

Hybrid silica-polysaccharide aerogels: promising new materials

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1. Introduction

The following research is based on the preparation of hybrid aerogels based on silica-polysaccharide without using additional cross-linkers. Silica aerogels themselves are known by their low density as well as low thermal conductivity. The mesoporous structure of silica aerogels leads to lowering the thermal conductivity of gaseous phase even below the values of air due to the Knudsen effect. The limitations of these materials are, however their poor mechanical properties. The polysaccharide aerogels, on the other hand, have better mechanical properties and higher thermal conductivities. Tetramethylortosilicate (TMOS) or tetraethylortosilicate (TEOS) are used as precursors in the production of silica aerogels. Furthermore, polysaccharide aerogels can be prepared only by the addition of methanol or ethanol [1,2]. The idea of the following research was to use methanol obtained after the hydrolysis of TMOS and use it for the gelation of polysaccharides [3]. This would mean that the additional alcohol to the system is unnecessary, since the alcohol released during the reaction is sufficient to convert the initially biphasic system into a homogeneous one [4].

In the presented work, tetramethylorthosilicate (TMOS) was used as inorganic precursor while various polysaccharides (alginate, pectin, xanthan and guar) were used as organic precursors. The mixture of inorganic and organic precursors resulted in stable wet gels, additionally dried using supercritical carbon-dioxide technique. Obtained materials were characterized using N₂ adsorption-desorption analysis, scanning electron microscopy (SEM), and thermogravimetry and scanning electron microscopy (TGA/DSC).

2. Materials and Methods

The hybrid gels were prepared by firstly obtaining of 2 wt % (pectin, alginate, xanthan and guar) and 4 wt % (pectin) of polysaccharide aqueous solutions. The solutions were mixed until homogenization at 400 rpm and 25°C for 1 h and then TMOS was added to each solution, respectively. The prepared polysaccharide-silica solutions were transferred to moulds and left until the gels were set. Obtained wet gels were aged in methanol for 5 h and further dried using supercritical CO₂ at 120 bar, 40°C for 6 h. Surface and cross-sectional morphologies of silica-polysaccharide hybrid aerogels prepared in this study were observed by using field emission scanning electron microscopy (FE-SEM) (HRSEM, Helios Nanolab FEI 650). The adsorption capacity, surface area, pore volume and pore size distribution were recorded on Micromeritics ASAP 2020 by nitrogen adsorption at 77 K. Thermogravimetric (TG) analysis was performed using a TGA/DSC1 Mettler Toledo in the temperature range of 30–600°C at a heating rate of 10°Cmin⁻¹. Thermal conductivity of hybrid aerogels was measured on HPDSC1 at the melting point of indium at 156.6°C [5]. True densities of aerogels were measured by gas pycnometer (Micromeritics AccuPyc II 1340) while the bulk densities were then determined as the ratio of mass to volume.

3. Results and discussion

Surface areas of 2 % guar, alginate, xanthan and guar aerogels are slightly lower from our previously published results on 4 % polysaccharide aerogels [1]. This is expected due to the larger macropore volume. However, silica reference sample has similar surface area to what is reported in the literature, this is around 800-1000 m²g⁻¹. By comparing surface area of prepared composites to blank polysaccharide aerogels, it was observed, that the surface area increased by all samples, but most drastically by guar-silica aerogels. Their surface area was 679 m²g⁻¹. This result is a confirmation of the presence of nanostructured silica aerogel phase in the pores of polysaccharide aerogels.

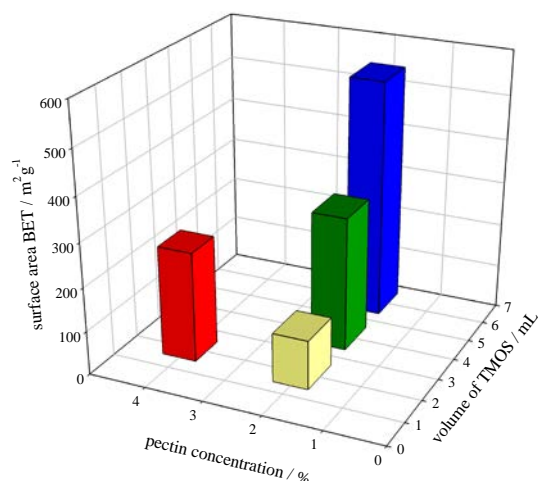


Figure 1. Surface areas pectin-silica hybrid aerogels

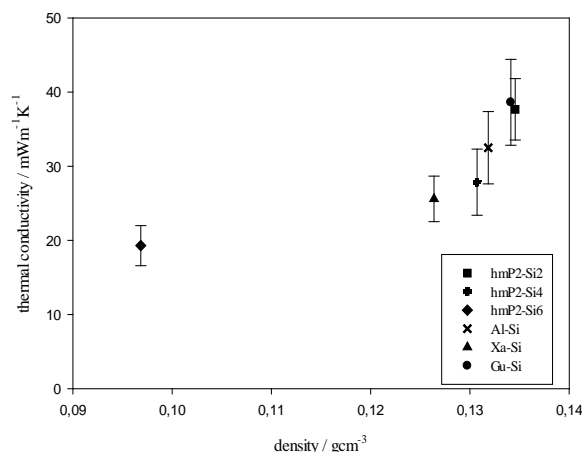


Figure 2. Thermal conductivity as the function of density

Addition of silica also improved the thermal stability of samples. The highest difference was observed again with guar-silica aerogels, where guar aerogels degraded to around 30% of their initial weight at 330 °C and hybrid aerogel degraded by only 16% at the same temperature. Thermal conductivity increased almost exponentially with higher aerogel density. Among the prepared hybrid aerogels, pectin-silica samples had the lowest thermal conductivity of 19 mWm⁻¹K⁻¹.

4. Conclusions

Prepared samples showed useful structural properties, including highly increased surface area compared to pure polysaccharide aerogels. Hybrid aerogels show high thermal stability and low thermal conductivity.

References

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