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Mechanical behavior of cellulignin based composites

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A powder derivative of acid pre-hydrolysis processing of cellulosic wastes, known as cellulignin, was used as filler in resin matrix composites. The flexural mechanical properties of cellulignin-polyester, epoxy or urea-formaldehyde matrix composites was evaluated. The results obtained show that the urea-formaldehyde and epoxy based composites can be used as alternative materials for low cost and low strength applications. Their advantages over the common wooden agglomerates or composites are presented and are based on the fact that cellulignin can be obtained virtually from any cellulosic waste. © *2001 Kluwer Academic Publishers*

1. Introduction

Cellulose based materials are widely spread all over the world, both in native and cultivated areas. The common characteristic of most agricultural crops, from grains to fruits and leguminous, is that only a fraction of the cultivated plant is used while a large mass of cellulosic waste has to be disposed after each harvest. For example, the annual harvest of rice in Brazil amounts to 10 millions of tons and about 2.5 millions of tons of rice husk are generated yearly [1]. Some of the wastes are already treated in order to obtain useful products or raw materials for industrial processes. For example, rice husk is used as fuel on rice processing industries. The ashes generated, that amount 30% of the fueled material, are a silica rich by-product [2] from which silicon carbide whiskers can be produced [3]. This material can also be used as filler in rubbers or thermoplastic polymers [4–6]. Other examples from the processing of wastes to obtain useful materials are fibres that can be obtained from banana trees and leaves [7, 8] and animal fodder that is produced from many sources, such as leaves and stalk points of sugar cane bagasse plant [9]. Nevertheless, an important fraction of all cellulosic wastes generated each year after harvesting, as well as from reflorestation areas, is lost due to non competitive prices for a derivative to be processed, lack of technology or even due to difficulties associated with easy transportation to a processing facility.

Recently a moderate temperature acid pre-hydrolysis of cellulose based materials was shown to successfully transform raw cellulose wastes such as leaves, stalks and other residues from grains, fruits, horticulture and grasses into a lignocellulosic material known as cellulignin [10]. This process has many advantages over the usual high temperature treatments used to process cellulose materials, and its derivative, cellulignin, is an entirely new, and very promising, raw material. In fact, cellulignin, can be used for animal forage and as an alternative fuel [10]. Cellulignin is obtained as a dark brown powder with a fibrous structure [11] and, therefore, could also be potentially used as filler in composite materials or in agglomerates, as a substitute for wood based materials.

In this work a study was undertaken in order to analyze the mechanical properties of cellulignin based composites. The results obtained are compared with the properties of common commercial materials and the advantages of this new engineering material are highlighted.

2. Experimental procedures and material

The cellulignin obtained by acid digestion of cellulosic wastes from chips of *eucalyptus sp.* is a dark brown powder composed of massive particles with lengths greater than 2 mm and showing a fibrous texture [10]. This material was milled and sieved and only the particles with lengths ranging from 180 to 600 μm were used in this work. The sieved particles have a needle like form with an average aspect ratio of about 2–5, Fig. 1. This needle like form is a convenient shape for a composite filler, because the higher the aspect ratio of a filler is, the higher its surface area to volume ratio

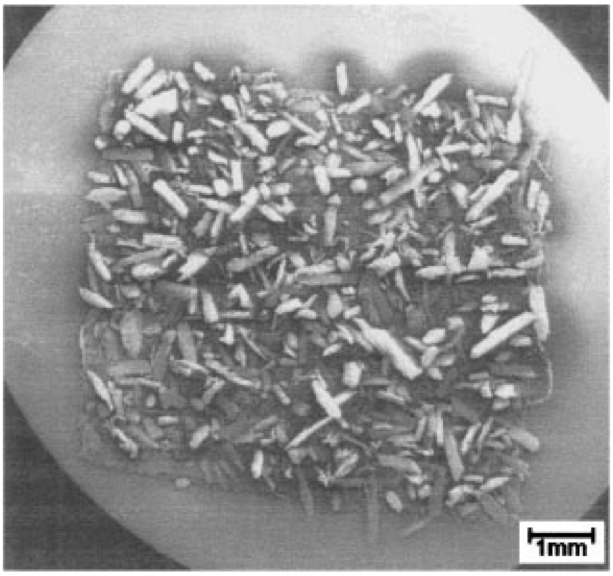


Figure 1 Needle like morphology of the cellulignin sieved particles.

[12]. Therefore, the interfacial area available for close contact between matrix and filler is increased and, theoretically, a more homogenous microstructure could be obtained. Besides of that, the mechanical behavior of particulate composites is increased when needle like particles are used. In fact, as it is well known, the efficacy of the load transfer to a fiber, or a needle like particle, increases as a function of the aspect ratio [13].

Three thermoset resins were used as the matrix phase, namely: urea-formaldehyde, polyester and epoxy. The polyester used was a commercial orthophtalic resin mixed with 2 weight percent of methyl ethyl ketone catalyst. The epoxy system was obtained by mixing the difunctional epoxy monomer, diglycidyl ether of bisphenol-A, with an aliphatic amine, triethylene tetramine. For this particular epoxy-hardener pair the stoichiometric ratio corresponds to 13 parts by weight of hardener per hundred parts of resin, phr. Both resins are cured at room temperature.

The effect of the formulation and processing conditions of the urea-formaldehyde resin on the mechanical properties of the bare resin was evaluated prior to the incorporation of cellulignin. Table I shows the different formulations analyzed and the processing conditions of time and temperature used. One can see from Table I that besides the resin monomer and hardener the resin formulations comprise an extender and water. The urea-formaldehyde resin is soluble in aqueous medium and, therefore, water is used to lower the resin viscosity in order to aid in the homogenization of the mixtures [14]. The use of a filler to extend the mixtures is recommended in order to decrease the cost of the resin [14]. A salt, coded M by the resin manufacturer, and wheat flour were used as hardener and extender, respectively. The formulation which showed the best results was the only one used as matrix in the composites.

The composites were fabricated by mixing together the proper quantities of resin and cellulignin in an orbital mixer. The weight fraction of resin was varied from 0.10 to 0.50. After continuously stirring the mixtures by 10–30 minutes the slurry obtained was cast in a steel mold with a cavity 114 mm long, 25 mm wide and 12 mm thick. The cure was done under a molding pressure of 35 MPa, following the cure schedule appropriate to each resin matrix. As the maximum length of the particles was much lower than the thickness of the test specimens (viz., $\approx 600\ \mu$m vs. 12 mm), the particles were mainly randomly distributed inside the composite without any preferential particle alignment direction. Nevertheless, in some instances, small clusters of particles laying on planes perpendicular to the thickness of the specimens could indeed be found, as it was shown by the fractographic analyis (see Fig. 7).

The different bare urea-formaldehyde resin formulations and composites were tested in flexion at a crosshead speed of 1 mm/min. A three point bending test apparatus was used with a span-to-depth ratio of 10. At least 6 specimens were tested per each material analyzed.

The analysis of the fracture surfaces of the test specimens was done by scanning electron microscopy, SEM. The samples were previously coated with a conducting film of carbon or gold-palladium alloy and the SEM analysis was performed with secondary electrons imaging and acceleration of the electron beam ranging between 15–20 kV.

3. Experimental results and discussion

The experimental results obtained for the different bare urea-formaldehyde resin formulations are shown in Table I. In Fig. 2 these results are plotted against the weight fraction of the extender, which was found to be the parameter that controls the mechanical behavior of the resin. In fact, as shown in Table I, the other parameters investigated, i.e., the time and temperature of cure and

TABLE I Experimental conditions used to analyze the bare urea-formaldehyde resin and experimental values of the modulus of rupture, MOR. The resin formulation is done in parts, in weight, per hundred parts of resin, phr

Formulation number	Resin formulation, phr			Cure conditions		MOR, MPa
	hardener	water	extender	time, minutes	temperature, °C	
01	10	15	–	15	130	9.4 ± 2.0
02	10	15	10	15	130	7.7 ± 1.2
03	10	15	20	15	100	7.1 ± 0.9
04	10	15	20	8*	30	6.8 ± 1.7
05	10	15	–	8*	30	8.8 ± 2.0
06	10	30	35	15	100	3.4 ± 0.8
07	8	50	50	15	110	2.3 ± 0.6
08	20	30	40	15	110	3.6 ± 0.6

*hours

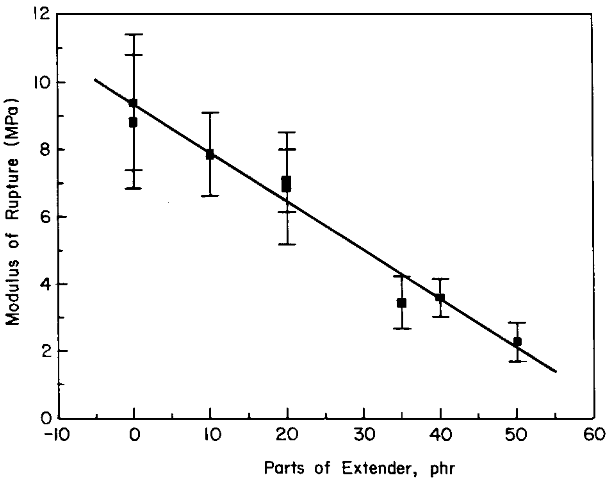
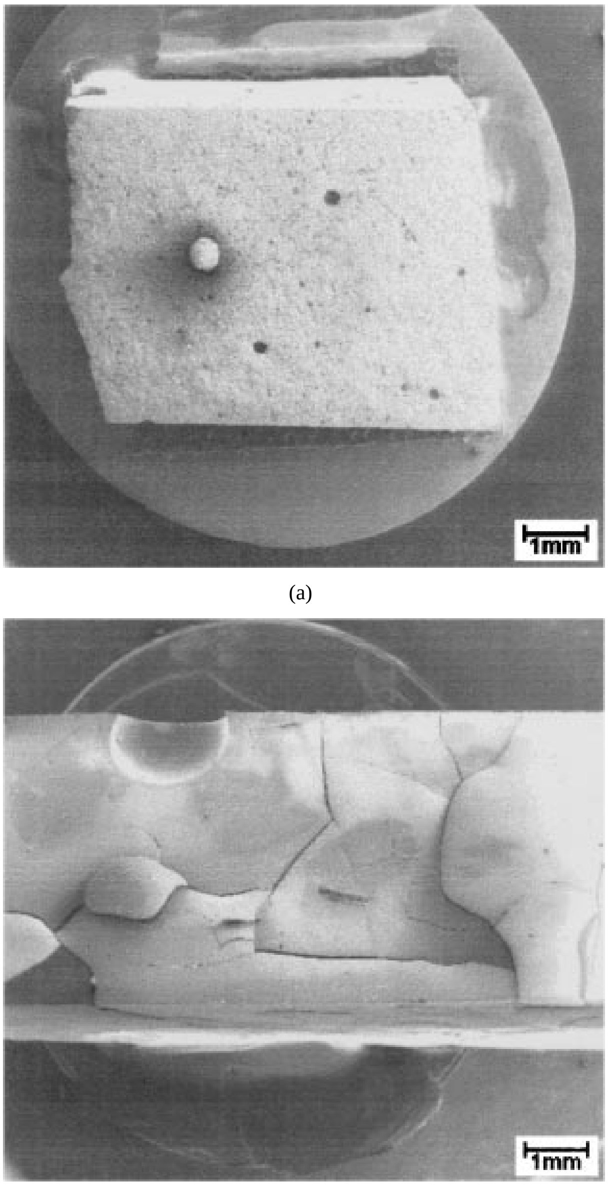


Figure 2 Variation of the modulus of rupture of the bare urea-formaldehyde resin as a function of the extender content.



(a)

(b)

Figure 3 Fracture surface of the urea-formaldehyde resin formulated with: a) 20 phr of extender and b) without extender.

the amount of hardener, did not bring strong changes on the values of the flexure strength. This behavior could be explained by analyzing the fracture surfaces of the test specimens. Although a severe mixing was done during the fabrication of the different resin formulations, the wheat flour used as extender tends to agglomerate. Therefore, as the amount of extender is increased, the microstructure of the bare resin becomes less homogeneous. Fig. 3 compares the fracture surfaces of the formulation 03, which contains 20 phr of extender, with that of formulation 01 fabricated without extender. Large clusters of extender, or large voids left by pulled out clusters, can be seen at the fracture surface of the material fabricated using extender, Fig. 3a. The fracture surface of the material without extender is much more smooth, Fig. 3b. At Fig. 4a one can see under higher magnification, the fracture surface of the extender containing compositions. The wheat flour particles are completely detached from the resin and cracks can be observed joining the particle's sites. These aspects apparently indicate that a low strength interface is developed between the particles and the resin. Fig. 4b shows that, indeed, the apparently smooth surface of the resin without extender has many topographic aspects, like voids, that can only be seen under higher magnifications.

Therefore, due to both the tendency of the wheat flour used as extender to agglomerate and the low strength of the extender-resin interface, the incorporation of extender reduces the mechanical performance of the bare urea-formaldehyde resin. From the above results the composites were fabricated using only the urea-formaldehyde system with formulation 01.

The experimental results of the cellulignin/urea-formaldehyde composites are shown in Table II. One can see that the values for the modulus of rupture are matrix dominated, since it increases as the content of resin is increased. In fact, the value of the modulus of rupture for the material with 100% of cellulignin, 3.2 ± 1.5 MPa, shows that cellulignin is a low strength material. This value has, however, to be regarded as representing the properties of the "green" material, obtained only by room temperature pressing of the cellulignin powder. The fractographic analysis of this material is reported elsewhere [11]. The main observed features are cracks running transversely to the loading axis, which resemble the cracks found in cross-ply laminates at plies showing low transversal strength, i.e., those plies with fibres laying at right angle with the loading axis [15]. Therefore, the presence of cracks running at planes perpendicular to the loading axis, whether they are formed by tensile or shear stresses, can be interpreted as common topographic characteristics of materials showing low transversal strength.

Although the values shown in Table II are very low as compared to the modulus of rupture from common inorganic fibre reinforced composites (e.g., $\sigma_r = 206.0$ MPa, for chopped glass fiber-epoxy composites with 20% volume fraction of fibres [16]), and even those from natural fiber reinforced composites (e.g., $\sigma_r = 43$ MPa for jute-polyester composites [17]), they are on the same level as those shown by wooden agglomerates and low density particle boards, that range

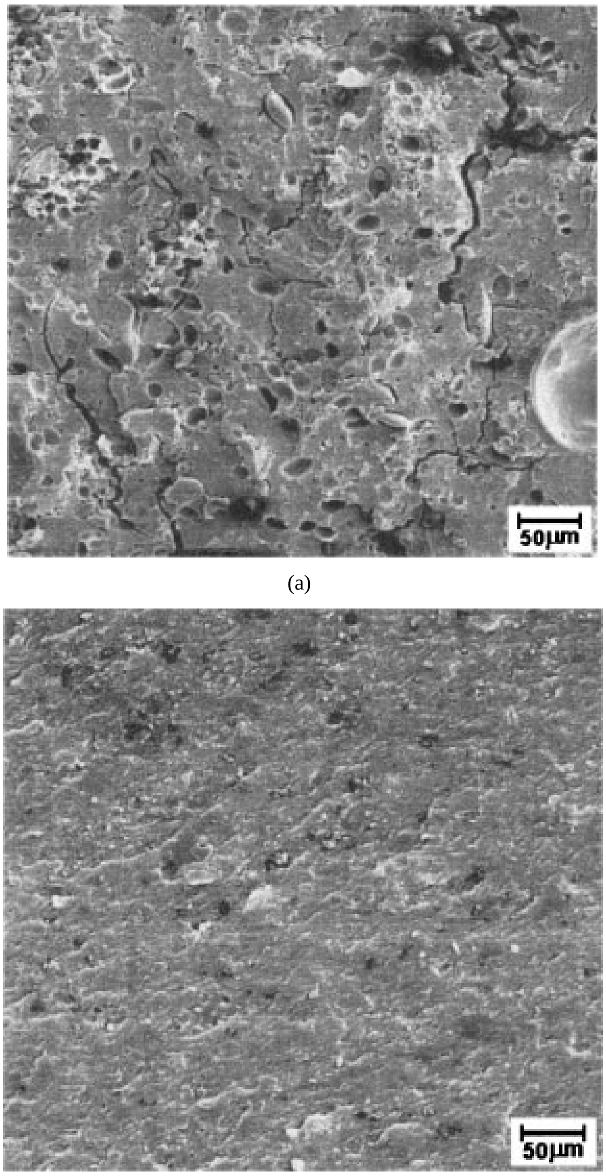


Figure 4 Topographic aspects of the urea-formaldehyde resin as a function of the amount of extender. a) Extender containing formulations characteristic surface features showing cracks joining the detached extender particles b) Characteristic homogeneous smooth surface observed for the formulations without extender.

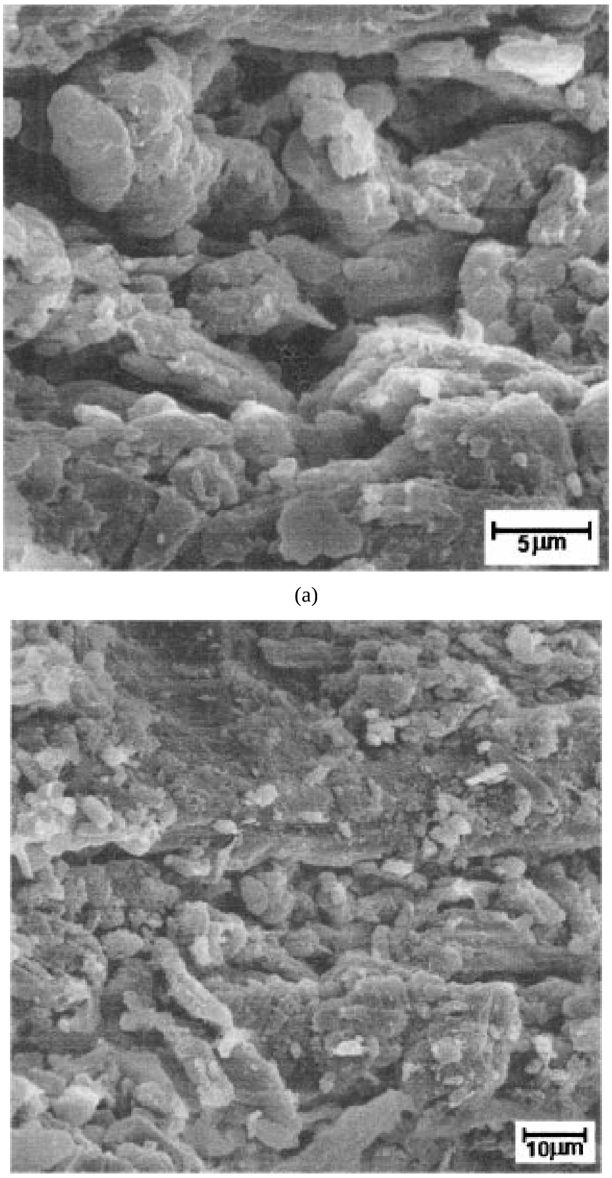


Figure 5 Fracture surface features of cellulignin- urea-formaldehyde composites with low resin content. a) Pores and particles without resin. b) Cracks laying at planes perpendicular to the plane of the applied three-point bend loads.

TABLE II Modulus of rupture of the cellulignin/urea-formaldehyde composites

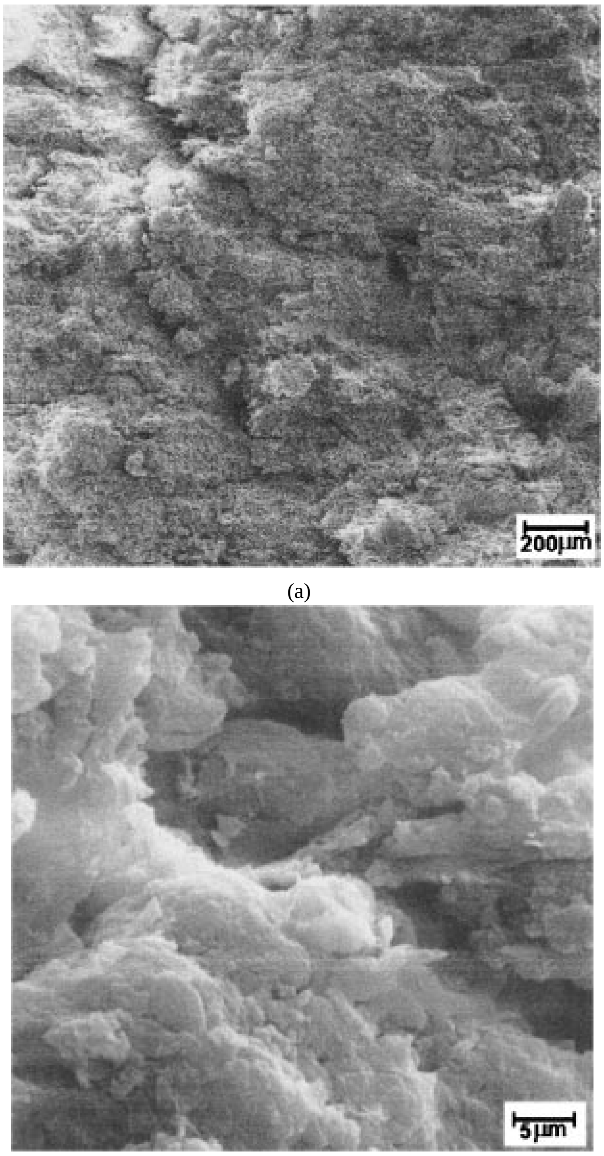
Parts of resin per hundred parts of filler	Modulus of rupture, MPa
8	3.7 ± 1.8
10	4.1 ± 1.7
12	4.6 ± 2.2
20	3.8 ± 0,7
50	6.7 ± 2.1

from 1.4 to 5.5 MPa [18] and from 5.5 to 9.7 MPa [19], respectively.

The fractographic analysis of the urea formaldehyde resin matrix composites with low resin content shows the common features observed for powder pressed materials, i.e., pores left between the particles and many loosely bonded particles. These aspects are presented in Fig. 5a. At the fracture surface of these materials one can also observe transversal cracks, as shown in Fig. 5b. The low transversal strength displayed by these composites is expected due to the lack of binding between many particles, that favors delamination by shear stresses under the three bending flexure test [20].

Transversal cracks are also present at the fracture surface of the urea-formaldehyde resin rich composites, as shown in Fig. 6a. The microstructure of these composites has, nevertheless, fewer number of pores and loosely bonded particles, Fig. 6b.

The experimental results obtained for the cellulignin filled epoxy and polyester matrix composites are shown in Table III. One can see that two different trends were obtained. The epoxy matrix composites showed the best mechanical results and even with amounts of resin as low as 10 phr, the values obtained for the modulus of rupture are among the best values reported for wooden



(a)

(b)

Figure 6 Same as Figure 5 for the composites with higher resin content. a) Transversal cracks. b) Pores and resin uncovered particles. These features are present in fewer number than that observed for low resin content composites.

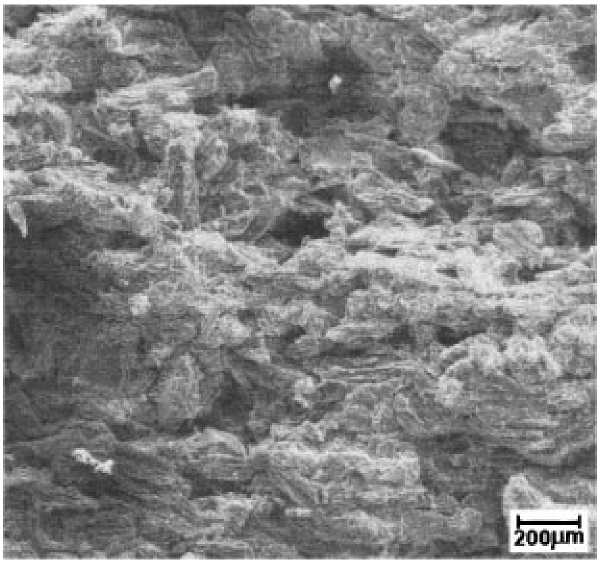


Figure 7 Fracture surface of the cellulignin-epoxy composites. Transversal cracks were not observed.

TABLE III Modulus of rupture of the cellulignin/epoxy and polyester composites

Epoxy composites	
Parts of resin per hundred parts of filler	Modulus of rupture, MPa
10	5.8 ± 0.8
20	6.2 ± 0.9
50	13.8 ± 0.7
Polyester composites	
Parts of resin per hundred parts of filler	Modulus of rupture, MPa
10	1.2 ± 0.1
20	1.7 ± 1.1
50	2.6 ± 0.2

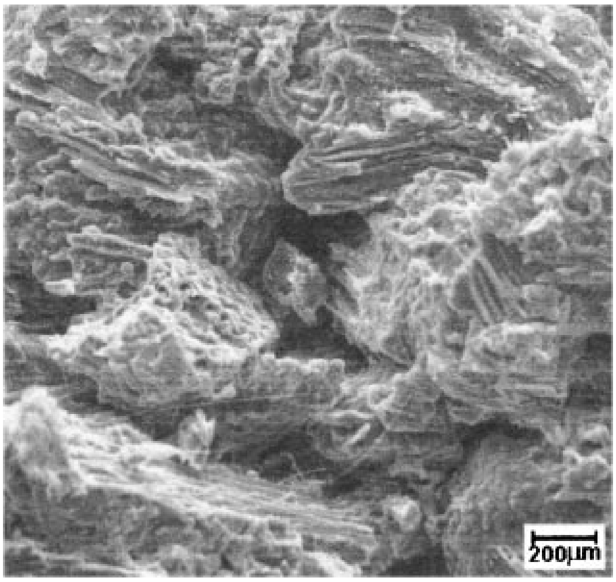


Figure 8 Broken cellulignin particles at the fracture surface of cellulignin-epoxy composites.

agglomerates [17] and chopped sugar cane bagasse-gypsum matrix [21]. The fractographic analysis of these composites shows also pores left by pressing procedure, but large transversal cracks were not observed, Fig. 7. A small number of broken cellulignin particles could also be found at the fracture surface of these composites, as shown in Fig. 8. This aspect reveals that a better interface strength was developed between the epoxy resin and the cellulignin filler. This better interface strength can be responsible for the improved mechanical properties showed by this composite.

The polyester matrix composites, on the other hand, showed very low mechanical properties, as depicted in Table III. The same fractographic aspects of pores and transversal cracks observed for the urea-formaldehyde matrix composites were also present, what could be interpreted as showing that a low strength interface was developed between the cellulignin particles and the polyester resin.

The difference in the values found for the urea-formaldehyde and polyester matrix composites could arise from the fact that urea-formaldehyde resins can form chemical bonding with cellulose based materials, since the methylol groups can react with the hydroxyl groups of cellulose [22, 23]. From the results obtained one could expect that only a poor mechanical anchoring is acting when the polyester matrix is used. The best results shown by epoxy matrix composites relatively to the urea-formaldehyde based composites were not completely identified. However, the epoxy matrix has much better mechanical properties than the urea-formaldehyde matrix. Common reported modulus of rupture for epoxy resins cured with aliphatic hardener range from 95 to 120 MPa [24], that is more than 9 times greater than the best value found in this work for a urea-formaldehyde resin. From the fractographic analysis it is also clear that a good epoxy resin impregnation occur and, therefore, the mechanical locking of the cellulignin particles was enhanced for the epoxy matrix composites.

From the results obtained one can classify cellulignin composites among the low strength materials that are, nowadays, used in low cost agglomerates, interior panels and furniture. The advantage of the development of these composites is based on the fact that the cellulignin filler can be obtained from practically any cellulosic residue. Therefore, what is now considered as a waste, such as the green parts of plants that are disregarded after each harvest, can be processed to obtain an useful material. In fact, the use of composites and agglomerates with cellulignin can be an attractive alternative to replace wooden based materials and, in so doing, help to reduce pressure on native forest areas. Not of minor importance is the use of cellulignin as an alternative fuel for electric power generation [11], what is considered as a way to reduce cellulignin costs and to add value to cellulosic wastes.

4. Conclusions

The experimental results obtained show that cellulignin/urea-formaldehyde or epoxy resin matrix composites can be useful materials to low strength-low cost applications. The use of the cellulignin powdered filler in composites or agglomerates has a great advantage over the common used fillers, because it is obtained from cellulosic wastes. Its use, therefore, is a way to reduce environmental problems by reducing cellulosic waste disposal. As cellulignin can virtually be obtained from any cellulose containing material, even usefulness herbage can be turned in a source of raw material for its production. Moreover, the development of this material could be an alternative way to replace common wooden based materials and, indirectly, an aid to reduce native forest destruction.

One could also expect that better mechanical properties can be obtained by varying some of the processing parameters used to produce the composites analyzed. The optimization of such parameters as molding pressure, size of the cellulignin filler and temperature of cure are now under way and are expected to bring relevant changes on the mechanical behavior of this promising new material.

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