Enhanced High Thermal Conductivity Cellulose Filaments via Hydrodynamic Focusing

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ASSOCIATED CONTENT
Supplementary Information

1. Methods for preparing cellulose filaments, and morphology of filaments.

Cellulose dispersion preparation: A TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl radical) CNF dispersion (charge density, 1780 μmol/g) was utilized (RHEOCRYSTAL, DSK) to prepare the CNFs. The dispersion had a total volume of 400 mL and consisted of 0.2 wt% CNF and distilled water. The dispersion was mechanically treated using a homogenizer (Microtec Physcotron) rotating at a speed of 7500 rpm for 10 min to achieve CNFs with a uniform length and then sonicated using an ultrasonic homogenizer (300 W, 19.5 kHz) for 10 min to homogenize the dispersion. Next, the CNF dispersion was ultra-centrifuged at 7500 rpm for 10 min to remove impurities and ultrasonically oscillated for 10 min to separate stable CNFs.

Flow focusing channel: The channel system used in this study consists of a stainless steel plate with the channel cut out (the channel cross-section is square with an area of 10⁻⁶ m²) sandwiched by two acrylic plastic plates locked with screws (Fig. 1). The inlets of the cellulose dispersion, distilled water, and salt or acid solution were attached to rubber hoses, and syringes were used to inject the fluids. Prior to filament fabrication, the channel was purged with distilled water to remove the bubbles and air entrapped inside the channel and avoid impurities in the cellulose filaments.

Cellulose filament preparation: The filaments were prepared via hydrodynamic assembly in the flow channel system with parameters shown in Table S-1 to induce the alignment of surface-charged nanofibrils. Ideally, the TEMPO CNFs rotate like rods under electric double-layer repulsion when the dispersion is injected into the main channel at a flow rate of 4.98 mL/h (Fig. 1). The shear force generated by the injected distilled water in sheath flow 1 (flow rate, 24.88 mL/h) make the nanofibrils orient in the flow direction. Next, hydrochloric acid was injected in sheath flow 2 (flow rate, 4.15 mL/h) to improve the alignment of the nanofibrils, which were then gelated into a gel thread by the diffusion of hydrogen ions due to Brownian motion from the sheath flows. The gel thread was ejected into an ethanol bath, where solvent exchange occurs to accelerate evaporation. Finally, the gel threads were removed from the ethanol bath and dried for 24 h in a 23 °C laboratory environment and we store filaments at experiment room conditions under around 70% relative humidity.

The geometry and process parameters of the flow channel system is the same as the previous work, except for using ethanol for the bath liquid instead of water to accelerate the evaporation of condensed water inside the filament to make a closer contact between fibrils, which was found to be important for thermal transport. The process parameters identified in the previous work to realize enhanced CNF alignment and mechanical properties were relevant for this work as well. Here, it is important to note that all the experiments were carried out for the same flow rates of main flow, sheath flow 1, and sheath flow 2. While this does realize reasonable reproducibility of high alignment of nanofibrils, the details such as diameter of the filament and the
The corresponding degree of crystallization in the range of interest in this work turned out to vary, which may not be so surprising as the diffusion of ions and the local concentration fibrils through the system is stochastic. Therefore, in this work, we use this “natural variation” to parametrize the diameter of the filament.

In this experiment, the alignment of fibrils was induced via shear and extension in the flow-focusing channel, and gelation occurred owing to the diffusion of ions that counteract the electric double-layer repulsion between the carboxylate surfaces, leading to gelation transition. Hydrogen bonding between carboxylate and oxygen atoms helps form crystal regions inside the filaments. Therefore, the simultaneous control of the orientation and bonding of the CNFs (crystallization) was achieved in the flow-focusing system. After drying, mechanical tension was applied to the cellulose filament. As the length of the filaments increased, the stress increased monotonically with increasing strain until it reached the yield strength. At the yield point, the stress increased slowly with further increases in strain until the fracture point was reached.

| Table S-1. Details of production conditions in flow-focusing channel system. |
|---------------------------------------------------------------|
| **Core flow** | **Sheath flow 1** | **Sheath flow 2** |
| Solution       | CNFs (0.2 wt%)    | Distilled water  | HCl (0.01 mol/L) |
| Flow rate [mL/h] | 4.15             | 4.98             | 24.88             |

2. Thermal conductivity measurement.

The T-type method is a useful tool for obtaining thermal conductivity of fiber materials. Fujii et al. measured the thermal conductivity of millimeter-long single carbon nanotubes using a suspended T-type nanosensor. In this study, we utilized the T-type thermal conductivity measurement setup shown in Fig. 2 to investigate the thermal properties of our cellulose filaments. The actual device is shown in Fig. S-1. Three copper blocks were used as heat sinks to maintain the system temperature using a Peltier module (OMRON Corporation). A platinum wire was suspended between two copper blocks by adhesion using silver paste. When a DC current is applied to the platinum wire, a temperature increase is generated along the platinum wire owing to Joule heating. When a test sample is attached to the platinum wire (one side of the test sample
is connected to the center of the platinum wire and the other side is connected to the third copper block by adhesion using thermal glue), heat is conducted through the test sample via the middle junction point, and the temperature varies along the platinum wire. From this variation, thermal conductivity of the cellulose filament at the T-junction could be extracted using a physical model. The filaments were fabricated, dried, stored in a lab environment with relative humidity of 70%. Thermal conductivity of filaments was measured under vacuum conditions (under $10^{-4}$ Pa) after stabilizing the pressure by pumping with a molecular pump for about 6 hours. More details are given in the following.

Figure S-1 Schematic of self-built T-type steady-state measurement setup. A platinum wire is suspended between two copper blocks. Filament is attached on the center of platinum wire and the third copper block. Aluminum wire bonding is used to connect copper blocks to the current source and voltmeter.

DC voltage is applied along a platinum wire, and by calculating the difference in heat flux with and without attaching sample onto the platinum wire, the thermal conductivity of test filament are obtained based on Eqs. (S-1) and (S-2).

$$\frac{\partial^2 T(x)}{\partial x^2} + \frac{q_0}{\kappa_m} = 0 \quad (S-1)$$
\[ q_0 = \frac{Q}{A_c L_m} - \frac{4g(T - T_0)}{D} \] (S-2)

Here, \( T(x) \) is the temperature distribution along the axis of platinum wire (\( x \)-axis), \( T_0 \) is the temperature of copper blocks (heat sinks). \( Q \) is the total heat generated by Joule heating, \( q_0 \) is the heat generated in each unit cell after subtracting the heat loss. \( \kappa_m \) is the thermal conductivity of platinum wire (hot wire). \( x \)-axis is taken along the longitudinal direction of the platinum wire, the test filament is connected to the middle point of the platinum wire at \( x=0 \), and the platinum is connected to the two copper blocks at \( x=\pm \frac{L_m}{2} \). \( A_m \) is the cross-section area of platinum wire. \( L_m \) is the length of platinum wire. \( D \) is the diameter of platinum wire. To reduce the effect of convective heat loss on the filament during the measurement, we performed experiment under vacuum condition at \( 10^{-3} \) Pa. The convective heat loss of the platinum wire is considered through the coefficient \( g \). \( S \) is the perimeter of platinum wire.

By solving Eqs. (S-1-S-2), the average temperature increase of Pt wire is obtained as:

\[ \Delta T = \frac{Q}{gL_m S} - \left( \frac{2Q}{gL_m^2 S \sqrt{\frac{gS}{\kappa_m A_m}}} \right) \tanh \left( \frac{L_m}{2} \sqrt{\frac{gS}{\kappa_m A_m}} \right) \] (S-3)

In experiments, measurements of two platinum wires with different lengths were performed, with \( \kappa_m \) and \( g \) as unknown parameters. Then \( \kappa_m \) and \( g \) could be estimated as 75 W/m-K and 2 W/m\(^2\)-K, respectively, by solving Eq. (S-3). In the following analysis of thermal conductivity of the filament, we used this 75 W/m-K as thermal conductivity of platinum.

The resistance of platinum wire with respect to square of current (Joule heating) is shown in Fig. S-2a and S-2b. The initial resistance of platinum for temperatures ranging from 40 K to 320 K is shown in Fig. S-2c. Then thermal coefficient of resistance can be obtained accordingly with first derivative of the resistance, as shown in Fig. S-2d. Temperature dependence of thermal conductivity of platinum wire is obtained and compared with reference value\(^5\) in Fig. S-3. It remains constant in the temperature range between 150 K to 300 K.
Figure S-2 Measured thermal conductivity of the Pt wire. a Electrical resistance of Pt wire under varying current. Red line denotes the averaged experimental data. b The fitting (red line) of the averaged data in a focusing on those with relatively high current (black square points). c Initial electrical resistance of Pt wire (without Joule heating) in a temperature range from 40 K to 320 K. d Thermal coefficient of resistant of Pt from 40 K to 320 K.

Figure S-3 Experimental thermal conductivity of Pt wire within temperature range from 40 K to 320 K, compared with the reference values\(^6\) (red circles).
Heat flux and temperature between the positions at $x=0^+$, and $x=0^-$ should be continuous, which is expressed as boundary conditions in Eq. (S-4).

$$\frac{T(0) - T_\infty}{R_s} = \kappa_s A_s \left( \frac{\partial T_{x=0^+}}{\partial x} - \frac{\partial T_{x=0^-}}{\partial x} \right)$$  \hspace{1cm} (S-4)$$

$$T(x = 0^+) = T(x = 0^-)$$

Here, $R_s$ is the thermal resistance of measured filament. Solving equations based on the above boundary conditions, the average temperature increase of Pt (with test sample) can be written as Eq. (S-5):

$$\Delta T = \frac{1}{\alpha} \left[ \frac{2}{\sqrt{mL_m}} \left( \sin \left( \frac{\sqrt{mL_m}}{2} \right) + \frac{n}{\sqrt{mL_s}} \left( 1 - \cos \left( \frac{\sqrt{mL_m}}{2} \right) \right) \right) \right] - 1$$  \hspace{1cm} (S-5)$$

where, $m = \frac{\alpha I^2}{\kappa_m A_m L_m R_0}$ and $n = \frac{\kappa_s A_s}{\kappa_m A_m}$.

$A_s$ is the cross-section area of filament, $\kappa_s$ is thermal conductivity of filament, $\alpha$ is thermal coefficient resistance of Pt, and $I$ is the applied current.

To validate the measurement accuracy, we also considered the systematic error including radiation of the sample to minimize the measurement errors. The ratio of heat radiation to total Joule heating can be expressed as:

$$\frac{Q_{\text{Radiation}}}{Q_{\text{total}}} = \frac{\varepsilon \sigma A_{\text{surface}} (T_{\text{avg}}^4 - T_0^4)}{\kappa_s A_s T_{\text{avg}}^0 - T_0}$$  \hspace{1cm} (S-6)$$

$\varepsilon$ is the emissivity of cellulose filament measured by FTIR (Fig. S-4) to be 0.47, $\sigma$ is the Stefan-Boltzmann constant $5.678 \times 10^{-8}$ W/m$^2$-K$^4$, $A_{\text{surface}}$ is the total surface area of cellulose filament, $T_{\text{avg}}$ is the average temperature of the entire cellulose filament, $T_0$ is the temperature at heat sink, $A_s$ is the average cross-section area of test cellulose filament, and $L_s$ is the length of test cellulose filament. Based on the calculation, the heat loss due to radiation through cellulose filament was found to be $\sim 10.3\%$ of the total heat conducted through the filament.

To predict the accuracy of the measured results, error analysis was performed. Since the thermal conductivity of filament $\kappa_s$ is defined as:
\[ \kappa_s = \frac{G L_s}{A_s} \]  

(S-7)

where, thermal conductance \( G \), the length of filaments \( L_s \), and the cross-section area of filaments \( A_s \), the random error can be characterized as follows.

\[ S_{\kappa_s} = \sqrt{\left( \frac{\partial \kappa_s}{\partial G} \right)^2 S_G^2 + \left( \frac{\partial \kappa_s}{\partial L_s} \right)^2 S_{L_s}^2 + \left( \frac{\partial \kappa_s}{\partial A_s} \right)^2 S_{A_s}^2} \]  

(S-8)

Figure S-4 Absorbance of CNF thin film measured by Fourier transform infrared spectroscopy (FTIR) to estimate inferred emissivity.

3. **Mechanical tension of filaments.**

As explained in the above Section 1, we applied the mechanical tension on cellulose filaments (Shimadzu company). The force sensor used with a maximum tensile force is 1N and testing speed is set at 5 mm/min. The strain-stress curve is shown in Fig. S-5. The stress increases with increasing strain monotonically, until it reaches the yield
strength. Then the stress increases slowly with further increasing the strain until the fracture point. With the cross-section area, the module can be obtained. As shown in Fig. S-6, the SEM observation shows that the cross section takes an ellipse shape, which means that the actual cross section area is about 83% of what is estimated from an optical microscope image of the largest filament width assuming a round cross section. The Young’s modulus of this filament is estimated as 22 GPa.

Figure S-5 Mechanical strain versus stress curve of filaments. From the origin, the stress increases with increasing of strain monotonically, until it reaches the yield strength. After that, the stress increases slowly with further increasing the strain until it reaches the fracture point.

Figure S-6 Cross-section image of one filament sample. It shows an ellipse shape and the actual area is around 83% of that estimated as a round shape. The Young’s modulus of this filament is estimated as 22 GPa.
4. Structure investigation.

Cellulose is a semicrystalline material that contains both crystalline and amorphous regions; in this study, crystallinity was used to denote the mass percentage of crystalline regions in the whole cellulose material. Raman spectroscopy is a useful tool for investigating the crystallinity of cellulose. To reveal the relationship between the thermal conductivity and microscopic structures of CNF filaments, we quantitatively investigated the structure of CNFs in the prepared filaments using Raman spectroscopy (RENISHAW INVIA with a 633 nm laser and 1800 l/mm grating). Non-polarized Raman spectroscopy was used to identify the crystallinity of the filaments, and linearly polarized Raman spectroscopy was used to identify the nanofibril orientations.

Prior to the measurement of filaments, silicon is used for calibration using the representative peak at 520.6 cm$^{-1}$ by microscope with 100 times magnification, 0.1% near-infrared laser state, acquisition exposure time of 30/s, and 3 times accumulations. After calibration, filaments are measured for the range from 30 to 3700 cm$^{-1}$. The spectral data is obtained with subtracting the baseline, and the smoothing process.

4.1 Crystallinity index of filaments: During crystallinity index analysis, the incident and scattered light were non-polarized. The inelastic scattering of the incident light by the cellulose molecule leads to a frequency shift in the Raman spectrum, which can be utilized to identify the underlying vibrational frequency. The vibrational frequencies of typical bonds of cellulose, such as C–C–O, C–C–C, C–O, C–C–H, and C–O–C, are well documented. For instance, the peak at 380 cm$^{-1}$ represents C–C–C, C–C–O, and C–O ring deformations (glucose ring deformation) in the cellulose molecule. The peak at 1096 cm$^{-1}$ represents the stretching of C–C or C–O atoms along the cellulose molecular chain. During the Raman spectroscopy measurements, one CNF filament was placed under a microscope with 100× amplification. The incident laser beam was linearly polarized, and a 1/4 wave plate was used to circularly polarize the scattered light to enable the characterization of the crystallinity of the filaments.

The frequency range of 250–1650 cm$^{-1}$ in the Raman spectra obtained, particularly the two peaks at 380 and 1096 cm$^{-1}$, was investigated to estimate the crystallinity of the cellulose materials. The shape and intensity of these peaks change significantly at different crystallinity levels. Previous studies found that the intensities of the peaks at 380 and 1096 cm$^{-1}$ change when the crystallinity of cellulose is altered by ball-milling. Thus, the intensity ratios of these peaks could be used to indicate the crystallinity index of cellulose.

Umesh et al. measured the crystallinity of 41 types of biomaterials, including sapwood, heartwood, and agricultural fibers, using near-IR FT-Raman and wide-angle X-ray diffraction (WXRD) measurements. The peak intensity ratios of these materials at 380 and 1096 cm$^{-1}$ were extracted, and their crystallinity was estimated by WXRD. The authors found a strong correlation between the Raman peak intensity ratio and...
crystallinity of cellulose and obtained a formula describing the correlation of the intensity ratio with the crystallinity index as follows:

\[
\text{Crystallinity index} = \frac{(I_{380}/I_{1096}) - 0.0286}{0.0065} \quad (3)
\]

Similar research was conducted by Agarwal et al.\textsuperscript{14} to determine the crystallinity of cellulose via Raman and WXRD measurements; here, the authors found that the ratio of the two peaks showed strong correlations with the theoretical crystallinity value, with an R\textsuperscript{2} value as high as 0.995. Two phases exist in bulk cellulose materials: one phase corresponds to the crystalline regions and the other phase represents the amorphous region\textsuperscript{15,16}. The crystallinity index of cellulose can be understood as the mass ratio of the crystalline region to the amorphous region\textsuperscript{17}.

Non-polarized Raman is performed along depth direction of cellulose filament to analyze the crystallinity of filament from surface (depth=0 µm) to 5.5 µm with increment of 0.5 µm by increasing the focal depth on test sample. (RENISHAW INVIA with 633 nm laser, 1800 grating and 600 lens VIS and CCD detector). From Fig. S-7, we can find that the crystallinity index of filament shows a decreasing trend with the depth to about 25% at depth over 2.5 µm.

![Figure S-7](image_url)

Figure S-7 Crystallinity index of a filament (with diameter of 16 µm) along the radius direction by using non-polarized Raman scattering. The depth is measured from the surface towards the axis of the filament.
4.2 Orientation of nanofibrils: The orientation of CNFs is another important factor influencing thermal conductivity, and approaches such as mechanical drawing, stretching, and extrusion have been used to improve the orientation of polymer fibrils, as mentioned earlier. Gierlinger et al. investigated the application of the orientations of cellulose and lignocellulose microfibers using polarized Raman spectroscopy\textsuperscript{18}. In their analysis, latewood fibers were selected because the fibrils of this type of wood fiber are naturally oriented parallel to the fiber axis with a deviation from this direction of less than 10°. The orientation of the fibers can be analyzed by changing the polarization light from perpendicular to parallel with respect to the fiber axis. From the Raman measurements, the authors found that most of the peaks, except that at 1377 cm\textsuperscript{-1}, change when the polarization direction is altered; the peak at 1377 cm\textsuperscript{-1} represents the H–C–C, H–O–C, and H–C–O bonds (on the side of the molecule). Interestingly, they found that the peak at 1096 cm\textsuperscript{-1} changed significantly (C–O and C–C bonds along the cellulose molecular chain). This peak changes with the polarization direction of the incident laser because scattering is sensitive to the orientation of the cellulose molecular chains. The other peaks showed only a minor dependence on the incident laser polarization direction. In this work, we adopted linear polarization for both the incident (parallel to the axial direction of the filament) and scattered light and normalized the peak intensity at 1377 cm\textsuperscript{-1} with that at 1096 cm\textsuperscript{-1} to identify the orientation of the CNFs. Note while orientation is a necessary condition to achieve high thermal conductivity, it is not a sufficient condition. This can be understood from the Fig. S-8 (a) and Fig. S-8(b), where orientation is not correlated with thermal conductivity (i.e. crystallinity) nor residual strain.

![Figure S-8](image)

Figure S-8 a Correlation between orientation and residual strain. b Correlation between orientation and thermal conductivity.

4.3 Characterization of termination and bonding: As illustrated in Section 4.1, non-polarized Raman is performed along depth direction of filament by increasing the focal depth on test sample. Normalized intensity of 1594 cm\textsuperscript{-1} represents\textsuperscript{19} the bonding of COO\textsuperscript{-} with Na\textsuperscript{+}. As shown in Fig. S-9 (a-b), the intensity of the normalized peak at 1594
cm$^{-1}$ indicates that $-\text{COONa}$ is rich in the center of the filament. By contrast, the surface of the filament shows smaller amount of $-\text{COONa}$. Since the charged negative carboxyl group should be bonded with either sodium ion or hydrogen ion, this suggests that the amount of $-\text{COOH}$ is rich on the surface and becomes less towards the center.

As explained in above Section 2, we performed FTIR spectroscopy to estimate emissivity of cellulose filament. We prepared a CNF thin film with the same ratio of solutions used to make the filament. The film was scanned from wavelength of 2 to 20 µm. An aluminum block is used as a baseline for background measurements. Next, we put CNF thin film on aluminum block, measure the absorbance spectrum, and subtract the baseline. The obtained spectrum is shown in Fig. S-4.

In addition, we performed an additional measurement using Micro-Fourier-transform infrared spectroscopy (Micro-FT-IR) to prove the hydrogen bonding highlighted under different diameter filaments (small, medium and large diameter). As shown in Fig. S-10, the obtained absorption spectra in the region between 3000-3600 cm$^{-1}$, corresponding to the stretching vibration of hydrogen bonds shows that wavenumbers of the peaks red-shifts and the distribution of the peaks become narrower with decreasing diameter. Details of Micro-FTIR measurement are as follows. Micro-FTIR was measured using IRT-5200 (Jasco) in the range from 800 to 4000 cm$^{-1}$ with 4 cm$^{-1}$ resolution. The signal was accumulated 100 times and averaged. Au mirror with thickness of 200 nm deposited on a glass substrate was used for background to evaluate its transmittance (nondestructive measurement) and obtain absorbance spectrum according to Kirchhoff’s law. Detector used is MCT fully cooled with liquid nitrogen and with aperture of 10 µm x 10 µm.

Figure S-9  

(a) Raman spectra of filament along radial direction. The depth is measured from the surface towards the axis of the filament.  

(b) Normalized Raman intensity at 1594 cm$^{-1}$. Near filament axis region shows rich in $-\text{COONa}$, and in contrast, surface region shows less $-\text{COONa}$. 


Figure S-10 Micro-FTIR spectra of CNF filaments with small (7.32 μm), medium (12.38 μm), and large diameters (21.43 μm). The results show the strengthening of hydrogen bonds with decreasing diameter.

Table S-2 Data summary of CI, diameter, thermal conductivity, and C-O-C shift of filaments.

| CI     | Diameter [μm] | TC [W/m-K] | C-O-C shift [cm⁻¹] |
|--------|---------------|------------|--------------------|
| 0.381  | 11.64         | 4.3        | 4                  |
| 0.38   | 9.84          | 4          | 5.2                |
| 0.414  | 13.65         | 4          | 5.1                |
| 0.392  | 13.65         | 3.3        | 6.2                |
| 0.39   | 12.26         | 3          | 4.7                |
| 0.435  | 12.25         | 4          | 4                  |
| 0.703  | 7             | 14.5       | 0                  |
| 0.63   | 7.63          | 12.5       | 1.98               |
| 0.614  | 7.42          | 9.5        | 1.1                |
| 0.524  | 9.89          | 6.2        | 0.8                |
| 0.731  | 9.77          | 5.5        | 4                  |
| 0.612  | 9.6           | 6          | 5.1                |
| 0.644  | 10.33         | 2.5        | 6.26               |
| 0.613  | 10.76         | 3.5        | 5.1                |
| 0.58   | 11.77         | 2.5        | 4.8                |
| 0.585  | 9.5           | 2.5        | 6.2                |
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