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Origins of B-type crystallinity in glycerol-plasticised, compression-moulded potato starches☆

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Abstract

The amount of B-type crystallinity in compression-moulded, glycerol-plasticised potato starches was strongly dependent on both the properties of the potato starch used and the applied processing conditions. The presence of amylose and the morphology of the potato starch used, but also processing parameters such as moulding temperature and water content during moulding affected the amount of B-type crystallinity in the materials and thus the ultimate mechanical properties of the plasticised starches. This indicated that the direct relation between composition and physical properties of processed starches is not always valid; processing parameters are important tools for controlling the physical properties of processed starches as they influence the amount of B-type crystallinity in the material. It was shown that the total amount of B-type crystallinity in the glycerol-plasticised potato starches should be considered as a summation of residual amylopectin crystallinity and recrystallisation of both amylose and amylopectin, being strongly dependent on the applied processing conditions. In order to explain the observed amount of B-type crystallinity in these starches, partial (co-)crystallisation of both amylose and amylopectin should occur at high moulding temperatures. The measured mechanical properties of the plasticised potato starches correlated well with the amount of B-type crystallinity observed in the materials. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Potato starch; Amylopectin; Amylose; Glycerol; B-type crystallinity

1. Introduction

The development of fully biodegradable, starch-based plastics is often reported in scientific literature and patents (see, e.g. Doane, 1994; Röper & Koch, 1990; Tomka, 1990 and references herein). In these materials, a variety of mechanical properties can be seen depending on composition or processing parameters. Examples of parameters affecting the mechanical properties of plasticised starches are starch source (van Soest & Borger, 1997), the water content during processing (Hulleman, Janssen & Feil, 1998) and plasticiser content (Lourdin, Bizot & Colonna, 1997; van Soest & Knooren, 1997; Myllymäki, Eerikäinen, Suortti, Forssell, Linko & Poutanen, 1997). A disadvantage of starch-based plastics is their sensitivity towards water and ageing. Variation of the water content of the material as a function of changes in relative humidity leads to shifting of the glass–rubber transition temperature T_g (e.g. Bizot, Le Bail, Leroux, Davy, Roger & Buléon, 1997) or to crystallisation of amylose and amylopectin (Joupilla & Roos, 1997). These effects cause (uncontrollable) changes in the mechanical properties. As can be concluded from thermal analysis and from changes in the mechanical properties, ageing also occurs by free volume relaxation (Shogren, 1992; Thiewes & Steeneken, 1997 and crystallisation into the B-type lattice (van Soest & Knooren, 1997).

The impact of the formation of B-type crystallinity on the mechanical properties of glycerol-plasticised potato starch has been described (van Soest, Hulleman, de Wit & Vliegenthart, 1996). Similar to synthetic polymers, an increase in the amount of B-type crystallinity resulted in an increase of the *E*-modulus and a decrease of the strain at the break of the material. Although amylose is thought to be a major source of B-type crystallinity formed during recrystallisation, it was also shown that in amylopectin gels (Ring et al., 1987) and in glycerol-plasticised waxy maize starch containing solely amylopectin (van Soest, de Wit & Vliegenthart, 1996), B-type crystallinity could be formed,

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Table 1
Characteristics of the potato starches used throughout this study

Description	Coding	Crystallinity	x_c [a]	Granular	Amylose content (%)
Regular potato starch	R	B-type	0.59	+	ca. 20
Destructurised potato starch	D	Amorphous	0.00	−	ca. 20
Amylopectin potato starch	A	B-type	0.49	+	< 1

[a] B-type crystallinity index as depicted in Fig. 2. Accuracy of the values: ± 0.05.

indicating that amylopectin itself is able to recrystallise into the B-type lattice at certain conditions. In starch plastics, the influence of amylose on the crystalline structure and physical properties of maize starches was determined (van Soest & Borger, 1997). The authors concluded that in these starches, amylose and amylopectin were involved in (co-)crystallisation into the B-type lattice. Although the formation of B-type crystallinity in plasticised starches has been observed and reported, the exact origins of B-type crystallinity in low-moisture, high-temperature plasticised starches are still unclear.

As the mechanical properties of thermoplastic starches are determined by the amount of B-type crystallinity, it is crucial for the development of thermoplastic starches with known and controllable properties to be able to predict the ultimate amount of B-type crystallinity after processing. Molecular and morphological characteristics of the starch such as amylose content or starch source will influence the mechanical properties as a function of the amount of B-type crystallinity which is induced in the processed material. This amount of B-type crystallinity also seems to be dependent on several processing parameters, and therefore it is stated that the assumed direct relationship between composition and physical properties, such as mechanical performance, of plasticised starches is only partially valid. Without knowing the processing history, which will have a strong impact on the amount of B-type crystallinity, ultimate mechanical properties cannot be predicted. In order to test the above mentioned, the origins of B-type crystallinity in various glycerol-plasticised, compression-moulded potato starches will be analysed by following the changes in the amount of B-type crystallinity as a function of starch morphology, presence of amylose and processing parameters, such as temperature and water content during compression moulding. The behaviour of three potato starches (granular, regular potato starch (B-type semi-crystalline, approximately 20% amylose), amylopectin potato starch (B-type semi-crystalline, <1% amylose) and destructurised potato starch (amorphous, approximately 20% amylose) will be investigated for this purpose.

2. Experimental

2.1. Description of the potato starches

The starches used throughout this study were regular potato starch (coded R), amylopectin potato starch (Apriori; coded A) and destructurised potato starch (Flocgel LV-W; coded D). These potato starches differed in several

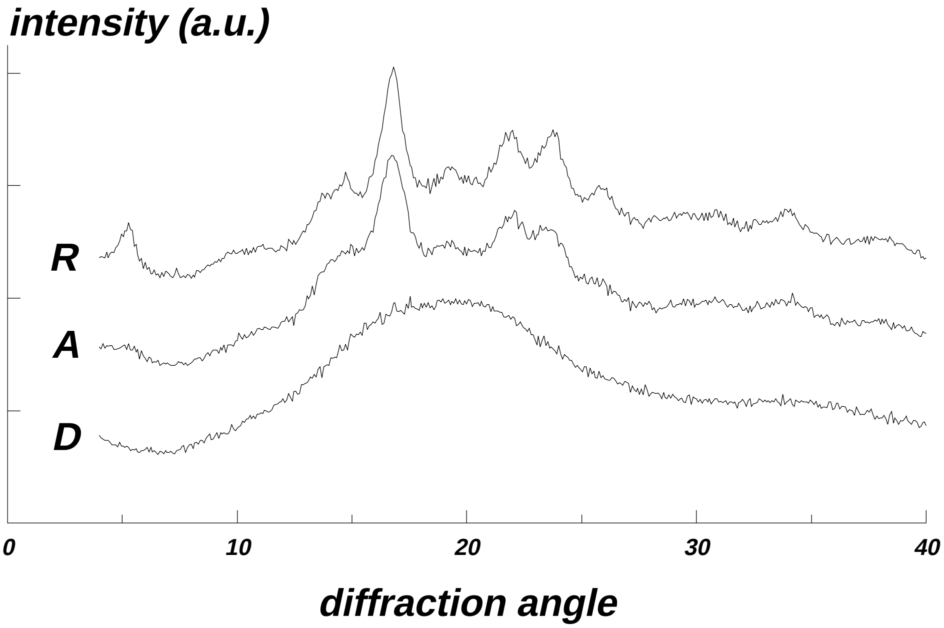

Fig. 1. WAXS-diffractograms of regular potato starch (R), amylopectin potato starch (A) and destructurised potato starch (D).

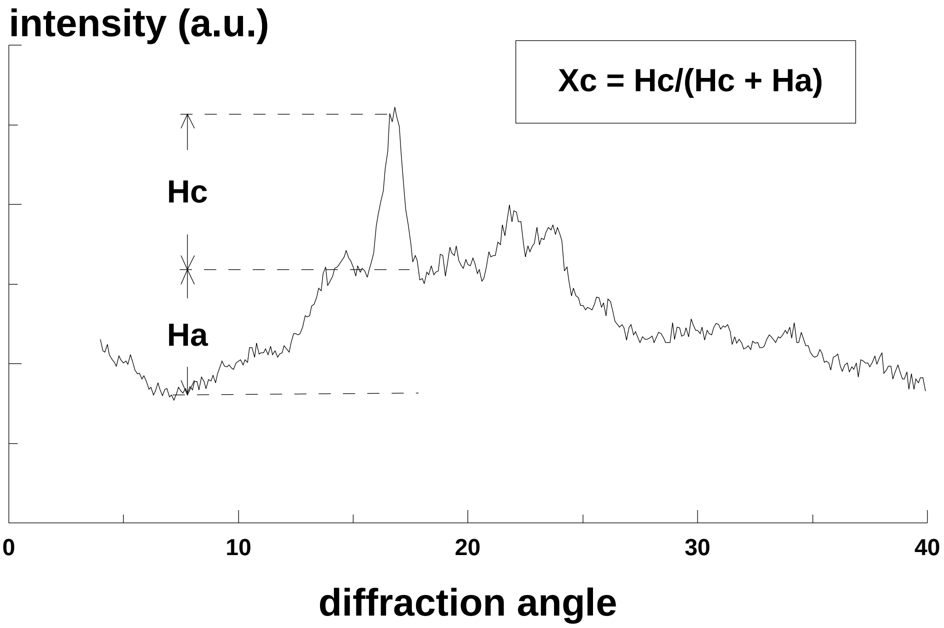

Fig. 2. Schematic description of the B-type crystallinity index x_c.

morphological and molecular aspects as listed in Table 1. A major difference between regular (R) and amylopectin (A) potato starch was the amylose content (respectively ≈ 20 and $< 1\%$ (w/w)). Both starches were granular with identical granule size distribution (data not shown), and semi-crystalline, showing a B-type organisation (crystallinity index $x_c \approx 0.59$ ($\pm$ 0.05) (R) and 0.49 ($\pm$ 0.05) (A); see Fig. 1). Destructurised potato starch (D) is a commercially available, cold-water soluble potato starch. Due to its pretreatment, the starch does not contain any residual granular structures and has lost all of its semi-crystalline organisation, leading to a coarse, amorphous product (see Fig. 1).

2.2. Preparation of starch–glycerol–water mixtures

The water contents of regular potato starch (Food Grade, AVEBE, Veendam, The Netherlands), amylopectin potato starch (Apriori; a gift from AVEBE, The Netherlands) and destructurised potato starch (Flocgel LV-W, AVEBE, Veendam, The Netherlands) were determined using a Sartorius MA40 infrared dryer by measuring the loss in weight after heating at 95°C for 4 min. Starch (dry matter) and glycerol (density 1.26 g ml^{-1}, Chemproha Chemical Distributors, The Netherlands) were mixed in the ratio 100:30 (w/w) for 20 min using a Bear Varimixer R40 (Woodshow & Co., Denmark). After equilibration for at least 24 h, the ratio of dry matter:glycerol:water in these premixes was varied between 100:30:11.2 and 100:30:40.0 (w/w/w) by adding precalculated volumes of water to these premixes. After adding water, these samples were mixed for 5 min using a Hobart N-50 mixer (Hobart, Canada). These mixtures were used for compression-moulding experiments at constant temperatures (160°C). For the experiments during which the moulding temperature was varied, the water content of the premixes was adjusted to a dry matter:-glycerol:water ratio of 100:30:30 (w/w/w). All premixes were equilibrated at least 24 h prior to compression moulding. The dry matter:water ratio, referred to as *W*, was calculated as $100 \times w_{\text{water}}/w_{\text{dry-starch}}$. In these experiments, *W* varied between 11.2 and 40.0. The value of *W* was limited to values lower than 40–45, as at higher *W* the materials were too weak to released from the mould undamaged. Premixes containing destructurised potato starch strongly aggregated on storing. These premixes were cryogenically milled directly before compression moulding.

2.3. Preparation of compression-moulded tensile bars

The starch–glycerol–water mixture (70 g) was applied to a mould (inner dimensions: 180 × 120 × 2 mm (l × w × h); outer dimensions: 300 × 350 mm). The sample was covered with PET-foil at both sides to facilitate mould release. The mould was placed in a hydraulic PHI press (City of Industry, California, USA). On the total surface of the mould, an initial pressure of 3–4 bar was applied. The mould was heated to 100°C at 10°C min^{-1}. At 100°C, the pressure was increased to 40 bar and the temperature was raised at 10°C min^{-1} to the set temperature. In the series wherein *W* was varied during compression moulding, the temperature was set at 160°C, which was maintained for 5 min. For the experiments in which the temperature was varied at constant *W*, the temperature was varied between 110°C and 190°C and maintained for 5 min. Subsequently, the mould was cooled to room temperature at 10–15°C min^{-1} and the mould content was released. The materials were equilibrated for 12–14 days at 20°C and 55% relative humidity

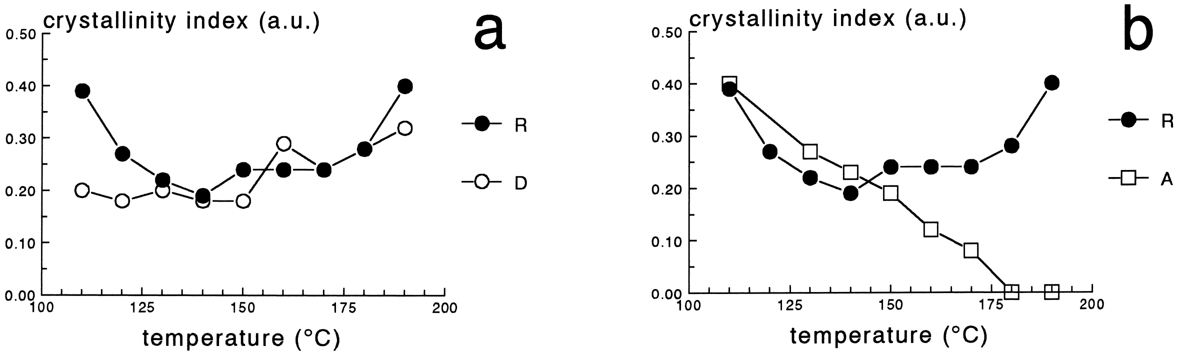

Fig. 3. B-type crystallinity index x_c versus moulding temperature for regular potato starch (R), amylopectin potato starch (A) and destructurised potato starch (D).

(r.h.). For several compositions, the produced sheets were directly frozen by immersion in liquid nitrogen, in order to analyse the crystal structures which were present directly after compression moulding.

2.4. Mechanical analysis

From the equilibrated compression-moulded plates, tensile bars were cut according to an adapted ISO1184-1983(E) method. Mechanical properties of the tensile bars were determined, at 20°C, on an INSTRON 4301 Universal Testing Machine, equipped with a load cell of 1 kN. Experiments were performed at a grip length of 60 mm and a cross-head speed of 10 mm min^{-1}. Strain at break (ϵ_b) was calculated relative towards a gauge length of 34 mm. Thickness of each tensile bar was measured in threefold before mechanical testing. Width of the tensile bars was 15 mm. For each material, 4–5 tensile bars were tested. After mechanical analysis, about 20 g of the material was placed in a KCH analytical mill A10 (Kinematica, Switzerland) and cooled by addition of small volumes of liquid nitrogen. The cooled sample was milled for 5–10 s and quickly transferred to a closed vessel to prevent water absorption.

2.5. Wide angle X-ray scattering

Diffractograms of powdered samples were recorded on a Philips diffractometer, at the settings as described in Hulleman et al. (1998). Based on the recorded diffractogram, a simple crystallinity index x_c was calculated (van Soest et al., 1996b).

Moisture determinations and polarised light microscopy were performed as described in Hulleman et al. (1998).

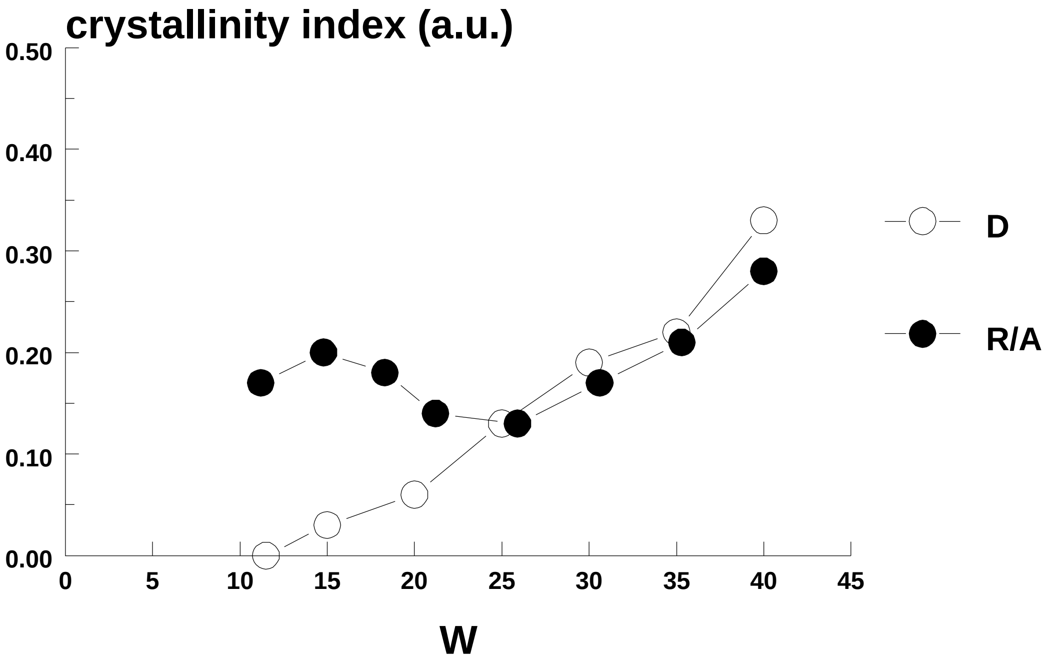

Fig. 4. B-type crystallinity index x_c versus W for regular potato starch (R), amylopectin potato starch (A) and destructurised potato starch (D).

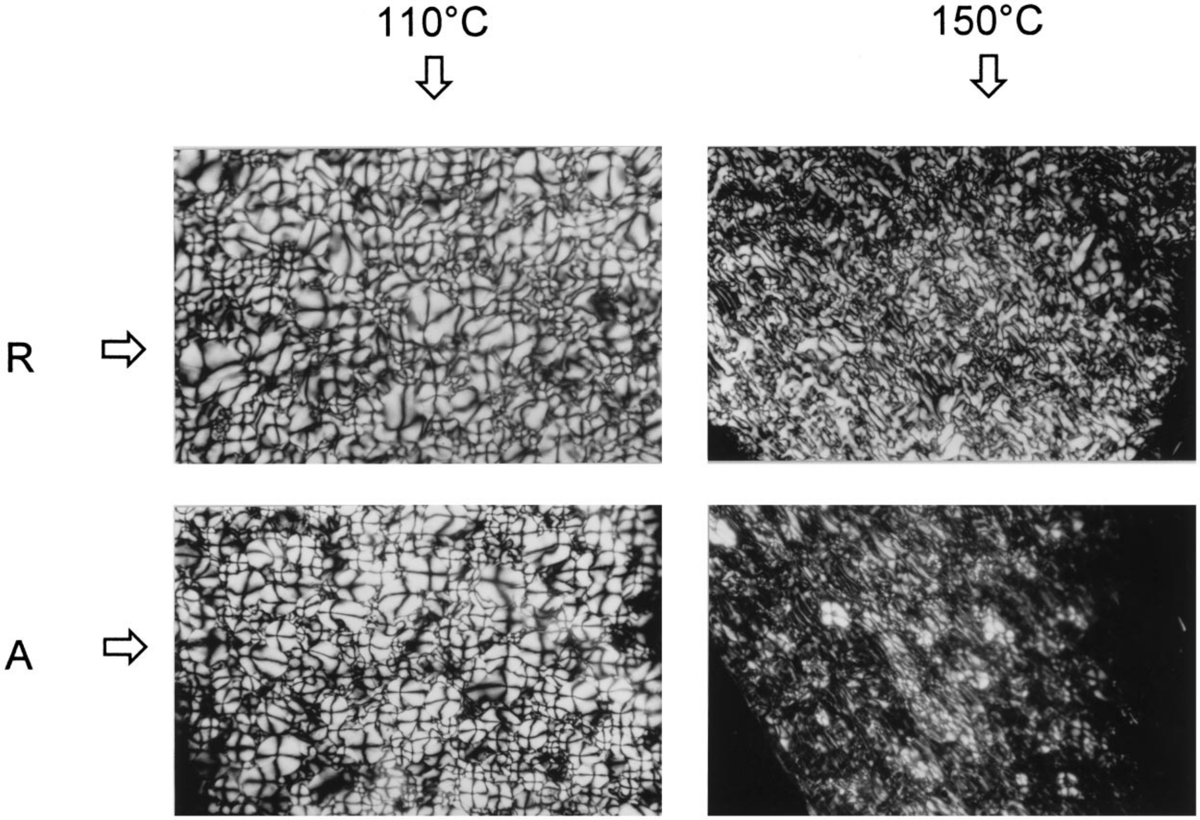

Fig. 5. Polarised light micrographs of regular potato (R) and amylopectin potato starch (A) at 110°C and 150°C.

3. Results and discussion

As the crystalline organisation of amylopectin in native, granular potato starches is of the B-type (see, e.g. Blanshard, 1987) and the lattice in which the starch polysaccharides recrystallised after or during processing was also of the B-type, the overall crystallinity in the plasticised potato starches could be represented using a simple B-type crystallinity index (x_c), as schematically depicted in Fig. 2.

3.1. B-type crystallinity in compression-moulded potato starches

When premixes, containing the potato starches R, D and A, glycerol and water in various ratios, were compression moulded and conditioned at 55% r.h. and 20°C for 2 weeks, translucent, relatively flexible plates were obtained with absolute water contents in the range of 11.0–13.0% (w/w). At these water contents, the T_g of the material is below room temperature (Hulleman et al., 1998; Lourdin, Coignard, Bizot & Colonna, 1997; Forssell, Mikkilä, Suortti, Seppälä & Poutanen, 1996). Although visually identical, the amount of B-type crystallinity in these materials, expressed as the B-type crystallinity index x_c was strongly dependent on the starch source (i.e. presence of native B-type crystallinity and amylose) as well as on the temperature and the water content during compression moulding (see also Hulleman et al., 1998). The crystallinity indices of all processed starches as a function of processing temperature and *W* are depicted in Figs. 3 and 4, respectively.

3.1.1. B-type crystallinity as a function of moulding temperature

3.1.1.1. Regular versus destructurised starch From Fig. 3(a), it is clear that the crystallinity index of moulded materials containing regular (R, ●) and destructurised (D, ○) potato starch only differed at relatively low moulding temperatures (below 130–140°C). Apparently, below these temperatures the melting of the semi-crystalline organisation of the native granule is incomplete. This is supported by DSC measurements (results not shown) in which the initial melting endotherm of the premixes containing regular potato starch:glycerol:water = 100:30:30 is found between ca. 84°C (T_{onset}) and 137°C ($T_{conclusion}$). As expected, the premix containing destructurised potato starch showed no melting endotherm. It is remarkable that materials containing destructurised potato starch contained B-type crystallinity, irrespective of the processing temperature. This meant that, even when starting from amorphous starch, recrystallisation of amylose and/or amylopectin into the B-type lattice occurred at all processing temperatures. For moulded regular potato starch, the total amount of B-type crystallinity at moulding temperatures below 130–140°C

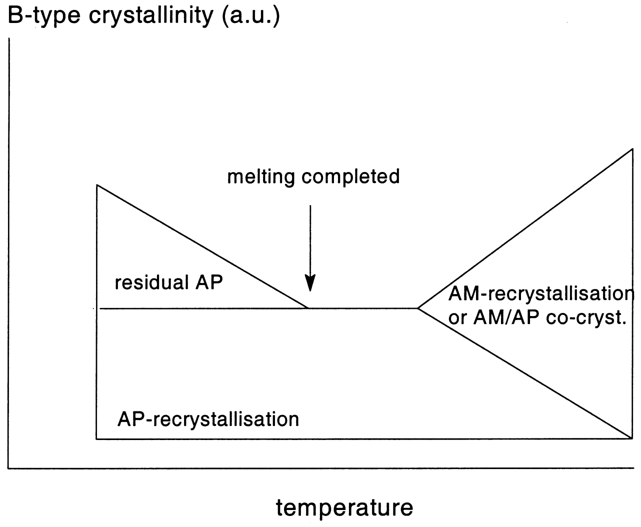

Fig. 6. Schematic description of the origin of B-type crystallinity in potato starches as a function of moulding temperature.

should be considered as a summation of residual crystallinity and recrystallisation, whereas above these temperatures only recrystallisation contributes to the total crystallinity. At moulding temperatures ≥ 160°C, both starches showed an increase in B-type crystallinity, originating from an increased level of recrystallisation into the B-type lattice.

Although melting in materials containing regular potato starch and amylopectin potato starch was completed at 130–140°C, as concluded from the DSC analyses on the premixes, residual birefringent structures were still observed up to moulding temperatures of 160°C. Examples of micrographs of regular and amylopectin potato starch, moulded at 110°C and 150°C, are shown in Fig. 5.

3.1.1.2. Regular versus amylopectin starch For regular (R) and amylopectin (A) potato starch, the crystallinity index x_c as a function of moulding temperature is depicted in Fig. 3(b). In contrast to regular potato starch, the B-type crystallinity index of amylopectin potato starch is gradually decreasing with increasing moulding temperature. Almost similar to regular potato starch, the melting endotherm of premixes containing amylopectin potato starch:glycerol:water = 100:30:30 is in the range 91–145°C (results not shown). Below 140°C, the amount of B-type crystallinity, like in regular potato starch, should be considered as a summation of residual amylopectin B-type crystallinity and recrystallisation into the B-type lattice. As for amylopectin potato starch, recrystallisation can only be attributed to recrystallisation of amylopectin, being also the major polysaccharide in regular and destructurised potato starch, it was assumed that for the potato starches used in this study, recrystallisation at relatively low moulding temperatures originates from recrystallisation of amylopectin.

Considering the identical crystallinities at low moulding temperatures ($T \leq 140$°C), the strong difference in B-type crystallinity at moulding temperatures higher than ≈ 150°C is remarkable. Above this temperature, melting was completed for both regular and amylopectin potato starch, as concluded from DSC experiments. Whereas regular potato starch showed an increased amount of B-type crystallinity at temperatures ≥ 150°C, amylopectin potato starch showed a gradually decreasing amount of B-type crystallinity with increasing moulding temperature, leading to completely amorphous materials when moulded at temperatures ≥ 180°C. Apparently, the presence of amylose strongly influences the formation of B-type crystallinity at moulding temperatures higher than 150°C. For this phenomenon, two mechanisms can be proposed: (i) recrystallisation of amylose: amylose, suggested to be in its amorphous state before processing (Blanshard, 1987), crystallises preferentially at higher moulding temperatures, whereas amylopectin is not able to recrystallise at these temperatures due to its lower crystallisation kinetics and mostly lower melting temperature (Miles, Morris & Ring, 1985; Ring et al., 1987) or (ii) amylose-induced recrystallisation of amylopectin by co-crystallising into the same B-type lattice (Mestres, Colonna & Buléon, 1988). This means that amylopectin itself is limited in its capacity to recrystallise when moulded at high temperatures. This could be due to an additional loss of order at the conformational level at higher temperatures such as the unfolding of (double) helical conformations to a truly amorphous, “chaotic” state, which limited nucleation. For both amylopectin potato starch and regular potato starch a (badly reproducible) endothermal transition was observed with an average onset temperature at 180–185°C and 165–170°C, respectively, which could be indicative of this transition. For

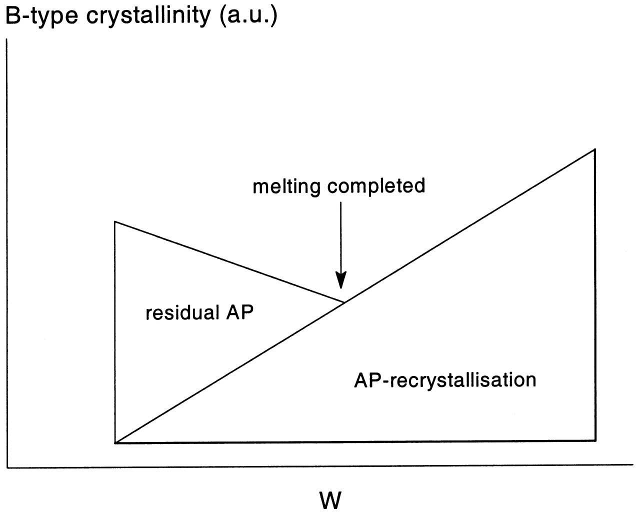

Fig. 7. Schematic description of the origin of B-type crystallinity in potato starches as a function of *W*.

amylose-containing regular starch, amylose could function at high temperatures as a nucleating polysaccharide for amylopectin, therewith inducing the formation of crystallinity.

One argument in favour of mechanism (ii) is the fact that the observed amount of B-type crystallinity in regular potato starch moulded at high temperatures (≥ 180°C; $x_c \geq 0.25$) cannot be attributed to amylose recrystallisation solely. Based on the amount of amylose available, being only 20% (w/w) of the polysaccharide fraction, part of the observed B-type crystallinity should originate from partial recrystallisation of amylopectin. As amylopectin potato starch does not recrystallise at higher moulding temperatures, the recrystallisation of amylopectin at higher temperatures is apparently mediated or initiated by the presence of amylose or the co-crystallisation with amylose. Based on the above mentioned arguments, a schematic description of the origins of B-type crystallinity in potato starches as a function of moulding temperature can be given, which is presented in Fig. 6.

3.1.2. B-type crystallinity as a function of W

In Fig. 4, the B-type crystallinity index as a function *W* is depicted. As mentioned in Section 2, *W* is a relative value indicating the water to dry potato starch ratio. Although only the B-type crystallinity index is shown, it should be mentioned that at low W ($W \leq 20$), small amounts of the so-called E_H-type crystallinity (Mercier, Charbonnierre, Grebault & de la Gueriviere, 1980) were observed. E_H-type crystallinity is attributed to the recrystallisation of amylose into a metastable, single-helical crystal structure (Mercier et al., 1980).

It is interesting that the B-type crystallinity index of regular potato starch and amylopectin potato starch showed a close to identical dependence on *W*. These starches are therefore depicted using a single marker. Apparently, when moulded at high *W*, the presence of amylose does not influence the recrystallisation into the B-type lattice and therefore amylopectin is thought to be the major polysaccharide recrystallising into the B-type lattice under these conditions. This supports mechanism (ii), which states that at relatively low moulding temperatures (160°C), amylopectin, although amorphous as determined by X-ray diffraction, is able to recrystallise or nucleate at the conformational, short range level it is still relatively ordered.

At $W \leq 25$, residual B-type crystallinity remained present in the materials containing regular and amylopectin potato starch, as could be concluded from the differences in B-type crystallinity index between regular and amylopectin potato starch and destructurised starch. Destructurised potato starch, being amorphous in the premix, remained amorphous when processed at low *W*, however, it showed a gradually increasing B-type crystallinity with increasing *W*. No differences between the three starches were observed at $W \geq 25$ (corresponding to a premix composition of starch:glycerol:water = 100:30: ≥ 25). At this *W*, melting of the premix containing regular or amylopectin potato starch is completed at 160°C, the temperature at which moulding was performed during these experiments. Besides observing residual B-type crystallinity at low *W*, originating from residual, crystalline amylopectin in the granule, recrystallisation (of presumably amylopectin) already started at low *W*, as concluded from the gradually increasing B-type crystallinity index for destructurised potato starch. Although in regular potato starch, amylose could co-crystallise at these conditions, it was concluded from the fact that the observed crystallinities of regular and amylopectin potato starch were identical, that most observed crystallinity at higher *W* originated from the recrystallisation of amylopectin. Based on the previous observations, the origins of B-type crystallinity as a function of *W* is schematically represented in Fig. 7.

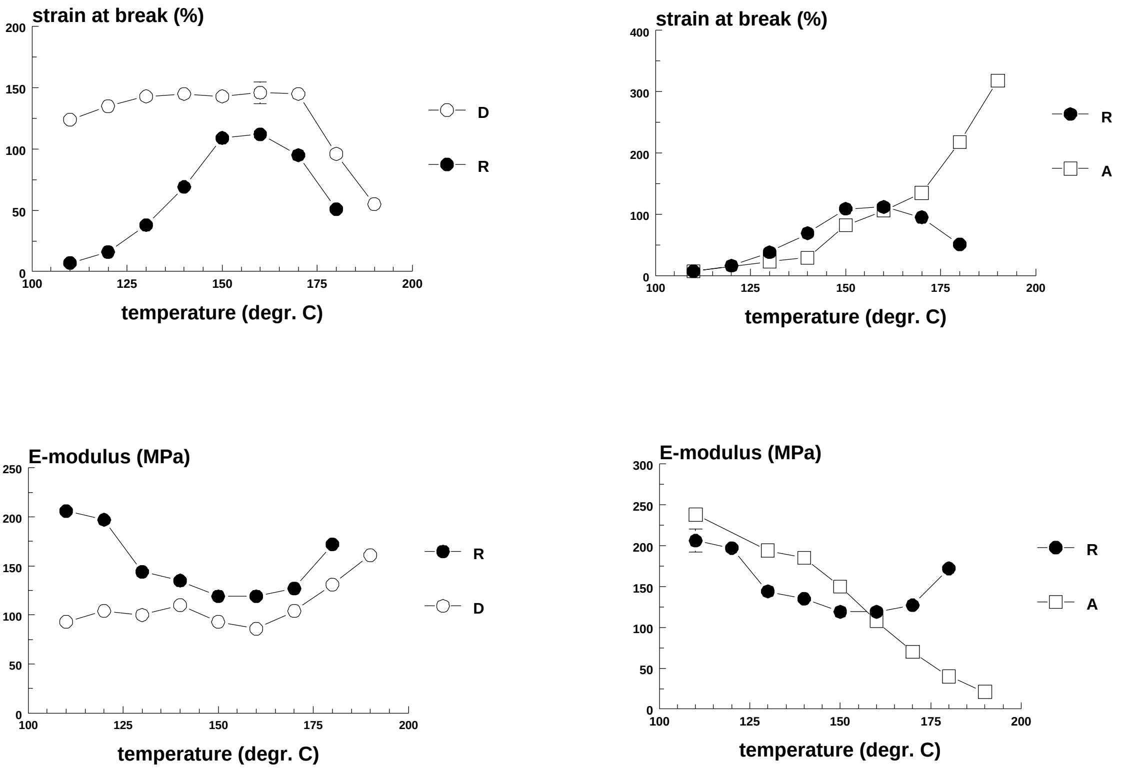

Fig. 8. *E*-modulus and strain at break as a function of moulding temperature for regular potato starch (R), amylopectin potato starch (A) and destructurised potato starch (D).

Although from the preceding experiments, insight is obtained in the origins of crystallinity, still little is known on the morphology of the crystalline zones in starches processed at low moisture contents and high temperatures. In potato starch granules, the crystalline zones are organised in repeating clusters of crystalline (approximately 60 Å) and amorphous zones (approximately 30 Å) (Cameron, 1992). It was observed during this study that even when melting was completed as determined with DSC and X-ray diffraction, still residual, non-birefringent and birefringent structures were present in the material (see Fig. 5). When still relatively fixed in this organisation due to low water contents, limited swelling and lack of shear stress, recrystallisation of the starch polysaccharides in this relatively fixed matrix could lead to revisualisation of these structures. This organisation will ultimately be lost at high moulding temperatures and other, lamellar, chain folded or spherulitic organisations will be formed, each morphology influencing the physical properties of the material. The strong macromolecular difference between amylose and amylopectin, will lead to a complex crystalline structure in the material (van Soest et al., 1996a).

3.2. Mechanical properties of the processed starches

The mechanical properties of compression-moulded starches are determined by the amount of B-type crystallinity in the material. Increasing the amount of B-type

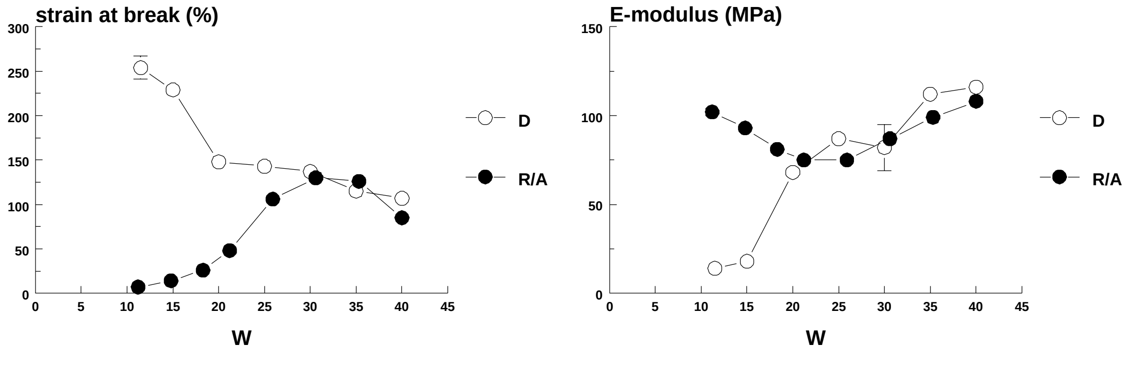

Fig. 9. *E*-modulus and strain at break as a function of *W* for regular potato starch (R), amylopectin potato starch (A) and destructurised potato starch (D).

crystallinity in glycerol-plasticised potato starches by conditioning at 90% relative humidity and 20°C followed by reconditioning, led to an expected increase in *E*-modulus and stress at break and a decrease in strain at break (van Soest et al., 1996a). These parameters are shown for all moulded starches as a function of moulding temperature and *W* in Figs. 8 and 9. When comparing the mechanical properties of the starches R, D and A with the variation of the B-type crystallinity index (Figs. 3 and 4), it can be concluded that for these starches a strong and expected correlation exists between the mechanical properties and the B-type crystallinity of the starches. As can be observed in Fig. 8, destructurised potato starch has a constant *E*-modulus ($\approx$ 100 MPa) and strain at break ($\approx$ 125–150%) at moulding temperatures lower than 170°C, associated with a constant B-type crystallinity. For regular potato starch, the *E*-modulus declined and strain at break increased with the moulding temperature increasing from 110°C to 150°C, which corresponds with the observed fall in overall B-type crystallinity, mainly caused by a more complete melting of the native crystallinity in the granule. For both starches, the *E*-modulus increased and strain at break decreased with increasing moulding temperature corresponding to the observed increase in B-type crystallinity. Comparison of regular and amylopectin potato starch leads to identical observations; for example for amylopectin potato starch, a gradual decrease in *E*-modulus and an increase in strain at break occurred with increasing moulding temperature, associated with an observed decrease in B-type crystallinity.

4. Conclusions

In this study, it was shown that the amount of B-type crystallinity is the major factor influencing the mechanical behaviour of compression-moulded, glycerol-plasticised potato starches. Differences in, e.g. molecular composition (amylose content) or morphology of the material (presence of native granular organisation) will influence the mechanical properties via the amount of B-type crystallinity present after processing. Also, by changing the processing parameters, such as temperature and water content during moulding it is possible to vary the amount of B-type crystallinity and therewith the properties of these materials.

It was shown that at low moulding temperatures, recrystallisation of amylopectin into the B-type lattice took place, irrespective of processing temperature. At low moulding temperatures, also residual B-type crystallinity originating from amylopectin was still present. At high moulding temperatures, the absence of amylose in amylopectin potato starch caused a reduced recrystallisation into the B-type lattice. Based on the results, a possible explanation for this behaviour was that at high moulding temperatures, amylopectin underwent an additional loss of order, which led to a limited recrystallisation in amylose-free amylopectin potato starch. Amylose, present in regular and destructurised potato starch, was able to recrystallise or to induce amylopectin recrystallisation at these conditions. As the observed amount of crystallinity could not be explained by solely amylose recrystallisation, (partial) co-crystallisation of amylose and amylopectin is probably occurring at high moulding temperatures. When melting was completed, as concluded from thermal analysis, still residual, birefringent granules were present in the materials moulded at relatively high temperatures suggesting the presence of a still high level of structural order within the granules.

When increasing the water content during moulding at 160°C, an identical increase in B-type crystallinity was observed for both regular and amylopectin potato starch, suggesting a major contribution of amylopectin to the overall crystallinity. At this temperature, amylopectin was able to recrystallise due to its still ordered state, as suggested above. Whereas at high water contents during moulding, probably mainly amylopectin recrystallisation took place, moulding at low water contents caused incomplete melting, leading to residual B-type crystallinity originating from amylopectin.

The measured mechanical properties of the plasticised potato starches correlated well with the amount of B-type crystallinity.

Acknowledgements

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