Available online at www.sciencedirect.com

ScienceDirect

Carbohydrate Polymers 66 (2006) 117–125

Carbohydrate Polymers

www.elsevier.com/locate/carbpol

Thermo-mechanical processing of sugar beet pulp. II. Thermal and rheological properties of thermoplastic SBP

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 22 February 2006; accepted 25 February 2006
Available online 17 April 2006

Abstract

Thermoplastic properties of extruded sugar beet pulp (SBP) are closely linked to water–polymer relationships. DSC analyses of water evaporation, water fusion and biopolymer relaxation according to SBP moisture content gave a more accurate estimation of SBP hydration steps than classical water adsorption isotherm. Three moisture contents (8%, 26%, 41% db) were then defined as limits of the different hydration behaviours. Melt viscosity measurements of SBP showed its shear thinning behaviour and the measured apparent viscosity is in the same range as thermoplastic starch viscosity. Using only water as plasticizer, to one temperature corresponded one moisture content to reach the optimal flowing properties: 110 °C/35%, 120°/25% and 130 °C/20%. This "plasticization" temperature has been estimated through DSC measurements of large amounts of moistened SBP in pressure-resistant pans. This new kind of DSC measurement revealed a new sample mass dependent second order transition between 140 and 180 °C, which temperature is linearly linked to the sample mass.

Keywords: Polysaccharide; Hydration; Plasticization; DSC

1. Introduction

The sugar beet pulp (SBP) is the by-product of the sugar extraction process. It consists mainly of polysaccharides from plant cell walls: arabinans and arabinoxylans hemicelluloses (Sun & Hughes, 1999), highly methylated and acetylated pectins (Oosterveld, Beldman, Schols, & Voragen, 2000) and cellulose microfibrils (Dinand, Chanzy, & Vignon, 1996). Due to such composition, SBP is therefore only used as a food complement to animal feed (Bach Knudsen, 1997). However, expensive drying process, low protein content and large amounts available have led to investigations to find some alternative uses for this material. Adding value to isolated compounds was considered first: alimentary fibres (Michel, Thibault, & Barry, 1988), cellulose microfibrils (Dinand, Chanzy, & Vignon, 1999), pectins (Oosterveld, Pol, Beldman, & Voragen, 2001; Turquois, Rinaudo, Taravel, & Heyraud, 1999) or ferulic acid (Micard, Renard, & Thibault, 1994). Raw pulp has as well been proposed as a cultivation substrate (Yoo & Harcum, 1999), for divalent cations complexation (Dronnet, Axelos, Renard, & Thibault, 1998), as a source of polyols for the production of urethanes and polyurethanes (Pavier & Gandini, 2000) as a source of fibre in biodegradable composites (Baar, Gebel, Imhof, & Mihalik, 1997; Turbaux, 1997) or for paper manufacture (Wong & Bregola, 1997). Development of SBP-based materials has been considered through the breakdown of the cell structure by chemical or enzymatic hydrolysis (Berghofer, Grzeskowiak, Mundlinger, Schleining, & Zenz, 1992) or by thermo-mechanical processing. In this previous study (Rouilly, Jorda, & Rigal, 2006), we have demonstrated that in specific conditions SBP can be processed by twin-screw extrusion, much like starch. While this process for starch involves the "melting" of granular structure, plasticization of SBP involves the non destructive breakdown of the

---

* Corresponding authors. Tel.: +33 5 62 88 57 25; fax: +33 5 62 88 57 30.
E-mail addresses: Antoine.Rouilly@ensiacet.fr (A. Rouilly), Luc.Rigal@ensiacet.fr (L. Rigal).

0144-8617/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.carbpol.2006.02.031

organized cell wall structure. SBP becomes then thermoplastic and could be described as a composite made of cellulose micro-fibrils embedded in a matrix constituted of hemicelluloses and pectins.

Biopolymers thermoplastic properties are not only linked to the increase of chains mobility with temperature increase but also to the presence of adsorbed water (Tomka & Sala, 1993). Water is a key factor of biopolymer stability, as it has been widely emphasized in food research (Slade & Levine, 1991). Moisture influences both crystalline and amorphous phases of the structure, and particularly, involves a large decrease of the glass transition temperature of the latter one, which has been intensively studied for almost all biopolymers (Di Gioia, 1998; Kelley, Rials, & Glasser, 1987; Morales & Kokini, 1997; Nicolls, Appleqvist, Davies, Ingman, & Lillford, 1995; Tomka, 1991).

Biopolymers water sorption is described by an isotherm (Fennema, 1996). Most of them have a sigmoid shaped isotherm combining the monolayer adsorption of the Langmuir model and the exponential behaviour of the Flory Huggis theory (Sala & Tomka, 1993). It is then possible to define three adsorption zones depending on the different water–biopolymer interactions (Fennema, 1996): the first one is linked to the monolayer formation in the BET model (Timmermann, Chirife, & Iglesias, 2001) corresponding to the hydration of ionic and highly polar groups, water is then considered a part of the solid. The second zone concerns the hydration of adsorbent free sites and the formation of further water molecules layers. In this zone, water is essentially retained by hydrogen bonds, and is then slightly mobile and non freezing. Addition of more water, in the last zone, involves glass transition of the amorphous chains. This freezing water can be physically retained in the structure or considered to be free water.

Unfortunately, obtaining satisfactory results from adsorption measurements with humidity controlled containers is fastidious and with new automatic devices the thermodynamic equilibrium is rarely reached at high humidity. But combining DSC analyses on the states transitions of the adsorbed water state and on water–biopolymer relationships, new hydration domains can be defined, as it is attempted in this paper. On the other hand, if these results allow a prediction of the influence of water content on physical–chemical properties of thermoplastic sugar beet pulp (TSBP), they are not sufficient to control a thermo-mechanical process. The effect of the mechanical compression on the adsorbed water, at temperatures above 100 °C, is never taken in account in glass transition measurements. Thus, we have developed a new kind of DSC analysis in pressure resistant pans to investigate the influence of sample mass, and by extrapolation of the sample bulk density, on a new thermal event; we believe to be linked to plasticization. It is then possible to predict transformation temperature of TSBP according to its water content and to its bulk density.

2. Materials and methods

2.1. Material

The sugar beet pulp (DM = 89.9%) originated at the Cagny site (France) was transformed following the previously defined twin-screw extrusion procedure (Rouilly et al., 2006). The salts used for sample conditioning were provided by Aldrich (St. Quentin Fallavier, France) and were of analytic purity.

2.2. Adsorption isotherms

Samples were dried for 15 days at 60 °C in a vacuum desiccator. They were then placed in some hermetic containers containing different saturated saline solutions which set the moisture level of the upper part of the container. Equilibrium was reached when sample mass does not vary more that 1% in 24 h. Their moisture content (MC) was obtained by drying at 105 °C during 24 h and expressed as percentage on a dry basis (db) (g water/100 g dry matter). The samples were then used for the DSC experiments.

Modelling of the isotherm was done according to the three-parameters Guggenheim–Anderson–de Boer (GAB) model, valid for a_w between 0.1 and 0.9 (Timmermann et al., 2001): $m = \frac{m_\mathrm{m} \cdot C \cdot K \cdot a_\mathrm{w}}{(1 - K \cdot a_\mathrm{w})[1 + (C-1) \cdot K \cdot a_\mathrm{w}]}$, where m is the equilibrium water content, m_m the monolayer moisture content, C the Guggenheim constant and K an energy constant correcting the properties of the multilayer molecules.

Curve modelling and derivation were obtained with Origin software (OriginLab System, Northampton, USA).

2.3. DSC analysis

This study was performed on a Pyris 1 power compensation calorimeter (Perkin Elmer) fitted with an Intracooler cooling system. The purge gas used was nitrogen of analytic quality at a flow rate of 20 ml/min. A temperature and energy calibration was carried out with indium ($T_\mathrm{f} = 156.6$ °C) and distilled water ($T_\mathrm{f} = 0$ °C) before the beginning of tests. DSC experiments to investigate relaxation were performed with 30 µl hermetic aluminum pans from 25 to 90 °C at 5 °C min^{-1}, water fusion analyses with hermetic stainless steel capsules from −60 to 60 °C at 10 °C min^{-1} and water evaporation analyses with 50 µl pin-hole aluminum pans from 30 to 180 °C at 10 °C min^{-1}. All these experiments were performed in triplicates.

Plasticization experiments were performed with hermetic 60 µl stainless steel capsules fitted out with 0-rings and resistant to an internal pressure of 40 bar (Perkin Elmer). They were carried out at a heating speed of 20 °C min^{-1} from 40 to 190 °C.

2.4. 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 1.8 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 and enable the direct calculation of the shear rate, the shear stress and the apparent viscosity (Willett, Jasberg, & Swanson, 1995). The TSBP and water, as appropriate, were mixed using Perrier 32.00 mixer (Montrouge, France). The mixture was then conditioned in an airtight container for 12 h at 25 °C, and tested for moisture content. The bulk density of the extrudates was measured and considered as constant at a value of 1.1 for the volume flow rate calculation. Viscosity (η) related to the shear rate (γ) was then modelled according to the power law: $\eta = K \cdot \gamma^{m-1}$, K being the consistency index and m the plasticity index (Vergnes & Villemaire, 1987).

3. Results and discussion

3.1. Hydration of TSBP

3.1.1. Adsorption isotherm

A sigmoid shaped isotherm tending to an infinite amount of water adsorbed in the presence of pure water was obtained for TSBP samples (Fig. 1). It demonstrated the presence of bound and unbound water and ensured no phase separation will occur during a thermo-mechanical process (Stepto, 2000). The GAB fitted very well SBP adsorption behaviour and corresponding coefficients were in the range of those of other biopolymers at the same temperature (Iglesias & Chirife, 1982). However m_m value 4.9% was low for polysaccharides and the C value 18.0 particularly high compared to results obtained with automatic apparatus (Roman-Gutierrez, Guilbert, & Cuq, 2002). But this kind of measurement is essentially used for comparative purposes (Micard, Belamri, Morel, & Guilbert, 2000; Tsiapouris & Linke, 2000) and does not give an accurate characterization of the hydration behaviour of biopolymers. The three different stages of water adsorption are defined in a generic way. By derivation of the modelled curve, it was only possible to detect the inflexion point, which should be the limit between the monolayer adsorption and the exponential Flory-Huggins and be close to the m_m value. For SBP samples, the water content corresponding to the inflexion was 5.6% and was slightly higher than the m_m value. In the high humidity region, the second derivative reached a maximum which should correspond to the glass transition of amorphous components of the sample at the analysis temperature (Fennema, 1996). The supplementary adsorbed water should then be freezing water and this value could mark the limit of the water bonding capacity of the material. But as from the fitting curve the value obtained was 36.3%, it was not enough to give a reasonable interpretation of the phenomenon. Some other experiments were necessary to characterize precisely the TSBP hydration properties.

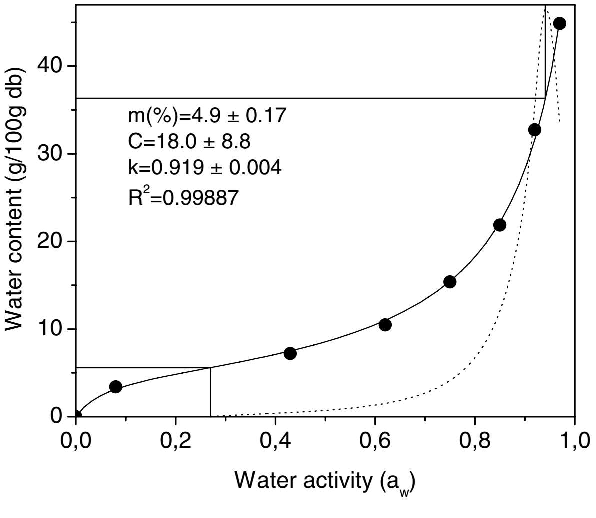

Fig. 1. TSBP water adsorption isotherm at 25 °C, its second derivative (dot lines) and the GAB modelling coefficients.

3.1.2. DSC analysis of SBP–water interactions

Three thermal events in low-moisture biopolymer systems are directly linked to water–biopolymer interactions: the fusion of the frozen “free” water, the evaporation of the adsorbed water and the relaxation phenomenon.

Relaxation is due to the stabilizing effect of water molecules on polysaccharides chains (Gidley, Cooke, & Ward-Smith, 1993). In the low humidity region, hydrogen polymer–polymer bonds stiffen the structure and their breakage involves an endothermic peak of relaxation. Relaxation is submitted to hysteresis (Takizawa & Nakata, 2000), has not only been observed on polysaccharides and its temperature stays constant with the moisture content of the samples: around 50 °C. On SBP analysis, the relaxation enthalpy increased to a maximum of 2.47 J/g of sample for a water content of 7.8% and decreased until peak complete disappearance for a water content exceeding 21.9% db. Its temperature was constant around 52 °C (Fig. 2).

According to our knowledge, the evolution of the vaporization enthalpy of the adsorbed water according to the adsorbent water content has never been reported. Experiments on TSBP samples showed a large increase of the enthalpy, in joules per grams of water, for moisture contents lower than 26–27% db. The low values, in the low humidity region, have been attributed to a short exposure time to heat, 8 min between 100 and 180 °C, while strong water–biopolymer interactions should have increase the enthalpy. Aguilera and colleagues proposed thus a value of 3.49 J/mg, instead of the classical value of 2.26 J/mg of pure water, for the vaporization of sorbed water (Aguilera, Cuadros, & Del Valle, 1998). After reaching a maximum of about 2.5 kJ/g of water, the enthalpy

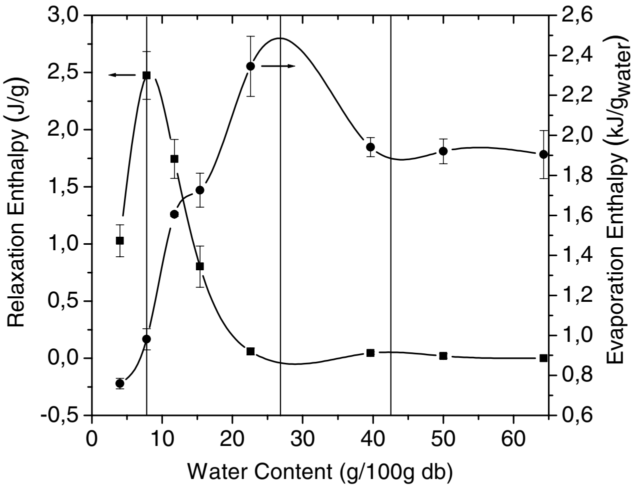

Fig. 2. Relaxation (■) and water evaporation (●) enthalpies of TSBP according to moisture content.

decreased to a plateau value around 1.9 kJ/g, for moisture contents higher than 40–42% db (Fig. 2).

For high moisture contents, a peak of freezing water fusion appeared around −5 °C. Even if integration of this peak should be taken carefully (Franks, 1991) as two types of crystallization may occur (Iijima, Nakamura, Hatakeyama, & Hatakeyama, 2000), by dividing the obtained value by 334 J/g (heat of fusion of pure water) and subtracting the result to the water content, the amount of non-freezing water for TSBP was 41.0 ± 3.4% db.

3.1.3. Water–SBP interactions according to water content

0–(≈)8%: the isotherm shape (Fig. 1) indicated clearly a stronger and quicker water adsorption in the low humidity region. This amount of water involves the strongest interactions, with ionic groups: galacturonic acid, ferulic acid, minerals (Franks, 1991), and the formation of a theoretical monolayer as it is expected from the GAB modelling ($m_m = 4.9\%$ db). But this theory does not take in account the organization of the polysaccharides under the stabilizing effect of water. New polymer–polymer hydrogen bonds appear in a particular configuration and maintain a structure of lower energy (Gidley et al., 1993) until a value of around 8% db is reached (Fig. 2). This value should be close to the inflexion of the adsorption isotherm (5.6%), pointing the hydration behaviour change, but was not.

8–(≈)26%: after reaching its maximum, the relaxation curve decreased until the complete disappearance of the peak. The sorption became faster and polymer–polymer interactions were replaced by water–polymer interactions. This amount of water hydrates all the polar groups in as much layers as it is possible and is linked by hydrogen bonds. The heat of evaporation increased and reached a maximum greater than the enthalpy of pure water. In this range, the water has a great influence on physical–chemical properties of biopolymers as it has a real plasticizing effect.

26–(≈)41%: the water was still non-freezing but the evaporation enthalpy decreased. Water should then be bonded to the material through other associations than secondary interactions with polar groups, involving hydration of non-polar groups or capillarity retained water (Damodaran, 1996). As the amount of apolar residues in SBP is really low, the second proposal seems more realistic.

>41%: water evaporation enthalpy was constant (Fig. 2) at a value lower than the enthalpy of pure water due to the contribution of bonded water. Bulk water accumulates in the material pores and follows polymer moves. This free water is then called sometimes hydrodynamic water. The vaporization enthalpy should then slightly increase in this range. In our conditions it stayed constant but the standard deviation of our measurements grew up with the water content. The maximum of the second derivative curve of the adsorption isotherm could correspond to this phenomenon and give a comparable result of 36.3% db (Fig. 1).

3.2. Melt rheology of TSBP

For food or material purposes, thermo-mechanical processing of biopolymers requires an increase of knowledge in melt rheology. Use of pre-shearing rheometer has permitted to develop rheological models for starch and although to point out all the important parameters (temperature, shear, water, plasticizer) as it is reported in the work of Martin, Averous, and Della Valle (2003). But studying the influence of water on biopolymer viscosity, without any other external plasticizer, restricts the experimental field. We have only been able to perform analyses at three different temperatures: 110, 120 and 130 °C for four moisture contents of approximately: 20, 25, 30 and 35% db (Fig. 3). In lower moisture conditions, self-induced heating under shear involved a large increase of the die temperature. And for high moisture content the TSBP was too sticky to ensure the feeding of the screw. That could have been predicted from the previous hydration characterization as above 35–40% the adsorbed water is "free". Best work conditions were so obtained for moisture contents around the limit value of 26% db.

For each temperature, increasing the moisture content involved an important decrease of the viscosity and a loss of regular flowing properties, reflected by a bad fitting to the power law (Table 1). This was due to water evaporation at the output of the rheological die. In regular conditions, TSBP was shear thinning and its viscosity was modelled with the power law. Obtained consistency K and pseudoplasticity m indexes were in the same range than those calculated for starch (Willett et al., 1995). m and K decreased when temperature or moisture content increased, as it is obvious for 20% db samples and at 110 °C, in good flowing conditions (Table 1).

But apart the interesting processing possibilities of TSBP for material applications, the rheological measurement pointed out another aspect of this kind of materials: the experimental window (temperature, MC) is very narrow. In fact, to one temperature corresponds one moisture content in the conditions used for this rheological

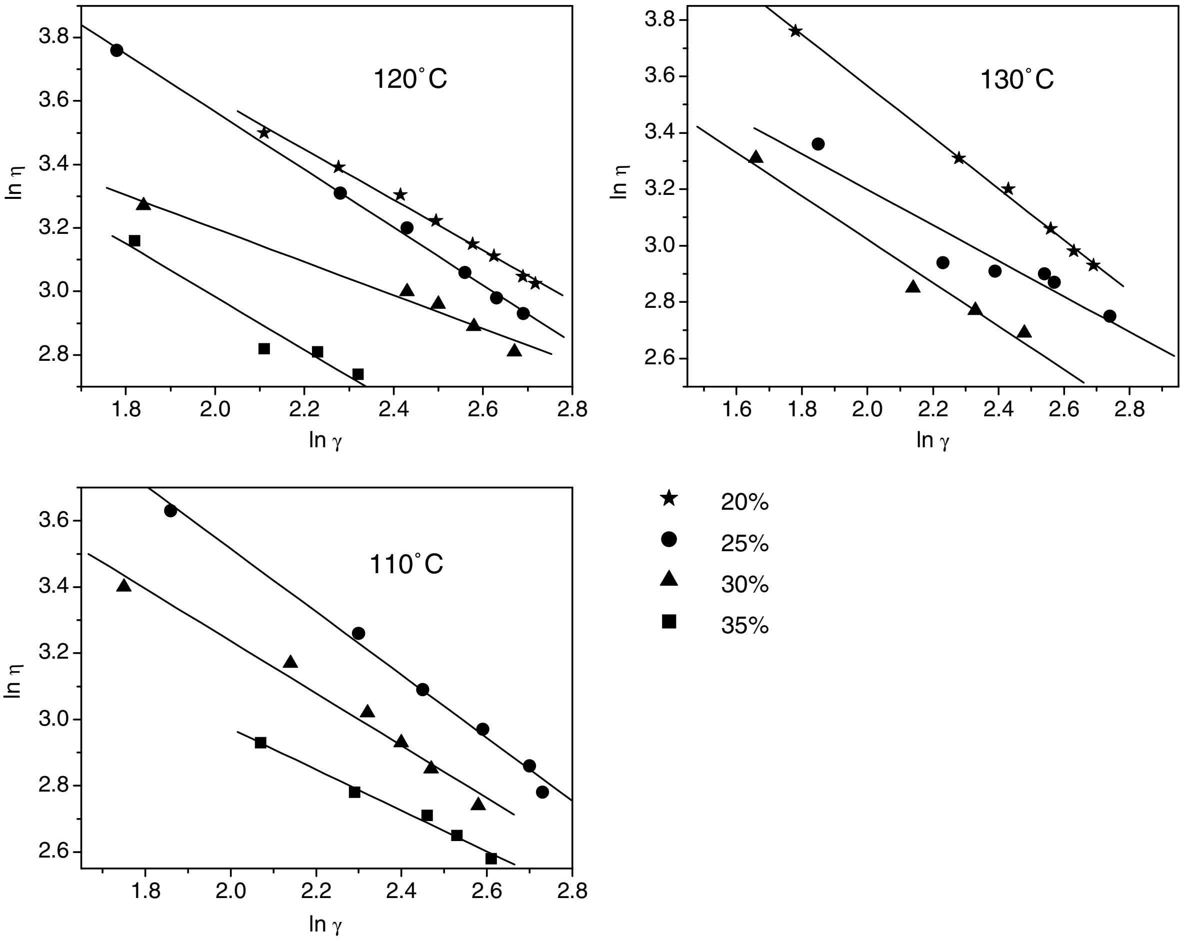

Fig. 3. Apparent viscosity (η) of TSBP according to shear rate (γ) at different moisture contents (% db) and temperatures.

Table 1
Power-law coefficients of the apparent melt viscosity of TSBP for increasing moisture contents and temperatures

Coefficient	Theoretical moisture content (%DM)			
	20	25	30	35
110 °C				
$MC_{measured}$ (% db)	–	24.8	30.6	32.3
Consistency *K* (Pa s)	–	262400 ± 65700	65000 ± 24000	16200 ± 3730
Power-law index *m*	–	0.05 ± 0.06	0.21 ± 0.06	0.38 ± 0.04
R^2	–	0.99659	0.98895	0.99359
120 °C				
$MC_{measured}$ (% db)	22.2	27.0	29.8	34.7
Consistency *K* (Pa s)	154880 ± 27088	243200 ± 28900	17782 ± 5340	45498 ± 49561
Power-law index *m*	0.204 ± 0.02	0.09 ± 0.02	0.474 ± 0.05	0.1625 ± 0.15
R^2	0.99659	0.99901	0.98826	0.96792
130 °C				
$MC_{measured}$ (% db)	22.5	27.8	32.8	–
Consistency *K* (Pa s)	45081 ± 3224	28773 ± 22990	36224 ± 20660	–
Power-law index *m*	0.297 ± 0.01	0.37 ± 0.4	0.232 ± 0.09	–
R^2	0.99921	0.94782	0.98646	–

measurement with a compression increasing the bulk density to about 1.1. For 110 °C, the corresponding moisture content would be close to 35% db (Table 1). The viscosity was the lowest with a good fitting. At 25% db, shear induced self heating involved an increase of the die temperature reaching 4 °C for high shear stress of about 400 s^{-1}. For 120 °C, for the same reasons it would be around 25% db and 20% db for 130 °C. This type of phenomenon has been observed for twin-screw extrusion of starch (Loercks et al., 2001) as well as for the extrusion of SBP (Rouilly et al., 2006). In the right combination of MC, temperature and pressure, polysaccharides materials undergo a transition step leading to a plastic appearance. During this stage, the material acquires interesting flowing properties and can be compressed to high density. Plasticization has found an analytical resonance only through starch granule "fusion" and never for amorphous polymers. Nevertheless DSC experiments in pressure resistant pans of TSBP samples revealed a new phenomenon at a temperature dependant from mass and moisture content of the sample and which could be linked to "plasticization".

3.3. DSC analysis of plasticization

3.3.1. DSC in pressure resistant pans

During any kind of thermo-mechanical process (extrusion, injection moulding, thermo-moulding), biopolymers are compressed in a constant volume. Evaporation of adsorbed water is hindered and biopolymers become plastic and flow. But compression can not be applied with classical thermal or thermo-mechanical analysis; all measurements are done in an open environment. In DSC for example, aluminium pans resist only at 2 bars (Aguilera et al., 1998) and are only used to avoid exchanges between the sample and the cell environment. In low moisture biopolymer system, only the events taking place at temperatures below 120 °C are monitored.

Stainless steel pressure resistant pans witherstand 40 bars (Perkin Elmer). New characterizations, in a narrow range of temperature because for the rubber O-ring, are then allowed: starch gelatinization (Stepto, 2000; Yu & Christie, 2001) or protein denaturation (Rouilly, Orliac, Silvestre, & Rigal, 2002) in low moisture conditions. In studying large amounts of amorphous biopolymer, a new event appears. It has been reported once as the exothermic peak of soy protein aggregation (Wang, Zhang, & Jane, 1996), but we think it is much more a second order transition.

3.3.2. A phenomenon linked to mass and MC of samples

The study of the DSC thermograms (Fig. 4) of large amounts (between 20 and 50 mg) of moistened TSBP samples, in pressure resistant pans, led to several remarks. First, the relaxation peak appeared at higher temperatures, almost 60 °C. This has been attributed to the higher heating rate applied for the use of these pans: 20 °C/min. Secondly, DSC thermograms of small amounts of sample were convex, as it has already been observed on gelatine analysis (Apostolov, Fakirov, Vassileva, Patil, & Mark, 1999). And finally for temperatures higher than 180 °C exothermic degradation seemed to take place as some air is trapped in the pan with the sample. The secondary transition was really obvious for high sample mass and high moisture content, but for small mass it was hard to detect and could be integrated as an exothermic event as well as an endothermic peak around 180 °C. The temperature of this baseline shift, the plasticization temperature (T_p), increased from 140 °C, for a moisture content of 44.9% db, to 175.9 °C, for 3.4%. And for a same moisture content, the temperature could drop from about 13 °C when the sample mass increased (Table 2). ΔC_p increased from 0.012 to 0.495 J/g °C with the rise up of the sample moisture content and was largely dependent of the sample mass too. These values of ΔC_p were in the same range than those calculated for glass transition of dry starch or proteins.

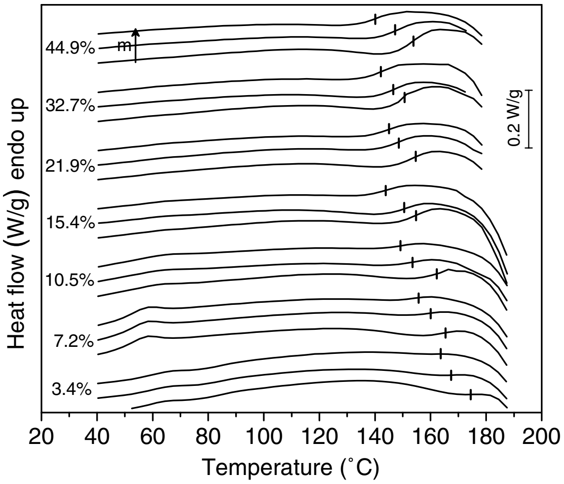

Fig. 4. DSC curves in pressure resistant pans of increasing mass of TSBP samples at different moisture contents (% db).

The influence of the sample mass on T_p could be interpreted as the broadening of this thermal event due to a decrease in the resolution (Yu & Christie, 2001), but not its influence on ΔC_p values (all the presented thermograms are normalized). The effect of the sample mass could then be related to the internal pressure inside the pan. Vapour pressure is unfortunately not linked to the sample mass and air compression inside the pan does not depend from the volume. We assumed so that internal pressure was close from the water vapour pressure, and it was in all cases higher than the admissible pressure for aluminium pans.

A plot of the plasticization temperature according to the TSBP moisture content, as it is done for glass transition, was impossible with this phenomenon. But for one moisture content, the relation between T_p and the mass was linear (Fig. 5). In a first approach, all the lines seemed parallel except the one for the highest moisture content. Looking at the calculated coefficients this difference became obvious: the intercept increased for a MC of 44.9% while it was always decreasing with the moisture content increase (Table 3). This could then be attributed to the appearance of freezing water. But more than another study of water–biopolymer relationships through the influence of water content on the two parameters of this regression, the linear relation allowed an extrapolation of the results. As it is impossible to fill the 60 µl volume of the pans with more than 50 mg (particularly with high moisture samples), while during thermo-mechanical processing TSBP bulk density reaches 1.1–1.2, the calculation of T_p for higher amounts provided some interesting data. It was then possible to plot

Table 2
Plasticization temperature, corresponding ΔC_p, and water vapour pressure at this temperature according to TSBP samples mass and moisture contents in pressure resistant pans

MC (% db)	Sample mass (mg)	T_p (°C)	WVP (bars)	ΔC_p (J/g °C)
3.4	25.55	175.9	9.1	0.066
	42.08	168.4	7.5	0.012
	48.57	162.5	6.6	0.012
7.2	30.27	164.2	6.8	0.096
	39.45	159.0	6.0	0.078
	50.76	153.5	5.2	0.066
10.5	27.02	160.2	6.2	0.159
	42.38	152.9	5.1	0.117
	51.98	148.5	4.6	0.100
15.4	25.16	154.1	5.3	0.272
	30.42	150.7	4.9	0.243
	43.53	143.7	4.0	0.211
21.9	24.6	152.2	5.0	0.317
	29.5	147.8	4.5	0.292
	37.5	144.4	4.1	0.267
32.7	21.25	150.9	4.9	0.448
	27.92	146.4	4.3	0.367
	34.08	142.1	3.8	0.321
44.9	18.59	153.4	5.2	0.495
	25.19	148.0	4.5	0.350
	34.42	140	3.6	0.265

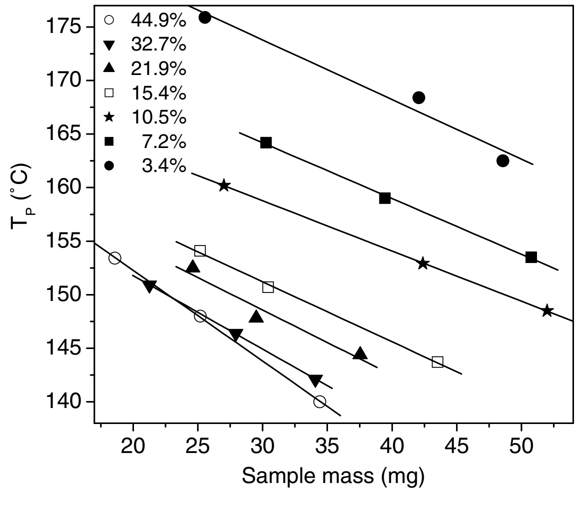

Fig. 5. Plot of the plasticization temperature of TBSP according to sample mass at different moisture contents (% db).

Table 3
Linear regression of the plot of plasticization temperature according to sample mass in the pressure resistant pan for different moisture contents

MC (%DM)	A (°C)	B (°C/mg)	R^2
3.4	190.5 ± 4.0	-0.56 ± 0.1	0.98423
7.2	179.8 ± 0.4	-0.52 ± 0.02	0.99904
10.5	172.8 ± 0.2	-0.469 ± 0.004	0.99995
15.4	168.0 ± 0.8	-0.56 ± 0.02	0.999
21.9	166.7 ± 4.4	-0.61 ± 0.1	0.9735
32.7	165.5 ± 0.2	-0.686 ± 0.001	0.99995
44.9	169.2 ± 0.4	-0.85 ± 0.01	0.99987

A is the intercept and B is the slope.

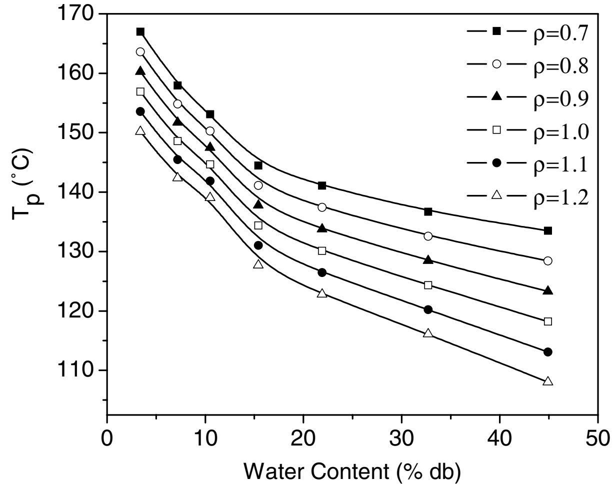

Fig. 6. Plot of the plasticization temperature of TBSP according to moisture content for an increasing bulk density (ρ).

T_p according to the water content for different bulk densities (Fig. 6). For $\rho = 1.2$, T_p decreased from 150 to about 110 °C in the humidity range studied, while for $\rho = 0.7$ it decreased from 170 to 133 °C. Low densities are unrealistic during thermo-mechanical processes, because pseudo hermetical conditions are reached through compression, but for the high values, the calculated plasticization temperature was in the range of the classical processing temperatures. It matched with the twin-screw extrusion conditions (Rouilly et al., 2006) and with the temperatures highlighted during rheological measurements. For a bulk density of 1.1, at 35% db, T_p would be around 118 °C, for 25%, around 124 °C and for 20% around 128 °C, while we previously found, respectively, 110, 120 and 130 °C.

4. Discussion

A new thermal event is revealed on these experiments in hermetical conditions. It is a second order transition whose baseline shift could be linked to polymer chains mobility to a change in the material heat capacity.

This plasticization temperature depends from the moisture content of the sample but also, as the phenomenon is not observed for small amounts of sample, of the internal pressure in the capsule. Determination of a plasticization pressure, corresponding to a moisture content, is unfortunately impossible. An equilibrium establishes itself between the water vapour in the pan free volume and the adsorbed water, depending on the temperature. When a specific pressure is reached, the supplementary heat could involve the excitement of the water molecules in the biopolymer network (plasticization temperatures are always above 100 °C) and then the movement, in a large scale, of these chains. This excitement could be responsible for the baseline shift.

Increasing the sample weight decreases the pan free volume, it is then saturated with water vapour faster and when plasticization occurs the sample is more hydrated. This could explain the decrease of T_p and ΔC_p when the sample mass increases, the more the chains are "solvated" or "plasticized" by the water molecules the more they are mobile.

This phenomenon could be then involved by a large scaled chains movement under water molecules excitement. This is consistent with the great changes (flowing, compressibility, aspect) observed in conditions of plasticization during twin-screw extrusion or any other thermo-mechanical process of thermoplastic sugar beet pulp.

5. Conclusion

Thermo-mechanical processing of biopolymers is closely linked to water–biopolymer relationships. Comparative analyses are easily obtained through classical water adsorption isotherms. But trying to separate the different kinds of water–biopolymer interactions, DSC analyses are more accurate. Studying three different events: water evaporation, relaxation and water fusion, four steps of the hydration of thermoplastic sugar beet pulp (TBSP) have been defined. The humidity range for thermo-mechanical processing was then well defined, as confirmed with melt viscosity measurements. TBSP, complex material composed manly of hemicelluloses, pectins and parietal cellulose, has the same rheological behaviour as starch.

But it was not enough to explain and understand the key phenomenon of these processes: "plasticization". We attempted to study the thermal properties of TSBP in hermetical conditions as close as possible from those obtained during thermo-mechanical processes, using large amounts of samples. A special event, we have integrated as a baseline shift, appeared between 140 and 180 °C. Its temperature and magnitude decreased when samples mass increased and samples moisture content decreased. As the temperature of this second order transition was linked linearly to the sample mass, extrapolation of the results to higher mass was then possible, approaching real thermo-mechanical conditions. The results give a good estimation of the processing temperatures observed during twin-screw extrusion and rheological measurements. This shift has so been assigned to a large-scaled movement of the biopolymer chains under water molecules excitement which could be responsible for plasticization. This study needs obviously further investigations, on other thermoplastics biopolymers, on the DSC measurement, on the thermograms analysis, on the extrapolation method, but could be promising for the understanding of biopolymers thermo-mechanical processing.

References

Aguilera, J. M., Cuadros, T. R., & Del Valle, J. M. (1998). Differential scanning calorimetry of low-moisture apple products. *Carbohydrate Polymers, 37*, 79–86.

Apostolov, A. A., Fakirov, S., Vassileva, E., Patil, R. D., & Mark, J. E. (1999). DSC and TGA studies of the behavior of water in native and crosslinked gelatin. *Journal of Applied Polymer Science, 71*, 465–470.

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.

Damodaran, S. (1996). Food proteins: An overview. In S. D. A. Paraf (Ed.), *Food proteins and their applications* (pp. 1–24). NY-Basel: Marcel Dekker.

Di Gioia, L. (1998). Effect of hydrophilic plasticizers on thermo-mechanical properties of corn gluten meal. *Cereal Chemistry, 75*(4), 514–519.

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

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

Dronnet, V. M., Axelos, M. A. V., Renard, C. M. G. C., & Thibault, J.-F. (1998). Improvement of the binding capacity of metal cations by sugar-beet pulp. 1. Impact of cross-linking treatments on composition, hydration and binding properties. *Carbohydrate Polymers, 35*, 29–37.

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

Franks, F. (1991). Hydration phenomena: An update and implications for the food processing industry. In H. Levine & L. Slade (Eds.), *Water relationship in food* (pp. 1–20). New York: Plenum Press.

Gidley, M. J., Cooke, D., & Ward-Smith, S. (1993). Low moisture polysaccharide system: Thermal and spectroscopic aspects. In J. M. V. Blanshard & P. J. Lillford (Eds.), *The glassy state in foods* (pp. 303–316). Nottingham University Press.

Iglesias, H. A., & Chirife, J. (1982). *Handbook of food isotherms: Water sorption parameters for food and food components*. New York: Academic Press.

Iijima, M., Nakamura, K., Hatakeyama, T., & Hatakeyama, H. (2000). Phase transition of pectin with sorbed water. *Carbohydrate Polymers, 41*, 101–106.

Kelley, S. S., Rials, T. G., & Glasser, W. G. (1987). Relaxation behaviour of the amorphous components of wood. *Journal of Material Science, 22*, 617–624.

Loercks, J., Pommeranz, W., Schmidt, H., Timmermann, R., Grigat, E., & Schulz-Schlitte, W. (2001). Thermoplastic starch utilizing a biodegradable polymer as melting aid. US 6, 235,815.

Martin, O., Averous, L., & Della Valle, G. (2003). In-line determination of plasticized wheat starch viscoelastic behavior: Impact of processing. *Carbohydrate Polymers, 53*, 169–182.

Micard, V., Belamri, R., Morel, M. H., & Guilbert, S. (2000). Properties of chemically and physically treated wheat gluten. *Journal of Agricultural Food Chemistry, 48*, 2948–2953.

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.

Morales, A., & Kokini, J. L. (1997). Glass transition of soy globulins using differential scanning calorimetry and mechanical spectroscopy. *Biotechnol. Prog., 13*, 624–629.

Nicolls, R. J., Appleqvist, I. A. M., Davies, A. P., Ingman, S. J., & Lillford, P. J. (1995). Glass transitions and fracture behaviour of gluten and starches within the glassy state. *Journal of Cereal Science, 21*, 25–36.

Oosterveld, A., Beldman, G., Schols, H. A., & Voragen, A. G. J. (2000). Characterization of arabinose and ferulic acid rich pectic polysaccharides and hemicelluloses from sugar beet pulp. *Carbohydrate Research, 328*, 185–197.

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. (2000). Oxypropylation of sugar beet pulp. 1. Optimisation of the reaction. *Industrial Crops and Products, 12*, 1–8.

Roman-Gutierrez, A. D., Guilbert, S., & Cuq, B. (2002). Distribution of water between wheat flour components: A dynamic water vapour adsorption study. *Journal of Cereal Science, 2002*, 247–355.

Rouilly, A., Orliac, O., Silvestre, F., & Rigal, L. (2002). Thermal denaturation of sunflower globulins in low moisture conditions. *Thermochimica Acta, 71080*, 1–7.

Rouilly, A., Jorda, J., & Rigal, L. (2006). Thermo-mechanical processing of sugar beet pulp. I. Twin-screw extrusion process. Carbohydrate Polymers, in press.

Sala, R., & Tomka, I. (1993). Water uptake in partially frozen and plasticized starch. In J. M. V. Blanshard & P. J. Lillford (Eds.), *The glassy state in foods* (pp. 483–489). Nottingham University Press.

Slade, L., & Levine, H. (1991). Beyond water activity: Recent advances based on an alternative approach to the assessment of food quality and safety. *Critical Reviews in Food Science and Nutrition, 30*(2–3), 115–360.

Stepto, R. F. T. (2000). Thermoplastic starch. *Macromolecules Symposium, 152*, 73–82.

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

Takizawa, T., & Nakata, Y. (2000). New small endothermic peaks with hysteresis commonly observed in differential scanning calorimetric study of biopolymer–water systems. *Thermochimica Acta, 352-353*, 223–231.

Timmermann, E. O., Chirife, J., & Iglesias, H. A. (2001). Water sorption isotherms of foods and foostuffs: BET or GAB parameters? *Journal of Food Engineering, 48*, 19–31.

Tomka, I. (1991). Thermoplastic starch. In H. Levine & L. Slade (Eds.), *Water relationships in food* (pp. 627–637). New York: Plenum Press.

Tomka, I., & Sala, R. (1993). On the equation of state of thermoplastic starch. In J. M. V. Blanshard & P. J. Lillford (Eds.), *The glassy state in foods* (pp. 475–482). Nottigham University Press.

Tsiapouris, A., & Linke, L. (2000). Water vapor sorption determination of starch based porous packaging material. *Starch/Stärke, 52*(2–3), 53–57.

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.

Vergnes, B., & Villemaire, J. P. (1987). Rheological behaviour of low moisture molten maize starch. *Rheologica Acta, 26*, 570–576.

Wang, S., Zhang, S., & Jane, J.-L. (1996). Effects of polyhydric alcohols on mechanical properties of soy protein plastics. *Journal of Macromolecular Science – Pure Applied Chemistry, AA33*, 557–569.

Willett, J. L., Jasberg, B. K., & Swanson, C. L. (1995). Rheology of thermoplastic starch: Effects of temperature, moisture content and additives on melt viscosity. *Polymer Engineering and Science, 35*(2), 202–210.

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.

Yu, L., & Christie, G. (2001). Measurement of starch thermal transitions using differential scanning calorimetry. *Carbohydrate Polymers, 46*, 179–184.