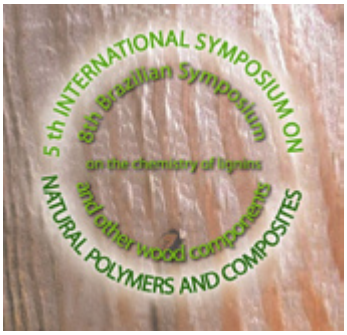

Thermal Behavior of Raw And Chemically Treated Sisal Fibers

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Abstract: *In this work mercerization, acetylation, and resorcinol/hexamethylenetetramine (R/H) solution treatments have been applied to sisal fibers to enhance adhesion with polymer matrices in composite materials. The thermal behavior of raw and chemically treated sisal fibers has been studied using the thermal gravimetric analysis (TGA) and the differential thermal gravimetry (DTG). The value of the initial decomposition temperature of sisal has been found to increase as a result of mercerization/acetylation treatment. Moreover, the rate of thermal degradation of fibers treated with R/H solution has been found to be lower than those of the raw fibers.*

Keywords: *sisal fiber, TGA, chemical treatment.*

Introduction

The sisal fiber from *Agave sisalana* is the most important leaf fiber in terms of quality and commercial use [1, 2]. The plant, which is native to Central America, has been used since pre-Columbian times. Nowadays, Brazil is the major producer with more than a million of people depending on this crop in the Northeast region of the country [3]. In recent years there has been an increasing interest in finding new applications for sisal-fiber reinforced composites on account of its low cost and density, high specific strength and modulus, no health risk, easy availability in some countries and renewability [2, 4]. Although sisal fiber is one of the most widely used natural fibers, a large quantity of this economic and renewable resource is still under-used [1,2]. The use of sisal fiber as a reinforcement in composites has raised great interest and expectations amongst materials scientists and engineers. The quality of the fiber-matrix interface is significant for the application of sisal fibers as reinforcement fibers for polymers and rubbers. Physical and chemical methods have been used to optimize this interface [5]. Moreover, it is very important to have knowledge about the influence of the processing temperatures in relation to the processing duration because there is always thermal stress during the manufacturing of natural fiber reinforced composite materials. Essential statements regarding the thermal stability of the natural fibers to be processed are obtained from the thermogravimetric analysis (TGA) [6].

In this work the thermal behavior of raw and chemically treated (mercerization, acetylation, and resorcinol/hexamethylenetetramine (R/H) solution treatments) sisal fibers has been studied using the thermal gravimetric analysis (TGA), and the differential thermal gravimetry (DTG).

Experimental Part

The samples of sisal fibers used in this work are from the variety *Agave sisalana*. The density of the fibers has been measured in a Micrometrics 1305 helium picnometer, as 1.26 ± 0.03 g/cm^3, and the diameter has been measured on 100 fibers using a Mitutoyo micrometer, as 114 ± 40 μm. The chemical composition of this variety of sisal has been determined, cellulose: 75.2 ± 0.3 %, hemicellulose: 13.87 ± 0.09 %, lignin: 7.98 ± 0.05 %, ash: 0.87 ± 0.01 % [7].

Prior to chemical modification, samples of sisal fibers have been washed in distilled water at 80 ± 2 °C for 1 hour. The washed fibers have been mercerized with 5% or 10% sodium hydroxide, at room temperature, 50 °C or 80 °C, for 1, 3 and 5 hours. For the acetylation treatment, raw and mercerized fibers have been immersed in glacial acetic acid for 1 hour at room temperature. They have then been separated and immersed in acetic anhydride containing drops of sulfuric acid for 5 minutes [2], filtered, rinsed up to pH 6 to 7 and then dried. For the resorcinol /hexamethylenetetramine (R/H) solution treatment, samples of raw, mercerized and mercerized/acetylated fibers have been immersed in the R/H aqueous solution (80/40, 40/20, and 20/8 g/L) for 1 hour and dried at 80 °C.

Thermogravimetric analysis (TGA) and differential thermogravimetry (DTG) have been obtained in TA Instruments 5100 - TGA 2050, in the temperature range from 25 to 800 °C, at a heating rate of 3 degree/min in an argon or nitrogen atmosphere.

Results and Discussion

Figures 1 and 2 show TGA and DTG profiles of raw, mercerized, raw/acetylated, and mercerized/acetylated sisal

fibers. The TGA results show that the initial weight loss depends on the sample. The mercerized/acetylated fibers show the smallest weight loss and the highest thermal stability. This may be due to an increase in the hydrophobicity of the fibers after the mercerization/acetylation treatment and, according to Albano *et al.* [8], to the substitution of OH groups for more voluminous ones, which brings about restrictions in the segmental mobility, thereby increasing the stiffness of the cellulose backbone. Its is also partially due to the fact that some components of the fiber, which degrade at a lower temperature, may be extracted during alkali treatment.

The DTG curves show an initial peak between 50 and 100 °C, which corresponds to water loss in all samples. After this peak, the DTG curve of the raw fibers shows three decomposition steps: a) the first decomposition peak at about 280 °C is attributed to thermal depolymerization of hemicellulose and the glycosidic linkages of cellulose; b) the second decomposition peak at about 340 °C is attributed to α-cellulose decomposition (weight loss approximately 70%); c) the small peak at 570 °C (weight loss around 20%) may be attributed to oxidative degradation of the charred residue. The thermograms show an improvement in the thermal stability of the modified fibers in relation to the raw fiber. The main decomposition temperature increases from 340 °C (raw) to 350 °C for the mercerized fibers, to 395 °C for the mercerized/acetylated fibers. There is a change in the degradation mechanism: in the mercerized/acetylated fibers there is only one stage, in the mercerized fibers and in the raw/acetylated fiber there are two, whereas for the raw fibers there are three. In the acetylated sisal fiber the peak due to oxidative degradation of the charred residue is missing, which indicates that the acetylated material is lost as volatile products and does not contribute to char formation. This behavior have been observed in all treatment conditions.

Results of TGA and DTG of raw, mercerized and mercerized/acetylated sisal fibers treated with resorcinol/hexamethylenetetramine (R/H) solution (40/20) are shown in Figures 3 and 4. The TGA results, Figure 3, show an initial weight loss, from 50 to 100 ºC, attributed to the vaporization of water present in the samples. Up to approximately 320 ºC, the rate of thermal degradation of treated fibers has been faster than those of raw fibers. However, from this temperature, the thermal behavior changes and the degradation rate becomes lower than those of raw fibers. At roughly 400 ºC, mercerized and mercerized/acetylated fibers have shown an pronounced loss weight. As expected, DTG curves, Figure 4, show the typical peaks of thermal degradation of the lignocellulose materials of raw and treated sisal. The curves have also shown peak at around 170 ºC, attributed to the resorcinol/hexamethylenetetramine cure reaction. These results have been observed in all treatment conditions. Thermal behavior of raw and treated fibers have shown that the biggest thermal stability of the fibers has been obtained with mercerization/acetylation treatment (from 200 °C to 300 °C).

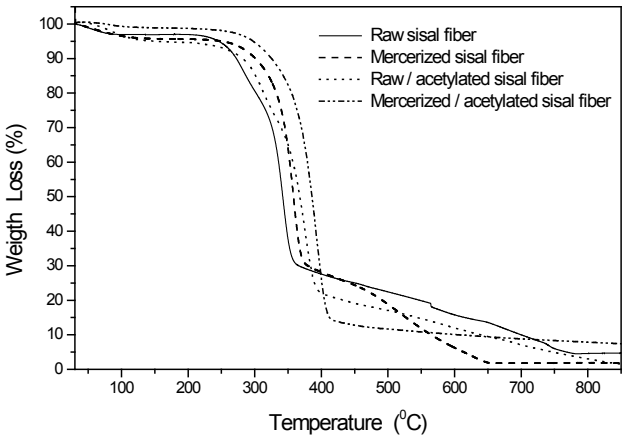

Figure 1: Thermogravimetric curves of raw and treated sisal fibers. Argon atmosphere. 3 degree/min.

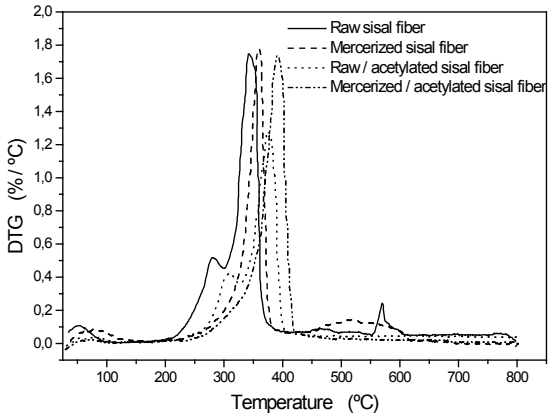

Figure 2: Differential thermogravimetric curves of raw and treated sisal fibers. Argon atmosphere. 3 degree/min.

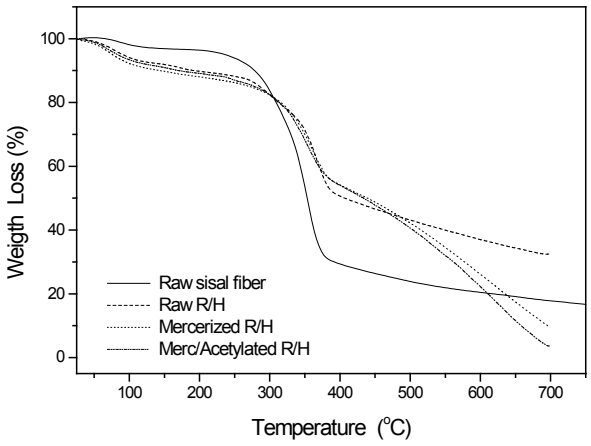

Figure 3: Thermogravimetric curves of raw, mercerized and mercerized/acetylated sisal fibers treated with resorcinol/hexamethylenetetramine (R/H) solution. Nitrogen atmosphere. 3 degree/min

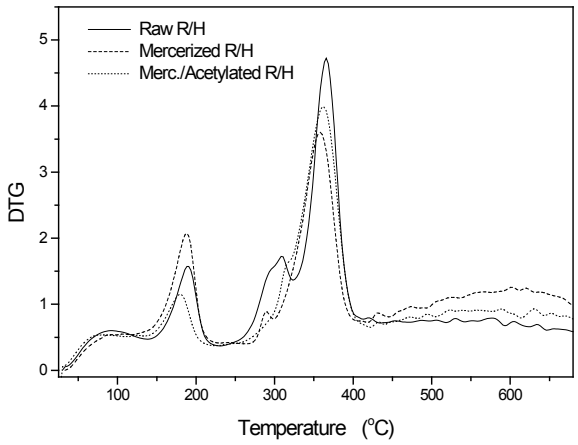

Figure 4: Differential thermogravimetric curves of raw, mercerized and mercerized/acetylated sisal fibers treated with (R/H) solution. Nitrogen atmosphere. 3 degree/min.

Acknowledgements

CNPq and Fapesp.

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