Mechanical Properties of Paper Saturated With a Hydrophobic Ionic Liquid

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Research into paper-based devices and ionic liquids has increased considerably in the past few years. Thus, the combination of paper-based devices with ionic liquids is also becoming an increasingly frequent research subject. However, the influence of the ionic liquid on the paper properties has been hardly considered. In this paper, the influence of a hydrophobic ionic liquid (1-butyl-3-methylimidazolium bis(trifluoromethyl-sulfonyl)imide) on the mechanical properties of laboratory paper, isotropic and oriented, made from eucalyptus sulfate and cotton linters, is investigated. The tensile strength, elastic modulus, and breaking strain of papers saturated with ionic liquid were about 60 to 90% of the dry paper characteristics. In contrast to water, the breaking strain did not increase in the presence of the ionic liquid. This is because the ionic liquid only slightly swelled the fibers.

DOI: 10.15376/biores.18.2.2842-2856

Keywords: Ionic liquid; Paper tensile strength; Lateral flow test; Paper wet strength; Microfluidic paper-based analytical device

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INTRODUCTION

Recently in sensing, there has been a renewed and increasing interest in microfluidic paper-based analytical device (µPAD) and ionic liquids (IL). The advantages of paper-based analytical devices are numerous: low production costs, transportable size, power-free internal pump due to capillary forces, as well as good biocompatibility and biodegradability (Shen *et al.* 2020; Tong *et al.* 2021). Using µPADs, it is possible to perform analyses of glucose (Gonzalez *et al.* 2016), heavy metals (Shen *et al.* 2017; Kamnoet *et al.* 2021), or phenolic pollutants (Qi *et al.* 2018), for example. Paper is also increasingly used as a basis for paper electronics (Tobjörk and Österbacka 2011).

Ionic liquids are a class of substances, *i.e.*, molten salts melting below 100 °C, featuring a wide liquid range, negligible vapour pressure, electrical conductivity, low flammability, and thermal stability. These properties depend on the nature of the anion and the cation as well as their chemical composition. Therefore, ILs can be tailored to address a desired behaviour, especially when comprising of organic molecules. ILs have been investigated in various fields (Zhang and Etzold 2016). They serve as an extracting agent in catalysis, as an electrolyte in fuel cells, as binder in electrodes, and many other applications.

Not surprisingly, ionic liquids are increasingly used in combination with paper-based devices. For example, in a paper-based supercapacitor where the IL functions as electrolyte (Pettersson *et al.* 2014; Wang *et al.* 2017). Furthermore, Sun *et al.* (2017) created a transportable paper-based sensor by applying graphite and a thermoresponsive pyrene-based ionic liquid to paper. Finally, Dossi *et al.* (2012) made a gas sensor based on a filter paper impregnated with an ionic liquid.

In summary, paper-based devices in combination with an IL are increasingly used in many applications. However, the influence of ILs on paper properties is rarely studied. For example, no publication could be found on the presence of ionic liquids affecting the mechanical strength of paper, which is important to know for applications and manufacturing processes. For example, there are many applications where an ionic liquid is brought into contact with paper, but is subsequently washed out, *e.g.*, in the production of µPADs with ionogels (Akyazi *et al.* 2016). In these cases, the paper strength could play a crucial role during processing. In contrast, the influence of water as well as moisture on paper strength has been part of numerous studies as described by Östlund and Niskanen (2021) as well as Johnson *et al.* (1983), among others. Some ILs dissolve cellulose and lignin, respectively, and thus they cannot be employed for the mentioned applications (Brandt *et al.* 2011; Glas *et al.* 2015).

This research studies how the paper strength changes compared to the dry state when the paper is saturated with an ionic liquid (in this case: 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [BMIm][NTf_2]) using isotropic paper as well as oriented paper made from unrefined eucalyptus sulfate and cotton linters pulp. It is expected that the paper strength characteristics of tensile strength, elastic modulus, as well as the breaking strain lie between the values of the dry paper as well as the water-saturated paper. It is expected that the characteristic values of the paper soaked in IL will be closer to the dry paper than to the values of the paper soaked in water, because it is a hydrophobic ionic liquid.

BACKGROUND

This section very briefly shows the influence of fiber orientation on the mechanical paper properties. Afterwards, it deals with the influence of water on paper strength properties when paper is soaked with water. At the end, the use of ionic liquids in fiber and paper applications is discussed.

The setup of the paper machine of commercially produced paper results in a preferred fiber orientation in the direction of the suspension flow or, in other words, in the machine direction. Consequently, more fibers are oriented in the machine direction (MD) than in the cross direction (CD) (Johnson *et al.* 1983; Norman and Söderberg 2001). The fiber orientation has an influence on many paper properties such as strength characteristics. The tensile strength in the main fiber direction, corresponding to MD, is greater than transverse to it, corresponding to CD (Johnson *et al.* 1983).

Paper Strength Properties in the Presence of Water

In the presence of water, the tensile strength of paper decreases. This can be attributed to two effects. First, water molecules penetrate between the fibers, weakening the hydrogen bonds. Secondly, fibers swell in the presence of water. As a result, the fibers become more flexible and the friction between the fibers decreases (Brückle 2012; Schäfer

et al. 2021). This allows the fibers to glide past each other and the main failure mechanism is fiber pull-out (Schäfer *et al.* 2021).

The decrease in tensile strength due to a liquid is described by the relative wet strength. The relative wet strength WS describes the tensile strength in the wet state σ_{wet} in a ratio to the tensile strength in the dry state σ_{dry}, see Eq. 1 (Brückle 2012):

$$WS = \frac{\sigma_{wet}}{\sigma_{dry}} \quad (1)$$

The elastic modulus, like the tensile strength, is greater in MD than in CD (Johnson *et al.* 1983). Because of the swelling of the fibers, the elastic modulus also decreases in water-saturated paper compared to dry paper (Persson *et al.* 2013). Persson *et al.* (2013) report that wet paper has an elastic modulus in the range of 10 MPa, whereas in the dry state the elastic modulus is in the range of 1 to 10 GPa, which is a factor of 100 to 1000.

The breaking strain behaves exactly opposite to the tensile strength and the elastic modulus. It is normally smaller in MD than in CD. The breaking strain increases in the presence of water because of the swollen fibers. In this state, they can better slide or be strained against each other (Brückle 2012). The effect of the increase in strain because the increasing water content is greater in CD than in MD (Johnson *et al.* 1983). According to Östlund and Niskanen (2021), paper in the dry state has a breaking strain of 1 to 5%.

Ionic Liquids in Combination with Pulp and Paper

Ionic liquids are molten salts with melting points below 100 °C. Some of these compounds are even liquid at room temperature (RT) and are thus called RTILs. Additionally, the abbreviation TSIL is often used, referring to task-specific ionic liquids, highlighting the interest in these kinds of materials. An overview over the history of ILs can be found in several reviews, such as in Welton (2018).

The ILs might be superior, where water or volatile organic compounds cannot be used, *e.g.*, when evaporation shall be prevented, for instance, in paper-based batteries or supercapacitors, where aqueous electrolytes would dry out. This undesired outcome can be overcome using an ionic liquid as an alternative, although the ion mobility is usually lower (Tobjörk and Österbacka 2011). Hydrophobic ILs can be obtained by incorporation of long aliphatic chains, often within the cation, or fluorination of organic anions as in bis(trifluoromethylsulfonyl)imide [NTf_2] and bis(pentafluoroethanesulfonyl)imide, extending the capabilities of ILs and enabling utilization in extraction for wastewater treatment and metal recovery (Wei *et al.* 2003; Domańska and Rękawek 2009; los Ríos *et al.* 2010; Regel-Rosocka and Wisniewski 2011; Hoogerstraete *et al.* 2013; Diabate *et al.* 2018).

A lot of research has been focused on fuel cells, batteries, and also supercapacitors, where ILs are investigated as electrolytes (Zhang and Etzold 2016). However, ILs can be found in processing of biomass, biopolymers, and paper (Brandt *et al.* 2011; Glas *et al.* 2015). Furthermore, extraction of cellulose out of industrial paper mill wastewater (Glińska *et al.* 2019) and hemicellulose from a kraft paper pulp (Roselli 2017) using an IL is reported. Viell *et al.* (2020) gave insights into the transformation process in wood treatment with ILs, while Spörl *et al.* (2018) demonstrated a fully recyclable all-cellulose composite, using 1-ethyl-3-methylimidazolium acetate.

The treatment with ILs has an influence on the physical properties of the material. Li *et al.* (2019) found that the pretreatment with [BMIm][Cl] improves the internal bond strength of the paper fibers and could also reduce the energy consumption of the refining

process. Ichiura *et al.* (2017) explain the increased wet strength of paper that was pretreated with [BMIm][Cl] as being due to partial dissolution of cellulose, forming a cellulose film on the surface and their hydrogen bonds. The anion of the IL plays an important role in the dissolution of cellulose. As concluded by Wang *et al*. (2012), the dissolution capabilities for cellulose follows acetate > chloride > formate > dicyanamide > [NTf_2]. In the publication of origin from Zhao *et al.* (2008), experiments were conducted at 110 °C and for most [NTf_2] compounds, dissolution was comparably low or below the detectable level, due to the low solubility. The role of the cation seems not as clear (Wang *et al*. 2012).

An increased tensile strength of aged paper was shown for the pretreatment with cholinium glycinate, which is explained by a possible antioxidant effect of this IL and bonds between adjacent chains of the cellulose (Scarpellini *et al.* 2016).

However, using different ILs, 3-alkyl-1-methylimidazolium tetrafluoroborates, 3-alkoxymethyl-1-methylimidazolium tetrafluoroborates, and 3-alkoxymethyl-1-methyl-imidazolium bis(trifluoromethanesulfonyl)imides, it was found that there were decreases the paper strength, which were attributed to weakened cellulose-hydrogen bounds, while the wettability was found to improve (Przybysz *et al.* 2005).

Even though ILs and their influence on paper strength has been investigated, the focus has been on pretreatments, where the paper is in contact with ILs before the measurements. To the best of the authors' knowledge, no research of tensile strength of IL soaked paper is documented. Thus, the present work considers a prominent, hydrophobic RTIL that shows neglectable cellulose dissolution capabilities. This RTIL, which has been intensively studied, well characterized (Vranes *et al.* 2012), and is commercially available, is 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [BMIm][NTf_2]. It is hence chosen as a model for tensile strength test of soaked paper in this work.

METHODS

Characterization of the Ionic Liquid

To characterize the IL and compare the results, its density, dynamic viscosity, and water content were measured. Therefore, the IL was measured as taken from the container. The density was determined as 1.4359 g mL^{-1} at 22 °C using an approximately 10 mL-sized pycnometer, priorly calibrated with purified water. The viscosity was determined as 44.5 mPas at 25 °C in a spindle viscometer DV-II+ (AMETEK Brookfield, Middleborough, MA, USA) with the spindle model S87 in a thermostatically controlled, open steel chamber. Water content was measured by Karl-Fischer-titration with a Metrohm model 720 KFS Titrino, Karl-Fischer-Roti® hydroquant C5 (Carl Roth GmbH + Co. KG, Karlsruhe, Germany) and HYDRANAL™ - dry methanol (Honeywell International Inc., Charlotte, NC, USA). The pristine IL contained 0.01 wt-% water (0.23 mol-%), while after being in contact with purified water for two weeks and occasionally shaking the content increased to 1.34 wt-% (24.06 mol-%).

Paper Production

Eucalyptus sulfate pulp (EuSu) and cotton linters, both unrefined, were used for paper production. In view of the subsequent application in µPADs, the pulp was not refined, since the goal was to produce a porous paper with low fines content. The length-weighted average fiber length is 0.87 ± 0.00 mm for EuSu (curl: 16.02 %, fibrillation: 1.24 %) and 1.06 ± 0.01 mm for linters (curl: 17.76 %, fibrillation: 1.30 %). The values

were determined with the Fiber Image Analyzer FS5 (Valmet, Espoo, Finland). The standard deviation refers to four measurements each. Isotropic laboratory sheets were produced using the Rapid-Köthen process according to ISO 5269-2 (2004) with a basis weight of approximately 50 g/m^2. In a laboratory paper, there is no preferred fiber direction within the fiberplane. Therefore, the paper strength properties are independent of the testing direction.

In addition, highly oriented paper sheets were produced with an experimental sheet former (Götzinger and Schabel 2019; Götzinger 2021). For the production of the highly oriented papers, a diluted fiber suspension with a consistency of 0.05% including CMC (carboxymethylcellulose sodium salt, Sigma-Aldrich, St. Louis, MO, USA, 55 mg/L) was first prepared. CMC serves as a dispersing agent to prevent flocculation (Götzinger and Schabel 2019; Götzinger 2021). In the experimental sheet former, the fiber suspension flows through a tube to a nozzle, where the fibers are aligned in the flow direction. The jet falls approximately tangentially from the nozzle onto a moving wire, where the suspension is dewatered directly through vacuum slots. In this way, the fiber is fixed on the wire, oriented in its direction. A shear flow is formed when the wire and the suspension have different velocities. This fixes one end of the fiber on the wire and the rest of the fiber aligns itself in the direction of the shear field, further increasing the fiber orientation. Thus, the degree of fiber orientation can be adjusted by the wire-jet velocity difference. An increase of the wire-jet velocity difference leads to an increase of the fiber orientation in the observed area. In oriented papers, there is a main fiber direction, so that paper strength properties are direction-dependent.

Götzinger (2021) investigated the influence of CMC on the stress-strain behavior of Rapid-Köthen laboratory sheets and could not observe any change in the stress-strain behavior due to CMC. Also by a conductivity titration based on Eyler *et al.* (1947) and by a complex titration based on Kessel (1985) of oriented papers with and without CMC, no differentiation between the samples was possible. The results indicate that most of the CMC is washed out with the white water during production (Götzinger 2021). Because CMC has no effect on stress-strain behavior, it was supplemented in the suspension for the production of oriented papers to avoid flocculation, but not in the production of Rapid-Köthen laboratory sheets because it is not needed for the production process.

Papers with a wire-jet velocity difference of 40 m/min and a basis weight of approximately 50 g/m^2 were produced for the analysis. Afterwards, the wet paper webs were dried in Rapid-Köthen sheet dryers (PTE, Pettenbach, Austria). The basis weight and thickness were subsequently measured for all papers.

Fiber Orientation Measurement

The degree of fiber orientation of the oriented papers was characterized by image analysis. Götzinger's method (Götzinger 2021) was used for this purpose. Before paper production, 0.3% of the dry fiber mass was dyed with a fluorescent yellow dye (Pergasol Yellow F-6GZ Liq., BASF, Ludwigshafen, Germany). In a climate-controlled state (ISO 187 1990), the papers were laid separately in a darkroom and were photographed (Nikon D300, Tokyo, Japan; with Nikon Y48 optical yellow filter, 508 dpi) under UV illumination (395 nm). Because of the slightly different degree of orientation, both the wire side and top side of the paper were captured.

Next, the image was preprocessed in MATLAB (R2020b, MathWorks, Natick, MA, USA), which includes converting the image to grayscale, adjusting the brightness, cropping the image area, and eliminating any wire marks that may be present.

Subsequently, a frequency distribution of the fiber orientation over an interval from -90° to +90° and a class width of 1° was created with Fiji (Schindelin *et al.* 2012) with the use of the Plug-In OrientationJ (Sage 2022), normalized to the area of 1. For fiber detection, the "Finite Difference" filter was used with a tensor width of 7 corresponding to the fiber width of 7 pixels. Firstly, the frequency distribution can be approximated by a von-Mises distribution, where the parameter κ can be considered as a parameter for fiber orientation. An increasing κ-value indicates an increase in anisotropy (Naito 2002). Secondly, the fiber orientation angle can also be determined, whereby a decreasing fiber orientation angle shows an increase in anisotropy (Naito 2002).

To characterize the produced papers, the wire and top side of five papers each were measured. The average fiber orientation parameter κ is 2.44 ± 0.39 for EuSu and 1.55 ± 0.04 for Linters. The average fiber orientation angle is 17.11 ± 1.33° for EuSu and 22.73 ± 0.33° for Linters.

Tensile Strength Measurement

The mechanical properties were measured on a Zwick/Roell Z010 universal machine (ZwickRoell GmbH & Co. KG, Ulm, Germany) in accordance with ISO 1924-2 (2008) under standard climatic conditions (ISO 187 1990). The paper strips were 15 mm wide. The standard specifies a free clamping length of 180 mm and a test speed of 20 mm/min. However, samples of this size cannot be produced either by the Rapid-Köthen method or on the experimental sheet former for highly oriented paper. Therefore, the free clamping length was reduced to 50 mm and the test speed was adjusted accordingly to 5.555 mm/min. For the highly oriented papers, samples were tested in the main fiber direction (MD) as well as in cross direction (CD). In each direction, nine to ten measurements were recorded. For the samples saturated in IL, only five measurements were recorded in each direction because of the required amount of IL.

All samples were tested under three conditions. First of all, the specimens were tested in dry condition. A 200 N load cell was used for the measurement. Second, the samples were tested in the water-saturated condition. Therefore, the samples were placed in a tub of distilled, air-conditioned water for 12 min. After 12 min, it was assumed that they were saturated with water because there was no change in the weight of the samples anymore. For testing, they were carefully removed from the tub after the 12 min, swabbed briefly, clamped into the tensile testing machine, and then measured. A 10 N load cell was used because of the low wet strength.

Lastly, the samples were soaked with the hydrophobic IL before measurement. A 200 N load cell was used again for the measurement. The samples could not be placed in a tub filled with IL as before with water, because in this case the consumption of the IL would have been too great. The required amount for the saturation of the samples was determined experimentally as 0.075 g, which corresponds to five drops from the used pipette. The required amount of IL (0.075 ± 0.026 g) was applied evenly to each sample and allowed to soak for 12 min. During this time, the IL had spread throughout the paper samples. This could be clearly seen from the change in transparency of the paper as well as the impression on the pad. When the soaked strip was removed from the pad, ionic liquid remained on the pad in fine drops. Consequently, the amount of the applied ionic liquid did not correspond to the amount that was later present in the paper during the measurement. After the conditioning, the tensile test was conducted.

Some samples failed in the clamping, especially the samples soaked in ionic liquid. Due to the small number of those, the measured values of the specimens that failed in or near the clamping were still used for the evaluation.

The tensile strength, elastic modulus, and breaking strain were determined for evaluation. The tensile strength is the maximum force at break related to the original paper cross-sectional area, which is calculated from the dry paper thickness and the width of the dry paper strip. To calculate the elastic modulus, a linear regression of the stress as a function of strain was performed. The regression was started at a strain of 0.1% and run for at least ten measurement points. As soon as the standard error of the regression was greater than 1%, the regression was completed in the linear range. The slope of the regression line is defined as the elastic modulus. The breaking strain is the relative change in length at break in relation to the original sample.

Measurement of the Fiber Swelling Capacity

Furthermore, the extent fibers swelled in the presence of water and IL compared to the dry state was measured. However, because the refractive index of air is far different from that of water or the IL, comparing fiber dimensions between these three conditions would be prone to imaging errors. Therefore, an oil that does not swell the fibers and has a refractive index close to that of water and the IL was used to obtain images of unswollen, *i.e*. "dry" fibers. Microscope images were taken with a Leica Confocal laser scanning microscope (TCS SP8, Leica Microsystems, Mannheim, Germany) of the oriented eucalyptus sulfate paper in the presence of three different liquids, namely water, the IL, and an oil, representing the dry state. The chosen oil (Cargille 7ML Refractive Index Liquid Series AA 1.42, Cargille Laboratories, Cedar Grove, NJ, USA) had a refractive index of 1.42, which by mixing with the IL closely matched the refractive index of the latter. This allowed confocal stacks of fibres measured in IL or this oil to be compared in terms of their spatial extent. Four (water, IL) or five (oil) images were taken for each sample. Using the microscope images, the fiber diameter was measured with ImageJ by a distance measurement. The diameter of the focused fibers was determined over the entire image. In total there were 90 measurements in oil, 60 in water, and 52 in IL.

RESULTS

The stress-strain curves in Fig. 1 illustrate the overall correlations, shown here for oriented eucalyptus sulfate paper. It can be clearly seen how the ionic liquid slightly reduced the tensile strength, the elastic modulus, and the breaking strain compared to the dry state. In addition, it is visible how water remarkably reduced the tensile strength as well as the elastic modulus and increases the breaking strain.

In the following figures, the tensile strength (Fig. 2), the elastic modulus (Fig. 3), and the breaking strain (Fig. 4) are presented for all samples in the different measuring conditions. A further diagram with adjusted axis can be found for each parameter, because either the values for the samples saturated with water or for the other two samples are comparatively small, depending on the considered parameter. The error bars indicate the standard deviation.

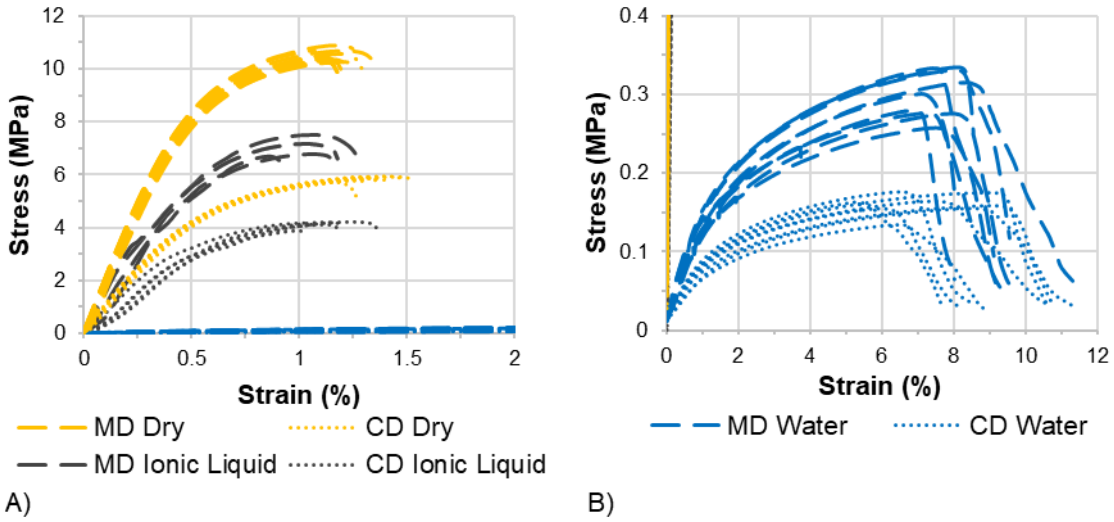

Fig. 1. Stress-strain diagram for oriented eucalyptus sulfate paper for dry state as well as water and ionic liquid saturated state. A) Strain on x-axis scaled to 2% for highlighting the graphs of dry sample as well as saturated with ionic liquid, B) stress on y-axis scaled to 0.4 MPa for highlighting the graphs in water saturated condition.

The tensile strength, shown in Fig. 2, was highest for the dry samples. The ionic liquid only slightly weakened the paper strength, whereas water drastically lowered it, as expected. In addition, the paper strength was higher in the predominant fiber direction than in the cross direction, which is also in line with the expectations. Furthermore, it can be observed that papers made from eucalyptus sulfate (EuSu) show higher strength values than those made from cotton linters. High strength properties are reported for refined linters (Sczostak 2009). Here, however, the fibers are short at approximately 1 mm, which reduces the strength properties of the cotton linters paper. Strength properties of papers made from unrefined fibers are generally small due to the weak fiber-to-fiber bonds (Sampson 2009).

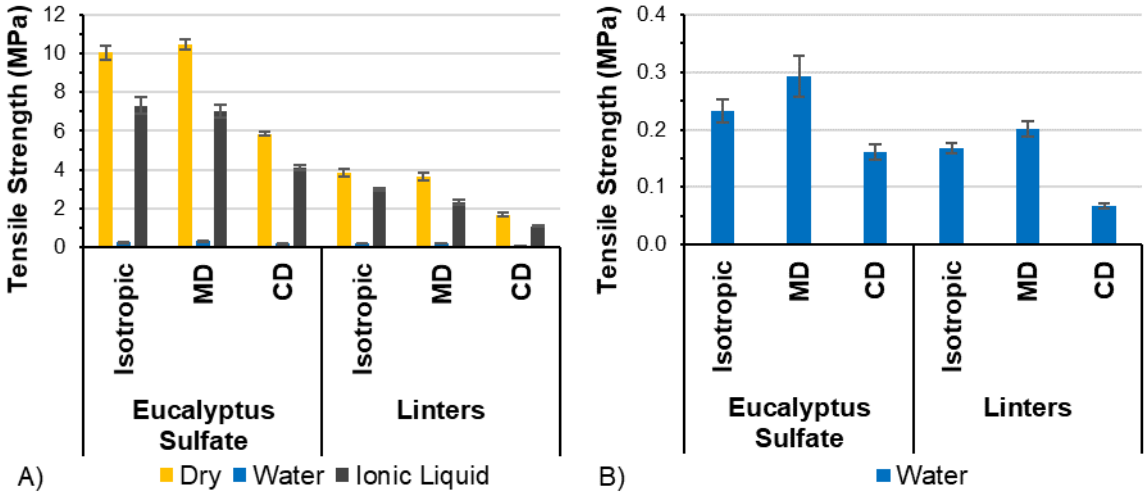

Fig. 2. The tensile strength for the isotropic as well as oriented eucalyptus sulfate and linters papers. The samples were tested in dry state and saturated with water or ionic liquid. For the oriented MD samples, the tensile direction corresponds to the main fiber direction, whereas for the CD samples the tensile direction is cross to the main fiber direction. The isotropic samples are Rapid-Köthen laboratory sheets. The error bars indicate the standard deviation. A) All conditions, B) only the samples saturated with water with adjusted axis.

Figure 3 shows the elastic modulus of the different samples. Again, it can be seen that the dry samples exhibited the highest elastic modulus. The ionic liquid slightly decreased the elastic modulus and water remarkably decreased the elastic modulus. In addition, deviations between samples increased because of the liquids. In contrast, the breaking strain increased noticeably with the addition of water, as Fig. 4 illustrates.

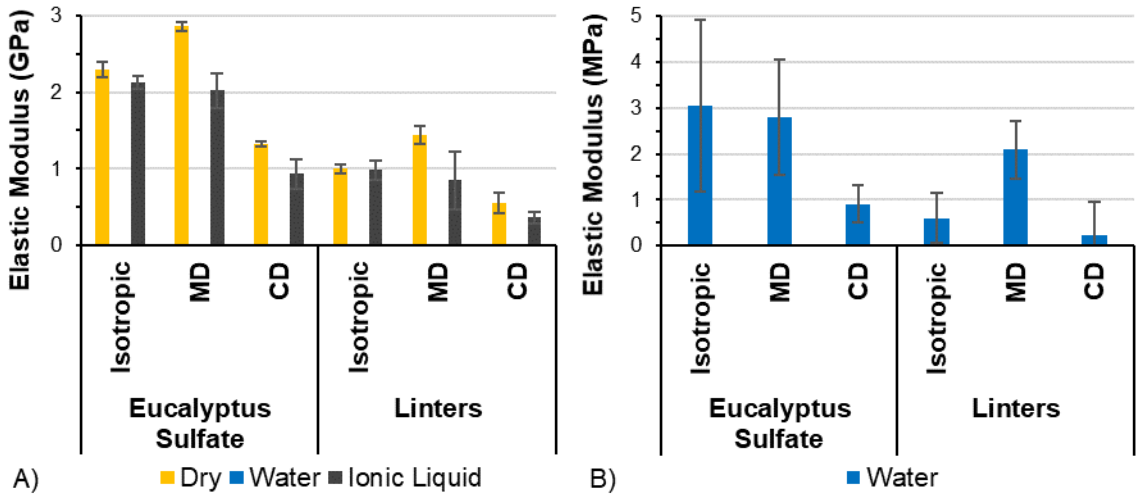

Fig. 3. The elastic modulus for the isotropic as well as oriented eucalyptus sulfate and linters papers. The samples were tested in dry state and saturated with water or ionic liquid. For the oriented MD samples, the tensile direction corresponds to the main fiber direction, whereas for the CD samples the tensile direction is cross to the main fiber direction. The isotropic samples are Rapid-Köthen laboratory sheets. The error bars indicate the standard deviation. A) All conditions (The bars from the samples saturated with water are very small and therefore not visible), B) only the samples saturated with water with adjusted axis and unit.

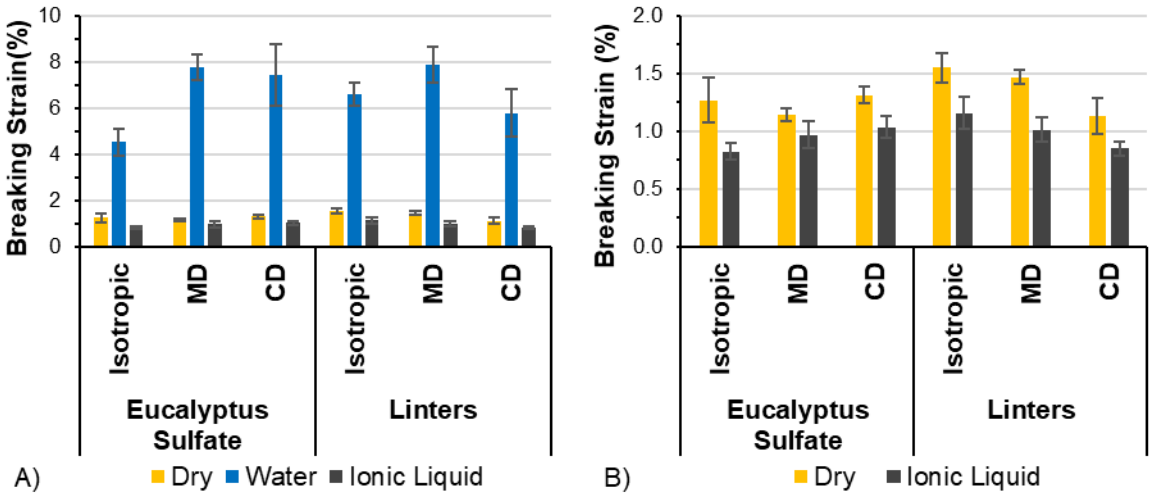

Fig. 4. The breaking strain for the isotropic as well as oriented eucalyptus sulfate and linters papers. The samples were tested in dry state and saturated with water or ionic liquid. For the oriented MD samples, the tensile direction corresponds to the main fiber direction, whereas for the CD samples the tensile direction is cross to the main fiber direction. The isotropic samples are Rapid-Köthen laboratory sheets. The error bars indicate the standard deviation. A) All conditions, B) only the dry samples as well as samples saturated with ionic liquid with adjusted axis.

It is noteworthy that the addition of the ionic liquid led to a small decrease in the breaking strain and not to an increase. It should be mentioned that in the dry state, the breaking strain in CD was only slightly higher (EuSu) or even lower (Linters) than in MD, which is unusual for oriented paper. Normally, the breaking strain in CD is much higher than in MD. This is because of the manufacturing process. The oriented papers were not produced on a commercial paper machine but on an experimental sheet former with following shrinkage-hindered drying. Further information can be found by Götzinger (2021).

Because the ionic liquid affected the paper tensile strength much less than water, the IL wet strength was correspondingly much higher and ranges between 64 and 77%, whereas the water wet strength was between 2 and 6%.

Microscope images (cf. Fig. 5) were used to measure the extent to which fibers swell in the presence of IL and water. It was found that the mean fiber diameter in oil, which approximately represents the dry state, was 11.29 ± 2.54 µm. The fiber diameter increased in the presence of the other liquids to 12.21 ± 2.74 µm in IL and 14.16 ± 2.95 µm in water. The fiber diameter in natural fibers is by nature widely distributed, which explains the large standard deviations.

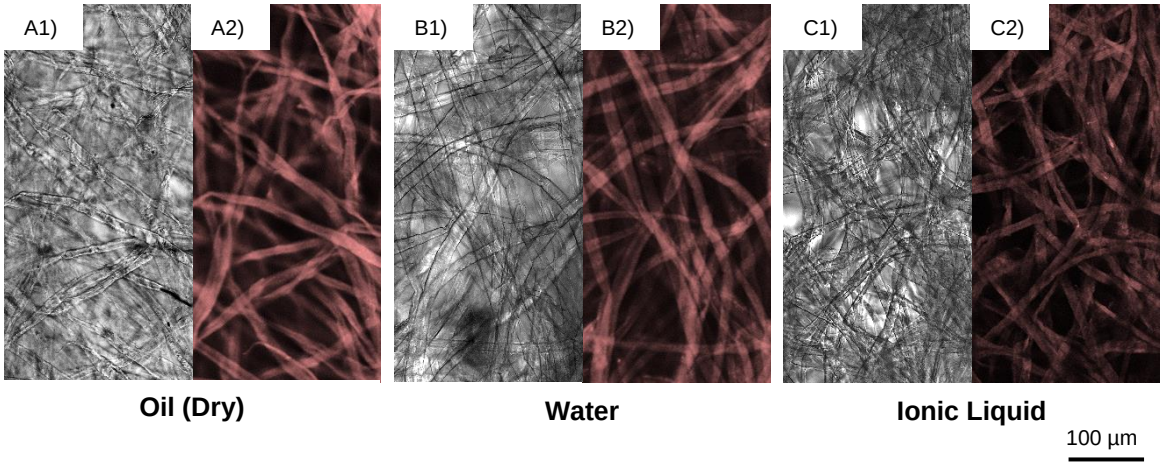

Fig. 5. Microscope and confocal images of eucalyptus sulfate paper, A1) microscope image, paper with oil, A2) the same area as confocal image, paper with oil, B1) microscope image, paper with water, B2) the same area as confocal image, paper with water, C1) microscope image, paper with IL, C2) the same area as confocal image, paper with IL.

DISCUSSION

As originally expected, the values of tensile strength as well as the elastic modulus of ionic liquid (IL) saturated paper were slightly lower than the characteristic values of dry paper. The two mentioned strength values of water saturated paper were much lower, as commonly known. Consequently, the presence of the hydrophobic IL slightly reduced the fiber bonds. It is conceivable that the ions or the water content in the IL partially break hydrogen bonds and reduce the van der Waals forces. Moreover, hydrophobic ILs probably form fewer hydrogen bonds (Dong and Zhang 2012; Hunt *et al.* 2015) to the fiber surface than water. The dissolution of cellulose in ILs is attributed to hydrogen bond interaction with acetate and chloride anions, which is low for [NTf_2] (Wang *et al.* 2012). It is conceivable that the hydrophobic IL might also interact with hydrophobic regions within

the paper material. This would lead to lower fiber bonding, and this in turn would lead to lower strength. However, the effect was much smaller than with pure water. In addition, the distance between the fibers would increase due to the presence of the IL, which also would lead to lower strength. The underlying cause cannot be comprehensively discussed, and further investigation is required.

It has often been shown that the breaking strain of paper increases remarkably in the presence of water. It is noteworthy that the breaking strain slightly decreased in the presence of IL compared to the dry state. This suggests that the fibers did not swell strongly because of the IL, which did not make the fibers more flexible and thus did not increase the breaking strain. Microscope images confirm that the fibers swelled only slightly in the presence of IL. The swelling might also result from the water contained in the IL.

It should be noted that only one hydrophobic ionic liquid was considered in this work. The exact effects on the strength properties will vary depending on the IL used. These measurements here are especially for initial guidance. It is assumed that an IL with a similar molecular structure will also affect the strength properties in a similar way. Moreover, the absolute values are also strongly dependent on the pulp and paper properties.

CONCLUSIONS

In this work, the effects of a hydrophobic ionic liquid on the mechanical paper properties were investigated when the paper was saturated with the ionic liquid 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [BMIm][NTf_2]. Knowledge of the change in mechanical properties is important for the application of ionic liquids in paper-based devices. For this purpose, isotropic, as well as oriented laboratory papers, made from unrefined eucalyptus sulfate and linters pulp were tested. The most important results of this study are the following:

1. The tensile strength, the elastic modulus, and the strain at break of papers soaked in the ionic liquid slightly decreased compared to the dry state. Because of the presence of the ionic liquid, the values were only 60 to 90% of the initial value. Thus, in subsequent applications of hydrophobic ionic liquids to paper-based devices, the mechanical properties of the paper can be expected to be only slightly reduced.
2. In comparison, the tensile strength and the elastic modulus of water-saturated papers substantially decreased and the strain at break increased considerably more. Consequently, the ionic liquid seems to weaken the fibre-fibre bonds noticeably less than water. Hence, in lateral flow tests with ionic liquids instead of aqueous solutions, the strength and the elastic modulus will be less weakened. However, the strain at break will not increase.
3. The fibers swell only slightly as a result of the ionic liquid.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge financial support from the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) – 405469627 and 465690040.

DIGITAL APPENDIX

Supporting information like the data of the thickness and basis weight measurement as well as the tensile strength measurement for all samples are available free of charge at https://tudatalib.ulb.tu-darmstadt.de/handle/tudatalib/3681 (DOI: 10.48328/tudatalib-1032).

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Article submitted: January 11, 2023; Peer review completed: February 11, 2023; Revised version received and accepted: February 17, 2023; Published: February 24, 2023.
DOI: 10.15376/biores.18.2.2842-2856