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Substitution degree and fatty chain length influence on structure and properties of Fatty Acid Cellulose esters.

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24 **Abstract**

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

38

39 **Keywords**

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

42

43 **1. Introduction**

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

49 dedicated to the fatty acylation of cellulose synthesis, either in heterogeneous (Wang & Tao,
50 1994; Chauvelon *et al.*, 2000; Freire, Silvestre, Pascoal Neto, Belgacem & Gandini, 2006) , or in
51 homogeneous media, such as LiCl/N,N-dimethylacetamide (Heinze *et al.*, 2000; Satgé, Verneuil,
52 Branland, & Krausz, 2004; Joly, Granet, Branland, Verneuil & Krausz, 2005) or ionic liquids (El
53 Seoud & Heinze, 2005; Huang *et al.*, 2011), mainly using fatty acyl chlorides or esters as
54 reagents. Some of these studies, including ours (Joly *et al.*, 2006; Crépy, Chaveriat, Banoub,
55 Martin & Joly, 2009), are dedicated to the determination of mechanical and/or thermal and/or
56 structural properties of Fatty Acid Cellulose Esters (FACEs) (Klarman, Galanti & Sperling,
57 1969; Sealey, Samaranayake, Todd & Glasser, 1996; Edgar *et al.*, 2001; Vaca-Garcia, Gozzelino,
58 Glasser & Borredon, 2003), which is a great deal if we consider the investigations on the
59 potential applications of such bio-based materials.

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

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

thermoplastic and hydrophobic FACE materials and in continuation of our previous works, the present study deals with the influence of substitution degrees (DS) on structure and properties of partially substituted FACES. We are dealing here with a complete range of FACES bearing fatty chains ranging from C10 to C16 with moderate to high DS values. The structural, thermal, thermomechanical analysis and chemical resistance of cellulose esters were systematically performed using Wide Angle X-ray Scattering (WAXS), Differential Scanning Calorimetry (DSC), and uniaxial tensile tests. The final goal of this investigation is to determine the structure-property relationships of FACES according to both degree of substitution and fatty chain length.

2. Experimental Part

2.1. Materials

All reagents were stored at room temperature and were used without further purification: microcrystalline cellulose (20 μ m, DP = 150, Aldrich); *N,N*-dimethyl-4-aminopyridine (DMAP, 99%, Acros); *N,N*-dimethylacetamide (DMAc, 99%, Acros); anhydrous lithium chloride (99%, Acros); decanoyl chloride (98%, Aldrich); lauroyl chloride (98%, Aldrich); myristoyl chloride (\geq 99%, Fluka); palmitoyl chloride (98%, Acros); chloroform (\geq 99%, Carlo Erba); methanol (\geq 99%, Carlo Erba); acetic acid (\geq 99%, Acros), hydrochloric acid (37%, Acros); sulphuric acid (95%, Acros); sodium hydroxide (\geq 99%, Acros); potassium hydroxide (\geq 99%, Acros). Deuterated chloroform was purchased from Aldrich and stored at 4°C.

2.2. Acylation of cellulose by acyl chlorides

In a typical experiment, a 20 g.L⁻¹ cellulosic solution, consisting in pre-treated cellulose in a 6.7% LiCl/DMAc (v/w) system (Joly, Granet & Krausz, 2003) (150 mL; 3 g; 18 mmol of anhydroglucose unit, 1 equiv.) and DMAP (6.6 g; 54 mmol; 3 equiv.) were stirred at 80°C until 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 (^1H -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

125 **2.4. Structural characterization**

126 Wide-Angle-X-ray Scattering (WAXS) experiments were carried out on a Genix microsource
127 (XENOCS) equipment using the Cu K α radiation ($\lambda=1.54$ Å). Primary beam was collimated and
128 monochromatized by a FOX2D-12Inf optic (Xenocs, France), and the WAXS patterns were
129 collected on a CCD VHR detector (Photonic Sciences). The experiments were led at room
130 temperature in transmission mode. Standard corrections were applied to the WAXS patterns
131 before their treatments. The intensity profiles were obtained by 360° azimuthal integration of the
132 2D WAXS patterns using the fit2D software®.

133

134 **2.5. Thermal behavior**

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

139

140 **2.6. Mechanical behavior**

141 Mechanical behavior was studied in uniaxial tensile mode using an Instron 4466 apparatus.
142 Tensile testing was conducted at room temperature, using specimens with L₀= 24 mm and l₀= 5
143 mm gauge length and width, respectively. The tensile tests were carried out at a constant
144 crosshead speed of 1.44 mm.min⁻¹ which corresponds to an initial strain rate of 1.10⁻³ s⁻¹. The
145 nominal stress σ and strain ϵ are defined conventionally as the ratio $F/(l_0 \cdot e_0)$ and $(L-L_0)/L_0$,
146 respectively.

147

148 **2.8. Contact Angle Measurements**

Contact angles were determined at room temperature and ambient humidity, using an Apollo Instruments OCA 20 contact angle apparatus operating with the sessile drop method, with a water drop of 3 μ L. All contact angles were measured on both sides of the drop by the ellipse-fitting calculation method, at a drop age of 1s. Each contact angle reported here is an average of at least 4 values obtained on the sample surface. A contact angle value higher than 90° indicates that the material sample surface is hydrophobic.

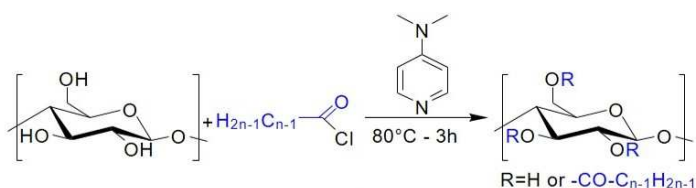
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156 **3. Results and Discussion**

Cellulose modification was performed in homogeneous media. This polysaccharide is known to be insoluble in classical organic solvents and water. Microcrystalline cellulose can be dissolved and chemically modified in aqueous NaOH solution (Elchinger et al., 2012), but this water-based solvent is not convenient as media for the synthesis of FACEs. Nevertheless, particular solvent systems such as lithium chloride/*N,N*-dimethylacetamide (LiCl/DMAc) (Dawsey & McCormick, 1990), have to be used to dissolve this polysaccharide. This solvent system is suitable for chemical reaction onto cellulose as it is underivatizing and do not degrade the natural polymer in time (Dupont, 2003).

Synthesis of plastic materials was performed by grafting fatty acids, used as internal plasticization, onto cellulose. Fatty acid chain lengths were ranged from decanoyl (C10) to palmitoyl (C16), corresponding to the major fatty acids found in vegetal oil triglycerides. FACEs (Figure 1) were obtained by a method described elsewhere (Crépy, Chaveriat, Banoub, Martin & Joly, 2009; Joly, Granet, Branland, Verneuil & Krausz, 2005), consisting in the reaction between fatty acid chlorides and cellulose. To trap HCl produced during reaction, we use DMAP, *i.e.* *N,N*-dimethylaminopyridine, a basic catalyst often used for this kind of reaction, in a large 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

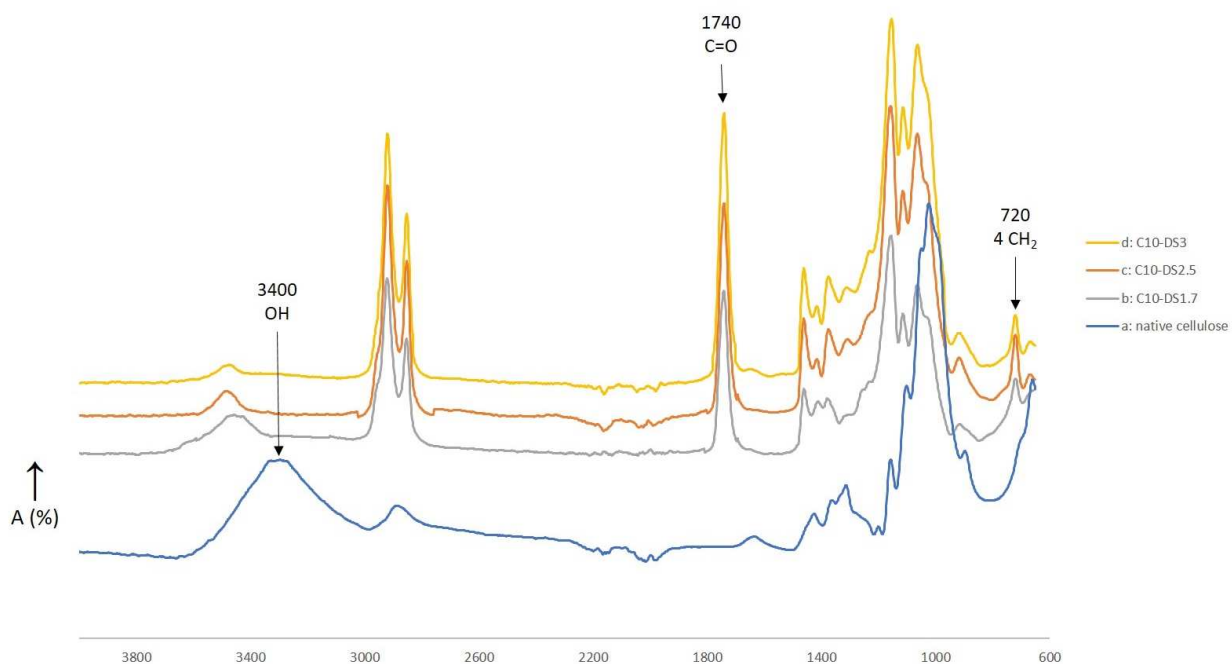
175
 176 **Figure 1:** fatty acid cellulose esters (FACEs).

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 $2800\text{-}2900\text{ cm}^{-1}$ (-CH- antisymmetric and symmetric stretching of -CH₂-
 185 and -CH₃), 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 -CH₂- groups (-CH₂)₄- rocking). That means that fatty chains have been directly
 189 grafted onto cellulose by an ester junction.

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. ^1H -NMR analysis

198 ^1H -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 ^1H -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 ^1H -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 & Saio (2012). However, in our study, only the fatty acid chains directly linked to the

cellulosic backbone, is used as an internal plasticizer. Figure 3 regroups FACES with traces of free fatty chains (Figure 3a) or DMAc (Figure 3b) in CEs films.

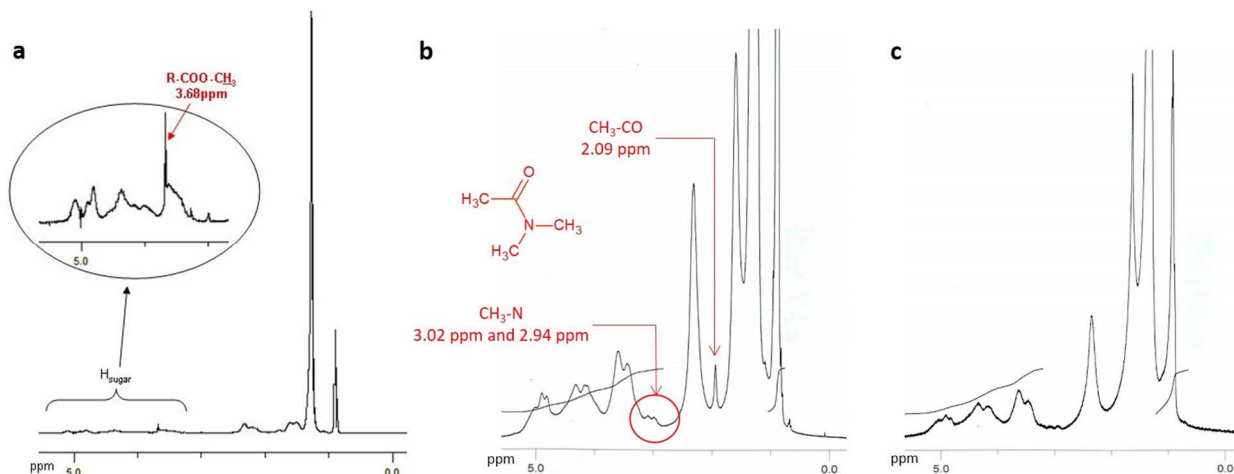


Figure 3: ¹H-NMR spectra of C12-DS3 containing free methyl fatty chains (a), or traces of DMAc (b), and pure C12 (c).

If the FACES are not pure, unexpected signals can appear on ¹H NMR spectra. A peak can be observed at 3.68 ppm and has already been identified in a previous work (Crépy, Chaveriat, Banoub, Martin & Joly, 2009) as free fatty acid methyl ester. Three other peaks can also be observed at 3.02 ppm, 2.9 ppm and 2.09 ppm, and were attributed to DMAc methyl groups. In order to evaluate the influence of both grafted fatty chain length and FACES degree of substitution, we have to be sure that residual solvent and free fatty acid methyl esters are eliminated, i.e. the missing of corresponding undesirable peaks on FACES ¹H NMR spectra. Consequently, purification steps are performed until complete disappearance of these undesirable peaks (figure 3c).

The degrees of substitution (DS) for all the cellulose derivatives were also evaluated using ¹H-NMR integrations and the results are reported in Table 1, according to the reaction conditions.

Table 1: Results of FACES synthesis. Molar conversion was determined according to DS of 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

FACES DS variation was studied according to the amount of fatty acid chloride introduced in the reaction mixture, but also to fatty chain lengths. The aim was first to graft enough fatty acid chains so that FACES exhibit thermoplastic properties, *i.e.* to obtain a minimal DS of 1.5 (Edgar et al., 2001). Thus, for C10 fatty chains, a DS of 1.7 was obtained using 5.5 eq. of fatty acid chloride (according to anhydroglucose unit amount). As expected, the higher the fatty acid chloride amount is, the higher substitution degree is, until a value of 3.0 using 9 eq. of decanoyl chloride. Comparing fatty chain length influence on DS, to obtain FACES with DS 1.7, the fatty acid chain amount can be decreased to 4.5 equiv. when increasing fatty chain length to 16 carbons. Even if the reactivity of fatty acids is supposed to slightly decrease with the increase of their chain length, this phenomenon seems to be thwarted by a steric effect favoring fatty acid chloride reaction, *i.e.* the longer the fatty chain is, the more it allows to separate polymer chains as well as the already grafted substituents, the more additional substituents have the space to react. This is also observed comparing other DS values according to fatty chain lengths and amounts, leading to conclude that, for a fixed DS value, the longer the fatty chain is, the lower the amount of fatty acid chloride is needed.

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.

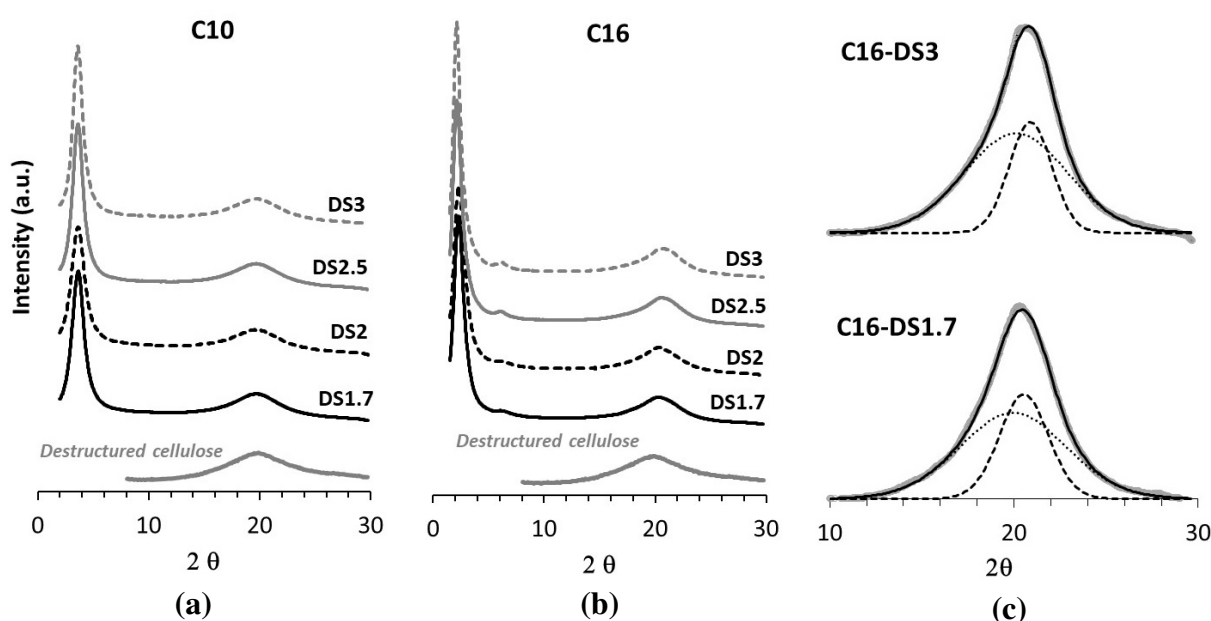
248

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 ($2\theta \approx 2-4^\circ$) and a broad and weak halo in the region $2\theta \approx$
253 $16-24^\circ$. 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 $2\theta = 10-28^\circ$ 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.



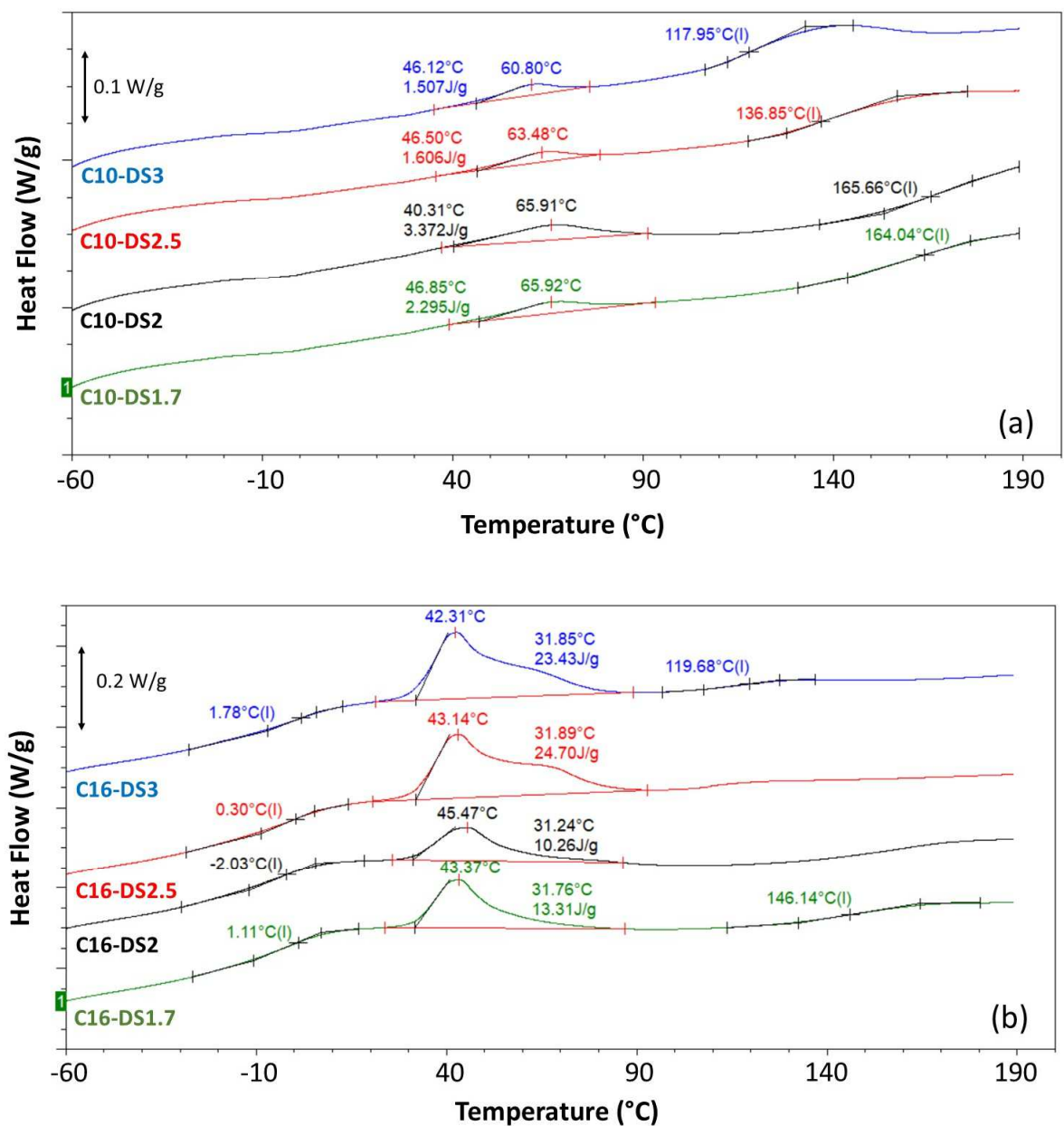
278
 279 **Figure 4:** X-ray diffractograms of the FACE cast films as a function of degree of substitution (a)
 280 case of C10 series (b) case of C16 series (c) deconvoluted peaks superimposed on the
 281 experimental curves for C16-DS3 and C16-DS1.7.

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-Keyriläinen et al. for
294 FACEs with DS lower than 1.0 (Willberg-Keyriläinen, 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 \pm 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

308 a temperature range lower than $T=-60^{\circ}\text{C}$, as previously shown for fully substituted FACEs
 309 (Crépy, Miri, Joly, Martin & Lefebvre, 2011).



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.

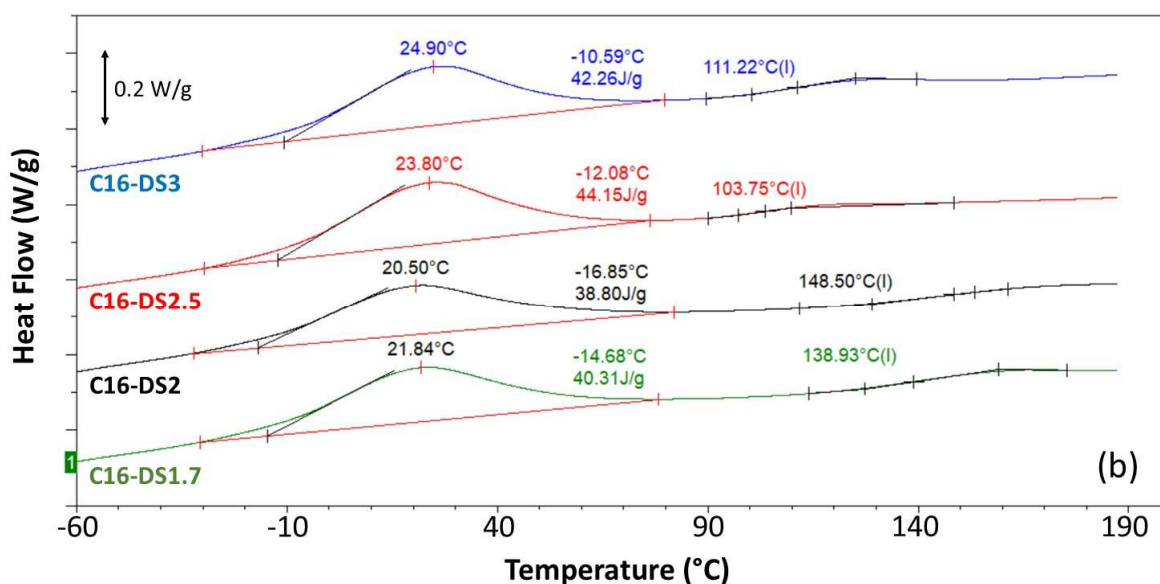
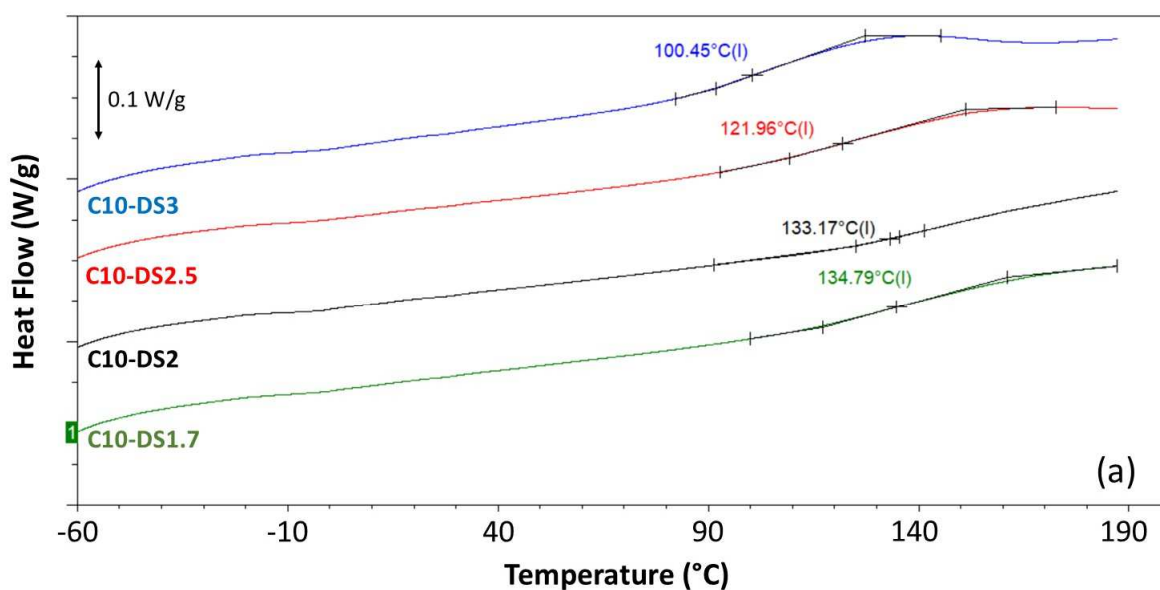
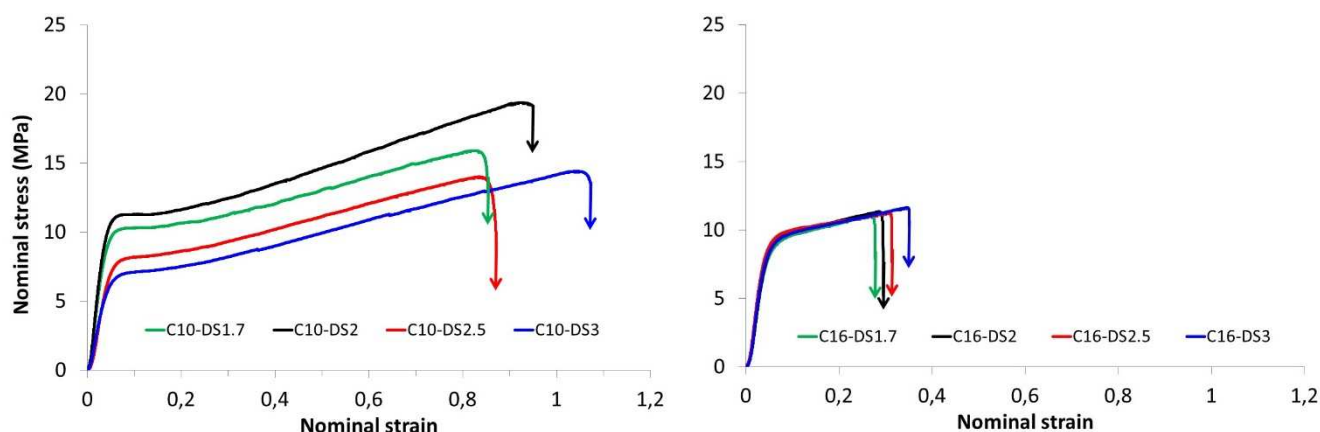


Figure 6: Second heating thermograms of the cellulose derivatives cast films (endotherm up) (a) case of C10 (b): case of C16.

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 $T=20^{\circ}\text{C}$. (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

$\theta(^{\circ})$	C10	C12	C16
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	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)	$\theta=25^{\circ}\pm 1^{\circ}$ Thin white film on the surface					
KOH (10mol/L)	$\theta=25^{\circ}\pm 1^{\circ}$ Thin white film on the surface					

We notice an increase of the hydrophobicity as fatty chain length increases in good agreement with previous study (Crépy, Chaveriat, Banoub, Martin & Joly, 2009). This behavior is strengthened as DS increases, according to higher amount of fatty chains.

Regarding chemical resistance, FACEs exhibit good stability in several acids, such as pure acetic acid, concentrated hydrochloric acid (37%) or sulfuric acid (until 5 M), whatever the fatty chain length and the DS are. By contrast, FACEs are destroyed after only a 2 h immersion in pure sulfuric acid. Moreover, when FACEs are immersed in potassium hydroxide or sodium hydroxide (until 10 mol/L), the contact angle decreases from about 95° to 25°. This change is attributed to the formation of a thin film of salt (sodium or potassium carbonate) covering the film surface, but no chemical surface modification occurred on the material chemical structure since no significant changes in FT-IR analyses were observed.

FACEs with DS1.7 seem to be as resistant as DS3. These results show a high stability of FACEs against strong acids (except pure sulfuric acid) and bases for a substantial time (until two weeks).

4. Conclusion

Fatty acid cellulose esters with different chain length (from C10 to C16) and various degree of substitution (from 1.7 to 3) have been successfully synthesized 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

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399

400 **6. References**

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