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Monolithic composites of silica aerogel with poly(methyl vinyl ether) and the effect of polymer on supercritical drying

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ABSTRACT

Novel monolithic and crack-free poly(methyl vinyl ether) (PMVE)-silica aerogel composites were synthesized using a modified sol–gel procedure. The presence of PMVE in solid network of the composite samples was confirmed by a variety of techniques including IR spectroscopy, TGA and BET. Extraction of ethanol from alcogel composite rods using $scCO_2$ was investigated both by experiments and simulations. Partial differential equations representing mass transfer within the composite alcogel phase and in the flowing $scCO_2$ phase were developed and solved using finite difference method. Mass of ethanol removed from the samples as a function of time were found to be in good agreement with model results using mass transfer coefficients regressed from the experimental data. Effect of the polymer content on the drying could be estimated by taking into account of porosity change with polymer incorporation. Drying time of the alcogel increased with increasing weight fraction of polymer in the silica network and gel thickness.

1. Introduction

Silica aerogels with very low densities, high porosities, high surface areas and controllable porous structures have been receiving increased attention as a promising class of materials as transparent thermal and acoustic insulators, fillers for paints and varnishes, catalytic supports and adsorbents [1–3]. However, fragility of silica aerogels prevents their widespread use. Incorporation of a polymer into the silica aerogel matrix is a favorable way to enhance mechanical strength of such materials [3–6]. Such nanostructured composites of silica aerogels with polymers are promising for use as core materials in vacuum insulation panels. An important factor which governs the economics of production of such panels is the capital and operating costs associated with the supercritical drying process and the effects of the polymer content on drying times. Therefore, an understanding of kinetics of drying of silica aerogel composites with supercritical CO_2 ($scCO_2$) and modeling of the process is important to provide insight into material development, scale-up and optimization of the composite aerogel manufacturing.

Composites of silica aerogels with polymers are generally synthesized by a two-step sol–gel method which involves consequent steps of hydrolysis, condensation, aging, solvent exchange and supercritical drying [1,2]. sol–gel method is also one of the preferred methods for the development of composites of silica aerogels with polymers since it is a low temperature technique. [3]. As polymers are sensitive to high temperatures, this procedure protects them from thermal degradation. Moreover, this technique allows mixing of the components at the nanoscale making it possible to synthesize inorganic–organic hybrids by the incorporation of organic/polymeric molecules to the inorganic matrices [3]. A variety of methods have already been developed to synthesize silica aerogel polymer composites such as co-condensation reactions with organically substituted precursors or polymers [3–7,23], liquid phase modifications using cross-linkers, stabilizing agents or coupling agents to attach styrene moieties [8], isocyanates [9–12] or epoxies [13,14] to the modified amine ends of the surface or liquid phase modifications without using any additional substance but with direct addition of the monomer in the initial solution [15–17]. Post synthesis modification techniques using supercritical fluid deposition [18–20] as well as the addition of molecular but nonreactive components to the precursor solution [15] appear to be other methods used for the synthesis of silica aerogel polymer composites.

In this study, we were able to synthesize monolithic composites of silica aerogels with poly(methyl vinyl ether) (PMVE) with *PMVE*

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content in the composite matrix ranging from 16 wt% to 52 by a two-step sol–gel *process. The* effect of the polymer content on the kinetics of supercritical drying was investigated both by experiments and simulations.

2. Materials and methods

2.1. Synthesis of silica aerogel PMVE composites

A modified two-step sol-gel process was used to synthesize silica aerogel PMVE composites. First, an equal weight percent mixture of tetraethylorthosilicate (TEOS) (from Alfa Aesar 98% purity) and ethanol (from Merck) was prepared. To this solution, a certain amount of PMVE solution (from Sigma Aldrich %50 wt in water) and then the acid catalyst, HCl, (from Riedel-de Haen with 37% purity) were added under continuous stirring to adjust the pH to around 2.0 where the rate of hydrolysis of the silica precursor was sufficiently high to complete hydrolysis within 40 min. Three samples were prepared with PMVE/TEOS mass ratios ranging from 0.055 to 0.31. Subsequently, NH_3 (from Aldrich 2.0 M in ethanol) as the condensation catalyst was added to accelerate condensation reactions and the resulting mixture formed a gel in approximately 10 min. The overall mole ratio of TEOS to water was 1:4, TEOS to HCl was 500:1, TEOS to ethanol was 1:4.5 and TEOS to NH_3 was 96:1. Shortly before gelation occurred, the sol was poured in cylindrical molds (diameter = 0.85 cm; length = 17 cm). Then, the wet gels, called as alcogels, were taken out from their molds and placed carefully in an equivolume mixture of ethanol and water and aged at 50 °C for 1 day. Subsequently, the alcogels were placed in a 75 ml pure ethanol bath for 3 days to remove all the impurities and water remaining in the pores of the alcogels. The ethanol was replaced once during this 3 day solvent exchange step. The concentration of water and impurities in ethanol was calculated to be very low and on the order of 10^{-2} mol/L. A photograph of one of the silica alcogel composite rods is shown in Fig. 1.

As the last step, ethanol was extracted from the silica alcogel rods via supercritical drying with CO_2 at 100 bar and 40 °C. For this step, the Speed SFE system (Applied Separations, model 7070, Allentown, USA) with a 26 ml tubular extraction vessel (length = 15.94 cm, diameter = 1.22 cm) was used. A schematic diagram of the extraction unit used in this study is shown in Fig. 2 which mainly consists of a high pressure extraction vessel in an oven, two filters at the top and the bottom of the vessel, a pump, a carbon dioxide cylinder, a cooler, a rotameter, and a control unit for controlling the temperature of the extractor and the expansion valve.

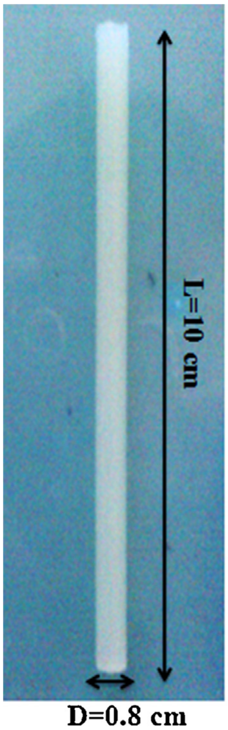

Fig. 1. A Photograph of one of the silica alcogel composite rods.

Primarily, the vessel was filled with pure ethanol to prevent the contact of the samples with air. Then, the synthesized composite rod was weighed and immediately immersed in ethanol in the vessel and mounted in the middle in upright position on the filter (7 in Fig. 2.) at the bottom of the vessel. Temperature of the vessel and of the micro-metering valve controlling the CO_2 flow rate were set to 40 °C and 80 °C, respectively and the vessel was preheated to the extraction temperature. Once the temperature was stabilized, the system was pressurized very fast with CO_2 until the desired operating pressure of 100 bar was reached. Excess amount of ethanol initially added to the vessel was rapidly removed from the vessel in about 5 min. The outlet micro-metering (9 in Fig. 2.) valve was adjusted to give the desired flow rate of CO_2 (3 L/min at standard conditions). The CO_2 stream from the extractor was expanded through the micro-metering valve (9 in Fig. 2.). The CO_2 stream mixed with ethanol was cooled by passing it through a vial immersed in a dry ice bath at ambient pressure and at −78 °C (12 in Fig. 2.). This caused the stream to separate into a gaseous stream rich in CO_2 and a liquid stream which is rich in ethanol. The gaseous stream was vented through a fume hood and the liquid stream was collected in glass vials. Ethanol collected in the vials was weighed within certain time intervals. After a certain period of time of the extraction, the vessel was depressurized slowly (around 0.17 bar/min) to prevent any cracks.

The flow rate was kept at 3 L/min at ambient conditions by adjusting the needle valve during the run and fluctuations were less than 5%. The pressure fluctuations during the run were kept to less than ±2 bars by adjusting the air pressure of the pneumatic pump and the temperature of the oven and the needle valve were controlled to ±1 K using a temperature controller. Mass balance closures for ethanol were within 10%. The densities of silica aerogels obtained in different runs but with the same reactant concentrations ranged from 0.13 to 0.15 g/cm^3.

2.2. Data processing of extraction of ethanol

Total amount of ethanol extracted from the alcogel is determined by the sum of the amount of ethanol in two outlet streams of the unit in Fig. 2 (gaseous and liquid streams).

$$m_{e,\text{total}} = m_{e,1} + m_{e,g} \tag{1}$$

where $m_{e,g}$ is the total amount of ethanol in the gaseous phase and $m_{e,l}$ is the total amount of ethanol in the liquid phase given by:

$$m_{e,1} = \sum_{i=1}^{i=n} m_i \tag{2}$$

where m is mass of ethanol collected in the vial submerged in the dry ice bath, i is number of vial and n is total number of vials.

Ethanol fraction in the gaseous stream can be calculated by Raoult's Law ($x_e P_e^* = y_e P$ where x_e mole fraction of ethanol in the liquid which is equal to 1 and y_e is mole fraction of ethanol in vapor phase, P_e^* is vapor pressure of ethanol and P is total pressure) assuming that the vapor stream leaving the vial is in equilibrium with the liquid in the vial. The collection vial was kept at −78 °C and ambient pressure. Since the vapor pressure of ethanol at −78 °C