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PREPARATION AND PROPERTIES OF SOME HYBRID AEROGELS FROM A SULFOPOLYBENZOBISTHIAZOLE-SILICA COMPOSITE

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PREPARATION AND PROPERTIES OF SOME HYBRID AEROGELS FROM A SULFOPOLYBENZOBISTHIAZOLE-SILICA COMPOSITE

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ABSTRACT

Aerogels were prepared so as to have a hybrid structure, by carrying out the supercritical drying process on composites consisting of an *in situ* generated silica network as the inorganic phase and a high-temperature polymer as the organic phase. The goal was to maintain the best properties of both components, for example, decreasing the brittleness of the ceramic phase by introducing a polymeric phase. A polybenzobisthiazole of very high thermal stability, with sulfonation to increase its reactivity, was chosen for the organic phase, and it was bonded to the silica phase by a silane coupling agent. A range of silica/polymer com-

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positions were investigated, and the resulting materials were characterized in terms of their moduli and ultimate properties in compression. Increase in the amount of polymer present decreased the moduli but increased deformabilities, yielding relationships that should be useful in the design of aerogels of optimized properties. Values of Poisson's ratio were also determined and used to estimate longitudinal sound velocities, which can be important in some applications of aerogel materials in general.

INTRODUCTION

Aerogels are a special class of materials with a highly porous structure. There are inorganic and organic aerogels as well as hybrid inorganic-organic aerogels of intermediate compositions. The unusual properties of aerogels such as extremely low thermal conductivity, slow sound propagation, and optical transparency recommend them for potential commercial applications, in spite of their unfortunate brittleness.

A number of years ago, aerogels were described as one of the top ten scientific and technological developments [1]. As their name implies, they are extremely porous materials, consisting more of air than gel [2, 3]. They are a special class of open-cell foams that have an ultrafine pore size (< 50 nm), connected porosity, high surface areas ($400\text{--}1000$ m² g⁻¹) and an ultrastructure composed of interconnected colloidal particles, or polymeric chains, with characteristic dimensions of 10 nm [4].

Because of their ultra-dispersed structures, aerogels have fascinating properties, including extremely low thermal conductivities (~ 0.002 W m⁻¹K⁻¹) [5, 6], unusual sound-propagation characteristics (sound velocities less than 100 m/s) [7], and unique optical properties. Recent applications include the development of thermal insulating windows [8], transparent thermal insulation for passive solar usage (e.g., to reduce the heating energy consumption of homes) [9], catalytic substrates with high surface areas [9], and detectors for Cerenkov radiation in high-energy particle physics [10]. Despite their highly unusual properties, there are some problems which impede aerogel commercial development, such as marked brittleness, limited transparency in some cases, and frequently a hygroscopic nature.

Traditionally, aerogels have been inorganic materials prepared by the sol-gel process [11, 12], which involves the hydrolysis and condensation of



metal alkoxides, e.g., tetraethoxysilane (TEOS) $[\text{Si}(\text{OEt})_4]$. It is also possible, however, to prepare novel aerogels from totally organic materials [13, 14] or from organic-ceramic hybrid materials [15-22]. In this sol-gel process, multifunctional monomers are cross linked into sol particles which then continue cross linking and, finally, form a continuous gel network. In order to preserve the gel structure from shrinking and cracking from the build-up of capillary forces during the drying process, super-critical drying is generally employed [15].

Recent studies have shown that the incorporation of small amounts of organic polymers into these fragile inorganic networks can dramatically increase their compression strength and toughness, improve their optical transparency, and decrease their hydrophilicity [15-22]. In the present investigation, some novel organic-inorganic hybrid aerogels are prepared. The organic component is a thermally-stable aromatic heterocyclic polymer, specifically a polybenzobisthiazole (PBT) which was sulfonated to increase its reactivity with a ceramic phase. The PBTs are rigid-rod polymers which are designed to maintain desirable properties at elevated temperatures [23]. They are being used for aerospace applications because of their exceptional weatherability and their resistance to hydrolytic attack and oxidation at elevated temperatures. The ceramic component will be a silica (SiO_2) network in-situ generated using tetramethylorthosilicate (TMOS) by the sol-gel hydrolysis-condensation process [11]. Recent experimental results have shown that the use of a bonding agent can significantly improve the properties of such organic-ceramic composites [24-26]. In the present systems, chemical bridges between the organic and ceramic phases of the hybrid material will be formed from the bonding agent *N,N*-diethylamino-propyltrimethoxysilane. The polymer was a sulfobiphenylpolybenzobisthiazole (SBPPBT II) synthesized in the Wright-Patterson Air Force Laboratories specifically for this project [27] (Figure 1).

The mechanical behavior of silica aerogels is characteristic of brittle, perfectly elastic materials [28], but a number of studies have been conducted to

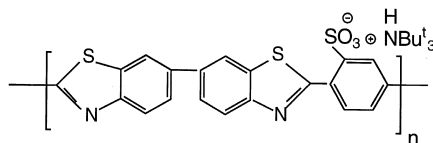


Figure 1. Structure of the SBPPBT II polymer.

investigate their elastic properties [29, 30]. The sound propagation characteristics for silica aerogels determined using both ultrasonic velocity measurements and mechanical property measurements have shown that they possess very low sound velocities [31-36]. It was hoped that introducing mechanically soft, elastic structures will make silica aerogels less brittle and promising acoustic materials, with applications in acoustic delay lines or high-temperature sound isolation [36]. The desirable low sound velocities in aerogels are due to low values of Young's modulus, which can be determined from compression measurements.

In the first part of this program, the goal was to produce novel aerogels from organic-ceramic hybrid materials, to study the effects of the amount of ceramic component present in the aerogel on compression strength, and sound velocity, and to provide guidance for the design of materials of optimized properties.

EXPERIMENTAL

Materials

The sample of SBPPBT II was prepared as described elsewhere [27], and the silane coupling agent was obtained from Huls America Inc. TMOS, tributylamine (99%), and methanol (99+%) were obtained from Aldrich.

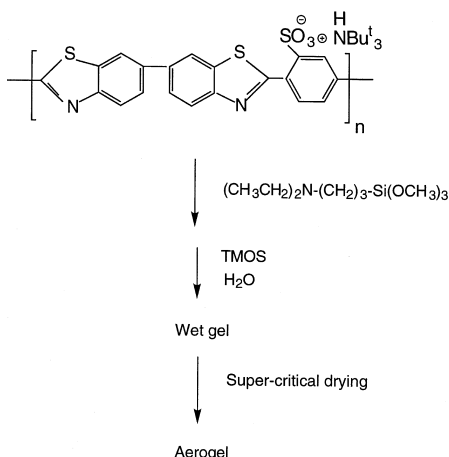
Preparation of Aerogels

The SBPPBT II-SiO₂ aerogels were prepared according to Scheme 1.

Specifically, SBPPBT II, methanol, and tributylamine were placed into a three-neck flask equipped with a mechanical stirrer, a condenser, and a nitrogen inlet and outlet. The mixture was held at 50°C for 36 hours under a very slow stream of nitrogen. If some methanol escaped from the solution during refluxing, more was added to maintain an approximately constant amount. After a clear, homogeneous solution was obtained, it was cooled to room temperature and the silane coupling agent and TMOS were added. The mixture was stirred for another two hours at room temperature, and a stoichiometric amount of water was added to give a very viscous solution.

Stoichiometric amounts of the polymer and silane coupling agent, and varying amounts of TMOS were thus used to prepare a series of aerogel samples. The amounts of SiO₂ were varied by varying the amount of TMOS, and the amount of silica calculated included contributions from hydrolysis of the





Scheme 1. Preparation of SBPPBT II-silica aerogels.

trimethoxysilane groups on the coupling agent. The resulting solutions were placed into small cylindrical sample vials (5-cm heights, 2-cm diameters), subsequently giving gels having cylindrical shapes. After the vials were sealed, gelation was permitted to occur. The gels were removed from the vials and immersed in methanol, which was subsequently used as an exchange solvent for the drying. The methanol was exchanged by fresh methanol several times until no optical waves were observable upon stirring for four days. A solvent-exchange process was used to remove the water (which is immiscible with liquid CO₂) from the pores of the gels. The gels were then placed into a E3000 critical point drying apparatus, and the methanol in the gels replaced by liquid CO₂, followed by supercritical drying at the critical point of CO₂ (31.5 °C and 1100 Psi). This process prevents the delicate gel structure from the shrinking and cracking usually caused by the capillary forces formed in the cell pores in the case of non-critical solvent evaporation from the gel.

Characterization Techniques

Bulk densities were determined from the weights and volume of the aerogel samples, and linear shrinkage extents by measurements of cylindrical sample diameters before and after the supercritical drying. Uniaxial compression was used to measure the moduli and ultimate strengths of the samples; uniaxial extension tests are not possible with materials too fragile for the required



clamping. These compression measurements were carried out at room temperature on an Instron testing machine, as a function of the amount of SiO₂ present in the aerogel. The initial heights of the samples were approximately 1.5 cm, and they were compressed at a cross-head speed of 0.02 in/min. Values of the Poisson ratio μ were determined from measurements of the sample dimensions before and after the compressions. Sound velocities were estimated from the stress-strain results.

RESULTS AND DISCUSSION

The SBPPBT II-SiO₂ aerogel samples prepared had the amounts of silica listed in the first column of Table 1. Columns two and three give values of the density and the relative linear shrinkage for the aerogels. The densities of the aerogels are seen to increase with increase in the amount of silica present, as expected, but the amount of shrinkage upon drying the gels did not vary in any significant way with the amount of silica present.

Figures 2 and 3 show the stress-strain results for the aerogels, where the strain is the relative change $\Delta h/h$ in height of the sample, at the low or moderate deformations most important in their applications and at some high deformations, respectively. In Figure 3, the stresses have been normalized with values of the density, the ratio being important in applications in which the material is transported. Values of Young's modulus were obtained from the initial slopes of

TABLE 1. Densities and Linear Shrinkages for the Aerogels

SiO ₂ :Polymer Weight Ratio	10 ³ Density (g/cm ³)	$\Delta D/D$ (%)
12.5:100	9.58	13.4
22.5:100	11.0	11.1
32.5:100	11.3	12.3
42.5:100	11.8	14.6
62.5:100	17.5	13.4

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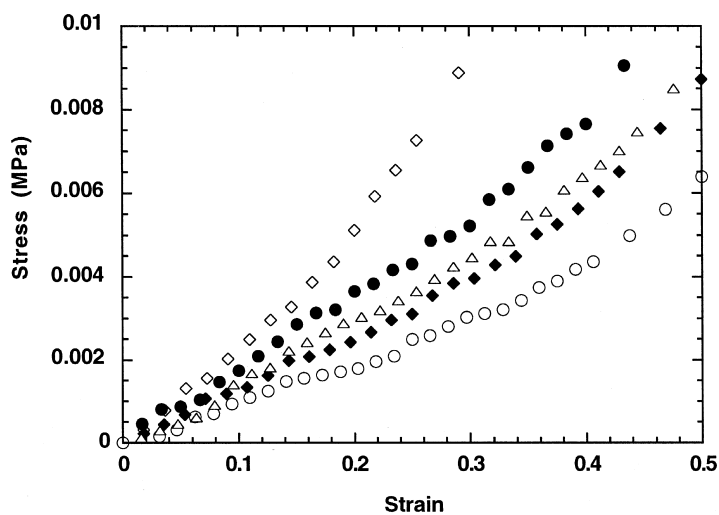


Figure 2. Compressional stress-strain isotherms for SBPPBT II-SiO₂ aerogels: 12.5:100 (○), 22.5:100 (◆), 32.5:100 (△), 42.5:100 (●), and 62.5:100 (◇), SiO₂:polymer weight ratio.

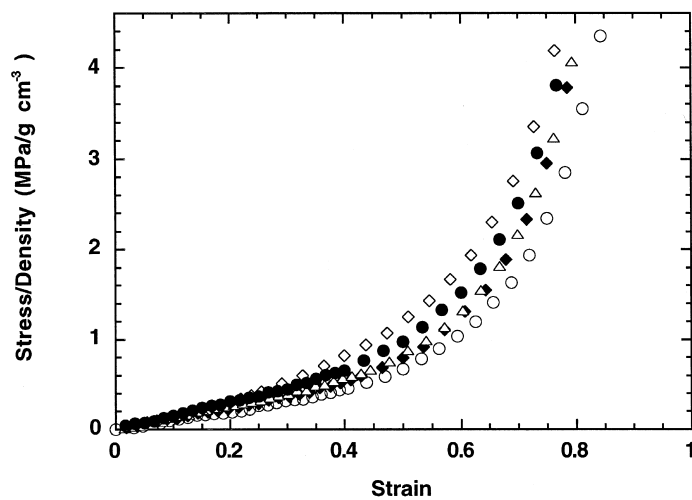


Figure 3. Compressional stress-strain isotherms in which the stress is normalized with the density; see legend to Figure 2.

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the stress-strain isotherms (Figure 2). The polymeric phase introduced into these aerogels is seen to give these samples considerable deformability, i.e., significantly reduced brittleness.

Values of the longitudinal sound velocity for silica aerogels have been determined using the equation

$$c_1 = [Y(1 - \mu)/\rho(1 + \mu)(1 - 2\mu)]^{1/2} \quad (1)$$

where c_1 is the longitudinal sound velocity (m/s), Y is the Young's modulus (N m^{-2}), μ is the Poisson's ratio, and ρ is the density (g/l) [36]. Table 2 presents the values of Y , μ , and c_1 of the resulting SBPPBT II-silica aerogels.

According to the literature, the maximum deformability of pure silica aerogels is very low ($\sim 10\%$) [30], however, there are cases where the deformabilities of such *in situ* generated materials are as high as 60% [15, 37]. These increases in deformability may possibly be due to non-hydrolyzed groups remaining in the structure after the sol-gel process is terminated. In any case, the deformabilities of the SBPPBT II-SiO₂ aerogels have been significantly increased in comparison to the silica aerogels; i.e. incorporating this organic polymer into the aerogels did substantially increase their deformability. In addition, the increase in the amount of polymer in these aerogels decreases both the Young's modulus and the yield strength (Figure 2). These observations suggest that incorporation of organic polymer decreases the inherent brittleness of silica aerogels.

As the amount of silica was increased, Young's modulus increased, as expected, but the Poisson ratio did not show any obvious trend. Values of the lon-

TABLE 2. Young's Moduli, Poisson's Ratios, and Longitudinal Sound Velocities

SiO ₂ :Polymer Weight Ratio	10 ³ Y (N m ⁻²)	10 ³ μ	c_1 (m/S)
12.5:100	9.74	3.82	31.8
22.5:100	12.3	1.50	33.4
32.5:100	14.2	3.14	35.4
42.5:100	17.5	0.99	38.5
62.5:100	22.3	1.02	35.7



itudinal sound velocity did generally increase with increase in the amount of silica. In brief, the results suggest that introducing organic polymer into these aerogels decrease their brittleness, while maintaining relatively low values of the longitudinal sound velocity.

CONCLUSION

Organic-inorganic aerogels were prepared using a high-temperature polymer and *in situ* generated silica. A range of silica/polymer compositions was investigated, and mechanical property measurements in compression indicated that increase in the amount of polymer present decreased the moduli but increased deformability. Thus, introducing the organic polymer into these aerogels was successful in reducing their brittleness.

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