



Mechanical and thermal properties of nanofibrillated cellulose reinforced silica aerogel composites



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ABSTRACT

We report on the mechanical and thermal properties of monolithic nanofibrillated cellulose (NFC) reinforced silica aerogel composites. Silica aerogel composites were made by dispersing NFC into polyethoxydisiloxane (PEDS-P_{750E20}) sols prior to gelation. Attempts to further improve the dispersibility of the NFC in ethanol were made using maleic anhydride (MA) as a surface-modifying agent. The effects of the NFC and MA-modified NFC on the properties of the aerogel composites were studied and compared to neat silica aerogel references made in the same manner. Surface-modification of the NFC using MA did not lead to any significant differences in any of the measured properties compared to the unmodified NFC. In general, the NFC reinforced silica aerogel composites did not exhibit notable improvements with regards to elastic modulus E , compressive strength σ_C , or fracture strain ϵ_F over neat silica aerogels of the same densities. However, improvements due to the NFC were seen in the tensile strengths of the aerogel composites which exhibited tensile strengths 25–40% higher than neat silica aerogels of the same densities. While BET analysis indicated that the mesoporous microstructure of the silica aerogel matrix was retained, thermal conductivity λ values increased by $\approx 11\%$ from 13.8 mW/m K to 15.3 mW/m K due to the presence of the NFC.

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1. Introduction

Silica aerogels have extraordinarily low thermal conductivities ($\lambda \approx 13$ mW/m K) [1] which have great potential in industrial applications such as thermal packaging and building construction [2–4]. The environmental and financial implications of these insulation materials have been illustrated by recent estimations that aerogel-based building insulation has the potential to reduce energy consumption by 30% and CO₂ emissions by 25% [5] in comparison to the conventional insulation materials currently used, e.g. polyurethane foam and expanded polystyrene (EPS) ($\lambda \approx 25$ –40 mW/m K) [6,7], and mineral wool insulation

($\lambda \approx 30$ –40 mW/m K) [8]. However, the high manufacturing costs and poor mechanical properties of silica aerogels should be overcome before large scale manufacture and widespread application become economically feasible.

Obviously, substantial progress has already been made since Kistler first produced silica aerogels from sodium silicate (water glass) solutions in 1931 by means of supercritical ethyl alcohol drying [9,10]. The costs to manufacture silica aerogels, *i.e.* time, labour, and equipment, have been significantly reduced due to developments in chemistry and processing techniques. For example, modern chemical precursors, such as tetramethyl orthosilicate (TMOS) [11], tetraethoxysilane (TEOS) [12], and polyethoxydisiloxane (PEDS) [13], require much shorter processing cycles and yield high quality aerogels. Also, the need for equipment intensive supercritical fluid drying of the aerogels can be circumvented using ambient pressure drying techniques [14,15]. As a result, silica aerogel-based insulation materials are commercially available nowadays in the form of fibre mats ($\lambda \approx 14.5$ –18 mW/

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m K) (Aspen Aerogels, Inc., USA) [16] and spray on plasters ($\lambda \approx 28$ mW/m K) (Fixit AG, Switzerland) [17] filled with silica aerogel granules. These insulation systems provide the brittle silica material with the necessary mechanical strength for building applications, with manageable losses in thermal insulation. Next generation aerogel-based insulation will be contingent upon even greater material strength and superior thermal properties. Promising solutions have been identified in the form of nanocomposites in which cross-linking polymers [18–20], nanoparticles [21], and reinforcement nanofibres [22,23] have been incorporated into monolithic silica aerogels.

This work focuses on nanofibrillated cellulose (NFC) as potential structural reinforcement materials in silica aerogel-based composites. Cellulose fibres are ubiquitous, lightweight, mechanically stable, and can be conveniently surface-modified for customized applications [24]. To date, only a few studies have been reported on the properties of composite materials consisting of silica aerogels and NFC [25–31]. In most of these cases, prepared cellulose gels are modified in silica sol solutions to create interpenetrating networks of silica and cellulose [25–29,31]. Homogenous distributions of cellulose is better achieved using "one pot" synthesis concepts, however issues with solubility, dispersibility, and chemical surface reactions may lead to undesired microstructures and properties [30]. While, these studies have composite materials that are relatively mechanically robust compared to neat silica aerogel materials, the thermal conductivity values reported for the composite materials of 26–45 mW/m K are substantially higher than those of neat silica aerogel systems [31].

In this work, we study the influence of randomly dispersed NFC on the mechanical, microstructural, and thermal properties of silica aerogel-based composite monoliths with the goal of improving the mechanical properties of the silica aerogel composites without substantial increases in thermal conductance. The NFC reinforced silica aerogel composites are produced from ethanol-based sols of a PEDS precursor, PEDS-P_{750E20}. Varying concentrations of NFC are incorporated into the sol prior to gelation to achieve homogenous distributions of fibres in the silica aerogel matrix systems. However, NFC is intrinsically hydrophilic and does not readily disperse in ethanol. In an attempt to improve the dispersability of the NFC in ethanol, separate batches of the NFC were surface modified using maleic anhydride (MA). Our hypothesis is that the esterification of NFC with MA allows for a hydrophobization of the nanofibres, while providing sufficient polarity so that the MA-modified NFC would form stable dispersions in ethanol. The effects of the MA-modified NFC reinforced silica aerogel composites were examined and compared to the silica aerogel composites produced from unmodified NFC. By comparing these results with an earlier systematic study on the mechanical, thermal, and microstructural properties of neat silica aerogels made from PEDS-P_{750E20} in ethanol-based sols [32], we are able to assess the influence of the NFC on the material properties of the silica aerogel composite. The addition of NFC, both unmodified and MA-modified, noticeably improved the tensile strength σ_T of the silica aerogel-based composite by 25–40% compared to neat silica aerogel monoliths of similar densities while increasing the thermal conductivity by $\approx 11\%$ from 13.8 mW/m K to 15.3 mW/m K. The elastic modulus E , compression strength σ_C , and fracture strain ϵ_F of the aerogel monoliths were not significantly affected.

2. Experimental methods

2.1. Nanofibrillated cellulose

Nanofibrillated cellulose (NFC) was supplied by Borregaard Industries Ltd., Norway, as a water suspension with a solid content of

3.27% w/w. The NFC was obtained by disintegrating the bleached sulfite wood pulp in a homogenizer which produced microfibrils with diameters in the range of 10–100 nm. The NFC suspension was solvent exchanged to ethanol over three cycles of centrifugation and redispersion. Homogenization and redispersion processes were carried out using a homogenizer (30 s at 5000 rpm, Ultra-Turrax T25 basic, Ika-Verke). All centrifugation operations were conducted at 3500 rpm for 15 min. The final NFC concentration in ethanol was $0.85 \pm 0.02\%$ w/w.

2.2. Preparation of maleic anhydride-modified NFC (MA-NFC)

To prepare the MA-NFC, 100 g of a 3.27% w/w NFC water suspension (i.e. about 0.0605 mol total hydroxyl groups) were first solvent exchanged with dimethylformamide (DMF) by three cycles of centrifugation and redispersion. After the last centrifugation step, the NFC in DMF suspension was introduced in a beaker and 160 mL of DMF were added. The mixture was homogenized for 30 s and introduced in a three-necked round-bottomed flask equipped with a condenser and a mechanical stirrer (RW 16 basic, Ika Werke). 19.8 g of MA (0.20 mol) and 4.78 g of pyridine (0.061 mol) were added and the reaction was allowed to proceed at 105 °C for 3 h, under nitrogen flow. Subsequently, the modified NFC was washed three times with an ethanol/acetone mixture (1/1 by volume) to eliminate any remaining non-bonded chemicals, and the washing was then repeated three times in pure ethanol. Each washing cycle included a homogenization and centrifugation step. The final MA-modified NFC concentration in ethanol was adjusted to $0.85 \pm 0.02\%$ w/w. The success of grafting was confirmed by FTIR spectroscopy, where a broad signal was detected between 1750 and 1690 cm^{-1} , corresponding to the carbonyl stretching vibrations of the ester formed and the acid terminal function [33].

2.3. Preparation of NFC aerogel for SEM

Unmodified and MA-modified NFC suspensions were diluted to 0.07% w/w and freeze-dried in liquid nitrogen.

2.4. Sample preparation

Research grade PEDS, a prepolymerized form of tetraethoxysilane (TEOS) containing a water-to-TEOS molar ratio of 1.5 and a SiO₂ content of 20% w/w in ethanol and referred to as PEDS-P_{750E20} (PCAS, France), was used as the silica gel precursor [13]. The NFC dispersions were homogenized by a homogenizer (Ultra-Turrax T25 basic, Ika-Verke) prior to sample preparation to redisperse the fibres and break apart agglomerates that may have formed during settling. Desired amounts of unmodified or MA-modified NFC dispersions were pipetted into beakers containing measured amounts of PEDS-P_{750E20}, and ethanol (F25-AF-MEK ethanol denatured with 2% methyl ethyl ketone (MEK), Alcosuisse, Switzerland) under constant stirring. Gelation was initiated by adding a 7.25 M solution of ammonium hydroxide (NH₄ OH) (Product No. 09861, Fluka, Germany) at 2% v/v of the NFC sol dispersion. The gelation-initiated sols were poured into polystyrene moulds, either 50 × 50 mm square boxes (Product No. 2965, Semadeni, Switzerland) to make samples for thermal conductivity measurements or 18 mm diameter cylindrical tubes (Product No. 1698, Semadeni, Switzerland) for mechanical tests. Gelation occurred in approximately 10 min, shortly after which the alcogels were covered with ethanol and aged overnight. Aging the gels resulted in isotropic shrinkage of approximately 10% v/v which allowed the gels to be easily removed from the moulds [13]. The alcogels were then transferred to glass beakers filled with ethanol and covered with aluminium foil.

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