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CHARACTERIZATION OF MALVA FIBERS THERMAL BEHAVIOR BY TGA/DTG AND DSC[1]

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Abstract

A natural malva fiber extracted from the plant has shown values of density and mechanical strength with potential for uses in engineering applications such as automobile interior parts and floating components. Moreover, natural fibers can also be used as insulating materials in packaging and building panels. In this case some thermal properties are required. Therefore, the objective of this work was to evaluate the thermal behavior of the malva fiber by means of TGA, DTG and DSC analysis. The TGA curves revealed weight loss related to release of humidity and molecular structure decomposition. Peaks in the DTG curves indicated two intervals in temperature associated with different decomposition processes. The only endothermic DSC peak found was attributed to the lignocellulosic water of hydration being lost around 121ºC.

Keywords: Malva fiber; Thermal decomposition; Water evolution.

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1 INTRODUCTION

In recent times, environmental aspects related not only to pollution caused by non-degradable synthetic leftovers, specially polymeric wastes, but also to climate changes as a consequence of industrial activities, are motivating the use of natural materials. A particular case is fibrous composites, like the fiber grass composites. These synthetic materials, made from non-renewable polymers, are practically non-degradable and contribute to global warming by the CO_2 emission associated with the energy required for the fabrication process. In spite of these environmental shortcomings, fiber materials are essential for the production of many items such as insulating chests, automobile cushion, construction panels, etc. An environmentally correct alternative to replace synthetic fibers composites is the naturally existing ones extracted from plants such as ramie and sisal. These have some environmental advantages of being renewable and degradable, these malva plant provide a negative contribution to CO_2 emission by absorbing greenhouse gas during the plant lifecycle. Malva fibers have been used since long time in simple items such as ropes and rugs. Today they are used in engineering applications related insulation in building panels(1,2) and finish parts in automobile interior components.(3)

In Brazil, the malva fiber obtained from the plant is being used as a great substitute for synthetic polymer composites. Recent work on the characterization of the malva fiber has shown its potential as a new engineering material with a density range that goes from 0,5g/cm^3 to 4,5g/cm^3. This malva fiber could be used in reinforcement systems.(4) Moreover, by its mechanical properties of strength and rupture, the malva fiber could be applied as reinforcement and insulation material. However, the thermal behavior of the malva fiber has not yet been evaluated. Therefore, the objective of this work was to conduct thermal gravimetric analysis, TGA and its derivate, DTG as well as differential scanning calorimetry, DSC, measurements up to a temperature associated with the degradation of this natural fiber.

2 EXPERIMENTAL PROCEDURE

The malva fibers investigated in this work were commercially supplied by Companhia Castanhal from Pará State, of the North Region of Brazil. Figure 1 illustrates the typical malva plant and fibers extracted from its stem.

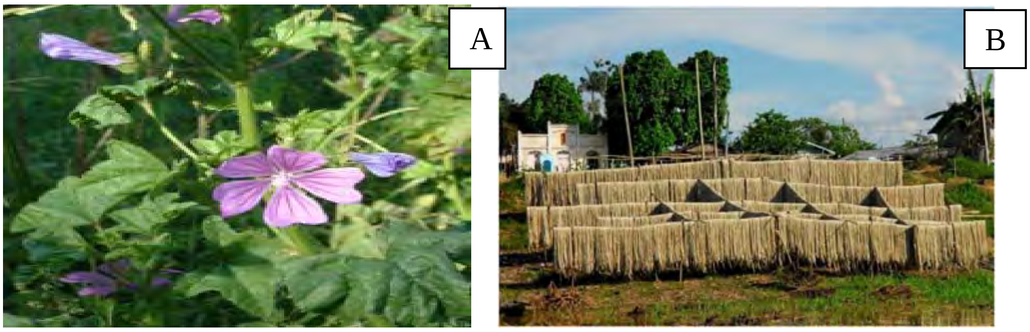

Figure 1. Malva plant (A), sun-dried of fibers after the defibrillation(B).

Samples of the malva fiber were prepared, for the thermal behavior characterization by TGA/DTG and DSC. The TGA/DTG analysis was carried out in a model 2910 TA Instrument (Figure 2a), equipment operating at a heating rate of 10ºC/min in the interval of temperatures from 23 to 800ºC. This operation was conducted under nitrogen and oxygen atmospheres. Thin discs with 2 mg in weight, corresponding to approximately 1 mm in thickness, were used as sample for the TGA/DTG analysis. The DSC analysis was carried out in a model 2010 TA Instrument (Fig. 2b), equipment operating from 25 to 250ºC. For this particular analysis a 15 mg sample of malva fiber was placed inside a tight-closed aluminum container.

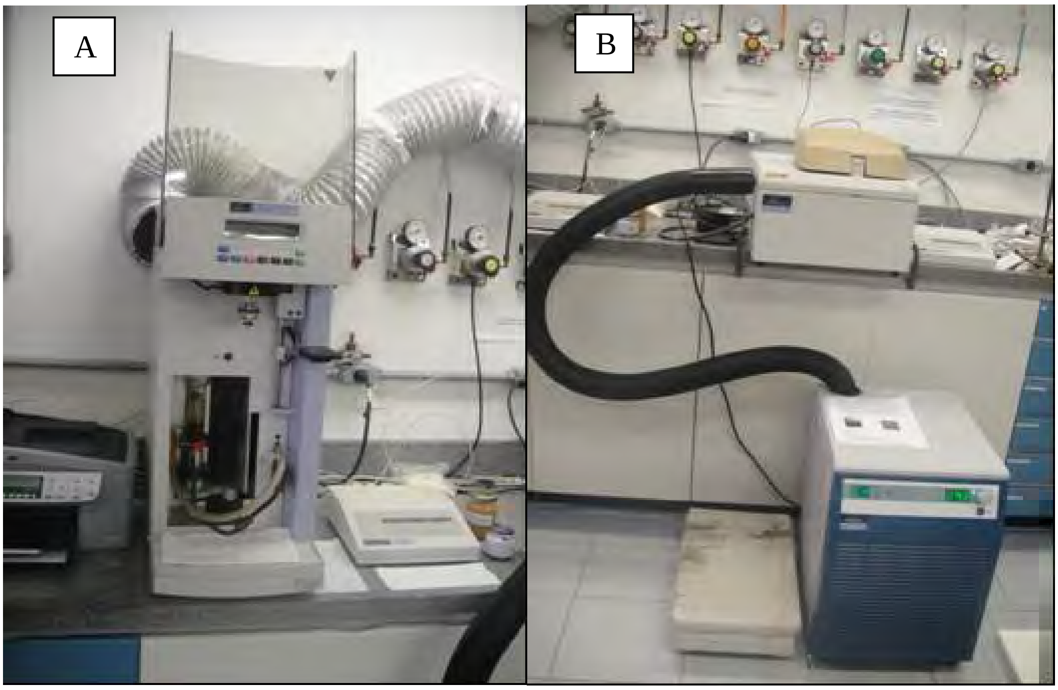

Figure 2 – Thermal analysis equipments: (A) TGA/DTG, and (B) DSC.

3 RESULTS AND DISCUSSION

The thermal stability of the malva fiber measured by the loss in weight through TGA performed with increasing temperature under oxygen (O_2) is shown in Fig. 3. In this figure it should be noticed that after a small initial drop in weight from 25 to 75ºC, the curve remain constant up to approximately 220ºC, characterizing a first constant stage. This initial drop in weight for natural materials is normally attributed to the release of water related to the humidity absorbed on the surface of a hydrophilic lignocellulosic structure.(5) After the first constant stage, a sharp decrease in weight then occurs until approximately 400ºC. This sharp decrease can be associated with the decomposition of the malva fiber lignocellulosic structure by rupture of its macromolecular chains.(6) With increasing temperature, a second constant stage in both TGA curves (Figure 3), exists up to the limit of 800ºC established for the analysis.

Even though 200ºC was indicated as the approximate end of the first constant stage in TGA curves, the onset of the malva fiber structure decomposition was determined by means of a formal procedure. The intercept of the horizontal extension of the first constant stage with the straight line, at the inflexion point, corresponding to the sharp decrease gives the onset of the structure decomposition. As shown in Fig. 3, this onset occurs at the relatively close temperatures of 300ºC for TGA.

The end of the malva fiber structure decomposition process can also be determined using a similar procedureThis was done by considering the intercept of the same straight line tangent at the inflexion point of the sharp decrease with the second stage horizontal line. In this case, the decomposition ends at 379°C for TGA. Here a relevant aspect to be noted is the different levels for the second constant stage,(7,8) (Figure 3), depending on the atmosphere of the thermogravimetric analysis.

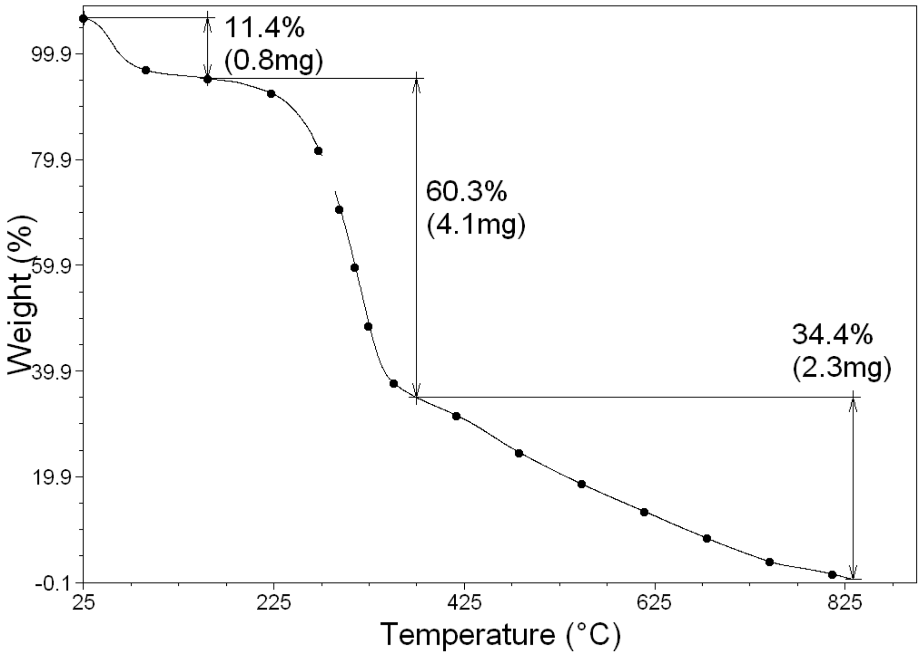

Figure 3. TGA curves to the malva fiber.

TGA curve at Fig. 3 shows the important levels of weight loss associated with events occurring to the malva fiber thermal degradation. The small first drop in weight due to the loss of absorbed humidity is relatively close, 11,4%. This result together with the close decomposition onset temperatures (Figure 3), indicates that the initial release of humidity is not affected by the existent atmosphere. By contrast, the sensible differences in weight loss during the structure decomposition, 60,3%, together with corresponding significant differences between the decomposition temperatures (Figure 3), indicate an effect of the atmosphere. This will be better understood in conjunction with the DTG curves.

The residual weight found at 825°C in the second stage, of 2,3%, corresponding to the thermal degradation in the malva fiber, can be interpreted as follows. However, the O_2 reaction during the malva fiber decomposition apparently left a thermal stable residue, probably oxides that did not decompose up to 800°C.

Figure 4 shows the DTG curves for the malva fiber under oxygen (O_2) atmosphere. The first peaks at the same temperatures of 54,1°C and same amplitude confirm that the release of humidity is not affected by the distinct atmospheres.

The peaks corresponding to the maximum rate of malva fiber decomposition, 316,3°C in O_2, indicate that oxygen induces a reaction with the malva fiber, causing a more effective degradation to occur at earlier temperatures. In fact the carbon and nitrogen that constitute the lignocellulosic structure of the malva fiber are expected to react with the oxygen releasing CO, CO_2 and H_2O. Additionally, other free elements in the structure, like Ca, K, Na, Fe, etc, may also react with the O_2 to form oxides associated with inert ashes.

A relevant aspect of the larger peaks in Fig. 4 is their broadening observed in the left side as shoulders around 280°C. This can be attributed to lower temperature peaks, apparently at 290°C that are concealed by the larger peaks.(9,10) Lower temperature peaks indicate a complex thermal degradation process related to the rupture of

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molecular chains with different energy levels.

Another feature in Figure 4 is the existence of small peaks at 459,9°C for O_2 atmosphere. This is apparently an indication of another effective loss of weight taking place at temperatures higher than that associated with the first peaks. In fact, the existence of two peaks in the DTG curve of a natural fiber and its polymer composite was reported(5,6) at similar intervals of temperature. The lower temperature peak was attributed to the decomposition of more rigid molecular segments while the higher temperature peak would be related to the decomposition of more flexible segments.(11)

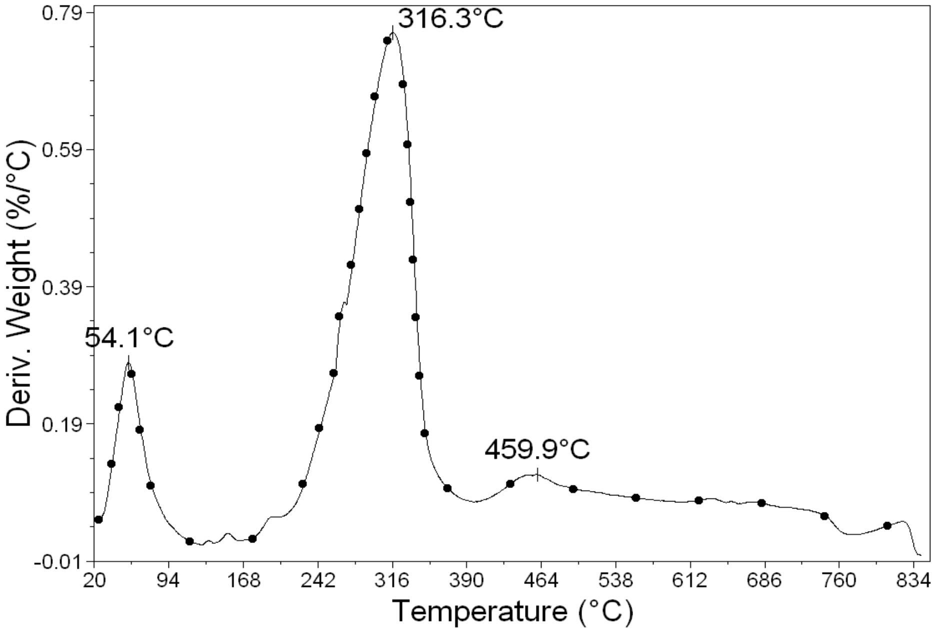

Figure 4. DTG curves for the malva fiber.

Figure 5 shows the DSC curve for the malva fiber. In this figure an endothermic event occurs in the interval of temperature from approximately 25°C to 225°C with a peak at 127,9ºC. It is suggested that the heat absorbed in this endothermic event, 135 J/g, could be related to the release of water associated with the hydration of the lignocellulosic structure of the malva fiber, before macromolecular chain degradation occurred.

Finally, the thermal analysis performed in the malva fiber indicated that this natural material loses a relatively small amount of absorbed water up to 55,6°C. Its macromolecular chain structure begins the thermal degradation process around 225°C and, under an oxidizing atmosphere, leaves a solid residue of less than 10% of its total weight. These characteristics establish the limits for engineering applications of the malva fiber, especially as an insulating material.

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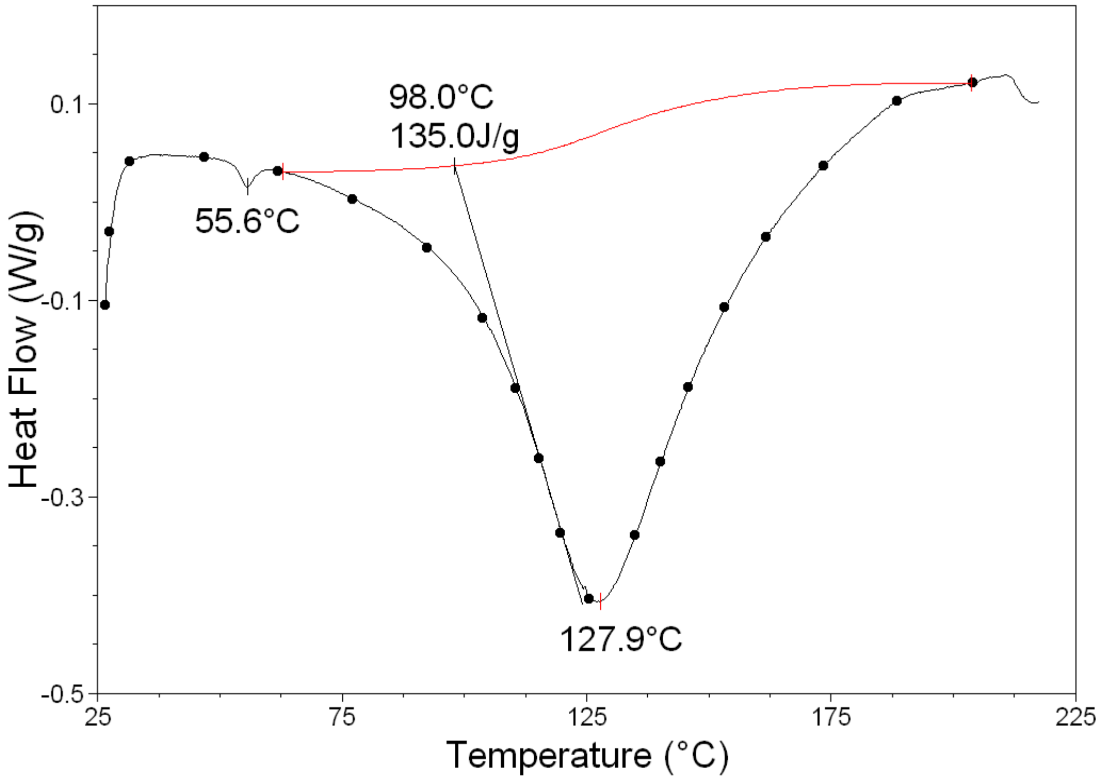

Figure 5. The DSC curve for the malva fiber heated under O_2 atmosphere.

4. CONCLUSIONS

- The thermal behavior of a malva fiber analyzed by TGA, DTG and DSC revealed evidences of water loss and structural decomposition. Up to 75ºC approximately 11,4% of humidity is released while the lignocellulosic water of hydration is lost around 121°C.
- Two events of structural decomposition displayed maximum weight loss associated with clear peaks at 316ºC and 459ºC, as well as apparently concealed peaks at 280°C, on oxygen atmosphere.
- Under oxygen, a constant amount around 9% of stable solid residue is formed as inert ashes from 400°C up to 825°C. This residue is composed of oxides from trace metals such as Ca, K, Na and Fe as contents of the malva fiber lignocellulosic structure.

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