CELLULOSE/BIOCHAR AEROGELS: THERMAL PROPERTIES AND LIFETIME PREDICTION

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Abstract – Aerogels can be applied in thermal insulation and because they are exposed to the action of temperature and weathering, it is necessary to know about the degradation kinetics and the thermal properties of these materials. For the production of aerogels, a suspension of cellulose is produced at a concentration of 1.5% (w/w), aerogel AC-1, and at this suspension was applied 40% (w/w) of biochar (to cellulose mass), aerogel AC-1.B40. The addition of biochar to the cellulose aerogel causes a decrease in the rate of degradation and loss of mass. The values of E_a showed no dependence on conversion degree (α) and two steps of degradation were observed for both samples, following the same degradation model (A→B→C). Regarding the lifetime prediction, the aerogel AC-1.B40 demonstrated to be more stable than AC. It means that after 1 year exposed to a temperature of 150 °C AC-1.B40 has not completely degraded as seen in the aerogel AC-1. In all, the addition of biochar to the cellulose aerogel is a great option for further production of thermal insulators.

Keywords: cellulose *Pinus elliotti*, biochar, aerogel, thermal analysis.

Introduction

Cellulose is the most abundant natural polymer in nature, as it is the main constituent of the cell wall of plants, and is also present in algae, fungi, animals, and bacteria. The three-dimensional structure formed by its fibers provides materials with excellent mechanical properties, in addition to being able to produce light and porous materials such as aerogel [1] [2].

Aerogels can be used as thermal insulation, and for this, is exposed to a certain temperature for a long period time, it is important to know the degradation kinetics, and, consequently, the lifetime prediction of materials is highly recommended. A *Pinus elliotti* cellulose was used as raw material for the production of aerogel and also for biochar, allowing this form to add a high value to this biomass combined with a low processing cost.

From the knowledge of the degradation kinetics and the lifetime prediction, it is possible to plan materials replacement before catastrophic failure occurs and determines a possible prediction of the behavior for the materials in a large range of temperatures. Additionally, thermal predictions can be made by accessible experimental conditions (TG) and by simulation [3] [4].

In the present study, Pinus elliotti cellulose was used as raw material for the production of aerogel and also for biochar, allowing this form to add a high value to this biomass combined with a low processing cost. This study investigates the influence of biochar in the aerogel regarding degradation kinetics and lifetime prediction of 1 year exposed at 150°C.

Experimental

The Pinus elliotti cellulose used was of the unbleached long fiber type supplied by the company Trombini - RS.

Initially, Pinus elliotti cellulose was ground in a stone mill for 5 hours at 4500 rpm, to obtain the cellulose suspension with 1.5% (w/w) cellulose fiber concentration [5].

The biochar (BC) was produced from cellulose residue pyrolysis with a heating rate of 5 ºC min^{-1}, isotherm time of 60 min, the final operating temperature of 800 ºC, and N$_2$ flow of 150 mL min^{-1} [6].

Aerogels were produced using the methodology presented by [6]. Initially, the cellulose suspension was centrifuged and BC was added to the supernatant at a concentration of 40% (to cellulose mass). The supernatant was drained over the precipitate and mechanically stirred for 5 min to completely homogenize the suspension. The final suspension was sonicated for 30 minutes and 50% amplitude (maximum equipment capacity - 500W). Finally, the suspension was frozen in an ultrafreezer in square molds and then lyophilized for 72 hours under vacuum at - 45ºC.

Thermogravimetric analysis (TG) was performed in a Shimadzu TGA-50 equipment in an N$_2$ atmosphere with 50 mL min^{-1} rate. Four different heating rates were used: 10, 20, and 40 °C min^{-1}, with temperature ranging from 25 to 600 °C. The mass of each sample was ca. 10 mg. The kinetic triplet composed by E$_a$ and A values, degradation model, and degradation mechanism was determined by Kissinger-Akahira-Sunose (KAS) and Friedman (FR) in the *Netzsch Thermokinetics* software [7]. After that, a year of lifetime prediction at 30-180 °C range was performed based on the previously obtained kinetic parameters.

Results and Discussion

Figure 1 presents the photograph of the aerogel AC-1 and AC-1.B40 as well as their thermogravimetric curves. In the photographs, it is possible to see the porous structure of the aerogel, which has a porosity greater than 94%. As previously mentioned, these aerogels can be used as thermal insulators due to their low thermal conductivity (0.024 W m^{-1} K^{-1}) [6]. And due to this application, where they can be exposed to high temperatures, it is essential to know about their thermal properties.

Analyzing the curves in Figure 1, cellulosic materials show two mass loss events: between 50 and 100ºC, related to the humidity present in the sample; and from 250ºC, related to cellulose degradation and decomposition and also to the lignin and hemicellulose present in aerogel. Still, it is observed that the aerogel AC-1, lost the highest percentage of mass at a higher speed than the aerogel AC-1.B40. Besides, the addition of the biochar to the aerogel AC-1.B40 reduces the rate of degradation and mass loss, showing greater thermal stability than the aerogel AC-1. This result can be justified by the insertion of the biochar in the aerogel AC-1.B40 since it is composed mainly of carbon, 68% while the AC-1 has about 34%.
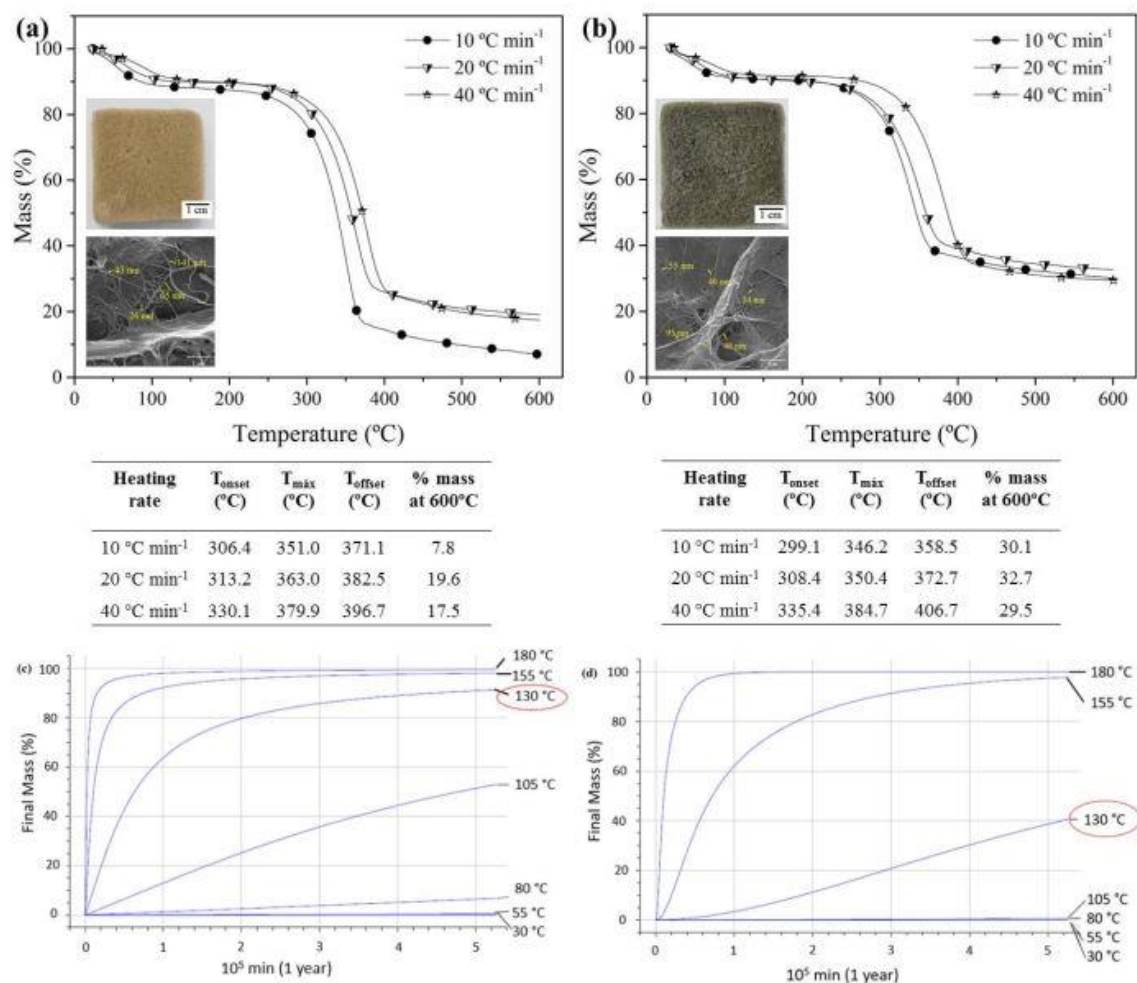
Figure 1 – TGA curves, micrographs and photographs: (a) AC-1 and (b) AC-1.B40.

As can be seen, when increasing the heating rate, Tonset gradually increases, because there is a shorter exposure time of cellulose to high temperatures at higher heating rates, in addition to the increase in the heating rate there is the displacement, from molecular events to higher temperatures [8] [9].

Table 1 shows the values of E_a and A calculated using the Friedman and Kissinger-Akahira-Sunose methods. As seen in Table 1, the aerogel AC-1 showed E_a and A values higher than AC-1.B40. This result corroborates with the literature, once Yao et al. [10] claim that cellulose is the main contributor to activation energy values. In other words, the higher content of cellulose in the sample leads to higher E_a values. Additionally to it, according to Vyazovkin et al. [11] E_a is associated with the energy barrier, so in this case, AC-1 presented more barrier to the heat transfer than AC-1.B40. Regarding A values, the same trend was observed.

Table 1- Ea and A mean values evaluated by FR and KAS methods

Sample	FR		KAS	
	E_a (kJ.mol^{-1})	A	E_a (kJ.mol^{-1})	A
AC-1	226.3 ± 32.9	26.9 ± 2.3	188.0 ± 3,5	13.45 ± 0.8
AC-1.B40	116.4 ± 21.4	7.6 ± 1.7	109.7 ± 23,9	6.7 ±1.7

From the parameters presented in Table 1, it was possible to simulate the experimental degradation curves based on the most common theoretical degradation mechanisms for the solid-

state [12]. The simulation was performed on the *Thermokinetics*, which has the advantage of the quality of the statistical analysis, and, consequently, minimizing operator error. More information about the software and how it works could be found elsewhere [13] [7]. The simulation was based on Waterloo's reaction pathway, which states that all compounds in solid-state degradated into volatiles and charcoal [14].

The results statistically suggest that two-steps degradation model (A→B→C), for both samples. The degradation model could be associated with main cellulose chain (A) which degrades in low molecular weight celluloses (B), which degrades in smaller cellulose chains, in the case of AC-1, or biochar particles, in the case of AC-1.B40 (C). Regarding the degradation mechanism, the addition of biochar did not influence it, since for both samples presented an autocatalytic degradation followed by other autocatalytic degradation mechanisms. The reported results corroborate with the literature [13] [15].

Based on all kinetics parameters obtained in the previous steps, a lifetime prediction predictions for both aerogels using the 30-180ºC temperature range (in steps of 25ºC) until 10^5 min (1 year) were performed and the resulting curves are shown in Figures 1(c) and (d).

In the range of 30-55ºC both aerogels have the same behavior, from 55ºC, the aerogel AC-1 has degraded over the years, reaching a loss of mass of 50% at a temperature of 105ºC. While the AC-1.B40 aerogel maintains its stability up to a temperature of 105ºC. At 130ºC, values for residual mass (%) were 90 and 40 for AC-1 and AC-1.B40, respectively. This shows that after 1 year of exposure to a temperature of 130ºC, the aerogel AC-1.B40 has greater thermal stability than the aerogel AC-1. At 155ºC, the aerogel AC-1 reaches 90% of mass loss in the first year of exposure, whereas the aerogel AC-1.B40 reaches this percentage of mass loss from the third year. Above this temperature, both aerogels reach maximum degradation up to two years of exposure. This demonstrates that the addition of the biochar to the cellulose aerogel acts synergistically concerning cellulose degradation, providing greater stability to the cellulose aerogel when it is exposed to temperatures above 105ºC for extended periods.

Conclusions

The addition of the biochar to the cellulose aerogel provides improvements in the thermal properties of the material, such as a reduction in the rate of thermal degradation and loss of mass, besides, there is an increase in the thermal stability of the aerogel AC-1.B40 (compared to the aerogel AC-1) when it is exposed to temperatures above 105ºC for extended periods.

Acknowledgements

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