Journal of Non-Crystalline Solids xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Journal of Non-Crystalline Solids

journal homepage: www.elsevier.com/locate/jnoncrysol

Tensile performance of silica-based electrospun fibrous mats

Jianjun Li*, Chujun Nie, Beibei Duan, Xu Zhao, Haibao Lu, Weilong Yin, Yibin Li, Xiaodong He*

National Key Laboratory of Science and Technology on Advanced Composites in Special Environments, Harbin Institute of Technology, Harbin 150080, PR China

ARTICLE INFO

Keywords:
Electrospinning
Tensile performance
Silica-based

ABSTRACT

To understand the relationship between mechanical behavior and fiber assembly in electrospun ceramic-based fibrous mats, the tensile performance of silica, silica/polydimethylsiloxane and silica/polymethyl methacrylate hybrid fibrous mats was investigated. Elastic-plastic behavior as a whole was confirmed in the silica-based fibrous mats. The initial isotropy and disordered networks with point contact between the randomly oriented fibers before the tensile test and the highly oriented fibrous bundles with side contact between the aligned fibers after the tensile test were observed using scanning electron microscopy.

1. Introduction

Ceramic fibers with intrinsically hard, inert and corrosion resistant features are attractive for their applications in areas such as catalysis, the electronic and photonic industry, environmental science, and energy technology [1]. Electrospinning is a powerful technique that can process viscoelastic solutions into continuous one-dimensional fibers with controllable diameters, compositions, and structures to fabricate non-woven mats [2–4]. Long-range periodic array or structure control in one-dimensional structures can also be realized by modifying the electrospinning setup [5–9]. During the past few years, the electrospinning technique has been developed successfully for ceramic systems to produce micro- and nanofibers. Viscoelastic inorganic precursory solutions [10–12] resulting from the sol-gel process can be used for electrospinning. The combination of sol-gel and electrospinning provides a straightforward route for the preparation of electrospun ceramic fibers. The flexible sol-gel chemical approach in combination with the concept of molecular-level incorporation of nanoscaled components, or organic polymers, can tailor inorganic structures into novel multifunctional hybrid materials, which may be applied in diverse areas, including mechanical improvement, [13–17] and filtration and self-cleaning [18,19]. Electrospinning in combination with the sol-gel technique has directly produced SiO_2, Al_2O_3, TiO_2, ZrO_2 and other fibers [20–22].

Silica is one of the most typical ceramic materials and is widely used in both academia and industry. Silica and modified silica materials prepared by the sol-gel process are functional materials with a wide range of applications, including controlled release, protective coatings, adsorption, chromatography, separation, biotechnology, energy conservation, cultural heritage restoration and environmental remediation [23,24]. Silica fibers can be electrospun from its sol made from hydrolysis and condensation of tetraethoxysilane (TEOS). Enhanced thermal and mechanical properties from silica and better flexibility due to the polymer provide multifunctional performance to silica-based polymer hybrids [25,26]. Silica sols can be electrospun into fibers without any carrier polymer [21]. Silica fiber has been synthesized on a large-scale with highly ordered mesoporous structure and continuous long fibers by employing electrospinning [27]. Flexible, high-heat-resistant, and amphiphobic mats were fabricated by (fluoroalkyl) silane (FAS) modification of electrospun pure silica nanofibrous mats [28]. In the process of preparing silica-based electrospun hybrid products, polymers and silica sol must be dissolved in a suitable organic solvent. The excellent solubility of silica sol in different solvent systems [29,30] makes it possible to prepare silica/polydimethylsiloxane (PDMS) and silica/polymethyl methacrylate (PMMA) electrospun hybrid products with controllable wetting behavior.

Mechanical behavior determines the practical applications of electrospun materials, especially ceramic-based products. Most studies on electrospinning have focused on the optimization of processing control parameters and improvement of functional performance. The effects of oriented morphology, structures and tensile properties on electrospun polymer-based nanofibers have been investigated [31–34]. A thorough understanding of the mechanical properties of electrospun ceramic-based fibrous mats is necessary. The elastic-plastic behavior of non-woven fibrous mats and a constitutive model, which captures the membrane stress-strain behavior as a function of fiber properties and the geometry of the fibrous network, have been investigated from the amorphous polyamide system [35].

Silica hybrid products, including aerogel, film, fiber and particle have been investigated in various applied fields. Our previous re-

* Corresponding authors.
E-mail addresses: ljj8081@gmail.com (J. Li), hexd@hit.edu.cn (X. He).

http://dx.doi.org/10.1016/j.jnoncrysol.2017.05.016
Received 10 December 2016; Received in revised form 25 April 2017; Accepted 15 May 2017

searches reported the fabrication and modification of silica fibrous mats obtained by electrospinning [8,26,29,30]. In this study, we evaluate the mechanical performance of electrospun silica-based (silica, silica/polymethyl methacrylate and silica/polydimethylsiloxane) fibrous mats under various conditions. The mechanical behavior of the mats was investigated by uniaxial tensile tests. The results provide a basic understanding of the relationship between the mechanical performance and the internal structures of electrospun fibrous mats.

2. Experimental

In this study, all the reagents were directly used without further dilution. Tetraethoxysilane (98%) was purchased from the Sigma-Aldrich Chemical Company. Polymethyl methacrylate (PMMA) was obtained from the Aladdin Company. Polydimethylsiloxane (99.7%), ethanol (99.7%), acetone (99.7%), dichloromethane (99.5%) and hydrochloric acid (37%) were supplied by the Tianjin Fengchuan Chemical Reagent Company. Polyethylene oxide (PEO, Mn = 900,000) was provided by the Changchun Jinghua Company.

Silica sol was prepared by the hydrolysis and condensation of tetraethoxysilane and the detailed experimental procedure is reported elsewhere [8]. Polyethylene oxide (PEO) is introduced into silica sols as an electrospinning carrier and it's concentration in silica sol is 1 wt%. Solid polymethyl methacrylate must be dissolved in acetone to become polymethyl methacrylate solution (0.1 g/mL) firstly. Liquid polydimethylsiloxane can be used directly. Silica sol can be mixed with polymethyl methacrylate in acetone or with polydimethylsiloxane in dichloromethane to get the mixtures for electrospinning.

Here a needle electrospinning apparatus (Beijing Future Material Sci-tech Company) was used. The flow rate of the mixtures was 2 mL/h and the distance between the needle and collector was 20 cm. The voltage was 24 kV. The scanning electron microscope (SEM) images were performed on the HITACHI SU8000. The tensile behavior of the electrospun mat was tested on tensile testing equipment (Instron 5944) with a tensile speed of 0.5 mm/min at room temperature. Dumbbell-shaped tensile specimens were prepared from isotropic electrospun silica-based fibrous mats.

3. Results and discussion

Our previous work investigated the influence of solvent on the spinnability and silica-based electrospun fibers. The correct viscosity of the precursory solution is essential for producing a continuous flowing stream of silica from the needle to the collector. The results reveal that acetone can lower the minimum concentration for electrospinning of silica sols, and the diameter of silica fibers decrease as the silica sol/acetone volume ratio decreases [29]. Experimental studies have demonstrated improvements in the modulus and strength of electrospun polymer nanofibers with reduced diameter [36]. In this manuscript the mechanical behavior of silica fibrous mats that were electrospun from different concentrations of silica sol in acetone is tested. The SEM images of electrospun silica fibers in acetone with 2:1 and 1:1 silica sol/acetone volume ratios are displayed in Fig. 1a) and b), illustrating the effect of silica sol concentration on the diameter of fiber. The average diameter of silica fiber spun with 2:1 silica sol/acetone volume ratio is approximately 1 μm, and the average diameter of silica fiber spun with 1:1 silica sol/acetone volume ratio decreases to 500 nm.

The mechanical performance of electrospun silica-based non-woven mats was quantitatively examined using uniaxial tensile tests. All the measured products were cut from the homogeneous region of the collected electrospun mats. To avoid compression damage from the clamp, specimen shaped thin protective cardboard pieces were fabricated to cover the tensile specimen and form a sandwich structure. After mounting the samples onto the instruments we cut off the protective cardboard using scissors (as shown in Fig. 2a)). Fig. 2b) presents the tensile stress-strain curves of electrospun silica fibrous

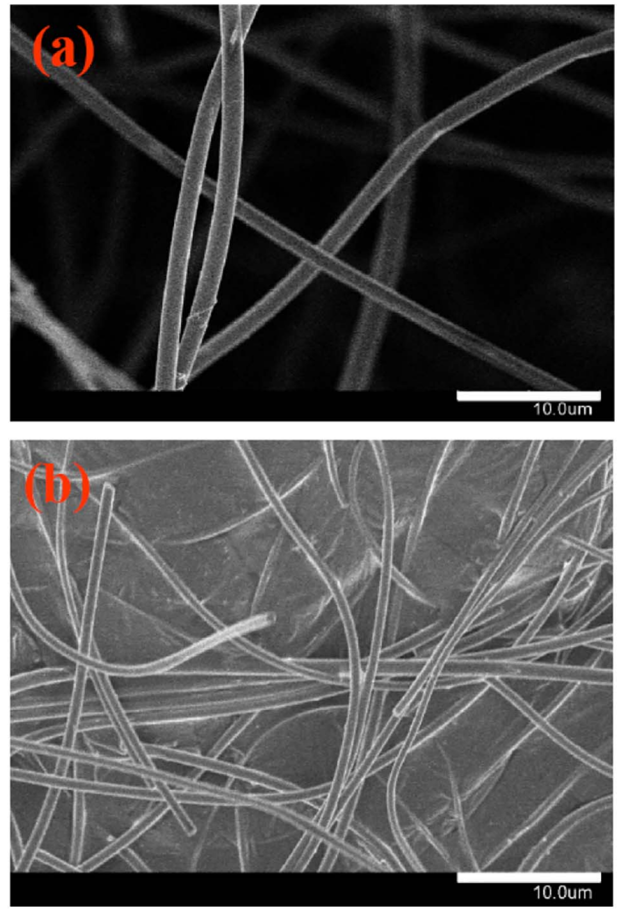

Fig. 1. SEM images of electrospun silica fibers made in acetone solvent with 2:1 (a) and 1:1 (b) Silica sol/acetone volume ratios.

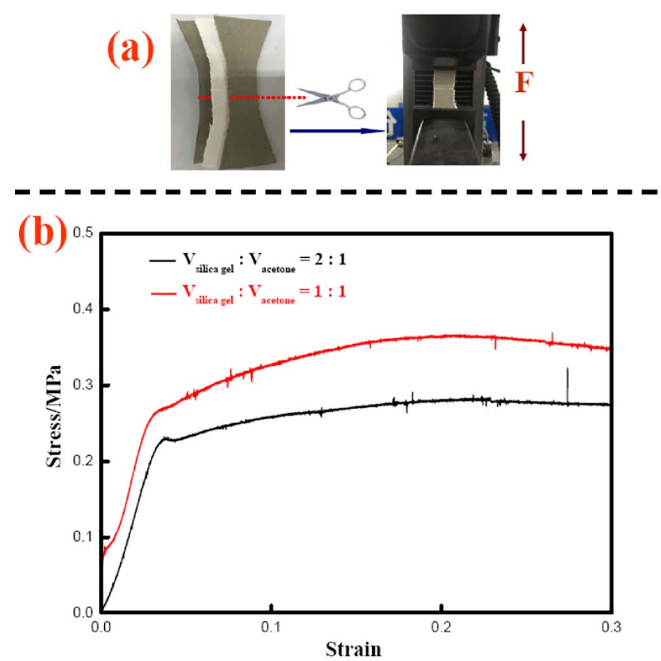

Fig. 2. (a): Silica fibrous mat with protective cardboard covers; (b): Tensile stress-strain curves of electrospun silica fibrous mats made in acetone solvent with 2:1 and 1:1 silica sol/acetone volume ratios.