Synthesis and Properties of Organic Xerogels from Pine Bark and Wood Polyphenols

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Abstract. The paper describes a promising route for the synthesis of novel organic xerogels from naturally occurring, renewable resources using pine-derived polyphenols as suitable initial precursors with relatively low cost. Methods of organic xerogels synthesis based on the use of condensed tannins and ethanol lignin isolated respectively from pine bark and wood are proposed. The effect of cross-linking agent nature – formaldehyde or furfuryl alcohol on the porous structure of resulting organic tannin (lignin)-formaldehyde and tannin (lignin)-furfuryl xerogels was established. Denser tannin-formaldehyde xerogels are subjected to shrinkage (up to 50 %) in processes of drying, and their bulk density ranges in 0.73–0.80 g/cm^3. Porous tannin-furfuryl xerogels almost do not shrink at drying and have bulk density 0.30–0.42 g/cm^3. The addition of ethanol lignin to the reaction mixture decreases the shrinkage of organic xerogels, whereas the addition of surfactant has a weak effect on the shrinkage. The chemical and porous structure of organic xerogels was investigated by FTIR, BET and SEM methods. FTIR results showed that lignin-containing xerogel possesses more numerous surface functional groups due to an inclusion of ethanol lignin in the gel structure. According to SEM, the three-dimensional network is characteristic for tannin-formaldehyde xerogels which is built from crosslinked polymer chains formed by globular particles with size about 40–50 nm. The tannin-furfuryl xerogels structure is formed by large agglomerates of particles with size up to 100–150 nm.

Keywords: pine tannin, ethanol lignin, organic xerogels, microstructure, porosity.

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Синтез и свойства органических ксерогелей
на основе полифенолов коры и древесины сосны

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Аннотация. В статье описывается перспективный путь синтеза новых органических ксерогелей из природных возобновляемых ресурсов с использованием полифенолов сосны в качестве подходящих исходных предшественников с относительно низкой стоимостью. Предложены методы синтеза органических ксерогелей, основанные на использовании конденсированных дубильных веществ и этаноллигнина, выделенных соответственно из коры и древесины сосны. Установлено влияние природы сшивающего агента – формальдегида или фурфурилового спирта на пористую структуру образующихся органических таннин(лигнин)-формальдегидных и таннин(лигнин)-фурфуриловых ксерогелей. Более плотные таннин-формальдегидные ксерогели подвержены усадке (до 50 %) в процессах сушки, и их насыпная плотность колеблется в пределах 0,73–0,80 г/см³. Пористые таннин-фурфуриловые ксерогели практически не дают усадки при высыхании и имеют насыпную плотность 0,30–0,42 г/см³. Добавление в реакционную смесь этаноллигнина снижает усадку органических ксерогелей, а добавление ПАВ слабо влияет на усадку. Химическую и пористую структуру органических ксерогелей исследовали методами FTIR, BET и SEM. Результаты ИК-Фурье показали, что ксерогель, содержащий лигнин, имеет большее количество поверхностных функциональных групп за счет включения в структуру геля этаноллигнина. По данным СЭМ, для таннин-формальдегидных ксерогелей характерна трехмерная сетка, построенная из сшитых полимерных цепей, образованных глобулярными частицами размером около 40–50 нм. Структура таннин-фурфуриловых ксерогелей образована крупными агломератами частиц размером до 100–150 нм.

Ключевые слова: сосновый таннин, этаноллигнин, органические ксерогели, микроструктура, пористость.

1. Introduction

In recent years, researchers pay considerable attention to the modification and optimization of methods for producing porous materials and polymers, in particular, organic and carbon aerogels – porous materials with three-dimensional nano-network structure. The known methods of organic gels synthesis are based on sol-gel polycondensation reactions of phenol, resorcinol, catechol, cresol and other polyphenol compounds with aldehyde (formaldehyde etc.) in a suitable solvent and following drying at special conditions (subcritical, supercritical or ambient drying) [1–4]. The improving methods of synthesis of organic gels using renewable wood biomass as raw materials are an actual research task [5–7]. In recent years the more environmentally friendly plant polyphenols such as tannins and lignin are used for synthesizes of polymer gels and resins [2, 6–9].

However, the major issue limiting is that the preparation of the most organic aerogels needs such expensive and time-consuming synthesis cycle as including drying step [10, 11]. Rigorous drying conditions (especially freeze drying and supercritical CO_2 drying) inevitably required because of the surface tension of liquids during drying [1, 2]. Therefore, replacing costly supercritical drying step by a simple, subcritical drying would be much cheaper and easier. Such more cost-effective method of drying of organic gels is for as drying at ambient conditions.

The commercial tannins isolated from bark or wood of acacia and mimosa (named wattle and quebracho tannins) have received the greatest demand in the gel synthesis. The base structural units of condensed quebracho tannins are mainly flavonoids of prorobinetidine (acacia) or prophisetinidine (mimosa) types [6, 9, 12, 13]. Procyanidin-type condensed tannins extracted from pine bark (*Pinus radiate, Pinus pinaster*) were used too to prepare the tannin-based foams with promising properties as insulation materials [14]. All of these types of tannin are typical representatives of phenol substances of pyrocatechol group and they are considered as condensed products of two or more units of flavan-3-(di-)ols.

A bark of Siberian pine *(Pinus Silver. Ros)* also is a perspective source of condensed tannins presented mainly by oligomers of procianidine and prodelfinidine flavonoids [15]. Therefore they will interact with aldehydes to form cross-links, as is the case with resorcinol- or phenol-formaldehyde systems [13, 16].

Lignin, as known, is polyphenol substance with reactive hydroxyl groups. So it can partially replace more expensive phenolic compounds of natural (tannins) or synthetic (resorcinol) origin in gelation reactions with aldehydes [9, 17]. Lignin isolated from a wood by using organic solvents, being a sulfur-free material is a more suitable source for synthesis of aerogels [8, 17, 18]. The use of branched lignin macromolecules in polycondensation reactions makes it possible to regulate the texture characteristics of resulting gels [8, 9, 19]. Despite the growing interest in the use of lignin as

a rich raw-material for the production of new functional materials, there are few studies on the use of organosolv lignins for the preparation of the corresponding aerogels.

It is known, the one strategy for minimizing shrinkage during the drying process may consist in using surfactants [20]. Surfactants able to decrease the surface tension of the solution to be evaporated, thus introducing additional porosity of gels. However, the influence of surfactants aimed for regulating the porosity of gels to shrinkage prevention on the solvent/polymer interface into pores at gel drying is ambiguity [13, 21].

Formaldehyde is the most widely used cross-linking agent in the synthesis of organic gels [9, 12]. Besides, such furan compounds as furfural aldehyde and furfuryl alcohol have also ability to participate in crosslinking reactions to chain or consecutive polymerization that supplies the obtaining of materials with valuable properties (foams, fibers, elastomers and others) [2, 6, 14, 22]. The furfuryl alcohol is the most important furan derivative produced on an industrial scale from hemicelluloses which contained in biomass [23], and it has a wide ranges of applications [7, 14, 22].

The present research has focused on the synthesis of organic xerogels prepared from pine tannins and additives of the ethanol lignin or surfactant, taken in various ratios with cross-linkers. In the given work, we have developed a sustainable and economical synthesis of organic xerogels on bases of polyphenol substances, isolated from pine bark (tannin) and from pine wood (ethanol lignin), performed using polycondensation reactions with formaldehyde or furfuryl alcohol, and by subsequent ambient condition drying. As a result of the study, the influence of the nature of polyphenols (tannins and ethanol lignin) and crosslinking agents (formaldehyde and furfuryl alcohol), ratio of polyphenol/ crosslinking agent and surfactant additives on the porous structure of the resulting gels was established. A special attention was dedicated to the different shrinkages occurring during the elaboration process. A thorough structural characterization of the obtained xerogels and their properties was carried out.

2. Experiments

2.1. Materials

The pine tannins (*T*) extracted by ethanol from the bark of Siberian pine (*Pine Silver Ros.*) were used for gel synthesis. The pine tannin extract (C – 57.3; H – 6.5; ash – 0.4 % mass) had a weight average molecular weight (M_W) of 1132 g/mol and a polydispersity of 1.915. The ethanol lignin (*L*) was isolated by pine wood treatment with 60 % ethanol solution at the temperature 180 °C according to technique described in [24]. The elemental lignin composition is: C – 67.0; H – 6.3; ash – 0.25 (% mass). The furfuryl alcohol of analytical grade (Belgium) was used as 98 % solution without additional purification. The 37 % solution of formaldehyde (Metafrax, Russia) was analytically grade. The non-ionic monooleate sorbitan Span®80 ($C_{24}H_{44}O_6$, Germany) of analytical grade was used as surfactant (S). The formaldehyde (*F*) and furfuryl alcohol (*FA*) were used as crosslinking agents.

2.2. Preparation of xerogel samples

Preparation of organic tannin-(lignin)-formaldehyde (*T+L*)/*F* alcohol gels was carried out in ethanol medium according to technique described in [9]. Synthesis of tannin-(lignin)-furfuryl (*T+L*)/*FA* gels was carried out with use of furfuryl alcohol according to technique described in [25] with some modification.

In typical experiment the polyphenolic substances were dissolved in ethanol in the required concentration and then formaldehyde solution was added. The mass ratios of polyphenolic component (tannin and lignin) to crosslinking agent (formaldehyde or furfuryl alcohol) were 1:1.5 and 1:2. The pH was adjusted to 3 for all samples by addition of 37 % HCl. The homogenous reaction mixture was placed in hermetically closed 25 ml glass tube and was kept at temperature 75±2 °C for 5 days in ventilated oven. After that the formed gels were removed from test tubes in the form of cylindrical samples and cut into fragments 15–20 mm in size. The samples were placed in a flask with ethanol, which was gently shaken using an orbital shaker at temperature 40 °C for three days. Ethanol was replaced daily to remove by-products of polycondensation from the pores of the gel.

Then the resulting gel samples were dried to a constant weight at 60 °C using a rotor evaporator under the ambient conditions.

2.3. Physico-chemical characterization

IR absorption spectra of organic xerogels were registered on FTIR spectrometer Shimadzu IR Tracer-100 in the range 4000–400 cm^{-1} with a resolution of 4 cm^{-1}. The samples were pressed in *KBr* matrix (3.0 mg/997 mg of the matrix). The spectral information processing was performed using the LabSolution IR software package.

The porous characteristics of xerogels were determined using the automatic adsorption analyzer ASAP 2020 (Micromeritics, USA). The nitrogen adsorption/desorption isotherms were measured at –196 °C in relative pressure (P/P_0) range from 0.005 to 0.995. The samples were preliminary degassed at temperature 80 °C under vacuum for 24 hours. The next parameters were used to characterize the porous structure: specific surface area determined by BET-method from adsorption branch of isotherm (S_{BET}), total pore volume calculated from N_2 adsorbed volume at P/Po ≥ 0.995 (V_{tot}). The calculations of micropore volume (V_{micro}) and micropore surface area (S_{micro}) were done with the use t-plot method, and micropore diameters were calculated by *DFT* method. The mesopore volume (V_{meso}) and average mesopore diameter (D_{meso}) were calculated from desorption curve of the adsorption isotherm, using of Barrett-Johner-Halendar model (BJH).

The apparent density ρ_{app} (g/cm^3) of the organic xerogel was calculated as a ratio between the mass of the crushed sample and the volume occupied by it using the results of three parallel measurements.

The CHN elemental analysis of samples was conducted on a Thermo Quest Flash EA-1112 elemental analyzer (Italy).

The microstructure of the samples was studied by scanning electron microscopy in secondary electrons with the use of SEM S 5500 (Hitachi, Japan). The samples were preliminary covered by platinum (about 1.5 nm) with the use of magnetron sputter coater K575X (England).

3. Results and discussion

3.1. Investigation of physico-chemical characteristics

The tannins and ethanol lignin isolated from pine bark and wood respectively were used for organic gel syntheses. The mixing of tannin pine extract (*T*) and formaldehyde *(F)* in a mass ratio 1:1.5 and 1:2 at room temperature leads to fast gel formation in both cases. The point of gel formation that is characterized the ability of the mixture to polymerize was achieved in the first case during the first

minute and in the second one for 10 minutes after mixing of the components. Thus formaldehyde can easy react with tannin molecules providing a crosslinking effect.

The photographs of the organic xerogels that retain the shape of blocks after stages of ageing, purification and vacuum drying are presented on Fig.1. The resulting tannin- formaldehyde xerogel (in proportion 1:1.5) prepared without any additives is a tight monolith block of brown color with smooth surface (Fig. 1a). The increase of T/F ratio to 1:2 results in the formation of looser xerogel with bulk density 0.73 g/cm^3 (Table 1).

The tannin-formaldehyde xerogels obtained under conventional drying conditions were very dense as subject to strong shrinkage (up 50 %) that is likely correlates to pore size. These xerogels have more bulk density (0.73–0.78 g/cm^3) as compared to T/F gel synthesized by us earlier in analogical manner from fir tannin but dried with using of freeze dryer (0.67 g/cm^3) [19]. As received in literature, narrower pores lead to higher capillary stresses and hence to higher volume losses upon drying [13]. The known organic T/F aerogels on the bases of querbacho tannins have yet the less bulk density values (0.44–0.56 g/cm^3) owing to their supercritical drying that minimizes the shrinkage [12].

The more visible variations in the block form of organic xerogel (Fig.1b) and its density are observed after the ethanol lignin (L) addition in quantity of 50 % to tannin mass. After drying it has the brown color and was less smooth surface characterized and lower bulk density (0.60 g/cm^3) in comparison with tannin-formaldehyde xerogel. During the drying its shrinkage was 30–35 %. It is known that the additions of lignin in the synthesis of aerogels and cryogels can reduce the shrinkage of the gel because

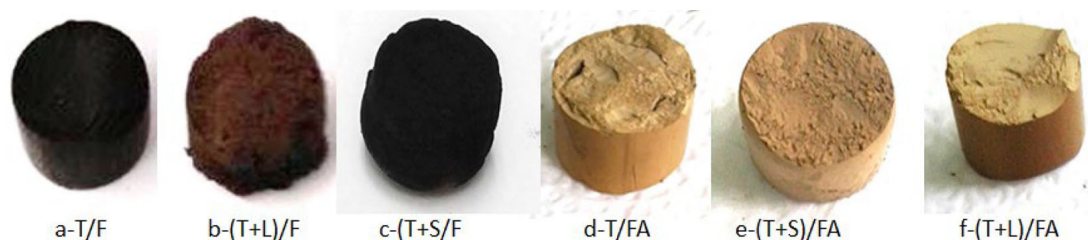a-T/F   b-(T+L)/F   c-(T+S)/F   d-T/FA   e-(T+S)/FA   f-(T+L)/FA

Fig. 1. Photographs of the samples of tannin-formaldehyde (a-c) and tannin-furfuryl (d-f) xerogels

Table 1. Characteristics of organic pine tannin-derived xerogels

Xerogel samples	Component proportion	C, % mass.	H, % mass.	Bulk density ρ, g/cm^3
T/F	1.0:1.5	63.5	6.3	0.78
T/F	1:2	60.4	5.2	0.73
(T+S)/F	1.0:1.5	62.4	6.1	0.80
(T+L)/F	1.0:1.5	65.9	4.6	0.60
T/FA	1.0:1.5	65.3	4.9	0.36
T/FA	1:2	66.0	5.3	0.42
(T+L)/FA	1.0:1.5	66.8	4.8	0.50
(T+S)/FA	1.0:1.5	64.7	5.1	0.30

large lignin molecules contribute to the formation of macropores during polycondensation [18, 26]. The obtained (*T*+*L*)/*F* xerogel probably is a copolymer of tannin and lignin macromolecules.

As noticed above, the addition of surfactant to reaction mixture can to decrease shrinkage of organic gel at drying. This effect may depend on the nature and concentration of the initial components, as well as on the strength of the crosslinking and the size of particles forming the gel [21]. We revealed that the addition of surfactant SPAN®80 to the *T*/*F* mixture did not prevent the shrinkage of the (*T*+*S*)/*F* xerogel at drying. On the contrary, the surfactant contributes to the formation of slightly more dense packing and increases bulk density of the resulting gel to 0.80 g/cm^3 (Table 1). During drying in vacuum, the sample *(T+S)/F* was subjected to shrinkage and become brittle, that led to partially destruction.

When furfuryl alcohol is used as crosslinking agent, the resulting gels are produced in the form of monolith blocks after heating at 73–75 °C for 2–3 hours. The gelation process in this case is longer than using formaldehyde due to the lower reactivity of furfuryl alcohol [27]. *T*/*FA* xerogels looking as the rigid and light blocks of yellow-brown color were obtained after drying (Fig.1d-e) The resulting sample with a *T*/*FA* ratio of 1:1.5 has extended cavities (Fig. 1d), and its bulk density is 0.36 g/cm^3. The appearance of these cavities is probably due to the fact that at low concentration of *FA* the resulting sol does not form a continuous polymer network, as observed for phenol-furfural gels [25].

The addition of pine ethanol lignin to tannin-furfuryl mixture (1:1.5) increases the bulk density of the xerogel (*T*+*L*)/*FA* from 0.36 to 0.50 g/cm^3. In contrast, the addition of surfactant to the *T*/*FA* mixture decreases the bulk density of the resulting gel to 0.30 g/cm^3. The samples of *(T+L)/FA* and *(T+S)/FA* gels after drying have no visible caverns in their texture (Fig. 1e, f).

In the case of the sample with *T*/*FA* ratio 1:2 the time of gel formation is decreased due to higher concentration sol particles. The increase in the number of crosslinks during polycondensation leads to a decrease in the size of the particles forming the gel and to the reinforcement of the gel. Along with the formation of a large number of crosslinks between tannin aromatic rings, the formation of methyl bridges between two furan rings is possible. The ability of furfuryl alcohol to undergo polycondensation in an acidic medium was reported in [27]. After drying the *T*/*FA* (1:2) xerogel keeps the shape of monolithic block with bulk density of 0.42 g/cm^3.

It is known that the shrinkage of organic gels takes place either due to the fragile network of the gel or due to the high capillary pressure inside of micropores of the gel matrix [9, 17, 21]. The density of cross-linking in gel precursors has significant effect on its microstructure and bulk density. Probably in our case the ethanol lignin acts as co-reagent in (*T*+*L*)/*FA* system and promotes the formation of additional links with furfuryl alcohol participation. The reduction of bulk density of the xerogel (*T*+*S*)/*FA* (1:1.5) is probably due to the weak fixation of surfactant molecules in gel matrix therefore; its molecules release the pores in the process of washing the gel with ethanol.

3.2. Microstructure and morphology

The morphology of tannin-containing xerogels obtained with the use of formaldehyde was characterized by SEM method. The cross-section images of organic xerogels of different composition are presented on Fig. 2. The matrix of *T*/*F* xerogel is formed by compact globular particles with size about 40–50 nm which are closely connected in chains forming a developed spatially cross-linked structure (Fig. 2a). The porous structure of this sample is represented by uniformly distributed pores
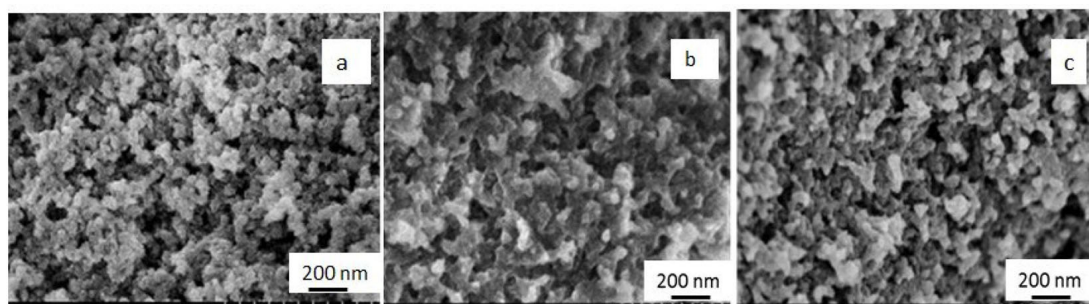
Fig. 2. SEM images of the organic tannin-formaldehyde xerogels

of 30–70 nm in size and by a few labyrinth channels between polymer chains with sizes up to 100 nm. The structure of *T*/*F* xerogel is very similar to resorcinol-formaldehyde and tannin-formaldehyde gels reported in literature [13, 16].

The spatial structure of (*T+S*)/*F* xerogel is less branched and more tough (Fig. 2b). It is based on a compact packing of rough spherical particles of distorted shape with a sizes ≤ 50 nm which form a matrix of with pores of preferred sizes 50–100 nm. The addition of surfactant slightly changes the porosity of T/F xerogel. The matrix of (*T+L*)/*F* sample (Fig. 2c) is formed mainly from conjoined globules with size about 50 nm and its structure contains the separate aggregates up to 200–250 nm in size. The pores distribution patterns in the matrix of this sample is less uniform compared to *T*/*F* xerogel. The average size of the pores is about 50 nm and there are open cavities up to 100 nm in size between particle aggregates.

As clearly seen from Fig.3, the internal structures of organic xerogels obtained with the use of furfuryl alcohol as linking agent in ratios 1:1.5 and 1:2 are markedly different from those of tannin-formaldehyde xerogels. The matrix of the sample of *T*/*FA* (1:1.5) is constructed from aggregates of fused globular particles with a size about of 100–150 nm (Fig. 3a). The xerogel porous structure is represented by open meso- and macropores with sizes of 50–150 nm. There are also separate cavities up to 200–300 nm in size. The close accretion of small globules (50 nm) in chains provides greater mechanical strength of the xerogel and the stability of its spatial structure to compression. The presence
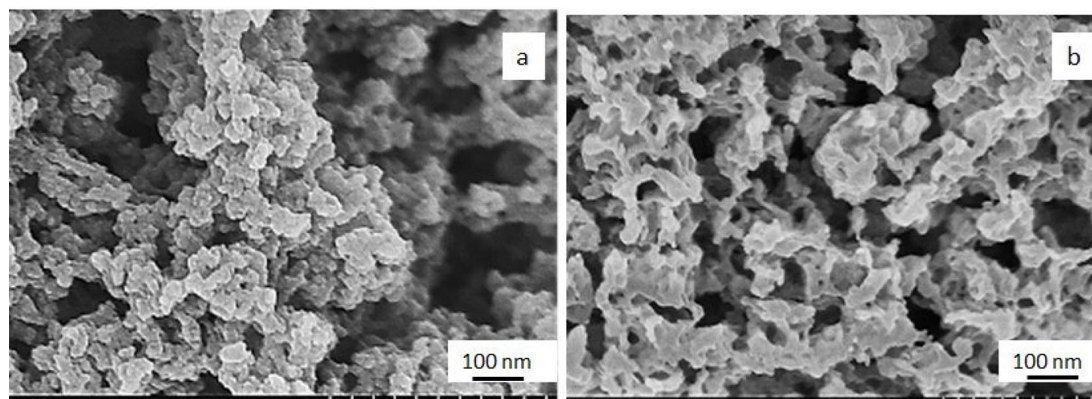

Fig. 3. SEM images of organic tannin-furfuryl xerogels in ratios: a – 1:1.5; b – 1:2

of relatively large numbers of voids between polymer chains contributes to the reduction of the density of *T/FA* xerogel.

At increase in the *T/FA* ratio from 1.5 to 2 changes the shape of the particles forming a rigid xerogel framework (Fig. 3b). The separate small particles (50 nm) are not observed in this structure. The closely spaced particles form a matrix with wide variety of labyrinth pores in shape and size (from units to hundreds of nanometers). The number of open pores and their dimension between xerogel particles is decreased with the increase of *T/FA* ratio. The absence of typical for organic xerogels nodular network structure allows classifying *T/FA* (1:2) sample to aerogel foams [6, 22].

According to SEM data the structures of tannin-furfuryl xerogels with the additives of lignin and surfactant (images not shown) are formed by aggregated particles of irregular shape and size (50–150 nm). The *(T+S)/FA* sample has a rough surface with large unstructured hollow cells. Some particles stick together into big aggregates about 1 μm size.

Comparison of the xerogels structure synthesized with the use of formaldehyde and furfuryl alcohol shows that *T/F* xerogel has more closely packing structure and small number of macropores. Sample of *T/FA* gel has less ordered structure and tight particle association in rigid cavernous matrix with large pores. Probably, during condensation process the formaldehyde molecules form more crosslinks with tannins than larger furfuryl alcohol molecules. As a result, *T/F* xerogel has a denser structure than *T/FA* gel.

3.3. Porous texture characteristics

Isotherms of nitrogen adsorption–desorption at –196 °C on the samples of tannin-formaldehyde (Fig. 4a) and tannin-furfuryl (Fig. 4b) organic xerogels (1:1.5) correspond to IV type typical for mesoporous materials [28].

The hysteresis loops inherent type IV isotherms indicate the condensation of nitrogen molecules in mesopores. The wider hysteresis loops and earlier start of capillary condensation indicate a wider pore size distribution in *(T+L)/F* sample (Fig. 4a, curve 1) compared to *T/F* one (Fig. 4a, curve 2) [12].

Presented in Table 2 data demonstrate such characteristics of porous structure of xerogels as specific surface area (S_{BET}), total pore volume (V_{tot}), diameter of pores (D_{pore}) and specific surface of micropores (S_{micro}). As seen, the main characteristics of porous structure of *T/F* (1:1.5) xerogel are
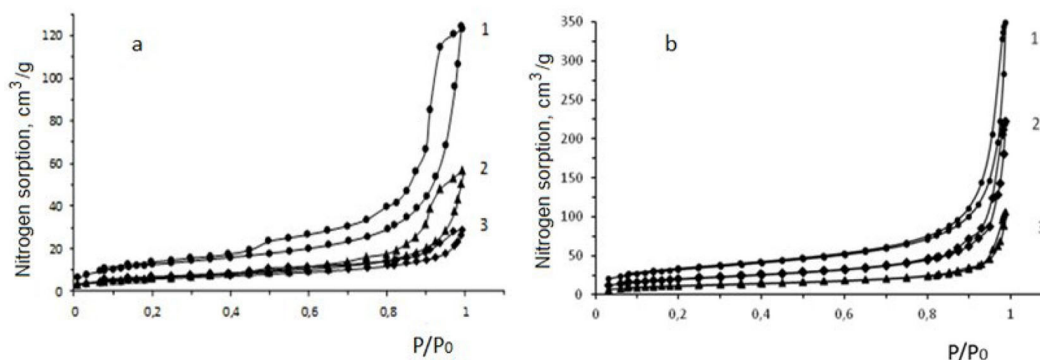

Fig. 4. Isotherms of N_2 adsorption-desorption on the tannin-formaldehyde (a): 1 – *(T+L)/F*, 2 – *T/F*, 3 – *(T+S)/F* and tannin-furfuryl samples (b): 1 – *T/FA*; 2 – *(T+S)/FA*; 3 – *(T+L)/FA* organic xerogels

Table 2. Characteristics of porous structure of tannin-formaldehyde and tannin-furfuryl organic xerogels

Sample	S_{BET}, м²/g	$V_{tot.}$, cm³/g	D_{pore}, nm	S_{micro}, m²/g	D_{meso}, nm	
					sorption	desorption
T/F, 1:1.5	21.1	0.05	4.1	4.0	6.4	4.6
(T+L)/F, 1:1.5	32.4	0.07	4.4	4.9	9.5	7.4
(T+S)/F, 1:1.5	15.5	0.06	4.3	2.3	12.1	10.9
T/F, 1:2	9.6	0.04	6.8	1.3	11.3	10.2
T/FA, 1:1.5	117.5	0.44	7.4	19.5	12.4	11.1
(T+S)/FA, 1:1.5	73.3	0.28	7.6	10.9	12.2	11.2
(T+L)/FA, 1:1.5	41.6	0.14	6.5	2.5	11.2	10.5
T/FA, 1:2	21.5	0.08	5.3	2.1	11.6	11.1

some changed in the presence of lignin and surfactant, and they vary within the following limits: S_{BET} between 15.5 and 32.4 m²/g; $V_{tot.}$ from 0.05 to 0.07 cm³/g; D_{pore} between 4.1 и 6.4 nm. The increase of T/F ratio to 1:2 in gel synthesis leads to a more pronounced reduction of the specific surface area of xerogel from 21.1 to 9.6 m²/g, surface area of micropores from 4.0 to 1.3 m²/g and to the increase of average pore diameter from 4.1 to 6.8 nm.

The sample of T/FA (1:1.5) xerogel has the higher values of S_{BET} 117.5 m²/g, S_{micro} 19.5 m²/g and V_{tot} 0.44 cm³/g. The additives of lignin and surfactant reduce these porous characteristics of tannin-furfuryl xerogels (Table 2). In a greater extend, to the decreasing in all parameters of porosity leads to the increase in the T/FA ratio from 1:1.5 to 1:2: the specific surface area declining from 117.5 to 21.5 m²/g, the average pore size from 7.4 to 5.3 nm, micropore surface from 19.5 to 2.1 m²/g and pore volume from 0.44 to 0.08 cm³/g.

The average pore diameter values (D_{meso}) calculated by BJH method are higher for T/FA xerogels (10.5–11.2 nm) than that for T/F samples. A close coincidence of the pore diameter values determined from adsorption and desorption isotherm may indicate a developed mesoporous structure of T/FA xerogels. A significant difference in the total pore volume for T/FA xerogels of various compositions (from 0.08 to 0.44 cm³/g) is probably due to the difference in the degree of cross linking of the gel framework during polycondensation of tannins with furfuryl alcohol.

3.4. FTIR-study

The chemical structure of organic xerogels was studied by FTIR method. It is revealed that the IR spectra of tannin-formaldehyde and tannin-furfuryl samples (Fig. 5) contain different absorption bands indicating the presence of significant number of functional groups and chemical bonds.

The wide absorption band for all samples in the region of 3400 cm⁻¹ belongs to the stretching vibrations of O–H absorption due to the phenolic and aliphatic hydroxyl groups. Absorption bands at 2970, 2930 and 2780 cm⁻¹ refer to vibrations of C–H bonds in CH_2- and CH_3-groups and in furan molecules. The intensive band at 1610 cm⁻¹ belongs to skeleton C–C vibrations of aromatic rings [29]. Absorption bands at 1460 and 1350 cm⁻¹ correspond to deformation vibrations of -CH_2- group in phenol structure [29]. The band around 1460 cm⁻¹ is associated with the formation of methylene bridges between the aromatic rings as described in the literature [18]. The presence of absorption bands
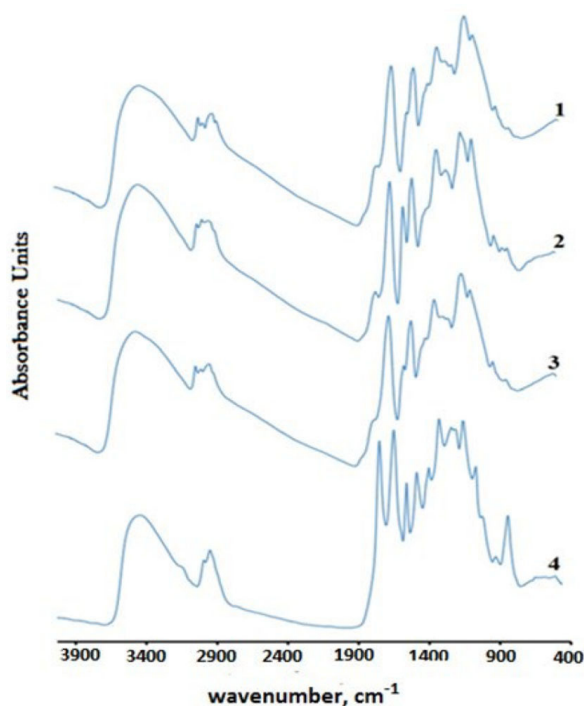
Fig. 5. FTIR spectra of organic xerogels (1:1.5): 1 – *T/F*; 2 – *(T+L)/F*; 3 – *(T+S)/F*; 4 – *(T+L)/FA*

in the region between 1194 and 1036 sm^{-1} indicates the formation during polycondensation process the methylene and methylene-etheric bridges which connect the aromatic rings [30].

The spectrum of *(T+L)/F* sample contains more complex functional groups due to the complicated linkages in the lignin component (Fig. 5, curve 2). An increasing in the intensity of absorption bands at 1278, 1034, 873 and 815 cm^{-1} characteristic of lignin of G-type (guaiacol) is observed that indicates the inclusion of ethanol lignin in the gel matrix during polycondensation process. Also, there is an observable peak at 1512 cm^{-1} in the IR spectrum of lignin-contained xerogel which is a characteristic peak for softwood lignin [18].

The IR spectrum of *(T+L)/FA* contain absorption bands at 1167 and 1020 cm^{-1}, which can be attributed to stretching vibrations of C–O–C bonds in -CH$_2$–O–CH$_2$- bridges or stretching vibrations of C-O bonds [30]. The absorption band at 1513 cm^{-1} likely indicates the present lignin in xerogel composition [18]. The increase of intensity of band at 1712 cm^{-1} that belongs to vibration of carbonyl group (–C=O) can point out the opening of the furan ring during polycondensation process [27]. The band at 789 cm^{-1} presented in spectrum of *T/FA* sample is characteristic of furan derivatives.

4. Conclusion

In summary, the novel organic xerogels synthesized by sol-gel polycondensation formaldehyde and furfuryl alcohol with non-toxic tannins and ethanol lignin isolated respectively from pine bark and wood were prepared by using a convenient drying process under reduced pressure. Correlations between synthesis parameters and final material properties were obtained. It was established that by

variation of the reaction mixture composition, and its ratios with crosslinking agent (formaldehyde or furfuryl alcohol) it is possible to regulate the characteristics of the porous structure of resulted xerogels and their properties.

It was found that the porosity of the tannin-formaldehyde T/F xerogels is lower than that of tannin-furfuryl xerogels. It depends in a greater extends from the nature of pine polyphenols and the crosslinking agent, as compared to the presence of surfactant additive. T/FA xerogels are stable to shrinkage and have lower density (0.3–0.42 cm^3/g), higher specific surface (up to 117.5 m^2/g) and pore volume (0.44 cm^3/g) compared to T/F xerogels. The microstructure of the tannin-formaldehyde xerogels is a spatially branched network of interconnected globular particles with a size about 40–50 nm in the case of tannin-formaldehyde xerogels. The tannin-furfuryl xerogels are formed by more large particles (up to 100 nm).

The knowledge gained in these studies, would allow researchers better to use as suitable pine-derived source tannins and organosolv lignin for a synthesis of organic and carbon xerogels.

References

[1] Vareda J.P., Lamy-Mendes A., Duraes L.A. Reconsideration on the definition of the term aerogel based on current drying trends. *Micropor Mesopor Mater. 2018*. 258, 211–216. http://dx.doi.org/10.1016/j.micromeso.2017.09.016.

[2] Szczurek A., Fierro V., Pizzi A., Stauber M., Celzard A. A new method for preparing tannin based foams. *Ind. Crops and Prod. 2014*. 54, 40–53. doi: 10.1016/j.indcrop.2014.01.012.

[3] Pierre A.C., Pajonk G.M. Chemistry of Aerogels and Their Applications. *Chem. Rev. 2002*. 102. 4243–4265. https://doi.org/10.1021/cr0101306.

[4] Rodrigues L.A., Parmentie J., Parra J.B., Thim G.P. Preparation of nodular carbon cryogel from simple and inexpensive polycondensation reaction of commercial modified black wattle tannin. *J. Sol-Gel Sci Technol. 2013*. 67, 519–526. https://doi.org/10.1007/s10971–013–3109–3.

[5] Zhao Sh., Malfait W.J., Guerrero-Alburquerque N., Koebel M.M., Nystrom G. Biopolymer Aerogels and Foams: Chemistry, Properties, and Applications. *Angew. Chem. Int. Ed. 2018*. 57. 7580–7608. https://doi.org/10.1002/ange.201709014.

[6] Pizzi A. Tannin-Based Biofoams, a Review. *Journal of Renewable Materials 2019*. 7(5), 477–492. http://dx.doi.org/10.32604/jrm.2019.06511.

[7] Delgado C., Santiago F.J., Fierro V., Pizzi A., Celzard A. Optimization of "green" tanninfuranic foams for thermal insulation by experimental design. *Materials and Design 2018*. 139, 7–15. https://doi.org/10.1016/j.matdes.2017.10.064.

[8] Mikova N.M., Ivanov I.P., Zhizhaev A.M., Tsyganova S.I., Kuznetsov B.N. Synthesis and Properties of Carbon Gels Based on Larch Bark Tannins and Hydrolysis Lignin. *Rus. J. Appl. Chem.* 2022. 95(3), 393–400. doi: 10.1134/S 1070427222030089.

[9] Grishechko L.I., Amaral-Labat G., Szczurek A., Fierro V., Kuznetsov B.N., Pizzi A., Celzard A. New tannin-lignin aerogels, *Ind. Crops Prod. 2013*. 41, 347–355. doi: 10.1016/j.indcrop.2012.04.052.

[10] Job N., The′ry A., Pirard R., Marien J., Kocon L., Rouzaud J.N., Béguin F., Pirard J.P. Carbon aerogels, cryogels and xerogels: influence of the drying method on the textural properties of porous carbon materials. *Carbon 2005*. 43(12), 481–2494. http://dx.doi.org/10.1016/j.carbon.2005.04.031.

[11] Kraiwattanawong K., Sano N., Tamon H. Influence of evaporation drying on the porous properties of carbon/carbon composite xerogels. *Polymers 2021*. 13(16), 2631. https://doi.org/10.3390/polym13162631.

[12] Amaral-Labat G., Szczurek A., Fierro V., Pizzi A., Celzard A. Systematic studies of tannin-formaldehyde aerogels: preparation and properties. *Sci Technol Adv Mater. 2013*. 14, 015001(13p). doi:10.1088/1468–6996/14/1/015001.

[13] Amaral-Labat G., Grishechko L. I., Fierro V., Kuznetsov B. N., Pizzi A., Celzard A. Tannin-based xerogels with distinctive porous structures. *Biomass and Bioenergy 2013*. Vol. 56, P. 437–445. doi:10.1016/j.biombioe.2013.06.001.

[14] Lacoste C., Pizzi A., Basso M–C., Laborie M-P., Celzard A. Pinus pinaster tannin/furanic foams: PART I. Formulation. *Ind. Crops Prod. 2014*. 52, 450–456. http://dx.doi.org/10.1016/j.indcrop.2013.10.044.

[15] Buzuc G. N., Lovkova M. Y., Ershik O. A., Sokolova S. M. A new source of Proanthocyanidins with antiarthritic activity: Purple marshlocks (Comarumpalustre L.) rhizome and roots. *Doklady Biochemistry and Biophysics 2008*. 421(1), 211–213. doi:10.1134/s1607672908040121.

[16] Tannert R., Schwan M., Ratke L. Reduction of shrinkage and brittleness for resorcinol-formaldehyde aerogels by means of a pH-controlled sol–gel process. *J. Supercritical Fluids 2015*. 106, 57–61. https://doi.org/10.1016/j.supflu.2015.06.021.

[17] Chen F., Xu M., Wang L., Li J. Preparation and characterization of organic aerogels by the lignin-resorcinol-formaldehyde copolymer. *BioResources 2011*. 6(2), 1262–1272.

[18] Jõul P., Ho T. T., Kallavus U., Konist A., Leiman K., Salm O.-S., Kulp M., Koel M., Lukk T. Characterization of Organosolv Lignins and Their Application in the Preparation of Aerogels. *Materials 2022*. 15. 2861. https://doi.org/10.3390/ma15082861.

[19] Mikova N. M., Levdanskiy V. A., Skwortsova G. P., Zhizhaev A. M., Lutoshkin M. A., Chesnokov N. V., Kuznetsov B. N. Structure and properties of organic xerogels derived from tannins and ethanol lignins of the Siberian fir. *Biomass Convers Biorefin. 2021*. 11, 1565–1573.

https://doi.org/10.1007/s13399–019–00561–8

[20] Worsley M. A., J. H. Satcher Jr., Baumann T. F. Influence of sodium dodecylbenzene sulfonate on the structure and properties of carbon aerogels. *J Non Cryst Sol. 2010*. 356(3), 172–174. https://doi.org/10.1016/j.jnoncrysol.2009.12.008.

[21] Wu D., Fu R. Requirements of organic gels for a successful ambient pressure drying preparation of carbon aerogels. *J. Porous Mater. 2008*. 15, 29–34. doi: 10.1007/s10934–006–9048–4.

[22] Basso M. C., Giovando S., Pizzi A., Celzard A., Fierro V. Tannin/furanic foams without blowing agents and formaldehyde. *Ind. Crops Prod. 2013*. 49, 17–22. https://doi.org/10.1016/j.indcrop.2013.04.043.

[23] Agirrezabal-Telleria I., Gandarias I., Arias P. L. Production of furfural from pentosan-rich biomass: Analysis of process parameters during simultaneous furfural stripping. *Bioresour Technol. 2013*. 143, 258–264. https://doi.org/10.1016/j.biortech.2013.05.082.

[24] Weinwurm F., Drljo A., Silva T. L.S., Friedl A. Principles of ethanol organosolv lignin precipitation: process simulation and energy demand. *Chemical Engineering Transactions 2014*. 39, 583–588. https://doi.org/10.3303/CET1439098.

[25] Wu D., Fu R. Fabrication and physical properties of organic and carbon aerogel derived from phenol and furfural. *J. Porous Materials 2005.* 12, 311–316.

[26] Grishechko L. I., Amaral-Labat G., Szczurek A., Fierro V., Kuznetsov B. N., Celzard A. Lignin-phenol-formaldehyde aerogels and cryogels. *Micropor. Mesopor. Mater. 2012.* 168, 19–29. https://doi.org/10.1016/j.micromeso.2012.09.024.

[27] Choura M., Belgacem N. M., Gandini A. Acid-catalyzed polycondensation of furfuryl alcohol: mechanisms of chromophore formation and cross-linking, *Macromolecules, 1996.* 29, 3839–3850. https://doi.org/10.1021/ma951522f.

[28] Gregg S. J., Sing K. S.W. Adsorption, Surface Area and Porosity, Academic Press, London etc., 1982, 303 https://doi.org/I:10.1149/1.2426447

[29] Pandey K. K. A study of chemical structure of soft and hardwood and wood polymers by FTIR spectroscopy. *Journal of Applied Polymer Science 1999.* 71(12), 1969–1975. https://doi.org/10.1002/(SICI)1097–4628(19990321)71:12 %3C 1969:: AID-APP6 %3E 3.0.CO;2-D

[30] Wen-Cui L., An-Hui L., Shu-Cai G. Characterization of the microstructures of organic and carbon aerogels based upon mixed cresol-formaldehyde. *Carbon 2001.* 39, 1989–1994. doi: https://doi.org/10.1016/S 0008–6223(01)00029-X