CHEMICAL MODIFICATIONS ON CURAUA FIBERS (Ananas erectifolius)


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Abstract

In this work, the effect of surface treatments, viz. mercerization and a multi enzyme complex, was investigated on curaua fibers by scanning electron microscopy (SEM) and thermogravimetric analysis (TGA). Scanning electron microscopy shows that all treatments, but the 2 %wt mercerization one, promote strong surface modifications on the fibers, removing the outer parenchyma-rich surface layer and exposing the inner fibrillar structure. The thermograms show an improvement in the thermal stability of the modified fibers in relation to the raw fibers. The main peak of DTG curve for the raw fibers occurred at 365°C, and all treatments increased this temperature. The treatments with 5%wt NaOH and enzymes apparently changed on a similar way the fiber surface. This is an outstanding result because the treatment with enzymes is cleaner than the treatment with NaOH. Therefore, if it could be used instead of the treatment with NaOH, a more environmental friendly treatment will be available to treat curaua surface fibers.

Keywords: enzyme treatment, alkali treatment, lignocellulosic fibers, curaua, composites

1. Introduction

Nowadays, a large number of lignocellulosic fibers are being used to reinforce resin matrix composites in many different industrial fields. In the automotive industry, for instance, the interior door panels and cushion seats are already being manufactured with these fibers. Lignocellulosic fibers such as curaua, sisal, flax, hemp and jute offer benefits as reduction in weight, cost, and CO2 emissions, as well as recycling. However, lignocellulosic fibers have some drawbacks. One of them is the usual lack of adhesion at the fiber-matrix interface. This weak interface arises due to the hydrophobic character of the common polymeric matrices and the hydrophilic character of lignocellulosic fibers. To increase the lignocellulosic fiber polymer interface several chemical and physical treatments like,
for example, mercerization (alkali treatment) and acetylation are proposed on the
literature [d’Almeida et al., 2006 and Boynar et al., 2003].

In this work, the effect of surface treatments, viz. mercerization and a multi
enzyme complex, were investigated on curaua fibers by infrared scanning electron
microscopy (SEM) and thermogravimetric analysis (TGA).

The treatments with 2, 5, 10 and 15%wt of NaOH solution and with a selected
enzyme (enzyme complex mixture, consisting of carbohydrates – arabinase, cellulase,
beta-glucanase, hemicellulase and xylanase), prepared from a selected strain of
Aspergillus aculeatus, were performed according to the procedures described in
another work for sponge gourd fibers [d'Almeida et al., 2007].

The mercerization treatment is described as following. The raw fibers were
immersed during one hour at room temperature in solutions with, respectively, 2 and
5%wt of NaOH solution. After that, the fibers were washed with flowing tap water
and left at rest for 24 hours to remove any residue of NaOH. The water bath was then
changed and the fibers were left for more 24 hours in immersion. The pH of this
second water bath was observed to be always near 7, indicating that the washing
treatment was effective.

A multi-enzyme complex produced from a selected strain of Aspergillus
aculeatus was also used to treat the surface of the fibers. This particular enzyme is
tailored to extract materials from plant cell walls, including hemicellulose and xylans.
Since the time of treatment varies from plant material to plant material when enzymes
are used, the ideal time of treatment was determined at first. For that, the absorbance
vs. treatment time curve was obtained using the Somogyi method. This method doses
the amount of reducing sugars. In short it consists of soaking a certain amount of the
fibers (9 grams) in 300 ml of distilled water with 4.5 pH during 24 hours. This
particular pH value was obtained using citric acid as described elsewhere. After that
the container with the fibers was placed in a water bath with a temperature ranging
from 40 to 50 °C, and 2 ml of the enzyme was then added. The container was
continuously shacked and dosing aliquots were extracted at 0 min, every 30 min
during the first 5 hours, and at 6, 7, 8, 24 and 48 hours of treatment. To neutralize
the enzyme the solution was soaked in a water bath at 100°C during 2 min. Following the
results obtained the raw fibers were treated for 4 hours, neutralized at 100 °C, washed
in flowing tap water and air dried.

Both treatments can remove hemicellulose and other polysaccharides adhered
to the fiber surface exposing, therefore, the inner cellulose fibrils and contributing to
increase the mechanical interlock at the fiber/matrix interface [Blezki and Gassan,
1999, Ray et al., 2001]. The enzyme treatment is particularly interesting because it
can be used to selectively remove, on a controlled way, polysaccharides that do not
contribute to the fiber mechanical properties. In fact, the enzyme treatment is
expected to substitute with advantages the more environmentally dirt mercerization
process. NaOH solutions are highly corrosive and have to be suitably treated before
disregarding them to the environment. And also, special care has to be taken while
handling these solutions during the treatment steps. The enzyme based treatment has
far smaller environmental impact.

The curaua fibers treated with 10 and 15%wt NaOH were too dry and stiff.
Thus, we present herein only the results for treatment with 2 and 10%wt NaOH.
Figure 1 presents the aspect of curaua fibers before and after the treatments. Figures 1(a) and 1(b) have the same overall surface features, and parenchymatic cells can be observed. The 2%wt NaOH treatment apparently only cleaned the fibers, removing any gummy tissues still attached to them. For the 5%wt NaOH (Figure 1(c)) and enzyme (Figure 1(d)) treatments, the surface was much more attacked, and the fiber external layer was removed, exposing the inner fibrillar structure. The removed material was probably mainly composed of hemicellulose and other polysaccharides [d’Almeida, 2007].

![Figure 1](image)

Figure 1-(a) Raw curaua fiber; (b) 2%wt NaOH; (c) 5%wt NaOH; (d) enzyme.

The thermogravimetric analysis of lignocellulosic fibers is a very useful tool that can be used to determine the temperature at which the material begins to degrade as well as to verify the fiber thermal stability. With this analysis, one can observe if a given treatment is reducing the hydrophilic behavior of the fibers or if it is changing their thermal characteristics. In this work, thermal analysis was used to study the effect of both NaOH and enzyme treatments on the thermal behavior of sponge gourd, with respect to the behavior of the raw fiber.

Figure 2 presents the TG and DTG curves obtained for the raw, NaOH treated and enzyme treated fibers. Apparently, all treatments contributed to increase the curaua fiber thermal stability, as can be seen on Figure 2; all treatments dislocated the loss weight and DTG curves to higher temperatures. This fact was stronger for enzyme treated fibers. In fact, the temperature at which the rate of degradation is greater increases with the all treatments with respect to that of the raw fiber.

![Figure 2](image)

Figure 2- (a) Tg and (b) DTG curves for raw, NaOH and enzyme treated fibers.

From the above results, it can be concluded that both treatments removed polysaccharides, what contributes to expose the inner microfibrillar cellulose fiber
structure. Considering that NaOH is a pollutant, toxic and corrosive product and that enzymes are environmental friendly, it is interesting to perform more analysis to enable the future use of enzymes in order to modify the surface of lignocellulosic fibers.

References