Preparation and characterisation of aerogel composites reinforced with electrospun nanofibre

Qiliang Chen, Yantao Chen, Huijun Wu & Xiaoqing Zhou

To cite this article: Qiliang Chen, Yantao Chen, Huijun Wu & Xiaoqing Zhou (2015) Preparation and characterisation of aerogel composites reinforced with electrospun nanofibre, Materials Research Innovations, 19:sup2, S2-185-S2-189, DOI: 10.1179/1432891715Z.0000000001413

To link to this article: https://doi.org/10.1179/1432891715Z.0000000001413
Preparation and characterisation of aerogel composites reinforced with electrospun nanofibre

Qiliang Chen\textsuperscript{1,2}, Yantao Chen\textsuperscript{1}, Huijun Wu\textsuperscript{*1,2} and Xiaoqing Zhou\textsuperscript{1,2}

Silica aerogels and their composites with electrospun poly(vinylidene fluoride) nanofibre were successfully fabricated using tetraethylorthosilicate as precursor and dimethyl sulphoxide as solvent via sol-gel process and ambient drying. The pure aerogel showed high transmittance for visible light and low thermal conductivity (0.026 W m\textsuperscript{-1} K\textsuperscript{-1}) and poor strength. Tensile, compress and blending strength of aerogel composite reinforced with electrospun nanofibre were dramatically enhanced 24, 32 and 3 times compared with pure aerogel, respectively. The composite materials could keep integrity even after being greatly bented and rolled. It also exhibited excellent thermal insulation property with thermal conductivity of 0.029 W m\textsuperscript{-1} K\textsuperscript{-1}, slightly higher than pure aerogel. This provides a facile method to prepare monolithic aerogel composites with high mechanical strength and thermal insulation performance.

Keywords: Aerogel, DMSO, Polyvinylidene fluoride, Electrospinning, Nanofibres

Introduction

Silica aerogels are low density non-crystal solids with high porosity up to 99.8\% and surface area in the range 500–1000 m\textsuperscript{2} g\textsuperscript{-1}, which are composed of ‘interconnected nano-particle’\textsuperscript{1,2}. Excellent thermal,\textsuperscript{3} optical,\textsuperscript{4} acoustic\textsuperscript{5} and catalytic properties\textsuperscript{6} from unique nanostructure has drawn many researchers attention to develop its potential scientific and industrial applications. Despite numerous potential applications, aerogels are not extensively used, because they are fragile and difficult to prepare in a large-scale industrial production.\textsuperscript{7}

Great effort was made to enhance mechanical properties of aerogel, such as addition of drying control chemical additives (DCCA),\textsuperscript{8} aging in alkoxide/alcohol solutions\textsuperscript{9,10} and chemical vapour deposition treatment with hydrophobic reagent.\textsuperscript{11} The results were not satisfied for aerogel application. Approaches such as incorporation of a secondary reinforcement materials including polymers,\textsuperscript{12} particles or fibres\textsuperscript{13,14} have been used to enhance mechanical properties of aerogel materials. Fibrous reinforcement has attracted extensive attention, because the aerogel composite can be endowed with monolith and flexibility. Liao et al.\textsuperscript{15} first impregnated glass fibre into silica aerogel and investigated influence of fibre alignment on mechanical and thermal properties. Zhang et al.\textsuperscript{15} adopted ceramic fibre to reinforce the silica aerogel, mechanical strength of the silica aerogels increased from 1.6 \times 10\textsuperscript{4} to 9.6 \times 10\textsuperscript{4} Pa with the doping of 10\% ceramic fibres, while the thermal conductivity is 0.029 W m\textsuperscript{-1} K\textsuperscript{-1}. To improve flexibility of aerogel composite, more and more researchers focussed on nanoscale fibre as reinforcement, which showed more compatibility with aerogel because of compatible scale in fibre diameter and aerogel nanopore. Feng et al.\textsuperscript{16} synthesised the carbon aerogel composites reinforced by carbon fibres via the pyrolysis of the resorcinol formaldehyde aerogels reinforced with oxidised polyacrylonitrile. Loy group\textsuperscript{17} presented strong aerogel composite introducing polyaniline nanofibres, which exhibited were electrically conducting (8.0 \times 10\textsuperscript{-8} to 1.83 \times 10\textsuperscript{-5} S cm\textsuperscript{-1}) when amount of polyaniline nanofibres ranged in 1.3–16.5 wt-%. Li et al.\textsuperscript{18} blended sepiolite fibre with silica sol and achieved excellent interfacial interaction in the sepiolite/silica aerogel composite, which appeared improvement of mechanical properties without sacrificing much thermal insulating performance. Shoushtari group\textsuperscript{19} showed silica aerogel/polyethylened terephthalate (PET) nonwoven fibre composite led to a stronger hydrophobicity and higher thermal insulation performance compared to the neat PET nonwoven. Our group\textsuperscript{13} investigated aerogel composite reinforced with three different microstructures electrospun poly(vinylidene fluoride) (PVDF) webs and found the composite with electrospun nanofibre presented good intact monolith, improved strength and the lowest thermal conductivity (0.028 W m\textsuperscript{-1} K\textsuperscript{-1}).

In this paper, pure aerogel and flexible aerogel composite reinforced with electrospun PVDF web were prepared with silica dimethyl sulphoxide (DMSO) sol. The effects of the electrospun PVDF on the thermal conductivity...
and the mechanical properties of the SiO₂ aerogels composites are evaluated.

Materials and methods

Materials

Tetraethylorthosilicate (>98%, TEOS), ethylalcohol (>99%, EtOH), N,N-dimethyl-formamide (>98%, DMF), dimethyl sulphoxide (>98%, DMSO), N-hexane (>99%) and trimethylchlorosilane (>95%, TMCS) were purchased from Baishi Co. Ltd. (China). Poly(vinylidene fluoride) was purchased from Guanghua Co. Ltd. (China). Poly(vinylidene fluoride) was purchased from Baishi Co. Ltd. (China).

Electrospinning of PVDF web

A total of 28 wt-% PVDF solutions were prepared by dissolving PVDF particles in DMF in a water bath at 65°C under magnetic stirring for 6 h, followed by cooling to room temperature with continuation of stirring for another 6 h. The PVDF solutions were, respectively, inserted into a plastic syringe with a stainless steel nozzle with the diameter of 1.0 mm for electrospinning by using an electrospinning apparatus (Model: NEU) from Kato Tech Co. Ltd., Japan. The apparatus consists of a syringe pump for supplying the PVDF solution, a grounded electrode for collecting the fibres, and a DC power for supplying high voltage. In electrospinning process, the voltage of 13 kV was applied to the stainless steel connected with the PVDF solution, and a DC machine (Sunthink, China) with a loading speed of 0.0012 Pa s and 200 nm as SEM image shows in Fig. 1a.

Preparation of silica sol

Silica sol was prepared by a two-step acid/base catalysed sol-gel process. In the first step, TEOS, DMSO, deionised H₂O and HCl were mixed in the molar ratio 1:7:1:1 × 10⁻³ and magnetically stirred for 30 min. The solution was then kept at room temperature for 24 h. In the second step, DMF as DCCA and NH₄OH as base catalyst were added in the sol to adjust pH at 6–8. The remainder H₂O was added in to accelerate the gelation process. The overall molar ratio of H₂O to TEOS was 2:1. The obtained silica sol without gelation was used for combination process with electrospun PVDF web.

In comparison with pure silica aerogel composite with DMSO, silica ethanol sol was prepared according to similar procedures, only solvent substitution of EtOH.

Synthesis of SiO₂ aerogel composites reinforced with electrospun PVDF web

The electrospun PVDF webs were added into the silica sol as framework and the PVDF/SiO₂ composites were obtained. The PVDF/SiO₂ composite gelled to monolith after 0.5–1 h. The composite gels were kept at room temperature for 2 days for further solidification to form silica monoliths. These monoliths were soaked in EtOH to exchange DMSO solvent in the pore. After that, the composite gels were aged in H₂O/EtOH (1:4, vol.) solution for 24 h and then TEOS/EtOH (1:4, vol.) solution for 24 h to strengthen the gel network. The water and ethanol solvents in the pores of the wet gel were exchanged with isopropanol and n-hexane, respectively. After being immersed in a solution of 10% vol. Trimethylchlorosilane/n-hexane at 35°C for about 8 h for surface modification, the monoliths were washed in n-hexane for 32 h. The SiO₂ aerogel composites reinforced with electrospun PVDF webs were synthesised by drying the monoliths at 70°C for 12 h followed by further drying at 100°C for 12 h. For comparison, the pure aerogels were prepared with the silica DMSO and ethanol sol without electrospun PVDF webs, respectively.

Instruments and characterisations

The as-synthesised SiO₂ aerogel composites reinforced with electrospun PVDF webs were coated with gold/palladium to be investigated on their morphology and microstructure by using a 1530VP scanning electron microscopy (SEM, LEO, Germany). The thermal conductivity was measured by a TPS2500 thermal conductivity apparatus (Hot Disk, Germany) in terms of a transient plane heat source method at room temperature. The testing power and period of the thermal conductivity apparatus were 10 mW and 20 s, respectively. The thermostability of the aerogel composites was measured by using a TGA400 thermal gravimetric analyzer (TG, PerkinElmer, USA) at the heating rate of 10°C min⁻¹. The surface hydrophobicity of the aerogel composites was determined using a Kruss DSA100 droplet scanning analysis (DSA, Germany) at a static analysis mode.

The bulk density of the aerogel composite was determined by measuring the weight and volume of the aerogel composites. The compression tests of the aerogel composite were carried out on a WHY-50 automatic pressure-testing machine (Hualong, China) at a time-displacement model with a loading speed of 2 mm min⁻¹. The bending modulus of the aerogel composites was investigated with a three point flexural bending method on a CMT6104 universal testing machine (Suntihink, China) with a loading speed of 5 mm min⁻¹ at room temperature.

Results and discussion

Morphology and microstructure of electrospin PVDF web

Figure 1 shows the morphologies and microstructures of electrospun PVDF web prepared with 28 wt-% PVDF in DMF solvent. Figure 1a exhibits the optical images of electrospun PVDF web cut in circle with the diameter about 12 cm. It can be observed that the PVDF web possesses integrity and high flexibility (Fig. 1b). The webs were composed of nanofibre with diameter between 1 μm and 200 nm as SEM image shows in Fig. 1c.

Morphologies of pure aerogel and aerogel composites reinforced electrospun PVDF web

The pure aerogel prepared with DMSO exhibited higher transparency than the aerogel with ethanol (Fig. 2a and b). These may attribute to two factors derived from different physical properties of DMSO and ethanol: DMSO is a polar aprotic solvent with higher viscosity (0.001996 Pa s at 20°C) and dipole moment (3.96 D) compared with ethanol (0.0012 Pa s and 1.69 D, respectively). High
1 Morphologies and microstructures of electrospun PVDF web prepared with 28 wt-% PVDF in DMF solvent: a, b optical image of electrospun PVDF web; c SEM image of electrospun PVDF web

2 Morphology of pure aerogel and aerogel composite based on electrospun fibre strengthened aerogels. a Pure aerogel prepared with DMSO solvent; b pure aerogel prepared with EtOH solvent; c, d aerogel composite materials prepared with DMSO solvent

3 Contact angle of pure aerogel and aerogel composites prepared with DMSO: a pure aerogel; b aerogel composite reinforced with electrospun PVDF nanofibre
viscosity solvent can reduce the rate of aggregation. This phenomenon can be observed from longer gelation time of gel prepared with DMSO; High dipole moment solvent DMSO possesses higher solubility for silica and incomplete hydrolysis compound of TEOS, compared with ethanol, resulting in less phase separation. Rapid aggregation and phase separation may lead to large colloid, which would augment light diffusion. Pure aerogel prepared with DMSO had uniform gel network and appeared higher transparency accordingly.

In Fig. 2, it can be observed that the SiO₂ aerogel composite specimens reinforced with the electrospun PVDF nanofibre showed intact integrity with a large size of diameter of 12 cm. From Fig. 2d, the SiO₂ aerogel composite specimen reinforced with the electrospun PVDF nanofibres showed good flexibility even if bended into a circle.

Figure 3 shows the contact angle of the pure aerogel and aerogel composites prepared with DMSO. It can be observed that the contact angle of the aerogel composite was slightly decreased to 137° relative to pure aerogel (143°). The composite also exhibited perfect hydrophobicity so that the aerogel composites could keep perfect thermal insulations even in moist environment.

Microstructure of SiO₂ aerogel composites reinforced electrospun PVDF webs

Figure 4 depicts that nanofibre exhibited rough surface caused by high rate electrospinning process and almost all of aerogel was separated from electrospun nanofibre aerogel in composite. The different phenomena were observed in aerogel composite prepared with EtOH, which was reported in our previous work. These may attributed from the solvent exchange process of DMSO and EtOH. Although the electrospun PVDF web possesses the lowest density, it shows the highest thermal conductivity. Aerogel composite has higher density 0·32 g·cm⁻³, compared with pure aerogel (0·23 g·cm⁻³), but thermal conductivity of composite is just slightly increased to 0·029 W·m⁻¹·K⁻¹ (pure aerogel, 0·026 W·m⁻¹·K⁻¹), achieving higher performance for thermal insulation. These may be attributed that super thermal insulate aerogel powder filled in the micron scale hole in PVDF web, attenuating thermal shortcut when nanofibres intersect or parallel.

Figure 5 shows the thermal gravimetric analysis of the pure aerogels and aerogel composites reinforced with

<table>
<thead>
<tr>
<th>Sample</th>
<th>Thermal conductivity (W·m⁻¹·K⁻¹)</th>
<th>Density (g·cm⁻³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure aerogel</td>
<td>0·026</td>
<td>0·23</td>
</tr>
<tr>
<td>Electrospun PVDF web</td>
<td>0·037</td>
<td>0·20</td>
</tr>
<tr>
<td>Aerogel composite</td>
<td>0·029</td>
<td>0·32</td>
</tr>
</tbody>
</table>

Table 1 Properties of pure aerogel, electrospun PVDF web and aerogel composite prepared with DMSO

Thermal properties of pure aerogel, electrospun PVDF web and aerogel composites

In Table 1, the pure aerogel prepared with DMSO exhibits high density, which may be ascribed to the incomplete solvent exchange of DMSO and EtOH. Although the electrospun PVDF web possesses the lowest density, it shows the highest thermal conductivity. Aerogel composite has higher density 0·32 g·cm⁻³, compared with pure aerogel (0·23 g·cm⁻³), but thermal conductivity of composite is just slightly increased to 0·029 W·m⁻¹·K⁻¹ (pure aerogel, 0·026 W·m⁻¹·K⁻¹), achieving higher performance for thermal insulation. These may be attributed that super thermal insulate aerogel powder filled in the micron scale hole in PVDF web, attenuating thermal shortcut when nanofibres intersect or parallel.

Figure 5 shows the thermal gravimetric analysis of the pure aerogels and aerogel composites reinforced with
Conductivity to 0 ambient drying. The composite achieved excellent dimethyl sulphoxide as solvent via sol-gel process andpressive strength of composite had even exponen-
tively. The unique preparation provided another prep-
ration way to obtain monolithic aerogel composite for
heat preservation application.

Table 2 Mechanical properties of pure aerogel and aerogel composite reinforced with electrospun PVDF web

<table>
<thead>
<tr>
<th>Sample</th>
<th>Tensile strength (MPa)</th>
<th>Compressive strength (MPa)</th>
<th>Bending strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure aerogel</td>
<td>0.07</td>
<td>0.11</td>
<td>2.09</td>
</tr>
<tr>
<td>Aerogel com-</td>
<td>1.7</td>
<td>3.5</td>
<td>6.3</td>
</tr>
</tbody>
</table>

Pure aerogel and aerogel composite prepared with DMSO.

Mechanical properties of pure aerogel and aerogel composite reinforced with electrospun PVDF web

Table 2 demonstrates the mechanical properties of the pure aerogel and aerogel composite reinforced with different electrospun PVDF web. It can be observed that all the mechanical properties of composite reinforced with electrospun PVDF nanofibre had been significantly increased, relative to pure aerogel. The tensile and compressive strength of composite had even been exponen-
tially augmented to 1.7 and 3.5 MPa, respectively. Although the bending strength was tripled to 6.3 MPa, the composite displayed highly flexible. These may be attributed to reinforcement and energy absorption of electrospun PVDF nanofibre.

Conclusions

Pure aerogel and aerogel composite with electrospun poly(vinyliden fluoride) nanofibre were successfully fab-
ricated using tetraethylorthosilicate as precursor and dimethyl sulphoxide as solvent via sol-gel process and ambient drying. The composite achieved excellent thermal insulation performance with the low thermal conductivity to 0.029 W·m⁻¹·K⁻¹ and higher application temperature to 172°C. The composite possessed high flexibility and tensile and compressive strength of it had been tremendously enhanced to 1.7 and 3.5 MPa respectively. The unique preparation provided another prep-
ration way to obtain monolithic aerogel composite for heat preservation application.

Acknowledgements

This research was supported by the Guangdong Province Natural Science Foundation for Distinguished Young Scientists, China (No. S2013050014139) and the Research Grant by Education Department of Guangdong Province, China (No. 2013KJCX0141).

References

16. J. Feng, C. Zhang, J. Feng, Y. Jiang and N. Zhao: ‘Carbon aerogel composites prepared by ambient drying and using oxidized polycry-
publications.html