

Aerogel from Sustainably Grown Bacterial Cellulose Pellicles as a Thermally Insulative Film for Building Envelopes

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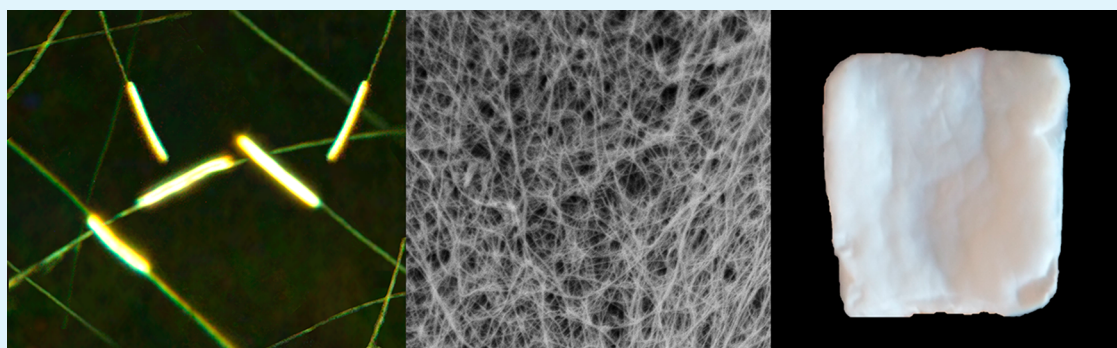
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ABSTRACT: Improving building energy performance requires the development of new highly insulative materials. An affordable retrofitting solution comprising a thin film could improve the resistance to heat flow in both residential and commercial buildings and reduce overall energy consumption. Here, we propose cellulose aerogel films formed from pellicles produced by the bacteria *Gluconacetobacter hansenii* as insulation materials. We studied the impact of the density and nanostructure on the aerogels' thermal properties. A thermal conductivity as low as 13 mW/(K·m) was measured for native pellicle-based aerogels that were dried as-is with minimal post-treatment. The use of waste from the beer brewing industry as a solution to grow the pellicle maintained the cellulose yield obtained with standard Hestrin–Schramm media, making our product more affordable and sustainable. In the future, our work can be extended through further diversification of food wastes as the substrate sources, facilitating higher potential production and larger applications.

KEYWORDS: cellulose aerogel, bacterial cellulose, insulation, building envelope, thermal conductivity, sustainable

INTRODUCTION

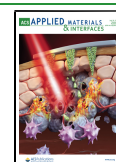
As the human population along with the demand for energy keep growing, the need for reducing energy consumption similarly increases. Residential and commercial building energy consumption amounts to ~40% of the total energy consumption in the United States and ~37% in the European Union.¹ The energy spent on heating and cooling buildings across the world is massive and should be reduced in the near future. Simply relying on regulations for new buildings will not cope fast enough with the present situation. Improving the overall insulative properties of existing edifices becomes mandatory to achieve such energy reduction goals. Understanding these issues, in 2014, the United States Department of Energy (DOE) issued a roadmap for emerging technologies regarding building envelope research and development, including the construction of new buildings and the retrofitting of existing buildings.² Therein, their performance target for retrofit products is to achieve a thermal resistance equivalent to an *R* value of 12 per inch of the material by 2025.

To address this goal, we investigated the fabrication of cellulose aerogels as a candidate to provide the required insulation in a product that is both sustainable and environmentally friendly. Cellulose is considered a green product as it is widely available and renewable, and is commonly extracted from wood pulp, cotton, and bacteria.^{3–5} Most recent applications of cellulose include 3D printed metamaterials,⁶ metal–organic frameworks (MOFs),^{7,8} and biomedical applications due to its biocompatibility^{9,10} and thermal insulative properties.^{11,12} Even with an increasing research interest in cellulose, most studies involve many processing steps such as cellulose extraction, purification, and

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post-treatments to obtain purified nanocellulose before fabricating a product.^{13,14} Considerable interest was found in directly drying bacterial cellulose pellicle into an aerogel after a few steps of solvent exchanges.¹⁵ This method streamlines the fabrication of cellulosic aerogels. Despite this very attractive idea, the ensuing material has so far not been bound to practical applications and has remained cost prohibitive for applications like building insulation due to the use of expensive growth media. A recent work compiled studies of alternative carbon sources and nutrients for growing cellulose.¹⁶ In particular, the use of beer brewing waste was demonstrated as an affordable alternative growth solution with high yields; however, the characterization of the ensuing materials did not focus on the properties related to thermal insulation of building envelopes.¹⁷

Here, we focused on developing cellulose aerogel insulative materials, directly produced by bacteria, that exhibited maximal thermal resistivity, while minimizing processing steps. We used waste from the beer industry to reduce the production cost of the aerogel while also optimizing parameters to maximize the thermal barrier properties. We explored the use of additives to tweak *in situ* the nanostructure of the aerogels. We thoroughly characterized the thermal properties of our samples and found them to satisfy the US DOE's next-generation building envelope insulation materials target of an *R* value of 12 per inch.² In addition, our fabrication approach is poised to both reduce production costs and lower the environmental impact of this technology by using waste as a nutrient source for the bacteria.

MATERIALS AND METHODS

Standard Hestrin–Schramm (HS) media was prepared as described in the literature.¹⁸ Briefly, the reference substrate final solution consisted of glucose (20 g/L), peptone (5 g/L), yeast extract (5 g/L), disodium phosphate (2.7 g/L), and citric acid (1.15 g/L). The pH of the HS solution was 6. The growth solution was derived from beer waste (BW) (fermented or not) obtained from local breweries in Boulder, Colorado. The acidic waste liquid is brown and contains sugars, proteins, flavor molecules¹⁹ such as acids and esters, various salts, and fibers, adding up to ~70 g/L of solid content. The exact composition varies somewhat depending on the exact waste used, but this did not seem to affect the results in terms of yield or properties of aerogel materials. After all, this waste is always based on malt and hop extracts. A few weight percent of ethanol can be present when fermented waste is used, which is consistent with a previous work.¹⁷

When preparing our initial source media, the pH was adjusted to 5.5 by adding a 2 M NaOH solution prior to autoclaving the solution for 30 min at 121 °C. Carboxymethyl cellulose (CMC) (15 g/L) was added to the growth medium before sterilization to yield thinner cellulose fibers. Once cooled down to room temperature, glucose was added to the solution immediately before inoculation with the bacteria. Different concentrations were tested. The optimal final glucose concentration in the BW-based solution was found at 10 g/L. For both the BW and HS media, the sugar solution was autoclaved separately under the same conditions and combined with the rest of the growth medium prior to use.

Gluconacetobacter hansenii (ATCC 53582) was purchased from ATCC and revived according to their suggested protocol. This particular bacterial strain has been selected as it is known to swiftly produce homogeneous cellulose pellicles.²⁰ The sample was rehydrated and transferred to a culture tube with 5 mL of HS growth media. The solution was kept in an incubator (26 °C and 60 rpm) for 5 days. The solution became slightly hazy, indicating successful bacteria revival. Agar culture plates were inoculated with the revived *G. hansenii* and incubated for 4 days. Single colonies were then collected and allowed to multiply for 5 more days in a 5 mL

culture tube in the incubator (26 °C and 60 rpm). The 5 mL solution was then injected in 1 L of either HS substrate or BW-based growth solution.

Cellulose production by *G. hansenii* is visible after a few days of incubation (26 °C static conditions) as a solid floating at the liquid air interface (Figure 1 a–d). Aerogel production from cellulose pellicles

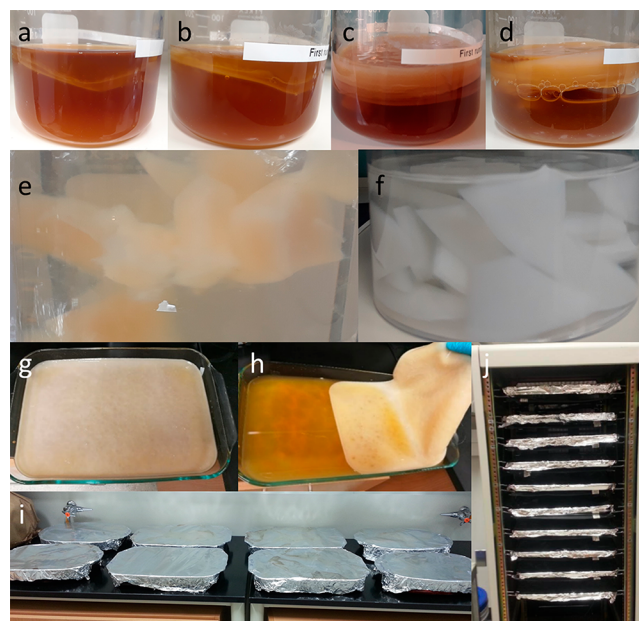


Figure 1. Production of a cellulose pellicle by bacteria using waste from the beer industry as a growth medium. First row: pictures of the growing pellicle close to the surface after (a) 3 days, (b) 7 days, (c) 10 days, and (d) 14 days. Second row: harvested pellicles are cut into pieces and washed first with (e) 1% NaOH at 80 °C then with (f) water. (g–j) Scaling up the cellulose production using larger pans. (g and h) Pictures of 0.1 m² fully grown cellulose pellicles. (i) Picture of 8 pans prepared for cellulose production. (j) Vertical racking of the pans to save space.

follows steps similar to previous literature reports¹⁵ and is described as follows. Pellicles are typically harvested after 3 weeks of growth (Figure 1h). The thickness of the pellicles varies between 1 and 20 mm depending on the nutrient concentration, the aspect ratio of the container, and the duration of the growth. To accelerate the washing step for the fabrication, the cellulose is cut into smaller pieces and washed with 1% NaOH at 80 °C for 1 h (Figure 1e). Then, the pellicles are washed with water until the pH remains neutral (Figure 1f). We explored scaling up the production of cellulose by increasing both the size and the number of pellicles produced at the same time (Figure 1 g–j). Up to 10 cellulose pellicles of ~0.1 m² (10 × 15 in.²) in size were produced in the laboratory at a given time.

Slowly, the cellulosic hydrogel's water is exchanged with ethanol by pure immersion. The solvent exchange is repeated five times at room temperature, with each step lasting for at least 6 h. The cellulosic alcogel is then dried via super critical CO₂ using a Tousimis Automegasamdri 915B critical point dryer. The chamber is filled with ethanol before placing the alcogel. After closing the lid, the system is cooled down and liquid CO₂ is injected. The ethanol present in the chamber is pushed out through the purge line as more CO₂ is added. Once most of the ethanol is purged, the machine is heated up to 40 °C, yielding a pressure of 1300 psi (8.96 MPa). Under these conditions, the CO₂ is supercritical. The remaining ethanol within the sample is exchanged with supercritical CO₂ and is collected at the bottom of the chamber due to an increased density. The system is left for several hours before releasing slowly the supercritical fluid (25 psi/min, 0.17 MPa/min) until the chamber is at atmospheric pressure. The cellulose is now an aerogel with a density ranging from ~6 to 28

mg/mL, depending on the growth conditions (duration, glucose concentration, use of CMC additive, etc.). To increase the density of the cellulosic aerogel, we plastically deformed the aerogels via uniaxial compression. The samples were squeezed uniformly across the sample using two wooden or plastic nonstick slabs covering the entire area of the sample before applying pressure. Using this method, densities up to 40 mg/mL were obtained.

The thermal conductivity, k , of aerogel films was measured using a comparative method,²¹ wherein the same heat flow is passed through a stack of aerogel and reference films of comparable area with the reference film facing the heat source and aerogel film facing the heat sink. Thus, by measuring the difference of temperatures at both surfaces of the films, the thermal conductivity was found as $k = k_0(\Delta T_0/\Delta T)(A_0/A)(d/d_0)$, where k_0 is the thermal conductivity of a reference film, d and d_0 are the respective thicknesses of the sample and reference, A and A_0 are the respective cross-section areas of the sample and reference ($A_0/A \approx 1$), and ΔT and ΔT_0 are differences between the temperatures at two surfaces of the sample and reference, respectively. As a reference, we used an aerogel with a comparably low thermal conductivity of $k_0 = 14 \text{ mW/(K}\cdot\text{m)}$ as confirmed by measurements using the guarded hot plate method in certified characterization facilities. The temperature of each film's surface was measured using the FluxTeq thermocouples and acquisition system.

Instrumentation. A thermogravimetric analysis (TGA) was performed in a N_2 atmosphere at 25–500 °C. TGA runs were performed in a Netsch STA 449 F1 Jupiter thermogravimeter with an alumina crucible at a heating rate of 10 °C/min. The thermal stability of the sample was calculated using a basic mass loss rate expression, dm/dt , and normalized to the total quantity of the lost mass.

Scanning electron microscopy (SEM) images were taken on a FEI Quanta 600 SEM at the National Renewable Energy Laboratory (NREL). The samples were sputtered with a thin layer ($<5 \text{ nm}$) of a Pt/Au mixture and imaged under 3 kV of accelerating voltage.

Fourier-transform infrared (FTIR) spectroscopy experiments were performed in the mid-infrared ($4000\text{--}500 \text{ cm}^{-1}$) region using a Nicolet 750 Magna FTIR spectrometer equipped with a Pike brand integrating sphere with a KBr beam splitter and an MCT/A detector.

UV–vis measurements were done on a Cary 500 scan UV–vis–NIR spectrometer equipped with a Labsphere DRA-CA-5500 integrating sphere.

Mechanical measurements were made using a DMA 850 from TA Instruments with a standard tension clamp attachment. The applied force and displacement of the clamp were recorded. The initial dimensions of the sample were used to convert the measurements to stress and strain using TRIOS software.

RESULTS AND DISCUSSION

Bacterial cellulose pellicles produced by *G. hansenii* cultured in HS media or the BW-based substrate look similar. The yield of produced cellulose per liter of culture medium after 3 weeks in HS media is 7 g/L while it is only 5.5 g/L for the as-received BW. The addition of 10 g/L glucose to the BW increased the yield to 6.5 g/L. A further increase to 20 g/L added glucose to the BW solution did not increase the cellulose yield. These results are in agreement with a previous research on the production of cellulose using beer waste with addition of glucose.¹⁷ From this, beer production BW-based waste medium appears to be a liable, economical alternative to HS medium for growing cellulose pellicles, as it can be obtained free of charge.²²

The studied bacteria directly excrete cellulose.²³ Several channels on their membrane produce a thin thread of cellulose nanofibrils. These nanofibrils aggregate into thicker ribbons due to hydrogen bonding (Figure 2a). When CMC is added to growth solutions, the aggregation of elementary fibrils is inhibited as the CMC molecules intercalate between cellulose fibrils (Figure 2b), prohibiting hydrogen bonding.²⁴ The native

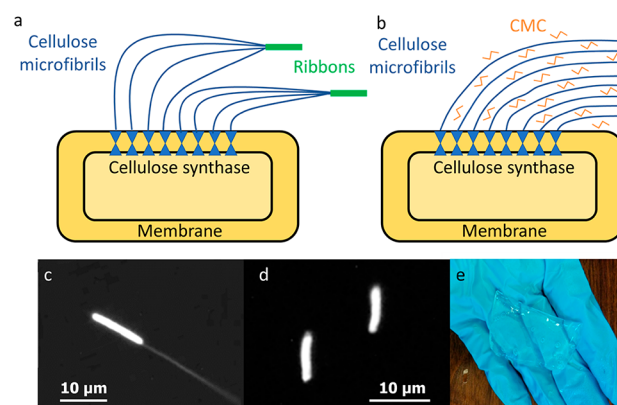


Figure 2. Schematics of cellulose production by a bacterium: (a) native cellulose and (b) cellulose produced with the CMC additive. In the absence of CMC, the microfibrils aggregate into ribbons, which can also further aggregate. CMC molecules intercalate between elementary fibrils through hydrogen bonding, preventing the aggregation of fibrils into ribbons. Dark-field microscopy images of bacteria producing cellulose (c) without and (d) with CMC. The thinner thread of cellulose (d) could not be optically resolved. (e) Picture of a transparent cellulose pellicle obtained with the CMC additive.

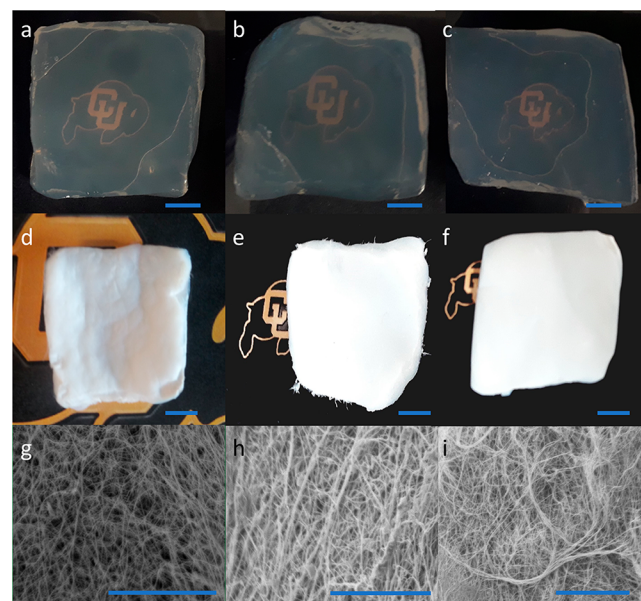


Figure 3. Cellulose pellicles grown with 1.5 wt % CMC additive yielding different densities once dried, depending on when the bacteria cellulose was harvested (first column, 7.2 mg/mL; second column, 9.4 mg/mL; third column, 11 mg/mL). Wet pellicles (a, b, and c) are transparent due to the thinner cellulose fibers and refractive index matching with water. The scale bar is 1 cm. After drying, the aerogels (d, e, and f) are opaque and flexible and (in lateral dimensions) measure $\sim 5 \times 5 \text{ cm}^2$. The scale bar is 1 cm. Corresponding SEM images (g, h, and i) of cellulose aerogels (d, e, and f, respectively) show a reduced thickness of the fibers due to the addition of CMC during growth. The scale bar is 5 μm .

production of cellulose by *G. hansenii* was imaged via dark-field optical microscopy (Figure 2c). However, in the presence of CMC, the thinner threads of bacterial nanocellulose could not be optically resolved via dark-field imaging (Figure 2d). As the bacteria were moving under the microscope and their primary motion mechanism requires the production of cellulose,^{25,26}

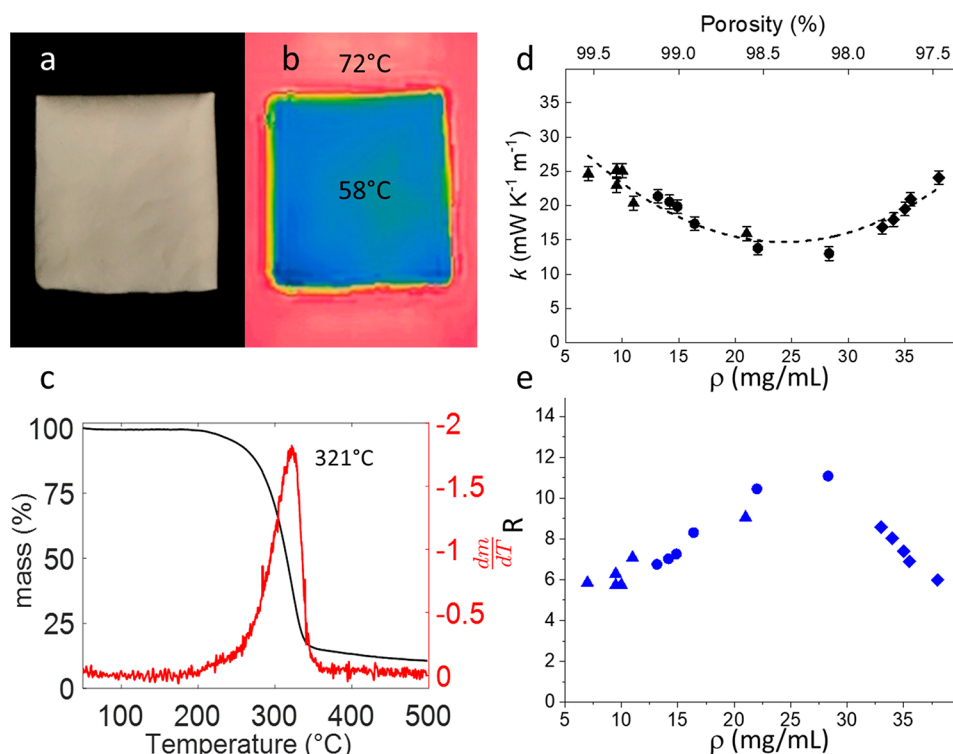


Figure 4. (a) Conventional photograph of a $\sim 4 \times 5$ cm² cellulose aerogel and (b) an infrared image of the aerogel (blue) on top of a hot surface (pink, 72 °C). The blue color indicates that the surface of the film remains cold (58 °C), qualitatively demonstrating the thermal insulative properties of the material. (c) Thermogravimetric analysis showing the thermal stability of the cellulose up to 230 °C and a maximum dm/dT at 321 °C. The cellulose aerogel characterized here was heated to remove moisture (~ 8 –10% of the initial weight) before performing the TGA experiments. Quantitative characterization allowed the measurement of (d) the thermal conductivity and (e) the R value per inch of the material versus the density or the porosity of the cellulose aerogel. Solid circles and triangles show the characteristics of cellulose without and with CMC, respectively. Solid diamonds represent the properties of samples having increased densities from uniformly squeezing cellulose samples without CMC.

we can confirm the production of cellulose with a reduced diameter due to CMC's addition. Cellulose hydrogel pellicles obtained with CMC additive are transparent (Figure 2e), consistent with the reduced light scattering and smaller diameters of its constituent nanofibers.

The transparency of cellulose pellicles grown in the presence of CMC is directly linked to the thinner cellulose constituting the pellicle. Furthermore, the pellicle density was lower when CMC was present. Regardless, the transparency did not persist once the pellicle was dried (Figure 3). Under optimal conditions, supercritical drying prevents hornification and shrinkage of the pellicle. The loss of transparency here is mainly explained by an increase of the refractive index contrast between the cellulose material and air, as compared to the much smaller contrast in the case of hydrogels. Three transparent pellicles harvested at different times yield different densities once dried (7.2, 9.4, and 11 mg/mL). SEM imaging of the aerogels shows the disordered cellulose fiber network whose diameter are in the tens of nanometers and can be as small as ~ 10 nm (Figure 3g, h, and i). These dimensions are in agreement with previous work using CMC²⁷ and are much smaller than within the native cellulosic aerogel.¹⁵ The absence of bundled fibers on the micrographs also confirms the very limited extent of hornification, if any, during the drying process. On the contrary, if hornification is of interest, the use of less polar solvents as intermediates, instead of ethanol, could be a lever to control the bundling of the nanofibers and thus

allow the tuning of the light scattering properties of the final sample.

The qualitative thermal characterization of our aerogels is shown on Figure 4a and b. The cellulose aerogel is placed over a hot surface (72 °C), and both traditional photography and infrared (IR) thermographs are shown. On the IR image (Figure 4b), the film remains blue (58 °C) while the hot back plate is pink, showing the relatively large difference in temperature between the two surfaces. The thermal stability of the film was assessed using TGA (Figure 4c). The mass stays stable with temperature up to ~ 230 °C where a drop is observed as the cellulose starts to degrade. The measured weight-loss rate is maximal at 321 °C. These results are comparable to published literature data, as expected for a pure cellulose sample.²⁸ An outgassing pretreatment at 60 °C was performed before recording the thermogravimetric data. During that process, moisture and adsorbed molecules are removed from the sample. Up to ~ 8 –10% of the total mass is removed with degassing, consistent with a previous work.²⁹ The outgassing pretreatment at 60 °C is an advised procedure for the maximization of the thermal insulation and allows for better durability of a product. This pretreatment was utilized before each thermal conductivity characterization for our samples reported in this work. The quantitative analysis of the thermal properties of the films was made using heat flux sensors (see Materials and Methods for details). The thermal conductivity (Figure 4d) and the R value per inch of material (Figure 4e) are given as a function of the measured density of

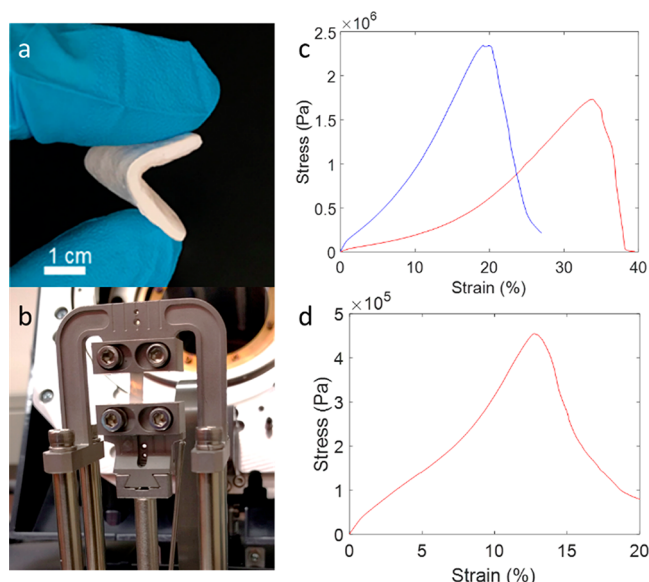


Figure 5. (a) Picture showing qualitatively the flexibility of a cellulose aerogel. (b) Picture of the device used for the mechanical analysis (DMA850 from TA). A cellulose aerogel is attached to the test clamp and locally appears translucent as it is being thinned and torn upon an applied tension. (c) Typical examples of standard pull results for a regular cellulose aerogel. During the measurement, the cellulose fibers are first aligned, and then they are elongated. Finally, they are torn in succession without showing catastrophic failure. The blue curve corresponds to a sample where the fibers were initially more aligned than in the sample corresponding to the red curve. (d) Measurement for a cellulose aerogel with a CMC additive of a similar density shows a weaker response while maintaining a similar maximal elongation.

the cellulose aerogel. The thermal conductivity includes contributions from gas conduction within the pores and across the networked cellulose fibers and emissivity-related contributions (we note that the contribution due to thermal-range emissivity can be disregarded for these materials at ambient temperatures). When the porosity is too high, the thermal energy transfer through gas conduction within the pores is significant, yielding a higher thermal conductivity. In that sense, smaller pores are preferred. However, when reducing the

pore size by increasing the density of fibers, the contribution of the latter to the thermal conductivity increases. It follows that minimal thermal conductivity is achieved when the competing factors of both the pore size and density of fibers are optimized. The optimum density is found at densities around 25 mg/mL, where the conductivity could be assessed to be as low as $k \approx 12\text{--}13 \text{ mW}/(\text{K}\cdot\text{m})$. The corresponding R value per inch is close to 12, meeting the DOE's 2025 performance target for emerging building envelope technologies.² The lowest measured value obtained was 13 mW/(K·m) for a sample whose density was measured to be 28 mg/mL. To the authors' knowledge, this is the lowest thermal conductivity reported for a cellulose aerogel.^{12,30,31} Standalone, these aerogels already present excellent insulation properties, but they would further outperform competing materials when embedded in multilayer insulation blankets (MLI).^{32,33} Briefly, within this envisaged embodiment of a building insulation material, our cellulose aerogel would be encapsulated between radiation reflective materials, such as a metal foil or films with metallized coatings, to reduce the radiant heat transfer of our system. The system can be more efficient when multiple alternating layers are used. Although demonstrating this is outside of this present work, we hypothesize that, overall, the thermal insulation would be enhanced, and the cellulose aerogel would be protected in this implementation. In particular, fire protection of the cellulose aerogel is a major concern and could be mitigated through encapsulation with specific films, such as multilayer polymer metal laminates.³⁴

Cellulose aerogels can easily be handled by hand and are quite flexible (Figure 5a). Their mechanical properties under tension were characterized using a DMA 850 from TA Instruments with a standard clamp (Figure 5b). Rectangle-shaped samples, ~6 mm wide and ~10–20 mm long, were cut using a razor blade. Characteristic stress versus strain curves are given for a native cellulose aerogel (Figure 5c) and a CMC-modified cellulose aerogel (Figure 5d). All curves show an initial regime where the fibers are aligned along the pulling direction. The initial Young's modulus E can be as low as 10–20 kPa. Then, the slope steepens as the fibers are pulled ($E \approx 100\text{--}150 \text{ kPa}$). The randomness of the cellulose network creates a variety of responses, and a maximum elongation

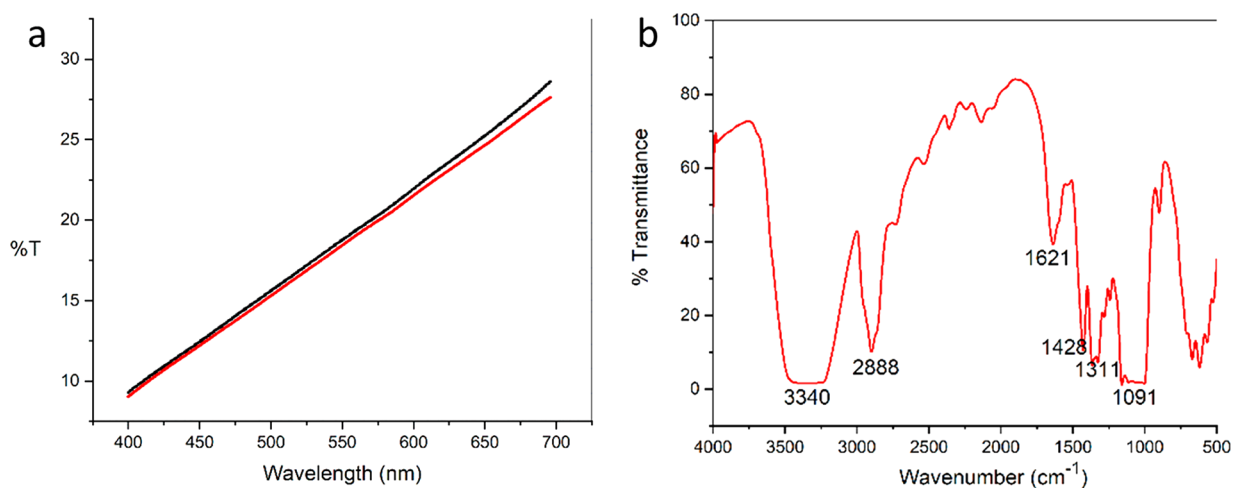


Figure 6. (a) Low-density cellulose aerogel visible transmission spectra showing ~20% of scattered transmission at 550 nm. Both the total transmission (solid black curve) and scattered transmission (solid red curve) are plotted. (b) FTIR measurement of the transmittance of a low-density cellulose aerogel.

before failure up to >30% elongation was measured. The cellulose aerogel with the CMC additive consists of thinner fibers, so they are less stiff than native ones ($E \approx 50$ kPa for the second regime). Even though cellulose aerogels are not tough materials, these results show they can be handled without risking film tearing, confirming the potential of bacterial cellulose as an insulative material for building envelopes. In addition, they are easily cut to any size and shape with a razor blade or a utility knife.

The white appearance of our cellulose aerogel is due to strong Mie scattering by its porous network structure. When the cellulose aerogel density is sufficiently low, $\sim 20\%$ of the visible light can be transmitted through as scattered transmission (Figure 6a) while it maintains a low thermal conductivity, similar to or lower than air. Sandwiching such cellulose aerogels between glass panes in an insulating glass unit (IGU) can provide appreciable diffuse light in applications such as sky lights, daylighting, and in various privacy windows while reducing solar heat gain and maintaining superior thermal insulation. The window will not heat up as the light is not absorbed but rather scattered. Looking beyond hot climates, this solution could be also useful for greenhouses where light needs to be spread equally on all the plants.³⁵ The FTIR spectrum shown in Figure 6b is typical for cellulose-based materials. The total absorption at around 1000 cm^{-1} indicates that the porous material would absorb mid-IR light from the blackbody emission of objects at room temperature. Then, because of the low thermal conductivity of the aerogel, the energy would be reemitted and reabsorbed multiple times but effectively reflected backward rather than penetrating through the aerogel film thanks to the aerogel's porous network. Overall, the transmission of this mid-IR energy linked to the radiation of an indoor object is expected to be low, and most of it should be reflected toward the inside of the building; however, the metalized coatings and metal foils briefly discussed above can be used to further reduce the emissivity contribution to the thermal barrier behavior of our materials.

CONCLUSIONS

In this work, we report the bacterial production of cellulose pellicles as insulative materials for building envelope applications. *G. hansenii* natively produce cellulose as part of their motility process. When grown in large colonies, the bacteria weave in concert a porous network of intertwined cellulose fibers, forming a nanoporous extracellular matrix. This cellulose pellicle, once harvested and dried with supercritical CO_2 , results in an aerogel. A considerably low thermal conductivity of $13\text{ mW/(K}\cdot\text{m)}$ was measured on native cellulose aerogels. This performance shows that our material is suitable for next generation thermal barriers for building envelopes. We also modified our pellicles using a CMC additive during the growth stage to keep the cellulose fibers thin, which could be of interest to control different properties of aerogel materials depending on the needs of specific applications. For example, the increased accessible area obtained with the thinner fibers could become useful in imparting hydrophobicity on aerogels through various surface modifications. One extra advantage of that CMC-enabled aerogel material is it can be cut to size but also sewn into larger pieces. Mechanical and thermal gravimetric characterizations confirmed the real potential of this material for the building envelope insulation industry. In particular, cellulose aerogels could be used in multilayer insulation blankets to not only

further increase the thermal insulation of the material but also add fireproofing properties. We showed that a substrate medium based on the waste from brewing beer yields a cellulose output similar to relatively expensive HS media while also allowing the optimization of the mesoscale structure and tune density needed to maximize thermal barrier properties. This strategy based on recycling waste not only reduces the cost but also makes the production sustainable. We expect to see other sources of waste, especially from the food industry, that perform as well as the beer waste we used for this research, which is one future research avenue to be pursued.

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Notes

The authors declare no competing financial interest.

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