# BIO-BASED CELLULOSE-BIOCHAR-PEG CRYOGELS FOR THERMAL INSULATION

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Unbleached cellulose from *Pinus elliotti* and polyethylene glycol (PEG) were used for the manufacturing of bio-based cellulose-biochar-PEG cryogels. The cryogels were prepared by the sol-gel method, where biochar was added to a cellulose/PEG suspension, and subsequently freeze-dried. Also, biochar from poultry little waste was employed as reinforcement, aiming to increase mechanical and thermal properties. The main results showed that, for cryogels with biochar (5.0 wt% in relation to cellulose) and PEG (5.0 wt% in relation to the cryogels mass), an increase of the compressive strength by about 30% was achieved. The thermal conductivity of the same samples with biochar reached similar results (0.041 W m<sup>-1</sup>.K<sup>-1</sup>). Therefore, the produced material has potential to be applied as thermal insulator as an environmentally friendly alternative, with the properties that meet the requirements for traditional thermal insulators.

Keywords: bio-based cryogel, cellulose, biochar, dynamic-mechanical properties

### INTRODUCTION

Among the factors related to climate change, energy consumption is one of the most relevant concerns, the civil construction sector being one of the highest consumers in this respect. According to the Energy Information Association,<sup>1</sup> it is projected that the energy consumption of commercial buildings, not belonging to the Convention on the Organization for Economic Cooperation and Development  $(OECD)^2$ , will represent about 64% of the energy consumption in 2050. Thus, strategies for greater insulation for better energy conservation and enhancement of sustainable energy strategies in the construction sector are needed.<sup>3</sup> With the gradual development and demand in materials for thermal insulation, traditional materials, such as polyurethane and polystyrene foams, do not meet the needs of society and industry due to their disadvantages of toxicity and non-renewability. In

this case, cryogels appear as an environmentally friendly alternative for such components designated for thermal insulation, also considered a revolutionary alternative to traditional petroleum-based thermal insulation materials.<sup>4</sup>

According to the IUPAC Gold Book, "Aerogel" is defined as "a gel comprised of a microporous solid in which the dispersed phase is a gas". Furthermore, its nomenclature may vary according to the drying method. For instance, when using lyophilization, the aerogel can be named as cryogel. However, among scientists, there is no consensus between these nomenclatures, often only the term aerogel being The research and development used. of aerogels/cryogels is driven by their extraordinary properties, such as low thermal conductivity (<0.05 W.m<sup>-1</sup>.K<sup>-1</sup>), low density (<0.1 g.m<sup>-3</sup>), high porosity (>90%), and surface area (>100 m<sup>2</sup>.g<sup>-1</sup>), Cellulose Chem. Technol., 58 (1-2), 91-99 (2024)

which make them attractive for applications such as thermal insulation in buildings, piping, home appliances, transportation, and aerospace engineering.<sup>5</sup>

Despite the aforementioned benefits in using aerogels/cryogels as alternative materials for thermal insulation, there are still some challenges that need to be surpassed for the application of such materials on industrial scale. For instance, Korhonen *et al.*<sup>6</sup> obtained cellulose cryogels and aerogels using NaOH-water solvent with freezedrying and drying with supercritical CO<sub>2</sub>, respectively. The results showed that the compressive modulus reached a maximum of 15 MPa for those crygels. Buchtová et al.<sup>7</sup> reached a maximum of 100 kPa in compression strength and no more than 10 MPa in compression modulus for aerogels prepared via dissolution-coagulation and different drying methods, using supercritical CO<sub>2</sub> (aerogels) or via freeze-drying (cryogels). In this tudy, cellulose of three different molecular weights was dissolved in an ionic liquid/dimethyl sulfoxide mixture and used. In fact, low mechanical response is an issue when these aerogels are designated for industrial application. For instance, some standard procedures, such as E1730-19, claims that a minimum of 206.8 kPa is required for a density lower than 41 kg.m<sup>-1</sup> for the use of foams in sandwich panels.8

Biochar (BC) is an alternative filler used as reinforcement in some materials. In a previous work, we reported that the use of 40 wt% biochar provided a 60% increase in the compressive strength of aerogels in relation to the control cellulose aerogel.<sup>9</sup> In addition to the benefits of using BC in composites, this bio-filler is a carbonrich material, produced from the pyrolysis of organic feedstock in the total or partial absence of oxygen. The thermochemical conversion of biomass for the production of BC is a common method and presents high efficiency in terms of product quality and yield.<sup>10</sup> Furthermore, this organic material, usually becomes more attractive due to its low cost, viability, abundance, and nontoxicity.<sup>11,12</sup> In addition to the use of fillers, according to Li et al.13 to extend cryogel applications, researchers ususally combine polymers (PAN fibers and PBZ membranes) and inorganic matter (carbon nanotubes and Fe<sub>3</sub>O<sub>4</sub> nanoplatelets) to form cryogels with improved properties, strong hydrophobicity, and good thermal insulating.

Therefore, the objective of this work was to develop cellulose-biochar-PEG crvogels. comprising a cellulose skeleton in combination with a water-soluble thermoplastic polymer (*i.e.*, polyethylene glycol (PEG)) and BC. PEG is an inexpensive polymer that possesses desirable properties, such as biocompatibility and biodegradability, well-suited for biomedical applications (bioconjugation, imaging, tissue engineering, etc.) due to its high solubility in aqueous media. Moreover, PEG can also be conjugated with drugs or attached to the surface of drug-encapsulating nanomaterials to augment in vivo stability and solubility and to reduce the clearance rate from circulation, thus optimizing drug efficacy. BC from poultry litter waste was chosen as the second nanofiller in this cryogel system as it has excellent mechanical properties, and a large amount of oxygen on the surface.

## EXPERIMENTAL

### Materials

The cellulose fiber used in this study was obtained from *Pinus elliottii*, supplied by the company Trombini (Fraiburgo – SC). Poultry litter waste (PLW) was used as biomass for biochar production, received from a farm in Antônio Prado – Brazil; it basically consisted of wood chips and sawdust. Polyethylene glycol (MM: 20000 g mol<sup>-1</sup>) reagent was purchased from Sigma-Aldrich S.A. and used as received.

# Production of bio-based cellulose-biochar-PEG cryogels

Figure 1 shows the production flowchart of biobased cellulose-biochar-PEG cryogels. Initially, the cellulose was mixed with distilled water at a concentration of 1.5% w/w. This mixture was then placed in a stone mill (Masuko Sangyo - model MKCA6-2J, Japan) for grinding the fibers. The grinding was carried out with the aid of an open rotor centrifugal pump to circulate the suspension, for a period of 5 h with a rotation of 2500 rpm. After obtaining the cellulose suspension, it was centrifuged for 5 min at 4500 rpm. The supernatant was heated to a temperature of 60 °C and then the PEG was mixed at a concentration of 5 and 10% w/w (in relation to the suspension of cellulose), based on our previous work,<sup>14</sup> until its complete solubilization (Suspension 1). The cellulose sediment was separated for further mixing.

Biochar was produced from poultry litter by the pyrolysis process, where approximately 100 g of poultry litter waste was placed in a benchtop reactor. The cylindrical quartz reactor operated under an atmosphere of nitrogen gas (N<sub>2</sub>) with a flow rate of 150 mL min<sup>-1</sup>. The oven temperature was then increased at a rate of 5 °C min<sup>-1</sup> until it reached 800 °C. The reactor

was kept at this temperature for 60 min (holding time), and then cooled, still with  $N_2$  flow, to room temperature. Total cooling time was approximately 10 h. After pyrolysis, the biochar formed was macerated to later be used in powder form.

To Suspension 1, biochar was added in concentrations of 5 and 10% w/w (in relation to the concentration of cellulose), based on our previous work,<sup>14</sup> to obtain Suspension 2, and kept under mechanical stirring for 5 minutes to homogenize the mixture. Then, Suspension 2 was mixed with the

sediment (cellulose), and mechanically stirred for 5 min. The suspension was sonicated for 5 min, frozen in an ultrafreezer at -80 °C for 24 h and then lyophilized in a lyophilizer (Liobrás – model LioTop L101, Brazil) for approximately 72 h. All equipment and more information about the processing parameters can be found in the work of Perondi *et al.*<sup>15</sup> Table 1 shows the nomenclature and concentrations of cellulose, PEG and biochar of cryogels, where the concentration.



Figure 1: Production flowchart of bio-based cellulose-biochar-PEG cryogels (Perondi et al.)<sup>15</sup>

Cravagal	Cellulose fibers	PEG	Biochar
Cryoger	(% m/m)	(% m/m)	$(\% \text{ m/m})^1$
CPB-1			0.0
CPB-2		5.0	5.0
CPB-3	1 4		10.0
CPB-4	1.4		0.0
CPB-5		10.0	5.0
CPB-6			10.0

Table 1 Nomenclature of bio-based cellulose-biochar-PEG cryogels

#### Characterization of bio-based cellulose-biochar-PEG cryogels

Apparent density was measured in accordance with ASTM D1622-08, the cryogel thickness and height were measured in triplicate using a caliper electronic Fowler – Model Pro-Max Electronic Caliper 54-200-777-1 (USA) to calculate the volume of the sample. The cryogel mass was then measured on an Ohaus®

AS200 balance (USA) and the apparent density ( $\rho_{criogel}$ ) was calculated by the ratio of the sample mass and volume.

The morphology of cryogenic fracture was analyzed by scanning electron microscopy (SEM, Tescan brand equipment – model FEG Mira 3 (Czech Republic)), coated with Au, and the acceleration voltage applied was 15 keV.

Thermogravimetric analysis (TGA) was performed in Shimatzu TGA-50 equipment (Japan) under the following conditions:  $N_2$  atmosphere, 50 mL min<sup>-1</sup> rate, and heating rate of 10 °C min<sup>-1</sup> from 30 to 800 °C.

Compressive strength was measured by compression tests following ASTM D695-15 standard. The tests were performed in a universal test machine  $EMIC^{\text{(B)}} - Model DL 2000$  (Brazil), with a compression speed of 1.3 mm min<sup>-1</sup> equiped with a load cell of 50 kN. The load necessary to reduce the thickness of the specimen by 50% of its initial thickness was measured and divided by the calculated cross-section area.

Dynamical-mechanical thermal analysis (DMTA) of the cryogels was performed using TA Instruments<sup>®</sup> Q800 (USA) apparatus, using a compression clamp. The temperature range was from -50 to 40 °C, mainly aiming to evaluate the glass transition temperature  $(T_g)$ , with oscillation responses at 1 Hz and heating rate of 3 °C min<sup>-1</sup>. The samples were conditioned in a temperature-regulated chamber by liquid nitrogen cooling. The DMTA measurement was also used to evalute the storage modulus (E'), loss modulus (E'') and damping factor (tan $\delta$ ) data.

### **RESULTS AND DISCUSSION**

The morphology of the bio-based cellulosebiochar-PEG cryogels was studied using scanning electron microscopy and can be seen in Figure 2 (a-c). The cryogels exhibited highly porous and interconnected structure, with cellulose fibers at the nanometer scale, due to the mechanical defibrillation process. The hydroxyl groups present on the surface of the fibers tend to form agglomerates due to their high contact surface.<sup>16</sup>

The results of apparent density, compressive strength and thermal conductivity of the cryogels are presented in Figure 3 (a, b and c). As can be seen, the concentration of biochar does not influence the properties tested, however the concentration of PEG presents changes, the concentration of 5% w/w of PEG showing the best properties. This can be explained by its higher apparent density, which increases its resistance to compression and thermal conductivity.

CBP cryogels had an apparent density from 0.073 to 0.130 g cm<sup>-3</sup> (Fig. 3 (a)), being dependent on the solids concentration (PEG), that is, the higher the solids concentration, the greater the apparent density. As seen by the statistical analysis presented in Figure 3 (a), the addition of biochar did not influence the relative density of the cryogels. This behavior was also reported previously.<sup>17,18</sup> The cryogels with higher PEG contents CBP-4, CBP-5, and CBP-6 presented apparent density above 0.120 g cm<sup>-3</sup>.

The solids concentration also influenced the compressive strength of cryogels, due to the increase in the apparent density of the cryogel, which makes it more rigid.<sup>19</sup> The higher the solids concentration, the higher the compressive strength (Fig. 3 (b)). Lazzari et al.<sup>17</sup> obtained the same behavior for the cellulose and biochar cryogel, reporting a compressive strength of 156 kPa for deformation of 70%, in the cryogel with 50 wt% of biochar. Luo et al.,20 who combined cellulose nanofibers with PVA and M-K10, obtained maximum compressive stresses of approximately 9.5 kPa for 60% strain, and 43.58 kPa for 80% strain. TPMA aerogels have the ability to recover their original shape after being compressed by a weight of 1000 g, being able to support  $3.3 \times 10^3$ times their mass.



Figure 2: SEM micrographs of bio-based cellulose-biochar-PEG cryogels at mag. 50 kx: (a) CBP-4, (b) CBP-5 and (c) CBP-6



Figure 3: Bio-based cellulose-biochar-PEG cryogels: (a) apparent density; (b) compressive strength; (c) thermogravimetric analysis: TG, thermal degradation profile as weight percent and DTG, derivative weight profile as weight percent; and (d) thermal conductivity (same letters indicate no statistical difference between samples in a column)

 Table 2

 Results of the analysis of thermogravimetry of bio-based cellulose-biochar-PEG cryogels

Cryogel	$T_{onset}(^{o}C)$	T <sub>peak</sub> (°C)	Residual mass (%)
CBP-1	387.17	410.12	3.1
CBP-4	380.52	410.19	3.0
CBP-5	372.76	409.18	0.5
CBP-6	373.41	409.54	2.5

TG and DTG curves (Fig. 3 (c)) show no mass loss in the region of 100 °C related to loss of moisture, as all the cryogels were oven dried before the test. The cryogels showed the same degradation behavior, with only a single mass loss event at 300-450 °C, referring to the pyrolysis of cellulose. As can be seen in Figure 3 (c), neither PEG nor Biochar has a great influence on the degradation of cryogels, the main decomposistion process starting around 180 °C for CBP-1 (182 °C), CBP-4 (180 °C), CBP-5 (181 °C), and CBP-6 (180 °C). Wan *et al.*<sup>21</sup> also related similar decomposition temperature of their cellulose and PEG aerogels around 180-200 °C.

The presence of the biochar and PEG in the bio-based cellulose-biochar-PEG cryogels causes a decrease of the  $T_{onset}$  and maintains  $T_{peak}$ 

temperatures (obtained by thermogravimetry derived from the curves), as can be seen in Table 2.

In spite of similar results, two differences in the thermal behavior can be highlighted: i) considering the temperature of 400 °C, a higher weight loss is presented by CBP-6, while a lower weight loss is verified by CBP-5. CBP-1 and CBP-4 showed intermediate behavior, ii) the residual mass showed the be lower for the CBP-5 compared to other cyogels. The faster weight loss can be attributed to the higher BC amount (that has lower thermal stability), as well as the lower residual weight loss due to total evaporation of the BC. Briefly, the lower the amount of BC, the faster the thermal degradation and the lower the residual mass at the final temperature. Porous materials, such as cryogels, exhibit the characteristic of having a thermal conductivity very close to that of stagnant air ( $0.025 \text{ W.m}^{-1}$ .K<sup>-1</sup>), precisely because their structure has over 90% porosity. For CBP cryogels, the conductivity ranged from 0.039 to 0.047 W m<sup>-1</sup> K<sup>-1</sup>. The small differences between the cryogels can be explained by the heterogeneous three-dimensional structure formed by the different sizes of ice crystals formed during the freezing of the gel and maintained after the freeze-drying. These results were also found in our previous works.<sup>9,17</sup>

The DMTA curves presented similar behavior for CBP-5 and CPB-6 cryogels (the only two tested). In spite of the differences observed in the storage and loss moduli, as well as in tan  $\delta$  curves, the values can be considered similar considering the y-axis scale (for E', the values were 45 and 48 MPa),<sup>22,23</sup> and consequently in E" and tan  $\delta$ . Also, the size (the lower the size the higher the maximum defect) of the samples cut to perform DMTA tests has an influence on the test results, since the aerogels comprise almost 90% air and some imperfections, such as edge curvature or small deformation of the inner cell, can occur. For this reason, the tests were not repeated. From the curves of E' (Fig. 4 (a)), it is apparent that the addition of the fillers has resulted in a decrease of the storage modulus, from 50 to 47 MPa, for CBP-5 and CPB-6, respectively. Usually, the incorporation of rigid particles tends to increase the storage modulus in the gassy region, due to the restriction imposed by the rigid particles in the soft matrix.



Figure 4: Dynamic-mechanical thermal curves: (a) storage modulus (E'); (b) loss modulus (E''); and (c) tan delta of CBP-5 and CBP-6

However, three main points have to be highlighted: i) biochar is not a rigid particle and hence the effect of the reinforcement would be more noticeable in the elastomeric region,  $^{24}$  ii) the aerogel has not enough interface to transmit the and tranfer stress received through the reinforcement to the matrix, because most of the material is composed of air, and iii) the agglomeration of the cellulose at lower temperatures tends to weaken the polymeric structure with higher temperatures. Hence, the reduction in the storage modulus with biochar can be attributed to some aggregation level of the biochar, which led to a softer material. A reduction of the storage modulus, about 40%, occurred from -45 to 35 °C, for both cryogels. This reduction is attributed to the glass transition temperature, in which an increase in the molecular

motion of the amorphous polymer chains promotes an expansion of the free volume and a decrease of the capacity to store energy.<sup>25</sup> This decrease is constant because the molecular motion increases contantly with temperature. For dense materials, such as composites, the glassy plateau tends to extend to higher temperatures, because more energy is required to deform the polymer chains,<sup>26</sup> contrary to aerogels, where most of the structure is composed of air.

When the ability to store energy is higher for a determined material, the ability to lose energy as heat is also higher. Below the glass transition temperature, the polymeric chains have not enough thermal energy to promote significant changes in the dynamic-mechanical response, hence no significant alterations in the E' curves are observed. With temperature, the polymeric chains start moving (according to the reptation theory), aiming to dissipate the energy received as heat. The higher the movement of the chains, the higher the space created (free volume) in the system.<sup>27,28</sup> Hence, if the sample needs to receive more energy to starts this cooperative motion, more energy is dissipated in the glass transition temperature (as can be observed in Fig. 4 (b)). This energy released is proportional to the previously received energy.

The tanð behavior (Fig. 4 (c)) of the cryogels varies only in the dissipation maximum and not in the peak position. These parameters give us an idea of the viscoelastic behavior of the aerogel, by dividing E" by E'. The temperature at tanð peak value of CBP-6 is lower than that of CBP-5 at -15 °C, which demonstrates that CBP-5 showed a lower damping factor compared to CBP-6. Table 3 presents some parameters calculated using DMTA curves. It can be noted that all parameters estimated are quite similar.

Table	3
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E'g (-45 °C) and E'r (35 °C), from storage modulus curves, E'' and Tg values from loss modulus curves, peak height (PH) and full width at half maximum (FWHM) from tan delta of cryogels



Figure 5: Schematic representation of the bio-based cellulose-biochar-PEG cryogels studied

Figure 5 shows a schematic representation of the CBP cryogels formation. First, the suspension was freeezed at -80 °C, where ice crystals are formed and the cellulose biochar is agglomerated. These agglomerations are very difficult to control and are maintaned in the final aerogel structure. Hence, for the same conditions, different CBP cryogel structures can be obtained, *i.e.*, of the same type, but disposed differently. In our case, many variables account for the DMTA results, including cryogel structure, biochar content, biochar dispersion, biochar agglomeration, among others. Our former studies<sup>17</sup> demonstrated that, independently of the material included in the CBP cryogels, the structure seems to not change significantly, because the freezing temperature is the same, altering only the type of the particles used. In our case, the most influencing factor is the cellulose content. As mentioned above, when freezing at -80 °C, the cellulose suspension tends to agglomerate, as ice crystals are formed. According to Ni *et al.*,<sup>29</sup> the mechanisms that contribute to the porous CBP cryogels formation are the ice crystal growth rate, nucleation rate, molecular entanglement, and sol structure. Variations in the pre-freezing temperature, PEG or biochar concentrations all had great influence on the morphology and size distribution of ice crystals and pores of CBP cryogels. In our case, as the freezing temperature and PEG content were the same, the factor that would have higher influence on the structure of the CBP cryogels is the biochar concentration (in the case of the DMTA curves).

# CONCLUSION

conclusion, the prepared bio-based In cellulose-biochar-PEG cryogels demonstrated a highly porous and interconnected structure, as observed in scanning electron micrographs. The addition of biochar did not significantly influence the apparent density of the cryogels, which was primarily dependent on the solids concentration (PEG). However, higher solids concentration led to increased apparent density and compressive strength, making the cryogels more rigid. Thermogravimetric analysis revealed a single mass loss event at 300-450 °C, attributed to the pyrolysis of cellulose, with minimal influence of PEG or biochar. The cryogels exhibited thermal conductivity close to that of stagnant air due to their high porosity.

Dynamic-mechanical thermal analysis indicated a reduction in storage modulus with the addition of biochar, attributed to the softer material resulting from potential aggregation of biochar. The glass transition temperature led to a decrease in storage modulus, showing a consistent reduction caused by increased molecular motion with temperature. The dissipation factor (tan $\delta$ ) demonstrated similar behavior for both cryogels, varying only in dissipation maximum. Schematic representation illustrated the complexity of the CBP cryogels' formation, emphasizing the influence of factors such as freezing temperature, PEG, and biochar concentrations on their structure.

comprehensive In summary, the characterization of the bio-based cellulosebiochar-PEG cryogels provides valuable insights into their structural, thermal, and mechanical properties. These findings contribute to the understanding of the interplay between components and processing conditions, laying the groundwork for further optimization and application of these cryogels in various fields.

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