Mechanical Behavior of Sheets Prepared from Sugar Beet Cellulose Microfibrils

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ABSTRACT: The mechanical behavior of films cast from sugar beet cellulose microfibrils was investigated through tensile tests. The obtaining of these microfibrils by chemical and mechanical treatments from the raw beet pulp is described. Depending on their purification level, individualization state, and moisture content, differences in tensile modulus are observed. It is found that pectins act as a binder between the cellulose microfibrils, which tends to increase the Young's modulus in dry atmosphere and to decrease it in moist conditions. The extraction of the cellulose microfibrils from the sugar beet cell wall and the obtainment of microfibril suspensions with partial individualization of the microfibrils by a mechanical treatment lead to the formation of a network of cellulose microfibrils within the film, which in turn increases the tensile modulus. Furthermore, the effect of the remaining pectins is compared with the effect of pectins previously removed and added to completely purified cellulosic microfibrils. As expected, once removed and so partly degraded, those pectins have nearly no influence on the mechanical properties. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **64:** 1185-1194, 1997

Key words: sugar beet pulp; cellulose microfibrils; pectins mechanical properties

INTRODUCTION

After the removal of sucrose, there exists a large amount of by-product in the sugar-refining factories, i.e., sugar beet pulp, which is traditionally pressed and dried to be marketed as cattle feed. Sugar beet pulp has been reported to contain large amounts of pectins (between 25 and 30%), hemicelluloses (25%), and cellulose (20%). The pulp also consists of protein and minerals.[1,2]

Pectins are composed of "smooth" $\alpha(1 \rightarrow 4)$-D-galacturonic acid regions alternating with "hairy" or ramified regions. These hairy regions are generally constituted of alternating α-D-galacturonosyl residues, which are 4-linked, and α-L-rhamnosyl residues, which are 2-linked, with approximately half of the rhamnosyl units carrying O-4 side chains containing mainly galactose and arabinose residues.[3]

Cellulose is a polydispersed linear polymer of poly-$\beta(1 \rightarrow 4)$-D-glucose with a syndiotactic configuration. Cellulose chains aggregate to form a fibril, a long thread-like bundle of molecules stabilized laterally by hydrogen bonds between hydroxyl groups of adjacent molecules. The molecular arrangement of these fibrillar bundles, called microfibrils, is sufficiently regular so that cellulose exhibits a crystalline X-ray diffraction pattern.

Paper sheets are constituted of cellulose microfibrils and are generally considered to be nonisotrope materials with a viscoelastic and non-linear mechanical behavior. Paper is classed either as a hydrogen bond network,[4–8] as a random fiber network,[9–13] or as an orthotropic continuous medium.[14]

Natural cellulose fibers are gaining attention

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as a reinforcing phase in thermoplastic matrices.[15–18] Their low density, a highly reduced wear of the processing machinery, and a relatively reactive surface may be mentioned as attractive properties, together with their abundance and low price. Nevertheless, such fibers are used only to a limited extent in industrial practice, which may be explained by difficulties in achieving acceptable dispersion levels. The dispersion level of cellulose fibers within a thermoplastic matrix is naturally subordinated to the processing technique used and to the physicochemical nature of the matrix, but also to the filler shape before adding to the polymer and to their interaction degree. The extraction step of cellulose microfibrils from the cell wall is therefore important in the final properties of the composites.

The aim of this work is to evaluate the mechanical behavior of sheets prepared from sugar beet cellulose microfibrils as a function of their purity level, according to successive chemical extractions, which also induces the interactions level, and of their topological arrangement, determined by homogenization treatments of the raw material. The effect of the moisture content on the mechanical properties of the microfibrils is also examined.

EXPERIMENTAL

Extraction of Pectins from Sugar Beet Pulp

Pressed and dried pulp was provided by "Laboratoire Fit, Générale Sucrière" (Nassandres, France), as pellets of about 7 mm in diameter. The pellets were hydrated into water, ground in a Waring blender apparatus for 10 min at a water-to-pulp ratio of 40 to 1, and filtered under vacuum on a 25-μm-pore-size Blutex nylon net (Tripette et Renaud, France). The pulp was extracted twice, and the solid residue was then treated with dilute hydrochloric acid ($0.05M$) for 1 h at 85°C, as described elsewhere by Rombouts and Thibault.[19] The pH of the pectin solution was adjusted to 4.5 with $2M$ sodium hydroxide, and the solution was dialyzed against distilled water and freeze dried. These pectins were dissolved in cold $0.05M$ sodium hydroxide solution and stirred overnight at 4°C under nitrogen in order to saponify the methyl and acetyl esters. The pH was adjusted again to 4.5 with $1M$ hydrochloric acid, dialyzed against distilled water, and freeze dried. The acid-soluble pectins were chemically heterogeneous and showed continuous variation of molecular weights, but from intrinsic viscosity measurements, the viscosity average molecular weights are generally around 40,000 and 45,000, as reported elsewhere by Guillon and Thibault.[20]

Preparation of Cellulose Microfibril Samples

The whole chemical and mechanical treatments together with the codification of the samples are reported in Figure 1 and described below.

Chemical Treatments: Removal of Pectinic and Hemicellulosic Polysaccharides

Sugar beet pulps were purified according to different chemical treatments.[21] The main objective of these treatments was to eliminate pectic substances, hemicelluloses, and phenolic molecules like lignin or polyphenols.

The alkali extraction with a 2% (w/w) sodium hydroxide (NaOH) solution for 2 h at 80°C was expected to hydrolyze pectins by a β-elimination process and solubilize them, because they are naturally insoluble in aqueous medium. This hydrolysis allows the solubilization of both pectins and hemicelluloses, which were then eliminated by filtration and rinsed by distillated water. The bleaching treatment with a sodium chlorite ($NaClO_2$) solution in a buffer medium (sodium acetate buffer pH = 4.9) for 2 h at 70°C under mechanical stirring was performed to remove phenolic compounds or molecules having chromophore groups, in order to whiten the pulps.

Despite these successive chemical treatments, calcium oxalate crystals still remain within the material. They can be removed by filtration on an appropriate sieve (pore size ranging between 20 and 70 μm). However, this technique does not allow the total removal of these crystals. It is also noteworthy that at this purification level, microfibrils are not individualized and are still associated within the cell wall. A further step consists of a mechanical treatment, as described in the next section.

For the preparation of sample C1, pellets were hydrated into water and ground in a Waring blender for 40 min at a water-to-pulp ratio of 40 to 1 (see Fig. 1) in order to facilitate the chemical accessibility. The suspension was filtered under vacuum on a 25-μm-pore-size Blutex nylon net, in order to remove the water-soluble components (sugars, salts) and some of the oxalate crystals.

The sample labeled C2 was prepared as follow.

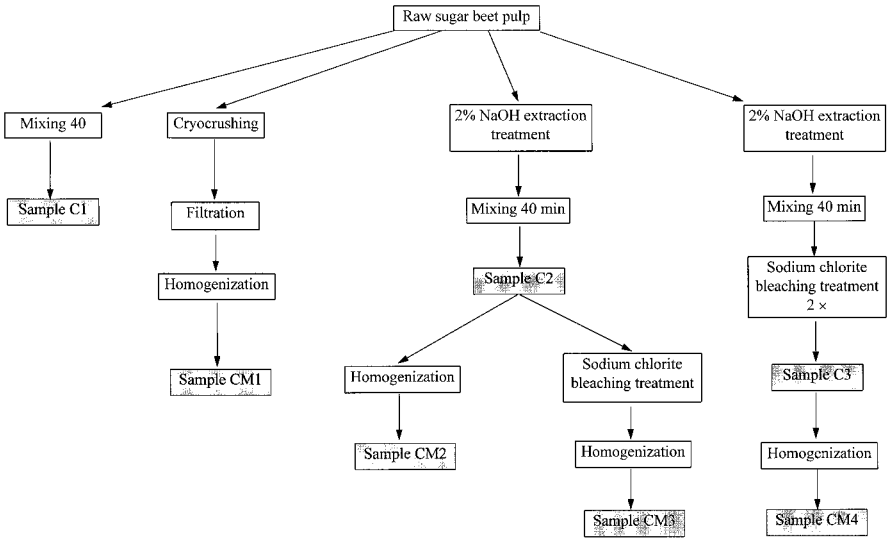


Figure 1 Chemical and mechanical treatments together with codification of the samples.

Pellets (20 g) were first dehydrated and then dispersed into 0.5*M* sodium hydroxyde solution (200 mL) under vigorous mechanical stirring at 80°C for 2 h. The sample was filtered under vacuum through a 25-μm-pore-size Blutex nylon screen; the residue was dispersed into 0.5*M* NaOH solution (200 mL) for 15 min at room temperature and filtered through a 25-μm-pore-size Blutex nylon screen. The cellulosic residue was washed with distilled water for several hours, until constant pH was reached, in order to remove most of the soluble mineral salts. The cellulosic residue was dispersed in distilled water, ground in a Waring blender apparatus for 40 min, and filtered. The yield, determined on the dry basis, was 68.3%.

In order to prepare sample C3, sample C2 was bleached according to Wise et al.[22] Ten grams of sample C2 was dispersed into 10 mL of a sodium chlorite, sodium acetate–buffered solution and vigorously stirred at 70°C for 2 h. The sample was filtered, and the yield, determined after drying, was 80.8%. A second chlorite bleaching treatment led, after filtration, to sample C3, with an overall yield for the two chlorite bleaching treatments of 79%.

Mechanical Treatment: Individualization of Cellulose Microfibrils

Two techniques of cellulose microfibril individualization were carried out, as described below.

Cryocrushing. Cryocrushing consists of the crushing of frozen pulp with liquid nitrogen. The freezing of the pulp leads to the formation of ice crystals within the cells. Under mechanical crushing, these crystals slash the cellular wall and release wall fragments. In order to remove calcium oxalate crystals, the crushed material is then diluted in water and abundantly strained.

Use of a Manton-Gaulin Apparatus. The Manton-Gaulin apparatus (APV France, Evreux, France)[23] was initially designed to homogenize and stabilize food ingredients. This apparatus operates according to the principle of high pressure and consists of a high-pressure plunger pump fitted with a homogenizing valve assembly. The suspension is propelled under the influence of a high-pressure gradient (500 bars) through two valves. The potential energy is therefore converted into kinetic energy (the suspension is accelerated until 300 m/s) and, within a very short time, into heat. As a consequence of this energy transfer, high shear and normal stresses, as well as high-energy particle collisions, occur in the processed medium. Their origins are inertial, frictional, and cavitational phenomena. This treatment on beet pulp dispersions for 0.5–3 h leads to a homogeneous suspension by microfibril individualization.

For the preparation of sample CM1, the pellets were first hydrated and cryocrushed and then were washed with water and filtered. A 2% (w/w) water suspension was prepared from this residue and homogenized at 500 bars for 2 h in a Manton-Gaulin apparatus.

Samples CM2 and CM4 were prepared from samples C2 and C3, respectively, by dispersing 4

g into 200 mL of distilled water and homogenizing at 500 bars for 2 h in the Manton-Gaulin apparatus. Sample CM3 was prepared from sample C2 by bleaching it one time and by applying next the homogenization treatment described above.

Film Casting

The objective of this work being the evaluation of the chemical purification (pectin and hemicellulose elimination) and mechanical treatments (cellulose microfibril individualization) on the mechanical properties of solid materials, solid films were prepared from the previously obtained suspensions. The air was removed by pumping the suspension under vacuum in order to avoid bubble formation in the material during drying. The residue was then cast into a plastic mold and stored at 37°C. After 48 h, evaporation was achieved and homogeneous beet pulp film was obtained.

Effect of Addition of Previously Removed Pectins to Purified Microfibrils. In order to control the cellulose/pectin ratio in the materials, films were prepared from purified cellulose microfibril suspensions and pectins previously extracted from the pulp. The cellulose microfibrils dispersed into water were mixed with the water pectin solution, with various amounts of pectins, in order to obtain films with a weight fraction of pectins ranging from 10 to 50% (sample codification, H10–H50). Films were prepared as previously described.

Effect of Moisture Content. Pectins are more hydrophilic than cellulose. It is then of interest to study the evolution of the mechanical properties with the moisture content. The tailored samples previously prepared were stored in dessicators containing saturated salt solutions for at least 5 days until used. Three relative humidity (RH) conditions were used, namely, 25, 58, and 75%.

Infrared Spectroscopic Measurements

The spectra of samples were recorded with a Perkin-Elmer 1720 X Fourier transform infrared spectrometer. Films were either ground and mixed with KBr (sample/KBr ratio, 1/99) to prepare pastilles or dispersed in water and evaporated as thin films directly observed.

Transmission Electron Microscopy

Transmission electron microscopy (TEM) observations were achieved with a Philips CM200 operated at 80 kV. A drop of a dilute cellulose microfibril suspension was deposited on carbon-coated grids and allowed to dry.

Scanning Electron Microscopy

A scanning electron microscope (SEM) from JEOL (JSM-6100) was used for studying the morphology of the materials containing extracted and added pectins. The films were fractured at the liquid nitrogen temperature. An observation of two sets of samples was made. The first one corresponded to films just after their fracture, and the second one corresponded to films that have been fractured and then submitted to an etching treatment by water in order to remove pectins from the surface. Indeed, the added pectins involved in tailored samples are soluble in water, contrary to original pectins.

Tensile Tests

The mechanical behavior of films of sugar beet cellulose microfibrils was analyzed with an Instron 4301 testing machine (UK) in tensile mode, with a load cell of 100 N capacity. The specimen was a thin rectangular strip (50 mm $\times$ 5 mm $\times$ 200 μm). Tensile tests were performed at a strain rate $\varepsilon = 2.8 \times 10^{-3}$ s^{-1} (crosshead speed = 5 mm/min) and at 25°C. For each measurement, it was observed that the strain was uniform along the sample, until its break. So, the strain ε can be determined by $\varepsilon = \ln(l/l_0)$, where l and l_0 are the length during the test and the length at zero time, respectively. The stress is calculated by $\sigma = F/S$, where F is the applied load and S is the cross-section. S is determined assuming that the total volume of the sample remains constant, so that $S = S_0 \times l_0/l$, where S_0 is the cross-section at zero time.

Data allow the plotting of stress versus strain curves, and the slope in the vicinity of $\sigma = \varepsilon = 0$ ($[d\sigma/d\varepsilon]_{\varepsilon \to 0}$) is equal to the tensile or Young's modulus (E). In order to have a more accurate comparison between the various materials, it is necessary to account for the film porosity, which can change in accordance with treatments. The corrected tensile modulus E_{corr} is calculated by taking into account the real cross-section S_{corr} of the sample:

$$S_{corr} = \frac{M}{\rho \times L} \quad (1)$$

where M and L are the weight and the length, respectively, of the sample, and ρ is the density of pure cellulose ($\rho = 1.5$ g/cm^3). The corrected tensile modulus E_{corr} is then determined from the slope at zero point of the curve $\sigma_{corr} = F/S_{corr} = f(\varepsilon)$. Stress and strain at break are not reported in this study because break always occurs in the vicinity of the jaws. This is due to the strip shape of the specimens. The values reported in this work result from the average of at least five measurements.

RESULTS AND DISCUSSION

Sugar beet pulps consisted of different cell walls associated together. The individualization of these different cells required chemical treatments to hydrolyze and solubilize the pectinic and hemicellulosic polysaccharides. The solubility of pectic substances depends not only on their molecular weight, but also on the presence of methyl esters, acetyl groups, and lateral chains. Any factor which tends to decrease the intermolecular binding possibilities leads to an increase of the macromolecular solubility. These factors may be of steric (presence of substituants) or of chemical nature (presence of ionizing groups). These two parameters are then very important in the case of pectic substances and hemicelluloses.

Thus, a polygalacturonic acid is insoluble in water but becomes soluble after the ionization of carboxylic groups by a monovalent cation. Moreover, pectic substances are able to create intermolecular bonds in the presence of calcium ion (Ca^{2+}), leading to an "eggs' box"-like structure which decreases the solubility of the pectins.

The alkali treatment allows the ionization of pectin carboxylic groups (CO_2H) and the formation of the corresponding sodium carboxylate (CO_2Na), which decreases the ability of hydrogen-type intermolecular bounds and prevents the "eggs' box"-like structure formation.

At low temperature and in alkaline medium, pectic substances are de-esterified without any effect on the degree of polymerization. On the other hand, heating favors β-elimination reactions, leading to a degradation (decrease of the degree of polymerization) and therefore to a greater solubility.

Cellulose can be also partially degraded during these extractions. To prevent this degradation, soda extraction duration is carefully controlled. Indeed, cellulose microfibrils are embedded in a pectin/hemicellulose matrix, which covers them almost completely. The soda extraction hydrolyzes only the surface substances. However, too concentrated alkaline solutions or too long reaction durations can induce undesirable reactions, like the "peeling" phenomenon which occurs on the polysaccharides' reducing end and continues by recurrent β-elimination. The 2% concentration soda solution used was low enough to avoid this "peeling" phenomenon on the cellulose molecules.

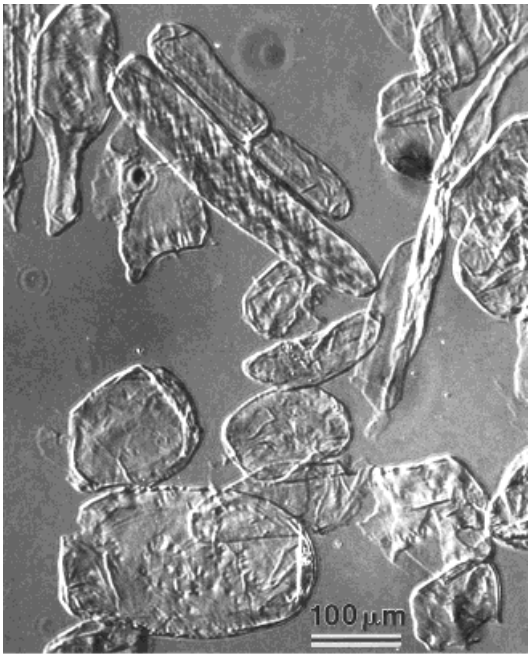
Infrared measurements were performed on sugar beet pulps at different steps of purification to follow the removal of the pectins. By this technique, it is possible to follow the removal of the pectins, due to the vanishing of the characteristic bands at 1,740 cm^{-1} (carboxylate groups) and at 1,590 and 1,240 cm^{-1} (acetyl and methyl ester groups, respectively).

Sodium chlorite in acetic buffer medium allows the removal of lignin and tannins, which yield the grayish color of the beet pulp. This way is the most widespread technique at the laboratory scale to remove lignin from plants. Lignin is rapidly oxidized by chlorine and chlorites. Lignin oxidizing leads to lignin degradation and to the formation of hydroxyl, carbonyl, and carboxylic groups, which facilitate the lignin solubilization in alkaline medium and then the purification of cellulose. The treatment by a sodium chlorite solution in sodium acetate buffer medium for 2 h removes most of the lignin. A further treatment is often required to fully bleach the suspension.

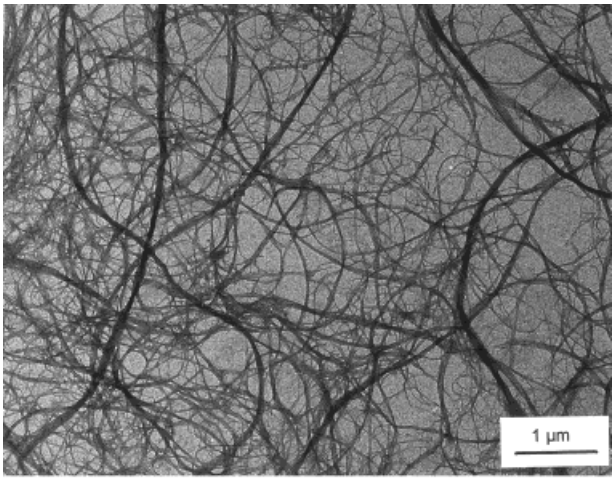
At this stage, the different cell walls are well individualized [see Figure 2(a)], but the microfibrils are still associated within the cell wall. In order to extract and individualize the microfibrils from the cell walls, a mechanical treatment is required. This can be performed with a Manton-Gaulin apparatus. The effect of this homogenization treatment is well displayed in Figure 2(b), which shows a micrograph of individualized cellulose microfibrils.

Effect of Chemical Treatment

A typical stress versus strain curve of a chemically treated beet cellulose microfibril film (sample C1) at 25°C is reported in Figure 3. This material exhibits a classic behavior, i.e., a linear behavior for strain smaller than 0.01 and a decrease of the slope $d\sigma/d\varepsilon$ versus increasing ε. The slope in the vicinity of $\sigma = \varepsilon = 0$, i.e., determined for $\varepsilon < 1\%$, is equal to the tensile modulus (E). Results are reported in Table I.



(a)



(b)

Figure 2 (a) Optical micrograph in Nomarski contrast showing individualized sugar beet cell wall and (b) Transmission electron micrograph showing individualized cellulose microfibrils after high-pressure mechanical treatment.

A decrease of the tensile modulus with purification level, and then with the gradual elimination of pectins, is shown in Table I. It is clear that cellulose microfibrils are stiffer in the presence of pectins. Pectins act as a binder between the cellulose microfibrils and improve the mechanism of load transfer toward microfibrils when the sample is subjected to a mechanical stress. This binding mechanism is governed by hydrogen bonding and/or covalent connections between pectins, hemicelluloses, and cellulose microfibrils.

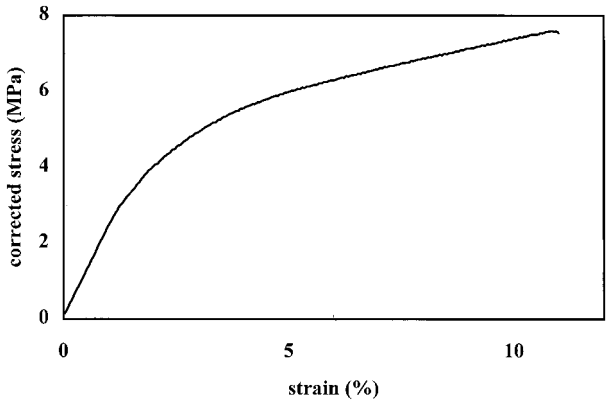


Figure 3 Typical stress versus strain curve for chemically treated sugar beet cellulose microfibril films (sample C1) at 25°C. $\varepsilon = 2.8 \times 10^{-3}\ s^{-1}$.

Effect of Mechanical Treatment

The tensile modulus of cellulose microfibril films as a function of the chemical treatment and after mechanical treatment in the Manton-Gaulin apparatus are presented in Table II. The same behavior as those previously reported for the tensile modulus is observed as a function of the purification level, i.e., the Young's modulus decreases with the gradual elimination of pectins. Figure 4 displays the evolution of the tensile modulus as a function of the purification level for both chemically (samples C) and chemically and mechanically (samples CM) treated microfibril films. The mechanical treatment of cellulose microfibrils induces a significant increase of the Young's modulus, whatever the purification step may be. The homogenization treatment leads to an individualization of cellulose fibers, as displayed by TEM in Figure 2, and to the formation of a strong network of microfibrils inside the material. Moreover, the modulus drop between purification steps 1 and 2 (which differ by the 2% soda extraction treat-

Table I Mechanical Properties of Chemically Treated Sugar Beet Cellulose Microfibrils

Sample	C1	C2	C3
E (GPa)	1.3	0.9	0.7
E_{corr} (GPa)	2.3	1.25	1.15

Table II Mechanical Properties of Chemically and Mechanically Treated Sugar Beet Cellulose Microfibrils

Sample	CM1	CM2	CM3	CM4
E (GPa)	2.3	1.85	2.0	1.8
E_{corr} (GPa)	3.2	2.7	2.65	2.5

ment) is smaller for individualized microfibrils (CM1 and CM2) than for undividualized pulps (C1 and C2). This result shows that the extraction and individualization of the microfibrils from the cell wall are more efficient when the pectin content is lower.

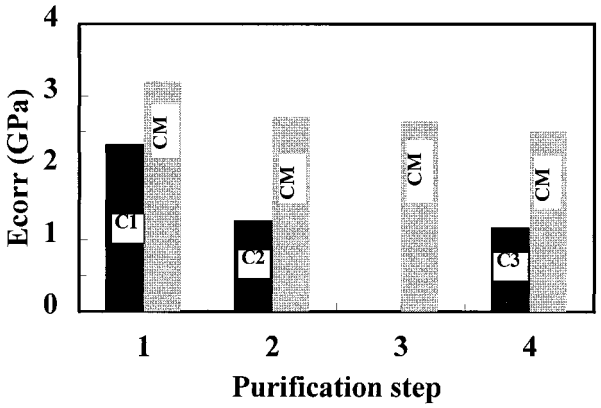


Figure 4 Evolution of the tensile modulus as a function of the purification level for both chemically (samples C in black) and chemically and mechanically (samples CM in gray) treated microfibril films.

Effect of Moisture Content

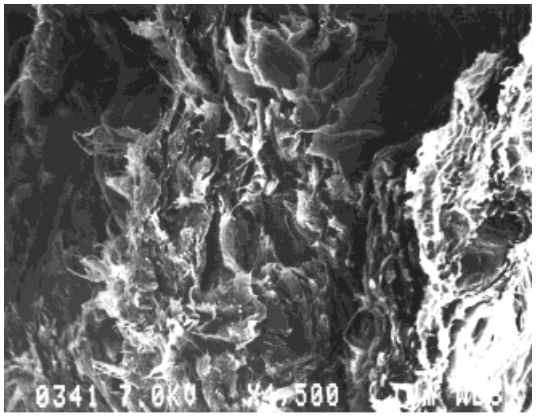
Tensile tests were performed on films containing controlled fractions of added pectins (tailored H10 to H50 materials) or original pectins (CM1 to CM4 samples) and stored at various relative humidity (RH) levels. Results are reported in Table III for tailored samples. We ascertain that no coherent evolutions for the tensile modulus are displayed as a function either of the pectin content or of the RH within the pulp.

The explanation of this phenomenon lies in the fact that the addition of pectins previously extracted from the pulp, and then resolubilized, acts differently than the natural pectins originally present within the raw material. In sugar beet cell wall, pectins surround cellulose microfibrils and lead to their cohesion. Extracted pectins are on one hand soluble in water, and their degree of polymerization is necessarily lower than those of natural pectins. On the other hand, during blending of the cellulose suspension with the pectin solution, pectins probably locate differently than in raw pulp. Instead of surrounding cellulose microfibrils, pectins occur as inclusions within the material. Interactions between both constituents are therefore strongly restricted. During tensile tests, the material acts as a microfibril network, the behavior of which is unaffected by the presence of pectin domains. This hypothesis is suitable to explain the inconsistency in the evolution of the tensile modulus as a function of pectin content. Moreover, pectins are strongly hydrophilic and will absorb most of the water present within the material. Because pectins do not interact with microfibrils, which in turn ensure the cohesion of the film, it is obvious that no consistent evolution of the modulus with the moisture content can be expected.

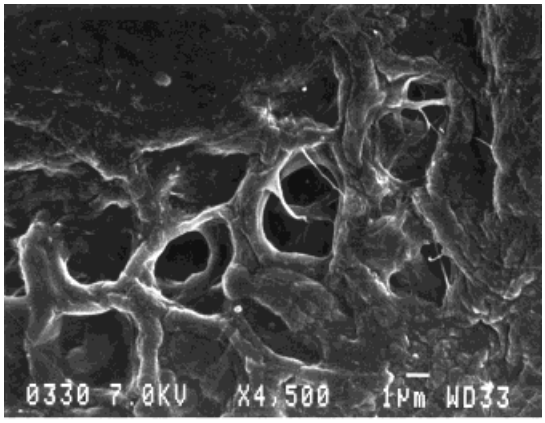
SEM was used to characterize the morphology

Table III Mechanical Properties of Sugar Beet Cellulose Microfibrils as a Function of RH Level and Added Pectin Content

Sample	H10	H20	H30	H40	H50
Pectin content (w/w %)	10	20	30	40	50
RH 25%					
E (GPa)	1.2	2.6	1.95	2.1	1.7
E_{corr} (GPa)	2.6	3.35	3.0	3.2	2.5
RH 58%					
E (GPa)		2.2	1.9	1.6	1.9
E_{corr} (GPa)		2.6	2.3	2.3	2.4
RH 75%					
E (GPa)	1.5	1.7	1.95	2.6	2.5
E_{corr} (GPa)	1.95	1.9	2.5	3.3	2.7



(a)



(b)

Figure 5 Scanning electron micrographs of (a) freshly fractured surface and (b) surface of fracture after the etching treatment by water of a 10% pectin-filled sample.

of cellulose/pectin films involving extracted and resolubilized pectins. Figure 5(a) shows the surface of a film, just after fracture, filled with 10% pectins. On this micrograph, pectin and cellulose domains cannot be directly identified. Figure 5(b) shows the surface of fracture for the film containing 10% pectins after etching by water. From the comparison between Figure 5(a) and (b), the evidence of the localization of pectins as inclusions within the cellulose network is given by the presence of holes which correspond to the dissolution of pectins inside the film.

To evidence the effect of moisture content on the mechanical behavior of beet pulps, we have then used films containing natural pectins. The evolution of pectin content can be determined by the different steps of purification, even if the cellulose/pectin ratio is not quantified. The mechanical properties of samples CM1 to CM4, which were chemically and mechanically treated, are reported in Table IV as a function of moisture content. In this table, the pectin content decreases from left to right, and the RH increases from the top to the bottom. The effects of the mechanical treatment and relative moisture content are shown in the three-dimensional diagram of Figure 6.

At 25% RH, the modulus rapidly decreases with the purification step, especially between steps 1 and 2, because most of the pectins are removed during this treatment. The modulus then remains practically constant during subsequent purification steps. At higher RH (58 and 75%), the modulus is nearly constant during the various treatments. This is probably because pectins are strongly hydrophilic. Indeed, in moist conditions, pectins absorb most of the water, which results in the softening of pectin domains. Their effect on the mechanical response of the pulp is then negligible. The material behaves like a microfibril network surrounded by a soft phase. It is worthy to note the very low value of the modulus of the CM1 sample, which presents the higher pectin content, in a highly moist atmosphere. This result is probably due to the difficulty of forming a microfibril network in the presence of a high amount of softened pectins.

Moreover, one can wonder at the moduli measured on the sheets prepared from sugar beet cellulose microfibrils, which are much lower than those reported for paper sheets[24] (11.7 GPa). We have tried to dehydrate a CM1 sample at 400K for 30 min. The modulus increases to 6 GPa (E_{corr} = 8.5 GPa). The difference between this value and the one reported by Smith et al.[24] is probably due to the high amount of pectins present in this sample, which is watertight.

CONCLUSIONS

Sugar beet cellulose microfibril films were processed by casting an aqueous suspension of pulp. The mechanical properties of these films were analyzed as a function of the purification step, of the cellulose microfibril individualization state, and of the moisture content.

Pectins naturally present in the pulp strongly influence the mechanical behavior of the film. Their elimination induces a decrease of the tensile modulus in dry atmosphere. Indeed, pectins act

Table IV Mechanical Properties of Sugar Beet Cellulose Microfibrils as a Function of RH Level and Treatment Step (the Pectin Content Decreases From Left to Right)

Sample	CM1	CM2	CM3	CM4
RH 25%				
E (GPa)	2.3	1.85	2.0	1.8
E_{corr} (GPa)	3.2	2.70	2.65	2.5
RH 58%				
E (GPa)	1.15	1.3	1.3	1.1
E_{corr} (GPa)	1.65	1.7	1.7	1.65
RH 75%				
E (GPa)	0.8	1.1	1.3	1.15
E_{corr} (GPa)	1.1	1.7	1.6	1.7

as a binder between the cellulose microfibrils and improve the mechanism of load transfer toward microfibrils when the sample is subjected to a mechanical stress. This binding mechanism increases the cohesion within the material, and it is due to hydrogen bonding and/or covalent interactions between pectins, hemicelluloses, and cellulose microfibrils. On the other hand, the Young's modulus decreases with the pectin content in a humid atmosphere. This phenomenon is due to the hydrophilic character of pectins, which constitute preferential sites of water localization and soften in the presence of moisture.

However, the addition of pectins previously extracted from the pulp, and then resolubilized, in the microfibril network does not lead to the same result. The degree of polymerization of the pectins decreases during the extraction, and pectins occur as inclusions within the material, whereas they are better dispersed and interact with hemicelluloses and cellulose microfibrils within the plant cell wall. The extracted pectins are not involved in the mechanical response of the pulp.

The tensile modulus increases with the duration of the mechanical treatment of the pulp. This treatment leads to an individualization of the microfibrils and then to the formation of a network of cellulose microfibrils within the material. We noticed that the individualization of the microfibrils during the mechanical treatment is all the easier because the pectin content is low.

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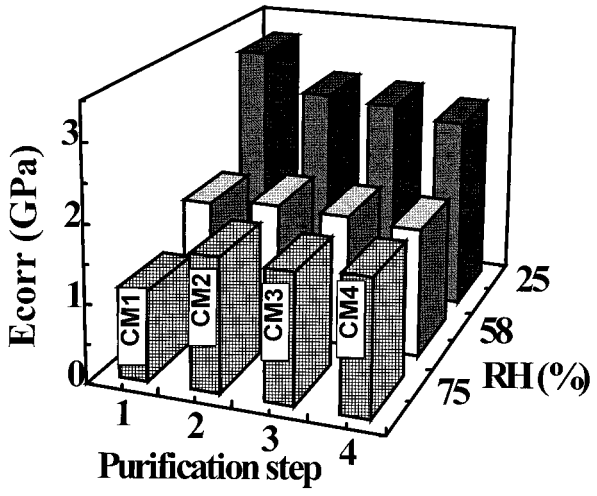

Figure 6 Evolution of the corrected tensile modulus as a function of the purification step and of the relative humidity.

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