1 **Effect of plasticizers on the mechanical and thermomechanical properties of cellulose-based**
2 **biocomposite films**

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6 **Abstract**

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

21 *Keywords:* Cellulose; hydroxyethyl cellulose; composite; plasticizer; deep eutectic solvent; thermoformability

22 **1. Introduction**

23 Oil-based packaging materials are one of the most prominent sources of persistent environmental pollutants
24 (Davis and Song, 2006; Derraik, 2002). Many oil-based materials have a low degree of biodegradability and
25 can contain residuals of toxic monomers, which may be highly disadvantageous, especially for food
26 packaging. Furthermore, the declining oil resources are one of the driving forces for seeking novel alternative
27 solutions for current applications, including the packaging industry, which continues to grow (Owen et al.,
28 2010).

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

37 Cellulose can be derivatized by several methods to improve formability of biopolymeric materials.
38 Esterification and etherification (Fox et al., 2011) or carbamation (Johan-Fredrik et al., 1985; Sirviö and
39 Heiskanen, 2017) can be used to convert cellulose into water-soluble semi-synthetic polymer. Soluble
40 cellulose derivatives can be utilized for solvent-casting to prepare films with varying functionalities. Although
41 methods, such as melt-processing in blow-film extrusion are preferred in an industrial scale, there are
42 several ways to utilize solvent-casting in large scale applications.(Siemann, 2005) However, chemical
43 modification can increase the fabrication cost and often requires chemicals that are environmentally
44 undesirable. One possibility to take advantage of both the cost and sustainability of natural fibers and the
45 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 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 thermoformabity) 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 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 minutes. 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^2) and a free-standing film was obtained after overnight drying at 40 ºC. 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.

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

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 ºC 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 films 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 ºC for 5 min and then heated, at a rate of 5 ºC/min, to 250 ºC 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 ºC (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 parameters used were 17 mm gap distance, 10 µm amplitude, 0.01 N preload force and 125% force track.

3. Results and Discussion

3.1. Tensile properties of plasticized biocomposites

*3.1.1 Effect of the single-component plasticizers on the tensile properties of CF-HEC composite*

Many packaging materials require high elongation at break in addition to good strength properties. However, many natural-based polymers have low ductility due to the strong hydrogen bonding between constituent molecules, which results in a stiff structure. This is particularly so with natural CF, which tend to form hydrogen-bonded networks when used as a filler or reinforcement agent, and this can decrease the biocomposites elongation. Therefore, several plasticizers were evaluated to improve the elongation by decreasing the hydrogen bonding between fibers and polymers. Glycerol is one of the most studied plasticizers (Vieira et al., 2011) as it is non-volatile, cheap (produced in high amounts as a side-product of biodiesel fabrication) and has low toxicity (Tan et al., 2013). When a small amount of glycerol (12.5% relative to the mass of HEC) was added to CF-HEC biocomposites, no change in the elongation at break was noted, and the strength decreased by around 25%. Generally, a decrease in the strength of polymeric materials is common when plasticizers are added because of the weaker interaction between polymeric chains (Sanyang et al., 2015) (Figure 1). The increased amount of glycerol (to 25 and 37.5% relative to the mass of composite) improved the elongation at break of the biocomposites significantly, and a maximum elongation at break of 11.8% was obtained (the elongation at break of the non-plasticized composite was 7.7%). Composite strength also decreased when glycerol content was increased, but it still remained at a relatively high level. When 25% glycerol was used, the tensile strength of the composite was 18 MPa, which is similar to, for example, alginate composite containing 50% birch pulp without plasticizers (Sirviö et al., 2014) and polypropylene containing bamboo fibers (Chen et al., 1998).
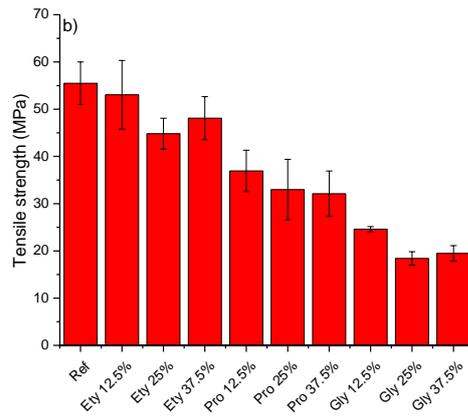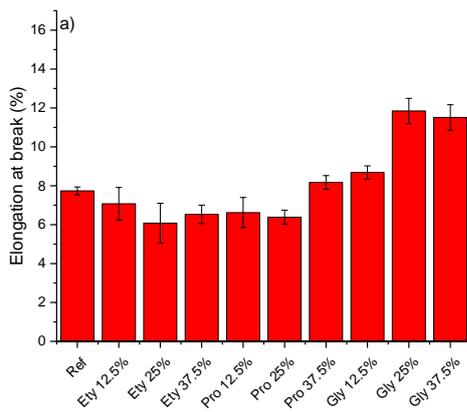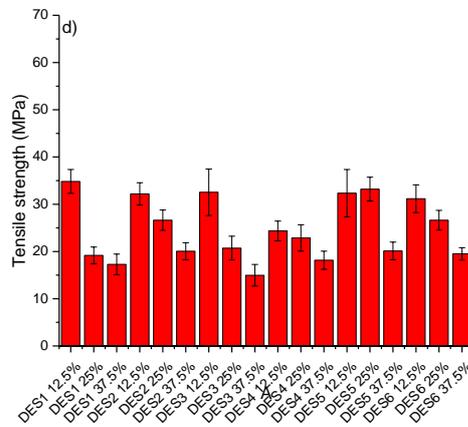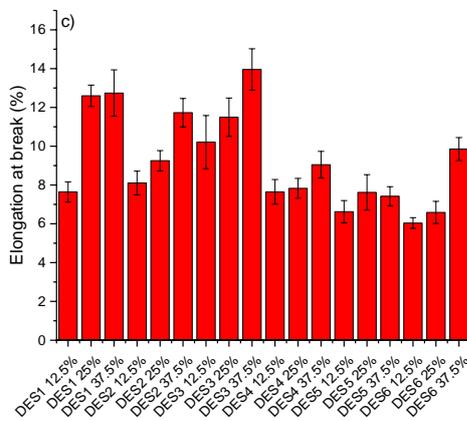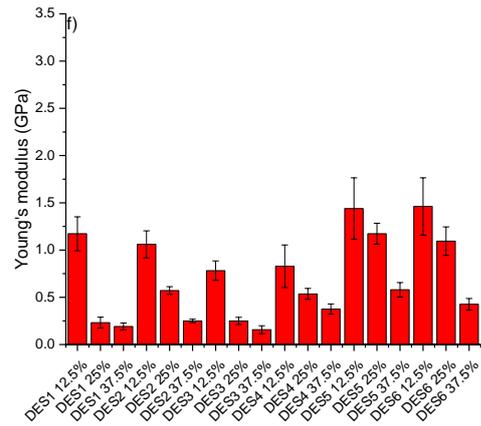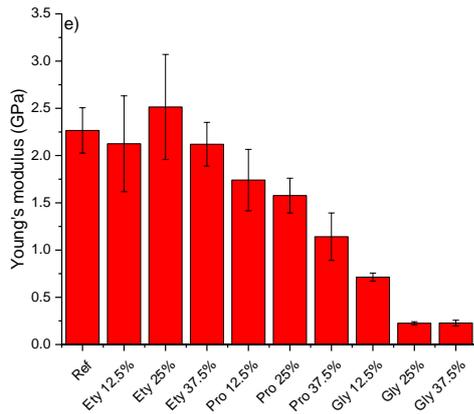
Figure 1. Elongation at break, tensile strength, and Young's modulus of the non-plasticized (Ref) and single-component plasticized (Ety, Pro, Gly), (a), (b), and (e), and of the DES-plasticized (DES1-DES6), (c), (d), and (f), CF-HEC (50:50 wt%) biocomposites. Error bars represent the standard deviation of the specimen.

Two cyclic carbonates, namely propylene and ethylene carbonate, were also tested as plasticizers for CF-HEC biocomposites. Organic carbonates are esters of carbonic acid and can be produced directly from carbon dioxide (North et al., 2010), thus making them attractive chemicals to be studied as plasticizers. However, in this case, both carbonates exhibited a small, or even negative, effect on both elongation at break and strength values. Of the two carbonates, the use of 37.5% propylene carbonate increased the elongation at break of CF-HEC composite by 5%, which is still lower compared to the composite containing 12.5% glycerol, indicating a low plasticizing effect of the cyclic carbonates on the CF-HEC composite. The poor performance of cyclic carbonates may be due to the low interaction between CF-HEC and the plasticizer.

The Young's modulus of plasticized composites followed similar trends to tensile strength. The introduction of glycerol significantly decreased the Young's modulus, whereas a small decrease was observed when propylene carbonate was used. Use of ethylene carbonate showed practically no effect on the modulus of composites. The introduction of efficient plasticizer (here glycerol) decreases the ability of the material to resist deformation, which results in loss of stiffness and can be observed as decrease of Young's modulus. (Lim and Hoag, 2013) On the other hand, introduction of ethylene carbonate might cause the undesirable disturbance of formation of composite (e.g. causes poor interaction between components), which is then reflected as poor mechanical performance. Similar decrease in tensile properties (elongation, strength and modulus) has been observed when high concentration of glycerol was introduced to sugar palm starch films.(Sanyang et al., 2015) Possible explanation was described as phase separation phenomenon.

3.1.2 Effect of the DES plasticizers on the tensile properties of composite

DES components were added directly into a water mixture of HEC and CF and allowed to form during drying. The DESs produced using choline chloride together with glycerol (DES1), glucose (DES2) and urea (DES3) exhibited relatively similar plasticizer effects compared to glycerol (Figure 1). The addition of 12.5% DES1 and DES2 had no effect on the elongation at break of CF-HEC biocomposites, whereas their further addition increased the elongation at break of biocomposites to similar, or even higher, elongation at break values compared to glycerol. When DES3 (based on choline chloride and urea) was used, even the small addition of 12.5% plasticizer increased the composite elongation at break to over 10%; however, high standard deviations were observed. Of the DES plasticized CF-HEC biocomposites, DES3 appeared to be the most efficient plasticizer, whereas DES formed between choline chloride and citric acid (DES4) had only a minor effect on the elongation at break (a elongation at break of 9.0% was obtained using 37.5% DES4). The tensile strengths of DES1–4 biocomposites were similar to those of biocomposites containing glycerol (i.e.

5

189 the addition of plasticizer significantly decreased the strength). Although glycerol has low toxicity and is
190 produced as by-product of biodiesel production, use of DESs as alternative plasticizer could have some
191 benefits. Evaporation of DESs can be even lower compared to glycerol as for example DESs based on
192 glycerol have lower vapor pressure compared to glycerol. In addition, urea based DESs exhibits significantly
193 lower vapor pressure compared to glycerol or glycerol-based DESs. (Shahbaz et al., 2016) Evaporation of
194 glycerol eventually leads to stiffening of the composite, which disadvantageous in many applications. In
195 addition, as urea can be produced from carbon dioxide, use of urea-based DES could be seen as
196 temperature carbon sink.

197 Both propylene and ethylene carbonates were also used as DES components (hydrogen bond donors) for
198 plasticizing the CF-HEC composite. Tetrabutylammonium bromide was chosen as a hydrogen bond acceptor
199 as neither of the carbonates formed DES with choline chloride. The propylene carbonate-based DES (DES
200 5) exhibited no plasticizing effect and also decreased the strength of composite (Figure 1). Conversely, the
201 use of 37.5% DES6 (based on ethylene carbonate and TBAB) increased the composite elongation at break
202 from 7.7 to 9.9%. This was still lower compared to glycerol and DES1-3. However, the results indicate that
203 DESs based on cyclic carbonates can act as plasticizers, if the polymeric matrix provides sufficient
204 interaction (i.e. hydrophobicity) with the plasticizer.

205 The Young's modulus of DESs plasticized composites were similar to those of single component plasticizer,
206 as the modulus values were significantly reduced by the addition of DESs. Decrease of the modulus was in
207 line with the decrease of tensile strength and increase of elongation at break.

208 **3.2 Dynamic mechanical analysis of biocomposites as a function of variable humidity**

209 *3.2.1 Effect of humidity on the dynamic mechanical properties of single-component plasticized composites*

210 The tan δ curves of biocomposites containing single-component plasticizers at different humidity levels are
211 presented in Figure 2 (storage and loss modulus curves are presented in Supporting Information, Figure S1).
212 Propylene carbonate and ethylene carbonate containing biocomposites exhibited similar tan δ curves
213 compared to reference composite, and the tan δ maximum was observed around 70% humidity level.
214 However, when glycerol was added, the tan δ peak gradually moved towards lower humidity region. At
215 plasticizer content of 12.5%, the tan δ peak occurred around a humidity of 55% (which is slightly higher
216 compared to the humidity where the tensile strength tests were performed: 50%). Further addition of glycerol
217 moved the tan δ peak towards even lower humidity level (also the shape of the peak broadened). These
218 results are in line with the results obtained in the tensile testing: at a glycerol content of 12.5%, the maximum
219 tan δ peak occurred at a higher humidity where tensile strength measurements were performed, and only a
220 minor effect on the tensile elongation at break was observed. At a glycerol content of 25 and 37.5%, the δ
221 peak shifted to lower humidity, and a good plasticization effect (in terms of improved elongation) was
222 observed. In the case of propylene carbonate and ethylene carbonate, no movement of the tan δ peak
223 maximum and no increased elongation at break values in the tensile test were noted.

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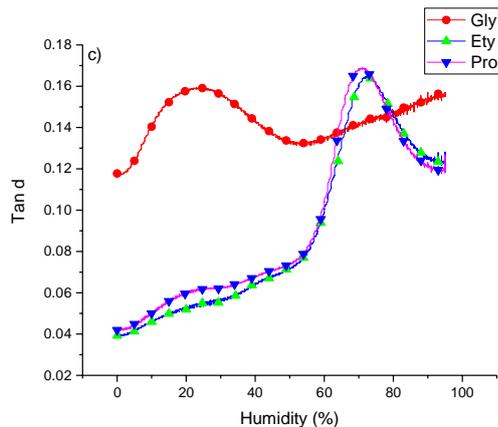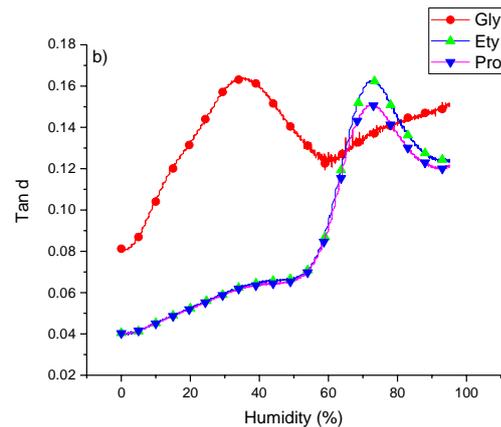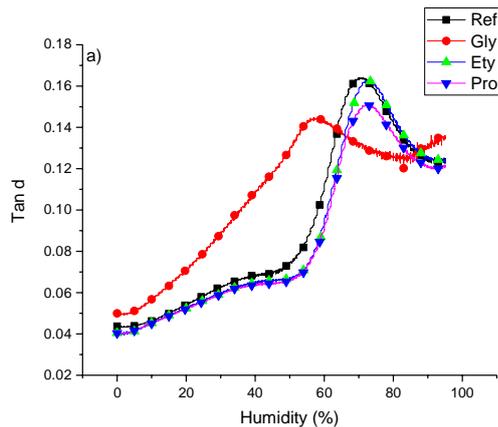
Figure 2. The tan δ curves of the single-component plasticized CF-HEC biocomposites at various humidity levels measured using DMA with plasticizer content of a) 12.5%, b) 25%, and c) 37.5%. The tan δ curve of the unplasticized CF-HEC biocomposite (Ref) is in figure 2a.

The better interaction of glycerol with water compared to that of cyclic carbonate with water could originate from the fact that glycerol can act both as hydrogen bond donor and acceptor. However, cyclic carbonates contains only hydrogen bond acceptors and cannot therefore act as hydrogen bond donor." In addition, carbonates have a rigid cyclic structure, which causes molecules to be more amphiphilic (has both hydrophobic and hydrophilic part), which prevents them from efficient interaction with water. However, glycerol is a freely rotating molecule, which can allow a better interaction with water compared to cyclic carbonates. The better interaction between water and plasticizer results in plasticization of CF-HEC biocomposites, as water act as an additional plasticizer. Act of water as plasticizer was also proposed for xylitol or sorbitol plasticized hardwood xylan.(Gröndahl et al., 2004) Softening of the material was observed after certain increase of the humidity. Further supporting results about the plasticization effect of water was obtained using DMA at elevated temperature (see section 3.3.1.).

3.2.2 Effect of humidity on the dynamic mechanical properties of the DES-plasticized biocomposites

Biocomposites containing DES as a plasticizer had similar tan δ curves compared to single-component plasticizers, as the best DES plasticizers (choline chloride together with urea and glycerol) exhibited a tan δ peak maximum between 20 and 50% humidity with a dosage of 25% (Figure 3). However, both DESs containing glucose (DES2) and citric acid (DES4) showed a tan δ maximum around the same humidity (between 40 and 60%), whereas the glucose-containing composite showed a higher improvement in the elongation at break. In addition, use of cyclic carbonate as part of the DES, instead of the pure chemical, had some effect on the DMA result at different humidity levels as tan δ was broadened and the maximum shifted toward lower humidity.
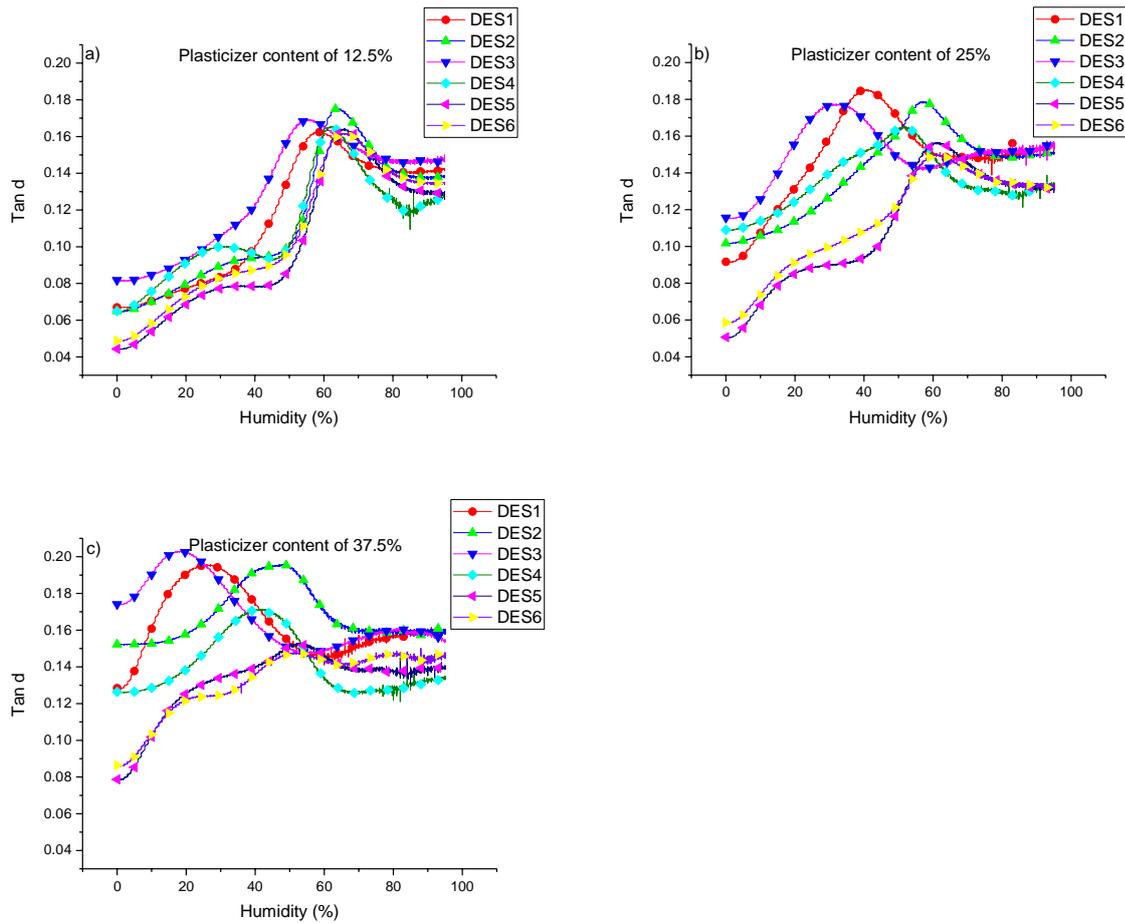
Figure 3. Tan δ curves of the DES-plasticized CF-HEC biocomposites at different humidity levels measured by DMA using plasticizer contents of a) 12.5%, b) 25%, and c) 37.5%.

Even though the results obtained by DMA at different humidity levels were slightly inconclusive, and further studies should be conducted, there was evidence that the addition of plasticizers made the biocomposites more responsive towards humidity. Increased responsiveness may be due to the improved adsorption of water on the composite or the applied plasticizer, which in turn may ease the polymer chains' ability to slide against each other. Previously, the presence of glycerol was reported as promoting water molecular up-take in the amaranth flour films, thus resulting in more ductile films (Tapia-Blácido et al., 2013).

3.3 Dynamic mechanical analysis of biocomposites as a function of variable temperature

3.3.1 Effect of temperature on the dynamic mechanical properties of single-component plasticized biocomposites

Thermomechanical properties provide an insight into the thermal behavior of the biocomposites, thereby indicating their potential thermoformability. In some packaging formulations, thermoformability may be beneficial to shape complex 3D structures. Conversely, for various applications, good thermal stability (i.e. the materials ability to resist thermally induced softening) may be more desirable. Here, DMA was used to measure the thermomechanical properties of the CF-HEC biocomposites.

The initial storage modulus of the CF-HEC composite decreased from 3,830 to 1,090 MPa when samples were heated from 30 to 200 ºC, which indicates that temperature induced loss of stiffness (Table 2). The addition of both glycerol and propylene carbonate decreased the initial storage modulus of biocomposites at 30 ºC. In the case of glycerol, the storage modulus started to decrease as a function of temperature. However, a minor increase can be observed at higher temperature; at 200 ºC, the storage modulus of

272 glycerol-containing biocomposites was higher (12.5% glycerol), similar (25% glycerol), or slightly lower
273 (37.5% glycerol) compared to pure composite without plasticizers. This may be due to the evaporation of
274 absorbed water at higher temperatures, which in turn reduced the plasticizing effect (as stated in the section
275 3.2, humidity was found to be one of the driving forces toward composite plasticization). In the case of
276 propylene carbonate, the storage modulus decreased gradually as a function of temperature, indicating it did
277 not have a similar effect to glycerol on the composite regarding the response to humidity. This is in line with
278 the tensile test measurements where only a minor effect on tensile strength was noted when propylene
279 carbonate was used as plasticizer. The storage modulus of ethylene carbonate plasticized composite
280 showed similar behavior as a function of temperature compared to pure CF-HEC composite as it was
281 observed that the addition of ethylene carbonate had only a minor effect on the storage modulus of
282 biocomposites.

283 Table 2. Storage moduli (MPa) of unplasticized (Ref) and single-component plasticized CF-HEC
284 biocomposites (50:50 wt%) at different temperatures.

Temperature (ºC)	Ref	Glycerol			Propylene carbonate			Ethylene carbonate		
		12.5 %	25 %	37.5 %	12.5 %	25 %	37.5 %	12.5 %	25 %	37.5 %
30	3830	2739	1689	866	3697	1959	1696	3363	3979	3132
100	3220	1517	841	507	3198	1852	1909	2753	2700	2899
150	1824	1199	945	704	2000	1016	1199	1498	1319	1687
200	1091	1227	1110	922	1275	634	807	998	891	1123

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286 The tan δ curve of the pure CF-HEC composite showed a linear increase between 100 and 140 ºC, which
287 indicates the softening of the composite; HEC has a glass transition temperature at 120 ºC (Kararli et al.,
288 1990) (Figure 4). In addition, both cyclic carbonate plasticized biocomposites exhibited similar properties, but
289 a minor increase in the maximum height of curves was observed. The glycerol plasticized biocomposites
290 showed a broad curve from around 40 to 100 ºC, after which, the curves started to decline. This further
291 indicates that drying of the composite at an elevated temperature decreased the softening effect of glycerol.
292 The glycerol's effect on the tan δ of CF-HEC composite was similar, as noted, to glycerol plasticized chitosan
293 (Ma et al., 2017). In addition, regarding the fixed plasticizer content, it has been observed that adding
294 moisture content decreased the glass transition temperature of starch films (Mathew and Dufresne, 2002). In
295 addition, previously the effect of the moisture on the plasticized wheat protein was observed, as the further
296 increase in the tan δ values was observed when moisture was lost during the heating. (Zhang et al., 2005)
297 The further increase in the tan δ values was proposed to be due to the change of the glass transition
298 temperature. In our case, this was observed as broad tan δ peak in the glycerol plasticized composites.

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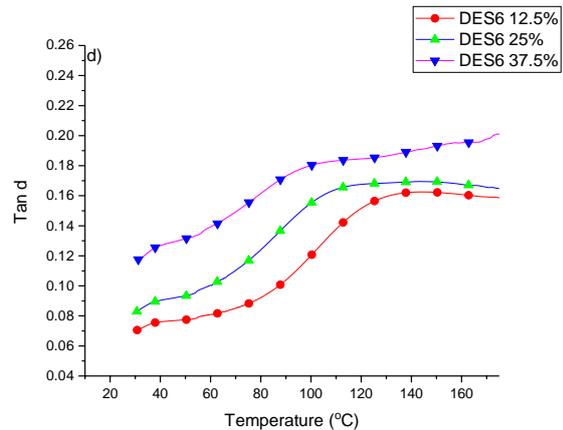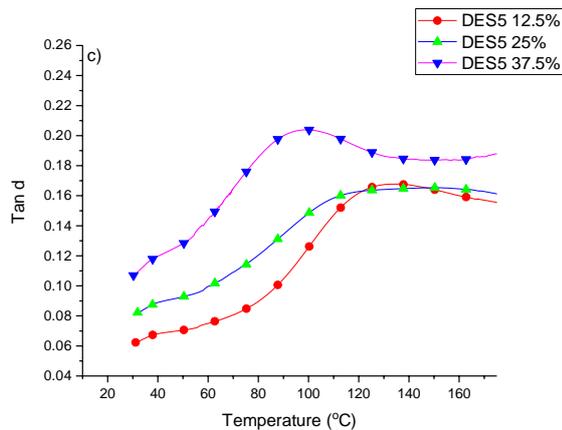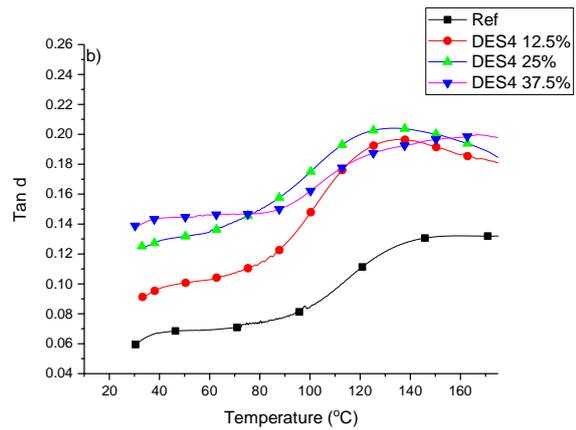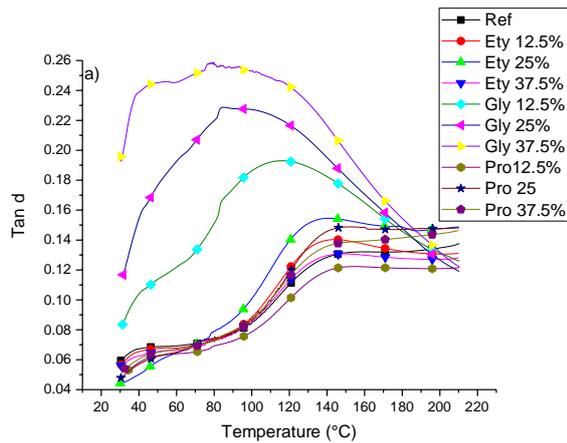
Figure 4. Tan δ curves of a) unplasticized and single-component plasticized, b) unplasticized and DES4, c) DES5, and d) DES6 CF-HEC biocomposites with plasticizer contents of 12.5, 25, and 37.5% at various temperatures measured by DMA.

3.3.2 Effect of temperature on the dynamic mechanical properties of the DES-plasticized biocomposites

Both DES1 and DES3 had similar effects to glycerol on the storage modulus as the storage modulus first decreased during heating from 30 to 100 ºC, after which, values began to rise (Table 3). Conversely, when DES2 was used as plasticizer, this effect was not so visible. Moreover, DES based on tetrabutylammonium bromide and cyclic carbonate exhibited a similar effect to cyclic carbonate alone, as the storage modulus gradually decreased with the addition of plasticizer and increasing temperature. It was also observed that some DES-plasticized biocomposites broke during the test at high temperatures. In particular, this occurred with DES containing citric acid, where high acid content might cause some hydrolysis of the biocomposites at higher temperatures.

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Table 3. Storage moduli (MPa) of DES-plasticized CF-HEC biocomposites (50:50 wt%) at different temperatures.

Temperature (°C)	DES1			DES2			DES3			DES4			DES5			DES6		
	12.5 %	25 %	37.5 %	12.5 %	25 %	37.5 %	12.5 %	25 %	37.5 %	12.5 %	25 %	37.5 %	12.5 %	25 %	37.5 %	12.5 %	25 %	37.5 %
30	3115	2104	1763	3843	3246	3071	3221	3916	1566	3365	2918	1711	3266	3732	2836	3916	3652	2692
100	1838	901	733	2165	1873	1954	1612	1588	536	2065	1653	1062	2155	1743	1000	2381	1676	1037
150	1187	976	892	1143	1042	983	981	1129	461	1050	879	-*	1223	1046	821	1185	1051	746
200	1035	975	1074	-*	1117	962	1077	1459	749	-*	-*	-*	958	890	-*	875	872	-*

*Sample broke during measurement

In the cases of DES1 and DES3 plasticized biocomposites, the tan δ curves were similar to the glycerol plasticized biocomposites (broad curve around 40 and 100 ºC, after which, the curve started to decline; see Supporting Information for curves). On the contrary, DES2 exhibited different softening behavior as a function of temperature (Figure 4). The maximum tan δ curve occurred at the same temperature compared to pure composite. However, with plasticizer content of 12.5%, the height of the tan δ maximum compared to the starting point at 30 ºC, was significantly higher. This may indicate that glucose- containing DES-plasticized CF-HEC composite is more thermoformable compared to pure composite. With higher plasticizer content, the increase of the tan δ height from initial value to maximum was not so evident, which may be due to the initial higher plasticity of composite with higher plasticizer content. These observations suggest that DES2 may have a slightly different plasticizing effect on the CF-HEC biocomposites compared to glycerol and DES based on choline chloride, together with glycerol and urea.

At plasticizer content of 12.5%, DES based on tetrabutylammonium bromide, together with cyclic carbonates, exhibited similar behavior compared to DES2 (Figure 4). However, the increase of plasticizer content decreases the maximum temperature of the peak of tan δ, and DES5 containing composite with plasticizer content of 37.5% exhibited a tan δ peak maximum below 100 ºC. High (intensity) of tan δ peak reflects the extent of mobility of the polymer chain segments and therefore indicates more viscose behavior (Hill et al., 2000). Due to the highest tan δ peak, DES6 plasticized composite had the highest thermoformability at the lowest temperature compared to reference and other plasticized composites. Results obtained here indicates that by choosing the right components, DESs could act as versatile alternative for more traditional plasticizers. Improved thermoformability might allow the production of composites based on HEC and CF to be utilized in larger scale, as thermoformability allows the use of methods, such extrusion, during the composite production.

4. Conclusion

Glycerol and DESs based on choline chloride, together with glycerol, urea and glucose, were identified as a potential plasticizer to improve ductility of composite films based on natural CF and chemically modified, water-soluble cellulose (HEC). Based on the DMA analysis at varying humidity, the addition of good plasticizer made biocomposites more responsive towards humidity. This in turn was observed as increased elongation as a result of good plasticization effect. The DES plasticizers based on mixtures of various components had a similar, or even slightly better, plasticization effect comparable to more traditionally used plasticizers, such as glycerol. Some DES-based plasticizers, especially tetrabutylammonium bromide and propylene carbonate, could also be used to increase the thermoformability of CF-HEC biocomposites, which may be desirable function in packaging applications. DES plasticizers based on cyclic carbonate were found to be potential environmentally friendly additives to produce natural plastics because carbonates, such as propylene carbonate, may be produced from carbon dioxide. More systematic investigation about the different compositions of DES should be conducted in future to give better insight about the mechanism of plasticization when DESs are used instead of single-component plasticizers. The results should then be demonstrated with the larger-scale and continuous methods, such as papermaking procedure or extrusion.

Conflict of interests
All authors certify that there is no conflict of interests in this study.

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