Thermal Degradation Kinetics and Lifetime Prediction of Cellulose Biomass Cryogels Reinforced by its Pyrolysis Waste

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Degradation kinetics is an important tool in order to understand and improve energy conversion and the final application of a material. Cellulose cryogels (CC) are a new class of materials that can be reinforced by several types of particle, including biochar. Apart from it, degradation kinetics and lifetime prediction of biomass cellulose cryogels reinforced by cellulose pyrolysis waste (BC) has been investigated using TG techniques and iso-conversional model free methods. Additionally, the same study was applied to cellulose cryogels reinforced by graphene nanoplatelets (NPG) to compare the behavior of a filler from waste (BC) and a noble filler (NPG). Furthermore, the influence of the addition of the fillers into the cellulose biomass were evaluated in terms of thermal stability and crystallinity. BC and GNP led to higher values of activation energies ($E_a$) calculated from model-free isoconversional methods and all samples degraded in two-steps. Finally, lifetime prediction was successfully applied and the CC cryogel became more stable over time, maintaining almost 80% of the mass for 1 year exposed at 180 °C. The results of this study shown that only cellulose biomass cryogels are more suitable to produce thermal insulators due to it higher thermal stability.

Keywords: Cryogels, biochar, graphene nanoplatelets, cellulose, degradation kinetics.

1. Introduction

The use of porous materials from biomass presents an alternative to polymers derived from fossil fuels such as polystyrene, polyurethane and, ethylene vinyl-acetate foams. Cellulose-based cryogels are a relatively new class of porous materials produced by replacing the liquid phase present in a gel with air (through freeze-drying or freeze-drying), without affecting its three-dimensional structure.1

These materials have characteristics such as high surface area and porosity, and therefore, they can be used in different areas. A potential application, according to recent studies, for cryogels is the use as thermal insulators2-6 for the fact that its thermal conductivity ($<0.04$ W m$^{-1}$ K$^{-1}$)2,7 is close to the thermal conductivity of stagnant air ($\sim 0.025$ W m$^{-1}$ K$^{-1}$).8 Additionally, they can be reinforced by fillers such as its pyrolysis waste (biochar), in order to improve some properties such as flame resistance, high electrical conductivity, and impermeability to water.

Thermal insulators reduce heat transfer between two media through conduction, convection, and radiation. The insulating capacity of a material is measured according to the thermal conductivity, that is, the lower the thermal conductivity the greater the insulating capacity. They can be applied in different areas, such as civil construction, textile industry, among others. In some applications, thermal insulators are exposed to high or low temperatures, for example, in heat exchangers where there are heated pipes, or in cold rooms for cooling and preserving food and medicines. For this reason, understand the kinetic degradation behavior is extremely important since there is a change in the temperature during shipping.10

Since cryogels might be applied as thermal insulants, understanding the thermal degradation and kinetics behavior is highly recommended. Thermal insulators might use in different environments and thermal conditions, and, consequently, thermal degradation can occur at different rates. Additionally, knowledge on the degradation kinetics on thermal insulant predicts the long-exposure behavior of the sample, saving uptime and cost. Kinetic studies give essential information such as activation energy (minimum energy required to start the reaction), pre-exponential factor (velocity of the reaction) and, reaction order (degradation mechanism)11-13.

For a reliable and complete kinetic study, the ICTAC (International Confederation for Thermal Analysis and Calorimetry) states that the study must follow the steps:
2. Materials and Methods

2.1. Materials

The materials used in the production of the aerogels were: *Pinus elliotti* cellulose (Trombini - RS) and graphene nanoplatelets (GNP) with carbon content > 99.5 wt% (Strem Chemicals, INC. - USA).

The chemical composition of cellulose was performed. Lignin was determined according to TAPPI T222 om-02. Extractives were determined by TAPPI T204 cm-97. Humidity, cellulose, and hemicellulose were determined by Van Soest Method. All results were determined in percentage by weight (% w/w).

2.2. Production of cellulose/BC and cellulose/GNP cryogels

*Pinus elliotti* cellulose, in solution, was ground in a stone mill for 5 hours at 4500 rpm, to obtain the cellulose suspension with 1.43 (% w/w) cellulose fiber concentration. The biochar (BC) was produced from cellulose pyrolysis with a heating rate of 5 °C min⁻¹, isotherm time of 60 min, a final operating temperature of 800 °C, and N₂ flow of 150 mL min⁻¹. The cryogels were produced using the methodology presented by²⁴. Initially, the cellulose suspension was centrifuged and BC or GNP was added to the supernatant at concentrations of 50 and 100% (relative to the cellulose mass), the final concentration of suspension is 2.14 and 2.86% w/w, respectively. The supernatant was mixed with the precipitate and mechanically stirred for 5 min to completely homogenize the suspension. The final suspension was sonicated in an ultra-freezer in square molds and then lyophilized for 72 hours under vacuum at –45 °C.

The samples were named: CC for the pure cellulose cryogel; CC100BC for cellulose cryogel containing 100% biochar (relative to the cellulose mass); CC50BC for cellulose cryogel containing 50% biochar (relative to the cellulose mass); CC100GNP for cellulose cryogel containing 100% graphene nanoplatelets (relative to the cellulose mass) and CC50GNP for cellulose cryogel containing 50% nanoplatelets of graphene (relative to the cellulose mass).

2.3. Characterization of cellulose/BC and cellulose/GNP cryogels

The analysis was performed on an X-ray diffractometer, Shimadzu - model XRD-6000 (Japan). The range analyzed was 20 = 10° to 40°, with a step of 0.05° and an integration time of 2 s. The crystallinity of the cryogels was calculated using Equation 1 This method was based on research carried out by Hermans and Weidinger²⁵.

\[
CI = \left( \frac{A_{\text{cryst}}}{A_{\text{total}}} \right) \times 100
\]  

(1)

where, CI is the crystallinity index (%); A_{\text{cryst}} is the sum of crystalline peak areas, and, A_{\text{total}} is the total area under the diffractograms.

The thermal properties were analyzed by thermogravimetric analysis (TG) Shimatzu TGA-50 equipment. Under conditions: N₂ atmosphere 50 mL.min⁻¹ rate, a heating rate of 10 °C.min⁻¹ from 30 to 800 °C.

The mass of each sample was ca. 10 mg. From TG curves, a theoretical study based on the chemical composition of *Pinus elliotti* (base of the cryogel) was performed based on Cabeza et al.²⁶ work. We choose to apply this approach since it allows observing the effect of each component on the TG curve and the evolution of each component’s char. The free spreadsheet developed (Biomass Modelling—Thermal degradation) is available at http://hpp.uva.es/software/.

For kinetic study, were four different heating rates were used in TG curves: 5, 10, 20, and, 40 °C min⁻¹, with temperatures ranging from 30 to 800 °C and N₂ atmosphere 50 mL.min⁻¹ rate. The kinetic study was followed by Vyazovkin studies²⁷,²⁸. Four steps were used for a complete kinetic degradation study. Firstly the Arrhenius parameters, activation energy (E_a) and pre-exponential factor (A) were calculated by two isoconversional methods: differential Friedman (FR) (Equation 2) and integral Kissinger-Akahira-Sunose (KAS) (Equation 3), in which R and T are the gas constant (8.314 J.K⁻¹mol⁻¹) and temperature (K), respectively.

\[
\ln\left( \frac{d}{dt} \right) = \ln\left( Af(\alpha) \right) - \frac{E_{FR}}{RT}
\]

(2)
\[
\ln \left( \frac{\beta}{T^2} \right) = \ln \left( \frac{AR}{E(\alpha)} \right) - \frac{E_{a,\text{KAS}}}{RT}
\]  

(3)

Where A is the pre-exponential factor, E is the activation energy, \( \alpha \) is the fractional reaction, R is gas constant and, T is the temperature.

Once \( E_a \) and A values were determined, the second step was determined by the degradation model followed by determining the degradation mechanism(s) \( f(\alpha) \). Last but not least, a prediction of properties for 10 years regarding loss mass at different temperatures were analyzed. All kinetic parameters and prediction of properties were simulated in the Thermokinetics software, from Neetzsch. More information about the software could be found elsewhere.\(^{12,18,22}\)

After that, lifetime prediction was done based on the previously obtained kinetic parameters used by the Thermokinetics Software. Lifetime prediction is performed in order to predict the behavior of the material when exposed to certain temperatures for long periods of time.\(^{16}\) More information regarding the steps could be found elsewhere.

3. Results and Discussion

3.1. Cellulose chemical composition

*Pinus Elliotti* cellulose had about 68.4 ± 2.1% (w/w) cellulose, 14.2 ± 1.4% (w/w) hemicellulose, 3.9 ± 0.6% (w/w) lignin, 10.62 ± 0.3% (w/w) extractives, and 7.43 ± 0.19% (w/w) moisture. The results were calculated considering the biomass in natura (wet basis). The sum of the four fractions does not reach 100%. This behavior could be related to the presence of other substances that are determined by none of the methods used.\(^{39}\) After wood processing for cellulose production, cellulose content increases and lignin decreases, however, for the present sample, there is the presence of lignin in its composition because this material press has not gone through the fiber bleaching process. According to\(^{38}\) the mechanical and physical properties of the fibers are influenced by their composition, higher levels of crystalline cellulose provide greater thermal stability. Fibers with higher levels of hemicellulose and extracts show thermal degradation at low temperatures, because they can absorb more moisture.

Based on the aforementioned chemical composition, Figure 1 shows the representative curve for 5 °C min\(^{-1}\) for *Pinus Elliotti*, using Cabeza’s approach. It is noteworthy that the lignin, when degraded, forms the highest amount of char between the components.

![Figure 1. Representative curve simulated with a heating rate of 5 °C min\(^{-1}\) for *Pinus Elliotti*, using Cabeza’s approach.](image)

Literature reports the thermal degradation of lignocellulosic materials in the following order: around 100 °C (elimination of water/humidity), around 200 °C (degradation of hemicellulose), around 270 °C (degradation of cellulose) and, around 400 °C (degradation of lignin)\(^{31-33}\). All the results presented in Figure 1 corroborates with the literature. Furthermore, some authors report that hemicellulose is the main responsible for the reaction order and thermal stability, cellulose for the degradation process and the Arrhenius parameters \( (E, A) \) and, lignin for the final tail\(^{11,22,34,35}\).

3.2. XRD and Crystalinity Index

Figure 2(a) shows the X-ray diffractograms of cellulose and cryogels samples studied. Cellulosic materials present 20 reflection assigned in 14.4° (1 -1 0), 16.3° (1 1 0), 22.3° (2 0 0) and, 34.3° (0 0 4) diffraction patterns of carbon crystallographic plane, and the 18.6° reflection assigned to the amorphous phase. These plans are characteristic of native cellulose.\(^{16,37}\)

Figure 2 (b) shows the diffractogram of the biochar and the cellulose/BC cryogels. The BC spectrum shows a strong broad diffraction peak at around 22 ° which is in keeping with the (0 0 2) diffraction patterns of carbon.\(^{38}\) As is already known, crystalline cellulose disappears during biomass pyrolysis. The peak at 29.3° in the spectra of cellulose/BC cryogels, according to\(^{39}\) is related to the characteristic graphite d-spacings that occur close to the 27°. Also, the d-spacings present fewer contrasts in the biochar compared to the raw material, which influences the spectra of cryogels due to the high concentration of biochar present in them, as there is an increase in the aromatization of the biochars’ molecular structures together with the crystalline crystal.\(^{39}\)

The cellulose/biochar cryogels XRD pattern is dominated by the crystalline cellulose in the original biomass.\(^{40}\) According to the diffractograms, the BC sample seems amorphous because the crystalline peaks are very wide, whereas the CC50BC and CC100BC samples present the crystalline and narrow peaks.
The XRD spectra of cellulose/GNP cryogels shown in Figure 2 (c), show the same pattern as the GNP spectrum, with a peak at ~ 26° associated with stacked crystalline graphitic sheets or bulk graphite. Cryogels show a weakening of this peak after the incorporation of GNPs, because the mass of GNP decreases when it is added to cellulose, which reflects a decrease in the degree of graphitization of cryogels.

The crystallinity index (Figure 2 (d)) of Pinus elliotti cellulose, calculated by Equation 1, was 79.9%, a value consistent with the literature. The cryogel crystallinity index is affected by the addition of the BC and GNP. CC50BC and CC100BC cryogels had a lower I.C. than CC50GNP and CC100GNP cryogels, which is expected since GNPs have peaks typical of crystal structures (Figure 2c).

3.3. Thermogravimetric analysis

According to the thermogravimetric curves, at heating rate of 10 °C min⁻¹, all samples showed a loss of mass around 100 °C, due to the loss of moisture present in them. Figure 3a shows the TG and DTG curves for cellulose, BC, and GNP. Cellulose presents the greatest loss of mass between 280 - 400 °C: degradation of the most reactive fraction of hemicellulose (150-350 °C), generating more non-combustible gases and more tar than cellulose; cellulose degradation (275-350 °C) responsible for the greater production of flammable volatiles; and degradation of lignin. In the case of lignin (250-500 °C), due to its highly complex structure, as it is a heterogeneous polymer, its crosslinking occurs in different ways, this is because lignin is derived from lignol precursors. Due to this, lignin has different stabilities, which directly reflects on its degradation behavior. Even starting at low temperatures, the degradation process occurs more slowly, so lignin is the main responsible for the formation of residual material (17.3%). The BC and GNP showed a loss of mass below 10% (4.2 and 7.2%, respectively), referring to the humidity present in the sample. The organic matter present in the cellulose is degraded during the pyrolysis process, for this reason, there is no considerable loss of mass in the BC sample.

For CC, CC50GNP, and CC100GNP (Figure 3bdf) it was possible to observe one main degradation peak. For all cryogels, the biggest event of mass loss occurs between 300 - 400 °C referring to the degradation of the major compounds (cellulose, hemicellulose, and lignin) of the cellulose used as raw material, as mentioned above. The incorporation of GNP to the cellulose cryogel, presented Tpeak value within the error range of the equipment, which shows that GNP did not change the thermal stability of cryogels. This behavior is also observed by for graphene oxide/cellulose aerogels nanocomposite. In the study presented by you hear an increase of 20°C in Tonset with the addition of 5% of GO in the regenerated cellulose/graphene oxide composite aerogel due to the strong interaction between the two raw materials.

![Figure 2. X-ray diffractograms: (a) cellulose Pinus Elliotti; (b) cellulose/BC cryogels; (c) cellulose/GNP cryogels and, (d) crystalline index.](image-url)
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forming the network reticulation three-dimensional effect of aerogel limiting the molecular activities of cellulose. After the decomposition of lignin, the biochar formation process is completed. As the temperature rises, from that point on, there is the formation of ashes. In this stage, there is a low loss of mass because the main components of the raw material have already been decomposed. This behavior was evidenced only for cryogels CC50BC and CC100BC (Figure 3c and 3e) cryogels that presented the second degradation peak, around 600 - 750 °C.

Figure 3. TGA curve and its derivative (DTG) for (a) cellulose, BC, and GNP; (b) CC; (c) CC50BC; (d) CC50GNP; (e) CC100BC and, (f) CC100GNP.
Table 1 shows the data taken from Figure 3 for the TG curves of cryogels, for the heating rate of 10 °C min\(^{-1}\). The residual masses of BC and GNP were 95.8 and 92.8%, respectively. The residual mass showed an increase of about 2-4 times of the cryogels to the cellulose and is associated with the inorganic compounds present in the BC and GNP.

3.4. Degradation kinetics and lifetime prediction

All the kinetic study reported here was based on the simulation of the samples from 100 to 500 °C, based on Figure 3 (TG) in which shows that the range is the main degradation. Additionally, at temperatures higher than 500 °C the char reside takes place, and our objective was to observe the influence of carbonaceous fillers on the degradation of cellulose cryogel. Regarding degradation kinetics, The TG and DTG curves obtained at four different heating rates (5, 10, 20, and 40 °C min\(^{-1}\)) and the simulated curves for the most probable degradation mechanisms, based on the best-fit curves and the statistics of these curves are displayed in Supplementary Material, for all cryogels.

As stated by ICTAC, the first step of the degradation kinetics is the determination of the dependency of \(E_a\) and \(A\) with the conversion degree (\(\alpha\)), and this relation is showed in Figure 4. The shape of all curves (Figure 4) are very similar and linear (for \(\alpha = 0.2-0.7\)), and the same behavior was reported by Neves et al.\(^{12}\) and Ornaghi et al.\(^{22}\). The linearity observed for all samples corresponds to a non-dependency of \(E_a\) and \(A\) with \(\alpha\). The \(\alpha=0.2\) to 0.7 range is reported in the literature as the main degradation step of cellulosic materials\(^{11,26}\).

Table 2 summarizes the mean values of \(E_a\) samples evaluated Friedman method (differential) and KAS method (integral) for \(\alpha=0.2 - 0.7\). An ANOVA one-way was performed

| Sample       | \(T_{onset,1}\) (°C) | \(T_{peak,1}\) (°C) | \(T_{offset,1}\) (°C) | \(T_{onset,2}\) (°C) | \(T_{peak,2}\) (°C) | \(T_{offset,2}\) (°C) | RW* (%) |
|--------------|----------------------|---------------------|----------------------|----------------------|----------------------|----------------------|---------|
| Cellulose    | 318.6                | 358.5               | 391.1                |                      |                      |                      | 17.3    |
| CC           | 318.6                | 352.7               | 391.0                |                      |                      |                      | 13.8    |
| CC50BC       | 282.4                | 333.8               | 369.4                | 674.4                | 697.8                | 709.9                | 28.1    |
| CC100BC      | 282.7                | 324.6               | 364.1                | 659.76               | 684.9                | 713.92               | 38.9    |
| CC50GNP      | 337.4                | 365.7               | 380.1                |                      |                      |                      | 39.4    |
| CC100GNP     | 321.8                | 343.5               | 361.6                |                      |                      |                      | 56.3    |

*RW – Residual weight

Figure 4. Dependence of \(E_a\) vs \(\alpha\) for all studies samples by a) Friedman method and b) KAS Method.
Table 2. Mean values of (E\textsubscript{a}) and A (α = 0.2 - 0.7) for all studied samples.

| Sample          | Friedman          | KAS       |
|-----------------|-------------------|-----------|
|                 | E\textsubscript{a} (kJ mol\textsuperscript{-1}) | Log A (1 s\textsuperscript{-1}) | E\textsubscript{a} (kJ mol\textsuperscript{-1}) | Log A (1 s\textsuperscript{-1}) |
| CC              | 126.2 ± 3.0       | 8.2 ± 0.2 | 119.6 ± 0.5\textsuperscript{*} | 8.3 ± 0.2 |
| CC50BC          | 131.3 ± 9.6       | 9.0 ± 0.6 | 121.1 ± 2.8\textsuperscript{*} | 8.8 ± 0.2 |
| CC50GNP         | 129.6 ± 4.1       | 8.4 ± 0.4 | 120.2 ± 2.5\textsuperscript{*} | 8.0 ± 0.1 |
| CC100BC         | 147.7 ± 11.6      | 10.4 ± 0.8| 141.6 ± 3.2\textsuperscript{*} | 10.4 ± 0.4 |
| CC100GNP        | 165.0 ± 61.0      | 11.5 ± 4.9| 145.0 ± 12.9\textsuperscript{*} | 10.5 ± 1.0 |

*Same letters indicate no statistical difference between samples in a column (Table S.1 – Supplementary Material).

on \( E\textsubscript{a} \) values for KAS method (Table S.1). Comparing the different samples, the incorporation of higher content of BC and GNP into the cellulose cryogel did influence the kinetic parameters, raising Ea and A values. Neves et al.\textsuperscript{16} studied kinetics degradation of microcrystalline cellulose and the \( E\textsubscript{a} \) value found was around 170 Kj mol\textsuperscript{-1} for KAS method\textsuperscript{16}, studied kinetics degradation of Pinus elliottii and the \( E\textsubscript{a} \) value found was around 180 kJ mol\textsuperscript{-1} for FWO method, Ali et al.\textsuperscript{28} studied kinetics degradation of coconut shell waste and the \( E\textsubscript{a} \) value found was around 100 kJ mol\textsuperscript{-1} for FWO method. We found, for CC sample (100% cellulose), \( E\textsubscript{a} = 119.6 ± 0.5 \) Kj mol\textsuperscript{-1} by KAS method, supporting the results trustworthiness summarized in Table 2. Its noteworthy that, the Tonset of both BC samples decrease around 30 °C in the DTG curves and the Ea values for both were higher, compared to CC samples, Tonset and Ea are not correlated. For instance, Tonset is determined in a specific point (DTG) and the Ea value is determined in a range of conversion degree. By observing Figure 3c and 3e, is possible to see that T onset was determined around 280 °C around 0.35 conversion degree whereas the Ea was determined in the conversion degree range of 0.2 to 0.7.

The plot of Friedman method (Figure S1) and KAS method (Figure S2) considering conversion degree range of \( \alpha = 0.2 – 0.7 \) for all samples could be found in the Supplementary Information. The second and third steps of a reliable kinetic degradation study, according to ICTAC, are the determination of the degradation model and the determination of the \( f (\alpha) \), respectively. The degradation model and degradation mechanism were determined statistically using an F-test tool based on previous studies\textsuperscript{12,22}, and the statistic results for the simulated curves (Figure S3) are shown in Supplementary Material. A reaction pathway for the vegetal fiber degradation model was the Waterloo’s degradation model, which states that all solid compounds decompose into volatiles and charcoal\textsuperscript{11,26}.

Firstly, all the samples were simulated using a one-step model (Figure S4), but a poor fit was obtained for all degradation models. Even though the samples appear to obey a single-step degradation due to its non-dependency of Arrhenius parameters with \( \alpha \) as aforementioned, a poor fit indicates that, at least, two degradation mechanisms are present\textsuperscript{12,13}. Apart from it, using the best single-step results, a two-step model and mechanisms were tested. Two-step degradation model was chosen based Benini et al.\textsuperscript{50}, Ali et al.\textsuperscript{11}, Pereira et al.\textsuperscript{51}, Hu et al.\textsuperscript{52} and Ornaghi et al.\textsuperscript{22}.

For the cryogel AC the most probable degradation model is \( A \rightarrow B \rightarrow C \) where: A seems to be cellulose and or lignin chains, B seems to be low molecular weight cellulose and/or lignin, and C: cellulose and/or lignin chars. For the cryogels produced using carbonaceous fillers (biochar and graphene nanoplates) the most probable degradation model is \( A \rightarrow 1 \rightarrow B \rightarrow 2 \rightarrow C \) where: A seems to be cellulose and or lignin chains, B seems to be low molecular weight cellulose and/or lignin, and C: cellulose and/or lignin chars and BC and GNP chars. Since two-step degradation mechanism was observed, two Ea values need to be reported: \( E\textsubscript{a1} = 141.7 \) kJ mol\textsuperscript{-1} and \( E\textsubscript{a2} = 100 \) kJ mol\textsuperscript{-1} for CC, \( E\textsubscript{a1} = 145 \) kJ mol\textsuperscript{-1} and \( E\textsubscript{a2} = 104 \) kJ mol\textsuperscript{-1} for CC50BC, and, \( E\textsubscript{a1} = 151.2 \) kJ mol\textsuperscript{-1} and \( E\textsubscript{a2} = 100 \) kJ mol\textsuperscript{-1} for CC50GNP, \( E\textsubscript{a1} = 180.3 \) kJ mol\textsuperscript{-1} and \( E\textsubscript{a2} = 124 \) kJ mol\textsuperscript{-1} for CC100BC and \( E\textsubscript{a1} = 191.2 \) kJ mol\textsuperscript{-1} and \( E\textsubscript{a2} = 130 \) kJ mol\textsuperscript{-1} for CC100GNP. The degradation mechanism for all samples was autocatalytic (Cn) followed by random nucleation (Fn) or autocatalytic (Cn or Bn). The results reported here corroborate with Ali et al.\textsuperscript{11}, Neves et al.\textsuperscript{12}, Ornaghi et al.\textsuperscript{22} and Benini e al.\textsuperscript{50}.

The thermal lifetime predictions of all cryogels were simulated using the \( E\textsubscript{a} \) values and degradation mechanism previously determined and the curves were simulated by one year of exposure at the 30-530 °C temperature range. This temperature range since thermal insulants can be exposed to a wide temperature range and based on TG curves (Figure 3). For a better visualization, was choose to analyze the mass consumption at 180°C (Figure 5) for all samples. The sample CC exposed for 1 year at 180 °C will lose around 15% of the mass, whereas the samples CC50BC, CC50GNP, CC100BC, and CC100NP will lose around 80%, 80%, 100%, and 90% of mass, respectively, at the same conditions as CC. This means that the incorporation of carbonaceous fillers into the cryogel increased the amount of mass degradation, become harmful in that sense. This behavior could be related to the fact that the sample AC has a certain amount of lignin harmful in that sense. This behavior could be related to the fact that the sample AC has a certain amount of lignin harmful in that sense. This behavior could be related to the fact that the sample AC has a certain amount of lignin harmful in that sense. This behavior could be related to the fact that the sample AC has a certain amount of lignin harmful in that sense. This behavior could be related to the fact that the sample AC has a certain amount of lignin harmful in that sense. This behavior could be related to the fact that the sample AC has a certain amount of lignin harmful in that sense. This behavior could be related to the fact that the sample AC has a certain amount of lignin harmful in that sense. This behavior could be related to the fact that the sample AC has a certain amount of lignin harmful in that sense. This behavior could be related to the fact that the sample AC has a certain amount of lignin.
4. Conclusions

Here we report the results of the study of the degradation kinetics of cellulose cryogels with the addition of carbonaceous fillers to verify the influence of these fillers on the degradation and lifetime of cryogels. Cellulose cryogels containing 50 and 100% of biochar and cellulose cryogels containing 50 and 100% graphene nanoplatelets were produced. The cryogel crystallinity index was affected by the presence of the carbonaceous particles, assuming higher values with the addition GNP. The incorporation of biochar to cellulose cryogels decreased its degradation temperature, while GNP increased. In the degradation kinetics the degradation mechanism present for all samples was autocatalytic (Cn) followed by random nucleation (Fn) or autocatalytic (Cn or Bn). In terms of thermal lifetime prediction, the incorporation of carbonaceous fillers to cellulose cryogels did not favor greater stability since pure cellulose cryogels exposed for 1 year at 180 °C lose about 15% of their mass, while samples containing BC or GNP even lose 80% or more of their mass. The results of this study shown that only cellulose biomass cryogels are more suitable to produce thermal insulators due to it higher thermal stability.

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Supplementary material

The following online material is available for this article:

- **Table S1** – One-way was performed on $E_a$ values for KAS method.
- **Figure S1** – Plot of Friedman method for all studied samples.
- **Figure S2** – Plot of KAS method for all studied samples.
- **Figure S3** – Simulated curves.
- **Figure S4** – Parameters were obtained after the nonlinear regression method through the thermal degradation mechanism. All fitting presented were R2>0.99 for the best fit.