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Preparation of mixed esters of starch or use of an external plasticizer: two different ways to change the properties of starch acetate films

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In view of the brittleness of acetylated starch-based materials, we investigated the possibility of obtaining internal plasticization of such products by preparing mixed esters of starch with both acetate groups and fatty-acid ester chains. We prepared such compounds and determined their compositions by use of quantitative solid-state NMR. The method detailed in this work is not usually used in the area of modified polysaccharides.

The presence of fatty-acid esters is shown to decrease the glass transition temperature. External plasticization of starch acetate by triacetin is also studied. A wide range of polymer–plasticizer compositions was investigated, and the variation of glass transition temperature is found to follow a Couchman law. The mechanical behaviour of mixed esters is also investigated. The introduction of fatty-acid esters is shown to depress the glass transition temperature and the α relaxation associated with the glass transition, corresponding to a plasticizing effect. The introduction of these substituents is shown to suppress the β relaxation, corresponding to a local antiplasticizing effect. However, the strength modulus of mixed esters remains almost unchanged compared to that of starch acetate, and the materials remain brittle in spite of internal plasticization. This is due to a decrease of glass transition temperature, which is not sufficient to produce a soft material. In contrast, external plasticization resulted in an increased flexibility, when sufficient amounts of plasticizer were used. © 1998 Elsevier Science Limited. All rights reserved.

INTRODUCTION

Starch is a natural polysaccharide that is renewable, biodegradable and of low cost. It has been widely studied for many years in the field of materials (Doane, 1992; Swanson *et al.*, 1993; Shogren *et al.*, 1993; Röper *et al.*, 1990; Griffin, 1994).

The hydrophilic nature of starch is a major constraint that seriously limits the development of starch-based materials. In fact, such products are highly water-sensitive, and their properties depend on the ambient humidity (Shogren *et al.*, 1993; Shogren, 1993).

Chemical derivatization has long been studied as a way to solve this problem and to produce waterproof materials. Depending on the nature of the substituents and on the degree of substitution (DS), the properties of modified starch can be varied in an extensive way (Light, 1990).

Esterification with organic acids (from acetic to fatty acids) is known to result in a thermoplastic and hydrophobic material, when the DS is high enough. Acetylation of starch has been widely studied for this purpose (Whistler *et al.*, 1944; Mullen *et al.*, 1942; Wolff *et al.*, 1951, 1957). Mullen *et al.* (1943) evaluated the industrial potential of starch acetates and mentioned the poor mechanical properties obtained, resulting from the presence of amylopectin (the highly branched component of starch). They also found that the properties of starch esters could be enhanced by increasing the size of substituents (butyrate, caproate), but these properties remained poor.

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Keeping in mind these conclusions, some workers focused on the properties of fatty esters but limited their investigations to esterification of amylose. Gros *et al.* (1962) demonstrated that it was possible to obtain a large elongation (400–600%) with films prepared from amylose and capric or lauric acid. When changing the nature of the fatty-acid ester from acetate to laurate, they observed a decrease in Young's modulus from 4 to 0.2 GPa. At the same time, a large depression of the melting temperature from 295 to 70°C was measured. In the same work, they prepared some mixed esters of amylose and showed that it was a way of promoting internal plasticization. However, the cost of amylose is very high and unsuitable for the production of a common plastic. For this reason, the production of partially substituted starch esters has been recently revisited, with the works of Shogren (1996) on acetates plasticized with water, and that of Sagar *et al.* (1995) on butyrates to hexanoates showing enhanced processability and mechanical properties especially when the starch esters were plasticized with dibutylphthalate. These authors all worked with high amylose-content starch, in order to decrease the influence of amylopectin.

In this work, we investigated two basically different ways of obtaining plasticization of starch acetates. On the one hand, we synthesized mixed esters in which the fatty-acid ester (caproate or laurate) acts as an internal plasticizer. On the other hand, glycerol triacetate (triacetin) was used to study external plasticization because this compound is well known to efficiently plasticize cellulose acetate (Suvorova *et al.*, 1995).

In order to carry out structural analyses of these starch derivatives, quantitative high-resolution ^{13}C NMR in both the liquid and solid phases was used. The need for solid-state NMR was due to the fact that the chemical modification resulted in polymers that were insoluble in the usual solvents (chloroform, methylene chloride, acetone, toluene, dimethylsulfoxide).

The experimental conditions required to obtain quantitative information from NMR either in the liquid or solid phase are actually well established (Attias *et al.*, 1987). In solution, a single spectra recorded under appropriate conditions (proton decoupling only during the acquisition of the NMR signals and long enough recovery periods between the scans) leads to signals that are directly proportional to the number of spin. While it is straightforward to get quantitative data from liquid NMR, to do so from solid-state NMR is much more complex. In fact, the high-resolution ^{13}C spectra of solids are recorded under cross-polarization (Hartmann *et al.*, 1962) and magic-angle spinning (CP/MAS) conditions (Andrew, 1981). The ^{13}C magnetizations are built-up through the dipolar interactions between the carbons and their surrounding protons. The dynamics of this process strongly depend on the nature of the carbons (CH_3, CH_2, CH, C). In fact, it is the sum of two processes that are:

- the exponential decrease of magnetization;
- the transfer of magnetization through cross-polarization.

Its analytical expression was established several years ago (Garroway *et al.*, 1979):

$$M = M_0[1 - \exp(-t_{cp}/T_{CH})]\exp(-t_{cp}/T_{1\rho H}) \qquad (1)$$

where M is the measured intensity, M_0 is the initial intensity of magnetization, T_{CH} and $T_{1\rho H}$ are two characteristic relaxation times of the system, and t_{cp} is the contact time (period of the CP/MAS experiment during which the ^{13}C magnetizations are built up).

M_0 is directly proportional to the number of spins, and, consequently, it can be used for quantitative analysis. Unfortunately, this parameter can never be measured directly and the values of M_0, T_{CH} and $T_{1\rho H}$ were computed by fitting the experimental intensities M recorded at different mixing times t_{cp} with the above analytical expression.

EXPERIMENTAL

Materials

A high amylose-content starch (Collys) from corn was kindly provided by Roquette (France). Caproic anhydride, lauric acid, glycerol triacetate (triacetin) and 1,3-dicyclohexylcarbodiimide (NDCC) were purchased from Aldrich (France). All solvents were used without further purification.

Synthesis

Our main interest is to obtain homogeneous chemical modification of starch. Such a homogeneity of the modification is necessary to obtain derivatives with reproducible properties. In a previous study (Fringant *et al.*, 1996), we determined the physical properties of starch acetates. These products had various degrees of substitution and were prepared by homogeneous deacetylation from a solution of starch triacetate in chloroform. In the present case, the homogeneous chemical modification was achieved by working with a destructured form of starch obtained by dissolution in hot DMSO, followed by precipitation from ethanol. Such a treatment allows the disintegration of the organized packing of the chains to obtain more isolated macromolecules with an increased accessibility of the reactive groups. With this more reactive form of starch, we prepared fatty esters by the classical method described by Gros *et al.* (1962) using acyl chlorides. Due to the higher accessibility of the starch, such conditions were too harsh (high tempertures, long reaction times, rapid production of hydrochloric acid in the reaction medium) producing major molecular degradation. Consequently, we adopted milder synthesis conditions, using anhydrides in pyridine.

Preparation of fatty anhydride

Since lauric anhydride was not commercially available, it was prepared by the dehydration of two equivalents of the corresponding acid. Lauric acid (16 g, 8 × 10^{-2} mol) was

Table 1. Quantities of reagents used for the preparation of mixed esters

Type of mixed ester	Acetic anhydride	Fatty anhydride	Acetate/sugar (mol/mol)	Laurate or caproate/sugar (mol/mol)
Acetate/caproate	2 ml	14.5 ml	1.7	5.1
Acetate/caproate	4 ml	9.7 ml	3.4	3.4
Acetate/caproate	6 ml	4.9 ml	5.1	1.7
Acetate/laurate	2 ml	24 g	1.7	5.1
Acetate/laurate	4 ml	16 g	3.4	3.4
Acetate/laurate	6 ml	8 g	5.1	1.7

dissolved in 250 ml of diethylether that had previously been dried over metallic sodium ribbons, and 9 g of *N,N′*-dicyclohexylcarbodiimide (NDCC), corresponding to a slight excess, 4.3×10^{-2} mol, were added to the solution. The mixture was stirred overnight at ambient temperature under nitrogen flow. The reaction produced an insoluble compound (hydrated NDCC), which was then filtered and discarded. The supernatant ether phase was evaporated under reduced pressure, resulting in a white wax of lauric anhydride as confirmed by FTIR: (disappearance of the hydroxyl band at 3000–3500 cm^{-1} and the appearance of a new band characteristic of the anhydride function at 1800 cm^{-1}).

Preparation of mixed esters

The procedure used here was the same as that described to prepare starch acetate (Wurzburg, 1964). Destructured Collys (2 g) was activated for 1 h in 20 ml of pyridine at 80°C under nitrogen flow. Then, a mixture of the two anhydrides dissolved in 50 ml of pyridine was added. The mixture was then stirred for 5 h at 60°C. After cooling, the clear viscous solution was precipitated with methanol. The resulting polymer was then carefully washed with methanol and dried. The quantities used are given in Table 1.

Characterization

Liquid NMR

NMR spectra were recorded at 25°C on a Bruker AC300 spectrometer operating at 75 MHz for carbon and using $CDCl_3$ as solvent. A 10 mm probe was used to enhance the signal/noise ratio. Because not all samples were completely soluble, only qualitative analysis was possible. For the soluble samples, the composition was determined by quantitative measurements using an inverse gated proton decoupling pulse sequence with a flip angle of 90° (14.5 μs). 8000 to 10000 pulses were collected with a repetition time of 20 s, such a duration was necessary to allow a complete relaxation of the system of spin. After Fourier transformation of the data, the integrations of the different signals were performed with the routine provided on Bruker software.

Solid NMR

Solid-state ^{13}C NMR spectra were obtained under CP/MAS conditions on a Bruker MSL 200 spectrometer operating at 50.3 MHz. A sample of 200–250 mg was placed in a double-bearing rotor made of zirconia. The spinning speed was set in the range 3300–3500 Hz.

The ^{1}H radio-frequency field strengh was set to give a 90° pulse duration of the order of 50 ms; the same value was used for the dipolar decoupling process. The ^{13}C radio-frequency field strength was obtained by matching the Hartmann–Han conditions. Chemical shifts were calibrated via glycine carbonyl signal, set at 176 ppm relative to tetramethylsilane. No special sequence, such as the TOSS sequence, was used to eliminate the spinning side bands, since such sequences give spectra that cannot be used for further quantitative treatments. Assignments of spinning side bands were performed by recording spectra at two different spinning rates.

In order to get quantitative information a dynamic study of the carbon magnetization build-up was performed by varying the contact time values from 10 μs to 20 ms. From these experiments, the quantitative intensities of the different signals were computed, using the simplex fitting progam (SIMFIT) provided by Bruker to fit the data with Eq. (1) and extract M_0. The delay between each acquisition was 10 s; 500–1000 transients were collected.

Properties

Glass transition

Glass transition temperatures were determined using a Perkin-Elmer differential scanning calorimeter (DSC7) equipped with a cooling device. Powder samples were weighed in aluminium pans which were then sealed. For the study of external plasticization, Collys triacetate was premixed with the desired amount of triacetin one day before measurements were made in order to obtain a homogeneous distribution of the plasticizer. The blend was composed of 100 g of starch derivative mixed with *X* g of triacetin and the composition is expressed in the text as "*X*% of plasticizer".

DSC samples were pre-conditioned by a rapid heating to 120°C to eliminate any residual solvent. Thermograms were recorded during heating at a scanning rate of 15°C/min. Glass transition temperatures were determined from the second scan (using the instrument software) in order to discard the influence of thermal history.

Table 2. Assignments of chemical shifts obtained by solid NMR for a mixed acetate/fatty-acid ester of starch

Region	Chemical shift (ppm)	Assignment
I_1	225–240	Carbonyl spinning side bands
I_2	165–180	Carbonyls
I_3	87–107	Carbonyl spinning side bands and sugar C-1
I_4	55–87	Sugar C-2, C-3, C-4, C-5, C-6
I_5	17–40	CH_2 in aliphatic side chains and CH_3 of acetate groups
I_6	10–17	CH_3 of alipahatic side chains

Tensile strength measurements

Mechanical properties were determined using an Instron device at 25°C. A constant rate of 0.4 mm/min corresponding to a strain rate of 0.0235/min, was used. The normalized H3 samples were cut from cast film prepared by slow evaporation (one night at ambient temperature to obtain the film) of a 5% (w/v) solution in chloroform. Before testing, the samples were equilibrated for two weeks in a controlled atmosphere at 57% r.h. and at a temperature of 25°C. This controlled atmosphere of 57% r.h. was chosen because of its usual use by many workers to obtain reproducible results when testing the mechanical properties of biopolymers. After conditionning, the water contents of the samples were in the range 3–5%.

DMTA

Dynamic mechanical thermal analysis (DMTA) measurements were made using a Metravib (France) device. Curves were recorded at different frequencies (1, 0.1, 0.01 Hz) during heating from 100 K at a scanning rate of 13 K/h. The samples tested were cut from cast films prepared as described before.

RESULTS AND DISCUSSION

Determination of composition of mixed esters by solid NMR

When they were soluble, the synthetized starch derivatives produced spectra with well-resolved signals. The spectrum of a mixed acetate/laurate ester is shown in Fig. 1. The assignments of the different signals present in the aliphatic region (10–40 ppm) were easily made on the basis of data found in the literature (Johnson *et al.*, 1972) and by comparison with the spectra obtained for the individual esters. Assignments are illustrated in Fig. 2. The identification given for the sugar region was taken from previous work (Fringant *et al.*, 1996).

Two typical solid-state NMR spectra of mixed esters are presented in Fig. 3. The NMR signals in the solid-state appear to be much broader (200 Hz) than those in solution. The lack of crystallinity in these materials leads to a dispersion of the chemical shifts, which is the cause of the signal broadening. Nevertheless, the signals are easily assigned by comparison with the spectra obtained in solution.

The spinning rates (3500–4000 Hz) that were used to record the spectra were not high enough to average completely

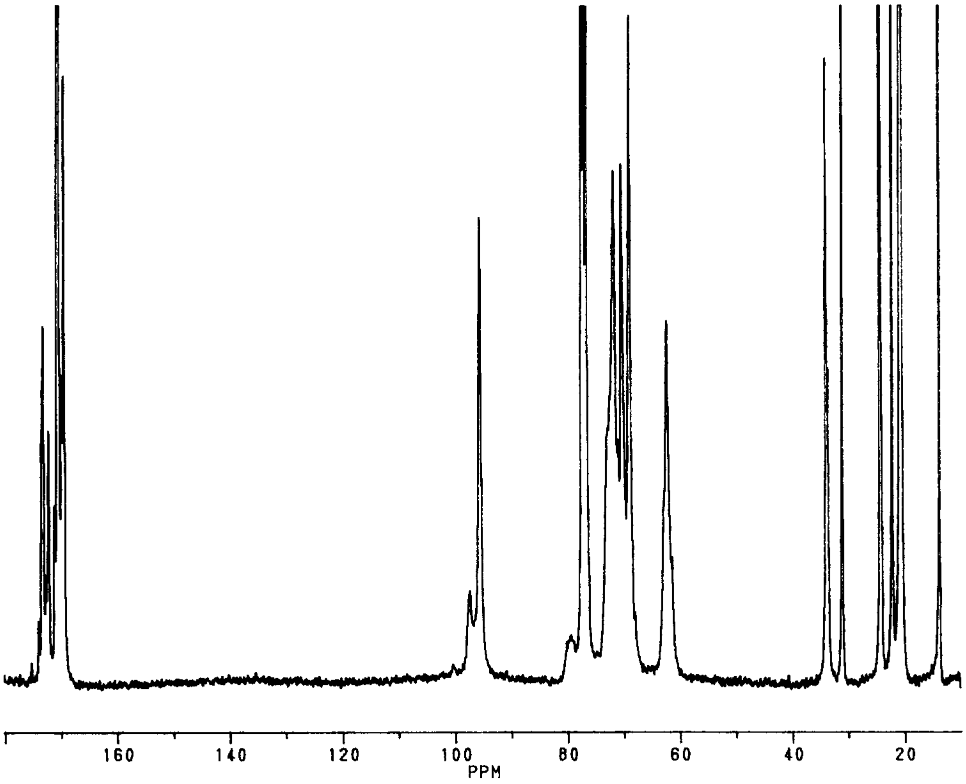

Fig. 1. Liquid ^{13}C NMR spectra of a mixed acetate/laurate starch ester.

Table 3. Composition of mixed esters determined from liquid and solid NMR measurements

Type of ester	From liquid-state NMR			From solid-state NMR		
	DS_{tot}	DS_{ali}	DS_{ace}	DS_{tot}	DS_{ali}	DS_{ace}
Acetate/laurate	2.95	0.57	2.35	3.1	0.5	2.6
Acetate/laurate				2.7	0.6	2.1
Acetate/laurate				2.5	0.1	2.4
Acetate/caproate	2.66	0.7	1.93	2.9	0.7	2.2
Acetate/caproate				2.3	1	1.3
Acetate/caproate				2.8	0.3	2.5

DS_{tot} = total degree of substitution; DS_{ali} = fatty-acid ester degree of substitution; DS_{ace} = acetate degree of substitution; accuracy of the values: ±8–10%.

the chemical shift anisotropy tensor of carbonyl groups. Consequently, this gives rise to spinning side bands, termed SSB in the spectra. These are easily identified by changing the spinning rate. For the quantitative exploitation of the data, the integrals of the spinning side bands were added to the integrals of the carbonyl signals as the carbonyl resonances are split in their isotropic signal and spinning side bands. Assignments and definitions of the integral regions are reported in Table 2.

Fig. 4A (1 and 2) display an example of the magnetization of the different spectral regions versus the contact time (t_{cp}). They illustrate the cross-polarization dynamics that appear to be dependent on the nature of the carbons. It can be seen that the maximum values of the magnetization M are obtained over a range of t_{cp} of 1–3 ms. In order to make quantitative measurements, it is necessary to obtain spectra with as good a definition of the different signals as possible. This was achieved by chosing a value of t_{cp} to allow the magnetization of all the different carbons to be as high as possible. Considering the results presented on Fig. 4, all the determinations of the degrees of substitution were made with the value of the contact time $t_{cp} = 1.5$ ms.

The different curves presented in Fig. 4B (1 and 2) result from the fitting of the experimental data with Eq. (1) which allows us to calculate M_0 and to normalize the values of observed intensities ($M_{t_{cp}}/M_0$). These curves allow the coefficients k_i used for the calculation of the degrees of substitution to be obtained as described below, whatever the chosen value of t_{cp}. Moreover, for long contact times, the evolution of magnetization is mainly described by an exponential decrease as can be seen in Eq. (1). It can be seen in Fig. 4B that for the highest values of t_{cp}, all the normalized magnetizations are of the same order of magnitude. This means that for all the carbons, in spite of the different chemical environments, a single relaxation ($T_{1\rho H}$) of the protons is implied and this indicates that our materials were sufficiently homogeneous. (Attias *et al.*, 1987).

It has to be mentioned that the calculated values of the parameter T_{CH} are in the order $T_{CHI_6} > T_{CHI_2} > T_{CHI_4}$; the numbers indicate the spectral region defined in Table 2. The T_{CH} order illustrates the difficulty in polarizing the methyl group of fatty-acid esters due to its high mobility.

By combination of the assignments with the normalized curves, one can deduce the following formulae that allow calculation of the different degrees of substitution for the modified polymers. Total degree of substitution:

$$DS_{tot} = [(I_1 + I_2 + (I_3 - I_4/5))/k_2]/[(I_4/5)/k_4]$$

Aliphatic side chains:

$$DS_{ali} = (I_6/k_6)/[(I_4/5)/k_4]$$

Acetyl groups:

$$DS_{ace} = DS_{tot} - DS_{ace}$$

The coefficients, k_i, are obtained from the normalized polarization curves and are calculated for each spectral region (I_i) as follows:

$$k_i = (M_{t_{cp}}/M_0)_i \qquad (2)$$

The degrees of substitution calculated from solid-state

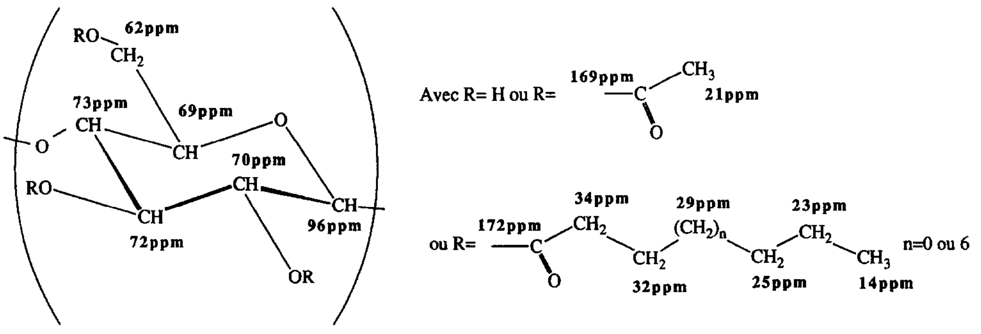

Fig. 2. Assignments of chemical shifts obtained by liquid NMR for a mixed acetate/fatty-acid ester of starch with fatty esters having more than six carbon atoms.

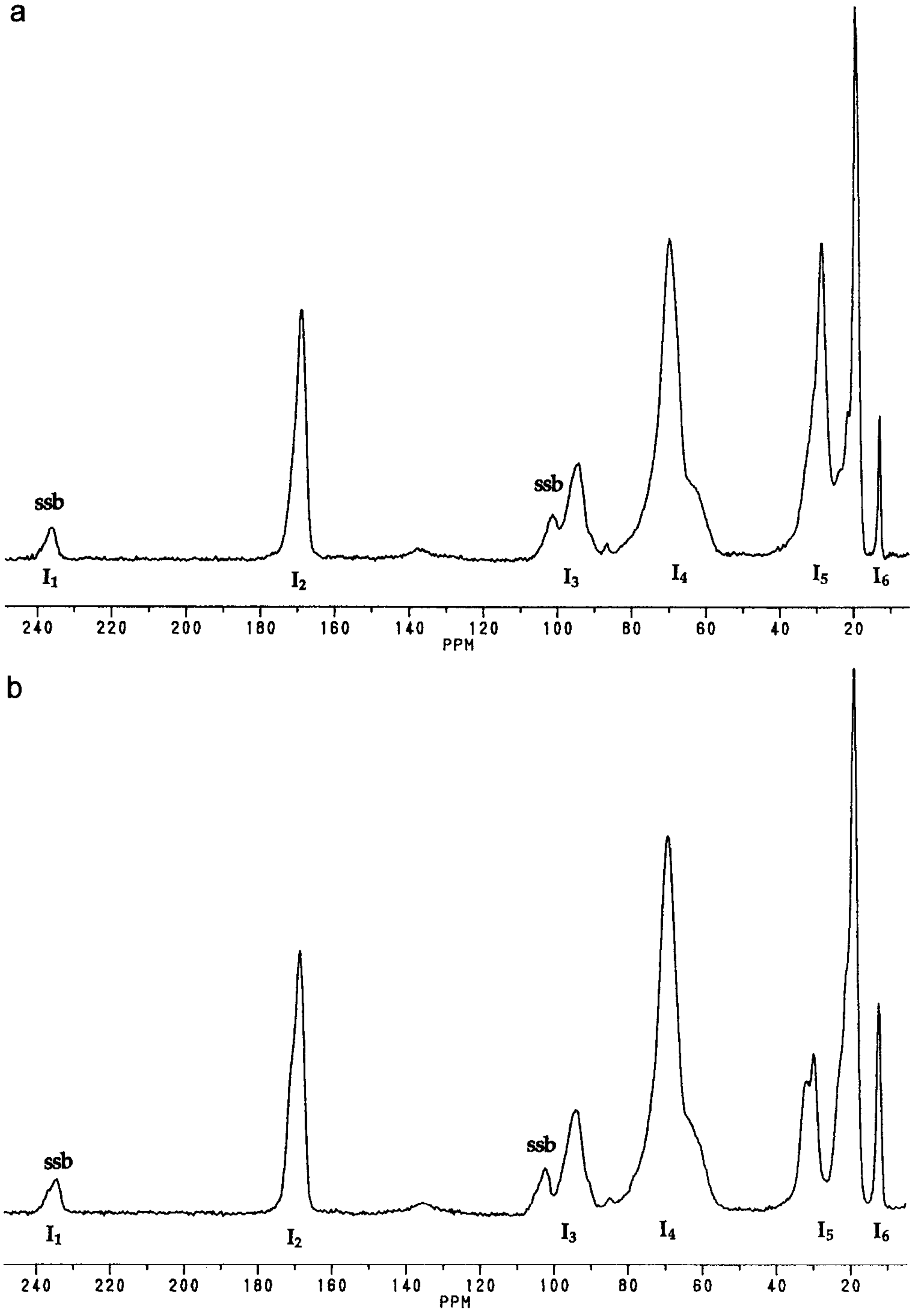

Fig. 3. Solid ^{13}C NMR spectra of (a) mixed acetate/laurate starch ester and (b) mixed acetate/caproate starch ester.

measurements are given in Table 3 and compared with the values obtained from liquid NMR measurements. It can be noticed that both methods provide a fairly good agreement when the polymers are soluble. The differences can be explained by many factors: e.g. the quality of the signal/noise ratio and the difficulty in correctly integrating the spinning side bands, which makes it difficult to obtain an experimental error smaller than about 10% for the DS extracted from solid NMR. However, these measurements allow us to estimate the composition of the mixed esters we prepared, in a simple and non-destructive way, and to compare their behaviour.

Thermal properties

The glass transition temperatures of mixed esters are given in Table 4 and compared with starch triacetate. It can be seen that whatever is the composition of mixed esters, the glass transition temperature is located below the value obtained for pure starch acetate having nearly the same

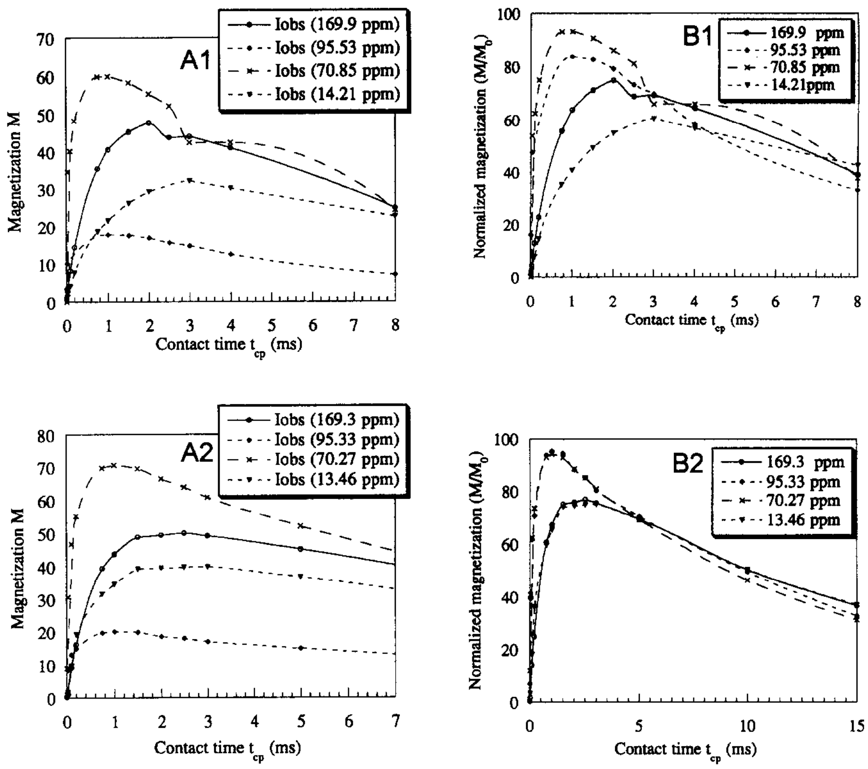

Fig. 4. Evolution of (A) magnetization and (B) normalized magnetization for (1) mixed acetate/laurate and (2) acetate/caproate ester.

DS. It is difficult to make a precise comparison between all samples, because the total degrees of substitution are slightly different. However, it is clear that there is a depression of the glass transition temperature, when the fatty-acid ester content increases (Gros *et al.*, 1962).

From these data, it appears that plasticization with laurate substituents is more efficient than with caproate; it was necessary to introduce a higher proportion of caproate to obtain the same shift in glass transition temperature as with a given proportion of laurate. This is consistent with literature results showing a decrease in the melting temperature of amylose fatty triesters when chain length increases. However, one can notice that even for a significant level of fatty-acid esters, the glass transition temperature remains much higher than ambient temperature.

The external plasticization of starch acetate by triacetin was also studied. The variation of the glass transition temperature with plasticizer content is shown in Fig. 5 (in this figure, the composition is given using true mass fraction of plasticizer). The decrease of T_g is clearly illustrated and shows the efficiency of triacetin in plasticizing the biopolymer.

The validity of the Couchmann–Karasz (Brinke *et al.*, 1983) model was examined. The DSC thermogram of pure triacetin was recorded, after rapid quenching to obtain the glassy state of the plasticizer, and is presented in Fig. 6. This allowed us to determine the parameters

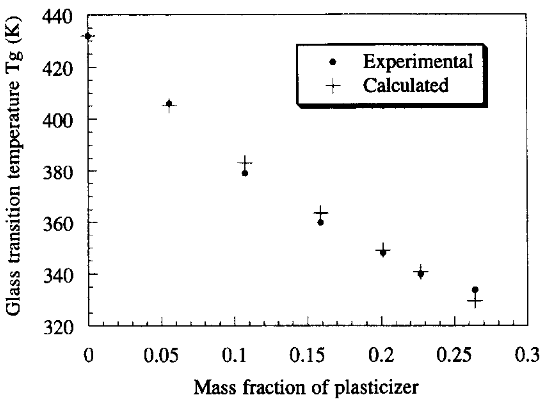

Fig. 5. Evolution of the glass transition temperature of Collys triacetate with the amount of plasticizer and comparison with the theoretical curve.

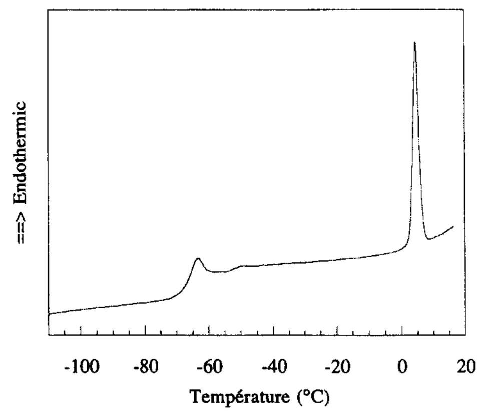

Fig. 6. Thermogram of glycerol triacetate after rapid quenching at 110°C. Scanning rate 15°C/min.

Table 4. Glass transition temperatures of mixed esters obtained by DSC

Type of ester	DS_{ace}	DS_{ali}	DS_{tot}	T_g (°C)
Acetate/laurate	2.1	0.6	2.7	89
Acetate/laurate	2.6	0.5	3.1	97
Acetate/laurate	2.4	0.1	2.5	136
Acetate/caproate	1.3	1	2.3	90
Acetate/caproate	2.2	0.7	2.9	114
Acetate/caproate	2.5	0.3	2.8	133
Acetate			3	155

required by the model which describes the variation of the glass transition temperature according to the following relation:

$$T_g = \frac{w_1 \times \Delta Cp_1 \times T_{g_1} + w_2 \times \Delta Cp_2 \times T_{g_2}}{w_1 \times \Delta Cp_1 + w_2 \times \Delta Cp_2} \qquad (3)$$

where T_{g_1} is the glass transition temperature of the pure polymer ($T_g = 433$ K, Fringant *et al.*, 1996), T_{g_2} that of triacetin ($T_g = 206$ K), w_1 and w_2 the weight fraction of each component, ΔCp_1 (0.23 J g^{-1} K^{-1}) and ΔCp_2 (0.5 J g^{-1} K^{-1}) the increment of heat capacity. The theoretical curve obtained from application of this model is shown in Fig. 5. A good agreement can be seen between the model and the experimental data, demonstrating that triacetin is a good plasticizer over a wide range of composition and that it is efficient in producing a material with a low T_g.

Mechanical properties

Among the different mixed esters prepared, only two were soluble in chloroform and permitted the preparation of cast films. Therefore, the determination of mechanical properties was limited to these two modified polymers. The values of tensile strength for the different plasticized acetate films are given in Table 5. The quantity of triacetin (45%) was chosen because it results in a sufficient flexibility of the films.

As can be seen from Table 5, the values of modulus obtained for mixed-ester films are not very different from the one obtained for non-plasticized acetate film. This is related to the fact that the value of glass transition temperature remains above ambient temperature; the materials remain in the glassy state ($T_g = 97$°C for acetate/laurate and $T_g = 114$°C for acetate/caproate), and their modulus is almost unchanged compared to that of unplasticized starch acetate film. In contrast, with triacetin, the modulus is much smaller than that without plasticizer when the content is high enough to produce a low glass transition temperature (T_g is in the range 30–40°C but could not be precisely determined by DSC for such a high plasticizer content).

Table 5. Mechanical properties of various starch ester films ($T = 298$ K, 57% r.h.)

Type of ester	Modulus (GPa)	Elongation at break (%)
Unplasticized acetate ($DS = 2.8$)	1.7	5
Acetate (2.35)/laurate (0.57)	1.3	3
Acetate (1.93)/caproate (0.7)	1.2	1
Plasticized acetate (45%)	0.16	13

Table 6. Characteristics of molecular relaxations of an unplasticized starch acetate film. The temperatures of the relaxations are determined at the frequency of 0.1 Hz

Temperature (K)	τ_0 (s)	E_a (kJ/mol)
140	1.7×10^{-11}	29
227	1.5×10^{-19}	82
404	1.9×10^{-54}	417

These differences in mechanical behaviour were illustrated by DMTA measurements. The curves obtained are presented in Fig. 7. Different molecular relaxations can be observed; they are named γ, β and α as temperature increases. The measurements have been made using different frequencies which allows the calculation of molecular motion characteristics for each relaxation. For these calculations, the characteristic temperature of the relaxation is determined for each measurement frequency; it corresponds to the maximum of the loss modulus E''. The relaxation time τ is determined by the relation $2\pi f\tau = 1$ where f is the frequency measurement. The characteristics of the relaxation are determined assuming an Arrehnius law:

$$\tau = \tau_0 \exp(E_a/RT)$$

where τ_0 is the pre-exponential time, T the characteristic temperature of the relaxation and E_a the activating energy.

Unfortunately, the resolution of our curves was sometimes low and these calculations were not always possible. The results obtained are presented in Table 6.

The γ relaxation for unplasticized acetate film is clearly visible. Its characteristics (low activation energy and characteristic time value of the same order as Debye time) are in

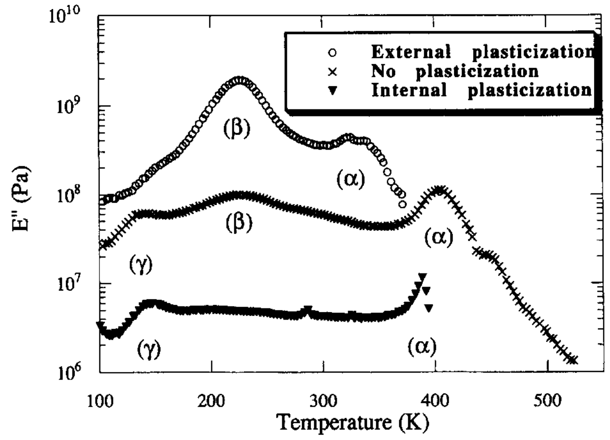

Fig. 7. Evolution of loss modulus with the temperature for different acetate films. Frequency measurements 0.1 Hz. Scanning rate 13 K/h.

agreement with a local non-cooperative motion of the side groups (acetate or non-substituted hydroxyl). This relaxation disappears with the addition of the external plasticizer, as is also the case with other systems (Nylon/water (Varlet *et al.*, 1990); cellulose/water (Montes *et al.*, 1994)). In the case of mixed esters, this relaxation is slightly enhanced. This is consistent with the rotation of aliphatic methyl groups that is easier than the rotation of acetate or non-substituted hydroxyl, as mentioned earlier with regard to the solid NMR results.

The α relaxation is unambiguously related to the glass transition; its characteristics (high activation energy and low characteristic time) are in total agreement with cooperative motions and its variation is in good agreement with the variation of the glass transition temperature determined by DSC.

The β relaxation is more difficult to explain. In the case of unplasticized acetate film, the calculated characteristics are relevant to a slightly cooperative local motion. Such relaxations have been observed for many polysaccharides (Scandolla *et al.*, 1991; Bradley *et al.*, 1976) and attributed to the motion of a limited number of sugar units. In the case of internal plasticization, such a relaxation is not observed, perhaps indicating a local antiplasticizing effect of fatty-acid esters. This effect could be explained by steric hindrance of fatty-acid esters that decreases the possibilities for local motion. In the case of external plasticization, an impressive β relaxation is observed. The calculated characteristic time is smaller (5×10^{-33} s instead of 10^{-17} to 10^{-19} s) and the activating energy is higher (143 kJ/mol instead of 50–80 kJ/mol) than usual values for such a relaxation. This is a reflection of significant cooperativity in this motion. This could be due to specific polymer–plasticizer interactions arising from the similarity in chemical structure between the polymer subtituents and the plasticizer. Another interpretation, which has to be kept in mind, is the possibility of a phase separation and a system with two glass transition temperatures. In this case, the observed relaxation would in fact be related to the glass transition of the most plasticized part of the system. The present results do not allow us to distinguish among these possibilities at this time.

The evolution of the amplitude of the β relaxation is in good agreement with the mechanical properties reported in Table 5. As is the case with many polymers, the ductilities of our samples were of the same order as the β relaxation height. The most brittle sample (mixed ester) was that for which no β relaxation was observed.

CONCLUSION

In this work, we investigated internal and external plasticization of starch acetates. We prepared mixed esters containing both acetate and caproate substituents, or acetate and laurate subtituents. We characterized the modified polymers by quantitative solid-state NMR. The composition of mixed esters, obtained by this method, has a limited precision, but was sufficient to make a comparison between the different products. Moreover, this method is non-destructive and simple, once the optimum conditions have been determined in a preliminary study.

We demonstrated that the depression of the glass transition temperature could be produced by increasing the size of the substituent or the proportion of the fatty-acid ester, in agreement with literature results. The external plasticization by triacetin was also demonstrated to be very efficient and to follow the Couchmann–Karasz law.

The influence of plasticization on mechanical properties was shown to be negligible for mixed esters in the composition range investigated. In contrast, external plasticization results in a material with an increased flexibility.

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