

# Silica Aerogel / Hydroxy-Terminated Poly(dimethylsiloxane) (PDMS(OH)) Nanocomposites by Reactive Supercritical Deposition

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## ABSTRACT

Transparent Vacuum Insulation Panels (VIPs) with low thermal conductivity values are under development for effective thermal insulation in buildings and household applications. Silica aerogels appear as the most promising nanostructured materials to be implemented as filler materials in transparent VIPs due to their transparency in addition to extremely low thermal conductivity. One drawback of silica aerogels is their poor mechanical properties which makes their utilization as monolithic and crack-free materials challenging. This problem can be overcome by reinforcing aerogels with polymers which results in improved resilience that would allow for practical utilization. Besides, the development of such composite materials brings in novel physical properties which open up new possibilities for unexplored application areas.

Monolithic composites of silica aerogels with hydroxyl-terminated poly(dimethylsiloxane) (PDMS(OH)) were developed using a reactive supercritical deposition technique. The technique is composed of two stages; the first stage includes the dissolution of PDMS(OH) in supercritical CO<sub>2</sub> that results in a single phase binary mixture and the second stage is the exposure of the silica aerogel to this single phase binary mixture. The deposition experiments were performed with various PDMS(OH) concentrations and at different temperatures. The effects on the polymer uptake and pore properties of the composites were investigated. The chemical composition and the pore structure of the deposited samples were characterized by ATR-FTIR and N<sub>2</sub> sorption analysis. The polymer uptakes were observed to increase with increasing PDMS(OH) concentration and deposition temperature. In addition, it was found that the transparency of the composites can be tuned with the amount of the polymer loaded to the samples.

## INTRODUCTION

The major contribution to global energy consumption originates from the amount of energy consumed in the buildings. Additionally, 70% of this amount is solely consumed for heating and cooling applications for both residential and commercial buildings. Under these circumstances, thermal insulation has been receiving increased attention and is considered as one of the most effective ways to reduce energy consumption. The efforts in development of more effective thermal insulation systems have concentrated on the improvement of existing materials as well as the development of novel materials with enhanced thermal insulation properties. Among various insulation systems, vacuum insulation panels (VIPs) with typical thermal conductivities of 3-5 mW/mK emerge as outstanding solutions for effective thermal insulation problem in buildings and household applications nowadays. The achievement of such low thermal conductivities in VIPs relies on the suppression of the gaseous convection by applying vacuum. Recently, the idea of transparent VIPs has been established in order to replace the conventional window glazing. Since then, research about development of

transparent materials that can be used in the transparent VIPs has been gaining increasing interest. Silica aerogels appear as the most promising nanostructured materials to be implemented in transparent VIPs due to their transparency and extremely low thermal conductivity.

Silica aerogels are nanostructured materials that have been attracting considerable attention due to their unique and intriguing properties such as low density, transparency, high surface area, high porosity and low thermal conductivity. More importantly, their properties can be tailored for a specific application either by manipulation of the synthesis parameters during the sol-gel process or by post-treatment of the synthesized aerogels [1-4]. However, silica aerogels are highly fragile materials due to their poor mechanical properties which make their utilization as monolithic and crack-free materials challenging. This problem can be overcome by reinforcing aerogels with polymers which results in improved resilience that would allow for practical utilization. There are different ways to produce polymer-silica aerogel composites. Among these techniques the reactive supercritical deposition is the most promising one since the transparency and porous structure of the material can be controlled and retained.

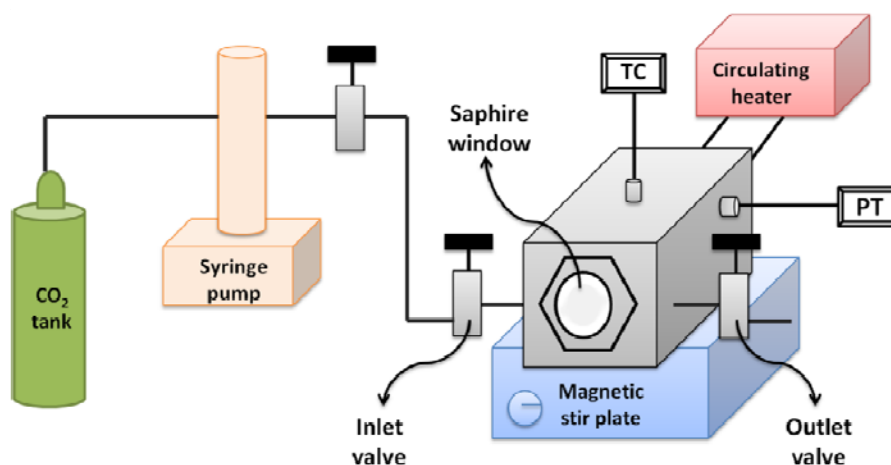
It is well known that many silane compounds have appreciable solubility in scCO<sub>2</sub> which can be exploited for the development of new ways to synthesize composites of silica aerogels with silicone based polymers [5-10]. In this study, a reactive supercritical deposition technique was employed to synthesize a composite of silica aerogel with hydroxyl-terminated poly(dimethylsiloxane) (PDMS(OH)). The polymer was deposited to aerogel from a single phase binary mixture of PDMS(OH)-CO<sub>2</sub>. The effects of polymer concentration and deposition temperature on the mass uptake and material properties were investigated. The deposited samples were characterized by N<sub>2</sub> sorption and ATR-FTIR measurements. The novel reactive supercritical deposition technique allows for the production of monolithic, crack-free, homogenous and transparent silica-PDMS(OH) aerogel composites in a controlled manner which may pave the way for the utilization of silica aerogels and their composites in various applications such as core materials in transparent vacuum insulation panels.

## **MATERIALS AND METHODS**

Hydroxy-terminated polydimethylsiloxane (PDMS(OH)) (99.9%) was purchased from Sigma Aldrich. The chemicals were used as received. Carbon dioxide (CO<sub>2</sub>) (99.998%) was purchased from Messer Aligaz.

The deposition experiments were performed in a constant volume high pressure view cell that is displayed in Figure 1. A certain amount of polymer was placed into the vessel together with the silica aerogel sample and the vessel was brought to desired temperature. A wire mesh was used to separate the aerogel sample from the polymer in order to avoid the contact of the sample with the liquid polymer which would destroy the aerogel structure. With continuous stirring, CO<sub>2</sub> was pumped into the vessel and the dissolution of the polymer in CO<sub>2</sub> occurred. When the desired pressure value was reached, a single phase binary mixture of PDMS(OH)-CO<sub>2</sub> was obtained in the vessel. The silica aerogel sample was exposed to this single phase mixture for 24 h. As the final step of the deposition, extraction with pure CO<sub>2</sub> was performed to remove the excess amount of polymer remaining in the vessel.

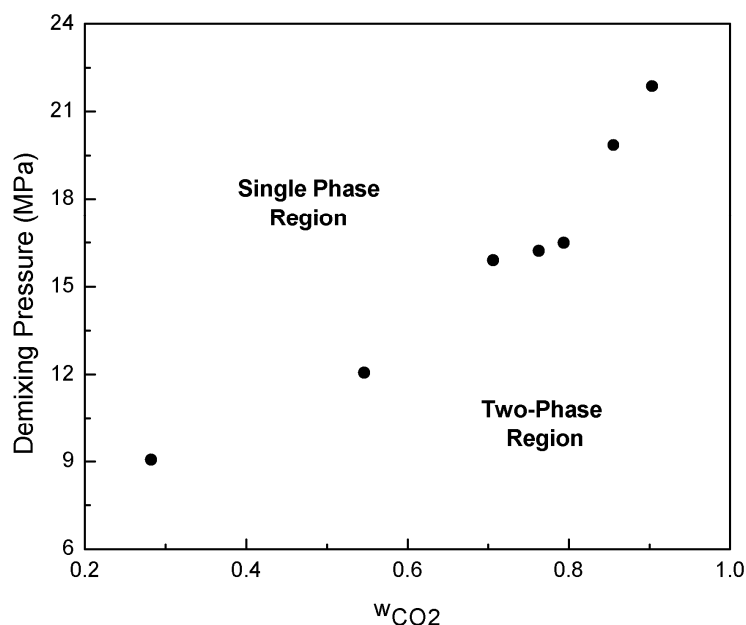
The mass uptake values of all the deposited aerogel samples were determined gravimetrically. The attenuated total reflectance (ATR) fourier transform infrared spectra (FTIR) were recorded on a Thermo Scientific Smart iTR to investigate the chemical composition of the samples. The pore properties of the samples were determined by N<sub>2</sub> adsorption-desorption measurements at 77 K (Micromeritics ASAP 2020).



**Figure 1:** Experimental setup (TC: Thermocouple, PT: Pressure Transducer)

## RESULTS

The supercritical deposition method is a two step procedure which involves the dissolution of PDMS(OH) in scCO<sub>2</sub> and the exposure of silica aerogel to the single phase PDMS(OH)-CO<sub>2</sub> binary mixture. Therefore initially, the phase behavior measurements were conducted to determine the demixing pressures of PDMS(OH)-CO<sub>2</sub> binary mixtures and the demixing pressure data were employed for the determination of the deposition conditions such that a single phase can be attained at the experimental temperature, pressure and concentration. The demixing pressures were measured at different temperatures for a wide composition range. Figure 2 displays the demixing pressures measured at 323.2 K.

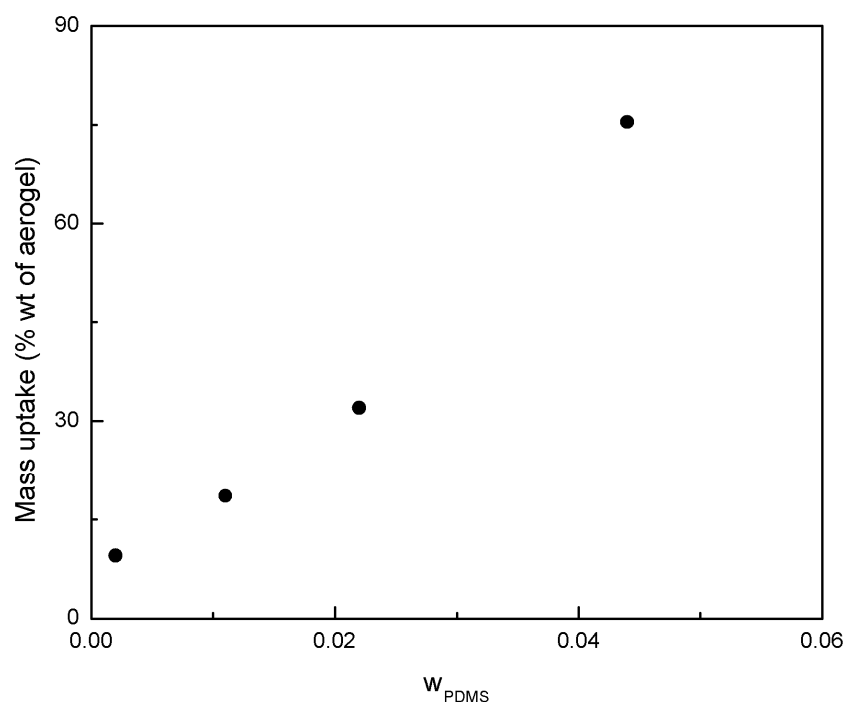


**Figure 2:** Demixing pressures of PDMS(OH)-CO<sub>2</sub> mixture at 323.2 K

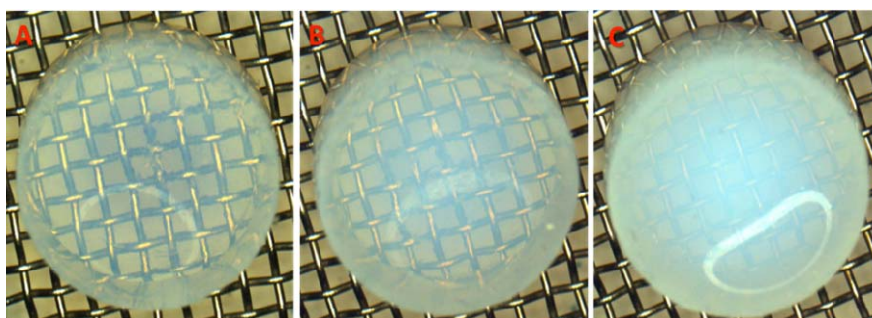
Deposition experiments with different initial PDMS(OH) concentrations were conducted at 323.2 K and 31 MPa for 24 hours and the effect of the polymer concentration on uptake amount was investigated. All of the deposited samples were obtained as crack-free monoliths.

Figure 3 displays the mass uptakes of the aerogel samples for different polymer weight fractions and shows that there is almost a linear increase in mass uptake with increasing initial PDMS(OH) concentration. This increase in mass uptake was attributed to the higher concentration gradients between the bulk and the surface obtained with higher polymer weight fractions which resulted in enhanced rates of diffusion and/or reaction of the PDMS(OH) molecules.

Figure 4 shows the images of the aerogel samples after the deposition. The transparency decreased with increasing polymer amount. However, it is important to note that the transparency can be controlled with the polymer amount deposited into the aerogels and can be retained with polymer uptakes up to 30 wt%.



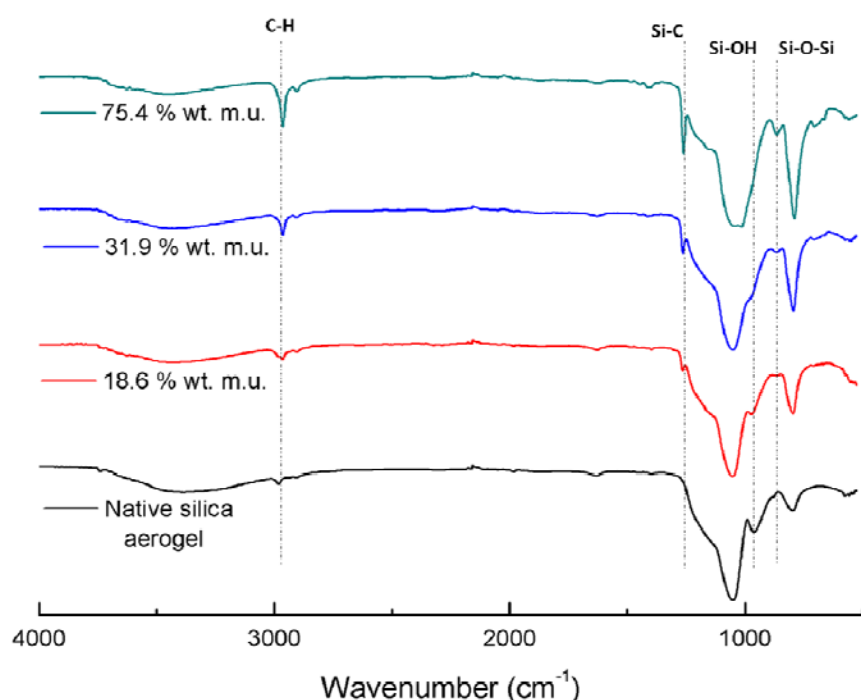
**Figure 3:** The mass uptake for different initial PDMS(OH) compositions in the vessel



**Figure 4:** Images of aerogel samples with A) 18.6 wt%; B) 31.9 wt% and C) 75.4 wt% mass uptakes

ATR-FTIR analyses were performed with the deposited samples and the spectra were compared with the native silica aerogel in Figure 5. There are three peaks indicative of the presence of the polymer in the aerogel sample. The peak at  $2963\text{ cm}^{-1}$  represents the C-H

stretching vibrations originating from the methyl side groups of PDMS(OH). The peak at  $1267\text{ cm}^{-1}$  is due to the Si-C stretching vibrations that originate from methyl side groups attached to the polymer backbone. The peak appearing at  $850\text{ cm}^{-1}$  for the deposited sample was attributed to  $\equiv\text{Si-O-Si}(\text{CH}_3)_2\text{-R}$  bond that were formed due to the condensation reaction between the  $\equiv\text{Si-OH}$  groups of the aerogel and  $\text{OH-Si}(\text{CH}_3)_2\text{-R}$  end groups of PDMS(OH). The intensities of the C-H and Si-C stretching vibration peaks as well as the Si-O-Si peak that signifies the reaction between PDMS(OH) and surface  $-\text{OH}$  groups of the silica aerogel increased accordingly with the increasing polymer amount in the deposited samples. Furthermore, the peak at  $960\text{ cm}^{-1}$  that was observed in native silica aerogel sample was attributed to stretching of Si-OH groups of the aerogel. The disappearance of this peak upon deposition additionally indicates the reaction between PDMS(OH) and the surface Si-OH groups of the aerogel.



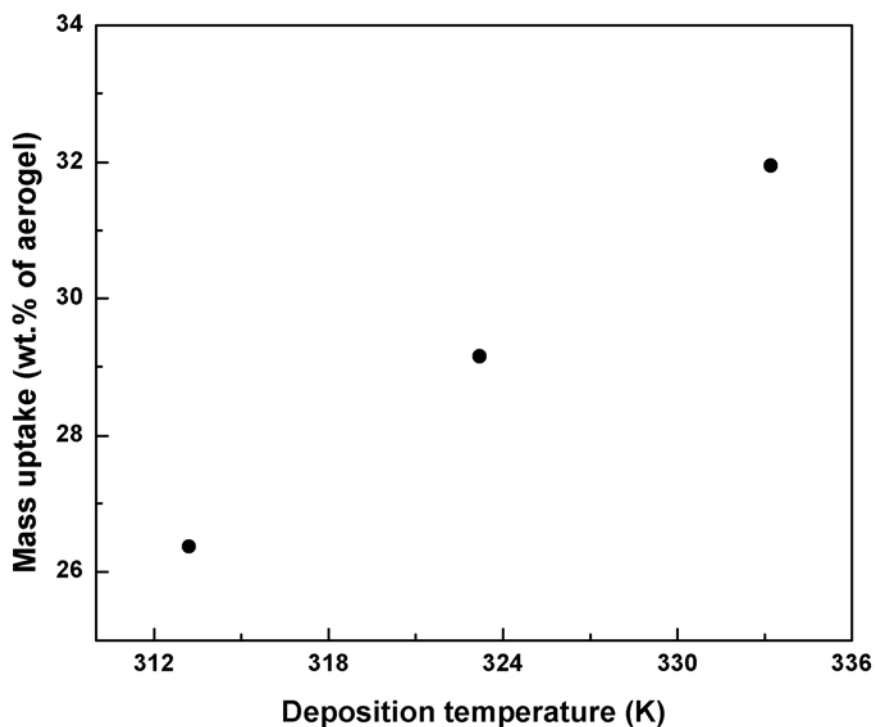
**Figure 5:** ATR-FTIR spectra showing the evolution of Si-C, C-H and Si-O-Si peaks upon deposition

The  $\text{N}_2$  sorption measurements were additionally performed with the deposited samples and the results were summarized in Table 1. With the increasing polymer uptake the density of the samples increased whereas the surface area and the pore volume decreased accordingly. The decrease in pore volume and surface area originated from the coating of the aerogel surface with the polymer layer [11].

**Table 1:** Densities and pore characteristics of the deposited aerogels

Mass Uptake (wt% of aerogel)	Density ( $\text{kg/m}^3$ )	BET Surface Area ( $\text{m}^2/\text{g}$ )	Total Pore Volume ( $\text{cm}^3/\text{g}$ )
18.6	188	596	4.14
31.9	215	454	3.04
75.4	276	280	2.06

Furthermore depositions were performed with the same polymer concentration at three temperatures, namely, 313.2 K, 323.2 K and 333.2 K. The mass uptakes of the deposited samples are displayed in Figure 6. It is obvious that there is almost a linear increase in mass uptakes with the increasing deposition temperature. The increasing temperature facilitated the reaction between the polymer and silica aerogel which resulted in increased reaction rates at higher temperatures. As a result higher amount of polymer molecules were bonded to the surface at elevated temperatures.



**Figure 6:** Mass uptakes of the aerogel samples deposited at different temperatures

## CONCLUSION

Silica-PDMS(OH) composite aerogels were developed by employing a reactive supercritical deposition technique. The technique is composed of two stages; first stage is the dissolution of PDMS(OH) in CO<sub>2</sub> that results in a single phase binary mixture of PDMS(OH)-CO<sub>2</sub> in the vessel and the second stage is the exposure of the silica aerogel samples to the single phase binary mixture. During the course of the deposition, the polymer molecules reacted with the surface -OH groups of the aerogel samples. It was shown that polymer uptakes as high as 75.4 wt% of aerogel could be attained depending on the polymer concentration in the binary mixture. The deposited samples retained their crack-free monolithic structure and the transparency of the aerogels could be preserved up to polymer loadings of around 30 wt%. In addition, the polymer uptake was determined to increase with increasing the initial polymer concentration and deposition temperature which was attributed to the enhanced reaction rates. According to ATR-FTIR results, the intensity of Si-C and C-H vibration peaks that originated from PDMS(OH) increased accordingly with the increasing polymer content in the deposited samples. Additionally, the results obtained from N<sub>2</sub> sorption analysis showed that the specific surface area and the pore volume of the deposited samples decreased with increasing polymer content due to the coating of the aerogel surface with the polymer layer. With the reactive supercritical deposition technique, various silane compounds

can be employed in the surface modification and the development of composites of aerogels which may lead to advancement of novel materials such as transparent VIPs, as well as novel processes to synthesize these materials.

**ACKNOWLEDGMENT.** We acknowledge the Financial Support of the NANOINSULATE (Development of Nanotechnology-based high performance Opaque & Transparent Insulation Systems for Energy-efficient Buildings) being funded by the EU Program EeB.NMP.2010-1 under grant agreement no. (260086).

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