

Molecular breakdown of corn starch by thermal and mechanical effects

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Abstract

The molecular weight reduction of corn starch at 30–43% moisture during thermal treatment at temperatures 90–160 °C and during well-defined thermomechanical treatment at temperatures 90–140 °C was investigated. Thermal treatment resulted, during the first 5 min in a decrease in molecular weight as measured by intrinsic viscosity, after which longer heating had no significant effect. Higher moisture contents and temperatures generally resulted in more breakdown, although the effect diminished at higher temperatures. The decrease in intrinsic viscosity during thermomechanical treatment at relatively low temperatures and moisture contents was shown to be only dependent on the maximal shear stress. At higher temperatures, thermomechanical breakdown could be split into a mechanical part depending on maximal shear stress and a thermal breakdown part, which was again time-dependent on the shorter time-scales only. Higher moisture content during thermomechanical treatment resulted in more thermal breakdown and lowered the shear stresses required for mechanical breakdown. Consequences for process design are discussed briefly.

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1. Introduction

The molecular weight of starch influences many properties of starch-based products, such as expansion rate, cold paste viscosity, water solubility and absorption, the degree of retrogradation and gelling properties (Bindzus, Fayard, Van Lengerich, & Meuser, 2002; Bruemmer, Meuser, Van Lengerich, & Niemann, 2002; Chinnaswamy & Bhattacharya, 1986; Mua & Jackson, 1997). The production of starch-based products often involves the application of a combination of (shear) stresses and thermal treatment, for example during extrusion. It is known that this combination leads to starch molecular weight reduction (Baud, Colonna, Della Valle, & Roger, 1999; Willett, Millard, & Jasberg, 1997).

Recently, it was shown that the extent of mechanical degradation of waxy corn starch is determined by the maximal shear stress during a thermomechanical treatment,

in the situation that thermal breakdown effects can be neglected (van den Einde et al, 2004). However, in many practical situations, the temperature is such that thermal degradation is important as well, next to shear-based effects. Fujio, Igura, and Hayakawa (1995) and Igura, Hayakawa, and Fujio (1997) showed that 15 min heating at 150 °C resulted in a decrease of molecular weight of corn and sweet potato starch. Byars (2003) found that thermal degradation effects were important during jet cooking of waxy corn starch.

The combined and simultaneous effects of heating and shearing on starch have not yet been clarified completely. Many studies conducted so far have focussed on the degradation of starch during extrusion and molecular weight reduction was explained quantitatively in terms of mechanical degradation only (Diosady, Paton, Rosen, Rubin, & Athanassoulis, 1985; Parker, Ollett, & Smith, 1990; Willett et al., 1997). Effects of more defined shear and temperature on starch degradation so far also resulted in quantitative explanations in terms of mechanical degradation only (Vergnes, Villemare, Colonna, & Tayeb, 1987).

The influence of moisture content on molecular weight reduction is another effect that has not been investigated

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Nomenclature		
C_1	first fit parameter in first order τ_{\max} model (–)	X_m (–) relative intrinsic viscosity of the molten fraction of the treated starch due to mechanical breakdown (–)
C_2	second fit parameter in first order τ_{\max} model (m^2/N)	X_{th} (–) relative intrinsic viscosity of the molten fraction of the treated starch due to thermal breakdown (–)
MC	moisture content (%)	Greek symbols
t	time (s)	$[\eta]$ intrinsic viscosity (ml/g)
t_{th}	time after the maximal shear stress was reached [time during which thermal effects were dominant compared to mechanical effects] (s)	$[\eta]_0$ intrinsic viscosity of native starch (ml/g)
X	relative intrinsic viscosity of the molten fraction of the treated starch compared to native starch	τ_{\max} maximal shear stress (N/m^2)

thoroughly. It has been suggested that increasing moisture content decreases the degree of starch degradation during heating and shearing processes such as extrusion (Chinnaswamy & Hanna, 1990; Wen, Rodis, & Wasserman, 1990) due to the reduction of the stresses occurring (Davidson, Paton, Diosady, & Larocque, 1984) since the melt viscosity is reduced. On the other hand, water might be involved in the chemical reactions that are leading to (thermal) degradation of starch, as suggested in a recent review by van den Einde, Goot, van der, and Boom (2003). Igura, Katoh, Hayakawa, and Fujio (2001) found that the effect of time–temperature history becomes large when processing starch at high moisture content. This suggests that the effect of moisture content might be more complex than only its effect through shear stresses.

In this study, a shear cell enabling a well-defined plain shear field was used to investigate the effects of simultaneous heating and shearing treatment on the molecular weight of regular corn starch at different moisture contents and temperatures in experiments in which both thermal and mechanical effects were important. The relative importance of heating was studied in separate experiments.

2. Materials and methods

2.1. Starch

Regular corn starch was obtained from Cargill BV. Starch was premixed with water as described earlier (van den Einde et al., 2004).

2.2. Heating treatment

Mixtures of corn starch were heat-treated in a mold with inner dimensions $100 \times 150 \times 2 \text{ mm}^3$ ($l \times w \times h$) or in a rotating sterilizing device. The mold was pressurized to avoid steam leakage. Pressure was in all cases put onto the outer raised edge of the mold, not on the sample, to avoid pressure effects. Further details on the mold used can be

found elsewhere (van Soest & Kortleve, 1999). Heat treatment in the mold and in the rotating sterilizing device was shown to reveal the same results in terms of degradation (results not shown). Temperatures, times and moisture contents are given in Table 1.

2.3. Heating–shearing treatment

Mixtures of corn starch and water were heated and sheared in the shearing device described earlier (van den Einde et al., 2004). Temperatures, times and rotation speeds are given in Table 2. Due to the steam pressure, no temperatures higher than 125 °C were possible

Table 1

Time (t), temperature (T) and moisture content (MC) during heat treatment and absolute ($[\eta]$) and relative (X) intrinsic viscosity of heat-treated corn starch

Experiment number	t (s)	T (°C)	MC (%)	$[\eta]$ (ml/g)	X (–)
Native	–	–	–	225	1
1	900	85	30	224	0.99
2	900	100	30	229	1.02
3	300	110	30	220	0.98
4	600	110	30	225	1.00
5	900	110	30	209	0.93
6	900	110	30	207	0.92
7	900	110	30	209	0.93
8	900	120	30	192	0.85
9	900	130	30	177	0.79
10	300	140	30	171	0.76
11	600	140	30	165	0.73
12	900	140	30	154	0.68
13	900	140	30	166	0.74
14	300	160	30	156	0.69
15	600	160	30	160	0.71
16	900	160	30	147	0.65
17	300	110	43	178	0.79
18	600	110	43	168	0.75
19	900	110	43	174	0.77
20	300	140	43	152	0.68
21	600	140	43	145	0.64
22	900	140	43	140	0.62
23	300	160	43	144	0.64
24	600	160	43	141	0.63
25	900	160	43	152	0.68

Table 2

Total treatment time (t) time after maximal shear stress (t_{th}), temperature (T), moisture content (MC), rotation speed (N), maximal shear stress (τ_{max}), absolute ($[\eta]$) and relative (X) intrinsic viscosity, and relative intrinsic viscosity of thermal part (X_{th} ; see text) of thermomechanically treated starch

Experiment number	t (s)	t_{th} (s)	T (°C)	MC (%)	N (rpm)	τ_{max} (10^4 Pa)	$[\eta]$ (ml/g)	X (–)	X_{th} (–)
26	960	130	90	30	75	5.11	147	0.65	1.03
27	1051	857	90	30	50	4.86	154	0.68	1.04
28	480	127	100	30	35	3.87	165	0.73	0.95
29	360	88	110	30	75	4.56	143	0.64	0.92
30	272	122	110	30	25	3.32	192	0.85	1.01
31	540	140	110	30	35	3.51	186	0.83	1.00
32	600	260	110	30	35	3.11	172	0.76	0.87
33	510	149	120	30	75	3.67	191	0.85	1.06
34	600	268	120	30	35	3.27	161	0.72	0.84
35	270	120	125	30	50	4.13	169	0.75	1.01
36	600	268	130	30	35	2.44	171	0.76	0.78
37	847	687	130	30	50	3.45	136	0.60	0.73
38	1153	1015	130	30	50	3.45	131	0.58	0.70
39	581	444	140	30	50	2.85	151	0.67	0.73
40	900	558	140	30	50	1.51	148	0.66	0.66
41	300	120	90	37	25	3.16	167	0.74	0.85
42	300	120	90	37	75	4.00	157	0.70	0.92
43	273	121	90	37	50	3.75	177	0.79	0.99
44	600	462	90	37	50	4.20	147	0.65	0.89
45	285	88	110	37	25	2.25	179	0.80	0.80
46	273	229	110	37	10	2.40	170	0.76	0.77
47	720	568	110	37	50	2.85	131	0.58	0.64
48	226	86	125	37	50	1.95	173	0.77	0.77
49	606	564	125	37	50	2.25	136	0.60	0.60
50	280	124	90	43	50	2.80	148	0.66	1.02
51	270	130	90	43	25	2.14	162	0.72	0.97
52	270	148	110	43	50	1.99	166	0.74	0.96
53	270	232	110	43	10	1.45	143	0.64	0.74
54	270	562	110	43	10	1.54	122	0.54	0.64
55	270	126	125	43	50	1.64	194	0.86	1.04
56	600	250	125	43	25	1.09	135	0.60	0.64

at 37 and 43% moisture, whereas at 30% moisture the maximum temperature was 140 °C. At higher temperatures, steam leakage took place, which was shown to have a large influence on all results obtained.

After the thermomechanical treatment, samples were dried and ground to fine powder under liquid nitrogen as described earlier (van den Einde et al., 2004).

2.4. Analysis

Intrinsic viscosity was determined as described earlier (van den Einde et al., 2004). The degree of degradation was calculated as the relative intrinsic viscosity X (Diosady et al., 1985). X-ray diffraction measurements on a Philips PC-APD PW 3710 powder X-ray diffractometer showed that no native crystalline could be found anymore in almost all samples (results not shown). Only samples heat-treated at $T \leq 140$ °C and 30% moisture showed some A-type crystals (approximately 12%), but as these samples were hardly degraded, the effect on X was minimal (maximally 0.01). Therefore, the calculation method described by

Diosady et al. (1985) could be simplified to:

$$X = \frac{[\eta]}{[\eta]_0} \quad (1)$$

3. Results and discussion

All the measured values are shown in Table 1 (heat-treated samples) and Table 2 (heated-sheared samples).

3.1. Breakdown by thermal effects only

Fig. 1 shows the measured relative intrinsic viscosity X as a function of temperature and moisture content after 15 min heat treatment. A higher temperature generally resulted in more starch breakdown, although the effect diminished at both high temperature and high moisture content. At 30% moisture, heat treatment at temperatures ≤ 110 °C induced only a small amount of starch degradation within 15 min ($X \geq 0.92$), which can probably be neglected in short-time experiments. Increasing moisture content

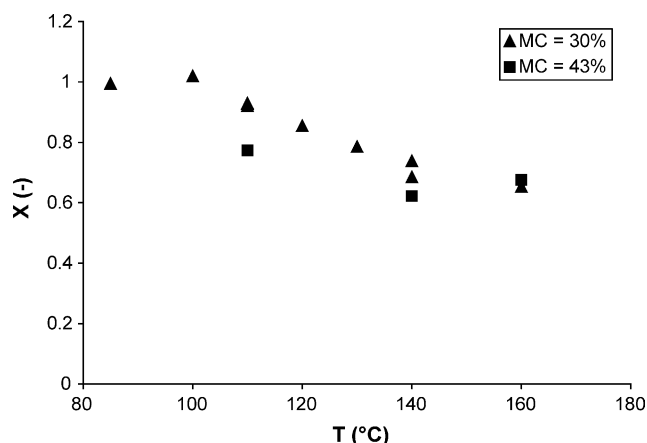


Fig. 1. Relative intrinsic viscosity X of low moistened starch heat-treated at different moisture contents as a function of temperature. Treatment time was in all cases 15 min.

generally resulted in more degradation. This effect of moisture content is in accordance with the hypothesis mentioned in the introduction that water may be involved in the occurring chemical reactions. The effect became less pronounced at higher temperatures (Table 1).

Fig. 2 shows that different treatment times (5, 10 or 15 min) did not result in significantly different degrees of breakdown at 30% moisture. Comparable results were obtained for 43% moisture. It seems that thermal treatment resulted in initial starch degradation only, after which the intrinsic viscosity remained approximately constant. As intrinsic viscosity measurements are only sensitive to endodegradation, it was also checked whether or not increase of time led to the formation of more water-soluble products, which are a measure for exodegradation. Water solubility of the product was in all cases low (0–7%) and different treatment times resulted in only very small differences, suggesting that exodegradation was also not significantly dependent on time. Although one would intuitively expect a first order degradation process, recent investigations by other researchers have revealed comparable results. Byars (2003) studied the degradation of waxy

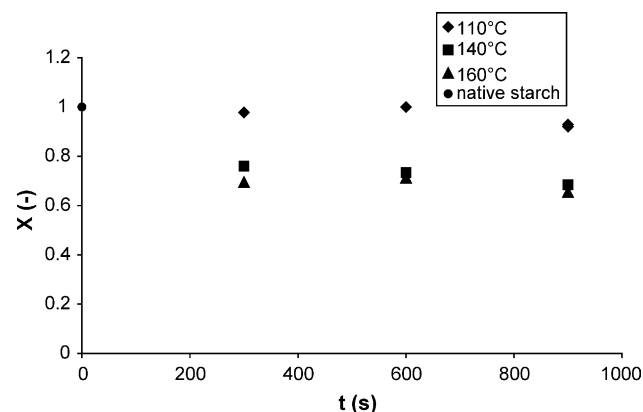


Fig. 2. The effect of treatment time on the relative intrinsic viscosity X of heat-treated low moistened starch at different temperatures. MC = 30%.

corn starch during heating in a jet cooker. The first few passes through the jet cooker resulted in significant decrease in intrinsic viscosity, whereas little additional breakdown was observed during further passes. Dintzis and Bagley (1995) found that the intrinsic viscosity value of waxy corn starch autoclaved at 120 °C remained constant with increasing holding time (21–60 min). Although the treatment time investigated was much longer than in this paper, their results also suggest time independence after an initial breakdown, in agreement with the results reported here.

3.2. Breakdown by shear

Fig. 3 shows the relative intrinsic viscosity X of thermomechanically treated low moistened starch as a function of maximally applied shear stress τ_{\max} and moisture content. In our earlier work (van den Eijnde et al., 2004), it was shown that when thermal effects were avoided, the mechanical breakdown of waxy corn starch at 30% moisture could be well described by a first order equation with the maximal shear stress τ_{\max} as the key parameter:

$$X_m = C_1 \exp(C_2 \tau_{\max}) \quad (2)$$

As explained in Section 3.1, the heating experiments showed that thermal effects play a role within 15 min at temperatures higher than 110 °C if moisture content = 30%.

Eq. (2) could indeed be fitted well to all the data at temperatures ≤ 110 °C, but also to the data obtained from short time experiments at 120 and 125 °C (Table 2, exp. no. 33 and 35). Thermal effects at 120 and 125 °C were found negligible due to the short times used in these two experiments and therefore these data could be used for fitting as well. Fitted parameters were $C_1 = 1.46$ and $C_2 = -2.45 \cdot 10^{-5} \text{ m}^2/\text{N}$. C_1 was higher than 1 suggesting that there is a threshold value for shear stress before regular corn starch breaks down (van den Eijnde et al., 2004). If the shear stress applied is lower than this threshold value, X_m remains at 1. The minimally required stress can be calculated by equating Eq. (2) to 1. Thus, the degradation equations become:

$$X_m = 1 \quad \text{if } \tau_{\max} < 2.32 \times 10^4 \text{ N/m}^2 \quad (3a)$$

$$X_m = 1.46 \exp(-1.63 \cdot 10^{-5} \tau_{\max}) \quad (3b)$$

$$\text{if } \tau_{\max} \geq 2.32 \times 10^4 \text{ N/m}^2$$

The R^2 value was 0.83, which suggests that a first order correlation, as found for waxy corn starch at 30% moisture content, can also be applied to regular corn starch at 30% moisture content. Samples treated for a longer time at 120 or 125 °C and samples treated at 130 or 140 °C clearly showed an additional thermal effect (Table 2), as was expected from the heating experiments.

At 43% moisture, the situation was somewhat different (Fig. 3). As stated in the introduction, water may be

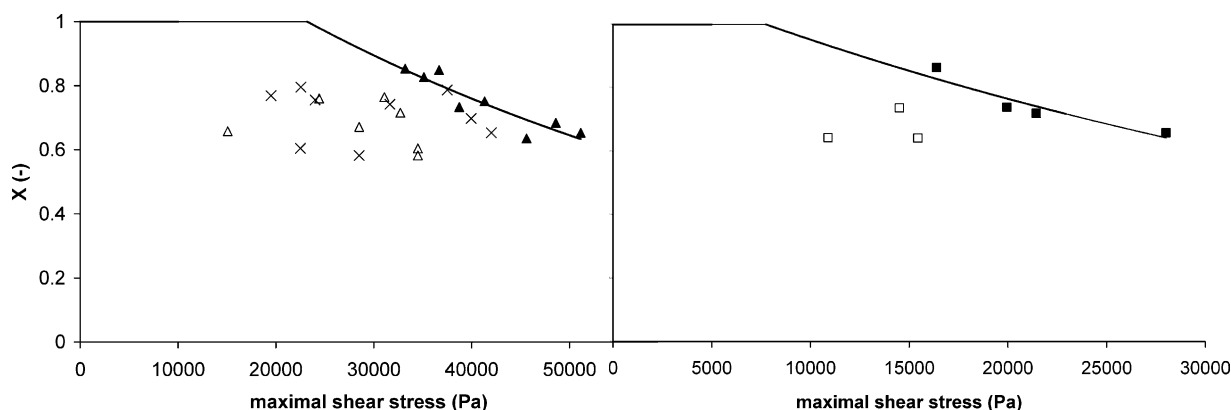


Fig. 3. Relative intrinsic viscosity X of thermomechanically treated low moistened starch as a function of maximally applied shear stress τ_{\max} and moisture content. \blacktriangle and \triangle : MC = 30%; \times : MC = 37%; \blacksquare and \square : MC = 43%. Closed symbols are used for experiments in which only mechanical effects are significant; open symbols indicate results from experiments in which thermal effects played a significant role. Lines indicate the fitted first order models.

involved in the occurring reactions. Therefore, it was expected that a higher fraction of water might destabilize the glycosidic bond and that the shear stresses required for breaking down the starch might be lower at higher moisture content. For this reason, a separate first order equation with the maximal shear stress τ_{\max} was fitted to those data that had received a relatively short treatment time after the maximal shear stress was reached (so that thermal effects were supposed to be almost negligible), resulting in:

$$X_m = 1 \quad \text{if } \tau_{\max} < 7.74 \times 10^3 \text{ N/m}^2 \quad (4a)$$

$$X_m = 1.18 \exp(-2.18 \cdot 10^{-5} \tau_{\max}) \quad (4b)$$

$$\text{if } \tau_{\max} \geq 7.74 \times 10^3 \text{ N/m}^2$$

($R^2 = 0.88$). The temperature at and above which thermal effects are important is approximately 110 °C. As expected, this is lower than at 30% moisture. Thermal effects during thermomechanical treatment are further discussed in Section 3.3.

At 37% moisture, data obtained at 90 °C were more or less comparable in breakdown to 30% moisture, although they were somewhat scattered (Fig. 3 and Table 2). At higher temperatures, in all cases more breakdown took place than expected from the 30% moisture shear-induced breakdown line (Fig. 3). This could be due to thermal effects during the thermomechanical treatment, as explained further in Section 3.3.

3.3. Breakdown by shear and heat

As explained in Section 3.2, part of the breakdown of starch in thermomechanically treated samples was due to thermal effects. As was found earlier, effects of shear stress are time-independent and the molecular weight of starch after shearing treatment is determined by the maximal shear stress applied. It was, therefore, assumed that mechanical breakdown is dominant during thermomechanical treatment until the time that this maximal shear stress is encountered. After this time, thermal effects may result in further

degradation of the starch. The mechanisms of breakdown by heat and shear were assumed to be independent. Therefore, it is logical to assume the following relation:

$$X = X_m X_{th} \rightarrow X_{th} = \frac{X}{X_m} \quad (5)$$

X_m was calculated according to Eqs. (3a) and (3b) for 30 and 37% moisture and according to Eqs. (4a) and (4b) for 43% moisture.

Fig. 4a shows X_{th} as a function of temperature at 30% moisture. The data points close to $X_{th} = 1$ are the ones in which thermal effects were supposed to be negligible and that were used for fitting the first order models described in Section 3.2 (Fig. 3). The other data in this figure clearly suggests that the data obtained from thermal experiments are not highly different from those derived from the thermomechanical experiments. This suggests that thermomechanical treatment can indeed be approximated as an independent combination of a mechanical treatment with the main parameter τ_{\max} and a thermal treatment. Combining Fig. 4a and Table 2 reveals that, in analogy with the heat-treated samples, all samples with $t_{th} > 300$ s could be described as dependent on temperature only and not significantly on treatment time (compare for example experiments 37 and 38). This finding can simplify the description of the effects of thermomechanical treatment: if time after the maximal shear stress exceeds a threshold, the treatment can be described as an addition of an effect of τ_{\max} and an effect of the temperature.

Fig. 4b shows X_{th} as a function of temperature at 43% moisture. The shape of the curve is comparable to the one obtained from the data at 30% moisture. In line with the expectations, the downward trend in X_{th} with temperature occurs at lower temperatures than at 30% moisture. The data obtained from the purely thermal experiments are not highly different from the ones derived from the thermomechanical treatment. This suggests that at 43% moisture also, a heating–shearing treatment can be approximated as a mechanical treatment with the main parameter τ_{\max} and

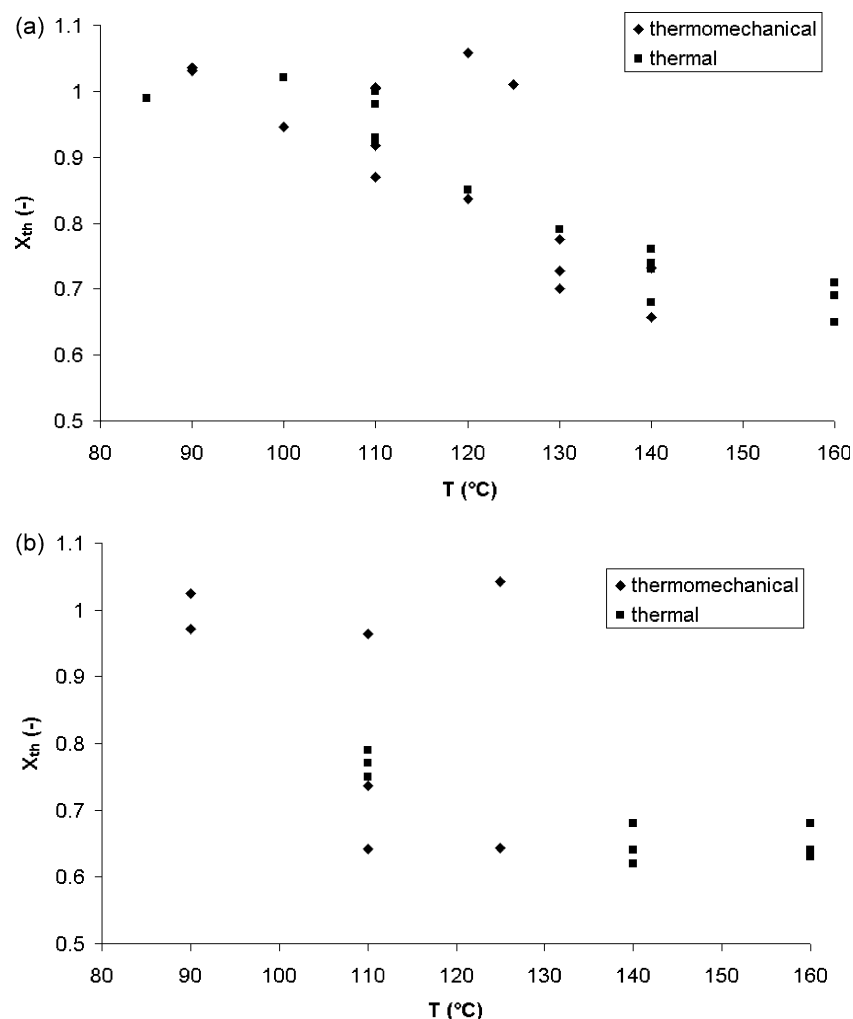


Fig. 4. Relative intrinsic viscosity due to thermal effects X_{th} of thermally and thermomechanically treated corn starch at (a) 30% and (b) 43% moisture as a function of temperature. Data points with X_{th} close to 1 were those being used for fitting the first order mechanical degradation lines in Fig. 3 (negligible thermal effects; see text).

an independent thermal treatment. The somewhat lower value found for X_{th} in experiment 54 (110 °C; Table 2) might be due to the following. Fig. 4b clearly shows that the difference in breakdown between 110 and 125 °C is high. Although temperature control during the experiment was reasonably accurate, a local increase of temperature to approximately 114 °C was shown to be possible. Taking into account the large dependence of breakdown on temperature in this regime, it may be possible that this higher temperature caused the additional breakdown.

At 37% moisture, reproducibility was less than at 30 and 43% moisture (Table 2) and data were highly scattered (Fig. 3). It seems that 37% is in the intermediate area between the two regimes. The behavior in this region appears to be complex as small changes in conditions will cause several effects to occur simultaneously, such as bond destabilization, effects on viscosity and thermal breakdown. Therefore, the behavior of the starch–water mixture in this region seems to be highly sensitive to small deviations in temperature or moisture content. In order to obtain

a complete view of all the influences on the starch degradation at 37% moisture, a higher accuracy than that possible with the current experimental setup may be necessary.

3.4. Consequences for product and process design

3.4.1. The role of water in starch breakdown

As described in the introduction, previous studies suggested that increasing moisture content decreased the degree of starch degradation during heating–shearing processes, due to the effect of lower stresses. Our study indicates that this statement is not always valid. As Figs. 2–4 and Tables 1 and 2 show, increasing moisture content has three different effects. It decreases the shear stresses, but it also increases the degree of thermal breakdown and it destabilizes the bond so that smaller stresses are required for mechanical breakdown. Hence, the relation between moisture content and degree of degradation is not linear, but more complex. It can even be expected that an optimum

occurs in breakdown at a certain moisture content, as changing moisture content will probably affect melt viscosity to a different extent than it will affect the degree of degradation. This is in accordance with results by Govindasamy, Campanella, & Oates, 1996. They found that increasing moisture content from 34 to 42% decreased the degree of starch degradation, but that increasing moisture content from 42 to 50% increased the degree of starch degradation during extrusion of sago starch. However, these authors suggested this to be caused by gelatinization, resulting in various extents of granular structure relaxation, rather than by thermal breakdown effects. Baud et al. (1999) found that degree of degradation after extrusion could not be related directly to the moisture content, which could be in accordance with the current results. These authors did not explain their result in terms of thermal degradation either.

3.4.2. Time (in)dependence of thermal breakdown

Another interesting result for process design is the unexpected partial time dependence of starch breakdown during heat treatment. Apparently, once a certain heating time is reached, no further starch breakdown will take place. This can be a useful feature, as it might be possible to change various product properties or inactivate undesired components without significantly affecting the starch molecular weight.

4. Concluding remarks

Effects of shear and thermal treatment on low moistened corn starch were unraveled in this work. Thermal breakdown was shown to have an effect during a limited time only. Upon further increasing the thermal treatment time, no additional breakdown takes place. Thermomechanical degradation could be divided clearly into a mechanical effect, depending on maximal shear stress, and an independent thermal effect, which was for (thermal) treatment times > 300 s only dependent on temperature and not on time. These findings suggest a convenient way to estimate the effect of thermomechanical treatment on starch molecular weight and can, therefore, be a useful tool in process design.

Increasing moisture content had three separate effects on starch molecular weight reduction: it decreased the stresses, increased thermal breakdown and decreased the stresses required for breakdown. This makes the effect of moisture content quite difficult to predict, but the findings described in this paper can provide the first guideline for estimating the effects of changing moisture content on starch molecular weight reduction.

The finding that shear and temperature effects can be considered independent may open up the possibility for relatively simple, but accurate models that could be used for design of processes that are more effective and efficient than the thermomechanical processes available today.

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