

# Polyvinyl Alcohol Aerogel for Efficient Removal of Moisture from Gaseous Streams

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## Abstract:

Hydrophilic polyvinylalcohol (PVA) aerogels were investigated for adsorptive humidity removal. Aqueous solutions of PVA were submitted to repeated freeze/thaw cycles and the resulting gels were dried with supercritical CO<sub>2</sub>. The effects of polymer concentration, thawing time and the number of freezing/thawing cycles on the final aerogel properties were investigated. Morphology of the pores at the surface and at the interior of the aerogel monoliths was studied. PVA aerogels had a broad pore size distribution and pores at the surface of the gels were smaller than the pores at the interior. Adsorption and desorption of water vapor on PVA aerogels were investigated in a closed batch system at 25 °C, 40 °C and 50 °C in 100% relative humidity of air for three hours. Moisture adsorption capacity of PVA aerogels at 50 °C was 41 wt%. The desorption studies indicated that more than 95% of the adsorbed moisture could be removed. Between the cycles, aerogels retained their shape and physical properties. The results reveal that PVA aerogels are promising adsorbents for humidity removal.

## 1. Introduction:

Adsorptive humidity removal is a technology that is being increasingly used to remove moisture from gaseous streams in a wide variety of applications such as drying in dishwashers, dehumidifiers and solar water harvesters for obtaining potable water from air. A wide variety of adsorbents with high capacity for moisture and good regeneration properties ranging from MOFs to zeolites are being investigated in many laboratories around the world for adsorptive humidity removal [1,2,3]. Aerogels are nanoporous materials with very high surface areas which make them attractive for use as adsorbents. There have been many studies on the adsorption of many chemicals ranging from toxic dyes to greenhouse gases on organic and inorganic aerogels with promising results [4]. However, studies on adsorption of water vapor on aerogels are limited. The few studies in the literature are on adsorption of water vapor on silica aerogels. However, major disadvantage of silica aerogels is that their adsorption capacities decrease considerably by repeated adsorption-desorption cycles of water [5]. The aim of the present study was to investigate the humidity adsorption and desorption capacities of hydrophilic PVA aerogel synthesized by cyclic freeze/thaw method.

## 2. Materials and Methods:

### 2.1. Sample preparation:

PVA with a degree of hydrolysis of 98–99% with an average molecular weight of  $3.1 \times 10^4$  g mol<sup>-1</sup>, was purchased from Sigma-Aldrich. PVA aerogels were prepared using a freeze/thaw method. Homogenous solutions of PVA with different polymer concentrations

were prepared by dissolving PVA in distilled water at 80°C. The resulting solutions were frozen at -20°C and then thawed at room temperature leading to the formation of a gel by gradual expulsion of water. Solvent exchange was carried out using water–ethanol mixtures. Subsequently, gels were dried by supercritical CO<sub>2</sub> at 100 bars and 313 K. The effects of polymer concentration, thawing time, and the number of freezing/thawing cycles on the final aerogel properties were investigated.

## 2.2. Morphology studies:

The morphology and porous structure of PVA sample submitted to four freezing/thawing cycles were examined by using a field emission scanning electron microscope (SEM) type ZEISS Ultra Plus, with an operating voltage of 3 kV. SEM images of samples from the surface and the interior of the PVA monoliths were taken. The pore size, pore volume, pore size distribution and Brunauer-Emmett-Teller (BET) surface area of sample were determined via nitrogen physisorption using a Micromeritics ASAP 2020 instrument.

## 2.3. Adsorption and desorption of water vapor measurements:

Adsorption of water vapor on PVA aerogel was investigated in a closed batch system at 25 °C, 40 °C and 50 °C in 100% relative humidity of air for three hours and desorption of water vapor using dry air was carried out at room temperature. Sample was weighed before and after conditioning and the adsorption capacity was calculated from the formula:

$$\% \text{ adsorption} = \frac{W_f - W_i}{W_i} \times 100$$

where  $W_i$  is initial weight and  $W_f$  is final weight.

## 3. Results and Discussion:

BET results indicated that the aerogel prepared using an aqueous solution 10% PVA concentration, frozen at -20°C for 10 hours, thawed for 2 hours at 25°C and subjected to four cycles had the highest surface area that was 76 m<sup>2</sup>/g. Thus, morphology, adsorption, and desorption of water vapor were investigated for these aerogels. Mean density value of aerogel monoliths prepared from 10% PVA solution was determined as 0.195 g/cm<sup>3</sup>. From BET results, the mean size of the pores was determined as 15 nm and pore size distribution was found between 1.7 nm to 64.7 nm.

Cyclic freeze/thaw is a physical crosslinking method which involves freezing the polymer solution at low temperature for a certain period of time followed by a slow thawing at room temperature. At first freezing step, free water inside the aqueous PVA solution freezes so ice crystals appear inside the sample. These ice crystals act as a porogen material by pushing PVA-PVA chains to each other and contribute to hydrogen bonding formation between polymer chains. Subsequently, a porous structure is obtained by melting of ice crystals between PVA chains at room temperature for at least three hours since rapid heating rate prevents the network stabilization [6]. Further freezing and thawing cycles were performed to improve the strength of the gels. Increasing the number of F/T cycles, resulted in an increase of polymer mass loss. Moreover, the average pores size decreased with increasing number of cycles. Four F/T cycles were found as optimum with gels that are sufficiently strong.

Morphology of the PVA aerogel sample was investigated by SEM (Fig1 and Fig2). Surface and interior of the PVA aerogel were examined separately, since a dense skin formation was

observed on the sample surface after drying with  $scCO_2$ . Denser polymer skin occurs with distortion of the sample due to collapsing of pores at the peripheral during diffusion of water molecules from bulk to the surface of the sample [7]. According to SEM results, there was a broad pore size distribution both at the surface and at the interior of the PVA aerogel monolith that are consistent with pore size distribution results from nitrogen physisorption data. Compared to the samples from the interior (Fig 2d), smaller pores (Fig 1c) were observed at the sample surface.

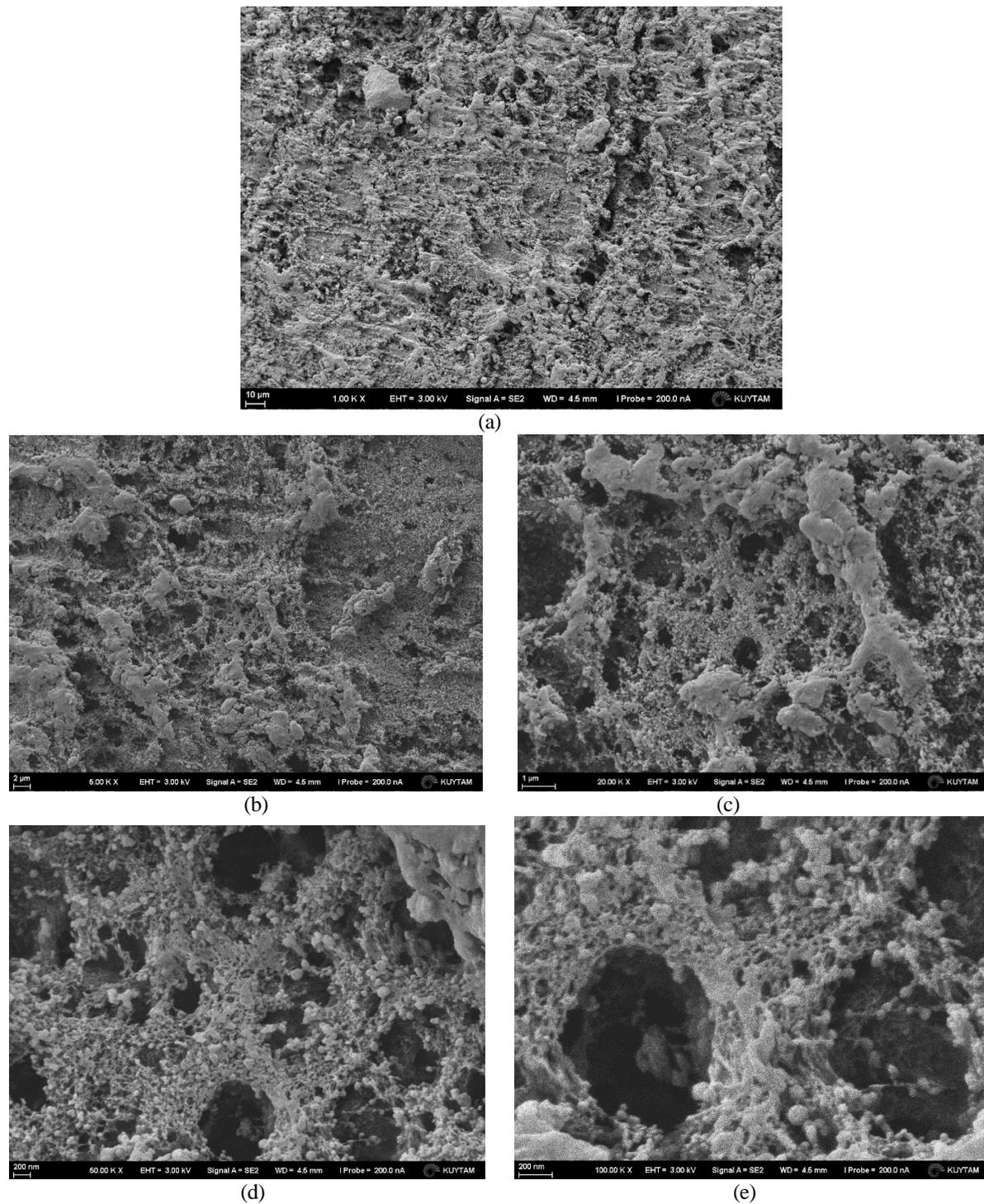


Fig 1: SEM micrographs of PVA (10%) aerogel monolith (surface) after 4 F/T cycles.

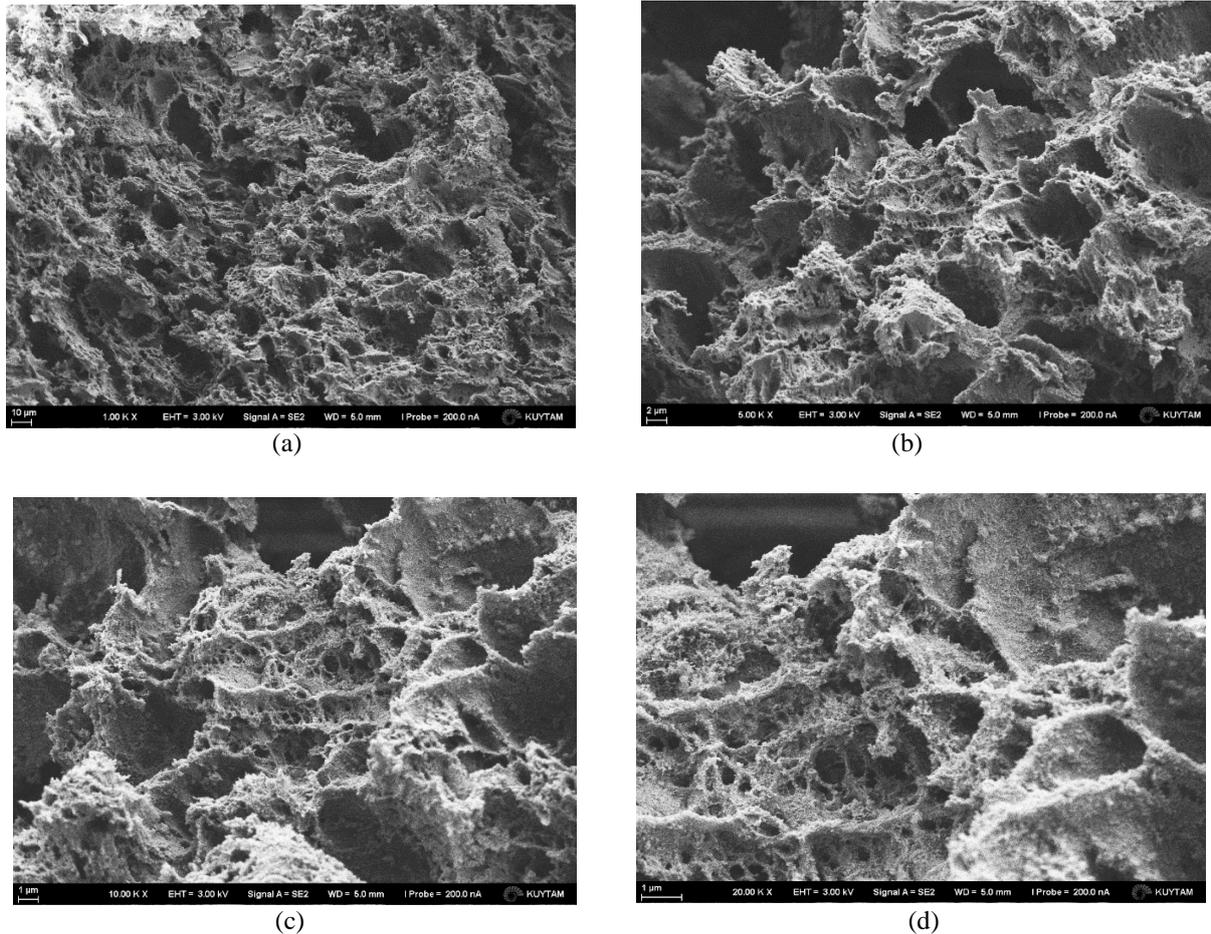


Fig 2: SEM micrographs of PVA (10%) monolith (interior) after 4 F/T cycles.

Moisture adsorption capacity of PVA aerogel at 40°C and 50°C was 36 wt% and 41 wt% respectively. During adsorption, gel volume also increased for both temperatures due to condensation of water vapor inside the pores. These gels deformed during desorption. However, at 25°C, the aerogel retained its shapes and physical properties after five adsorption and desorption cycles. Moisture adsorption capacity of PVA aerogel at 25 °C was determined as 25 wt%. More than 95% of the adsorbed moisture could be removed after each desorption cycle.

#### 4. Conclusion

In the present study, PVA aerogels prepared with different freeze thaw cycles and polymer concentrations were investigated in order to develop alternative adsorbents for humidity removal applications. The aerogel prepared using an aqueous solution 10% PVA concentration, frozen at -20°C for 10 hours, thawed for 2 hours at 25°C and subjected to four cycles had the highest surface area that was 76 m<sup>2</sup>/g. In order to optimize the aerogel strength, 4 F/T cycles were applied.

According to morphological and structural investigations, broad pore size distribution between 1.7 nm to 64.7 nm was found both at the surface and at the interior of the PVA aerogel monolith. Larger pores were observed at the interior while smaller pores were at the surface of the aerogel. Denser structure was on the surface of the PVA aerogel monolith. The structural properties revealed that the mean pores size was 15 nm so the PVA aerogel can be categorized as mesoporous material.

Moisture adsorption capacity of PVA aerogel was investigated inside the batch system at 25°C, 40°C and 50°C was found as 25 wt%, 36 wt% and 41 wt%, respectively. However, aerogel did not retain its shape during adsorption at 40°C and 50°C. On the contrary, after five adsorption and desorption cycles at 25°C, PVA aerogel resisted the deformation and preserved its dimensional integrity. At the end of the each desorption cycles, over 95% of the adsorbed moisture was removed. Consequently, PVA aerogels can be alternative adsorbents for moisture removal.

## 5. Acknowledgements

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## 6. References

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