Available online at www.sciencedirect.com
ScienceDirect
Carbohydrate Polymers 66 (2006) 81–87
Carbohydrate Polymers
www.elsevier.com/locate/carbpol

Thermo-mechanical processing of sugar beet pulp. I.Twin-screw extrusion process

A. Rouilly *, J. Jorda, L. Rigal

Laboratoire de Chimie Agro-Industrielle, UMR 1010 INRA/INP-ENSIACET, 118 route de Narbonne, F-31077 Toulouse Cedex 04, France

Received 16 September 2005; received in revised form 23 January 2006; accepted 18 February 2006
Available online 4 April 2006

Abstract

Sugar beet pulp (SBP) is the raffinate of sugar extraction. Composed of empty vegetal cells, three quarters of it consist of polysaccharides. As it is cheap and produced in great quantities SBP is a potential raw material for industrial applications other than cattle feeding. Twin-screw extrusion modified its structure and destructuring level depended on the specific mechanical energy provided (SME). By gradually increasing this energy, the rate of soluble matter increased, cell structure was progressively destroyed and SBP rheological behaviour was modified. For an SME of 745 W h kg^{-1}, SBP examined through a scanning electron microscope showed a structure similar to that of a composite formed by a continued matrix consisting mainly of pectin and hemicelluloses filled with cellulose microfibres. Plasticized SBP was then formed by injection-molding. Thus treated, SBP becomes a cheap alternative to the use of thermoplastic starch for the production of biodegradable materials.

Keywords: Twin-screw extrusion; Rheology; Thermoplastic; Injection-molding

1. Introduction

A third of the world production of sugar comes from sugar beet (*Beta vulgaris*). One ton of sugar beet (saccharine content 16%) provides a dried weight of around 130 kg of sugar and 50 kg of a by-product, sugar beet pulp (SBP). Pulp output in Europe was more than 6 Mt in 2002 and its price after dehydration was approximately 0.1 € per kg^{-1} (CGB, 2000).

The industrial sugar extraction process consists of a counter-current hot water circulation which preserves cell structure and avoids co-extraction of parietal compounds. Thus, sugar beet pulp is made of vegetal cells drained of their vacuolar sap, but whose membranes have not been affected (Dinand, Chanzy, & Vignon, 1996). These cell walls are primary as harvesting takes place as soon as the tuber reaches its maximum size and weight. SBP consists mainly of cell wall polysaccharides in almost equal proportions as compared to the dry matter, that is approximately 25% cellulose, 25% hemicellulose and 25% pectin. It also contains a small quantity of lignin (Okojie & Sargent, 1990). More precisely, the cellulose in sugar beet cell walls is made of 2–4 nm in diameter fibril arrangements (Dinand et al., 1996) of low crystallisation level (Heux, Dinand, & Vignon, 1999) embedded in a matrix consisting of arabinans and arabinogalactans (Sun & Hughes, 1999) linked by covalent bonds to highly methylated and acetylated pectic chains.

Due to its composition, SBP is considered as forage or as foodstuffs (Bach Knudsen, 1997), and is therefore used only as a food complement to animal feed. However because of high-cost dehydration and low protein content, alternative uses have to be investigated to avoid the waste of a large amount of the production. Enhancing the value of the extracts was considered first: food fibres (Michel, Thibault, & Barry, 1988), cellulose microfibrils (Dinand, Chanzy, & Vignon, 1999; Togrul & Arslan, 2003), pectins (Oosterveld, Pol, Beldman, & Voragen, 2001; Turquois, Rinaudo, Taravel, & Heyraud, 1999) or ferulic acid

* Corresponding author. Tel.: +33 5 62 88 57 25; fax: +33 5 62 88 57 30.
E-mail address: Antoine.Rouilly@ensiacet.fr (A. Rouilly).

0144-8617/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.carbpol.2006.02.025

(Mathew & Abraham, 2004; Micard, Renard, & Thibault, 1994). Raw SBP was also used as a cultivation substrate (Yoo & Harcum, 1999), for divalent cations complexation (Dronnet, Renard, Axelos, & Thibault, 1997; Reddad et al., 2002), as a source of polyol for the production of urethanes and polyurethanes (Pavier & Gandini, 2000a, 2000b) or as a source of fibre in the composition of biodegradable materials (Baar, Gebel, Imhof, & Mihalik, 1997; Turbaux, 1997) or for paper manufacture (Wong & Bregola, 1997). Structural modification of SBP was only considered from two different points of view: chemical or enzymatic hydrolysis for the production of a paste to be used in the manufacture of packaging (Berghofer, Grzeskowiak, Mundlinger, Schleining, & Zenz, 1992) and parietal polysaccharides solubilization by extrusion-cooking to improve its nutritional properties (Ralet, Thibault, & DellaValle, 1991).

The aim of the first part of this work is to demonstrate that twin-screw extrusion in extreme conditions makes it possible to break sugar beet cell structure while avoiding thermal degradation. This process liberates the non cellulosic cell wall polysaccharides from their native organization and SBP acquires some interesting thermoplastic properties and can be injection-molded. The obtained material mechanical properties are tested.

2. Materials and methods

2.1. Material

The sugar beet pulp (DM = 89.9%) originated at the Cagny site (France). Before being processed it was coarsely grinded through a 6 mm grid.

2.2. Extrusion

A Clextral BC45 co-rotating twin screw extruder (Firminy, France) was used. Its barrel was divided into seven 20 cm sections for a total length of 1.4 m. It could be fitted with a converging 10 mm diameter die in at its end, over which was placed a demultiplication plate bored by eight 2 mm diameter holes and holding a granulating blade. The profile of the screw was of variable screw elements with two sections of mechanical constraint (Fig. 1). The screw elements used in Section 1 were chosen to help water impregnation and to apply a first mechanical stress. They were some blocks of either kneading disks (Mal0) or kneading paddles (Mal2) orientated one from another with variable angles or some notched wheels (MEL). The length of this section was always 100 mm. The second zone was dedicated to high shear treatment under compression. The screw elements used were either some twin lead reverse screws (C_2FC) or some single lead reverse screws (C_1FC) of a length of 50 mm. The rest of the screw configuration was made of double lead screws with a pitch of 33 or 25 mm. A typical screw configuration is shown on Fig. 1.

The electrical power of the motor was measured continuously and allowed the specific mechanical energy to be calculated (N'Diaye & Rigal, 2000). Barrel in Section 2 and die were equipped with pressure and temperature sensors (Fig. 1). The temperature of the barrel was programmed at 25/25/70/70/70/70/70 °C. It increases by self-overheating in stress areas to an equilibrium temperature depending on the operating parameters. The amount of water introduced was expressed by the L/S mass ratio of the water input flow rate to the dry matter input flow rate.

2.3. Solubility

Three samples of each extrudate of approximately 3 g were dried and weighed. They were then soaked in 50 ml of distilled water at 25 °C. Suspensions were stirred regularly in a discontinuous manner during 24 h, then filtered. Solid residues were then dried and weighed. The difference between the initial mass and the final mass compared to the initial mass led to the determination of the content of soluble matter.

2.4. Colorimetry

Samples were finely grinded through a 1 mm grid before analysis on a Minolta CM-508i spectrocolorimeter (Ramsey, USA) in the referential $L^*a^*b^*$.

2.5. Adsorption isotherms

Samples were dried for 15 days at 60 °C in a vacuum desiccator before being placed in the hermetic containers containing the saturated saline solutions which set the moisture level of the upper part of the container (Rouilly, Orliac, Silvestre, & Rigal, 2001). Equilibrium was reached when sample mass did not vary more that 1% in 24 h. Their

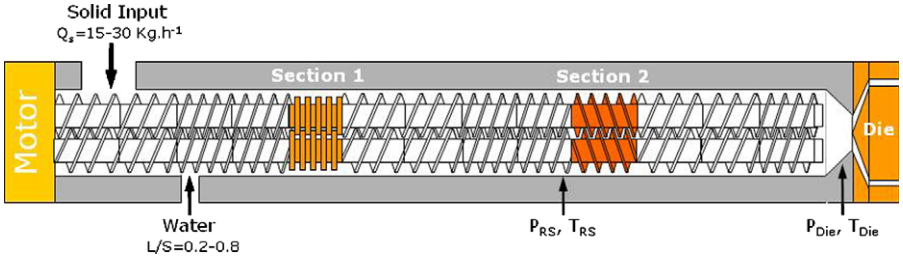

Fig. 1. Schematic representation of the twin-screw extruder configuration.

moisture content was then obtained by drying at 105 °C during 24 h.

2.6. Microscopy

Scanning electron microscopy observations were carried out on a LEO 435VP. All samples were dried at 60 °C during 48 h in a vacuum desiccator before being metallized.

Optical microscope was a Nikon SMZ1500 assisted with Lucia software. Maximum resolution of the microscope was 0.25 μm.

2.7. Rheology

Melt viscosity measurements were carried out on a Rheomex Haake system (Karlsruhe, Germany) consisting of a single-screw extruder (18 mm diameter screw and 2.0 compression rate) fitted with a 3 mm diameter capillary rheometric die of a L/D ratio of 10. The mass flow rate and die pressure were continuously monitored according to screw rotation speed to calculate the shear rate, the shear stress and the apparent viscosity. For analytical purposes, moisture content of SBP was set at 20%, temperature at 130 °C. Extrudate apparent density was measured and considered as constant at a value of 1.2 for the volume flow rate calculation.

For most thermoplastics, the shear stress is linked the shear rate by a power law-type model:

$$\tau p = K\gamma^m.$$

The shear rate and shear stress can be used to obtain a curve showing the viscosity at the wall of the material tested by applying the following equation, known as the Ostwald de Waele equation:

$$\eta = \tau p/\gamma p = K\gamma_p^{m-1}. \quad (1)$$

The values of m are between 0 and 1 for thermoplastic materials, which explains their shear thinning behaviour. The values of the K coefficients (consistency) and m (pseudo-plasticity index) were obtained by linear regression of log 10 values of the real viscosity as a function of the log values of the shear rate. This measurement, carried out in a single capillary, did not take edge effects into account. In addition, attempts to perform the Bagley correction using different capillary geometries (L/D) were unsuccessful because of a too large pressure variation. Therefore the measurement did not allow calculation of absolute values of viscosity and all the viscosity values reported herein are apparent viscosity values, calculated from Eq. (1).

2.8. Gel permeation chromatography

Water soluble biopolymers were extracted in water at 70 °C during 2 h. They were then precipitated in ethanol before being diluted in deionized water to a concentration of around 2000 ppm. A 100 μl volume of these solutions was finally injected with a Dionex (Voisins le Bretonneux, France) P580 pump equipped with an automated sample injector in a line of one PL Aquagel-OH 30 8 μm and two PL Aquagel-OH mixed 8 μm columns from Polymer Laboratories. Eluant was a buffer solution of sodium nitrate (0.2 M) and dihydrogenphosphate (0.01 M) with a flow rate of 1 ml.min^{-1} at 25 °C. Calibration was made with pullulans of molecular weight ranging from 0.18 to 788 kDa.

2.9. Production of injection-molded samples

The equilibrated samples (80% DM) were injected with a Billion H280/90TP injection press (Oynnax, France). The temperature profile selected was 40/70/110/130 °C for all mixtures. The resulting materials were in the form of standardised rectangular bars (80 mm × 10 mm × 4 mm) (ISO294, 1996) and standardised dumbbells (150 mm × 10 mm × 4 mm) (ISO527-2, 1993). After conditioning in humidity-controlled chambers until equilibrium (60%; 25 °C), the bars were subjected to flexural strength tests (ISO178, 2001). The standardised dumbbells were used to measure the mechanical properties of the materials during tension tests (ISO527-2, 1993). Sven specimens of each were tested.

3. Results and discussion

3.1. Influence of the specific mechanical energy

To study the influence of the specific mechanical energy different screw elements have been tested in Sections 1 and 2 in a configuration without die (Table 1). Screw speed and L/S ration were kept constant, respectively, at 200 t min^{-1} and around 0.3.

In softer conditions, Ralet et al. (1991) have shown that extrusion treatment results in solubilization of the pectic compounds: galacturonic acid and arabinose contents of the soluble phase were particularly high. In these experiments, the solubilization appeared only when SME reached 500 W h kg^{-1} as the ratio of soluble fraction increased from 13.2% for the raw pulp to 28.2% and 47.4%, respectively, for EP4 and EP5 (Table 1).

The increase of SME supplied to the pulp in the extruder was due to the use of screw elements of increasing shear effect in zone 1, especially for the notched wheels (MEL) but the effect of the reverse screw element in zone 2 was more obvious. From a twin lead reverse screw (C_2FC) to a single lead one (C_1FC) compression of the returning matter was increased and SME increased. Use of two reverse screw elements resulted in the highest SME: 681.5 W h kg^{-1} (Table 1). In these conditions of shear and compression, temperature in the second section increased over 100 °C and water evaporation took place as revealed by extrudate moisture content lower than the dehydrated raw pulp one. The extrusion-cooking process of SBP resulted as well in the production of a strong smell and a change in pulp colour. With SME increase, the lumi-

Table 1
Solid input rate (Q_S), intensity (I), temperature (T_{RS}) recorded during extrusion process

Trial	Zone 1	Zone 2	Q_S (kg h^{-1})	I (A)	T_M (°C)	SME (W h kg^{-1})	Solubles (% MS)	DM (%)	L^*	a^*	b^*
RP	–	–	–	–	–	–	13.2	89	71.7	0.26	10.4
EP1	MAL2 −60°	C_2FC	19.8	28	98	213.4	14.2	76.8	72.5	0.20	8.8
EP2	MAL2 90°	C_2FC	19.1	42	95	320.3	14.9	82.3	70.4	0.46	9.3
EP3	MEL	C_1FC	16.8	51	93	442.2	14.7	73.6	68.0	0.56	8.7
EP4	MAL2 90°	C_1FC	15.3	58	114	552.2	28.2	88.2	68.9	0.63	10.6
EP5	MAL0	C_2FC (×2)	17.1	80	112	681.5	47.4	92.3	55.0	3.12	12.4

Calculated specific mechanical energy (SME), rate of soluble matter, dry matter content and colorimetric measurements of corresponding extrudates. L/S ratio is 0.3 for all experiments.

nance L^* decreased while the red parameter a^* increased drastically to a value of 3.12 for EP5. The yellow parameter first decreased for SME lower than 500 W h kg^{-1} and finally increased to a higher value than the reference value for the raw pulp (Table 1). These results were characteristic of a degradative treatment of SBP.

3.2. Influence of L/S ratio

From the previous experiments it could be concluded that the volumic expansion of water vapour after the reverse screw caused the degradation of SBP constitutive biopolymers. To avoid this phenomenon the extruder has been fitted with a die creating a second compression zone along the screw configuration. As we let the temperature establish itself by self-heating, in these conditions L/S ratio determinated the physical-chemical properties of the mixture.

The screw configuration was constituted of kneading disks in the first section and of a double lead reverse screw in the second. The die was fitted with pressure and temperature sensors.

Decreasing L/S ratio from 0.80 to 0.31, SME increased from 269.1 to 745.3 W h kg^{-1} while die temperature raised up to 123 °C (Table 2). As for the experiments without die, changes in physico-chemical properties appeared when SME reached 500 W h kg^{-1}. The fraction of water soluble matter increased drastically from 13.6% to 31.0% corresponding respectively to EP7 and EP8. The behaviour was exactly the same when looking at the apparent viscosity curves, EP6 and EP7 had a comparable behaviour while viscosity tended to decrease for EP8 and was really lower for EP9: its viscosity was lower than 1000 Pa s when shear rate was higher than 280 s^{-1} (Fig. 2). Relatively high viscosity for EP6 grade has been attributed to a slightly higher dry matter ratio than 80% during measurement. Rheology of extruded SBP seemed then to be linked to the solubilization of the cell wall polysaccharides. For Trial EP9 the same L/S ratio as those of the first trials without die has been used. In these conditions SBP was treated with the highest SME (i.e., 745.3 W h kg^{-1}) and the highest temperature was reached (i.e., 123 °C). However, SBP was not degraded: dry matter of the extrudate was 76.3%, EP9 had a pasty texture, and L^* and b^* values, corresponding, respectively, to white and yellow, decreased continuously. Finally the soluble fraction content of EP9 was lower than for EP5.

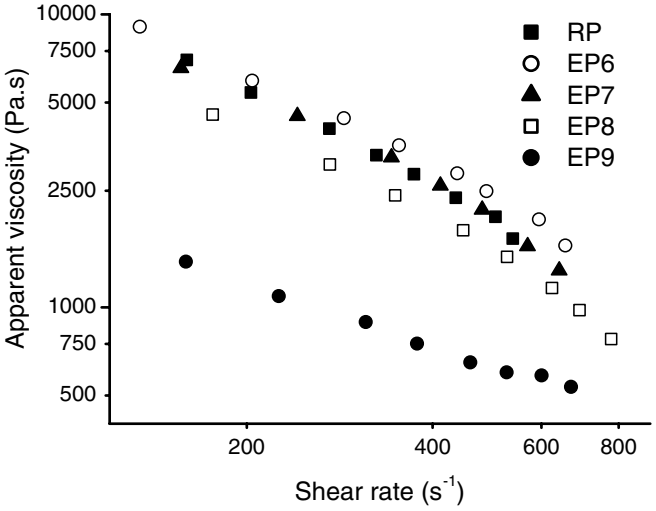

Fig. 2. Extrudates apparent viscosity at 130 °C (80% DM) according to the shear rate (die: 3 mm in diameter and L/D = 10).

Table 2
Solid input rate (Q_S), ratio of liquid flow rate to solid input rate (L/S), intensity (I) and maximum temperature (T_{max}) recorded during extrusion process with a die

Trial	Q_S (kg h^{-1})	L/S	I (A)	T_{max} (°C)	$P_{D\ (bars)}$	SME (W h kg^{-1})	DM (%)	Soluble (% DM)	L^*	a^*	b^*
RP	–	–	–	–	–	–	89	13.2	71.7	0.26	10.4
EP6	16.3	0.80	27	72	53	269.1	49.5	11.7	67.9	0.81	8.96
EP7	15.3	0.65	49	110	76	424.6	58.2	13.6	65.5	0.83	8.71
EP8	17.2	0.58	60	114	78	512.1	55.4	31.0	59.3	0.85	8.72
EP9	14.9	0.31	86	123	70	745.3	76.3	37.8	55.0	1.53	8.05

Calculated specific mechanical energy (SME), rate of soluble matter, dry matter content and colorimetric measurements of corresponding extrudates.

Twin-screw "plasticization" of SBP was obtained through thermo-mechanical treatment under compression. Pressure was not a determining factor but a limitating one. Die pressure was stable around 70 bars for the trials EP7 to EP9 (Table 2).

3.3. SBP destructuring

SBP is constituted of empty parenchymal cells (Fig. 3a). Solubilization of some of the pectic substances during twin-screw extrusion has already been observed (Ralet et al., 1991), but the change in rheological properties of extruded pulp must be caused by a more important structural change: the breakage in some extent of the cell structure.

Adsorption isotherms of the extruded grades from 6 to 9 and of the raw pulp (Fig. 4) gave some additional results on their structure. In the water activity range of 0.1–0.7, sorbed water amount increase is directly linked to the increase of water soluble matter (Table 2) and so to the increase of free hydroxyl groups. This result was confirmed by the molecular weight of hot water extracted polysaccharides from RP and EP9 (Table 3). Molecular weight of EP9 extracts were 30% lower than those of RP extracts. Therefore the mass adsorbed at the equilibrium increased with the specific mechanical energy supplied during the twin-screw extrusion. But in the high humidity range ($P/Po > 85\%$) the higher this energy was, the lower was the adsorbed amount of water. This phenomenon is characteristic of the cell structure breakage. In this humidity range the adsorbed water is sometimes called "freezing water" and is not bound to polymers by secondary interactions but is retained physically (Fennema, 1996). Empty cells absorption capacity by capillarity is high and results in SBP swelling ability. SBP destructuring was then responsible for the decrease of water adsorption in the high humidity range. Partial loss of the cell structure appeared during twin-screw extrusion when SME increased. Adsorption behaviour of EP8 grade was surprising. Its sorbed water uptake at 97% RH was the lowest while its SME and soluble matter rate were, respectively, only 512.1 W h kg^{-1} and 31%. This could be due to a pressure effect as recorded pressure during the experiment was maximum but it has still to be investigated.

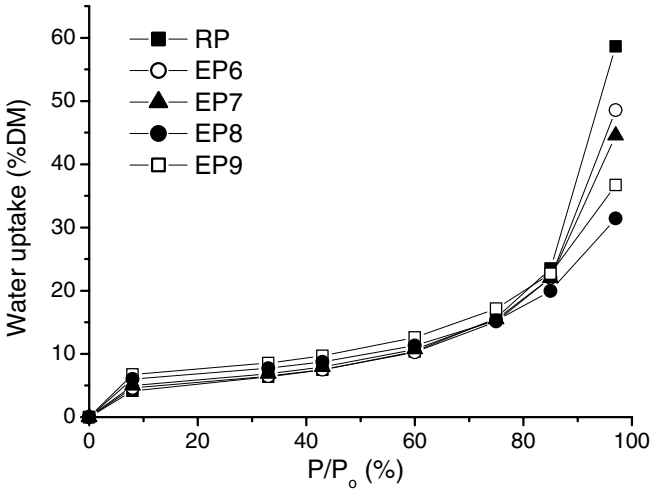

Fig. 4. Adsorption isotherms at 25 °C of the different obtained extrudates.

Table 3
Molecular weight of water soluble (70 °C, 2 h) components measured by GPC

	RP	EP9
Mn	31,108	20,456
Mw	154,789	92,650
Mz	347,114	244,557
Ip	498	453

The structure evolution was clearly observed on micrographs. With the treatment severity increase, micro-structure became thinner and thinner and cells disappeared (Fig. 3b), and for the EP9 grade the observed structure was a continuous matrix in which the cellulose microfibres should be embedded (Fig. 5).

Solubilization of a part of the pectic substances is caused by the cell structure breakage. Non-cellulosic cell-wall polysaccharides – more than the half of dry SBP weight – form then a continuous matrix having a thermoplastic behaviour, at least for EP9 grade. Solubilization concerns

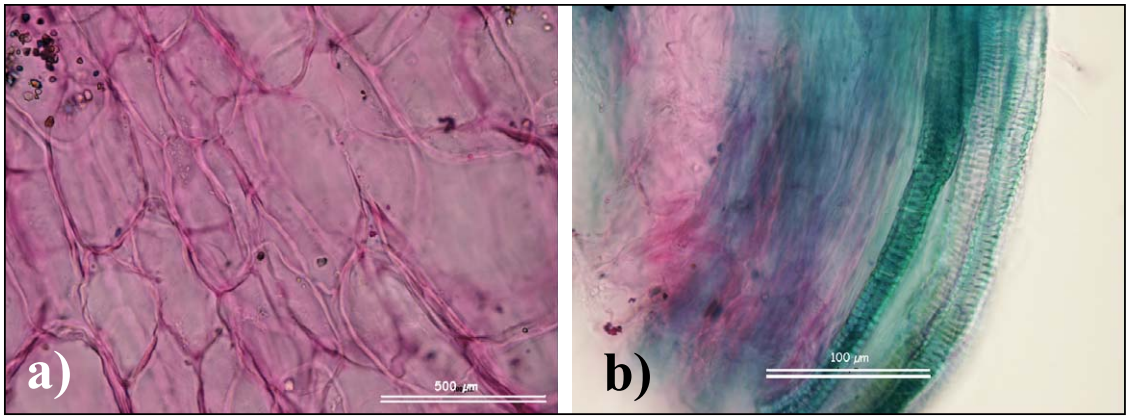

Fig. 3. Raw SBP (a) and plasticized EP9 (b) observed by optical microscopy.

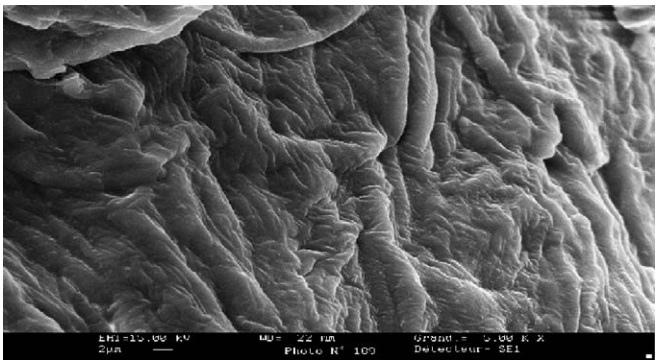

Fig. 5. Scanning electron micrographs of the EP9 extrudates (G = 5000).

Table 4
Power law coefficients of extrudates viscosity modelling (130 °C, 20% MC) and corresponding correlation coefficient

	K (Pa s^m)	m	R^2
RP	2,064,429	−0.116	0.9948
EP6	1,593,675	−0.047	0.9924
EP7	2,001,704	−0.1154	0.981
EP8	2,145,359	−0.171	0.9828
EP9	45,761	0.312	0.9928

essentially pectic substances as revealed by high rate of arabinose and galacturonic acid in the solubilized fraction in the Ralet et al. study (Ralet et al., 1991).

The cell wall breakage could explain the surprising rheological behaviour of the SBP extruded grades observed with the power-law modelling (Table 4). Negative pseudo-plasticity indexes have only been reported in particular cases for starch (Willett, Millard, & Jasberg, 1997) and were attributed to starch degradation. In our study, the increase of shear rate in the capillary die during viscosity measurement of partially destructured SBP samples could induce cell wall breakage in a larger extent in the operating conditions used: 130 °C and 80% DM. During the analysis the disentanglement of the network was obtained not only by disruption of weak interactions but although of covalent bonds and that could be responsible for the negative pseudo-plasticity indexes calculated. For EP9, the destructuring process should then be complete as a normal thermoplastic behaviour is observed: $m = 0.312$ and $K = 45{,}761$.

3.4. Injection-molding of the plasticized SBP

Highly destructured SBP (EP9) got some suitable flowing properties to be formed by injection-molding. Rehydrated to a 20% moisture content, EP9 was effectively processed in a conventional injection-molding press with a 130 °C nose temperature and a 1500 kg cm^{-2} injection pressure. After reequilibration of its moisture content at 60% HR, the formed material was dense (1.4) and stiff (Table 5), like most starch-based materials (Rouilly & Rigal, 2002). Like all non-modified agro-materials, without the addition of an external plasticizer (i.e., glycerol) molded

Table 5
Properties of EP9 injection-molded samples

Property	Injected samples
Density (g cm^{-3})	1.40 ± 0.02
Bending modulus (GPa)	4.2 ± 0.2
Flexural strength (MPa)	34.6 ± 1.2
Young's Modulus (GPa)	2.0 ± 0.2
Tensile strength (MPa)	17.5 ± 1.8
Tensile strain (%)	1.1 ± 0.3

SBP was brittle: tensile strain around 1% for a tensile modulus of 2 GPa. And as EP9 had a water soluble content around 40% (Table 3), molded material were very hydrophilic and disintegrated when soaked in water.

4. Conclusion

In specific twin-screw extrusion conditions: two compression zones and with a liquid/solid ratio of 0.32, sugar beet pulp can be plasticized. Its cellular structure is destroyed and some of the cell-wall polysaccharides are shortened while avoiding thermal degradation. SBP becomes then thermoplastic and can be considered as a composite material made of a non-cellulosic cell-wall polysaccharides matrix filled with cellulose microfibres. Formed by injection-molding, the SBP based material is dense and stiff but brittle. Thus modified SBP constitutes a cheap alternative to thermoplastic starch.

References

Baar, A. G., Gebel, W., Imhof, U. & Mihalik, H. (1997) Process for producing mouldings with a barrier layer made of biodegradable material, and mouldings produced according to this process, WO 97/10293.

Bach Knudsen, K. E. (1997). Carbohydrate and lignin contents of plant materials used in animal feeding. *Animal Feed Science and Technology, 67*, 319–338.

Berghofer, E., Grzeskowiak, B., Mundlinger, N., Schleining, G., & Zenz, H. (1992). Biologisch abbaubares Verpackungs-und/oder Hüll-Material und Verfahren zu seiner Herstellung, EP 0,506,650.

Confédération Générale des planteurs de Betterave. (2000) La betterave en 2001.

Dinand, E., Chanzy, H., & Vignon, M. R. (1999). Suspensions of cellulose microfibrils from sugar beet pulp. *Food Hydrocolloids, 13*, 275–283.

Dinand, E., Chanzy, H., & Vignon, M. R. (1996). Parenchymal cell cellulose from sugar beet pulp: Preparation and properties. *Cellulose, 3*, 183–188.

Dronnet, V. M., Renard, C. M. G. C., Axelos, M. A. V., & Thibault, J.-F. (1997). Binding of divalent metal cations by sugar-beet pulp. *Carbohydrate Polymers, 34*, 73–82.

Fennema, O. R. (1996). Water and ice. In O. R. Fennema (Ed.), *Food chemistry* (pp. 17–95). Marcel Dekker Inc: NY-Basel.

Heux, L., Dinand, E., & Vignon, M. R. (1999). Structural aspects in ultrathin cellulose microfibrils followed by ^{13}C CP-MAS NMR. *Carbohydrate Polymers, 40*, 115–124.

ISO178 (2001). ISO Standard. Plastics – Determination of flexural properties.

ISO294 (1996). ISO Standard. Plastics – Injection-moulding of test specimens of thermoplastic materials.

ISO527-2 (1993). ISO Standard. Plastics – Determination of tensile properties – Part 2: Test conditions for moulding and extrusion plastics.

Mathew, S., & Abraham, T. (2004). Ferulic acid: An antioxidant found naturally in plant cell walls and feruloyl esterases involved in its release and their applications. *Critical Reviews in Biotechnology, 24*, 59–83.

Micard, V., Renard, C. M. G. C., & Thibault, J.-F. (1994). Studies on enzymic release of ferulic acid from sugar beet pulp. *Lebensmittel-Wissenschaft Und Technologie, 27*, 59–66.

Michel, F., Thibault, J.-F., & Barry, J. L. (1988). Preparation and characterisation of dietary fibre from sugar beet pulp. *Journal of The Science of Food and Agriculture, 42*, 77–85.

N'Diaye, S., & Rigal, L. (2000). Factors influencing the alkaline extraction of poplar hemicelluloses in a twin-screw reactor: Correlation with specific mechanical energy and residence time distribution of the liquid phase. *Bioresource Technology, 75*, 13–18.

Okojie, N. F., & Sargent, D. (1990). *Alkaline diffusion*. San Fransisco: Sugar Processing Research Conference, pp. 145–173.

Oosterveld, A., Pol, I. E., Beldman, G., & Voragen, A. G. J. (2001). Isolation of feruloylated arabinans and rhamnogalacturonanes from sugar beet pulp and their gel forming ability by oxidative cross-linking. *Carbohydrate Polymers, 44*, 9–17.

Pavier, C., & Gandini, A. (2000a). Oxypropylation of sugar beet pulp. 1. Optimisation of the reaction. *Industrial Crops and Products, 12*, 1–8.

Pavier, C., & Gandini, A. (2000b). Urethanes and polyurethanes from oxypropylated sugar beet pulp I. Kinetic study in solution. *European Polymer Journal, 36*, 1653–1658.

Ralet, M.-C., Thibault, J.-F., & DellaValle, G. (1991). Solubilization of sugar-beet pulp cell wall polysaccharides by extrusion-cooking. *Lebensmittel-Wissenschaft Und Technologie, 24*, 107–112.

Reddad, Z., Gerente, C., Andres, Y., Ralet, M.-C., Thibault, J.-F., & Le Cloirec, P. (2002). Ni(II) and Cu(II) binding properties of native and modified sugar beet pulp. *Carbohydrate Polymers, 49*, 23–31.

Rouilly, A., Orliac, O., Silvestre, F., & Rigal, L. (2001). DSC study on the thermal properties of sunflower proteins according to their water content. *Polymer, 42*, 10111–10117.

Rouilly, A., & Rigal, L. (2002). Agro-materials: A bibliographic review. *Journal of Macromolecular Science part C: Polymer Reviews, 42*, 441–479.

Sun, R. C., & Hughes, S. (1999). Fractional isolation and physico-chemical characterization of hemicelluloses and cellulose from sugar beet pulp. *Carbohydrate Polymers, 36*, 293–299.

Togrul, H., & Arslan, N. (2003). Production of carboxymethyl cellulose from sugar beet pulp, cellulose and rheological behaviour of carboxymethyl cellulose. *Carbohydrate Polymers, 54*, 73–82.

Turbaux, M. E. M. (1997) Composite ecological and recyclable material for moulding granules, FR 2,745,818.

Turquois, T., Rinaudo, M., Taravel, F. R., & Heyraud, A. (1999). Extraction of highly gelling pectic substances from sugar beet pulp and potato pulp: Influence of extrinsic parameters on their gelling properties. *Food Hydrocolloids, 13*, 255–262.

Willett, J. L., Millard, M. M., & Jasberg, B. K. (1997). Extrusion of waxy maize starch: Melt rheology and molecular weight degradation of amylopectin. *Polymer, 38*, 5983–5989.

Wong, E., & Bregola, M. (1997). Use of sugar beet pulp for making paper or cardboard, WO 97/30215.

Yoo, S. D., & Harcum, S. W. (1999). Xanthan gum production from waste sugar beet pulp. *Bioresource Technology, 70*, 105–109.