Influence of Annealing on the Pasting Properties of Starches from Varying Botanical Sources

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ABSTRACT

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Pea, potato, wheat, and rice starches were annealed for 24 hr. Differential scanning calorimetry data were collected; pasting characteristics were determined using the Brabender Viscoamylograph and the Newport Scientific Rapid Visco-Analyser (RVA); and amylose leaching during heating in the viscoamylograph was examined. Differential scanning calorimetry data showed an increased gelatinization temperature and enthalpy, and a narrower gelatinization temperature range for all starches. Viscoamylograph viscosity curves showed that annealing resulted in an increased peak viscosity (except for potato starch), and an increased viscosity upon cooling. The amount of amylose leached from the granules was not linked to viscosity changes. Less amylose was leached from the granules of annealed pea and potato starches. The amount of solubilized amylose was practically unchanged (slightly

decreased) after the annealing treatment for rice starch, whereas annealed wheat starch showed a slightly increased leaching of amylose. Except for pea starch, RVA results were comparable to the results from the viscoamylograph. In a dimethyl sulfoxide (DMSO) and water mixture (92.5:7.5, w/w), viscosity changes were not consistent for all annealed starches. For annealed pea, wheat, and rice starches, the onset of solubilization occurred at lower temperatures. The increased peak viscosity was attributed to a higher rigidity and resistance to shear of the starch granules. For annealed potato starch, the viscosity was decreased. A higher rigidity and increased resistance to heat and shear of the starch granules are probably the main causes of the viscosity changes due to annealing, both in water and in a DMSO-water mixture.

Annealing of granular starches involves incubation in excess water, for a certain period of time, at a temperature above the glass transition temperature but below the gelatinization temperature.

The first observations of the effects of annealing on starch were probably reported by Gough and Pybus (1971), although those authors did not use the term. Using Kofler hot-stage microscopy, they observed both an increase of the gelatinization temperature and a decrease of the gelatinization temperature range as a result of annealing. Their findings were confirmed later by differential scanning calorimetry (DSC) experiments (Yost and Hoseney 1986; Krueger et al 1987a,b; Münzing 1989; Knutson 1990; Tester and Morrison 1990; Larsson and Eliasson 1991; Lopez and Lopez 1991; Stute 1992) and by small angle light scattering (Marchant and Blanshard 1978, 1980). In addition to increased gelatinization temperatures and decreased gelatinization temperature ranges, increased gelatinization enthalpies were noted as well. However, Yost and Hoseney (1986), Larsson and Eliasson (1991), and Stute (1992) observed no change of the gelatinization enthalpy after annealing. Possible explanations for the phenomena include crystallite growth or perfection (Yost and Hoseney 1986; Tester and Morrison 1990; Larsson and Eliasson 1991; Lopez and Lopez 1991), a partial melting of the crystallites followed by a realignment of the polymer chains (Marchant and Blanshard 1978, 1980), development of crystallinity in the amorphous regions of the granule (Krueger et al 1987a,b; Münzing 1989), interactions between amylose and amylopectin (Knutson 1990), or alterations of the coupling forces between crystallites and the amorphous matrix (Stute 1992) as a result of the annealing process.

So far, not much work has been reported with regard to the pasting properties of annealed starches. The pasting properties of annealed potato starch were investigated by Stute (1992) and

Hoover and Vasanthan (1994). Hoover and Vasanthan (1994) also reported the pasting behavior of annealed wheat, lentil, and oat starches, while Schierbaum and Kettlitz (1994) did so for annealed rye starch. It is clear from the literature that for all the starches investigated, annealing affects the pasting properties in some way, but the observed effects differ depending on the source of the starch.

The purpose of our work was to perform further investigations concerning the influence of annealing on the pasting properties of starches from varying botanical sources. The examined starches included wheat and rice starch (A-type), potato starch (B-type), and pea starch (C-type). Maize starch (A-type) was not included in the experiments. Krueger et al (1987a) reported that commercial maize starch is already annealed during the isolation process because wet milling includes a lengthy steeping step at temperatures above 45°C. Viscosity development was measured with a Brabender Viscoamylograph as well as a Newport Scientific Rapid Visco-Analyser (RVA). Amylose leaching experiments were performed in an attempt to relate the annealing viscosity changes to the amount of amylose leached from the granules during the heating cycle in the Brabender Viscoamylograph. Also studied was the viscosity development of the native and annealed starches in a dimethyl sulfoxide (DMSO) and water mixture (Cooreman et al, in press).

MATERIALS AND METHODS

Pea starch (Nastar), rice starch, and potato starch (Meridal G) were obtained from Cosucra (Momalle, Belgium), Remy (Wijgmaal, Belgium) and Amylum (Aalst, Belgium), respectively. Wheat starch (Meriwit AA) was obtained from Amylum as well. Pure potato amylose (A0512) was obtained from Sigma Chemical Co. (St. Louis, MO). DMSO (highest purity grade) was obtained from UCB (Gent, Belgium).

Annealing Procedure

A starch suspension (1:2, w/w) was heated for 24 hr in a sealed container in a water bath at a constant temperature. The annealing temperatures were chosen as a function of the gelatinization temperatures of the native starches (Table I), i.e., 3–4% below the

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gelatinization peak temperatures (in °K) as determined by DSC. The annealing temperature was 50°C for potato and pea starch, 45°C for wheat starch, and 55°C for rice starch. After a 24-hr incubation period, the starch suspension was Buchner-filtered and the residue was dried overnight (room temperature, air stream).

DSC

DSC experiments were performed using a Seiko DSC-120 (Kawasaki Kanagawa, Japan). Indium and tin were used as standards. Approximately 5 mg of starch were accurately weighed in an aluminum sample pan. Water was added to obtain a ratio of 1:2 (w/w). The sample pan was hermetically sealed and then heated from 5 to 150°C at a rate of 4°C/min. An empty pan was used as reference. The transition temperatures reported are for onset (T_o), peak (T_p), and completion (T_c). The enthalpy (ΔH) of gelatinization was determined by integration of the endotherm. Each sample was analyzed in triplicate. The pooled standard deviations were 0.2°C for T_o, 0.1°C for T_p, 0.4°C for T_c, and 0.9 mJ/mg for ΔH.

Viscosity Curves

Viscoamylography was performed using a viscoamylograph (Visco-amylograph, Brabender, Duisburg, Germany) equipped with a 700 cm·g cartridge. The temperature-time conditions for starch suspensions (6.6%, w/w; 500 g total weight) were: a heating step from 35 to 95°C at a heating rate of 1.5°C/min; a holding phase at 95°C for 20 min; a cooling step from 95 to 35°C at 1.5°C/min; and a holding phase at 35°C for 20 min. To investigate the repeatability of the method, a control rice starch was analyzed six times at the same concentration (6.6%). The standard deviation for the peak viscosity was 3 BU (the difference between the maximum and minimum value was 7 BU). The standard deviation for the end viscosity was 9 BU (with a difference between the maximum and minimum value of 25 BU).

Rapid viscosity analysis was performed using a Rapid Visco-Analyser (RVA) (Newport Scientific, Sydney, Australia). The temperature-time conditions for starch suspensions (6.6%, w/w; 25 g total weight) were: a heating step from 50 to 95°C at 6.43°C/min (after an equilibration time of 1 min at 50°C); a holding phase at 95°C for 8 min; a cooling step from 95 to 50°C at 6.43°C/min; and a holding phase at 50°C for 17 min. As with the viscoamylograph method, the repeatability of the RVA method was investigated by analyzing a control rice starch six times at the same concentration (6.6%). The standard deviations of the peak viscosity and the end viscosity were both 1 rapid visco unit (RVU) (the difference between the maximum and minimum value was 2 RVU).

Viscosity profiles of starch (6.6% dry matter) in a DMSO-water

mixture (92.5:7.5, w/w) were recorded as described by Cooreman et al *(in press)*. The temperature-time conditions included a heating step from 25 to 75°C at 5°C/min and a holding phase at 75°C for 30 min. In contrast with the temperature-time conditions used for the suspensions in water, the cooling step was eliminated. Again, the repeatability of the RVA DMSO-water method was investigated by analyzing a control rice starch five times at the same concentration (6.6%). The standard deviations were 5 RVU for the peak viscosity (with a difference between the maximum and minimum value of 14 RVU) and 4 RVU for the end viscosity (with a difference of 8 RVU between the maximum and minimum value).

Amylose Leaching

Starch suspensions (0.66% [w/w] for rice, pea, and wheat starch or 0.33% [w/w] for potato starch) were heated in the Brabender Visco-amylograph. Suspensions were isolated after different time intervals and immediately centrifuged at 1,500 × *g* for 10 min. Both the total carbohydrate (phenol-sulfuric acid method, Dubois et al 1956) and the amylose content (blue value
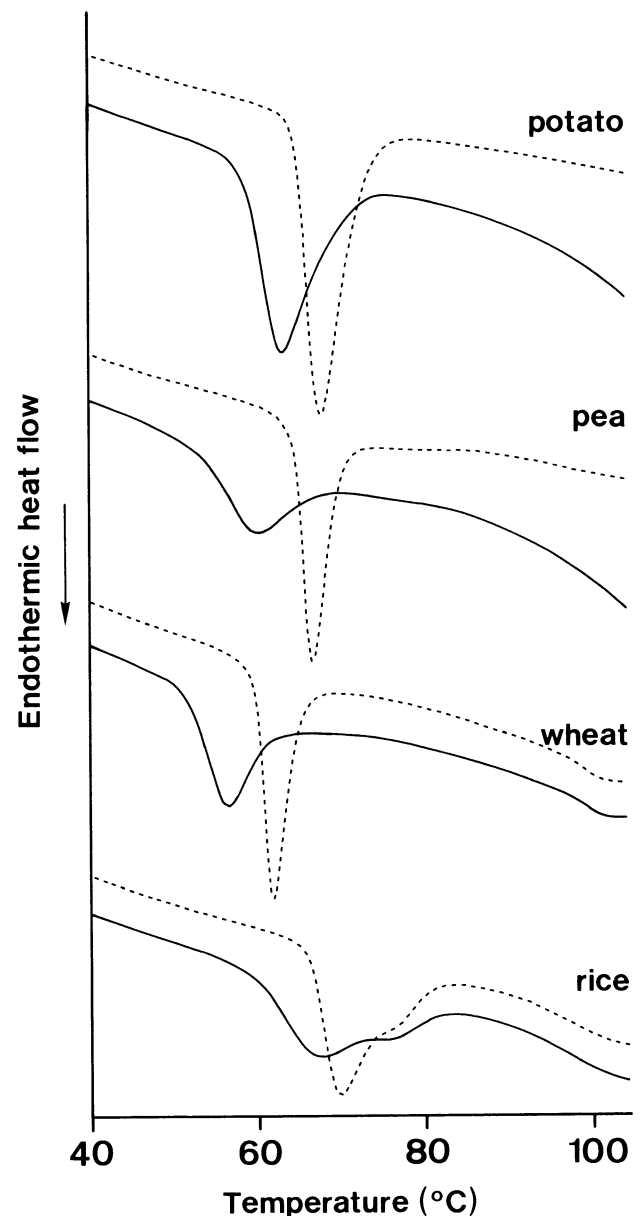

Fig. 1. Differential scanning calorimetry patterns of native (——) and annealed (----) starches.

TABLE I
Thermal Characteristics of Native and Annealed Starches: Onset (T_o), Peak (T_p), and Completion (T_c) Temperatures (°C), Gelatinization Enthalpy (ΔH)[a], and Gelatinization Range ($T_c - T_o$)

Starch	T_o	T_p	T_p'[b]	T_c	ΔH[a]	$T_c - T_o$
Potato						
Native	58.6	63.0	...	72.2	19.2	13.6
Annealed	64.8	67.7	...	73.0	19.9	8.2
Pea						
Native	53.5	59.8	...	66.9	9.7	13.4
Annealed	65.2	67.5	...	71.0	12.2	5.8
Wheat						
Native	51.5	56.2	...	61.6	10.6	10.1
Annealed	59.7	61.7	...	64.9	11.0	5.2
Rice						
Native	59.7	67.8	75.3	82.6	13.0	22.9
Annealed	66.2	70.0	...	81.2	14.2	15.0

[a] ΔH in mJ/mg of starch.
[b] Peak temperature of second rice starch endotherm.

procedure, Gilbert and Spragg 1964) of the supernatant were measured. Amylose content was determined at least in duplicate. To that end, supernatant (1.0 ml) was pipetted into a 50-ml flask. After addition of 0.1N NaOH (0.5 ml), the sample was boiled for exactly 3 min and immediately cooled in an ice bath. Samples were neutralized with 0.1N HCl (0.5 ml), then 20.0 ml of a potassium hydrogentartrate solution (5.0 g/l) was added. Distilled water ($\approx$43 ml) and 0.5 ml of an iodine solution (200 mg of I_2 and 2 g of KI per 100 ml) was added, and the total volume was adjusted to 50 ml with distilled water. The thoroughly mixed solution was allowed to rest 20 min at room temperature. Absorbance was measured at 680 nm. Pure potato amylose was used for the calibration curve.

RESULTS

DSC

The results of the DSC experiments are shown in Figure 1 and Table I. Annealing increases gelatinization temperatures. Increases for T_o and T_p were more pronounced than for T_c. An ΔH increase was also observed. The gelatinization temperature range ($T_c - T_o$) was drastically reduced. The gelatinization endotherm of native rice starch consists of two peaks (Fig. 1), therefore two peak temperatures (T_p and T_p') are given in Table I. Annealing moved the first peak to a higher temperature, while the second peak appeared as only a shoulder of the first peak (Fig. 1).

The largest effects of annealing on the thermal characteristics of starch were observed for pea starch. An increase in T_p of 7.7°C was noted, together with an ΔH increase of 2.5 mJ/mg and a decrease in the gelatinization temperature range of 7.6°C. Annealing had the smallest effect on T_p for rice starch, which increased 2.2°C.

Viscoamylograph Curves

Viscosity curves of native and annealed starches are shown in Figure 2 (note difference in scales), the pasting characteristics are shown in Table II.

As a result of annealing, the T_o of viscosity development was increased by 5°C for potato starch. In contrast, this parameter

remained practically unchanged for annealed pea starch, and it was even shifted slightly to a lower temperature for annealed wheat and rice starch. For annealed potato starch, maximum viscosity development shifted toward a higher temperature and a lower value. For annealed wheat and pea starch, the viscosity development during the heating phase and the 95°C holding phase was markedly increased. For rice starch, this viscosity development was only slightly increased. Annealing increased the viscosity during the cooling phase for all starches.

RVA Curves

Shear rates are higher in the RVA cup than in the viscoamylograph cup (Deffenbaugh and Walker 1989). There are also differences in sample size, stirring geometry, and temperature-time conditions. The RVA profiles are shown in Figure 3 (note difference in scales), and the pasting characteristics are shown in Table II.

The viscosity behavior of suspensions of potato, wheat, and rice starches showed that the relative annealing effect recorded by the RVA was approximately the same as that recorded by the viscoamylograph. However, for annealed rice starch, the onset of viscosity development was unchanged in the RVA profile as opposed to a decrease of this parameter in the viscoamylograph profile. The more pronounced viscosity peak for wheat starch in the RVA viscosity profile is of interest.

The RVA results for pea starch were not entirely in agreement with the viscoamylograph results. The viscosity of annealed pea starch increased in the viscoamylograph profile but not in the RVA profile. The plateau viscosity at 95°C was approximately unchanged (slightly increased), and the end viscosity decreased. Furthermore, the RVA profile showed a shift of the onset of viscosity development to a higher temperature, while this parameter was unchanged in the viscoamylograph profile.

Amylose Leaching

To correlate viscosity changes from annealing with amylose leaching during the heating cycle, the amount of soluble amylose (as well as the amount of soluble total carbohydrates) in the starch suspension were determined after isolation at different
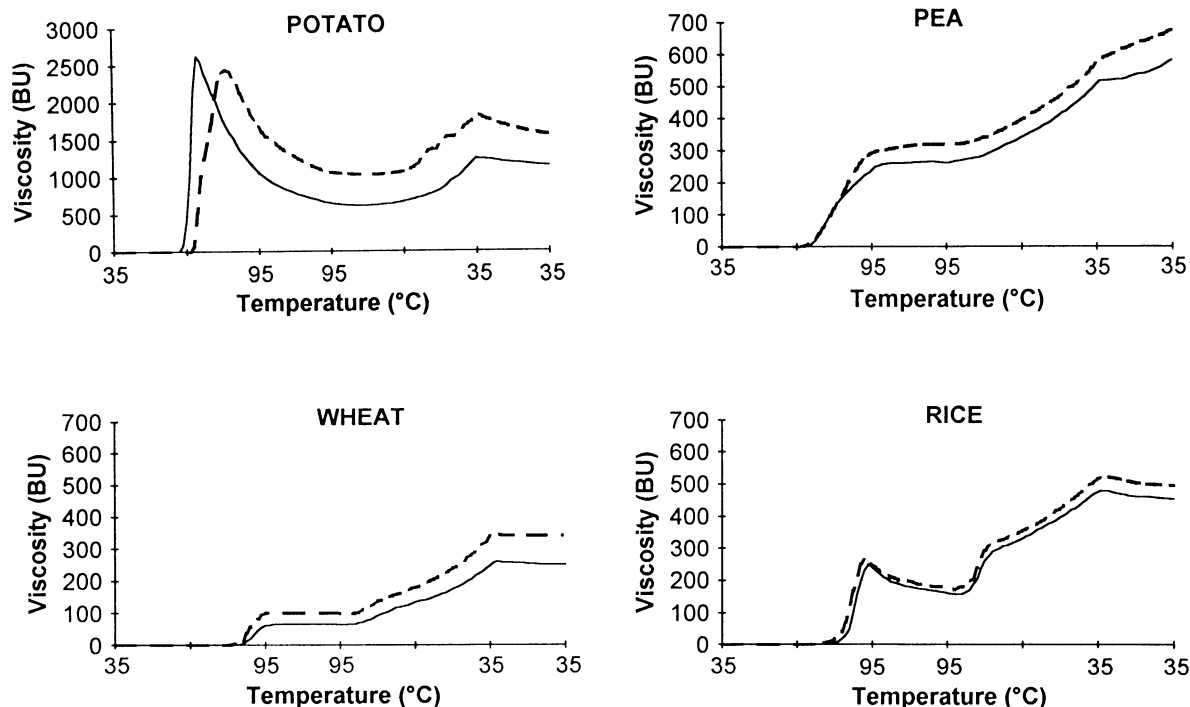

Fig. 2. Viscosity curves of native (——) and annealed (----) starches measured with a Brabender Viscoamylograph. BU = Brabender units. (Note differences in scale)

stages in the viscoamylograph cycle. The results are shown in Figure 4 and Table II. The amount of leached amylose was expressed as the percentage of the total starch (dry weight). The amounts of leached carbohydrates followed the same tendencies as the amounts of leached amylose (results not shown).

For the native starches as well as for the annealed starches, an increasing amount of amylose was leached from the starch granules with increasing temperature and increasing time at 95°C. For native starches, this observation confirms earlier results by Tester and Morrison (1990) and Radosta et al (1992).

TABLE II
Effects of Annealing on Different Starches

Technique	Parameter	Potato		Pea		Wheat		Rice	
		Native	Annealed[a]	Native	Annealed[a]	Native	Annealed[a]	Native	Annealed[a]
Brabender Viscoamylograph	Onset temp. (°C)	62	5	68	0	83	−3	77	−3
	Viscosity (BU)[b]								
	Peak	2,620	−180	260[c]	60	65	35	250	15
	End	1,145	415	580	95	250	90	455	40
Rapid Visco-Analyser (RVA)	Onset temp. (°C)	64	5	67	4	86	−4	85	0
	Viscosity (RVU)[d]								
	Peak	405	−31	59[e]	3	37	28	52	10
	End	148	76	101	−12	49	25	65	18
Amylose leaching (%)[f]	35 min	13.0[g]	−2.8[g]	20.6	−4.0	9.2	−0.1	4.5	−0.2
	40 min	27.2	−9.2	24.1	−3.6	24.1	2.6	14.5	−0.9
	60 min	38.7	−12.3	27.4	−2.6	29.5	0.7	21.6	−0.7
RVA in dimethyl sulfoxide and water mixture	Onset temp. (°C)	50	−2	54	−1	47	−2	39	−5
	Viscosity (RVU)								
	Peak	321	−60	75	28	139	12	174	31
	End	162	−39	42	1	36	3	37	7

[a] Change in the parameter as a result of annealing; a negative sign implies a decrease.
[b] Brabender units.
[c] Pea starch shows no peak viscosity, reported value is the viscosity after 60 min (95°C).
[d] Rapid visco units.
[e] Pea starch shows no peak viscosity, reported value is the viscosity after 16 min (95°C).
[f] Percent of total starch content.
[g] Values measured at peak viscosity time, i.e., after 23 and 31 min for native and annealed potato starches, respectively.
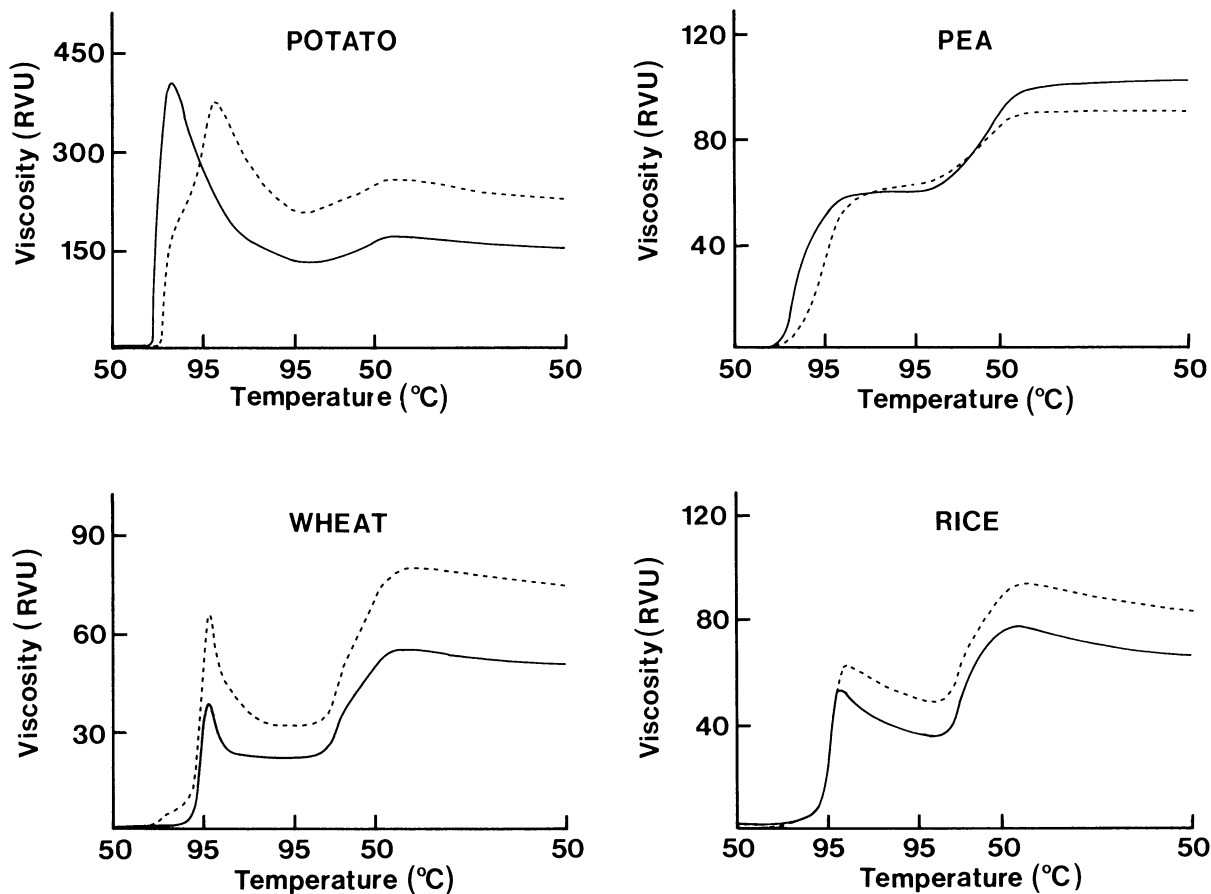

Fig. 3. Viscosity curves of native (——) and annealed (----) starches measured with a Rapid Visco-Analyser. RVU = Rapid visco units. (Note differences in scale)

The amount of leached amylose was substantially reduced for annealed pea and potato starches and only slightly reduced for annealed rice starch. For annealed wheat starch, however, there appears to be a slight increase in leached amylose content.

Pasting Properties in DMSO-Water

The pasting curves of the native and annealed starches in DMSO-water (92.5:7.5, w/w) are shown in Figure 5 (note difference in scales); the pasting characteristics are shown in Table II.

For annealed pea, wheat, and rice starches, a shift of the onset of viscosity development to a lower temperature was observed, together with a shift of the viscosity peak to a higher value and a lower temperature. The end viscosity for pea and wheat starches was not affected by the annealing process, although rice starch had a slightly higher end viscosity. Viscosity behavior of annealed potato starch was totally different from that of the other annealed starches. The onset of viscosity development was decreased as it was for the other starches, but the peak and end viscosities were decreased.

DISCUSSION

DSC

Irrespective of the botanical source or crystal type, annealed starches showed the same relative results when measured in water by DSC: an increase in the gelatinization temperature and enthalpy, and a narrower gelatinization temperature range. Therefore, whatever its exact mechanism, all starch crystal types respond to annealing in a similar fashion.

Viscosity and Amylose Leaching

Miller et al (1973) and Colonna and Mercier (1985) described the molecular events that occur in starch granules of normal genotypes during the heating cycle in the Brabender Viscoamylograph. Slight granule swelling and loss of birefringence occur earlier than any appreciable viscosity increase. Initially, during the pronounced viscosity increase, further swelling of the granules

occurs, accompanied by limited leaching, followed by excessive swelling and solubilization above 90°C. This results in loss of granular integrity, although the granules do not totally disintegrate. Thus, swelling of the granules can take place before starch starts to solubilize (Doublier 1981). Amylose is preferentially solubilized, and an increased leaching temperature causes an increase in the molecular mass of the leached amylose (Ghiasi et al 1982; Radosta et al 1992).

Different views exist with regard to the factors that determine the viscosity development during heating of the starch granules in water. According to Schoch (1969) and Evans and Haisman (1979), viscosity development is determined by the formation of a tightly packed array of swollen, deformable granules. Schoch and Maywald (1968) report that the hot paste viscosities of starches are determined by the extent of swelling of the starch granules and the resistance of the swollen granules to dissolution by heat or fragmentation by shear. On the other hand, according to Miller et al (1973), leaching of macromolecules that form an entangled network is the main factor in viscosity development during the heating of the starch granules. In agreement, Ziegler et al (1993) reported that leached amylose makes a great contribution to the viscosity for corn starch. According to Doublier et al (1987) and Lineback and Rasper (1988), several factors control the viscosity during pasting, including swelling of the granules and the amount of solubilized starch. In summary, therefore, it can be stated that both the formation of a tightly packed array of swollen, deformable granules, and the leaching of macromolecules can contribute to viscosity development in starch pastes.

Upon cooling, the amylose molecules aggregate, leading to gel formation (Miles et al 1985). Thus, the viscosity increase on cooling is a measure of the retrogradation tendency of the starch.

One striking observation was the absence of a consistent increase of the onset of viscosity development for all starches (Table II, Figs. 2 and 3). An increase would be expected, based on the consistent increase of the DSC gelatinization temperature of the annealed starches (Fig. 1 and Table I).

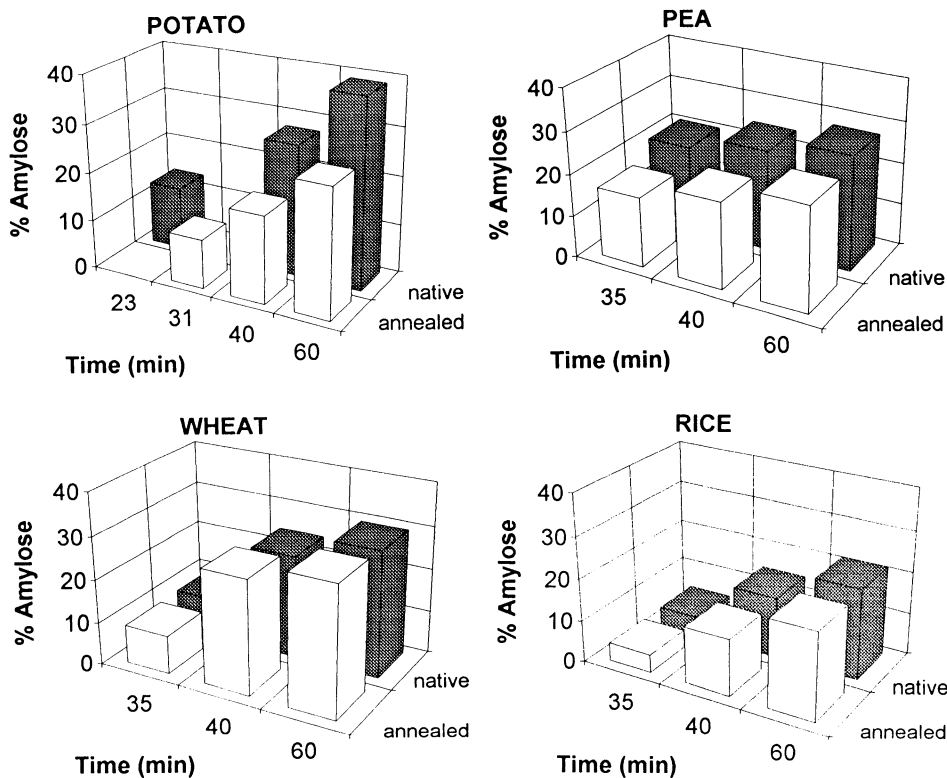One pasting property common to all the annealed starches we

Fig. 4. Amylose leaching for native and annealed starches. % Amylose = percentage of total starch.

examined (except for pea starch in the RVA) was increased viscosity upon cooling (Figs. 2 and 3, Table II). According to Loh (1992), the viscosity of the starch gel formed upon cooling is mainly determined by the amount and molecular weight of the amylose leached from the granules, but it seems likely that the remnants of the gelatinized granules also contributed to this viscosity. Indeed, a starch gel consists of a mixture of swollen gelatinized granules and molecularly dispersed macromolecules leached from the granules (Ring 1985). Amylose leaching did not increase after annealing for any of the examined starches, except wheat (Fig. 4, Table II); thus one can speculate that the remnants of the granules indeed contribute to viscosity. Annealing may make the swollen gelatinized granules or "ghosts" more rigid and resistant to shear, resulting in a higher viscosity on cooling.

Potato starch (B-type). The shift of the onset of viscosity development and the viscosity peak to a higher temperature, the decrease of the peak viscosity, and the increase of the viscosity upon cooling (measured with both the Brabender Viscoamylograph [Fig. 2] and the RVA [Fig. 3]) for annealed potato starch confirm results of Stute (1992) and Hoover and Vasanthan (1994). Stute (1992) ascribes these changes to the reduced swelling power of the annealed potato starch, which improves the shear stability, leaving more intact granules (ghosts) after heating. This then leads to a higher viscosity upon cooling. These changes would be the result of the modified coupling forces between the crystallites and the amorphous matrix (Stute 1992). Amylose leaching decreases for annealed potato starch (Fig. 4, Table II), which may indicate that the reduced peak viscosity of annealing may be caused not only by the reduced swelling power (Stute 1992) but also by the reduced amylose leaching (of course, the two latter phenomena could be related).

Pea starch (C-type). The increased viscosity for annealed pea

starch (Fig. 2) measured by the viscoamylograph can be ascribed to an increased resistance of the granules to heat and deformation resulting from an enforcement of the intragranular binding forces, rather than to an increased leaching of amylose, because annealing clearly reduces the solubilization of this macromolecule. Even if the swelling power is reduced as a result of annealing (Hoover and Vasanthan 1994), a viscosity increase during heating is still possible. Indeed, at the relatively high concentrations we used, starches with a low swelling power could produce a higher viscosity than starches with a high swelling power because at high concentrations the inherent deformability of the granules dominates the rheology of the system during heating (instead of the swelling power at low concentrations). One would expect starches with a low swelling power to have a much lower deformability, leading to a higher viscosity (Evans and Lips 1992).

The RVA results for pea starch (Fig. 3) were not consistent with the corresponding viscoamylograph results (Fig. 2). The viscosity determined with the RVA in the 95°C holding phase was practically unchanged, and the end viscosity decreased as a result of annealing. Therefore, we investigated some factors that could affect the viscoamylograph and RVA evaluation of the impact of annealing on starch pasting properties (unpublished data). Different evaluations of the annealing effect on pea starch pasting properties were caused mainly by the different heating and cooling rates applied in the different instruments, rather than by the different measuring geometry, sample size, or shear rate conditions. Furthermore, the annealed pea starch seemed to be more resistant to heating rate than was the native starch. Indeed, the maximum viscosity during heating of annealed pea starch was unchanged with increased heating rate; an increase of this viscosity was observed for native pea starch (unpublished data). This may explain the different evaluation of the annealing effect with the visco-
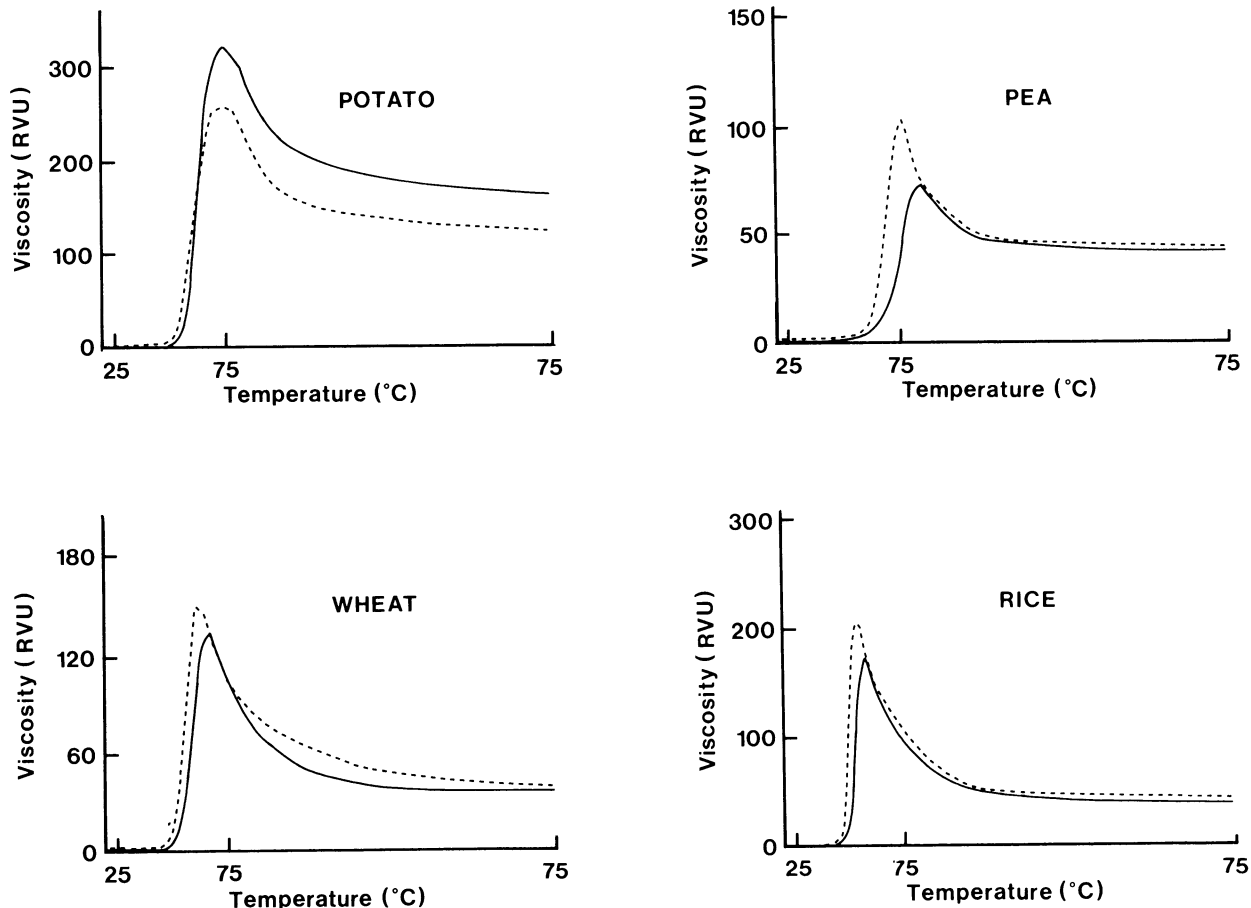

Fig. 5. Vicosity curves for native (——) and annealed (----) starches in a dimethyl sulfoxide (DMSO) and water mixture (92.5:7.5, w/w) measured with a Rapid Visco-Analyser. RVU = Rapid visco units. (Note differences in scale)

amylograph and the RVA.

Wheat and rice starches (A-type). The viscoamylograph pattern of annealed rice starch (Fig. 2) shows a slightly increased viscosity. The amylose leaching does not change for annealed rice starch (Fig. 4). Thus again, as for pea starch, the viscosity increase as a result of annealing cannot be related to an increased amylose leaching.

Annealed wheat starch showed an increase in viscosity during heating and cooling (Fig. 2, Table II). In contrast with the other starches, amylose leaching was slightly increased (Fig. 4, Table II) after annealing. This indicates that the slightly increased amylose leaching could partly account for the viscosity increase of wheat starch but does not rule out the possibility that increased resistance of the granules toward heat and shear may also have contributed to the viscosity increase. RVA results for wheat starch (Fig. 3) were consistent with viscoamylograph results (Fig. 2), although the more pronounced viscosity peak for wheat starch in the RVA profile was of interest. Previous experiments (unpublished data) indicated that this was probably caused by the higher shear rates in the RVA.

Viscosity Development in DMSO-Water

The viscosity development of starches in a 92.5:7.5 DMSO-water mixture (Cooreman et al, *in press*) was also studied with the RVA. The gelatinization mechanism of starch granules in DMSO-water is different from that in water alone. DMSO dissolves granular starches without appreciable swelling and without molecular degradation of the starch (Leach and Schoch 1962). Adding 5–15% water to DMSO enhances the rate of solution of the starch. The granules dissolve by surface erosion (potato starch) or by granule fragmentation (corn starch). Granules retain their polarization crosses during dissolution in DMSO (French 1984). No gelation or retrogradation upon cooling takes place in DMSO-water. Cooreman et al (*in press*) investigated the pasting properties of cross-linked maize starches in DMSO-water. The viscosity increase induced by cross-linking starches (as compared to the native starch) was ascribed to the reduced solubilization and the higher rigidity of the insolubles, while the contribution of the soluble fraction to the viscosity increase was considered minimal (Cooreman et al, *in press*).

Onset of viscosity development shifted to a lower temperature for annealed pea, wheat, and rice starches, which were characterized by a higher peak viscosity than their native counterparts (Fig. 5, Table II). In keeping with results by Cooreman et al (*in press*), the higher peak viscosity for annealed pea, wheat, and rice starches can be ascribed to a higher rigidity of the annealed starch granules. Thus, although the onset of solubilization occurs at a lower temperature after annealing, increased rigidity and resistance to shear lead to a higher viscosity peak during further heating. After prolonged heating of pea and wheat starch at 75°C, both the native and the annealed starch granules must be solubilized completely, or to the same degree, because end viscosity remained unchanged by annealing (Fig. 5). The slightly higher end viscosity of the annealed rice starch (Fig. 5, Table II) indicates an incomplete dissolution of the annealed rice starch granules. The decreased peak and end viscosities of annealed potato starch were more difficult to interpret.

CONCLUSIONS

While DSC results showed that, irrespective of starch crystal type, annealing consistently leads to increased endotherm temperatures and enthalpies, the changes in pasting properties as a result of annealing are not the same for all starches and are dependent on the measuring system (Brabender Viscoamylograph vs. RVA). Changes in amylose leaching behavior do not explain changes in viscosity curves. The viscosity changes (in water) are probably the result of an increased resistance of the starch granules toward heat and shear. One pasting property common to all annealed starches is increased viscosity upon cooling, which may be attributed to more rigid "ghosts" in the starch gels. In this respect, it would be very useful to study the dynamic rheological properties of these starch gels.

For all starches (except potato starch), the viscosity changes in DMSO-water may also be ascribed to an increased rigidity of the annealed starch granules. On the basis of our data, it is not possible to confirm or exclude one or more hypotheses formulated in the literature concerning the molecular mechanism of annealing. Introduction of other new techniques to investigate the annealing phenomena will be necessary.

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