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# Thermo-mechanical properties and blend behaviour of cellulose acetate/lactates and acid systems: Natural-based plasticizers

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# 1           **Thermo-mechanical properties and blend behaviour of cellulose** 2           **acetate/lactates and acid systems: Natural-based plasticizers**

3

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16

## 17   **ABSTRACT**

18   This work brings together thermo-mechanical and structural information for plasticized cellulose  
19   acetate (CA) by lactates and octanoic acid. CA are processed with plasticizer due to their high Tg and  
20   their strong H-bonding network. We prepared CA / plasticizer blends by corotative twin screw  
21   extruder and by solvent casting methods. **The study of the different relaxations and of the glassy**  
22   **zone modulus was performed by dynamic mechanical analysis (DMA). The miscibility range of**  
23   **cellulose acetate blends were identified by the analysis of the tan  $\delta$ . Depending on the composition**  
24   **of the system, one or two transitions are noted, this last result indicates the presence of a phase rich**  
25   **in CA and another in plasticizer.** To connect this information to crystallinity and molecular  
26   organization, X-ray diffraction analyses were carried out. **The disappearance of crystallinity allows the**  
27   **plasticization of previously inaccessible zones, causing a glassy modulus drop of more than 1000**  
28   **MPa.**

29   **Keywords:** Cellulose acetate, plasticization, miscibility, thermo-mechanical properties, X-ray  
30   diffraction.

## 31 1. Introduction

32 In recent years, the interest in biopolymers has been increasing continuously. Cellulose acetate is a  
33 biobased and biodegradable polymer manufactured from cellulose, which is one of the most  
34 abundant renewable organic resources on Earth, and excess of acetic anhydride (Wu et al., 2004). A  
35 part of the hydroxyl groups is converted to acetyl groups using esterification reactions. The most  
36 common degree of substitution (DS) is 2.5 partly due to melting properties (Kamide & Saito, 1985).  
37 To improve flexibility and processability by lowering the glass-transition, cellulose diacetate is  
38 blended with plasticizers (Lee et al., 2005; Vieira, da Silva, dos Santos, & Beppu, 2011; Wypych,  
39 2012).

40 In the literature, there are many studies on thermal and mechanical properties of plasticized  
41 cellulose acetate. Samples are especially characterized by dynamic mechanical analysis and  
42 differential scanning calorimetry.(Bao, Long, & Vergelati, 2015; Kawai & Hagura, 2012; Lee et al.,  
43 2005; McBrierty, Keely, Coyle, Xu, & Vij, 1996; Scandola & Ceccorulli, 1985a; Seymour, Weinhold, &  
44 Haynes, 1979; Vidéki, Klébert, & Pukánszky, 2007).

45 Over the past few years, the worldwide production of plasticizers has been around 5 million tons per  
46 year. They were used in about 60 different polymers and 30 groups of products (Białecka-Florjańczyk  
47 & Florjańczyk, 2007). Modifying polymers by the addition of plasticizers is not a recent practice in the  
48 manufacturing of plastic products. Their use began in the late 19<sup>th</sup> century. Plasticizers represent  
49 about one third of the global market of plastic additives (Rahman & Brazel, 2004).

50 The main plasticizers used to plasticize cellulose acetate are triacetin (food packaging & cigarette  
51 filters and other), diethyl phthalate (glasses & adhesive tape and other), triphenyl phosphate  
52 (photographic films and other) among others (Wypych, 2017). Triacetin and diethyl phthalate are  
53 among the best plasticizers of cellulose acetate due to their high boiling points (respectively 260 and  
54 298 °C). This reduces the plasticizer weight loss during the mixing process (Quintana, Persenaire,  
55 Lemmouchi, Bonnaud, & Dubois, 2014). It should be noted though that some of the commonly used  
56 plasticizers are not eco-friendly.

57 There is an increasing interest for natural based plasticizers to develop new bio-based materials  
58 made from biodegradable and renewable resources. It seems to be more appropriate to use natural  
59 based plasticizers to manufacture biopolymers (Vieira et al., 2011). Lactates are esters formed from  
60 lactic acid (Pereira, Silva, & Rodrigues, 2011), and octanoic acid (OA) is a fatty acid mainly found in  
61 edible oils and milk of various species (Lizhi, Toyoda, & Ihara, 2008; Nair et al., 2005). They are  
62 natural solvents so they could be named green solvents. They have higher boiling points than other  
63 solvents which come from biomass. Ethyl lactate (ELL) and butyl lactate (BL) are particularly

64 attractive due to their lower vapour pressures than some traditional solvents: they have a lower VOC  
65 (volatile organic carbon) character. (Lomba, Giner, Zuriaga, Gascón, & Lafuente, 2014)

66 In this study, lactates and octanoic acid was used as external plasticizers of cellulose acetate to  
67 decrease the Tg and suppress the high degree of crystallinity of CA. The objectives of this work are to  
68 study the effect of these eco-friendly additives on thermo-mechanical, structural properties and  
69 morphologies of CA materials.

## 70 2. Materials & methods

### 71 2.1 Materials

72 CA was supplied by Acetow GmbH (Freiburg, Germany). The DS of CA was 2.45, i.e. combined acetic  
73 acid  $\approx$  55.63 %. Ethyl lactate (ELL,  $\geq$  98 %, food grade CAS No.: 687-47-8), butyl lactate,  $\geq$  97 %, food  
74 grade, CAS No.: 34451-19-9) and octanoic acid (OA,  $\geq$  98 %, food grade, CAS No.: 124-07-2) were  
75 purchased from SIGMA-ALDRICH.

76  $^1\text{H}$  NMR analysis solvent acetone- $d_6$  and pyrrole (purity  $\geq$  99%) were both supplied by Acros  
77 Organics.

78

### 79 2.2 Experimental procedure

#### 80 2.2.1 Preparation of CA / plasticizer samples

81 In this study, two types of processing to prepare plasticized cellulose acetate were used due to the  
82 wide range of plasticizer rates under study. In fact, the extrusion process is impossible for blends  
83 containing less than 15 wt% of plasticizers due to the very low plasticization and also for blends with  
84 more than 40 wt% of plasticizers due to their very low viscosity at high temperature. So, solvent cast  
85 method was used for mixtures without or with very small amount of plasticizers and for mixtures  
86 with up to 70 wt% of plasticizers.

87 A corotative twin-screw extruder Clextral BC 21 was used to prepare compounds composed of 15 to  
88 40 wt% of plasticizer, with a screw speed of 100rpm at a feeding rate of 2 kg/h. Cellulose acetate  
89 powder, dried for 72 h under vacuum at 70 °C, was inserted in zone 1 using a weight-feeder. A liquid  
90 plasticizer was injected by a volumetric pump in zone 2. The extruder was connected to a water  
91 cooling bath and a granulator.

92 For samples plasticized between 0 and 70 wt%, 2 g of CA / plasticizer mixtures were dissolved in 20  
93 mL of acetone. The solutions were placed 24h under stirring and then poured into an evaporation

94 bell, composed of a PTFE mold closed with a perforated glass lid on the top, at room temperature  
95 during 150 h.

### 96 2.2.2 NMR Spectroscopic Measurements

97 <sup>1</sup>H NMR analyses were performed by a Bruker Advance III spectrometer working at 400 MHz  
98 equipped with a 5 mm multinuclear broadband probe (BBFO+) with z-gradient coil. The solute  
99 concentration was 60 to 80 mg.mL<sup>-1</sup> in acetone d6. The analysis was performed at a 298 K  
100 temperature. To analyse and quantify internal plasticization of CA, 1/3 of the solute weight was  
101 added in pyrrol.

102 The amount of plasticizer was analyzed by NMR because the target concentration of a blend was not  
103 equal to the real concentration, in particular for the mixtures obtained by an extrusion process.

### 104 2.2.3 Dynamical mechanical analysis (DMA)

105 The dynamical mechanical analysis was carried out by means of a dynamical mechanical thermal  
106 analyser Q800 (TA instruments). A wide range of temperatures (-100 °C to +220 °C) were  
107 investigated. A constant heating rate of 2 °C.min<sup>-1</sup> and frequencies of 1 Hz were used. Transition  
108 temperatures were determined using the inflexion point of the storage modulus curve and the glassy  
109 zone modulus was determined using the minimum of tangent  $\delta$  according to *C. Liu et al.* (Liu, He,  
110 Ruymbeke, Keunings, & Bailly, 2006). CA/plasticizer samples were preconditioned at 30 % of relative  
111 humidity for 60 h before thermo-mechanical analysis.

### 112 2.2.4 Small-angle X-ray scattering (SAXS) and Wide-angle X-ray scattering (WAXS)

113 SAXS/WAXS experiments were carried out at the European Synchrotron Radiation Facility (ESRF) in  
114 Grenoble (France) on the BM2-D2AM beamline. The incident photon energy was set to 18 keV.  
115 Samples with a thickness between 800 and 1000  $\mu\text{m}$  were directly placed in the beam path. The SAXS  
116 and the WAXS signals were detected simultaneously using two 2D XPad solid state detectors. For  
117 SAXS acquisition, the sample-to-detector distance was set at about 1.15 m and a beam stop with a  
118 diameter of 2 mm was used. For WAXS acquisition, the sample-to-detector distance was set at 10  
119 cm. The q-calibration ( $q = 4\pi\sin(\theta)/\lambda$ ;  $2\theta$ : scattering angle) was achieved using a silver behenate  
120 powder standard for SAXS and a chromium(III) oxide (Cr<sub>2</sub>O<sub>3</sub>) powder standard for WAXS. The  
121 scattering contribution of air was subtracted from the scattering intensity of the samples. The image  
122 data treatments took into account the flat field response. The intensity was further normalized by  
123 the incident flux, and the sample thickness and l-calibration were achieved with a glassy carbon  
124 standard. The scattering profiles of the intensity I as a function of the scattering vector q were  
125 obtained by azimuthally averaging the corrected images.

## 126 2.2.5 Scanning electron microscope (SEM)

127 The morphology of the samples was observed by a scanning electron microscope (Hitachi S 3000 N)  
128 with a tungsten filament and high vacuum operated at 10 kV. The surface of samples was prepared  
129 with a cryo-ultramicrotome RMC MTXL. All the samples were gold-palladium-coated by sputtering to  
130 produce electrical conductivity.

131

## 132 3. Results and discussion

### 133 3.1 Thermal properties of systems

134 Based on a dynamical mechanical analysis, we identify the effect of lactates and octanoic acid used  
135 as external plasticizers on relaxation peaks. DMA spectra of samples containing 5 to 70 wt% of  
136 plasticizer were compared to one another.

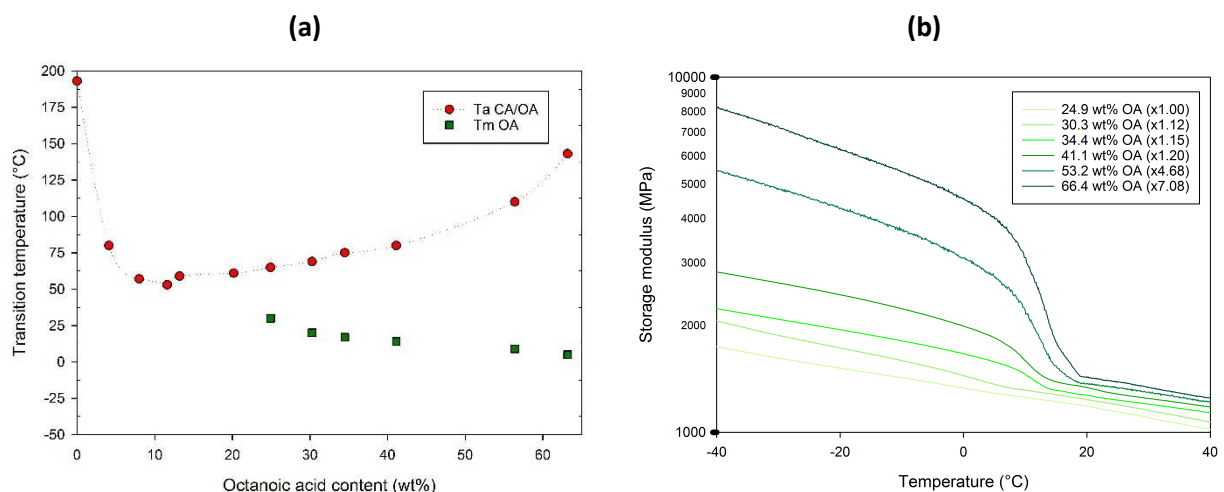


Figure 1: (a) Transition temperatures of CA/OA blends, according to the real plasticizers content. (b) Storage modulus measured at 1Hz according to temperature for CA mixtures containing different OA real content.

137

138 Thermal properties of CA / OA tested samples were investigated by DMA. Results were presented in  
139 Fig. 1a. With low amounts of octanoic acid as plasticizer, a decrease in  $\alpha$  relaxation temperature  
140 could be observed, which is considered as the glass transition temperature of the system. The Tg  
141 decreased around 50°C with less than 10 wt% of OA. At low rate, OA was a very good plasticizer of  
142 the CA system. With plasticizer rates higher than 25 wt%, the Tg of the blends CA / OA shifted to high  
143 temperatures.

144 According to storage modulus curves (Fig. 1b), all the cellulose acetate blends containing between 25  
145 to 66 wt% of OA remained unmixed. In fact, all of them presented a drop around 17 °C which  
146 increase with the OA content. This drop can be attributed to the melting temperature of pure OA

147 (Inoue, Hisatsugu, Suzuki, Wang, & Zheng, 2004), indicating that, a phase separation occurred in the  
 148 blend (between CA and OA). The extent of the drop around 17 °C increases with the OA content. The  
 149 quantity of OA that has demixed, which does not plasticize CA chains, increased. It seemed that after  
 150 a definite composition, between 20 wt% and 25 wt%, octanoic acid which was added to the mixture  
 151 led to the formation of a two-phase system with an OA-pure phase. The increase of T<sub>g</sub> for increasing  
 152 OA content suggests that some of the OA which plasticized CA at lower concentration could migrate  
 153 to the OA -pure phase. That is to say, additional acid had more affinity with the pure OA phase than  
 154 with CA / OA phase, and as consequence, less octanoic acid was available for the plasticization of CA  
 155 chains.

156 This demixing phenomenon of octanoic acid could be confirmed by SEM (Fig. 2). The sample  
 157 containing about 20 wt% of octanoic acid had a completely homogeneous surface, while the sample  
 158 containing 40 wt% of OA shows a porous structure.

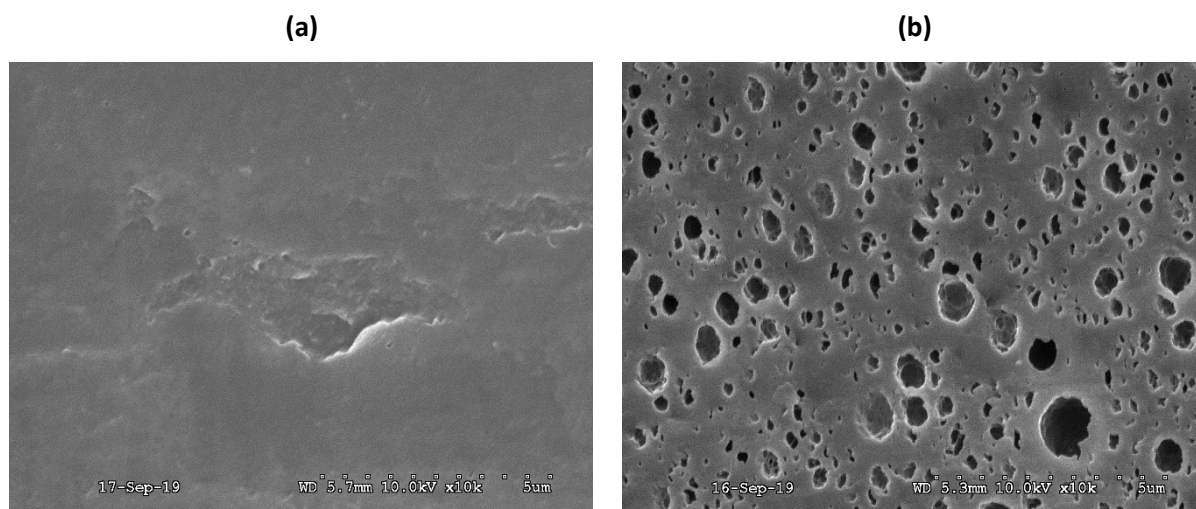


Figure 2 : Scanning electron micrographs X 10 000 from the prepared surfaces of cellulose acetate blends containing (a) 20.2 wt% of OA and (b) 41.1 wt% of OA.

159 Fig. 3 show the variation of the T<sub>g</sub> of CA / lactates blends obtained by DMA at a frequency of 1 Hz as  
 160 a function of the lactates content, for CA / BL and CA / ELL blends respectively. On these graphs, the  
 161 experimental values of the glass transition temperature could be fitted by the Fox equation (Fox,  
 162 1956).

$$1/T_{g,b} = \sum w_i/T_{g,i} \quad (1)$$

163  
 164 Where T<sub>g,b</sub> and T<sub>g,i</sub> are respectively the glass transition temperature of the blend and of the  
 165 components (CA and plasticizers), and w<sub>i</sub> is the mass fraction of component i.

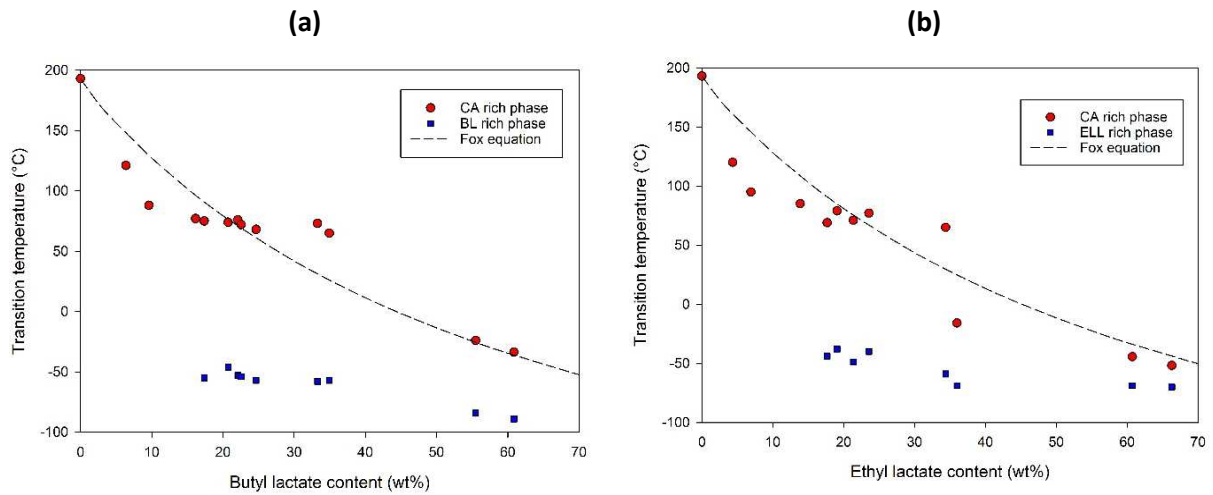
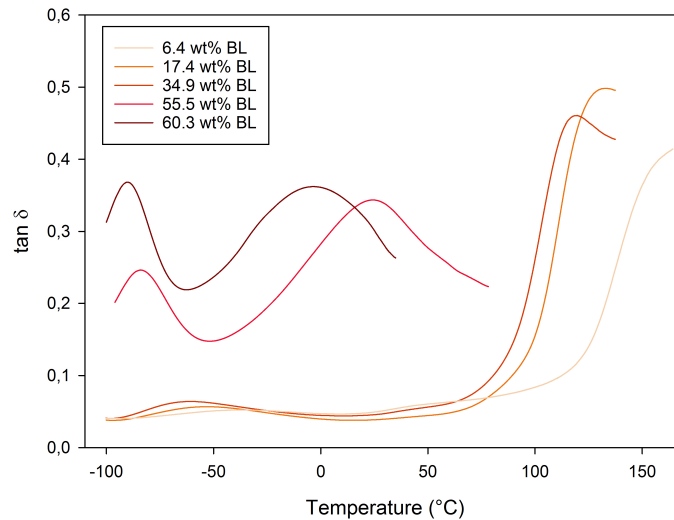


Figure 3 : Transition temperatures of (a) CA/BL blends (b) CA/ELL blends, according to the real plasticizers content.

166

167



168

169 Figure 4: Tan  $\delta$  measured at 1Hz according to temperature for CA mixtures containing different real BL content.

170

171

172 By measuring the glass transition temperature by DMA, it was possible to make a first  
173 characterization of the miscibility range of cellulose acetate / lactates blends.

174 It can clearly be seen that for lactates content up to 20 wt %, a single transition is found, which  
175 suggests that the mixture is monophasic and that its components are completely miscible. This  
176 transition corresponds to the glass transition of the blend which decreased first, with the increasing  
177 plasticizer contents. The reduction of Tg of cellulose acetate related to the effect of external  
178 plasticization has already been shown (Liu et al., 2006; Vidéki et al., 2007).



179 For lactates contents higher than 20 wt %, a second transition was found at lower temperature. It  
180 was pointed out that two phases of CA / plasticizer mixtures could be observed. The amplitude of  
181 this second relaxation increased with plasticizers rate (Fig. 4). It was possible to differentiate it from  
182 cellulose acetate  $\beta$  secondary relaxation, because it shifted to lower temperatures, thus introducing  
183 the concept of rich phases in cellulose acetate and rich phases in plasticizer (Bao et al., 2015; Kawai &  
184 Hagura, 2012). Other descriptions are found in the literature, assuming a complete and  
185 homogeneous miscibility of the plasticizer in the matrix. The secondary relaxation of the mixture  
186 would be due to specific polymer/plasticizer interactions (Seymour et al., 1979) or be produced by  
187 diluted chain movements in the plasticizer (Scandola & Ceccorulli, 1985b).

188 When it was possible to observe the relaxation of the plasticizer rich phase, a plateau around 75 °C  
189 for the relaxation of rich CA phase occurred. In other words, the transition temperature of this phase  
190 no longer decreased. For these blends compositions, values are not predicted correctly by Fox  
191 modelling.

192 Subsequently, with increasing amounts of lactates, experimental transitions got closer to the values  
193 obtained by the Fox equation. The two relaxations then had an equivalent intensity.

194 The Fox equation assumes no specific interactions between components of the mixture, such as  
195 hydrogen bonds (which preponderate in CA/lactates blends). The observed deviations can be also  
196 explained by this fact.

197

### 198 3.2 Thermo-mechanical properties of systems

199 Dynamical mechanical analysis of CA / lactate blends also allowed studying the glassy zone modulus  
200 as a function of plasticizers rate. It was summarized in Fig. 5.

201 For blending compositions with 0 to 10 wt% of plasticizer in which there was a decrease in  $\alpha$

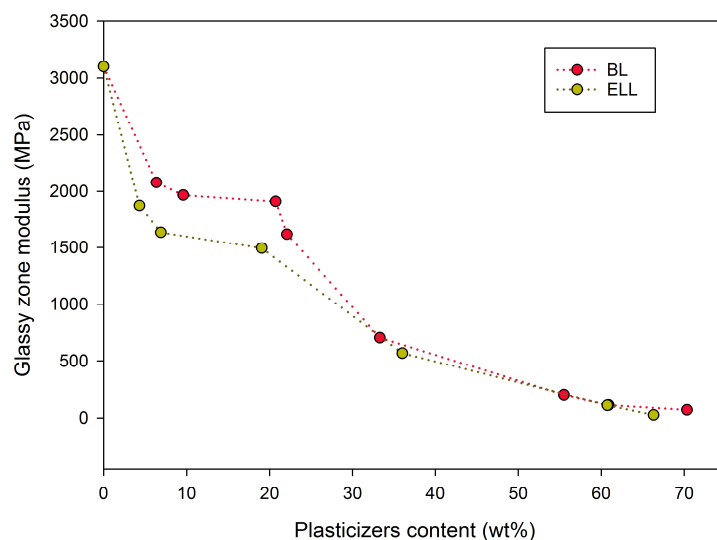


Figure 1: Glassy zone modulus temperature of CA/BL and CA/ELL blends, according to the real plasticizers content.

202 transition, a drop of the glassy zone modulus plateau was also observed. For concentrations of  
203 plasticizers above 10 wt%, composition at which a plasticizer rich phase appears, the glassy zone  
204 modulus stabilizes. Above 20 wt% of plasticizers, a second modulus drop appeared. According to Fig.  
205 7 crystallinity vanished at the same rate. A second modulus plateau was perceived next to 50 wt%.  
206 This last one could be analysed as cellulose acetate chains diluted in lactates, which were then a  
207 major part in the blend.

### 208 3.3 Effect of plasticizer on the crystallinity and molecular organization.

209 It is known that cellulose acetate is a partially crystalline polymer and transition from the glassy to  
210 the rubbery state is due to amorphous fractions of polymers. Scandola M. and al. (Scandola &  
211 Ceccorulli, 1985b) have hypothesized that small amounts of plasticizers only solvate the amorphous  
212 regions. To solvate the crystalline fraction of the polymer, higher amounts need to be used. They  
213 have also assumed that the whole sample could be uniformly diluted, owing to complete solvation of  
214 the crystalline fraction.

215 According to this, they hypothesized that if cellulose acetate retained its crystallinity after adding a  
216 small content of plasticizer, the composition of amorphous regions of cellulose acetate should be  
217 different from the nominal composition of the mixture. Given that it is amorphous regions that  
218 influence the glass transition of the blend, this may be an additional explanation to the difference  
219 with theoretical Tg values predicted by Fox equation.

220 The effect of plasticizers on the degree of crystallinity of cellulose acetate is briefly discussed in this  
221 section. Fig. 6 and 7 show X-ray diffraction profiles at small and wide angles of samples prepared via  
222 solvent casting method and give additional information on plasticizing effects.

223 The presence of periodic structures generates scattering peaks; abscissa of these peaks correspond  
224 with the average inter-domain distance also called *d*-spacing.

225 It can be described by:

$$d = 2\pi/q^* \quad (2)$$

226 where  $q^*$  is the  $q$  value corresponding to the maximum intensity in  $\text{\AA}^{-1}$  and  $d$  is the  $d$ -spacing value in  
227  $\text{\AA}$ .

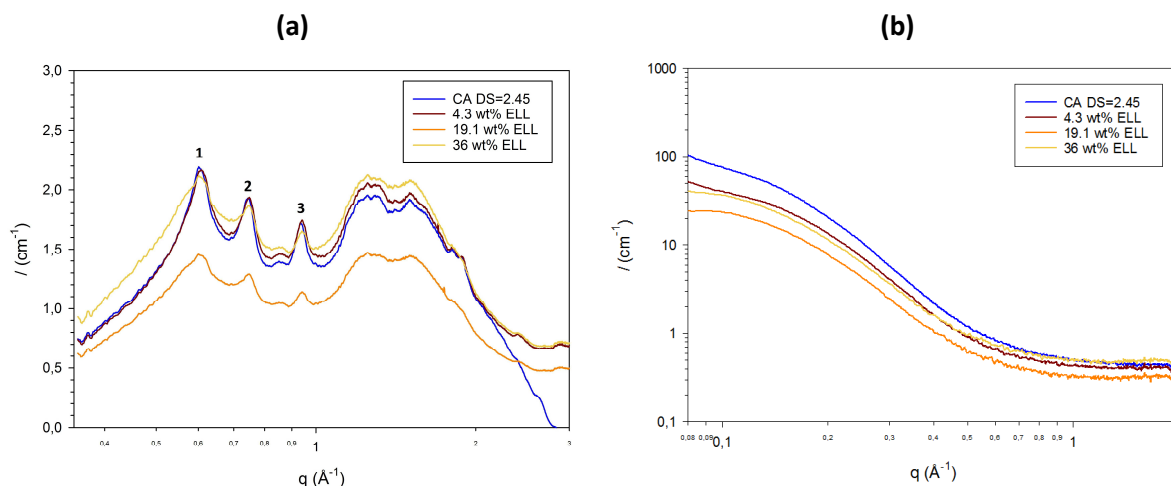


Figure 6: (a) WAXS and (b) SAXS profiles, CA/ELL blends

228  
 229 Fig. 6 corresponds to SAXS and WAXS profiles for CA / ELL blends. For these systems, in WAXS  
 230 profiles, we can clearly see that crystallinity is preserved with the addition of ELL. The three  
 231 characteristic crystalline peaks of unplasticized cellulose acetate can be identified. We can observe  
 232 them at d-spacings of  $d_1=10.5$ ,  $d_2=8.4$  and  $d_3=6.8$  Å and their values are in agreement with literature  
 233 values (Fawcett et al., 2013; Yu BAO, 2015). Nonetheless, the intensity of the peaks decreases with  
 234 the increasing ELL content. SAXS curves also present the same profile, undoubtedly inherited from  
 235 the presence of the crystallites.

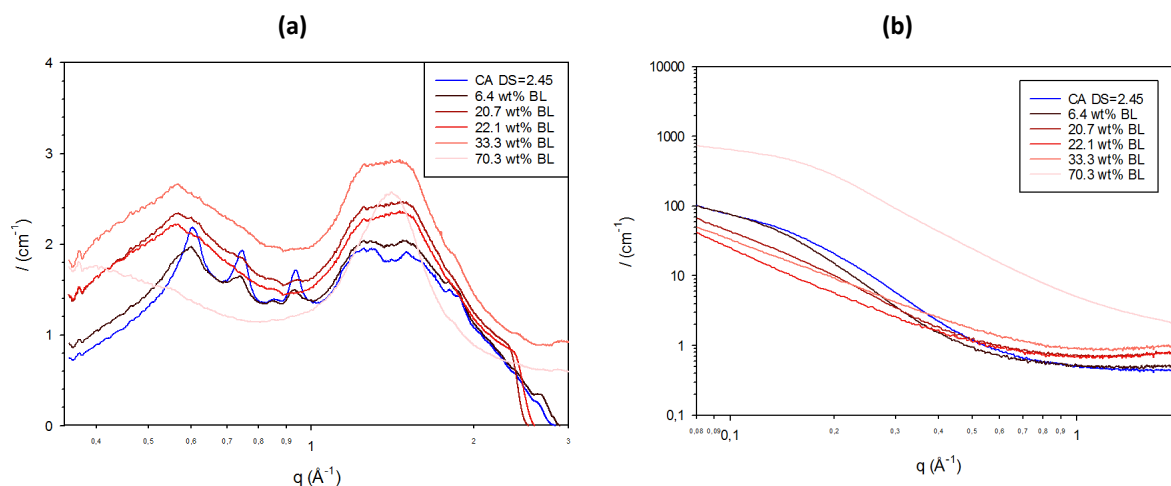


Figure 7 : (a) WAXS and (b) SAXS profiles, CA/BL blends

236  
 237 WAXS profiles of CA / BL systems (Fig. 7a) show an assignment of crystallinity according to the  
 238 composition of the blend. At BL contents larger than 20 wt%, the crystallinity is no longer visible. The  
 239 SAXS analysis (Fig. 7b) permits to highlight the evolution of the diffusion with blend composition. In

240 other words, the plasticizer has affected the structure. As seen previously, beyond 20 wt% of BL, the  
241 crystallinity was no longer observed. It may be hypothesized that the response of the amorphous  
242 phase is examined. Beyond 33 wt% the slope is affected. This suggests a more open molecular  
243 organization due to the presence of plasticizer. At 70 wt% of BL, a change appears in the profile. The  
244 hypothesis can be made that after a relatively high BL content, it acts as a solvent for the CA. The  
245 structure seems diluted.

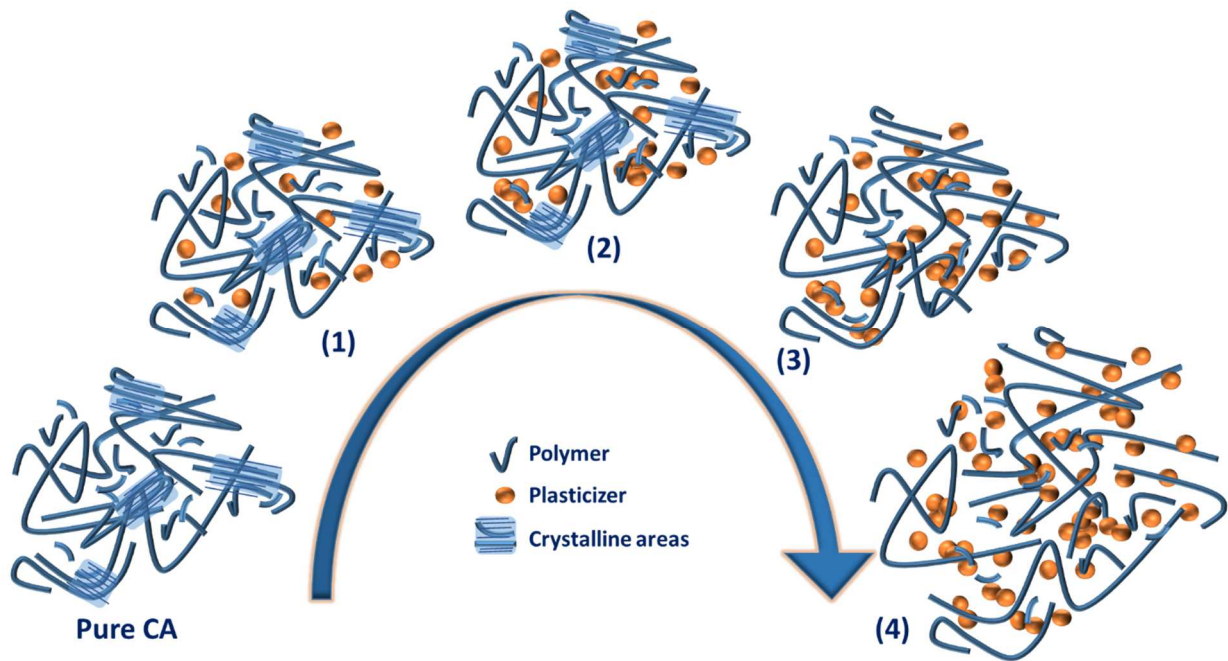
246 It appears that ELL is a less active solvent than BL. We suggest that this phenomenon should be  
247 attributed to the lack of compatibility between ELL / CA, hence the ELL being rejected by the  
248 crystalline phase in the amorphous phase. Therefore the crystalline phase is not affected.

249

### 250 3.4 Blends behaviour and miscibility

251 Five different regions have been suggested during the cellulose acetate plasticization process with  
252 the increasing content of plasticizers as shown in a schematic drawing (Fig. 8). Pure CA was described  
253 as a polymer formed of short and long chains with a low degree of crystallinity (Bao et al., 2015). At  
254 low plasticizer content (region n°1), lactate molecules are mixed homogeneously with CA. The  
255 polymer amorphous phase is plasticized by the plasticizer. It leads to a decrease in Tg and glassy  
256 plateau modulus of the blend with the increasing plasticizer content. Then when the plasticizer  
257 content increases (region n°2), a portion of the plasticizer regroups to create a plasticizer-rich phase  
258 containing short CA chains (Spurlin, Martin, & Tennent, 1946) . At these compositions, blends are not  
259 totally miscible. There is a plateau for the main transition of the CA-rich phase and for the glassy  
260 zone modulus. This assumes that in this phase, the plasticizer rate does not increase or only  
261 marginally.

262



263

264 *Figure 8: Schematic representation of the behaviour of cellulose acetate with the increasing plasticizer content.*

265

266 With a higher plasticizer content, a modulus drop was observed and X-ray diffraction analyses have  
 267 shown a disappearance of crystallinity and more spacing between CA chains, which indicates that the  
 268 molecular mobility of the CA-rich phase is affected by the plasticizer (region n°3). In a mixture with  
 269 even more plasticizer (region n°4), the behaviour of the blend is totally different. Short and long CA  
 270 chains have been dissolved by plasticizer. The structure of the mixture is significantly more open, the  
 271 plasticizer governs the molecular mobility. A possible interpretation for this behaviour is that the  
 272 plasticizer-rich phase, which is scattered in the CA-rich phase, has developed enough to break  
 273 intermolecular H-bonding. These hydrogen bonds may be at the origin of a closer molecular  
 274 organization. A high threshold of plasticizer could eliminate them.

275

## 276 4. Conclusions

277 The dynamical properties of plasticized cellulose acetate have been examined by dynamical  
 278 mechanical analysis, structural properties and crystallinity were investigated by X-ray diffraction for a  
 279 more detailed description of blends. For octanoic acid, a decrease of the glass transition temperature  
 280 followed by an unmixing of the system, as a function of plasticizer content, was observed. Although it  
 281 is not a good plasticizer at high content, at low concentration 10 wt% allowed a drop in Tg of  
 282 approximately 150 °C. Through the correlation between DMA and WAXS/SAXS results, the

283 plasticizing effect of lactates on cellulose acetate were studied in detail. We interpreted data and  
284 with the help of the literature, it allowed us to highlight mechanisms regarding miscibility and phase  
285 separation in the strongly H-bonded of cellulose acetate blends with the increasing plasticizer  
286 content. With low lactates in blends, only one relaxation transition was detected by DMA, it was  
287 identified as  $\alpha$  relaxation. A decrease of this glass relaxation, as a function of plasticizer content was  
288 observed, CA/lactates blends are miscible. From 15 wt% of lactates above the miscibility limit, two  
289 relaxations were detected, introducing the concept of CA-rich phase and plasticizer-rich phase. With  
290 an increasing amount of lactates, CA/lactates blends became amorphous. The plasticizer affect the  
291 structure that it cannot affected previously, between 20 and 40 wt% of lactates, a glassy modulus  
292 drop of approximately 1500 MPa was observed. Systems with high lactate content were strongly  
293 affected by the plasticizer-rich phase, CA-rich phase and plasticizer-rich phase transitions are closer  
294 indicating the disappearance of intermolecular interactions. These three green solvents are good  
295 candidates for making plasticized cellulose acetate by extrusion because they provide a decrease in  
296 T<sub>g</sub>, crystallinity and glassy modulus. Nevertheless octanoic acid need to be used under 30 wt%. The  
297 description of these systems need further examination for understanding the chemical mechanisms  
298 regarding miscibility and phase separation.

299

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