SYNTHESIS AND PROPERTIES OF HYBRID AEROGEL MATERIALS BASED ON LIGNOSULFONATE AND SILICA USING SUPERCRITICAL DRYING

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DOI: 10.56651/lqdtu.jst.v1.n01.622.pce

Abstract

In this study, the sol-gel method was used for the synthesis of hydrogels based on liquid glass and sodium lignosulfonate. Isopropyl alcohol was used to subsitute water in the hydrogel structure, preventing linear shrinkage and maintaining the water content in the range of 1-4.8%. Subsequently, these hydrogels were subjected to supercritical drying at 40°C and a pressure of 12 MPa in a 250 mL device together with a supercritical CO_2 consumption of 100 Nl/h, resulting in a hybrid aerogel with a specific surface area reaching 483 m^2/g. The resulting aerogels have a micro-mesoporous structure with average pore sizes of 3-50 nm and a total pore volume ranging from 0.27 to 2.19 cm^3/g. These hybrid aerogel materials have a noticeably low density (i.e., as low as 0.055 g/cm^3).

Keywords: *Aerogel; supercritical drying; silicon dioxide; sodium lignosulfonate.*

1. Introduction

Materials science is focused on developing novel materials with unique properties and versatile applications. Among these materials, aerogels have attracted widespread attention from scientists around the world due to their solid structure that features high porosity, specific surface area, low density, and large pore volume [1, 2]. These characteristics make aerogels highly suitable for many applications, particularly including sound and thermal insulation materials [3], gas and liquid absorbents [4, 5], catalysts and catalyst carriers [6], energy storage devices [7], and sensitive elements in gas sensors [8]. Aerogel materials that are based on organic compounds and silicon dioxide synthesized through the sol-gel method have demonstrated the ability of functional groups in organic molecules to interact with inorganic matrices [9]. A recent study on the combination of sodium lignosulfonate and silicon dioxide has revealed that the aerogel material's structure is formed through hydrogen bonding between the OH groups of sodium lignosulfonate and the oxygen atoms of the siloxane chains of SiO_2 [10, 11].

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Technical lignin, including sodium lignosulfonate, is a type of multifunctional aromatic polymer based on natural lignin that has been modified through wood digestion (in alkaline or acidic media) or hydrolysis. These polymers possess a range of functional groups (e.g., methoxyl, carbonyl, hydroxyl, carboxyl, and sulfo groups) within their macromolecular structure, making them amenable to further modification. By utilizing self-organization with highly dispersed silicic acid sol, engineering lignin can be modified to synthesize compounds with a wide range of useful properties, such as polymeric fillers for pharmacology, electroactive mixtures for microelectronics, biosorbents for medicine, and catalyst carriers for catalysis [12].

Various factors, such as synthesis parameters and type of solvent substituting water in the hydrogel structure during multi-step solvent exchange, significantly impact the properties of aerogels. Multi-step solvent exchange is necessary to preserve the original gel structure and prevent shrinkage and cracking, which can adversely affect the quality of the final aerogel monoliths. Furthermore, the supercritical drying process plays a crucial role in the formation of the distinctive properties of aerogels as it enables the preservation of the three-dimensional pore structure. Indeed, this three-dimensional pore structure gives rise to aerogels' unique properties, such as high porosity and large surface area [13].

Supercritical fluid is a state whereby the liquid and vapor phases are no longer separate, resulting in a fluid with a high density similar to that of a liquid and a low viscosity like that of a gas [14]. The diffusion coefficient of supercritical fluids is intermediate between those of liquids and gases [15]. During supercritical drying, the organic solvent in the gel structure is gradually removed using supercritical fluid to avoid structural changes in the original gel and preserve its nanostructure. The supercritical gel drying process is the most complex, technologically advanced, and expensive step in the production of aerogels. Conventional heat drying or freeze-drying can produce highly porous materials, but the original gel structure is destroyed. In the case of freeze-drying, crystals formed inside the gel can lead to the formation of large pores, resulting in a decrease in the specific surface area [16]. Therefore, the use of supercritical fluids for gel drying enables the production of aerogels with all the necessary properties, such as high specific surface area, high porosity, and low density [17]. The key difference between the supercritical drying method and other drying methods is that no phase boundary is formed in the porous structure of the gel during drying.

In this study, hydrogels were synthesized using sodium lignosulfonate and liquid glass as a common source of SiO_2 via the sol-gel method. In a multi-step solvent exchange process to replace water from the original gel structure, isopropyl alcohol was used as an organic solvent due to its low toxicity, availability, and good solubility in water and supercritical CO_2 used in the subsequent drying step. The gel following solvent exchange was dried using supercritical CO_2. The influence of sol-gel synthesis conditions on the porous structure of the lignosulfonate-based and liquid-glass hybrid aerogel materials was analyzed using modern analytical methods.

2. Experiment

2.1. Chemicals

Sodium lignosulfonate was obtained from Industrial Holding AMK-Group Co., Ltd. (Moscow, Russia), while liquid glass with a molar ratio of SiO_2/Na_2O of 3.4 was procured from Prime Chemicals Group Co., Ltd. (Moscow, Russia). Isopropanol (≥ 99.8%) was used as the solvent, and sulfuric acid (95.6%) was added as the gelation agent, both of which were sourced from Rushim Co., Ltd. (Moscow, Russia).

2.2. Preparation hydrogels and aerogels

The synthesis process of hybrid aerogels from liquid glass and lignosulfonate is depicted in Fig. 1.

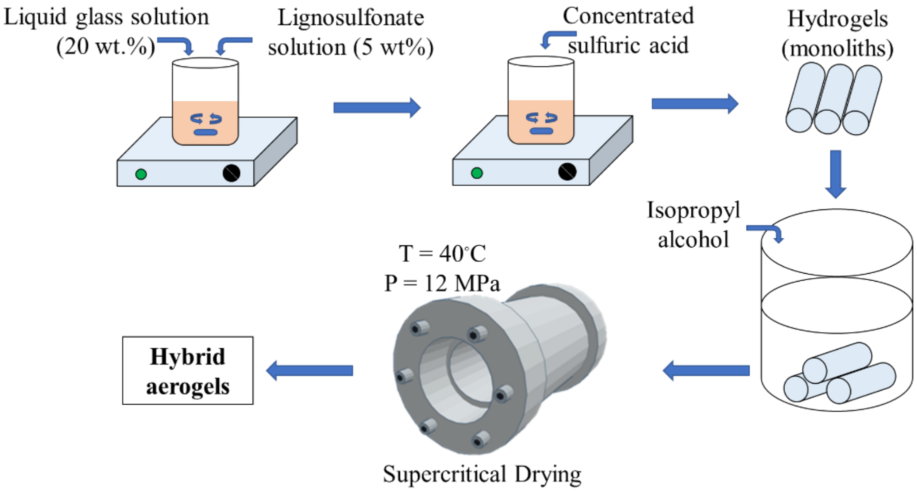

Fig. 1. Scheme for the synthesis of aerogel monoliths based on silicon dioxide and lignosulfonate.

To prepare the hydrogel monoliths, sodium lignosulfonate was dissolved in deionized water and filtered through filter paper to obtain a 5 wt% solution of lignosulfonate. Liquid glass was dissolved in deionized water to obtain a 20 wt% solution with the concentration of the sol calculated from SiO_2. The solutions were stirred for 10 minutes at a constant temperature of 25°C and 500 rpm using a magnetic stirrer. Hydrogels were formed by mixing a 5% solution of lignosulfonate into a 20% glass solution in different volume percentages of the lignosulfonate solution (10%, 30%, 50%, and 60%). The mixture was stirred for an additional 10 minutes at 25°C and 500 rpm, and then concentrated sulfuric acid was slowly added until a pH of 7.5 was observed, as measured using a 2100-OHAUS pH-meter. The hydrogels were matured for 24 hours at room temperature and then washed several times with deionized water to remove dissolved salts. The presence of residual SO_4^{2-} ions in the washing water was tested using a solution containing Ba^{2+} ion. The next step involved a multistep solvent exchange using isopropyl alcohol to remove water from the hydrogels. During each step, the concentration of isopropyl alcohol was increased, with at least 24 hours between each step. In this work, the following solvent exchange steps were used: 10%, 30%, 60%, 90%, and 100% isopropyl alcohol concentration. The final stage involved supercritical drying to obtain aerogel monoliths.

2.3. Supercritical drying procedure

We utilized our own experimental setup to dry the hydrogel with supercritical CO_2 in a high-pressure apparatus with a volume of 250 mL [18, 19]. Fig. 2 depicts the schematic diagram of the supercritical drying system.

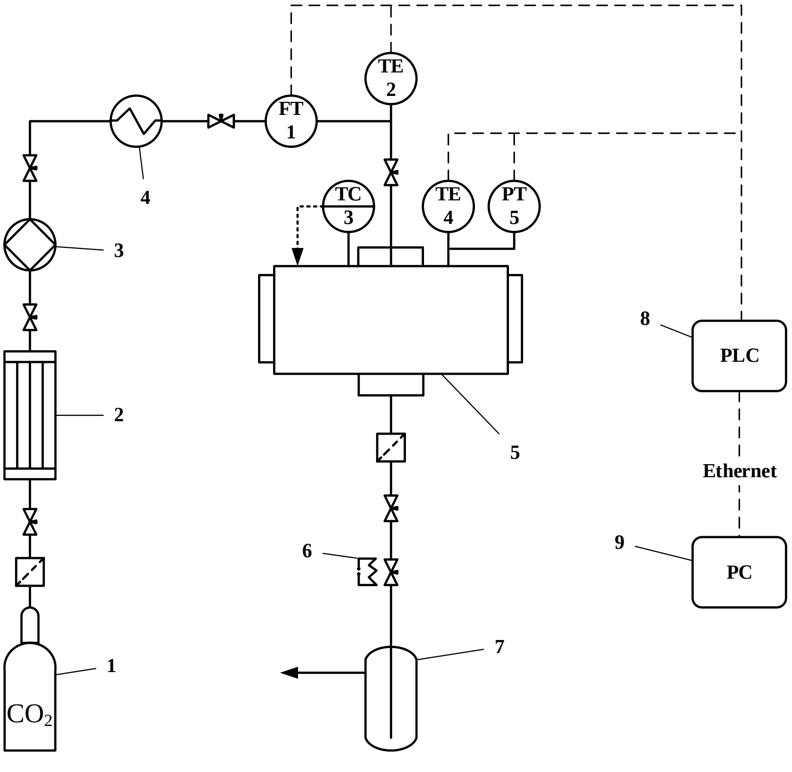

Fig. 2. Scheme of the supercritical reactor: 1 - CO_2 tank; 2 - condenser; 3 - piston pump; 4 - heater; 5 - high pressure reactor with a volume of 250 mL; 6 - heating element; 7 - separator; 8 - programmable logic controller (PLC); 9 - personal computer (PC); TC3 - temperature controller; FT1 - Coriolis flowmeter; TE2, TE4 - thermocouples; PT5 - pressure sensor.

Liquid CO_2 is supplied from a tank (1) to a condenser (2), where it is cooled to 278 K to prevent gas phase formation. The pressure of the CO_2 is then increased to 12 MPa using a G35 pump (3) from Maximator GmbH, Germany. Prior to carrying out the drying process in a high-pressure reactor with a volume of 250 mL (5), the liquid CO_2 is passed through a heater (4) to reach a temperature of 40°C. The supercritical drying apparatus (Fig. 2) is equipped with several instruments, including a thermocouple (TE2) and a Coriolis flowmeter (FT1, MINI CORI-FLOW ™ M13 Coriolis flowmeter from Bronkhorst High-Tech B.V., Netherlands) at the inlet to the high-pressure vessel, a thermocouple (TE4), a pressure sensor (PT5) to measure the pressure and temperature inside the vessel. The data from TE2, FT1, TE4, and PT5 is transferred to a programmable logic controller (PLC, 8), and then to a personal computer (PC, 9), where it is displayed and stored. The temperature inside the high-pressure vessel is controlled using a temperature transducer (TC3), and heating is provided by a flexible heating cable located on the housing of the high-pressure vessel. The CO_2 flow is regulated using a system of valves at the outlet of the high-pressure vessel.

The supercritical drying process can be divided into four main stages. During the first stage, the apparatus is pressurized with liquid carbon dioxide using a pump (3), and the drying parameters are established at 40^{o}C and 12 MPa. At the second stage, the solvent is displaced from the free volume of the apparatus by maintaining a constant liquid CO_2 flow rate. This stage is characterized by a constant drying rate, and most of the solvent is removed during this stage. The duration of the second stage is determined by the intensity of convective transport in the free volume of the apparatus, which is dependent on the CO_2 flow rate. For hydrogel monoliths, we carried out this stage at a flow rate of 100 Nl/h for 1 hour. The third stage involves the diffusional exchange of the solvent inside the pores of the hydrogels with supercritical carbon dioxide. For hydrogel monoliths, we carried out this stage at a constant flow rate of supercritical CO_2 of 100 Nl/h for 6 hours. During the fourth stage, depressurization is carried out at a rate of 4 bar/min, and the aerogels are subsequently removed from the apparatus. The entire supercritical drying process lasts for 8 hours.

2.4. Analytical experiments

The internal structure of aerogels plays a crucial role in determining their unique properties, such as porosity, specific surface area, and pore size distribution. The linear shrinkage andapparent density of aerogels is also important properties that can be easily measured and is frequently used as quality indicators [20]:

$$V_{pores} = \left(\frac{1}{\rho_{apparent}} - \frac{1}{\rho_{true}} \right) \tag{1}$$

$$\phi = \left(1 - \frac{\rho_{apparent}}{\rho_{true}} \right).100\% \tag{2}$$

$$\rho_{apparent} = \frac{m}{V} \tag{3}$$

$$L = \left(\frac{l_{ini} - l_{fin}}{l_{ini}} \right).100\% \tag{4}$$

where ρ_{true} is true density of the samples (g/cm^3); l_{ini} is the initial linear size of the sample (cm); l_{fin} is the final linear size of the sample (cm); m is the mass of the sample (g); and V is the sample volume (cm^3).

The texture of the aerogel was characterized using low-temperature N_2 adsorption-desorption analysis (NOVA 2200e Analyzer). Prior to analysis, samples were dried under vacuum (< 1 MPa) at 60°C for 20 hours. The specific surface area was determined using the BET (Brunauer-Emmett-Teller) method, while the average pore diameter was calculated using desorption techniques and the BJH (Barrett-Joyner-Halenda) analysis. Furthermore, the morphologies of the aerogels were examined using scanning electron microscopy (SEM) (JEOL 1610LV, JEOL Ltd., Tokyo, Japan). All analytical experiments were performed at the core facilities centre of Mendeleev University of Chemical Technology of Russia.

3. Results and discussion

In this study, hybrid aerogels produced using liquid glass and lignosulfonate were found to preserve the bulk shape of the original hydrogels while exhibiting an exceptionally light weight, as illustrated in Fig. 3.

Fig. 3. Physical shape and light weight of a hybrid aerogel based on silicon dioxide and lignosulfonate.

The obtained hybrid aerogel materials were cylindrical monoliths. The nitrogen adsorption-desorption isotherm at 77 K for aerogels in monoliths form composing of silicon dioxide with lignosulfonate is shown in Fig. 4.

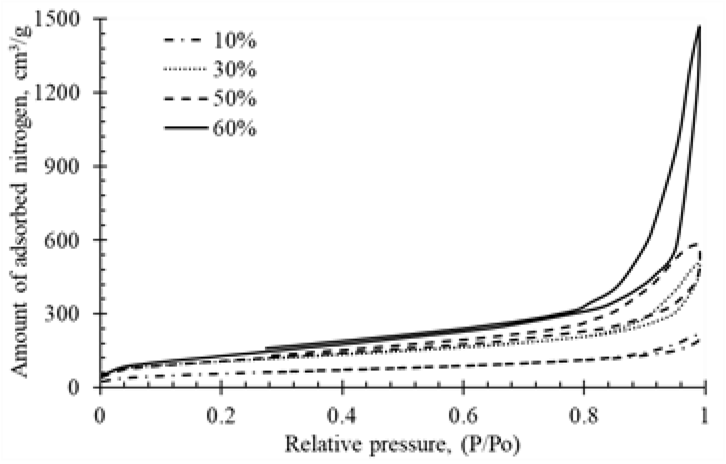

Fig. 4. Nitrogen adsorption-desorption isotherms at 77 K for hybrid aerogels in the form of monoliths based on silicon dioxide and lignosulfonate.

The isotherms obtained are classified as type IV according to the IUPAC classification, typical of mesoporous materials with capillary condensation [21]. An increase in the concentration of lignosulfonate results in an increase in adsorbed nitrogen, indicating an increase in the total pore volume. The BJH pore size distribution of the hybrid aerogels prepared using different ratio of silica and lignosulfonate is presented in Fig. 5. The curves showed the existence of mesopores with diameters ranging from 3 nm to 50 nm. It is noteworthy that at lignosulfonate volume percentage of 60%, pore sizes could reach up to 120 nm. This is attributed to the formation of microparticles within the aerogel structure resulting from the heightened concentration of lignosulfonate, which in turn leads to an expansion of pore diameter. This assertion is reinforced by the SEM image and aligns with the findings presented in the reference [10].

SEM images of silicon dioxide-based aerogels with lignosulfonates are presented in Fig. 6. As the concentration of lignosulfonate increases, the solid components in the aerogel structure tend to agglomerate and compact, resulting in the formation of macropores.

Table 1 presents the characteristics of hybrid aerogels based on silicon dioxide and lignosulfonate: specific surface area S_{BET}, m^2/g; mesopore volume V_{BJH}, cm^3/g; the volume of all pores V_{pores}, cm^3/g is calculated by formula (1); porosity ϕ, % is calculated by formula (2); apparent density $\rho_{apparent}$, g/cm^3 is the ratio of the mass of the sample to the entire volume it occupies (including pores and voids), which is calculated by formula (3); linear shrinkage L, % is associated with the inevitable shrinkage processes during such stages as solvent replacement, supercritical drying, which is calculated by formula (4). Linear shrinkage was calculated from the stage of gelation to obtaining material after supercritical drying.

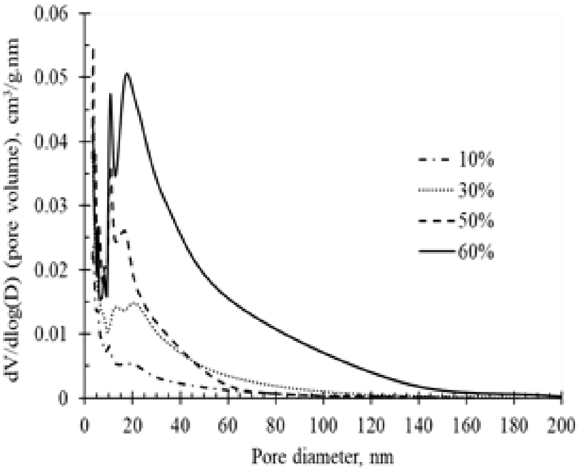

Fig. 5. Pore size distribution for hybrid aerogels in the form of monoliths based on silicon dioxide and lignosulfonate.

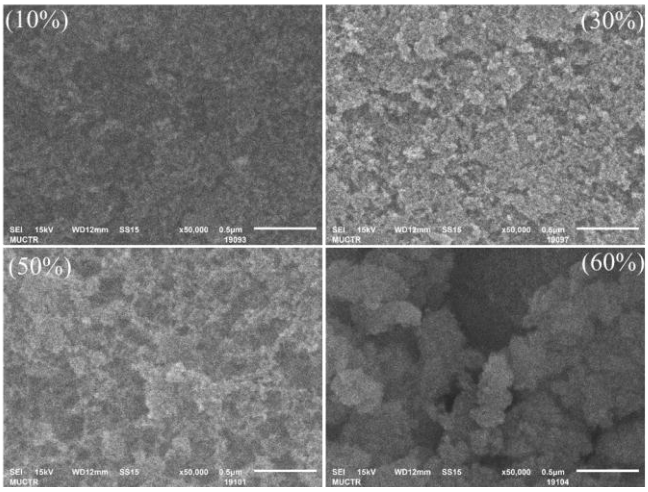

Fig. 6. Surface porous structure morphology of hybrid aerogels based on silicon dioxide and lignosulfonate.

Table 1. Characteristics of hybrid aerogels based on silicon dioxide and lignosulfonate

Sample	S_{BET}, m²/g	V_{BJH}, cm³/g	V_{pores}, cm³/g	ϕ,%	$\rho_{apparent}$, g/cm³	L,%
10%	206	0.27	7.20	95	0.132	4.8
30%	375	0.66	7.82	95	0.121	3.2
50%	396	0.80	14.96	97	0.065	1.6
60%	483	2.19	17.79	97	0.055	1.0

Table 1 reveals that an elevation in lignosulfonate concentration resulted in an increase in specific surface area of the hybrid aerogel to 483 m^2/g and mesopore volume to 2.19 cm^3/g, surpassing the values of 450 m^2/g and 2.0 cm^3/g reported in the previous study [10]. Additionally, the incorporation of lignosulfonate aided in reducing the linear shrinkage of the aerogel structure during synthesis. Consequently, the aerogel's porosity rose from 95% to 97%, and the density of the hybrid aerogel decreased from 0.132 g/cm^3 to 0.055 g/cm^3. The results suggest that replacing water with isopropyl alcohol in the initial hydrogel and utilizing this supercritical drying condition have resulted in positive outcomes for the creation of hybrid aerogels that employ liquid glass and lignosulfonate as their primary components.

4. Conclusion

The hybrid aerogel materials were synthesized by combining liquid glass and lignosulfonate, achieving remarkable porosities up 97%. By using isopropyl alcohol to displace water from the initial hydrogel structure, the gel's form and texture were maintained, as evidenced by minimal linear shrinkage varying between 1% and 4.8%. By increasing the lignosulfonate concentration and employing supercritical drying at 40°C and 12 MPa pressure in a 250 mL apparatus, along with a supercritical CO_2 flow rate of 100 Nl/h, a hybrid aerogel with a high specific surface area ranging from 206 m^2/g to 483 m^2/g was successfully produced. The resulting aerogels exhibited a micro-mesoporous structure, with average pore sizes ranging from 3 to 50 nm and total pore volumes between 0.27 and 2.19 cm^3/g. As the lignosulfonate concentration increased, pore sizes expanded up to 120 nm. These hybrid aerogel materials have remarkably low densities, reaching values as low as 0.055 g/cm^3.

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TỔNG HỢP VÀ ĐẶC TÍNH CỦA VẬT LIỆU AEROGEL LAI DỰA TRÊN LIGNOSULFONATE VÀ SILICA SỬ DỤNG SẤY SIÊU TỚI HẠN

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Tóm tắt: Trong nghiên cứu này, phương pháp sol-gel được sử dụng để tổng hợp hydrogel dựa trên thủy tinh lỏng và natri lignosulfonat. Rượu isopropyl được sử dụng để thay thế hàm lượng nước trong cấu trúc hydrogel, ngăn ngừa sự co ngót tuyến tính và duy trì nó trong khoảng từ 1% đến 4,8%. Sau đó, các hydrogel này được sấy khô siêu tới hạn ở 40°C và áp suất 12 MPa trong thiết bị 250 mL cùng với mức tiêu thụ CO_2 siêu tới hạn là 100 Nl/h, tạo ra một aerogel lai có diện tích bề mặt riêng đạt 483 m^2/g. Các aerogel thu được có cấu trúc vi mô xốp với kích thước lỗ trung bình nằm trong khoảng từ 3 đến 50 nm và tổng thể tích lỗ rỗng nằm trong khoảng từ 0,27 đến 2,19 cm^3/g. Những vật liệu aerogel lai này có mật độ thấp, giá trị nhận được là 0,055 g/cm^3.

Từ khóa: *Aerogel; sấy siêu tới hạn; silic đioxit; natri lignosulfonat.*

Received: 22/02/2023; Revised: 27/03/2023; Accepted: 20/04/2023; Published: 27/04/2023

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