Mechanical Properties of Pulp Delignified by Deep Eutectic Solvents

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Mechanical properties were evaluated for pulp delignified by four deep eutectic solvents (DES). The DES systems were based on choline chloride and lactic acid (1:9), oxalic acid:dihydrate (1:1), malic acid (1:1), and the system alanine:lactic acid (1:9). The results indicated that the type of DES system used influenced the delignified pulp's mechanical properties including tensile, burst and tear indexes, tensile length, and stiffness. The most suitable DES systems were choline chloride:malic acid (1:1) and alanine:lactic acid (1:9), which achieved the best aforementioned mechanical properties compared to the other DES systems. The weakest performance in the process of pulp delignification was the system with choline chloride and oxalic acid dihydrate (1:1).

Keywords: Deep eutectic solvents; Mechanical properties; Pulp; Delignification

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INTRODUCTION

The most available source of biomass is lignocellulose in the form of fiber or pulp. These raw materials can be converted into many chemicals and materials and can be used in the paper industry in the form of pulp. For every fractionation, the use of a solvent is required and using a recyclable solvent is ideal (Tang *et al.* 2017). However, lignocellulose processing is limited by the material's very low solubility in water and some organic solvents. Deep eutectic solvents (DESs) are used in the process of dissolution and fractionation, and may also be used in the post-delignification process. Deep eutectic solvents are mixtures of hydrogen bond acceptors and hydrogen bond donors with a melting point much lower than that of either of its components. They have been the focus of interest in past years due to their unique properties (de Morais *et al.* 2015). The DESs have promising potential for applications in the pulp, paper, and recycling industries (CEPI 2013; Hiltunen *et al.* 2015; Suopajärvi *et al.* 2017). The DESs are considered green solvents due to their biodegradability, recyclability, non-flammability, low toxicity, low price point, and availability. A significant amount of DESs can be prepared directly from low toxic natural components (Dai *et al.* 2013). However, the toxicity of DES can be higher compared to its individual components (de Morais *et al.* 2015; Sirviö *et al.* 2016), but the toxicity greatly depends on the organism exposed to the DES (Juneidi *et al*. 2015).

Due to the formation of hydrogen bonds between the DES components, DESs are characterized by a large depression or freezing point (Vigier *et al.* 2015). Since DESs introduction, several research papers have been published on their use in the delignification process (de Dios 2013; Francisco *et al.* 2012; Jablonsky *et al.* 2015; Kumar *et al* 2016; Choi *et al.* 2016; Skulcova *et al.* 2016). Among other advantages, DESs may be used for the dissolution and hydrolysis of some lignocellulosic components, such as lignin, under mild conditions compared to other methods (Majova *et al.* 2017a). In their recently published works, Majova *et al*. (2017a, 2017b) documented that delignification by DESs requires neither temperature higher than 100 °C nor increased pressure. The delignification of woody biomass by DESs at higher temperatures (120 °C, 145 °C, and 180 °C) was performed at work Alvarez-Vasco *et al.* (2016). However, thermal degradation of DES was not evaluated. The thermal stability of DESs was described in a paper by Haz *et al.* (2016). The authors investigated the temperature dependence of the thermal stability of DESs based on choline chloride and organic acids. The authors' subsequent work documents that there is a weight decrease of up to 37% (for choline chloride and malonic acid) at 100 °C. Due to their low energy consumption during their engagement in the pulp processing, DESs represent a very promising alternative to conventional delignification solvents (Majova *et al.* 2017a). In this study, the results obtained for the delignification of pulp by DESs composed of choline chloride and three organic acids, as well as alanine and lactic acid, are offered. The delignified pulp was characterized by mechanical properties such as tensile index, tensile length, burst index, tear index and stiffness.

EXPERIMENTAL

Materials

All chemicals were obtained from Sigma Aldrich (Bratislava, Slovakia). The solvents were stirred in a water bath at 70 °C to 80 °C to form a homogeneous liquid. Four deep eutectic solvents were used for the experiment. The DESs were mixed from choline chloride, oxalic acid dihydrate, malic acid, lactic acid (90% solution), and alanine (Table 1).

Table 1. Deep Eutectic Solvents

Sample	HBA : HBD	Molar ratio	Density (g/cm^3) at 25 °C	Viscosity (mPa·s) at 28 °C
DES1	ChCl : oxalic acid dihydrate	1:1	1280	126.1
DES2	ChCl : malic acid	1:1	1299	494.3*
DES3	ChCl : lactic acid	1:9	1217	70.9
DES4	Alanine : lactic acid	1:9	1230	168.0

ChCl- choline chloride, HBA- hydrogen bond donor, HBD- hydrogen bond acceptor; *at 80 °C

The hardwood kraft pulp was obtained from Mondi SCP, Ružomberok, Slovakia (pulp 1) and BUKÓZA HOLDING a.s., Hencovce, Slovakia (pulp 2). Characteristic chemical properties of the pulp before and after DES delignification are listed in Table 2 (Majova *et al.* 2017b).

The pulp sample was mixed with DES and treated at 60 °C for 2 h. The sample was washed using hot water to a neutral pH, filtered, and air-dried. The Kappa number and viscosity were determined by standard procedures (TAPPI T236 cm-85 (1996); TAPPI T230 om-94 (1996)) described elsewhere (Majova *et al.* 2017b).

Table 2. Characteristic Chemical Properties of Pulp Before and After DES Delignification

Sample	Kappa No.	Viscosity (mL/g)	DP	CS	*Slc*$_\kappa$ (%)	*Efc*$_\kappa$ (%)
Kraft pulp 1 *[1]	21.7	789	1157	-	-	-
DES1	13.3	648	930	0.243	5.96	38.7
DES2	13.2	772	1130	0.023	52.02	39.2
DES3	13.5	775	1134	0.020	58.27	37.8
DES4	12.3	784	1149	0.006	206.48	43.3
Kraft pulp 2 *[2]	14.3	851	1258	-	-	-
DES1	11.1	490	683	0.842	0.88	22.4
DES2	12.3	780	1113	0.131	2.82	14.0
DES3	11.8	745	1085	0.160	2.34	17.5
DES4	11.2	800	1160	0.084	6.01	21.7

* [1]Mondi SCP, Ružomberok Slovakia; [2]BUKÓZA HOLDING, a. s., Hencovce, Slovakia
DP – degree of polymerization,
CS – cellulose chain scission number
Slc$_\kappa$ – The selectivity of delignification (expressed as a decrease in Kappa number, κ, on the unit change of the intrinsic viscosity)
Efc$_\kappa$ – The efficiency of delignification (expressed as a decrease in Kappa number on the unit change of the initial Kappa number of pulp)

To determine mechanical properties, handsheets were prepared from pulp and subjected to measurements. All pulps were beaten at 2300 (pulp 1) or 2900 (pulp 2) revolutions in a PFI beater (Paper Testing Instruments GmbH, Laakirchen, Austria). The tensile index, tensile length, burst index, tear index, stiffness, and brightness of the handsheets were measured using standard TAPPI methods. The freeness of beaten pulps was measured according to TAPPI T227 om-94 (1994). The handsheet for testing of papermaking properties was formed according to TAPPI T205 sp-95 (2002). The handsheet of each beating condition was measured for optical and strength properties such as brightness (TAPPI T452 om-98 (1996)), stiffness (ISO 2493-1 (2010)), tensile strength (TAPPI T494 om-88 (1996)), tearing strength (TAPPI T414 om-88 (1996)), and bursting strength (TAPPI T403 om-91 (1996)).

RESULTS AND DISCUSSION

Some properties of the pulps are given in Table 2. The residual lignin content of the pulp is expressed using the Kappa number. In this work, pulps with different initial Kappa numbers, namely 21.7 (pulp 1) and 14.3 (pulp 2), were used.

It was evident (Table 2) that pulp with a higher initial lignin content underwent a more efficient delignification when pre-treated by DESs.

In recently published work, Majova *et al.* (2017b) described the effect of DES on the delignification of pulp by parameters such as degree of polymerization, cellulose chain scission number, selectivity of delignification and efficiency of delignification. The results showed that pulp with a higher initial Kappa number or lignin content would possess a greater fraction of easily removed lignin fragments. Summarized of the results in work Majova *et al*. (2017b) shown that the selectivity and efficiency of delignification the best performance was achieved by the DES composed of alanine and lactic acid.

The impact of DES on pulp delignification may be explained as follows. Alvarez-Vasco *et al.* (2016) discovered that DES can selectively cleave ether linkages in biomass lignin and facilitate lignin removal from biomass. The mechanism of DES cleavage of ether bonds between phenylpropane units was confirmed, and the results showed that DES has the ability to selectively cleave ether bonds without affecting C-C linkages in lignin. But on the other side, it is also necessary to point out that solvent properties of DES, such as acid strength play also important role in the mechanism of hydrotropic lignin dissolution and extraction from pulp (Soares *et al.* 2017). The best performance of delignification was achieved by the DES composed of alanine and lactic acid. In this case the change in the degree of polymerization was minor (Majova *et al.* 2017b).

Mechanical properties of the kraft pulps were measured for comparison before and after the DES treatment, and the results are given in Table 3. Pulp 1 and pulp 2 were beaten at 2300 revolutions and 2900 revolutions, respectively. The final degree of beating, 30 °SR (Shopper-Riegel number), was achieved for pulp 1 when DES2, DES3, and DES4 were applied. When DES1 was applied, a higher degree of beating (39 °SR) was reached due to a more noticeable degradation of cellulose in the pulp. For pulp 2, a higher number of revolutions (2900) had to be used to achieve 30 °SR. The DESs were subsequently applied to the original (unbeaten) pulp 2. After delignification by the DESs, pulp 2 was beaten at 2900 revolutions. The final level of beating reached 30 °SR to 34 °SR in for DES2 through DES4. For delignification using choline chloride and oxalic acid, considerable pulp degradation occurred during beating and the level of beating at 2900 revolutions reached 60 °SR. It follows from the presented results that if greater pulp degradation occurred from a DES application, it was observed during pulp beating. In other words, the pulp with more profound cellulose degradation and a lower lignin elimination selectivity required less beating energy to reach the same level of beating (30 °SR).

Strength properties of both kraft pulps 1 and 2 were determined, and it was found that tensile index, tensile length, and tear index were higher for pulp 1 than for pulp 2 (before DES treatment). The burst index was the same for both pulp samples (4.2 kPa·m^2/g). The brightness was lower for pulp 1 than for pulp 2.

Table 3. Mechanical Properties of Kraft Pulps Before and After DES Treatment

Sample	DES System	Beating (°SR)	Tensile Index (Nm/g)	Tensile Length (km)	Burst Index (kPa·m^2/g)	Tear Index (mN·m^2/g)	Stiffness (mN)	Brightness (%)
Kraft pulp 1*[1]	-	30	72.02	7.3	4.2	7.1	126	27.02
Pulp 1	DES1	39	56.32	5.7	2.9	3.7	102	35.06
	DES2	30	66.37	6.8	3.7	6.2	126	32.33
	DES3	30	62.49	6.4	3.6	6.4	131	34.05
	DES4	30	63.00	6.4	3.6	6.6	130	33.38
Kraft pulp 2*[2]	-	30	67.28	6.9	4.2	6.3	123	31.09
Pulp 2	DES1	60	49.61	5.1	2.2	3.2	100	38.31
	DES2	34	67.89	6.9	3.8	5.4	128	33.81
	DES3	32	68.14	6.9	4.0	5.5	126	35.77
	DES4	30	67.38	6.9	4.1	6.1	123	34.63

* [1]Mondi SCP, Ružomberok Slovakia; [2]BUKÓZA HOLDING, a. s., Hencovce, Slovakia

Fiber strength properties and the structure and bonding of pulp in handsheets depend on individual fiber characteristics, such as fibrillation and density (Fiserova *et al* 2016). The bonding strength between fibers results from the physical contact with hydrogen bonding between hydroxyl groups on the fiber’s surface (Liu *et al* 2013). The tensile indices of pulp 1 after DES treatments were considerably lower than that of the untreated pulp 1 sample. The tensile strength of the samples decreased with the removal of lignin. This trend is not well adapted to the fiber bonding effect (Hedjazi *et al.* 2009). As residual lignin is removed, the fibers become more elastic (Yang *et al*. 2003). This facilitates closer contact between the fibers and thus increases the bonding area. Increased delignification is generally accompanied by further cellulose damage, which has been observed in other pulping and delignification processes (Guay *et al.* 1998). In contrast, the high hemicellulose content in chemical pulp has a beneficial effect on interfiber bonding (Kordsachia and Patt 1988). This result was not confirmed in this study because the hemicellulose content was not determined. Similar results were seen for burst index and tear index. The burst index is closely related to the degree of hydrogen bonding between fibers. More hydrogen bonding between fibers will increase the burst index because more force is needed to break the surface of the sample (Liu *et al.* 2013). After DES application, there was a slight decrease in burst index and therefore less hydrogen bonding.

Tear index depends on the paper’s fiber length (Hassan *et al.* 2014). The average fiber length in a raw material may not change during the pulping and delignification process. The degree of hydrogen bonding depends on the fiber properties and the severity of the chemical treatment applied to the fiber (Zhao *et al.* 2002). After the application of DES delignification, the tear indices decreased. The smallest decrease in tear index was seen after the application of DES4 for both pulps. The decrease of tear index for treated pulp by DES during the delignification progress could be explained by changing of fiber deformability. With the lignin removal, fibers become more deformable which decrease the tear index of the fiber network (Li *et al.* 2016). The measured data documented that the highest degradation of cellulose was achieved using DES1 at both pulp. For treated pulp 2 by DES1 the degradation of cellulose was higher than for pulp 1.

The stiffness values of pulp 1 and the treated pulp were very similar. In some samples, the stiffness was higher for the treated pulp than for pulp 1 (for samples after DES3 and DES4 treatment). The brightness of the pulp was higher after treatment in all cases because DES treatment markedly decreased the lignin content, and therefore the Kappa number, which made the pulp brighter.

The tensile index of pulp 2 after DES treatment remained almost unchanged for three of the four samples. The fourth sample showed a remarkably lower tensile index than untreated pulp 2. The DES1 was composed of oxalic acid, which aids the disintegration of cellulose chains, and caused decreased tensile properties, as seen for the DES1 pulp compared to untreated pulp. Tensile length and burst index were similar for pulp 2 and the pulp after DES treatment (except for DES1). The tear index was lower for the treated pulp because delignification caused a decrease in the degree of polymerization that impacted the mechanical properties of pulp. The stiffness of beaten pulp after DES2 (128 mN), DES3 (126 mN), and DES4 (123 mN) treatment is very similar to initial kraft pulp 2 (123 mN). At treatment of pulp by DES4 stiffness reached 100 mN, however, this pulp was beaten on the 60 °SR at 2900 revolutions. For all samples, the brightness after treatment was higher.

CONCLUSIONS

1. The DES delignification has potential to replace oxygen delignification after kraft pulping. In this study, the pulp was delignified with different DES systems based on choline chloride and lactic acid (1:9), oxalic acid dihydrate (1:1), lactic acid (1:9), and alanine:lactic acid (1:9).
2. It has been shown that pulp with a higher initial lignin content will have a greater fraction of easily removable lignin fragments. Additionally, the results of this study showed that the type of DES influenced the mechanical properties of delignified pulp such as tensile, burst and tear indices, tensile length, and stiffness.
3. The best systems were choline chloride:malic acid (1:1) and alanine:lactic acid (1:9), for which the best mechanical properties were reached.

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