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The effect of thermomechanical treatment on starch breakdown and the consequences for process design

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Abstract

Macromolecular degradation of starch by heating and shear forces was investigated using a newly developed shear cell. With this equipment, waxy corn starch was subjected to a variety of heat and shear treatments in order to find the key parameter determining the degree of macromolecular degradation. A model based on the maximal shear stress during the treatment gave an improved prediction compared to existing models in literature based on specific mechanical energy input (SME) or shear stress multiplied by time ($\tau \cdot t$). It was concluded that molecular weight reduction of starch at the temperatures investigated (85–110 °C) is a time-independent process, during which the starch molecules are broken down virtually instantaneously by high shear force within time scales investigated. Consequences for design of shear based processes (especially extrusion) are shortly discussed.

Keywords: Starch; Molecular weight reduction; Shear; Melting; Extrusion; Intrinsic viscosity

1. Introduction

Starch is an ingredient that determines product properties, such as cohesiveness, water solubility and cold paste viscosity of many food products. Previous studies have shown that the molecular weight of the starch is an important property in this respect (Bindzus, Fayard, van Lengerich, & Meuser, 2002; Bruemmer, Meuser, van Lengerich, & Niemann, 2002).

Production of starch based products often comprises a combination of shear and thermal treatment, for example in extrusion processes. It is well known that the combination of shear and thermal treatment leads to molecular breakdown, but the exact cause and control of this effect are still matters of uncertainties. This is partly due to the fact that the shear rates, shear stresses and temperatures are rather inhomogeneous in most process equipment and therefore difficult to control. Nevertheless, the use of extrusion trials led to development of empirical models describing the relation between molecular weight and process parameters. Parker, Ollett, and Smith (1990) concluded that molecular breakdown relates to the specific mechanical energy (SME) input during extrusion, defined as the capacity transferred by the screws per unit of mass or volume (Meuser, van Lengerich, & Reimers, 1984). Diosady, Paton, Rosen, Rubin, and Athanassoulias (1985) obtained a first-order correlation between the molecular weight reduction and shear stress multiplied by time ($\tau \cdot t$), thereby suggesting time–shear equivalence in molecular breakdown of starch.

Some authors presented a different approach by using equipment with more defined shear and temperature gradients. Vergnes, Villemaire, Colonna, and Tayeb (1987) carried out an important study, describing the effect of well-defined shear and temperature on macromolecular degradation. They used a self-built rheometer with pre-shearing to simulate extrusion cooking and concluded that mechanical energy input during

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Nomenclature

C_1	first fit parameter in first-order model (−)
C_{1a}	first fit parameter in first-order SME model (−)
C_{1b}	first fit parameter in first-order $\tau{\cdot}t$ model (−)
C_{1c}	first fit parameter in first-order $\tau_{\max}$ model (−)
C_{2a}	second fit parameter in first-order SME model (m^3/J)
C_{2b}	second fit parameter in first-order $\tau{\cdot}t$ model ($m^2/(N\ s)$)
C_{2c}	second fit parameter in first-order $\tau_{\max}$ model (m^2/N)
f	fraction of non-crystalline material (−)
H	height of the cone (m)
MW	molecular weight (Da)
n	number of experiments (−)
p	number of parameters (−)
R	radius of the cone at the top of the shearing zone (m)
RSS	residual sum of squares (−)
s	standard deviation
SME	specific mechanical energy (J/m^3)
SME_{SC}	specific mechanical energy as calculated for the new shearing device (J/m^3)
t	time (s)
V	volume (m^3)
X	relative intrinsic viscosity of the non-crystalline fraction of the treated starch compared to native starch (−)
Greek symbols	
γ	shear rate (s^{-1})
$[\eta]$	intrinsic viscosity (ml/g)
$[\eta]_i$	intrinsic viscosity of the non-crystalline starch fraction (ml/g)
$[\eta]_{rs}$	intrinsic viscosity of the crystalline starch fraction (equals intrinsic viscosity of native starch) (ml/g)
θ	angle of the shear zone of the newly developed shearing device (°)
τ	shear stress (N/m^2)
$\tau_{\max}$	maximal shear stress (N/m^2)

the treatment determined macromolecular degradation of the starch. Igura, Hayakawa, and Fujio (1997) used a flow tester equipped with a capillary tube to show qualitatively the impact of heating at 150 °C and shearing on macromolecular degradation of various starches. They showed that longer time heating gave the same degree of degradation as a shorter time heating–shearing treatment, suggesting an equivalence of shear and heating time at this temperature.

Grandbois, Beyer, Rief, Clausen-Schaumann, and Gaub (1999) and Beyer (2000) presented a fundamental approach. They investigated the molecular strength of the glucosidic bonds, and the effect of extensionally applied forces on these bonds using atomic force microscopy. One of their conclusions was that breakdown of a covalent bond in an amylose molecule takes place almost instantaneously in case the force applied exceeds the bond strength. If their outcome is applied to an extrusion process of a starch-containing product, it implies a dependency of the molecular weight reduction on the maximal force during the treatment, rather than on treatment time. This seems to be in contradiction with the empirical studies described above.

The aim of this study was therefore to investigate which fundamental process parameter determines starch macromolecular degradation during a heating–shearing treatment. For this purpose, a new device was developed, which enabled the separation of the effects of shear force, shear rate, time and temperature. Experimental data of this device were used to find the key parameter to starch molecular weight reduction. The outcome of the key parameter study was used to explain the pattern of starch molecular weight reduction during extrusion cooking.

2. Theory

2.1. Measurement and quantification of starch degradation

Shear forces are known to induce endodegradation of the high molecular weight compounds in starch (Baud, Colonna, Valle, & Roger, 1999; Davidson, Paton, Diosady, & Larocque, 1984). The intrinsic viscosity $[\eta]$ is especially sensitive to this type of degradation, even if the actual molecular weight reduction is limited and difficult to measure by chromatographic methods. Furthermore, a good correlation was found between the molecular weight of corn amylopectin as measured by chromatography in combination with laser light scattering and the intrinsic viscosity (Millard, Dintzis, Willett, & Klavons, 1997), suggesting that $[\eta] \sim \mathrm{MW}^{0.29}$. Therefore, the intrinsic viscosity can be used as a measure for the molecular weight.

Some studies suggest that the crystalline part of the starch is not susceptible to a mechanical treatment. According to these investigations, only the non-crystalline parts can be degraded. As a result of this, the intrinsic viscosity needs to be corrected. Diosady et al. (1985) suggested the following correction

$$X = \frac{[\eta]_i}{[\eta]_{rs}} \tag{1}$$

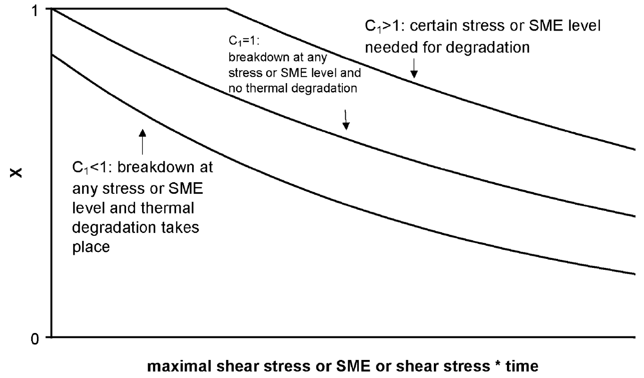

Fig. 1. Effect of the value of parameter C_1 on the models described in Section 2.

$$[\eta]_\mathrm{i} = \frac{[\eta] - (1-f)[\eta]_\mathrm{rs}}{f} \tag{2}$$

where f denotes the fraction crystalline starch; $[\eta]$ and $[\eta]_\mathrm{rs}$ denote the intrinsic viscosity of the treated and of the native starch, respectively. X represents the relative intrinsic viscosity ($0 < X < 1$) and can be used as a measure for starch degradation. $X = 1$ denotes that starch was not degraded.

2.2. Modeling and key parameter study

Models relating the decrease in intrinsic viscosity and process parameters were developed by Parker et al. (1990) and Diosady et al. (1985). Parker and co-workers related the intrinsic viscosity to the specific mechanical energy during extrusion. Diosady and co-workers related the intrinsic viscosity to the product of shear stress and time. Their models can be written as

$$X = C_{1a}\exp(-C_{2a}\cdot \mathrm{SME}) \tag{3}$$

and

$$X = C_{1b}\exp(-C_{2b}\cdot \tau t) \tag{4}$$

respectively, where SME denotes the specific mechanical energy, τt denotes the product of shear stress and time and C_{1a} and C_{1b} are constants. Parker and co-workers did not include the melt correction described in Section 2.1, which means that they assumed that $f = 1$.

Contrary to these studies, the fundamental investigations of Beyer (2000) and Grandbois et al. (1999) suggest the maximal shear stress to be the key parameter. In analogy with the models described above, the following correlation can be derived:

$$X = C_{1c}\exp(-C_{2c}\cdot \tau_\mathrm{max}) \tag{5}$$

The value of the constant C_{1a}, C_{1b} or C_{1c} depends on whether or not thermal breakdown takes place and on whether or not native starch can handle a certain shear stress or mechanical energy input before breaking down (Fig. 1). If thermal breakdown takes place, the value is expected to be lower than 1. If no thermal breakdown takes place and the native starch can handle a certain shear stress or mechanical energy input before breaking down, the constant is higher than 1. In this case, $X = 1$ if the stress or mechanical energy input level is lower than minimally required for breakdown (Fig. 1). If the native starch breaks down at any shear stress or mechanical energy level but no thermal breakdown takes place, the constant is equal to 1.

The use of the shear cell described below allowed us to compare the different models and thus to find the key parameter to starch degradation.

3. Materials and methods

3.1. Starch and water

Waxy corn starch was used in all experiments. Intrinsic viscosity and percentage of crystalline material of the native starch are given in Table 1. Before processing, starch was pre-mixed with water to a moisture content of 30% (w water/w total). Experiments were carried out 1 day after

Table 1
Treatment conditions and results for a mixture of waxy corn starch and 30% water processed in the shear cell

Exp. no.	Rotation speed (rpm)	T (°C)	t (s)	τ_max (10^4 Pa)	$\tau\cdot t$ (10^6 Pa s)	SME (10^9 J/m^3)	% crystalline	$[\eta]$ (ml/g)
Native	–	–	–	–	–	–	26.0	165
1	10	110	900	0.74	1.66	0.96	13.5	126
2	35	110	900	1.29	1.32	1.33	14.8	114
3	75	110	750	1.31	4.59	11.20	11.2	97
4	35	100	900	1.17	1.60	2.12	17.2	128
5	35	100	900	1.25	1.41	2.21	17.2	113
6	75	100	1200	1.97	3.67	10.50	11.2	81
7	75	100	900	2.60	2.07	7.29	14.6	82
8	75	85	960	2.46	3.53	9.66	15.3	89
9	75	85	1200	2.63	5.80	24.10	12.5	80
10	75	85	960	3.05	4.48	20.20	12.2	71

Exp. no.: experiment number; T : temperature; t : treatment time; τ_max : maximal shear stress during the measurement; $\tau\cdot t$: shear stress multiplied by time; SME: specific mechanical energy; % crystalline: percentage of A-type crystals as measured by X-Ray diffraction; $[\eta]$: intrinsic viscosity.

pre-mixing in order to allow equilibrium of water over the starch.

3.2. Heating–shearing treatment in the shear cell

The starch–water mixture was thermomechanically treated in a newly developed shearing device. This new device was based on a cone and plate rheometer concept. It was designed and sized at pilot scale. Thickness of the product layer was kept small compared to the diameter of the cone, in order to apply the desired shear rates at relatively low rotation speeds, thereby avoiding circular flow and guarantee ideal flow conditions. The engine was chosen in such a way that shearing stresses up to 4×10^4 Pa, comparable to extrusion processes, were possible.

The shearing device and its dimensions are shown in Fig. 2. After the shearing zone (1) was filled, the starch–water mixture was heated by the electrical heating elements (2) in the cone and sheared between the rotating plate (3) and the non-rotating cone (4). A thermocouple (5) monitored the sample temperature. As soon as the temperature set point was reached, the engine was started. During the treatment of sample 1, rotation speed was kept constant at 10 rpm, corresponding to a shear rate of 24 s^{-1}. During the treatment of samples 2, 4 and 5, a rotation speed of 35 rpm was applied. To avoid slip and inhomogeneous samples, the rotation speed was obtained in the following steps: the rotation speed was first set at 10 rpm for 300 s, and then at 35 rpm until the end of the run. During the treatment of samples 3 and 6–10, a rotation speed of 75 rpm was applied, again obtained in steps: the rotation speed was first at 10 rpm for 300 s, then at 35 rpm for 250 s, then at 50 rpm for 110 s and finally at 75 rpm until the end of the run. The use of different rotation speed combinations made it possible to change the shear stress and mechanical energy input. Sample size was 130 g in all experiments. Times and temperatures are shown in Table 1.

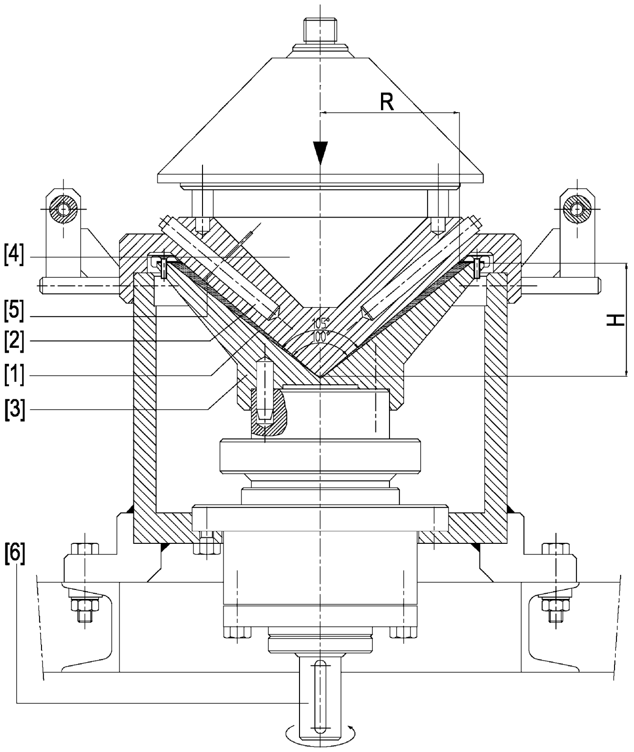

Fig. 2. A newly developed shear cell for applying well-defined shear and temperature to low moistened starch. Cone angle = 100°, shear zone angle $\theta = 2.5°$, $R = 0.1$ m, $H = 0.082$ m.

Shear stress during the treatment was determined by measuring the torque (6). The specific mechanical energy input during the treatment in the shear cell ($\mathrm{SME_{SC}}$) was calculated according to (based on Vergnes et al., 1987):

$$\mathrm{SME_{SC}} = \frac{\int_0^t \mathrm{torque}\cdot\gamma\cdot \mathrm{d}t}{V} \tag{6}$$

Also shear stress (τ) and shear stress multiplied by time ($\tau\cdot t$) were calculated from the torque measurements.

After the thermomechanical treatment, the shear cell was opened and the heated–sheared sample was directly frozen. Prior to further analysis, samples were dried in an oven at 130 °C to 10% water content. After drying, the samples were immersed in liquid nitrogen and ground to pass a 366 μm sieve.

3.3. Analysis

Intrinsic viscosity $[\eta]$ of the samples was measured at 25 °C with an Ubbelohde viscometer (Fujio, Igura, & Hayakawa, 1995). Starch was dissolved in 1 M KOH for 45 min and six concentrations in the range of 0.5–2 mg/ml were used (solvent flow time = 332 s). Values of the intrinsic viscosity measurement could be reproduced within a range of 5%.

Crystallite type of the starch and percentage of crystalline material was determined using a Philips PC-APD PW 3710 powder X-Ray diffractometer.

3.4. Mathematical comparison of models

In order to find the key parameter to starch degradation, the models described in Section 2 were fitted to the data. In order to find the best model and thus the key parameter for starch degradation, two methods were used. As a first indication, the R^2 values were compared. Secondly, the Akaike information criterion was used (Akaike, 1973):

$$\mathrm{AIC} = n\ln(s^2) + 2p + \frac{2p(p+1)}{n-p-1} \tag{7}$$

$$s^2 = \frac{\mathrm{RSS}}{n} \tag{8}$$

The criterion states that if two models are compared, model 2 is considered to give a better fit than model 1 if $\mathrm{AIC}_1 - \mathrm{AIC}_2 > 5$.

Furthermore, the intercepts of the fits can be considered physically correct only if they are equal to or higher than 1 (Section 2). Therefore, also the fitted values of the intercept were used to compare the models.

4. Results and discussion

4.1. Paste formation and melting

In all experiments, a melt with small powdery fractions was obtained, comparable to the results of Barron, Buleon, Colonna, and Valle (2000) on heating–shearing treatment of pea starch below the melting temperature. X-Ray diffraction measurements showed that indeed part of the material was not molten (Table 1) and that all samples displayed A-type crystals, the same type as the native starch.

Development of the shear stress in time appeared to be sensitive to the exact conditions during preparation and filling. Therefore, starting with the same conditions could lead to a variety in shear stresses (τ, SME; Table 1). Therefore, it was decided to relate the measured process data to the product properties.

4.2. Macromolecular degradation during heating–shearing treatment

In all samples, macromolecular degradation took place as evident from a decrease in intrinsic viscosity (Table 1). In order to find the key factor to starch degradation, Eqs. (3)–(5) were fitted to the data (Figs. 3–5). The parameter values obtained, the correlation coefficients (R^2 values) and the values for the Akaike information criteria are shown in Table 2. The first-order SME and $\tau \cdot t$-based literature models yielded low R^2 values (<0.67), whereas an acceptable fit ($R^2 = 0.933$) could be obtained using a first-order model based on the maximal shear stress $\tau_{\max}$. The calculated Akaike criteria showed that the $\tau_{\max}$ based model described the data significantly better than the SME and $\tau \cdot t$ based models: the difference between the Akaike criteria was higher than 5. Thus, at the temperatures investigated the process of starch degradation on a macroscopic scale is time independent within time scales investigated, which is in agreement with the fundamental conclusion by Beyer (2000) for cleavage of covalent bonds.

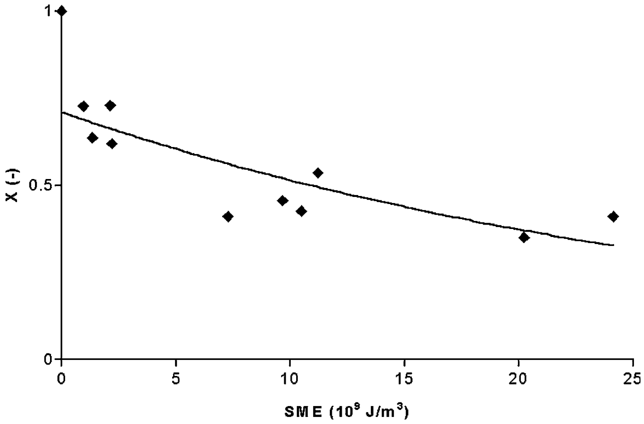

Fig. 4. Relative intrinsic viscosity X of heated- and heated–sheared waxy corn starch (water content 30%) as a function of SME. Points are the measurements, the line is the fitted first-order model.

The value of the constant C_{1c} in the $\tau_{\max}$ based model was 0.95. As long as no thermal degradation takes place, one would expect the value to be at least 1 (Section 2). Although the uncertainty in the intrinsic viscosity experiments is such that the value is not significantly different from unity, it may be an indication that some thermal degradation took place. In order to check this, heating without shearing was applied both at 85 and 110 °C for 15 min. The sample treated at 110 °C had an intrinsic viscosity of 158 g/ml. This very small difference from the value of native starch might explain why the constant C_{1c} in the $\tau_{\max}$ based model was slightly below 1. Thermal treatment at 85 °C decreased the intrinsic viscosity to 140 ml/g. This value was found in many replications of this experiment. This might be related to the solubility of the starch. After the thermal treatment at 85 °C it was very

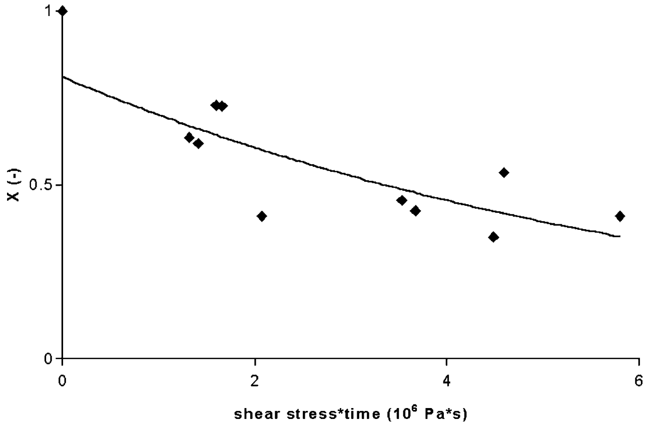

Fig. 3. Relative intrinsic viscosity X of heated- and heated–sheared waxy corn starch (water content 30%) as a function of $\tau \cdot t$. Points are the measurements, the line is the fitted first-order model.

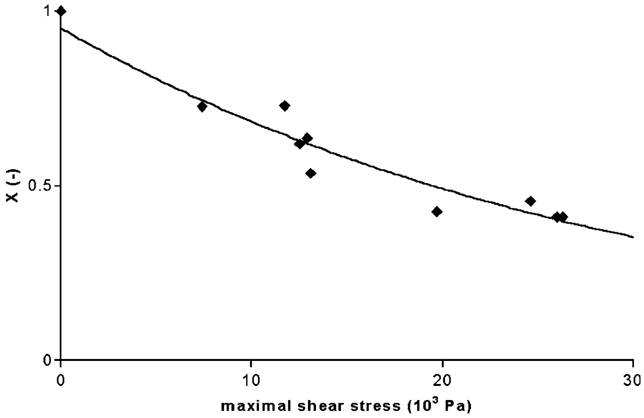

Fig. 5. Relative intrinsic viscosity X of heated- and heated–sheared waxy corn starch (water content 30%) as a function of maximal shear stress $\tau_{\max}$. Points are the measurements, the line is the fitted first-order model.

Table 2
Fit parameters, R^2 and AIC values for different first-order models including melt correction (see text) fitted to the data given in Table 1

Model	C_1	C_2	R^2	AIC
Diosady et al. (1985); $X = C_1 \exp(-C_2 \cdot \tau t)$	0.81	1.44×10^{-7}	0.64	−46.6
Parker et al. (1990); $X = C_1 \exp(-C_2 \cdot \mathrm{SME})$	0.71	3.22×10^{-11}	0.66	−44.8
New model; $X = C_1 \exp(-C_2 \cdot \tau_{\max})$	0.95	3.30×10^{-5}	0.93	−66.2

difficult to dissolve the starch in a KOH solution. This might be responsible for the low intrinsic viscosity measured subsequently. However, these solubility problems were not observed on any of the thermomechanically treated samples. Comparison of samples 7 and 9, which have the same maximal shear stress but different treatment temperatures (Table 1), clearly shows that the effect described above was not found in the heating–shearing experiments.

The constants C_{1a} and C_{1b} in the $\tau \cdot t$ and SME based models, respectively, were significantly lower than 1 (Table 2). The thermal effects described above cannot account for these low values of the constants, showing that the physical background of these models cannot be correct. Again, this indicates that the time independent model should be used to predict starch degradation at the temperatures and process times investigated.

The fact that Vergnes et al. (1987) found a good correlation between SME in a rheometer, implying a kind of time–shear equivalence, may be explained from the applied higher temperatures (140–180 °C). Thermal, time-dependent effects are not negligible anymore at these temperatures, so that a correlation with time is expected. Furthermore, possible interactions between thermal and shear effect might occur at these temperatures as well, which could further induce an effect of time on the results.

4.3. Explanation of degradation effects during extrusion processes

From the measurements, we suggest the following degradation pattern during extrusion at the temperatures investigated.

As long as all material is powdery, no degradation takes place because no significant shear force is applied to the starch molecules, as also found by Colonna, Melcion, Vergnes, and Mercier (1983). As the material begins to melt, shear stress is applied to the starch, causing the larger molecules in the non-crystalline parts to be degraded. The degradation pattern now becomes more complex as viscosity and shear stress on one hand decrease due to the breakdown of the macromolecules, but on the other hand increase due to further melting of the material. Furthermore, the breakdown will be inhomogeneous, because the shear rate, and thus the shear stress, varies locally in the extruder. Thus, it is expected that the degradation continues in time along the length of the extruder, although the degradation process itself is time-independent.

During extrusion trials, the SME is coupled to the shear stresses along the barrel. Typically, higher maximal shear stresses in the extruder lead to a higher torque on the engine and thus to a higher SME. Therefore, it is not surprising that in extrusion processes a good correlation between SME and starch breakdown can be obtained as, for example, found by Parker et al. (1990) and Willett, Millard, and Jasberg (1997).

Using the degradation pattern described above, we are now able to formulate how to prevent undesired degradation during extrusion (at the temperatures investigated in this paper) and to review how well the extruder performs if molecular weight reduction is a desired process.

According to our insights, undesired macromolecular degradation during extrusion processes can be reduced by decreasing the screw speed or increasing the depths of the gaps, so that the maximal shear stress is lower. The expected effect of screw speed is in accordance with data of Valle, Boché, Colonna, and Vergnes (1995) on extrusion of potato starch. It is also in agreement with data of Valle, Colonna, Patria, and Vergnes (1996) on extrusion of waxy corn starch and with data of Colonna and Mercier (1983) on extrusion of manioc starch, although in these two studies the effect of screw speed was investigated at higher temperatures, so that thermal effects may have to be taken into account. Increasing the moisture content will also lower the maximal shear stress and thus reduce the macromolecular degradation, although thermal effects might be more important at higher moisture content, as indicated by Igura, Katoh, Hayakawa, and Fujio (2001). The expected effect of moisture content is in accordance with data of Chinnaswamy and Hanna (1990) on extrusion of corn starch and with data of Davidson et al. (1984) on extrusion of wheat starch.

On the other hand, if molecular reduction is desirable, the inhomogeneity of conditions in an extruder is a source of inefficiency, as only the high shear spots in the extruder are effective.

5. Concluding summary

At the temperatures investigated, the maximal shear stress during heating–shearing treatment was found to be the key parameter determining the degree of macromolecular degradation of starch. This conclusion could be drawn only by means of separating the effects of shear and time showing that the newly developed shear cell is a useful tool in understanding effects of shear, temperature and time on the properties of low moistened starch and probably other materials.

The degree of macromolecular degradation during extrusion processes can be reduced by decreasing the maximal shear stresses by decreasing screw speed or increasing the depths of the gaps, but the residence time does not play a role for the breaking process itself. Increasing moisture content also decreases the maximal shear stress, although it might also affect thermal breakdown effects. The results presented can form a basis to develop predictive models enabling exact description of starch degradation.

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