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Effect of degree of substitution on the mechanical and thermomechanical properties of lauroyl cellulose ester films

Nicolas Joly,[1] *Patrick Martin,*[1] *Luc Liénard,*[2] *Delphine Rutot,*[2] *Fabrice Stassin,*[2] *Robert Granet,*[3] *Pierre Krausz*[3] *and Jean-Paul Cavrot*[4*]

[1] Centre Technologique des Agroressources, IUT de Béthune, Département Chimie, B.P.819, 62408 Béthune cedex, France.
[2] Nature for Innovative and Sustainable Solution (Natiss asbl.), Rue de la Sucrerie, 10, 7800 Ath, Belgique.
[3] Laboratoire de Chimie des Substances Naturelles (EA1069), Faculté des Sciences et Techniques, Université de Limoges, 123 av. Albert Thomas, 87060 Limoges cedex, France.
[4] Laboratoire de Chimie Physique Appliquée, I.U.T. de Béthune, Parc de la Porte Nord, 62700 Bruay la Buissière, France.

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Abstract: Cellulose-based plastic films were prepared in homogeneous media with a range of lauroyl fatty acid attachments by ester formation, expressed as the degree of substitution (DS). The esters were cast to form films and their mechanical properties studied. This study showed a surprising relationship between DS and elastic modulus as well as DS and tensile strength, where a peak was observed at DS 2.4. The unexpected variation of static elastic modulus (E) was confirmed by dynamic mechanical analysis (DMA) and this trend was also observed for glass transition temperature (T_g). These results are discussed in relation to sample cohesion.

Introduction

Petroleum reserves will be exhausted in less than one century, so it is necessary to find alternative raw materials for fuels in the plastics industry. Cellulose (polysaccharide of β–D-glucose units attached by $\beta(1\rightarrow4)$ linkages) is natural, renewable, abundant, biodegradable polymer and available in plentiful, and is arguably one of the most appropriate alternatives to petroleum-based plastics. For this reason several studies have been undertaken to assess the potential of this polysaccharide in various areas, including composites [1] and plastics [2, 3]. Cellulose is well known to produce plastic films when it is esterified by fatty acids [4]. Thus a number of studies have focused on the synthesis of fatty acid cellulose esters using conventional heating methods [5, 6] (half to few hours), microwave irradiation (few minutes) in heterogeneous [7] and homogeneous conditions [8] respectively. These studies have shown that the ability of cellulose to be converted into films due to fatty acid attachment is dependant on: (i) the degree of substitution (DS), which is

defined as the number of fatty acid chains attached per anhydroglucose unit; (ii) the synthesis conditions.

In continuation of our previous works, [9] we now report on the manner in which the DS value influences the thermomechanical properties of cellulose lauroyl ester plastic films.

Results and discussion

Description of synthesized cellulose ester samples

Each acylation was conducted under the same reaction conditions using 3 equiv. (per anhydroglucose unit) of *N,N*-dimethylaminopyridine (DMAP) as basic catalyst. DMAP catalytic activity does not influence the reaction results, but due to its basicity, it is able to neutralize the hydrochloric acid produced during the acylation reaction. This neutralization is necessary for casting plastic films with favorable mechanical properties required for this study. The results obtained with varying amounts of lauroyl chloride are shown in Table 1. The synthesis performed with lauroyl chloride equivalents below 3 did not produce plastic films. Such cellulose esters are characteristic of those with DS values lower than 1.5, which are insoluble in chloroform and cannot be converted into plastic films by casting; hence they are not recorded in Table 1.

Tab. 1. Results obtained for the acylation of cellulose with lauroyl chloride under conventional heating (90°C, 30 minutes), in the presence of 3 equiv. of DMAP.

Entry	Equiv. lauroyl chloride	R_{mass} [a)] (%)	R_{mol} [b)] (%)	DS
1	4	204	69	1.72
2	5	301	90	2.09
3	6	320	91	2.23
4	6.5	330	90	2.33
5	7	339	91	2.42
6	7.5	342	92	2.46
7	8	361	94	2.50
8	9	365	94	2.57

[a] mass yield (ratio between the product weight and initial cellulose weight).
[b] molar yield (ratio between the mole number of acylated anhydroglucose units, calculated according to the DS value).

The variation of DS according to the lauroyl chloride amount follow the same evolution as described previously [9]. It is to be noted that the reaction has good reproducibility, with a deviation on DS of 5%. Every plastic formed in these experiments were observed to be translucent and flexible.

FT-IR and ^{1}H NMR analyses

A comparison of the FT-IR spectra of cellulose and plastic films (Figure 1) clearly show the relative efficiency of acylation. For cellulose esters, a decrease in the intensity of the characteristic band for hydroxyl groups and a shift from 3290 to 3463 cm^{-1} due the consequent loss of the hydrogen bonding as normally observed in cellulose was observed. This decrease in intensity occurs with a concomitant

appearance of a band around 1740 cm^{-1} characteristic of carbonyl ester groups. A band at 1153 cm^{-1} characteristic of a C-O-C ester stretching vibration was also observed in the spectra obtained for the cellulose esters. As expected, comparison between both cellulose ester spectra showed an increase in the DS, according to a slight decrease of O-H group band intensity. The presence of the aliphatic fatty chains of lauroyl ester was also readily detected by the absorbance observed at 2918 and 2849 cm^{-1} corresponding to the symmetric and asymmetric C-H stretching, and the appearance of a small peak at 711 cm^{-1} characteristic for at least four linearly connected CH_2 groups.

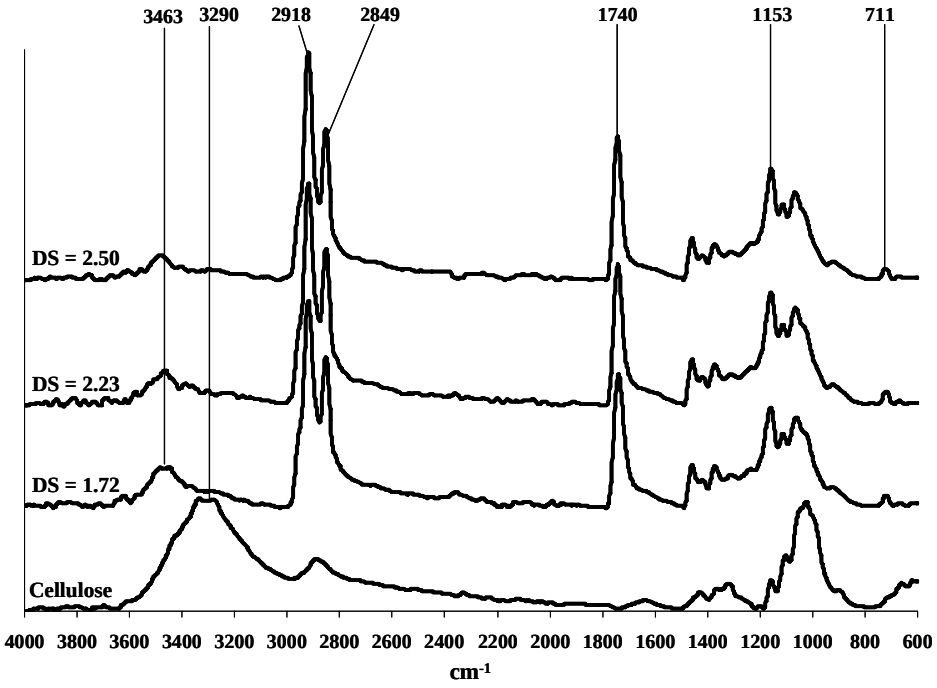


Fig. 1. Comparison between cellulose and cellulose ester FT-IR spectra.

^1H NMR spectroscopy was used to determine the DS for each cellulose ester prepared and to confirm attachment of the lauroyl chains onto cellulose, by integration of the characteristic signals of fatty acid protons at 0.89 ppm (ending CH_3, t, 3 H), 1.26 ppm ($(CH_2)_8$, m, 16 H) and 2.32 (CH_2 in α position of carboxylic function, t, 2 H) respectively.

Mechanical properties

The literature [10] has reported that the glass transition temperature (T_g) of cellulose laurates decreases with an increase in DS, until 78°C when a maximum DS of 3 is reached. Consequently, the tensile tests performed at room temperature are far from T_g of the materials in this study and, as a consequence, correspond, in all cases, to the solid-state mechanical behavior. A typical dynamometric curve obtained during the tensile tests of cellulose ester plastic films is shown in Figure 2.

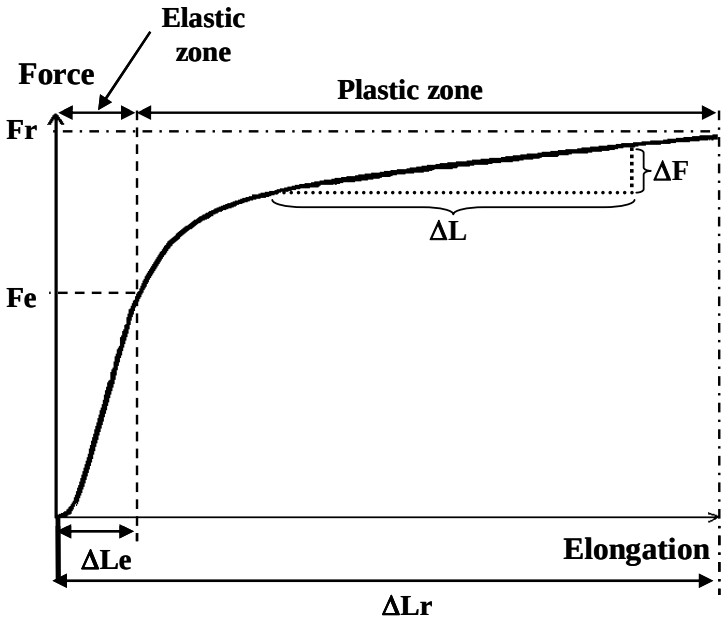


Fig. 2. Dynamometric curve recorded during cellulose esters tensile tests.

It can be seen that no strain softening occurs, *i.e.* the deformation is homogeneous up to the failure point.

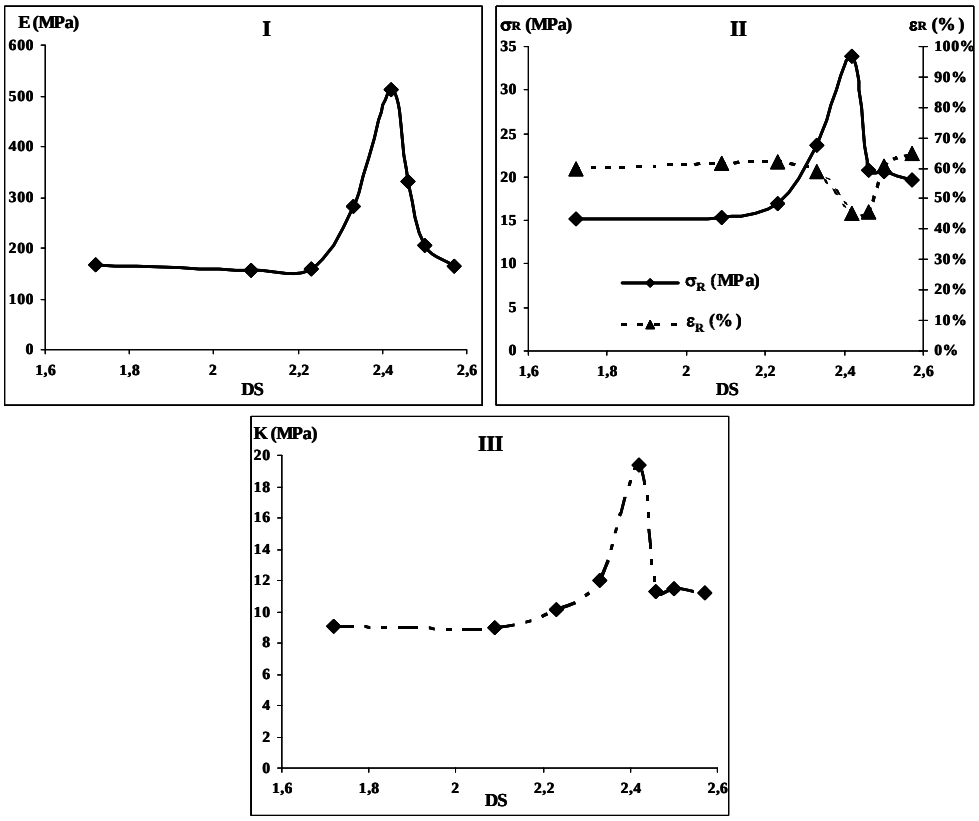


Fig. 3. Evolution of elastic modulus E (I), tensile strength σ_R and tensile strain level ε_R (II) and strain hardening coefficient K (III) versus DS for cellulose ester films.

The relationship of different mechanical parameters versus the DS is presented in Figure 3. An unexpected variation of the mechanical properties was observed in which *E*, σ_R and *K* values were found to increase drastically close to the DS value of 2.42 (Table 2, entry 5). For this particular DS value, the sample stiffness reaches 512 MPa, which corresponds to the elastic modulus of commodity plastics such as polyethylene. At the same time, this sample becomes less ductile with a strong increase in tensile strength (up to about 35 MPa), and decrease in strain at break (down to about 40%). The strain hardening coefficient, which measures the ease of plastic deformation propagation, also reaches a maximum value at DS = 2.42, which correlates well with the less ductile behavior of the sample. It seems that a DS value of 2.42 is indicative of a more cohesive structure. These mechanical properties (*E*, σ_R and *K*) are close to those of commodity plastics, but the ductility is lower.

DMA results

Dynamic mechanical analysis (DMA) was performed to obtain more information on pertaining molecular motion in relation the structure and possible interactions between the chemical groups involved. Figure 4 shows the typical variation in loss factor (tan δ) and storage modulus (E') of the plastic **4** measured over the temperature range from -70 to 200°C. The same relationship between E' and the experimental temperature were observed for all of the plastics in this study. The dynamic storage modulus was found to decrease rapidly between -70 and -10°C, slowly from 0°C, and finally more rapidly once more. Thus, three relaxation peaks were observed. The main transition T_α observed at the higher temperatures is accompanied by the most significant decrease of E', and is attributed to the glass transition of the polymer [10]. The two secondary transitions appear at lower temperatures, T_β as a shoulder on the main transition peak and T_γ which is well separated from the others.

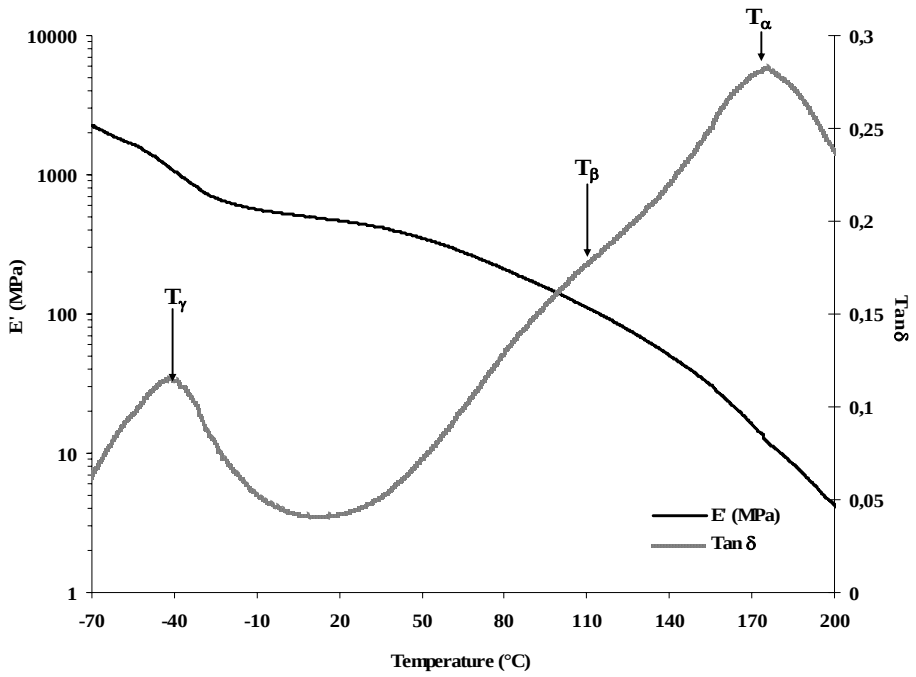


Fig. 4. Example of DMA thermogram obtained for the sample **4**.

The transition temperatures and dynamic storage modulus are depicted in Table 2 for each plastic. A close correlation is observed between the dynamic storage modulus E', determined by DMA, and the elastic modulus E, obtained from tensile tests, with a maximum value at DS = 2.42. The transition temperatures follow a similar trend, where T_β and T_α are at a maximum for the product with DS = 2.42, while T_γ declines to a minimum.

As a consequence, the polymer with DS = 2.42 shows the largest separation between T_α and T_γ. This surprising behaviour might be due mobility characteristics resulting from interactions between the ester groups and the remaining hydroxyl groups.

Tab. 2. Experimental data (α, β and γ transition temperatures and dynamic modulus E') obtained by DMA of cellulose esters.

Entry	DS	T_α (°C)	T_β (°C)	T_γ (°C)	E' (MPa)
1	1.72	130	79	-36	0.210
2	2.09	129	82	-37	0.212
3	2.23	132	95	-37	0.192
4	2.33	172	112	-38	0.442
5	2.42	190	138	-41	0.526
6	2.46	175	119	-44	0.467
7	2.50	138	95	-41	0.243
8	2.57	131	90	-37	0.201

Conclusions

Cellulose esters were synthesized successfully with various degrees of substitution in the range 1.7 to 2.6. The mechanical properties of each sample were investigated and showed an unexpected relationship with DS values. Instead of a linear variation, the elastic modulus and the tensile strength were found to reach a maximum value at DS = 2.42. The DMA study of these cellulose-based plastic films also showed an unexpected variation for transition temperatures and storage modulus, in both cases with a maximum at DS = 2.42.

Fatty acid polysaccharide ester plastic films are promising materials to replace petrochemical commodity plastics and have potential uses such as mulching films. The investigations on mechanical properties of other plastics based on natural polymers, such as hemicelluloses and inulin [11] are underway.

Experimental part

Materials

Microcristalline cellulose (Aldrich, 20µm), lauroyl chloride (Acros, 98%) and *N,N*-dimethyl-4-aminopyridine (Acros, 99%) were used without further purification.

Solvents were purified and stored by using conventional methods. Lithium chloride (Acros, 99%) was stored under vacuum.

Cellulose ester synthesis

Cellulose esters were synthesized using a method described elsewhere [9]. Cellulose was first dissolved in lithium chloride / *N,N*-dimethylacetamide (LiCl/DMAc) by a method in which solvent exchanges were applied before solubilizing in a solution of 6.7% (wt./vol.) LiCl/DMAc (concentration: 1 g of cellulose in 50 mL of the LiCl/DMAc) [12].

Acylation was performed by adding lauroyl chloride and DMAP as catalyst to a solution of cellulose. This mixture was then heated at 90°C for 30 min and the resulting cellulose ester was recovered and purified by a classical method consisting of successive precipitations and redissolving respectively with methanol and chloroform, and drying before casting. In a typical experiment, 3 g of cellulosic substrate (150 mL of a stock solution accounting for 18.5 mmol of anhydroglucose units) was mixed with various amounts of lauroyl chloride (0 to 9 equiv. per anhydroglucose unit, 0 to 166.5 mmol, 0 to 38.7 ml). The amount of catalyst was fixed at 3 equiv. per anhydroglucose unit (55.5 mmol, 6.78 g).

Film forming

Each product was converted into plastic film by casting**:** cellulose esters (white powders) were dissolved in chloroform (150 mL), and then the solvent was allowed to evaporate in a fume cupboard at ambient pressure at room temperature. The recovered films have a thickness ranging from 200 to 350 µm depending on the amount of cellulose ester obtained during the ester preparation.

Chemical Characterization

Each product was characterized by FT-IR spectroscopy using a FT-IR Bruker Vector 22 equipped with a diamond reflection accessory. ^{1}H NMR Spectroscopy was performed in $CDCl_3$ using a Bruker DRX-300 Spectrometer (operating at 300.13 MHz) and served to determine the degree of substitution (DS) by an integration method described elsewhere [9]. The DS is defined as the number of fatty chains attached per anhydroglucose unit and has been shown to have a maximum value of 3.

Mechanical properties

Cellulose ester plastic films (20×20 cm) were converted into dumbbell shaped samples. Ten tests were performed on each film, at room temperature, using an Instron 3201® uniaxial tensile machine. Characteristic parameters of the dumbbell shaped samples are gauge length (L_i) of 50 mm, width (l_i) of 12 mm and a thickness (e_i) ranging from 200 µm to 350 µm. The strain rate $\dot{\varepsilon}$, defined as the ratio of the moving crosshead speed to the gauge length, was fixed at 3.3×10^{-4} s^{-1}.

Some mechanical parameters were deduced from these tests. The elastic modulus *E* was determined from the slope of the linear part of the dynamometric curve (Fig. 2) using the conventional definition expressed as equation 1,

$$E = \frac{F_e \times L_i}{e_i \times l_i \times \Delta L_e} \qquad (1)$$

where F_e is the elastic force corresponding to the elastic elongation ΔL_e, L_i the initial gauge length of the sample, e_i the initial thickness of the sample and l_i the initial width of the sample.

The tensile strength σ_R was calculated as the true failure stress, according to equation 2,

$$\sigma_R = \frac{F_R}{S_f} \qquad (2)$$

where F_R is the failure force and S_f the sample section at break.

Similarly, the tensile strain ε_R was calculated according to equation 3,

$$\varepsilon_R = \frac{\Delta L_R}{L_i} \times 100 \qquad (3)$$

where ΔL_R is the elongation of the sample at failure and L_i the gauge length.

Finally the strain hardening coefficient was determined according to the equation 4,

$$K = \frac{\Delta F \times L_i}{\Delta L \times S_i} \qquad (4)$$

where $\Delta F/\Delta L$ is defined as the slope of the linear part of the dynamometric curve in the plastic region (see Figure 2) and L_i and S_i are, respectively, the gauge length and the initial section of the sample. This last parameter is a measure of the plastic deformation ability of the sample.

Dynamic mechanical analyses

Dynamic mechanical analysis (DMA) was undertaken on films using a DMA Q800 from TA Instruments in multi frequency strain mode, equipped with film tension clamps. Analyses were performed from -70 to 200°C with a frequency of 1 Hz and a heating rate of 5°C/min. During testing, the dynamic mechanical parameters E' (storage modulus), E'' (loss modulus) and tan δ (loss factor) were recorded as a function of temperature.

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