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Homogeneous acylation of Cellulose diacetate: Towards bioplastics with tuneable thermal and water transport properties

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ABSTRACT:

In this study, we report a simple, non-degrading and efficient homogeneous acylation of cellulose diacetate (CDA) by using a large panel of commercially available acylating aliphatic moieties, differing in their structure (fatty, ramified, bulky, cycloaliphatic, aromatic, more or less spaced from the cellulose backbone), in view of generating a library of well-defined cellulose mixed esters with enhanced thermoplasticity. As reflected by a lowering of the glass temperature (T_g), the covalent grafting confers an improved mobility to the cellulose chains, by disrupting the initial H-bonds. In particular, it appears that the gain in free volume is tailored by the substituent structure and that acylating reagents consisting in a terminal bulky moieties spaced from CDA chains by a linear chain efficiently separate macromolecular chains without generating detrimental stiffening interactions (low T_g around 125 °C). Moreover, free-standing films easily prepared by solvent casting exhibit relevant water transport properties, which are closely dictated and tuned by the water solubility of the cellulose mixed ester.

KEYWORDS: cellulose diacetate, cellulose mixed ester, acylation, plasticization, T_g , fatty chains, water permeability

1. Introduction

For a number of years, much attention has been focused on research to replace petroleum-based commodity plastics by biosourced materials offering competitive properties. In this frame, cellulose diacetate (CDA), the most important ester of cellulose is an excellent candidate produced and available at industrial scale (Simon, Muller, Koch, & Muller, 1998; Rustmeyer, 2004) mainly used as synthetic fibers in the manufacture of cigarette filters and textile field. CDA is characterized by a degree of substitution (DS) between 2.2 to 2.7, i.e. an average of 2.2 to 2.7 acetate groups per one anhydroglucose unit (AGU). In this DS range, cellulose acetate is soluble in acetone, allowing for its transformation into filaments through wet spinning processes employed at the industrial scale (Edgar, Buchanan, Debenham, Rundquist, Seiler, Shelton, & Tindall, 2001). However, for plastic applications, cellulose diacetate is not easily melt-processable and cannot be shaped as such by conventional extrusion or injection processes. Indeed, due to the presence of strong intermolecular and intramolecular hydrogen bonds developed between the residual hydroxyl functions, the glass temperature (T_g) is high compared to more conventional thermoplastics and the melting temperature of cellulose diacetate is close to its decomposition temperature ($\sim 240^\circ\text{C}$) (Kamide, & Saito, 1985). Consequently, the processing window is too narrow. Therefore, it is challenging to obtain melt-processable cellulose diacetate without thermal degradation and the cornerstone to target a thermoplastic processing of CDA is to disrupt the hydrogen-bonded network. For this purpose, CDA needs to be plasticized. Plasticization enhances the overall CDA chain mobility and as a consequence lowers the T_g . Typically, low molecular weight external plasticizers are added to cellulose acetate (Park, Misra, Drzal, & Mohanty, 2004; Wypych, 2004; Fordyce, & Meyer, 1940; Lee, & Shiraishi, 2001; Selinger, & Brine, 1988). Small molecules such as phthalates (McBrierty, Keely, Coyle, Xu, & Vij, 1996), triacetin (Quintana, Persenaire, Lemmouchi, Sampson, Martin, Bonnaud, & Dubois, 2013), glycerol

(Gutiérrez, De Paoli, & Felisberti, 2012), or lactones (Warth, Mulhaupt, & Schätzle, 1996) have been currently used because of their good compatibility with cellulose acetate, their low cost and their easy handling. Ionic liquids, such as 1-butyl-3-methylimidazolium chloride, have also been used as efficient plasticizer of cellulose acetate (Bendaoud, & Chalamet, 2014). Nowadays, plasticized cellulose acetate is utilized in various fields (aeronautic, films for photography or eyeglass frames) notably because of its interesting transparency, gloss and silky feel properties (Edgar, Buchanan, Debenham, Rundquist, Seiler, Shelton, & Tindall, 2001). However, these processes require generally a substantial amount of plasticizers (~ 30 wt.%). These additives can be subjected to exudation towards the surrounding medium or to volatilization which is prone to jeopardize the initial properties of the materials, leading to a weakening of its performance and its accelerated aging. Additionally, the plasticizer migration could imply serious hazards to health or environment (Quintana, Persenaire, Bonnaud, & Dubois, 2012; Ghiya, Dave, Gross, & McCarthy, 1996). Thus, for many applications, this kind of melt-processable CDA materials is impractical. In order to circumvent this issue, the covalent attachment onto the cellulose acetate backbone of molecules able to directly play the role of plasticizers appears as a relevant approach (defined as internal plasticization). The grafted substituents are expected to destroy H-bonds and consequently to promote the overall motion of the macromolecular chains. Also, the conversion of hydroxyl groups can impart CDA with much new functionality. As a function of the acetylation degree, cellulose acetate offers reactive hydroxyl sites able to be chemically substituted (Joly, Granet, Branland, Verneuil, & Krausz, 2005; Frisoni, Baiardo, & Scandola, 2001; Nishio, 2006). To that extent, cellulose acetate was subjected to various chemical modifications in melt state or in solvent conditions. The existing literature mainly concerns the modification of cellulose acetate having a DS between 2.1 to 2.5 through esterification derivatizations. One can cite works

dealing with reactions with cyclic esters, such as ϵ -caprolactone (Szamel, Domjan, Klébert, & Pukánszky, 2008) and/or L-lactide (Vidéki, Klébert, & Pukánszky, 2007; Chenghu, Jinming, Yuxia, Jian, Jin, Jun, & Jiasong, 2004), with preformed oligomers of ϵ -caprolactone (Klébert, Nagy, Domján, & Pukánszky, 2009) or even with maleic anhydride (Lee, & Shiraishi, 2001) in presence or not of catalyst (Yoshioka, Hagiwara, & Shiraishi, 1999) and generally achieved in bulk reactive extrusion process (Warth, Mülhaupt, & Schätzle, 1997). However, external plasticizers were often concomitantly added into the reactional medium to be used as processing aids. Therefore, cellulose acetate chemical modification in solution appears as an attractive approach because of the possibility to achieve the chemical derivatization at low temperature and to easily remove the solvent after the reaction. Such approach was also exploited for the thermoplasticization of raw cellulose in view of broadening its range of applications (Chen, Zhang, Xiao, Tian, & Zhang 2018; Tanaka, Iwata, & Iji 2017). Regarding cellulose acetate derivatization, the main concern of this work, we can cite the Iji team, which has significantly attempted to modify cellulose acetate in solvent medium (dioxane). For example, these authors were interested in CDA (DS = 2.1 and DS = 2.4) modifications with cardanol. For this purpose, they used an acyl chloride cardanol (Iji, Moon, & Tanaka, 2011) and an isocyanate-functionalized cardanol, allowing for the formation of ester and urethane linkage (Tanaka, Honzawa, & Iji, 2013). Significant decreases of T_g , depending on the extent of modification, were reported especially for CDA modified by the acyl chloride cardanol. The authors evidenced insufficient thermoplasticity for CDA modified with isocyanate modified cardanol, and they ascribed it to too high interactions between the side grafts. Thus, they demonstrated that the substitution of acetyl by propionyl group considerably improved the thermoplasticity of the cardanol-bonded cellulose derivative. Otherwise, the same team described the post-modification of cardanol-modified CDA (through the esterification route)

with aliphatic and aromatic acylating reactants, such as heptanoic acid chloride, lauric acid chloride, stearic acid chloride, and benzoic acid chloride alone or in mixture (Iji, Toyama, & Tanaka, 2013). As a function of the DS, they measured lower T_g values around 147-149°C. Stearic acid chloride was also bonded onto non-modified CDA and T_g of 155°C and 145°C were collected for cellulose mixed esters with a DS of 0.31 and 0.51, respectively. Note that the same authors were interested in the addition of reinforcing agents, such as olefin resins (Kiuchi, Soyama, Iji, Tanaka, & Toyama, 2014), modified silicones (Soyama, Kiuchi, Iji, Tanaka, & Toyama, 2014) or polyester resins and glass fibers (Soyama, & Iji, 2017) into CDA bearing cardanol moieties in order to improve the impact and the bending strength of the resulting composites.

In summary, despite many attempts dedicated to the post-modification of cellulose diacetate, the generation of cellulose diacetate-based melt-processable materials is still challenging, since they constitute highly appealing target biosourced polymers for large scale bioplastic applications. In this study, we investigated the homogeneous cellulose diacetate acylation and the close relationship existing between the structural characteristics of the acylating reagents and the final properties of the cellulose mixed esters. For this purpose, cellulose diacetate ($DS_{CDA} = 2.45$) is modified with a large panel of aliphatic acid chlorides (Fig. 1), by targeting different extents of modification ($0.05 < DS_{grafts} < 0.5$).

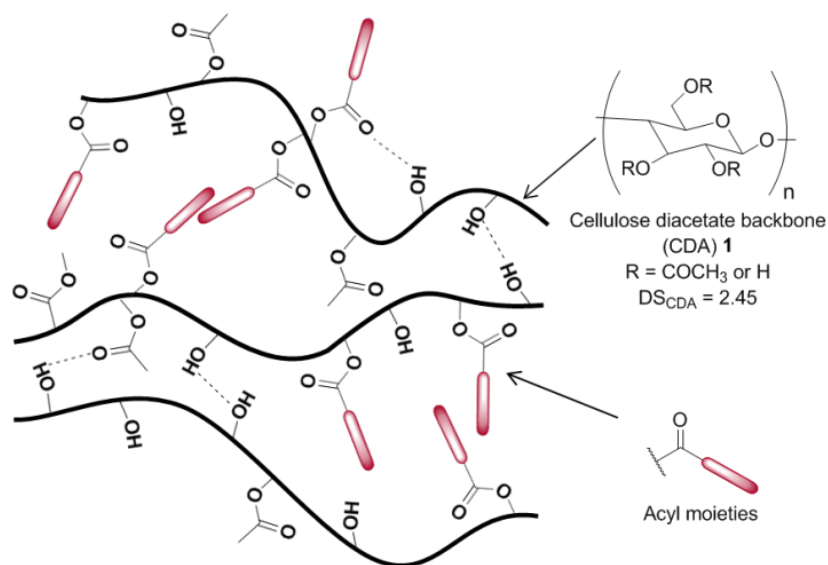


Fig. 1. Acylation of cellulose diacetate with acyl chlorides.

The selected acylating reagents differ in their chemical structure: series of fatty acyl with various chain lengths, ramified, more or less bulky, aromatic or cycloaliphatic with a spacer more or less short. The resultant cellulose mixed esters are in-depth characterized and a specific focus is devoted to the influence of the structural characteristics of the substituents on the plasticization effect. Finally, cellulose mixed ester-based films, successfully prepared by solvent casting are analyzed by dynamical mechanical analysis and the water transport properties of the cellulose diacetate-based thermoplastics are assessed. This work offers an attractive route to design promising bioplastics with tailored thermoplasticity and water permeability.

2. Experimental

2.1 Materials

Cellulose diacetate (CDA) **1** (DS in acetate groups, $DS_{CDA} = 2.45$) was supplied by Solvay (DS = average number of hydroxyl groups substituted by acetate groups per anhydroglucose unit (AGU)). Triethyl amine was supplied by Aldrich. Methanol and 1,4-dioxane were supplied by Carlo Erba. Butyryl chloride, hexanoyl chloride, octanoyl chloride, decanoyl chloride, dodecanoyl chloride, myristoyl chloride, stearoyl chloride, oleoyl chloride, furoyl chloride, 3,3-dimethylbutyryl chloride, cyclohexanecarbonyl chloride, cyclohexylacetyl chloride, 2-ethylhexanoyl chloride, 1-adamantanecarbonyl chloride, 1-phenylcyclopentanecarbonyl chloride, 4-heptylbenzoyl chloride and hydrocinnamoyl chloride were used as received from Aldrich. They were purchased at the highest commercial quality, and were used without further purification.

2.2 Characterizations

Infrared analysis (IR). FTIR spectra were recorded with a Nicolet iS10 (ThermoFisher Scientific) using attenuated total reflectance (Smart iTR Diamond) ATR and collecting 32 scans from 500 to 4000 cm^{-1} .

Size exclusion chromatography (SEC). Size exclusion chromatography (SEC) of cellulose diacetate and esterified cellulose acetate derivatives were carried out at 50 °C on a chromatograph connected to a Viscotek pump (1 mL/min) and Rheodyne 7725i manual injector (100 μL loop) using a combination of detectors (Viscotek VE3580 refractometer RI at 50°C and Viscotek T60A viscometer at room temperature), two Viscotek I-MBHMW-3078 columns and one Viscotek I-MBLMW-3078 column, 300 \times 7.5 mm (polystyrene/divinylbenzene) and pre-column viscotek I-GUARD-0478 and DMF/LiNTf₂ (10

mM) as the eluent. The samples were prepared in DMF/LiNTf₂ at a concentration of 3 mg/mL and filtered through 0.45 μm pore size PTFE filter prior to the measurements. *Nuclear Magnetic Resonance*. NMR spectra were recorded with Bruker 400 spectrometer (¹H: 400 MHz, 298 K and 64 scans; ¹³C: 100 MHz, 298K, 6000 scans) with CDCl₃ and DMSO-d₆ (only for samples 17a and 17b – Table 2) as solvents. The chemical shifts (δ, ppm) are referenced to the residual solvent peak in reference to the work done by Buchanan on the NMR characterization of the cellulose acetate (Buchanan, Edgar, Hyatt, & Wilson, 1991). The DS values of the final products (DS_{grafts}) were calculated from ¹H NMR spectra as follow:

$$DS_{graft} = \frac{7 \times I_{\delta_{graft}}}{3 \times I_{\delta_{3.0-5.5}}}$$

where $I_{\delta_{graft}}$ corresponds to the integral of a well-defined peak assigned to a chemical group belonging to the graft and $I_{\delta_{3.0-5.5}}$ represents the integral of the multiple peaks from δ3.0 to δ5.5 ascribed to **glucose protons**. Typical ¹H and ¹³C NMR spectra of cellulose acetate derivatives (hexanoate and hydrocinnamate) are shown in Fig. 3 and Fig. 4. *Thermogravimetric analysis (TGA)*. TGA measurements were performed under nitrogen (90 mL/min) using a TA Instruments TGA Q500 apparatus at a heating rate of 10 °C/min up to 580 °C. The thermal decomposition temperatures T_{d5%} and T_{dmax} stand for the temperature corresponding to a weight loss of 5% and to the maximum to the derived curve, respectively. *Differential scanning calorimetry (DSC)*. DSC analyses were carried out on a TA instrument Q10 or Q20 DSC. The samples were placed in sealed aluminium cells. The esterified cellulose derivatives were heated from 0 °C to 220°C (three heating cycles) and then cooled down from 220°C to 0°C (two cooling cycles) with a heating rate of 10°C/min under nitrogen atmosphere. The glass transition temperature (*T_g*) was determined from the second heating run and corresponds to the middle point.

Dynamical mechanical analysis (DMA). DMA experiments under shear mode were performed with a DMA/SDTA861° Mettler Toledo apparatus, equipped for rectangular samples and working in shear mode. Values of the shear storage, G' , and loss moduli, G'' , as well as the tangent of the loss angle, $\tan \delta = G''/G'$, were determined. This apparatus was especially dedicated to the study of films and composite materials. The average typical dimensions of the samples were $10 \times 8 \times 0.120\text{-}0.150 \text{ mm}^3$. The tests were performed under isochronal conditions at 1 Hz and each sample was heated from room temperature to 220°C at a heating rate of $3^\circ\text{C}\cdot\text{min}^{-1}$.

Water vapor transmission rate. Water vapor transmission rates (WVTR) were determined at 5°C and for a partial pressure gradient equal to 98-75% RH. WVTR were measured by the “wet cup method”. Films (typical thicknesses around $50 \mu\text{m}$) were sealed with epoxy glue between two aluminium foil masks, leaving an uncovered film area of diameter of 2.2 cm. The systems were then sealed on a hermetic lid of a glass jar of volume 32 mL. All actual exchange surfaces after deposition of epoxy resin were recalculated by optical analysis. The cup containing a potassium sulfate saturated aqueous solution (98% HR) was placed in a glove box humidified with sodium chloride saturated aqueous solution (75% HR) placed in a cold room (5°C). The water vapour partial pressure gradient was 2 mbar.

2.3 Synthesis of cellulose mixed ester by acylation of cellulose diacetate

Illustration with acylation by using butyryl chloride. CDA **1** (500 mg, 1.89 mmol, 1 eq/OH) was dissolved in 1,4-dioxane (9.5 mL, [0.2M]) by stirring at 90°C under a dry nitrogen atmosphere. Then, the reaction mixture was cooled to room temperature and anhydrous triethyl amine (0.26 mL, 1 eq/OH) was added. A solution of butyryl chloride (98 μL , 0.94 mmol, 1 eq/OH) in dehydrated 1,4-dioxane (4.7 mL, [0.2M]) was then slowly added drop

wise, and the mixture was refluxed for 15 hours under a nitrogen atmosphere. The reaction solution was poured into methanol (60 mL) at room temperature under vigorous stirring to isolate a solid product. The precipitated product was then filtered by filtration and washed with methanol (three times, 60 mL). The resulting white product was dried overnight at 80°C to obtain the sample **2** (459.5 mg, DS_{CDA} 2.45/DS_{Butyryl} 0.27, 98% yield). ¹H-NMR [CDCl₃, ppm]: δ0.92-1.00 (m, CH₃), 1.66 (m, CH₂), 1.94-2.12 (m, OAc), 2.33 (m, CH₂), 3.54 (CH_{sugar unit}, H₅), 3.70 (CH_{sugar unit}, H₄), 4.06 (CH_{sugar unit}, H₆), 4.41 (CH_{sugar unit}, H₁, H₆), 4.79 (CH_{sugar unit}, H₂), 5.07 (CH_{sugar unit}, H₃). The weight yield was calculated by dividing the mass obtained (calculated from the DS obtained from the ¹H NMR spectrum) by the theoretical mass obtained by considering quantitative esterification. The experimental protocol described above was used to prepare all acyl-bonded CDA. The operating conditions in terms of amount of acyl chloride were changed to vary the extent of the CDA modification (DS_{grafts}), as indicated in Table 1. The products resulting from the esterification with myristoyl chloride, and stearoyl chloride were more extensively purified (samples 7 and 8) due to the presence of additional undesired by-products. Therefore, after precipitation in methanol, the powder was filtrated and was subjected to extensive washing steps: - one washing in a mixture of diethyl ether/ethanol (1/1 v/v) during 1h, - three washings in ethanol and, - three washings in diethyl ether. The resulting white product was dried overnight at 80 °C to obtain the samples 7 and 8.

Solubility of cellulose mixed esters in organic solvents. The solubility of cellulose ester derivatives was determined by test tube solubility measurements. Each sample was introduced in a given solvent at a concentration of 50 mg/mL at room temperature for 24 hours and the samples were macroscopically referenced as soluble (+) or insoluble (-). The solvents tested are toluene, dimethyl sulfoxide, chloroform, tetrahydrofuran, ethanol, dichloromethane and acetone.

Preparation of cellulose mixed ester-based films by solvent casting. For dynamical mechanical analysis, the acylated CDA derivatives were dissolved in chloroform (**under mild agitation conditions by using a magnetic stirrer at around 300 rpm**) at a concentration of 10 wt %. The solutions were stirred for at least 24h at room temperature and then poured into a silicone mold covered with Teflon. The films were further air dried at room temperature to promote the slow solvent evaporation. Slow solvent evaporation prevents films from surface damaging and air bubbles. Final plasticized CDA films are measured as 2 cm in diameter and 120-150 μm thickness and are optically transparent (Fig. 6).

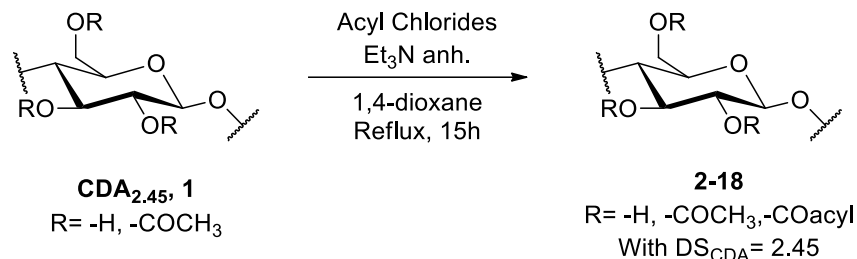
For water vapor transmission rates measurements. 50 mg of esterified CDA derivative was dissolved in 2 mL of dichloromethane. The solutions were stirred for at least 7h at room temperature and then poured into a 3 cm diameter glass petri dishes to promote slow solvent evaporation during at least 17 h. Typical film thicknesses were around 50 μm to perform suitable water permeation kinetics.

3. Result and discussion

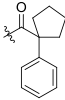
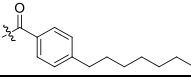
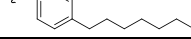
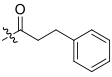
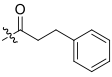
Acylation of cellulose diacetate: generation of cellulose mixed esters

Cellulose mixed esters were generated through a homogeneous acylation of cellulose diacetate ($DS_{\text{acetate}} = 2.45$) in dioxane with a series of commercially available aliphatic acid chloride moieties in presence of trimethylamine (table 1, samples 1 to 18). It is well known that acid chloride-mediated esterification in basic conditions is particularly efficient and proceeds in mild and not harsh conditions (low temperature, low reaction time). Triethylamine acts as i) a proton scavenger able to neutralize the progressive formation of HCl, avoiding any acidic hydrolysis of the glucosidic bonds and ii) as a reaction catalyst. Aiming at gaining insight on the influence of the structural characteristics of the substituent, a large panel of acylating reagents was utilized, such as fatty acyl with various chain lengths and having or not unsaturation (butyryl chloride, hexanoyl chloride, octanoyl chloride, decanoyl chloride, dodecanoyl chloride, myristoyl chloride, stearoyl chloride and oleoyl chloride samples 2 to 9, which correspond to the major fatty acids found in vegetable oil triglycerides), ramified (3,3-dimethylbutyryl chloride, 2-ethylhexanoyl chloride, samples 10 and 11), cycloaliphatic derivatives disposed more or less near to the cellulose chain (cyclohexanecarbonyl chloride and cyclohexylacetyl chloride, samples 12 and 13), very bulky (1-adamantanecarbonyl chloride, sample 14), heterocyclic (furoyl chloride, sample 15) and aromatic acid chlorides with various structures: crowded with an aliphatic ring, or associated with a linear chain besides or not the acyl function (1-phenylcyclopentanecarbonyl chloride, 4-heptylbenzoyl chloride and hydrocinnamoyl chloride, samples 16,17,18).

Table 1 Experimental conditions used for acylation of cellulose diacetate and features of the resulting cellulose mixed esters.



| N° | R (acyl) | Eq acyl chloride/O H | DS ^a | T _{d5%} (°C) ^b | T _{dmax} (°C) ^c | Residual mass% ^d | T _g (°C) ^e |
|------------------|---------------------|----------------------|-----------------|------------------------------------|-------------------------------------|-----------------------------|----------------------------------|
| 1 | $\text{CDA}_{2.45}$ | - | - | 321 | 367 | 10.7 | 192 |
| 2 | | 0.5 | 0.27±0.01 | 326 | 371 | 11.6 | 173 |
| 3 | | 1.0 | 0.32±0.02 | 302 | 359 | 12.0 | 162 |
| 4a | | 0.5 | 0.21±0.01 | 309 | 369 | 10.8 | 171 |
| 4b | | 0.8 | 0.26±0.01 | 339 | 375 | 10.3 | 158 |
| 4c | | 1.0 | 0.27±0.01 | 338 | 374 | 10.1 | 158 |
| 4d | | 1.3 | 0.31±0.02 | 340 | 376 | 9.2 | 157 |
| 5 | | 5.0 | 0.23±0.01 | 327 | 370 | 12.1 | 162 |
| 6 | | 5.0 | 0.22±0.01 | 342 | 378 | 8.8 | 161 |
| 7* | | 1.0 | 0.21±0.01 | 336 | 373 | 10.7 | 158 |
| 8a** | | 1.0 | 0.31±0.02 | 321 | 366 | 11.7 | 150 |
| 8b | | 5.0 | | <i>Product + by-products.</i> | | | |
| 9a | | 0.5 | 0.11±0.01 | 336 | 376 | 10.8 | 170 |
| 9b | | 5.0 | 0.24±0.01 | 330 | 379 | 12.0 | 160 |
| 10a | | 0.5 | 0.18±0.01 | 308 | 371 | 10.9 | 178 |
| 10b | | 5.0 | 0.41±0.02 | 322 | 370 | 10.6 | 168 |
| 11a | | 0.5 | 0.07±0.01 | 248 | 367 | 12.0 | 188 |
| 11b | | 5.0 | 0.23±0.01 | 277 | 368 | 11.5 | 164 |
| 12a | | 0.5 | 0.11±0.01 | 324 | 378 | 11.5 | 182 |
| 12b | | 5.0 | 0.45±0.02 | 266 | 339 | 13.9 | 174 |
| 13a | | 0.5 | 0.10±0.01 | 295 | 371 | 9.6 | 173 |
| 13b | | 5.0 | 0.45±0.02 | 336 | 369 | 12.7 | 164 |
| 14a | | 0.5 | 0.11±0.01 | 270 | 368 | 12.2 | 192 |
| 14b | | 5.0 | 0.30±0.02 | 306 | 361 | 11.3 | 186 |
| 15a ^f | | 0.5 | 0.22±0.01 | 246 | 364 | 12.2 | <i>Nd</i> |
| 15b ^f | | 5.0 | 0.33±0.02 | 277 | 366 | 11.9 | 175 |

| | | | | | | | |
|-----|---|-----|-----------|-----|-----|------|-----|
| 16 |  | 0.5 | 0.24±0.01 | 343 | 376 | 12.2 | 194 |
| 17a |  | 0.5 | 0.09±0.01 | 294 | 374 | 10.9 | 169 |
| 17b |  | 5.0 | 0.14±0.01 | 318 | 372 | 12.1 | 179 |
| 18a |  | 0.5 | 0.21±0.01 | 300 | 366 | 12.2 | 174 |
| 18b |  | 5.0 | 0.52±0.03 | 323 | 374 | 11.6 | 125 |

^a Calculated from ¹H NMR spectroscopy.

^b Temperature corresponding to a weight loss of 5%.

^c Temperature corresponding to the maximum of the derived TGA curve.

^d For complete thermal degradation, determined by TGA.

^e Glass temperature determined *T_g* by DSC

* Additional purification in ethanol/diethyl ether mixture. ** Additional purification in ethanol/diethyl ether mixture and esterification in dioxane with 10% of dichloromethane

The reaction mixture was poured into methanol and after multiple washings, cellulose mixed esters were recovered in good yield (> 90%), as white powder. For samples 7 and 8a, more extensive purification steps were achieved. Indeed, the presence of undesired by-products was emphasized and additional washings in ethanol/diethyl ether mixtures were required for the purification. The reproducibility of the acylation derivatizations was verified. The solubility of each acyl-bonded cellulose diacetate derivatives was investigated in various common solvents such as toluene, DMSO, CHCl_3 , THF, CH_2Cl_2 , EtOH and acetone, to be compared to unmodified cellulose diacetate (Table S1). Firstly, note that all acylated derivatives remain soluble in dioxane during the esterification reaction. As for unmodified CDA, the cellulose mixed esters are soluble in DMSO, THF, acetone and DMF and most of esterified CDA derivatives become soluble in chlorinated solvents, such as CH_2Cl_2 and CHCl_3 (except for 10a, 15 a and 15b). The derivatives are insoluble in very apolar or polar solvents, as toluene and EtOH. The esterification ligation step enlarges the range of good solvents which would facilitate the characterization in solution. As it is crucial to maintain the CDA chain integrity in the course of the acylation, the cellulose mixed esters were analysed by size exclusion chromatography in DMF (Fig. 2).

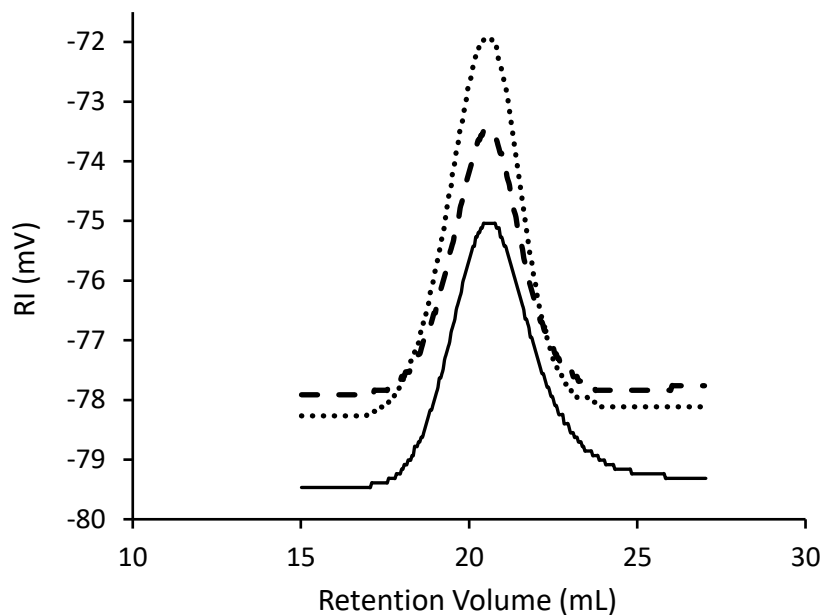


Fig. 2. SEC curves of cellulose diacetate (—), sample 3 (- -) and sample 18b (...).

As examples, SEC traces of CDA, samples 3, and 18 b are displayed in Fig. 2. The quasi-superimposition of elution peaks from SEC chromatograms shows that the acylated CDA derivatives and unmodified CDA have comparable molecular weights. The experimental reaction conditions used for the acylation are quite soft and no chain degradation occurs during the acylation procedure. Nonetheless, a slight narrower mass distribution for the cellulose mixed esters can be detected, probably due to a chain fractionation and the removal of low molecular weight chains induced by the precipitation steps. The cellulose mixed esters were analysed by NMR spectroscopy. Fig. 3 and Fig. 4 illustrate ^1H and ^{13}C NMR spectra of **sample 3 and 18b** and confirm that the acyl groups have been successfully tethered to the cellulose backbone. Additionally, NMR analyses demonstrate the integrity of the cellulose mixed esters. Acetate protons, arising from cellulose diacetate, appear as multiplets from 1.75 to 2.2 ppm. Protons assigned to **glucose units** of cellulose are visible between 3.4 and 5.3 ppm

(H1 to H6). As a result of the esterification ligation, new protons attributed to the covalently bonded substituents, either fatty chains (protons Ha, Hb, Hc, Hd and He, Fig. 3 (a)) or aromatic moieties (Hd, Hd, Hf, Hg, Hh, Fig. 4 (a)) can be identified. The success of the acylation was also confirmed by ^{13}C NMR spectroscopy through the appearance of the expected carbon signals, such as the carbon of the aromatic rings around 130 ppm for cellulose acetate hydrocinnamate (Fig. 4, (b)). The acylation reaction statistically occurs on both the residual primary and secondary OH groups of the cellulose **glucose** units. Indeed, as reported in literature, contrary to etherification of cellulose (including protective/deprotective groups), esterifications by direct reaction with activated acyl moieties in homogeneous medium were not regioselective, even for the use of bulky acylating reagents (Fox, Li, Xu, & Edgar, 2011; Xu, Li, Tate, & Edgar, 2011).

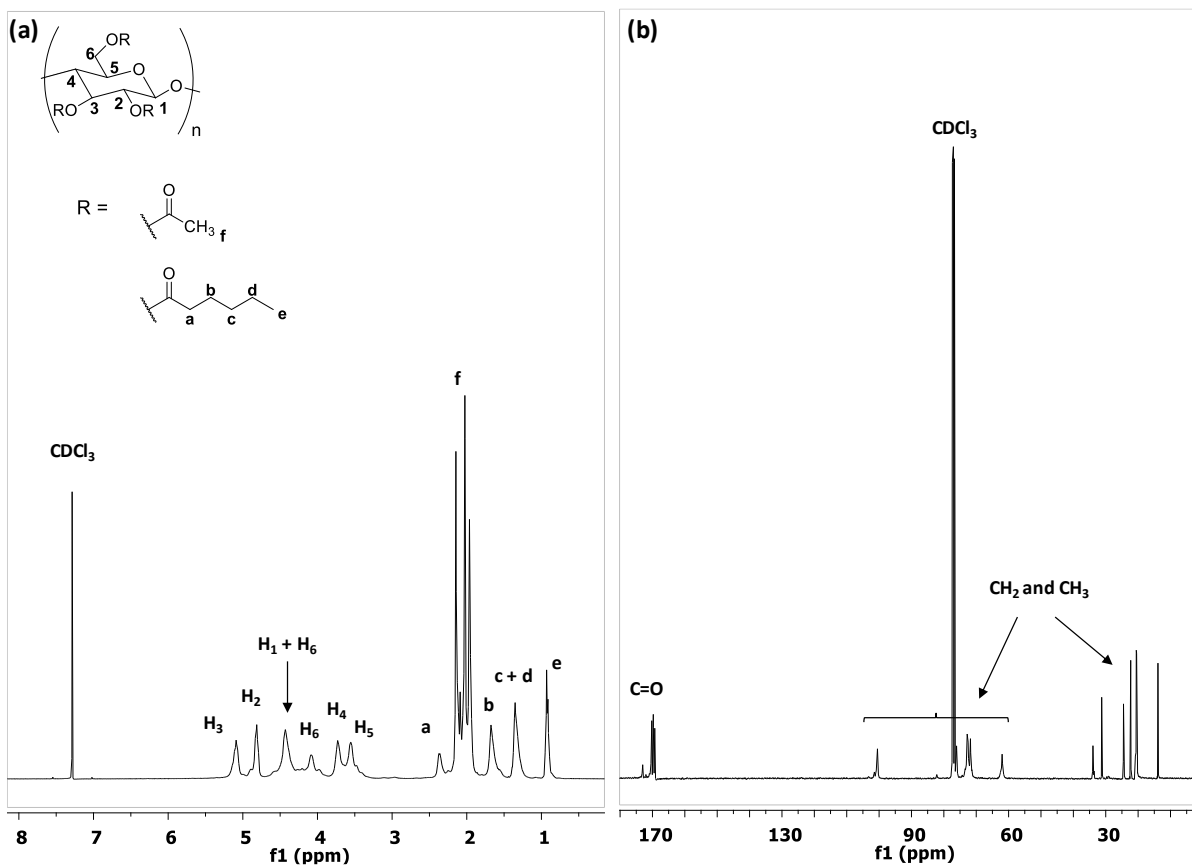


Fig. 3. ^1H (a) and ^{13}C (b) NMR spectra of **sample 3 cellulose acetate hexanoate** ($\text{DS}_{\text{Hexanoate}} = 0.32$) (CDCl_3 , 298 K).

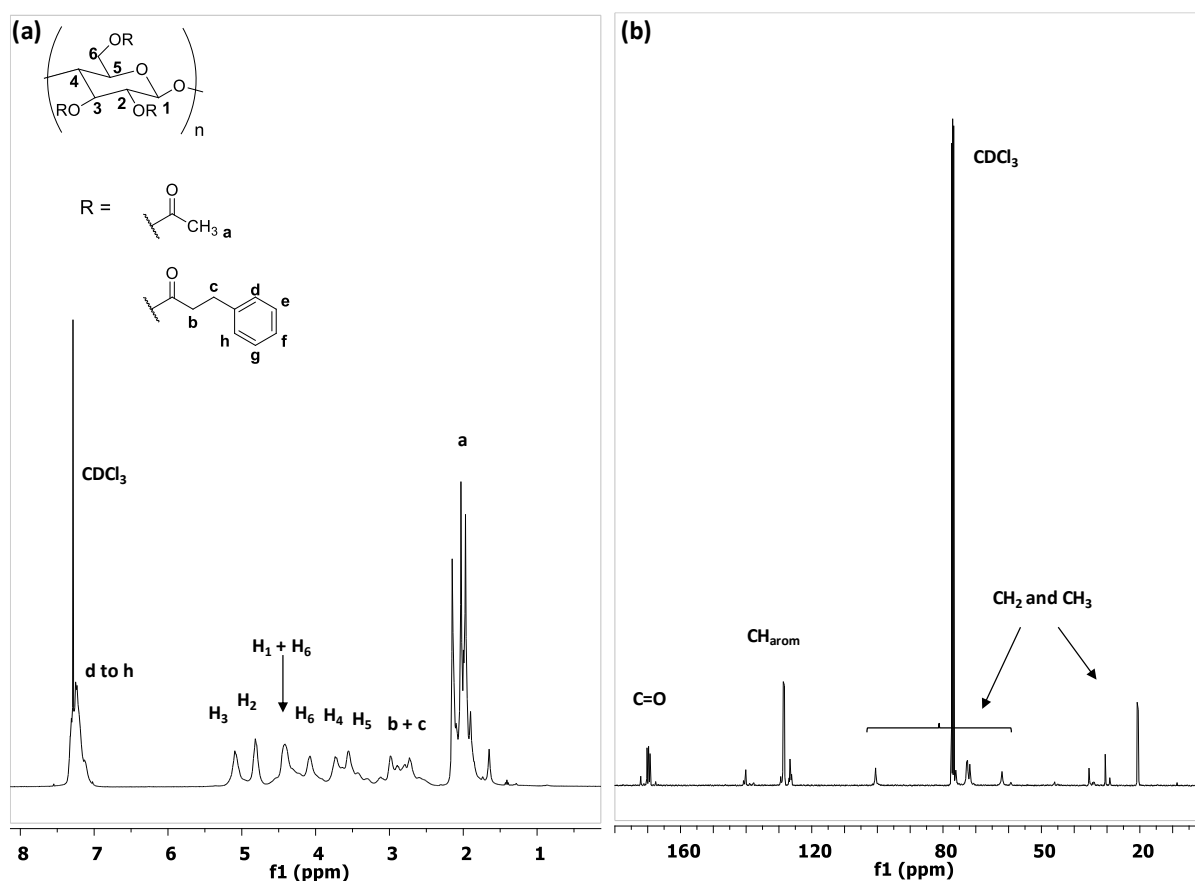


Fig. 4. ^1H (a) and ^{13}C (b) NMR spectra of sample 18b cellulose acetate hydrocinnamate ($\text{DS}_{\text{Hydrocinnamate}} = 0.52$) (CDCl_3 , 298 K).

The $\text{DS}_{\text{grafts}}$ of the cellulose mixed esters was calculated from ^1H NMR spectroscopy by using the integration of CDA backbone protons and the one of the protons of the bonded substituent (see experimental part for more details). As commonly reported for esterification of polysaccharide by acyl chlorides (Crépy, Chaveriat, Banoub, Martin, & Joly, 2009; Chen, Zhang, Xiao, Tian & Zhang, 2018), acylation is not quantitative (see conditions and DS values gathered in Table 1). This can be reasonably ascribed to the high water sensitivity of the acid chloride derivatives. Also, the residual OH groups of CDA are strongly implied into the formation of intra and interchains H-bonds (origin of the high T_g of CDA), which probably impair the OH reactivity. However, satisfying DS values are obtained. Table 1

clearly shows that the reactivity is closely dependant on the chemical structure of the used acylating reagent. As expected, the reactivity of fatty acyl chlorides is decreased with the increase of the length of the fatty chain. When long acylating chains were used, the presence of undesired carboxylic acid and methyl ester was evidenced, at the expense of targeted CDA acylation. Regarding the more bulky acid chloride molecules (ramified, cyclic, heterocyclic and aromatic) no clear tendency can be drawn. We can only assume that not only the cellulose diacetate acylation is dependent on the solvent sensitivity of the acylating reagents but it is also linked to *i*) the steric hindrance effects induced by the aliphatic groups bearing the acid chloride group and to *ii*) the effects of electronic density and polarity which both are closely dependent on the structural characteristics of the acyl modifiers. Also, it is reasonable to admit that the formation of intermolecular interactions (such as Van der Waals interactions or π - π stacking) between the side groups could impede the reactivity. The 4-heptylbenzoyl chloride derivative seems to be the less reactive modifier, and the use of hydrocinnamoyl chloride leads to the highest DS values. Moreover, the influence of the acyl chloride/CDA hydroxyl groups ratio was addressed (samples 4 and 9-18, Table 1). It results that the extent of modification is significantly enhanced by an increase of the amount of the acylating reactant. In summary, a library of cellulose mixed esters with well-defined structures and differing in their structural parameters was successfully generated by a one-step, non-degrading and simple homogeneous acylation of cellulose diacetate in solvent medium. Furthermore, by adjusting the feed ratio, the DS could be tuned.

Thermal properties of the cellulose mixed esters.

The thermal stability of all cellulose mixed esters was characterized by thermogravimetric analysis. The thermal decomposition temperatures ($T_{d5\%}$, T_{dmax}) and the residual mass after the complete thermal degradation are gathered in table 1. Examples of TGA of CDA, samples

2 and 18b are given in Fig. S1, S2 and S3. Globally, the degradation temperatures (around 300 °C) are quite similar, as reported in literature (Tanaka, Iwata, & Iji, 2017; Glasser, Samaranayake, Dumay, & Davé, 1995). Good thermal stability is not affected by the acylation procedure, which is a key point when melt-processable materials are targeted. Moreover, the only single decomposition peak visible in TGA curve demonstrates that the esterified CDA derivatives, recovered after precipitation, washings, and drying are not contaminated by solvents or any other ungrafted molecules. No water uptake is visible in TGA traces due to the rather apolar character of the CDA derivatives imparted by both acetate groups and additional aliphatic bonded substituents. Otherwise, each derivative was analysed by differential scanning calorimetry. As shown in DSC thermograms, no endothermic peak corresponding to a melting phenomenon was identified, even for derivatives esterified with long acyl chains, contrary to some published works dealing with cellulose fatty ester (Tanaka, Iwata, & Iji, 2017; Glasser, Samaranayake, Dumay, & Davé, 1995; Crépy, Chaveriat, Banoub, Martin, & Joly, 2009). This difference in crystalline behaviour is much probably due to the amount of bonded aliphatic chains, which is lower in our case (lower DS_{grafts} values). Glass temperatures (T_g) were determined as the middle point on the second heating ramp. The collected T_g values are summarized in table 1, and examples of DSC curves obtained for CDA, and samples 9a, 13b and 18b are displayed in Fig. 5.

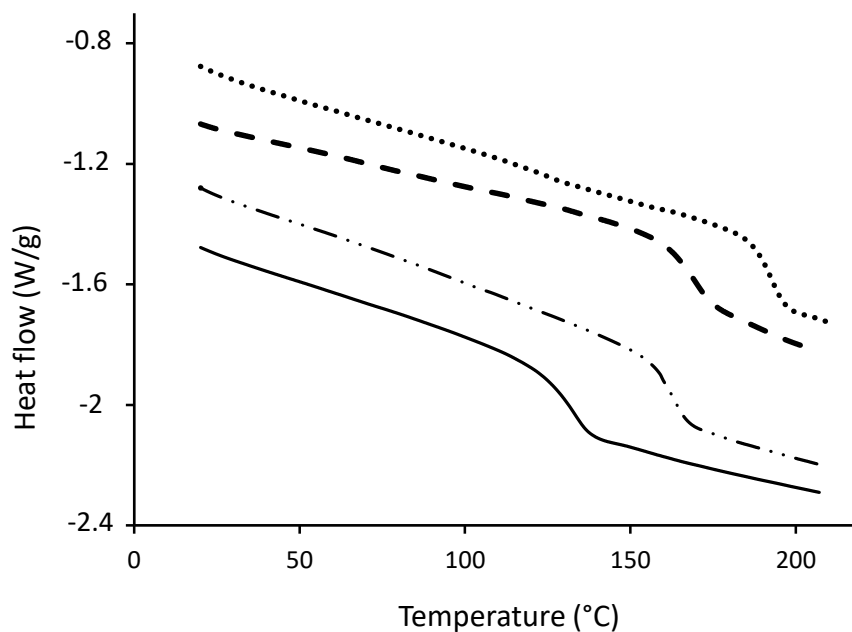


Fig. 5. DSC curves of cellulose diacetate (...) and cellulose diacetate acylated with oleyl chloride (sample 9a) (- -), with cyclohexylacetyl chloride (sample 13b) (-.-.) and with hydrocinnamoyl chloride (sample 18b) (-).

First, as expected, we can observe that the grafted aliphatic acyl moieties lead to a decline of T_g . Such a decrease of T_g is solely ascribed to the effect of the bonded substituent, since as emphasized by NMR and thermogravimetric analysis, no residual molecule (solvent, water, ungrafted acid chlorides), able to act as external plasticizers, has been detected. Thus, the attached aliphatic moieties are able to destroy H-bonds, increasing the distance between the polymer chains and thus improving the overall macromolecular mobility, as schematically represented in Fig. 1. Interestingly, the degree of the plasticizing effect is closely dependant on the extent of the esterification and, especially on the chemical structure of the substitutes. In order to assess the influence of the size of the grafted fatty acyl on the plasticizing effect, the evolution of T_g versus the chain length for a given DS (around 0.24) is depicted in Fig. 6 (samples 2 to 9).

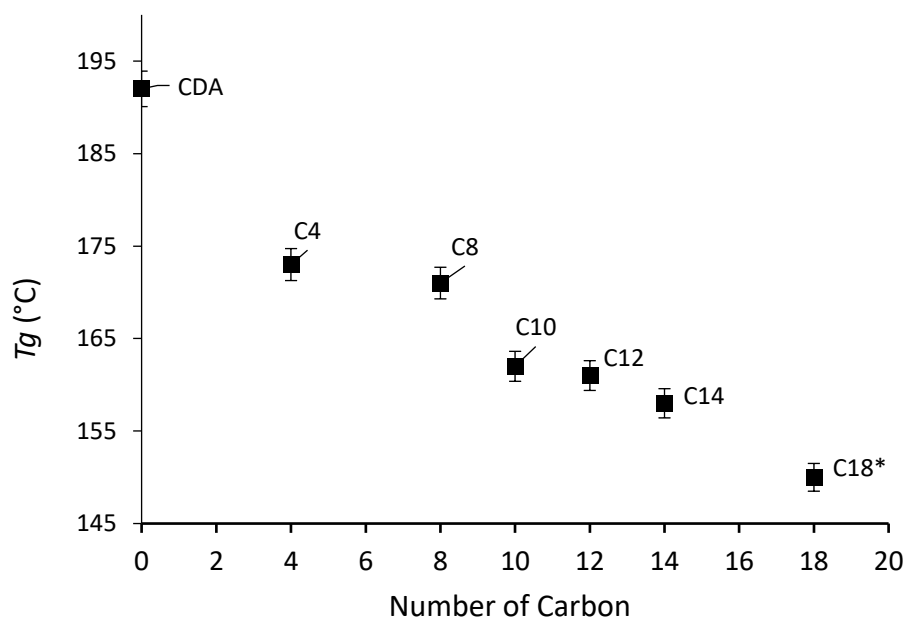


Fig. 6. Evolution of T_g values of the cellulose mixed esters as a function of the number of carbons of the fatty acyl substituent for a given DS around 0.24 (*: except for C18 with DS = 0.31). For comparison, the T_g of unplasticized CDA is given.

Fig. 6 shows that the T_g noticeably decreases with the increase of the length of the fatty chain. It decreases from 192 °C (for unmodified CDA) to 173 °C for a C4 acid chloride, to 158 °C for an acid chloride with 14 carbons, and to 150 °C for 18 carbons (with a slightly higher DS, around 0.31). Such a substantial lowering of T_g stems from the degree of flexibility of the pendant fatty chains, which is promoted by the chain length. Supplementary free volume is created when the size of the substituent lengthens. This contributes to an enhancement of the freedom degree of the polysaccharide chains, as reported in literature (Vaca-Garcia, Gozzelino, Glasser, & Borredon, 2003). Note that the benefit effect of the chain length of fatty esters on the plasticization can be annihilated for high degrees of substitution for which local crystalline phases could be detected. The presence of an unsaturation along the aliphatic

chain reduces the mobility, being not favorable for a T_g lowering (Sample 7 compared to sample 9b, table 1). This is consistent with previous work stipulating that the presence of double bond in aliphatic chain bonded to cellulose chain jeopardizes the ductility (Crépy, Chaveriat, Banoub, Martin, & Joly, 2009). Interestingly, the increase of DS for one given structure of acid chloride (samples 4a, b, c and d, Table1) conduces to a significant decrease of T_g (from a T_g of 171°C to 157°C, for a DS = 0.21 and 0.31, respectively). Different conclusions can be drawn from the use of more bulky acylating reagents (samples 10 to 18). First of all, T_g is decreased by a DS increase, irrespective of the structure of the substituent. Regarding the effect of the structural characteristics of the acyl moieties, we focused on the comparison of cellulose mixed esters with the highest DS. It appears that the incorporation of ramified substituents (3,3-dimethylbutyryl chloride and 2-ethylhexanoyl chloride, samples 10 and 11) leads to a T_g reducing of around 20 °C. For the cycloaliphatic acid chlorides, the plasticizing effect is more pronounced for cellulose diacetate esterified with cyclohexylacetyl chloride (sample 12), compared to the one derived from the use of cyclohexanecarbonyl chloride (sample 13). Thus, longer segment between the bulky moieties (here the aliphatic ring) and the cellulose backbone is beneficial to improve the flexibility. Without spacer, the expected beneficial steric effect of these modifiers is counterbalanced by the fact that the bulky aliphatic groups are not far enough from the cellulose backbone. Consequently, the side groups can undergo interactions with the hydrophobic plane of glucose unit of cellulose skeleton, being detrimental for a mobility gain. The acylation with 1-adamantane carbonyl chloride is not particularly valuable since no noticeable T_g change could be detected, compared to unmodified cellulose diacetate. This stems from the too strong bulkiness of adamantyl moieties which are sterically hindered and not able to act as efficient plasticizers, as recently reported in literature (Chen, Zhang, Xiao, Tian, & Zhang, 2018). This can induce a

too regular organization of the macromolecular chains (Granstrom, Kavakka, King, Majoinen, Makela, Helaja, Kilpelainen, 2008). The introduction of furoyl groups yields to a moderate T_g decrease (sample 15, Table 1). Concerning the series of aromatic modifiers (samples 16, 17, 18, Table 1) major differences on the plasticizing effect emerge. As underpinned for cellulose mixed ester bearing adamantyl side groups, phenylcyclopentanecarbonyl grafts (sample 16) are too sterically hindered, and are disposed too near to the cellulose main chain. Moreover, these substituents can develop intermolecular interactions (dipolar interactions and π - π stacking between the aromatic rings). Contrary to what had been expected, this oversized rigid ester group contributes to rigidify the modified cellulose diacetate derivative. By focusing on samples 17 and 18, it ensues that acid chlorides composed of both aromatic and linear aliphatic segments are particularly suited to provide an efficient plasticizing effect to cellulose diacetate. The linear part can be considered as a soft segment (Chen, Zhang, Xiao, Tian, & Zhang, 2018). Indeed, in spite of particularly low DS_{grafts} values for samples 17 ($DS = 0.09$, and $DS = 0.14$), a significant T_g decrease is measured. Given these noteworthy results, it would have been relevant to target CDA derivatives with higher DS , but it was not possible due the poor reactivity of 1-phenylcyclopentanecarbonyl chloride. The CDA derivative acylated with hydrocinnamoyl chloride appears as the more promising acylated cellulose sample. The reactivity of hydrocinnamoyl chloride is high enough to generate a completely substituted CDA derivative ($DS = 0.52$ for sample 18b). Both this high degree of modification combined to the well-suited chemical structure of the hydrocinnamoyl groups allow for a markedly lowering of T_g to a value of 125 °C. Such low T_g , obtained from the esterification of commercially available cellulose diacetate (with $DS_{\text{CDA}} = 2.45$), has not been reported so far in the literature. Thus, an acylating reagent constituted of a linear spacer segment directly anchored to the cellulose backbone with a terminal bulky aromatic group appears as the

optimal structure to efficiently separate macromolecular chains without generating detrimental stiffening interactions. Indeed, linear chains located at the end of the bulky moieties attached to cellulose chains can undergo additional physical interactions, impeding the motion of the polymer chains. Moreover, a high extent of modification contributes to enhance the thermoplastic properties of the cellulose mixed esters.

Properties of casted cellulose mixed esters films.

A large variety of solution methods was explored to prepare polymer films, such as electrospinning for example, allowing for the formation of membranes composed of cellulose nanofibers (Lee, Nishino, Sohn, Lee, & Kim, 2018; Wencheng, Hou, Jang, Bai, Zhu, Gao, Wei, Mo, & Lang, 2018). Herein, we aimed at preparing rather dense films without peculiar morphology and we turned to the use of the solvent casting method to prepare cellulose mixed ester free-standing films. This experimental route is particularly simple and requires not sophisticated laboratory equipment (see details in experimental section). Moreover, the solubility ability in a large panel of common organic solvent of the cellulose mixed esters synthesized in this work is advantageous for the preparation of plastic films by casting. After a controlled step of solvent evaporation, homogeneous and optically transparent self-supported films without macroscopic defect were obtained, as shown in Fig. 7. It was checked that reproducible film can be obtained and that there is no solvent residual within films. As depicted in Fig. 7 d', the film stemming from the sample 18b: cellulose acetate hydrocinnamate with a DS_{graft} of 0.52 is particularly flexible and ductile with sufficient mechanical properties to be easily handled without any damage (contrary to the film processed from unmodified cellulose diacetate). This is the result of the efficient plasticizing role of the bonded aliphatic moieties, which enhances the overall chain mobility (as also reflected by the T_g decrease, Table 1).

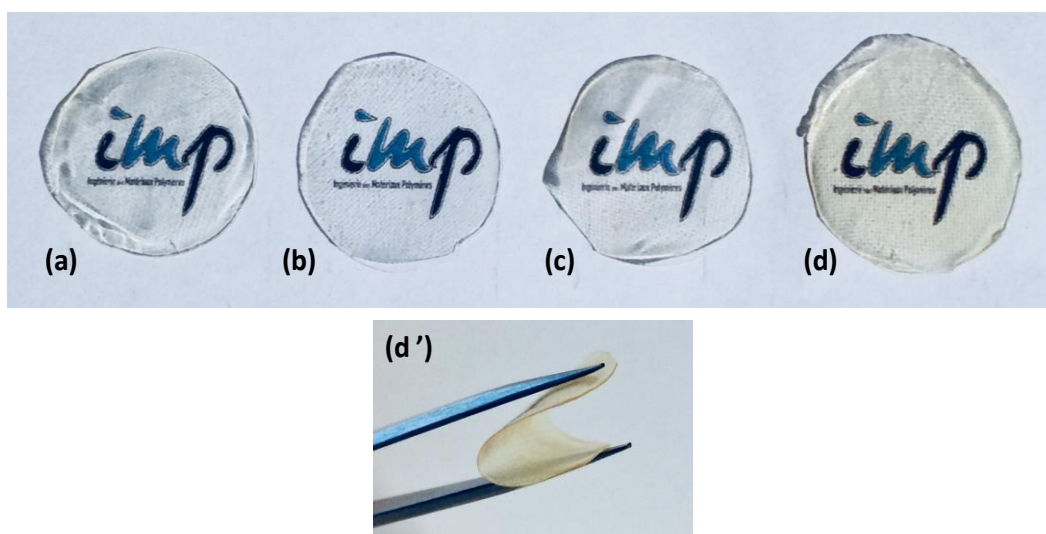


Fig. 7. Self-supported films of acylated CDA derivatives prepared by solvent casting from: (a) Cellulose acetate stearate (sample 4d), (b) Cellulose acetate dodecanoate (sample 6), (c) Cellulose acetate cyclohexanecarbonate (sample 12b) and (d) and (d') Cellulose acetate hydrocinnamate (sample 18b) at room temperature.

The cellulose mixed esters-based films were characterized by dynamical mechanical analysis (DMA) under shear mode, and the evolution of the shear storage (G') and loss moduli (G'') was monitored as a function of the temperature. Note that it is quite delicate to perform reproducible DMA on unmodified cellulose diacetate film, due to its strongly brittle and fragile character and to its thermal degradation. The thermomechanical behaviour of films processed from samples 12b and 18b, are given in [Fig. 8 \(a\) and \(b\)](#), respectively. Other examples of DMA thermograms are provided in [Fig. S4](#) and [Fig. S5](#).

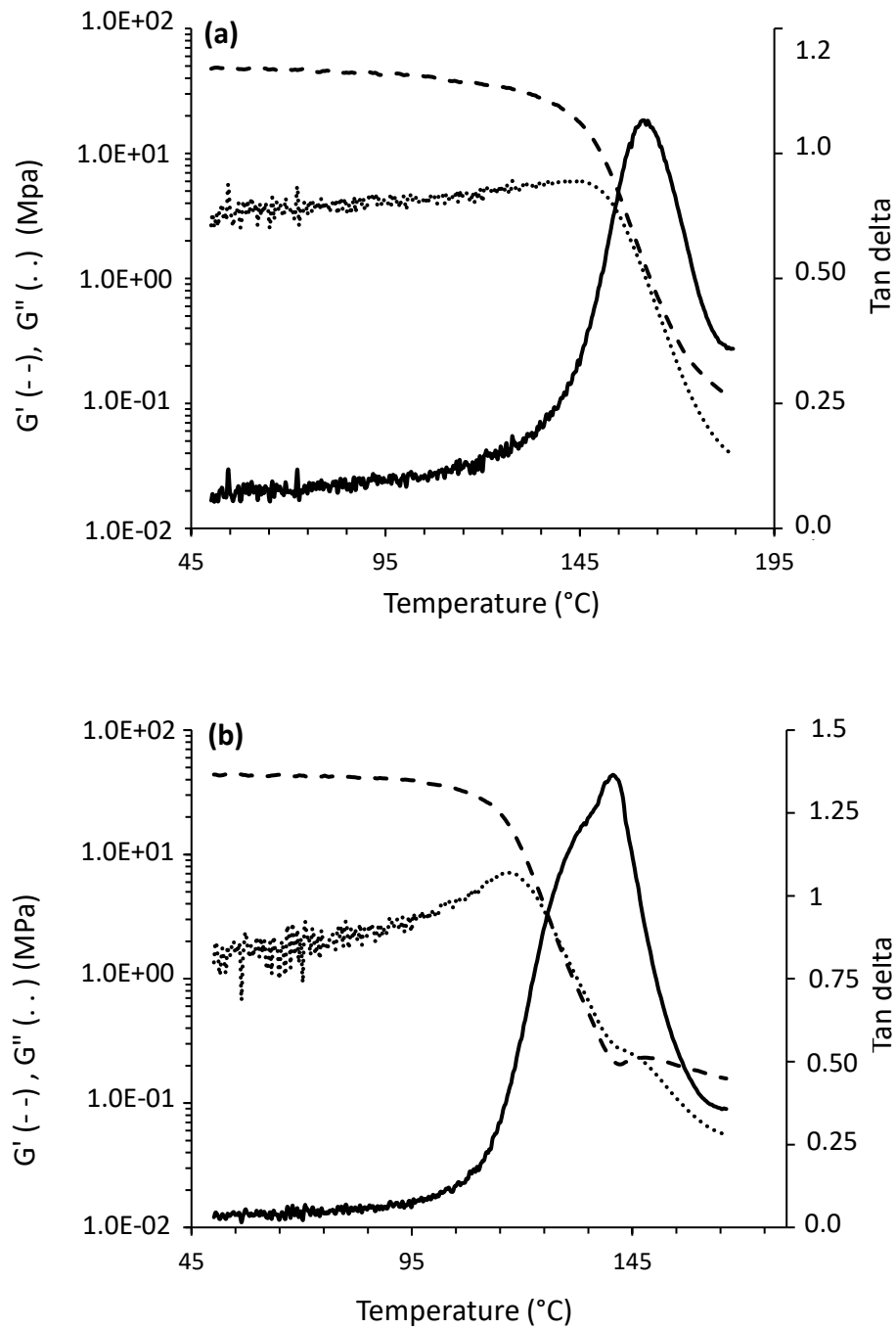


Fig. 8. Evolution of moduli G' (---) and G'' (...) and of the loss tangent ($\tan \delta$) (—) as a function of temperature of films made from (a) Cellulose acetate cyclohexanecarboxylate (sample 12b, DS = 0.45), and (b) cellulose acetate hydrocinnamate (sample 18b, DS = 0.52).

Note that we deliberately started the DMA at temperature higher than room temperature, thus the secondary sub-glass relaxation transitions of cellulose (β - and γ - relaxations), usually measured at negative temperatures (Bendaoud, Chalamet, 2014; Vaca-garcia, Gozzelino, Glasser, Borredon, 2003; Vidéki, Klébert, & Pukanszky, 2017) could not be detected on the DMA curve. Also, the β' transition, often associated to hydrated cellulose acetate and related to the loss of water associated with different groups, could not be identified in the two thermograms (Vaca-garcia, Gozzelino, Glasser, Borredon, 2003; Vidéki, Klébert, & Pukanszky, 2007). The upper α thermomechanical relaxations (the maximum of $\tan \delta$), corresponding to the glass transition phenomena of samples 12b and 18b were close to 165 and 135°C, respectively. These values are of the same order of magnitude than the thermal transitions determined from differential scanning calorimetry and indicate the beginning of segmental movement of large units of CDA chains (Table 1). Such decreased T_α values for cellulose acetate cyclohexanecarboxylate and particularly for cellulose acetate hydrocinnamate result from the covalent grafting of the aliphatic substituent, which significantly enhances the motion and the flexibility of polysaccharide chains by disrupting the H-bonds developed between OH groups. We can note a more significant width of the α relaxation peak for the film casted from sample 18b, which reveals a wider distribution of relaxation times, corresponding to more or less mobile modified cellulose chains. The mobility dispersity can originate from an uneven distribution of the substituents along the cellulose chain.

Additionally, water vapor transmission rates (WVTR) were determined on some selected casted films in order to assess the impact of acylation on water transport properties. These transport properties are very interesting to be evaluated, for applications in the packaging field for example. Herein, WVTR were made at 5°C to take into account the real conditions for

packaged fresh food. **Fig. 9 depicts** the water permeability of unmodified cellulose acetate and of various cellulose mixed esters, such as samples 2, 4b, 5, 7 and 8a (CDA bearing fatty chains differing in the chain length by keeping the DS_{graft} nearly constant around 0.24). Also, the samples 9a, 9b, 13a, 11b, 13b, and 18b were analyzed. These samples were selected in view of gaining insight on the effect of the substituent structure and on the extent of the modification (both having a role on the mobility and the hydrophobicity).

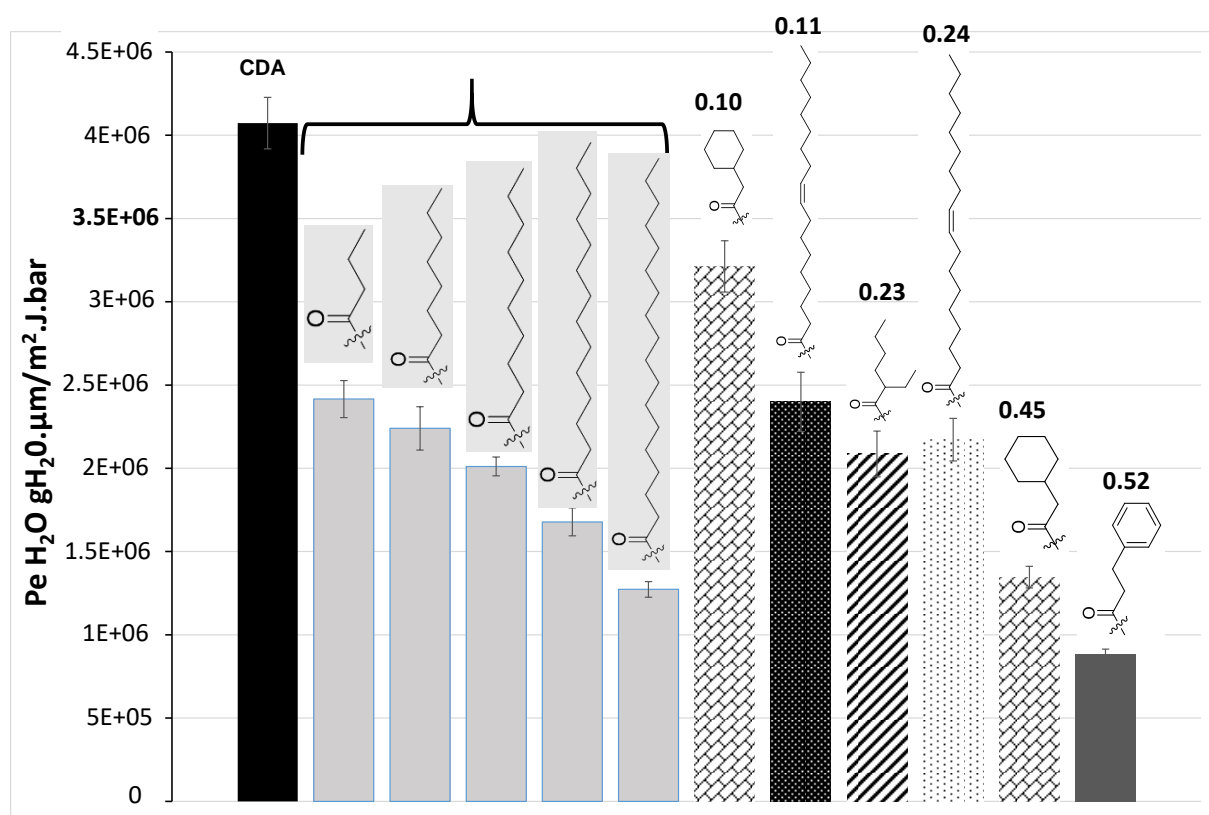


Fig. 9. Water vapour permeability of unmodified CDA and cellulose mixed esters-based films (samples 9a, 9b, 13a, 11b, 13b, and 18b) measured at 5° C. DS for cellulose fatty esters is around 0.24 and for the other samples, the DS is directly indicated near the chemical structure of the substituent.

Firstly, compared to unmodified cellulose acetate, we can observe that the water permeability of the acylated CDA samples substantially decreases, irrespective of the bonded substituents. Water transport properties are thus significantly modified by the covalent grafting. These experimental values are at the same order of magnitude that the permeability coefficients reported for cellulose acetate plasticized by small molecules (dibutyl phthalate, polyethylene glycol, and propylene glycol) added at high concentration of 40% w/w of dry polymer weight (Rao & Diwan, 1997). The authors obtained (after conversion) values varying from 2 to 6. 10^6 $\text{g}\cdot\mu\text{m}\cdot\text{m}^{-2}\cdot\text{J}^{-1}\cdot\text{bar}^{-1}$. From a general statement, the permeability P proceeds through a solution-diffusion mechanism, that is to say that P is the product of the solubility S of the permeate by its diffusion coefficient D , through the well-known relationships $P = DS$ given from Fick's first law (Brody, & marsh, 1997). Polymer chains must “move aside” to open up the path for water. Permeability is thus related to chain mobility, being here affected by both the internal plasticization induced by the covalent grafting of acyl moieties (T_g decrease, Table 1, Fig. 6) and by the external plasticization due to the absorbed water at high hydration rate. Meanwhile, when the plasticization effect governs the permeability changes through $P = DS$, the permeability is expected to increase (through an increase of the D diffusion coefficient D). However, here the permeability values of all cellulose mixed esters are decreased. This is probably due to the water solubility, which is considerably depleted by the presence of side apolar substituents, and by the consumption of the residual hydroxyl groups OH onto the cellulose acetate backbone. Consequently, in our case, the permeability is mainly governed by the water solubility, which is closely dictated and controlled by the hydrophobic nature of the bonded aliphatic moieties. Also, note that the water permeabilities were measured at 5°C , which can screen the benefit plasticizing effect of the grafted acyl modifiers. Concerning the cellulose fatty esters with a $\text{DS}_{\text{grafts}}$ around 0.24, Fig. 9 shows that the water permeability

decreases when the length of the fatty chain increases. As previously explained, the permeability of the esterified CDA derivatives is mainly governed by the water solubility, which is understandably reduced by the increase of the size of the fatty chains. For the other cellulose mixed esters bearing ramified, cycloaliphatic, unsaturated aliphatic chain or aromatic moieties as side groups (samples 9a, 9b, 13a, 11b, 13b, and 18b), one can see that the water permeability values are in the same range of the ones of CDA fatty esters (for rather comparative DS). From this series of experiments, it appears that the predominant factor affecting the water permeability is the degree of substitution (DS_{grafts}). Indeed, the lowest water permeability values were obtained for the highest DS, that is to say cellulose acetate cyclohexylacetate with a DS of 0.45 (sample 13b) and cellulose acetate hydrocinnamoate with a DS = 0.52 (sample 18b). The complete substitution of OH groups seems to be a prerequisite to target low water permeability for applications in packaging food. In this frame, cellulose acetate hydrocinnamoate (sample 18b) is the ideal candidate.

4. Conclusion

A large library of cellulose mixed esters was synthesized through a simple and homogeneous acylation of cellulose diacetate, by using a series of commercially available aliphatic acid chloride modifiers differing in their chemical structure (fatty chains with different length, ramified, bulky, aliphatic or aromatic rings disposed more or less near to cellulose backbone). It results that the covalent introduction of the acyl moieties leads to a significant lowering of T_g , as a consequence of the enhancement of the overall mobility of the macromolecular chains. The degree of the internal plasticization is dictated by both the extent of modification, and especially by the structural features of the bonded substituent. The gain in mobility is promoted when the length of the ester fatty chain increases. Besides, an ideal structure was highlighted and it consists in a terminal bulky and rigid moiety (particularly aromatic) spaced

from the cellulose skeleton by a linear aliphatic segment (reduction of T_g around 67 °C). This suited structure generates a large enough free volume without generating detrimental physical interactions. The cellulose mixed esters were processed by solvent casting into self-handing films. DMA showed that α - mechanical transitions are in agreement with the T_g values. The analysis of water permeability evidenced that the grafting of aliphatic acyl moieties leads to a significant decrease of the water transport properties. The permeability is controlled by the water solubility of the cellulose mixed esters, which is linked to the apolar character of the grafted molecule and to the DS values. Further experimentations are under progress to identify CDA films presenting original gas selectivity (CO_2/O_2) required for ready to use food. The melt processing ability of the more promising esterified CDA derivatives by conventional processes will be subsequently studied and the mechanical properties will be evaluated, in order to target specific industrial applications.

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Supporting Information. Solubilisation analysis in various solvents, TGA curves, DMA curves.

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Table of Contents Entry

Homogeneous acylation of Cellulose diacetate: Towards bioplastics with tuneable thermal and water transport properties

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