to remove the excess of water),

$$M_t / M_\infty = k t^n \qquad (2)$$

where M_t is the water content at time t, and M_∞ is the water content at equilibrium (Comyn 1985). The line obtained by plotting $\log M_t/M_\infty$ as a function of time was used to determine k and n from the intercept and slope, respectively. The diffusion coefficient D of water in the specimen was calculated with equation 3,

$$M_t / M_\infty = 4/L \left(D t / \pi \right)^{1/2} \qquad (3)$$

where L is the specimen thickness (Comyn 1985).

RESULTS AND DISCUSSION

Lyocell and Cotton Fibers Characterization

Table 1 shows the composition and other properties of the lyocell and cotton fibers used in the present study.

Lyocell fibers are obtained by separating the cellulose from the other components of wood, which is composed of lignin, cellulose, and polyoses (hemicellulose). After the extraction of these components, the material obtained can contain residues of lignin and other constituents of the lignocellulose fiber. Regarding the cotton, the lignin present in the plant, such as in the stalk, in principle could contaminate the fiber. The results in Table 1 indicate that the contents of cellulose and holocellulose (cellulose+hemicellulose) differed by no more than the standard errors, so the two values can be taken as being equal, which indicates that there were no polyoses in the fiber. Lignin was not detected in either fiber (Table 1).

Table 1. Properties of lyocell and cotton fibers

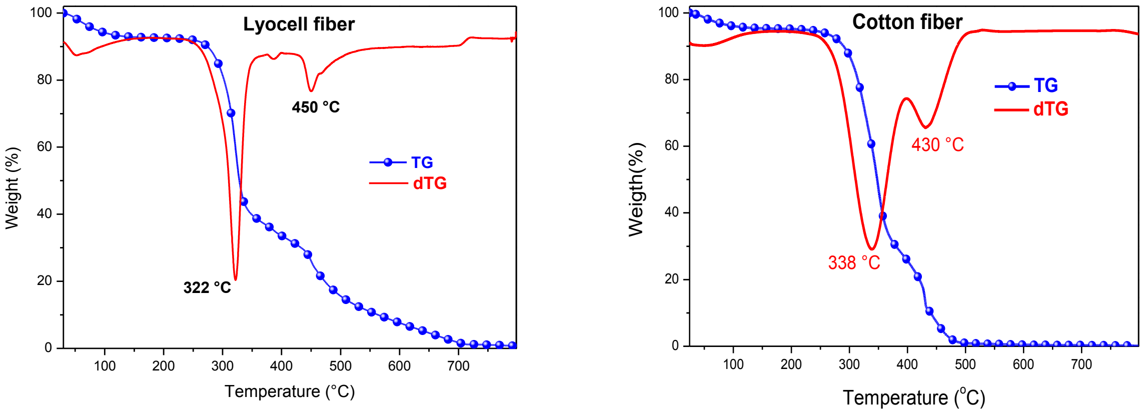
Property	*Content* * *(%)*	
	Lyocell	*Cotton*
Moisture	9.3 ± 0.1	5.3 ± 0.1
Ash	0.9 ± 0.1	1.3 ± 0.1
Lignin	0.0	0.0
Holocellulose	98.0 ± 0.2	96.3 ± 0.1
Cellulose	97.5 ± 0.3	96.0 ± 0.3
Crystallinity	77	87

***** ±: Standard deviation

The crystallinity index was higher for cotton (87%) compared to lyocell fibers (77%) (Table 1). The crystallinity of cellulosic fibers can influence the mechanical properties of their composites (Isogai et al. 2009; Carrillo et al. 2010).

Thermal Analysis

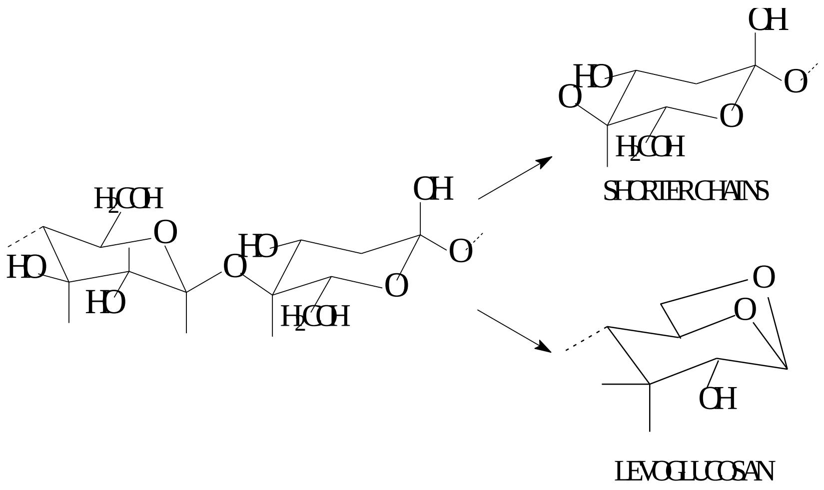
Thermogravimetric analysis (lyocell and cotton fibers) curves are shown in Fig. 2.



(a) (b)

Fig. 2. TG and dTG curves of (a) lyocell and (b) cotton fibers (in synthetic air, 20 mL min^{-1}; 10 ºC min^{-1})

The first weight loss (around 10%) observed in TG curves of lyocell and cotton fibers (Fig. 2a, 2b, respectively) correspond to volatilization of the residual moisture. The loss of structural water occurs at temperatures over 100 ºC, because these molecules are strongly bound to the cellulosic fibers due to its hydrophilic character. The evolution of water from cellulose occurs at various temperatures, because many reactions involved in the degradation of this polysaccharide form water. The first step of cellulose decompose-tion usually involves an intra-molecular reaction with the elimination of water, which forms levoglucosan and also depolymerization reactions that lead to shorter chains (Scheme 1) (Klemm et al. 2001):



Scheme 1. Intra-molecular reaction forming levoglucosan and depolymerization reactions that result in shorter chains (Klemm et al. 2001)

Other reactions may occur, such as the cleavage of glycosidic bonds (C-H, C-O, C-C), dehydration, decarboxylation, and decarbonylation (Almeida et al. 2010; Scheirs et al. 2001). The products generated in this first stage decompose at higher temperatures with the release of volatiles.

For the lyocell fiber, a considerable mass loss was observed from 250 °C to 320 °C (nearly 60%; Fig. 2a, TG curve) because of the thermal decomposition of cellulose (Suñol et al. 2007; Wu et al. 2008). For the cotton fiber, the thermal decomposition of cellulose occurred from 255 °C to 340 °C (nearly 60%; Fig 2b, TG curve). This step of cellulose decomposition led to differential loss peaks (dTG) at 322 °C for lyocell and at 338 °C for cotton.

In a previous study, in which linter celluloses with different degrees of crystallinity were considered (Morgado 2011), a shift to lower temperature in the differential loss peaks (dTG) was observed for the sample with lower degree of crystallinity, as was observed for the lyocell fiber, which was less crystalline than the cotton fiber (Table 1). The intermolecular hydrogen bonds between chains are stronger in the crystalline domains than in those of the non-crystalline regions and require more energy to break before the decomposition process can proceed.

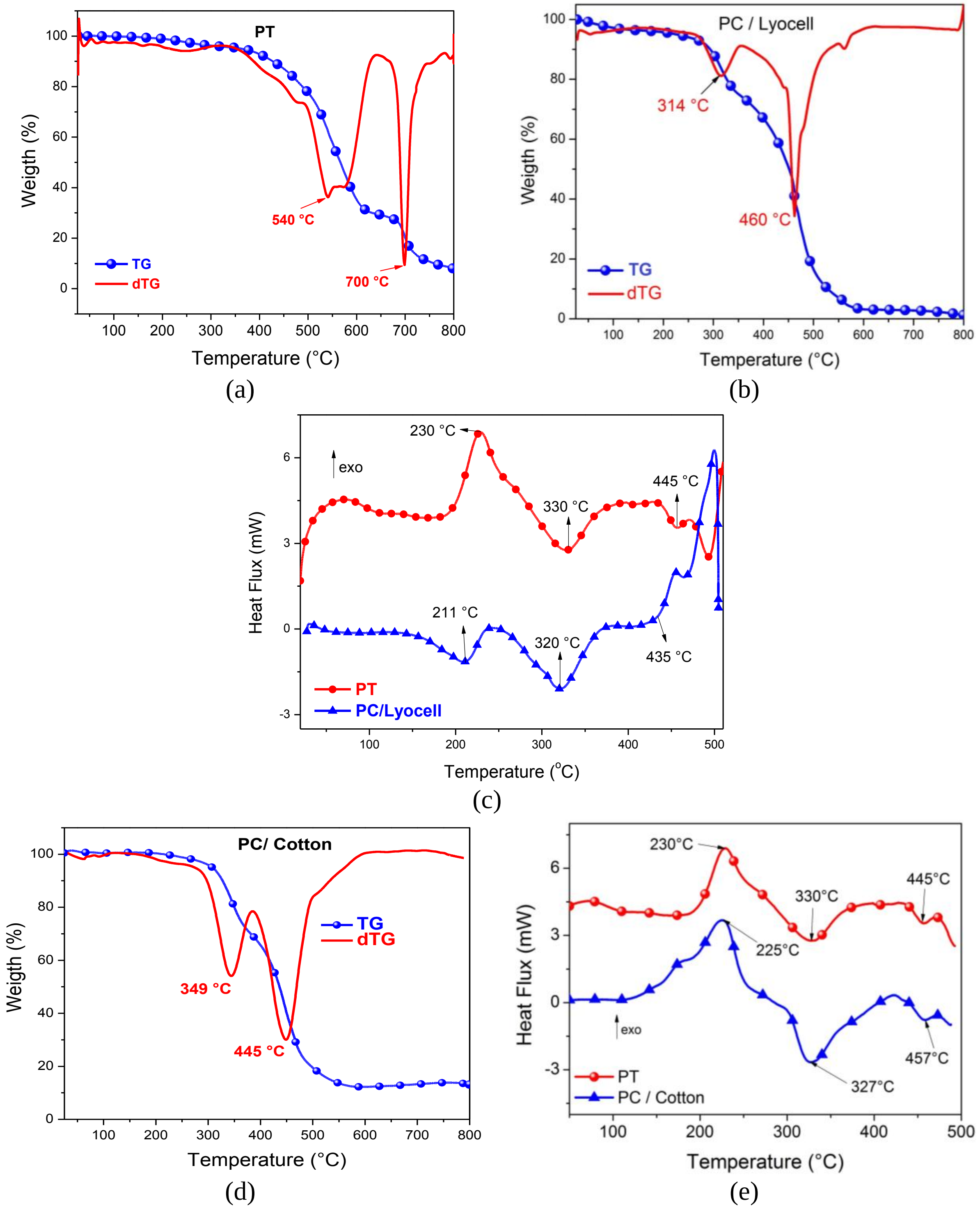
Low-intensity differential loss peaks (dTG curves) were observed at 450 °C and 430 °C for the lyocell and cotton fibers (dTG curve, Fig. 2a, 2b), respectively, which can be attributed to the release of volatiles relating to the decomposition of the by-products of the previous stage. This may have been favored by the air atmosphere in which the samples were submitted during analysis.

TG and DSC curves for the phenolic thermoset and their respective composites are shown in Fig. 3. The phenolic composite reinforced with lyocell and cotton fibers (Fig. 3b, 3d) showed a greater loss of mass up to 100 °C than the phenolic thermoset (unreinforced matrix, PT) in the TGA (Fig. 3a) due to the presence of hydrophilic fibers in the composites, as discussed previously (Fig. 2a, 2b).

The mass loss between 250 and 350 °C came from the decomposition of cellulose (Fig. 3b, 3d) and from events related to the matrix (similar behavior was observed for the phenolic thermoset (Fig. 3a). From 400 to 500 °C, the mass loss (50.5%) was higher for the composites, because they have a lower thermal stability than the neat thermoset due to the presence of fibers (lyocell and cotton) in the former, that decompose at temperatures lower than the neat thermosets (Paiva and Frollini 2006).

In the neat thermoset, during DSC analysis (Fig. 3c), a residual cure of the matrix can occur, which probably explains the exothermic peak at 230 ºC. At 330 ºC, an endothermic peak was observed that could be related to the vaporization of the volatiles formed during decomposition. The endothermic peak close to 450 ºC can also be related to volatiles released during decomposition of the thermoset.

The DSC curve for the phenolic composite reinforced with cellulosic fibers (Fig. 3c, 3e) exhibits thermal events related to both the matrix and the cellulosic fibers. Peaks were observed at 211 °C (endothermic, Fig. 3c) and 225 °C (exothermic, Fig. 3e) for composites reinforced with lyocell and cotton fibers, respectively, whereas an exothermic peak was observed for the neat thermoset (230 ºC), as previously mentioned. The shift to the lower temperature when the composites are compared to the neat thermoset is probably caused by the beginning of the decomposition of fibers near these temperatures.



(a) (b)

(c)

(d) (e)

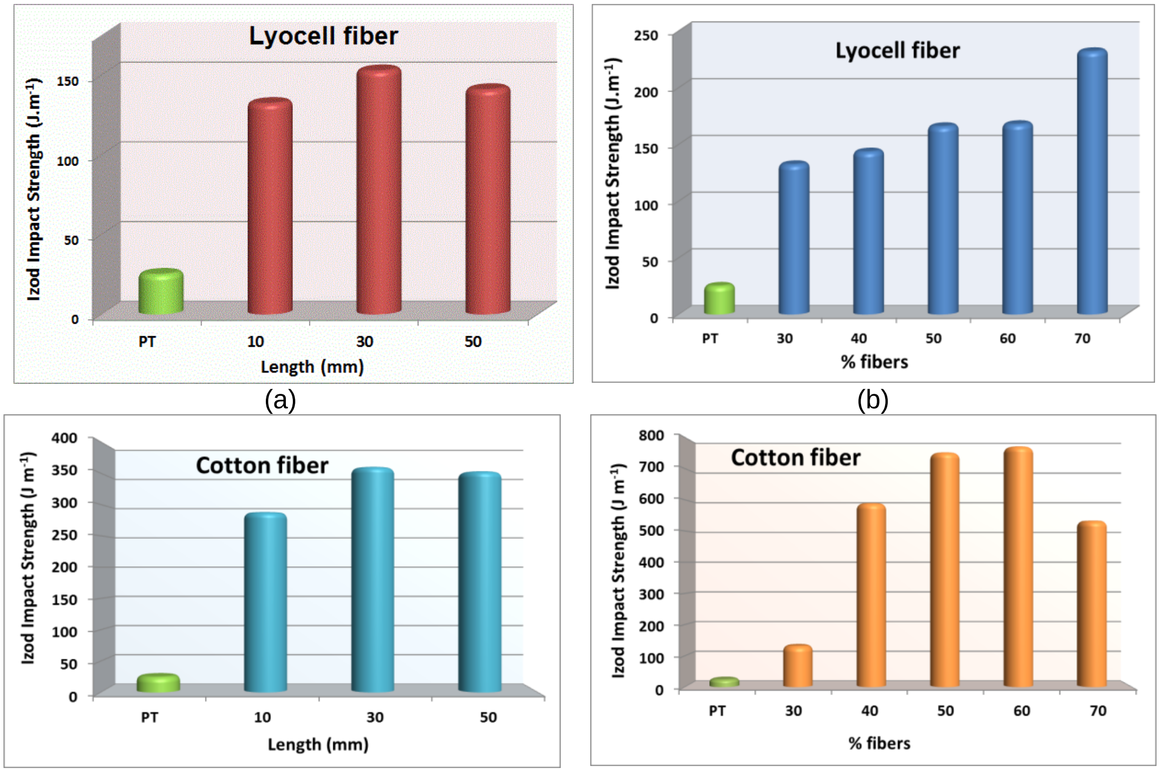
Fig. 3. (a) TG and dTG curves and (c) DSC curves of the phenolic thermoset (PT) and (b, c) phenolic composite (PC) reinforced with lyocell fiber (50 wt%) and (d, e) phenolic composite (PC) reinforced with cotton fiber (50 wt%) (synthetic air, 20 mL min^{-1}; 10 ºC min^{-1})

Considering the composite reinforced with lyocell, the endothermic event related to the vaporization of the volatiles generated during both matrix and fiber decompositions outweighed the exothermic peak related to the decomposition, and the net result was the endothermic peak at 211 °C. Thereafter, endothermic peaks related to the decomposition of the phenolic polymer can be observed near 330 and 445 °C, which are the temperatures observed for the neat thermoset (Fig. 3c, 3d).

The other composites tested in the present study had TG and DSC curves that were similar to those discussed above.

Izod Impact Strength

Figure 4 presents the impact strength of lyocell and cotton fibers reinforced phenolic composites for several fiber lengths (Fig. 4a, 4c) and fiber percentages (Fig. 4b, 4d). The impact strength was not influenced significantly by changing the length of the fibers, considering the standard deviation (Fig. 4a). However, a tendency toward higher impact can be observed when the length of lyocell fibers increased from 10 to 30 mm and toward lower impact when the length increased from 30 to 50 mm.



(a) (b)

(c) (d)

Fig. 4. Izod impact strength of phenolic thermoset (PT) and related composites reinforced with lyocell fibers: (a) at various fiber lengths (30 wt% fibers); (b) at various fiber contents (length fibers: 10 mm), cotton fibers: (c) at various fiber lengths (30 wt% fibers); (d) at various fiber contents (length fibers: 50 mm). Lyocell: the lowest standard deviation was ±14 Jm^{-1} (at 30 wt%) and the highest was ±24 Jm^{-1} (at 40 wt%), cotton: the lowest standard deviation was ±15 Jm^{-1} (at 30 wt% cotton fiber) and the highest was ±28 Jm^{-1} (at 40 wt% cotton fiber).

For lyocell fibers, it was observed that some of the 50 mm length fibers were bent after impregnation with the resin, which can affect the impact resistance of the composite. For the composites reinforced with cotton fibers (Fig. 4c), the impact strength increased as the length of the fiber increased from 10 to 50 mm, exhibiting values near the 30 and 50 mm cotton fiber composites. In this case, no bending was observed for the 50 mm fibers after their resin impregnation.

Lyocell fibers of 10 mm were chosen for the study on the variation of the fiber content. There were two reasons for this choice: First, composites with fibers of length 10 and 30 mm (30 wt%) exhibited close values of impact strengths. Second, the shorter 10 mm fibers do not bend when impregnated by the resin. To also assess the effect of varying percentage of fibers in composites reinforced with longer fibers, cotton 50 mm fibers were chosen for this study, since these fibers do not exhibit bending after impregnation by the resin, as observed for lyocell fibers. Considering the average diameters of the fibers, namely, 9.9 ± 0.6 and 16.6 ± 2.8 µm, for lyocell and cotton, respectively (determined from SEM images, as shown in Fig. 5, and others that are not shown), a length of 10 mm indicates an aspect ratio (length/diameter) of approximately 1010 for lyocell and 3012 for cotton fiber (at a length of 50 mm). It must be noted that the aspect ratios were calculated from the fiber diameters determined from the SEM images, which are related to the actual reinforced matrix, and not from the diameters of the respective yarns. These reduced values in diameter were generated by the separation of bundles of filaments, as a result of the excellent impregnation of the yarn by the liquid phenolic resin, in the first stage of preparation of the composite. The small diameter of the fibers inside the matrix, combined with their relatively long lengths, led to meaningful values of aspect ratios.

Thermoset phenolic polymer by itself has useful properties, although it is fragile compared to other materials, as mentioned. The presence of lyocell and cotton fibers led to considerably higher values for the impact strength, as compared to that of the neat thermoset (25 Jm^{-1}, Fig. 4).

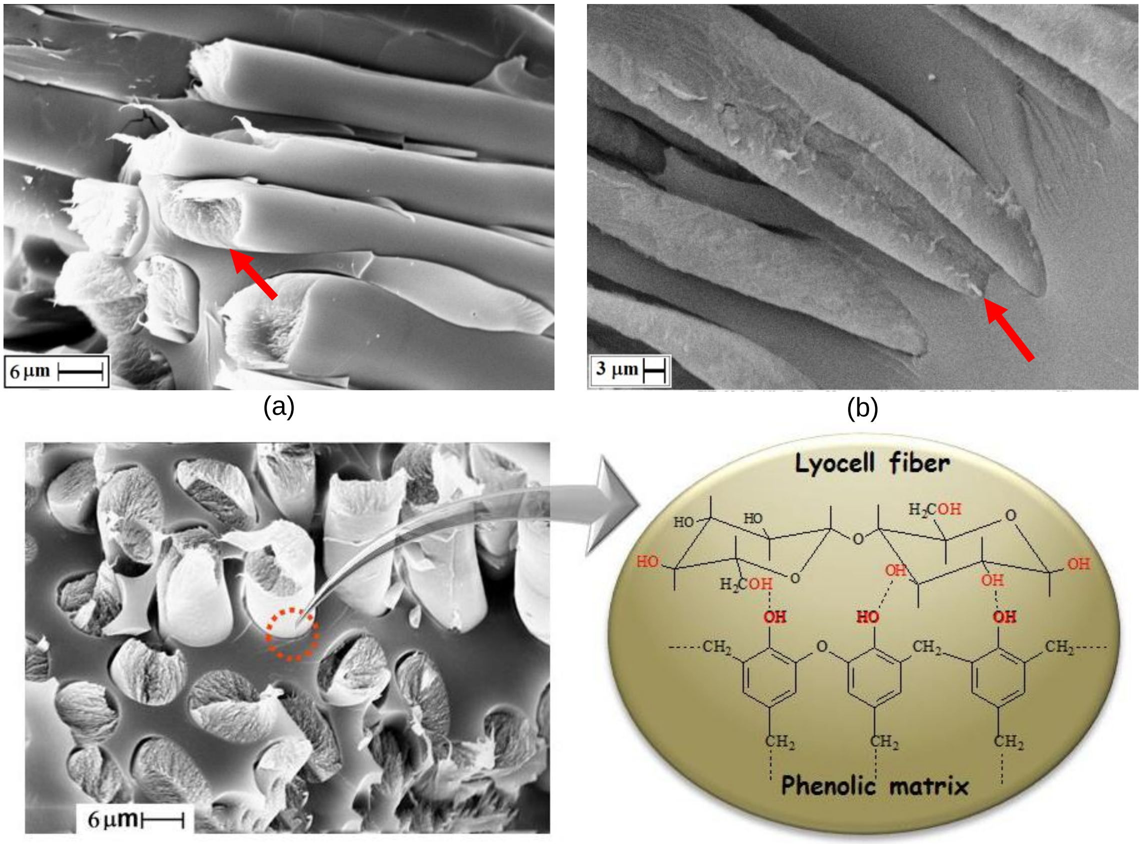
The Izod impact strength of composites reinforced with cotton fibers increased when the proportion of the fibers rose from 30 w% to 50 w% (Fig. 4d). In this case, the large quantity of fibers increased the absorption and distribution of the energy impact. When 60 wt% of fibers were used, considering experimental errors, the impact strength was the same for 50 wt% cotton fibers, and for 70 wt% cotton composite, the contact of fiber to fiber apparently increased, affecting the mechanisms of matrix/fibers transferring energy and hence the mechanical properties.

Concerning lyocell fibers, the results indicated that the impact strength of the composites reinforced with this fiber gradually increased with the percentage of reinforcing fibers, although the values referring to the composites strengthened with 30 and 40 wt% fibers were relatively close together when one considers the standard deviations (±14 and ±24 Jm^{-1}, respectively) (Fig. 4b).

Cellulose content and fiber crystallinity are important factors for the mechanical properties of fibers. However, when fibers with different diameters are compared, the aspect ratio of fibers should be taken into account, given that this parameter can have a strong influence on the mechanical properties of composites. Considering the amount of fiber that led to the highest impact strengths (60 and 70 wt% for cotton and lyocell, respectively, Fig. 4), it can be observed that the composite reinforced by cotton (10% less fiber compared to the composite reinforced by lyocell) presented an impact strength approximately three times higher than the composite reinforced by lyocell. Considering the aspect ratio of the fibers that reinforced these composites (3012 and 1010 for cotton and lyocell, respectively), the ratio between these two values is also approximately three. Thus, these results indicate that the two fibers have a good capacity to reinforce a phenolic matrix, with some advantage for cotton, which can be attributed to the higher crystallinity of this fiber (87%) compared to lyocell (77%, Table 1).

SEM

Figure 5 shows micrographs of the fractured surfaces of samples (after the Izod impact test). In general, a similar behavior was observed for lyocell and cotton fibers in the SEM images, with some advantage for cotton fibers, when compared to lyocell (data not shown). It is possible to see the efficient covering of the fiber by the matrix (Fig. 5a, 5b) and homogeneous distribution of fibers in the matrix (Fig. 5b, 5c). The homogeneity (of lyocell fiber distribution in the matrix) decreases with increasing fiber length (from 50 mm; micrographs not shown), which could explain the decrease in impact strength at 50 mm (Fig. 4a).



(a) (b)

(c)

Fig. 5. SEM images of fractured surfaces of phenolic composites reinforced with lyocell fibers (length: 10 mm); (a) 30, (c) 70 wt%; and cotton fibers (length: 50 mm); (b) 50 wt%.

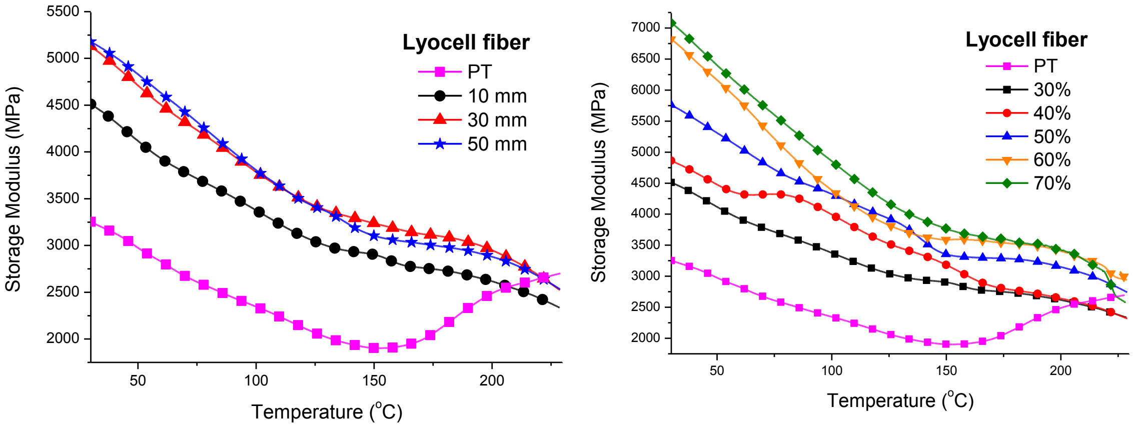
In general, the micrographs of the composites show the breakage of fibers near the plane of fracture of the matrix (Fig. 5c), which points to a good fiber-matrix interaction. Notably, few fibers were pulled free of the matrix with the pull-out mechanism, which indicates that adhesion between the fibers and the matrix was strong (Sreekala et al. 2000; Trindade et al. 2005; Paiva and Frollini 2006). The hydroxyl groups (polar groups) present in the matrix and on the cellulosic fibers interact to form hydrogen bonds (Fig. 5c, right side), which produce a strong adhesion at the interface (Silva et al. 2011; Joseph et al. 2008). The interactions between the fibers and the matrix, schematically shown for lyocell (Fig. 5c, right side), are certainly present when the reinforcement corresponds to the cotton. Neither voids nor crack propagation was observed in the matrix region. Microvoids, which are mainly a consequence of the vaporization of water generated by the condensation reaction, which occurs during curing of the matrix, can decrease the mechanical properties of the composite (Trindade et al. 2008). Good penetration of the resin among the fibers and the high pressure during the preparation of the composite (experimental) decreases the number of voids considerably.

Even when 70 wt% of cotton fiber was used as reinforcement, the covering of the matrix was efficient (micrograph not shown). However, the higher concentration of fibers increased fiber-fiber contact, reducing the Izod impact strength (Fig. 4d).

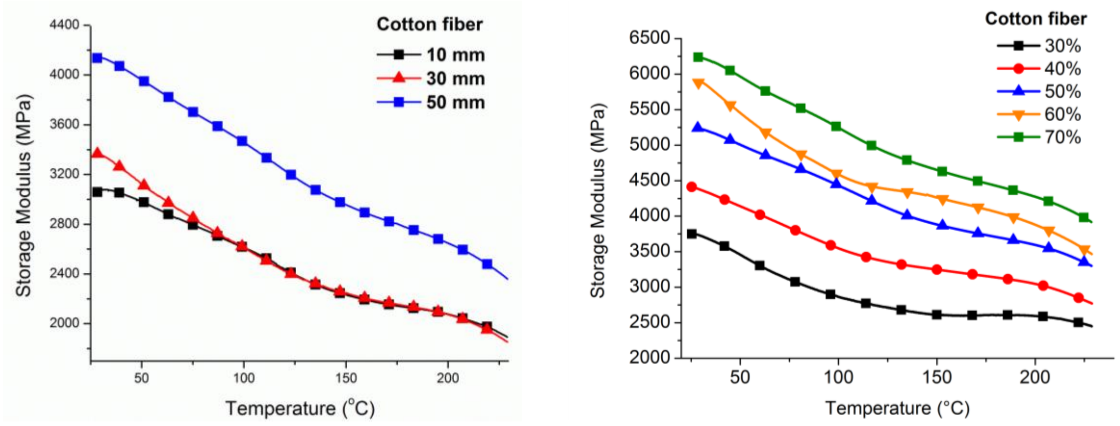
DMTA

The phenolic thermoset, lyocell and cotton composites were analyzed using DMTA (Fig. 6 and 7). The DMTA results for the composites reflect to the interaction between the components (fibers and matrix) at the interface. Next to the interface there is also an interphase; that is, a region of the matrix enveloping the fiber that has different properties from the other regions. In the case of the neat thermoset, the DMTA results are related mainly to the mobility of the segments between the crosslinking points (Trindade et al. 2005; Paiva and Frollini 2006).

For the phenolic thermoset, E’ increased from 150 ^{o}C, which suggests that a residual cure occurred during scanning. Importantly, the cross-linked structure of the thermoset phenolic was not complete. The increase in E’ from 150 ^{o}C, was generally lower for the composites than for the thermoset (Fig. 6).

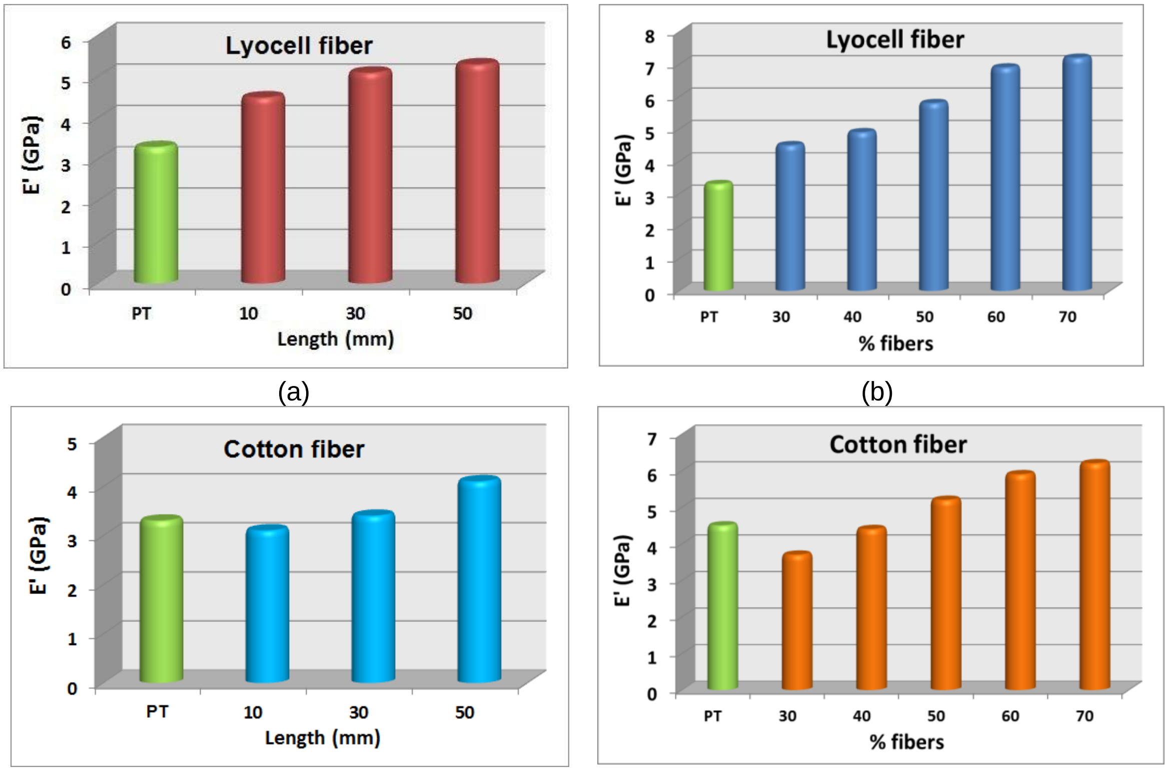


(a) (b)



(c) (d)

Fig. 6. Storage modulus E' values for the thermoset (PT) and composites reinforced with (a) lyocell and (c) cotton fibers of length 10, 30, and 50 mm (30 wt%); (b) composites reinforced by lyocell at 30, 40, 50, 60, and 70 wt% (length: 10 mm); (d) composites reinforced with cotton at 30, 40, 50, 60, and 70 wt% (length: 50 mm). Lyocell: the lowest standard deviation was ±74 MPa (at 40 wt%, 10 cm) and the highest was ±265 MPa (at 60 wt%, 10 cm), cotton: the lowest standard deviation was ±117 MPa (at 30 wt%, 3 cm) and the highest was ±272 MPa (at 30 wt%, 5 cm).

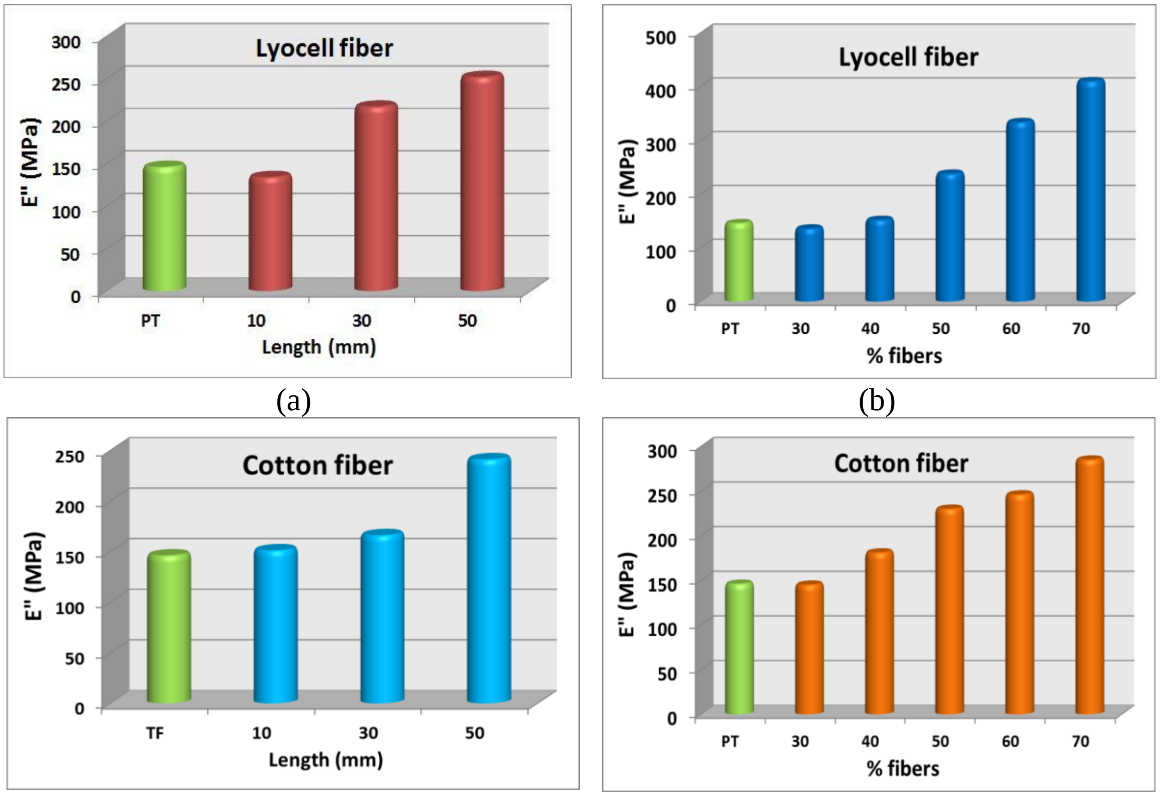


(c) (d)

Fig. 7. Storage modulus E' values for the thermoset (PT) and composites reinforced with (a) lyocell and (c) cotton fibers of length 10, 30, and 50 mm (30 wt%); (b) composites reinforced by lyocell at 30, 40, 50, 60, and 70 wt% (length: 10 mm); (d) composites reinforced with cotton at 30, 40, 50, 60, and 70 wt% (length: 50 mm); at room temperature (25 °C). The error between the three trials ranged from ±0.03GPa (10 mm, 30 wt% lyocell fiber) to ±0.37GPa (10 mm, 50 wt% cotton fiber.

In the composites reinforced with cellulose (lyocell and cotton) fibers, it was observed that there was a steady increase in the storage modulus of the material as the fiber length or mass content of fibers increased (Fig. 6 and 7). This is due to an increase in the rigidity of the material, because the cellulose is a highly crystalline material that can act as an internal link in the matrix (Barbosa et al. 2010; Ramires et al. 2010). In Fig. 7, it can be observed that the behavior of the composites reinforced with cellulosic fibers (both lyocell and cotton fibers) was similar when the fiber lengths (Fig. 7a, 7c) or percentages (Fig. 7b, 7d) varied.

Ramires et al. (2010) reported comparative results for composites reinforced with microcrystalline cellulose, and the strength of interaction of the microfibers with the matrix was assessed from the *E”* results. An improvement in the interaction at the interface had led to lower energy dissipation and a lower value of *E”*. In this context, in the present study, the values of *E”* (Fig. 8b, 8d) indicated that an increase in the amount of both fibers in the matrix decreased the strength of adhesion because the values of E” decreased with the amount of fibers.



(a) (b)

(c) (d)

Fig. 8. Loss modulus E” values, at room temperature (25 ^{o}C), for the thermoset (PT) and composites reinforced with (a) lyocell and (c) cotton fibers of length 10, 30, and 50 mm (30 wt%); (b) composites reinforced by lyocell at 30, 40, 50, 60, and 70 wt% (length: 10 mm); (d) composites reinforced with cotton at 30, 40, 50, 60, and 70 wt% (length: 50 mm). The error between the three trials ranged from ±6GPa (10 mm, 30 wt% cotton fiber) to ±25GPa (50 mm, 30 wt% lyocell fiber).

Water Absorption

The composites (reinforced with lyocell or cotton fibers) were analyzed for water absorption. The samples were cut from plates prepared in advance, and thus on the sides of these samples the fibers were directly exposed to water, as the test was conducted by immersing the samples in water. These conditions (i.e., sides not covered by the matrix and immersion in water) were chosen to represent the harshest conditions that the material could be exposed to for a certain application.

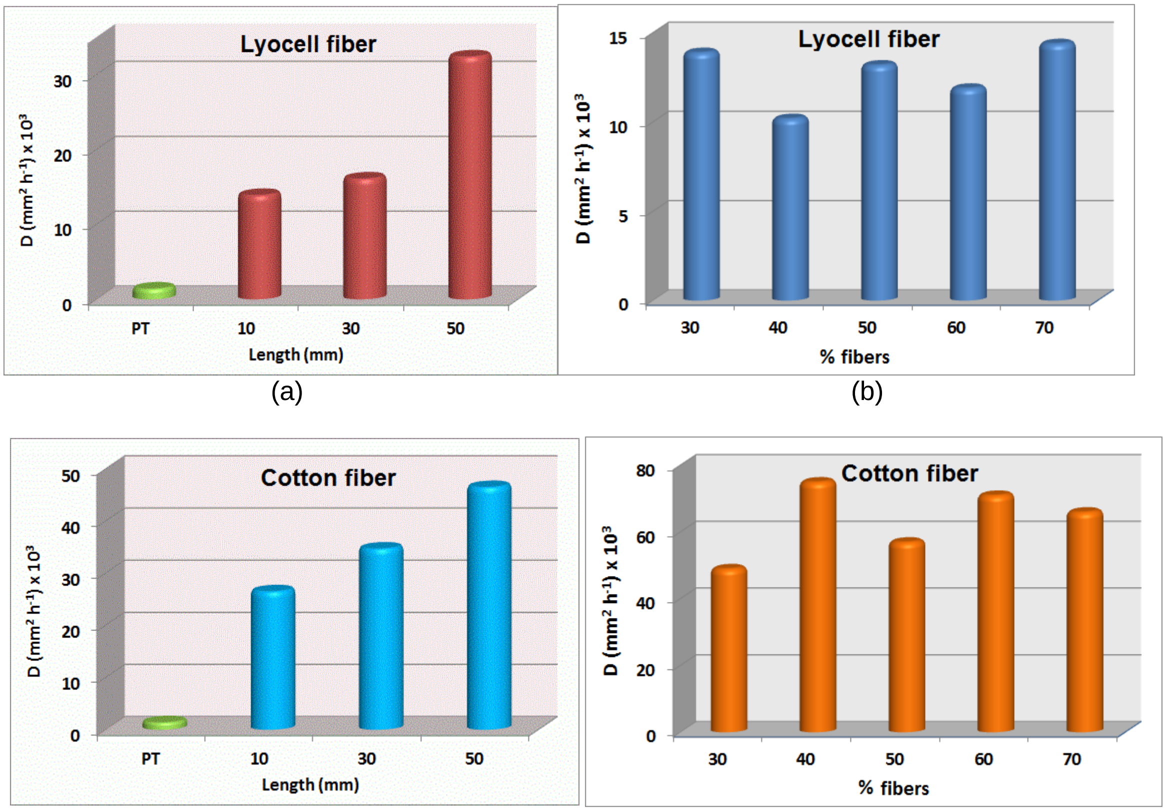
The fiber/matrix interaction intensified when the fibers were well coated by the matrix, which also reduced their hygroscopicity. Thus, the results of water absorption can also be used to gain information about the adhesion at the fiber-matrix interface.

The diffusion of water in the bulk of the composite is strongly influenced by the speeds at which the hydrogen bonds were broken and re-established, such as between H_2O/H_2O, H_2O/polymeric matrix, and H_2O/fibers, throughout the composites. Moreover, the water molecules are considered to diffuse through the matrix, the fibers, and the interface (Megiatto et al. 2009).

In this study it is assumed that water absorption by the composites normally follows Fick's law of diffusion, since the exponent n was found to be near 0.5 for all composites. The value of k (Eq. 2) gives information on the affinity between the material and water molecules (Comyn 1985; Megiatto et al. 2008) and was found to be near 0.1 for all composites. The mechanism of water diffusion is different between the matrix and fibers. The fibers have a porous structure, in which the water molecules form strong hydrogen bonds with hydroxyl groups of the celluloses. In the matrix, the water molecules interact with polar groups (Megiatto et al. 2009). In this material, impregnation of the fiber by the resin was, in general, efficient and resulted in homogeneous composites (Fig. 5) with protected and waterproofed fibers.

The diffusion coefficient of water was considerably lower in the neat thermoset than in the composites (Fig. 9a, 9c). This result suggests that the polar groups of the neat thermoset resin were considerably more available to interact with water in the former (neat thermoset) than in the phenolic matrices in composites. In other words, in the phenolic composites, it appears that the hydrogen bonds developed mainly between the matrix and the fiber rather than between the matrix and the water. Figures 9a and 9c show that the diffusion coefficient D increased with the fiber length. The number of fiber ends decreases with the increase in their length, and the covering of these ends by the less hydrophilic matrix was probably especially efficient. Thus, fewer hydrogen bonds were likely developed between the fiber and water, which accelerated the diffusion of this molecule through the composite with longer fibers. The amount of water absorbed by the longer fibers (50 mm in length) at the point of saturation (after 3 days) was the lowest observed, corresponding to approximately 3.0 and 4.0 wt% for lyocell and cotton, respectively. These data corroborated those of the diffusion coefficient.

The results (Fig. 9b, 9d) showed no correlation between the percentage of the fiber (lyocell and cotton) and the diffusion coefficient. Despite the number of fibers varying over a wide interval (30 to 70 wt%), the D values varied only slightly. These results can be taken as an indication that the impregnation of the fibers by the resin was not negatively affected by the increase in the percentage of fibers, which confirms the ease of impregnation of the fibers by the resin. In addition, the amount of absorbed water showed no correlation with the percentage of fibers, ranging approximately between 3.0 and 4.5 wt% for both fibers.



(a) (b)

(c) (d)

Fig. 9. Water diffusion coefficient ***D*** for (a) phenolic thermoset (PT) and phenolic composites reinforced with (a) lyocell and (c) cotton fibers of lengths 10, 30, and 50 mm (30 wt%); (b) composites reinforced with lyocell fibers at 30, 40, 50, 60, and 70 wt% (length: 10 mm); (d) composites reinforced with cotton fibers at 30, 40, 50, 60, and 70 wt% (length: 50 mm). The error between the three trials ranged from ±0.01 (30 mm, 30 wt% lyocell fiber) to ±0.09 (10 mm, 30 wt% lyocell fiber).

Composites reinforced with cotton fiber presented higher values of ***D*** when compared with composites reinforced with lyocell fiber (Fig. 9). Increasing the efficiency of filling and covering of the highly hydrophilic fibers by the less hydrophilic matrix accelerated the diffusion of water molecules and increased is the value of ***D***. The better filling and covering of the fibers of cotton, compared with lyocell, may be another factor that has led to the higher impact strength of the composites reinforced with cotton (Fig. 4).

CONCLUSIONS

1. Lyocell and cotton fibers obtained from natural and renewable resources yielded good results when added as reinforcement to a phenolic matrix. Furthermore, it was possible to replace 70% wt% of the synthetic material by the fiber.

2. Lyocell and cotton fibers, with structures consisting only of cellulose chains, have a more hydrophilic character than the phenolic matrix. Taking into account this characteristic, the water absorption results were satisfactory.
3. The impregnation process ensures the proper covering of the fibers by the matrix, leading to strong interaction at the fiber-matrix interface and thus to good adhesion, as indicated by the SEM images. This in turn leads to good impact strength. In this context, the composites reinforced with 70 wt% of lyocell (10 mm in length) can be emphasized, highlighting the composite reinforced with 60 wt% of cotton (50 mm in length).

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