Cellulose Nanofibril Aerogels: Synergistic Improvement of Hydrophobicity, Strength, and Thermal Stability via Cross-Linking with Diisocyanate

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Supporting Information

ABSTRACT: A facile gelation cross-linking approach was devised to fabricate meso- and macroporous cellulose nanofibril (CNF) aerogels with multiple improved properties. CNF hydrogels made using a freezing–thawing method with a 94 kPa modulus were solvent exchanged with acetone and then cross-linked with methylene diphenyl diisocyanate (MDI) to produce aerogels with significantly improved compressive properties that follow a power law increment against aerogel density with impressive 1.69, 2.49, and 1.43 scaling factors for Young’s modulus, yield stress, and ultimate stress, respectively. The optimally cross-linked aerogels had nearly tripled specific surface area (228 m²/g) and doubled pore volume (1 m³/g) from numerous new 9–12 nm wide mesopores as well as significantly improved thermal stability (43% char residue at 500 °C vs 9.1% for un-cross-linked aerogel). Cross-linking also made the amphiphilic CNF aerogel highly hydrophobic and capable of completely separating chloroform from water via simple filtration. These nanocellulose aerogels show great promise for efficient and continuous separation of oils and hydrophobic liquids from water.

KEYWORDS: aerogel, cellulose nanofibril, hydrophobic, cross-linking, oil–water separation

INTRODUCTION

Aerogels are uniquely porous materials with ultralight weight and ultrahigh porosity and were first reported in the early 1930s. While most aerogels are silica, carbon, or synthetic polymer-based, those derived from sustainable and renewable materials are particularly enticing, among which cellulose aerogels present novel attributes such as low thermal conductivity, flexibility, excellent wet resiliency, etc. Cellulose aerogels have been most commonly produced by multistep sol–gel processes involving cellulose dissolution, regeneration in nonsolvents, and solvent exchange to media suitable for either supercritical-drying or freeze-drying. These processes typically demand the use of large quantities of solvents and chemicals such as N-methylmorpholine-N-oxide (NMMO), alkali hydroxide/urea, sodium hydroxide, calcium thiocyanate tetrahydrate, lithium chloride/dimethylacetamide (LiCl/DMAc), lithium chloride/dimethyl sulfoxide (LiCl/DMSO), ionic liquid, etc. As these processes required dissolution of cellulose, the native cellulose I crystalline structure is destroyed to regenerate into either amorphous or cellulose II structures. Nanocelluloses, the crystalline I domains isolated is destroyed to regenerate into either amorphous or cellulose II

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disocyanate, CNF hydrogels were first fabricated by freezing—thawing (FT) and were then solvent exchanged to acetone, a solvent for disocyanate, enabling disocyanate reaction with CNFs in the acetone gel. Drying the cross-linked acetone gel in air can lead to structural collapse. Therefore, the acetone gel was solvent exchanged to tert-butanol, a solvent suitable for freeze-drying, and then freeze-dried to yield aerogel. The cross-linked CNF aerogels were characterized in terms of morphologies, mechanical properties, thermal stability, specific surface area, etc. and were also applied for oil—water separation.

EXPERIMENTAL SECTION

Materials. Pure cellulose was isolated from rice straw to 36% yield by a three-step 2/1 toluene/ethanol extraction and acidified NaClO₂ (1.4%, pH 3−4, 70 °C, 6 h) and KOH (5%, 70 °C, 2 h) isolation process reported previously. CNFs were derived from the isolated pure cellulose by employing 5 mmol/g NaClO₂/cellulose at pH 10, and then neutralizing the solution to pH 7 by adding 0.5 M NaOH, followed by mechanical blending (Vitamix 5200) at 37 000 rpm for 30 min. Hydrochloric acid (1N, certified, Fisher Scientific), acetone (historical grade, Fisher Scientific), tert-butanol (certified, Fisher Scientific), methylene diphenyl disocyanate (98%, Sigma-Aldrich), triethylamine (99.7%, extra pure, Sigma-Aldrich), chloroform (HPLC grade, EMD), methylene blue (certified biological stain, Fisher Scientific), and Sudan IV red (Allied Chemical) were used as received without further purification. All water used was purified using a Milli-Q plus water purification system (Millipore Corporation, Billerica, MA).

Cellulose Nanofibril Hydrogels and Acetone Gels. Aqueous CNF suspensions (0.6%) were fabricated into hydrogels by either FT or hydrochloric acid (HCl) gelation. FT hydrogels were formed by freezing CNF aqueous suspension at −20 °C for 4 h and then thawing it at ambient temperature. HCl hydrogel was obtained by addition of 1 mL of HCl (1 N) on top of 8 mL of CNF aqueous suspension under static state in a refrigerator (4 °C) overnight. Both FT and HCl hydrogels were immersed in HCl (0.2 N) to further protonate the surface carbonyls for enhanced gelation and were then exchanged with acetone into acetone gels.

Cross-Linking with Diisocyanate. For cross-linking, the CNF acetone gels were placed in 80 mL of acetone containing MDI at 1:1, 2:1, and 4:1 MDI:CNF mass ratios with 20 μL of triethylamine as a catalyst at room temperature for 48 h. After reaction, the solution became turbid with white precipitate, and the cross-linked CNF acetone gels were washed thoroughly with acetone to remove unreacted reagents. Both un-cross-linked and cross-linked CNF acetone gels were further exchanged to tert-butanol and then freeze-dried (−50 °C, 0.05 mbar) in a freeze-drier (FreeZone 1.0L Benchtop Freeze-Dry System, Labconco, Kansas City, MO). The CNF aerogels from FT and HCl gelation were designated as FT-CNFn and HCl-CNFn aerogels, respectively, and those cross-linked at 1:1, 2:1, and 4:1 MDI:CNF ratios were designated as CNF1MDI, CNF2MDI, and CNF4MDI aerogels, respectively.

Characterization. The optical transmittance of 0.6% CNF suspension and FT- and HCl-CNFn hydrogels (2 mm-thick) was recorded from 350 to 800 nm using an Evolution 600 UV−vis spectrophotometer. The density of all CNF aerogels was calculated based on the dimension (length and diameter) and mass of a piece of cylindrical aerogel, as measured using a digital caliper and balanced to 0.01 mm and 0.1 mg resolution, respectively. The liquid contact angles on un-cross-linked and cross-linked FT-CNFn aerogel were visualized by dropping 10 μL of water (dyed with methylene blue) or chloroform (dyed with Sudan IV) on the aerogel surface.

The absorption capacity of CNF aerogels toward water and chloroform was measured by immersing the aerogel into 20 mL of liquid and allowing it to saturate, and the surface liquid was blotted with filter paper and weighed. The absorption capacity (g/g) was calculated as

$$\text{absorption capacity} = \frac{(w_e - w_0)}{w_0}$$

(1)

where $w_e$ and $w_0$ are weights of fully saturated and dry aerogels, respectively.

The cyclic absorption capacities of un-cross-linked and cross-linked FT-CNFn aerogels toward chloroform were determined by completely evaporating the previously absorbed chloroform in air and then reabsorbing it following the previous method. CNF aerogel was cut along the cross sections with a sharp razor, mounted with conductive carbon tape, sputter coated with gold, and imaged by a field emission scanning electron microscope (FE-SEM) (XL 30-SEFEG, FEI/Philips, United States) at a 5 mm working distance and 5 kV accelerating voltage. FTIR spectra of CNF aerogels as transparent KBr pellets (1:100, w/w) were obtained from a Thermo Nicolet 6700 spectrometer. The spectra were collected at ambient conditions in the transmittance mode from an accumulation of 128 scans at a 4 cm⁻¹ resolution over the regions of 4000−400 cm⁻¹. Thermogravimetric analyses (TGA) of CNF aerogels were performed on a TGA-50 thermogravimetric analyzer (Shimadzu, Japan). Each sample (5 mg) was heated at 10 °C/min from 25 to 500 °C under nitrogen (N₂) (50 mL/min). The specific surface area and pore characteristics of CNF aerogels were determined by N₂ adsorption at 77 K using a surface area and porosity analyzer (ASAP 2020, Micromeritics, United States). Approximately 0.1 g of each sample was degassed at 35 °C for 24 h. The equilibration time was set as 15 s for mesoporous materials to ensure data accuracy. The specific surface area was determined by the Brunauer−Emmett−Teller (BET) method from the linear region of the isotherms in the 0.06−0.20 relative P/P₀ pressure range. Pore size distributions were derived from desorption branch of the isotherms by the Barrett−Joyner−Halenda (BJH) method. The total pore volumes were estimated from the amount adsorbed at a relative pressure of P/P₀ of 0.98. Compressive tests were performed on 10 mm-long cylindrical CNF aerogels using an Instron 5566 equipped with a 5 kN load cell and two flat-surface compression stages. The loading compressive rates were set to the same constant (1 mm/min). Young’s modulus was determined from the initial slope (strain of less than 0.02) of the σ−ε curve. The yield stress ($\sigma_y$) was determined at the
end of elastic region, and the ultimate stress ($\sigma_u$) was determined at strain ($\varepsilon$) = 0.8. Oil–water separation was investigated using CNF4MDI aerogel (3 mm-thick) in between a vacuum suction filtration device. A phase-separated mixture of water:chloroform (200 mL, 50:50 v/v) was poured on top of aerogel membrane and filtered without pulling any vacuum. This filtration-assisted separation was repeated 10 times to investigate the reusability.

■ RESULTS AND DISCUSSION

**CNF Aerogel Characterization.** The coupled TEMPO mediated oxidation and mechanical defibrillation produced 1–2 nm-thick and 500–1000 nm-long CNFs that contain 1.29 mmol/g surface C6 carboxylate groups, of which 86% are sodium carboxylate. While the electrostatic repulsion among the negatively charged surface carboxylates keeps CNFs suspended in aqueous media over time, aqueous CNF suspensions at as low as 0.6% were viscous due to interfibril hydrogen bonding among the abundant surface C2, C3, remaining C6 hydroxyls, and protonated carboxyls as well as entanglement among high aspect ratio flexible fibrils. To induce gelation of aqueous CNFs at such a low concentration, inter-CNF association was promoted by two external stimuli, i.e., slow freezing to increase local CNF
concentrations followed by thawing (FT) and protonation with HCl to reduce interfibril electrostatic repulsion.

Both FT- and HCl-CNF hydrogels appeared translucent with slightly higher clarity in the latter (Figure 1a). This was corroborated by the visible light transmittance (10–24%) of the FT-CNF hydrogel lower than that (31–43%) of the HCl-CNF hydrogel (Figure 1c). The light transmittance of both CNF hydrogels much lower than that the original 0.6% CNF suspension with only 1/5 the thickness of the light path was clear evidence of greater CNF association induced by either slow freezing or reduced electrostatic repulsion. For aqueous CNF suspension, the 33% light transmission at 350 nm, much lower than the 84% at 800 nm, was likely from greater scattering at wavelengths closer to the size of CNFs as in aqueous colloidal systems.

Both FT- and HCl-CNF hydrogels were solvent exchanged with acetone and then tert-butanol and were finally freeze-dried, producing white opaque aerogels with respective densities of 6.9 and 8.3 mg/cm³ (Figure 1b). In the sequential solvent exchanges with acetone and tert-butanol, neither gels exhibited dimensional changes from the original hydrogels, indicating no major impact on CNF association or organo-gel structure. However, the solvent exchanged FT-CNF aerogel had a density slightly lower than that (8.1 mg/cm³) of the same CNFs from only freezing (−20 °C) without solvent exchanges. One possible explanation is that, during solvent exchange, the surface bound organic solvent (acetone and tert-butanol) could inhibit close and compact assembly of CNFs, leading to a less-dense structure.

The two aerogels had grossly different morphologies. FT-CNF aerogel showed a cellular structure of biomodally distributed very large 200–500 μm-wide irregularly shaped honeycomb-like cells with thin walls of closely packed self-assembled CNFs with numerous ca. 50 nm-wide and hundreds of nanometers-long slit-like spaces (Figures 2a–c). In contrast, HCl-CNF aerogel was mostly fibrillar, with interfibrillar spaces ranging from hundreds of nanometers to tens of micrometers wide (Figures 2d–f). A few very fine fibrils were observed in FT-CNF aerogels, whereas hardly any film-like pieces were found in HCl-CNF aerogels. The major morphological differences between the two are the cellular structure with distinctly different bimodal distributed pores of the former, i.e., by 3 orders of magnitude, and the fibrillar structure of the latter.

BET nitrogen adsorption–desorption behaviors of these aerogels provided further details on pores less than 100 nm and features discerned by the high-resolution SEM. Both aerogels showed type IV isotherms, typical of mesoporous materials (Figure 3a). FT-CNF aerogel showed an asymmetric H2 hysteresis loop between 0.6 and 0.8 P/P0 in addition to a less intensive H1 type hysteresis loop at above 0.9 P/P0 (Figure 3b). The H2 hysteresis was attributed to pore blocking or percolation effect in ink-bottle pore structures of the mesopores, consistent with the narrow slit width observed on the walls. The primary sharp peak centered at 6 nm followed by a shallow one from 20 to 100 nm further indicates the dominance of mesopores in FT-CNF aerogel. The HCl-CNF aerogel showed an H1 hysteresis of nearly parallel adsorption and desorption branches at P/P0 above 0.9 and a small peak at 8 nm followed by a much larger and broader peak centered at 62 nm, indicating significantly more macropores than mesopores, also consistent with SEM observations. As expected, the fibrillar HCl-CNF aerogels had higher specific surface (209 m²/g) and pore volume (0.96 cm³/g) than those of the much better self-assembled FT-CNF aerogel (123 m²/g and 0.37 cm³/g, respectively), which is due to the more fibrillar structure of HCl-CNF aerogel as opposed to the well-assembled film-like structure for FT-CNF aerogel (Figure 2).

Both FT- and HCl-CNF aerogels exhibited similar thermal behaviors, i.e., similarly hygroscopic, containing 7–8.2% moisture, losing 75% of mass from 200 to 345 °C, but had significantly different chars of 9.1 and 3.6% at 500 °C, respectively (Figure 3c). While HCl-CNF aerogel produced similar extent of char as native cellulose, the two and half times higher amount of char from FT-CNF aerogel was attributed to its much more extensively assembled and packed film-like structures and lower specific surface to heat exposure. Both aerogels were flexible and could be compressed to up to 0.8 strain while remaining physically intact, showing three stress–strain regions of initial linear elastic and then plastic deformation and the final densification (Figure 3d). FT-CNF aerogel showed a steeper linear elastic deformation region with a more than doubled Young’s modulus of 94 kPa but less than half 0.05 yield strain as compared to the 44 kPa Young’s modulus and 0.13 yield strain for HCl-CNF aerogel. While both aerogels showed similar 31–33 kPa ultimate stress, when normalized by density, FT-CNF aerogel had significantly higher specific Young’s modulus (13.6 MPa/g·cm³) and slightly higher ultimate stress (4.5 MPa/g·cm³) compared to those of the HCl-CNF aerogel (5.3 and 4.0 MPa/g·cm³, respectively). Again, the significantly higher specific modulus of FT-CNF aerogel is attributed to the well-assembled CNF walls in an interconnected honeycomb structure.

The specific ultimate stress of FT-CNF aerogel is 44 times that of glutaraldehyde cross-linked TEMPO oxidized from eucalyptus pulp frozen at −78 °C (~0.3 MPa/g·cm³ specific ultimate stress at 0.8 strain). The specific Young’s modulus of FT-CNF aerogel is over three times higher than that of freeze-dried silylated aerogel from homogenized oat straw nanocellulose frozen at −196 °C (4.1 MPa/g·cm³ specific Young’s modulus at 6.7 mg/cm³) and ca. 70% higher than that of aerogel from enzymatically degraded and homogenized softwood pulp microfibrillated cellulose frozen at −196 °C (8 MPa/g·cm³ specific Young’s modulus at 7 mg/cm³) or −180 °C (8–9 MPa/g·cm³ specific Young’s modulus at density of 20–30 mg/cm³) but is similar to that of TEMPO oxidized softwood nanocellulose aerogel unidirectionally frozen at 15 K/min (~13.5 MPa/g·cm³ specific Young’s modulus at 5.6 mg/cm³). Because the latter was frozen at a slow rate and also consisted of a honeycomb-like structure, the higher modulus in both cases was consistent with more extensive assembling of CNFs into the well-packed thin wall in the honeycomb structure.

FT-CNF aerogel absorbed 112.1 and 100.8 mL/g of water and chloroform, respectively, without observable deformation, indicating amphilipicity with slightly higher hydrophilicity. In contrast, HCl-CNF aerogel shrank immediately upon exposure to the same liquids, releasing trapped air bubbles and absorbing only 28.0 and 30.2 mL/g water and chloroform, respectively, about a third of those absorbed by the FT-CNF aerogel. The shrinking of HCl-CNF aerogel was attributed to the fibrous structure that collapsed from the surface tension of absorbed liquid. On the basis of the higher mechanical strength and better shape retention with absorbed liquids, further cross-linking with MDI was applied to only FT-CNF aerogel.

MDI Cross-Linking of FT-CNF Aerogel. FT-CNF hydrogels were solvent exchanged into acetone gels, and then cross-linked with MDI using triethylamine as a catalyst. On the basis of the 4.19 mmol/g surface hydroxyls and 1.29 mmol/g carboxyls/carboxylates for CNFs calculated from the surface charge density.
and crystallite dimensions determined from conductometric titration and X-ray diffraction, respectively,
the 1:1, 2:1, and 4:1 MDI:CNF w/w ratios were calculated to be 1.45:1, 2.90:1, and 5.80:1 isocyanate to total carboxyl or NCO:OH/COOH+COO$^-$ molar ratios for CNF1MDI, CNF2MDI, and CNF4MDI, respectively, all with excess MDI cross-linker. Neither acetone exchange nor MDI cross-linking caused dimensional changes, but the cross-linked acetone gels became more opaque (Figure S1), which is believed to be due to the reduced pore spaces on the film surface that prevent light transmittance. All MDI-cross-

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**Figure 4.** SEM images of MDI-cross-linked aerogels: (a, d, and g) CNF1MDI, (b, e, and h) CNF2MDI, and (c, f, and i) CNF4MDI.

**Figure 5.** Characteristics of MDI cross-linked FT-CNF aerogels: (a) FTIR spectra, (b) TGA, (c) BET specific surface area (inset is specific surface area and total pore volume, and (d) BJH pore size distribution.
MDI cross-linked FT-CNF aerogels retained honeycomb structures (Figures 4a–c) similar to those of the un-cross-linked one (Figure 2a) but, in contrast to the smooth pore wall (Figure 2b), the cell walls were covered with aggregates that increased in number and size with increasing MDI ratios (Figure S3 and Figures 4d–f). Closer inspection on the pore walls also showed that slit-like spaces tens of nanometers in length remained present after cross-linking (Figures 4g–i) but increasingly filled at higher MDI levels, as indicated by arrows. These MDI aggregates were found tightly attached or anchored on the cell walls, which may strengthen the structure, as is be discussed later.

Cross-linking between MDI and the hydroxyls/carboxyls on FT-CNF aerogel was confirmed by the appearance of two new peaks at 1540.8 and 1234.2 cm$^{-1}$, corresponding to the C–N stretching and N–H bending of amides II and III, respectively (Figure 5a). The characteristic aromatic skeletal vibration at 1511.9 and 1598.7 cm$^{-1}$ ascribed to the vibration of isocyanate (N=O) in MDI also appeared on the cross-linked aerogels and increased in intensity with increasing MDI:CNF ratios, showing increasing presence of unreacted isocyanates. However, the unreacted isocyanate peaks did not intensify to the same extent as the urethane nor the aromatic skeletal, indicating MDI participated more in cross-linking than not. Nevertheless, these unreacted isocyanates offer reactive sites for introducing other functionalities on the aerogel surfaces.

MDI-cross-linked CNF aerogels had lower moisture contents (determined at 150 °C) of 3.8, 4.2, and 2.3% for CNF1MDI, CNF2MDI, and CNF4MDI, respectively, significantly less hygroscopic by 50% for CMF1MDI and CNF2MDI and over 70% for CNF4MDI, which is mostly due to the aromatic groups in the MDI structure. The MDI-cross-linked aerogels also decomposed at a rate ($-0.45\%$ °C$^{-1}$) considerably lower than that of FT-CNF ($-0.79\%$ °C$^{-1}$) but in the same 200–350 °C range (Figure 5b), retaining higher mass at the end of the primary stage of decomposition, i.e., 350 °C. The derivatives of these TGA curves showed a peak at 268 °C ascribed to degradation of carboxylated CNF surface chains, while the primary degradation peak centered at around 321 °C for FT-CNF, CNF1MDI, and CNF2MDI and slightly higher at 331 °C for CNF4MDI (Figure S4). Most significantly, the char residues significantly increased to 34.7, 36.1, and 43.3% with increasing MDI ratios from the 9.1% for FT-CNF. The more than tripled and quadrupled char residues could be ascribed to the aromatic moiety and low oxygen content in MDI along with lower decomposition rates, contributing to the improved thermal stability of MDI cross-linked CNF aerogel.

MDI-cross-linked FT-CNF aerogels showed similar type IV BET nitrogen adsorption–desorption isotherms with the typical H1 hysteresis at $P/P_0$ above 0.7 (Figure 5c). However, the MDI-cross-linked FT-CNF aerogels exhibited significantly increased pore volumes and smaller mesopore sizes, shifting from the clearly bimodal pore distribution of the FT-CNF aerogel, i.e., a sharp peak at 6 nm and a shallow broad peak centered at 60 nm, to close to monodistributed pore sizes of the CNF4MDI aerogel (Figure 5d). The average pore size enlarged from 6 nm for the un-cross-linked aerogels to 9.4, 10.6, and 12.0 nm, the pore volume increased from 0.37 m$^3$/g to 0.87, 1.00, and 0.94 m$^3$/g, and the specific surface increased from 128 m$^2$/g to 216, 228, and 228 m$^2$/g for CNF1MDI, CNF2MDI, and CNF4MDI, respectively. These improved mesoporous structures had 2.35, 2.70, and 2.54 times higher specific surface area and 1.75, 1.85, and 1.80 times higher pore volume, respectively, compared to those of the un-cross-linked aerogel. The nearly tripled specific surface area and close to doubled pore volume of all three cross-linked FT-CNF aerogels was con...
linked aerogels indicated the creation of numerous new mesopores with cross-linking. As slit-like spaces tens of nanometers wide were well-preserved after cross-linking, the additional specific surface area and pores were thought to be from either within MDI aggregates or in the interspaces between MDI aggregates and CNF cellular wall surfaces. The slightly lowered specific surface area and pore volume of CNF4MDI may be attributed to the substantial filling of the mesopores, as observed from the SEM images (Figure 4). Clearly, significant pore generation is attributed to cross-linking alone, while slightly more was observed with 2:1 MDI:CNF or CNF2MDI aerogel. Furthermore, these cross-linking effects are highly positive as opposed to the severe reduction of 700 m²/g specific surface area to as low as 8 m²/g on silica aerogel cross-linked with poly(hexamethylene disocyanate).38,39

The MDI cross-linked FT-CNF aerogels CNF1MDI, CNF2MDI, and CNF4MDI exhibited significantly higher modulus of 127, 204, and 209 kPa, or 1.35, 2.2, and 2.2 times that of the un-cross-linked aerogel (94 kPa), respectively (Figure 6a), clearly evident of strengthening via increasing MDI cross-linking. Both yield stress and strain increased as the MDI ratio increased, from the respective 3.6 kPa and 0.05 for the un-cross-linked to 13.8 kPa and 0.1 or nearly 4 times and 2-fold increases for optimally cross-linked aerogel, respectively. The ultimate stress also increased with increasing MDI, doubling to 66 kPa for the CNF4MDI aerogel. However, linear elastic deformation could only sustain for up to 0.1 compressive strain for CNF4MDI, followed by a large plastic deformation, leading to nonrecovery compression.

Because the cross-linked aerogels also densified with the MDI cross-linking, Young’s modulus (E), yield stress (σy), and ultimate stress (σu) were plotted against their density (ρ) in log–log scale (Figures 6b–d) and fitted with power law expression

$$E \text{ or } \sigma \sim \rho^n$$

where n is the scaling factor. All mechanical properties increased with increasing densities with a scaling factor n greater than 1, showing nonlinear relationships. The scaling factors for Young’s modulus, yield stress, and ultimate stress of MDI cross-linked FT-CNF aerogels were 1.69, 2.49, and 1.43, respectively. This is in contrast to the 1 scaling factor, i.e., no scaling law effect, previously observed for TEMPO oxidized cellulose nanofibril aerogels with densities ranging from 4 to 40 mg/cm³. Therefore, the scaling law effect was attributed to the cross-linking of CNFs with the rigid MDI molecules, imposing greater improvement in mechanical properties over slightly increased aerogel density.

**Liquid Affinity and Separation of MDI Cross-Linked FT-CNF Aerogel.** The un-cross-linked FT-CNF aerogel was amphiphilic, capable of absorbing slightly more water (112.1 mL/g) than chloroform (100.8 mL/g) (Figures 7a and e), corresponding to filling 78 and 70%, respectively, of the pore volume of 144.3 mL/g calculated from aerogel density (6.9 mg/cm³) and crystalline cellulose density (1600 mg/cm³). All MDI-cross-linked FT-CNF aerogels became clearly more hydrophobic with water beading up on the surfaces (Figures 7b–d). The increasingly larger water contact angles with higher MDI levels (Figures 7b and c) are consistent with enlarging absorption capacity differences between nonpolar chloroform and polar water (Figure 7e). While the absorption of both polar and nonpolar liquids decreased with increasing cross-linking, chloroform absorption decreased moderately to 81.7, 58.5, and 63.6 mL/g, respectively, but water absorption dropped most sharply to 52.8, 18.1, and 5.3 mL/g for CNF1MDI, CNF2MDI, and CNF4MDI, respectively, owing to the increased hydrophobicity. The decrease in chloroform absorption is due to increased density after cross-linking, corresponding to a decrease in the pore absorption capacities of 121.3, 101.4, and 86.3 mL/g for CNF1MDI, CNF2MDI, and CNF4MDI, respectively. However, the chloroform absorption corresponded to 68, 50, and 47% of the pore capacities, showing no particular trend with respect to MDI levels. These chloroform absorption capacities of MDI-cross-linked CNF aerogels are in fact slightly higher than the 58–70% capacities of the lighter (2.7–8.1 mg/cm³ densities) uncross-linked aerogels, suggesting slightly improved pore accessibility.

The cyclic absorption of chloroform was conducted by evaporating the absorbed chloroform prior to the next absorption cycle (Figure 7f). Chloroform absorption decreased substantially in the first three cycles and stabilized after 5 cycles to 29.9, 34.2, 41.5, and 57% for FT-CNF, CNF1MDI, CNF2MDI, and CNF4MDI, respectively. Such decreased absorption was...
attributed to shrinkage in both lateral and thickness directions, and the extent of shrinkage decreased with increasing MDI levels (Figure S5). Consistent with the least dimensional shrinkage from cross-linked at the highest level, CNF4MDI aerogel showed the highest relative absorbency, indicating that the MDI cross-linked structure is more rigid to resist shrinkage caused by the surface tension during liquid evaporation.

Separation of oil from water was evaluated via simple filtration using the most hydrophobic and least hydrophilic CNF4MDI aerogel (Figure 8). Equal chloroform (dyed in Sudan IV red) and water were mixed and immediately phase separated. Upon being poured over a 3 mm-thick CNF4MDI aerogel disc filter (Figure 8d), chloroform permeated through the lipophilic CNF4MDI aerogel into the flask below, while water was retained above by the hydrophobic aerogel filter, effectively separating water and oil. The used aerogel filter retained some chloroform, as shown by the red color, but remained effective in separating the chloroform–water mixture for at least ten times. This fast and repetitive filtration capability of this MDI-cross-linked CNF aerogel filter demonstrated clearly its potential applications for efficient and cyclical separation of oils and hydrophobic pollutants from water without being limited by the actual absorption capacity of the materials.

**CONCLUSIONS**

Gelation of TEMPO oxidized CNFs via FT produced hydrogel that was less transparent than that produced by protonation with HCl. Both hydrogels were solvent exchanged to acetone then tert-butanol and were finally freeze-dried into similarly white opaque FT- and HCl-CNF aerogels with respective densities of 6.9 and 8.3 mg/cm³ but distinctly different morphologies and properties. FT-CNF aerogel had an irregularly shaped honeycomb-like structure with large 200–500 μm-wide cells with self-assembled CNF mesoporous thin walls, bimodally distributed 6 and 60 nm pores, and slit-like spaces hundreds of nanometers long compared to the mostly fibrillar structure of HCl-CNF aerogel. Solvent exchanging and cross-linking FT-CNF hydrogels with MDI further optimized the thermal stability (char from 9.1 to 43%), strength (Young’s modulus from 94 to 209 KPa), and hydrophobicity (reduced water absorption from 95.3% to 5.3 mL/g water and 63.6 mL/g chloroform). The significantly more hydrophobic MDI-cross-linked CNF aerogels could completely separate chloroform from water by simple filtration. These hydrophobic macro- and mesoporous MDI-cross-linked CNF aerogels can serve as robust media for efficient and continuous separation of oils and hydrophobic liquids from water via simple filtration.

**ASSOCIATED CONTENT**

* Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.6b13577.

Photos of MDI cross-linked FT- and HCl-CNF acetone gel and aerogel, SEM images and DTGA spectra of MDI cross-linked FT-CNF aerogel, and photos of FT-CNF...
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