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Effects of poly(vinyl alcohol) additions on the structure of silica xerogels

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ABSTRACT

Poly(vinyl alcohol)/silica hybrid xerogels were prepared from sonohydrolysis of tetraethoxysilane (TEOS) and additions of water-solution of poly(vinyl alcohol) (PVA). The samples were studied by small-angle X-ray scattering (SAXS), nitrogen adsorption, and differential scanning calorimetry (DSC). On drying at room temperature the resulting xerogels exhibit a fairly bimodal porous structure composed by small mesopores and micropores. The pore size distribution of the mesopores was found to follow approximately a power-law with the pore size. The micropore structure was associated to an evolution at a high resolution level of the mass fractal structure of the original wet gels. The role of the PVA addition on the pore structure of the xerogels is to diminish the specific surface area and the pore volume without to change substantially the pore mean size.

1. Introduction

A large variety of silica based glass and glass ceramics has been obtained by sol–gel process from the hydrolysis of tetraethoxysilane (TEOS) [1,2]. The overall process involves hydrolysis and polycondensation reactions up to the formation of a gel. The wet gel structure is frequently described as a continuous solid network embedded in a large volume fraction liquid phase. Supercritical drying (aerogels), freeze drying (cryogels), and evaporation drying (xerogels) are the usual methods in dried gel production.

The pore structure and the properties of the final product depend strongly on the starting materials and on the conditions of hydrolysis, aging and drying of the gels [3], and, also, on the addition of chemical and structural modifiers. Particularly, the incorporation of organic polymers in the silica structure to form organic/inorganic hybrids [4–7] has proportioned the obtaining of materials with interesting structural properties. The synthesis and characterization of organic/inorganic hybrids aim mainly to improve the properties of silica gels with respect to their fragility, brittleness, and moisture sensitivity, which limit their application in several fields.

Poly(vinyl alcohol) (PVA) has been utilized for the fabrication of hybrids by incorporating PVA with TEOS using water as a solvent [4–7]. The improved mechanical properties of the hybrids are due to hydrogen bonding between PVA and silanol on silica [7]. It has been also reported that OH groups on PVA molecules react with silanol groups during the sol–gel reactions [7].

In this work, we studied mainly by small-angle X-ray scattering (SAXS) and nitrogen adsorption the effects of the additions of poly(vinyl alcohol) on the structure of the resulting TEOS-derived poly(vinyl alcohol)/silica hybrid xerogels. An interesting and original correlation between the structural properties as determined by SAXS and by nitrogen adsorption has been observed in these systems.

2. Experimental

The samples were prepared from the sonohydrolysis of mixtures of 25 ml of TEOS, 8 ml of deionized water, and 5 ml of 0.1 N HCl as a catalyst, so the hydrolysis water/TEOS molar ratio was equal to 6.45 and the pH approximately equal to 2.0. Sonohydrolysis was promoted during 10 min under a constant power (~0.7 W/cm^3) of 20 kHz ultrasonic radiation to obtain homogeneous sols. The quantity of V_x ml of a 5.5% by weight water-solution of poly(vinyl alcohol) (PVA), prepared from a fully hydrolyzed PVA solid powder sample (Sigma–Aldrich CAS9002 89-5), plus $(20 - V_x)$ ml of water were added to the hydrolyzed sols and the sonication was applied for 2 min more for complete homogenization. V_x was varied to 0,

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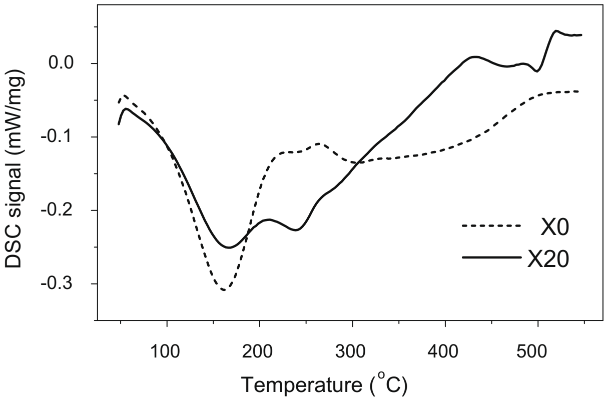

Fig. 1. DSC testing carried out at a heating rate of 10 °C/min for pure silica X0 and PVA/silica hybrid X20 xerogels.

4, 8, 14, and 20 ml to yield the xerogel samples X0, X4, X8, X14, and X20, respectively. The water dilution was desired in order to obtain a set of sols with different PVA concentrations and approximately the same silica concentration (~1.8×10^{-3} mol SiO_2/cm^3). The pH of the sols were yet increased up to about 4.5 by addition of 3.5 ml 0.1 N $NH_4(OH)$ in order to accelerate the gelation process, before the samples were cast in sealed plastic containers for gelation and aging. Monolithic wet gels were obtained after 30 days aging at 40 °C and, then, monolithic xerogels by slow drying at room temperature. The samples were powder ground (~200 μm) and studied by differential scanning calorimetry (DSC), small-angle X-ray scattering (SAXS) and nitrogen adsorption.

The SAXS experiments were carried out using synchrotron radiation with a wavelength $\lambda = 0.1608$ nm. The experiments were conducted using the SAXS beamline of the LNLS synchrotron radiation facility, Campinas, Brazil [8]. The beam was monochromatized by a silicon monochromator and collimated by a set of slits defining a pin-hole geometry. A 2D position sensitive X-ray detector (CCD display), with 79 μm/pixel in both the directions, was used to record SAXS intensity as a function of the modulus of the scattering vector $q = (4\pi/\lambda)\sin(\theta/2)$, where θ is the scattering angle. The experimental setup allowed us to get SAXS data from $q_0 = 0.08$ nm^{-1} to $q_m = 2.0$ nm^{-1} with increments of $\Delta q = 1.98 \times 10^{-3}$ nm^{-1}. The data were corrected by the sample attenuation and the parasitic scattering, and normalized with respect to the beam intensity and the logarithm of the attenuation, which is proportional to the thickness of the sample.

Nitrogen adsorption isotherms were obtained at liquid nitrogen temperature using an ASAP 2010 Micromeritics apparatus. The samples were degassed at 120 °C for no less than 24 h before the adsorption tests. The adsorption data were analyzed for the BET specific surface S_{BET}, the total pore volume per mass unit V_p, as the total volume of nitrogen adsorbed at a point close to the nitrogen saturation pressure, the pore mean size $l_p = 4V_p/S_{BET}$, and the mesopore size distribution (PSD), as determined by the classical Kelvin equation and the Harkins and Jura model for cylindrical pores, and also for the micropore volume V_{mi} and micropore surface S_{mi} as determined by t-plot method [9].

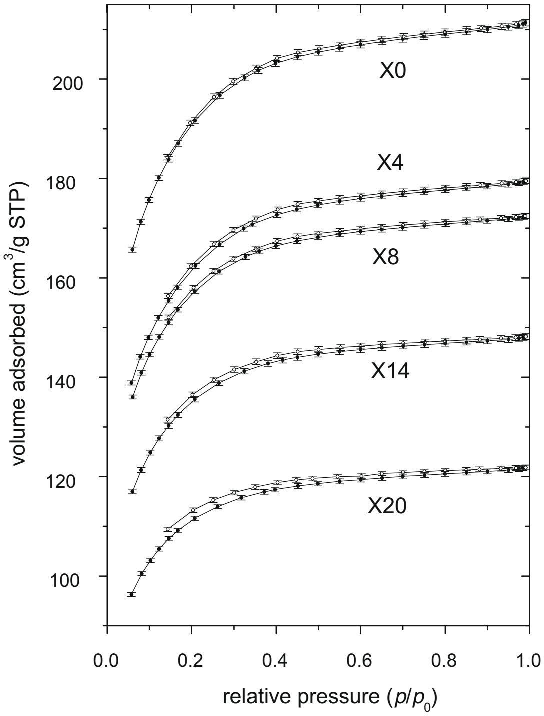

Fig. 2. Nitrogen adsorption isotherms for pure silica and PVA/silica hybrid xerogels.

3. Results

Fig. 1 shows the DSC testing for pure silica X0 and PVA/silica hybrid X20 xerogels carried out under nitrogen atmosphere with a heating rate of 10 °C/min. The curves show an endothermal peak at about 160 °C which is due to liberation of water from the micropores and adsorbed water weakly bound to the material. A second endothermal peak at about 240 °C which appears only for the hybrid X20 xerogel in Fig. 1 is due to the melting point of the polymer. This suggests the presence of fairly crystallized polymeric material in the hybrid xerogels. A very weak exothermal peak is apparent at about 270 °C in both the samples which is due to residual organic material decomposition. Above 300 °C, the hybrid xerogel exhibits a continuous upward base line shifting, which should be due to the continuous decomposition of the additional residual organic material present in the hybrid xerogels. An endothermal peak due to pyrolysis or carbonization of residual organic material is yet apparent at about 500 °C in the hybrid X20 xerogel.

Fig. 2 shows the nitrogen adsorption isotherms measured at the liquid nitrogen temperature for the xerogels. The isotherms are more properly classified as type I, according to IUPAC classification [10]. Table 1 shows the values for the BET specific surface area S_{BET}, the total pore volume per mass unit V_p, and the pore mean size l_p, as determined from the adsorption isotherms. Table 1 also shows the values for the micropore volume V_{mi} and the micropore surface S_{mi} as determined by t-plot method from the adsorption data.

Table 1
Characteristics of the pore structure of the xerogels as determined from nitrogen adsorption data.

	S_{BET} (m^2/g)	V_p (10^{-1} cm^3/g)	l_{BET} (nm)	S_{mi} (m^2/g)	V_{mi} (10^{-1} cm^3/g)
X0	659 ± 5	3.27 ± 0.05	1.98 ± 0.03	311 ± 4	1.44 ± 0.03
X4	559 ± 5	2.77 ± 0.05	1.98 ± 0.03	252 ± 4	1.16 ± 0.03
X8	541 ± 4	2.67 ± 0.05	1.97 ± 0.03	256 ± 4	1.19 ± 0.03
X14	467 ± 4	2.29 ± 0.04	1.97 ± 0.03	221 ± 3	1.02 ± 0.02
X20	384 ± 4	1.89 ± 0.03	1.96 ± 0.03	190 ± 3	0.88 ± 0.02