

## Reinforcing silica aerogels with tungsten disulfide nanotubes



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### ARTICLE INFO

#### Article history:

Received 5 February 2015

Received in revised form 16 July 2015

Accepted 16 July 2015

Available online 20 July 2015

#### Keywords:

Silica aerogel

Nanocomposite

Inorganic nanotubes

Tungsten disulfide nanoparticles

Mechanical properties

### ABSTRACT

Silica aerogels are unique solids with extremely high porosity (>99.5% air by volume), transparency and low density. With their high surface area and thermal resistivity they make excellent heat insulators. However, due to their fine structure they are fragile and therefore impractical for structural applications. To improve their mechanical properties we suggest incorporation of minute amounts of tungsten disulfide nanotubes. Nanotubes of tungsten disulfide are known for their high mechanical strength, strain and thermal stability. Adding some 0.1–1 wt% of tungsten disulfide nanotubes to a variety of polymers clearly lead to substantial improvement in their mechanical properties.

The current study reports the preparation of silica aerogels compounded with small amounts of tungsten disulfide nanotubes. Three-point bending and uniaxial compression tests of the composite aerogel revealed 85% and 23% improvement in the composite material toughness, respectively.

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### 1. Introduction

Aerogels are amongst the most porous solid material known. Since their pores are filled with air they are very light and insulate heat very well. The combination of low weight and high thermal insulation makes them suitable for space exploration applications [1].

Silica aerogels are normally prepared from Si-alkoxide precursors through sol–gel chemistry [2]. The gel formed is made of very thin walls, few nanometers thick, in a random structure and surrounded by meso-sized pores. In order to dry these delicate materials supercritical drying is used. By transferring the pore fluid to supercritical phase it is possible to vent it out with no capillary forces. Thus, supercritical drying is essential to achieve dry material without collapse of the fine porous structure.

A major limitation of dry silica aerogels is their mechanical fragility, i.e., they exhibit low fracture toughness [3]. Different approaches have been proposed to improve the strength and fracture toughness of silica aerogels [4]. One method includes dispersing fillers such as fibers in the silica matrix. Several studies reported the improved mechanical behavior of aerogels filled with different kinds of fibers [5–7]. The properties of the composite aero-

gel depend on those of the filler and on the interaction between the filler and the matrix.

Important parameters include: (1) The size and aspect ratio of the fibers; (2) the concentration and dispersion of the fibers in the host matrix and (3) the fiber–silica matrix interaction. These considerations suggest that inorganic nanofibers with high crystalline order which can disperse well in the matrix will endow substantial improvements to the mechanical behavior of the aerogel.

Nanoparticles (NPs) from inorganic layered compounds with hollow-core structure are a relatively new class of materials. The first inorganic NPs made from tungsten disulfide (WS<sub>2</sub>) and molybdenum-disulfide (MoS<sub>2</sub>) were reported in 1992 and 1993, respectively [8,9]. The growth mechanism of WS<sub>2</sub> fullerene like (IF) NPs was elucidated and resulted in the synthesis of a pure phase [10]. IF-WS<sub>2</sub> nanoparticles (“industrial grade”) are currently produced in large scale and are commercially used as superior solid lubricants for a variety of tribological applications and for polymer reinforcement. Recently, a comprehensive understanding of the growth mechanism for inorganic nanotubes (INT)-WS<sub>2</sub> resulted in pure phase and scaled up synthesis (up to 150 g/day) [11]. The INTs are 1–20 micron long with diameter of 30–150 nm (aspect ratio of 100 and larger).

Fig. 1 shows a scanning electron microscopy (SEM) (a) and transmission electron microscopy (TEM) (b) images of typical WS<sub>2</sub> nanotubes. The TEM analysis clearly reveals the perfectness of the INT crystalline structure and almost no defects on their surface.

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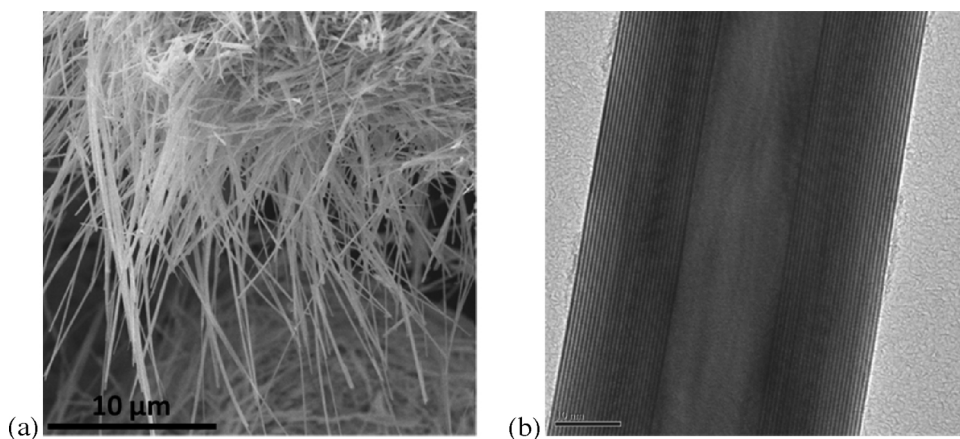


Fig. 1. Defect free INT-WS<sub>2</sub>; (a) SEM image. (b) TEM image (scale bar 10 nm).

More recently, nanotubes and fullerene-like NP from numerous other layered compounds were reported [12,13]. Their structure is analogous to multiwall carbon nanotubes (MWCNT). Similarly to MWCNT these nanoparticles consist of several closed layers held together by van-der-Waals forces. The outer surface of the WS<sub>2</sub> IF/INTs consists a layer of inert sulfur atoms. Both theory and experiment show that the intermolecular forces between these inorganic nanoparticles are very weak [14]. Consequently, they are loosely aggregated and can easily be dispersed in solutions. Moreover, it was demonstrated that dispersing agents are generally not required [15,16] to form stable suspensions in viscous fluids, like polymer blends and fluids undergoing rapid gelation.

The mechanical properties of individual nanotubes were studied in some detail before [17,18]. The Young's modulus of WS<sub>2</sub> nanotubes was found to be around 150 GPa; their tensile strength—16–20 GPa and their strain  $\varepsilon > 10\%$ . In addition, the WS<sub>2</sub> nanotubes are chemically stable up to a temperature close to 350 °C in oxidative atmosphere and beyond 1000 °C in a reducing or neutral atmosphere. These results suggest that such nanotubes could be very useful for reinforcing different polymers and inorganic phases, like the aerogels.

The controllable structure and properties of WS<sub>2</sub> nanotubes, their capability to form uniform dispersion in polymer matrices and good INT-polymer interfacial interaction are of utmost importance for the preparation of polymer composites with enhanced mechanical and thermal behavior. Accordingly, substantial effort has been paid in various laboratories to study the effect of adding minute amounts of WS<sub>2</sub> nanotubes on the mechanical and thermal properties of different polymers. Indeed, adding tiny amounts (0.1–2 wt %) of nanotubes to various polymer matrices lead to improved mechanical and thermal behavior of the nanocomposites.

The studied polymers include polymethyl methacrylate (PMMA) [19], room temperature vulcanized (RTV) silicone adhesive [20], nylon [21], polypropylene [22], epoxy [23,24] and polyurethane (PU) [25] among others. As an example, in the case of electrospun PMMA nanofiber mesh, the addition of 1% WS<sub>2</sub> nanotubes improved the tensile strength by more than 600 kPa, and the Young's modulus increased from  $10.16 \pm 0.02$  MPa to  $102.08 \pm 3.60$  MPa (improvements of  $\sim 900\%$ ) for the composite material (at room temperature) [19]. In addition, it was shown that INT-WS<sub>2</sub> nanotubes could beneficially influence the crystallization behavior of poly(3-hydroxybutyrate) (PHB), which is one of the most extensively studied and utilized biodegradable and renewable thermoplastic polyester [26]. It was shown that the WS<sub>2</sub> nanotubes accelerate the crystallization of PHB, and an

increment of 36.3 °C in the crystallization temperature of PHB was observed for as little as 0.1 wt% INT added, and this in comparison with 5.5 °C obtained for MWCNT.

These results suggested that adding small amounts of INT-WS<sub>2</sub> should moderately affect the structure and weight of aerogels, while their mechanical behavior could be considerably improved. This is the subject of the present publication.

## 2. Experimental

### 2.1. Materials

WS<sub>2</sub> nanotubes (INT-WS<sub>2</sub>) were provided by NanoMaterials Ltd. (Israel) [27]. The synthesized material contained 10–20% WS<sub>2</sub> platelets (2H phase) and was not further purified for the present experiments. Silica gel forming reagent, tetraethyl orthosilicate (TEOS) (reagent grade, 98%, density:  $0.933 \text{ g mL}^{-1}$ ), ammonium hydroxide (28–30 wt% in water, ACS reagent), and ammonium fluoride ( $\geq 98.0\%$ , ACS reagent) were purchased from Sigma-Aldrich. High purity ethanol (ACS specifications) was acquired from J.T. Baker.

### 2.2. Sample preparation

Silica and INT-WS<sub>2</sub>/silica composites were prepared according to the base-catalyzed tetraethyl orthosilicate (TEOS) polymerization method, which is described briefly below. “Stock solution” was prepared by mixing ammonium fluoride (463 mg) and ammonium hydroxide (5.695 mL) in 25 mL of double distilled water (DDW). An “alkoxide solution” consisted TEOS and ethanol in 1:2.2 mL ratio respectively. The “catalyst solution” was prepared by mixing stock solution during sonication with DDW and ethanol at 0.074:1.4:2.2 mL ratio, accordingly. The molar ratio of the total mixture TEOS:Ethanol:H<sub>2</sub>O:NH<sub>4</sub>F:NH<sub>4</sub>OH was 1.0:17.0:17.7:0.003:0.02 respectively.

INT-WS<sub>2</sub> powder was added to the ethanol-water phase of the “catalyst solution”. The mixture containing the INT-WS<sub>2</sub> was manually mixed and then sonicated three times in a water filled beaker at room temperature. Each sonication period was 3 min long. This short sonication was sufficient to achieve good dispersion of the nanotubes. The ultrasonic bath (MRC, AC-120H) operated at frequency of 50 kHz. In order to prevent overheating of the solution the water in the beaker was replaced every 2 min. Stock solution was added to the ethanol/water/INT mixture to make the catalyst solution. The catalyst solution was mixed with the alkoxide solution and then poured into Teflon molds for gelation. After 25–20 min the molds with the gel were transferred into ethanol bath for 7 days of

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