A journey with bacteria: from waste to nematic colloids & gels & to smart windows

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Windows & energy: not a simple problem

- 20% building energy is lost through windows
- $500-$1000 loss per household each year
- Globally, comparable to 50% of energy from coal-based electric power plants

http://www.blindalley.com
Thermos & a triple-silver, triple-pane solution

→ Heat exchange: emission & thermal conduction
→ Silver coating to reflect radiation;
→ Vacuum between walls to minimize the thermal conduction;

→ What if all windows in US were triple-pane, vacuum, with triple-silver coatings?
→ Carbon dioxide emission reduction by about 70 millions tons per year [1]


• Very expensive,
• Tinted (not fully transparent)
• Hard to install, often structurally incompatible
• Do not fully solve the problem…
What would be ideal?

→2 problems – thermal conduction (~60%) & IR emission (~40%)

Replace or retrofit glass with a material that has:
→Perfect thermal insulation
→Perfect visible transparency
→Infrared reflectivity, ideally tunable to be different depending on exterior T
→Solar heating in IR good in winter but not during summer

Ideal spectra for summer
Ideal spectra for winter

Such materials do not exist...
Aerogels from Liquid crystals of cellulose?

→ Aerogels have low thermal conduction;
→ Made from disordered networks of silica colloidal nanoparticles (<1% solid);
→ Non-transparent in visible;
→ Emissivity in IR barely altered
Magic (statistical physics) of self-assembly

- Cellulose nanorods (4-6 nm diameter, 2-3 microns long)
- Free energy is minimized in the LC phase
Properties of 6.5-inch cellulose aerogels so far

As a thermal barrier on cold/hot surfaces

Note: transmission better than that of 92% of glass due to lower effective refractive index

<table>
<thead>
<tr>
<th>Aerogel Parameters</th>
<th>Measured value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Visible Light Transmission</td>
<td>96.6%</td>
</tr>
<tr>
<td>Haze</td>
<td>2.8%</td>
</tr>
<tr>
<td>Color Rendering Index</td>
<td>0.90</td>
</tr>
<tr>
<td>Thermal conductivity</td>
<td>11.5-13.5 mW/K/m</td>
</tr>
<tr>
<td>U value</td>
<td>~0.6 BTU/sf/F/hr</td>
</tr>
</tbody>
</table>
Haze: physical origins

→ haze is a function of particle size $r_0$ relative to a wavelength $\lambda$ of light
→ shorter (blue) wavelengths are scattered more & longer (red/infrared) less

$r_0 << \lambda \rightarrow$ Rayleigh scattering

Rayleigh scattering is strongly color selective $I \sim \lambda^{-4}$

$r_0 \approx \lambda \rightarrow$ Mie scattering

Hazy day
Haze & Scattering in Cellulose Aerogel

→ Scattering due to imperfections of the surface or nanoporous network
→ Macropores (≥100 nm) are responsible for Mie scattering
→ Nanopores (<50 nm) are responsible for Rayleigh scattering

SEM image of aligned aerogel

aerogel consist of fibrous skeletons and pores

→ Strategy for reducing haze:
→ Very thin 4nm nanofibers and <50 nm nanopores
Experimental Haze Characterization

ASTM D1003 is the accepted standard for haze measurements.
Bacterial workforce to make it inexpensive

→ $5 \times 10^{30}$ bacteria on Earth

→ Acetobacter xylinus
→ Consume food/beer industry waste
→ Produce cellulose nanorods

Beer “wort” from local breweries

Nanocelulose production by bacteria

- Autoclave to sterilize, introduce *Acetobacter xylinus* and wait for cellulose growth!
Large Scale Bacterial Cellulose Growth

Kilograms of nano-cellulose in the lab produced with ease!
Production of aerogel by bacteria

Dark field microscopy of *a. hansenii* at work

Schematic of *acetobacter* producing cellulose

Cellulose microfibrils stick together via hydrogen bonding to make cellulose fibers

- Thick cellulose fibers are one of the sources for strong scattering and haze in aerogels
- Preventing hydrogen bonding between microfibrils can result in producing of cellulose fibers of smaller diameters

*A. Xylinum* at work

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*Brown et al., PNAS 73, 4565 (1976)*
Production of aerogel by bacteria

- Sodium carboxymethyl cellulose (~1.5%) is added to a culture solution to prevent hydrogen bonding between cellulose fibrils.

A. xylinum bacteria with a thick cellulose fiber before adding SCC

A. xylinum bacteria after adding SCC

Thin cellulose fibrils are not visible
Bacterial Cellulose Aerogel

Acetobacter Hansenii
- About 1g/L/week
- Highly pure
- Opaque, high concentration pellicles

Minimally processed cellulose aerogel directly made from a cellulose bacterial biofilm pellicle and grown by *Acetobacter hasenii*

- Cheap, Large Scale Production
- Green production
Bacterial Cellulose Aerogel

- Lower the fabrication cost;
- Green fabrication process;
- Selected Finalist of NASA iTech.

Hydrogel

Alcogel

Aerogel

Sodium carboxymethyl cellulose

Cellulose microfibers

Cellulose II

Cellulose synthase

Cysteamin monomers

Lipopolysaccharide envelope

1 cm

1 cm

75°C

55°C
CNF aerogel via polysiloxane

Principle:

Functionalized CNFs + Polysiloxane precursor

Liquid crystalline CNF aerogel obtained by polysiloxane crosslinking
From fluid-like to solid liquid crystal film

Cellulose nanorods

Negatively stained TEM using phosphotungstic acid

→ Ordered colloidal LC -> hydrogels -> organogels -> aerogels...

→ Liquid crystal phase at <.5% by vol.
→ CNF gels via polysiloxane crosslinking
→ Flexible transparent aerogel
Manufacture of cellulose aerogels

1. Raw cellulose (Bacterial cellulose)
2. Nanofibers (TEMPO-mediated oxidation)
3. Surface modification (quaternary amine)
4. Critical point drying
5. Polysiloxane
6. Acetic acid
7. Surfactant
8. Urea
9. Hydrogel
10. Alcogel
11. Aerogel
12. Age at 60°C for 3 days
13. Wash with water and solvent exchange to isopropanol
14. Ambient drying

15. Raw cellulose (Bacterial cellulose)
16. Nanofibers (TEMPO-mediated oxidation)
17. Polysiloxane
18. Nitric acid
19. Surfactant
20. TMAOH
21. Hydrogel
22. Alcogel
23. Organogel
24. Aerogel
25. Age at 80°C for 3 days
26. Wash with water, methanol and solvent exchange to isopropanol
27. Solvent exchange to heptane
28. Ambient drying
Liquid crystalline order within aerogels

→ Birefringent because of the ordered internal structure of nanofibers
→ Liquid crystal aerogel with the “frozen” order
Mechanical Robustness, Flexibility & Hydrophobicity

Mechanical robustness & flexibility

6.5” (diagonal), 2.5 mm thick

Hydrophobicity
Fabrication of aerogel using sustainably-derived cellulose

Cellulose aerogel from bacterial cellulose produced from beer wort waste

→Note: transmission better than that of 92% of glass!

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Parameters | Measured value |
---|----------------|
Visible Light Transmission | 96.6%          |
Haze             | 2.8%           |
Thermal conductivity of aerogels

Thermal conductivity $k$ measures the heat conducting capability of a material:

$$Q = -k A \Delta T$$

where $Q$ is the heat flow, $A$ is the cross-sectional area, and $\Delta T$ is the temperature difference between the hot and cold sides.

$$k = \frac{QL}{A \Delta T}$$

The dimension of $k$ is $\text{W/Km}$.

Ultra-low thermal conductivity

→ Measurement challenge: laser flash approach – conductivity too low to be accurate

http://thermalanalysislabs.com

→ High-accuracy Heat Flow Meters (Japan, Canada, USA)
→ For specially prepared samples to further boost accuracy
→ Comparative/reference high-accuracy measurement of thermal conductivity

→ Thermal conductivity of non-transparent aerogels <10mW/(km) achieved in past
→ We achieved & measured 11.5 mW/(km) in transparent aerogels!
Methods for thermal conductivity measurements

- **Guarded Hot Plate (GHP)** method is the most optimal for measurements of small $k$!

- **Transient Plane Source**: $k$-range (W/mK) 0-2
- **Modified Transient Plane Source**: $k$-range (W/mK) 0-100
- **Laser Flash Diffusivity**: $k$-range (W/mK) 0-500

References:

Thermal conductivity measurements: Guarded Hot Plate method

- Guarded Hot Plate method using a heat flow meter HFM 436: Kyoto (Japan)

  - Requires large samples
  - High sensitivity to small $k$!!!

Measurement of thermal conductivity: comparative/reference method

Knowing the thermal conductivity $k_2$ of the reference material one can find the thermal conductivity of the sample.

\[ Q_1 = k_1 \frac{A_1}{L_1} \Delta T_1 \quad Q_2 = k_2 \frac{A_2}{L_2} \Delta T_2 \]

\[ Q_1 = Q_2 \]

\[ k_1 = k_2 \frac{A_2}{A_1} \frac{\Delta T_2}{\Delta T_1} \frac{L_1}{L_2} \]

Measurement of $U$-value: comparative/reference method

$U$-value measures the rate of heat transfer

$$Q = UA\Delta T$$

$$U = 1/R$$

The lower $U$-value, the better ability to resist heat conduction

$$[U] = \left[ \frac{W}{Km^2} \right] = \left[ \frac{BTU}{^\circ F ft^2 hr} \right]$$

$$U_1 = U_2 \frac{A_2}{A_1} \frac{\Delta T_2}{\Delta T_1}$$
Measurement of thermal conductivity: comparative/reference method setup

Temperature controller

Hot stage

Infra-red FLIR camera imaging
Measurement of thermal conductivity: comparative/reference method

Standard: polysiloxane $k_2=0.013$ W/mK*

Sample: aerogel film

$$k_1 = k_2 \frac{A_2 \Delta T_2}{A_1 \Delta T_1} \frac{L_1}{L_2}$$

- Quick and flexible
- Can measure small area samples

*G. Hayase et al., Appl. Materials & Interfaces 6, 9466 (2014)
*G. Zu et al., Chem. Mater. 30, 2759 (2018)
AIR FILMS heat transfer parameters

Heat transfer parameters measured with a comparative method

- Quick and flexible
- Can measure small area samples
- Samples under different conditions, chemistry and composition
Cellulose Aerogel on the window

- 6.5” (diagonal), 2.5 mm thick;
- Cold outside, picture taken from inside;
- The window pane had to be thoroughly cleaned to match low-haze characteristics of our aerogel films!

→ Thermal conductivity 2.5 times lower than that of air!
→ Thermal superinsulation!
Ambient drying & scaling cellulose aerogels

Colloidal dispersion

Hydrogel

Heptane gel

Ambient dried aerogel

Acrylic mold with silicone rubber spacer

4" × 5" × 3mm

1m² × 3mm
Facilities for fabricating meter-square scale aerogels

Home-built curing system

Thermal barrier

Precursor solution

Glass mold

Metal sheet

Heating band

Thermal barrier

Heating bands (2 kW)

m² glass mold with 3mm-thick spacer

1.1m
Facilities for fabricating meter-square scale aerogels
Fabrication of meter-square scale aerogels

Pumping the precursor solution

m²-hydrogel

m²-hydrogel in the water tank
We developed a safe way to scale up (together with EHS and Fire marshall)
Characterization of square-foot composite aerogels

- Composite aerogel
- Thermally insulating
- Visible transparent

Glass container

60°C water

Ice water
Flexible!

Transmission: 95.3%

Haze: 1.9%
Durability?

- Cellulose is hydrophilic & hygroscopic
- Durability challenge?
- Nanostructure + chemical surface modification & additives: super-hydrophobicity achieved!
- UV, humidity, soaking, baking…
- Super-durability achieved!

Water is repelled from the aerogel surface

24h at 80°C, 80% humidity, the intense under UV

500W Hg UV bulb

Visible Transmission after durability testing: no change detected
Haze after durability testing: only 0.6% change

Thermal Conductance after durability testing: less than 1.7% change
Advanced Fenestration Durability Analysis

NREL maintains multiple systems to perform controlled weatherization and exposure testing

Differential Thermal Cycling Unit

Solar and Thermal Weatherization

Thermal Cycling Stress Testing
• Highly insulating windows including framing

Controlled Solar and Thermal Exposure
• Materials and assembly durability
• Dynamic window technologies

See Also:  http://www.nrel.gov/pv/performance_reliability/indoor_testing.html
Differential Thermal Stress Testing

NREL’s DTCU is capable of controlling the temperature and RH independently on both sides of a fenestration sample, or wall section at the same time.

Sample Temperature Range: -50°C to 110°C
Relative Humidity: 5–95%
Thermal ramp rate maximum of 2°C/min
Sample Size Maximum: 45” x 45” x 8”

The DTCU is installed in the Optical Characterization Lab
Dynamic Window Durability Testing

Atlas XR260 Weatherometer

Standard for ASTM 2141-14
Absorptive Electrochromic Durability Testing

Supporting development of other dynamic IG technologies.

Environmental Conditions
Irradiance = 1 Sun ASTM AM 1.5
Temperature: -10°C to 60°C (Ambient)
Optimized climate-dependent spectral transmission?

Ideal spectra for summer

Ideal spectra for winter

→ Perfect visible transparency
→ Infrared reflectivity, ideally tunable to be different depending on exterior $T$
→ Solar heating in IR good in winter but not during summer

→ Can we do it with nano-cellulose liquid crystals again?
Imparting low-e properties onto aerogel films

- Single film only reflects radiation of same handedness satisfying Bragg’s law (LCP)
- Sandwiching films & nematic aerogel doubles reflection

Biomimetic Photonic Structure

Single Photonic Layer

Sandwiched Photonic Layer

- All cellulose-based self-assembled film
- Flexible, scalable fabrication
Modeling three-layer helicoidal films

Parameters of the multilayered film

- Thickness of the films
  CLC:NLC:CLC → 150μm:2690μm:150μm
- Pitch of cholesteric $p=6.4\mu m$
Scalable Production of Cellulose Nanomaterials

Cotton Cellulose
Bacteria Cellulose
Hard, Soft Wood Pulp
Microcrystalline Cellulose

H$_2$SO$_4$
45°C
Purify

+ Commercial CNCs (e.g. Cellulose Lab)

Optimizing the Cellulose Nanocrystal Reaction

- Continuous sonication reduces reaction time (8h → 2h)
- Large-scale centrifuge facilitates additional centrifuge cycles, reduces dialysis time (3d → 2d)
- Almost half as much acid needed (as presented by Vladyslav)
Low-e photonic layers with designable IR reflection to optimize depending on climate
Color Rendering

Following ISO Standard 9050:2003

Color rendering: how color of an object appears to human eyes and how well subtle variations in colors are revealed.

$R_a = 95\%, \text{ CNF aerogel}$

$R_a = 84\%, \text{ CNC-based low-E film}$
Cellulose nanorod aerogel films enable disruptive smart window film technology

- Transparent in visible, IR-reflective
- Thermally insulating
- Flexible, mechanically robust
- Inexpensive
- Retrofitting & new installed products

- Self-assembly of cellulose nanorods derived from the waste
- Cost-effective manufacturing of ordered aerogels (under $5 per square foot)
- Large-scale production of encapsulated flexible AIR FILMS
Applied products for retrofitting

**Key phase III goals:** Further improve parameters, scale to square meters, develop pilot production approach, more durability tests

### Prototype Target Table

<table>
<thead>
<tr>
<th>Metric/Property</th>
<th>Prototype 1.5, Phase II</th>
<th>Prototype 2, Phase II</th>
<th>Prototype 3, Renewal Phase III</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quarter Due</td>
<td>Q6 (all just accomplished)</td>
<td>Q9 (2/2019)</td>
<td>Q14 (5/2020)</td>
</tr>
<tr>
<td>Metric/Property</td>
<td>Size/description</td>
<td></td>
<td></td>
</tr>
<tr>
<td>U (BTU/sf/F/hr)</td>
<td>6.5 inch, ≤3 mm thick aerogel</td>
<td>6.5 inch diameter, ≤3 mm thick film</td>
<td>Square-meter, ≤3 mm film</td>
</tr>
<tr>
<td>Haze</td>
<td>&lt;5%</td>
<td>&lt;3%</td>
<td>&lt;2%</td>
</tr>
<tr>
<td>Visible light transmission (Tvis)</td>
<td>&gt;80%</td>
<td>&gt;85%</td>
<td>&gt;90%</td>
</tr>
<tr>
<td>Color rendering index (Rn)</td>
<td>&gt;0.8</td>
<td>&gt; 0.9</td>
<td>&gt; 0.92</td>
</tr>
<tr>
<td>Exterior temperature for interior condensation (C)</td>
<td>Reported</td>
<td>Reported</td>
<td>Less than -5</td>
</tr>
<tr>
<td>Thermal conductance</td>
<td>20 W/K/m²</td>
<td>10 W/K/m²</td>
<td>10 W/K/m²</td>
</tr>
<tr>
<td>Exterior temperature (C) at which the interior pane surface has radiative temperature of 11 deg C</td>
<td>Reported</td>
<td>4</td>
<td>Less than 0</td>
</tr>
<tr>
<td>Durability testing, including, mechanical strength, water infiltration, UV degradation, thermal cycling and thermal gradient tests</td>
<td>Not reported</td>
<td>Pass 1 week moisture/heat test, thermal cycling test, 1 day UV exposure test</td>
<td>Pass 2 weeks moisture/heat test, thermal cycling test, 1 week UV exposure test</td>
</tr>
<tr>
<td>Manufacturing cost, as in the TEA</td>
<td>Pathway to $5/ft²</td>
<td>Pathway to $3/ft²</td>
<td>&lt;$3/ft²</td>
</tr>
<tr>
<td>Median service lifetime</td>
<td></td>
<td></td>
<td>&gt;10 years</td>
</tr>
</tbody>
</table>
## Key phase III goals: Demonstrate, further improve parameters, scale to square meters, & develop pilot production approach

### Installed products for new windows

- Enabled by the phase II breakthroughs, though not planned initially
- Key phase III goals: Demonstrate, further improve parameters, scale to square meters, & develop pilot production approach

### Prototype Comparison

<table>
<thead>
<tr>
<th>Metric/Property</th>
<th>Prototype 2.5 (Phase III)</th>
<th>Prototype 3 (Phase III)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quarter Due</td>
<td>Q11 (5/2029)</td>
<td>Q14 (5/2020)</td>
</tr>
<tr>
<td>Metric/Property \ Size/description</td>
<td>6.5 inch diameter, ≤3 mm thick aerogel film between two 3mm thick panes of glass</td>
<td>Square-meter, ≤3 mm thick aerogel film between two panes of 3mm thick glass</td>
</tr>
<tr>
<td>U (BTU/sf/F/hr)</td>
<td>&lt;0.5</td>
<td>&lt;0.3</td>
</tr>
<tr>
<td>Haze</td>
<td>&lt;2%</td>
<td>&lt;1%</td>
</tr>
<tr>
<td>Visible light transmission (T(_{vis}))</td>
<td>&gt;80%</td>
<td>&gt;85%</td>
</tr>
<tr>
<td>Color rendering index (R(_a))</td>
<td>&gt; 0.9</td>
<td>&gt; 0.92</td>
</tr>
<tr>
<td>Exterior temperature for interior condensation in degrees C</td>
<td>Reported</td>
<td>Less than -10</td>
</tr>
<tr>
<td>Exterior temperature at which the interior pane surface has radiative temperature of 11°C(^{(9)})</td>
<td>0</td>
<td>Less than -5</td>
</tr>
<tr>
<td>Durability testing, including, mechanical strength, water infiltration, UV degradation, thermal cycling and thermal gradient tests</td>
<td>Pass 1 week moisture/heat test, thermal cycling test, 1 day UV exposure test</td>
<td>Pass 2 weeks moisture/heat test, thermal cycling test, 1 week UV exposure test</td>
</tr>
<tr>
<td>Manufacturing cost, as in the TEA</td>
<td>Pathway to &lt;$10/ft(^2)</td>
<td>&lt;$10/ft(^2)</td>
</tr>
<tr>
<td>Estimated median service lifetime</td>
<td>&gt;20 years</td>
<td>&gt;20 years</td>
</tr>
</tbody>
</table>
Conclusions & outlook

→ Liquid Crystal Aerogels to enhance Window Efficiency
→ Multi-layer cholesteric films to yield the low-e character
→ Solving both the thermal conductivity and emissivity problems

Thank you !!!