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Facile synthesis of sponge reinforced monolithic silica aerogels with improved mechanical property and excellent absorptivity

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ABSTRACT

Silica aerogels (SA) with low density were reinforced with monolithic polyurethane sponge (PUS) using the sol–gel method at ambient pressure. The product (PUS reinforced SA) presents good features of high hydrophobicity and lipophilicity after the surface is modified by trimethylchlorosilane (TMCS). In the product, the nanoporous SA granules were held by the PUS skeleton. The SA has excellent absorptivity for various solvents and oils. Moreover, the aerogels demonstrate remarkable elasticity which overcomes the fragility of pure SA without PUS. Furthermore, the preparation process is also cost effective hence the PUS reinforced SA could be recommended as solvent/oil absorbent for the water pollution industry.

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1. Introduction

Water contaminations caused by oils or organic solvents can severely threaten the people and environment [1]. To control the accidental and unconscious release of oil/organic liquids effectively, a wide range of oil remediation materials have been employed as absorbents [2], dispersants [3] and so on. Among them, the hydrophobic porous materials are commonly used due to their excellent features such as low density and high porosity [4]. The hydrophobic aerogels, such as the polyvinyl alcohol–cellulose nanofibril hybrid aerogels (PACNHA) [1], the methyltriethoxysilane based aerogels [5] and the silica aerogel (SA) coated polymer sponge [6] have all showed excellent absorptivity to oils. However, the used precursors for these materials are usually very expensive.

Tetraethylorthosilicate (TEOS), on the other hand, is a cheaper precursor and the TEOS based hydrophobic SAs can be made through surface modification. The SA with modified surface has high porosity and large surface area [7]. SAs modified with –CH_3 can function very well in sorption of organics and the adsorption capacity is 10 times higher than that of activated carbon [8]. However, shrinkage and cracking could happen to SA during drying at ambient pressure [7]. The SA usually cracks into many small pieces after an adsorption–desorption cycle [9]. Therefore it is not suitable to be directly applied in solvent/oil sorption in water pollution industry.

The TEOS based SA with large specific surface area has been made previously at ambient pressure [10]. However, the mechanical properties need to be improved for commercial uses. In this study, the PUS, served as skeleton, was introduced to the sol–gel based SA preparation process. The modified aerogels present a very effective absorptivity for organic liquids and it can be recycled for more than 10 times. Besides, the mechanical properties have also been significantly improved compared to either pure SA or PUS.

2. Experiments

Preparation of sponge reinforced silica aerogels: The analytical pure reagents used for producing the alcogels were the same as our previous work [10]. The PUS samples were sonicated in acetone and DI·H_2O and then dehydrated at 80 °C. Certain amount of TEOS and EtOH were mixed and stirred at the presence of DI·H_2O. 0.1 M HCl was added to the solution to reduce the pH value down to 3–4 for catalyzing the hydrolysis. The alcosol was heated up using 45 °C water bath for 6 h. Then 0.5 M NH_4OH was added to the stirring sol to increase the solution pH to 6–7 to catalyze the condensation. Refined PUS with appropriate dimension was put into the sol. The PUS should be squeezed and the mixture was sonicated in an ultrasonic water bath for 5 min to remove the bubbles within the pores completely. The gelation would take place within 2 h.

After gelation, EtOH was added to the alcogel for aging in the 45 °C water bath for 6 h. Meanwhile ethanol was replaced by n-hexane twice within 12 h. Then 15 vol% TMCS/n-hexane solution was added to modify the gel. The replacement and modification were conducted in the 45 °C water bath. The modified gels were dehydrated at ambient pressure. The dehydration process was carried out at 60 °C for 4 h and then 100 °C for 12 h.

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Characterization methods: The PUS reinforced SA was cut into several cubic pieces, the mass and size were measured respectively. Then the density can be obtained through mass/volume. The contact angle was measured using KSV CAM 200 contact angle goniometer (Helsinki, Finland) at ~20 °C. Compression test was conducted using an Instron (E3000K8953) (250 N load, 0.5 mm/min) in which the sample size is 10 mm long, 10 mm wide and 20 mm high. The microstructure of the aerogels was studied using a FESEM (SIRION 200, FEI, USA).

The obtained samples with a size of 30 mm × 30 mm × 30 mm were immersed into mixtures prepared using various types of solvents/oils and water with a 1:1 volume ratio. The absorption process was fast and generally reached equilibrium within a few minutes. Then the soaked samples were taken out and weighed after the aerogel surface was swiped using a filter paper to remove extra surface solvent/oil [11]. The absorptivity (Q) was determined using following equation

$$Q(\%) = \frac{(W - W_0)}{\rho_L V_0} \times 100\% \qquad (1)$$

where W_0 and W are the weights of aerogels respectively before and after absorption, V_0 is the aerogel volume, and ρ_L is the density of absorbed solvent/oil.

3. Results and discussion

The PUS is porous material with a pore diameter of approximately 700 μm (Fig. 1a). The PUS skeleton did not crack or collapse during the preparation process and considerable amount of SA particles attached to the skeleton surface as shown in Fig. 1b. The SA granules fixed in the PUS skeleton presented nanoporous structure (Fig. 1c). The granules were held by the PUS skeleton without damaging the skeleton. In addition, the compressive stress of the silica aerogel granules is considerable. As a result, monolithic, crack free and large scale PUS reinforced SA was produced (Fig. 1d). And the overall compressive stress improved significantly which will be discussed in the following section.

As the molar ratio of precursor to solvent will affect the properties of PUS reinforced SAs significantly, the molar ratio of EtOH (solvent) to TEOS (denoted as N) was set 6, 8, 10, 12, 14, and 16 respectively. With the nanoporous SA particles embedded in the macropores of PUS, the overall bulk density and porosity of the PUS reinforced SA is as low as 0.152 g/cm^3 (corresponding porosity is 94.3%), as shown in Fig. 2a. For high molar ratio, TEOS condensed in a much large volume of EtOH environment which results in weak linkages between the silica particles. The weak linkages lead to poor mechanical strength of the gel network and the pores will collapse during the dehydration process at ambient pressure. On the other hand, for low N, the volume of EtOH is small, the pores formed by condensation were also small and the capillary pressure of small pores is higher than that of bigger pores [12], so that the small pores will be more easily destroyed. Therefore in both cases, the pores in the aerogels will collapse and the aerogels will lead to shrinkage. Thus the molar ratio of EtOH to TEOS was set as 10 while studying the following mechanical property and solvent/oil absorptivity.

Once the surface is modified by TMCS, the aerogel becomes hydrophobic (Fig. 2e, contact angle: 161°) and oleophilic. As shown in Fig. 2b and c, once a small piece of PUS reinforced SA was submerged in the gasoline and water mixture, the gasoline was quickly absorbed without absorbing the water. The gasoline filled PUS reinforced SA could be left floating on the water without any oil release or water absorption. A water droplet can stay at the surface of PUS reinforced SA whereas a gasoline droplet will be completely absorbed immediately once contacted to the aerogel surface. The absorption process usually takes less than 2 s (Fig. 2d).

Mechanical property: To study the mechanical property, the compressive stress as a function of extension was tested as shown in Fig. 3. Both PUS reinforced SA and PUS can be compressed by more than 50% because of the high porosity. The PUS reinforced SA completely recovered to its original shape with no mechanical failure after being subjected to 50% strain (Fig. 3a). For the PUS, only 0.036 MPa is needed to compress 86% of its original length (Fig. 3b). However, the maximum stress at 50% for PUS reinforced SA is 0.38 MPa (Fig. 3c), which is much higher than that of PACNHA [1], pure methyltriethoxysilane [5] and methyltrimethoxysilane [13] derived SA. The maximum stress before failure is shown in Fig. 3d.

Absorptivity: As the surface is modified by TMCS, the PUS reinforced SA is superhydrophobic and superoleophilic. To quantify the absorptivity, the absorption performance of PUS reinforced

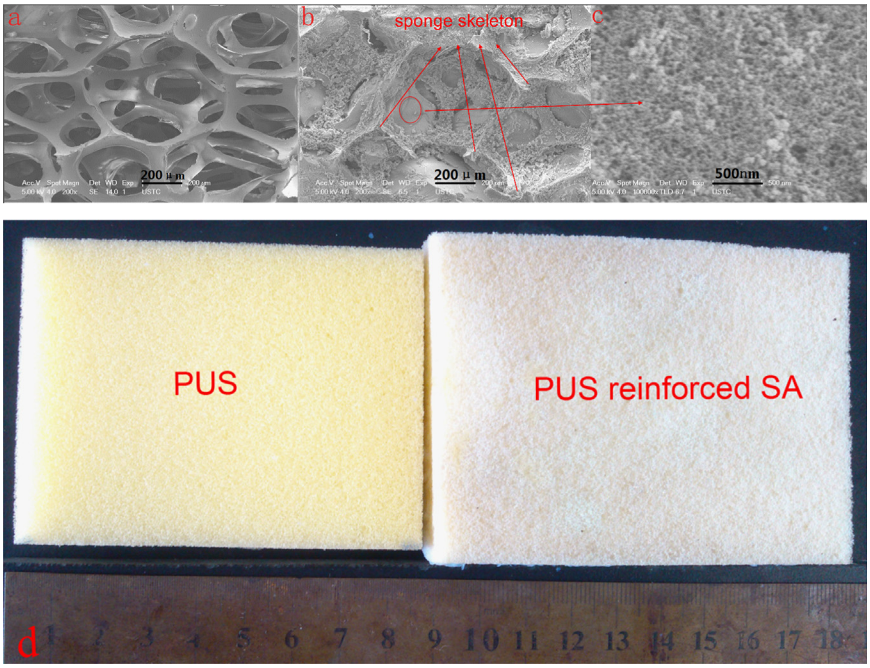

Fig. 1. SEM image of (a). PUS; (b). PUS reinforced SA (molar ratio (EtOH/TEOS) = 10); (c). silica aerogels within the PUS pores; (d). optical images of PUS, monolithic and crack free PUS reinforced SA.

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