Preparation and researching the properties of organic aerogels based on epoxy resins

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Abstract. The aim of this work was to develop methods for the synthesis of organic gels based on epoxy resins and the production of their aerogels. In general, aerogels are obtained from gel samples that consist of a high-molecular spatial network and a low-molecular dispersion medium - solvent. Various drying methods are used to remove liquid from gel pores, the most reliable of which, allowing to obtain samples of aerogels with undamaged spatial structure, is drying in supercritical fluid medium. As a result of the work the aerogels of different density were obtained, the dependence of density on the solvent content in the samples was revealed. The obtained aerogels were characterized by density, studied by infrared spectroscopy to assess the degree of polymerization of the resin, as well as using the BET method to determine the specific surface area of the samples and obtain its dependence on the catalyst content and curing conditions.

1. Introduction
To date, much attention has been paid to obtaining, studying the properties and introducing into production aerogels - highly porous solid gels in which the liquid phase has been completely replaced by the gas phase. Due to the fact that in the pores of the aerogel is a gas rather than a liquid, these substances have an extremely low volume density (the lightest have a density of about 0.001 g/cm³ [1]). They also demonstrate a number of properties unique to these materials, such as high strength, sorption capacity [2], low thermal and acoustic conductivity [3] etc.

The method of aerogel production consists of two stages: preparation of gels, whose pores are filled with solvent, and removal of liquid solvent with its replacement by gas. There are three main methods for drying gels in total: heating to boiling point of the solvent, freeze drying and supercritical drying. The first method is not suitable for the production of aerogels, as the transition of the solvent from the liquid phase to the gas phase due to the capillary effect and the huge surface tension (inversely proportional to the pore radius) breaks the gel structure.

The method of freeze drying (lyophilic drying) is based on sublimation of the solvent in cryogenic conditions in vacuum bypassing the liquid phase and, accordingly, the negative effect of the capillary effect. The result is a gel in whose pores the liquid was replaced by gas. However, this method is not suitable for drying, for example, hydrogels, where water acts as a solvent, because it expands when frozen, so that the structure of the gel can be destroyed. This is why the gels thus dried are released under the name of cryogels [1].
The method of supercritical drying, similar to the method of freeze drying, is based on the transfer of liquid to the gas without the formation of a mobile interface and, accordingly, capillary effects. The sample is placed in a reaction vessel and the pressure and temperature in it is raised to values above the critical for the solvent. The solvent passes from the liquid state to the supercritical state (supercritical fluid), in which the surface tension forces are no longer present - as a consequence, there is no capillary effect either. The pressure in the vessel is then changed so that the solvent is transferred from the supercritical state to the gaseous state and is removed from the vessel. This process results in an aerogel with an undamaged spatial structure [1]. Due to the fact that for organic solvents the critical values of pressure and temperature are rather high (for example, 4.7 MPa and 235.5 °C for acetone, 21.8 MPa and 374 °C for water), their achievement is very difficult, while for carbon dioxide the critical values are only 7.3 MPa and 35 °C. Therefore, supercritical drying is divided into "cold" using the supercritical fluid of carbon dioxide and "hot", where the critical pressure and temperature are reached for the solvent used [3].

The most common are aerogels obtained from various inorganic (SiO2, TiO2, Fe2O3, etc.) and carbon materials. Such aerogels are used as protective coatings for walls, ceilings and parts of equipment exposed to heavy wear and tear; as liquid and gas filters, and as space dust traps on the Stardast. In addition, aerogels can be obtained from organic materials (polyvinyl alcohol, cellulose, xanthan, polyisocyanates, etc.) [1, 4]. Some of these aerogels can be used in various bio compatible systems. Others are used as additives in combined organic-inorganic aerogels to increase strength and plasticity [1]. The structure and properties of aerogels based on resorcinol-formaldehyde resins have been most well researched [5], which, for example, showed lower thermal conductivity than silica aerogels (0.012 W/m*K versus 0.016 W/m*K) [6], they are also promising for use as separators of gases and liquids, sorbents for contaminants, precursors for carbon nanoparticles and aerogels, which are considered as components of promising energy sources. [1]. At the same time, there is no data in the literature on the use of epoxy resins and binders based on them to produce organic aerogels of no less well-known and very widely used polymers forming a strong three-dimensional network [7, 8]. Epoxy resins are a large class of compounds containing oxirane cycles, capable of forming various 3D cross-linked structures under the action of various hardeners (polyamines, carboxylic acid anhydrides, etc.).

Therefore, the purpose of this work was to develop a methodology for obtaining gels and aerogels based on epoxy resins, to study their thermophysical properties, as well as to evaluate the specific surface area and determine their possible applications.

2. Experimental

For the production of gels based on epoxy resin as reagents for the initial mixture took: epoxy diene resin ED-20 (based on DGEBA, the manufacturer of FKP "Zavod im. Sverdlovs Plant", 22,8-23 wt.% of epoxy groups, Figure 1 (a)), curing catalyst 2,4,6-bis(dimethylamine methyl)phenol (alkphen, DMP-30, Figure 1 (b)), acetone (ch.p.), CO2 (ch.p.).

(a)  

(b)

Figure 1. Structural formulas of initial compounds - ED-20 epoxy resin (a) and 2,4,6 bis(dimethylamine methyl)phenol (b).

2.1. Gel synthesis
In the process of preparation of the mixture to the resin attachment the calculated amount of acetone was added so that the total acetone content in the samples changed from 20 to 80 wt% (A-20, A-40, A-60 and A-80, respectively), and then a catalyst curing 1 wt%. After that the obtained mixtures were thermostatically controlled at 50°C for 5 in hermetically sealed polypropylene ampoules.

In the second series in ED-20 solutions with acetone concentration of 60 and 80 wt% varied catalyst concentration from 1 to 10 wt%: A-60 series (x = 1, 2, 3, 4, 5, 10 wt %) and A-80 series (x = 3, 5, 10 wt %). After that the received mixtures were thermostatically staticked at temperature 50°C during 15 days in hermetically sealed polypropylene ampoules.

Density of initial solutions at 23°C was determined by pycnometric method.

At the end of the resin curing process, the samples were washed in acetone for 1 week (acetone was changed daily). The samples were then dried in a CO₂ supercritical fluid atmosphere.

2.2. Supercritical drying
Drying was carried out on R250Sys Thar Instruments. The sample was placed in the reactor, which was then filled with liquid CO2 and heated to 35°C. The pressure in the vessel was gradually increased to 250 bar and it was kept in the vessel for 5 minutes, then reduced to 80 bar and then raised again to 250 bar. The cycle was repeated 10 times, after which the samples were taken out of the reaction vessel.

2.3. Characterization of aerogels
The bulk densities of the samples were calculated by their mass to volume ratio. Aerogels’ shrinkage was estimated by the change of their geometric volume compared to the geometric volume of wet gels.

IR spectra of samples were recorded using the Alpha Bruker FTIR spectrometer (KBr tablets).

The specific surface area values were determined using a 5-point Brunauer, Emmett and Teller (BET) method at the relative pressure range of P/P0 = 0.05–0.25; the correlation coefficients of the corresponding linear regressions in the coordinates of the BET equation were not less than 0.9975. Pore volume distributions were determined according to the Barrett, Joyner and Halenda (BJH) method, by the analysis of a desorption branch of an adsorption-desorption isotherm (28 points). Prior to measurements, samples were flushed with a dry helium flow for 16 hours at 45°C (Quadrasorb SI) or vacuum dried at room temperature (Autosorb-1 Quantachrome).

3. Results and discussing
The polymerization reaction in the mixture ED-20 - DMP-30 - acetone took place according to the scheme shown in Figure 2.

![Figure 2. Schematic representation of epoxy resin polymerization process.](image)

As a result of curing of ED-20 epoxy resin it was possible to obtain samples of cross-linked polymers in the form of gels at the concentrations of solvent 20, 40, 60 and 80 wt %, the photos of which before and after SC-drying are shown in Figure 3. Samples of A-20 and A-40, transparent solid and heavy cylinders, are gradually covered with cracks at long exposure times both without and after SC-drying (Figure 3 (a - c)). Samples of A-60 and A-80 are opaque, after SC drying they become noticeably lighter than the hardened resin and samples of A-20 and A-40. But A-60 occupies the whole volume corresponding to the initial solution, and A-80 occupies from 20 to 50 % of the initial volume.
It can be noted that the color of dried samples correlates with the concentration of the hardener - the more it is, the more saturated the color (Figure 3 (d - g, i - k)). It should also be noted that samples for a long time even after SC-drying, vacuuming and / or heating to 100°C retain a weak aroma of acetone, which disappears in the samples of series A-60 and A-80 only after prolonged (more than 100 hours) vacuuming at room temperature or heating above 130°C. As a result of the latter, samples of all series are significantly reduced in size and their density is close to that of the cured resin.

Figure 4 shows the type of dependencies of density of initial solutions and samples of obtained aerogels on acetone content in them. As expected, the density of the initial solutions changes smoothly. The density of samples with acetone content of 20 and 40 wt.% after SC drying is close to the density of cured resin, and with increasing acetone content it decreases sharply. At change of quantity of the curing catalyst in samples of A-60 and A-80 series the density practically does not change.

Figure 3. Type of gel samples A-20 - A-80 immediately after gel synthesis (a), A-20 after 1 week (b) and 1 month after synthesis (c), aerogels after SK drying: A-60-1, A-60-3, A-60-5, A-60-10 (d-g), and after trimming to measure the bulk density of A-60-1 (h), A-80-3, A-80-5, A-80-10 (i-k).
3.1. ИК-спектроскопический анализ

Analyzing the results obtained by infrared spectroscopy of SC-dried samples (Figure 6), one can draw conclusions about the close to quantitative course of the curing process of resin polymerization accompanied by the opening of epoxy groups. The infrared spectra shown in Figure 6(b) lack the characteristic absorption bands of the epoxy group in the region 971 and 915 cm\(^{-1}\), while in the infrared spectra of the ED-20 resin these bands are pronounced. In the spectra of samples with acetone content of 20 and 40 wt.%., shown in Figure 6, in the region 1710-1712 cm\(^{-1}\), there are absorption peaks corresponding to the fluctuations of the keto group C=0 acetone [9], from which we can conclude that the obtained samples even after drying contain a significant amount of acetone.

Figure 4. Dependence of the density of the stock solutions in acetone (a) and aerogels after SC drying (b) of the acetone content wt.%. 

(a)
(b)
3.2. Specific surface area estimation by Brunauer-Emmet-Teller (BET) method

The specific surface area was also determined for the samples by the BET method [9, 10, 11]. The research was carried out on two sorbetometers in order to evaluate the consistency of the results obtained with different methods of sample pre-treatment (vacuum drying and dry helium blowing). The results are presented in Figures 7 and Table 1.

Apparently, it is because of the fact that the number of catalysts in the samples of A-60-series differed, the values of specific surface area in them are reduced from 146 to ~7 m$^2$/g in proportion to the increase in DMP-30 concentration from 1 to 4 wt.%, and then virtually unchanged and remains equal to 6.4-7 m$^2$/g (Figure 7).

We believe that the reason for the reduction of the specific surface area of S may be a significant acceleration of resin polymerization with an increase in the catalyst content, as well as insufficient solubility of catalysis products in acetone, which is a complex with charge transfer, see Figure 1. The latter hypothesis is confirmed by the fact that when the order of application of the catalyst - addition to the resin and subsequent dissolution of the mixture in acetone, in the resulting mixture there is a flaky residue, which is not observed when the catalyst is added to drugs. It is also possible that gels with closed porosity are formed in samples with a large amount of catalyst, the area of which cannot be determined by the BET method.

Another factor affecting the size of the surface area is the duration of the curing process (Figure 7). Apparently, at a prolonged exposure at 50°C the polymer relaxing tightens pores or their estuaries as a result of nitrogen cannot penetrate into pores, adsorption can occur and the experimental value of the specific surface area is much lower than the real value.

Figure 5. IR-spectra of the resin ED-20 and samples A-20 - A-80 after SC drying: general view (a), in the region of oscillations of groups C=O (b) and oxirane cycle (c).

The spectra are normalized by the characteristic band of aliphatic CH2 group oscillations.
**Figure 6.** Dependence of specific surface area of samples on catalyst DMP-30 content.

**Table 1.** Dependence of density and specific surface of aerogel samples on the share of acetone in the initial mixture.

| Sample   | Share of acetone | Bulk density of acetone solution, g/cm³ | Bulk density after SC-drying, g/cm³ | Specific surface, m²/g | Autosorb-1 Quantachrome | Quadrasorb SI |
|----------|------------------|----------------------------------------|-------------------------------------|------------------------|--------------------------|----------------|
| A-60     | 0.603            | 0.920                                  | 0.481                               | 146                    | -                        | -              |
| A-60-1   | 0.605            | 0.919                                  | 0.512                               | 75,1-65,9              | 57,3-60,8                | -              |
| A-60-2   | 0.608            | 0.478                                  | -                                   | 22,8-23                | -                        | -              |
| A-60-3   | 0.562            | 0.478                                  | 0.565                               | -                      | 16,1                     | -              |
| A-60-4   | 0.616            | 0.487                                  | -                                   | 6,4                    | -                        | -              |
| A-60-5   | 0.621            | 0.491                                  | -                                   | 7,4                    | -                        | -              |
| A-60-10  | 0.641            | 0.598                                  | -                                   | 3,6-5,7                | <3                       | <3             |
| A-80-3   | 0.806            | 0.256                                  | 2,64                                | -                      | <3                       | <3             |
| A-80-5   | 0.810            | 0.842                                  | 0.220                               | -                      | <3                       | <3             |
| A-80-10  | 0.820            | 0.212                                  | 3,8                                 | -                      | <3                       | <3             |

For the A-80-x series, it has been noticed that the introduction of a large number of catalysts makes it possible to obtain gels of a larger volume (as the number of catalysts increases, the height of the resulting array increases and the bulk density decreases slightly). This can be explained by the fact that more embryos are formed simultaneously in a unit of volume and the resulting gel particles do not have time to precipitate, stick together and fill a larger volume of the solution.

With the Barrett, Joyner and Halenda (BJH) method determined pore volume distributions for sample A-60-1 (Figure 7(b)). The sample contains only mesopores and macropores.
The reason for the reduction of the specific surface area can be a significant acceleration of resin polymerization with increasing catalyst content. In this case, more resin comes into reaction and macromolecules are formed which do not have time to form a structure with a large number of pores. Another factor affecting the size of the surface area may be the duration of the curing process and the closing of pores by oligomeric molecules. As a result, nitrogen cannot be adsorbed in closed pores, and because of this, the experimental value of the specific surface area is much smaller than the real value.

A-60-1: total pore volume 0.47 cm$^3$/g, average pore radius 132 Å. The pores are slotted, the distribution shows the size in the mesopores area.

A-80-3: specific surface $S_{sp} = 2.64$ m$^2$/g, total pore volume $V_p = 0.026$ cm$^3$/g, average pore radius $r = 198$ Å.

A-80-10: specific surface $S_{sp} = 3.8$ m$^2$/g, total pore volume $V_p = 0.018$ cm$^3$/g, average pore radius $r = 93$ Å.

4. Conclusion
In the course of this work it was possible to develop an experimental methodology for the synthesis of gels based on epoxy resins; the possibility of obtaining aerogel samples from them was shown. IR-spectroscopic analysis showed almost quantitative process of epoxy resin polymerization and presence of solvent in some samples after drying in the atmosphere of supercritical fluid. Primary data on the properties of epoxy resin-based aerogels were obtained. The BET method for gel and aerogel samples evaluated the specific surface area and specific compressive strength characteristics. It was shown that aerogel samples have rather low density (~0.5 g/cm$^3$ - 0.2 g/cm$^3$). The dependences of density and specific surface area values on the curing catalyst content and on the acetone content have been obtained.

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