# THERMAL INSULATING PROPERTY OF AN OPTICALLY-ACTIVE POLYURETHANE-BASED SILICON AEROGEL

by

## Ling LIN<sup>*a,b*</sup> and Chaoxia WANG<sup>*a*\*</sup>

<sup>a</sup> Key Laboratory of Eco-Textile, Ministry of Education, School of Textiles and Clothing, Jiangnan University, Wuxi, China

<sup>b</sup> School of Textile and Clothing, Yancheng Institute of Technology, Yancheng, China

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Improving the mechanical property of the silicon aerogel while maintaining its excellent thermal insulation performance is still a big challenge in developing the next-generation thermal insulation materials. To solve this problem, the optically active polyurethane aerogel composite is developed via the sol-gel method to combine the advantages of the thermal insulation performance of the silicon aerogel and the mechanical property of the end-capped siloxane optically-active polyurethane. The prepared composite is characterized by the SEM, the Fourier transform infrared spectroscopy, the absorption-desorption curve, the thermal analysis, and the mechanical property. Results show that the composite has intact pores with high surface area and pore volume, leading to excellent thermal insulation and mechanical performance. Moreover, its thermal insulation performance is greatly enhanced due to the better distributed small pores and the thermal reflective effect of binaphthyl groups which collaboratively block heat loss from thermal conduction and thermal radiation. The thermal stability is similar to silicon aerogel and its heat resistance temperature is 445 °C. The addition of macromolecular polymers increases the contact points between particles, the contact areas between particles of the network skeletons, and the supporting effect of the skeleton material, which ensures the stability of the material structure. The compressive modulus of prepared composite is up to 2.465 MPa, which is 600 times more than that of the pure  $SiO_2$  aerogels.

Key words: optically-active polyurethane, organosilicon modification, aerogel composite, mechanical properties, thermal insulation

#### Introduction

Heat is transferred through thermal conduction, convection and radiation [1-4]. The human body is constantly exchanging heat with the environment, and thermal insulation is essential for humans to withstand external threats from the environment. Clothing and building are the two classical examples of thermal insulation that protect humans from the cold environment and maintain the wellbeing and comfort [5]. Despite the structural design of clothing, the intrinsic thermal conduction and radiation properties of materials are also important in developing thermal insulation gears.

Searching for new materials with a novel structure and a low thermal conductivity together with thermal radiative insulation is always on the agenda of developing thermal insu-

<sup>\*</sup> Corresponding author, e-mails: wangchaoxia@sohu.com; janegirl007@163.com

lation gears. The SiO<sub>2</sub> aerogel, an important thermal insulation material, is light and has a low thermal conductivity because air occupies most of its volume [6, 7], so it is widely used as nano-porous insulation materials in different areas [8-10]. However, its applications are greatly limited due to its poor thermal stability and brittle nature. The network scaffold usually consists of a polymer rich in -OH groups, bringing mechanical properties together with shape stability to the SiO<sub>2</sub> aerogel [11-13]. Flexible polymers have been widely used to strengthen the SiO<sub>2</sub> aerogel, but the polymer should have thermal stability and insulation performance, especially the performance to resist and reflect infrared radiation.

Polyurethane has been extensively used as protective coating on different subjects, defending against different threats such as water, liquids, chemicals, and to some extent, heat [14, 15]. Especially, the optical polyurethane (OPU) has an evident infrared radiation reflection index to provide an excellent thermal radiative protection [16]. However, the coated membrane is likely to be broken during its usage due to its poor interface binding between the coating and fabrics [17, 18].

In this study, the optically active polyurethane aerogel composite (OPUSA) is developed using the sol-gel method to combine the thermal insulation performance of the SiO<sub>2</sub> aerogel with the mechanical properties of OPUS. It is shown that the combination of the endcapped siloxane optically-active polyurethane (OPUS) and SiO<sub>2</sub> is a feasible method to compensate for their respective weaknesses. This research provides a technical basis for improving the thermal stability of OPUS and a way to enhance the mechanical property of SiO<sub>2</sub> aerogels.

## Experimental

### Materials

Tetraethoxysilane (TEOS), glycerol, caustic soda and ethanol (95%) were provided by China National Pharmaceutical Group Co. Ltd., hydrochloric acid and ammonium hydroxide were provided by Tongsheng Chemical Co. Ltd (Jiangsu, China), N-Hexane, (3-Aminopropyl) triethoxysilane and trimethylsilyl chloride were provided by Alladdin Chemical Co. Ltd (Shanghai, China). All the chemicals were in analytical grade and were used without further purification.

#### Preparation

The synthesis route of OPUS is shown in fig. 1, where 8.50 g isophorone diisocyanate (IPDI) and 18.75 g Polycarbonate diol (PCDL) were simultaneously added at a molar ratio 5.1: 2.5 into a three-necked flask equipped with a mechanical stirrer and a reflux condenser to perform pre-polymerization at 75 °C for 1.5 hours. The 1.51 g DMPA was then added to reactor with the prepolymer for the chain extending at 75 °C for 1.5 hours. One drop of catalyst dibutyltin dilaurate was added to catalyze the chain extension reaction. The 2.15 g Sbinaphthol (BINOL) dissolved in 40 mL anhydrous THF was added dropwise into the system to react with the isocyanate group (NCO) further at 75 °C for another 3 hours. The obtained OPU was then modified by a slightly excessive amount of silicane coupling agents KH-550 and a small number of catalyst at 75 °C for 2 hours until there was no NCO group in the system, resulting in OPUS.

The obtained OPUS was then modified by silicane coupling agent KH-550 through hydrolysis, resulting in OPUSA, fig. 2. The concentration of OPUS in the OPUSA aerogel was changed in the synthesis stage so as to analyze the effect of OPUS concentration on the properties of OPUSA<sub>2</sub> aerogel. The concentration of OPUS was controlled to be 0, 5, 8, 10, 12,

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### Figure 1. The synthesis route of OPUS

and 15 wt.%, respectively, which were corresponding to samples of  $SiO_2_0$ , OPUSA\_1, OPUSA\_2, OPUSA\_3, OPUSA\_4, and OPUSA\_5, respectively.

## Characterization and measurements

The FESEM (Nova NanoSEM 450); Absorption-desorption and pore size (TriStar II 3020 tester, Micomeritics, US); FTIR spectra (NEXUS-670); TG and DSC (STA 449C) were used for analysis.



Figure 2. Schematics of the fabrication process of OPUSA aerogel



Figure 3. The SEM images of OPUSA aerogel composites for different samples; (a) SiO<sub>2</sub>\_0, (b) OPUSA\_1, (c) OPUSA\_2, (d) OPUSA\_3, (e) OPUSA\_4, and (f) OPUSA\_5 (insets: detailed views)

Thermal insulation performance was tested on a heat platform with a temperature of 46 °C. The compression module was tested on an RGD-5B compression module testing machine. The compression deformation was 50% of the original height of the composite aerogel.

### **Results and discussion**

#### Microstructure

Figure 3 shows the SEM images of OPUSA aerogel composites with different weight percentages of OPUS. The SiO<sub>2</sub> aerogel in fig. 3(a) has a smooth surface, and the detail view on the surface (Inset) suggests that it has an even grain structure morphology composed of numerous particles. The OPUSA aerogel has a typical porous structure, and the surface is quite rough compared with the SiO<sub>2</sub> aerogel. Moreover, the OPUSA aerogel has a larger particle size than that of the pure SiO<sub>2</sub> aerogel, as shown in the detailed views (Insets). Figure 3 shows that the increase of OPUS from 5 wt.% to 10 wt.% has limited effects on the particle size of the OPUSA aerogel. However, with further increase of the OPUS percentage, the particle size of the OPUSA aerogel increases evidently, large pores are observed, and the porosity and pore size decrease. Aerogel particles tend to aggregate at a low percentage of OPUS such as the sample of OPUSA\_2.

Figure 4(a) shows the adsorption-desorption curves of the OPUSA aerogel. The profile of the curves is in IV shape, suggesting a mesoporous structure of the aerogel with pore

size of 2-50 nm. At a higher relative pressure of  $P/P_0 > 0.5$ , the curves show hysteresis (H3 hysteresis loop) because of concentrated capillary effects [19-21], indicating the tunnels are long and narrow with open ends. The surface area and pore volume of the OPUSA aerogel have been calculated to be 634.02 m<sup>2</sup>/g and 1.43 cm<sup>3</sup>/g, according to BET and BJH methods, respectively. Pore size distribution curves in fig. 4(b) show a broad distribution of pores in the OPUSA aerogel. When the percentage of OPUS is 10 wt.%, a narrow peak exists at 16 nm with a distribution range of less than 55 nm, suggesting an evident mesoporous structure in the OPUSA aerogel.

### Chemical structure

Figure 5 shows the FTIR spectra of the OPUSA aerogel. The spectra show absorbing peaks around 1078, 960, 1650, and 2980 cm<sup>-1</sup> plus 850 and 755 cm<sup>-1</sup>, corresponding to



Figure 4. Adsorption-desorption (a) and pore size distribution (b) of the OPUSA aerogel

the Si-O-Si stretching vibration, Si-OH stretching vibration, -OH vibration, C-H stretching vibration, and Si-C in Si-CH<sub>3</sub>, respectively. The absorbing peak at 1650 cm<sup>-1</sup> is attributed to the C=O stretching of allophanate reacted from – NCO and NH<sub>2</sub>. No evident absorbing peak is observed for –NCO at 2270 cm<sup>-1</sup>, suggesting that the reaction between KH550 and OPUS is fully completed. The peak at 1715 cm<sup>-1</sup> is the characteristic peak of C=O, and the peaks around 2780-2980 cm<sup>-1</sup> are C-H absorbing peak in –CH<sub>2</sub> and CH<sub>3</sub>, 1250 cm<sup>-1</sup> for C-N stretching absorbing peak, and 1470 cm<sup>-1</sup> for C=C vibration peak. These peaks prove the existence of the binaphthyl group. The addition of OPUS to the OPUSA aerogel introduces several



Figure 5. The FTIR spectra of OPUSA aerogel with different concentrations of OPUS

functional groups such as binaphthyl group into the composite aerogel, which will provide some extra thermal protection capacity to the as-developed aerogel.

## Thermal analysis

Figure 6 shows the thermal stability of the pure SiO<sub>2</sub> aerogel, OPUS and the OPUSA composite (15% OPUS). The TG-derivative is used to represent the thermogravimetric analysis results of the OPUSA composite in fig. 6(a). As can be seen from fig. 6(a), the mass loss of the OPUSA composite is due to the mass loss of OPUS chains and SiO<sub>2</sub> aerogels. About 9% of the mass loss within 100 °C is due to the evaporation of the absorbed water and most of the ethanol solvent in the sample. It is evident that the adding of OPUS in the OPUSA aerogel has resulted in a big weight loss around 400 °C with fewer residues at 1000 °C. From the TG-derivative curve, the peak mass loss occurs at 445 °C. It is mainly caused by the thermal decomposition of OPUS long chain and the thermal oxidation of Si-CH<sub>3</sub> on the OPUSA skeletons. There is a small mass loss between 650 and 750 °C, which may be caused by the further cracking of the  $-CH_2$  group in the aerogel. There is no significant mass loss after

700 °C. From the TG-DSC analysis, it is apparently that the OPUSA composite can withstand a temperature of up to 445 °C.



Figure 6. The TG and DSC curves of OPUSA (a) and TG curves of SiO<sub>2</sub>, OPUS, and OPUSA (b)

Table 1 shows the thermal insulation performance of the OPUSA aerogel. The surface temperature of the OPUSA aerogel increases rapidly in the first 5 minutes, but only a small increase is observed even after 30 minutes. It is found that the OPUSA aerogel as thermal insulation layer has a stable insulation performance. The surface temperature of the SiO<sub>2</sub> aerogel after 30 minutes is 41.1 °C, only 4.9 °C lower than that of the hotplate. By contrast, the surface temperature of the OPUSA aerogel is around 34.8 °C–38.5 °C after 30 minutes (up to 11.2 °C difference with the hotplate), suggesting an evident improved thermal insulation performance. The enhanced thermal insulation performance is due to the better distributed small pores after introducing OPUS and the thermal reflective effect of binaphthyl groups which block heat loss from thermal conduction and thermal radiation.

Sample	Time [minutes]						
	0	5	10	15	20	25	30
SiO2_0	22	34.8	36	38.5	39	40.8	41.1
OPUSA_1	25.9	35.7	36.1	38.4	37.2	36.5	36.3
OPUSA_2	25.3	33.8	37.4	37.8	38.3	38.5	38.5
OPUSA_3	25.3	34.1	35.5	36.0	35.9	36.0	35.9
OPUSA_4	25.2	32.7	34.3	34.6	34.8	35.1	34.8
OPUSA_5	25.5	36.4	37.8	37.7	37.9	38.3	38.5

Table 1. Thermal insulation effect of OPUSA aerogel [°C]

### Mechanical properties

The compression tests were carried out on OPUSA aerogel composites with different contents of OPUS. The stress-strain curves are shown in fig. 7 and the compression resilience column graph after 50% compression of their height is presented in fig. 8. The increase of OPUS in the aerogel has greatly enhanced its compression capacity together with tenacity.



Figure 7. Stress-strain curves of the OPUS, SiO<sub>2</sub>, and OPUSA

The aerogel composites reinforced by OPUS have higher compressive strength. The compressive modulus of 15% OPUS composite aerogel is up to 2.465 MPa, which is more than 600 times that of the pure  $SiO_2$  aerogels. The addition of macromolecular polymers increases the contact points between particles, the contact areas between particles of the network skeletons, and the supporting effect of the skeleton material, which ensures the stability of the material structure.

The elastic moduli of the OPUSA composites with different OPUS contents are listed in tab. 2. The elastic modulus of the composite aerogel is higher than that of pure  $SiO_2$  and



Figure 8. Column graph of compression resilience ratio of OPUSA composites

OPUS, which indicates that the combination of OPUS and  $SiO_2$  aerogel can improve the elastic modulus synergistically. With the increase of the OPUS content from 0 to 15%, the elastic modulus first increases and then decreases. The optimal content of OPUS to achieve the maximum elastic modulus is 10%. In the composite system, the proper proportion can make the two tightly bonded, and this strengthening greatly increases the elastic modulus.

Table 2. Elastic modulus of OPUS, SiO<sub>2</sub>, and OPUSA composites with different OPUS contents

Samples	OPUS contents [%]	Elastic modulus [MPa]
SiO2_0	0	0.023
OPUS	100	0.013
OPUSA_1	5	0.069
OPUSA_2	8	0.048
OPUSA_3	10	0.861
OPUSA_4	12	0.044
OPUSA_5	15	0.073

#### Conclusions

The OPUSA aerogel composite has successfully prepared using a sol-gel process from precursors OPUS and TEOS. The as-prepared OPUSA aerogel is non-transparent with excellent shape stability and elasticity. The pore size analysis suggests the OPUSA aerogel has an evident mesoporous structure. The thermal stability of the OPUSA aerogel is similar to that of the SiO<sub>2</sub> aerogel and its heat resistance temperature is as high as 445 °C. The surface temperature of the OPUSA aerogel increased evidently within 5 minutes in the thermal insulation test, and the temperature difference reached to 11.2 °C after 30 minutes. The enhanced thermal insulation performance is due to the better distributed small pores after introducing OPUS and the thermal reflective effect of binaphthyl groups which block heat loss from both thermal conduction and thermal radiation. When the OPUS concentration was increased to 10%, the scaffold of the OPUSA aerogel became stronger with excellent tenacity and all the pores were distributed more evenly with excellent elasticity, as a result the compression mechanical properties were improved greatly.

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