Substitution degree and fatty chain length influence on structure and properties of fatty acid cellulose esters

Lucie Duchatel-Crépy, Nicolas Joly, Patrick Martin, Adeline Marin,
Jean-Francois Tahon, Jean Marc Lefebvre, Valérie Gaucher

HAL Id: hal-03006969
https://hal.univ-lille.fr/hal-03006969v1

Submitted on 21 Jul 2022

1 **Substitution degree and fatty chain length influence on structure and**

2 **properties of Fatty Acid Cellulose esters.**

3

4 Lucie Duchatel-Crépy,[a] Nicolas Joly,[b*] Patrick Martin,[b] Adeline Marin,[c] Jean-Francois Tahon,[c]

5 Jean-Marc Lefebvre,[c] Valérie Gaucher [c*]

6

7 [a] Univ. Artois, EA 4515, Laboratoire de Génie Civil et géo–Environment (LGCgE), F–62400,

8 Béthune, France

9 [b] Univ. Artois, UnilaSalle, Unité Transformations & Agroressources, ULR7519, F-62408,

10 Béthune, France.

11 Fax: +33 (0)3 21 68 49 57; E-mail: nicolas.joly@univ-artois.fr.

12 [c] Univ. Lille, CNRS, INRA, ENSCL, UMR 8207 - UMET - Unité Matériaux et Transformations,

13 F-59000 Lille, France.

14 Fax: +33 (0)3 20 43 65 91; E-mail: valerie.gaucher@univ-lille.fr.

15

16 Corresponding authors:

17 Nicolas Joly; Postal address: Univ. Artois, UnilaSalle, Unité Transformations & Agroressources,

18 ULR7519, 1230 rue de l'Université, BP819, F-62408 Béthune cedex; Tel.: +33 (0)3 21 63 23 00;

19 Fax: + 33 (0)3 21 68 49 57; E-mail address: nicolas.joly@univ-artois.fr.

20 Valérie Gaucher; Postal address: Univ. Lille, CNRS, INRA, ENSCL, UMR 8207 - UMET -

21 Unité Matériaux et Transformations, Bât. C6, F-59000 Lille, France, France; Tel: + 33 (0)3 20

22 33 64 16 ; Fax: + 33 (0)3 20 43 65 91 ; E-mail address: valerie.gaucher@univ-lille.fr.

23

Abstract

A series of fatty acid cellulose esters (FACEs) with both various degrees of substitution (from DS=1.7 to 3) and side chain length were obtained by grafting aliphatic acid chlorides (from C10 to C16) onto cellulose backbone, in a homogeneous LiCl/DMAc medium. These materials were characterized by Fourier Transformed InfraRed (FTIR) and Nuclear Magnetic Resonance of Proton (^{1}H NMR) spectroscopies, as well as Wide Angle X-ray Scattering (WAXS), Differential Scanning Calorimetry (DSC), mechanical analyses and chemical resistance to concentrated acid and alkali solutions. Whatever the alkyl chains length and the DS, all samples displayed a layered structure composed of a planar arrangement of parallel cellulosic backbones with fully extended flexible side chains oriented perpendicular to the planar structure without interdigitation. The alkyl chains were able to crystallize as soon as they are long enough. As the DS decreased, the plasticizing effect of the alkyl chains was less pronounced and their ability to crystallize was improved. Regarding the mechanical behavior and the chemical resistance, similar results were observed whatever the DS is.

Keywords

Fatty Acid Cellulose Esters; layered type structure; side-chain crystallinity; structure-properties relationships

1. Introduction

Cellulose is considered as the most abundant raw polymer on earth, since it is estimated that about 5.10^{10} tons of cellulose are generated each year throughout the world (Pérez, 2000). In accordance, many studies have been focused, for the last 3 decades, on the use of cellulose as an alternative to the non-renewable petroleum-based polymers for the synthesis of bio-based and potentially biodegradable materials. Among all these researches, an almost large part are

dedicated to the fatty acylation of cellulose synthesis, either in heterogeneous (Wang & Tao, 1994; Chauvelon *et al.*, 2000; Freire, Silvestre, Pascoal Neto, Belgacem & Gandini, 2006) , or in homogeneous media, such as LiCl/N,N-dimethylacetamide (Heinze et al., 2000; Satgé, Verneuil, Branland, & Krausz, 2004; Joly, Granet, Branland, Verneuil & Krausz, 2005) or ionic liquids (El Seoud & Heinze, 2005; Huang et al., 2011), mainly using fatty acyl chlorides or esters as reagents. Some of these studies, including ours (Joly et al., 2006; Crépy, Chaveriat, Banoub, Martin & Joly, 2009), are dedicated to the determination of mechanical and/or thermal and/or structural properties of Fatty Acid Cellulose Esters (FACEs) (Klarman, Galanti & Sperling, 1969; Sealey, Samaranayake, Todd & Glasser, 1996; Edgar et al., 2001; Vaca-Garcia, Gozzelino, Glasser & Borredon, 2003), which is a great deal if we consider the investigations on the potential applications of such bio-based materials.

In a previous work (Crépy, Miri, Joly, Martin & Lefebvre, 2011), we have demonstrated for the first time, the structure-properties relationship of fully substituted FACEs bearing various fatty chains (from C8 to C16), and we have notably demonstrated an original structural model in which the cellulosic backbones display a planar organization, together with an arrangement of the alkyl side chains perpendicular to the cellulose backbone without interdigitation. The methodology and the analytical strategy, we have developed in this study, allowed a lot of research team to go further in their studies of structure properties relationship of biobased or synthetic polymers (Danjo & Iwata, 2018; Li et al., 2018; Qian et al., 2018).

Furthermore, it is well known in the scientific community specialized in polysaccharide chemistry, and for instance fatty acid polysaccharide esters, that DS and fatty chain length are the main parameters able to directly influence properties of FACE-type materials. For example, it was clearly shown that FACEs with DS higher than 1.5 exhibit thermoplastic properties and solubility in organic lipophilic solvents (Wang & Tao, 1995; Edgar et al., 2001), whereas a lower DS allows especially hydrophobicity of FACEs (Peydecastaing et al., 2011). Interested in

74 thermoplastic and hydrophobic FACE materials and in continuation of our previous works, the

75 present study deals with the influence of substitution degrees (DS) on structure and properties of

76 partially substituted FACEs. We are dealing here with a complete range of FACEs bearing fatty

77 chains ranging from C10 to C16 with moderate to high DS values. The structural, thermal,

78 thermomechanical analysis and chemical resistance of cellulose esters were systematically

79 performed using Wide Angle X-ray Scattering (WAXS), Differential Scanning Calorimetry

80 (DSC), and uniaxial tensile tests. The final goal of this investigation is to determine the structure-

81 property relationships of FACEs according to both degree of substitution and fatty chain length.

82

2. Experimental Part

2.1. Materials

85 All reagents were stored at room temperature and were used without further purification:

86 microcrystalline cellulose (20μm, DP = 150, Aldrich); *N,N*-dimethyl-4-aminopyridine (DMAP,

87 99%, Acros); *N,N*-dimethylacetamide (DMAc, 99%, Acros); anhydrous lithium chloride (99%,

88 Acros); decanoyl chloride (98%, Aldrich); lauroyl chloride (98%, Aldrich); myristoyl chloride (≥

89 99%, Fluka); palmitoyl chloride (98%, Acros); chloroform (≥ 99%, Carlo Erba); methanol (≥

90 99%, Carlo Erba); acetic acid (≥ 99%, Acros), hydrochloric acid (37%, Acros); sulphuric acid

91 (95%, Acros); sodium hydroxide (≥ 99%, Acros); potassium hydroxide (≥ 99%, Acros).

92 Deuterated chloroform was purchased from Aldrich and stored at 4°C.

93

2.2. Acylation of cellulose by acyl chlorides

95 In a typical experiment, a 20 g.L^{-1} cellulosic solution, consisting in pre-treated cellulose in a

96 6.7% LiCl/DMAc (v/w) system (Joly, Granet & Krausz, 2003) (150 mL; 3 g; 18 mmol of

97 anhydroglucose unit, 1 equiv.) and DMAP (6.6 g; 54 mmol; 3 equiv.) were stirred at 80°C until

98 complete solubilization. Fatty acyl chloride (4.5 to 9 equiv. per anhydroglucose unit according to

99 fatty acid chloride) was then added and the mixture was heated classically at 80°C during 3

100 hours (Joly et al., 2006; Vaca-Garcia, Thiebaud, Borredon & Gozzelino, 1998). The reaction

101 media was poured into methanol (3 vol) to precipitate cellulose fatty esters and the solid was

102 purified by a repeated solubilization/precipitation process using chloroform and methanol,

103 respectively, and finally dried in air at room temperature (Satgé et al., 2002).

104 FACEs were obtained as white powders or cotton like solids according to both fatty chain length

105 and DS. These products were converted into films by casting in chloroform (10 g of FACE in

106 100 mL of chloroform). All cast films were translucent and ductile.

107 A similar protocole (synthetic and purification conditions) was performed onto cellulose solution

108 without the introduction of fatty acyl chloride, in order to obtain a non-derivatized cellulose after

109 the same synthetic pathway, so-called "destructured cellulose". This product was used as

110 standard for X-ray analyses.

111

112 **2.3. Chemical Characterization**

113 Every film has been characterized by Fourier Transformed InfraRed (FTIR) spectroscopy using

114 an Agilent Cary630 apparatus equipped with an ATR accessory.

115 Nuclear Magnetic Resonance of Proton (^{1}H-NMR) spectroscopy was performed in $CDCl_3$ using

116 a Bruker DRX-300 Spectrometer (operating at 300 MHz) to determine both purity and degree of

117 substitution (DS) by an integration method described elsewhere (Joly, Granet, Branland,

118 Verneuil & Krausz, 2005). The DS is defined as the number of fatty chains linked per

119 anhydroglucose unit (maximum value of 3).

120 Resistance tests to strong acids and basis consisted in a complete immersion of dumbbell-shaped

121 samples, until two weeks, in several acid or base solutions. After their immersions, they were

122 washed with water and dried before contact angle measurements. The control sample

123 corresponds to dumbbell-shaped samples before immersion.

124

2.4. Structural characterization

Wide-Angle-X-ray Scattering (WAXS) experiments were carried out on a Genix microsource (XENOCS) equipment using the Cu K_α radiation (λ=1.54 Å). Primary beam was collimated and monochromatized by a FOX2D-12Inf optic (Xenocs, France), and the WAXS patterns were collected on a CCD VHR detector (Photonic Sciences). The experiments were led at room temperature in transmission mode. Standard corrections were applied to the WAXS patterns before their treatments. The intensity profiles were obtained by 360° azimuthal integration of the 2D WAXS patterns using the fit2D software[®].

133

2.5. Thermal behavior

DSC measurements were carried out on a Perkin-Elmer Diamond apparatus. The temperature and the heat flow scales were calibrated from the melting of high purity indium and zinc samples. About 10 mg of each FACE film sample was used in the heating/cooling cycle experiments conducted at 20°C.min^{-1} under nitrogen atmosphere.

139

2.6. Mechanical behavior

Mechanical behavior was studied in uniaxial tensile mode using an Instron 4466 apparatus. Tensile testing was conducted at room temperature, using specimens with L_0= 24 mm and l_0= 5 mm gauge length and width, respectively. The tensile tests were carried out at a constant crosshead speed of 1.44 mm.min^{-1} which corresponds to an initial strain rate of 1.10^{-3} s^{-1}. The nominal stress σ and strain ε are defined conventionally as the ratio $F/(l_0*e_0)$ and $(L-L_o)/L_o$, respectively.

147

2.8. Contact Angle Measurements

149 Contact angles were determined at room temperature and ambient humidity, using an Apollo

150 Instruments OCA 20 contact angle apparatus operating with the sessile drop method, with a

151 water drop of 3 μL. All contact angles were measured on both sides of the drop by the ellipse-

152 fitting calculation method, at a drop age of 1s. Each contact angle reported here is an average of

153 at least 4 values obtained on the sample surface. A contact angle value higher than 90° indicates

154 that the material sample surface is hydrophobic.

155

156 **3. Results and Discussion**

157 Cellulose modification was performed in homogeneous media. This polysaccharide is known to

158 be insoluble in classical organic solvents and water. Microcrystalline cellulose can be dissolved

159 and chemically modified in aqueous NaOH solution (Elchinger et al., 2012), but this water-based

160 solvent is not convenient as media for the synthesis of FACEs. Nevertheless, particular solvent

161 systems such as lithium chloride/*N,N*-dimethylacetamide (LiCl/DMAc) (Dawsey & McCormick,

162 1990), have to be used to dissolve this polysaccharide. This solvent system is suitable for

163 chemical reaction onto cellulose as it is underivatizing and do not degrade the natural polymer in

164 time (Dupont, 2003).

165 Synthesis of plastic materials was performed by grafting fatty acids, used as internal

166 plasticization, onto cellulose. Fatty acid chain lengths were ranged from decanoyl (C10) to

167 palmitoyl (C16), corresponding to the major fatty acids found in vegetal oil triglycerides. FACEs

168 (Figure 1) were obtained by a method described elsewhere (Crépy, Chaveriat, Banoub, Martin &

169 Joly, 2009; Joly, Granet, Branland, Verneuil & Krausz, 2005), consisting in the reaction between

170 fatty acid chlorides and cellulose. To trap HCl produced during reaction, we use DMAP, *i.e.*

171 *N,N*-dimethylaminopyridine, a basic catalyst often used for this kind of reaction, in a large

172 amount (3 eq. according to glucose unit) to allow both acylation reaction (catalyst action) and

173 protection of cellulosic backbone from hydrolysis (base action). In these reaction conditions, we

174 can consider that cellulose is not damaged during the process.
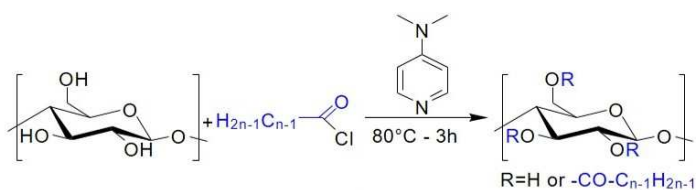
| R	Structure	Name
H	H	-
C10 (n = 10)		Decanoyl
C12 (n = 12)		Lauroyl
C14 (n = 14)		Myristoyl
C16 (n = 16)		Palmitoyl

176 **Figure 1:** fatty acid cellulose esters (FACEs).

177

178 **3.1. FTIR analysis**

179 A comparison of the FTIR spectrum of native cellulose with cellulose laurate shows the relative

180 efficiency of acylation (Figure 2): a decrease in the intensity of the hydroxyl group characteristic

181 band at 3400 cm^{-1} (-OH stretching) and its shift to 3600 cm^{-1} were observed (compared to the

182 native cellulose spectrum). This difference indicates that a part of -OH groups was substituted.

183 This phenomenon is concomitant with an increase in the intensity of the -C-H alkyl bonds

184 characteristic signals at 2800-2900 cm^{-1} (-CH- antisymmetric and symmetric stretching of -CH$_2$-

185 and -CH$_3$), corresponding to the presence of fatty long chains. The appearance of two new bands

186 is also observed; the first one at 1740 cm^{-1} (-C=O stretching), corresponding to the vibration of

187 ester carbonyl groups, and the second one at 720 cm^{-1} characteristic for at least four linearly

188 connected -CH$_2$- groups (-(CH$_2$)$_4$- rocking). That means that fatty chains have been directly

189 grafted onto cellulose by an ester junction.

8

190   Same results are obtained whatever the substituent chain length is. Moreover, the increase of

191   fatty acid chloride amount introduced in the reaction media lead to an intensity increase of the

192   band at 1740 cm^{-1} (-C=O) is (Figure 2). This evolution suggests the growth of fatty FACEs

193   degree of substitution (DS).
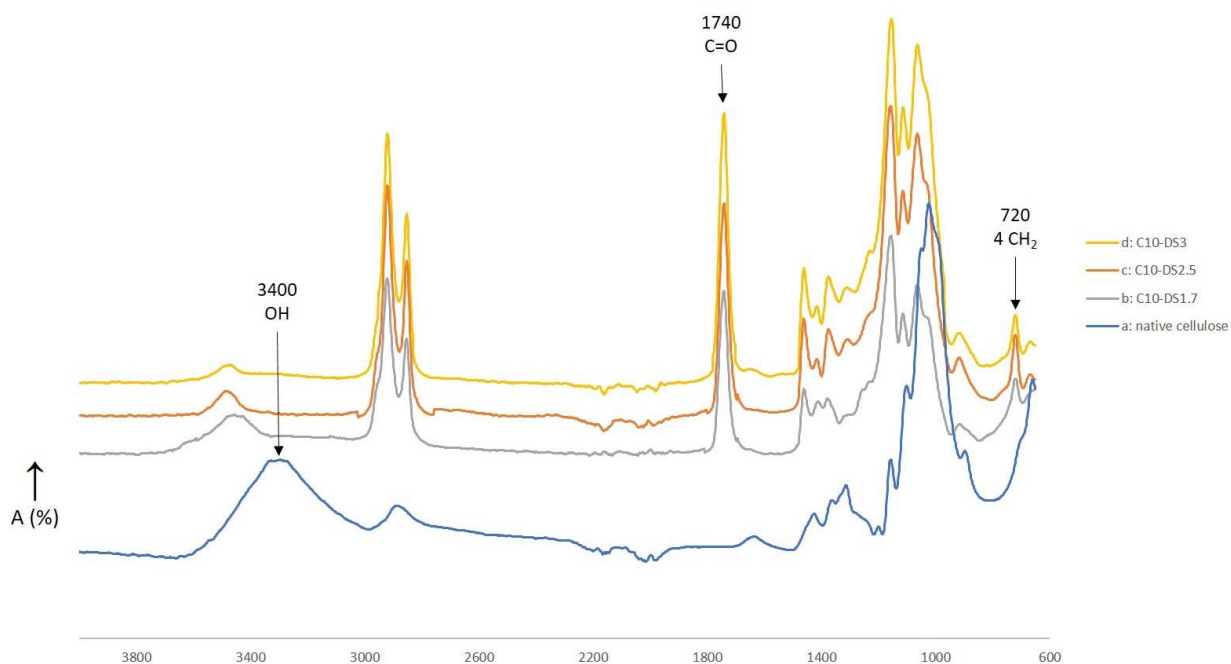
194

195   **Figure 2:** FTIR spectra of native cellulose (a) and C10 films (b, c and d) with different DS.

196

197   **3.2. ^{1}H-NMR analysis**

198   ^{1}H-NMR spectroscopy was used to estimate quantitatively the presence and amount (degree of

199   substitution, DS) of the fatty chains on cellulose backbone. Note that ^{1}H-NMR spectra were

200   similar for all FACEs, irrespective of their fatty chain lengths. The acylation of cellulose was

201   confirmed by integration of the characteristic signals of fatty acid protons from 0.89 to 2.34 ppm,

202   and of the cellulosic backbone from 3.0 to 5.50 ppm (carbohydrate protons).

203   ^{1}H-NMR spectroscopy was also used to make sure FACEs films were free of solvent (DMAc) or

204   methyl fatty esters. Indeed, solvents and fatty acid esters are usually used as plasticizer in plastic

205   films, according to Ning, Xingxiang, Haihui & Jianping. (2009) and Mantese Sander, Nicolau,

206   Guzatto & Saios (2012). However, in our study, only the fatty acid chains directly linked to the

9

207   cellulosic backbone, is used as an internal plasticizer. Figure 3 regroups FACEs with traces of

208   free fatty chains (Figure 3a) or DMAc (Figure 3b) in CEs films.

209
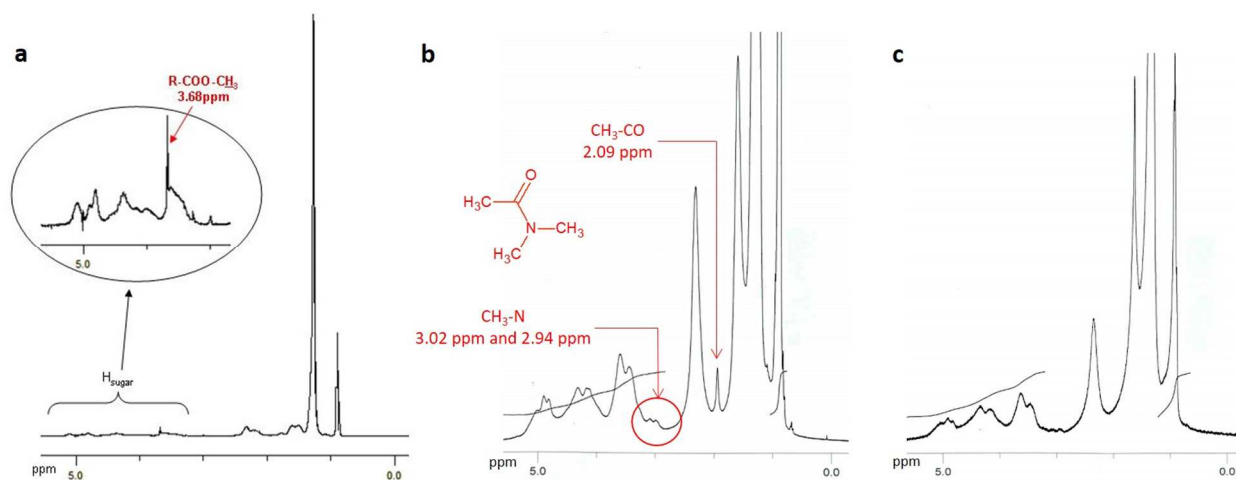
211   **Figure 3:** ^{1}H-NMR spectra of C12-DS3 containing free methyl fatty chains (a), or traces of

212   DMAc (b), and pure C12 (c).

213

214   If the FACEs are not pure, unexpected signals can appear on ^{1}H NMR spectra. A peak can be

215   observed at 3.68 ppm and has already been identified in a previous work (Crépy, Chaveriat,

216   Banoub, Martin & Joly, 2009) as free fatty acid methyl ester. Three other peaks can also be

217   observed at 3.02 ppm, 2.9 ppm and 2.09 ppm, and were attributed to DMAc methyl groups. In

218   order to evaluate the influence of both grafted fatty chain length and FACEs degree of

219   substitution, we have to be sure that residual solvent and free fatty acid methyl esters are

220   eliminated, i.e. the missing of corresponding undesirable peaks on FACEs ^{1}H NMR spectra.

221   Consequently, purification steps are performed until complete disappearance of these undesirable

222   peaks (figure 3c).

223   The degrees of substitution (DS) for all the cellulose derivatives were also evaluated using [1]H-

224   NMR integrations and the results are reported in Table 1, according to the reaction conditions.

225 **Table 1:** Results of FACEs synthesis. Molar conversion was determined according to DS of

226 FACEs versus anhydroglucose unit amount in starting cellulose.

FACE name	C10				C12				C14				C16			
Fatty acid chloride (eq.)	5.5	6	8	9	5	5.5	7.5	9	4.5	5	6.5	8	4.5	5	6.5	8
DS (±0.1)	1.7	2	2.5	3	1.7	2	2.5	3	1.7	2	2.5	3	1.7	2	2.5	3
Weight increase (%)	135	157	195	253	157	203	241	267	166	214	252	276	171	226	255	289
Molar conversion (%)	90	89	87	92	88	93	90	84	83	87	83	77	78	83	76	72

227

228 FACEs DS variation was studied according to the amount of fatty acid chloride introduced in the

229 reaction mixture, but also to fatty chain lengths. The aim was first to graft enough fatty acid

230 chains so that FACEs exhibit thermoplastic properties, *i.e.* to obtain a minimal DS of 1.5 (Edgar

231 et al., 2001). Thus, for C10 fatty chains, a DS of 1.7 was obtained using 5.5 eq. of fatty acid

232 chloride (according to anhydroglucose unit amount). As expected, the higher the fatty acid

233 chloride amount is, the higher substitution degree is, until a value of 3.0 using 9 eq. of decanoyl

234 chloride. Comparing fatty chain length influence on DS, to obtain FACEs with DS 1.7, the fatty

235 acid chain amount can be decreased to 4.5 equiv. when increasing fatty chain length to 16

236 carbons. Even if the reactivity of fatty acids is supposed to slightly decrease with the increase of

237 their chain length, this phenomenon seems to be thwarted by a steric effect favoring fatty acid

238 chloride reaction, *i.e.* the longer the fatty chain is, the more it allows to separate polymer chains

239 as well as the already grafted substituents, the more additional substituents have the space to

240 react. This is also observed comparing other DS values according to fatty chain lengths and

241 amounts, leading to conclude that, for a fixed DS value, the longer the fatty chain is, the lower

242 the amount of fatty acid chloride is needed.

11

243   Considering molar conversions, the unrecovered products may be eliminated during purification

244   process, meaning that they are FACEs with DS lower than 1.5, whatever the fatty chain length is.

245   Moreover, it appears that, even if DS3 is easier to obtain for C16 fatty chain, molar yields

246   decrease when increasing fatty chain length / with the increase of fatty chain length. On the

247   contrary, reactivity of fatty acid chloride increases when fatty chain length decreases.

248

249   **3.5. Structural characterization**

250   Figures 4a and 4b show the diffractograms of C10 and C16 series and of destructured cellulose

251   powder for information purpose. Whatever the degree of substitution is, all FACE films exhibit a

252   major reflection in the low angle region ($2\theta \approx 2\text{-}4°$) and a broad and weak halo in the region $2\theta \approx$

253    $16\text{-}24°$. The location of these reflections is not influenced by the degree of substitution but only

254   by the fatty chain length. Regarding the broad halo, it is related to both amorphous cellulosic and

255   fatty alkyl chains. Concerning fully substituted FACEs, previous study has shown that a part of

256   the alkyl chains is able to crystallize into a α-hexagonal packing as soon as the alkyl chains are

257   long enough (Crépy, Miri, Joly, Martin & Lefebvre, 2011). To investigate the effect of the DS on

258   the alkyl chain organization, a deconvolution of the I (2θ) profiles in the region $2\theta = 10\text{-}28°$ has

259   been performed using Peakfit software for C16-DS1.7 and C16-DS3. Two Pearson functions are

260   needed to fit the experimental diffractograms of both materials (Figure 4c). Considering that the

261   Pearson function with the narrower 'Full Width at Half Maximum' is related to the crystalline

262   part of the material, this result shows that as for the fully substituted cellulose palmitate, a part of

263   the alkyl chains is also crystallized for the lowest DS.

264   Regarding the diffraction in the low angle region, its presence reveals that all studied materials

265   organize into a layered type structure, as shown in a previous study dealing with fully substituted

266   FACEs (Crépy, Miri, Joly, Martin & Lefebvre, 2011). This structure is composed of a planar

267   arrangement of parallel cellulosic backbones with fully extended flexible side chains oriented

268   perpendicular to the planar structure without interdigitation. Note that this specific organization

269   may explain the fact that C16 needs less fatty acid chloride equivalent than C10 for a similar DS

270   as reported previously. Thus, the layered structure implies that the longer the fatty side chain is,

271   the higher the space between cellulosic backbones is. This phenomenon minimizes the steric

272   hindrance which may facilitate the grafting in the case of longer chains compared to shorter

273   chains.

274   To summarize, contrary to the alkyl chain length, the degree of substitution does not

275   significantly impact the structural organization of FACEs: in the studied DS range, all materials

276   exhibit a layered structure in which the alkyl chains are perpendicular to the cellulosic chains

277   planes and a part of them is able to crystallize.
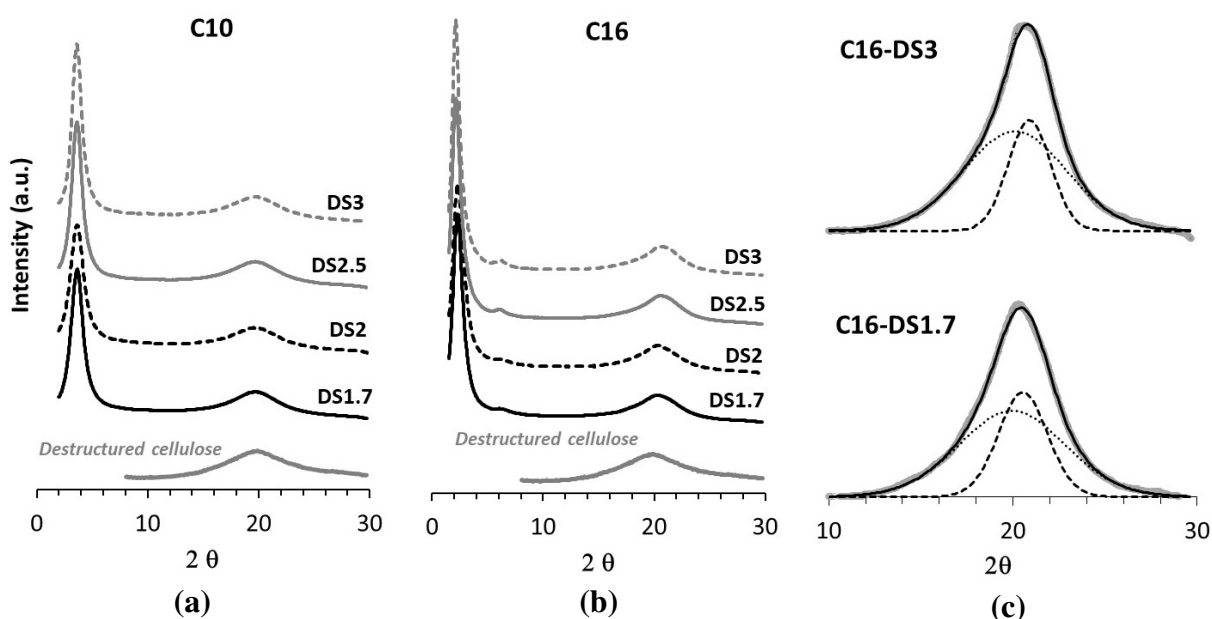
278

279   **Figure 4:** X-ray diffractograms of the FACE cast films as a function of degree of substitution (a)

280   case of C10 series (b) case of C16 series (c) deconvoluted peaks superimposed on the

281   experimental curves for C16-DS3 and C16-DS1.7.

282

283   **3.3. Thermal behavior**

284 The thermal behavior of the C10 and C16 derivatives as a function of degree of substitution

285 during the first heating is illustrated in Figures 5a and b. Several thermal events occur depending

286 on the fatty chain length: one or two broad heat capacity jumps related to glass transitions and a

287 broad endothermic peak were observed. The high temperature glass transition, T_{g2}, related to the

288 cellulosic backbone, tends to decrease as the DS increased. A T_{g2} drop of around 40°C and 30°C

289 is observed for respectively C10 and C16 cellulose derivatives as the DS increases from 1.7 to 3.

290 The plasticizing effect of alkyl chains is more sensitive to the degree of substitution than to the

291 fatty chain length. This may be related to the reduction of the intramolecular H bonds number as

292 the DS is increased. The endothermic peak above room temperature is related to the melting of

293 crystals composed of a part of alkyl-side chains as reported by Willberg-Keyrilaïnen et al. for

294 FACEs with DS lower than 1.0 (Willberg-Keyrilaïnen, Vartiainen, Harlin & Ropponen, 2017).

295 No clear influence of the degree of substitution is observed while the melting peak area increases

296 significantly with the side chain length. Whatever the degree of substitution is, the temperature

297 of the melting peak of C10 is located around 60°C and characterized by a low area around 1 to 4

298 J/g. By comparison, the more important area and broadness of the endotherm in the case of C16

299 derivatives reveals a higher crystal content with a broad crystal thickness distribution. However,

300 no clear trend of the DS on the crystal content of C16 is evidenced from Figure 5b. The value of

301 peak area changes from 12+/-2 J/g for the lowest DS (DS1.7 and DS2) to 24 J/g for the highest

302 DS (DS2.5 and DS3). However, one may specify that samples underwent different long-term

303 annealing at 25°C. So the study of the effect of degree of substitution on the crystal melting will

304 be more relevant on thermograms recorded during the second heating. The low glass transition

305 temperature, T_{g1}, is observed in the case of C16 cellulose derivatives at around -2°C whatever

306 the DS is. This transition is ascribed to the alkyl chain fraction which is not involved in the

307 crystalline phase. The glass transition T_{g1} is not observed in the case of C10 because it occurs in

14

308 a temperature range lower than T=−60°C, as previously shown for fully substituted FACEs

309 (Crépy, Miri, Joly, Martin & Lefebvre, 2011).
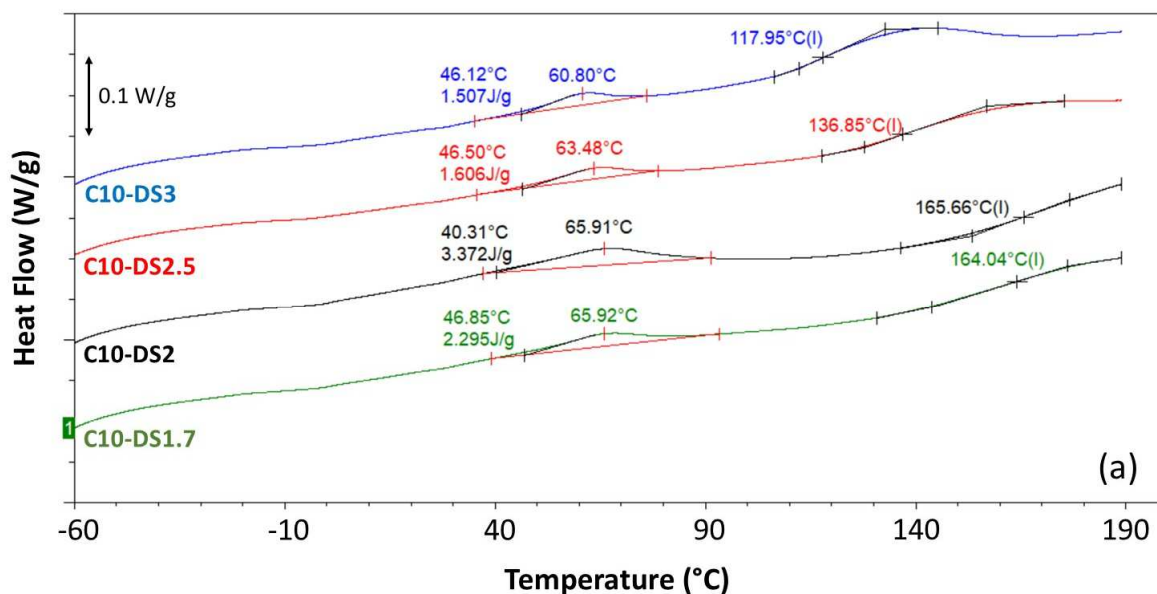
310
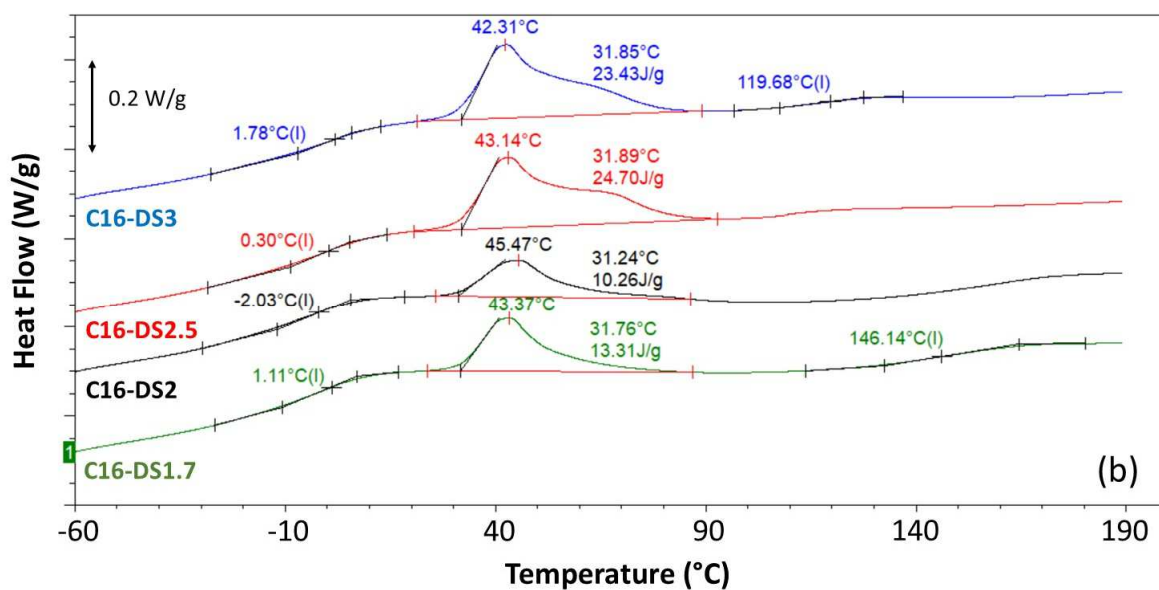
311

312 **Figure 5:** First heating thermograms of the cellulose derivatives cast films (endotherm up) (a)

313 case of C10 and (b) case of C16.

314

315 The thermograms recording during the second heating are illustrated in Figures 6a and 6b. In

316 addition to the improvement of the plasticizing effect of alkyl chains as a function of DS (as

317 observed during the first scan), the crystal melting peak attributed to a part of alkyl side chains is

318   only observed for C16 cellulose derivatives. This indicates that crystals in the first scan result

319   from annealing of samples stored at room temperature. Melting point during the second scan

320   occurs at temperature below the one recorded during the first scan and the melting peak area is

321   almost constant whatever the DS. This means that similar crystals (thickness and content) are

322   formed in all C16 derivatives as soon as samples are undergone to similar thermal treatment.

323   Considering that C16-DS1.7 contains around half-less alkyl chains than in C16-DS3, this

324   indicates that the ratio of alkyl chain involved in crystal phase is twice higher in material with

325   DS1.7. This observation suggests that alkyl chains substitution pattern is rather homogeneous

326   along the cellulosic chains. Indeed, if this is not the case, there will be some regions with higher

327   local DS and regions with lower local DS than the average DS. In the most extreme situation, the

328   former region will be composed of fully substituted cellulosic chains while in the latter, the

329   cellulosic chains will be not substituted at all. In such case, one should expect a crystal content

330   relative to the amount of alkyl chains equal to the one obtained for fully substituted cellulose

331   fatty esters which is not observed. Also, the change of crystallinity with respect to alkyl chain

332   content rather supports a homogeneous distribution of alkyl chains along the cellulosic chains.

333   The improvement of alkyl chains crystallization ability as the degree of substitution decreases

334   may be ascribed to a steric hindrance of alkyl chains less pronounced as the degree of

335   substitution is decreased.

16

336

337
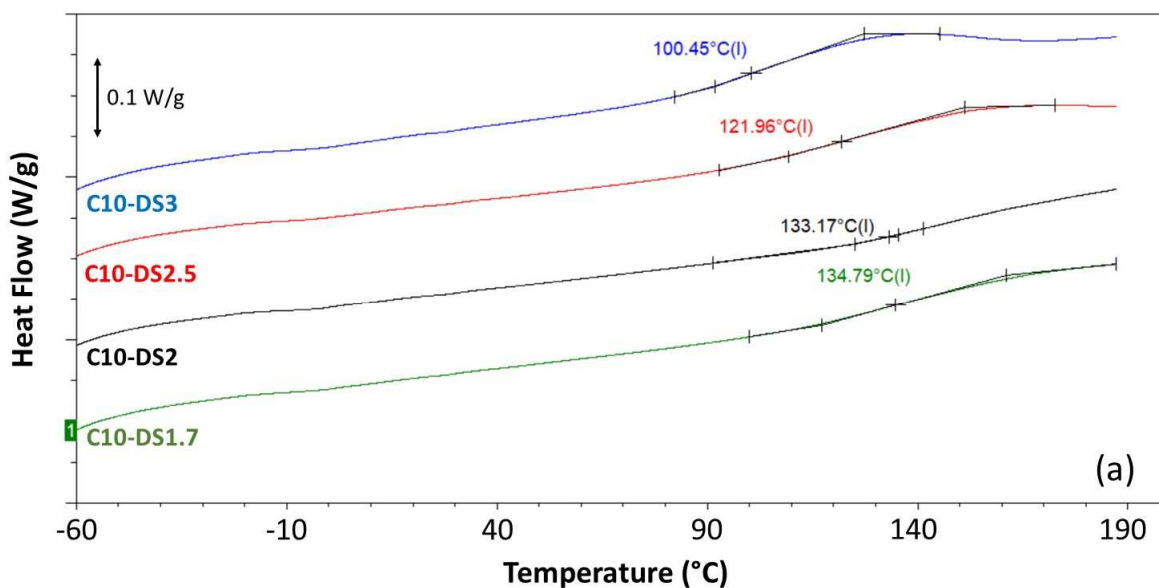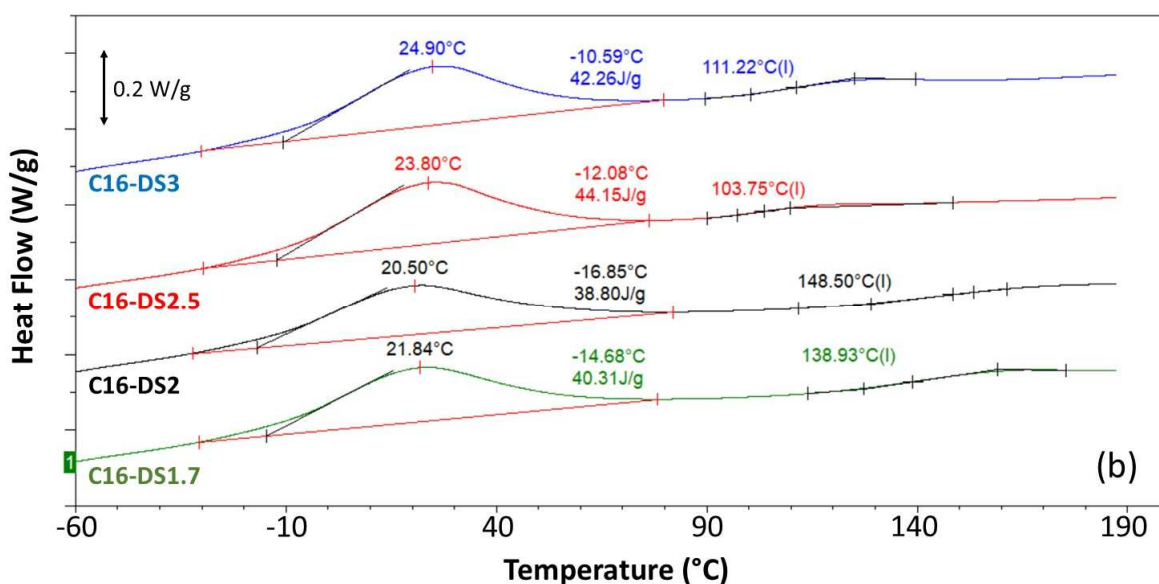
Figure 6: Second heating thermograms of the cellulose derivatives cast films (endotherm up) (a) case of C10 (b): case of C16.

3.6. Uniaxial tensile behavior

Figures 7a and 7b display the nominal stress–strain curves of the C10 and C16 derivatives films tested at room temperature. All samples exhibit a ductile behavior with a decrease of the strain at break as the alkyl chain length is increased. As the degree of substitution is increased, a drop of the stress level is observed in the case of the C10. This behavior may be related to the more

346 pronounced plasticizing effect of the alkyl chains as DS is increased, as previously shown in the

347 thermal behavior section. By contrast, no effect of the DS is evidenced for the cellulose palmitate

348 derivatives. In that case, the presence of crystals may occult the plasticizing effect of the alkyl

349 chains. From a mechanical point of view, all these results suggest that there is no need to fully

350 substitute FACEs.
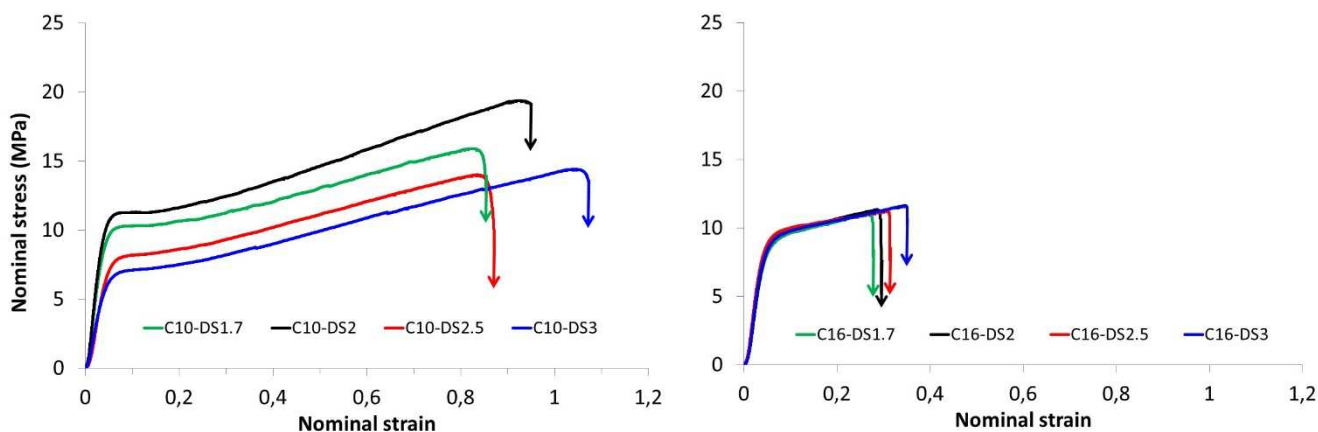
351 **Figure 7:** Nominal stress–strain curves under uniaxial drawing at T=20°C. (a) case of C10 (b)

352 case of C16.

353
354 **3.7. Resistance tests to strong acids and bases**

355 The stability of FACEs has been evaluated for the more and the less substituted, and results are

356 regrouped in Table 2. FACEs are composed of a polysaccharide, which is sensitive to acid-

357 catalyzed hydrolysis of osidic bonds, and fatty acid esters able to be saponified in basic

358 conditions. Considering both potential chemical degradation routes, our aim was to observe the

359 variation of surface hydrophobicity according to immersion of FACEs samples in acidic and

360 alkali solutions with different concentrations.

361 **Table 2:** Stability tests of FACEs with different DS after immersion in aqueous acidic or basic

362 solutions, using contact angle (θ) measurement.

363

θ(°)	C10	C12	C16

18

	DS1.7	DS3	DS1.7	DS3	DS1.7	DS3
Control sample	93	97	95	100	97	107
H₂O	No significant change					
CH₃COOH (99%)	No significant change					
HCl (37%)	No significant change					
H₂SO₄ (5mol/L)	No significant change					
H₂SO₄ (95%)	Complete decomposition after 2 hours					
NaOH (10mol/L)	θ=25°±1° Thin white film on the surface					
KOH (10mol/L)	θ=25°±1° Thin white film on the surface					

364

365 We notice an increase of the hydrophobicity as fatty chain length increases in good agreement

366 with previous study (Crépy, Chaveriat, Banoub, Martin & Joly, 2009). This behavior is

367 strengthened as DS increases, according to higher amount of fatty chains.

368 Regarding chemical resistance, FACEs exhibit good stability in several acids, such as pure acetic

369 acid, concentrated hydrochloric acid (37%) or sulfuric acid (until 5 M), whatever the fatty chain

370 length and the DS are. By contrast, FACEs are destroyed after only a 2 h immersion in pure

371 sulfuric acid. Moreover, when FACEs are immersed in potassium hydroxide or sodium

372 hydroxide (until 10 mol/L), the contact angle decreases from about 95° to 25°. This change is

373 attributed to the formation of a thin film of salt (sodium or potassium carbonate) covering the

374 film surface, but no chemical surface modification occurred on the material chemical structure

375 since no significant changes in FT-IR analyses were observed.

376 FACEs with DS1.7 seem to be as resistant as DS3. These results show a high stability of FACEs

377 against strong acids (except pure sulfuric acid) and bases for a substantial time (until two weeks).

378

379 **4. Conclusion**

380 Fatty acid cellulose esters with different chain length (from C10 to C16) and various degree of

381 substitution (from 1.7 to 3) have been successfully synthetized in homogeneous medium and

382   converted into films by casting. From a structural point of view, all materials exhibit a layered

383   structure in which the alkyl chains are perpendicular to the cellulosic chains planes, whatever the

384   DS and chain lengths are. As soon as the alkyl chain length is long enough (C16), the lower the

385   DS is, the higher the alkyl chain is able to crystallize. Regarding the mechanical behavior, all

386   FACEs films exhibit a thermoplastic behavior which more depends on alkyl chain length than on

387   the DS. In particular, a significant increase of the stress level combined with a drop of the strain

388   at break are clearly observed as the fatty chain length increases. By contrast, no major effect of

389   the DS on mechanical behavior is observed, especially for FACEs with long alkyl chain length.

390   Concerning their chemical resistance, all FACEs exhibit high stability in both acid and bases

391   whatever the DS. This study highlights for the first time that there is no gain to fully substitute

392   cellulose esters since FACEs with a DS between 1.7 and 3 exhibit similar mechanical properties

393   and chemical resistance to acidic and basic solutions. Various applications may be considered for

394   these FACEs such as chemical bottle coatings, or acid or base protection films.

395

399

6. References

400   **6. References**

401   Chauvelon, G., Gergaud, N., Saulnier, L., Lourdin, D., Buléon, A., Thibault, J.F., & Krausz, P.

402   (2000). Esterification of cellulose-enriched agricultural by-products and characterization of

403   mechanical properties of cellulosic films carbohydrate. *Carbohydrate Polymers*, *42*, 385-392.

404

20

405 Crépy, L., Chaveriat, L., Banoub, J., Martin, P., & Joly, N. (2009). Synthesis of cellulose fatty

406 esters as plastics – Influence of the degree of substitution and the fatty chain length on

407 mechanical properties. *ChemSusChem, 2*, 165-170.

408

409 Crépy, L., Miri, V., Joly, N., Martin, P., & Lefebvre, J.-M. (2011) Effect of chain side length on

410 structure and thermomechanical properties of fully substituted cellulose fatty esters.

411 *Carbohydrate Polymers*, *83*, 1812-1820.

412

413 Danjo, T., & Iwata, T. (2018). Syntheses of cellulose branched ester derivatives and their

414 properties and structure analyses. *Polymer, 137,* 358-363.

415

416 Dawsey, T.F., & McCormick, C.L. (1990). The lithium chloride/dimethylacetamide solvent for

417 cellulose: a litterature review. *Journal of Macromolecular Science Reviews Macromolecular*

418 *Chemistry and Physics, 30*, 405-440.

419

420 Dupont, A.L. (2003). Cellulose in lithium chloride/*N,N*-dimethylacetamide, optimisation of a

421 dissolution method using paper substrates and stability of the solutions. *Polymer*, *44*, 4117-4126.

422

423 Edgar, K.J., Buchanan, C.M., Debenham, J.S., Rundquist, P.A., Seiler, B.D., Shelton, M.S., &

424 Tindall, D. (2001). Advances in cellulose ester performance and application. *Progress in*

425 *Polymer Science, 26*, 1605-1688.

426

427 Elchinger, P.H., Faugeras, P.A., Zerrouki, C., Montplaisir, D., Brouillette, F., & Zerrouki, R.

428 (2012). Tosylcellulose synthesis in aqueous medium. *Green Chemistry*, *14*(11), 3126-3131.

429

430 El Seoud, O.A., & Heinze, T. (2005). Organic esters of cellulose: New perspectives for old

431 polymers. In Polysaccharides 1: Structure, Characterization and Use; Book Series: Advances in

432 Polymer Science; Edited by: T. Heinze. *186*, 103-149.

433

434 Freire, C.S.R., Silvestre, A.J.D., Pascoal Neto, C., Belgacem, M.N., & Gandini, A. (2006)

435 Controlled heterogeneous modification of cellulose fibers with fatty acids: Effect of reaction

436 conditions on the extent of esterification and fiber properties. *Journal of Applied Polymer*

437 *Science*, *100*(2), 1093-1102.

438

439 Heinze, T., Dicke, R., Koschella, A., Kull, A.H., Klohr, E.A., & Koch, W. (2000). Effective

440 preparation of cellulose derivatives in a new simple cellulose solvent. *Macromolecular*

441 *Chemistry and Physics*, *201*, 627-631.

442

443 Huang, K., Xia, J., Li, M., Lian, J., Yang, X., & Lin, G. (2011). Homogeneous synthesis of

444 cellulose stearates with different degrees of substitution in ionic liquid 1-butyl-3-

445 methylimidazolium chloride. *Carbohydrate Polymers*, *83*(4), 1631-1635.

446

447 Joly, N., Granet, R., & Krausz, P. (2003). Crosslinking of Cellulose by Olefin Metathesis.

448 *Journal of Carbohydrate Chemistry*, *22*, 47-55.

449

450 Joly, N., Granet, R., Branland, P., Verneuil, B., & Krausz, P. (2005). New methods for acylation

451 of pure and sawdust - extracted cellulose by fatty acid derivates – thermal and mechanical

452 analyses of cellulose-based plastic films. *Journal of Applied Polymer Science*, *97*, 1266-1278.

453

454 Joly, N., Martin, P., Liénard, L., Rutot, D., Stassin, F., Granet, R., Krausz, P., & Cavrot, J.P.

455 (2006). Effect of degree of substitution on the mechanical and thermomechanical properties of

456 lauroyl cellulose ester films. *E-Polymers*, *70*, 1-9.

457

458 Klarman, A.F., Galanti, A.V., & Sperling, L.H. (1969). Transition temperatures and structural

459 correlations for cellulose triesters. *Journal of Polymer Science*, *7*, 1513-1523.

460

461 Li, J., Wang, H., Kong, L., Zhou, Y., Li, S., & Shi, H. (2018). Phase Transition and Side-Chain

462 Crystallization of Poly(methyl vinyl ether-alt-maleic anhydride)-g-Alkyl Alcohol Comb-like

463 Polymers, *Macromolecules, 51*, 8922-8931.

464

465 Mantese Sander, M., Nicolau, A., Guzatto, R., & Saios, D. (2012). Plasticiser of oleic acid

466 polyester on polyethylene and polypropylene. *Polymer Testing*, *31*, 1077-1082.

467

468 Ning, W., Xingxiang, Z., Haihui, L., & Jianping, W. (2009). *N,N*-dimethylacetamide/lithium

469 chloride plasticized starch as solid biopolymer electrolytes. *Carbohydrate Polymers*, *77*, 607-

470 611.

471

472 Peydecastaing, J., Vaca-Garcia, C., & Borredon, E. (2011) Interactions with water of mixed

473 acetic-fatty cellulose esters. *Cellulose*, 18, 1023-1031.

474

475 Pérez, S. (2000). Initiation à la Chimie et à la Physico-Chimie Macromoléculaires. 1st ed; GFP

476 Ed: Strasbourg, France, Vol. 13, Chapter 1.

477

478 Qian, Y.Q., Han, N., Bo, Y.W. , Tan, L.L. , Zhang, L.F., & Zhang, X.X. (2018). Homogeneous

479 synthesis of cellulose acrylate-g-poly (n-alkyl acrylate) solid–solid phase change materials via

480 free radical polymerization. *Carbohydrate Polymers*, 193, 129-136.

481

482 Satgé, C., Verneuil, B., Branland, P., Granet, R., Krausz, P., Rozier, J., & Petit, C. (2002). Rapid

483 homogeneous esterification of cellulose induced by microwave irradiation. *Carbohydrate*

484 *Polymers*, *49*, 373-376.

485

486 Satgé, C., Verneuil, B., Branland, P., & Krausz, P. (2004). Synthesis and properties of

487 biodegradable plastic films obtained by microwave-assisted cellulose acylation in homogeneous

488 phase. *Comptes Rendus Chimie*, *7*, 135-142.

489

490 Sealey, J.E., Samaranayake, G., Todd, J.G., & Glasser, W.G. (1996). Novel cellulose derivatives.

491 IV. Preparation and thermal analysis of waxy esters of cellulose. *Journal of Polymer Science:*

492 *Part B: Polymer Physics*, *34*, 1613-1620.

493

494 TAPPI Press-Viscosity of pulp (capillary viscosimeter method). (1990) TAPPI test methods

495 1991. (1990). Atlanta: Tappi Press. 1, Ref. T230 om-89.

496

497 Vaca-Garcia, C., Thiebaud, S., Borredon, M.E., & Gozzelino, G. (1998). Cellulose esterification

498 with fatty acids and acetic anhydride in lithium chloride/*N,N*-dimethylacetamide medium.

499 *Journal of the American Oil Chemists' Society*, *75*, 315-319.

500

501   Vaca-Garcia, C., Gozzelino, G., Glasser, W.G., & Borredon, M.E. (2003). Dynamic mechanical

502   thermal analysis transitions of partially and fully substituted cellulose fatty esters. *Journal of*

503   *Polymer Science: Part B: Polymer Physics*, *41*, 281-288.

504

505   Wang, P., & Tao, B.Y. (1994). Synthesis and characterization of long-chain fatty-acid cellulose

506   ester (FACE). *Journal of Applied Polymer Science*, *52*, 755-761.

507

508   Wang, P, & Tao, BY (1995) Synthesis of cellulose-fatty acid esters for use as biodegradable

509   plastics. *Journal of Environmental Polymer Degradation*, 3, 115–119.

510

511   Willberg-Keyrilaïnen, P., Vartiainen, J. Harlin, A., & Ropponen, J. (2017). The effect of side-

512   chain length of cellulose fatty acid esters on their thermal, barrier and mechanical properties.

513   *Cellulose, 24,* 505-517.