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Production of cellulose carbamate using urea-based deep eutectic solvents

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Abstract Cellulose carbamate is a bio-based, biodegradable, and environmentally friendly material and thus an interesting alternative to petroleum-based polymers or fibers from cellulose produced using the viscose process for producing fibers from cellulose. In this study we described an efficient and green method to prepare cellulose carbamates by using deep eutectic solvents. Three different urea-based deep eutectic solvents were used with different molar ratios and cellulose consistency. Nitrogen content of cellulose carbamates increases when cellulose consistency increases from 5 to 20%. Also, the reaction temperature affects the nitrogen content. In addition, the cellulose crystallinity decreases during the carbamation reaction with 20% cellulose consistency using any of the three deep eutectic solvents studied, when the sample is processed in a high-consistency reactor. By selecting suitable parameters, the nitrogen content of cellulose carbamates can be easily adjusted to a desired level.

Keywords Cellulose · Urea · Cellulose carbamate · Deep eutectic solvent · DES

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Introduction

Cellulose is one of the most abundant and oldest natural polymers on earth and, hence, can be regarded as an important raw material with multiple purposes such as textiles, papers, foods, cosmetics, and biomaterials (Edgar et al. 2001). It is a linear polymer that consists of $\beta(1 \rightarrow 4)$ linked D-glucose units. These units are very prone to associate with each other via strong inter- and intra-molecular hydrogen bonds and hydrophobic interactions forming resistant microfibrillar network structures (Lindman et al. 2010), which are practically insoluble in water and in conventional organic media. The poor solubility of cellulose sets remarkable challenges on its chemical processing into various end-products. Therefore an industrial need for novel, viable chemistries is evident.

Cellulose carbamate (CCA), due to its bio-based, biodegradable and biocompatible properties, is considered as an environmentally friendly material and thus provides an interesting alternative to petroleum-based polymers (Mormann and Michel 2002; Yin et al. 2007). Cellulose carbamate also has relatively high stability at room temperature, which enables long storage periods (Fu et al. 2015). The cellulose carbamate process is a well-known alternative to the commonly known viscose process for producing fibers from cellulose. Industrial tests have shown that cellulose carbamate can be processed feasibly on viscose spinning machines (Klemm et al. 2005; Yin et al. 2007; Guo et al. 2009). In recent years the viscose process has been considered

less favorable due to its environmental issues and recycling difficulties (e.g. carbon disulfide is commonly used). As a result, cellulose carbamate has emerged as one of the most promising alternatives to viscose in the near future (Zhang et al. 2013). In conventional processes, cellulose carbamates with the nitrogen content (N%) of 1–2.5% are prepared by treating cellulose with urea above its melting point (Fu et al. 2015). On a laboratory scale, cellulose carbamates can also be synthesized using a supercritical carbon dioxide method (Yin et al. 2007; Yin and Shen 2007; Zhang et al. 2013), a microwave assisted method (Guo et al. 2009, 2010; Fu et al. 2014) and organic medium methods (Yin et al. 2007; Guo et al. 2009, 2010). In all cases, high temperature (>135 °C) has been a prerequisite for sufficient cellulose carbamate formation. However, lower reaction temperatures could be beneficial to minimize side reactions and prevent cellulose thermal degradation. Furthermore, a reaction medium that efficiently open up cellulose structure and thereby provide even distribution of carbamate groups could significantly improve the end-product quality and performance, e.g. in fiber spinning.

Environmental consciousness and green chemistry development are setting the targets for the next generation of industrial chemical processes for cellulose versatile modification. Ionic liquids (ILs) are known for their environmental impact and clear advantages in a wide range of applications and processes, however most ILs have hazardous toxicity and poor biodegradability (Zhang et al. 2012). Deep eutectic solvents (DES, also referred as low melting solvent mixtures by some authors) are closely related to ILs and have usually many advantages compared to ionic liquids, such as low price of starting materials, nontoxicity, biodegradability and biocompatibility (Florindo et al. 2014; Smith et al. 2014; Wahlström et al. 2016). DESs are eutectic mixtures consisting of two or more components, a hydrogen bond donor and a hydrogen bond acceptor that together have a lower melting point than the individual components. A well-known example is the mixture of choline chloride (melting point 302 °C) and urea (melting point 132 °C), which form DES with melting point of 12 °C (Abbott et al. 2003). Furthermore, DESs can be formed using various quaternary ammonium salts and carboxylic acids, and the physical properties of DESs are determined by the composition of the mixture, while their phase behavior is similar to ionic liquids. (Abbott et al. 2004; Zhang et al. 2012; Smith et al. 2014) DESs have

now become of growing interest both at academic and industrial levels, which is further verified by the increasing number of publications dedicated to the use of DESs in recent literature (Zhang et al. 2012). The use of DESs has been reported in many applications such as processing of metals (Abbott et al. 2005, 2006), biodiesel purification (Abbott et al. 2007), biomass processing (Hiltunen et al. 2016; Wahlström et al. 2016) and biocatalysis (Gorke et al. 2008; Zhao et al. 2011).

Herein we present a new method to prepare cellulose carbamates using urea-based DESs by using three different DESs with two different molar ratios as examples of cellulose carbamation. The effects of DESs molar ratio, cellulose consistency and reaction temperature on cellulose carbamation formation were tested.

Experimental

Materials

Urea, betaineHCl, betaine, and choline chloride were purchased from Sigma-Aldrich in the highest purity grade and were used as received. The cellulose material in this study was Never-dried Enocell hardwood dissolving pulp produced by Stora Enso, Finland.

Formation of DES

DESs were prepared using the method described by Abbott et al. (2003). DES components were mixed together with different molar ratios and heated at 100 °C until a clear homogeneous liquid was formed. The liquid was slowly cooled and the freezing point was taken as the temperature at which the first solids began to form.

Preparation of cellulose carbamate

Preparation of cellulose carbamate in glass reactor (5% consistency).

In a typical procedure, cellulose (20 g in dry weight, 68% dry-matter content) was mixed with an earlier-formed DES solution in the standard mechanical laboratory glass reactor, which was preheated to a constant temperature. The reactor was equipped with a vacuum line to remove water. The mixture was stirred for 20 h at a constant temperature. Purification was performed by dialyzing the sample against water using a membrane

(Biotech RC, SpectrumLabs, USA) with a cut-off of 3.5 kD. The reaction mechanism is shown in Scheme 1.

Preparation of cellulose carbamate in a high-consistency reactor (10 and 20% consistency).

In a typical experiment, a high-consistency DIT reactor (CV Helicone Mix Flow, Design Integrated Technology USA, Inc.) was preheated to a constant temperature. Ready-made DES solution and cellulose (20 g dry weight, 68% dry-matter content) were added to the reactor. The reactor was equipped with a vacuum line to remove water. The mixture was stirred for 20 h at a constant temperature. Purification was performed by dialyzing the sample against water using a membrane (Biotech RC, SpectrumLabs, USA) with a cut-off of 3.5 kD.

Nitrogen analysis

Total nitrogen content (N%) of cellulose carbamates was determined using the Kjeldahl titration method.

Fourier transform infrared spectroscopy (FT-IR)

FT-IR measurements were carried out using a Nicolet iS50 FT-IR equipped with Omnic software and an ATR sampling accessory (Thermo Fisher Scientific Inc., Rockford, IL, USA) between 400 and 4000 cm^{-1}. 32 scans were taken for each sample with a resolution of 4 cm^{-1} in transmittance mode.

Nuclear magnetic resonance (NMR)

The solid state ^{13}C CP/MAS NMR spectroscopy (ssNMR) was performed using an Agilent 600 MHz NMR spectrometer (Agilent Technologies, USA) with a magneticflux density of 14.1, equipped with a 3.2 mm triple resonance magic angle spinning (MAS) probehead operating in double resonance mode. The number of accumulated scans was 5000, with 10 s delay between successive scans. Contact time in cross polarization (CP) was 3 ms, and MAS rate in the experiments was 10 kHz. All ssNMR experiments were carried out at room temperature.

Charge density measurements

Charge density of cellulose carbamate samples were measured using Mütec PCD-03 particle-charge detector (Herrsching, Germany). The samples were titrated at pH 4 using 0,001 N polydiallyldimethylammonium chloride (polyDADMAC) as the titrant.

X-ray powder diffraction (XRD)

X-ray powder diffraction (XRD) data of cellulose carbamates were recorded with a Philips X'Pert MPD diffractometer (Philips Research Laboratories, Netherlands) equipped with a primary beam and a curved graphite monochromator Cu Kα1 radiation (1.5406 Å; 40 kV, 50 mA). A proportional counter detector, PW3011/10, was used to collect the data in a 2θ range of 5°–40° with a step size of 0.02°.

Results and discussion

DES formation

In this study three different urea-based deep eutectic (DES) systems, urea:choline chloride, urea:betaineHCl and urea:betaine, were tested with different molar ratios (from 6:1 to 1:2). Freezing points of the
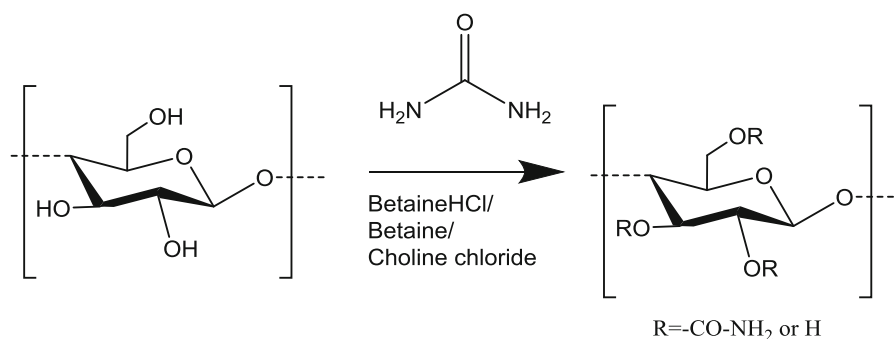
Scheme 1 Reaction scheme for synthesizing cellulose carbamates

R=-CO-NH$_2$ or H

tested urea-based DESs have been presented in a phase diagram (Fig. 1). Generally, DESs have a large depression of freezing point and most DESs are liquid between 25 and 70 °C (Zhang et al. 2012). All of the three tested urea-based mixtures have been earlier reported as deep eutectic solvents. For example, Abbott et al. (2003) studied urea:chloline DESs and they found that when the molar ratio 2:1 was used, the freezing point was 12 °C. Sharma et al. (2013) reported urea:betaineHCl DES with a molar ratio of 4:1, which was liquid at room temperature. Zeng et al. (2016) have reported urea-betaine DESs. They found that urea and betaine formed DESs when molar ratios of 3:1 to 1:1 were used. Our freezing point results correlate well with these findings. It is desirable to use an excess of urea to ensure that consumption of urea in the cellulose carbamate formation does not break the DES solvent system. Therefore, based on these freezing point results, molar ratios of 2:1 and 4:1 were chosen to be used in the carbamation reactions.

Preparation of cellulose carbamate

Cellulose carbamation reactions were carried out using different DES systems, consistencies and temperatures. Cellulose carbamations with 5 wt% cellulose consistency were carried out using a glass reactor, while a high-consistency twin-screw DIT reactor was used for 10 and 20 wt% cellulose consistency reactions. The reaction temperature also varied: both

95 and 120 °C were used. Nitrogen content (N%) of cellulose carbamates were determined using the Kjeldahl titration method and the N% for each sample has been presented in detail in Table 1.

Cellulose carbamates were analyzed with a FT-IR spectrometer. Figure 2 shows the FTIR spectra of native cellulose and cellulose carbamates with nitrogen contents of 1.1 and 4.2%, respectively. When cellulose carbamates are compared to starting cellulose, a new absorption peak at ~ 1710 cm^{-1} can be observed. This peak is due to the stretching vibration of the carbonyl (C=O) in the base of urethane and shows that urea has reacted with cellulose. It can also be concluded that the carbonyl absorption peak correlates quite well with nitrogen content: the higher N%, the bigger absorption peak. This view is in line with published results (Nada et al. 2000). Absorbance of cellulose hydroxyl groups at 3330 cm^{-1} also decreases when carbamation takes place, which correlates well with the increased reaction of urea with the OH of cellulose chains (especially primary OH groups) (Nada et al. 2000; Yin and Shen 2007).

Cellulose carbamates were also analyzed using solid-state ^{13}C NMR spectroscopy (ssNMR). ssNMR spectra of starting cellulose and cellulose carbamate with 4.2 N% are presented in Fig. 3. Cellulose carbamates give a clear signal at 160 ppm, which is due to the carbonyl carbon of the carbamate group. Methyl groups of the betaineHCl/betaine/choline chloride were not observed, which also confirms that after
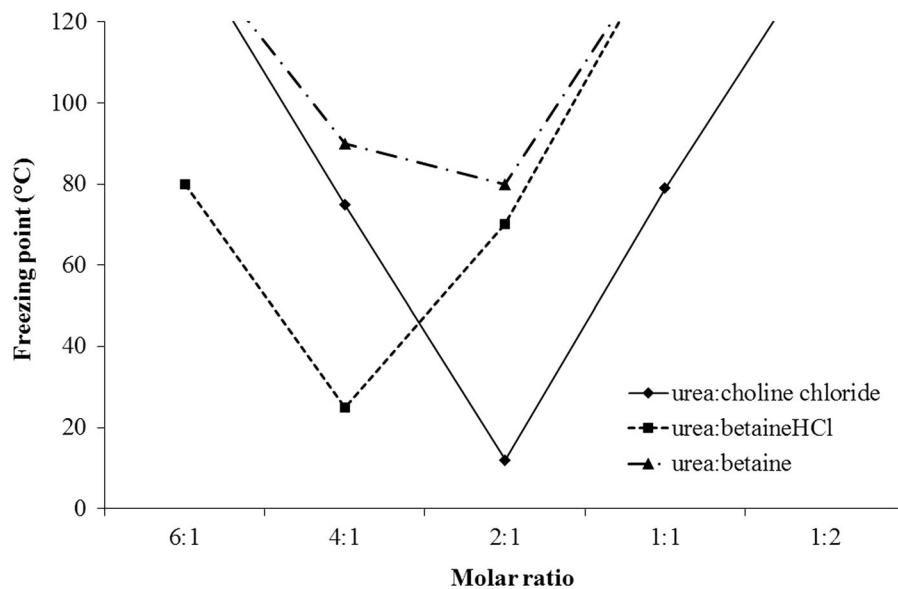
Fig. 1 Phase diagram of the tested DES systems

Table 1 N% of cellulose carbamates according to Kjeldahl method

DES	Molar ratio	Temperature (°C)	N%[a]		
			5%[b]	10%[b]	20%[b]
Urea:choline chloride	2:1	95	0.1	0.2	0.9
		120	0.5	0.7	2.4
	4:1	95	0.1	0.3	1.1
		120	0.6	1.0	2.3
Urea:betaine	2:1	95	0.4	1.0	2.4
		120	1.1	1.2	5.5
	4:1	95	0.6	1.4	5.2
		120	0.7	3.2	7.4
Urea:betaineHCl	2:1	95	2.0	1.2	4.2
		120	3.3	1.7	5.6
	4:1	95	5.2	2.2	5.2
		120	3.3	1.4	6.7

[a] Nitrogen content according to Kjeldahl method

[b] Cellulose consistency (wt%)

Fig. 2 FT-IR spectra of native cellulose (**a**), cellulose carbamates with 1.1 N% (urea:betaine 2:1) (**b**), and cellulose carbamate with 4.2 N% (urea:betaine HCl 2:1) (**c**)
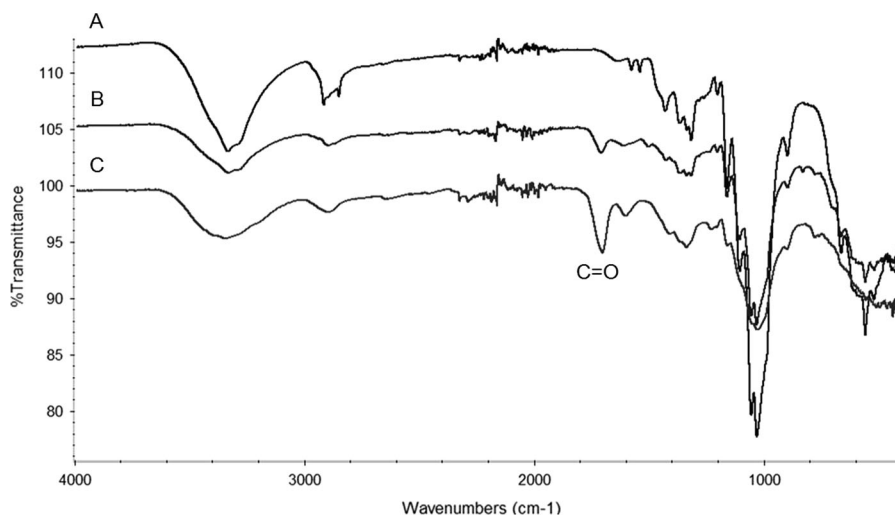
purification the reactions produces pure cellulose carbamate.

In addition, none of the cellulose carbamate samples had a cationic charge, which also confirms that no side reactions, e.g. cationization reaction, occurred even though the samples have a rather high nitrogen content.

Cellulose hornification means that stiffening of the polymer structure takes place upon the cellulose drying process (Kato and Cameron 1999; Fernandes Diniz et al. 2004). When wood pulp fibers are dried, the internal fiber volume shrinks, because of the structural changes in wood pulp fibers. If fibers are re-suspended in water, the original water-swollen state is not regained (Fernandes Diniz et al. 2004). In the carbamation reactions, we have used cellulose, which

was air-dried to a 68% dry content. This chosen dry content was a compromise, because it is known that very dry cellulose is severely hornificated, which is not desirable for our purposes. On the other hand, also a large amount of water (i.e. low cellulose dry content) could disturb the carbamation reaction due to water possibly destroying the DES system by preventing its interaction with cellulose fiber. Weise (1997) has investigated the cellulose hornification effect and found that at above the 40% dry content, cellulose already started to hornificate. When the dry content of cellulose reaches 70%, water removal no longer affects cellulose irreversibly.

The consistency of cellulose in the DES system and carbamation reaction seems to have a significant effect

Fig. 3 ssNMR spectra of native cellulose (*red*) and cellulose carbamates with 4.2 N% (urea:betaine HCl 2:1) (*blue*). (Color figure online)
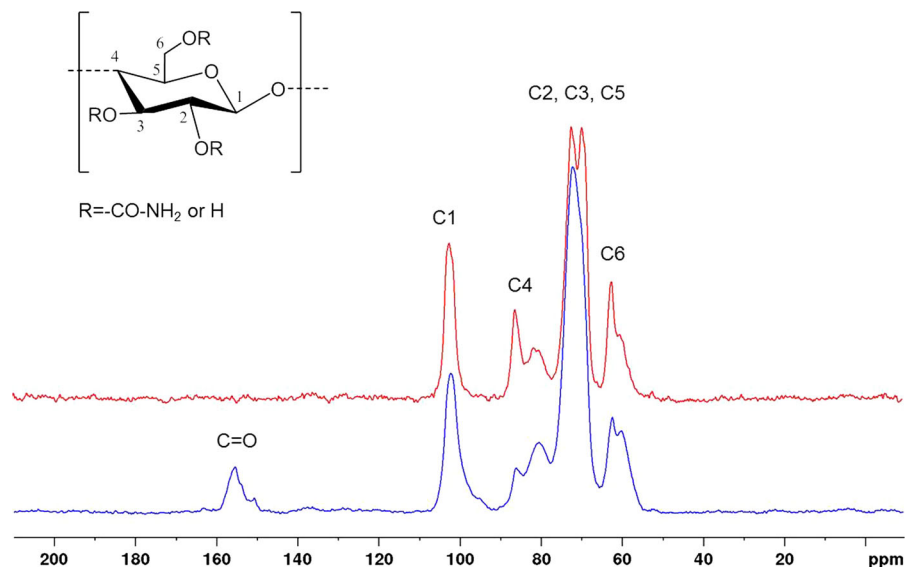
on the nitrogen content of carbamates (Fig. 4). Nitrogen content (N%) in all tested DES systems increases when cellulose consistency increases. Carbamation reactions with 20% cellulose consistency resulted in much higher N% than the 5% consistency reaction. This may be a result of the shearing effect of the high-consistency reactor, which causes a peeling effect of the cellulose fiber S1 layer, thus opening the fiber structure and improving chemical reactions. The highest N%s were reached using the urea:betaine DES system.

Also, the temperature of the carbamation reaction affects the nitrogen content (Fig. 5). When 120 °C was used as a reaction temperature instead of 95 °C, N% of cellulose carbamates are somewhat higher. Yin et al. (2007, 2013) have found the same effect, when using the urea method with supercritical CO_2 in high pressure (180–200 bar). They concluded that the nitrogen content of cellulose carbamate was quite low when the temperature was below 120 °C and N% increased significantly with increasing temperature. This is logical as the higher temperature favors the carbamate formation reaction due to the higher rate of isocyanic acid formation (Lundström et al. 2009). However, high temperatures may also result in increased decomposition of the cellulose and its derivatives and formation of various urea dimerization and trimerization products. When urea-based DESs were used in the carbamation process, the required reaction temperature is lower and thus the

decomposition of cellulose is minimized. It is generally known that urea conversion into isocyanic acid does not take place below the urea melting point (135 °C), which is needed for carbamation (Lundström et al. 2009). In DES systems the urea melting point is significantly lower and thereby the formation of isocyanic acid could also take place at lower temperatures.

The molar ratio of DES systems also has an effect on the N% of cellulose carbamate. When the amount of urea increased, the N% also increased. In the case of urea:betaineHCl, we observed that N% increased from 5.6 to 6.7 when the urea content increased from 31 wt% (molar ratio 2:1) to 42 wt% (molar ratio 4:1), when 20% consistency was used. Guo et al. (2010) have found the same effect, and report also that when urea content increased from 10 to 50 wt%, the nitrogen content increased from 1.25 to 2.9%. Therefore, by selecting the suitable parameters, the N% of cellulose carbamates can be easily adjusted to a desired level.

Crystallinities of cellulose carbamates were analyzed using the ssNMR C4 peak separation method (Newman 2004; Park et al. 2010) and powder XRD. In the ssNMR spectra, the peak at 99 ppm is assigned to the C4 carbon in the crystallized part of cellulose and the peak at 85 ppm is assigned to the C4 carbon of the cellulose amorphous part. The crystallinity degree of cellulose can be calculated by dividing the area of cellulose crystallized part by the total area assigned to the C4 carbon peak. Based on these ssNMR results, it

Fig. 4 N% of cellulose carbamates prepared with different DES systems
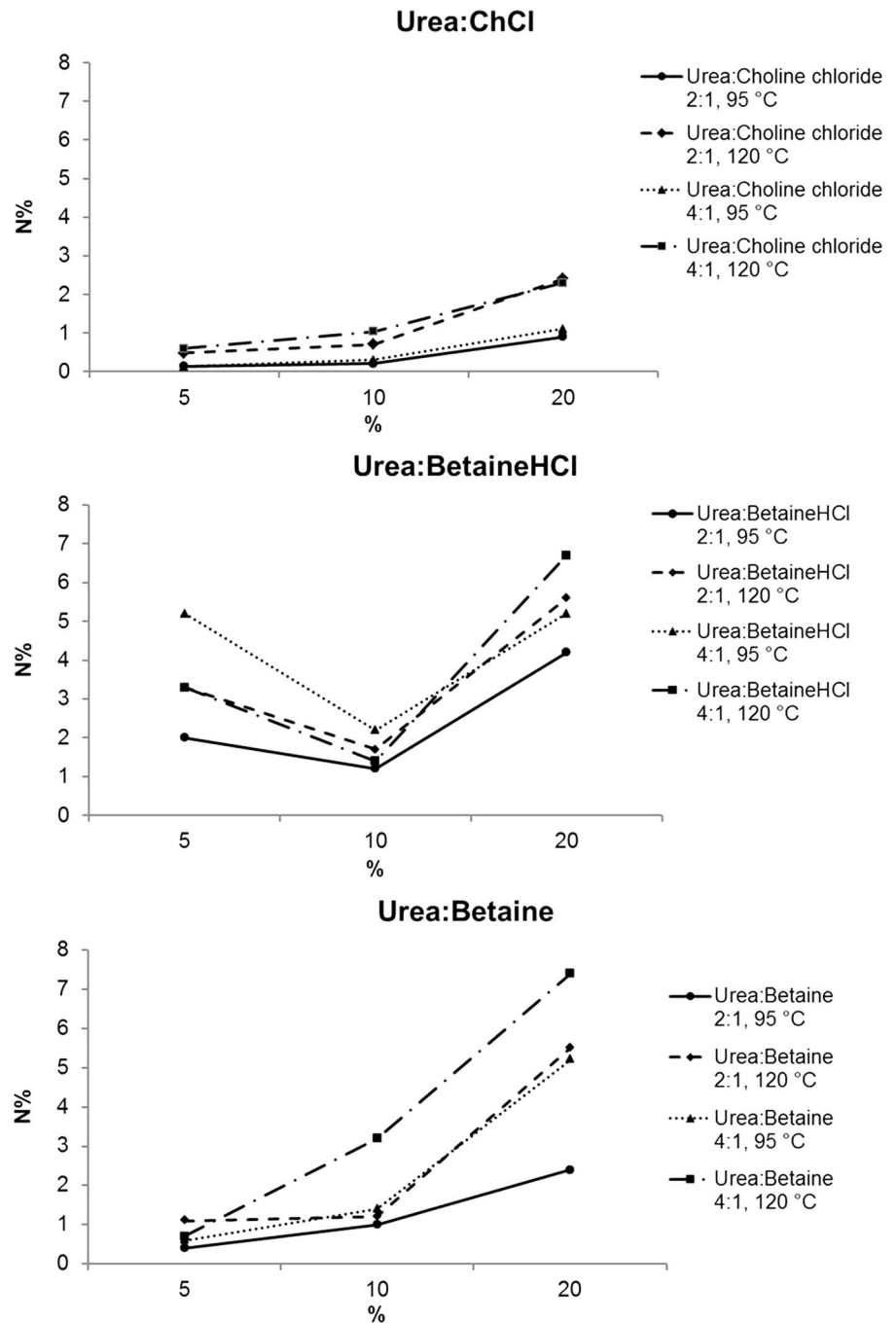
can be said that the cellulose crystallinity decreases during the carbamation reaction when a high-consistency DIT reactor was used in 20% cellulose consistency. The crystallinity of the starting cellulose was 56% and it decreased to 30% when 20% consistency was used; the N% being 4.2%. From the powder XRD measurements the crystallinity indexes were calculated using the Segal method (Segal et al. 1959). The crystallinity index decreased 40% (from 80 to 48%) when 20% consistency was used for the urea:betaineHCl 2:1 sample (Fig. 6). A similar effect was observed also for other DES samples processed at high
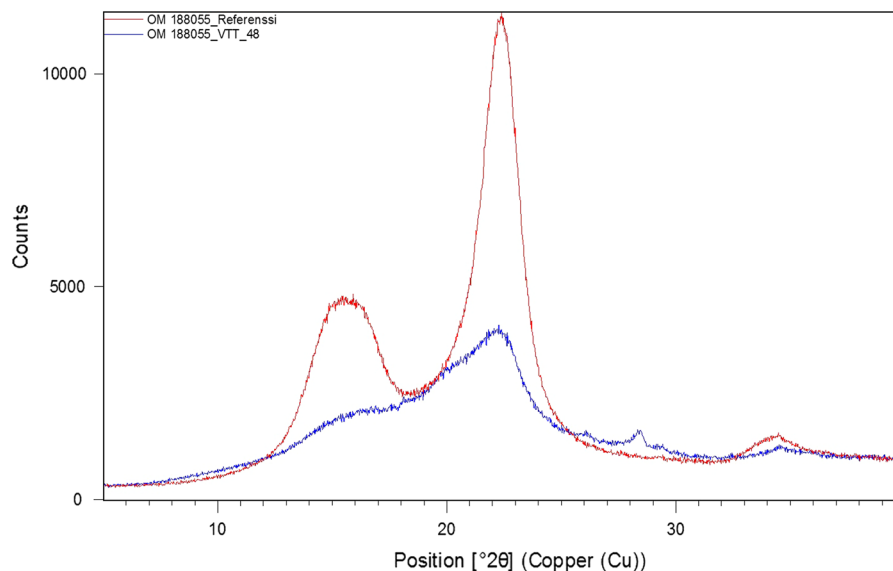
Fig. 5 N% of cellulose
carbamates prepared with
different temperature
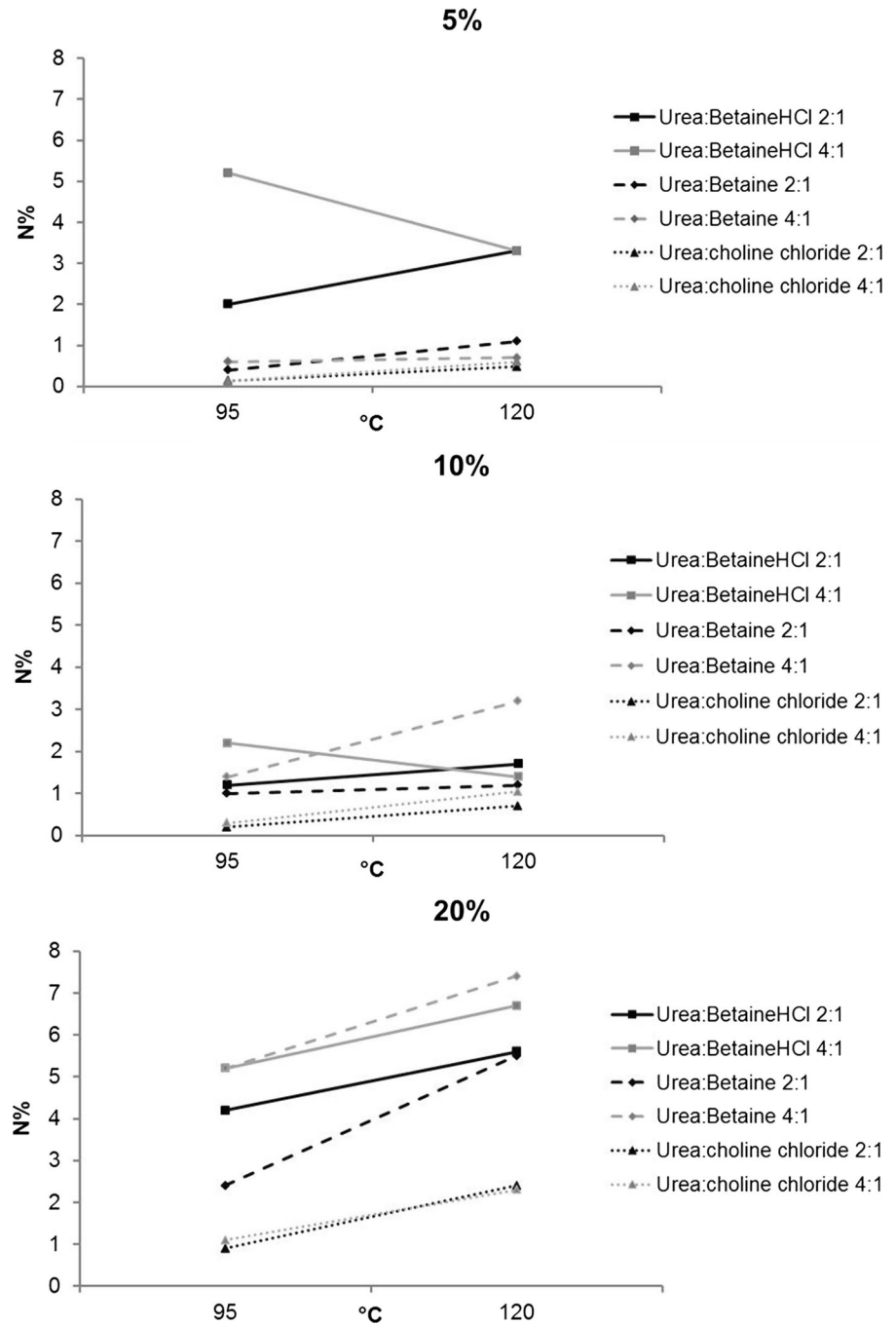
consistency. The powder XRD analyses results are in line with crystallinities measured by the ssNMR method. This supports the conclusion that the carbamation reaction in high consistency decreases the cellulose crystallinity. This is most probably due to the fact that the formation of carbamate reduces structural

organization and the density of hydrogen bonds and these together partially destroy the crystalline structure of cellulose. Zhang et al. (2013) have also analyzed crystallinity of cellulose carbamates by XRD. They found that the degree of crystallization of cellulose carbamates decreases significantly when

Fig. 6 XRD analysis of native cellulose (*red*) and cellulose carbamates with 4.2 N% (urea:betaine HCl 2:1) (*blue*). (Color figure online)

the –OH group of cellulose was substituted by urea, while producing carbamates by the supercritical CO2 method. They found that when N% was increased from 1.2 to 4.4%, the crystallinity degree of the samples decreased from 63.5 to 51.9. Guo et al. (2009) confirmed the same effect in their experiments: the crystallinity degree of cellulose carbamates decreased from 72 to 64% when N% increased from 0.65 to 2.4%.

Conclusions

We have demonstrated an efficient and green method to prepare cellulose carbamates by using deep eutectic solvents. Using urea-based DES solvents, cellulose carbamate can be synthesized without any additional solvents at low temperature. The nitrogen content can be adjusted by tuning consistency and temperature with selected DESs. N% increases when cellulose consistency increases from 5 to 20%. The highest nitrogen content was reached using a urea:betaine DES system. In addition, the cellulose crystallinity decreases during the carbamation reaction with 20% cellulose consistency using any of the three deep eutectic solvents studied, when the sample is processed in a high-consistency reactor. By selecting suitable parameters, the nitrogen content of cellulose carbamates can be easily adjusted to the desired level.

References

Abbott A, Capper G, Davies D, Rasheed R, Tambyrajah V (2003) Novel solvent properties of choline chloride/urea mixtures. Chem Commun 1:70–71

Abbott A, Boothby D, Capper G, Davies D, Rasheed R (2004) Deep eutectic solvents formed between choline chloride and carboxylic acids: versatile alternatives to ionic liquids. J Am Chem Soc 126:9142–9147

Abbott A, Capper G, Davies D, Rasheed R, Shikotra P (2005) Selective extraction of metals from mixed oxide matrixes using choline-based ionic liquids. Inorg Chem 44:6497–6499

Abbott A, Capper G, Davies D, McKenzie K, Obi S (2006) Solubility of metal oxides in deep eutectic solvents based on choline chloride. J Chem Eng Data 51(4):1280–1282

Abbott A, Cullis P, Gibson M, Harris R, Raven E (2007) Extraction of glycerol from biodiesel into a eutectic based ionic liquid. Green Chem 9:868–872

Edgar KJ, Buchanan CM, Debenham JS, Rundquist PA, Seiler BD, Shelton MC, Tindall D (2001) Advances in cellulose ester performance and application. Prog Polym Sci 26:1605–1688

Fernandes Diniz JMB, Gil MH, Castro JAAM (2004) Hornification—its origin and interpretation in wood pulps. Wood Sci Tecnol 37:489–494

Florindo C, Oliveira F, Rebelo L, Fernandes A, Marrucho I (2014) Insights into the synthesis and properties of deep

eutetic solvents based on cholinium chloride and car-
boxylic acids. ACS Sustain Chem Eng 2:2416–2425

Fu F, Zhou J, Zhou X, Zhang L, Li D, Kondo T (2014) Green
method for production of cellulose multifilament from
cellulose carbamate on a pilot scale. ACS Sustain Chem
Eng 2:2363–2370

Fu F, Xu M, Wang H, Wang Y, Ge H, Zhou J (2015) Improved
synthesis of cellulose carbamates with minimum urea
based on an easy scale-up method. ACS Sustain Chem Eng
3:1510–1517

Gorke J, Srienc F, Kazlauskas R (2008) Hydrolase-catalyzed
biotransformations in deep eutectic solvents. Chem Com-
mun 10:1235–1237

Guo Y, Zhou J, Song Y, Zhang L (2009) An efficient and
environmentally friendly method for the synthesis of cel-
lulose carbamate by microwave heating. Macromol Rapid
Commun 30:1504–1508

Guo Y, Zhou J, Wang Y, Zhang L, Lin X (2010) An efficient
transformation of cellulose into cellulose carbamates
assisted by microwave irradiation. Cellulose 17:1115–
1125

Hiltunen J, Kuutti L, Rovio S, Puhakka E, Virtanen T, Ohra-aho
T, Vuoti S (2016) Using a low melting solvent mixture to
extract value from wood biomass. Sci Rep 6:32420

Kato KL, Cameron RE (1999) A review of the relationship
between thermally-accelerated ageing of paper and horni-
fication. Cellulose 6:23–40

Klemm D, Heublein B, Fink HP, Bohn A (2005) Cellulose:
fascinating biopolymer and sustainable raw material.
Angew Chem Int Ed 44:3358–3393

Lindman B, Karlström G, Stigsson L (2010) On the mechanisms
of dissolution of cellulose. J Mol Liq 16:76–81

Lundström A, Andersson B, Olsson L (2009) Urea thermolysis
studied under flow reactor conditions using DSC and FT-
IR. Chem Eng J 150:544–550

Mormann W, Michel U (2002) Improved synthesis of cellulose
carbamate without by-products. Carbohyd Polym 50:201–
208

Nada A, Kamel S, El-Sakhawy M (2000) Thermal behavior and
infrared spectroscopy of cellulose carbamates. Polym
Degrad Stab 70:347–355

Newman RH (2004) Homogeneity in cellulose crystallinity
between samples of Pinus radiate wood. Holzforschung
58:91–96

Park S, Baker J, Himmel M, Parilla P, Johnson D (2010) Cel-
lulose crystallinity index: measurement techniques and
their impact on interpreting cellulose performance.
Biotechnol Biofuels 3:10

Segal L, Creely JJ, Martin AE, Conrad CM (1959) An empirical
method for estimating the degree of crystallinity of native
cellulose using the X-ray diffractometer. Text Res J
29:786–794

Sharma M, Mukesh C, Mondal D, Prasad K (2013) Dissolution of
α-chitin in deep eutectic solvents. RSC Adv 3:18149–18155

Smith E, Abbott A, Ryder K (2014) Deep eutectic solvents (DESs)
and their applications. Chem Rev 114:11060–11082

Wahlström R, Hiltunen J, de Souza Pitaluga, Nascente Sirkka
M, Vuoti S, Kruus K (2016) Comparison of three deep
eutectic solvents and 1-ethyl-3-methylimidazolium acetate
in the pretreatment of lignocellulose: effect on enzyme
stability, lignocellulose digestibility and one-pot hydroly-
sis. RSC Adv 6:68100–68110

Weise U (1997) Characterization and mechanisms of changes in
wood pulp fibres causes by water removal. Acta Polytechnic
Scandinavica, 249, Finnish University of Technology

Yin C, Shen X (2007) Synthesis of cellulose carbamate by
supercritical CO2-assisted impregnation: structure and
rheological properties. Eur Polym J 43:2111–2116

Yin C, Li J, Xu Q, Peng Q, Liu Y, Shen X (2007) Chemical
modification of cotton cellulose in supercritical carbon
dioxide: synthesis and characterization of cellulose car-
bamate. Carbohyd Polym 67:147–154

Zeng C, Qi S, Xin R, Wang Y (2016) Synergistic behavior of
betaine-urea mixture: formation of deep eutectic solvent.
J Mol Liq 219:74–78

Zhang Q, Vigier K, Royer S, Jérôme F (2012) Deep eutectic
solvents: syntheses, properties and applications. Chem Soc
Rev 41:7108–7146

Zhang Y, Yin C, Zhang Y, Wu H (2013) Synthesis and Char-
acterization of cellulose carbamate from wood pulp, assis-
ted by supercritical carbon dioxide. Bioresources 8(1):
1398–1408

Zhao H, Baker G, Holmes S (2011) New eutectic ionic liquids
for lipase activation and enzymatic preparation of biodie-
sel. Org Biomol Chem 9(6):1908–1916