Carbohydrate Polymers 75 (2009) 125–129

Contents lists available at ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

The preparation of lignocellulosic aerogels from ionic liquid solutions

Olli Aaltonen *, Olli Jauhiainen

VTT Process Chemistry, P.O. Box 1000, 02044 VTT, Finland

ARTICLE INFO

Article history:
Received 5 May 2008
Received in revised form 2 July 2008
Accepted 3 July 2008
Available online 10 July 2008

Keywords:
Aerogels
Cellulose
Lignocellulose
Lignin
Xylan
Critical point drying
Supercritical
Carbon dioxide
Ionic liquids

ABSTRACT

Nanofibrillar aerogels were prepared from cellulose, spruce wood and from mixtures of cellulose, lignin and xylan. The lignocellulosic polymers were first dissolved in an ionic liquid and coagulated from solution by adding aqueous ethanol. The obtained gel was washed with ethanol and liquid carbon dioxide and finally dried by releasing the carbon dioxide from the porous structure at supercritical temperature to obtain the aerogel. The bulk densities of the biopolymer aerogels ranged from 25 to 114 g/l and the internal surface areas (BET) from 108 to 539 m^2/g depending on the biopolymer mix and on the polymer concentration in the ionic liquid solution. All aerogels were compressible and consisted of nanofibrillar biomaterial network with open-pore structure.

1. Introduction

Interest towards ultralightweight cellulose aerogels has arisen due to their green status, biodegradability and their potential use as nanostructured, bio-based materials for thermal insulators, supercapacitors, storing media for gases in fuel cells, filtermaterials for extremely fine particles, drug delivery systems, drug coating purposes, etc (Hoepfner, Ratke, & Milow, 2008; Jin, Nishiyama, Wada, & Kuga, 2004; Rosenau, 2007; Tan, Fung, Newman, & Vu, 2001). Aerogels can be produced from a solution of a biopolymer which forms a gel network by entrapping the original solvent. The solvent within the gel network is then replaced by air without collapsing the biopolymer network.

Cellulosic aerogels were first prepared from cellulose and nitrocellulose "jellies" in ordinary organic solvents. Kistler (1931) and co-workers described the solvent exchange of such jellies followed by drying in supercritical propane without collapsing the aerogel structure.

Nanofibrillar cellulose aerogels have also been prepared by the dissolution of cellulose in hot, aqueous calcium thiocyanate followed by regeneration and a carefully controlled drying procedure (Hoepfner et al., 2008; Jin et al., 2004). During cooling the hot calcium thiocyanate/cellulose-solution undergoes a sol-to-gel transition at 80 °C. The cellulose aerogels had densities from 10 to 100 g/l and surface areas from 70 to 220 m^2/g depending on the concentration of cellulose in the thiocyanate solution and on the drying method.

Another way to produce cellulose aerogels is to first prepare a cellulose solution with a one-component, non-aqueous and non-derivatizing cellulose solvent. The solution is then transformed into a gel by adding a polar non-solvent. The cellulose solution need not be complete in that it may still contain undissolved cellulose fragments. The cellulose solvent must be capable of disrupting the intermolecular hydrogen bonds while simultaneously preserving the polymer backbone of cellulose in essentially an undegraded state.

Such cellulose solvents include *N*-methyl morpholine *N*-oxide (NMMO) which is used as a cellulose solvent in the commercial Lyocell-fiber process. Innerlohinger, Weber, and Kraft (2006) and Rosenau, Liebner, Potthast, Haimer, and Wendland (2007) have produced aerogels from dissolving pulp using Lyocell dopes. The specific densities of the cellulose aerogels ranged from 20 to 260 g/l depending on the cellulose content of the Lyocell dopes and on the regeneration procedure.

Substituted pyridinium and imidazolium salts are known, non-aqueous and non-derivatizing cellulose solvents. They belong to a group known as ionic liquids which have recently received immense research interest as low vapor pressure reaction media and as catalysts in organic chemistry.

The story of organic salts or ionic liquids in cellulose dissolution started with Graenacher's work as early as 1934. He found that

* Corresponding author. Tel.: +358 405020181.
E-mail address: olli.aaltonen@vtt.fi (O. Aaltonen).

0144-8617/$ - see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.carbpol.2008.07.008

N-ethyl pyridinium chloride dissolves cellulose. The melting point of the ethyl pyridinium salt is approximately 118 °C and the cellulose solutions tend to become too viscous for practical use. Therefore an organic solvent, either dimethyl formamide or dimethyl sulfoxide has been added to the solution (Husemann & Siefert, 1969) to lower the melting point of the solvent, to facilitate cellulose dissolution, to reduce cellulose degradation, and to make it possible to spin filaments of precipitated cellulose from the solution. Although spinning is technically possible (Aaltonen, Karvinen, Komppa, Pohjola, & Pohjola, 1977), the two-component solvent system was considered too complex and further research to develop an alternative to the viscose process was dropped at that time. It was not until 2002 that interest in non-aqueous, organic salts in cellulose dissolution revived with the discovery that alkyl-substituted imidazolium chlorides also dissolve cellulose (Swatloski, Spear, Holbrey, & Rogers, 2002). The benefit of imidazolium salts over pyridinium chloride is that up to 10% cellulose-containing solutions can be obtained at around 100 °C. Kilpeläinen, Xie, King, Granström, and Heikkinen (2007) have shown that not only pure cellulose but also wood and thermomechanical pulp can be dissolved in a number of substituted imidazolium chlorides and in imidazolium dicyanamide.

We have not found publications about producing aerogels from cellulose or lignocellulose biopolymers dissolved in ionic liquids. The only reference found that is in that area is a recent report that gel formation occurs when cellulose, dissolved in 1-butyl-3-methylimidazolium chloride, is kept at room temperature for 7 days (Kadokawa, Murakami, & Kaneko, 2007).

Combining the knowledge that (a) cellulose and wood can be dissolved in an ionic liquid (Kilpeläinen et al., 2007; Swatloski et al., 2002), (b) an ionic liquid solution of cellulose forms a gel when absorbing water (Kadokawa et al., 2007), and (c) that the collapse of aerogel structures during liquid removal can be avoided by extracting the liquid with a supercritical solvent (Kistler, 1931), we initiated a study into the possibility of producing aerogels or aerogel-like nanostructures from wood and from mixtures of lignocellulose polymers.

This is a report of our research in the production of ultralightweight aerogels from cellulose, cellulose–lignin, cellulose–lignin–xylane mixtures and from spruce wood using 1-butyl-3-methylimidazolium chloride as the solvent for the biopolymer material. To prepare the biopolymer aerogels from ionic liquid solutions the biopolymer solution was first coagulated in aqueous ethanol. While other antisolvents would also do, one reason for choosing ethanol was that its concentration in water can be selected freely. This gives the possibility to adjust the hydrophility of the coagulation bath over a range. A solvent exchange was then made by replacing the ionic liquid and water with anhydrous ethanol. Then ethanol was replaced with liquid carbon dioxide. The other reason for choosing ethanol for this phase was that it is completely miscible with carbon dioxide under sufficient pressure. Therefore it can be easily washed from the hydrogel with liquid carbon dioxide. Finally the gels were dried by releasing carbon dioxide from the biomaterial at above the critical temperature of pure carbon dioxide.

The polymeric materials for this study were selected so that they represent the main components of the lignocellulosic materials which may be soluble in ionic liquids: cellulose, lignin and hemicellulose. Additionally, softwood was chosen as presumably representing the most demanding raw material. Bleached softwood pulp was chosen to represent relatively pure cellulose in fiber form. For the lignin model compound we used sodalignin. Sodalignin is sulfur-free and obtained commercially from the cooking of non-wood plants with caustic soda. Sodalignin is recovered from the cooking black liquor. Xylan was chosen as the model compound to represent hemicellulose. Xylan is a xylose polymer and the most abundant hemicellulose component in hardwoods and in many non-wood plants. The choice of biopolymer mixtures was made to gather knowledge on how the different main biopolymer components of a lignocellulose matrix contribute to or prevent the aerogel structure formation. By selecting different biopolymer compositions one may expect that the surface and physical properties of the nanofibrillar aerogel could be adjusted.

2. Materials

Cellulose was air-dry pulp sheets that were shredded by hand and used as such in dissolution. The sheets were bleached and dried softwood Kraft pulp from a Finnish pulp mill.

Xylan was from birch wood and acquired from Sigma: xylose residues $\geqslant$90% by HPAE.

Lignin was Protobind 1000 sodalignin powder from Granit S.A., Switzerland.

Spruce wood (Finnish Picea Abies) was crushed, Wiley-milled, and sieved. Drying was done in ambient air at room temperature. Two particle size fractions were used: (a) <1 mm, (b) <0.2 mm.

CO_2 (99.7%, food-grade) was from Oy Aga Ab, Finland.

Ionic liquid was 1-butyl-3-methylimidazolium chloride from Merck KGaA, Darmstadt.

Ethanol was of technical grade, absolute (99.5%) from Primalco Oy, Finland.

Water was ion-exchanged MilliQ-grade prepared in-house.

3. Experimental

To study the dissolution, coagulation, gelling, and aerogel formation properties of different lignocellulosic polymers the biopolymer compositions in the ionic liquid solution and the ethanol concentration of the first coagulation bath were varied.

Material combinations tested were:

- cellulose
- sodalignin
- cellulose + sodalignin
- cellulose + sodalignin + xylan
- spruce wood

3.1. Dissolution

Biopolymers (1.5–3.7 g) were mixed with 50 g of 1-butyl-3-methylimidazolium chloride (C_4mimCl) in a 100 ml rotavapor flask. The flask was immersed in an oil bath at 130 °C and rotated for at least 4 h. The solution was observed visually and if the solution appeared unsatisfactory heating was continued up to 27 h.

3.2. Coagulation and solvent exchange

The suspension or solution obtained from the dissolution step was poured, while hot, onto a petri dish to form a less than 10 mm thick layer. The solution was then either (a) immediately immersed in the first coagulation bath or (b) kept in a humid atmosphere for days so that it slowly adsorbed moisture from air before it was immersed in the first coagulation bath. In cases where the concentration of the lignocellulose polymer in the ionic liquid remained low the solution occasionally started to crystallize while being kept at room temperature. Such solutions were not brought to coagulation. Visually complete or near-complete solutions were stable and remained liquids despite being at a temperature much below the melting point of the pure ionic

liquid. The first coagulation bath was a room temperature, aqueous ethanol solution with either 10, 50 or 90 wt% ethanol. The bath was replenished at least three times before finally immersing the precipitate in pure ethanol, which also was replenished at least three times. The immersion time in each bath was typically at least overnight. The washed solid cake was stored completely immersed in ethanol.

3.3. Aerogel production

A 5 × 5 mm piece was cut from the washed biomass cake, submerged in ethanol, and transferred to a 30 ml high-pressure viewcell. Ethanol was added to the cell to immediately immerse the piece of biomass gel in the liquid. Liquid CO_2 was pumped into the cell at room temperature and approx. 70 bars pressure to completely fill the cell. After about 2–3 h part of the liquid was withdrawn from the cell while keeping the biomass completely submerged in liquid. This could be confirmed visually through the cell window. The cell was filled with fresh, liquid CO_2. This ethanol-to-CO_2 solvent-exchange cycle was repeated a number of times until approximately 130 ml CO_2 had been used. Finally the content of the cell was heated to above the critical temperature of CO_2 so that no liquid–vapor-interface could be formed during pressure reduction. The cell was slowly depressurized to obtain the dry aerogel piece of biomass polymer. The aerogel was characterized by measuring the density, BET-surface, BJH-average pore size and by taking SEM pictures. The SEM pictures shown in Figs. 1–5 are from surfaces of the aerogel materials revealed by first making a cut with a knife and then breaking the material by hand. If the solvent exchange procedures were incomplete, i.e. either ionic liquid or ethanol residues were left in the porous biomass, the structure collapsed during pressure reduction in the final stage of CO_2 drying. The bulk density of each aerogel sample was obtained by weighing the sample and dividing the weight by sample volume, measured with a micrometer. The BET-surface area and BJH-pore dimensions were obtained with a TriStar 3000 unit (Micrometritics Inc.). The unit measures and calculates nitrogen adsorption and desorption isotherms at 77 K and uses the isotherms to calculate the surface area and nanometer-range pore sizes of the sample. The method is based on the theory of combined physical adsorption and capillary condensation of a gas in the pores (Barrett, Joyner, & Halenda, 1951; Brunauer, Emmett, and Teller, 1938).

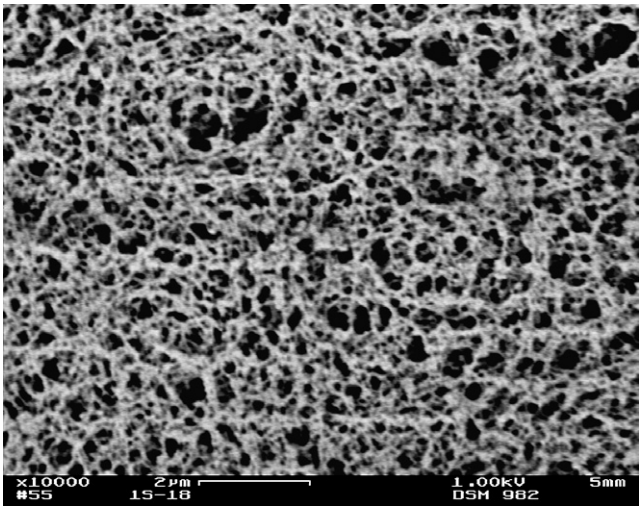

Fig. 1. SEM picture of an aerogel produced from bleached cellulose pulp (Experiment no. 1).

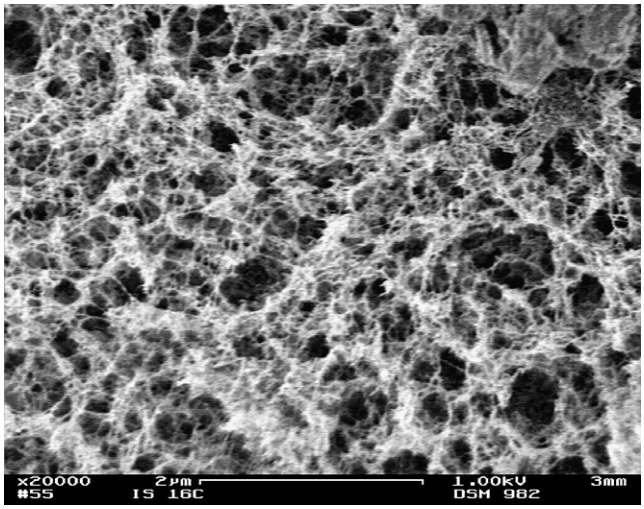

Fig. 2. SEM picture of an aerogel produced from cellulose/sodalignin – mixture (Experiment no. 4).

4. Results and discussion

By visual inspection the solutions obtained with spruce sawdust were never quite clear. Using the finer screened sawdust fraction (particles through 0.2 mm holes) and drying the wood powder thoroughly under vacuum resulted in visually more homogeneous solutions than when using coarser sawdust. However, even those dispersions contained visible traces of undissolved wood particles and the dispersion appeared to contain a jellylike substance. In contrast, completely clear solutions in the ionic liquid were obtained from cellulose, lignin, xylan, and their mixtures.

In the experiments where the sodalignin fraction in the biopolymer mix was either 67 or 100 wt% the solution in the ionic liquid did not precipitate as a gelled network. Instead, it either did not visibly coagulate at all or it formed a mass of particles which did not form a gel. In these experiments with high lignin fractions no precipitation occurred when the coagulation bath contained 90 wt% ethanol and particles appeared when the ethanol concentration was 10 wt%. In all experiments where lignin was part of the polymer mix and a solid precipitate was obtained, we observed partial dissolution of lignin in the bath. This could be seen from the increasing brown color of the bath with increasing ethanol concentration. Not all coagulation trials with spruce wood were successful either. Comparing experiments 10 and 11 shows that no precipitate could be obtained from a solution/dispersion where spruce sawdust had been heated in the ionic liquid for about 21 h. However, a good gel-like precipitate was obtained from an otherwise similar experiment, but with much shorter dissolution time. The stability of cellulose and other lignocellulosic polymers in ionic liquids deserves a study of its own. In this work we only checked how the pH of solutions develop during wood dissolution. Although a 10 wt% water solution of the as-received C_4mimCl is neutral (pH 7.2), the pH of the heated (20 h) spruce solution, dispersed in water, had dropped to pH 3.3. The resulting pH was dependent on the dissolution time. After 4.5 h of heating wood in the ionic liquid, the pH of the water dispersion was pH 4.4. In contrast, heating pure C_4mimCl at 130 °C for up to 30 h did not cause its water solution to become more acidic.

With a suitable biopolymer mix and with a not too long dissolution time aerogels were successfully obtained from biopolymer ionic liquid solutions. We did not detect any significant differences in gelling and subsequent aerogel formation between experiments where the biopolymer solution was first kept in moist air and those

trials where the biopolymer solution was immersed in an aqueous bath immediately after the dissolution step. The concentration of ethanol in the aqueous bath (from 10 to 90 wt% EtOH) did not have any visible effect on gelling and aerogel formation either.

The key parameters are listed in Table 1. The characterization of the obtained aerogels is in Table 2.

The microstructures of the aerogels produced from the different biopolymer solutions in 1-butyl-3-methyl imidazoliun chloride were viewed with Scanning Electron Microscopy. SEM micrographs are shown in Figs. 1–5. All samples display characteristic open-pore network structures which are independent of the composition of the lignocellulose polymer mix. The microstructure pore diameters range from approximately 100 nm in the cellulose/lignin/xylan-aerogel (Fig. 3, Experiment 8) to about 4 μm in the wood aerogel (Fig. 5a, Experiment 13). All polymer material appears to be incorporated in the web-structure. There are no signs of separate particles of any kind in the SEM pictures. However, the network structure in wood aerogels (Figs. 4 and 5) is perhaps a little bit more branch-like than in the aerogels prepared from the mix of isolated polymers or cellulose (Figs. 1–3). The micropore sizes between wood aerogels from parallel experiments differ greatly. (Fig. 4a vs. b and Fig. 5a vs. b). Since the differences are not in line with the differences in the coagulation bath compositions one may assume that at least the wood aerogel samples were inhomogeneous. Applying mixing in the coagulation and solvent exchange stages might yield more homogeneous materials and more rapid overall preparation time.

Table 1
Conditions and results in the dissolution and coagulation stages of the aerogel-formation experiments. In all experiments approximately 50 g of C_4mimCl was used in the dissolution step.

Experiment no.	Biomaterial in C_4mimCl - solution				Dissolution time at 130 °C (h)	Ethanol concentration in the first coagulation bath (wt%)	Appearance of the coagulate
	Cellulose (g)	Lignin (g)	Xylan (g)	Wood (g)			
1	1.5				4	90	Gel
2		1.5			2	90	No coagulate
3		1.5			2	10	Particles
4	2.0	1.0			27	90	Gel
5	2.0	1.0			27	90	Gel
6	0.5	1.0			4	90	No coagulate
7	0.5	1.0			4	10	Particles
8	2.0	0.7	1.0		8	50	Hard gel
9				1.5	10	10	Gel
10				1.5	10	90	Gel
11				1.5	21	90	No coagulate
12				1.5	21	10	No coagulate
13				2.0	4.5	90	Gel
14				2.0	4.5	10	Gel

Table 2
Characterization of the biopolymer aerogels obtained from ionic liquid solutions after solvent exchanges and drying from supercritical carbon dioxide

Experiment no.	Aerogel bulk density (g/l)	BET-area (m^2/g)	BJH-adsorption average pore diameter (nm)	BJH-desorption average pore diameter (nm)
1	48	539	55	35
4	31	210	25	26
5	25	217	42	17
8	114	213	27	14
9	50	122	32	17
10	37	n.d.	n.d.	n.d.
13	54	108	25	10
14	55	108	25	22

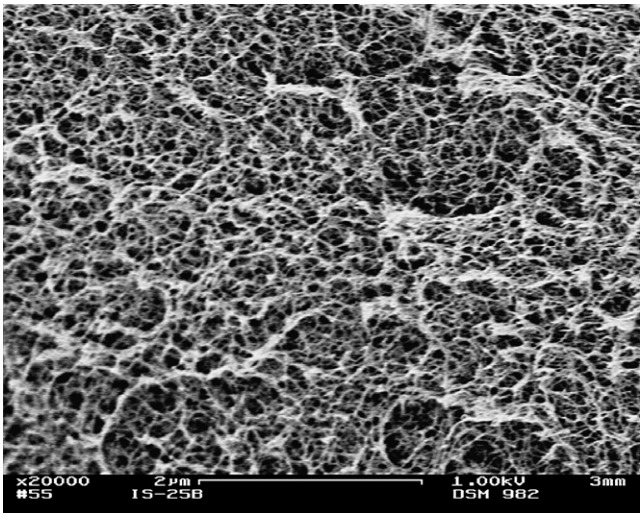

Fig. 3. SEM picture of an aerogel produced from cellulose/sodalignin/xylan – mixture (Experiment no. 8).

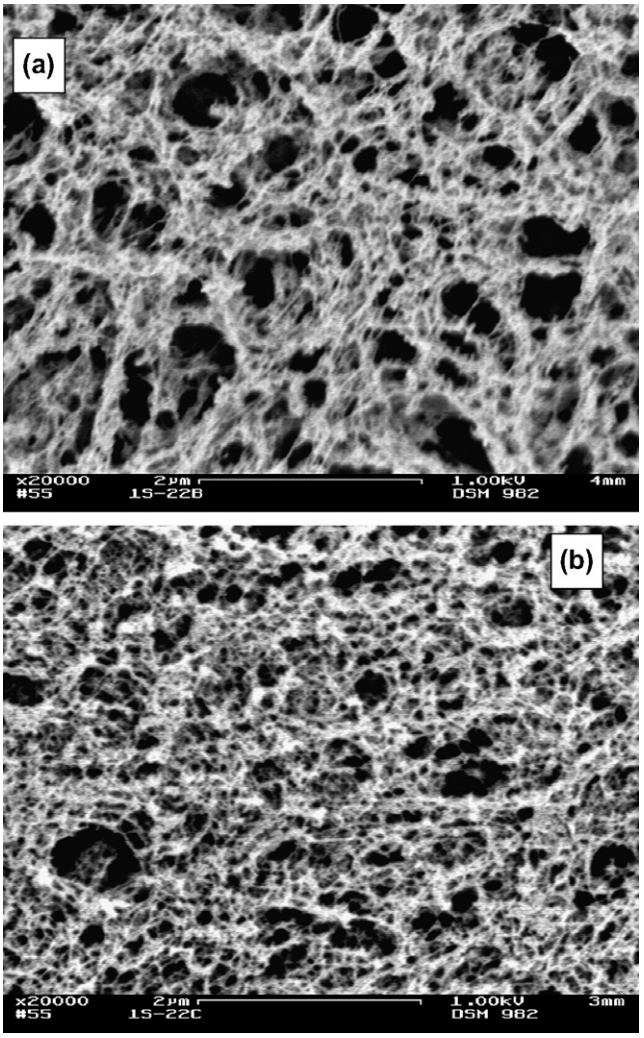

Fig. 4. SEM pictures of aerogels produced from spruce wood, coagulated in baths containing (a) 10 wt% EtOH and (b) 90 wt% EtOH (Experiments 9 and 10, respectively).

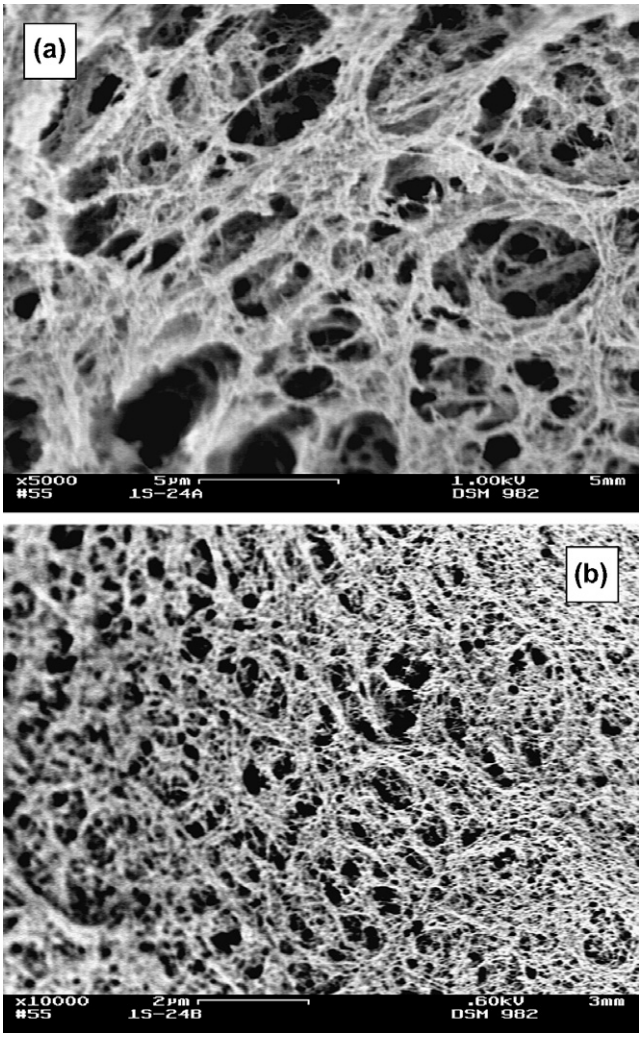

Fig. 5. SEM pictures of aerogels produced from spruce wood at slightly different dissolution conditions than in Experiments 9 and 10. Coagulations in (a) 90 wt% EtOH and (b) 10 wt% EtOH (Experiments 13 and 14, respectively).

The aerogel materials obtained from cellulose and from its mixtures with lignin and xylan were very soft and compressible. The materials could be flattened between fingers and after releasing pressure they only slightly recovered their volume. These microporous products could be easily disintegrated to fibrous or powder-like material by rubbing between fingers. Aerogels made from wood were much harder. They exhibited much more structural strength than the aerogels prepared from cellulose or cellulose mixtures. The obtained aerogels were sensitive to the electron beam in the Scanning Electron Microscope. Too much acceleration voltage caused a collapse of the nanofibrillar structure; the material appeared to vanish. Therefore the acceleration voltage in SEM was restricted to approximately 1 kV.

By visual inspection cellulose aerogels were completely opaque and shining white. A brownish color increased with the amount of lignin in the polymer mix.

The ability of ionic liquids to dissolve a number of biopolymers without derivatization makes them a flexible and interesting medium for producing aerogels from biopolymer mixtures. It should be possible, for example, to adjust the hydrophilicity and biocompatibility of the nanofibrillar aerogel by changing the polymer mix.

Acknowledgements

The authors gratefully acknowledge Mr. Unto Tapper for the skillful scanning electronic microscopy of the samples and the 'Biorefinery Research Program' of VTT for funding the work.

References

Aaltonen, O., Karvinen, J., Komppa, V., Pohjola, L., & Pohjola, V. J. (1977). Properties of rayon spun from cellulose dissolved into *N*-ethylpyridinium chloride solution. *Paperi ja Puu, 11*, 739–742.

Barrett, E. P., Joyner, L. G., & Halenda, P. P. (1951). The determination of pore volume and area distributions in porous substances. I. Computations from nitrogen isotherms. *Journal of the American Chemical Society, 73*, 373–380.

Brunauer, S., Emmett, P. H., & Teller, E. (1938). Adsorption of gases in multimolecular layers. *Journal of the American Chemical Society, 60*, 310–319.

Graenacher, C. (1934). Cellulose solution. US Patent Office, Pat. No. 1,943,176.

Hoepfner, S., Ratke, L., & Milow, B. (2008). Synthesis and characterization of nanofibrillar cellulose aerogels. *Cellulose, 15*, 121–129.

Husemann, E., & Siefert, E. (1969). *Macromolecular Chemistry, 128*, 288–291.

Innerlohinger, J., Weber, H. K., & Kraft, G. (2006). Aerocellulose: Aerogels and aerogel-like materials made from cellulose. *Macromolecular Symposia, 244*, 126–135.

Jin, H., Nishiyama, Y., Wada, M., & Kuga, S. (2004). Nanofibrillar cellulose aerogels. *Colloids and Surfaces A: Physicochemical Engineering Aspects, 240*, 63–67.

Kadokawa, J., Murakami, M., Kaneko, Y. (2007). Formation of cellulose gel with ionic liquid and preparation of regenerated cellulose from the gel. Abstracts of Papers, 234th ACS National Meeting, Boston, MA, USA, August 19–23.

Kilpeläinen, I., Xie, H., King, A., Granström, M., & Heikkinen, S. & Argyropoulos, D. S. (2007). Dissolution of wood in ionic liquids. *Journal of Agricultural and Food Chemistry, 55*, 9142–9148.

Kistler, S. S. (1931). Coherent expanded aerogels and jellies. *Nature, 127*, 3211–3741.

Rosenau, T., Liebner, F., Potthast, A., Haimer, E., Wendland, M. (2007). Ultralightweight cellulose aerogels from NBnMO-stabilized lyocell dopes. *Research Letters in Materials Science*, Vol. 2007, Article ID 73724..

Swatloski, R. P., Spear, S. K., Holbrey, J. D., & Rogers, R. D. (2002). Dissolution of cellulose with ionic liquids. *JACS Communications, 124*, 4974–4975.

Tan, C., Fung, B. M., Newman, J. K., & Vu, C. (2001). Organic aerogels with very high impact strength. *Advanced Materials, 13*, 644–646.