Ionic liquids as solvents for making composite materials from cellulose

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Abstract. Some imidazolium-based ionic liquids (ILs) are able to dissolve microcrystalline cellulose to form 10 wt% solutions. This allows easy production of cellulose composite materials by mixing the respective solutions. The purpose of this work was to make an environmentally friendly novel material using cellulose as a binder to be an alternative for classical binders in electrically conductive materials. Eleven ILs were used to dissolve cellulose. The ILs included two ILs previously untested for this application. Monofilaments composed of three types of cellulose and carbon aerogels were prepared. Solutions of cellulose and carbon aerogels were made into electrically conducting materials. Regeneration of cellulose and composites from ILs was performed using water, ethanol, and acetone. From those antisolvents water proved to be the most effective. The solutions were made into films and fibre extrusions. The used ILs were successfully recovered and reused after regeneration of cellulose. This further strengthened the belief that dissolving cellulose with ionic liquids is a 'green process'.

Key words: materials chemistry, cellulose, carbon aerogels, ionic liquids, composite materials, ionogels.

1. INTRODUCTION

Cellulose has been used as a chemical raw material for more than 150 years. It has many commercial applications, serving as a raw material to produce e.g. paper, pharmaceutical compounds, textiles, etc. (Kennedy, 1987). Cellulose is also widely used in polymer and paint industries (Hon and Shiraishi, 2000; Yu et al., 2009). There are examples of applying cellulose as a reinforcement material in nanocomposites, electronic devices, and fuel cell membranes (Gilbert, 1994; Khalil et al., 2012; Miao and Hamad, 2013). The substance has also been considered as a feasible feedstock for biofuel production (Carroll and Somerville, 2009).

In recent years, microfibrillated cellulose, also called nanofibrillated cellulose, has become a topic of interest in many scientific studies. In nature, a certain number of individual cellulose molecules are brought together and packed into elementary fibrils in the size range of 3–5 nm. These units are aggregated into larger units of microfibrils in the range of 15–20 nm, thus forming the second hierarchical level in the plant cell wall (Klemm et al., 2011). These kinds of cellulose nanofibres can be harvested also from certain bacteria (Lavoine et al., 2012).

Cellulose is a widely used material (Klemm et al., 2005). However, its applications are limited due to a small amount of solvents to dissolve it. For example, it is insoluble in water and most common organic solvents. Also, its separation from natural lignocellulosic biomass is difficult (Sannigrahi and Ragauskas, 2013). Dissolving cellulose is difficult due to its highly ordered fibril structure and strong hydrogen bonding network. Finding renewable and environmentally friendly resources to dissolve cellulose has become a matter of concern (Liebert, 2010; Domínguez de María, 2013).

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Recent developments indicate that cellulose can be dissolved in NaOH/thiurea and NaOH/urea aqueous solutions directly and relatively fast. However, the solution can easily gel, thus it still is not a strong solving solution. Compared to previously mentioned systems a NaOH/thiurea/urea system is more effective for dissolving cellulose (Jin et al., 2007).

Despite the fact that there are ways to dissolve cellulose it is still complicated when compared to dissolving cellulose directly in ionic liquids (ILs). Some ILs are capable of breaking the hydrogen bonds of cellulose's extensive fibrillated structure without derivatization (Swatloski et al., 2002). Acidic ILs have been used to dissolve microcrystalline cellulose (Ding et al., 2012), wood and sawdust (Wang et al., 2010), and sugarcane (Lan et al., 2013). However, only some ILs can dissolve cellulose. According to the literature, most popular ILs used to dissolve cellulose under conventional heating (<100 °C) are imidazolium-based ones: AMIMCl, BMIMCl, BMIMAc, EMIMAc, EMIMCl, EMIM DEP (Fukaya et al., 2010; Wang et al., 2012). The ability of these liquids to dissolve cellulose mostly depends on the anion present, whose basicity and hydrogen-bonding ability play a key role in this process, but also the nature of the cation is important (Brandt et al., 2013).

When testing different IL anions the results have shown that their interaction strength with the cellulose is in a declining order as follows: chloride anion > acetate anion > alkylphosphate anion > tetraflouroborate anion > hexaflourophosphate anion (Vitz et al., 2010). The last mentioned ILs with non-coordinating anions, $[BF_4]^-$ and $[PF_6]^-$, do not dissolve cellulose. The increasing chain length of the attached alkyl groups on cations seems to reduce the effectiveness of the ILs in dissolving carbohydrates (Klemm et al., 2005; Ding et al., 2012).

The information collected on the dissolution of cellulose is still somewhat chaotic because of the different types of cellulose, concentration values, and conditions (i.e. temperature, heating method, etc.) presented. Methods of dissolving cellulose in ILs vary including the following conditions: magnetic stirring with heating, conventional heating, ethanol treatment, mechanical milling (Lan et al., 2013). Also, the purity of ILs (especially their water content) is an important parameter. The fact that cellulose can also degrade in an IL, besides dissolving, is not fully studied.

It has been shown that cellulose can be dissolved in certain ILs up to 25 wt% (Pinkert et al., 2009). In addition, to produce solutions with 25 wt% of cellulose microwave heating and short period of heating time was used (El Seoud et al., 2011; Ha et al., 2011). Short heating periods are necessary for the reason that microwave heating creates a possibility of cellulose degradation. From practical point of view solutions with 5 wt% of cellulose are easier to prepare and handle because of lower viscosity.

Regeneration of cellulose from an IL solution can be done by introducing an antisolvent to the IL and cellulose solution. The antisolvent will weaken and even destroy the hydrogen bonds formed between cellulose and IL. The antisolvent has to be miscible with the IL and a precipitant for cellulose (Zhang et al., 2011; Gupta et al., 2013a). It is proposed that water, ethanol, acetone, methanol, and acetonitrile can be used as antisolvents for regenerating cellulose from ILs (Zhu et al., 2006). Water was recognized as the most effective solvent for breaking the bonds between the IL and cellulose in solution, subsequently helping to form the bonds between cellulose molecules (Swatloski et al., 2002). On the other hand, the presence of water in the IL hinders the dissolving of cellulose drastically. It has been shown that even 1% of water present in an IL makes dissolving cellulose impossible (Gupta et al., 2013b).

The macroscopic morphology of the regenerated cellulose depends on the contacts of the antisolvent with the ionic liquid and cellulose solution. Rapid mixing or a continuous stream of the antisolvent leaves cellulose in powdered form. Fibres and rods can be made with extrusion into the antisolvent. Films can be obtained with casting or covering plates (Luo and Zhang, 2010).

The ILs have a good potential for making new materials because they act as solvents for natural polymers such as cellulose and as dispersive media for inorganic nanoparticles or mesoporous materials. One of the examples of hybrid materials is ionogels where ILs and porous inorganic materials are combined (Néouze et al., 2006). The common material for ionogels is silica aerogel but carbon materials can also be successfully used. Cellulose composites with electrically conductive components provide opportunities to form materials with high electrical conductivity and switchable electrical and optical properties due to cellulose's wide range of morphological forms (Moon et al., 2011; Nakagaito and Yano, 2014). The most of research has been done with carbon nanotubes to make conductive cellulose composites where they show excellent mechanical properties and electrical conductivity, as well as thermal stability (Shi et al., 2013; Hamedi et al., 2014).

Experiments have shown that carbon nanotubes in their powdered form can form gels with imidazolium-based ILs. These gels are formed in very mild conditions in a wide range of compositions; they are very homogeneous and stable for a long time. The molecular orientation of ILs is considered responsible for the gelling system, which is more likely ruled by a great number of weak physical interactions among carbon particles (Fukushima et al., 2003). Thus ionogels have the properties of both a solid polymer and a liquid IL. Ionogels can be moulded and have many applications, including in actuators (Fukushima et al., 2005; Néouze et al., 2006). Mixing carbon nanotubes with ILs has shown the possibility of producing actuators with fast movement (Yamato et al., 2012). These actuators have

consisted of carbon materials as the conductive material, a polymer as the binder, and ILs as electrolytes. Polymers such as poly(vinylidene fluoride–hexafluoropropylene) (PVdF–HFP) are materials that usually serve as binders in carbon aerogel electrode materials (Kruusamäe et al., 2013).

Experiments have shown that carbon aerogels can be well dispersed in ILs forming a gel-like material that could be a component of composites. Carbon aerogels are highly porous materials with a large specific surface area, usually made from porous supercritically dried organic aerogels pyrolysing these at high temperatures. Synthesis and processing parameters allow tuning carbon material structure and properties, including pore distribution, pore volume, and surface area (Al-Muhtaseb and Ritter, 2003; Zubizarreta et al, 2007; ElKhatat and Al-Muhtaseb, 2011; Amaral-Labat et al., 2012).

To change the electrical properties of carbon aerogels doping can be used (Maldonado-Hódar, 2013). Having homogeneous dispersion of IL–carbon, the material can be mixed with IL–cellulose solutions, and this mixture can be used to make carbon aerogel composite films and monofilaments, where the IL is removed with water. This process demonstrates the possibility of producing extrusions using cellulose dissolved in ILs and having carbon material as the conducting material in them. The ILs used can be regenerated and reused.

The main objective of this work was to produce electrically conducting composite materials using an IL as the solvent, carbon aerogel as the conducting material, and cellulose as the binder. This combination has not been attempted in the available literature. The possibility of replacing the classical binders with a more environmentally friendly material – cellulose – was investigated. We give a more systematic approach to dissolving cellulose in ILs and later regenerating it than has been reported so far in the literature. Results for previously untested ILs for dissolving and regeneration of cellulose are also presented.

2. MATERIALS AND METHODS
2.1. Ionic liquids

Based on the literature, the following 11 ILs were selected:

1-allyl-3-methylimidazolium chloride	(AMIMCl)
1-ethyl-3-methylimidazolium chloride	(EMIMCl)
1-butyl-3-methylimidazolium chloride	(BMIMCl)
1-butyl-3-methylpyridinium chloride	(BMpyCl)
1-ethyl-3-methylimidazolium acetate	(EMIMAc)
1-butyl-3-methylimidazolium acetate	(BMIMAc)
1,3-dimethylimidazolium methyl sulfate	(DMIMMeSO$_4$)
1-butyl-3-methylimidazolium methyl sulphate	(BMIMMeSO$_4$)
1-ethyl-3-methylimidazolium diethyl phosphate	(EMIM DEP)
1-butyl-3-methylimidazolium hexafluorophosphate	(BMIMPF$_6$)
1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide	(BMIMTf$_2$N).

The ILs used in this work were obtained from Sigma-Aldrich, IOLITEC, and Merck KGaA with purities ranging within 95–98%. No further processing except vacuum drying was done to the ILs. The ILs dissolving cellulose were selected to be as comparable with one another as possible. The properties of the selected ILs can be found in Table 1.

Table 1. Properties of the ILs used. NA – not available; g/mol IL – mass of cellulose dissolved per mol of IL

IL	Molecular weight, g/mol	Density, g/cm^{3} [a]	Melting/Freezing point, °C [a]	Cellulose dissolving conditions	Cellulose solubility, wt%	Cellulose solubility, g/mol IL
AMIMCl	158.63	1.1660[b]	49–51	100 °C for 12 h[c]	10–20[d,e]	15.9–34.9[d]
EMIMCl	146.62	1.112	77–79	90 °C for 12 h[d,e]	4–12[d,e]	5.9–17.6[d]
BMIMCl	198.26	1.086	~70	83–90 °C for 12 h[d,e]	5–18[d,e]	8.7–NA[d]
BMpyCl	185.69	NA	93–113	105 °C for 12 h[d,e]	5–39[d,e]	9.3–72.4[d]
EMIMAc	170.21	1.027	>30	90 °C for 12 h[d,e]	5[d,e]	8.5[d]
BMIMAc	198.26	1.055	<−20	70–100 °C for NA[d]	12–15.5[d]	23.8–30.7[d]
DMIMMeSO$_4$	208.24	1.33	NA	90 °C for 24 h[e]	NA[f]	NA
BMIMMeSO$_4$	250.32	1.210	NA	NA	NA	NA
EMIM DEP	264.26	1.157	19–21	65 °C for NA[e]	10[d]	23.6[d]
BMIMPF$_6$	284.18	1.38	6.5	90 °C for 12 h[e]	0[d,e]	0[d,e]
BMIMTf$_2$N	419.36	1.44	1	110 °C for NA[d]	<0.5[d]	<2.1[d]

[a] Producer data.
[b] (Wu et al., 2010).
[c] (Kosan et al., 2008; Janesko, 2011).
[d] (Wang et al., 2012).
[e] (Pinkert et al., 2009).
[f] In a test with indulin the IL dissolved it over 50 wt% (Pinkert et al., 2009).

Different ILs were used to get some kind of a systematic overview of their dissolving properties in similar conditions. No data were found in the literature on ILs containing sulphates. Two ILs, $BMIMPF_6$ and $BMIMTf_2N$, were selected for comparisons as ILs that do not dissolve cellulose.

2.2. Cellulose

Three types of cellulose were used. One type, the bleached chemo-thermomechanical aspen pulp, was obtained from the company Estonian Cell. This material (designated by L) was dried in an oven at 90 °C until no weight loss was observed. The cellulose was white with peeling layers.

Another type of cellulose was microcrystalline cellulose (MC) for chromatography with a particle size of 20 μm. It was obtained from the Latvian chemical company BIOLAR. MC is a white powder and was used without any preprocessing.

A third type of cellulose was microfibrillated cellulose, or the so-called nanocellulose (NF). The pulp of nanocellulose was obtained from VTT Technical Research Centre of Finland, with a dry material content of 3.5%. This NF gel was freeze-dried to obtain a dry porous structured cellulose material to be used in experiments.

2.3. Carbon aerogels

The carbon aerogels used in this investigation were made from organic aerogel based on 5-methylbenzene-1,3-diole (5-methylresorcinol) (5-MR). These aerogels were made according to the instructions of Pérez and Peikolainen described in (Pérez-Caballero et al, 2008).

Two types of organic aerogels were made from 5-MR, water (W), formaldehyde (FA), and sodium carbonate (Cat). The differing factor of these types was the mole ratio of 5-MR and Cat. The mole ratios of all the components were as follows: W/5-MR = 45, 5-MR/FA = 0.5, 5-MR/Cat = 30 or 90. The carbon samples are referenced as CCat30 and CCat90, respectively. By varying the amount of the catalyst the porosity of the aerogel was influenced. The pore size distribution of the used carbon aerogels is shown in Fig. 1. The different parameters of the used carbon aerogels are presented in Table 2.

The organic gels were made in distilled water and the solvent was changed to acetone before supercritical drying. Drying was performed according to the procedure described in (Pérez-Caballero et al, 2008). The supercritical extraction system, a double clamp autoclave 100 mL in volume by NWA Analytische Meßgeräte GmbH, Germany, was used.

The pyrolysis of the dried organic aerogels was achieved in an inert N_2 atmosphere in a tube-shaped oven. The oven used was Carbolite MTF 12/25/400,
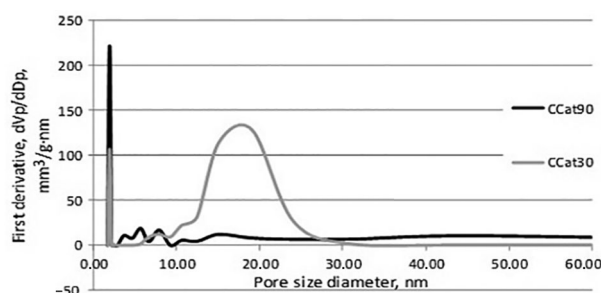

Fig. 1. Pore size distribution of carbon aerogels used in this work.

Table 2. Parameters of carbon aerogels used in this work

Parameter	CCat30	CCat90
BET surface area, m^2/g	461.7	490.0
Langmuir surface area, m^2/g	625.5	659.6
Total pore volume, mm^3/g	1395	1040
Micropore volume, mm^3/g	48.63	49.34
Micropore area, m^2/g	138.0	140.0
Non-microporous surface area, m^2/g	323.7	349.9

Great Britain. The final temperature of pyrolysis was 900 °C. The gel was hold at that temperature for 60 min. After the program ended, the oven was let to cool down to room temperature. The aerogels were then ground using a ball mill vibrator from Narva, Brand-Erbisdorf, Germany, and sieved to get fractions <0.04 mm in size.

2.4. Dissolving and regenerating cellulose and composites

Solutions of cellulose in IL (10 wt%) were made. Cellulose was dissolved in IL by heating the solution for 12 h with stirring performed manually every 6 h. The heating temperature depended on the melting temperature of the IL. Solutions of BMpyCl and AMIMCl were heated up to 110 °C, other solutions were heated to 85 °C. Mixtures of carbon aerogel and IL were made (also 10 wt%). From these solutions composites were prepared.

Three types of antisolvents – water, ethanol, and acetone – were used for the regeneration of cellulose and cellulose composites. The dissolved cellulose composites were cast into a rectangular mould and submerged into an antisolvent. Excessive amounts of antisolvents were used so that the regenerating material was completely submerged. The formed film was left still in the antisolvent for 24 h before removed. Later the experiments were repeated, the antisolvent being intensively agitated.

A syringe was used to make extrusions in a form of string. Two different needles with inner diameters 0.60 mm and 0.76 mm were used. Water was used as the
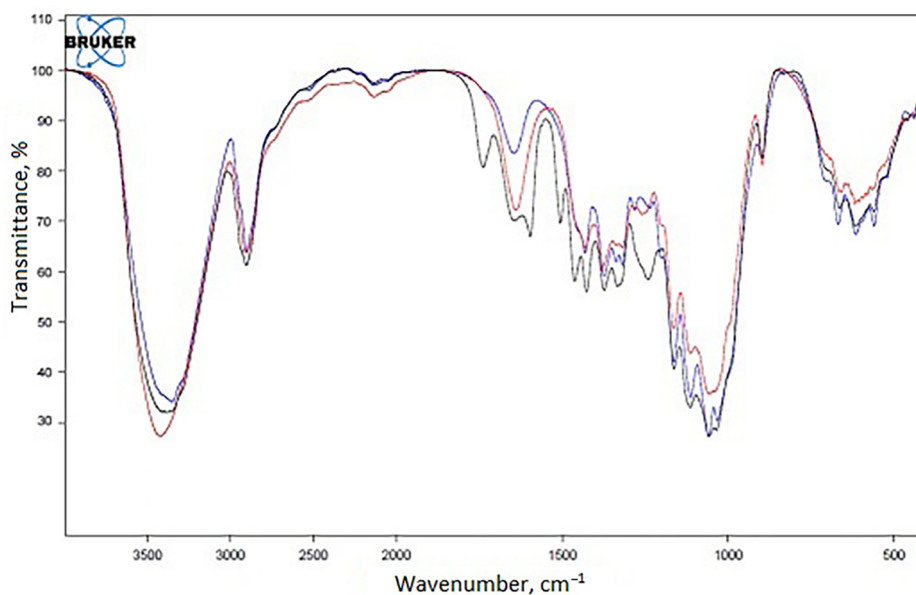
Fig. 2. IR spectra of different cellulose materials (L – blue, MC – black, NF – red) used in this work.

antisolvent in this case and the string was left in the water for 5 min before removed. After removing the composite string from water it was left to dry in open air. Later its electrical resistance and contraction were measured.

The antisolvent with IL was later collected for the regeneration of IL.

2.5. Infrared spectroscopy of cellulose and IL solutions

All solutions where the ILs were able to dissolve cellulose were analysed with infrared (IR) spectroscopy. The IR spectra were recorded with Bruker Tensor 27 FTIR spectrometer in the scanning range 400–4000 cm^{-1}, with a resolution 4 cm^{-1}. For each spectrum 64 scans were averaged. The IL solutions were placed between KBr windows and three types of cellulose were each mixed with dry KBr and pressed to pellets to record the spectrum. The IR spectra of each cellulose type can be seen in Fig. 2.

For all the composite films and monofilaments the electrical resistance (in kΩ) was measured using a multimeter LCR Meter LCR200 by EXTECH Instruments (Taiwan) with 1 mm distance between the measuring probes.

3. RESULTS AND DISCUSSION

3.1. Cellulose dissolution and regeneration

Eleven types of ILs were tested with three types of cellulose. All the possible combinations are demonstrated in Table 3. Also, it was observed whether the solution took a solid or a liquid form.

The best dissolution properties were demonstrated by the ILs with Cl$^-$ and Ac$^-$ anions. This confirms the information obtained from the literature. Also EMIM DEP dissolved every type of cellulose almost completely. The ILs with the MeSO$_4^-$ anion did not dissolve cellulose enough to qualify as good solvents for making cellulose and carbon aerogel composites.

Both BMIMPF$_6$ and BMIMTf$_2$N made cellulose softer but demonstrated almost no solubilizing properties as expected (Swatloski et al., 2002; Weingärtner, 2008; Zhao et al., 2008; Zavrel et al., 2009; Wang et al., 2012).

Of the three types of celluloses MC solubilized fastest taking only a couple of hours to dissolve. Out of the 11 ILs chosen for experiments AMIMCl, EMIMCl, BMIMCl, BMpyCl, EMIMAc, BMIMAc, and EMIM DEP dissolved every type of cellulose used at 10 wt% level. More electronegative anions led to better cellulose solubilizing abilities.

Those seven IL and cellulose solutions were used to make cellulose films, which were later submerged in antisolvents under the same conditions without stirring or continuous washing. After 24 h the films were removed and let to dry. The colour change of all the cellulose, and thus their purity, was followed. Cellulose with its white natural colour and dry surface was deemed pure from IL. Films dissolved in Cl$^-$ and submerged in water gave the best results, regenerating cellulose almost without any colour. The cellulose dissolved in IL with Ac$^-$ anions mostly retained its coloration. The cellulose dissolved with EMIM DEP retained some of its coloration but regenerated into purer cellulose than from ILs with Ac$^-$ anions.

The cellulose regenerated in ethanol and acetone retained some of its coloration, which was due to some

Table 3. Dissolution of different types of cellulose (L – chemo-thermomechanical pulp, MC – microcrystalline cellulose, and NF – microfibrillated cellulose) in ionic liquids with 10 wt%. S – solubilizing, PS – partially solubilizing, NS – non-solubilizing, L – liquid, NL – solid (non-liquid)

Ionic liquid	L		MC		NF	
AMIMCl	S	NL	S	L	S	L
BMIMCl	S	NL	S	NL	PS	NL
EMIMCl	S	NL	S	NL	PS	NL
BMpyCl	S	NL[a]	S	NL[a]	S	NL[a]
BMIMAc	S	NL	S	L	PS	NL
EMIMAc	S	NL	S	L	S	L
BMIMMeSO$_4$	PS	L	NS	L	PS	L
DMIMMeSO$_4$	NS	L	NS	NL	PS	NL
EMIM DEP	S	NL	S	L	PS	NL
BMIMPF$_6$	NS	NL	NS	NL	NS	L
BMIMTf$_2$N	NS	L	NS	L	NS	NL

[a] BMpyCl is very hygroscopic (Sashina et al., 2013) and care must be taken when operating in the open air.

ILs remained in the cellulose film when the antisolvent was not stirred. When the solvent was actively stirred, there were no coloration and impurities. Ionic liquids differ in the solubility in solvents (Figs 3 and 4).

Out of the three antisolvents used water demonstrated the best regeneration properties. The amount of antisolvent left in the composites, i.e. coloration, was estimated visually. All the samples were submerged in excess of antisolvent, and the amount of the antisolvent compared to the amount of the IL. Acetone retained high amounts of ILs in all types of cellulose after 24 h submersion. This was especially true in case of EMIMAc or BMIMAc. Ethanol acted poorly, retaining ILs in every cellulose film. This points to the need for a longer contact time and an active stirring of the antisolvent for these cases. It was confirmed in the second experiments where an active stirring of solvent was performed and well-regenerated cellulose samples were obtained. It was also demonstrated by IR spectra showing no large differences in regenerated cellulose samples in Figs 3 and 4.

The only IL and cellulose solution that did not form films was BMpyCl solution. Upon submerging into the antisolvent the BMpyCl and cellulose film dissipated within minutes in water. According to observations in this work, BMpyCl does not actually dissolve cellulose but destroys the polymer.

The IR spectra of regenerated cellulose indicate the influence of regenerating solvents, water and ethanol (Figs 3 and 4). They extract almost all ILs from the film while acetone leaves under the same conditions ILs in the composite.

The fact that water can form more hydrogen bonds with IL ions is the reason why it regenerates more cellulose from IL as compared to ethanol and acetone. Ethanol and acetone, having larger molecules than water, face more trouble moving between cellulose polymers. Because Cl$^-$ and Ac$^-$ anions break hydrogen bonds in cellulose, they are more strongly attracted to water molecules with their stronger hydrogen bonds when compared to ethanol and acetone.

The same eleven ILs were tested with three types of carbon aerogels to make homogeneous mixtures. How-
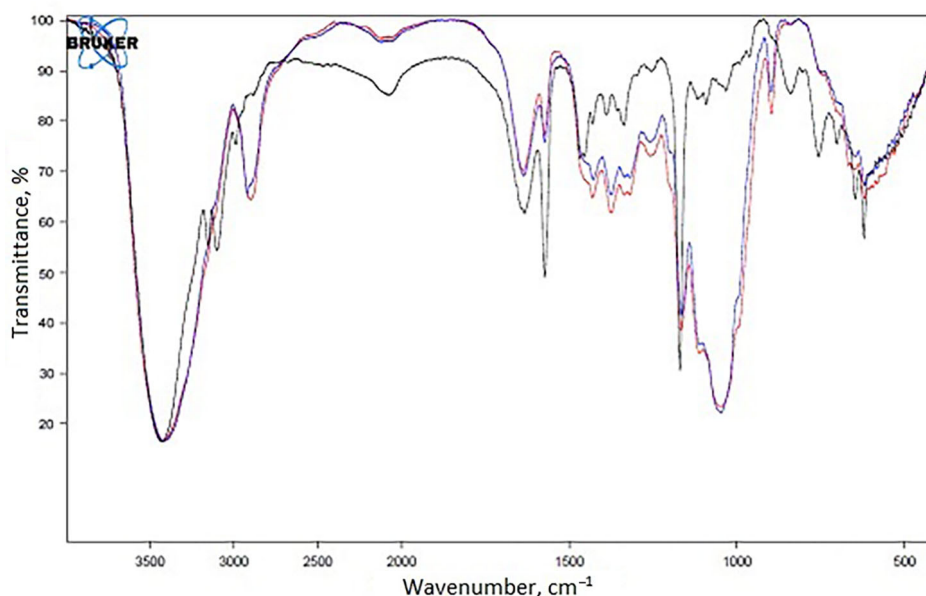

Fig. 3. Infrared spectra of regenerated IL(EMIMCl)–NF cellulose solutions with different solvents (water – blue, ethanol – red, and acetone – black).
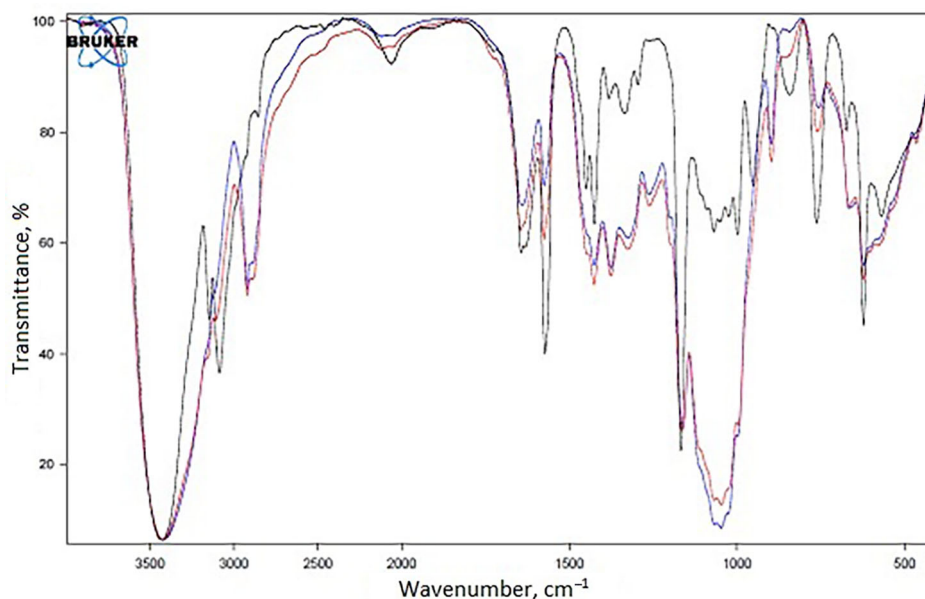
Fig. 4. Infrared spectra of regenerated IL(AMIMCl)–NF cellulose solutions with different solvents (water – blue, ethanol – red, and acetone – black).

ever, the mixture with carbon aerogel CCat30 with more catalyst was prone to precipitate from the IL. The mixture with carbon aerogel CCat90 with less catalyst was still homogeneous after seven days. To get a homogeneous mixture of carbon aerogel and IL it is important to stir the mixture right before the mixing with cellulose and IL solution.

The ILs AMIMCl, EMIMCl, BMIMCl, BMpyCl, EMIMAc, BMIMAc, and EMIM DEP were used to make carbon and cellulose composites because these were the only ILs capable of dissolving a satisfying amount of cellulose. Also, water, ethanol, and acetone as antisolvents were used to regenerate the composites. All the composites acquired a black surface due to the carbon aerogel.

All composites except BMpyCl formed a strong film to handle. These composites dissipated in every antisolvent, leaving only a black and brown powder in the moulds.

3.2. Carbon aerogel and cellulose composite monofilaments

Cellulose and IL solutions were used to make fibre with a syringe. This process was repeated with cellulose and carbon aerogel solutions. The monofilaments were regenerated in water because out of the three anti-solvents tested, water was the most effective. The regeneration time was reduced from 24 h to 5 min because it was observed that the coloration of the dis-solved cellulose in ILs did not change dramatically any more after a couple of minutes of regeneration in water.

When the ILs and cellulose solution made contact with water, ILs started visibly to solubilize in water, leaving a semiopaque suspension around the regenerating string. The suspension dissipated in minutes and no visible IL dissipation was detected.

After regeneration in water cellulose L left a twisting string with a disorganized rough surface, MC usually left a semiopaque string with a smooth surface, and NF left a winding string with an organized rough surface. Monofilaments were not made from NF dissolved in EMIMCl because it was not possible to get a homo-geneous solution and large chunks remained in the solution.

The coloration of cellulose monofilaments was similar to that of cellulose films in regeneration. Due to the shorter time of regeneration in the antisolvent the nature of cellulose also started to play a certain role in its regeneration. Cellulose L, which has the most chaotic configuration of molecules, retained much of ILs, especially ILs with Ac⁻ anions. In this case also the stirring of the antisolvent exerted some influence on the regeneration, retaining less ILs in films.

The SEM images of the cellulose samples regene-rated in the antisolvent (Fig. 5) clearly show different structures of regenerated cellulose depending on the starting material: in the case of microfibrillated cellulose NF (Fig. 5C) and even more in the case of bleached chemo-thermomechanical pulp L (Fig. 5A), non-homo-geneous surfaces can be observed. Sample L has a fibrous structure, which points to the difficulties in solubilizing natural cellulose material. This was in correlation with the initial observations at the macro-
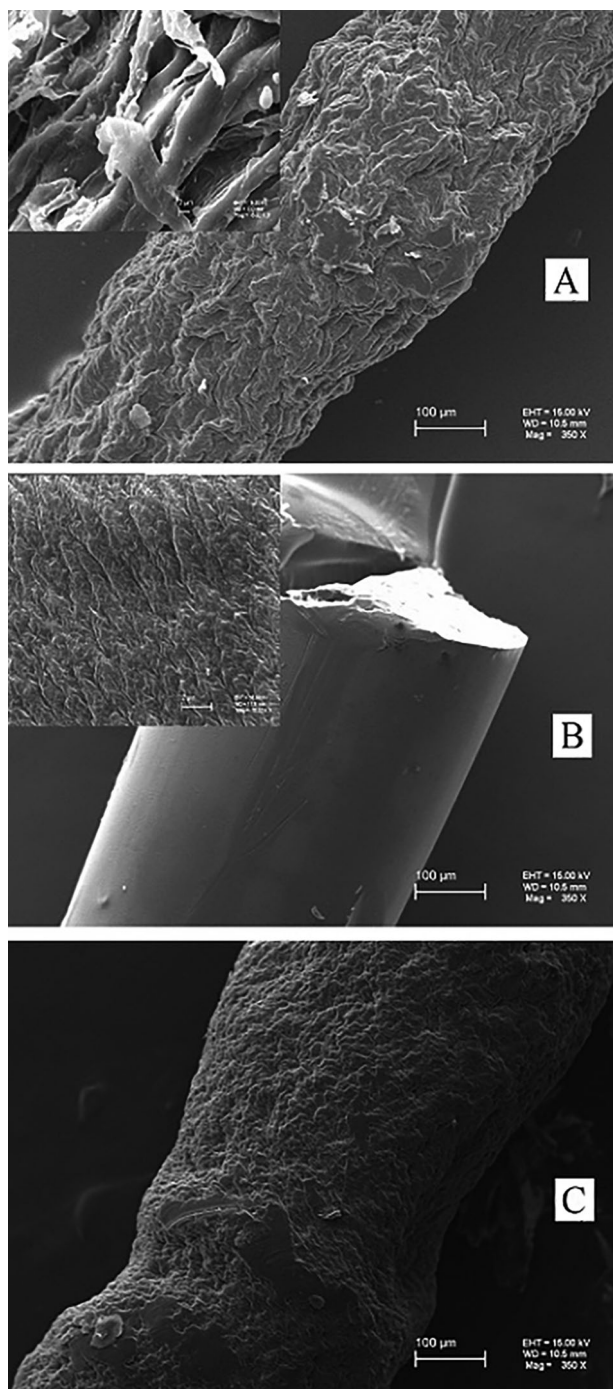
Fig. 5. SEM images of different previously EMIMAc-dissolved cellulose samples regenerated in water: (A) L string, (B) MC string, (C) NF string.
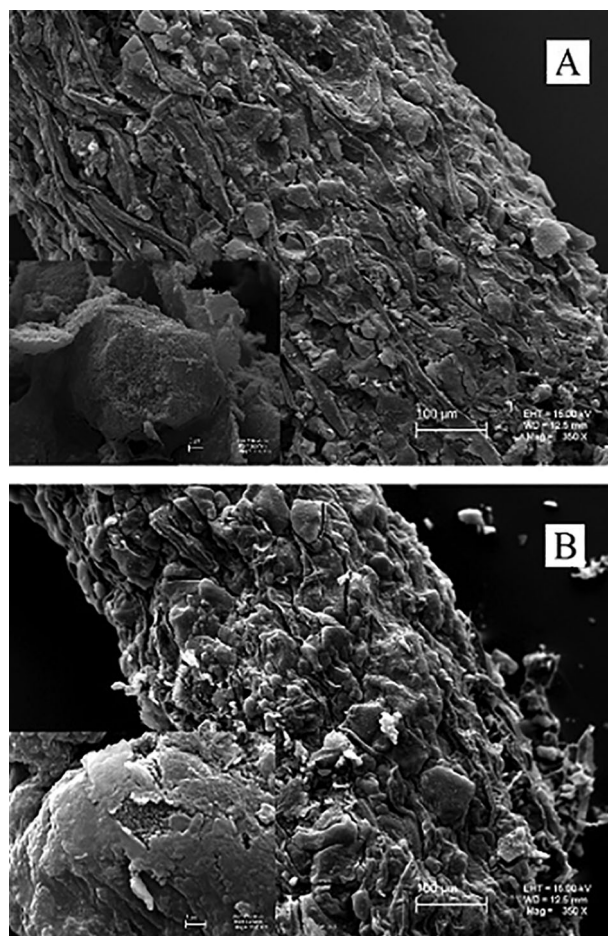

Fig. 6. SEM images of cellulose composites with carbon aerogel CCat90 powder previously dissolved in IL and regenerated in water. Carbon aerogel can be seen lodged into the structure of cellulose. (A) dissolved in EMIMCl and regenerated L composite string, (B) dissolved in EMIM DEP and regenerated NF composite string.

scopic scale. The more chaotic the cellulose molecules are (i.e. the more the composition resembles the natural cellulose composition), the rougher and the more chaotic the produced fibre will be.

A similar trend is seen in the case of cellulose and carbon aerogel composites. In the SEM images (Fig. 6)

a fibrous structure of regenerated cellulose can be seen, wrapping the small pieces of carbon aerogel. The nano-porous structure of carbon aerogels is seen at greater magnifications. It can also be seen that aerogel is not swollen with cellulose: cellulose and carbon aerogel are well distinguished.

The contraction of cellulose monofilaments was 31–62% (measured by change in the diameter of the fibre). The contraction of carbon cellulose composite mono-filaments remained between 7% and 52%. All types of cellulose exhibited a tendency to contract almost a half of the diameter they initially had (Fig. 7). There was no difference in contraction between different types of cellulose or between different carbon aerogels (Figs 7 and 8). The composites containing carbon aerogel exhibited greater contraction compared to pure cellulose (Figs 7 and 8). The high porosity of carbon aerogel plays a part in this effect. Some composites reduce their
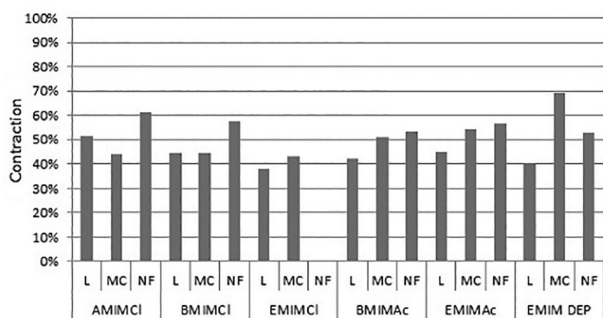
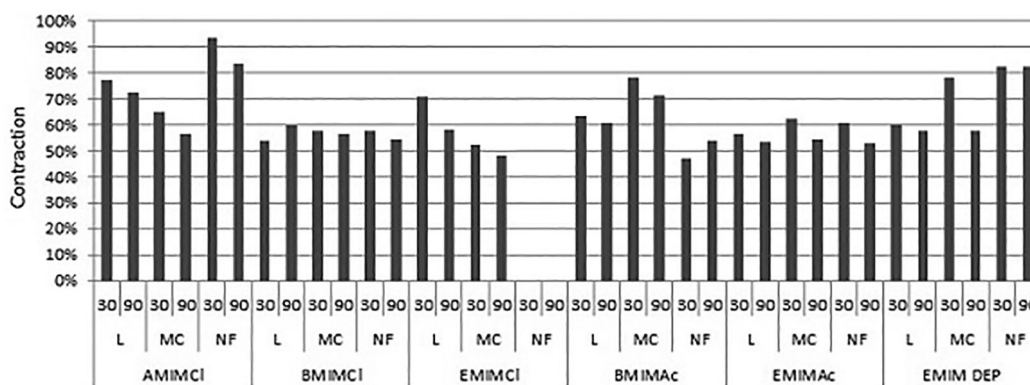**Fig. 7.** Contraction of cellulose monofilaments.

Fig. 8. Contraction of carbon aerogel and cellulose composite monofilaments.

due to its ionic nature. This holds true for all combinations of ionic liquids tested. When there was an active stirring and washing of the filament, no big difference in electrical resistance between the samples (within limits of measurement uncertainty) was detected.

From these data it can be concluded that the regeneration process should be carried out with good stirring and a long washing time. An option might be ultrasonic agitation as opposed to mechanical stirring used in this research. However, those types of composites in case of which some amount of IL remained in the composite could be used in the production of sensors or moving actuators. Ion-conducting smart materials

diameters to only about 10% of their initial width. This has to be taken into consideration when planning to use this material as a conducting fibre. Fibres regenerated in acetone had several times the conductivity compared to samples regenerated with other two antisolvents (Fig. 9). This is due to IL left in the material.

The electrical resistance in composite monofilaments was similar to the trends observed in composite films. The origin of cellulose did not play any detectable role in the conductivity of the composites made (Fig. 9). Films containing carbon aerogel CCat90 showed higher conductivity. This indicates that some IL remained in the sample after the regeneration.

The dependence of the electrical resistance of films and composites on regenerating solvents when regeneration was performed under similar conditions without stirring the antisolvent can clearly be observed. Films regenerated with ethanol showed higher conductivity than those regenerated with water. Films regenerated with acetone showed at least an order of magnitude lower electrical resistance as compared to materials regenerated with water and ethanol. The ionic liquid left in the composite lowers the electrical resistance

with three layers (two electrodes and a membrane to separate them) need ions in the electrodes (Kruusamäe et al., 2013).

Our results suggest that acetone is not a good solvent for regenerating composites, especially from ILs with Cl^- anions. The order of the electrical resistance of films regenerated by acetone is as follows: IL with $Cl^- < Ac^- < DEP^-$ anions. The materials developed in this work have a possible application in environmentally friendly electrodes.

4. CONCLUSIONS

Fabrication cellulose composite materials was investigated. The main objective was to produce environmentally friendly and electrically conductive materials.

From the eleven ILs used for dissolving cellulose only six (AMIMCl, BMIMCl, EMIMCl, BMIMAc, EMIMAc, EMIM DEP) were able to dissolve it to make 10 wt% solutions while one (BMpyCl) degraded the cellulose. From the three types of cellulose used, the micro-crystallized cellulose showed the best solubility because of its purity and homogeneity.
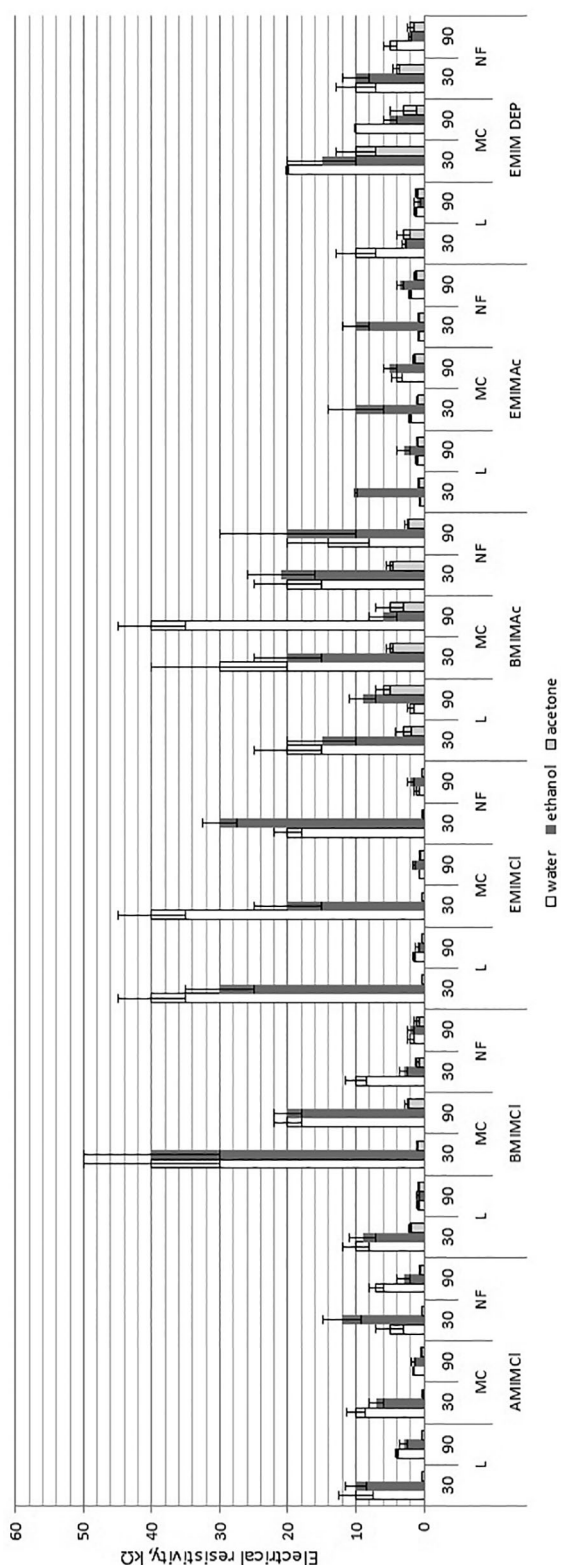
Three different antisolvents were used – water, ethanol, and acetone – to regenerate cellulose from IL solutions. Of these antisolvents, water was the most effective to regenerate cellulose and dissolve ILs out from the composite.

Two carbon aerogels with different structural parameters (specific surface area and pore size) were used to make carbon aerogel composite films and mono-filaments. A new kind of cellulose–carbon composite was characterized. Out of the two carbon aerogels the one made with a higher surface area showed higher electrical conductivity. From the three antisolvents used acetone regenerated composites with electrical conductivity as low as 300 Ω and as high as 50 kΩ. Water regenerated IL from the composite more effectively, thus producing composites with higher electrical conductivity, with the lowest of 500 Ω and highest 10 MΩ.

Also, the contraction of regenerated fibres was measured. The majority of the fibres shrank more than half of their width. This gives an opportunity to produce very thin fibres using only extrusion.

The ILs used to dissolve cellulose were successfully regenerated, which further strengthens the belief that dissolving cellulose with ionic liquids is a 'green process'.

For further testing more types of ILs should be used in similar conditions to get a more systemic approach to dissolving cellulose and other natural polymers in ionic liquids. Moreover, the possible application of cellulose composites as a material for moving actuators should also be investigated.

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Fig. 9. Electrical resistivity of carbon aerogel cellulose composite materials.

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Tselluloskomposiitide valmistamine ioonsete vedelike abil

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Antud töös uuriti tselluloosi ja süsinikaerogeelide komposiitide valmistamist. Töö peaeesmärk oli valmistada keskkonnasõbralik ja elektrit juhtiv materjal.

Üheteistkümnest valitud ioonsest vedelikust suutsid vaid kuus (AMIMCl, BMIMCl, EMIMCl, BMIMAc, EMIMAc, EMIM DEP) tselluloosi 10 wt%-ni lahustada ja üks (BMpyCl) lagundada. Mikrokristalne tselluloos lahustus kõikides tselluloosi lahustavates ioonsetes vedelikes kolmest kasutatud tselluloosist (mikrokristalne, nanofibrilleeritud, töötlemata tselluloosimass) kõige paremini ja seda tänu oma puhtusele ning homogeensusele.

Seitsmest ioonse vedeliku ja tselluloosi lahusest valmistati kiled, kasutades tselluloosi ioonsest vedelikust regenereerimiseks kolme erinevat antilahustit: vett, etanooli ning atsetooni. Nendest kolmest antilahustist oli tselluloosi regenereerimiseks ja ioonse vedeliku komposiidist väljalahustamiseks kõige tõhusam vesi.

Süsinikaerogeel-komposiitkilede ja monofilamentide valmistamiseks kasutati kaht eri tüüpi süsinikaerogeeli, mis erinesid oma struktuurparameetrite (eripindala ning pooride suuruse) poolest. Iseloomustati uut tüüpi tselluloossüsinikaerogeeli komposiiti. Suurema eripindalaga süsinikaerogeel oli suurema elektrilise juhtivusega. Tselluloosi atsetooniga regenereerimine ei lahustanud välja kogu ioonse vedeliku hulka ja neis kiledes ilmnes elektriline takistus 300 oomist 50 kilo-oomini. Vesi oli valitud antilahustitest tselluloosi regenereerimiseks ja komposiidist ioonse vedeliku väljalahustamiseks kõige efektiivsem ning võimaldas valmistada komposiite juhtivusega 500 oomist 10 megaoomini.

Mõõdeti ka regenereeritud fiibrite kokkutõmbuvust. Enamik fiibreid kahanes rohkem kui poole diameetri võrra. See võimaldab, vaid ekstrusiooni kasutades, valmistada väga õhukesi fiibreid.

Tselluloosi lahustamiseks kasutatud ioonsed vedelikud regenereeriti edukalt, mis tõendab veelgi, et tselluloosi lahustamine ioonsete vedelikega on loodussäästlik protsess.

Edasisteks uuringuteks soovitame teha katseid rohkemate ioonsete vedelike tüüpidega ühesugustes tingimustes. Seeläbi oleks võimalik luua süsteemsemad teadmised tselluloosi ja muude looduslike polümeeride lahustamiseks ioonsetes vedelikes. Lisaks võib uurida tselluloskomposiitide võimalikku rakendust liikuvates aktuaatorites.