Cellulose Esterification with Fatty Acids and Acetic Anhydride in Lithium Chloride/*N,N*-Dimethylacetamide Medium

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ABSTRACT: Homogeneous esterification of cellulose with saturated fatty acids (*n*-octanoic to *n*-octadecanoic) was accomplished with acetic anhydride co-reactant in lithium chloride/*N,N*-dimethylacetamide (LiCl/DMAc) medium. Cellulose mixed triesters (CMT) were obtained after 5 h at 130°C with an average of 2.2 acetyl groups and 0.8 fatty substituents per anhydroglucose unit. A mixed acetic-fatty anhydride, formed *in situ,* accounts for the grafting of the fatty moiety. The purified products were characterized and compared to the analogous cellulose simple fatty triesters (CST) that were synthesized from fatty acid chlorides in pyridine medium. Dynamic contact angle with water, glass transition, and storage moduli were correlated with the length of the fatty substituents. The CMT proved to be highly hydrophobic and more mechanically resistant than the CST.
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KEY WORDS: Cellulose esters, contact angle, dynamic mechanical properties, fatty acid chlorides, fatty acids, glass transition, hydrophobicity, mixed anhydrides.

Ten percent of the world pulp production is transformed into cellulose derivatives, i.e., 4.4 million tons per year (1). In particular, the market of cellulose organic esters amounted to 815 thousand tons in 1985 (2). However, only cellulose esters and mixed esters of the aliphatic C_2 to C_4 carboxylic acids are used to an industrially significant extent, expressly in the coatings, film, textile, and cigarette filter industries. Such lower esters are generally synthesized from the corresponding carboxylic acids and their anhydrides.

On the contrary, higher cellulose esters have not yet found a large industrial impact. Their characteristics have not been thoroughly studied, and their synthesis methods are to some extent uneconomical. Preparation of the fatty cellulose esters requires more drastic methods than the lower series. They are generally prepared from a fatty acid chloride. This powerful reagent produces aggressive hydrochloric acid as a by-product of the esterification reaction. To limit cellulose acidic degradation, pyridine (3) and triethylamine (4) have been used to neutralize HCl as it is formed. Recent progress has allowed the esterification of cellulosic materials with fatty acid chlorides without any base or solvent to remove gaseous HCl from the reaction system by applying a nitrogen stream (5) or vacuum (6).

Unlike fatty acid halides, fatty acids are esterifying agents that do not induce cellulose degradation. However, their extremely low reactivity toward cellulosic hydroxyl groups prevents the esterification reaction. Certain molecules, such as dicyclohexylcarbodiimide and 4-pyrrolidinopyridine (4), *p*-toluenesulfonyl chloride (7,8), methanesulfonyl chloride (9) or trifluoroacetic anhydride (TFAA), have been employed to transform carboxylic acids into more reactive entities. With the TFAA or "impelling" method, several fatty esters of cellulose or wood have been prepared (10–12). A variation on this method that involves acetic anhydride, hydroquinone, and, optionally, potassium acetate has been used to fix acrylic acids onto cellulose (13).

In this work, we present a cellulose esterification technique that employs saturated fatty acids (from *n*-octanoate to *n*-octadecanoate) and inexpensive acetic anhydride co-reactant to yield a cellulose mixed acetic-fatty triester (CMT).

We have chosen the lithium chloride/*N,N*-dimethylacetamide (LiCl/DMAc) system to study the performance of this esterification method and to prepare different CMT samples. It has been demonstrated by nuclear magnetic resonance (NMR) studies that this system is a true solvent for cellulose, i.e., the polysaccharide is neither degraded nor transformed into a derivative (14). In this manner, cellulosic hydroxyl groups are readily accessible, and diffusion and crystallinity limitations are avoided.

The dynamic thermomechanical properties and the hydrophobic character of these novel esters have been evaluated and compared to those of cellulose simple fatty triesters (CST). The latter were synthesized by adapting the acid chloride-pyridine method (3). The characterization of CST, especially hydrophobicity, adds new elements to other works previously reported (8,15).

EXPERIMENTAL PROCEDURES

Materials. Alpha cellulose (4% pentosans) was obtained from Sigma (Saint-Quentin Fallavier, France). Reagent-grade chemicals were purchased from Aldrich (Saint-

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Quentin Fallavier, France) and were used without further purification or treatment.

Cellulose dissolution. Cellulose (10 g) was dissolved in 500 mL of fresh LiCl/DMAc solvent (9% wt/wt) at 90°C under mechanical stirring for 30 min. A particle-free solution was obtained under such conditions.

Synthesis of CMT. A mixture of fatty acid (2 eq/cellulose OH), acetic anhydride (2 eq/OH), and $HClO_4$ catalyst (0.0003 eq/OH) was stirred for 1 h at 90°C. The hot mixture was poured into a previously prepared cellulose (10 g dry basis) solution. The whole was then refluxed under mechanical stirring for 5 h at 130°C. The esterified cellulose was recovered at the end of the reaction by precipitation with 3 vol (1500 mL) of 50% aqueous ethanol. The suspension was vacuum-filtered over fritted glass, thoroughly washed with ethanol (5 × 100 mL) and with deionized water (3 × 100 mL), then purified by Soxhlet extraction with ethanol for 16 h. Finally, the powder was dried at 105°C to constant weight and stored in a desiccator at room temperature.

Synthesis of CST. Cellulose (10 g) was suspended in excess pyridine (250 mL) at room temperature. Fatty acid chloride (2 eq/OH) was added to the heterogeneous mixture, and the whole was refluxed under mechanical stirring in an oil bath at 130°C for 2 h. One volume (250 mL) of 50% aqueous ethanol was added to stop the reaction. The mixture was vacuum-filtered over fritted glass. The solid was thoroughly washed with ethanol (5 × 100 mL) and with acetone (2 × 100 mL), then purified by Soxhlet extraction with acetone for 16 h. Finally, the cellulose ester was dried at 50°C to constant weight and stored in a desiccator at room temperature.

Proton NMR. Cellulose esters were dissolved in $CDCl_3$ to obtain the ^1H NMR spectra in a Bruker ARX (Wissembourg, France) 400 MHz instrument. The seven protons of the anhydroglucose unit were located in the 3.0–5.5 ppm region and those from the acyl substituents in the 0.8–2.4 ppm region.

Gas chromatography–mass spectrometry (GC–MS). Identification of the esterifying agent was carried out with a gas chromatograph (Hewlett-Packard 5890, Labege, France) and a mass-selective detector (Hewlett-Packard 5971) at a potential of 70 eV for ionization by electron impact. Separation was performed by a 50 m × 0.22 mm × 1 µm dimethylpolysiloxane BP1 (SGE, Villeneuve Saint Georges, France) fused-silica capillary column. The column was temperature-programmed from 50–220°C (5°C/min). The injector and detector temperatures were 220 and 250°C, respectively. The carrier gas helium was fixed at 22 psi.

Elemental analyses. C, H, N, and O elemental analyses were made by the Control Laboratory of the ENSCT (Toulouse, France) with an Elemental Analyzer 1106 (Carlo Erba Strumentazione, Les Ulis Cedex, France).

Thermomechanical properties. Samples were hot-molded (100°C for CST and 190°C for CMT) in a laboratory press (4 ton) to obtain a probe of 30 × 12 × 3 mm and then allowed to cool at room temperature. Dynamic-mechanical tests were carried out at 5 Hz in a dynamic mechanical thermal analyzer DMTA MkII from Rheometric Scientific (Marne la Vallee, France). Studies were performed in a single-cantilever bending module with a 14-mm span. The storage modulus (E) and the loss factor (tan δ) were measured in the −70 to +200°C range at a heating rate of 4°C min^{-1}. Glass transition (T_g) was defined as the temperature that corresponded to the maximum in the loss factor.

Hydrophobicity. Dynamic contact angle (DCA) between water and the cellulose esters was evaluated through a Cahn's DCA Analyzer DCA-322 (Cahn Instruments Inc., Cerritos, CA). The samples were hot-pressed (same as above) to obtain thin regular films. The software calculates the DCA value when the sample is slowly introduced (60 µm/s) in pure water [high-performance liquid chromatography (HPLC)-grade], and its apparent weight is registered. Moreover, the difference between the initial and the final weight determined the water adsorbed by the sample during the testing period (about 30 min). The measurements were repeated on the single sample until a constant DCA was reached. At least two different films were used for every sample.

RESULTS AND DISCUSSION

Esterification. Cellulose was readily esterified by the fatty acid chloride–pyridine mixture. The CST obtained in this medium showed a compact plastic consistency. Degree of substitution (DS) for CST was determined by elemental analysis by using the theoretical formula

$$C_{6+n\cdot DS}H_{10+2\cdot DS\cdot(n-1)}O_{5+DS}$$

where n stands for the number of carbon atoms in the acid residue. Practically, three fatty substituents were introduced in every anhydroglucose unit regardless of the size of the aliphatic substituent (Table 1). The weight increase (WI) of each cellulose sample, due to the grafting of fatty substituents, was consistent with its DS value and showed that no extensive degradation of the polymer took place, contrary to other synthesis methods (5).

On the other hand, the mixed esterification method with fatty acids grafted an average of 0.8 fatty chains and 2.2 acetyl groups per anhydroglucose unit to yield a cellulose tri-

TABLE 1
Synthesis of Cellulose Simple Fatty Triesters from Fatty Acid Chlorides[a]

Cellulose triester	DS[a]	$WI_{(DS)}$ (%)[b]	WI_{actual} (%)[c]
n-Octanoic	3.00 ± 0.01	234	226
n-Decanoic	2.98 ± 0.01	283	271
n-Dodecanoic	2.99 ± 0.02	336	335
n-Tetradecanoic	3.01 ± 0.02	390	387
n-Hexadecanoic	2.96 ± 0.06	435	436
n-Octadecanoic	2.93 ± 0.09	481	461

[a] Degree of substitution (DS) and weight increase (WI) of cellulose samples. Mean and standard deviation from three elemental analyses.
[b] Calculated from the DS mean value.
[c] Experimental error = ±3%.

TABLE 2
Synthesis of Cellulose Mixed Triesters (CMT) (acetate–alkanoate) from Fatty Acids and Acetic Anhydride

Fatty substituent	DS_a (acetic)	DS_f (fatty)	DS (total)	DS_a/DS_f	$WI_{(DS)}$ (%)[a]	WI_{actual} (%)[b]
n-Octanoic	2.19	0.81	3.00	2.70	120	100
n-Decanoic	2.18	0.82	3.00	2.66	134	115
n-Dodecanoic	2.18	0.82	3.00	2.66	149	131
n-Tetradecanoic	2.27	0.72	2.99	3.15	152	147
n-Hexadecanoic	2.24	0.74	2.98	3.03	167	155
n-Octadecanoic	2.24	0.71	2.95	3.15	175	167

[a] DS and WI of the cellulose samples. Calculated from the corresponding DS values.

[b] Experimental error = 3%. See Table 1 for abbreviations.

ester. The acetylation reaction was slightly favored when longer fatty acids, which are less reactive, were used (Table 2). The two substituents in mixed esters were identified and quantitated by ^1H NMR spectroscopy (Fig. 1). Again, no significant mass loss due to degradation was detected for the samples.

Mechanism of reaction for mixed esterification. The reaction with octanoic acid was chosen as a model for this study. When acetic anhydride co-reactant was not added to the esterifying mixture, reaction over the same time under the same temperature conditions resulted in the formation of cellulose octanoate in extremely low yields (DS < 0.10). This indicated that the mixed esterification method does not consist of two simultaneous independent esterification reactions. Acetic anhydride co-reactant influenced the grafting of most fatty chains.

The GC–MS analysis of the esterifying mixture, i.e., stirred hot mixture of fatty acid, acetic anhydride and $HClO_4$ catalyst, revealed the formation of a new compound (52% relative amount) that could not be identified by the mass spectral library (NBS54). It is known that trifluoroacetic anhydride and a monocarboxylic acid react to form a mixed trifluoroacetic-carboxylic anhydride (11). The new compound was thus supposed to be an acetic-fatty mixed anhydride formed by the analogous Reaction 1:

$$\begin{aligned} &\mathrm{RCOOH + CH_3 \cdot CO \cdot O \cdot CO \cdot CH_3} \\ &\rightarrow \mathrm{R \cdot CO \cdot O \cdot CO \cdot CH_3 + CH_3COOH} \end{aligned} \qquad [1]$$

To verify this hypothesis, acetic-octanoic anhydride standard was synthesized by a described method (16) that does not involve any of the original reagents in the esterifying mixture: sodium acetate and octanoyl chloride. The standard was analyzed by GC–MS under the same conditions as the esterifying mixture. Retention time and mass spectrum for the standard were the same as those for the unknown product derived from octanoic acid and acetic anhydride (Table 3). The molecular peak at m/z = 186, the intense octanoyl RCO- fragment at m/z = 127, and the acetyl RCO- fragment at m/z = 43 provided additional evidence for identification of the mixed anhydride. The mixed anhydride in the esterifying mixture was formed in 68% yield from acetic anhydride and octanoic acid.

Mixed anhydrides can dissociate in the presence of an acid catalyst to form the corresponding acylium ions, which account for the cellulose esterification (Scheme 1). Two paths are possible. The more abundant acylium ion is the one whose carboxylic acid has a higher p*K* (13). Any fatty acid has a p*K* greater than that of acetic acid; consequently, fatty acylium ion formation is favored. However, although the reactivity of the acetylium ion is much higher, the acetylation reaction is

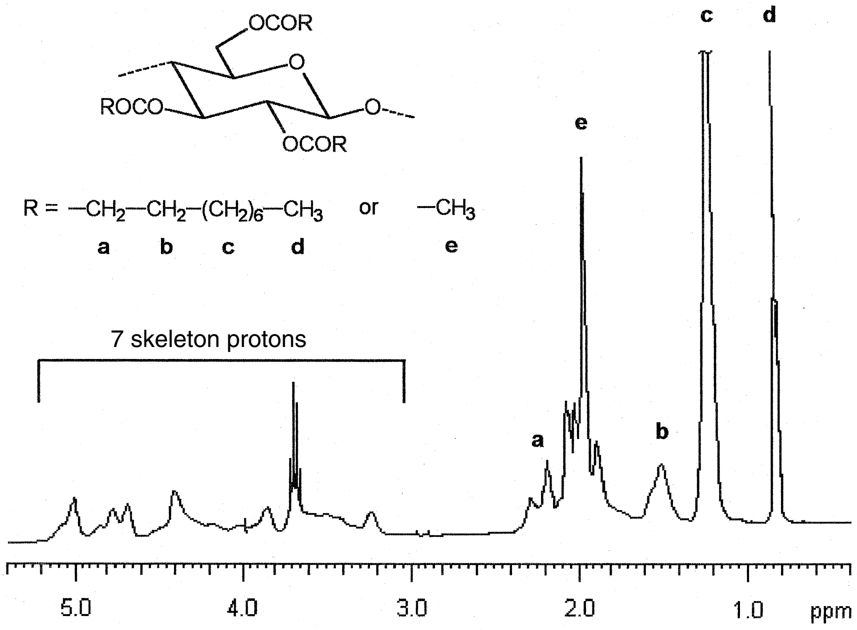
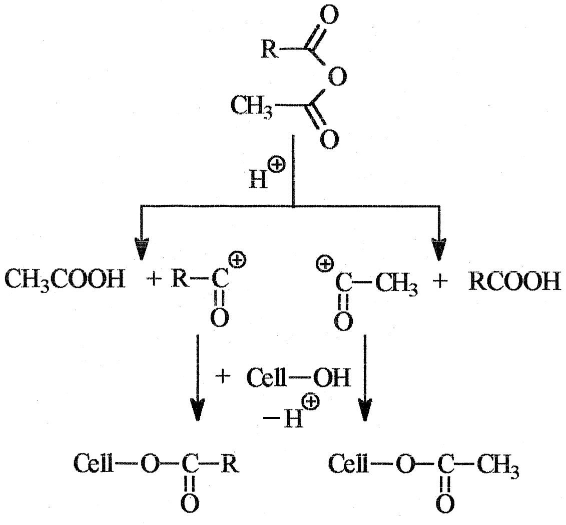


FIG. 1. Proton nuclear magnetic resonance spectrum of cellulose mixed acetic-decanoic triester in $CDCl_3$ (DS_{acetyl} = 2.18; $DS_{decanoyl}$ = 0.82). DS, degree of substitution.

TABLE 3
Mixed Acetic-Octanoic Anhydride Identified by Gas Chromatography–Mass Spectrometry (GC–MS)

	Retention time (min)	Mass spectral data [*m/z* (%)]
Unknown compound in esterifying mixture	36.41	127 (100); 57 (39); 41 (23); 55 (18); 43 (16); 29 (11); 42 (10); 27 (7); 98 (5); 84 (5); 39 (5); 186 (3)
Standard[a]	36.37	127 (100); 57 (26); 41 (15); 55 (12); 43 (10); 29 (7); 42 (6); 27 (5); 98 (5); 84 (4); 39 (4); 186 (3)

[a] Synthesized from sodium acetate and octanoyl chloride according to Reference 16.



SCHEME 1

at the expense of fixing simultaneously an important proportion of acetyl substituents.

Hydrophobicity. DCA of both kinds of esters were evaluated and correlated to the number of carbon atoms in the fatty substituent (Fig. 2). As expected, the presence of more fatty chains per anhydroglucose unit makes CST more repellent to water than CMT. Nevertheless, hydrophobicity was quite high for both kinds of cellulose esters (DCA ≥89°). Their DCA values increased asymptotically with the size of the fatty chain, and for CST, a plateau at 115° was reached for esters longer than C_{12}. Because CMT possess numerous acetyl groups with lower water repellency, a fatty chain longer than C_{12} can still compensate and increase slightly their hydrophobicity. However, their asymptotical value appears to be about 10° lower than that of CST. In addition, we have tested commercial (Aldrich) cellulose triacetate ($n = 2$) as a reference compound to verify the trends of the DCA curves. This polymer bears only one kind of aliphatic substituent, as CST do, but it also can be considered as a "cellulose mixed acetic-acetic triester." Both curves meet at this point. Moreover, no water sorption was detected to the nearest 0.0001 g for any of the samples during the immersion period (30 min).

Thermomechanical properties. DMTA in the bending mode showed remarkable differences between mixed and fatty cellulose triesters. For any homologous simple and mixed esters, the latter were more rigid at the same temperature (Fig. 3). Flexibility of the fatty chains and the space created between the cellulosic chains by long substituents decrease the mechanical resistance of CST. Indeed, the storage moduli for the CST were at least 25 times lower than those for CMT (Fig. 4). A slight diminution of *E* was observed when the side chains of CST were lengthened. On the contrary, no influence of the fatty chainlength on *E* for CMT was detected. We concluded that the abundant short acetyl groups

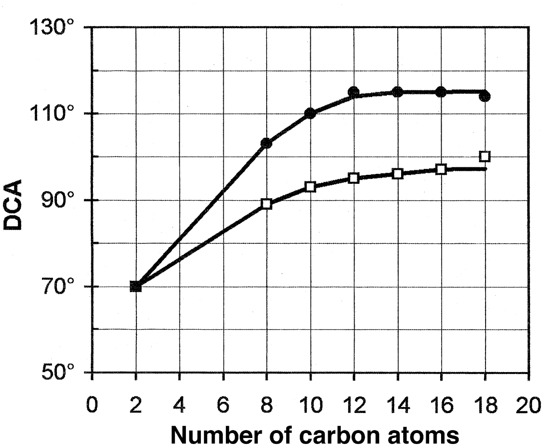


FIG. 2. Dynamic contact angle (DCA) of the cellulose esters with water: (□) mixed triesters; (●) simple triesters for different fatty substituent sizes.

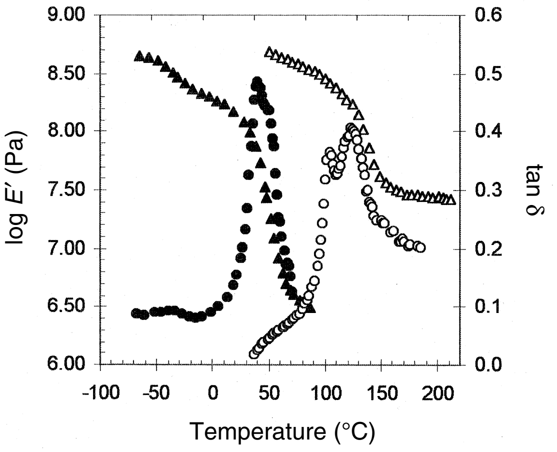


FIG. 3. DMTA data recorded at 5 Hz in bending mode. (▲), (●) log *E′*, tan δ for cellulose trioctanoate; (△), (○) log *E′*, tan δ for cellulose mixed acetic-octanoic triester ($DS_{acetyl} = 2.19$; $DS_{octanoyl} = 0.81$). See Figure 1 for abbreviation.

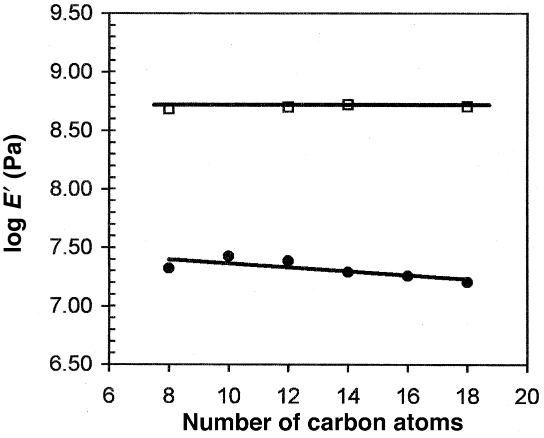


FIG. 4. *E*′ of cellulose esters: (□) mixed triesters; (●) simple triesters for different fatty substituent sizes. See Figure 3 for abbreviations.

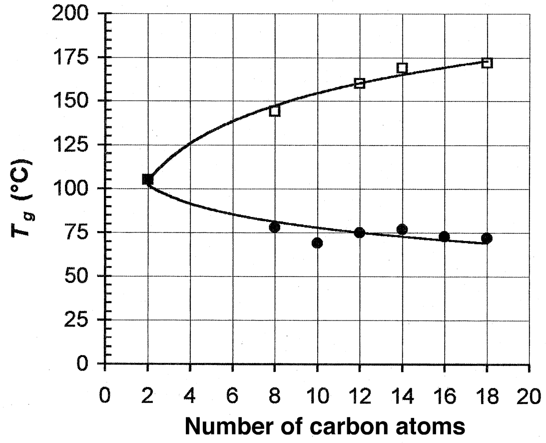


FIG. 5. Glass transition (T_g) of cellulose esters: (□) mixed triesters; (●) simple triesters for different fatty substituent sizes.

in CMT regulate their rigidity. This fact, combined to the rise of the molecular weight of the polymer, accounts for the unexpected regular increase of T_g when the size of the fatty substituent in CMT grows (Fig. 5).

In conclusion, the esterification of cellulose with unmodified fatty acids and acetic anhydride in DMAc/LiCl medium allowed the grafting of fatty acyl groups into cellulose, along with a dependent acetylation, thanks to the formation of a mixed anhydride. The obtained mixed esters were highly hydrophobic and more mechanically resistant than the corresponding fatty simple triesters. This synthesis method employs cheaper reagents than the existing parallel techniques, and it does not form corrosive HCl as a by-product. Further investigation should be carried out to exclude any cellulose solvent to exploit this technique as a process of low environmental impact.

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