



## Effect of plasticizers on the mechanical and thermomechanical properties of cellulose-based biocomposite films



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### ABSTRACT

Biocomposites based on natural cellulose fibers (CF) and hydroxyethyl cellulose (HEC), were produced in the form of green packaging films. The effect of the different single-component plasticizers (glycerol, propylene carbonate and ethylene carbonate) on the mechanical and dynamic thermomechanical properties of the films were studied. Moreover, the softening effect of the two-component plasticizer based on deep eutectic solvents (DESs) was addressed. Of the single-component plasticizers, glycerol was found to be the most efficient by increasing the elongation at break of the composite by 53%. A similar, or even better, increase in elongation at break (up to 81%) was obtained with DESs based on choline chloride and glycerol, glucose or urea. Based on the dynamic mechanical analysis at varying humidity, the performance of plasticizers was strongly attributed to the humidity. The DES based on tetrabutylammonium bromide and propylene carbonate was most efficient at providing thermoformability to the composite by lowering the thermal softening temperature. Based on the obtained results, DESs are a highly promising plasticizers for the cellulose-based biocomposites with similar or even better plasticizing effect compared to conventional plasticizer. In addition, DESs can be used to improve the thermoformability of biocomposites, by lowering the thermal softening temperature.

### 1. Introduction

Oil-based packaging materials are one of the most prominent sources of persistent environmental pollutants (Davis and Song, 2006; Derraik, 2002). Many oil-based materials have a low degree of biodegradability and can contain residuals of toxic monomers, which may be highly disadvantageous, especially for food packaging. Furthermore, the declining oil resources are one of the driving forces for seeking novel alternative solutions for current applications, including the packaging industry, which continues to grow (Owen et al., 2010).

Cellulose is the most abundant biopolymer on earth and has been long utilized in many applications, such as paper and cardboard (Brown and Saxena, 2000). In its natural form in wood, cellulose exists in fibrous form, which can be utilized, for example, in papermaking. However, due to its fibrous structure, it is difficult to produce continuous, film-like materials, which could be applied in food packaging. Due to its strong hydrogen-bonding network, cellulose has a poor thermoformability meaning that cellulose degrades before melting and fibers cannot be thermally melted to continuous films. In addition, cellulose is practically insoluble in most common solvents. Due to the restricted processability, conventional methods, such as extrusion are not feasible to produce films from cellulose fibers (Pandey et al., 2014).

Cellulose can be derivatized by several methods to improve formability of biopolymeric materials. Esterification and etherification (Fox et al., 2011) or carbamation (Johan-Fredrik et al., 1985; Sirviö and Heiskanen, 2017) can be used to convert cellulose into water-soluble semi-synthetic polymer. Soluble cellulose derivatives can be utilized for solvent-casting to prepare films with varying functionalities. Although methods, such as melt-processing in blow-film extrusion are preferred in an industrial scale, there are several ways to utilize solvent-casting in large scale applications (Siemann, 2005). However, chemical modification can increase the fabrication cost and often requires chemicals that are environmentally undesirable. One possibility to take advantage of both the cost and sustainability of natural fibers and the formability of cellulose derivatives, is the production of biocomposites (Bledzki and Gassan, 1999). In these biocomposites, cellulose derivatives form the continuing matrix, whereas the cellulose fibers (CF) function as fillers. In some cases, CF fillers can act as reinforcement agents when the mechanical strength of cellulose derivatives is not high enough for material applications (Li et al., 2007). However, introduction of fibers usually decrease biocomposites ductility, especially when a large amount of filler is utilized (Wang et al., 2017). The ductility of cellulose-based biocomposites can be improved by adding plasticizers. Plasticizers are commonly low molecular weight chemicals that can

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interfere with the hydrogen bonding ability of cellulose biocomposites, resulting in higher elongation properties. In addition, plasticizers can be used to convert non-thermoformable materials into thermoplastic. For example, glycerol can be used to produce thermoplastic starch (Da Róz et al., 2011).

Deep eutectic solvents (DESs) are novel type of chemicals used as solvents, reagents, and catalysts in various applications (Paiva et al., 2014). They can be obtained from widely available and multiple times cheaper chemicals. DESs are recognized as promising plasticizers for different natural polymers (Leroy et al., 2012; Wang et al., 2015; Zdanowicz and Johansson, 2016). The fabrication of both thermoplastic starch (Abbott et al., 2014) and chitosan (Galvis-Sánchez et al., 2016) have been reported based on the use of DESs. In addition, DESs exhibits low toxicity and are readily biodegradable (Juneidi et al., 2015), which are desirable properties, especially, in food packaging applications. Some of the DESs are suggested to have antimicrobial properties, which are desired especially in food packaging (Wen et al., 2015). Currently there is a scarcity in the knowledge about the influence of DESs as plasticizers for cellulose biocomposites or the plasticization effect of the DESs compared to the more traditional plasticizers, like glycerol.

A potential approach to produce composite materials from cellulose fibers and soluble cellulose derivatives would be the modification of well-known paper making method. In the papermaking, cellulose fiber suspension is filtered through a wire screen, which results in formation of fiber network, i.e. fiber web on the screen. The web is further dried and post-treated to produce paper. This approach could potentially be applied to produce also composites with a high fiber content in a continuous process. Although the use of water-soluble cellulose derivatives would definitive results in low retention levels (i.e. loss of polymer within the filtered water), the fiber web can likely retain the polymer around the fibers in some extent. The retention can also be improved using retention agents (to improve the interaction between the constituents), with designed wire screen and by adjusting the viscosity of water solution. However, this development needs that the properties of composites containing high level of fibers are better understood. Especially, the deformation properties (elongation and thermoformability) are important features as continuous composite production could be combined with 3D shaping of the composite to produce strays for food applications, for example (Tanninen et al., 2017).

In this study, composite films were produced from mechanically treated softwood cellulose fibers (CF), together with hydroxyethyl cellulose (HEC), using solvent casting from the aqueous dispersion of CF in HEC solution. HEC was used as a continuous matrix to introduce formability properties, whereas different plasticizers were studied to further improve the elongation at break properties of biocomposites. Glycerol, propylene carbonate and ethylene carbonate were studied as single-component plasticizers. Two-component DESs were also addressed as plasticizers (DESs were based on choline chloride with glycerol, glucose, urea, or citric acid, and tetrabutylammonium bromide with propylene or ethylene carbonate). The mechanical properties of CF-HEC biocomposites were measured by tensile testing, whereas the thermomechanical properties were evaluated using dynamic mechanical analysis (DMA). DMA studies were also conducted in different relative humidity levels.

## 2. Experimental

### 2.1. Materials

Mechanically treated bleached softwood kraft pulp (Khakalo et al., 2017) was used as a cellulose material. The cellulose, xylan and glucomannan contents of the pulp were 80.3%, 10.4% and 8.4%, respectively, as determined by high-performance anion-exchange chromatography (HPAEC-PAD). The lignin content (TAPPI-T Method 222 om-02) of the pulp was 0.9%. Hydroxyethyl cellulose (average Mv ~1,300,000), urea, glycerol, and glucose were obtained as p.a. grades

**Table 1**  
Composition of DESs used as plasticizers.

	Hydrogen bond acceptor (HBA)	Hydrogen bond donor (HBD)	Molar ratio (HBA:HBD)
DES1	Choline chloride	Glycerol	1:2
DES2	Choline chloride	Glucose	1:2
DES3	Choline chloride	Urea	1:2
DES4	Choline chloride	Citric acid	1:1
DES5	Tetrabutylammonium bromide	Propylene carbonate	1:2
DES6	Tetrabutylammonium bromide	Ethylene carbonate	1:2

from Sigma Aldrich (Germany). Propylene and ethylene carbonates, citric acid and tetrabutylammonium bromide (TBAB) were obtained as p.a. grades from TCI (Germany). All chemicals were used without further purification. Deionized water was used throughout the experiments.

### 2.2. Preparation of the cellulose biocomposites

HEC was first dissolved in water to obtain a 1% solution, the desired amount of CF was then added (the HEC-CF ratio was 50:50), and the suspension was mixed for 15 min. Ratio of 50:50 was chosen to represent equal amount of both materials. This ratio was also shown to produce composites with good handling properties (easy to remove from polystyrene plate). The suspension was then cast on a polystyrene plate (grammage of film was 90 g/m<sup>2</sup>) and a free-standing film was obtained after overnight drying at 40 °C. For plasticization, 12.5, 25, and 37.5% plasticizer, relative to the total amount of HEC and CF, was added to the film-forming suspension (all percentages represent weight-percentages). The compositions of two-component plasticizers based on DESs are presented in Table 1. Individual DES components were added to the aqueous solution of HEC and CF and were allowed to form while drying.

### 2.3. Mechanical properties of biocomposites

The tensile tests were conducted using a universal material testing machine (Instron 5544, USA) equipped with a 100 N load cell. The composite films were cut into thin strips with a specimen width of 5 mm. For the tensile testing, a 40 mm gauge length was set under a strain rate of 4 mm/min, and six specimens were measured. Using a Lorentzen & Wettre thickness tester (Sweden), the thickness of each specimen was determined as an average from three random locations on the specimen. Film thicknesses ranged from 14 to 44 µm. The tests were conducted in 50% RH at a temperature of 23 °C and under a preload of 0.05–0.1 N. The specimens were conditioned for one day in the measurement environment before testing. Five samples from each film were measured and results are presented as average.

### 2.4. Dynamic mechanical analysis

The thermomechanical properties of the films were measured by DMA (TA Instruments DMA Q800, USA) equipped with tension (film) clamps and operating in multi-frequency mode. For the studies conducted under different relative humidity conditions, the DMA was also equipped with a DMA-RH Accessory. The rectangular specimens were prepared in the same way as for the tensile tests. DMA at variable temperature was conducted as follows: specimens were first equilibrated at 30 °C for 5 min and then heated, at a rate of 5 °C/min, to 250 °C using 17 mm gap distance, 15 µm amplitude, 0.05 N preload force and 125% force track. The specimens measured in variable RH were allowed to equilibrate first at 30 °C (RH 0%) for 120 min. Then, RH was stepped up at a rate of 1%/min until RH 95% was reached, and the sample was subsequently maintained isothermally for 60 min. The

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