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CHARACTERISATION OF A PHENOLIC RESIN AND SUGAR CANE PULP COMPOSITE

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Abstract - Polymeric materials are increasingly replacing metallic materials as a result of their properties. In this work a composite of phenolic resin and sugar cane pulp was developed. The sugar cane pulp has been previously alkalinised, dried, and milled and the particles had been classified in a range of grain sizes. Experimental assays were performed, varying the proportion of the resin and the reinforcement and the size of the cane pulp fibre, keeping the pressure and moulding temperature constant. These composites were characterised according to physical and chemical properties, through test bodies produced in moulds according to ASTM standards. The experiments performed showed that the use of sugar cane pulp as reinforcement in polymeric composites represents an option for reducing costs in industrial applications, thus suggesting a significant industrial applicability of the product.
Keywords: polymeric composite, phenolic resin, sugar cane pulp.

INTRODUCTION

The substitution of metallic materials by polymeric materials is a growing trend, partly resulting from the fact that in many industrial applications these materials have advantages over metallic materials, especially when increased resistance to corrosion, low thermal and electric conductivity, and low density are required.

With a view towards the changing needs of the market, the research and development of new materials, including thermofixed resin composites, has been the objective of many scientific studies.

A composite is a material developed by combining two or more components, one of which is a structural component (glass fibre, carbon fibre, vegetable fibres etc.) and the other a matrix component (resin), to obtain specific characteristics and properties (Mano, 1991). Recent years have witnessed rapid growth in the use of polymeric composites reinforced with fibre, producing a combination of high performance, great versatility, and other advantages at a favourable cost. One of the fibres used for these polymeric products, cellulose fibre, has become an important class of strengthening materials (Joly et al., 1996; Beshay and Hoa, 1992).

Plant fibres have characteristics of great interest in the area of polymeric composites; these include low density, low cost, biodegradability, flexibility in processing, and little need for treatment equipment. (Agrawal et al., 2000; Canché-Escamilla et al., 1999). Plant fibres are becoming an economic and ecological alternative as reinforcement and bulk agents in plastics, since these fibres can gradually substitute for the synthetic fibres regarded as traditional materials (for example, glass fibre), thus opening up new market possibilities for agricultural countries (Nothenberg, 1996).

Phenolic resins are some of the principal thermofixed synthetic polymers, the third most important polymeric matrix for composites (Lubin, 1969), and are also known for their high temperature resistance (Knop and Pilato, 1985; Kopf and Little, 1991). Pure phenolic resin can be obtained through the condensation reaction between phenol (C_6H_5OH) and formaldehyde (CH_2O), producing methylene bridges between the phenol molecules (Figure 1).

In the presence of given reagents this resin can form crosslinks under the influence of light or heat, resulting in a rigid material. The material forms a three-dimensional network that will not soften on subsequent heating and can be removed from its mould without the need to wait for it to cool (Vlack, 1984). Due to the widespread use of phenolic resin, composites have diverse applications, such as laminates for table-top coverings, desks, dividers, doors, brake pads, moulded electrical components, etc. (Mano, 1991).

Brazil is a large-scale producer of sugar cane due to the large sugar and alcohol industries, generating, as a result, a large quantity of pulp that is usually burnt to produce heat. The pulp, a fibrous, lignocellulose residue, the remnant of the sugar cane, constitutes a heterogeneous collection of particles of different sizes that vary between one and 25mm, with an average size of 20mm. The pulp is composed of cellulose, hemicellulose, and lignin as the principal natural polymers. It also contains small quantities of other compounds collectively classified as impurities. The chemical composition of the pulp for the fractions most frequently employed is given in Table 1.

The present study was aimed at developing and characterising the physical and chemical properties of a new type of composite material, using phenolic resin as the polymeric matrix and cane pulp as the strengthening element.

This study was developed in two phases: a) development of the composite, involving treatment of the sugar cane pulp, alkalinisation, drying, grinding and granulometric classification, formulation of the composite, and pressing and b) characterisation of the properties of the composite.

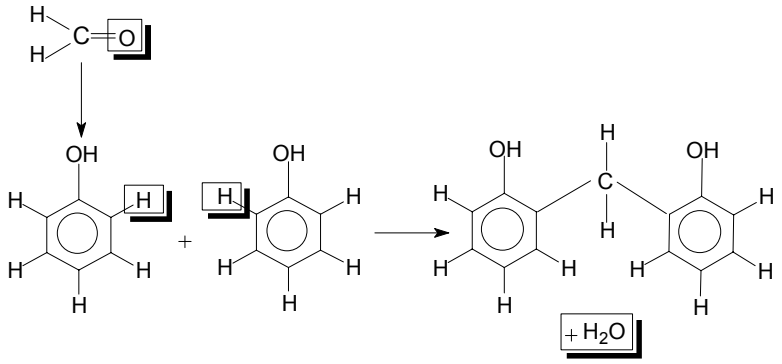


Figure 1: Condensation reaction for the formation of phenolformaldehyde.

Table 1: Chemical composition of the cane pulp.

	Whole Pulp	Fibre Fraction	MedullarFraction
Cellulose	46.6	47.7	41.2
Hemi-cellulose	25.2	25.0	26.0
Lignin	20.7	19.5	21.7

ICIDCA (1999)

MATERIAL AND METHODS

Development of the Composite

Test bodies of the composite were prepared with different grain sizes and cane pulp compositions, using an experimental plan described by Neto et al. (1996).

a) Neutralisation of the Cane Pulp

The cane pulp used in this study results from extraction of the cane syrup by grinding. As a result of the bacterial flora present in the cane pulp, the fermentation reactions proceed rapidly, leading to the formation of volatile products with unpleasant odours, as well as acidifying the medium. Therefore, this degradative process was neutralised by immersing the cane pulp in an aqueous solution of $Ca(OH)_2$. After the neutralisation bath the cane pulp was left in a sieve for removal of excess water (1 to 1:30h).

b) Drying of the Cane Pulp

After being neutralised, the cane was dried in a drying and sterilisation oven (model TE – 393/1 – TECNAL) for 3h at a temperature of 110°C.

c) Grinding and Granulometric Separation of the Cane Pulp

After drying the cane pulp was ground in a mill designed for plant tissues (Willye – ELOS)**.** The granulometric separation of the ground cane pulp was carried out in a granulometric sieve separator, in which the size ranges separated are indicated by the following code: G1 (35-80 mesh) and G2 (80-170 mesh).

d) Formulation of the Test Body

Phenolic resin (phenolformaldehyde) of the Novolak type, obtained from Alba Química and designated Thor MD 278 (ρ = 1.27 g/cm^3), was used in this study. There is hexamethylene tetramine (hexamine), which acts as a reticulation agent, in the formulation of this resin. Calcium stearate was used to improve the mobility of the product within the mould and the interaction between particles.

The test bodies varied in composition according to the quantity of resin and cane pulp and the grain size. In order to assess the composition and size range that represented the optimal properties of the system under study, a complete 2^2 experimental planning was used, in which was elaborated a planning matrix to minimize and to organize the experiments. In this planning was assessed the influence of the two factors, composition of the test body and grain size of the cane pulp for density, absorption of water, morphology and resistance to traction.

According to the experimental planning matrix, four experiments were to be performed for each assay; Table 2 summarises the experiments carried out, in which the responses to each experiments where analysed in graphs related to each assay type.

f) Pressing

The phenolic resin, together with the cane pulp and the additives, was mixed in a container, and the final mixture (physical mixture) was homogenised. After homogenisation of the mixture, the pressing phase was carried out by placing the mixture in a mould prepared according to ASTM standards, in which shape and size vary according to assays. A heated hydraulic press (model - SCHULZ – PHS 15t ICO Comercial S.A.) was used to bring about the thermofixation of the phenolic resin. A pressure of 150kgf/cm^2 was employed for 10 to 15 min at a temperature of approximately 170°C.

Table 2: Experiments conducted based on the experimental planning matrix.

Experiments	Composition of *C.P. (%)	Grain size of cane pulp (mesh)
1	C2	G2
2	C1	G2
3	C2	G1
4	C1	G1

*C1 = 69% resin/29% pulp/2% calcium stearate
C2 = 29% resin/69% pulp/2% calcium stearate
**G1 = 35- 80 mesh;
G2 = 80-170 mesh

Characterisation of the Composite

a) Density

According to Mano (1991), the density of a material reflects its chemical structure and its molecular organisation. Thus, more crystalline regions are more compact, whilst more amorphous regions are more voluminous. Polymeric materials are all comparatively light, and the majority of polymers have a density in the range of 0.9 to 1.5 g/cm^3 with a greater concentration of values close to 1. The density of the test bodies prepared in this study was determined according to the ASTM D792-66 standard, which describes the determination of different densities.

b) Resistance to Water:

Water resistance in polymers is assessed by the absorption of humidity, resulting in an increase in the dimensions of the piece, which hinders their application in precision situations. In addition, the variation in humidity can result in the formation of a network of microfractures on the surface of the artefacts and alter their electrical and mechanical properties. The sensitivity to water is related to the grade of cure of phenolic resins; for example, in the case of incomplete cure, the laminates in contact with the water swell change their size and undergo delamination, according to Mano (1991). The water absorption assay according to the method described in the ASTM D570 – 77 standard**,** in which the percentage of water absorbed by the sample is measured, was used.

c) Scanning Electron Microscopy (SEM)

The morphology of the composite in question, which is the interaction between fibre and matrix, was examined by scanning electron microscopy. The composite samples were fractured mechanically by hammer and covered with gold and examined in a Philips XL 30 microscope.

Tensile strength: The tensile strength, or resistance to breaking traction of a material, is measured by the charge applied to the material per unit area at the point of breaking (Mano, 1991). The traction assays carried out using EMIC DL 500/1000/2000/3000 equipment and methods ASTM D 412, D 638 and D 882 describe the assays.

RESULTS AND DISCUSSION

A photograph of the test body of the composite obtained, produced according to the ASTM D792-66 standard used in the assays, can be seen in Figure 2 below.

Figure 3 contains the density values for the composites with different percentages of cane pulp fibres and grain size distributions.

It can be seen that the density of the composites in relation to percentage of cane pulp fibres suffered a reduction with the increase in the fraction of fibres. This is due to the low density of the cane pulp in relation to the phenolic resin. The grain size, did not show significant influence on the density of the composite.

The micrographs of the composites obtained by SEM revealed a weak adhesion, i.e., the interaction between the fibre and the matrix was inefficient. This can be seen in Figure 4(a), which shows regions in which the fibres are released from the matrix during the fracture of the test body; this finding is also known as the "pullout" mechanism. In Figure 4(b) it can be seen that the cane pulp fibres are not covered by the polymeric matrix (phenolic resin), indicating also weak fibre-matrix adhesion. According to Bisanda (1993), in order to obtain improvement in the interaction between the fibre and the matrix, the fibres should be submitted to a treatment called "mercerization", where the fibres are treated with NaOH solution.

This treatment improves the adhesive characteristics of the fibre surface due to the removal of natural and artificial impurities from the surface. Consequently, the mercerised fibres have an increased surface tension as well as wetting ability, thus improving the entanglement between the matrix and the rough surface of the fibres. According to Tita (2001), comparing the results of composites with untreated fibres and those composites with mercerised fibres, it can be seen that composites with mercerised fibres show a greater fibre-matrix interaction, leading to an improvement in mechanical properties, such as resistance to impact.

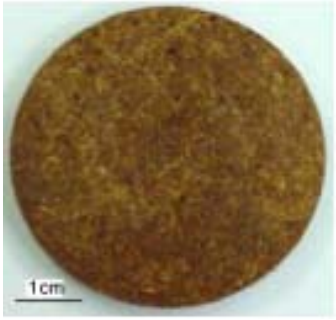


Figure 2: Composite test body.

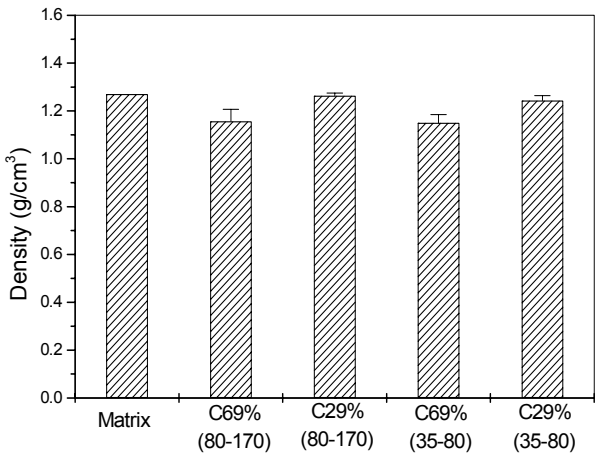
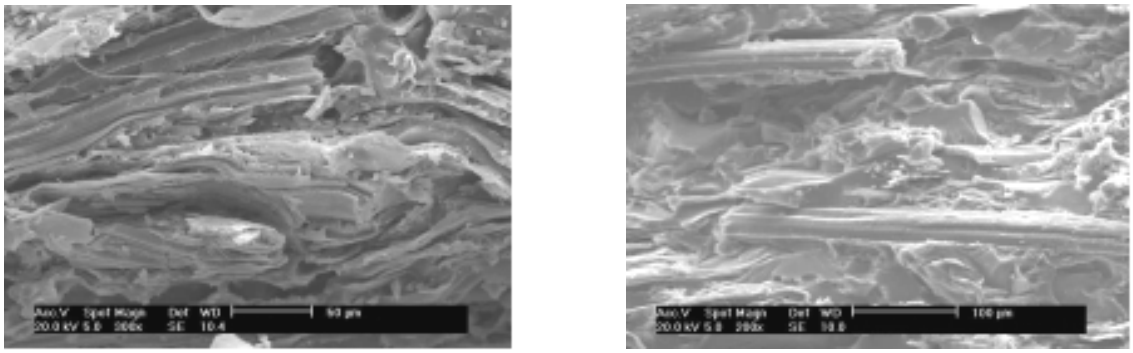


Figure 3: Density of the composites as a function of percentage of fibre and grain size.



(a) 300X magnification (b) 200X magnification

Figure 4: (a) Micrograph of the fracture of composite with 69% fibres and a granulometry of 35-80 mesh, (b) Micrograph of the fracture of composite with 29% fibres and a granulometry of 80-170 mesh.

In Figure 5 it can be seen that the absorption of water, on the order of 12% for the composites with higher percentage of cane pulp fibres (69%), increased in relation to pure resin (matrix), whilst the composites with a lower percentage of cane pulp fibres (29%) showed absorption on the order of 3%. According to references cited by George et al; (1998) for hydrophilic fibres, such as cellulose fibres, an increase in water absorption may be expected. Cellulose fibres are difficult to dissolve due to their highly crystalline nature, although they tend to retain liquid in their fibrilar spaces.

The high values of water absorption obtained may be due to the weak adhesion between the fibre and the matrix, as shown in Figures 4a and b. Since the hydrophylicity of the fibres can be reduced by chemical treatment (e.g., mercerisation), in which hydroxyl groups of the cellulose react with functional groups of the coupling agent, resulting in a satisfactory interaction between the fibre and the matrix, then the possibility of hydroxyl groups coming into contact with water molecules is considerably reduced (George, 1998). Another important factor that contributes to the absorption of water is the quantity of fibres that are inserted in the matrix, as can be seen from the results shown in Figure 5, in which a large percentage of fibres (69%) incorporated in the matrix significantly increases the absorption of water. The grain sizes didn't interfere in the absorption of water.

Tensile strength and stretching along the fracture are properties that are highly dependent on the interfacial adhesion between the phases present, since if the adhesion is not perfect, there is a strong probability of creating a flaw that would lead to breakage of the material in the interfacial region. The absence of adhesion leaves this region weaker (Bledzki and Gassan, 1999; Bledzki et al., 1997; Felix and Gatenholm, 1991).

Figure 6 shows the resistance to traction values for composites with different fibre percentages and grain sizes. It was found that the resistance to traction

for the fraction with 29% fibres was greater than that for the fraction with 69%; these values are within the expected range, according to similar results obtained by Joseph et al. (1999), using short fibres of sisal in a polyester matrix with fibre fractions between 10% and 50%. The resistance to traction of the composites increased with fibre fractions of between 20 and 50%, whilst for fractions lower than 20% the loading was found to be inefficient and for those above 50% there was an excessive interaction between the fibres, decreasing the resistance to traction. The influence of fibre granulometry in the tensile strength, in the case of 69% fibre fractions, for grain sizes of 80 to 170 mesh, was 36% higher than for grain sizes of 35 to 80 mesh. This behaviour was similar to 29% fibre fractions with the variation of 8%. This effect was probably due to the size of the granulometric bands used, below the critical length.

According to Joseph et al. (1999), in composites reinforced with short fibres there is a critical length of fibre necessary if maximum resistance is to be achieved. If the length of the fibre employed as reinforcement is shorter than the critical length, the fibre will be loosened from the matrix and the composite will break at low tensions.

Another important factor that may have contributed to these results is the weak adhesion between the fibre and the matrix, increasing the fragility of the material and putting in jeopardy the mechanical properties of the composite.

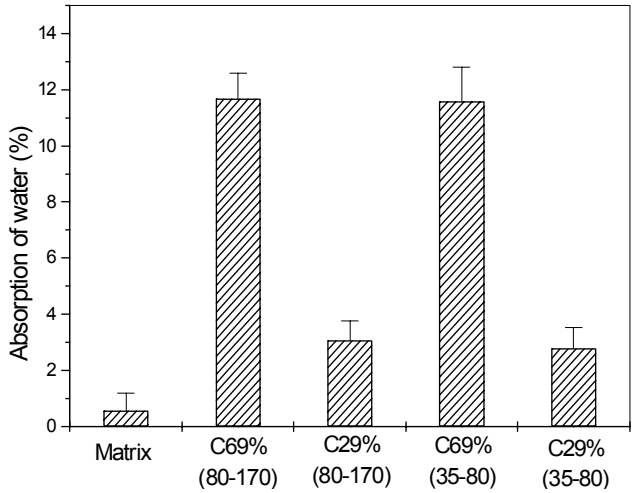


Figure 5: Absorption of water by the matrix and the composites with different percentages of fibre and grain sizes.

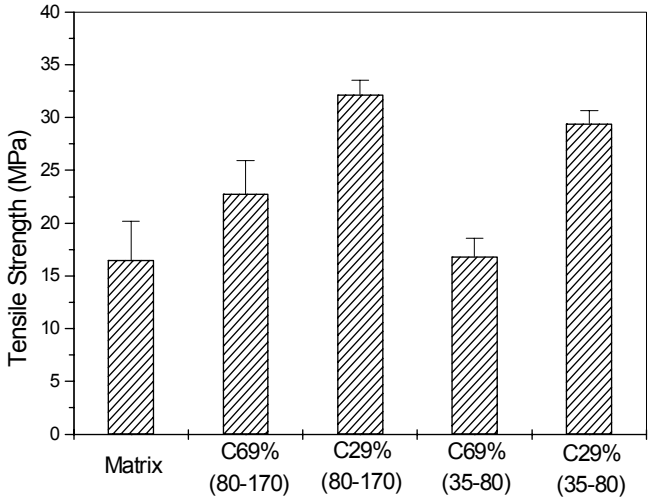


Figure 6: Resistance to traction for the matrix and the composites with different percentages of fibre and grain sizes.

CONCLUSIONS

From the results presented in this study it can be seen that the use of cane pulp fibres as a strengthener in phenolic resin represents a very viable alternative, since it provides an option for reducing costs in industrial applications, such as in the substitution of synthetic fibres, by vegetable fibres, and also for promoting environmental preservation.

The results obtained by SEM analysis demonstrated the weak adhesion between the fibre and the matrix, thereby affecting the assays for water absorption and resistance to traction. The density assays of the composites under study revealed a decrease of 8,5 % in the densities of the test bodies with 69% fibre fractions, while the variation in density with the granulometry of the fibres was not significant. The water absorption assays showed that with the increase in the fraction of cane pulp fibres in the composite (from 29 to 69%) the increase in water absorption was four times greater. Also, in this case the influence of granulometry was not significant.

The results obtained with the traction resistance assays demonstrate that traction increases with the proportion of fibres, reaching a maximum value at 29% fibres, whilst at a proportion of 69% fibres there was a decrease in these values where the resistance of traction was 40 % less than the maximum performed, due to the excessive interaction between the fibres, decreasing the values for resistance to traction of the composite. The influence of the grain sizes and fibre fractions on tensile strength was studied in this work. In the case of 69% fibre fractions, the value of the tensile strength for grain sizes of 80 to 170 mesh was 36% higher than for grain sizes of 35 to 80 mesh. This behaviour was similar to 29% fibre fractions with the variation of 8%. This effect can be possibly explained by the fibre length that was below the critical length.

Further experiments in this area will involve the pre-treatment of the sugar cane pulp fibres with NaOH to improve the adhesion between fibre and matrix.

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