Open cell aerogel foams with hierarchical pore structures

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ABSTRACT

A new class of macroscopic materials — the open cell aerogel foams (OCAFs) — are developed in this work that combine the attributes of open cell polymer foams and mesoporous polymer aerogels in single materials. The OCAFs have two functional elements — the large body of the materials is air-filled open cells with typical cell size greater than 1 μm and the walls between the open cells consisting of mesoporous aerogel formed by the polyurea strands of typical diameter 50 nm. The common foaming technologies cannot be easily adapted to obtain OCAF. This paper evaluates a strategy based on the use of templates of co-continuous immiscible polymer blends. The open cell macropores are created by selective dissolution of polystyrene from its co-continuous blend with polyethylene oxide. The gel networks of polyurea are then synthesized inside the macropores. Finally, the polyethylene oxide phase is removed by dissolution and the resultant material is dried under supercritical condition to obtain the OCAF. It is found that polyurea gel networks are initiated on the surfaces of polyethylene oxide template by nucleation and growth mechanism. The resultant polyurea OCAFs exhibit bulk density ~0.06 g/cm^3, BET surface area ~130 m^2/g, mesoporous solid networks, high air permeability, and close to 1500% weight gain in a few seconds when exposed to pump oil.

1. Introduction

Aerogels are highly porous, lightweight materials that offer high specific surface area, low thermal conductivity, and high porosity. Silica aerogels are first to receive the attention of researchers due to their excellent thermal stability and structural tunability [1,2]. In 1989, Pekala reported the first organic aerogel synthesized by the polycondensation of resorcinol and formaldehyde (RF) [3]. Following that, various organic aerogels were produced based on different polymers, for instance polyimide [4,5], syndiotactic polystyrene [6], and polybenzoxazine [7,8].

Polyurea aerogels were first mentioned in a U.S. patent [9]. The inventors presented a series of organic polyisocyanate-based aerogels including those of polyurea, polyurethanes, and polyallophanate. Lee et al. synthesized polyurea aerogels by reacting Jeffamine® with ethylene diphenyl diisocyanate (MDI) catalyzed by triethylamine (TEA) [10]. These authors studied the relationship between the bulk density and the thermal conductivity of polyurea aerogels. The specimens with a bulk density of 0.16 g/cm^3 showed thermal conductivity of 13 mW/(m·K) which is comparable with the values obtained for RF aerogels and silica aerogels. The polyurea aerogels with low density (0.06 g/cm^3) exhibited a fibrillar morphology while the one with a density of 0.1 g/cm^3 exhibited a denser and particulate morphology. Lee et al. [10] indicated that the large pores in the fibrillar morphology may increase the thermal transport rate via gaseous natural convection and radiation. The contributions of solid conduction heat transfer also increases with an increase of the solid content. These results indicate that the design of polyurea aerogels with the best thermal insulation properties is not a simple task and that studies on optimization of processing methods is required to attain such objectives.

Morphology variation in polyurea aerogels as function of solids concentration was earlier studied by Leventis and co-workers [11]. Polyurea networks with high crosslink density were synthesized from trifunctional isocyanate molecules and water. Polyurea aerogels with a wide range of bulk density (0.016–0.055 g/cm^3) were prepared and characterized. The networks of polyurea aerogels were constituted of polymer fibrils when the bulk density was no more than 0.13 g/cm^3. However, the networks of aggregated globules were observed for materials of bulk density~0.19 g/cm^3. These two morphological forms were the results of distinct aggregation mechanisms. For example, at low concentration, a reaction-limited aggregation led to strands, while at high concentration, a cluster-cluster crowding occurred to yield globular morphologies.

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Shinko et al. [12] used MDI, 4,4′-oxydianiline (ODA) or 2,2′-dimethylbenzidine (DMBZ), and 1,3,5-tris(4-aminophenyl)benzene (TAB) to synthesize a group of polyurea aerogels by varying the number of repeat unites (n) of polyurea oligomers. It was found that n determined the gelation time, e.g., longer gelation time for greater values of n. In the case of materials synthesized using ODA as the diamine, a greater n caused higher shrinkage due to higher extent of hydrogen bonding in the aerogels. Moreover, n had direct impact on the compression modulus of the aerogels, e.g., higher crosslinking density (smaller n; higher TAB content) resulted in higher compression modulus.

In the present work, a new class of materials, the open cell aerogel foams (OCAFs) that combine the attributes of polymer foams and mesoporous aerogels in single materials is reported. The structure of OCAFs can be divided into two parts, the interconnected and thus open macropores with size around 5 μm and the mesoporous aerogel cell walls. Leventis et al. [11] indicated an interesting material that combines the large foam-like macroporosity with nanoporous wall. It was created by trapping CO_2 bubbles in the gel during an ultrafast gelation process. In this case, CO_2 works as the porogen as is generally used in manufacturing polyurethane foams [11]. However, the parameters, such as the total volume of CO_2 and the dispersity of the bubbles in the gel system are difficult to control in production of stable products.

In this work, thermoset polyurea (PUA) aerogels were used in the synthesis of OCAFs where macroporosity and macropore distribution within the materials were easily controlled. The sol-gel synthesis of PUA gel occurred in a macroporous polyethylene oxide (PEO) template which was prepared through selective dissolution of atactic polystyrene (PS) from a co-continuous, immiscible PS/PEO blend. The PEO template was later removed and the resulting macroporous PUA gel was washed using acetone followed by supercritical drying to obtain the OCAF. This paper answers several key questions. First, it focused on the mechanism of formation of PUA gel network inside the macroporous PEO template. Specifically, the influence of PEO on the morphology of PUA gel networks was evaluated. Second, the paper evaluated if the hierarchical pore structures of OCAFs could improve the liquid uptake and the gas permeability through OCAFs. The properties of PUA aerogel monoliths and OCAFs were evaluated as a function of the concentration of the solids in the sol.

2. Experimental section

2.1. Materials

Monomer Desmodur N3300A triisocyanate was acquired from Covestro LLC. (Pittsburgh, PA). Triethylamine (TEA), tetrahydrofuran (THF), acetone, atactic polystyrene (PS, M_w ~ 192,000 g/mol) and polyethylene oxide (PEO, M_w ~ 300,000 g/mol) were purchased from Sigma Aldrich. Vacuum pump oil 19 was obtained from VWR (Radnor, PA).

2.2. Preparation of macroporous PEO template

30 g of PEO and 30 g of PS powder were dry blended and mixed in a Brabender Plasticorder mixer at 170 °C for 10 min at a rotor speed of 50 rpm and cooled to room temperature for further use. The blend was ground to powder state and compression molded at 170 °C and 21 MPa pressure into 2.8 cm diameter disks. The disks were soaked in THF for 24 h at room temperature to remove the PS phase and subsequently dried at room temperature to obtain the PEO template.

2.3. Synthesis of PUA gel, aerogel monoliths, and open cell aerogel foams (OCAF)

The sols of PUA were prepared by dissolving Desmodur N3300A, water, and TEA in acetone using the recipe presented in Table 1. TEA serves as a catalyst for isocyanate-water chemical reactions. 5 mL of the sol was poured into a glass mold of inner radius 1 cm and allowed to stand at room temperature for a prescribed time-period to obtain gel specimen. The specimen names listed in Table 1 also contain information about the molar concentration of the isocyanate. For example "PUA-0.1 M", refers to the sol that contained 0.1 mol/L of Desmodur N3300A. The gelation times varied with isocyanate concentration as follows - 6 h for specimen PUA-0.1 M, 3 h for specimen PUA-0.15 M, and 45 mins for specimen PUA-0.2 M. All gels were aged for 12 h before taking out of the mold. The gel specimens of volume about 5 cm^3 were then washed with fresh acetone (50 mL) for six times with 6 h intervals in order to remove any unreacted moieties.

The PUA gel specimens were dried using supercritical CO_2 to obtain the PUA aerogels. For this purpose, the gel specimens filled with acetone were brought in contact with liquid CO_2 in an autoclave and soaked for 2 h followed by drainage of the solvent and refilling. The soaking and washing steps were repeated 5 times after which the chamber was heated to 50 °C and kept at 11.5 MPa pressure for 1 h (critical point of CO_2 are 31 °C, 7.4 MPa). The chamber was depressurized at 50 °C for venting of CO_2 and aerogel specimens were recovered.

Note that "PUA Aerogel" in this paper refers to the aerogel monoliths to distinguish them from the open cell aerogel foams, "PUA OCAF". The PUA OCAF specimens were obtained by supercritical drying in carbon dioxide of PUA gels grown inside the PEO templates. For this purpose, the PEO templates were immersed in the sol of PUA for 1 min to fill the macropores of PEO templates (Fig. S2), immediately placed in a polypropylene container of inner radius 25 mm, and kept under sealed condition for gelation and aging over a period of 12 h. The resultant materials were washed with deionized water 4 times in 6 h intervals and with acetone 6 times in 6 h intervals. The PUA OCAF materials were dried under supercritical condition of carbon dioxide following the same procedure as presented above for PUA aerogels.

2.4. Characterization

The aerogel monoliths were of cylindrical shape while OACFs were of circular disk shape (Fig. S1). The mean and standard deviation of bulk density (ρ_b) values were obtained from the mass and volume of five (5) representative specimens for each recipe. The mean and standard deviation of skeletal density (ρ_s) were determined from ten (10) measurements using a helium pycnometer (Accupyc 1340, Micromeritics). The porosity (p) was obtained from the mean values of skeletal density and bulk density according to Equation (1).

$$p = \frac{\rho_s - \rho_b}{\rho_s} \times 100\% \tag{1}$$

Brunauer−Emmett−Teller (BET) surface area and pore size distribution of the specimens were obtained from N_2-sorption isotherms at 77 K, analyzed using a Micromeritics Tristar II 3020 analyzer. For each specimen a mean and standard deviation of BET surface area and pore volume were obtained from three (3) measurements. The morphology of the specimens was probed using scanning electron microscopy (SEM; JEOL JSM5310) at an operating voltage of 8 kV. Infrared (IR) spectra were recorded on a Bruker FT-IR Alpha spectrophotometer using a Platinum ATR accessory. The