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Physical properties of acetylated starch-based materials: relation with their molecular characteristics

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In order to obtain thermoplastic starch-based materials with a reinforced hydrophobicity, amylose and amylopectin were acetylated following the pyridine–acetic anhydride procedure. An amylose-rich starch triacetate was saponified under controlled conditions to obtain products with different acetyl contents. The adsorption of water by these polymers equilibrated in a 98% r.h. atmosphere was studied using thermogravimetric analysis and differential scanning calorimetry. A slight increase of non-freezing water content is observed when the acetyl content increases up to DS $\approx$ 1.3–1.4. For higher acetyl contents, the hydrophobicity of the material is efficiently enhanced and no more freezing water is adsorbed. Tensile strength measurements were performed on films with different amylose acetate–amylopectin acetate ratios: no variation of the tensile modulus (2.5 ± 0.5 GPa) was observed when composition changed, but the elongation at break was strongly decreased when the amylopectin acetate content increased. The influence of acetyl content on thermal properties was also studied. The position of glass transition (~150°C in the dried state) was unchanged when DS ranged from 1.7 to 3, and moved towards higher temperatures when the acetyl content decreased. This thermal characteristic when DS $>$ 1.7 will allow easy processing of these materials. Copyright © 1996 Elsevier Science Ltd.

(Keywords: starch; amylose; amylopectin)

INTRODUCTION

For the last ten years, there has been an important resurge of interest in the development of non-food applications of polymers from biomass. Among these, starch has been widely studied in the area of biodegradable materials[1-3].

Starch is a polymer of D-glucose stored in granules (organized in amorphous and crystalline regions) as a reserve in most plants[4-6]. Chemically, it is mainly composed of two very different macromolecules[7] whose proportion depends on the botanical origin of starch.

Amylose[8] is a very weakly branched polymer of D-glucose in which the repeating units are linked by $\alpha(1-4)$ linkages. It exhibits a typical molecular weight of more than 10^5. The stereoregularity[9] of amylose allows formation of complexes with a wide variety of complexing agents (iodine, lipids, etc.).

Amylopectin[10], the second component of starch, is a highly branched polymer of D-glucose. Branching points are $\alpha(1-6)$ linkages. Amylopectin molecular weight is not well known but is probably in the region of more than 5×10^6. The widely accepted structure of this compound is cluster type.

In most naturally occurring starches, the ratio amylose/amylopectin lies near 25/75, but some new varieties produce higher amylose yielding starches (70/30).

Research dealing with the use of starch for the preparation of new materials can be classified into three types.

1. Starch can be used as a filler in blends with synthetic polymers. It is then compounded in its granular form mainly with polyethylene[11]. The biofragmentability of such products was reduced due to the inaccessibility of starch granules for the enzymes.
2. To overcome this problem, a second approach is to mix extruded starch with synthetic polymers[12]. Indeed, starch can be considered as a thermoplastic material. In fact, the glass transition (T_g) of this polymer lies above its decomposition temperature when the polymer is dried[13], but the addition of water (which is a very efficient plasticizer of polysaccharides) drastically reduces the T_g[14]. Starch has been extruded using a wide variety of plasticizers. The homogeneous melt obtained is then coextruded and moulded with other synthetic thermoplastic materials[15]. In this approach, one important problem is the incompatibility of hydrophilic starch with synthetic polymers. To overcome the problem of chemical incompatibility of starch, a wide range of copolymerizations of synthetic monomers onto starch chains has been developed[16-18]. The copolymers obtained in this way can be processed as compatibilizing agents. However, the use of such copolymers is limited because of the high costs of such copolymerizations. Blends with partly hydrophilic synthetic

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polymers are preferred. The industrialized product resulting from this second approach is Mater-Bi® developed by Ferruzzi. This product is obtained by mixing thermoplastic starch with a partly hydrophilic synthetic copolymer (ethylene–acrylic acid copolymer)[19].

3. The last way to develop starch-based materials is to use extruded starch in the same manner as any thermoplastic material[20]. Various plasticizers[21] have been used to change the mechanical properties of such materials. The major drawback of this approach lies in the sensitivity to water exposure of the materials obtained. The plasticizers used are usually hydrophilic (glycerol, sorbitol, etc.) and can be washed by water. Moreover, it is necessary to add water to starch before extrusion processing. The evaporation of this non-equilibrium water content during ageing of material is accompanied by a change in material properties: the material becomes brittle. Another drawback is the hydrophilic nature of starch. Depending on the atmospheric relative humidity, starch can adsorb a more or less significant quantity of water. As T_g is very sensitive to water content, the mechanical properties of the materials undergo important changes with variation of relative humidity.

These considerations led us to try to develop new starch-based materials through homogeneous chemical modification of starch in order to increase its hydrophobicity. Examination of the literature and preliminary studies made in our laboratory showed that the most interesting chemical modification is acetylation. This reaction allows the preparation of a thermoplastic and hydrophobic material. Surprisingly, whereas some papers deal with the mechanical properties[22,23] of amylose triacetate, no data are available in the literature concerning the influence of derivatized amylopectin on such properties.

The purpose of this paper is to study the behaviour of acetylated components of starch and to investigate the influence of acetyl content on their thermal properties and hydration.

EXPERIMENTAL

Materials

Amylose was extracted by aqueous leaching[7] from pea starch, kindly provided by Cosucra (Holland): a suspension of 50 g of starch was added to 1.5 l of hot water (83°C). The temperature was maintained for 30 min with gentle shaking under nitrogen flow. The suspension was then centrifuged (4500 rev min^{-1}) for 20 min. The supernatant was cooled after adding n-butanol (9.5% by volume) and the amylose–butanol complex was allowed to crystallize for 16 h at room temperature. The complex was then centrifuged (12 000 rev min^{-1}) for 20 min. The complex was resuspended in a water/n-butanol mixture (9.5% by volume). The suspension was heated under nitrogen flow until dissolution of the complex. After recrystallization of the complex, the solution was centrifuged and the solid was then washed several times with ethanol, acetone and diethylether. After drying at room temperature, the extraction yielded about 5 g of a white powder.

Waxilys starch provided by Roquette (France) was considered to be composed of amylopectin essentially free of amylose. It was acetylated in its granular form or after pretreatment. This pretreatment was done to destructure the crystalline organization and consisted of the dissolution of waxy starch in dimethylsulfoxide and precipitation with ethanol.

A high amylose content starch (Collys, provided by Roquette France) was acetylated in its granular form.

All reagents (pyridine, acetic anhydride) were analytical grade and were used without further purification.

Procedures

Basic acetylation. Amylose, amylopectin and Collys were acetylated following the method of Whistler and Hilbert[23], with slight modifications. In order to acetylate the different starchy products in the mildest conditions and to avoid as much as possible molecular degradations, a preliminary study was made to demonstrate the difference in reactivities of the various starchy products.

Starch (used as a general term for amylose, Waxilys, whether destructured or not, and Collys) was activated in hot pyridine at the activating temperature (T_a) for a certain activating time (t_a) under nitrogen flow. The temperature was then decreased to the reaction temperature (T_r) and a given quantity of acetic anhydride was added slowly. The mixture was allowed to react for a certain time (t_r). The experimental conditions are given in *Table 1*.

After cooling, the product was precipitated with diethylether, washed with ethanol/water mixture, diethylether and dried.

Homogeneous controlled saponification. In order to obtain a homogeneous distribution of acetyl groups

Table 1 Experimental conditions for preparation of acetylated products

Starchy product	Quantity of starch (g)	Quantity of pyridine (ml)	Quantity of anhydride (ml)	T_a (°C)	t_a (min)	T_r (°C)	t_r (min)	DS
Amylose	2	100	8	80	120	60	360	2.8
Granular Waxylis	2	100	8	80	120	60	360	1.3
Pretreated Waxylis	2	100	8	80	120	60	360	2.6
Amylose	10	200	40	70	60	65	360	2.7
Granular Waxylis	7.5	250	30	85	180	70	1200	2.6
Pretreated Waxylis	7.5	250	30	80	120	50	960	2.6
Collys	50	700	200	85	120	60	600	3

Table 2 Experimental conditions used for controlled saponification of Collys triacetate at ambient temperature

	DS value							
	2.7	2.5	2	1.7	1.4	1	0.6	0.15
[KOH] (mol l^{-1})	0.01	0.01	0.02	0.04	0.02	0.05	0.1	0.2
Quantity of TBAOH[a] (ml)	3.2	3.2	10	3.2	10	20	20	20
Reaction time (min)	90	300	180	150	540	150	240	300

[a] 1 M TBAOH in methanolic solution

along the polymer chain, the saponification of fully acetylated product was conducted according to an original procedure. Triacetate of Collys (6 g) was dissolved in 240 ml of dichloromethane. The solution was shaken with aqueous potassium hydroxide (240 ml). As the hydrophobicity of dichloromethane does not allow diffusion of KOH, it is necessary to add a basic phase-transfer catalyst agent. The use of tetrabutylammonium hydroxide (TBAOH) dissolved in methanol enables good reaction efficiencies to be obtained. Depending on the concentration of KOH, on the quantity of TBAOH and on the reaction time, it was possible to obtain a wide range of acetyl contents. The experimental conditions are given in *Table 2*.

After completion of the reaction at the desired level, the product is precipitated with ethanol. The precipitate is then washed with water/ethanol mixtures until the pH reaches a neutral value. Washing is completed with diethylether and the product is then dried.

Analytical procedures. The intrinsic viscosity of the extracted amylose was measured using a capillary viscosimeter (Fica Viscomatic MS). The solvent was 1 M KOH, the temperature 25 ± 0.1°C and the concentration of the solution was 0.005 g ml^{-1} (dried basis).

The purity of amylose was checked by a spectrophotometric determination of the CLI[24] (iodine affinity). A synthetic linear amylose was used as reference.

Infra-red spectra were recorded using a Perkin Elmer FTIR 1720X apparatus. Spectra of powders were obtain by mixing 3 mg of acetate with 100 mg of dry KBr and by pressing the resulting powder into a disk.

N.m.r. spectra were recorded using $CDCl_3$ as solvent. Homonuclear measurements were made on a Bruker AC 300 spectrometer and heteronuclear measurements on a Varian Unity 400 spectrometer.

The determination of acetyl content was made following the procedure of Wurzburg[25] based on saponification with an excess of KOH back-titrated with hydrochloric acid.

Thermal properties study. Thermal properties of the samples were studied using a Perkin Elmer differential scanning calorimeter (DSC7), equipped with a cooling device. The powders were weighted (15–20 mg) in aluminium capsules, which were then sealed. Two holes were made in the capsules to allow evaporation of any residual solvent. The samples were conditioned by rapid heating to 120°C for 10 min to eliminate any residual solvent. The differential scanning calorimetry (d.s.c.) curves were recorded in the temperature range from 25 to 300°C upon heating with a scanning rate of 15°C min^{-1}. An empty capsule was used as a reference.

Hydration study. The samples were equilibrated for three weeks in a 98% relative humidity (r.h.) atmosphere. This level was obtained by exposing the powders to the vapour of a saturated $CuSO_4.5H_2O$ solution in closed desiccators at 25°C.

The total water content of the sample after equilibrium was determined by thermogravimetric analysis (t.g.a.). A Setaram-TGDTA92-12 apparatus was used. Hydrated samples (20–30 mg) were heated from 20 to 130°C at a scanning rate of 10°C min^{-1}. Tests were continued until the first derivative of the weight loss curve equalled zero. During loading, samples were exposed to ambient atmosphere for an average period of 1 min.

The d.s.c. apparatus was used to determine the amount of freezing water. D.s.c. curves were obtained in the temperature range from −40 to 20°C upon heating with a scanning rate of 2°C min^{-1}. Indium (T_m = 156.64°C) and n-dodecane (T_m = −9.65°C) were used for calibration. Samples were weighed (15–20 mg) in aluminium capsules, which were then sealed. During sealing, samples were exposed to ambient atmosphere for approximately 1 min. Sample enthalpies were calculated using pure water as reference.

Total water (W_c) was determined by t.g.a., freezing water (W_f) by d.s.c. and non-freezing water (W_{nf}) in accordance with Hatakeyama *et al.*[26], taking into account the dry matter as reference:

$$W_c = m_{(H_2O\ evap)}/m_s \quad (g/g) \quad (1)$$

$$W_f = \Delta H_s(1 + W_c)/\Delta H_{H_2O} \quad (g/g) \quad (2)$$

$$W_{nf} = W_c - W_f \quad (g/g) \quad (3)$$

in which $m_{(H_2O\ evap)}$ is the mass (in grams) of evaporated water determined by t.g.a., m_s the dried mass of the sample used for t.g.a. measurements, ΔH_{H_2O} the enthalpy of melting per gram of pure water, and ΔH_s the enthalpy of melting per gram of hydrated sample used for d.s.c. measurements.

Mechanical properties. Starch acetate films were prepared by casting. Dichloromethane was chosen as a volatile solvent for the highly substituted starch acetates. A casting solution (5% w/v) was prepared by dissolving the starch acetate in the solvent in order to obtain a clear viscous solution. Solutions were poured onto glass. The slow evaporation of the solvent resulted in a transparent film. Films were then cut to obtain the desired testing geometry.

Before testing, the pieces of film were allowed to equilibrate for two weeks in a 57% r.h. controlled atmosphere, in order to obtain reproducible results.

Tensile strength measurements were made at the temperature of 25°C using a Rheometrics Solids

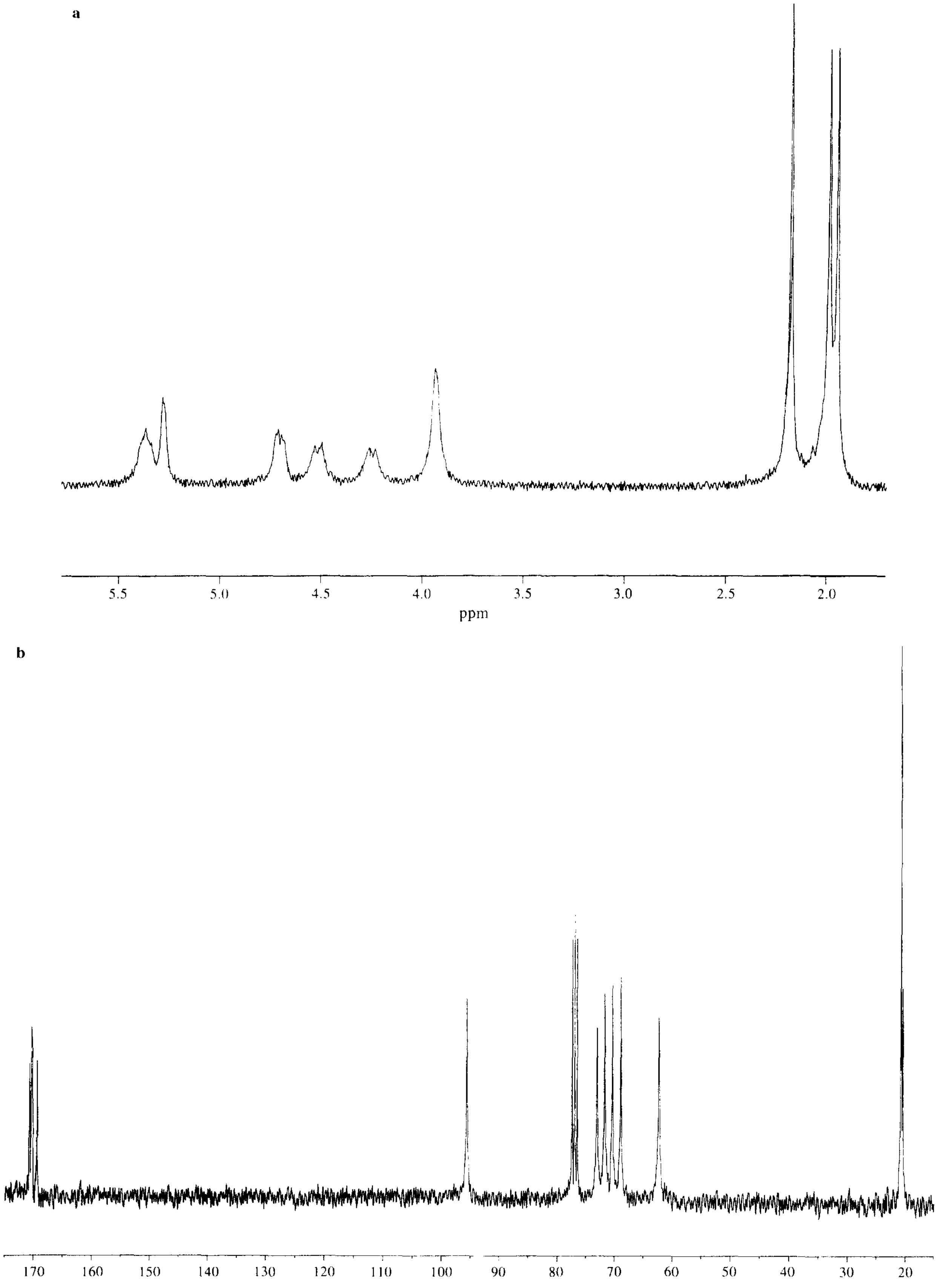

Figure 1 N.m.r. spectrum of starch triacetate: (a) ^{1}H n.m.r.; (b) ^{13}C n.m.r.; (c) two-dimensional heteronuclear ^{13}C–^{1}H n.m.r.

Analyser RSAII. A constant strain rate of 0.0001 s^{-1} was applied to the sample until break. The values given in the next section are the average of at least five measurements.

Dynamic mechanical thermal analysis (d.m.t.a.) measurements were made using a Rheometrics Solids Analyser (RSAII). D.m.t.a. curves were recorded in the temperature range from −120 to 250°C upon heating

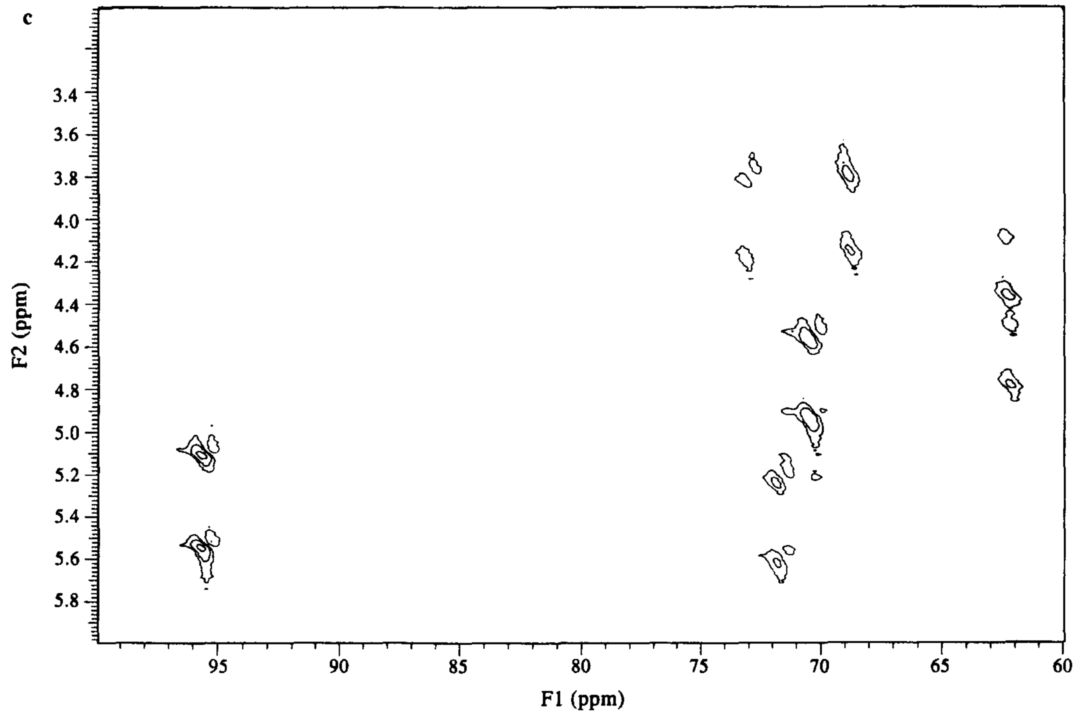

Figure 1 (*Continued*)

with a scanning rate of 3°C min^{-1}. A strain of 0.05% was applied with a frequency of 1 Hz.

RESULTS AND DISCUSSION

Synthesis and characterization

The purity of our pea amylose was checked by spectrophotometric determination of the CLI. The value measured in our experimental conditions was 17.5 g of complexed iodine per 100 g of dry amylose. The value determined with pure synthetic amylose was 17.8 g. The difference between these values is not significant as it is in the range of experimental error for such a spectrophotometric determination. Our amylose was consequently considered as pure enough and free of contamination by a large amount of amylopectin.

The value of intrinsic viscosity of our amylose in 1 M KOH solution at 25°C was 206 ml g^{-1}. This value allows the average viscometric molar mass to be estimated by using the Mark Houwink law. The molar mass determined was $M_v \approx 770\,000\ \mathrm{g\,mol}^{-1}$.

The experimental conditions of acetylation are given in *Table 1*. From the first part of this table, it can be seen that the acetylation of the different starchy products in the same conditions result in very different DS values. The molecular organization of polymeric chains in starch granules greatly decreases the accessibility and the reactivity of amylopectin. Moreover, when comparing the results obtained with amylose and destructured amylopectin, it can be noticed that the reactivity of amylose is higher.

As can be seen in the second part of *Table 1*, the products used in this study have a DS value somewhat lower than 3 (2.6–2.7). They will be called amylose acetate or amylopectin acetate in the following.

Whereas both amylopectin samples (whether pretreated or not) have the same DS, a significant difference between these products should be mentioned. In the case of the product prepared from granular starch, a residual birefringence could be observed under polarized light. This fact means that some of the granules were not sufficiently acetylated to break the molecular organization.

The acetyl content of the various products was determined by a chemical method[25] and the structure was checked by nuclear magnetic resonance (n.m.r.) and infra-red (i.r.) spectroscopy.

All the typical n.m.r. spectra and assignments are given in *Figure 1* and *Table 3*. The C_1 and C_6 peaks can be unambiguously attributed on the ^{13}C n.m.r. spectrum. The H_1 peak was determined with the heteronuclear correlation map. The observation of ^1H n.m.r. spectrum modifications after homonuclear decoupling at the frequency of H_1 allowed the H_2 peak to be located. This procedure made it possible to assign the different signals of each spectrum except for the C_4 and C_5 peaks. As the range of the other carbon atoms for starch acetate is similar to that observed for amylose, we attributed the C_4 and C_5 peaks in the same way as in the amylose spectrum.

Table 3 Chemical shifts and assignments of n.m.r. signals for acetylated derivatives

$\delta\ ^1H^a$	Position	$\delta\ ^{13}C^a$	Position
5.36	H_3	170.7–170.3–169.4	C=O
5.27	H_1	95.6	C_1
4.71	H_2	73.1	C_4
4.49	H_6	71.8	C_3
4.27	$H_{6'}$	70.5	C_2
3.93	H_4	68.9	C_5
3.93	H_5	62.3	C_6
2.18–1.99–1.95	$-CH_3$	20.8–20.5	$-CH_3$

[a] All chemical shifts are expressed in ppm and referred to tetramethylsilane

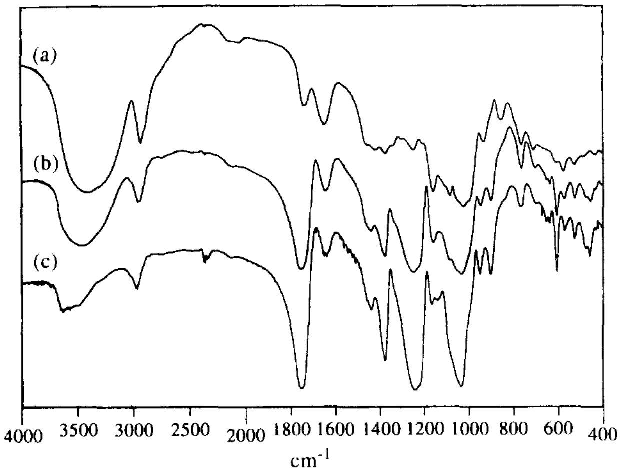

Figure 2 I.r. spectrum of acetylated starch with various DS values: (a) 0.14; (b) 2; (c) 3

The evolution of the i.r. spectrum with variation of the acetyl content is given in *Figure 2*. These spectra are characterized by the presence of three important bands: a C=O stretching band at 1750 cm^{-1}, a C–CH$_3$ deformation band at 1375 cm^{-1}, and a C–O stretching band at 1240 cm^{-1}.

Thermal properties

All the d.s.c. traces presented in this part were recorded after a first scan followed by rapid quenching. This was considered as a pretreatment necessary in order to obtain reproducible results in the absence of any hydration.

Typical thermograms obtained with amylose acetate and amylopectin acetate are presented in *Figure 3*. Both curves exhibit a drop of the baseline characteristic of a glass transition and located near 150°C. The change in heat capacity (C_p) values associated with this transition is identical for both polymers and is equal to 0.3 J g^{-1} K^{-1}. This value is in the range of ΔC_p associated with the glass transition of many polymers.

Whereas the thermogram of amylopectin acetate exhibits only a thermal decomposition (not shown in *Figure 3*) at higher temperatures (> 270°C), an exothermic peak followed by an endothermic one can be observed on the thermogram of amylose acetate. As a result of the pretreatment, a glassy state of the polymer is obtained after rapid quenching. When the temperature increases over the glass transition value, local motions of the polymer chains are allowed. Some parts of the amylose acetate chains can arrange and crystallize[27]. This phenomenon is associated with the exothermic peak. This crystallization was equally demonstrated by X-ray diffraction of the powder after annealing above the glass transition temperature. The endothermic peak corresponds to the melting of the crystallized part of the polymer. The values of the enthalpy associated with both peaks are identical and equal to ~10 J g^{-1}.

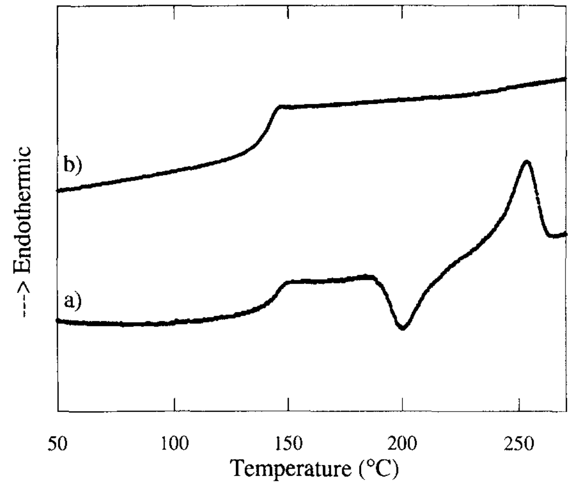

Figure 3 Typical d.s.c. traces for (a) amylose acetate (DS = 2.7) and (b) amylopectin acetate (DS = 2.6). Scanning rate 15°C min^{-1} (increasing temperature)

When the samples are maintained at a temperature higher than T_g before quenching (annealing treatment), rescanning of the sample leads to a decrease of the crystallization peak but the melting peak remains constant. This corresponds to the fact that a part of the polymer crystallized during annealing and that only the residual crystallizable part of the polymer crystallizes during scanning. This allowed us to study the kinetics of crystallization. The results are presented in *Figure 4*. At 170°C, a long time corresponding to an induction period is shown. The rate of crystallization is as usual very much influenced by annealing temperature.

D.s.c. was used to investigate the possibility of interaction between both components. In aqueous solution, amylose and amylopectin are incompatible[28] and lead to phase separation. Such a phenomenon or the presence of interactions between amylose acetate and amylopectin acetate in the solid state could be of great importance in explaining the mechanical properties.

The thermograms of two different mixtures of both acetates were recorded and are presented in *Figure 5*. Each mixture contained the same weight of both acetates. One was prepared only by mechanical mixing of the powders (b) and the other by preparation of a solution of the two acetylated polymers followed by coprecipitation with a non-solvent (c).

The d.s.c. curve of the mechanical mixture exhibits no difference from that of pure amylose acetate (a) except in the values of the enthalpies (crystallization and melting), which represent half the values measured in the case of pure amylose acetate. In fact, if this value is related to the quantity of amylose acetate present in the

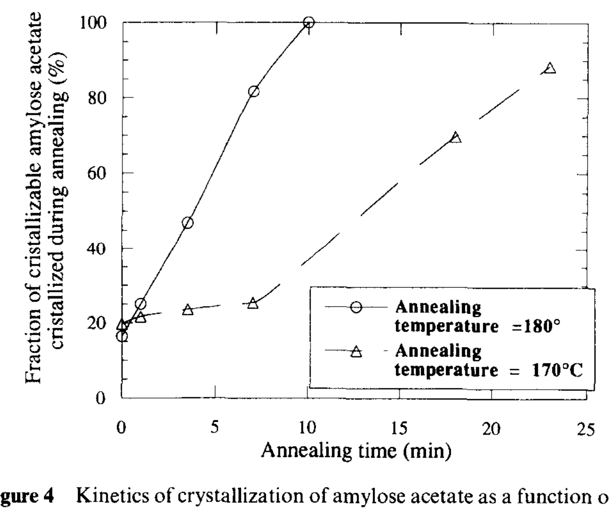

Figure 4 Kinetics of crystallization of amylose acetate as a function of annealing time

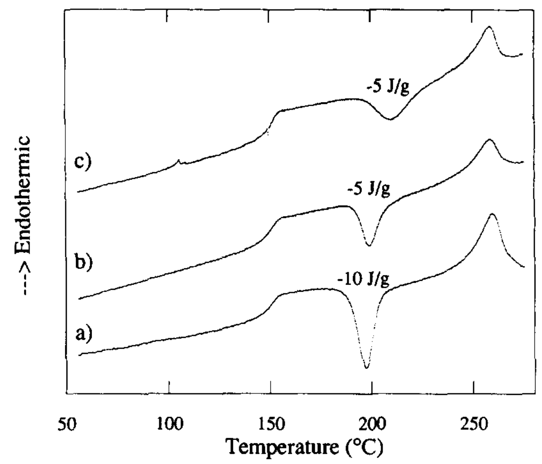

Figure 5 D.s.c. curves of acetylated starch components in mixture. (a) Amylose acetate 100%; (b) amylose acetate–amylopectin acetate (50/50), mechanical mixture; (c) amylose acetate–amylopectin acetate (50/50, coprecipitated mixture

mixture (50%), there is no difference between the samples.

On the contrary, the d.s.c. curve of the coprecipitated mixture exhibits a crystallization peak shifted towards higher temperatures and the peak is much larger than that observed in *Figure 5b*. This indicates that some interactions develop between both acetylated components. However, the value of the enthalpy of crystallization is also half the value measured for pure amylose acetate. This shows that even if the crystallization requires a more important thermic activation to occur due to the interactions, these are not strong enough to decrease the part of amylose that can crystallize; moreover, the melting peak remains unchanged.

These results seem to indicate that both acetylated components of starch can interact but that the interactions are weak.

The last part of our interest in the d.s.c. measurements was to investigate the influence of the degree of substitution on the thermal properties. The thermograms are presented in *Figure 6*. It can be seen that the position of the glass transition remains almost constant when the DS is larger than 1.4. For lower values of the DS, the glass transition temperature is shifted towards higher temperatures and cannot be determined for the less acetylated product. It can also be noticed that the thermal stability of the product is seriously decreased for the lowest values of acetyl contents. It can be noticed that no crystallization is observed when DS is lower than 2.7. This fact reinforces our assumption of a homogeneous distribution of acetyl groups along the polymeric chains.

Mechanical properties

We investigated the mechanical behaviour of some starch acetate films in order to see how the mechanical properties depend on the proportion of both components. The mechanical behaviour of amylose triacetate has been widely studied but there are no data available concerning amylopectin acetate and mixtures of both components. Films were made with various ratios of both components. When amylopectin acetate contents were higher than 60% (w/w), the films were too brittle to be manipulated. It was impossible to obtain a film with amylopectin acetate alone, as already mentioned by other authors[22,29].

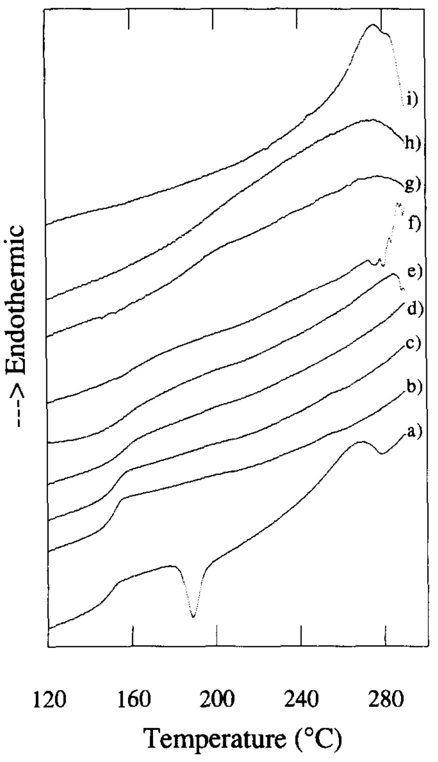

Figure 6 D.s.c. curves of acetylated Collys with different DS values: (a) 3; (b) 2.7; (c) 2.5; (d) 2; (e) 1.7; (f) 1.4; (g) 1; (h) 0.6; (i) 0.15

The stress–strain curves obtained for the different films are presented in *Figure 7*. These curves show that there is a very important change in mechanical behaviour when amylopectin acetate content increases. The stress–strain curves obtained with amylose acetate–rich film are typical of any thermoplastic material:

- at the beginning, the stress increases rapidly and is proportional to the strain—this is the elastic reversible strain area;
- the stress then increases and reaches a maximum—the strain is no more reversible;
- in the last area, the stress decreases slightly until break—this part is called the plastic strain area.

When the amylopectin acetate content increases, the plastic strain area slowly disappears and if the content is high enough, the stress–strain curve is reduced to the elastic reversible strain area.

The Young's modulus can be determined at the beginning of the curves and the measured value was 2.5 ($\pm$0.5) $\times 10^9$ Pa. This value was independent of the film composition. This does not seem surprising as it is well known that the strength of a material below T_g is mainly assured by short-range interactions such as hydrogen bonding or Van der Waals interactions. The chemical natures of both components of our films are similar and we can expect that the interactions are similar too.

Apparent yield stress remains constant up to 25% of amylopectin acetate and corresponds to 4% strain. On the contrary, the strain to break decreases continuously. For the highest amylopectin acetate contents, the brittle behaviour dominates. The evolution is shown in *Figure 8*. The elongation strongly decreases with the

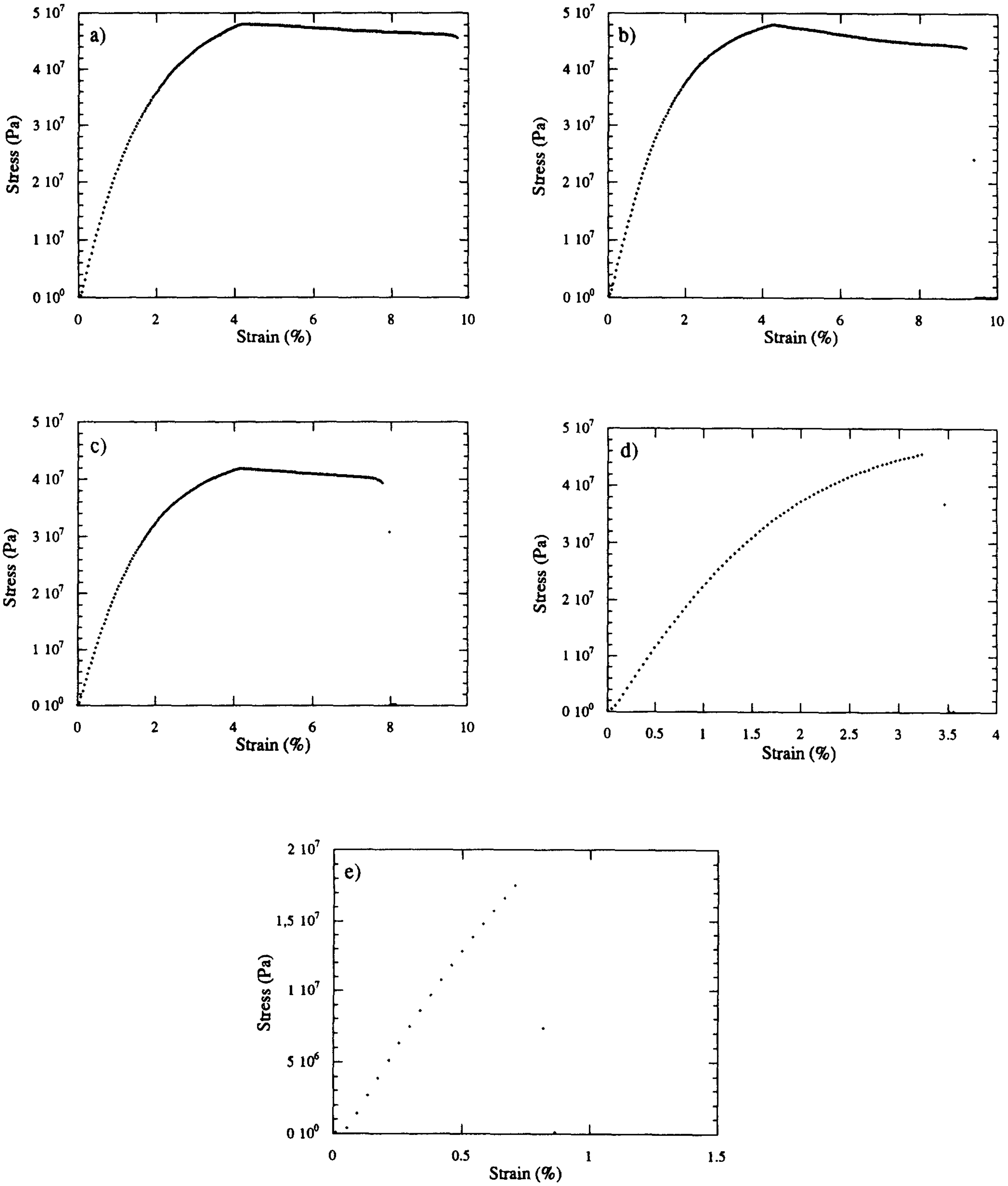

Figure 7 Evolution of the stress–strain curves obtained with films containing various ratios of amylose acetate (A) and amylopectin acetate (B): (a) A = 100%; (b) A/B = 90/10; (c) A/B = 75/25; (d) A/B = 60/40; (e) A/B = 40/60. $T = 25°C$. Strain rate 0.0001 s^{-1}

amylopectin acetate content. This can be explained through consideration of the amylopectin structure.

It is generally accepted that the configuration of amylopectin is a small dense sphere[30]. It can be assumed that the configuration of amylopectin acetate is rather similar. Moreover, the highly branched nature of amylopectin is well established[10]. The presence of such small and densely packed branches does not enable the chains to form a strongly entangled network, which is generally responsible for the high values of elongation at break. This assumption is in good agreement with the low degree of interaction demonstrated by d.s.c. measurements.

From the above results, it can be concluded that the behaviour of amylose acetate and amylopectin acetate are similar when considering the small strain range. As

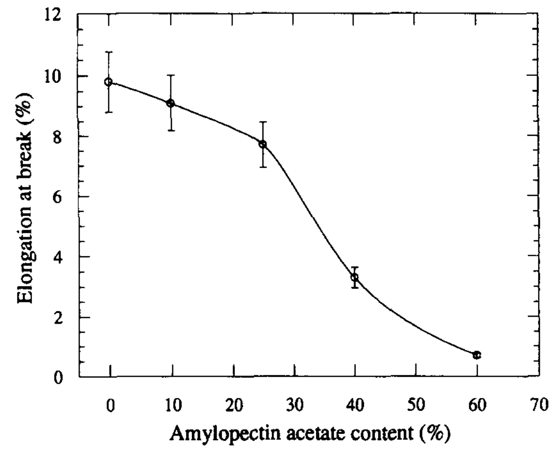

Figure 8 Variation of the elongation at break during tensile strength measurements as a function of the amylopectin acetate content

tensile measurements were made at room temperature, we wanted to know if the above conclusion is reached over a wide range of temperature. This was done by d.m.t.a. measurements. The experimental curves are given in *Figure 9*. It can be seen that there is no significant difference between the curves (E', E'' and $\tan\delta$ as a function of temperature) obtained with pure amylose acetate film and with a film containing a high percentage of amylopectin acetate when taking into account a range of temperatures varying between 20 and 170°C. The variations of all the physical variables when the temperature reaches 160°C are characteristic of the glass transition already mentioned in the d.s.c. results. Local motions of polymer chains are allowed and the modulus (E') decreases greatly. The small increase observed for temperatures higher than T_g are attributed to the recrystallization of amylose acetate. This recrystallization reinforces the rigidity of the material. It was observed that after such tests the amylose acetate samples were brittle after cooling, whereas they were flexible before heating above T_g.

The evolution of E' for temperatures lower than ambient temperature is rather different. For both types of films, the increase in temperature goes with a decrease in modulus, but the decrease is more pronounced in the case of the amylopectin acetate-rich material. Moreover, the values obtained with this material are higher than those obtained with pure amylose acetate. This can be explained by the structure of amylopectin. The packing of the chains increases the rigidity of the material at low temperature where the possibility of local motions is very restricted and consequently the modulus is higher.

It should be mentioned that we did not observe any difference in mechanical behaviour between the film prepared with any of the amylopectin acetates (whether or not destructured Waxilys was used). This indicates that a low proportion of non- or weakly acetylated granules has no reinforcement effect, as would be expected when considering the composite nature of such a material.

Hydration study

Hydration of acetylated starch was studied by measurements of the total adsorbed water and freezing adsorbed water contents for samples with a wide range of acetyl contents equilibrated in a 98% r.h. atmosphere.

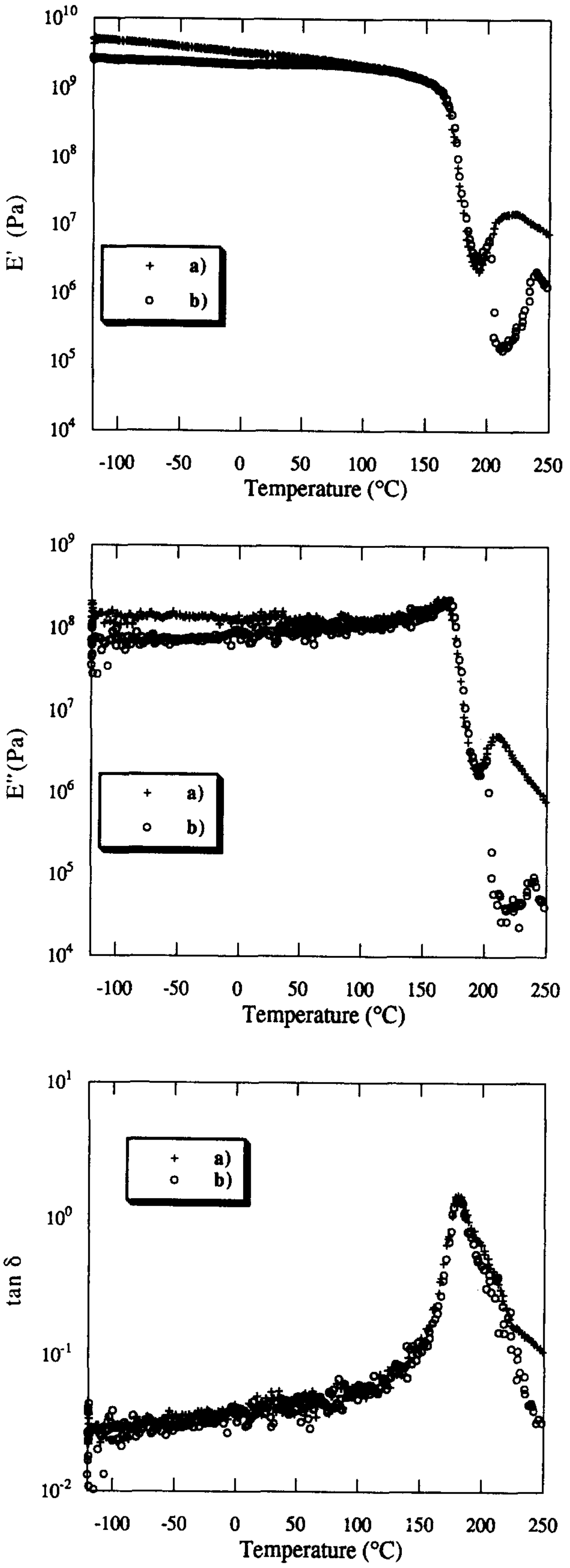

Figure 9 D.m.t.a. measurements with films containing various ratios of amylose acetate (A) and amylopectin acetate (B): (a) A = 100%; (b) A/B = 60/40

The results of these measurements are reported in *Figure 10*. The quantities of water in this figure are referred to the weight of dry samples. Two domains of hydration can be observed in this figure. For DS ranging from 0 to 1.3–1.4, both types of water molecules

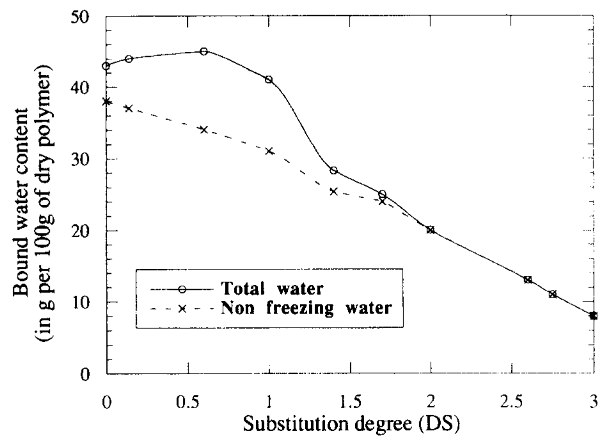

Figure 10 Variation of the water contents (total and freezing) adsorbed at 98% r.h. by acetylated starch as a function of DS

(i.e. freezing and non-freezing) are observed. The non-freezing water is the only one observed for r.h. ranging from 0 to 80%. For higher values of DS, only non-freezing water can be demonstrated. Moreover, the quantity adsorbed per gram of product decreases significantly in this higher DS range. This has to be taken with care as the molecular weight of the repeating unit undergoes a constant increase with DS variation. For this reason, the results of hydration measurements have been reported as the number of water molecules per repeating unit in *Figure 11*.

The expression used to determine this number of water molecules is given below:

$$n = W_{\mathrm{nf}}(162 + 42\mathrm{DS})/18 \qquad (4)$$

where n is the number of non-freezing water molecules per repeating unit, W_{nf} is the non-freezing water content (in g/g), 18 is the molecular weight of one water molecule, 162 is the molecular weight of the non-acetylated repeating unit and 42 is the difference between the molecular weight of the acetyl group corresponding to the chemical modification and the molecular weight of the hydrogen belonging to the hydroxyl group prior to modification.

The curves presented in *Figure 11* clearly confirm the presence of two domains of hydration. In these two domains, the characteristics of interacting non-freezing water molecules must be different.

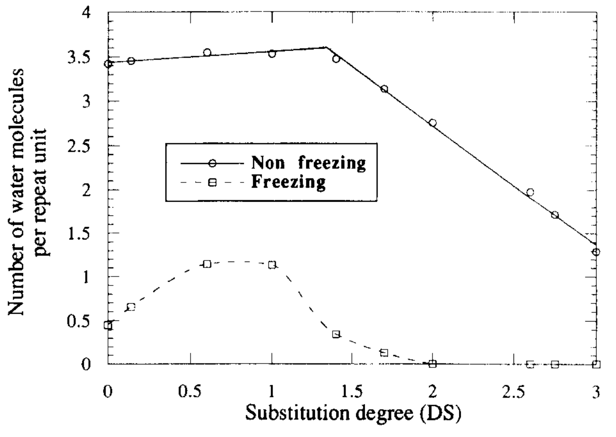

Figure 11 Variation of the number of water molecules adsorbed by repeat unit as a function of DS

The non-freezing water molecules are generally recognized as the molecules in direct interaction with the different hydration sites. In the case of acetylated products, these sites can be classified into three types, considering that the oxygen atom of the glycosidic bond does not interact with water molecules[31]:

- non-substituted hydroxyl groups;
- acetyl groups;
- oxygen atom of the ring.

Assuming that the characteristics of each hydration site remained unchanged with the variation of DS for both hydration modes, we calculated these characteristics using the linearity of the curves.

For DS ranging from 0 to 1.3–1.4, we consider that the number of acetyl groups was not sufficient to change the behaviour of the hydroxyl. Consequently, we kept the number of water molecules bound per hydroxyl group equal to 1, as is the case for non-substituted amylose[31]. Using the linearity of the curve presented in *Figure 11*, we determined that the number of non-freezing water molecules bound per acetyl group was 1.2 and per ring oxygen atom was 0.4.

For higher values of DS, we assumed that the characteristic of the oxygen atom of the ring was unchanged. This hypothesis allowed us to calculate the hydration characteristics of the other sites. We found that each hydroxyl group bound 1.7 water molecules and that each acetyl group bound 0.3 water molecules.

We interpret these numbers by assuming strong interactions between the acetyl groups on the polymeric chain. Some authors working on the anomeric effect have found evidence of the existence of unexpected effects attributed to some interactions induced by the acetyl groups[32]. The nature of such interactions is not well known.

For the lowest values of acetyl content, the number of acetyl groups is not sufficient so that they behave as if they were isolated. They are slightly more hydrophilic than the hydroxyl groups owing to the polarity of the C=O bond. When the DS increases, the acetyl groups associate and are not available to interact with water molecules. They efficiently increase the hydrophobicity

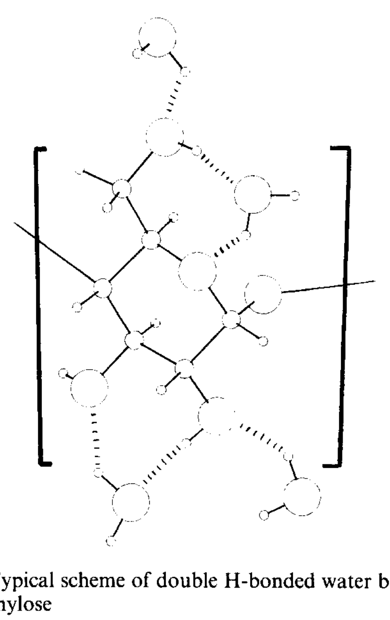

Figure 12 Typical scheme of double H-bonded water bridge for non-acetylated amylose

of the product. On the contrary, the hydrophilic character of the hydroxyl groups is reinforced: each hydroxyl group can potentially bind two water molecules as a donor or as an acceptor of hydrogen bonding. When studying amylose, this is not observed because when two hydroxyl groups are close enough, the water molecules are double H-bonded as presented in *Figure 12*.

CONCLUSION

From the above studies, it can be deduced that acetylation is an efficient chemical modification for obtaining thermoplastic starch-based materials with reinforced hydrophobicity. This reaction has to be completed until reaching a DS higher than 1.7 to be very efficient. This conclusion was drawn from hydration investigations which demonstrated that even at 98% r.h., no freezing water exists in the material. The d.s.c. measurements showed that in this range of DS, T_g becomes independent of DS and is located near 150°C. The thermal stability of the material is also increased by chemical modification. All this is consistent with the classic processing methods used in the thermoplastics field.

We have also demonstrated that the presence of amylopectin acetate in such materials strongly influences the mechanical properties. Amylopectin acetate behaves as a very rigid and brittle material owing to strong intramolecular interactions and low entanglement.

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REFERENCES

1 Röper, H. and Koch, H. *Starch* 1990, **42**, 123
2 Doane, W. M. *Starch* 1992, **44**, 293
3 Griffin, G. J. L. *Polym. Degrad. Stability* 1994, **45**, 241
4 Whistler, R. L. and Paschall, E. F. 'Starch: Chemistry and Technology', Academic Press, New York, 1967
5 Banks, W. and Greenwood, C. T. 'Starch and its Components', Edinburgh University Press, Edinburgh, 1975
6 Wurzburg, O. B. 'Modified Starches: Properties and Uses', CRC Press, Boca Raton, 1986
7 Schoch, T. J. in 'Advances in Carbohydrates Chemistry' (Eds W. W. Pigman and M. L. Wolfrom), Vol. I, Academic Press, New York, 1945, p. 247
8 Hizukuri, S., Takeda, Y., Usami, S. and Takase, Y. *Carbohydr. Res.* 1981, **94**, 205
9 French, D., Pulley, A. O. and Whelan, W. J. *Starch* 1963, **10**, 349
10 Manners, D. J. *Carbohydr. Polym.* 1989, **11**, 87
11 Griffin, G. J. L. *Adv. Chem. Ser.* 1974, **134**, 159; Griffin, G. J. L. U.S. Pat. 4,016,117, 1977
12 Warner-Lambert Company, Eur. Pat. 0,408,503, 1990
13 Orford, P. D., Parker, R., Ring, S. G. and Smith, A. C. *Int. J. Biol. Macromol.* 1989, **11**, 91
14 Kalichevsky, M. T., Jaroszkiewicz, E. M., Ablett, S., Blanshard, J. M. V. and Lillford, P. J. *Carbohydr. Polym.* 1992, **18**, 77
15 Fanta, G. F., Swanson, C. L. and Shogren, R. L. *J. Appl. Polym. Sci.* 1992, **44**, 2037
16 Liu, M., Cheng, R., Wu, J. and Cheng, M. *J. Polym. Sci., Polym. Chem.* 1993, **31**, 3181
17 Narayan, R., Lu, Z. J., Chen, Z. X. and Stacy, N. *Polym. Prepr.* 1988, **2**, 106
18 Patel, A. R., Patel, M. R., Patel, K. C. and Patel, R. D. *Angew. Makromol. Chem.* 1985, **136**, 135
19 Butterfly S. R. L. Int. Pat. WO 90/10671, 1990
20 Tomka, I. *Adv. Exp. Med. Biol.* 1991, **302**, 627
21 Shogren, R. L. in 'Biodegradable Polymer Packaging' (Eds C. Ching, D. L. Kaplan and E. L. Thomas), Technomic Lancaster, Lancaster, 1993, p. 7028
22 Wolff, I. A. *Ind. Eng. Chem.* 1968, **50**, 1552
23 Whistler, R. L. and Hilbert, G. E. *Ind. Eng. Chem.* 1944, **36**, 796
24 Kuge, T. and Ono, S. *Bull. Chem. Soc. Jap.* 1960, **33**, 1273
25 Wurzburg, O. B. in 'Methods in Carbohydrate Chemistry' (Ed. R. L. Whistler), Vol. IV, Academic Press, New York, 1964, p. 287
26 Hatakeyama, H., Iwata, H. and Hatakeyama, T. in 'Cellulose and its Derivatives' (Eds J. F. Kennedy, G. O. Philipps, D. J. Wedlock and P. A. Williams), Ellis Horwood, Chichester, 1985
27 Sarko, A. and Marchessault, R. H. *J. Am. Chem. Soc.* 1967, **89**, 6454
28 Kalichevsky, M. T. and RIng, S. G. *Carbohydr. Res.* 1987, **162**, 323
29 Mullen, J. W. and Pacsu, E. *Ind. Eng. Chem.* 1943, **35**, 381
30 Salemis, P. and Rinaudo, M. *Polym. Bull.* 1984, **12**, 283
31 Durette, P. L. and Horton, D. *Carbohydr. Res.* 1971, **18**, 57
32 Fringant, C., Tvarovska, I., Rinaudo, M., Mazeau, K. and Desbrieres, J. *Carbohydr. Res.* 1995, **278**, 27