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# 1 Viscoelastic behaviour of cellulose acetate/triacetin blends by rheology in the 2 melt state

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14 Declarations of interest : none.

15

## 16 Abstract

17

18 The viscoelastic behaviour of cellulose acetate **with a degree of substitution (DS) of 2,45** plasticized  
19 by triacetin was studied at short times by dynamic oscillatory measurements. Two distinct regimes  
20 and unexpected scaling behaviour according to plasticizer content were highlighted. The dynamics of  
21 chains and their structural organization are not modified up to 35wt% of triacetin. The rheological  
22 behaviour is led by a constant correlation length corresponding to the distance between strong  
23 intermolecular interactions subsisting in the melt state at high temperature even in the presence of  
24 plasticizer. This particular structure involves the apparition of strain hardening effects during uniaxial  
25 extensional flow tests and an important elasticity corresponding to the apparition of a Weissenberg  
26 effect at really low shear rates during shear sweeps. Intramolecular hydrogen bonds are responsible  
27 of the high rigidity of cellulose acetate chains. Plasticized cellulose acetate in the melt state belongs  
28 to the class of associating polymers and its rheological behaviour is mainly led by stickers.

29

30 **Keywords :** *Cellulose acetate, plasticizer, rheology, viscoelasticity, dynamics of chains, intermolecular interactions*

31

## 32 1. Introduction

33

34 Among cellulose derivatives, cellulose acetate (CA) is the most widely produced ester for  
35 thermoplastic applications (Balsler et al., 2004; Ganster & Fink, 2013). In this case, hydroxyl groups of  
36 anhydroglucopyranose (AGU) units that compose cellulose are replaced by acetyl groups during an  
37 acetylation process. Cellulose acetate properties depend on the degree of substitution (DS)

38 corresponding to the average number of hydroxyl groups replaced in an AGU unit. The melt  
39 processing of CA is possible only for a degree of substitution close to 2,5 (Kamide & Saito, 1985).  
40 Even in this cases, the temperature window for processing is narrow because the glass transition  
41 temperature ( $T_g$ ) is close to the decomposition temperature (Mohanty, Wibowo, Misra, & Drzal,  
42 2003; Quintana, Persenaire, Bonnaud, & Dubois, 2012). In order to facilitate the transformation in  
43 the melt state, external plasticization with low molecular weight plasticizers is a common solution (B.  
44 Wang et al., 2016; Zepnik, Kabasci, Kopitzky, Radusch, & Wodke, 2013).

45 The use of eco-friendly plasticizer as triacetin (TA) rather than widely used phthalate plasticizers is  
46 necessary for the development of cellulose acetate based materials (Wypych, 2017). The usual  
47 plasticizer content mixed with cellulose acetate is generally between 15 and 35wt% in the different  
48 applications to optimize both process and final mechanical properties (Balsler et al., 2004; Ganster &  
49 Fink, 2013). However, miscibility for the CA/TA mixture is not achieved over the whole range of  
50 composition. Some previous study (C. Bao, 2015) have shown by means of modulated DSC (MDSC),  
51 dynamic mechanical analysis in temperature (DMTA) and neutron scattering at small angles (SANS)  
52 that in the case of triacetin, phase separation occurs for 20 wt% TA introduced in bulk cellulose  
53 acetate (25 wt% for DEP). Then, two phases are observed, one considered as rich in CA and a second  
54 one, rich in plasticizer. Phase separation and partial miscibility results in a double  $T_g$  behavior for TA  
55 content above 20 wt%. For CA-rich phase the decrement of  $T_g$  is clearly significant (up to  $-200\text{ }^\circ\text{C}$ ).  
56 For TA-rich phase,  $T_g$  is weakly dependent on the composition and close to that of the plasticizer.

57 Cellulose acetate chains have an important rigidity and are considered as semiflexible or even  
58 inflexible because of residual intramolecular hydrogen bonds within a chain despite the esterification  
59 reaction (Hsieh & Kadla, 2012; Kawanishi, Tsunashima, Okada, & Horii, 1998; B. Wang et al., 2016). Its  
60 persistence length is maximum for DS close to 2,5 and constituted of 19 AGU units which correspond  
61 to 10 nm (Kamide, 2005a). Moreover, in the solid state, the distance between two neighboring  
62 chains is estimated around 1 nm because of residual intermolecular hydrogen bonds formed by free  
63 hydroxyl groups along chains (C. Bao, 2015). The existence of interactions between OH side groups of  
64 different chains is highlighted by several studies (Kamide, 2005b; Puleo, Paul, & Kelley, 1989).

65 The rheological behaviour of cellulose acetate in solution has been widely studied for different  
66 solvents (Ferrarezi, Rodrigues, Felisberti, & Gonçalves, 2013; Kawanishi, Tsunashima, & Horii, 2000;  
67 C. S. Wang & Fried, 1992). However, to the best of our knowledge, there are surprisingly very few  
68 studies that analyzed the viscoelastic behaviour of plasticized cellulose in the melt state and  
69 therefore for cellulose acetate / triacetin blends. The viscoelastic properties of cellulose acetate of  
70 DS 2,5 plasticized by 15wt% of triacetin or triethyl citrate (TEC) were studied by Small Amplitude  
71 Oscillatory Shear (SAOS). Similar curves were obtained for both plasticizer and shown typical shear  
72 thinning behaviour. According to the authors, "*externally plasticized cellulose acetate shows a  
73 rheological behaviour typical for conventional thermoplastics*" (Erdmann, Kabasci, Kurek, & Zepnik,  
74 2014). Additional study investigated rheological behaviour at large deformations and high shear rates  
75 (Zepnik et al., 2013). The shear viscosity of cellulose acetate / TEC systems as a function of shear rate  
76 was studied at  $220\text{ }^\circ\text{C}$  for plasticizer contents of 15, 20 and 25wt%. The authors reported that it is  
77 possible to produce a master curve thanks to a concentration-dependent shift factor. Under uniaxial  
78 extensional flow, a strain hardening effect was highlighted for the three TEC contents for low strain.  
79 In their case, an increasing amount of plasticizer shifts the maximum of the strain hardening to  
80 higher extension rates. Then, there is an elongational thinning region which is independent from TEC  
81 concentration. However, the authors did not underline the particularity of the strain hardening effect  
82 that occurred whatever the TEC content was.

83 According to the few results available in the literature, the presence of intermolecular and  
 84 intramolecular interactions between cellulose acetate chains is highlighted in solution but was not  
 85 reported at high temperature in the melt state. The aim of this paper is to study the effect of the  
 86 plasticizer content on the viscoelastic behaviour and the structural organization of cellulose  
 87 acetate/triacetin blends in the melt state. To do that, viscoelasticity of plasticized cellulose acetate  
 88 was characterized both in linear and nonlinear domains to determine whether or not interactions still  
 89 remain in the melt state despite the presence of plasticizer. Moreover, because there is no study  
 90 reporting this in the literature, the effects on the chains dynamics and flow behaviour of cellulose  
 91 acetate for different triacetin contents has been investigated over the complete phase diagram.

92

## 93 2. Experimental section

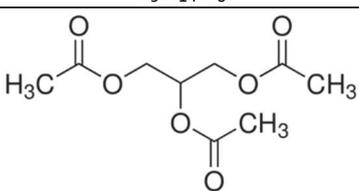
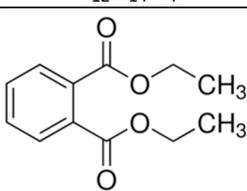
94

### 95 2.1 Materials

96

97 Cellulose acetate (powder, Mw = 93 000 g/mol and polydispersity index of 2,2) with a degree of  
 98 substitution of 2,45 was supplied by Acetow GmbH (Freiburg, Germany). Triacetin (TA) (purity  $\geq$   
 99 99,5%) was produced by Lanxess (Köln, Germany). Diethyl phthalate (DEP) whose grade is Provichem  
 100 1622 (purity  $\geq$  99,5%) was purchased from Proviron (Oostende, Belgium) and used as a reference  
 101 (Table 1). Samples with plasticizer content from 0 to 100wt% were prepared to study the complete  
 102 phase diagram.

103

Properties	Triacetin (TA)	Diethylphthalate (DEP)
CAS number	102-76-1	84-66-2
Chemical formula	C <sub>9</sub> H <sub>14</sub> O <sub>6</sub>	C <sub>12</sub> H <sub>14</sub> O <sub>4</sub>
Chemical structure		
Molar mass (g/mol)	218	222
T <sub>boiling</sub> (°C)	260	298
Density (at 25°C)	1,16	1,12
T <sub>g</sub> (°C)	-70	-88

104

Table 1 : Properties of plasticizers

105

106 The plasticizer contents were controlled and validated by <sup>1</sup>H NMR spectroscopy measurements. The  
 107 analysis solvent was acetone-d<sub>6</sub> (purity  $\geq$  99%) and pyrrole (purity  $\geq$  99%) was used as a reference to  
 108 quantify the plasticizer content by weight thanks to a comparative method. They were both supplied  
 109 by Acros Organics (Geel, Belgium). Measurements were carried out with a Bruker AVANCE III 400MHz  
 110 spectrometer.

111

## 112 2.2 Sample preparation

113

114 Cellulose acetate powder was dried at 70°C for at least 24h before processing. Two complementary  
115 methods were used to manufacture films of plasticized cellulose acetate. Melt processing was used  
116 for samples up to 35wt% of plasticizer while solvent casting method has been chosen above this  
117 content to overcome extrusion limitations. Films thickness was set between 0,5mm and 1mm to  
118 optimize samples for rheological measurements. The effect of processing method has been  
119 investigated for samples with 10, 20 and 35wt%.

120

### 121 2.2.1 Melt processing

122

123 A co-rotating twin screw extruder Leistritz ZSE 18 MAXX was used to incorporate plasticizer for melt  
124 processing up to 35wt%. The screw diameter (D) was 18mm and the screw length was 44 D. A flat die  
125 was used to produce films. The injection of the liquid plasticizer was first done with a peristaltic  
126 pump and cellulose acetate powder was added thanks to a lateral hopper. The screw speed and the  
127 temperature were adapted according to the plasticizer content from 150 rpm and 220°C at 10wt% of  
128 plasticizer to 200 rpm and 175°C at 35wt% of plasticizer.

129

### 130 2.2.2 Solvent casting method

131

132 Regarding the casting method, cellulose acetate and plasticizer were dissolved in acetone at a  
133 concentration of 10wt%. Acetone is an efficient and common solvent for cellulose acetate with DS of  
134 2,45 and presents the advantage to be volatile for the solvent casting method. The solutions were  
135 mixed for 24h at room temperature thanks to a magnetic stirring bar. After this step, the solutions  
136 were poured in a PTFE mold closed with a glass upper part drilled on the top in order to control the  
137 slow evaporation of acetone. This device was optimized by former works (C. Y. Bao, Long, &  
138 Vergelati, 2015). The evaporation time depends on the plasticizer content.

139

## 140 2.3 Characterization methods

141

### 142 2.3.1 Shear rheology tests

143

144 The linear viscoelastic properties were measured with a TA Instruments ARES or ARES G2 rheometer  
145 equipped with stainless-steel parallel plates of diameter 8 or 25 mm according to the material  
146 compliance (8 mm diameter for measurements from 0 to 35wt% of plasticizer, 25mm diameter for  
147 measurement from 50 to 90wt% of plasticizer). Small amplitude oscillation shear (SAOS) experiments  
148 were performed from 100 to 0,1 rad/s at fixed strain amplitude well within the linear regime, at  
149 different temperatures according to the plasticizer content (Table 2). Master-curves were built from  
150 several frequency sweeps and using the time-temperature superposition (TTS).

151 For samples with plasticizers contents between 10 and 35wt%, a gas convection oven has been used  
152 to reach the experimental temperature range (from 120 to 220°C). To prevent the loss of plasticizer

153 from the sample by evaporation, the samples were protected by a bell cover that ensure saturation  
154 of the environment with plasticizer vapour (Wee & Mackley, 1998). Regarding samples containing  
155 higher plasticizer contents, the experimental temperature range (from -10 to 100°C) allows the use  
156 of a Peltier system (APS) without bell cover considering the natural limitation of drying effects for  
157 such system.

158 Shear sweeps test were also performed for samples containing up to 35wt% of triacetin. Grooved  
159 parallel plates have been used in order to limit slippage (grooved cone-plate was not available).  
160 Then, it is worth to note that, as no Rabinowitsch corrections (Rabinowitsch, 1929) have been  
161 applied to the results, the following results are only qualitative and will be discussed for comparison  
162 purpose only.

163

### 164 2.3.2 Uniaxial extensional tests

165

166 For samples containing up to 35wt% of plasticizer, the transient uniaxial extensional viscosity was  
167 measured with a Sentmanat Extension Rheometer (SER) extensional rheology system mounted on an  
168 Anton Paar MCR 301 rheometer. The measurements were performed at 180°C for different  
169 extensional-strain rate ( $\dot{\epsilon}$ ) from 0,03 s<sup>-1</sup> to 1 s<sup>-1</sup>. Before each test starting, samples were previously  
170 conditioned several minutes at the measurement temperature in order to homogenize its  
171 temperature.

172

### 173 2.3.3 Measurement of the glass transition temperature

174

175 According to the triacetin content, two complementary methods have been used to determine the  
176 glass transition temperature (T<sub>g</sub>).

177 Glass transitions of the samples with plasticizer content up to 35wt% were determined by differential  
178 scanning calorimetry (TA Instruments Q10). Around 5 to 10 mg of plasticized cellulose acetate was  
179 analyzed. In accordance with previous studies, heating rate of 10°C/min was applied from -80 to  
180 160°C (Kamide & Saito, 1985; McBrierty, Keely, Coyle, Xu, & Vij, 1996; Sousa et al., 2010). Glass  
181 transition temperatures were determined from the second heat so as to suppress the influence of  
182 thermal history. An average was done with at least 3 measurements.

183 For better accuracy, dynamic mechanical thermal analysis was preferred for plasticizer amount  
184 above 35wt%. The glass transition temperatures were determined with a TA Instruments ARES  
185 rheometer equipped with a nitrogen tank by applying temperature sweeps at cooling rate of 4°C/min  
186 and at a frequency of 1 rad/s within the linear domain. An average was done with at least 5  
187 measurements. The results were analyzed and used in the light of a former study that determined  
188 the glass transition temperature of phases with high content of plasticizer by modulated differential  
189 scanning calorimetry (MDSC) (C. Bao, 2015).

190

## 191 3. Results and discussion

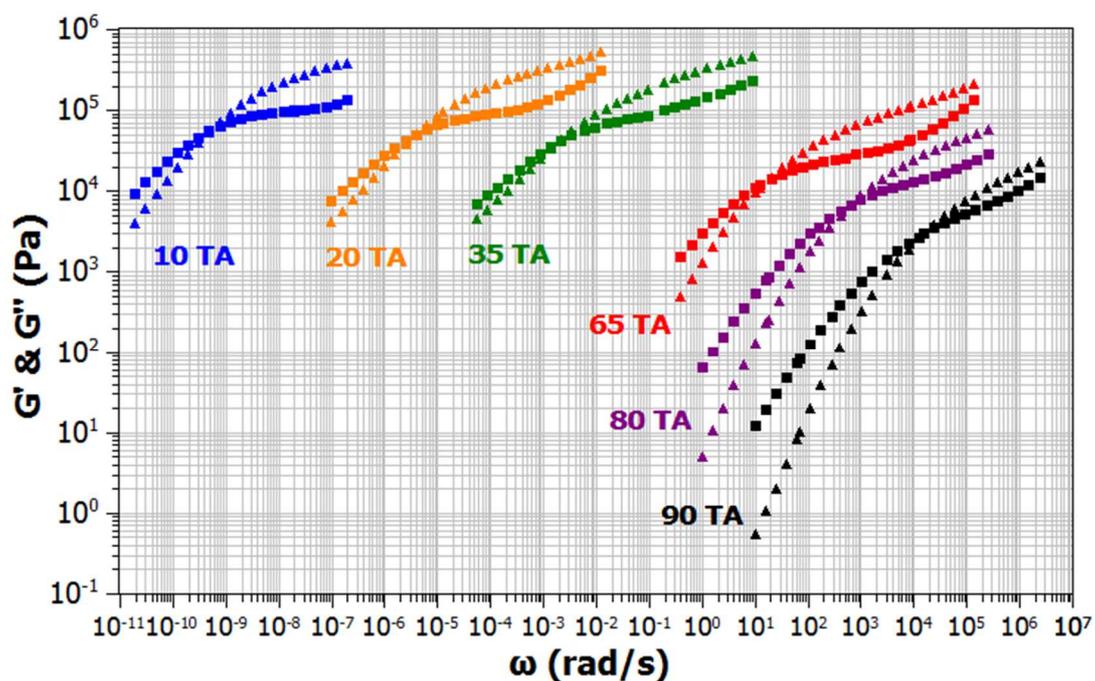
192

193 3.1 Evolution of rheological parameters according to triacetin content

194

195 The viscoelastic behaviour of cellulose acetate plasticized by triacetin was studied at short times by  
 196 dynamic oscillatory measurements. Master curves were obtained for samples containing between 10  
 197 and 90wt% of plasticizer (Figure 1). A reference temperature of 100°C was chosen to compare the  
 198 different samples. One can notice that the rubber plateau is not clearly defined suggesting a certain  
 199 polydispersity and strong coupling from the glass transition zone to the terminal zone. Whatever the  
 200 triacetin content is, the shape of complex relaxation modulus seems quite classical. Then, in the  
 201 following, main viscoelastic parameters have been inferred from the master curves and have been  
 202 analyzed in more detail as a function of the polymer content for figure 2 and figure 3 to analyse the  
 203 scaling behaviour.

204



205

206 Figure 1 : Comparison of master curves at 100°C as a function of triacetin content with  $G'$  ( $\blacktriangle$ ) and  $G''$   
 207 ( $\blacksquare$ ).

208

209 3.1.1 Rubber plateau modulus

210

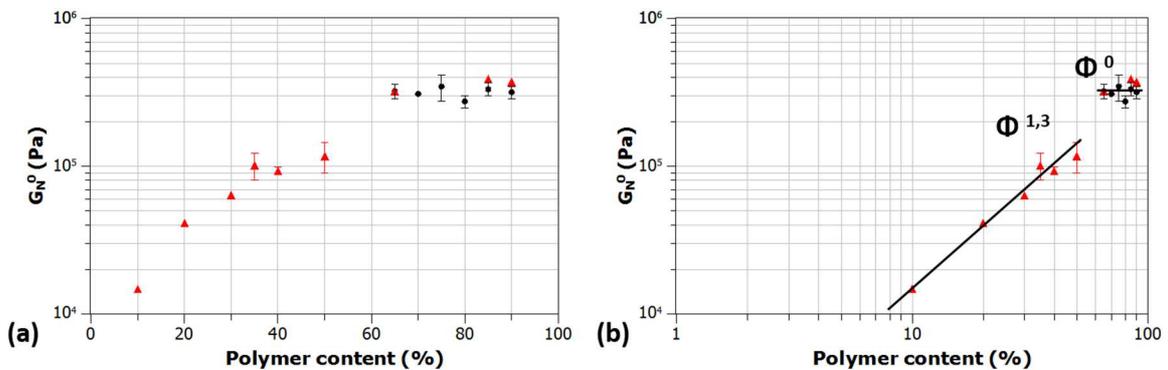
211 The rubber plateau modulus  $G_N^0$  is determined at the minimum of the damping factor  $\tan \delta$  (Liu, He,  
 212 Ruymbeke, Keunings, & Bailly, 2006).

213 
$$G_{N_{exp}}^0 = G'(\omega)_{\tan \delta \min} \quad (1)$$

214 Two different regimes are visible according to the triacetin content (Figure 2-a). First, up to 35wt%,  
 215 the plasticizer has no significant effect on the rubber plateau modulus. Then, above 50wt% of  
 216 triacetin,  $G_N^0$  decreases in a more classical way but its value remains high even at 90wt% of triacetin  
 217 where the dilute (unentangled) regime is not reached yet. Strong interactions still exist between the  
 218 chains that contribute to elasticity. This fact is in agreement with some results found in the literature

219 concerning cellulose acetate in solution. It is worth to note that these behaviours are not related to  
 220 the manufacturing processes (Figure 2). For low triacetin content up to 35%, the fact that the rubber  
 221 plateau modulus remains unaffected is unexpected if the cellulose acetate chains are considered as  
 222 classical linear entangled chains. This atypical result suggests that correlation lengths in tube  
 223 conformation are governed by strong **but labile** interactions that still exist even at high temperatures  
 224 and that remain unaffected up to 35wt% of triacetin. These interactions called stickers in this paper  
 225 **are characterized by a finite lifetime enabling connection and reconnection leading to transient**  
 226 **network formation (Brassinne, Cadix, Wilson, & Ruymbeke, 2017). For this system, stickers** may be  
 227 related to strong hydrogen bonds present even in the melt state and despite the addition of  
 228 plasticizer. According to the literature hydrogen bonds may subsist at high temperature. Indeed, in  
 229 the case of **hydroxyl**-functionalized polypropylene, 50% of the hydrogen bonds initially presents were  
 230 kept between chains at 250°C (Gupta et al., 2016). Moreover, for triacetin content above 35% (Figure  
 231 2-b), the plateau modulus follows scaling behaviour in  $\Phi^{1,3}$  whereas  $\Phi^{2 \text{ to } 2,2}$  is expected in the case  
 232 of linear entangled chains in the melt state.

233



234

235 *Figure 2 : Evolution of  $G_N^0$  as a function of polymer content, lin-log plot (a) and log-log plot (b) using*  
 236 *melt processing (●) and solvent casting (▲). Two regimes are visible, both with unexpected scaling*  
 237 *behaviours whatever the processing method.*

238

239 The same conclusions can be obtained from the evolution of the mass between entanglements ( $Me$ )  
 240 inferred from the experimental value of the rubber plateau modulus  $G_N^0(\Phi)$ .

$$241 \quad Me(\Phi) = \frac{\rho(\Phi) \times R \times T}{G_N^0(\Phi)} \quad (2)$$

242  $\rho(\Phi)$  is the density according to the polymer content and calculated by a linear law of mixture.  
 243 Because of the weak variation of the density when plasticizer is added, the polymer volume fraction  
 244 ( $\Phi$ ) and mass fraction ( $W$ ) are assumed to be similar.  $R$  is the ideal gas constant, and  $T$  is the  
 245 temperature in K.

246 The mass between entanglements is rather stable or slightly decreasing up to 35wt% of triacetin.  
 247 Above this value, this correlation length increases with a scaling exponent of -0,4 which is clearly  
 248 different from -1 to -1,2 expected for linear entangled chains. Because of the presence of strong  
 249 interactions between neighboring cellulose acetate chains, this correlation length rather corresponds  
 250 to a mass between stickers ( $M_s$ ) than a mass between entanglements. However, above a critical  
 251 triacetin content, it seems that the plasticizer is physically able to suppress some interaction but the  
 252 chains dynamics still not controlled by entanglements.

253

### 254 3.1.2 Relaxation times

255

256 The relaxation time ( $\lambda_n$ ) retained to compare the different samples is related to the low frequency  
257 crossover point of  $G'$  and  $G''$  that corresponds to shortest relaxation times in the terminal relaxation  
258 spectrum:

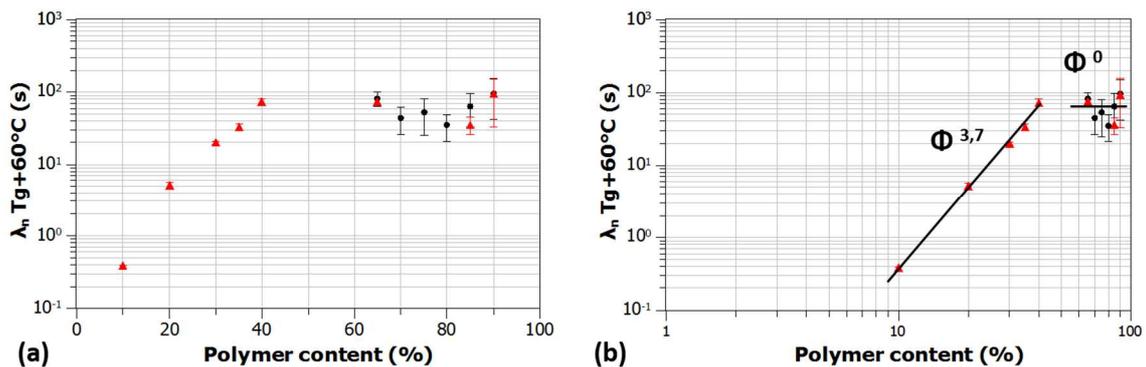
$$259 \lambda_n = \frac{\eta_0}{G_N^0} \quad (3)$$

260 where  $\eta_0$  is the newtonian viscosity.

261 To analyze the global dynamics of the plasticized cellulose acetate chains, it is necessary to overcome  
262 the strong effect of the plasticizer on the dynamics at the monomer scale. Thus, in order to compare  
263 all the samples at the same free volume (or at the same local dynamics), the relaxation times  
264 associated are analyzed at the same distance to the  $T_g$  ( $T_g+60^\circ\text{C}$ ) (Figure 3-a).

265 As for  $G_N^0$ , two distinct regimes are visible. Up to 35wt% of triacetin, the relaxation times remains  
266 constant whatever the triacetin content is. Despite the efforts made to have a fine repeatability for  
267 the acquisition of the data, there is still some noise mainly due to the accuracy on glass transition  
268 measurement. However, there is a noteworthy difference of behaviour compared to the samples  
269 with plasticizer contents above 60wt%. For contents lower than 35wt%, there is no effect of the  
270 triacetin on the relaxation times and on the global dynamics of the chains. The mechanisms are  
271 similar whatever the triacetin content is at the scale of the whole chains at short times. When the  
272 triacetin content exceeds a critical content, the relaxation times determined at iso-friction conditions  
273 evolve as  $\Phi^{3.7}$  (Figure 3-b) which is straight different from the scaling law  $\Phi^1$  observed for linear  
274 entangled chain (Watanabe, 1999). **Thus, for plasticizer contents above 60wt%, an important change**  
275 **of the structural organization of cellulose acetate chains appears because of the excess of plasticizer**  
276 **which leads to the physical disruption of stickers.**

277



278

279 *Figure 3 : Evolution of  $\lambda_n$  at the same distance to  $T_g$  (iso-friction conditions) as a function of polymer*  
280 *content lin-log plot (a) and log-log plot (b) for melt processing (●) and solvent casting (▲).*

281

282 As for the rubber plateau modulus, the correlation length that controls the relaxation mechanisms is  
283 linked to the stickers. These interactions are not affected by triacetin up to 35wt% and the global  
284 chain structure is not modified. In this range of triacetin content, plasticizer seems to fill the free

285 volume defined between two consecutive stickers but the resulting osmotic pressure is not sufficient  
286 to unstick the chain associations. Then, the plasticizer only modifies the local environment of the  
287 chains at the monomer scale but no change in the structure and in the global dynamics at the scale  
288 of the bulk is observed. Rheological parameters depending on the whole chain dynamics remain  
289 unaffected up to the critical content of 35wt%. Above this value, the constant correlation length  
290 cannot be held.

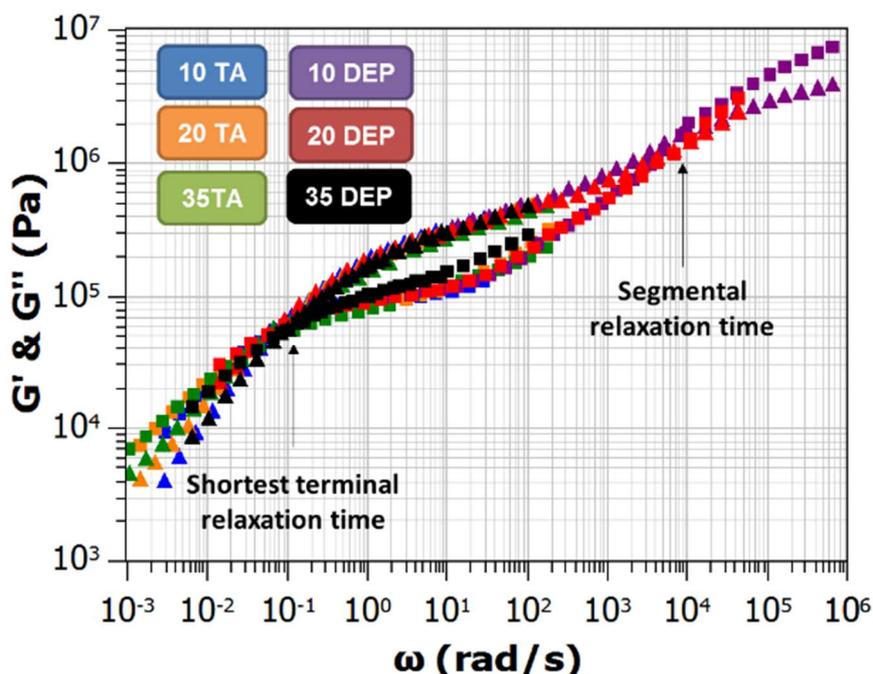
291

### 292 3.2 Independence of the relaxation mechanisms at short times according to the 293 nature of the plasticizer

294

295 The viscoelastic behaviour of extruded samples containing between 10 and 35wt% of diethyl  
296 phthalate (DEP) was studied by SAOS. The resulting master curves are then compared at the same  
297 distance to  $T_g$  with those obtained using triacetin as plasticizer. Interestingly, **even if the**  
298 **measurements were not realized within the same temperature range,** it seems that a unique master  
299 curve can be obtained for all the samples indifferently plasticized by triacetin or DEP (Figure 4). A  
300 similar rubber plateau is obtained no matter is the plasticizer and its concentration. None of the  
301 plasticizer has an effect on the rubber plateau modulus or its frequency span up to 35wt% of  
302 plasticizer. The nature of the plasticizer has no effect on the relaxation times at  $T_g+60^\circ\text{C}$ . In this  
303 frequency range, global chain dynamics are mainly controlled by stickers concentration and lifetime.

304



305

306 Figure 4 : Comparison of master curves at the same distance to  $T_g$  for plasticized cellulose acetate  
307 chains with triacetin or DEP contents between 10 and 35wt%.

308

### 309 3.3 Non-linear viscoelasticity of plasticized cellulose acetate

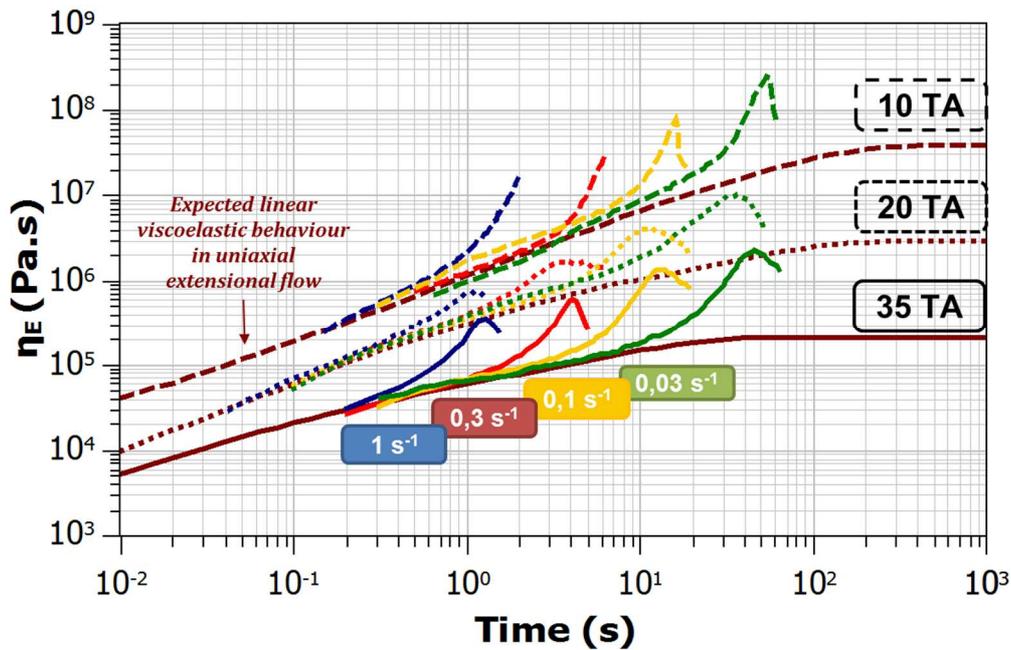
310

311 3.3.1 Uniaxial extensional flow at low plasticizer contents

312

313 Uniaxial extensional flow has been applied to cellulose acetate sample plasticized with triacetin  
 314 contents from 10 to 35wt% (Figure 5). All the results have been compared to the Troutonian  
 315 behavior (Trouton, 1906) in order to highlight the non-linearity of the transient viscoelastic response.

316



317

318 *Figure 5 : Evolution of the elongational viscosity at 180°C for different  $\dot{\epsilon}$  for 10 (---), 20 (...) and 35wt%*  
 319 *(—) of triacetin.*

320

321 Whatever the triacetin content is, a clear positive deviation (namely strain hardening) from the  
 322 Troutonian behaviour determined from SAOS measurements is noticed for the different extensional-  
 323 strain rates. The more  $\dot{\epsilon}$  increases, the shorter is the apparition time of this strain hardening. The  
 324 Troutonian viscosity decreases as a function of the triacetin content but the strain hardening effect  
 325 remains noteworthy. Again, this behaviour is not consistent with simple linear entangled systems and  
 326 it is possible to link it to the presence of strong interactions between cellulose acetate chains in the  
 327 melt state that remains active at the time scale of the extensional test. These interactions still exist at  
 328 high temperature and even for low extensional-strain rates. The presence of stickers may thus  
 329 explain the apparition of the strain hardening effect in uniaxial extensional flow. During stickers  
 330 “close state” lifetime, active elastic segments of average mass  $M_s$  are extended in the flow direction  
 331 until their maximum elasticity is reached leading to the rising of transient extensional viscosity.

332 This rubber like behaviour was thus compared with a Lodge model commonly used to quantify  
 333 rubber elasticity in the transient regime in the melt state (Barnes, Hutton, & Walters, 1989; Beraux,  
 334 2004; Carrot & Guillet, 2000) (Figure 6). The theoretical viscosity ( $\eta_{Lodge}$ ) associated to the model is  
 335 obtained from :

336 
$$\eta_{Lodge}(t) = \frac{\sigma_{Lodge}(t)}{\dot{\epsilon}(t)} \quad (4)$$

337 The Lodge stress model ( $\sigma_{Lodge}(t)$ ) is calculated from:

$$338 \quad \sigma_{Lodge}(t) = \int_{-\infty}^t m(t-t') \times \underline{\underline{C}}_t^{-1}(t') \times dt' \quad (5)$$

339 where  $m(t-t')$  stands for the memory function determined from the relaxation time spectrum ( $G_i, \lambda_i$ ):

$$340 \quad m(t-t') = \sum_i \frac{G_i}{\lambda_i} \times e^{-\frac{(t-t')}{\lambda_i}} \quad (6)$$

341 And the Finger's tensor defined as :

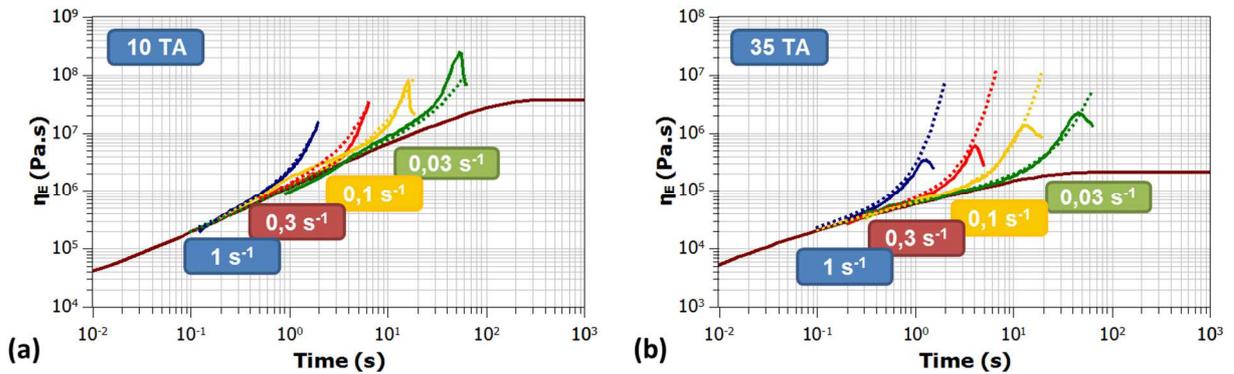
$$342 \quad \underline{\underline{C}}_t^{-1}(t') = \begin{bmatrix} e^{-2(\varepsilon(t')-\varepsilon(t))} & 0 & 0 \\ 0 & e^{\varepsilon(t')-\varepsilon(t)} & 0 \\ 0 & 0 & e^{\varepsilon(t')-\varepsilon(t)} \end{bmatrix} \quad (7)$$

343

344 The experimental transient extensional viscosities follow pretty well the theoretical values obtained  
 345 with the Lodge model up to 35wt% of triacetin whatever  $\dot{\varepsilon}$  is. The strain hardening amplitude is well  
 346 predicted by Lodge model. The samples containing 35wt% of triacetin had a better reproducibility.  
 347 According to this result, there are certainly long-life interactions at the timescale of the test which  
 348 prevent chain slippage even for the lowest  $\dot{\varepsilon}$  and therefore the longest experimental time.

349 Because of strong intermolecular interactions between stretched cellulose acetate chains, there is no  
 350 stretch relaxation of the species that should contribute to the lowering of the strain hardening as for  
 351 branched entangled polymers. For samples containing 70wt% of triacetin, a weaker and unclear  
 352 strain hardening is also visible (Report to supporting information).

353



354

355 *Figure 6 : Comparison of experimental elongational viscosities (—) and Lodge model (---) for 10 (a)*  
 356 *and 35wt% of triacetin (b) at 180°C.*

357

358 For better quantitative analysis, results are normalized by the Troutonian behaviour. The normalized  
 359 viscosity ( $\eta_{normalized}$ ) is :

$$360 \quad \eta_{normalized} = \frac{\eta_E}{3\eta(t)} \quad (8)$$

361 To suppress the effect of the elongation speed, this normalized viscosity is plotted as a function of  
 362 the Hencky strain ( $\varepsilon_H$ ) corresponding to :

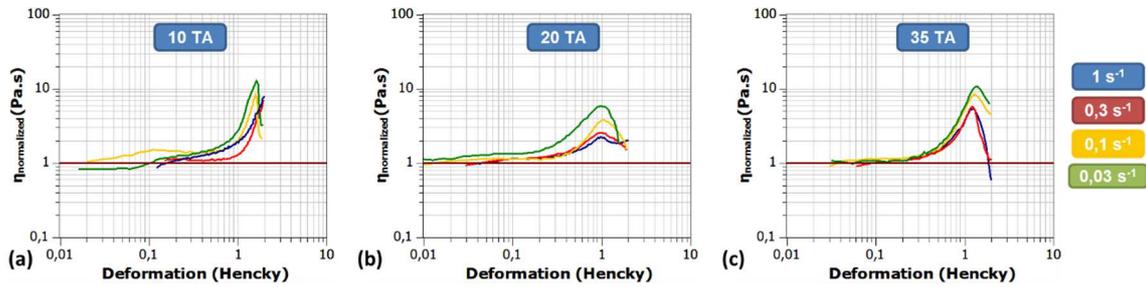
363

$$\varepsilon_H = \ln \frac{L}{L_0} \quad (9)$$

364

It seems that the intensity of the strain hardening effect does not depend on the triacetin content (Figure 7). The values are slightly lower for 20wt%. However, the apparition of strain hardening is abrupt in all the cases and there is clearly a critical strain of the system before the starting of the strain hardening which can be estimated between 0,4 and 0,6 Hencky. Moreover, a similar limited deformation around 1 Hencky is visible whatever the triacetin content is. These results confirm that, as observed for SAOS experiments, the extensional behaviour is similar from 10 to 35wt% of plasticizer corresponding to no changes in the structure at the scale of several chains. These results suggest that, up to 35wt%, the length of active elastic segments is the same whatever the plasticizer content is.

373



374

Figure 7 : Normalized viscosity as a function of the Hencky strain ( $\varepsilon_H$ ) for 10wt% (a), 20wt% (b) and 35wt% (c) of triacetin at 180°C.

375

376

377

### 3.3.2 Rigidity of cellulose acetate chains

378

Taking advantage of the results obtained by uniaxial extensional flow, the rigidity of plasticized cellulose acetate chains has been investigated. The Flory characteristic ratio ( $C_\infty$ ) was estimated assuming that elastic segment between two consecutive stickers has a finite extension which is reached at the onset of the strain hardening (critical deformation,  $\varepsilon_c$ ).

The theory of rubber elasticity based for crosslinked chains network was used to estimate from the critical deformation. To do that, the hypothesis that the network created by stickers is stable in the timescale of the test so that all the segments between two consecutive stickers are elastically active and confer an elastic behaviour to the system. From a definition of the entropy according to the extension ratio ( $\lambda$ ), it is possible to use the following equation to determine the resulting stress ( $\sigma$ ) :

389

$$\sigma = E \left( \lambda - \frac{1}{\lambda^2} \right) = E \times \varepsilon \quad (10)$$

E is the Young modulus and  $\varepsilon$  is the strain. In the case of an affine and homogeneous deformation, the critical extension ratio is defined by :

392

$$\lambda_c = \frac{r_{max}}{r_0} \quad (11)$$

The length  $r_{max}$  is the end to end distance of the chain segment between two consecutive stickers in fully extended configuration whereas  $r_0$  corresponds to its equilibrium value without any applied stress. This length ( $r_0$ ) is related to the number of monomers between two stickers (N) and the size of the monomer (b) by :

396

397 
$$r_0^2 = C_\infty \cdot N \cdot b^2 \quad (12)$$

398 With  $N = \frac{M_s}{m_0}$  where  $M_s$  is the mass between stickers defined in section 3.1.1 and  $m_0$  is the monomer  
399 molar mass.

400 The following system of equations enable to determine the critical extension ratio ( $\lambda_c$ ) from  
401 molecular parameters :

402 
$$\left. \begin{array}{l} r_0^2 = C_\infty \cdot N \cdot b^2 \\ r_0 = \sqrt{C_\infty \cdot N} \cdot b \\ r_{max} = N \cdot b \end{array} \right\} \lambda_c = \frac{N}{\sqrt{C_\infty \cdot N}} = \sqrt{\frac{N}{C_\infty}} \quad (13)$$

403 Then it is possible to express the critical deformation as follows :

404 
$$\varepsilon_c = \sqrt{\frac{N}{C_\infty}} - \frac{C_\infty}{N} \text{ because } \varepsilon_c = \lambda_c - \frac{1}{\lambda_c^2} \quad (14)$$

405 **Finally, the characteristic ratio  $C_\infty$  is estimated from equation 14 which is solved taking a monomer**  
406 **mass ( $m_0$ ) of 265 g/mol for cellulose acetate with a DS of 2,45 and a critical deformation ( $\varepsilon_c$ ) between**  
407 **0,4 and 0,6 according to experimental results. The mass between stickers ( $M_s$ ) is considered as**  
408 **constant up to 35wt% of triacetin and its value is around 12000 g/mol at 180°C according to the**  
409 **rubber plateau modulus ( $G_N^0$ ) determined by SAOS measurements.**

410 Equation 14 gives a value of  $C_\infty$  between 30 and 34 according to the critical deformation retained.  
411 This estimation is rather close to the value of 36 found in the literature (Lapasin & Pricl, 1995).  
412 Cellulose acetate chains are highly rigid because of **primary and secondary** intramolecular hydrogen  
413 bonds within a chain (Hsieh & Kadla, 2012; Kawanishi et al., 1998). In the melt state, the presence of  
414 plasticizer seems to not have an evident effect on the presence of the intramolecular interactions  
415 because of the conservation of a similar  $C_\infty$ . This result also confirms that, for plasticized cellulose  
416 acetate, elasticity stems from elastic segments between “close state” stickers which lead to strain  
417 hardening effects when solicited above a critical deformation during uniaxial extensional flow.

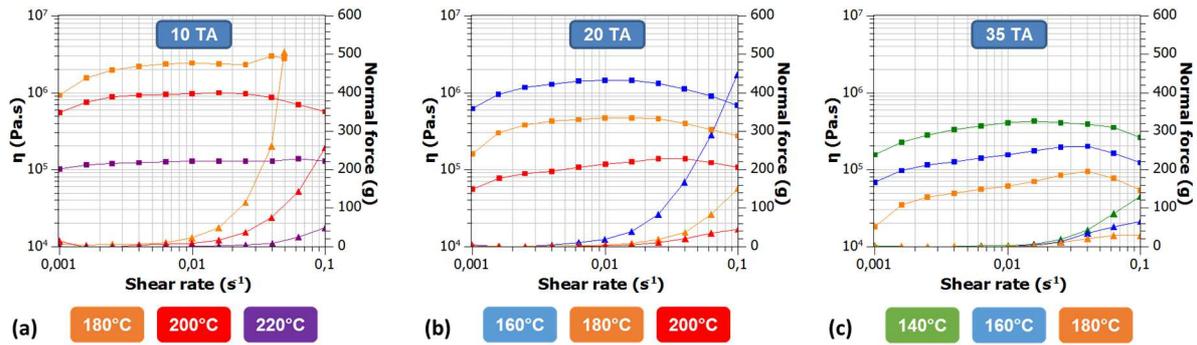
418

### 419 3.4 Large amplitude shear experiments at low plasticizer contents

420

421 For transient networks such as entanglements, strong elastic behaviour is observed under  
422 elongational flow whereas strain softening is always observed under shear flow. In order to check if  
423 this behaviour could be verified for this system, large amplitude shear experiments have been carried  
424 out for low plasticized samples. Because of experimental constraints described in section 2.3,  
425 measurements were performed with parallel-plate fixture. Therefore, the results are only qualitative  
426 and elasticity effects of plasticized cellulose acetate were then highlighted following the evolution of  
427 the normal force generated by sheared samples (Figure 8). The increase of the normal force is  
428 classically related to the Weissenberg effect appearing after a critical shear rate because of the  
429 development of a strong elasticity in the polymer. The critical shear rate for Weissenberg effect  
430 seems not really depend on plasticizer content and temperature. On the contrary, the intensity of  
431 this effect depends strongly on plasticizer content and temperature for the range of shear studied.

432



433

434 *Figure 8 : Evolution of the steady-shear viscosity (■) and the normal force (▲) as a function of shear*  
 435 *rate at different temperatures for 10 (a), 20 (b) and 35wt% (c) of triacetin.*

436

437 In any case, the Weissenberg effect appeared at really low shear rates and without any noteworthy  
 438 modification of the viscosity. Once again, this surprising behaviour may be related to the presence of  
 439 stickers between cellulose acetate chains. According to some results in the literature concerning  
 440 hydroxyl-functionalized polypropylene (PPOH) copolymers, hydrogen bonds could be responsible for  
 441 the high elasticity of a polymer during shear sweeps (Gupta, Yuan, Mike Chung, Cakmak, & Weiss,  
 442 2016). If the temperature increases, the network formed by hydrogen bonds is weakened and the  
 443 association time of the stickers decrease (Brassinne, Cadix, Wilson, & Ruymbeke, 2017). At the same  
 444 temperature, the triacetin content also influences the association time and have an effect on the  
 445 intensity of the Weissenberg effect.

446 However, cellulose acetate is well known to contain small amount of crystalline phase even beyond  
 447 the glass transition temperature  $T_g$  that could act as crosslink points and could be responsible for the  
 448 specific rheological behavior. When the degree of substitution decreases to 2,5, transitions related to  
 449 crystallinity are visible but their intensity turns out to be quite low, especially for X-ray diffraction  
 450 (XRD) measurements (T.G. Fawcett et al., 2013) or by mechanical analysis dynamic (DMA) (M.  
 451 Scandola & G. Ceccorulli, 1985.). Several papers have shown that pure cellulose acetate (not  
 452 plasticized) of degree of substitution 2.45 has a degree of crystallinity from 9 to 16% (M. Sousa et al.,  
 453 2010; C. Bao, 2015) and therefore are predominantly amorphous. Moreover, crystallinity decreases  
 454 for plasticized CA (M. G. A. Vieira, M. A. da Silva, L. O. dos Santos & M. M. Beppu 2011; M. Bocqué, C.  
 455 Voirin, V. Lapinte, S. Caillol & J.-J. Robin, 2016 ; M. Scandola & G. Ceccorulli, 1985). Actually, the role  
 456 of crystallinity on the peculiar rheological response can be ruled out because, if crystalline phase is  
 457 present and acts as crosslink, plasticized CA should behave as rubber with permanent long term  
 458 elasticity while terminal flow of plasticized CA is observed (Figure 1 and 4).

## 459 4. Conclusion

460

461 Thanks to the evolution of rheological parameters, it has been shown that rubber elasticity of  
 462 plasticized cellulose acetate is not related to classical entanglements but rather to another  
 463 correlation length corresponding to the distance between strong but labile interactions, called  
 464 stickers, between cellulose acetate chains. The stickers could be related to residual hydrogen bonds  
 465 between cooperative hydroxyls groups of two AGU units of neighboring cellulose acetate chains.  
 466 Stickers are characterized by a finite lifetime enabling connection and reconnection leading to  
 467 transient network formation. Therefore, plasticized cellulose acetate in the melt state has  
 468 characteristics of associating polymers.

469 Up to a critical content of 35wt%, the plasticizer could be localized in the free volume defined  
470 between two consecutive stickers of neighboring cellulose acetate chains. Therefore, the plasticizer  
471 modifies the local environment of the chains at the monomer scale but there is no modification of  
472 the structure at the scale of the bulk and the rheological parameters depending on the whole chain  
473 remained unaffected. These stickers confer an unusual viscoelastic behaviour to cellulose acetate at  
474 short times and unexpected scaling behaviour regarding the different rheological parameters studied  
475 by SAOS. Moreover, if the samples are compared at the same distance to T<sub>g</sub>, no effect of the nature  
476 of the plasticizer on the dynamics of chains is found up to 35wt%. On the timescale studied by  
477 dynamic oscillatory measurements, the global molecular dynamics are unaffected by the addition of  
478 plasticizer.

479 The strong interactions between cellulose acetate chains also have an effect at high deformation and  
480 confer unusual flow behaviour. A strain hardening effect, whose intensity is not dependent upon the  
481 triacetin content up to 35wt%, was noticed thanks to uniaxial extensional flow at different  
482 extensional-strain rates. Strain hardening appears at a same critical deformation for the different  
483 plasticizer content and the results fit with a Lodge model. It means that there are indeed permanent  
484 interactions on the experimental timescale. The strong elasticity of the polymer was also highlighted  
485 thanks to shear sweeps because of the apparition of a Weissenberg effect after a critical shear rate.  
486 This phenomenon appeared at really low shear rates and without any noteworthy modification of  
487 the viscosity. According to the literature, hydrogen bonds could be responsible of the high elasticity  
488 of a polymer during shear sweeps.

489 This work opens the way for further investigation of the structural organization of cellulose acetate  
490 chains in the melt state and more particularly the organization of the chains according to their molar  
491 mass and the study of long term relaxation.

492

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494

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