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Carbohydrate Polymers 55 (2004) 237–243

Carbohydrate Polymers
www.elsevier.com/locate/carbpol

Cassava bagasse-Kraft paper composites: analysis of influence of impregnation with starch acetate on tensile strength and water absorption properties

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Received 20 November 2002; revised 28 July 2003; accepted 29 July 2003

Abstract

A fibrous residue rich in non-extracted starch (bagasse) obtained from the industrial production of cassava starch was used to obtain a composite that is similar to cardboard, through a technique used in small scale artisan production of recycled paper. A mixture of 90% cassava bagasse and 10% of Kraft paper was used for the production of these composites. Kraft paper was added as a source of long fibres, in order to improve the mechanical properties of the material. The prepared material has similar characteristics to the molded fibre packaging made using recycled paper, as used in egg boxes. However, cassava bagasse has advantages over recycled paper, in view of the fact that it is obtained from known and renewable sources. The impregnated and non-impregnated materials were submitted to tests of tensile strength and to direct contact with water by complete immersion of the samples. The cassava bagasse-Kraft paper composites obtained had a slight resistance to direct contact with water. The water mass absorbed by the materials impregnated with starch acetate was approximately half that of the materials without impregnation. However, the impregnation had little influence on the tensile strength of the tested samples. Starch acetate is therefore an attractive additive for use in the manufacture of waterproof materials, such as disposable trays.

Keywords: Composites; Cassava bagasse; Starch acetate; Water absorption; Tensile strength

1. Introduction

Cassava, *Manihot esculenta Crantz*, is one of the main sources of industrial starch, being cultivated throughout the Brazilian territory, consumed in great quantities, and being important for the preparation of many typical food dishes in Brazil and in other tropical countries (Pandey, Soccol, Nigam, Soccol, Vandenberghe, & Radjiskumar, 2000; Cereda, 1994). In the industrial process to produce cassava starch, the solid residue (bagasse) resulting from the extraction is composed of fibrous materials and starch that has not been extracted. The amount of bagasse produced in industry is significant, being approximately 900 kg of bagasse, with 85% moisture, for each ton of processed root (Leonel, Cereda, & Roau, 1999). The composition of the bagasse depends on the cassava's origin as well as on the processing procedure, but it is predominantly starch (40–60%) and fibre (15–50%) plus small quantities of proteins and lipids (Pandey et al., 2000).

In Brazil, cassava bagasse is a problem for the starch industry because it has a high percentage of water, which makes drying and transport expensive. Because of this problem, many companies deposit this waste on neighbouring land, after which it is carried away to be used in animal feed (Cereda, 1994). The improper disposal of the material represents an environmental problem and the waste of a raw product, which could be used for other purposes.

In recent years, research has been directed towards ways of transforming agro-industrial residues into by-products. Pandey et al. (2000) have used the cassava bagasse as a substrate in microbiological processes, obtaining products

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doi:10.1016/j.carbpol.2003.07.007

of greater additional value, such as aroma and flavour compounds. The use of the bagasse for the production of disposable trays and supports for plants has been presented in symposia, but scientific studies have not been published. It is also important to note that, these trays are biodegradable, reducing the impact caused by the discharge into the environment of materials derived from petroleum.

Cassava starch has also been studied as a raw material for the production of biodegradable films, which are transparent, but with low resistance to direct contact with water and poor mechanical properties (Dufresne & Vignon, 1998; Larotonda, 2002; Lörcks, 1998; Roesser, Nevling, Rawlins, & Billmers, 2000; Tomka, 2000). Starch is a natural polymer consisting of amylose (linear glucose chains) and amylopectin (ramified glucose chains) units, whose percentages can be different depending on the origin of the starch (Buléon, Colonna, Planchot, & Ball, 1998; Dufresne & Vignon, 1998).

Starch's hydrophilic nature is the main limitation for the development of biodegradable materials from it (Curvelo, Carvalho, & Agnelli, 2001). Many studies have been directed at the chemical modification of the starch as an alternative way to improve its properties and applications, such as in the acetylation of starch, modifying the molecular structure and allowing the attainment of a thermoplastic and hydrophobic material (Fringant, Desbrières, & Rinaudo, 1996; Graaf, Broekroelofs, Janssen, & Beenackers, 1995; Treadway, 1946; Feuer, 1998).

The objective of this work was to develop biodegradable composites from the cassava bagasse and Kraft paper, and to evaluate the influence of its impregnation with starch acetate on the tensile strength and on the water absorption of these materials.

2. Materials and methods

Dried cassava bagasse was supplied by AMIFAR Ind. e Com. Ltda., Deodápolis, MS, Brazil, with the following composition: 63.1% starch and 36.9% fibre.

Ten parts of water for each part of bagasse was weighed and heated, under continuous stirring, up to 70 °C and then maintained at this temperature for 40 min by means of a temperature-controlled hot plate. Under these conditions, the starch is gelatinized and adhered to the fibres producing a homogeneous mass, which was then placed in a Meteor model Rex-1. A pre-dispersion of Kraft paper was also prepared in a mixer, in the mass ratio 100:1 (water/Kraft paper) for 10 min.

The mixture of bagasse-water and Kraft paper-water suspensions were maintained under mechanical stirring for 5 min, in order to obtain a 9:1 (w/w) pulp bagasse/Kraft paper relation. Water was added to this pulp (water/pulp mixture = 3:1) to allow a more fluid suspension. Similar to the artisan procedure used to obtain recycled paper, screens of nylon with dimensions 30 × 40 cm, were immersed in pulp mixture and lifted up to the surface, allowing the draining of the water. The screens were placed in a ventilated oven at 100 °C for 2 h.

2.1. Specimen preparation and impregnation with starch acetate

Samples were obtained with dimensions close to 25 × 100 mm. The average thickness of each sample was calculated from measurements taken at four distinct points, using a digital external Mitutoyo micrometer, model Digimatic, with a precision of 0.001 mm. The samples were weighed on a GEHAKA digital balance, model BG 2000. The specific gravity of each sample was determined using its weight and volume, which was calculated from its dimensions (width, length and thickness). Samples with similar thicknesses were selected and placed in a dessicator containing a saturated solution of NaCl (relative humidity 75%), which was then put into an oven maintained at 25 °C.

The synthesis of starch acetate was partially based on the process given in US Patent no. 5.710.269 (Feuer, 1998), substituting the catalytic agent MSA (methane sulfonic acid) with concentrated sulfuric acid. The degree of substitution (DS) of synthesized starch acetate was determined through the methodology proposed by Wurzburg (1964). The highest possible DS is 3, because there are three hydroxyl groups (OH) available for substitution on each anhydroglucose unit (Lepeniotis & Feuer, 1997; Miladinov & Hanna, 2001). Narayan, Bloembergen, and Lathia (1999) showed that starch acetate with a DS between 1.2 and 1.7 presents better mechanical properties, water resistance, processability, and rate of biodegradation. The DS of the starch acetated obtained was 1.41.

Solutions of starch acetate in chloroform at ratios of 1:5 and 1:10 (w/v) were placed in a small container that in turn was placed in dessicators, where the samples of composites were immersed and kept for 5 and 10 min. For vacuum impregnation experiments, the dessicator was maintained at a vacuum of 600 mmHg. Different conditions of impregnation were used in order to study the influence of the impregnation time and concentration of starch acetate solution on the resulting tensile strength and water absorption (Table 1).

2.2. Scanning electron microscopy

The samples were analyzed by scanning electron microscopy (SEM) using a Philips, model Xl-30. Samples of cassava bagasse sheets were covered with a fine gold layer using a BAL—TEC, model SCD 005 sputter coater. All micrographs were obtained using an accelerating voltage of 20 kV.

Table 1
Different conditions of impregnation with starch acetate

Materials	Ratio starch acetate/chloroform (w/v)	Time of impregnation (min)	Conditions
A = without impregnation	–	–	–
B	1:10	5	Atmospheric pressure
C	1:10	5	Vacuum
D	1:10	10	Atmospheric pressure
E	1:5	5	Atmospheric pressure
F	1:5	10	Atmospheric pressure
G	1:5	10	Vacuum

2.3. Quantitative analysis of sample impregnation with starch acetate

To prove that starch acetate, besides forming a film on the material surface, also filled part of the internal porous space of the samples, two quantitative analyses were made: (i) measurement of mass and thickness variations and (ii) mercury porosimetry analyses.

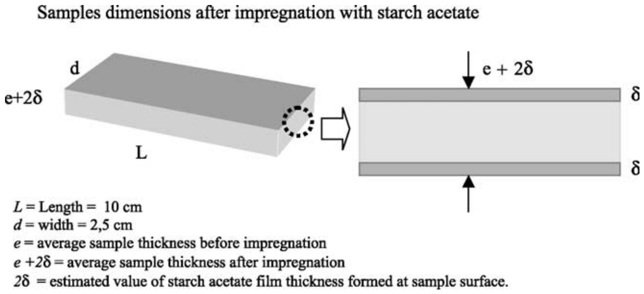
In the first, sample dimensions were determined using a micrometer (accuracy 0.001 mm) for thickness measurements and a rule (accuracy 0.5 mm) for width and length determination. Measurements were made before and after samples impregnations, these data being compared to determine coated film thicknesses, which were then used, together with starch acetate density value, to determine film volumes and weights. Fig. 1 shows the notation used for the determination of sample dimensions. Eqs. (1) and (2) were used to determine film volumes and film masses, respectively.

$$V_{\text{film}} = Ld2\delta \tag{1}$$

$$m_{\text{film}} = \rho_{\text{film}} V_{\text{film}} \tag{2}$$

In order to determine starch acetate film density, some films were obtained by casting in glass plates. After that, they were dried and milled, and then used to prepare water suspensions with known concentrations. Starch acetate film density was obtained by picnometry determinations.

Weight variations (Δm_{film}) of the samples promoted by impregnations were determined by measurements of sample weights before and after impregnation with starch acetate solution. The comparison of weight variations of the samples (Δm_{film}) with film weights determined by their dimensions (thickness, length and width) and density can indicate whether starch acetate penetrates inside sample pore spaces.



L = Length = 10 cm
d = width = 2,5 cm
e = average sample thickness before impregnation
$e + 2\delta$ = average sample thickness after impregnation
2δ = estimated value of starch acetate film thickness formed at sample surface.

Fig. 1. Determination of sample dimensions.

In the second, mercury porosimetry of impregnated and non-impregnated samples was carried out using a Porosizer Micromeritics 9320. Pressure steps, waiting 60 s to attain equilibrium between liquid mercury and capillary pressures, were used in all tests.

2.4. Mechanical and water absorption tests

Tensile strength analysis was carried out following the standard ASTM—D828 (1997), using an EMIC DL 2000 universal device with an R 2797 (500 N) load cell and speed of operation of 5 mm/min.

The water absorption study was based on the standard ABNT NBR NM ISO 535 (1999) that is derived from the Cobb method. It consists of a gravimetrical analysis in which a sample is weighed before and after its immersion in distilled water for 1 min.

For water absorption experiments, five samples from the same group were used to establish the average values of water absorption for each group. In tensile strength experiments, 12 samples from the same group were used in order to determine average values of elongation and rupture tension.

3. Results and discussion

3.1. Scanning electron microscopy

Fig. 2 shows a SEM micrograph of the surface and cryo-fractured surfaces of non-impregnated and starch acetate impregnated samples. Fig. 2(a) displays the micrographs of fibre of Kraft paper and bagasse fragments, forming a heterogeneous porous material. The impregnation with starch acetate modified notably the surface of the material, making it more homogeneous, in spite of the presence of fractures on the sample surface, as shown in Fig. 2(b). These fractures were formed during the drying of the films, when the chloroform (that was used to dissolve the starch acetate) was evaporated. Similar fractures were reported by Larotonda (2002) in starch acetate films obtained by casting. The empty spaces left by the solvent are substituted by air that promotes the appearance of film fractures (Eichler, Ramon, Ladyzhinski, Cohen, & Mizrahi, 1997). Fig. 2(c) and (d) shows the cryo-fractured surfaces of the impregnated samples at 25 × and 100 × magnification, respectively. These micrographs show the internal porosity of the material and the predominance of the impregnation close to the sample surface.

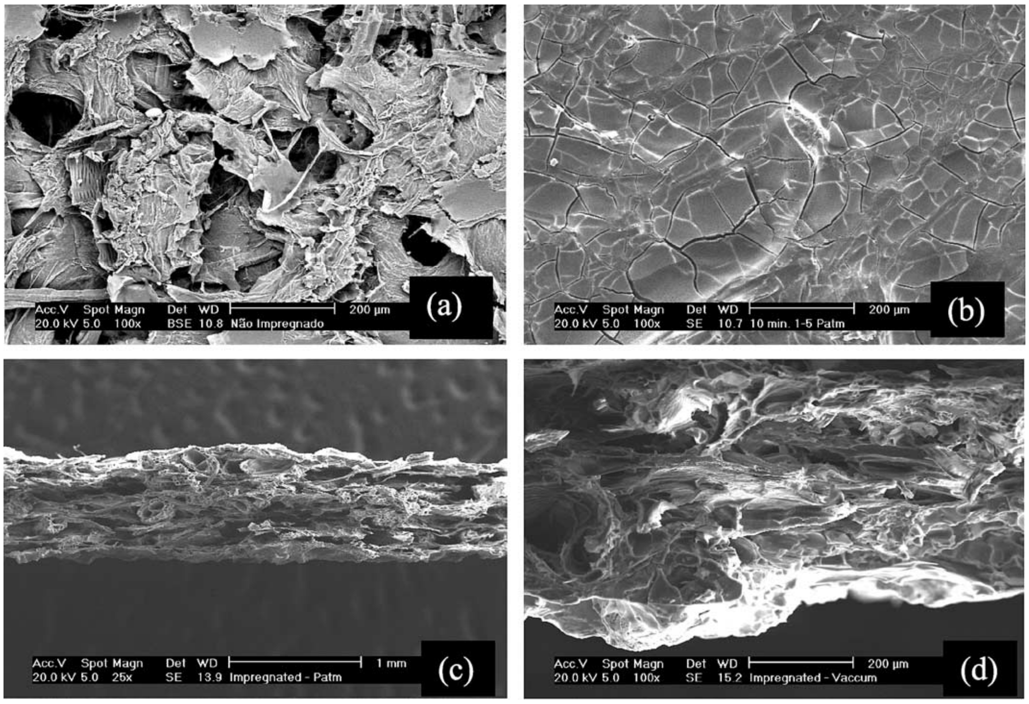


Fig. 2. SEM of the cassava bagasse sheet samples. (a) Surface of non-impregnated sample at 98 × magnification. (b) Surface of impregnated sample at 100 × magnification. (c) Cross-section of impregnated sample under atmospheric conditions at 25 × magnification and (d) cross-section of impregnated sample under vacuum conditions at 100 × magnification.

3.2. Thickness and bulk density of the samples

The influences of the impregnation with starch acetate on the increase in thickness and specific mass of the prepared materials are presented, respectively, in Table 2 and Fig. 3. Samples B and C showed an increase in the specific mass of 15 and 34%, respectively. For samples F and G the specific masses increased by 50 and 71%, respectively. The greater increase in the specific mass of samples C and G can be explained by the application of the vacuum which removes the air contained in the material, facilitating the entrance of starch acetate and allowing the filling of the pores at the surface and in the internal layers of the material. Thus, the thickness did not suffer great changes, but the quantity of starch acetate in the materials C and G were higher.

A comparison of average values of m_{film}, calculated by Eq. (2), and weight variation Δm promoted by impregnation is showed in Table 3. For samples C and G, weight variations promoted by impregnation were 42 and 65% greater than film weights determined by Eq. (2). These results indicate that at least half of the acetate starch acetate present in the samples penetrated inside the samples porous spaces. These results agree with the mercury porosimetry results, which are presented below.

Table 2
Increase in thickness of the samples after the impregnation with starch acetate under different conditions

Materials	Thickness—before impregnation (mm)	Thickness—after impregnation (mm)	Increase of thickness (mm)
A	0.836	–	–
B	0.898	0.953	0.055
C	1.042	1.096	0.054
D	0.878	0.956	0.078
E	0.900	1.014	0.114
F	0.931	1.082	0.151
G	1.081	1.146	0.065

A = non-impregnated; B = 5 min, 1:10; C = vacuum, 5 min, 1:10; D = 10 min, 1:10; E = 5 min, 1:5; F = 10 min, 1:5; G = vacuum, 10 min, 1:5.

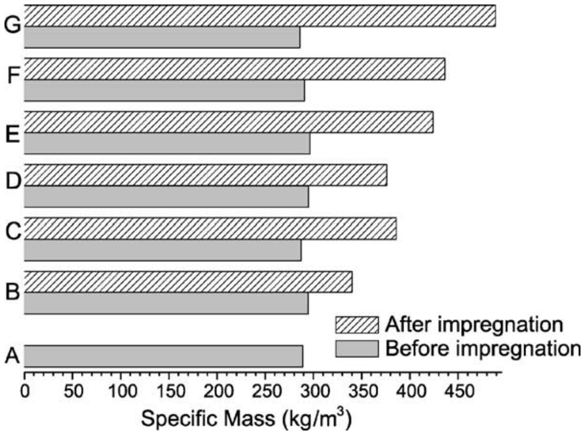


Fig. 3. Influence of impregnation with starch acetate on the specific mass of the samples (A = non-impregnated; B = 5 min, 1:10; C = vacuum, 5 min, 1:10; D = 10 min, 1:10; E = 5 min, 1:5; F = 10 min, 1:5; G = vacuum, 10 min, 1:5).

Table 3
Comparison of average values of m_{film}, calculated by Eq. (2), and weight variation Δm promoted by impregnation

Materials	Average mass$_{\mathrm{film}}$ (g), determined by Eq. (2)	Variation coefficients of mass$_{\mathrm{film}}$ (%)	Average Δm (g), determined by weight	Variation coefficients of Δm (%)	Comparison between mass$_{\mathrm{film}}$ (g) and Δm (g), (%)
B	0.1848	44.20	0.1464	23.37	26.0
C	0.1800	42.80	0.3085	10.94	42.0
D	0.2614	23.20	0.2518	3.70	3.8
E	0.3844	15.31	0.4080	5.31	5.9
F	0.5080	11.04	0.5042	8.30	0.8
G	0.2210	15.40	0.6290	17.00	65.0

B = 5 min, 1:10; C = vacuum, 5 min, 1:10; D = 10 min, 1:10; E = 5 min, 1:5; F = 10 min, 1:5; G = vacuum, 10 min, 1:5.

3.3. Mercury porosimetry

Mercury porosimetry analysis was carried out with non-impregnated and impregnated samples, using 0.249 and 0.331 g, respectively. Non-impregnated material presented porosity close to 0.76, while impregnated one presented porosity close to 0.60. This result indicates that the impregnation procedure promoted the intrusion of starch acetate solution into sample porous spaces. Average pore diameters determined by porosimetry analysis were 0.37 and 0.18 μm, respectively, indicating that large pores were impregnated preferentially. Total pore area was the same in the two cases, close to 22.5 m^2/g. This result occurred due the smaller pores, which represent the main contribution to total pore area, not being impregnated.

Sample bulk densities of the samples before and after impregnation, determined by mercury porosimetry, were 362 and 585 $\mathrm{kg/m}^3$, respectively, which is also an effect of starch acetate impregnation.

3.4. Mechanical tests

Table 4 shows the average values obtained from experimental results of maximum tensile strength, maximum elongation at breaking point, and variation coefficients for the different prepared materials.

Fig. 4 presents the average curves obtained in the analysis of tensile strength against elongation for all prepared samples. The dispersions of tensile strength in the rupture were between 9 and 17.5% and the variation coefficients for the elongations at the point of rupture were between 6.2 and 12.6%. Therefore, there were no significant differences in the values for mechanical properties for impregnated and non-impregnated samples. The fracture lattice present in the starch acetate films formed on the sample surfaces prevented an increase in tensile strength.

3.5. Water absorption tests

The impregnation of the samples with starch acetate provoked reductions in the water absorption, as presented in Fig. 5. Non-impregnated samples absorbed four times more water compared with samples F and G, which had minor water absorption rates. As these materials were immersed for 10 min in starch acetate dissolved in chloroform, at a ratio of 1:5 (w/v), it can be concluded that there occurred a reduction in the water absorption with the increase in immersion time and starch acetate solution concentration. The comparison of materials B and C with F and G showed that the impregnation under atmospheric pressure presented results similar to those obtained under vacuum.

Table 4
Values of maximum tensile strength, maximum elongation at break and variation coefficients for the materials prepared from bagasse with 10% Kraft paper and impregnated with starch acetate

Materials	Average maximum tensile strength (MPa)	Variation coefficients of tensile strength (%)	Average maximum elongation at break (%)	Variation coefficients of elongation at break (%)
A	4.07	12.3	3.88	9.4
B	4.34	11.3	3.94	12.6
C	4.00	17.5	3.61	7.6
D	3.29	14.7	4.25	8.5
E	3.25	9.0	4.36	6.6
F	3.61	11.5	4.24	10.3
G	3.99	14.5	3.35	6.2

A = non-impregnated; B = 5 min, 1:10; C = vacuum, 5 min, 1:10; D = 10 min, 1:10; E = 5 min, 1:5; F = 10 min, 1:5; G = vacuum, 10 min, 1:5.

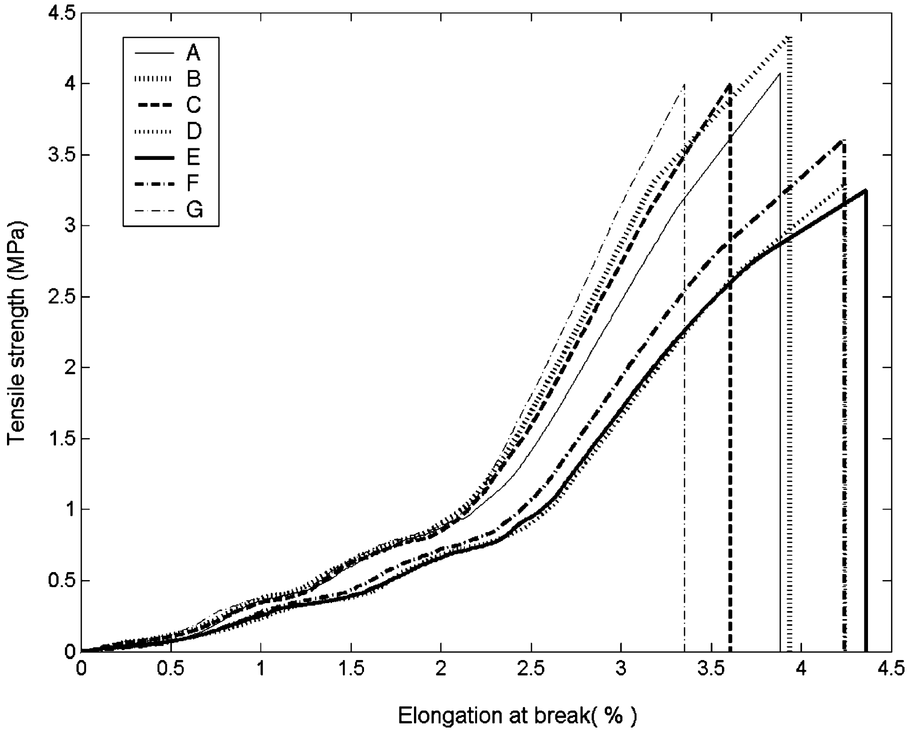


Fig. 4. Influence of impregnation with starch acetate on tensile strength and maximum elongation at rupture (A = non-impregnated; B = 5 min, 1:10; C = vacuum, 5 min, 1:10; D = 10 min, 1:10; E = 5 min, 1:5; F = 10 min, 1:5; G = vacuum, 10 min, 1:5).

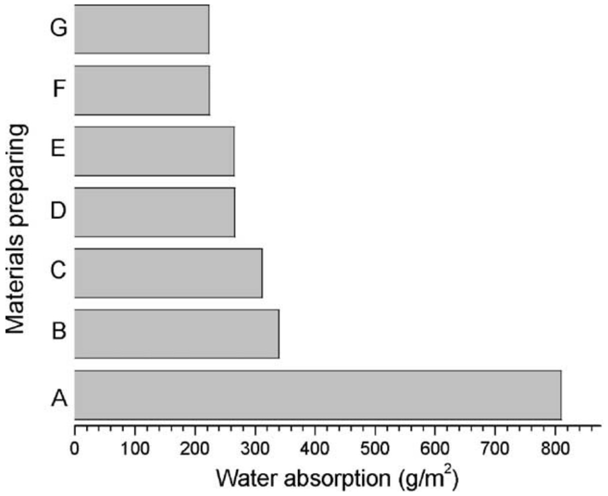


Fig. 5. Water absorption of the different samples (A = non-impregnated; B = 5 min, 1:10; C = vacuum, 5 min, 1:10; D = 10 min, 1:10; E = 5 min, 1:5; F = 10 min, 1:5; G = vacuum, 10 min, 1:5).

4. Conclusions

Cassava bagasse with 10% Kraft paper added to it can be used for the manufacture of cardboard. The results indicate that impregnation of hygroscopic materials with starch acetate had a great influence on the reduction of water absorption, which decreased to a quarter of the initial absorption in the best of cases. The materials impregnated under atmospheric pressure produced results for water absorption similar to those obtained under vacuum, showing that the impregnation depends on other variables such as the time of immersion and the concentration of starch acetate in the solution.

The evident chain of fractures in the starch acetate film on the sample surfaces was a problem for the improvement of the tensile strength of the impregnated materials. Therefore, the starch acetate impregnation employing cassava bagasse with 10% Kraft paper is an interesting alternative for reducing water absorption. Moreover, the use of starch acetate in the impregnation of hygroscopic materials offers an attractive replacement for the use of the starch, adding value to this raw material and providing an incentive to agricultural producers.

Complementary studies must be conducted to modify the leaf fibres and stems of the cassava plant so that these can be used as long-fibre sources in the mixture with cassava bagasse. This alternative can make the production process of bagasse trays economically practicable, since the required materials are freely available close to the industrial sites.

Acknowledgements

The authors wish to thank CAPES and CNPq for the financial support provided.

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