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Influence of silica derivatizer and monomer functionality and concentration on the mechanical properties of rapid synthesis cross-linked aerogels

L.S. White [a], M.F. Bertino [a, *], S. Saeed [b, c], K. Saoud [b, *]

[a] Department of Physics, Virginia Commonwealth University, Richmond, VA 23060, USA
[b] Department of Physics, Virginia Commonwealth University, Doha, Qatar
[c] Department of Metallurgy and Materials Engineering, Pakistan Institute of Engineering and Applied Sciences (PIEAS), Islamabad, Pakistan

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ABSTRACT

The relationship between both monomer functionality and concentration and the mechanical properties of cross-linked aerogels was investigated. For this, alcogels were synthesized using a gelation solution containing an alkoxide (tetramethyl orthosilicate, TMOS) to form the oxide gel skeleton, trimethoxysilylpropyl methacrylate (MTMS) to attach a coupling acrylic group to the pore walls, an acrylic monomer, a photoinitiator (Eosin Y) and a tertiary amine acting as base catalyst for gelation and as polymerization co-initiator. The gelation solvent was the ethanol–water azeotrope mixture (4.4% water by volume). After gelation, alcogels were cross-linked by photopolymerization using green light and were dried using the ethanol–water azeotrope as a supercritical fluid. Densities, shrinkage, surface areas, pore sizes, moduli and specific energy absorptions of the resulting monoliths were measured and found to depend very strongly on MTMS and monomer concentration and, to a lesser extent, on monomer functionality. Optimization of the gelation solution composition allowed for the fabrication of aerogel composites with Young's modulus of 257 MPa and specific energy absorption of 19.4 J g^{-1}, which makes them possible candidates for ballistic protection applications.

1. Introduction

Aerogels are unique porous materials with low thermal conductivity, low dielectric constants and high acoustic impedance, making them attractive materials for insulation applications [1]. Their fragility and lengthy processing has prevented, to date, their widespread use. Fragility issues were addressed in 2002 by the Leventis group [2]. This group developed a method for cross-linking of the skeletal oxide nanoparticles with a polymer without overly compromising surface area and porosity. Processing issues have been recently addressed by the groups of Anderson and Carroll [3] and by our own group [4]. In these methods, aerogels are prepared using one-pot chemistry and dried using supercritical organic solvents. In previous work done by our group, native silica and cross-linked aerogels were produced in a matter of hours without requiring solvent exchange [4]. The composites fabricated with our method had Young's moduli on the order of a few tens of MPa. While these moduli were within expectations for cross-linked aerogels [1,5], they were not sufficient to make aerogels useful for applications requiring high mechanical resilience, such as ballistic protection [1,6]. For these applications, a modulus of hundreds of MPa and an energy absorption of tens of J g^{-1} are required. In our previous work, we showed that the modulus of the composites could be increased by several times when the functionality of the cross-linking monomer was increased [4]. This result was in agreement with general trends of polymer chemistry, which show that the modulus of composites increases with the functionality of the cross-linker [5,7–9]. We therefore decided to further investigate the role of functionality and attempt fabrication of aerogels with a high modulus potentially suitable for ballistic protection applications. Monoliths cross-linked with varying concentrations of a penta-functional acrylate, acrylated dipentaerythritol (DPHA), or a difunctional acrylate, hexanedioldiacrylate (HDDA) and trimethoxysilylpropyl methacrylate (MTMS) were fabricated and characterized. The role of MTMS was scrutinized carefully, as its

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* Corresponding authors.
E-mail addresses: mfbertino@vcu.edu (M.F. Bertino), s2kmsaou@vcu.edu (K. Saoud).

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concentration represents the number of coupling sites of the polymer to the oxide skeleton, and the mechanical properties of monoliths depend strongly on the concentration of the coupling group. For example, it has been reported that the modulus doubles when the molar concentration of Si attached to a coupling group is increased from 15% to 30% [10]. Composites with increasing MTMS concentrations were fabricated in an attempt to further increase the modulus of cross-linked monoliths. The result of this study was the finding that the mechanical strength of the composites depends strongly on MTMS concentration and, to a lesser extent, on monomer concentration and functionality. In addition, power law dependencies existed between the modulus (Y) and the density (ρ) of the monoliths. The exponents of these power laws varied over a very wide range (from about 0.7 to about 4.5) and depended strongly on monomer type and MTMS concentration. Synthesis parameters were optimized to fabricate composites with a modulus of up to 257 MPa and an energy absorption of up to 19 J g^{-1}. These are high values for aerogel composites and are comparable to those of aerogels which were successfully used for ballistic protection [5]. Significantly, the composites were fabricated in a matter of hours without requiring multiple, day-long solvent exchanges, as is the case for cross-linked aerogels produced by more conventional methods such as supercritical CO_2 drying [11].

2. Experimental

2.1. Chemicals

Tetramethyl orthosilicate (TMOS), trimethoxysilylpropyl methacrylate (MTMS), methyldiethanolamine (Amine), and Eosin Y were purchased from Acros Organics. 1,6-Hexanediol diacrylate (HDDA) was purchased from Sigma–Aldrich, the structure of which is shown in Fig. 1a. It has a density of 1.01 g ml^{-1} at 25 °C and a molecular weight of 226 g mol^{-1}. A sample of 2-Propenoic acid, 1,1′-[2-[[3-hydroxy-2,2-bis[[(1-oxo-2-propen-1-yl)oxy]methyl]propoxy]methyl]-2-[[(1-oxo-2-propen-1-yl)oxy]methyl]-1,3-propanediyl]ester (DPHA), in a purity of 99%, was provided by Allnex SA, Belgium, the structure of which is shown in Fig. 1b. It has a density of 1.17 g ml^{-1} at 25 °C and a molecular weight of 524 g mol^{-1}. All reagents were used as-received. The ethanol–water azeotrope mixture (containing 4.4% water and 95.6% pure ethanol by volume) was used as gelation solvent and as supercritical fluid in the drying process. Unless stated otherwise, all references to ethanol in this manuscript refer to the ethanol–water azeotrope mixture.

2.2. Fabrication of cross-linked aerogels

The specific composition of the gelation solution for every sample presented in this work is reported in detail in Table S1. Briefly, gelation solutions contained TMOS to form the silica gel backbone, MTMS to derivatize the pore walls with an acrylic moiety, a monomer to cross-link the silica nanoparticles of the gel backbone, methyldiethanolamine as both base catalyst and co-initiator and Eosin Y as polymerization initiator. Eosin Y absorbs strongly in the green region of the light spectrum, so samples were illuminated with green LEDs. In addition, Eosin Y combined with a tertiary amine as a co-initiator is a very efficient visible-light polymerization initiator that is commonly used to polymerize acrylic resins. The mechanism of polymerization and its optimum concentration for aerogel synthesis are reported in previous work [4,12–16]. In all experiments, the concentration of TMOS and tertiary amine was kept constant at 0.88 ml (5.91 mmol) and 0.05 ml (0.44 mmol), respectively. Solutions were prepared by combining precursors, ending with the addition of amine. The gelation solutions were thoroughly mixed, and gelation occurred within 30 min. One batch of samples was prepared in which MTMS concentration was varied between 0.98% (0.04 ml, 0.17 mmol) and 24% (1.28 ml, 5.39 mmol) by volume (v/v) of the gelation solution, while maintaining a constant volume of HDDA (1.12 ml, 5.00 mmol) (Samples H1–H4 in Table S1). Experimentation was also done with samples containing both HDDA and DPHA monomers. Three samples were prepared using a constant volume of MTMS (0.04 ml, 0.17 mmol) and the concentration of DPHA and HDDA was varied over the three samples, the sum of the weight of the monomers always totaling 2.1 g (Samples M1, M2, and D1 in Table S1). Higher monomer concentrations yielded monoliths that cracked during supercritical drying. BET analysis of these monoliths showed that they had extremely low surface areas (below about 10 m^2/g). Probably, the low surface area slowed release of the solvent during depressurization of the autoclave and lead to cracking of the monolith. In experiments using solely DPHA, four batches of samples were prepared. The first batch (Sample D2 in Table S1), used to examine the effect of exposure time on the composites, consisted of ten samples prepared using the same gelation solution and exposed for increasing amounts of time. The results of this experiment are discussed in the SI section “Exposure Time,” with results detailed in Figure S1. In the second batch (Samples D3–D6 in Table S1), MTMS concentration was varied between 0.87% (0.04 ml, 0.17 mmol) and 21.94% by volume (1.28 ml, 5.39 mmol) while maintaining constant TMOS (0.88 ml) and DPHA (1.624 ml, 3.63 mmol) concentrations. The third and fourth batches of DPHA samples were prepared by varying DPHA concentration between 0% and 35% (1.624 ml, 3.63 mmol) by volume of the gelation solution, while maintaining TMOS (0.88 ml) and MTMS concentrations. So, the third batch (Samples D7–D11 in Table S1) was prepared using the DPHA concentrations reported above and a constant low volume of MTMS (0.04 ml, 0.17 mmol). The fourth batch (Samples D12–D16 in Table S1) was prepared using the DPHA concentrations reported

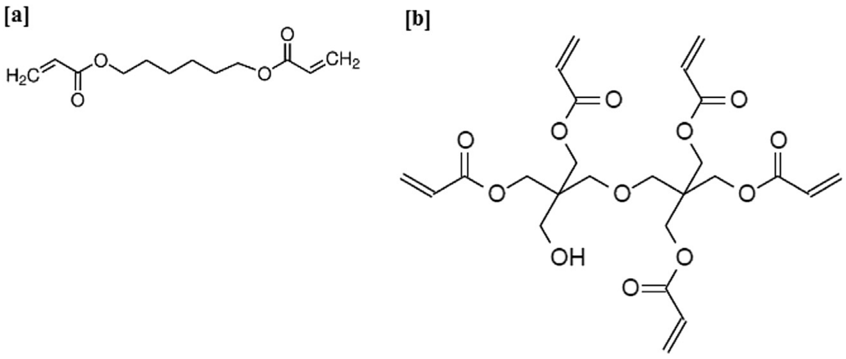

Fig. 1. [a] Hexanedioldiacrylate (HDDA), [b] Acrylated Dipentaerythritol (DPHA) monomer molecules used for cross-linking.