

# Preparation of organic and carbon xerogels using high-temperature–pressure sol–gel polymerization



Iman Naseri, Ali Kazemi, Ahmad Reza Bahramian\*, Mehdi Razzaghi Kashani

Polymer Engineering Department, Faculty of Chemical Engineering, Tarbiat Modares University, P.O. Box 14115-114, Tehran, Iran

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## ABSTRACT

To prepare organic gels at temperatures higher than normal boiling point of solvent, a method was developed using sol–gel polymerization in atmosphere saturated by vapor of solvent. To illustrate the advantages of proposed method, two series of gels were prepared using the conventional ( $T_{\text{curing}} = 70\text{ }^{\circ}\text{C}$ ) and the high temperature ( $T_{\text{curing}} = 140\text{--}170\text{ }^{\circ}\text{C}$ ) sol–gel polymerization. While no drying shrinkage was observed in our proposed method, 5–18% linear shrinkage occurred in conventional method depending on resin concentration in sol. Moreover, rising of curing temperature reduced the required time for preparation of organic gels from 5 days to lower than 5 h. The effects of processing parameters were investigated on physical and mechanical properties of organic xerogels. The results revealed that resin concentration significantly affects both density and compressive strength of final xerogels. While the curing temperature had no obvious effect on density, the raising of curing temperature significantly enhance the strength of organic xerogels. Carbon xerogels prepared by pyrolysis of novolac aerogels in inert atmosphere. The textures of the carbon xerogels were denser than corresponding organic xerogels, as evidenced by scanning electron microscopy (SEM) images.  $\text{N}_2$  adsorption tests indicated that carbon aerogels were mainly meso or macroporous depending on resin concentration in initial sol.

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## 1. Introduction

Carbon aerogels, a unique class of high-surface-area materials, are considered extremely attractive materials as adsorbents, electrochemical capacitors, catalyst supports and high-temperature thermal insulation materials due to their controllable pore size distributions, high surface areas, and very low electrical resistivity and low thermal conductivity [1–3]. Generally, there are four steps in the preparation of carbon aerogels, namely sol–gel polymerization of raw materials, solvent exchange, supercritical drying and pyrolysis process, all of which affect porosity and morphologies of carbon aerogels [4–6]. However, the conventional process involves long gelation time, expensive resorcinol and high cost of supercritical drying device [7–8]. The total process of carbon aerogel preparation requires approximately 2 weeks [9]. In recent years, many efforts have been made to shorten and simplify the production process based on elimination or shortening of one or more of the steps in the traditional process. In 1999 Qin et al. prepared organic gels by using direct supercritical acetone drying [10]. However, high critical temperature of acetone avoids using of this

drying method in large scale productions [11]. In 2008 Reub et al. was reported preparation of organic aerogels by using HCl as catalyst instead of conventional basic catalysts. The use of acid catalyst significantly reduced gel time. The gelation time varied from few seconds to minutes [12]. To eliminate solvent exchange step, Qin reported preparation of organic aerogel through alcoholic sol–gel process [9].

However, the large difference between appropriate temperature for curing of raw materials (based on differential scanning calorimetry, DSC) and normal boiling point of common organic solvents is one of the most important reasons for long process time and high drying shrinkage in conventional sol–gel polymerization. Actually, to avoid boiling of solvent and blowing of resin as a consequence of rapid curing and releasing of by-products, the curing temperature in the conventional sol–gel polymerization is selected below the normal boiling point of solvent [13]. This means the sol–gel polymerization should be conducted at relatively low temperature (typically less than  $100\text{ }^{\circ}\text{C}$ ) which is far from appropriate temperature for curing of monomer or resin. Conducting sol–gel polymerization at low temperatures has two defects. On the one hand, the low temperature sol–gel polymerization leads to slow curing reactions and hence, long required time for preparation of organic gel. On the other hand, the low temperature sol–gel polymerization leads to low crosslink density and modulus of the final gel.

\* Corresponding author. Tel.: +98 21 8288 4938; fax: +98 21 8288 4931.

E-mail address: [abahramian@modares.ac.ir](mailto:abahramian@modares.ac.ir) (A.R. Bahramian).

Basically, the crosslink density of organic aerogel is a key parameter that needs to be considered for aerogel applications. Highly cross-linked organic gel not only provides high structural stability in order to preserve its structure after solvent removal, but also introduces high char yield after pyrolysis to construct carbon aerogel [13]. Due to ring opening curing mechanism of benzoxazine resin and using of xylene as a high boiling point solvent ( $T_b = 135^\circ\text{C}$ ), Lorjaj reported preparation of organic and carbon aerogels at relatively high temperature ( $T_{\text{curing}} = 130^\circ\text{C}$ ). This high temperature sol-gel polymerization ( $130^\circ\text{C}$ ) led to not only reduction in process time, but also very little shrinkage observed after drying of the gels at ambient conditions [13]. However, toxicity of xylene and being inappropriate in the case of poly-condensation curing are disadvantages of this method.

The objective of this work is developing a method for preparation of organic gels at temperatures much higher than normal boiling point of solvent, regardless of normal boiling point of solvent and applicable to poly-condensation curing reactions. To achieve this goal, sol-gel polymerization in solvent vapor saturated atmosphere was proposed. Our hypothesis is that the saturated atmosphere could affect final structure of gel through three different mechanisms. First, it prevents the removal of solvent inside the sol. Second, the saturation pressure acts like a mechanical press and prevents from blowing of resin as a consequence of rapid releasing of volatile by-products in a short period of time. Finally, elevation of boiling point as a consequence of increasing surrounding pressure avoids boiling of solvent inside the sol.

## 2. Experimental details

### 2.1. Sample preparation

Two series of novolac gels prepared by using sol-gel polymerization reaction of novolac resin (IP 502, Resitan Co. Iran) and hexamethylene tetramine (HMTA) in 2-propanol (Dr. Mojallali Co. Iran). The novolac resin contained 9 wt.% of HMTA. The concentrations of solid components in the solutions were adjusted to desired values, set in the range of 10–40 wt.%.

To prepare organic gels by using conventional low temperature sol-gel polymerization, the homogeneous mixed solutions were poured into polypropylene (PP) vials with 14 mm diameter, sealed and cured at  $70^\circ\text{C}$  for 5 days. To prepare organic gels in solvent vapor saturated atmosphere, the solutions were cast in poly (tetrafluoroethylene), PTFE, molds. In contrast to conventional, the gel is prepared in an open mold. Then, the mold was put in an autoclave containing the required amount of solvent. Actually, the mold was put in a bath of solvent inside the autoclave. Then, the autoclave sealed and its temperature increased to the curing temperature and kept for 5 h. Finally, the resultant gels were dried at ambient pressure condition according to the cycle of  $25^\circ\text{C}$  for 24 h,  $90^\circ\text{C}$  for 24 h,  $120^\circ\text{C}$  for 24 h and  $140^\circ\text{C}$  for 4 h. Fig. 1 shows the effect of the atmosphere pressure of polymerization on structure of final product. In absence of pressure, releasing of volatile by-products and boiling of solvent cause blowing of solution and appearing of bubble in sol respectively.

Carbon aerogels were prepared by pyrolysis of novolac aerogels. Pyrolysis was conducted under a constant  $\text{N}_2$  gas flow of  $200\text{ cm}^{-3}\text{ STP/min}$ . The furnace was heated to  $250^\circ\text{C}$  at  $10^\circ\text{C/min}$  and maintained at  $250^\circ\text{C}$  for 15 min. Then, it was heated to  $550^\circ\text{C}$  at  $10^\circ\text{C/min}$  and kept at  $550^\circ\text{C}$  for 30 min. Finally, the furnace was heated to  $800^\circ\text{C}$  at  $10^\circ\text{C/min}$  and kept at  $800^\circ\text{C}$  for 180 min. The furnace was allowed to cool to room temperature under protection of  $\text{N}_2$ .

Fig. 2 shows the production processes of aerogels using high temperature and conventional sol gel polymerization.

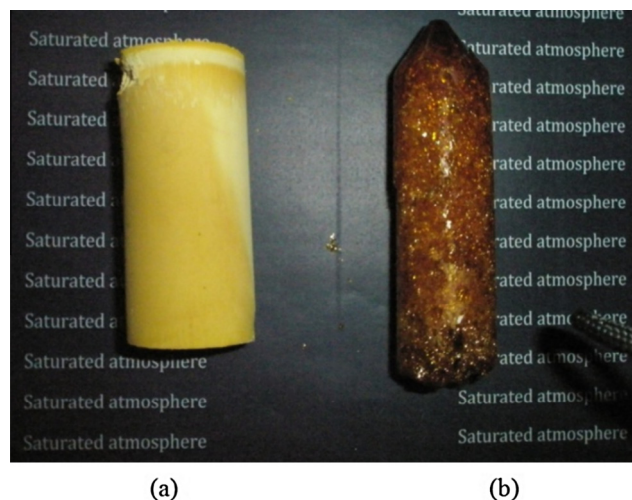


Fig. 1. The effect of polymerization condition on the final structure of samples in (a) sol-gel polymerization at elevated pressure and (b) sol-gel polymerization at ambient pressure.

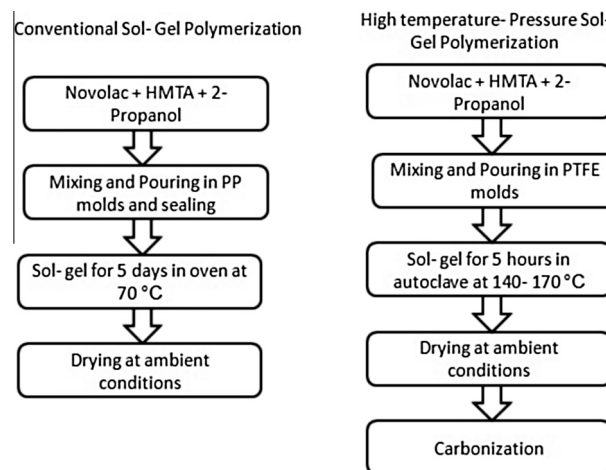


Fig. 2. Schematic representation of production processes.

### 2.2. Characterizations

The linear shrinkage of the samples was calculated by Eq. (1), from the diameters of the samples ( $D$ ) before and after ambient pressure drying.

$$L_{\text{shL}} (\%) = \frac{D_{\text{after}} - D_{\text{before}}}{D_{\text{before}}} \times 100\% \quad (1)$$

The apparent density of aerogels was calculated by measuring the dimension and the mass of the cylindrical sample. The skeletal density was measured by helium pycnometry (Accupye 1330, micromeritics, USA). Before density measurements, the samples were dried at  $120^\circ\text{C}$  in vacuum oven overnight in order to avoid the distorting effect of the adsorbed water on the volume measurement. A DSC (Netzch Co. Germany) was used to perform dynamic cure experiment. Approximately 10 mg of resin was placed in an aluminum pan. Dynamic temperature scan was conducted from 25 to  $300^\circ\text{C}$  at heating rate of  $5^\circ\text{C/min}$  in  $\text{N}_2$  atmosphere. The pyrolysis of novolac aerogel was characterized using a Thermal Analysis instrument Thermo Gravimetric Analyzer, TGA, (Mettler Co. Swetzerland) at a heating rate of  $10^\circ\text{C/min}$  in  $\text{N}_2$  atmosphere. A field emission SEM was used to study the structure of novolac and carbon aerogels.

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