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# Possibilities for the Physical Modification of Cellulose Shapes Using Ionic Liquids

*Frank Wendler,* Birgit Kosan, Markus Krieg, Frank Meister*

**Summary:** Functional cellulose shapes offer valuable properties for innovative application potentials in textile and medical products. Thereby excellent textile physiological properties of cellulose are allowed to be connected with novel application characteristics like bioactivity, electrical conductivity, heat storage or ability to adsorb liquids or gases. A very advantageous way to modify the properties of fibres, films or textile structures is to introduce particular additives via the Lyocell process. Regard to technical applications, functional additives will be able to incorporate themselves in the shape matrix and, in the case of using *N*-methylmorpholine-*N*-oxide monohydrate (NMMO) as solvent, implicate massive technological difficulties and deterioration of properties of the spinning dope. Beside a couple of limiting moments, ionic liquids (ILs) offer as direct solvents an excellent chance for physical modification of cellulose shapes. In contrast to NMMO, they exhibit a significantly higher thermal stability as well as a higher chemical resistance. ILs exhibit most widely a better dissolving capability for a number of different polymers. First results of the development of adsorber materials as well as novel bioactive fibres will be discussed and fibre characteristics will be given.

**Keywords:** additives; antibacterial activity; cellulose; ionic liquids; lyocell fibres

## Introduction

Direct dissolution of cellulose without derivatization applied for dry-wet/wet spinning of polymer solutions has been emerged to an efficient tool for the design of textile functional materials.[1–3] With the advancement of essential technological know-how for the manufacturing of cellulosic staple and endless fibres in a technical range (Lyocell process) in the foreground, the development tends to innovative functional fibres from the late ‘90s of last century. The ongoing progress yields on one side textile processible fibres with novel cross-sections and innovative dry-wet shaping techniques, e. g. blow casting and melt blowing, and on the other hand a series of completely new cellulosic functional fibres.[4,5]

*N*-Methylmorpholine-*N*-oxide monohydrate (NMMO) – up to now the exclusively used solvent in technical scale, possesses by reason of its chemical structure a number of properties which could have a drastically impact on process safety and efficient process conducting. By presence of oxidable or reducible compounds and temperatures clearly above 100 °C an intensified degradation of the solvent is expected, in worst cases with severe effects. These side reactions investigated already in the beginning of dry-wet spinning development,[6,7] may be triggered by a variety of impurities of the raw materials as well as typical reactants in the manner of air oxygen or free protons to be found in process environment.[8] Consequently, a serious deterioration of the economic viability of

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Centre of Excellence for Polysaccharide Research, Thuringian Institute for Textile and Plastics Research, Breitscheidstr. 97, D-07407 Rudolstadt, Germany
E-mail: wendler@titk.de
Member of the European Polysaccharide Network of Excellence (EPNOE) www.epnoe.eu

the process has to be taken into account connected with yield losses of recycled solvent and regenerated fibre with diminished features or in case of autocatalytic solvent decomposition with highly charged runaway reactions. Especially the latter gave rise to accidents not only during development but also by conducting of technical shaping plants. Moreover, in the case of modified solutions by the admixture of functional additives the start of thermal irregularities is shifted to lower temperatures.[9] In addition, it has to be mentioned that the preferably used solvent NMMO exhibits a very specific dissolution behaviour most widely limited to cellulose and only a few other polysaccharides. Not least these disadvantages promoted the search for alternative direct solvents as a continuously task.

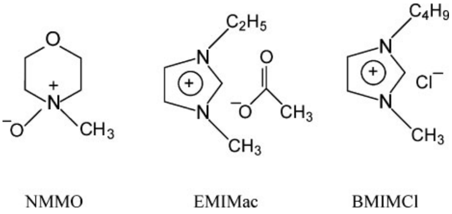
Thus, of actual importance are the activities concerning the direct dissolution of polymers in ionic liquids (ILs). In particular the 1-alkyl-3-methylimidazolium salts proved to be suitable solvents for cellulose.[10,11] Beside efficient dissolution efficiency special features such as the workability of polymer solutions at moderate and room temperatures, negligible vapour pressures under typical processing conditions as well as comparable chemical and thermal consistency, distinguish the ILs from other polymer solvents.[12–14]

The present report describes the solution behaviour of cellulose in ILs in the presence of functional additives, textile properties of the shaped bodies and further examinations regard to the thermal stability of ILs.

## Experimental Part

### Materials

*N*-Methylmorpholine-*N*-oxide (NMMO) was purchased from BASF (Ludwigshafen, Germany) and used as 50% (v/v) aqueous solution. The ionic liquids (ILs, Scheme 1) 1-ethyl-3-methylimidazolium acetate (EMIMac), mp. −45 °C and 1-butyl-3-methylimidazolium chloride (BMIMCl), mp. 73 °C were purchased from BASF (Ludwigshafen, Germany) and Solvent Innovation (Köln, Germany) without further purification. An eucalyptus pulp with a degree of polymerization (DP) of 569 and a bleached beech sulphite pulp characterized by the following data: $\alpha$ - cellulose 90.6%, (DP) 495, carboxyl groups 6.9 μmol/g, carbonyl groups 48.3 μmol/g, moisture 7.5% were used. Modification was provided with the following additives: activated charcoal, strong reactive (Grain size <10 μm; A.U.G. Döberitz, Germany); activated charcoal, medium reactive (Grain size <10 μm; Blücher, Erkrath, Germany); nano-scaled silver particles (porous MicroSilver BG™, 80–140 nm and colloidal NanoSilver BG™, 5–20 nm).



**Scheme 1.**
*N*-methylmorpholine-*N*-oxide (NMMO) and ionic liquids used in this study: 1-ethyl-3-methylimidazolium acetate (EMIMac) and 1-butyl-3-methylimidazolium chloride (BMIMCl).

### Preparation of Cellulose Solutions

The preparation of cellulose solutions was carried out in a special vertical kneader system, linked with a RHEOCORD 9000 (HAAKE). Temperature, torque moment and revolutions per minute (rpm) vs. reaction time were determined on-line. For the dissolution process the cellulose was disintegrated by means of an ultraturrax shearing step in water, was separated from excessive water and was transferred in the aqueous *N*-methylmorpholine-*N*-oxide or ionic liquid. The obtained stable suspension was poured in the vertical kneader system. Afterwards the water was removed at temperatures between 90 and 130 °C, a reduced pressure between 700 and 5 mbar and a shearing rate of 10 to 80 rpm. The resulting cellulose solution was analytically characterized and used for a further dry-wet shaping process. The details of the solution preparation were described in previous publications.[15]

### Spinning Trials

A self-made piston spinning equipment, which consists of a heatable cylinder, a spin package, an air-conditioned air gap, a spinning bath, a turning round godet and a take-off godet, was used for the shaping trials. The spinning dope is fed definitely to the spin package by a precise drive of the piston. Spin package contains the filter package, a heat exchanger and the spinneret. The heat exchanger permits beside a homogenization of the mass temperature also a continuous increasing of the spinning dope temperature from 80 to 120 °C at short dwell periods directly before the entrance into the spinneret. The air gap arranged between spinneret and coagulation is continuously movable between 10 and 150 mm through a vertical height adjustment. It is conditioned by means of a gas flow with definite temperature and moisture. The coagulation bath passes the spinning box, circulates by means of a pump and is adjustable in the height between 10 and 150 mm. A turning round godet collects the capillary skein and transports it over a traverse to the take-off godet. Finishing is carried out discontinuously after cutting the initial wet fibres into staples of uniform length.

### Differential Scanning Calorimetry (DSC)

Measurements were performed on a Mettler Toledo DSC 822e device with a heating rate of 10 K/min from room temperature up to 160 °C. The value of the first visually detectable deviation from the base line corresponds to the onset temperature, which indicates the initial thermal degradation.

### Reaction Calorimetry

Thermal investigations were realized with the Systag reaction calorimeter RADEX (mini-autoclave).[16] Approximately 2 g of the cellulose/NMMO solution were used in the steel vessel (design pressure: 100 bar) equipped with bursting disk and an internal sensor device for temperature determination. In the case of cellulose/IL solutions 1 g was weighed in a glass container which was inserted into the steel vessel. The vessel is kept by a temperature controlled steel/aluminium jacket. Ensuring a defined thermal resistance of the airspace between jacket and vessel, the temperatures of sample and jacket are measured continuously. For dynamic measurements (screening), the vessel was heated with a heating rate of 0.75 K/min from room temperature up to 300 °C followed by holding this temperature for 1 h dwell time. The onset temperature ($T_{on}$) was determined by plotting the deviation of pressure with respect to time (dp/dt) against the temperature and registering the temperature at the threshold value of 0.0002 bar/s.

### Determination of Fibre Properties

For fibre characterization the fibre fineness (DIN EN ISO 1973), wet and conditioned tenacity as well as elongation at break (DIN EN ISO 5079), loop tenacity (DIN 53843, Part 2), wet abrasion resistance[17] and water retention behaviour (DIN 53814) have been measured.

### Antibacterial Activity

The permanence of the antibacterial activity before and after defined washing was carried out according to JIS Japanese Industrial Standard (JIS L 1902: 2002) with the test strains *Staphylococcus aureus* ATCC 6588 and *Klebsiella pneumoniae* ATCC 4352. The total antibacterial activity was estimated with the calculation *log cfu (igc)18h – log cfu (sample)18h = total antibacterial activity* where *cfu* is colony forming units and *igc* is internal growth control. Criteria of evaluation for antibacterial activity are declared by the standard method: slight 0.5–1; significant $> 1$ - $<3$; strong $\geq 3$.

### Nephelometry

Nephelometric measurements were provided for the solvents *N*-methylmorpholine-

*N*-oxide monohydrate and 1-ethyl-3-methylimidazolium acetate. After dilution with a CASO bouillon (0,001% - 1%) the growth of the test strain *staphylococcus aureus* was conducted with a microplate nephelometer (NEPHELOstar Galaxy, BMG, Offenburg, Germany). Measurements (%NTU: nephelometric turbidity unit) were done every hour and put into growth curves with a total incubation time of 24 h.

### Intake Capacity

A desiccator with a beaker containing 25 ml toluene or carbon tetrachloride was used to maintain a saturated atmosphere. After 1 h, a second beaker with 1 g of the fibre was exposed into the desiccator for 24 hours. The weight gain of the fibre was measured.

## Results and Discussion

### Thermal Properties of Ionic Liquids (ILs) and Cellulose/IL Solutions

Direct dissolution of cellulose requires temperatures above 85 °C to produce homogeneous solutions within economically acceptable time. Under industrial conditions cellulose solutions are expired to mechanical shearing and enhanced temperatures over longer time periods. The physical dissolution process is attended by degradation reactions due to interactions of the solvent with cellulose and impurities of by-products or heavy metals. Autocatalytic reactions can initiate exothermicities, so-called thermal runaway reactions, which may end up in deflagrations.[8] Thus, besides the demands for efficient solubilization and non-derivatization the solvents has to be stable up to temperatures quite far above the process temperature.

The beginning of exothermicity can be detected by the onset temperature ($T_{on}$) using dynamic calorimetric measurements (DSC). Figure 1 displays the DSC curves of cellulose solutions in BMIMCl and NMMO as well as of pure NMMO. Whereas the cellulose/BMIMCl solution shows neither an endothermic melt peak nor an exothermic degradation peak, both NMMO and the cellulose/NMMO offers the typical start of melting near 70 °C and the pronounced exothermicity beginning at about 160 °C. By using of DSC, BMIMCl and further 1-alkyl-3-methylimidazolium salts used as cellulose solvents do not exhibit any thermal degradations up to temperatures of 220 °C and higher. However, investigations of cellulose/IL solutions showed similar to cellulose/NMMO solutions decreasing degree of polymerization (DP) values of the dissolved cellulose.

To quantify the stability of the cellulose/IL solutions the DP as a function of temperature and storage time was investigated.[18] The results are displayed in Figure 2. A slight decrease of molecular weight can be determined after spinning dope preparation which is caused by the mechanical shearing. The dopes are stable up to storage temperatures of 120 °C which is above the processing temperature. When exposed to 150 °C DP is decreased up to 29% after 8 h. Therefore, a stabilization of the system is necessary. Consequently, a combination of several chemical inhibitors against cellulose degradation as well as pH buffering of the anion has to be applied and is a topic of further research. Especially in the case of modified solutions by the admixture of functional additives, degradation reactions of both cellulose and solvent could be a sensitive problem.

DSC permits fast temperature screenings with relatively high heating rates that is a critical issue studying cellulose solutions, especially in NMMO, with comparably long induction periods of autocatalytic reactions and may give inaccurate onset temperatures as discussed in detail in ref. [16] Additionally, due to the small sample mass (about 10 mg) these measurements have a limited reproducibility being a problem in particular for modified cellulose/NMMO solutions containing, e.g. char coal and silver ions. Another disadvantage is the inability of realizing the typical self-heating of larger reaction masses.

Determination of the slope of pressure by means of the Systag calorimeter

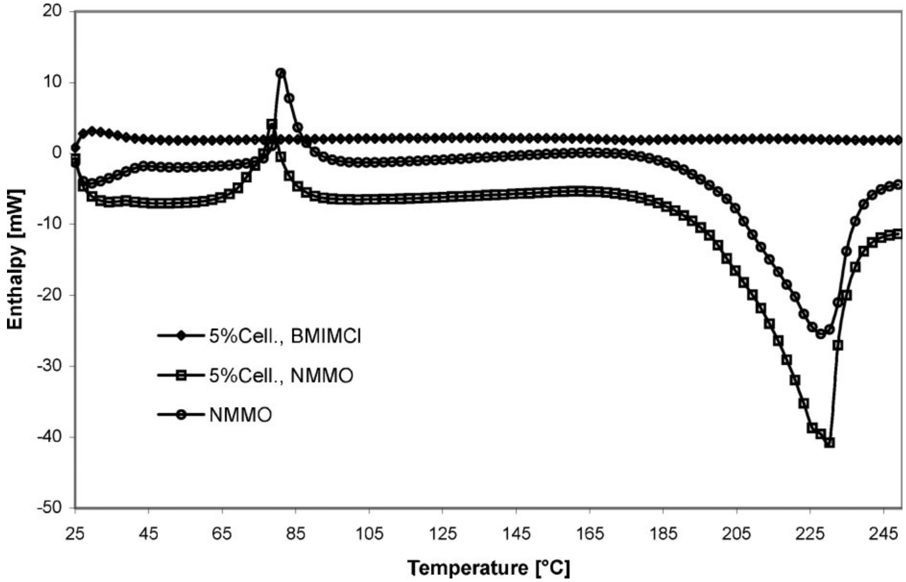


***Figure 1.***
DSC measurements: Relationship between temperature and enthalpy of cellulose solutions in 1-*N*-butyl-3-methylimidazolium chloride (BMIMCl) and *N*-methylmorpholine-*N*-oxide (NMMO) as well as pure NMMO.

RADEX (mini-autoclave) with sample amounts of 1–2 g exhibits higher sensitivity and gives also information about gas evolution even at lower temperature. Cellulose/NMMO solutions with and without additives give onset temperatures in the range 130–160 °C.[9] Compared to DSC measurements, the mini-autoclave measurements allow to differentiate much better resulting in a more accurate characterization of the influences of stabilizers and additives on the thermal behaviour of the cellulose dissolved in different media. Moreover, long term storage resistance (isoperibolic examinations) at certain temperatures can complete the knowledge of thermostability as described previously.[16]

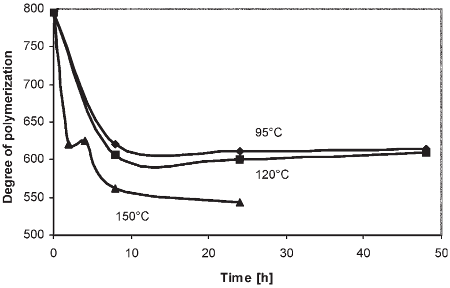


***Figure 2.***
Stability of spinning dopes in EMIMac: Relationship between degree of polymerization and time for different temperatures (12 wt.-% Linters, DP795) adapted from Hermanutz et al.[18]

In Table 1 $T_{on}$ for cellulose dissolved in NMMO and different ILs are summarized. Compared to NMMO the ILs tested possesses $T_{on}$ of 202 °C for BMIMCl and 183 °C for EMIMac. By increasing the cellulose concentration in EMIMac, a slight reduction of $T_{on}$ to 176 °C was observed. This reduction can be eliminated and a value of 181 °C appears after addition of the stabilizer system NaOH/propyl gallate that is commercially applied to stabilize cellulose/NMMO solutions.[19,20] $T_{on}$ of EMIMac is minor compared to BMIMCl. Influences of type of anion were also described in the above mentioned references, however, data about acetate containing imidazolium salts are missing. By that reason and the fact that acetates are promising alternatives to chloride ILs, further studies are ongoing.[21] Even EMIMac possesses extraordinary features com-

***Table 1.***
Comparison of onset temperatures ($T_{on}$) of cellulose (bleached beech sulphite pulp) solutions in NMMO and different ionic liquids. *Stabilizer: 0.04% NaOH, 0.06% propyl gallate.

| Solvent | Concentration of cellulose | Molar ratio cellulose: solvent | $T_{on}$ [°C] |
|---|---|---|---|
| NMMO | 12 | 8.8 | 146 |
| BMIMCl | 12 | 6.8 | 202 |
| EMIMac | 9 | 9.6 | 183 |
| EMIMac | 23.5 | 3.1 | 176 |
| EMIMac* | 23.5 | 3.1 | 181 |

pared to BMIMCl, because it is non-corrosive, non-toxic and higher concentrated cellulose solutions (>20 wt.-%) can be realized.[18]

Further advantage is the efficient functionalization of cellulosic matrices in solutions of ILs by physical incorporation of additives, e.g. metallic nano-scaled particles or adsorption materials. While the low thermal stability of NMMO against catalytic degradation restricts the incorporation of this type of substances at a technical scale, in ILs it succeeded most widely without problems.

Cellulose solutions produced by this route and added with relatively high amounts of nano-scaled silver particles do not suffer from a setback of onset temperatures compared to cellulose/NMMO solutions as depicted in Table 2. A cellulose solution in BMIMCl mixed with 0.1% of silver starts at approx. 200 °C to decompose whereas the cellulose/NMMO solutions shows first thermal activity at 145 °C. By addition of medium or strong reactive activated charcoal only a slight decrease is to be registered compared to the pure solvent and an unmodified cellulose/IL solution. Using NMMO as solvent the $T_{on}$ is not exceeding an amount of 137 °C, which is only 37 °C above the operating temperature. As mentioned above, an effective stabilization is necessary and is a further focus of research.

## Modification of Cellulosic Shapes in Ionic Liquids

Although the zero shear viscosities at 85 °C of cellulose solutions with equal concentration strongly depend on kind of IL, fibers with acceptable textile-physical properties can be spun both by means of dry-wet and wet technology.[22] Employing 1-ethyl-3-methylimidazolium acetate up to 20% of cellulose can be dissolved and regenerated (Table 3).

Another positive feature of ILs is the ability to dissolve beside cellulose both native and synthetic polymers. Here, only one example can be described. Collective dissolution of cellulose and polyacrylonitrile (PAN) is quite possible and ultimately functional fibers can be accomplished. Surprisingly, a consecutive dissolution could be shown: firstly cellulose and afterwards PAN are dissolved independent from kind and composition of the polymer mixture.[23,24] The produced fibers exhibit

***Table 2.***
Comparison of onset temperatures ($T_{on}$) of cellulose (bleached beech sulphite pulp) solutions in NMMO and ionic liquids with different additives.

| Concentration of cellulose | Ionic liquid | Additive | Concentration of additive | $T_{on}$ |
|---|---|---|---|---|
| [%] | | | [%] | [°C] |
| 12 | NMMO | MicroSilver | 0.1 | 145 |
| 12 | BMIMCl | MicroSilver | 0.1 | 200 |
| 12 | NMMO | Activated charcoal, strong reactive | 6 | 137 |
| 12 | BMIMCl | Activated charcoal, strong reactive | 6 | 197 |
| 18 | EMIMac | Activated charcoal, medium reactive | 9 | 177 |
| 23.5 | EMIMac | Activated charcoal, medium reactive | 11.75 | 176 |

***Table 3.***
Textile-physical properties of fibres spun from different ionic liquids (Cellulose: eucalyptus pulp).

| | | Solution | | | | |
|---|---|---|---|---|---|---|
| | | 1 | 2 | 3 | 4 | 5 |
| Cellulose concentration | % | 13.6 | 15.8 | 13.2 | 18.9 | 19.6 |
| Solvent | | BMIMCl | EMIMCl | BMIMAc | BMIMAc | EMIMAc |
| Fineness | dtex | 1.46 | 1.84 | 1.67 | 1.64 | 1.76 |
| Tenacity, cond. | cN/tex | 53.4 | 53.1 | 44.1 | 48.6 | 45.6 |
| Elongation, cond. | % | 13.1 | 12.9 | 15.5 | 12.9 | 11.2 |
| Loop tenacity | cN/tex | 33.1 | 29.5 | 22.1 | 25.1 | 19.9 |
| Wet abrasion test | T | 61 | 37 | 17 | 22 | 24 |
| Water retention value | % | 64.6 | 68.2 | 79.3 | 71.4 | 68.1 |
| DP of the fiber | | 514 | 493 | 486 | 479 | 515 |

a series of extraordinary properties. Table 4 displays the textile parameters and the clearly reduced water retention ability.

Moreover, at a cellulose/PAN volume ratio of about 50:50 a considerably rise of fibrillation resistance of the blend fibres was ascertained. Improvement of fibrillation tendency goes with a drop of water retention value as declared for pure cellulose fibres. The double logarithmic display of wet abrasion test vs. water retention value shows a strict linear dependence (Figure 3).

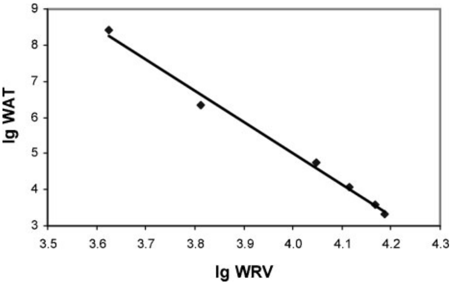


***Figure 3.***
Double logarithmic relationship between wet abrasion test (WAT) and water retention value (WRV) of the dried cellulose/PAN blend fibres.[24]

The spinning process with the application of nano-scaled silver particles proceeds up to 0.1% without any impact on textile physical parameters (Table 5) compared to unmodified fibres (Table 3). A crucial issue concerning the functional effect of the fibre is the homogeneity of silver particles in the spinning solution. The addition of silver as a suspension in NMMO assures sufficient distribution in the fibre. Desired silver content is adjustable with a recovery rate of approx. 70%. What is noteworthy in the application of colloidal silver in those concentration ranges is that it results in fibres of very high whiteness.[25]

***Table 4.***
Textile-physical properties of fibres modified with polyacrylonitrile (PAN) and spun from EMIMac. Cellulose: eucalyptus pulp.

| | | Solution | | | | | |
|---|---|---|---|---|---|---|---|
| | | 6 | 7 | 8 | 9 | 10 | 11 |
| Mass relation cellulose/PAN | | 100/0 | 90/10 | 80/20 | 70/30 | 60/40 | 50/50 |
| Volume relation cellulose/PAN | | 100/0 | 87/13 | 75/25 | 64/36 | 53/47 | 43/57 |
| Solid content | | 11.2 | 12.1 | 13.9 | 15.2 | 17.2 | 19.2 |
| Cellulose concentration | | 11.2 | 10.9 | 11.1 | 10.6 | 10.3 | 9.6 |
| Fineness | dtex | 1.7 | 1.7 | 1.7 | 1.7 | 1.7 | 1.7 |
| Tenacity, cond. | cN/tex | 50.3 | 44.6 | 35.1 | 30.4 | 23.9 | 19.4 |
| Elongation, cond. | % | 11.7 | 10.6 | 9.2 | 15.5 | 10.3 | 12.9 |
| Elongation, wet | % | 12.8 | 12.2 | 12.9 | 18.2 | 16.9 | 28.9 |
| Loop tenacity | cN/tex | 22.2 | 19.5 | 18.6 | 16.6 | 11 | 13.1 |
| Wet abrasion test | T | 28 | 36 | 59 | 114 | 618 | 4466 |
| Water retention value | % | 65.9 | 64.4 | 61.3 | 57.3 | 45.3 | 37.5 |

***Table 5.***
Textile-physical properties of fibres modified with nano-scaled silver particles spun from different ionic liquids. Cellulose: bleached beech sulphite pulp.

| | | Fibre 1 | Fibre 2 | Fibre 3 |
|---|---|---|---|---|
| Concentration of cellulose | % | 12 | 23.5 | 23.5 |
| Ionic liquid | | BMIMCl | EMIMac | EMIMac |
| Type of additive | | MicroSilver | MicroSilver | NanoSilver |
| Concentration of additive | % | 0.1 | 0.1 | 0.05 |
| Fineness | dtex | 1.80 | 1.62 | 1.56 |
| Tenacity, cond. | cN/tex | 42.3 | 55.9 | 50.8 |
| Elongation, cond. | % | 10.6 | 9.1 | 10.0 |
| Loop tenacity | cN/tex | 22.3 | 9.6 | 22.9 |

***Table 6.***
Test results of antimicrobial activity of solvents fibres modified with MicroSilver and NanoSilver spun from NMMO and ionic liquids. *after washing.

| Fiber | Type of additive | Solvent | Antimicrobial activity | |
|---|---|---|---|---|
| | | | *Staphylococcus aureus* | *Klebsiella pneumoniae* |
| 1 | 0.1% MicroSilver | BMIMCl | non antibacterial | non antibacterial |
| 2 | 0.1% MicroSilver | EMIMac | strong antibacterial | strong antibacterial |
| 2* | 0.1% MicroSilver | EMIMac | significant antibacterial | strong antibacterial |
| 3 | 0.05% NanoSilver | EMIMac | strong antibacterial | strong antibacterial |
| 3* | 0.05% NanoSilver | EMIMac | slight antibacterial | strong antibacterial |
| 4 | – | EMIMac | slight antibacterial | non antibacterial |
| 5 | – | NMMO | significant antibacterial | non antibacterial |
| Solvent | – | NMMO | non antibacterial | non antibacterial |
| Solvent | – | EMIMac | slight antibacterial | non antibacterial |

Table 6 summarizes the antimicrobial activity of fibers modified with nano-scaled silver particles. Fibres with porous MicroSilver show antimicrobial effects only for higher concentrations (from 0.1%). Because of the formation of aggregates, the antimicrobial performance of nanoscaled particles is achievable only by increasing the concentration. On the other hand, fibres with colloidal NanoSilver exhibit a higher performance (from 0.05%) as reported earlier in detail.[25] Further it can be drawn from the table, using chloride containing ILs as solvent no antimicrobial effect is detectable. Even the application of acetate gives a strong antimicrobial effect for both test strains. After defined washing (40 times, 60 °C) a strong effect is measured for *Klebsiella pneumoniae* and a significant one for *Staphylococcus aureus* in the case of 0.1% MicroSilver.

In addition, the antibacterial activity of the solvent EMIMac solely was investigated in more detail. Although the produced fibres are washed after spinning intensively, it has to be taken into account that there are residues of solvent in the fibre, which might be responsible for slight irregularities. Consequently, the effect of EMIMac on the growth of *Staphylococcus aureus* was measured by nephelometry. Compared to NMMO, which did not show any antibacterial activity, the ionic liquid

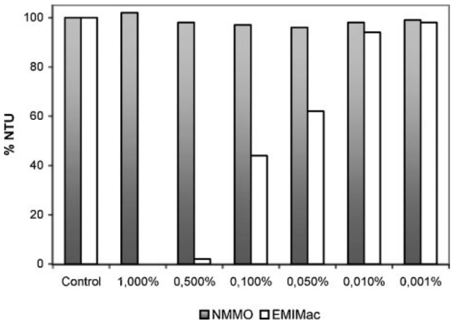


***Figure 4.***
Nephelometric measurements of the effect of EMIMac compared to NMMO (Control CASO bouillon) on growth of *Staphylococcus aureus* after 12 h for different concentrations.

***Table 7.***

Textile-physical properties of fibres modified with activated charcoals (50% with respect to cellulose) and spun from ionic liquids. Cellulose: bleached beech sulphite pulp.

| | | Fibre 6 | Fibre 7 | Fibre 8 |
|---|---|---|---|---|
| Concentration of cellulose | % | 12 | 18 | 18 |
| Ionic liquid | | BMIMCl | EMIMac | EMIMac |
| Activated charcoal | | strong reactive | strong reactive | medium reactive |
| Fineness | dtex | 2.18 | 3.07 | 2.86 |
| Tenacity, cond. | cN/tex | 12.9 | 12.2 | 11.7 |
| Elongation, cond. | % | 9.9 | 12.8 | 12.4 |
| Loop tenacity | cN/tex | 3.6 | 5.95 | 3.06 |

exhibits after 12 h at a concentration of 0.5% a clear bacteriostatic effect (Figure 4). On condition that the residue concentrations of solvent lie in the ppm – range (<0.01%) only less influences are to be assumed. Further investigations are in progress, in particular regard to purity monitoring of the shaped fibres. However, the strong difference between NMMO and EMIMac is remarkable, which confirms the harmless effect of NMMO as well as possibly new application routes for ionic liquids.

A composition of 50% cellulose and 50% adsorption materials, e.g. activated charcoal, result in fibres, which can be processed by conventional techniques to form non-wovens with sufficient mechanical stability and uniform charcoal loading (Table 7). The charcoal particles are evenly distributed in the whole fibre. Additionally, the cellulose acts as a three-dimensional carrier that is responsible for the mechanical stability.[26]

Non-wovens made there from have been investigated concerning its adsorption ability of organic compounds from the vapours as displayed in Figure 5. In general, it should be noticed that carbon tetrachloride has a higher ability to adsorption on activated charcoal than toluene. The differences between carbon tetrachloride and toluene in its adsorption behaviour can be explained by specific properties of the compounds. An equilibrium state has been reached and stabilized after one day,

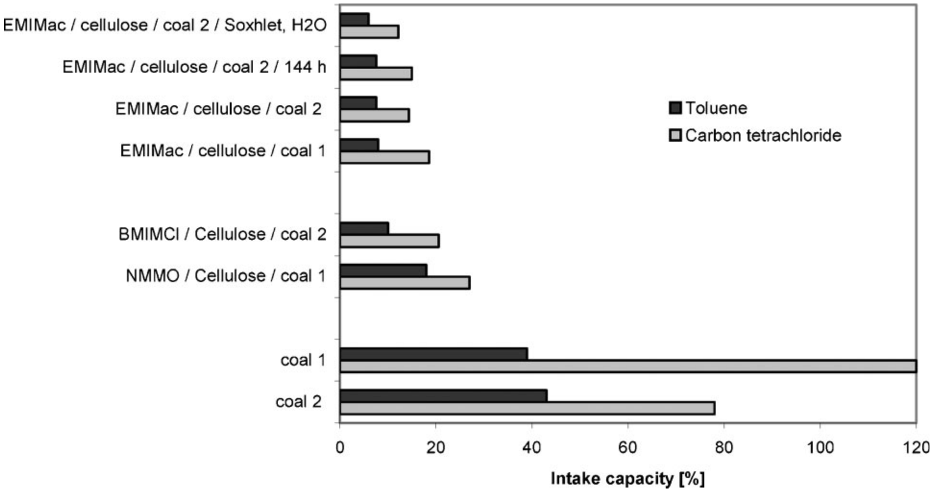


***Figure 5.***

Intake capacity of different activated charcoals (1 – medium reactive, 2 – strong reactive) and fibers spun from NMMO and ionic liquids. The adsorption time is 24 h except where denoted.

however, the equilibration loading level is already reached after 8 h.

The fibres have a lower affinity towards carbon tetrachloride and toluene than the pure active charcoal. Thus, a certain amount of the adsorbent must be inactive. First investigations of the produced fibres from ILs revealed that the adsorption effect do not reach the efficiency of the NMMO spun fibres. Reason might be aroused from the insufficient solvent extraction during fibre after-treatment. An additional reaction time in the desiccator as well as *Soxhlet* extraction brought no improvement of the intake capacity.

## Conclusion

Direct dissolution of cellulose and dry-wet shaping in ionic liquids provide regenerated fibres of high tenacity with versatile applications in the textile-technical sector. Main inconveniences of the so far used solvent *N*-methylmorpholine-*N*-oxide monohydrate (NMMO) were the incorporation of metallic nano-scaled particles and adsorber materials, thermal and chemical instability as well as high selectivity for almost exclusive dissolution of cellulose. In opposite to NMMO ionic liquids (ILs) exhibit a distinctively thermal resistance. The relative high decomposition temperatures of ILs are reflected in the onset temperatures ($T_{on}$) of cellulose/IL solutions ensuring higher process temperatures with lower risk of exothermic reactions and therefore, enhanced process safety. A slight decrease of $T_{on}$ with higher cellulose concentration was ascertained, which can be compensated by an effective stabilization. Activated charcoal and nano-scaled materials also minimize $T_{on}$. However, this decline is low compared to modified cellulose/NMMO solutions and can be attenuated by stabilizers, too. Structure/property relations with regard to the alkyl chain length and the anion/cation as well as recycling procedures will be a matter of further research. Multicomponent fibres with unexpected properties can be derived from consecutive dissolution of cellulose and polyacrylonitrile (PAN) in ILs and shaping of those. Both polymers develop inside the fibre cluster an own structure. The water retention behaviour increases as well as the wet abrasion resistance with enhancement of PAN content in the fibre. First efforts regard to the functional cellulose fibres containing nano-scaled silver particles and activated charcoal revealed reduced effects compared to cellulose fibres from NMMO. The investigations of the produced fibres showed that both the bioactive and the adsorption capacity do not reach the efficiency of the samples produced from NMMO yet. Here and on the development of simply technological capabilities towards recycling of ILs the focal points of actual research activities are to be laid.

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