THERMAL BEHAVIOR OF BURITI BIOFOAM

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Abstract

A natural biofoam extracted from the petiole of the buriti palm tree has shown values of density and mechanical strength with potential for uses in engineering applications such as automobile interior parts and floating components. Moreover, foams can also be used as insulating materials in packing 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 buriti biofoam 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.

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 that of foam materials, like the Styrofoam®, fabricated by a foaming process in which a blowing agent is added to heated polystyrene giving rise to a low density sponge like structure [1]. These synthetic materials, made from non-renewable petroleum derived 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, foam materials are essential for the production of many items such as insulating chests, drinking cups, lifebuoys, automobile cushion, construction panels, etc. An environmentally correct alternative to replace synthetic foams is the naturally existing foam extracted from plants such as cork and balsa wood that is lighter than water with densities below 0.3 g/cm^3. In addition to the environmental advantages of being renewable and degradable, these natural biofoams provide a negative contribution to CO_2 emission by absorbing greenhouse gas during the plant lifecycle. Natural biofoams have been used since long time in simple items such as corks for wine bottles and small buoyants. Today they are used in engineering applications related to thermal insulation in building panels [2] and soft parts in automobile interior components [3].

In the north Amazonian region of Brazil, a natural biofoam obtained from the buriti palm tree is being used as a modest substitute for Styrofoam® in insulating pieces like icebox. A recent work [4] on the characterization of the buriti biofoam has shown its potential as a new engineering material with a density lower than 0.1 g/cm^3 in association with relatively lower absorbed humidity and open porosity. This biofoam could be used in floating systems. Moreover, by its mechanical properties and evidence of ductile rupture, even at the liquid nitrogen temperature of -196ºC, the buriti biofoam could be applied as insulation material for very low temperature application [4]. However, the thermal behavior of the buriti biofoam 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 foam.

Experimental Procedure

The buriti biofoam was supplied by one of the co-authors, N.S.S. Santos, who brought it from her own property in the state of Para, north of Brazil. The aspect of as received pieces of biofoam is shown in Fig. 1.

Figure 1 – The as received buriti biofoam

Samples of the buriti biofoam were cut from one of the as received pieces, Fig. 1, for the thermal behavior characterization by TGA/DTG and DSC. The TGA/DTG analysis was carried out in a model 2910 TA Instrument, Fig. 2(a), equipment operating at a heating rate of 10ºC/min in the interval of temperatures from 25 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. 2(b), equipment operating from 25 to 250ºC. For this particular analysis a 15 mg sample of buriti biofoam was crushed and placed inside a tight-closed aluminum container.

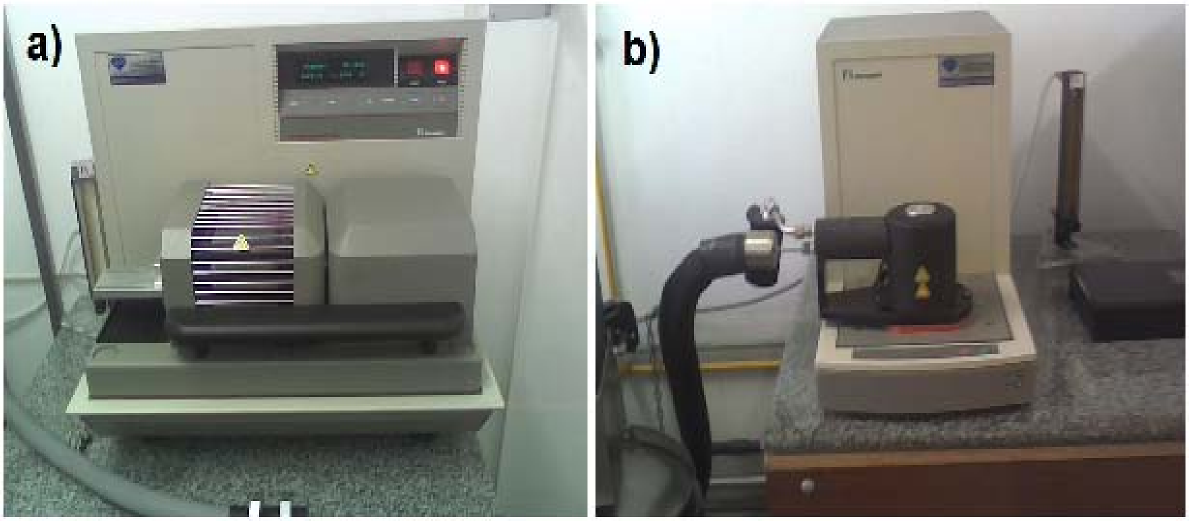

Figure 2 – Thermal analysis equipments: (a) TGA/DTG, and (b) DSC

Results and Discussion

The thermal stability of the buriti biofoam measured by the loss in weight through TGA performed with increasing temperature under oxygen (O_2) and nitrogen (N_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, both curves for O_2 and N_2 remain constant up to approximately 160ºC, 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 475ºC under O_2 and 550ºC under N_2. This sharp decrease can be associated with the decomposition of the biofoam lignocellulosic structure by rupture of its macromolecular chains [5]. With increasing temperature, a second constant stage in both TGA curves, Fig. 3, exists up to the limit of 800ºC established for the analysis.

Even though 160ºC was indicated as the approximate end of the first constant stage in both O_2 and N_2 TGA curves, the onset of the biofoam 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 268ºC and 263ºC for TGA under O_2 and N_2, respectively.

The end of the biofoam structure decomposition process can also be determined using a similar procedure. This 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 and 421ºC for TGA under O_2 and N_2, respectively. Here a relevant aspect to be noted is the different levels for the second constant stage, Fig. 3, depending on the atmosphere of the thermogravimetric analysis. The interpretation of results presented in Fig. 4 contributes to the understanding of this difference in the levels of the second constant stage.

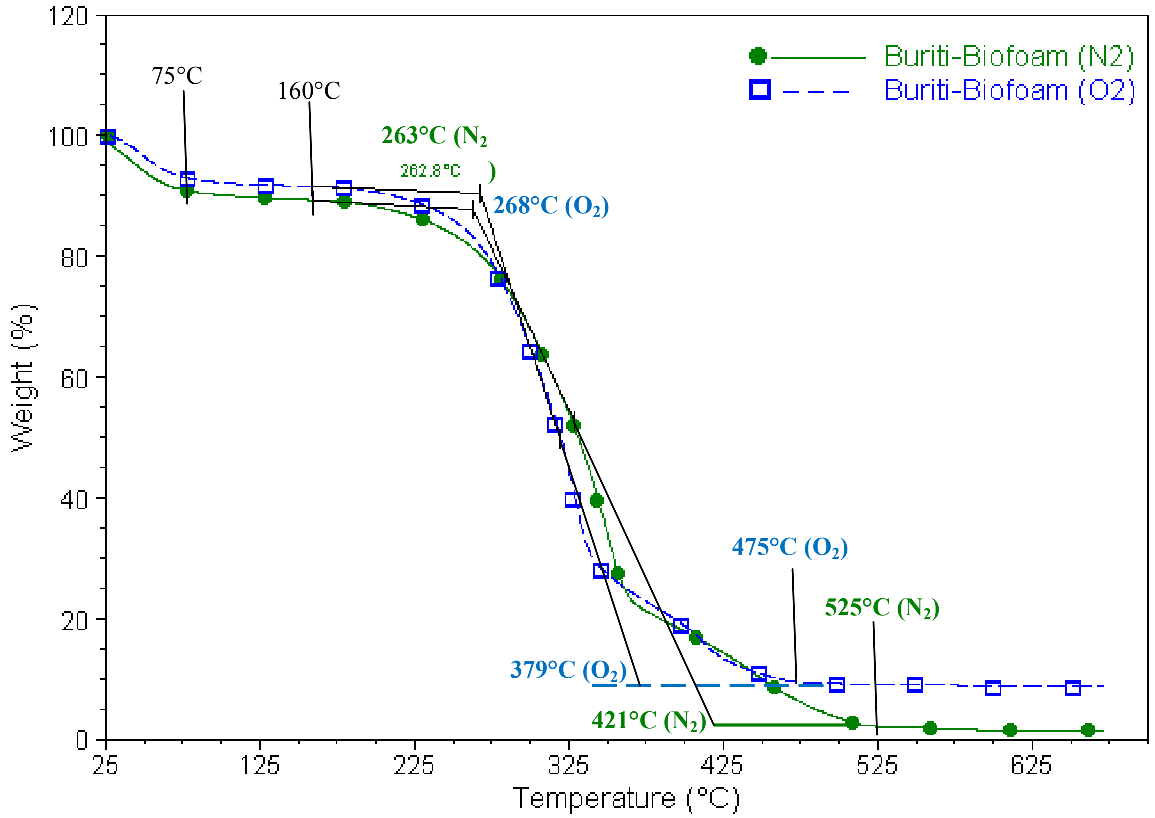

Figure 3. TGA curves showing the main temperatures associated with thermal events occurring to the buriti biofoam.

Figure 4 uses the same TGA curves of Fig. 3 to show the important levels of weight loss associated with events occurring to the buriti biofoam thermal degradation. The small first drop in weight due to the loss of absorbed humidity is relatively close, 8.2% and 10.4%, for TGA under O_2 and N_2 respectively. This result together with the close decomposition onset temperatures, Fig. 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, 82.7% for O_2 and 88% for N_2, together with corresponding significant differences between the decomposition temperatures, Fig. 3, indicate an effect of the atmosphere. This will be better understood in conjunction with the DTG curves.

The residual weight found at 525°C in the second stage, of 9.1% when O_2 was used as carrier gas and 1.6% in N_2, corresponding to the thermal degradation in the buriti biofoam, can be interpreted as follows. Under N_2, practically no residual matter is left after 525°C. However, the O_2 reaction during the buriti biofoam decomposition apparently left a thermal stable residue, probably oxides that did not decompose up to 800°C.

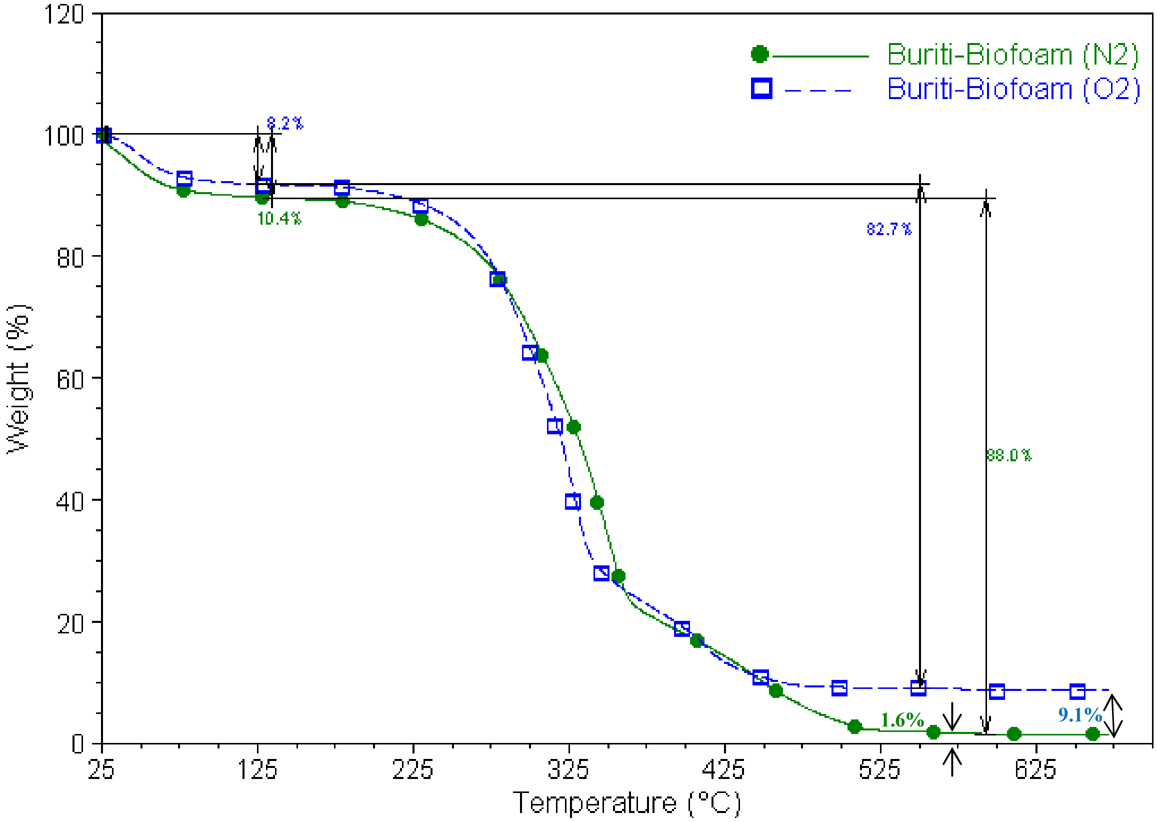

Figure 4. TGA curves showing the main levels of weight loss associated with thermal events occurring to the buriti biofoam.

Figure 5 shows the DTG curves for the buriti biofoam under oxygen (O_2) and nitrogen (N_2) atmospheres. The first peaks at the same temperatures of 50°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 biofoam decomposition, 329°C in O_2 and 349°C in N_2, indicate that oxygen induces a reaction with the buriti biofoam, causing a more effective degradation to occur at earlier temperatures. In fact the carbon and nitrogen that constitute the lignocellulosic structure of the biofoam 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. This could justify the high temperature amount of 9.1%, Fig. 4, of stable residues in TGA under O_2 atmosphere.

A relevant aspect of the larger peaks in Fig. 5 is their broadening observed in the left side as shoulders around 300°C. This can be attributed to lower temperature peaks, apparently at 290°C in O_2 and 310°C in N_2 that are concealed by the larger peaks. Lower temperature peaks indicate a complex thermal degradation process related to the rupture of molecular chains with different energy levels. In Fig. 5, the similar shape of the shoulders might correspond to the same degradation process for both atmospheres.

Another feature in Fig. 5 is the existence of small peaks at 414°C for O_2 and 446°C for N_2 atmospheres. 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 [6].

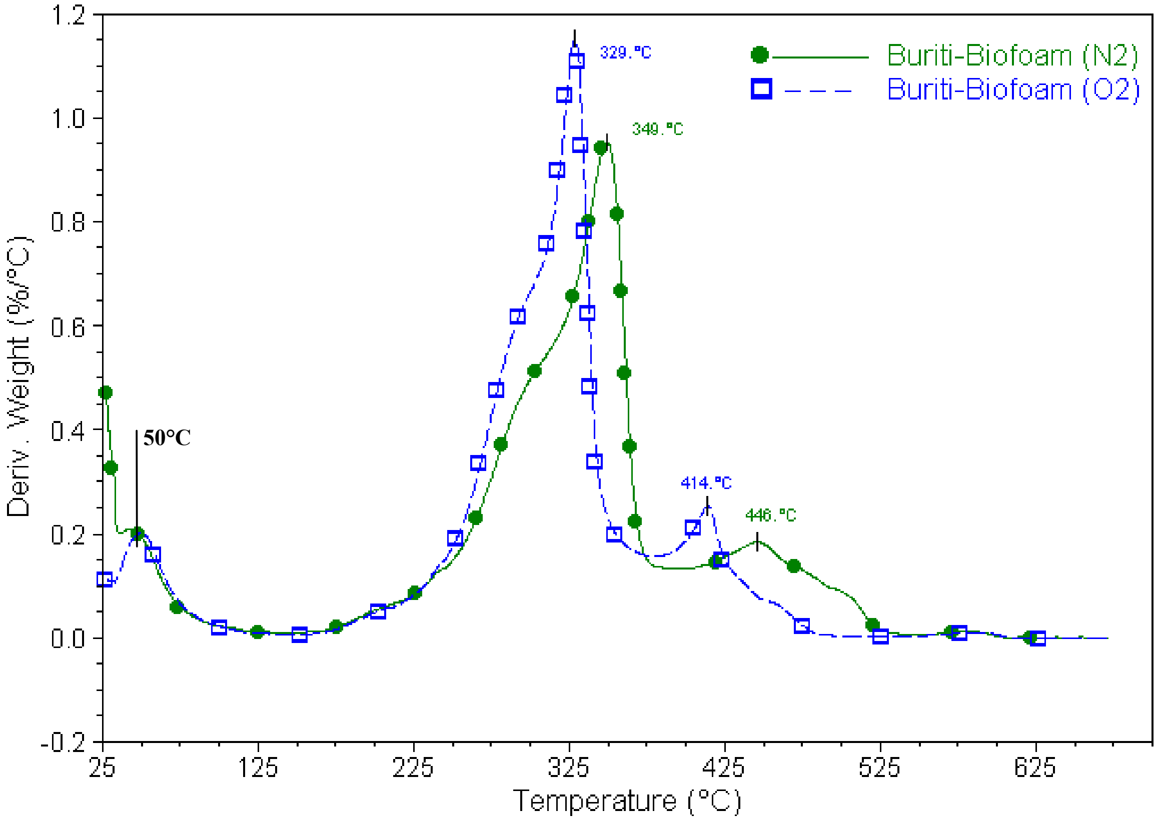

Figure 5. DTG curves for the buriti biofoam.

Figure 6 shows the DSC curve for the buriti biofoam. In this figure an endothermic event occurs in the interval of temperature from approximately 30°C to 200°C with a peak at 105ºC. It is suggested that the heat absorbed in this endothermic event, 106 J/g, could be related to the release of water associated with the hydration of the lignocellulosic structure of the biofoam, before macromolecular chain degradation occurred.

Finally, the thermal analysis performed in the buriti biofoam indicated that this natural material looses a relatively small amount of absorbed water up to 75°C. Its macromolecular chain structure begins the thermal degradation process around 260°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 buriti biofoam, especially as an insulating material.

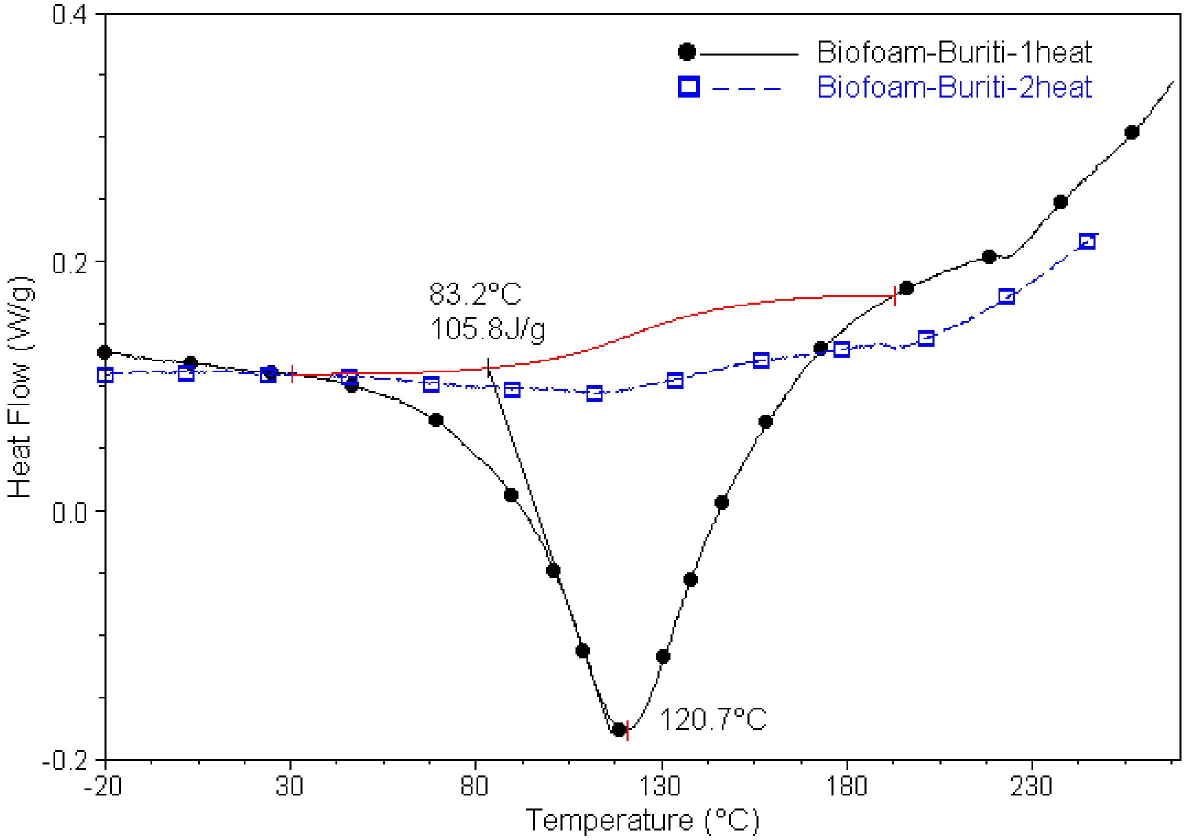

Figure 6. The DSC curve for the buriti biofoam heated under N_2 atmosphere.

Conclusions

- The thermal behavior of a buriti biofoam analyzed by TGA, DTG and DSC revealed evidences of water loss and structural decomposition. Up to 75ºC approximately 10% 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 329/349ºC and 414/446ºC, as well as apparently concealed peaks at 290/310°C, depending respectively on oxygen or nitrogen atmosphere.
- Under oxygen, a constant amount around 9% of stable solid residue is formed as inert ashes from 525°C up to 800°C. This residue is composed of oxides from trace metals such as Ca, K, Na and Fe as contents of the buriti biofoam lignocellulosic structure.

Acknowledgements

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