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Esterification of cellulose-enriched agricultural by-products and characterization of mechanical properties of cellulosic films

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Abstract

Two agricultural by-products, wheat bran and maize bran have been examined for their suitability to be transformed into biomaterials by esterification by lauroyl chloride. Influence of biochemical characteristic of cellulose (cellulose content, viscosity-average degree of polymerization, crystallinity) was studied on eight samples enriched in cellulose after chemical removal of heteroxylans and lignin. After an acidic pre-treatment, esterification was carried out with lauroyl chloride and an optimized reaction time of 8 h was used.

Chemical compositions were similar for all cellulose esters obtained, but cellulose content of initial material had a marked influence on the amount of esterified product. A film was easily obtained by casting and the mechanical (tensile strength and elongation), thermomechanical and calorimetric properties were determined. The possible role of grafted fatty acid as internal plasticizer was finally discussed.

Keywords: Wheat bran; Maize bran; Cellulose; Esterification; Cellulose laurate; Films; Mechanical; Thermomechanical; Calorimetric

1. Introduction

Synthetic polymers are vital to the economy and quality of life but their waste is becoming a serious ecological problem. Biopolymers can be good candidates for replacement of synthetic polymers but they have to offer comparable quality (barriers and mechanical properties, low cost, etc.,…) (Kaplan, Mayer, Ball, Mc Cassie, Allen & Stenhouse, 1993). Cellulose derivatives are widely used by various industries for their properties which are greatly dependent on substituent nature (Engelhardt, 1995). Cellulose-based films have been extensively studied, either for their efficient oxygen and hydrocarbon barrier properties of edible film of cellulose ethers (Kamper & Fennema, 1984a,b; Park, Weller, Vergano & Testin, 1993), or for the interesting filmogenic properties of long chain fatty acid esters (Benhaddou et al., 1995; Gault & Ehrmann, 1926; Kwatra, Caruthers & Tao, 1992; Wang & Tao, 1994, 1995). A pre-treatment is usually needed before esterification of cellulose by long chain fatty acid (Benhaddou et al., 1995; Gault & Ehrmann, 1926; Wang & Tao, 1994, 1995). The acidic activation using sulfuric acid, improved the accessibility and chemical reactivity of cellulose. Previous works have shown that this treatment led to a partial hydrolysis of cellulose into short chains and that some esterification of cellulose by sulfuric acid occurred. The presence of the bulky ionic sulfate group leading to a swelling effect and partial hydrolysis of the chains improved the accessibility of cellulose to chemical reagent and therefore its reactivity (Chauvelon et al., 1999).

Maize bran and wheat bran, two important and very cheap agricultural by-products, are mainly composed of cell wall polysaccharides, about 750 and 640 mg/g, respectively (Chanliaud, Saulnier & Thibault, 1995; Ralet, Thibault & Della Valle, 1990; Saulnier, Vigouroux & Thibault, 1995). Heteroxylans and cellulose are the main polysaccharides for the two by-products and wheat bran also contains some lignin (80 mg/g) (Chanliaud et al., 1995; Ralet et al., 1990; Saulnier et al., 1995). The chemical extraction of noncellulosic polysaccharides lead to a cellulose enriched residue containing more than 500 mg/g of cellulose (Brillouet & Mercier, 1981; Chauvelon et al., 1999; Saulnier et al., 1995).

These two by-products are therefore interesting sources of cellulose to prepare laurate ester films. However, the esterified product yield ((g/g) of initial sample) obtained from cellulose-enriched residue is lower than when pure cellulose is used (Chauvelon et al., 1999). In this article, we have therefore studied different ways of extraction of noncellulosic polymers and we have tried to improve the

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Table 1
Wheat bran and maize bran residues composition (mg/g) and viscosity-average degree of polymerization ($\overline{DP_v}$), nd, not determined

Treatment	Wheat bran No	Wac_1 H_2SO_4[a]	Wac_2 Wac_1 $NaC1O_2$	$Walk_1$ KOH H_2O_2[b]	$Walk_2$ $NaClO_2$ KOH[c]	Walk3 $NaClO_2$; KOH + H_2O_2[b]	Maize bran No	$Malk_1$ KOH $NaBH_4$[d]
Yield of residue (mg/g)	1000	Nd	nd	205	201	159	1000	224
Arabinose	136	15	6	94	66	22	135	55
Xylose	248	77	84	145	142	52	249	116
Mannose	5	9	13	11	13	14	6	12
Galactose	10	1	1	8	8	0	37	21
Glucose	206	398	600	617	605	681	289	658
Glucuronic acid	31	17	11	18	2	13	38	20
Cellulose	153	383	581	573	554	630	173	603
Heteroxylans[e]	425	110	102	265	218	87	459	212
Lignin	75	169	132	26	7	2	18	7
Protein	108	101	30	4	2	5	58	2
Ash	12	5	1	17	26	32	8	29
$\overline{DP_v}$[f]	nd	330	270	640	940	660	Nd	1250

[a] H_2SO_4 0.5 mol/l (industrially).
[b] KOH 2 mol/l + 1% (v/v) H_2O_2.
[c] KOH 2 mol/l.
[d] KOH 1.5 mol/l + 1% (w/v) $NaBH_4$.
[e] Heteroxylans = arabinose + xylose + galactose + glucuronic acid.
[f] Calculated using cellulose content as concentration.

esterification yields. The mechanical and thermomechanical properties of the laurate cellulose films were finally studied.

2. Materials and methods

2.1. Materials

Destarched wheat bran and enriched-cellulose residue recovered after treatment of the wheat bran with sulfuric acid (Wac_1) were provided by ARD (Pomacle, France). Destarched maize bran was provided by Ulice (Chappes, France).

2.2. Preparation of the Cellulose-enriched residues

2.2.1. Delignification of wheat bran (Green, 1963; Wilkie, 1979)

Destarched wheat bran or Wac_1 (100 g) was stirred and heated in deionized water (1.5 l) until temperature reached 70°C, then glacial acetic acid (18 ml) and sodium chlorite monohydrate (25 g) were added. After 1 h, the same amounts of acetic acid and sodium chlorite were added and the mixture was stirred for 1 h. The residue was recovered by filtration (pore diameter < 15 μm) and washed with water until washing water reached pH 5. The delignified residue was finally washed with 95% ethanol (3 times, 500 ml), then acetone (3 times, 500 ml), and dried in an oven at 40°C overnight. 79 g of dried residue were recovered and ground (particles diameter < 0.5 mm).

2.2.2. Alkaline extraction of heteroxylans

Sample (100 g/l) was stirred with 2 mol/l potassium hydroxide for wheat bran (Chauvelon et al., 1998) and 1.5 mol/l for maize bran (Chanliaud et al., 1995) at 100°C for 2 h. Sodium borohydride (10 g/l) (Whistler & BeMiller, 1958) or hydrogen peroxide (10 ml/l) (Amjed, Jung & Donker, 1992; Gould, Jasberg & Cole, 1989) was added in some experiments (Table 1). The residue was recovered after centrifugation (15,000 g, 30 min) and washed with deionized water (3 times, 600 ml). The mixture was adjusted to pH 6 with glacial acetic acid. The residue was washed with 95% ethanol (3 times, 500 ml), then acetone (3 times, 500 ml), and dried in an oven at 40°C overnight. The dried residue was finally ground (particles diameter $<$ 0.5 mm).

2.3. Chemical modification and films elaboration

Cellulose enriched sample (3 g) were activated by immersion at room temperature in 50 ml of a dilute solution of 0.5 mol/l sulfuric acid for 1 min (Benhaddou et al., 1995; Gault & Erhmann, 1926), then after draining on filter (pore diameter < 15 μm), the material was dried at 40°C for 48 h.

"Activated" material (3 g) was ground, then stirred with toluene (50 ml), lauroyl chloride (42 ml) and pyridine (15 ml) at 80°C (Benhaddou et al., 1995). Insoluble particles were removed by centrifugation (3380 g, 20 min, 20°C) and the ester was precipitated by adding 98% ethanol (400 ml). After 16 h at 4°C, the precipitate was recovered by filtration (pore diameter < 15 μm) and washed with ethanol (3 times, 50 ml) to remove residual pyridine and lauroyl chloride. Cellulosic ester (170 g/l) was then dissolved in toluene. A film of cellulosic ester was realized by the casting method. The solution of polymers solubilized in toluene was evenly spread on a glass plate maintained at room temperature until a total solvent vaporization during 16 h.

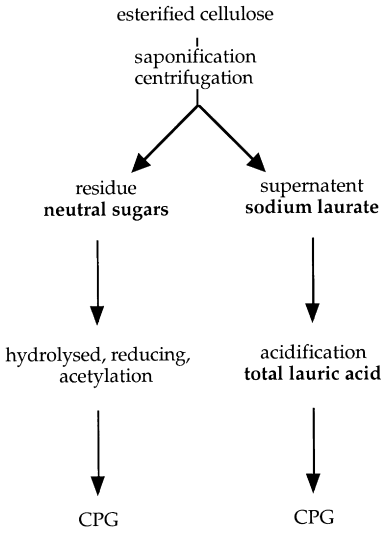

Fig. 1. Chemical characterization of cellulose laurate.

2.4. General methods

All results are expressed relative to the dry matter content determined by drying at 120°C for 3 h.

Ash was measured after incineration overnight at 500°C then for 2 h at 900°C.

Uronic acids were quantified by colorimetry using *m*-hydroxybiphenyl as chromogen (Thibault, 1979) after hydrolysis (30 min in 13 mol/l sulfuric acid at room temperature, then 3 h in 1 mol/l sulfuric acid at 100°C).

Proteins (N × 6.25) were determined by a semi-automatic Kjeldhal procedure.

Lignin was quantified by the method of Klason (1931).

Individual neutral sugars were analyzed by gas–liquid-chromatography (GLC) (Englyst & Cummings, 1988) after total hydrolysis and derivation of the monomers into alditol acetates. Cellulose-rich residues were "pre-hydrolysed" 2 h in 13 mol/l sulfuric acid at 30°C then hydrolysed 2 h in 2 mol/l sulfuric acid at 100°C (Chauvelon et al., 1998). Cellulosic glucose was estimated by the difference between glucose content as measured by GLC with (total glucose) and without (noncellulosic glucose) pre-hydrolysis. Films (10 g/l) were first de-esterified at 40°C during 16 h in 0.5 mol/l sodium hydroxide solution prepared in pure methanol (99.9%). The residue was recovered by centrifugation (2250 g, 15 min) and washed with pure methanol to remove any remaining traces of salts. The residue was then washed with deionized water to remove any remaining trace of methanol. The supernatant was recovered to determine lauric acid content (Fig. 1). The residue was finally freeze-dried and analyzed by GLC as described for cellulose enriched residues.

Lauric acid was measured after saponification of esterified product in 0.5 mol/l hydroxide sodium solution prepared in pure methanol as described above. Supernatant (Fig. 1) was acidified by addition of 100 μl of 1 mol/l hydrochloric acid. Free lauric acid was recovered in a solution of pure methanol, without saponification of esterified cellulose. Lauric acid was then analyzed by GLC on BP 21 SGE (12 m × 0.32 mm) capillary column at 150°C, using hydrogen (0.35 bar) as carrier gas. Capric acid was used as the internal standard.

The degree of substitution in the text refers to the molar ratio between lauric acid and total neutral sugar determined in the cellulosic film.

Viscosity-average degree of polymerization ($\overline{DP_v}$) of the cellulose was determined from the values of intrinsic viscosities determined in 0.5 mol/l cupriethylenediamine with an Ostwald viscosimeter (diameter: 0.46 mm, viscologic TI 1 SEMATech, Nice-France). Six determinations were realized at 25°C for each dilution (5.0, 3.3, 2.5, 1.7, 1.25, 0.8 mg/ml) of cellulosic solutions. The intrinsic viscosity was determined by extrapolation of the straight line of the reduced viscosity at concentration zero. The viscosity-average molar mass was determined by the Mark–Houwink–Sakurada relationship (Marx & Schultz, 1955; Marx-Figinni & Schultz, 1975).

$$[\eta] = 1.0110^{-4}\bar{M}_v^{0.9}$$

The mechanical behavior of films of cellulose laurate was analyzed with an Instron 1122 with a load cell of 100 N capacity. Measurements were repeated at least 6 times (10 × 20 mm). Tensile tests were performed at a crosshead speed of 20 mm/min at room temperature.

Dynamic thermomechanical analyses were carried out on a Rheometric Scientific DMTA IV apparatus. The storage and loss modulus (respectively E' and E''), and tan δ (tan $\delta = E''/E'$) were measured in the −60 to +100°C range at a frequency 1 Hz and a heating rate of 3°C/min. Events temperature pre-determined to the maximum in the tan δ.

Measurements of calorimetric properties of the materials were performed by differential scanning calorimetry (DSC) on automated DSC 121 equipment (SETARAM, France). Films were cryogrinded using a cryo-grinder (Spex 6700, Avantec) and placed in pressure-tight DSC cell (about 100 mg of matter per cell). A first scanning was performed from −70 to +70°C to erase any thermal events which might have occurred during the preparation and storage of the sample. After a rapid cooling (60°C/min) to −70°C, actual measurement was performed during a second scanning at 3°C/min.

3. Results

3.1. Composition of the cellulose-enriched residues

Cellulose-enriched materials were obtained by extraction of heteroxylans and lignin from wheat and maize brans. Wheat and maize brans (Table 1) were mainly constituted of arabinose (~140 mg/g) and xylose (~250 mg/g) from

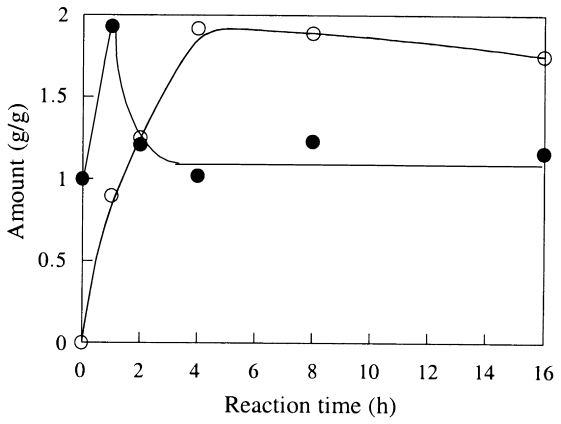

Fig. 2. Kinetic of esterification of Wac_2: yield in ester (weight in gram of recovered esterified sample per gram of starting sample, closed symbol) and in residue (weight in gram of recovered residual particles per gram of starting sample, open symbol).

arabinoxylan, and glucose (~210 and ~290 mg/g for wheat bran and maize bran, respectively), mostly from cellulose. Lignin represented about 80 mg/g in wheat bran, a value higher than in maize bran (~20 mg/g). These compositions are in agreement with previously published data (Bataillon, Mathaly, Nunes Cardinali & Duchiron, 1998; Brillouet & Mercier, 1981; Chanliaud et al., 1995).

To remove heteroxylans and lignin from destarched wheat bran, various chemical treatments were tested (Table 1). A cellulose content varying from 383 to 630 mg/g was obtained and the amount of residues left varied from 159 to 205 mg/g. Acidic extraction removed mostly heteroxylans (~95%), but lignin was not extracted. Delignification of Wac_1, using sodium chlorite removed less than 50% of lignin. Thus, Wac_1 and Wac_2 were rich both in lignin and in cellulose. Alkaline treatment removed lignin (~83 to 99%) and a large part of heteroxylans (~90%), but residual heteroxylans represented from 90 to 270 mg/g of the residue. About 25% of glucose was also lost during alkaline treatment, probably due to oxidative "peeling" (Whistler & BeMiller, 1958).

Only one treatment was applied to remove heteroxylans from maize bran. The cellulose content reached 603 mg/g and the amount of residue left was about 225 mg/g. About 90% of heteroxylans was removed and the amount of residual heteroxylans reached about 210 mg/g.

The average-viscosity degree of polymerisation was dependent on the extraction treatment (Table 1). Acidic treatment hydrolysed amorphous cellulose and the chain length was very short (330 and 270) and comparable to cellulose Avicel (Chauvelon et al., 1999). The longest cellulose chain length was obtained for $Malk_1$ ($\overline{DP_v} \sim 1,250$); the addition of sodium borohydride prevented cellulose chains from oxidative "peeling" (Whistler & BeMiller, 1958). The alkaline treatment realized without sodium borohydride led to a cellulose with intermediate chain length (640–940). Whatever the cellulose-enriched residue, a very low crystallinity level probably of type I was observed as previously reported (Chauvelon et al., 1999).

3.2. Kinetic of esterification

Esterification of cellulose by lauroyl chloride was very efficient for pure cellulose like a cellulose (Vaca-Garcia, Thiebaud, Borredon & Gozzelino, 1998; Wang & Tao, 1994, 1995), paper or cotton (Benhaddou et al., 1995) or microcrystalline cellulose (Chauvelon et al., 1999). The amount of esterified product was lower for cellulose-enriched agricultural by-product such as maize bran or wheat bran than for pure cellulose (~0.7 g/g and about ~3 g/g for cellulose-enriched residues and pure cellulose, respectively) (Benhaddou et al., 1995; Chauvelon et al., 1998, 1999). To improve the yield in esterified product, a kinetic of esterification of Wac_2 was realized (Fig. 2). Both cellulose laurate soluble in toluene, and residual particles insoluble in toluene, were obtained after esterification. The amount of ester and residual particles reached about 3 g/g, but the amount of ester increased with the reaction time and became constant after 4 h of esterification. At the beginning of the reaction, a higher amount of residual particles was observed (Table 2). The rate of substitution was probably not sufficient to make the product soluble in toluene. Finally, the amount of residual particles decreased to a constant value of about 1 g/g after 3 h of esterification.

The proportion of glucose recovered in cellulose laurate

Table 2
Influence of esterification time (h) on recovery in cellulose (%), esterified and free lauric acid content (mg/g) and degree of substitution (DS)

Time	Cellulose laurate				Residual particles[a]		
	Recovery in cellulose[b]	Esterified lauric acid	Free lauric acid	DS	Recovery in cellulose[c]	Esterified lauric acid	Free Lauric acid
1	25.6	491	5	2.3	46.8	305	77
2	37.4	596	2	2.7	25.3	459	12
4	40.7	514	3	2.5	20.1	426	14
8	55.4	529	83	2.4	15.0	484	4
16	46.9	575	17	2.9	25.2	458	8

[a] Insolubles particles in toluene at the end of the reaction.
[b] 100 × (glucose in cellulosic film)/(glucose in initial sample).
[c] 100 × (glucose in residual particles)/(glucose in initial sample).

Table 3
Amounts of esterified product and residual particles (g/g), recovery in cellulose (%), sugar composition (mg/g) and degree of substitution (DS) after esterification of cellulose-enriched by-products

	Cellulose laurate					Residual particles[a]	
	Amount[b]	Recovery in cellulose[c]	Noncellulosic polysaccharides	Cellulose	DS	Amount[b]	Recovery in cellulose[d]
Wheat Bran	0.27	5.7	106	44	2.6	2.07	81.9
Wac_1	1.64	59.1	23	170	2.5	1.13	19.5
Wac_2	1.89	55.4	21	170	2.4	1.23	15.0
$Walk_1$	2.53	66.6	35	162	2.8	0.64	10.4
$Walk_2$	1.86	62.0	25	202	2.1	0.64	20.8
$Walk_3$	1.35	50.5	64	226	1.9	1.16	34.5
Maize Bran	0.75	27.6	47	107	2.8	1.91	56.2
$Malk_1$	1.98	39.9	44	133	2.5	1.00	27.3

[a] Particles insoluble in toluene at the end of the reaction.
[b] Weight in grams of recovered ester (of residual particles) per gram of initial sample.
[c] 100 × (glucose in cellulose laurate)/(glucose in initial sample).
[d] 100 × (glucose in residual particles)/(glucose in initial sample).

and residual particles was dependent on reaction time (Table 2). After 8 h of reaction, the best yield in esterified product and recovery in cellulose were obtained (~1.9 g/g and 55% for yield in esterified product and recovery in cellulose, respectively). The chemical composition of cellulose laurate was very similar whatever the reaction time as shown by the relatively low variation of degree of substitution, (2.3–2.9). No dependence of the reaction time on the degree of substitution was observed. Cellulose laurate was probably soluble in toluene for this rate of substitution. A few amount of free lauric acid was still present both in cellulose laurate and in residual particles. These particles were also rich in esterified lauric acid and probably in noncellulosic compounds such as heteroxylans or lignin. Hydroxyl groups of these two polymers were probably esterified, which could explain the high amount of residual particles. The total recovery of glucose in cellulose ester and residual particles was only about 70%, suggesting that cellulose content might have been underestimated although optimized conditions have been used for the determination of cellulose.

3.3. Esterification of cellulose-enriched by-products

Esterification of wheat bran and maize bran (Table 3) led to a low amount of cellulose laurate (0.27 and 0.75 g/g for wheat bran and maize bran, respectively) and a high amount of residual particles (~2 g/g). Esters were rich in lauric acid and in noncellulosic compounds, such as arabinose and xylose, and only a small amount of glucose was present. Films were clear, slightly colored (yellow) but very sticky. The main part of cellulose was recovered in the residual particles (~80% for wheat bran and ~60% for maize bran). The better esterification yield observed for maize bran could be explained by its very low lignin content. As a matter of fact, lignin could act as a competitor for the esterification reagent and/or had a negative influence on cellulose accessibility.

A higher amount of cellulose laurate and a lower amount of residual particles were obtained (0.64–1.23 g/g) when cellulose-enriched residue were used (1.35–2.53 g/g). The main part of cellulose was recovered in cellulose laurate (~60%), excepted for $Malk_1$ where only 40% of cellulose was recovered in ester in spite of the low amount of cellulose recovered in residual particles (27%, Table 3). For other samples, total recovery of glucose in ester and in residual particles was about 85%. Esters were rich in lauric acid, glucose and exhibited a low amount of noncellulosic sugars. Degree of substitution varied from 1.9 to 2.8, which probably corresponded to a good solubility in toluene. Previous work have shown that cellulose laurate solubility in tetrahydrofuran or chloroform was favored for substitution degree varying from 1.2 to 2.5 (Samaranayake & Glasser, 1993a,b).

Table 4
Mechanical properties of film obtained from cellulose laurate

	Mechanical properties	
	Tensile strength[a] (MPa)	Elongation[a] (%)
Wac_1	1.8 (±0.2)	130 (±38)
Wac_2	2.1 (±0.1)	158 (±41)
$Walk_1$	1.8 (±0.2)	105 (±44)
$Walk_2$	2.5 (±0.2)	53 (±24)
$Walk_3$	2.0 (±0.3)	176 (±44)
$Malk_1$	2.3 (±0.1)	149 (±39)

[a] Values in parantheses are standard deviations.

3.4. Mechanical properties

Films were flexible, clear and only slightly colored (yellow) as previously reported (Wang & Tao, 1995; Chauvelon et al., 1998). Mechanical properties of films are reported in Table 4. Tensile strength was about 2 MPa whereas elongation varied from 53 to 180%. The high standard deviation (standard deviation range between

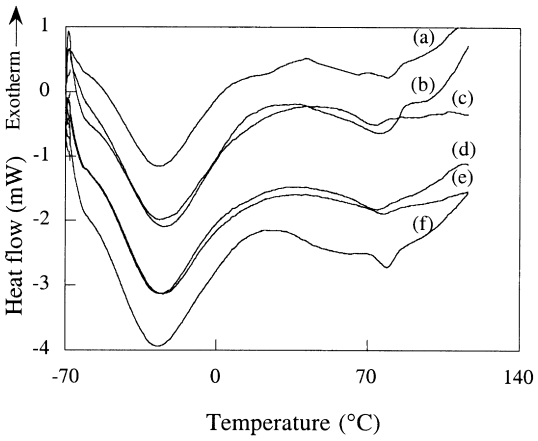

Fig. 3. DSC heating scans of various cellulose laurate: (a) $Malk_1$; (b) Wac_2; (c) $Walk_2$; (d) $Walk_3$; (e) Wac_1; (f) $Walk_1$.

0.1–0.3 MPa and 24–84% for tensile strength and elongation, respectively) indicated heterogeneity within a film. A shrinkage of the cross-section of the film occurred upon tensile stress.

3.5. Calorimetric and thermomechanical properties

Differential scanning calorimetry revealed two events whatever the cellulose laurate sample (Fig. 3). A first large endotherm peak occurred at a temperature of about −25°C for all samples except $Malk_1$ where a temperature of −37°C was measured (top of the peak). A second weak endotherm peak occurred between 60 and 80°C. Thermomechanical properties of Wac_2, $Walk_3$, and $Malk_1$ reveal a common behavior for all samples. Two molecular relaxations were observed (Fig. 4). One occurred between −40°C to −48°C for all samples. A second relaxation occurred at higher temperature (60–70°C) and was characterized by an important drop in E' and E'' modulus which values became too low (10^4, 10^5 Pa) for the sensitivity of DMTA apparatus. The appearance of the DMTA curve was assigned to α relaxation which molecular mobility is generally associated to glass transition (T_g). However, the unusual behavior of the DSC curves together with the easy distortion of the films at room temperature suggest caution about this interpretation. Sealey, Samaranayake, Todd and Glasser (1996) found higher temperatures for β (−26°C) and α relaxations (95°C) although mechanical properties at room temperature indicated a film easily distorted, suggesting the possible role of grafted fatty acid as internal plasticizer. Sealey et al. (1996) assigned the first transition as a low-temperature melt endotherm ($T_{m,l}$) and the second transition as glass transition (T_g). They found higher transition temperature (−15°C for $T_{m,l}$ and 94°C for T_g) but this variation between measurements was well known and largely observed by previous authors (Glasser, Samaranayake, Dumay & Davé, 1995). It could be explained either by gradual loss of moisture (Glasser et al., 1995) or by physical aging of the polymer (Struik, 1978). Glasser et al. (1995) shown that the thermal transition of cellulose esters cannot be determined with any precision in the presence of residual hydroxyl groups that cause moisture retention.

4. Discussion

Wheat bran and maize bran needed different treatment for an efficient extraction of noncellulosic polymers. The main difference between wheat and maize bran was their lignin content, and more drastic treatment (concentration in alkali,

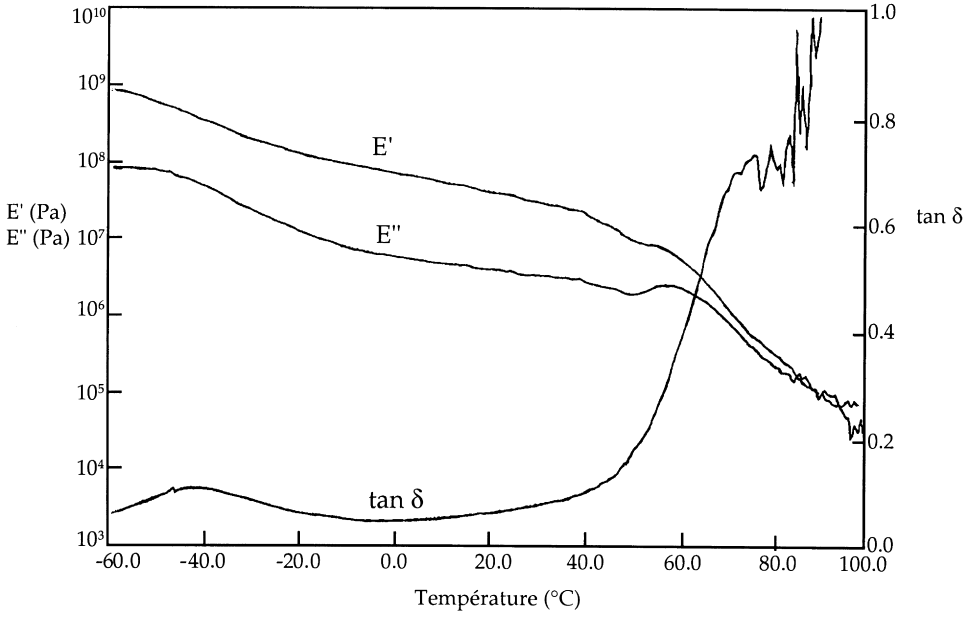

Fig. 4. DMTA data recorded at 1 Hz for cellulose laurate from Wac_2.

pre-treatment with sodium chlorite or alkaline treatment with hydrogen peroxide) was necessary for wheat bran, which had a high lignin content. Acidic treatment removed heteroxylan very efficiently but left a residue rich in lignin, with a cellulose of short chain length due to partial hydrolysis. Alkaline treatment removed both lignin and heteroxylan but the amount of residual heteroxylan was more important than after acidic treatment. The addition of sodium borohydride was an efficient way to prevent degradation of cellulose by oxidative peeling.

An esterification time of 8 h was selected allowing the best yield of cellulose laurate and the lowest amount of by-product. However, the amount of cellulose laurate increased with the cellulose content of the starting material. The two initial brans were rich in noncellulosics compound (heteroxylans, protein and lignin) embedding cellulose microfibrils, and probably preventing esterification of cellulose. Esterification of samples Wac_1 and Wac_2 rich in lignin gave cellulose laurate but also quite large amount of residual particles, suggesting that lignin was probably also esterified but remained insoluble in toluene. Besides chemical composition of cellulose laurate was similar whatever the initial cellulose.

Cellulose laurate exhibited a plasticized polymer behavior without addition of any plasticizer unlike others biopolymers as starch (Lourdin, Coignard, Bizot & Colonna, 1997) or proteins (Fairley, Monahan, German & Krochta, 1996). Long chain fatty acid cellulose ester exhibited similar mechanical properties and it has been shown that elongation increased with the degree of substitution whereas the tensile strength decreased (Wang & Tao, 1995). Esterified fatty acid seemed to act as internal plasticizer since increased of degree of substitution led to the same change of mechanical properties (Wang & Tao, 1995) that additional plasticizer for biopolymer like starch. However, our event, which could be a glass transition was detected at a temperature largely above room temperature, which was surprising, considering the elongation at room temperature. These two events revealed by DMTA appeared in the same range of temperature than the transitions evidenced by DSC. A possible explanation is that at very low temperatures one obtains crystallization of the side chains. The endothermic peak represents the transition of the side-chains from ordered into disordered states. This melting does not mean that the cellulose chain is melting. On the contrary, the chains could be well in a rather coiled state but frozen-in, i.e. in the glassy state. The alpha process at high temperatures has to be assigned to the glass transition of the macromolecular, i.e. the onset of segmental motions of the cellulose backbone. Sealey et al. (1996) have described comparable results and they assigned the two events to a low-temperature melt endotherm at −26°C and a glass transition at 95°C. The same authors suggested that a plasticization effect occurred for cellulose ester when chain length of substituent increased from C2 to C6 due to increased spacing between cellulose chains. Mobility of polymer was increased and T_g decreased. However, as chain length of fatty acid became larger than C6, T_g increased due to steric hindrance of bulky substituent, which diminished mobility of polymer.

Our results showed that it is possible to obtain films from agricultural by-products such as wheat bran and maize bran and their mechanical and thermomechanical properties seemed to be interesting. Furthermore, it would be interesting to realized a more economical and ecological esterification of cellulose-enriched residue, avoiding the use of pyridine to limit acidic degradation of cellulose (Fritz & Schenk, 1959). Hydrochloric acid produced by fatty acid chloride during reaction could be removed by applying a nitrogen stream (Thiebaud & Borredon, 1995) or vacuum (Kwatra et al., 1992). Homogeneous esterification of cellulose with fatty acid could also be realized using the lithium chloride/*N*,*N*-dimethylacetamide system (Samaranayake & Glasser, 1993a,b; Sealey et al., 1996; Vaca-Garcia et al., 1998).

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