CNC-machinable boehmite nanofiber–melamine–formaldehyde composite aerogels and derivatives for thermal insulation and optical applications

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Abstract. Composite aerogels combining melamine resin and boehmite nanofibers were successfully prepared using a sol–gel reaction in a mixed solvent of aqueous acetic acid and *N*,*N*-dimethylformamide. The composite aerogel exhibits low thermal conductivity and surface processability, making it a potential thermal insulating material for electronic substrates. Transparent γ-alumina aerogels and black alumina-graphite aerogels with designed surface topography were also prepared through CNC machining and calcination. These aerogels with precise surface structures are expected to have applications in fields such as optical materials.

Keywords. aerogels, boehmite nanofibers, composites, mechanical properties, thermal insulation, optical properties, CNC milling

Monolithic aerogels have several outstanding physical properties, such as low thermal conductivity and low refractive index.[1,2] They have been used as high-performance lightweight thermal insulators and as materials for physics experiments.[3,4] However, their low bulk density and light weight make them difficult to handle like everyday porous plastic materials, such as urethane foam. As a result, their use has been limited to specialty applications. In aerogel research, the delicate structure of aerogels results in persistent problems related to mechanical strength. Their brittleness makes bulk aerogels difficult to process once produced. Aerogels typically have a porosity greater than 90 % and their microstructure is composed of nanoscale particles. The necks between the particles in aerogels are easily broken[5] by even small impacts, and cracking, chipping and complete collapse occur rapidly during machining. As a result, it has been nearly impossible to produce precise shapes and sizes. However, if aerogel cutting can be realized, monolithic aerogels will have greater flexibility in terms of bulk shape and can be customized for use in specific applications. Aerogels with complex material geometries can be used in a variety of novel applications, such as thermal insulators that adhere to electronic substrates, lenses that take advantage of the low refractive index, and acoustic materials with controlled sound transmission. In recent years, there have been an increasing number of reports of aerogel composites with improved mechanical properties.[6,7] In contrast, few studies have focused on precision post-processing.

In recent years, there has been a growing trend to use stacked 3D printers to produce aerogels with specific shapes.[8,9] This technology allows the fabrication of materials with complex shapes, such as hollow structures, with a high degree of design freedom. However, there are still many situations, not only in the case of aerogels, where 3D printer modeling lacks processing precision. On the other hand, CNC milling can achieve higher accuracy than 3D printing by adjusting the cutting conditions. In fact, CNC micromilling is still preferred over 3D printing for accuracy and cost reasons in the fabrication of microfluidic devices that require high precision.[10] CNC milling also allow faster cutting when processing large bulk samples or curved surface patterns by changing end mills as needed. Therefore, it is important to consider precision machining of aerogels using CNC milling when looking at application development.

This study investigates high-strength porous materials composed of boehmite nanofibers (BNFs; aluminium hydroxide oxide) incorporated into a polymer that acts as an aerogel backbone and their processability. Boehmite nanofibers are one-dimensional structures about 4 nm in diameter, produced by hydrothermal synthesis from aluminum isopropoxide, with the fiber length that can be extended to several thousand times its diameter.[11,12] Commercially available BNF sol dispersed in aqueous acetic acid solutions can be used to produce nanofiber-reinforced porous skeletons when composited with resins obtained from acid-catalyzed aqueous sol–gel reactions.[13–15] This reaction significantly improves the mechanical properties of the composites; for example, porous polymethylsilsesquioxane composited with BNFs exhibited higher compressive, flexural, torsional, and frictional strengths than its uncomposited counterpart. Those composites have been used to develop water-repellent cell culture substrates because the improved strength allows patterning by milling on the surface.[16] This report extends on our previous findings and reports on our research into precision-machinable BNF–melamine resin (BM) aerogels.

Melamine(–formaldehyde) resin is a representative thermoplastic resin, along with phenol–formaldehyde and resorcinol–formaldehyde resins; their use in the fabrication of monolithic porous materials and aerogels has been reported.[17–19] Water-soluble methylolmelamine, a partial polymerization product of melamine and formaldehyde, is industrially available and can be used as a precursor to prepare monolithic gels in acidic aqueous solutions. In this study, melamine resin aerogels were prepared using Nikaresin S-260 (Nippon Carbide Industries Co., Inc., Japan) as a precursor with acetic acid as a catalyst. In a simple aqueous acetic acid solution, the melamine resin undergoes phase separation as soon as it is formed, and its skeletal structure tends to coarsen. To address this issue, the gelation of the melamine resin in an aqueous acetic acid solution with various organic solvents was tested. A 1:1 mixture of 1 M acetic acid solution and *N,N*-dimethylformamide (DMF) was found to be sufficient to suppress phase separation and produce an aerogel with light transmittance (Figure 1a). The preparation of transparent melamine resin aerogels has been reported using a method that involves supercritical drying after a combination of 4 days of gelation treatment and 5 days of solvothermal treatment with trifluoroacetic acid.[20] However, with this method, wet gels are formed within 3 h under ambient pressure and milder conditions, and transparent aerogels can be reproducibly obtained by supercritical drying. Even when BNF (Alumisol-F3000, Kawaken Fine Chemical Co., Japan) with an average length of 3000 μm was added to the starting composition, the mixed sol did not noticeably aggregate and gelled in a fraction of the time (Fig. 1b). After supercritical drying of the organogels, white composite aerogels were successfully obtained. The detailed process for the synthesis of melamine resin/BM aerogels is as follows. First, x g of methylolmelamine ($x = 0.5$, 1.0, 1.5) was dissolved in a mixture of 5 mL of aqueous acetic acid solution containing y % by weight of BNF ($0 \leq y \leq 5.0$) and 5 mL of DMF. The mixture was then incubated in a sealed vessel at 80°C for 24 h. The wet gels were then removed from the vessel and immersed in methanol, 2-propanol and hexane in that order for washing and solvent exchange. Finally, the wet gel was dried by supercritical drying to obtain the final sample "BMx-y", where $y = 0$ is a pure melamine resin aerogels and the rest are BM composite ones. The process was easily scalable and could produce more than 100 mL of aerogel at a time. However, the compositional range within which defect-free and reproducible BM aerogels could be produced was limited. It was observed that when a small amount of methylolmelamine ($x = 0.5$) was used in the initial composition, the aerogels were prone to uneven shrinkage during drying. On the other hand, when higher amounts of methylolmelamine ($x = 1.5$) were used, the viscosity increased and numerous bubbles developed in the bulk material. At the optimum amount of methylolmelamine ($x = 1.0$), no bubbles remained in the bulk. However, it was difficult to obtain samples without any bubbles on the surface.

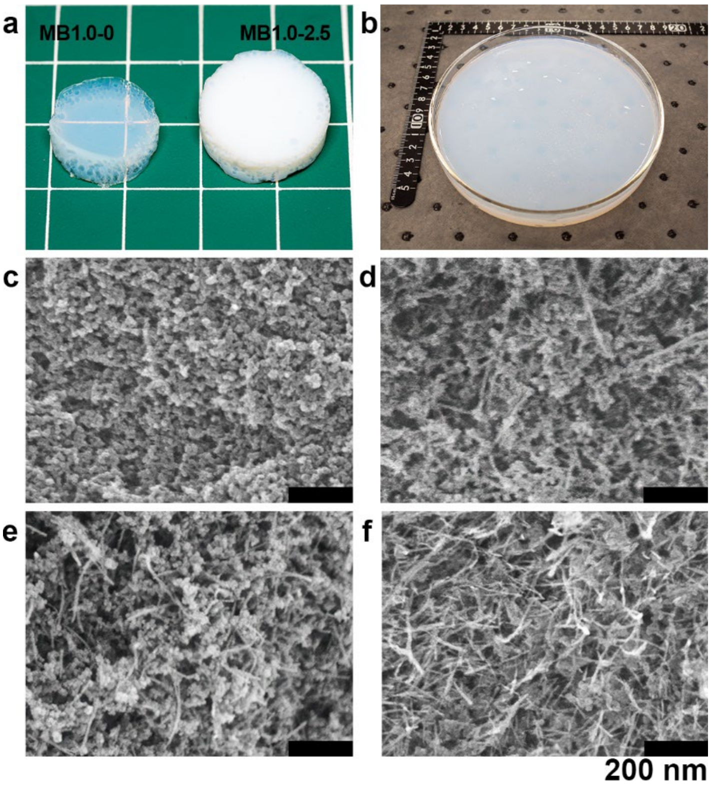

Figure 1. (a) Photograph of the light-transmissive melamine resin aerogel and white BM aerogel. (b) Photograph of BM 1.0-2.5 gelled on a 100 mL scale. Scanning electron microscopy (SEM) images of BM *x*-*y*: (c) BM1.0-0, (d) BM1.0-1.0, (e) BM1.0-2.5, (f) BM1.0-5.0.

The addition of nanofibers to composite aerogels can have an impact on the physical properties and processability of the aerogels. Table 1 lists the physical properties of the aerogel samples obtained at different melamine resin quantities and BNF concentrations. It can be observed that the pure melamine resin aerogels, BM*x*-0, experienced shrinkage during the drying process. However, in the composite aerogels containing nanofibers, this shrinkage was suppressed and the bulk density and Young's modulus were reduced. An increase in the BNF concentration resulted in the loss of the continuous structure of the melamine resin aerogel (Figures 1c-f), and the specific surface area decreased accordingly. The pure melamine resin aerogel BM1.0-0 was found to be prone to nonuniform shrinkage when its fabrication scale was increased, which can lead to the loss of porosity and a decrease in performance such as visible light transmission and mechanical strength against impact. In contrast, the composite aerogel was obtained with good reproducibility, suggesting that the addition of BNFs can help stabilize the aerogel structure during drying and prevent nonuniform shrinkage. Boehmite nanofiber-melamine resin composite aerogels exhibited elasticity (Figure S1) and were clearly more resistant to chipping and abrasion than silica aerogels. The thermal conductivity of the composite aerogels was measured by the heat flowmeter method and showed a minimum value of 0.0214 mW m^{-1} K^{-1} for BM 1.0-2.5. The difference in thermal conductivity between samples can be explained by solid phase heat transfer: increase in bulk density due to drying shrinkage in BM 1.0-1.0 and increase in BNF amount with higher thermal conductivity in BM 1.0-5.0.[21]

As a result of the improved mechanical properties resulting from compositing, it was possible to engrave letters and fabricate arbitrary concave and convex shapes on the surface of BM1.0-2.5 by using a CNC milling machine (Figure 2). The ability to machine the surface of BM1.0-2.5 to form square pillars with a length of 0.5 mm without difficulty promotes the application of the composite aerogel as a heat insulating material for electronic substrates with uneven surfaces.

Table 1: Physical properties of the melamine resin/composite aerogels BM*x*-*y* and BNFs.

Sample	Density [g cm^{-1}]	Young's modulus [kPa]	BET surface area [m^2 g^{-1}]	Thermal conductivity [W m^{-1} K^{-1}]
BM 0.5-0	0.273	4.16	576	-

BM1.0-0	0.287	7.94	626	-
BM1.0-1.0	0.158	2.73	589	0.0240
BM1.0-2.5	0.139	2.57	561	0.0214
BM1.0-5.0	0.136	0.696	389	0.0267
BM1.5-0	0.263	10.2	649	-
BNF	-	-	380	-

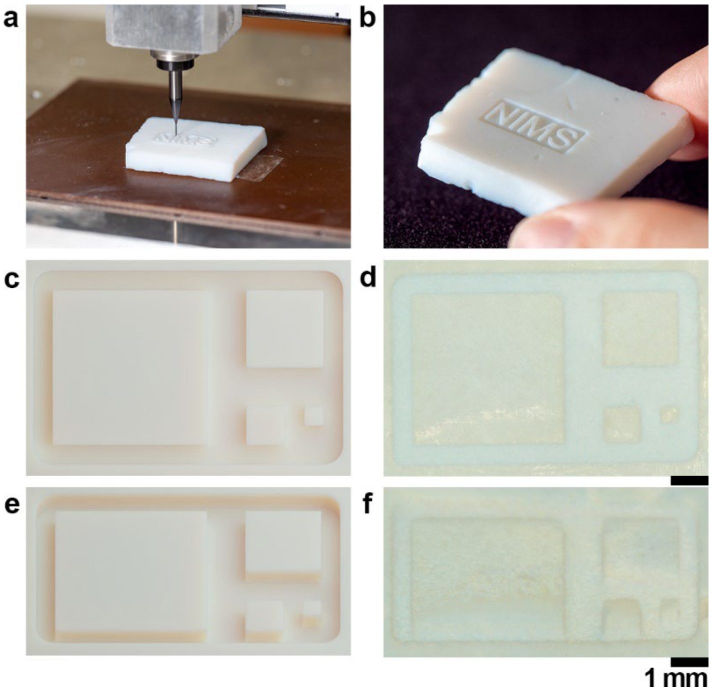

Figure 2. Photographs of (a) BM1.0-2.5 subjected to CNC milling and (b) the machined sample. (c) Computer graphics produced from CAD data used for CNC milling and (d) digital microscope image of an actual sample of BM1.0-2.5. The depth of cut is 0.5 mm. (e,f) Tilt-observation computer graphic/actual images of (c) and (d), respectively.

Some researchers have reported the preparation of monolithic porous materials by using melamine resin as a mold or support material and firing it under oxidizing conditions.[22–24] I attempted to fabricate light-transmissive γ-alumina aerogels with designed surface morphology by oxidizing and removing the melamine portion of surface-shaped BM aerogels at 500 °C. Among the BM composites, the calcined BM1.0-1.0 and BM1.0-2.5 aerogels underwent significant shrinkage and collapse of their shape (Figure S2). However, BM1.0-5.0 was heat treated in air and transformed to a transparent alumina aerogel with almost no shrinkage, retaining their shape after heat treatment in the air, as shown in Figures 2c-e. The transparent aerogel transmitted 79.2% of visible light at a wavelength of 550 nm at a thickness of 5 mm (Figure S3). In a previous study, pure BNF aerogels were obtained through the supercritical drying of a BNF sol after gelation with a base or phosphoric acid;[25,26] however, it was challenging to directly process the surfaces of these nanofiber structures. Processing strength was significantly enhanced once composited with the melamine resin, allowing the design of transparent aerogels. The calcination of BM1.0-5.0 in a nitrogen atmosphere yielded black aerogels, while maintaining their bulk shape (Figures 3f-h). Bulk density analysis, SEM (Figure 3e-f), energy dispersive X-ray spectroscopy (Figure S4), and micro-Raman spectroscopy (Figure S5) results suggest that during pyrolysis, the melamine resin adhered to the surface of graphite while bundling alumina nanofibers. The structure exhibited a reflectance of <0.7% at visible light wavelengths (Figure S6). Carbon aerogels obtained by calcination of resorcinol–formaldehyde aerogels in an inert atmosphere have been reported to exhibit high absorption rates because the incident light is efficiently absorbed, while being reflected through porous media.[27,28] It is considered that light confinement may occur in a similar manner in the alumina–graphite aerogels. The key to the fabrication of these transparent/black aerogels was the rate of temperature increase. The temperature increase rate must be constant at 100 °C/h (or much slower; the operating program is shown in Figure S7, Supporting Information) because aerogels tend to shrink if the temperature is increased rapidly. This should allow the aerogel to heat uniformly from the surface to the interior and slowly release the generated gases. To the best of our knowledge, no studies have reported similar findings on aerogels, especially with the ability to accurately process the aerogel surfaces using a CNC milling machine. Aerogels have been utilized as optical materials in various physical experiments,[29,30] and we anticipate that their application scope can be further expanded through the implementation of surface processing techniques.

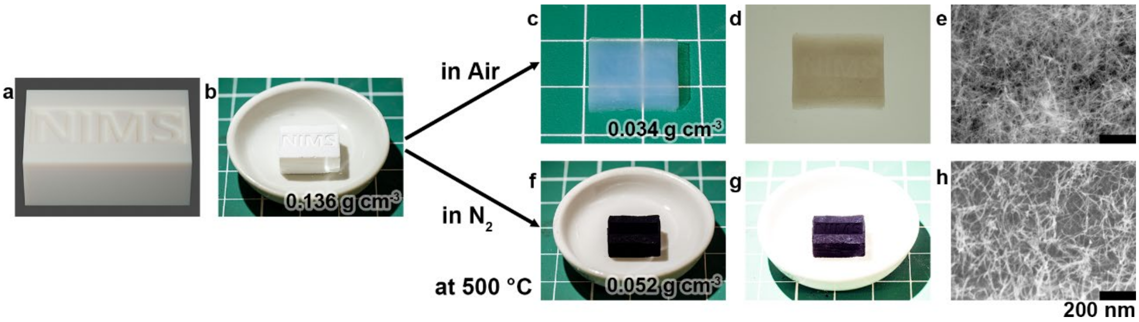

Figure 3. (a) Computer graphic produced from CAD data used for CNC milling, (b) Photograph of actual BM 1.0-5.0. The letters "NIMS" are engraved on the sample surface at a depth of 0.2 mm. The background grid spacing is 10 mm. (c) Photograph of the transparent alumina aerogels obtained by heat treatment in air. (d) Photograph of the same sample as (c) taken on an LED board. (e) SEM image of the transparent alumina aerogel. (g, f) Photograph of black alumina-graphite aerogel obtained in N_2; the two photographs were generated from the same data at different brightness levels to make the appearance and surface conditions easier to see. (h) SEM image of the black alumina-graphite aerogel.

In summary, CNC-machinable composite aerogels were successfully prepared using the melamine resin and BNFs. A mixture of aqueous acetic acid and DMF was used to prepare the melamine resin gel from methylolmelamine, allowing the reaction to expedite the fabrication process. The addition of BNFs to this mixed solvent did not cause any significant agglomeration in the resulting gel, thereby facilitating the complexation process. The physical properties and processability of the obtained BM composite aerogels were investigated. The addition of BNFs to the melamine resin enhanced the physical properties of the aerogel because of the suppression of shrinkage during gelation and supercritical drying, resulting in a decrease in the bulk density and Young's modulus. The BM composite aerogels, possessing low thermal conductivity (0.0214 W m^{-1} K^{-1}) and the surface processability with sub-millimeter accuracy, have a potential application as a thermal insulating material for electronic substrates. Additionally, transparent γ-alumina aerogels with an intact surface design were produced by heating the surface-processed BM aerogel to 500 °C in air to remove the melamine components. Calcination of the same BM aerogel in a nitrogen atmosphere produced alumina-graphite aerogels with high light absorption as well. The successful fabrication of aerogels with designed surface topography and optical features was attributed to the low heating rate, which minimized aerogel shrinkage and preserved the nanofiber structure. The aerogels with precise surface morphology obtained by CNC machining and appropriate thermal treatment in this study are expected to have applications in optical materials and other fields.

Note

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