Low-Density, Mutually Interpenetrating Organic–Inorganic Composite Materials via Supercritical Drying Techniques

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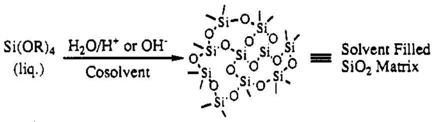
Low-density SiO_2 aerogels are an interesting class of materials for which commercial applications have been hampered by their brittle mechanical properties, hygroscopic nature, and sometimes limited transparencies. We have been interested in addressing these key problems by developing methods of homogeneously incorporating organic polymers within the SiO_2 framework. The formation of low-density organic–inorganic aerogel materials that show improved properties over conventional aerogels is reported. Two approaches are presented, both of which rely on supercritical CO_2 exchange during the drying process. The first approach involves addition of preformed polymers poly(2-vinylpyridine) (PVP), poly[methyl methacrylate-*co*-(3-trimethoxysilyl)propyl methacrylate)] (PMMA-TMSPM), and silanol-terminated poly(dimethylsiloxane) (PDMS) to the sol–gel precursor solutions, while the second approach involves forming the organic polymer cross-linked poly(*N,N*-dimethylacrylamide) (PDMA) in situ. In both cases bonding of the organic phase to the SiO_2 structure is important and crosslinking of the organic polymer further improves their properties. The mechanical, optical, and hydroscopic properties of these materials are reported.

Introduction

Among the several options that exist for the drying of solvent-filled, SiO_2 gels synthesized through the sol–gel process,[1] the supercritical drying process[2] is unique in allowing for the preparation of ultralow-density aerogel materials. Porous aerogels with densities as low as 0.003 g/cm^3 have been reported.[3] Although quite fragile, aerogels have fascinating properties including extremely low thermal conductivities ($\approx$0.002 W m^{-1} K^{-1})[4] and sound propagation characteristics (sound velocities less than 100 m/s have been reported).[5] The current commercial applications of sol–gel materials are impressive but limited. Recent examples include the pioneering work on the development of thermal insulating windows,[6] sol–gel-derived luminescent solar concentrators (LSC),[7] and collectors for Cerenkov radiation.[8] Despite their highly unusual properties, sol–gel materials have yet to reach their full potential. Some of the problems that have impeded their commercial development include their highly brittle character, sometimes limited transparency, and hygroscopic nature. Through our efforts to directly address these problems, we wish to report that incorporating small amounts of organic polymers into these fragile inorganic networks dramatically increases their compression strength and toughness, improves their optical transparency, and decreases their hydrophilicity.

The sol–gel process[1] involves the homogeneous hydrolysis and condensation of metal alkoxides (typically tetramethoxy or tetraethoxy orthosilicates, TMOS and TEOS, respectively) in the presence of cosolvents to form highly cross-linked, solvent filled gels (eq 1). Once formed,



(1)

the gelled SiO_2 network must be dried, requiring the removal of excess water, cosolvent(s), and the liberated alcohol (typically ethanol or methanol). It is the drying process that effectively prevents the practical and reproducible synthesis of monoliths or thick films with dimensions greater than a few millimeters, because these objects tend to shrink, crack, and shatter (shrinkages of 50–75% are common).[9] The shrinking and cracking are caused by drying stresses generally attributed to large capacity forces generated in the very small (<10 nm) pores of the gel.[10] By replacement of the pore solvents with a supercritical fluid (primarily CO_2 at 31 °C and 71 atm in this current work), the meniscus and associated capillary forces are eliminated and the fluid can then be removed leaving the low-density, ramified network intact and relatively uncompressed.[11] Due to miscibility problems, exchanging in supercritical CO_2 can be accomplished only by first replacing the pore solvents with an intermediate exchange

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solvent that is fully miscible with supercritical CO_2. Good exchange solvents include methanol, ethanol, isopropyl alcohol, pentane, and acetone.

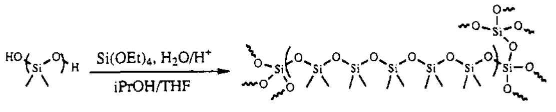
Results and Discussion

On the basis of our previous work on reinforcing sol–gel-derived xerogel networks by interpenetrating them with organic polymers,[12] we sought to develop a similar protocol applicable for these low-density aerogel materials. The primary requirement for success with this approach is the identification of organic polymers that are soluble in both the supercritical CO_2 as well as the intermediate exchange solvents. Polymers that are insoluble in any of the processing mediums rapidly phase separate or precipitate in the gel and opaque, noncohesive materials result. A secondary consideration is the inadvertent leaching of the organic polymer from the gel during the solvent exchange processes. Although a number of polymers can be uniformly incorporated into gels during the synthesis stage, many are nearly quantitatively removed during the processing steps. In some cases such as cellulose acetate (MW = 30 000, 33% acetylated), the polymer is only partially extracted, but the majority of it migrates to the surface of the SiO_2 sample rather than being uniformly distributed throughout. Ultimately, the best systems we found all employed different strategies to bind the polymer to the SiO_2 network so that these leaching and homogeneity problems could be surmounted.

Of the numerous polymers that were examined, four have been found to be appropriate for formation of these low-density, aerogel composites: poly(2-vinylpyridine) (PVP), poly[methyl methacrylate-*co*-(3-(trimethoxysilyl)propyl methacrylate)][13] (PMMA-TMSPM), silanol-terminated poly(dimethylsiloxane) (PDMS), and cross-linked poly(*N*,*N*-dimethylarylamide) (PDMA). The general procedure for formation of these composites first involves targeting a density by setting the total weight of the solids (polymer plus expected weight of SiO_2) in the appropriate amount of total solvent that defines the approximate volume of the final sample. Typically, the polymer, TMOS, and water are mixed with the appropriate amount of cosolvent (i.e., methanol, formamide, formic acid, THF, acetone, etc.) and the pH is adjusted to approximately 5. After gelation (10–20 h) and aging (1–14 days), the gels are soaked in 3–5 washings of the exchange solvent over a total period of 5–10 h in order to remove the catalyst, water, cosolvent, and the alcohol. Upon complete exchange, the gels are transferred to a high-pressure autoclave and liquid CO_2 (ca. 10 °C, 60 atm) is then exchanged for the intermediate solvent. Once this final exchange is complete, the temperature (ca. 40–45 °C) and pressure (80–100 atm) are increased until the system is above the critical point for CO_2. The supercritical fluid is then slowly removed yielding an optically transparent, low-density aerogel composite.

High-quality, transparent aerogel composites can be prepared that contain up to 38% linear PVP. Two molecular Weight PVP samples were examined, M_n = 50 000 and 200 000, with no discernible differences noted in the bulk properties of the composites obtained. Unlike other linear polymers that were examined (poly(vinyl alcohol), cellulose monoacetate, cellulose triacetate, poly(methyl vinyl ether), poly(*N*-vinylpyrollidone), Xanthan, poly(methyl methacrylate), and poly(ethylene oxide)), PVP shows little if any leaching from the gels during the solvent exchange and drying processes. Presumably this is due to extensive hydrogen-bonding interactions between the pyridine acceptors and the free silanols of the inorganic network. We also found that the mechanical properties of the PVP composites could be improved even further by incorporating small amounts of $CuCl_2$ that acts to cross-link the PVP by binding to multiple pyridinyl moieties on different polymer chains (*vide infra*).

To successfully incorporate other linear polymers into these composites, methods for forming direct covalent bonds between the two phases had to be employed. This can readily be accomplished using silanol terminated PDMS (M_n = 2,000) in a 3:1 isopropyl alcohol/THF solvent system.[14] Under the reaction conditions, the silanol end groups of the PDMS cocondense into the inorganic framework (eq 2).



(2)

Although linear PMMA readily leaches out (ca. 100% leaching observed) of the inorganic gels during the solvent-exchange process, we found that good methacrylate composites could be formed by using PMMA-TMSPM copolymers containing 1–10% of the propyl(trimethoxysilyl) moiety. Cocondensation of these PMMA-TMSPM copolymers with TEOS yields gels that discharge less than 1% of the polymer during processing. These PMMA-TMSPM copolymers were synthesized using standard free radical techniques (AIBN in benzene at 70 °C) and typically had molecular weights (M_n) ranging between 40 000 and 60 000. Successful, highly transparent aerogel composites were prepared with polymer concentrations as high as 50% by weight using these PMMA-TMSPM copolymers.

Alternatively, the polymers can be synthesized in situ by simultaneously carrying out the sol–gel condensation reaction and an independent free-radical polymerization of the appropriate vinyl monomer. This latter approach is particularly important because it allows the incorporation of crosslinks within the organic polymer to form two truly interpenetrating networks. For example, free radical polymerization of *N*,*N*-dimethylacrylamide containing 1–5% *N*,*N'*-methylenebisacrylamide cross-linking agent can be initiated in situ using ammonium persulfate (APS) and *N*,*N*,*N'*,*N'*-tetramethylethylenediamine (TMEDA) at room temperature. Near-quantitative polymerization of the acrylamide moieties is obtained under actual composite forming conditions using the APS/TMEDA initiator as evidenced by IR spectroscopy (Scheme 1).

We have synthesized samples of these materials with densities ranging from 0.5 to ca. 0.1 g/cm^3. Materials with densities less than 0.1 g/cm^3 can be easily prepared, but

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[15] Samples were predried in a vacuum over at ca. 120 °C and then suspended in a sealed vessel at 26 °C over a reservoir of water (the relative humidity within the vessel was not measured).

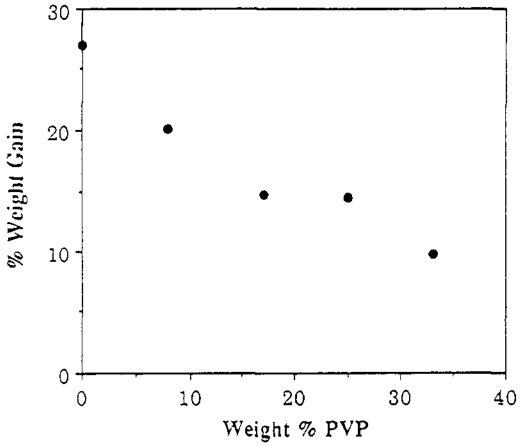


Figure 1. Water absorption by a constant-density (0.2 g/cm^3) series of SiO_2–PVP aerogel composites.

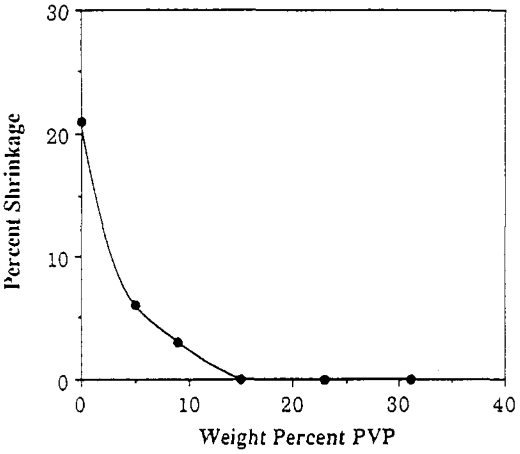
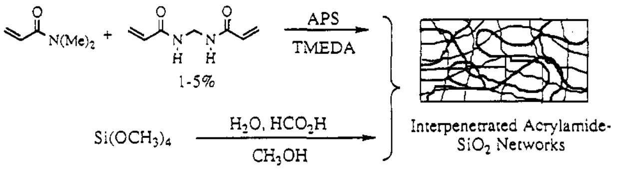


Figure 2. Percent shrinkage of a constant density (0.2 g/cm^3) series of aerogel PVP composites upon a 5-h exposure to atmospheric moisture.

Scheme 1



reproducibly forming flawless, uniform samples suitable for mechanical testing was difficult at these low densities.

The benefits realized by interpenetrating small amounts of organic polymer (ca. 5–20% by weight) into the inorganic networks are many. For example, upon exposure to ambient moisture, inorganic aerogels dried using supercritical CO_2 will absorb water and shrink (presumably due to continued silanol condensation reactions). Figure 1 shows the weight gain by a series of SiO_2–PVP aerogels when they are exposed to moist atmosphere[15] for 2 h, while Figure 2 shows their one-dimensional shrinkage.[16]

Clearly, inclusion of the PVP within these aerogels decreases their hydrophilic character and at loadings greater than 15% completely arrests their shrinkage. We attribute these changes to an increase in the bulk hydrophobic nature of these composites due to the presence of the polymer.

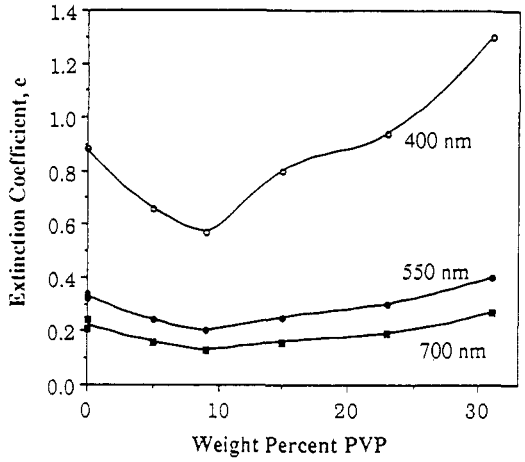


Figure 3. Extinction coefficients, *e*, at 400, 550, and 700 nm for a series of aerogel–PVP composites.

Additionally, we have found that the optical clarity of aerogels can be improved by the incorporation of PVP into these materials. This can be seen from the plot of molar extinction coefficient as a function of PVP content for a series of samples of uniform density (Figure 3).

In this series, the transparency is observed to go through a maximum value at ≈10% PVP. The most important factors in determining the transparency of a composite are the shapes and sizes of the domains and the relative difference between the refractive indexes between the two phases. The magnitude of scattering loss is exponentially dependent upon the ratio of the refractive indices across an interface: $I/I_0 \propto \exp[-K(n_p/n_m - 1)]$, where n_p and n_m are the refractive indexes of the pores and matrix, respectively.[17] For porous glass with air-filled pores, the ratio n_p/n_m is approximately 0.685. Completely replacing the air in the pores with polymer (PMMA) increases this ratio to 1.02 and in theory should substantially diminish the scattering loss. Such refractive index matching can only be partially responsible, however, in that we are doping these highly porous samples with only small amounts of polymer, and other polymers also with favorable refractive indexes do not show these same significant improvements. More likely, the polymer is influencing the structure of the inorganic component in some as yet undetermined way. Unfortunately, ongoing light-scattering and electron microscopy studies have not yielded definitive answers to this question.

Finally, we have found that incorporating PVP within the SiO_2 framework substantially alters and improves their mechanical behavior. Typical SiO_2 aerogels are frail materials that undergo catastrophic brittle failure at very low stresses. PVP-modified aerogels, however, exhibit diametrical behavior in that they undergo ductile yielding under stress. A comparison of the compression stress–strain curves for two samples of equal density, a pure SiO_2 aerogel and a 16% PVP/SiO_2 aerogel, is shown in Figure 4.

The amount of polymer included in the composite is key to determining the composite's properties. In general, by incorporation of organic polymers into aerogels there is a decrease in both the initial modulus at low strains and

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(16) A reviewer suggests that these are usually large shrinkages and water absorptions to observe for CO_2-dried aerogel materials. Although the actual magnitude of these values may vary from sample to sample depending upon the extent dehydration, pore structure, silanol content, etc., the relative trend is the important factor. We thank the reviewer for his comments.

(17) Richerson, D. W. *Modern Ceramic Engineering*; Marcel Dekker: New York, 1982.

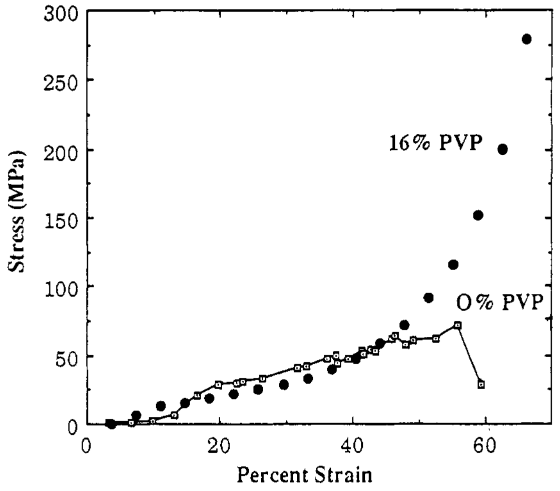

Figure 4. Comparison of the compression stress–strain curves for a pure SiO_2 aerogel (d = 0.2 g/cm^3) and composite aerogel doped with 16% linear PVP (d = 0.2 g/cm^3).

the offset yield strength but a substantial increase in the compressive strength (at high strains) of the composite materials relative to pure SiO_2 samples. Hence, the polymer–SiO_2 composites are less brittle and more ductile that their pure inorganic counterparts. Within a series of polymer–SiO_2 composites, both the modulus and compressive strength of the aerogel composites increase with increasing PVP content up to approximately 16–18% and then they begin to decrease. By 25% PVP, the properties deteriorate below those of pure SiO_2 aerogels of comparable densities. Like any other linear polymer, PVP does not form free standing aerogels on its own. In our view, as the volume percent of non-network-forming polymer (PVP) increases, it acts to impede complete formation of the inorganic network to such an extent that the bulk properties ultimately suffer. We felt that this limitation of the linear PVP could be overcome by incorporating cross-links into its structure. Under any conditions attempted, we were unsuccessful at forming high-quality composites by cross-linking the PVP *in situ* using a common divinyl comonomers such as divinylbenzene, ethylene glycol bisacrylate, or *N,N'*-methylenebisacrylamide. In all cases opaque gels always resulted and the polymerizations were usually not quantitative as monitored by IR spectroscopy. In the worse cases, two phase systems resulted that had little mechanical integrity. However, on the basis of the well-known coordination chemistry of Cu^{2+},[18] we found that by adding $CuCl_2$ to the PVP–SiO_2 aerogels, materials with superior properties resulted. For example, the offset yield strength of the 25% PVP–SiO_2 aerogel can be increased 320% (22 vs 5 MPa) and the Young's modulus by 1000% (11 vs 1 MPa) by addition of copper salts (1.1 wt % $CuCl_2$, Figure 5). Control aerogel samples prepared using $CuCl_2$ (0.5 and 1.1 wt %) without added PVP show no similar increase in properties.

This increase in both modulus and yield strength is consistent with the formation of copper-bridged crosslinks between pyridinyl moieties on neighboring polymer chains. Hence, loads are now distributed between two-crosslinked, three-dimensional networks rather than one network and one linear polymer.

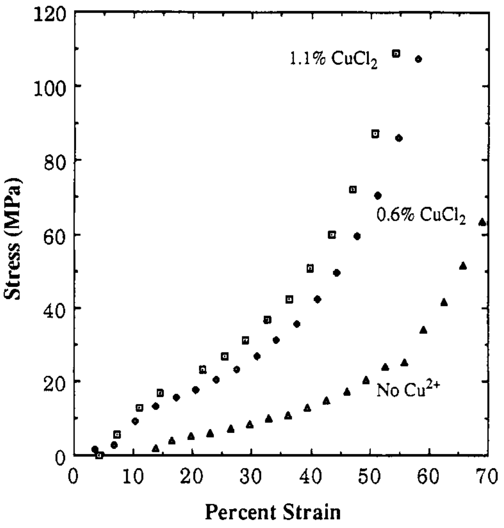

Figure 5. Comparison of the compressional stress–strain curves for a series of SiO_2–PVP (25%) aerogels (d = 0.2 g/cm^3) containing varying amounts of $CuCl_2$ cross-linking agent.

Conclusions

We have shown that the properties of traditional aerogels can be altered and improved by the incorporation of small amounts of organic polymers into their structures. Specifically, organic polymers tend to reinforce the inorganic framework, decrease their hydrophilicity and improve optical transparency. Further improvements to the mechanical behavior can be realized by the in situ crosslinking of the organic polymer using Cu(II) salts.

Experimental Section

General Techniques. All chemicals were obtained from commercial suppliers and used without further purification with the exception of 2-vinylpyridine and divinylbenzene. PVP of two different molecular weights was used (M_n = 50 000 (Reiline 240) and 200 000 (Reiline 2200)). 2-Vinylpyridine was destabilized (inhibitor *tert*-butylcatechol) with 0.5 M Na_2CO_3. The destabilized monomer was then distilled under a vacuum of 200 mTorr at 30 °C and stored at −40 °C. Divinylbenzene was destabilized (inhibitor *tert*-butylcatechol) in the same manner but was not distilled and was also stored at −40 °C. Infrared spectra were recorded on a Perkin-Elmer 1600 series FTIR spectrometer. Supercritical drying was performed in a BioRad autoclave of maximum pressure 172 bar. ^1H NMR was performed on a Bruker AM-400 spectrometer operating at 400 MHz in the UC Berkeley NMR facility. Gel permeation chromatography was performed on a Hewlett-Packard 1050 series liquid chromatography pump equipped with a HP Model 1047 refractive index detector and HP Model 3396A integrator. Separations were effected by 10^5-, 10^4-, 10^3-, and 10^2-Å Waters Ultrastyragel columns run in series. Molecular weight was calibrated relative to narrow molecular weight polystyrene standards (M_n = 4 000–600 000) purchased from Scientific Polymer Products Inc. Tetrahydrofuran (THF) was used as the mobile phase. Elemental analyses were performed by the Microanalytical Laboratory at the College of Chemistry, University of California, Berkeley.

General Formation and Solvent Exchange of Solvent-Swollen Gels. The components of the gels were added to small vials of either 6- or 8-mL total volume via 1-mL graduated pipettes which are accurate to ±0.002 mL or via 100-μL syringes for addition of smaller volumes. Solid components (polymers, radical initiators, and bisacrylamide) were added as solutions in one of the cosolvents. Gelation took place in sealed vials. Gelation time is defined as the time between the addition of the final component of the gel and the point at which no movement or flow is observed when the vial is inverted. Once the gelation point was reached, the vial was kept closed while aging occurred.

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(18) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 5th ed.; John Wiley & Sons: New York, 1988.

Gels were generally allowed to age for 1-3 days. The cap was then loosened or completely removed so that the solvent swollen gel could dry. Once sufficiently dried such that they no longer adhered to the vial walls, the gels were removed from vials by gently tapping the inverted vial or, in some cases, breaking the glass to remove the gel. In the interest of low-density aerogels requiring low shrinkage at this stage, drying time and subsequently densification and shrinkage were kept to a minimum. Thus, gels were removed from vials and submerged in exchange solvents as soon as possible after gelation. Gels were soaked in the exchange solvent for a few hours or unti no mixing waves were present upon stirring. The exchange solvent was then either discarded or saved for later evaporation to test for leaching, and the same volume of fresh solvent was added. This process was repeated three or four times. Volumes in each exchamge were generally 10-20 mL depending on gel volume.

General Supercritical Drying Procedure. Once the exchange process was finished, the gels were usually supercritically dried within a day. Swollen only in exchange solvent, the gels were transferred to a small permeable wire basket which was resting in a beaker filled with exchange solvent just above the basket level. The basket was equipped with dividers such that as many as nine gels could be supercritically dried at one time. The supercritical apparatus chamber was then filled to about three-quarter volume (approximately 150 mL) with exchange solvent, and the basket was transferred to the chamber which was then sealed. CO_2 was bled in at a rate of approximately 1 atm/min until the maximum tank pressure of 60 atm was reached. With the tank open all the way, the exhaust valve was slowly opened so that the exchange solvent slowly dripped into a collection vial at a rate of about 1 drop every 10 s. The entire exchange process typically took 2-4 h. The collected solvent was usually saved and evaporated to analyze for any leached material.

Once all the exchange solvent was bled from the apparatus and only CO_2 escaped from the exhaust valve, the exhaust and inlet values were closed. At this point, any remaining exchange solvent was allowed to leach from the gel into the CO_2 for an hour. After this period, the inlet valve was reopened and any additional exchange solvent was bled from the exhaust valve. The valves were then closed again and the CO_2 tank shut off. The temperature in the apparatus was then slowly increased at a rate of approximately 10 °C/h via a regulatory ethylene glycol/H_2O temperature bath that jacketed the chamber. The pressure naturally increased as the temperature was raised and was held between 80 and 100 atm via a pressure release valve on the top of the apparatus. Temperature was maintained at 40-45 °C (T_c of CO_2 = 31 °C, P_c = 71 atm) with pressure between 80 and 100 atm for at least 4 h. Supercritical CO_2 was then allowed to escape as a gas from the pressure release valve at a rate of 1 atm/min at most. When the pressure in the chamber returned to atmospheric pressure, the basket containing the aerogels was removed.

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