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# Featherlight, Mechanically Robust Cellulose Ester Aerogels for Environmental Remediation

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#### **S** Supporting Information

**ABSTRACT:** A unique combination of well-established synthesis procedures involving chemical cross-linking, careful solvent exchange to water, and subsequent freeze drying is used to produce ultralight (4.3 mg/mL) and highly porous (99.7%) cellulose diacetate (CDA) aerogels with honeycomb morphology. This versatile synthesis approach is extended to other nonaqueous polymers with hydroxyl functionalities such as cellulose acetate propionate and cellulose acetate butyrate to produce a single component polymer aerogel. These aerogels demonstrate a maximum water and oil uptake of up to 92 and 112 g/g, respectively. The honeycomb morphology provides a maximum compression strain of 92% without failure and reaches a compressive stress of 350 kPa, for 4 w/v % CDA aerogels (4%), which is higher than that reported for cellulosic aerogels. The 4% CDA aerogel were rendered hydrophobic and oleophilic via chemical vapor deposition with organosilane. The modified CDA aerogel surpasses their counterparts in maintaining their mechanical integrity for fast oil cleanup and efficient oil retention from aqueous media under



marine conditions. These aerogels are identified to be reusable and durable for a long period.

# 1. INTRODUCTION

Kistler, in 1931, prepared the first aerogel by supercritical drying of the solvent in the gel.<sup>1</sup> Subsequent development of supercritical CO<sub>2</sub> drying process made aerogel synthesis relatively fast and safer.<sup>2</sup> However, it was not until NASA's stardust mission, which captured high-speed cosmic particles using silica aerogels, that aerogels gained media attention in 2006.<sup>3</sup> Many novel aerogels have been synthesized since then, including carbon nanotubes,<sup>4,5</sup> graphene,<sup>6,7</sup> quantum dots,<sup>8</sup> polyimides,<sup>9</sup> cellulose,<sup>10</sup> and nanocellulose.<sup>11,12</sup> The definition of aerogels also developed over time. However, an important feature shared by all aerogels is the removal of the solvent from wet gel with minimum shrinkage to give high pore volume, usually higher than 90%.<sup>13,14</sup>

Even though a plethora of aerogels have been reported in the last decade, not much work has been carried out on singlecomponent polymer aerogels. Polymers have been used largely as a reinforcing material to improve elastic properties of inorganic aerogels.<sup>15–17</sup> In addition, although single-component aerogels from aqueous-based polysaccharides such as alginate, pectin, starch, chitin, chitosan, agar, and cellulose have been synthesized, their wet strength is questionable.<sup>14,18</sup> Polyurethane aerogels are one of the earliest synthetic polymer aerogels reported, which are formed by polycondensation of isocyanates and alcohols.<sup>19</sup> The isocyanates are, however, generally toxic and very reactive, which may sometimes prove hazardous to the surroundings.<sup>20</sup> Meador and co-workers have worked extensively with nonaqueous polyimide aerogels and have demonstrated improved mechanical properties for these aerogels.<sup>9,21</sup> In this study, we demonstrate single component aerogel synthesis from a different class of polymers, namely, cellulose esters, that are nonaqueous polymers with hydroxyl functionality.

Cellulose esters are polymers derived from the abundantly available cellulose but are easy to process than their parent cellulose owing to reduced intramolecular hydrogen bonding.<sup>22</sup> The aerogel synthesis approach is developed on cellulose acetate, which is extended to cellulose acetate propionate (CAP) and cellulose acetate butyrate (CAB), exhibiting a wide-range capability of this approach. Surprisingly, there have been few attempts at making aerogels from cellulose esters. Tan et al.<sup>23</sup> prepared aerogels by urethane linkage of cellulose acetate and cellulose butyrate followed by supercritical drying. The study was later reproduced by Rigacci and co-workers with cellulose acetate aerogels.<sup>24,25</sup> However, both of these efforts produced aerogels with high density (>0.1 g/mL) and low pore

Received: May 8, 2017 Accepted: June 6, 2017 Published: August 8, 2017 volume (<90%). The aerogel synthesis process usually involves solvent exchange prior to supercritical  $CO_2$  drying to replace water in the pores with a solvent that has high affinity for liquid  $CO_2$  such as acetone or ethanol. Here, we propose an alternative method where the gel is prepared in acetone but a solvent is exchanged to water prior to freeze drying. This approach produces ultralight cellulose acetate aerogels (4.3 mg/mL) with high pore volume (>99%). Moreover, the 4 w/v % cellulose acetate (4%) aerogel, with a density of 24.3 mg/mL, demonstrates unprecedented mechanical properties with a maximum compression strain of 92% without failure and a compressive stress of 350 kPa, which is higher than that reported for cellulosic aerogels.

Furthermore, 4% cellulose diacetate (CDA) aerogels selectively separate oil from a simulated spill in water without any observable disintegration of the material. The oil spill is highly detrimental to our ecosystem, and the prevalent technologies proposed to deal with oil spills, such as oil skimming, in situ burning, mechanical containment and utilization of dispersants, solidifiers, and degrading microorganisms, 26-31 are either inefficient or environmentally unfriendly. In this type of scenario, the use of sorbents is attractive because it is easy to deploy and do not generate byproducts. However, commercially used polypropylene mats that suffer from low sorption capability (typically less than 10 g/g of substrate) are difficult to recover (they are not buoyant) and are not biodegradable. Here, we have shown that the cellulose acetate aerogels present an attractive option for oilspill remediation owing to better wet strength, impressive mechanical integrity, durability, fast oil uptake, and oil retention under marine conditions.

# 2. RESULTS AND DISCUSSION

We begin by describing the formation and properties of a CDA aerogel. The versatility of the synthesis procedure is demonstrated by extending it to CAP and CAB. This is followed by conversion of CDA aerogels into their hydrophobic and oleophilic analogues, which are examined for their performance in simulated oil-spill remediation.

2.1. Aerogel Synthesis and Properties. Aerogel formation occurs in a three-step sequence starting with the synthesis of the organogel (gel in acetone), which is converted into a hydrogel (gel in water) and then into the final form (aerogel). Figure 1a shows the first step in the process in which the organogel is formed by the cross-linking reaction via ester linkages between hydroxyl groups in CDA and anhydrides of pyromelletic dianhydride (PMDA). While the formation of strong, self-standing gels at low CDA concentration (4 w/v %) (Figure 1a) indicates good cross-linking, direct evidence comes from the comparison of Fourier transform infrared (FTIR) spectra (Figure 1b) of the aerogel with that of CDA flakes. The main differences between the two FTIR spectra are (a) out of plane angular vibrations of aromatic sp<sup>2</sup> C–H bends (from 690 to 900 cm<sup>-1</sup>) and (b) aromatic C=C stretch ( $\sim$ 1500 cm<sup>-1</sup>). These two peaks indicate the presence of aromatic cross-linker in the aerogel. Also, the lack of paired bands for C=O stretch (indicative of anhydride groups between 1800–1830 cm<sup>-1</sup> and 1740-1775 cm<sup>-1</sup>) suggests that all PMDA reacted with the CDA hydroxyl groups. A slight broadening of O-H stretch at 3476  $\text{cm}^{-1}$  is assigned to the increased number of O–H bonds via the carboxylic groups formed. The strong acetyl C-O and alkoxy C-O peaks at 1220 and 1032 cm<sup>-1</sup>, respectively, indicate the presence of C-O-C stretching in the glucopyr-



**Figure 1.** (a) Proposed cross-linking reaction between CDA chains and cross-linker PMDA with the image showing the gelation of CDA solution into acetone-based organogel after the gel was set for 24 h and (b) FTIR spectra of CDA flakes and aerogels.

anose ring. These peaks combined with prominent carbonyl peak (C=O stretch) at 1736 cm<sup>-1</sup> confirm the presence of ester groups in CDA. The peaks at around 2950 cm<sup>-1</sup> are because of sp<sup>3</sup> C–H stretch, and the peak at 1368 cm<sup>-1</sup> corresponds to C–H bend.

We then examine to what extent the organogel swells (or shrinks) as we transition it to its final aerogel form via the intermediate hydrogel state, by measuring its density at each stage. Such information is important to understand the underlying structural changes a material undergoes during aerogel formation, an area in which very little work exists. Table 1 shows the densities of the organogel, hydrogel, and aerogel together with the aerogel pore volume, which are further depicted in Figure 2a. The organogel and hydrogel densities were calculated by assuming that all of the liquid was replaced with air without changing the volume of the gel (see Supporting Information for calculations).

Several features are evident from the data. First, the bulk densities of the 2 and 4% aerogels are much lower than the

Table 1. Density Values and Aerogel Pore Volume

	2%	4%	6%	8%
organogel density (mg/mL)	20.0	40.3	60.7	81.4
hydrogel density (mg/mL)		19.3 ± 1.6	50.8 ± 1.2	93.3 ± 2.1
aerogel density (mg/mL)	4.3 ± 0.7	$23.4 \pm 1.0$	$77.2 \pm 1.6$	$110.2 \pm 1.2$
aerogel pore volume (%)	99.7 ± 0.1	98.2 ± 0.1	94.1 ± 0.1	91.2 ± 0.1

calculated organogel density, unlike that for the 6 and 8% aerogels. The smaller density is likely due to the extensive swelling of the gels during gradual solvent exchange with water, along with small shrinkage during freeze drying. Second, we find (Figure 2a) that the 4% hydrogel does not exhibit appreciable shrinkage during freeze drying, as indicated from a very small increase in the aerogel density from hydrogel density. By contrast, the 6 and 8% hydrogels exhibit a large shrinkage during freeze drying. Third, the 8% CDA gels seem to shrink during the solvent exchange (whereas the 2, 4, and 6% gels swell during the solvent exchange). This observation is consistent with the strong intermolecular hydrogen bonding exhibited by CDA, which is expected to be stronger at the high CDA concentration that limits solvent penetration. Finally, owing to its extensive swelling, the 2% aerogel is ultralight and highly porous (density of 4.3 mg/mL and pore volume of 99.7%, Figure 2b). This is one of the lightest reported cellulosebased aerogels (see Table S2, for comparison).

The morphology of the aerogels was examined using a scanning electron microscope. The radial cross-section of the 4% aerogels shows irregularly shaped pores formed by filmlike walls of the assembled CDA [scanning electron microscopy (SEM) image in Figure 2c, inset]. The image reveals that the pore size is dictated by the rate of freezing.<sup>22</sup> Water in the hydrogels nucleate forming ice crystals that squeeze out the cross-linked CDA polymer and compress them into thin walls. The crystals then sublime during the drying process leaving behind cylindrical pores with an average diameter of 50  $\mu$ m. The CDA aerogels exhibit a low Brunauer-Emmett-Teller (BET) surface area  $(3.4 \text{ m}^2/\text{g})$  as compared to aerogels obtained from other cellulosic sources likely because of the large pore size of the aerogels. Figure S1 shows the  $N_2$ adsorption-desorption isotherm for the aerogel along with the pore size distribution in the inset. The lack of any distinct peak below 500 Å indicates the lack of micro- or mesoporosity. Assuming that the CDA aerogel is composed of cylindrical macropores, with a diameter range of 50-100  $\mu$ m running throughout the aerogel along the radial axis and the wall thickness of 1  $\mu$ m (Figure S2), we calculate the surface area to be in the range of  $1.6-3.2 \text{ m}^2/\text{g}$ , which agrees well with the value measured by  $N_2$  adsorption (see Supporting Information). This agreement further supports the lack of microporosity in the aerogel.

The porous morphology, including thin-walled structures observed in the cross-linked CDA aerogels, results in highly



**Figure 2.** (a) Comparison of the measured and the calculated density of organogels and hydrogels assuming that all solvents were replaced with air while maintaining the size of the gel. Data for 2% hydrogel density are not reported because the high swelling of the respective organogel during the solvent exchange made the hydrogel fragile for handling during measurements, (b) image of the 2% aerogel (density 4.3 mg/mL) on a dandelion leaf, (c) compressive stress—strain profile for 4% aerogels with the maximum compressive stress of 350 kPa and maximum strain of 92%. It is to be noted that the desired shape of the 2% aerogel was difficult to synthesize owing to the breakage of the gel during the sequential solvent exchange process. Hence, the compression testing of 2% aerogel was not performed. Along the same lines, owing to the relatively high concentration of polymer in 6 and 8% CDA gels, the final aerogel product for these gels have unavoidable artifacts during solvent exchange and freezing steps. The stress—strain curve for the 6 and 8% aerogels are not reported here. However, we found that both the 6 and 8% aerogels consistently yielded below 30% strain (Figure S3). Inset of the SEM image shows the radial cross-section of 4% CDA aerogel and (d) water uptake and kerosene oil uptake (g/ g of aerogel) as exhibited by the different aerogels.



Figure 3. SEM images of 4% (a) CAP and (b) CAB aerogels. Inset shows camera images of the respective aerogels. (c) Water and oil uptake by the three types of aerogels. (d) Liquid volume uptake normalized with the available pore volume per gram of the aerogel for all three aerogels.



**Figure 4.** Images showing the water-contact angle; (a) water wicks through the surface of the unmodified CDA aerogel, high water-contact angle at (b1) the top surface and (b2) transverse cross-section of the modified aerogel, (c) water uptake by the modified aerogel just after silanation (t = 0) and the same aerogel sample after 4 months. Inset images demonstrate high water-contact angle on the modified aerogel surface, and (d) the graph demonstrates that the modified aerogel retains its hydrophobicity even after 48 h.

compressible systems (see compressive stress-strain curve of 4 w/v % CDA aerogel, Figure 2c). Cross-linking a gel with relatively high polymer concentration gives an aerogel with a maximum compressive strength of 350 kPa, which is larger than the values reported for cellulosic aerogels (see Table S1). In contrast to the brittle behavior of silica aerogels,<sup>32</sup> the 4% CDA aerogel exhibits a high compression strain (92%) without failure. The high compression strains are generally comparable to carbon nanofiber aerogels and are higher than those of the cellulosic aerogels reported.<sup>12,33-36</sup> Interestingly, the 4% aerogel does not exhibit any yielding, suggesting that the relatively high concentrations of CDA used during synthesis (4 w/v %) renders strength and high compressibility to the aerogel.

Given the high pore volume and the closed cell morphology, the CDA aerogels are expected to perform ideally for liquid uptake, as confirmed experimentally (Figure 2d) for oil and water uptake. The 2% aerogels showed the highest water sorption of 92 and 112 g/g of aerogel, although capillary forces caused their collapse during evaporation. The 4, 6, and 8% CDA aerogels, however, were strong enough to sustain the capillary forces. The liquid uptake recorded for CDA aerogels in this study is comparable to the liquid uptake reported for nanocellulosic aerogels (see Table S2 and references therein). Figure S4 shows the liquid uptake (oil and water) relative to the available pore volume. The marginally higher water uptake compared with the available pore volume in 4, 6, and 8% aerogels suggests a significant finding in that sorption may take place both in the pores and on the polymer. Moreover, a ratio of oil uptake less than 1 may imply entrapment of air bubbles during sorption.

Article



**Figure 5.** (a) Snapshots from Movie S1 demonstrating the separation of spent kerosene oil from oil/water stagnant media. Reusability of the aerogel is demonstrated in the figure; (b) graph for the mass balance of the water and oil before and after separation indicating the complete removal of oil with very negligible sorption of water; (c) reusability of the aerogel was tested for 10 cycles of sorption and desorption (by mechanical compression) of *n*-hexane; (d) snapshots from Movie S2 to demonstrate the separation of dyed kerosene oil from oil-in-water-stirred system (kerosene: 6 g, deionized (DI) water: 100 g, aerogel: 0.26 g, and stirring rate: 500 rpm); and (e) snapshots from Movie S3 demonstrating the separation of high viscosity spent motor oil from motor oil/water-stirred system to model oil spill in a turbulent sea (motor oil: 7 g, DI water: 100 g, and aerogel: 0.35 g). Upper photographs show the side view of the beaker used for the study prior to the addition of the modified aerogel ("initial system"; upper left photograph) and an overhead view of the instant that the aerogel was added to the beaker (t = 0 s; upper right photograph).

To demonstrate the versatility of our aerogel synthesis approach, CAP and CAB aerogels were synthesized. Both of these are nonaqueous polymers where some of the hydroxyl groups are replaced by propionate and butyrate functional groups (Figure S5). SEM images of 4% CAP and CAB aerogels are shown in Figure 3a,b, which exhibit a honeycomb structure similar to that observed before for the CDA aerogel. Yet again, we were able to prepare one of the lightest single component polymer aerogels starting from a relatively high concentration of 4 w/v %. The density and the pore volume of CAP were measured to be  $13.0 \pm 0.9 \text{ mg/mL}$  and  $99.0 \pm 0.1\%$ , respectively. The density of CAB was slightly on the higher side, that is,  $27.9 \pm 3.2 \text{ mg/mL}$  but still 10 times lower than that reported for the earlier cellulose ester-based aerogels.<sup>23,24</sup> Compared with CDA aerogels, the 4% CAP and CAB aerogels exhibit lower water uptake (Figure 3c) because of increased hydrophobicity arising from longer carbon chain functional groups, namely, propionate and butyrate. The oil uptake is the highest for CAP owing to the largest available pore volume, validated from Figure 3d, where the liquid uptake is normalized with the available pore volume, and for oil uptake, the ratio is  $\sim$ 0.8 for all three types of aerogels. The similar morphological and bulk characteristics of CAP and CAB aerogels to CDA aerogels suggests that the mechanical properties of CAP and CAB aerogels will not be much different from that of CDA aerogels. Hence, they were not measured.

The low density, high pore volume, and impressive mechanical property of cellulose ester aerogels offer a strong potential for their use in cleaning oil spills by selective uptake of oil from water. The unmodified CAP and CAB aerogels may be ideal for selective separation of oil. However, we selected 4% CDA aerogels to test for the further studies of oil-spill remediation to identify whether the comparatively less hydrophobic CDA aerogels have the potential to be rendered more hydrophobic and oleophilic by chemical vapor deposition (CVD) with an organosilane. This may expand the scope of these cellulose ester aerogels.

2.2. Aerogel Modification To Reduce Water Uptake. To increase the hydrophobicity and oleophilicity of CDA aerogels, the CVD with trichloro-octylsilane (TCOS) was used to cap free hydroxyl functionalities with the hydrophobic chains. As shown in Figure 4a, a water droplet completely wicks through the surface of the unmodified 4% CDA aerogel, whereas a modified 4% CDA aerogel shows a water-contact angle exceeding 120° on both surfaces of the aerogel (Figure 4b1). Moreover, the fact that the transverse cross-section of the modified aerogel exhibits a high water-contact angle (Figure 4b2) indicates that TCOS diffuses below the surface of the aerogel, rendering the bulk aerogel hydrophobic. In general, all observed contact angles for the modified aerogels were greater than 120°. Note, however, that the typical large variation in contact angle values is due to the uneven surface on the aerogel. An X-ray photoelectron spectroscopy (XPS) survey scan of the top surface and transverse cross-section of the modified aerogel (Figure S6a) further confirms the diffusion of TCOS into the bulk of the aerogel. The calculated Si/O at. % at the top surface and in the center is 19 and 2 at. %, respectively. It is likely that the diffusion of TCOS inside of the bulk of the aerogels can be further increased by increasing the CVD exposure. However, a 2 h exposure to TCOS proved sufficient as the modified aerogels (2 h CVD) retained their hydrophobicity for months as indicated by the high water-contact angle on their surface  $(>120^{\circ})$  and the low water uptake (<3 g/g of aerogel, Figure)4c). It is to be noted that the samples were stored under the



Figure 6. Uptake of various liquids by modified aerogels. (a) Setup of wicking experiments showing immersion of cuboidal aerogel into the liquid of interest. The bottom face of the liquid is immersed 1.5 mm below the liquid surface. (b) Liquid uptake rate for three oils.

atmospheric condition for 4 months. This reflects the stability and durability of the modified aerogel over a long period.

The samples of the modified and unmodified 4% CDA aerogels were subjected to water sorption test for 48 h, with their behavior monitored after placing them on the surface of water. The unmodified CDA aerogel quickly sorbed water, between  $\sim$ 35 and 40 g/g aerogel in the course of approximately 48 h, whereas the TCOS-modified CDA aerogel was hydrophobic and sorbed less than 3 g/g aerogel during the same time period (Figure 4d). These data demonstrate that the modified aerogel is stable and retains its hydrophobicity even after constant exposure to water for 48 h.

2.3. Oil Separation. The TCOS-modified 4% CDA aerogel was tested in various scenarios of oil-in-water systems to evaluate their liquid uptake properties and mechanical integrity. The model oil used in these studies was a spent kerosene grade oil (viscosity of  $\sim 1-2$  cP). A sample of 0.26 g of the modified aerogel was placed into a jar, which contained 10.5 g of oil and about 59.4 g of water. The photographs of Figure 5a show the process of the selective sorption over time of the oil from the oil/water mixture by the modified aerogel. The aerogel was saturated with oil within a minute, as shown in Figure 5a(ii,iii). The oil-loaded aerogel was hand-pressed, as shown in Figure 5a(iv), to recover the oil and was reused to remove the oil remaining in the oil/water mixture, as shown in Figure 5a(v,vi). Movie S1 demonstrates the separation of oil from the oil/water mixture. The mass balance of the liquids from the separation shown in photographs of Figure 5a is shown in Figure 5b. The weight of the water, oil, and aerogel was measured before the experiment, and the weight of the oil pressed from the aerogel was measured after the experiment. The weight of the used aerogel and the remaining water was measured to complete the mass balance. The data shown in Figure 5b show that about 83 wt % of the kerosene oil was recovered, with the unrecovered oil staying trapped in the aerogel. In addition, the water sorption by the CDA aerogel was negligible (about 0.02 wt %), which suggests that the recovered oil could be reused.

No major changes in the aerogel structure were observed after multiple cycles of sorption and mechanical compression. The reusability of the modified aerogels was tested via *n*-hexane sorption and desorption by mechanical compression (Figure 5c). We found that a TCOS-modified 4% CDA aerogel can be subjected to at least 10 cycles of sorption and compression before undergoing structural failure. As shown in Figure 5c, the modified aerogel can sorb over 25 times its weight of *n*-hexane in the first cycle and can still sorb about 10 g of n-hexane per gram of aerogel even after 9 cycles of sorption/compression.

The modified aerogels were further tested under shear conditions in an oil-in-water medium (Movie S2). The spent kerosene was dyed red for better observation. Figure 5d shows the photographs to indicate that a clear solution is obtained within a minute because nearly all of the dyed oil is soaked up by the modified aerogel. The modified aerogel retains both oil and its mechanical integrity even in the stirred media, indicating its utility for oil-spill cleanups in the agitated media. To further simulate high viscosity oil spill in a turbulent environment (typical in marine environments), a stirred oil-in-water system was prepared (Movie S3), in which the oil used was spent motor oil (spent car oil with a viscosity of about 170 cP). As indicated by the photographs of Figure 5e, the modified aerogel sorbed all of the high viscosity motor oil within 2 min, even in the stirred media.

The rate of oil uptake was measured via wicking experiments using a tensiometer (CAHN DCA-312). The aerogels were cut into a cuboid shape and lowered into the liquid (see Figure 6a). Extreme care was taken to cut the aerogels in one direction to ensure that the pore alignment was same in all measured samples. The bottom edge (surface) of an aerogel was submerged 1.5 mm below the surface of a given liquid to ensure continuous contact of the aerogel with the solvent during the course of the experiment. Kerosene oil, crude oil, and motor oil were the liquids used with viscosity 1.4, 10, and 168 cP, respectively. Figure 6b shows the liquid uptake rate by the modified aerogel. We observe that the low-viscosity kerosene oil wicks the modified aerogel instantaneously, in contrast to the high-viscosity motor or crude oil. Motor oil with the highest viscosity has the slowest liquid uptake rate, as expected. The maximum uptake of crude oil is the highest, as crude oil  $(0.97 \text{ g/cm}^3)$  has a higher density than kerosene oil  $(0.8 \text{ g/cm}^3)$ . It should be noted that the wicking rate of any oil can be further tuned by changing the surface energy of the aerogel with other compounds such as fluorocarbons. The liquid uptake can also be tuned by changing the pore size of the aerogel, which in turn can be altered by controlling the freezing rate. These surface and bulk modifications are, however, subjects of further studies.

# 3. CONCLUSIONS

A versatile method to synthesize a single component polymer aerogel from a nonaqueous polymer with hydroxyl functionality is presented and demonstrated with cellulose esters. A unique combination of chemical cross-linking, solvent exchange, and freeze drying process was used to produce ultralight (4.3 mg/mL) and highly porous (99.7%) CDA aerogels for the first time. A low density cellulose ester aerogels (<30 mg/mL) were easily synthesized even with a relatively high starting concentration of the polymer (4 w/v %). The honeycomb morphology was provided by 4% CDA aerogels with high compressive strength (up to 350 kPa) and maximum strain of about 92%. These 4% CDA aerogels could be modified to render them hydrophobic and oleophilic and can be potentially used to selectively clean oil from oil spills in the rough marine environments.

# 4. EXPERIMENTAL SECTION

**4.1. Materials.** CDA (acetyl: 39.8% and hydroxyl: 3.5%), CAP (propionyl: 42.5% and hydroxyl: 5%), and CAB (butyryl: 46% and hydroxyl: 4.8%) were provided by the Eastman Chemical Company and used as received. Acetone (99%), ethanol, triethyl amine (TEA), TCOS, and the cross-linking agent 1,2,4,5-benzenetetracarboxylic acid (also known as PMDA) were purchased from Sigma-Aldrich. DI water was used. Dry ice was prepared in the laboratory using a liquid CO<sub>2</sub> cylinder with a siphon tube bought from Airgas (NC). All solvents used for wicking measurements were 99% pure and were bought from Sigma-Aldrich. Spent kerosene oil and motor oil together with Texas crude oil were used for experimental purposes.

4.2. Gelation of Cellulose Esters. CDA gels were synthesized using a PMDA cross-linker as reported earlier.<sup>37</sup> Briefly, a homogeneous solution of CDA in acetone was formed by stirring it in a 100 mL Pyrex bottle for 24 h. The stoichiometric amount of PMDA required for complete crosslinking was calculated by assuming that one PMDA molecule reacts with two hydroxyl groups on different CDA chains (Figure 1a). The CDA/PMDA molar ratio of 2:1 is required for complete cross-linking, but for this study, CDA/PMDA molar ratio of 8:1 was used to prevent the formation of a rigid crosslinked structure and to have free hydroxyl groups available for further modification. CDA solutions (2, 4, 6 and 8 w/v %) with the PMDA cross-linker were stirred for approximately 5 h to ensure complete dissolution. To this solution, 0.5 vol % of catalyst TEA was added while stirring for another 30 s. The solution was then transferred to a cylindrical mold and allowed to set into a gel for 24 h. Thereafter, the obtained organogels, hydrogels, and aerogels are referred to by using the concentration of the initial CDA solution (2, 4, 6, and 8%). The 4% CAP and CAB gels were prepared similarly.

**4.3. Solvent Exchange.** The acetone-gelled cellulose ester was subjected to sequential solvent exchange steps to gradually replace acetone with DI water. The gel was placed in a mixed solution of acetone and DI water; the volume of the DI water was five times the volume of the gel and was replaced every 12 h to allow enough time for the gels to reach equilibrium with the solution. A total of six such exchanges were performed with the following ratios of acetone/DI water used in sequence: 90:10, 75:25, 50:50, 25:75, 10:90, and 0:100. After the final exchange, the gel was kept in DI water for 24 h. This gel in water is termed as hydrogel.

**4.4.** Aerogel Synthesis. The hydrogel was frozen by completely immersing the gel in a dry ice/ethanol bath for 20 min. The frozen hydrogel was then transferred to a lyophilizer (Labconco FreeZone 2.5 Freeze Dryer) operating at -53 °C

and 0.113 mbar, which is lower than the triple point of water.<sup>38</sup> The freezed hydrogel was dried for  $\sim$ 24 h to obtain the aerogel.

**4.5. Aerogel Modification.** The CDA aerogels were subjected to CVD with TCOS to convert them hydrophobic and oleophilic.<sup>39</sup> A bottle-in-a-bottle setup was used for this purpose (Figure S6b), where TCOS was kept in the smaller container, and the aerogel was kept on a wire mesh atop. The system was kept in an oven at 80 °C for 2 h.

**4.6. Density, Pore Volume, and Surface Area.** Aerogel density ( $\rho_a$ ) was calculated by measuring its mass and volume. The aerogel was cut into cuboidal shape using a sharp clean blade. The mass of this cut aerogel was measured using an analytical balance, Fisher Scientific Accu-225D, which has the least count of 0.1 mg, and the volume was determined by using the dimensions (digital Vernier caliper). It is to be noted that the 2% aerogel was cut into small cuboidal shapes to measure its volume. Average density is reported after five measurements. The pore volume of the aerogels was calculated using eq 1

Pore volume =  $(1 - \rho/\rho_{CE}) \times 100\%$  (1)

where  $\rho_{\rm a}$  is the bulk density of aerogel,  $\rho_{\rm CE}$  is the bulk density of cellulose esters, 1.3 g/mL for CDA, 1.27 g/mL for CAP, and 1.2 g/mL for CAB.<sup>40</sup>

The BET surface area was measured by N<sub>2</sub> absorption and desorption isotherms using Micromeritics ASAP 2020. About 0.1–0.2 g of the sample was first degassed for 3 h at 115 °C prior to the analysis. BET analysis was carried out for a relative pressure of 0.01–0.3 at –196 °C.

**4.7. Chemical Analyses.** FTIR in the attenuated total reflectance mode (FTIR-ATR) was conducted using a PerkinElmer spectrophotometer. Samples were analyzed using the PIKE MIRacle accessory equipped with a GE crystal. The spectrum was collected for 256 scans and corrected for background noise. The multipoint baseline correction was realized for each spectrum.

**4.8.** Scanning Electron Microscopy. Imaging was recorded using a field-emission scanning electron microscope (FESEM), FEI Verios 460L. The aerogels were fractured under liquid  $N_2$  using a sharp clean blade to image the radial cross-section. The samples were fixed on the metal stub using a double-sided carbon tape. The as-prepared SEM samples were coated with a 5 nm layer of gold and platinum to capture secondary electrons from the surface and thus reduce charging.

**4.9. Mechanical Compression Testing.** The freeze-dried aerogels synthesized for compression testing were molded in 20 mL syringes with a height/diameter ratio of 2:1. The top and bottom part of a cylindrical aerogel was made smooth by using a sharp clean blade. Compressive stress-strain curves were obtained using an Instron Series IX with compressive loads of 0.5 N, which were lowered at the rate of 5 mm min<sup>-1</sup>.

**4.10. Sorption Test.** The aerogel was immersed in a liquid and allowed to saturate. After immersion, the surface of the saturated aerogel was blotted with a paper wipe to remove surface liquid and weighed. Liquid uptake was calculated using eq 2

$$Liquid uptake = \frac{W_{ab} - W_{a}}{W_{a}}$$
(2)

where  $W_{ab}$  and  $W_a$  are the weights of saturated and dry aerogels, respectively. Note, for sorption of organic solvents, the blotting step was avoided to prevent wicking of the solvent

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to the paper wipe. Instead, the saturated aerogels were weighed immediately.

**4.11. Reusability Tests.** A representative solvent of a low surface energy oil, *n*-hexane, was used to test the reusability of modified aerogels. Loaded aerogels were mechanically compressed between paper wipes to remove the solvent and weighed again to ensure at least 70% of the solvent was squeezed out. The process of sorption and compression was repeated until the aerogel lost its mechanical integrity, which was identified when the aerogel was not able to recoil back as observed by the unaided eye. The average data with standard deviation are reported after repeated tests with three different samples.

### ASSOCIATED CONTENT

#### **S** Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.7b00571.

Separation of oil and water using cellulose acetate aerogel, CVD setup, XPS survey scan, tables for CDA aerogel comparison with reported cellulosic aerogels, structure of cellulose esters, nitrogen adsorption– desorption data, compressive strength and liquid uptake of various aerogels, and density calculations (PDF)

Demonstration of separation of spent kerosene oil obtained from cleaning the pump, spent kerosene oil from oil-in-water stirred emulsion system, and spent motor oil (obtained from the oil change) from water in a stirred system to model oil spill in a turbulent ocean (ZIP)

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#### Notes

The authors declare no competing financial interest.

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