

Crystallinity in starch bioplastics

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Abstract

Thermoplastic starch (TPS) materials have been prepared by kneading, extrusion, compression moulding and injection moulding of several native starches with the addition of glycerol as a plasticizer. Two types of crystallinity can be distinguished in TPS directly after processing: (i) *residual crystallinity*: native A-, B- or C-type crystallinity caused by incomplete melting of starch during processing; (ii) *processing-induced crystallinity*: amylose V_H-, V_A- or E_H-type crystallinity which is formed during thermomechanical processing. The amount of residual crystallinity is related to processing conditions like processing temperature or applied shear stress. The composition of the mixture indirectly influences the amount of residual crystallinity. Lower amounts of glycerol cause a reduction in residual crystallinity. This effect is attributed to the increase in melt viscosity at decreasing plasticizer content, which causes an enhancement of shear stress on the melt. It has been concluded that composition and processing parameters are interrelated. Processing-induced crystallinity, also influenced by processing parameters, is caused by the fast recrystallization of amylose into single-helical structures. Increasing the screw speed during extrusion or increasing residence time during kneading causes an increase in single helical type crystallinity. The amount of crystallized amylose is proportional to the amount of amylose. The addition of complexing agents like calciumstearate or the presence of lysophospholipids cause the crystallization of amylose into these type of structures. In waxy starches, containing no amylose, obviously no V- or E-type crystallinity is formed.

Keywords: Thermoplastic starch; Crystal structure; Processing; Amylose

1. Introduction

A growing interest exists in non-food applications of starch. Especially thermoplastic starch (TPS) which can be used as bioplastics are under investigation. The mechanical properties of TPS bioplastics must be similar to the properties of commodity plastics like polyethylene and polypropylene, to be able to replace commodity plastics. As with synthetic polymers, the mechanical properties of TPS depend

on the crystallinity of the constituting polymers (Lai and Kokini, 1991; Van Soest et al., 1995b).

Native starches are biosynthetically assembled as semi-crystalline granules. The type of native, crystalline structure, labelled as A-, B- or C-type, depends on starch source. To obtain a TPS material, granular starch is thermomechanically processed by kneading, extrusion, injection moulding, compression moulding or blow moulding with the aid of plasticizers such as water, glycerol or urea and additives such as lecithin or monoglycerides. During processing of native starches, the semicrystalline

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structure, as present in the granule, is melted and the granular supramolecular structure is completely or partially destroyed as can be observed with differential scanning calorimetry (DSC), X-ray diffraction (XRD) and polarised light microscopy (PM). Depending on processing conditions and storage conditions, such as temperature and relative humidity, the amorphous starch blend of amylose and amylopectin recrystallizes into several crystal structures. A-, B- and C-type crystallinity and several V-type structures have been reported for low and medium moisture starch food products such as cakes, bread and several extrusion cooked starch products (Chinnaswamy et al., 1989; Eliasson, 1994; Riisom et al., 1984).

Native A- and B-type crystal lattices consist of double helical, six-fold structures. The difference between A- and B-type crystallinity is the packing density of the double helices in the unit cell (Imberty et al., 1991). The B-type structure is described as a more loosely packed hexagonal assembly of the helices with a column of water molecules present in the centre of the hexagonal arrangement, whereas in the A-type structure, this column of water is replaced by a double helix. The C-type structure is thought to be an intermediate structure of the A- and B-type.

Several V-type structures have been characterized (Winter and Sarko, 1974a, b; Yamashita and Hirai, 1966; Yamashita and Monobe, 1971; Zobel, 1968). In general, these crystalline complexes of amylose are prepared by the addition of a complexing agent to a (metastable) solution of amylose, which is followed by precipitation of the complex. In the crystalline precipitate, formed with a broad range of hydrophobic and hydrophilic components, amylose adopts a left-handed, single helical conformation (Gidley and Bociek, 1988; Veregin et al., 1987; Winter and Sarko, 1974a, b; Yamashita and Hirai, 1966; Yamashita and Monobe, 1971; Zobel, 1968). Compared to the double helical A- and B-type lattices, the V-type lattice has a relatively large cavity, which is thought to contain the complexing compound. Depending on the origin of the complexing agent and the crystallization medium, crystalline structures with different numbers of glucose residues per turn have been reported (Gidley and Bociek, 1988; Helbert and Chanzy, 1994; Rutschmann and Solms, 1990; Yamashita and Hirai, 1966; Yamashita and Monobe, 1971). Besides the variation in number

of glucose residues per turn, the structures also differ in the packing mode of the single helices in the unit cell (Helbert and Chanzy, 1994).

Several granular starches have been shown to contain significant amounts of free fatty acids or monoglycerides (Biliaderis and Seneviratne, 1990a, b; Kugiyama and Donovan, 1981; Kugiyama et al., 1980; Sievert and Holms, 1993). By means of XRD no long range order is observed, although by solid-state NMR spectroscopy the presence of a single helical conformation of amylose and the occurrence of a fatty acid methylene resonance are evident (Morisson et al., 1993a, c). This suggests a rather imperfect lattice organisation of the amylose complexes in the granule. Extrusion cooking of manioc starch in the presence of fatty acids, caused the formation of two amylose crystal structures with long range order (Mercier et al., 1980). The single helical structure, stable at low moisture content, denoted as E_H , is shown to transform into the V_H form by increasing water content of the sample. The relative abundance of both type of structures is affected by extrusion temperature (Mercier, 1989). Differences between the two morphologies are found in arrangement of the single helices in the crystal lattice.

For the preparation of TPS bioplastics, glycerol is used as a plasticizer. Little attention has been given to the formation of crystalline structures in glycerol-containing, low moisture, TPS materials. The purpose of this work is to identify the various crystal structures by structural analysis of glycerol-containing TPS, with differences in composition, processing and thermal history. After identification, the type and amount of structure will be related to processing parameters and composition.

2. Experimental

2.1. Materials

Potato starch and potato starch amylose-V were obtained from Avebe (Foxhol, The Netherlands). Waxy corn starch was obtained from Cerestar Gruppo Ferruzzi (Volvoorde, Belgium). Wheat starch was obtained from Doittau Amidon Haussy, Avebe. Rice starch was obtained from Remy Industries (Wigmaal-Leuven, Belgium) and corn starch from Amylum (Aalst, Belgium). Corn starch amylose (C-

AM) and amylopectin (C-AP) (practical grade) were obtained from Sigma (Bornem, Belgium).

2.2. Processing

Kneading and extrusion. TPS was prepared by kneading or extruding of the various starches using a Haake Rheocord 90 system equipped with a mixer or a laboratory-scale extruder. Other extruders used, are the Clextral BC45 and the Extruco TSE76. Prior to extrusion the starches were mixed with water, glycerol and additives, such as lecithin or glycerol monostearate. The following extrusion parameters were varied: back-pressure, torque, screw rotation speed and temperature profile along the extruder barrel. Kneading times and screw speeds are 10 min and 50 rpm, respectively, unless mentioned otherwise.

Compression moulding. Starches (45 g) premixed with the additives were processed in a PHI press (City of Industry). The mould consisted of five stainless steel plates with the dimensions 30×35 cm. The middle plate had a rectangular hole with the dimensions $100 \times 150 \times 2$ mm. To facilitate mould release, the sample was covered at both sides with PET foil. An initial pressure of 4000 kg was applied on the mould. The mould was heated to 100°C and the pressure was increased to 40 tonnes, after which the temperature was increased to 100 – 200°C at a rate of $10^\circ\text{C}/\text{min}$. The curing time was 5 min. The mould was cooled to room temperature at a rate of 10 – $15^\circ\text{C}/\text{min}$ and the materials were released from the mould.

Injection moulding. Premixes or TPS granulates were injection moulded using a DEMAG D60 NCI-IK. The following parameters were adjusted for the various compositions: temperature profiles, screw-speed, pressure, cycle-time, cooling-time, mould-temperature.

2.3. Instrumental analysis

X-ray diffraction. Samples were measured with a Philips PC-APD diffractometer (Model PW 3710) equipped with an Anton Paar TTK temperature chamber. Diffractograms were recorded in the reflection mode in the angular range 4 – 40° (2θ). The

CuK_α -radiation (1.542 \AA), generated at 40 kV and 50 mA, was monochromatized using a $15 \mu\text{m}$ Ni filter. The diffractometer was equipped with a 1° divergence slit, a 15 mm beam mask, a 0.2 mm receiving slit, and a 1° scatter slit. Radiation was detected using a proportional detector. Diffractograms were recorded from powders or intact tensile bars using a multipurpose sample stage. Diffractograms were smoothed (Savitsky-Golay, polynome: 2, points: 15) and baseline corrected by drawing a horizontal line through the valley in the diffractogram at 7° (2θ). The height (H_c at a specific diffraction maximum) or the area (A_c) of the crystalline diffraction was measured relative to the height (H_t) or area of the total diffraction (A_t) of the peak measured from the baseline.

Differential scanning calorimetry. Measurements were performed with a Perkin-Elmer DSC-7. Calibration was done with Indium ($\Delta H_{\text{fusion}} = 28.59 \text{ J/g}$, melting point ($T_{\text{onset}} = 156.60^\circ\text{C}$) and gallium ($\Delta H_{\text{fusion}} = 79.91 \text{ J/g}$, melting point ($T_{\text{onset}} = 29.78^\circ\text{C}$). An empty pan was used as a reference. Samples were weighed accurately into stainless steel pans and sealed hermetically. For obtaining the melting profile, samples of 30–40 mg were heated from 20 to 200°C at a rate of $10^\circ\text{C}/\text{min}$.

2.4. Preparation of highly crystalline single helical-type reference compounds

Potato starch amylose (6.0 g) was heated to 50°C in 100 ml dimethylsulfoxide until all amylose was dissolved and glycerol monostearate (600 mg) dissolved in 10 ml dimethylsulfoxide was added to the solution. The total mixture was heated to 90°C , 250 ml water of 90°C was added and the solution was kept at 90°C for 6 h. The solution was cooled to room temperature and the white precipitate was centrifuged off and washed three times with 500 ml ethanol/water 60/40 (v/v) with intermediate centrifugation. The white powder was dried at ambient conditions. The formed V_H -type structure was converted into the V_A -type by storage for two weeks in methanol. The dry $V_{\text{isopropanol}}$ -type structure was prepared by dissolving 3 g amylose-V in 300 ml 1 M sodium hydroxide, neutralizing with concentrated hydrochloric acid to pH 7 followed by heating to

80°C. Isopropanol (500 ml) was added to the hot solution and slowly cooled to 50°C. The precipitate was washed with 50 ml isopropanol and dried at 45°C in vacuo for three days and at 100°C for 1.5 h.

3. Results and discussion

3.1. Identification of crystalline structures in TPS

3.1.1. Identification of residual crystallinity

Residual A- and B-type crystallinity is observed in TPS dependent on the native crystal structure. These structures occur when the energy input is too low during processing to completely melt the native crystals as discussed below. For C-type crystallinity (pea starch) the same phenomenon is expected to occur, although no experiments have been performed with this starch type. The main reflections as measured in native starch of the A-, B- and C-type structure are summarized in Table 1.

Table 1
The crystallographic parameters of A-, B- and C-type crystals

Type	Angle ($^{\circ}$, 2θ)	d -Value (\AA)	Intensity ^a
A-waxy corn	14.8	6.00	s
	16.6	5.35	vs
	17.7	5.01	s
	22.6	3.92	vs
	26.3	3.39	w
	30.1	2.96	m
	33.2	2.70	w
B-potato	5.5	16.2	m
	10.8	8.17	m
	14.8	5.99	s
	17.0	5.21	vs
	19.3	4.60	s
	22.1	4.03	vs
	23.8	3.74	s
	26.1	3.42	w
	30.9	2.90	w
34.0	2.64	m	
C-pea	14.8	5.98	s
	16.8	5.29	vs
	17.6	5.03	m
	22.6	3.93	s
	30.2	2.96	w
	33.5	2.67	w

^a s = strong; m = medium; w = weak; v = very.

Table 2

The crystallographic parameters of V_H -type crystals

Angle ($^{\circ}$, 2θ)			d -Value (\AA)	Intensity ^a
Prepared from solution	TPS extrusion	Literature	Literature	Literature
7.2	7.1	7.5	11.8	s
		13.0	6.8	vs
12.7	12.6	13.3	6.5	s
		14.9	5.9	w
16.7		17.0	5.2	m
18.3		18.8	4.7	m
19.5	19.4	19.8	4.5	vs
22.1	22.1	22.2	4.0	m
		22.6	3.9	m
24.9		25.2	3.5	m
		28.8	3.1	w

^a s = strong; m = medium; w = weak; v = very.

3.1.2. Identification of processing-induced crystallinity

By XRD, three crystal structures of the single helical amylose type have been observed in the TPS materials depending on processing conditions and composition as discussed later. This is shown in Fig. 1a. The structures are identified as single-helical amylose crystals denoted in literature as V_A , V_H and E_H by comparison of the diffraction data of the TPS materials with literature and diffraction data of the prepared reference compounds. The diffractograms of the reference compounds are shown in Fig. 1b.

The diffraction parameters of the most frequently observed structure are summarized in Table 2. The crystal lattice, denoted as V_H , has a 6-fold left-handed helix in an orthorhombic unit cell with the dimensions: $a = 13.65$, $b = 23.70$ and $c = 8.05$ \AA (space group $P2_12_12_1$) (Rappenecker and Zugenmaier, 1981; Zobel et al., 1967) or in a hexagonal unit cell with the dimensions: $a = b = 13.65$ and $c = 8.05$ \AA (space group $P6_522$) (Brisson et al., 1991). The deviations of the parameters of the complex prepared from the solution and the complex found in the bioplastics from the parameters as given in literature are probably caused by differences in hydration of the unit cell. The presence of a complexing agent inside the helix has not yet unambiguously been proven.

A second diffraction pattern observed in TPS materials is assigned to the V_A structure. The diffraction

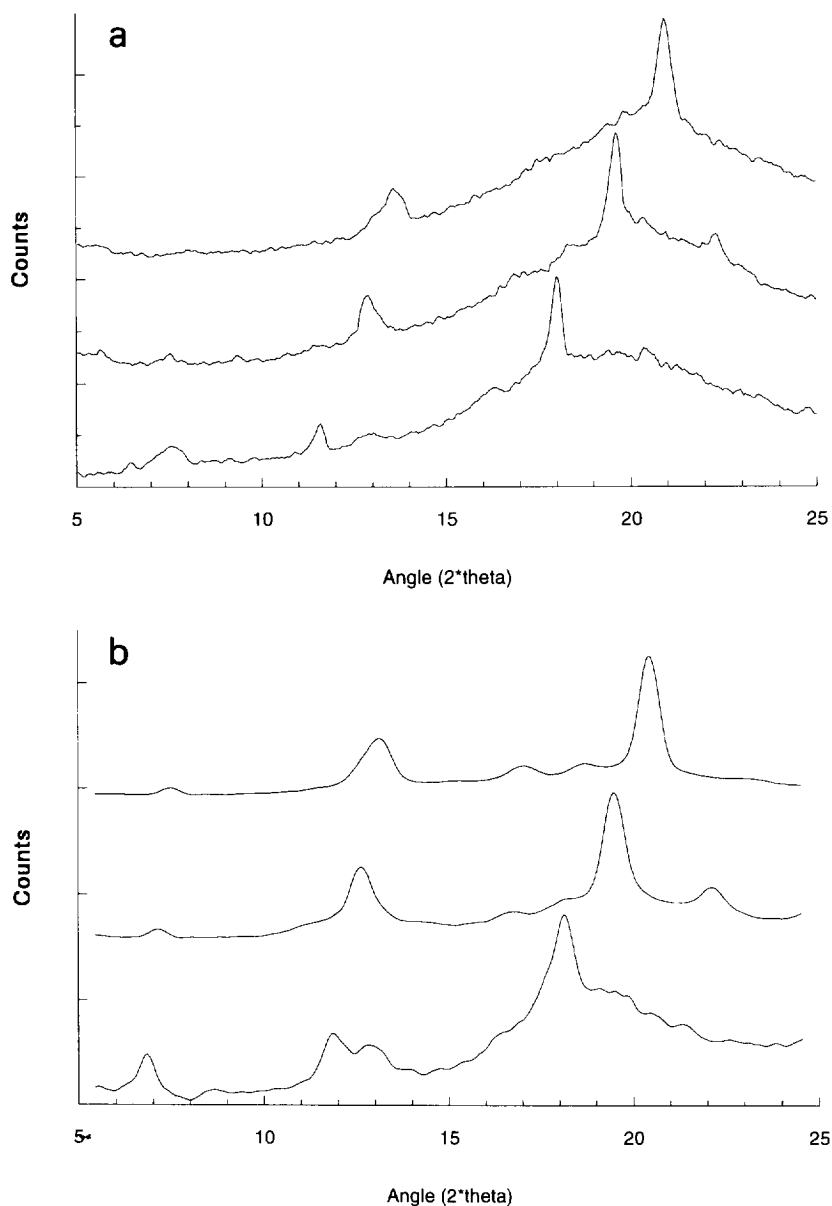


Fig. 1. The diffractograms of the three V-type structures, E_H , V_H , and V_A (from bottom to top) in thermoplastic starch (a) and crystallized from solution (b).

parameters of this structure are summarized in Table 3. Its lattice is indexed as an orthorhombic unit cell with the dimensions: $a = 13.0$, $b = 22.5$ and $c = 7.9$ Å (space group $P2_12_12_1$) (Winter and Sarko, 1974a,b). These unit cell parameters are based on fibre XRD patterns. The V_A lattice has more contracted amylose helices and contains less water than the V_H lattice.

Intermediate forms between the hydrated lattice V_H and the anhydrous lattice V_A are known, probably caused by differences in hydration of the unit cell (Zobel et al., 1967).

The third observed amylose single helical structure is identified as the E_H structure (Mercier et al., 1980) and the diffraction parameters are summarized

Table 3
The crystallographic parameters of the V_A type crystals

Angle (°, 2θ)		d-Value (Å)		Intensity ^a
Prepared from solution	TPS (injection moulding)	Literature	Literature	Literature
7.8	7.4	7.9	11.2	s
		13.4	6.6	vs
13.5	13.2	13.6	6.4	vs
15.7		15.8	5.6	m
17.5				m
19.4		19.4	4.6	m
20.9	20.6	20.8	4.3	vs
26.3		26.3	3.4	w

^a s = strong; m = medium; w = weak; v = very.

in Table 4. In the dry form, the lattice has been described as a 7-fold single helix in a hexagonal unit cell with the dimensions $a = b = 14.7$ Å (Yamashita and Monobe, 1971). In its wet form, the lattice has recently been described as a six-folded helix in an orthorhombic unit cell with the dimensions: $a = 28.3$, $b = 29.3$ and $c = 8.0$ Å (Buléon et al., 1990). The crystal structure is formed in the presence of bulky complexing agents like isopropanol, acetone or tert-butanol. Crystallites described by Yamashita and Monobe (1971) have larger peak widths than the crystalline structures found in the processed bioplastics from which it can be concluded that the TPS crystallites have significantly larger dimensions.

3.2. Influence of processing parameters and composition

3.2.1. Residual crystallinity

(1) Processing parameters — *Temperature*: In Fig. 2, two typical examples are shown of the occurrence of residual crystallinity in kneaded potato starch at temperatures of 90 and 116°C and in extruded potato starch at temperatures of 90 and 140°C. At the lower temperatures, some residual crystallinity is observed after processing. After processing at the high temperatures, the materials do not contain any residual crystallinity though some E_H-type crystallinity is observed due to crystallization of amylose. The observed residual crystallinity is of the B-type for the potato starch materials but this is obviously related to the crystalline structure in the native source.

Table 4
The crystallographic parameters of E_H-type crystals

Angle (°, 2θ)		d-Value (Å)		Intensity ^a
Prepared from solution	TPS (extrusion/kneading)	Literature	Literature	Literature
6.8	6.6/ 7.1	6.9	12.8	m
11.8	11.6/12.0	12.0	7.4	m
12.8				m
18.0	18.0/18.4	18.4	4.8	s
24.9				w

^a s = strong; m = medium; w = weak; v = very.

Shear stress: By comparison of the XRD patterns of compression moulded materials with extruded materials, it is shown that complete melting of the granular crystals takes place at lower temperatures or shorter time scales during extrusion. An increase in shear seems to facilitate the melting of the granular crystallinity indirectly by a local increase in temperature and by increasing the accessibility of the plasticizers to the granular starch resulting from an increased breakdown of the granules. The screw speed during extrusion is related to the applied shear stress although residence time decreases. At low plasticizer content, the shear energy applied has been shown to control the breakdown of the granular structure (Lai and Kokini, 1991).

(2) Composition — The melting of the granular crystallinity is related to glycerol and water content as determined by DSC measurements (Van Soest et al., 1995a). How plasticizer content affects the processing of starch under shear stress conditions still is subject of investigation.

3.2.2. Processing-induced crystallization

(1) Processing parameters — *Residence time*: The influence of the residence time on the formation of E_H-type crystallinity is shown in Fig. 3a for kneading of potato starch–glycerol–water mixtures. The material is amorphous after kneading for 1 min at 130°C. An increase in residence time leads to a increase in the amount of E_H-type crystallinity. A possible reason for the increase in crystallinity with increasing residence time is the increase in the amount of applied shear and the degree of disruption of the starch granule with increasing residence time. The

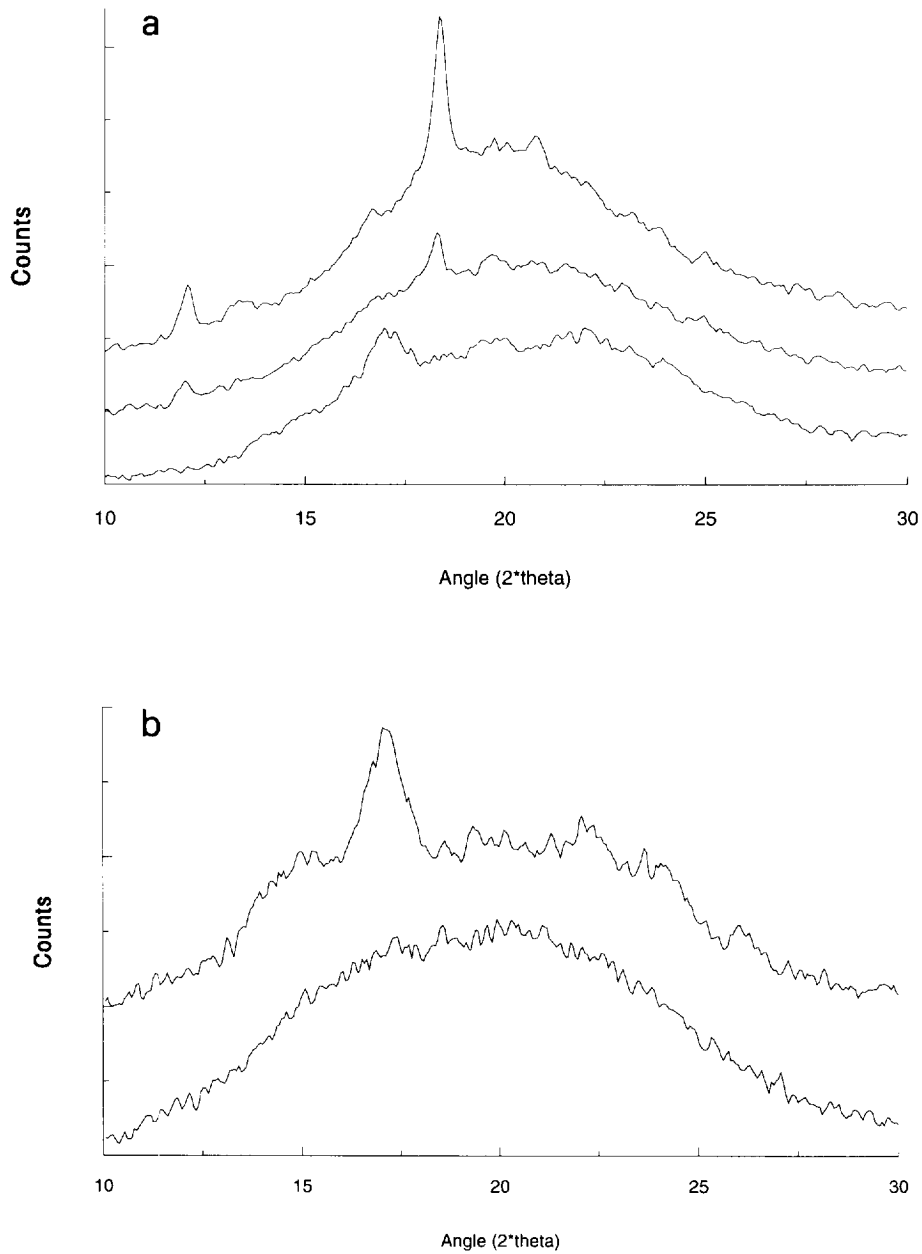


Fig. 2. Diffractograms of thermoplastic starch after processing of potato starch by kneading (top) and by extrusion (bottom). Kneading was performed at a starch–water–glycerol ratio of 100:32:32 (w/w) and at 90, 116 and 130°C (bottom to top). Extrusion was performed at a starch–water–glycerol ratio of 100:21:30 (w/w) and at 90 and 140°C (bottom to top).

shear stress, combined with the liberation of amylose by the disruption of the granular structure, yields an amorphous polymer melt with possibly highly stretched amylose. This orientation can induce

the formation of amylose crystallinity after cooling.

Screw speed: An increase in screw speed leads to an increase in the formation of single helical

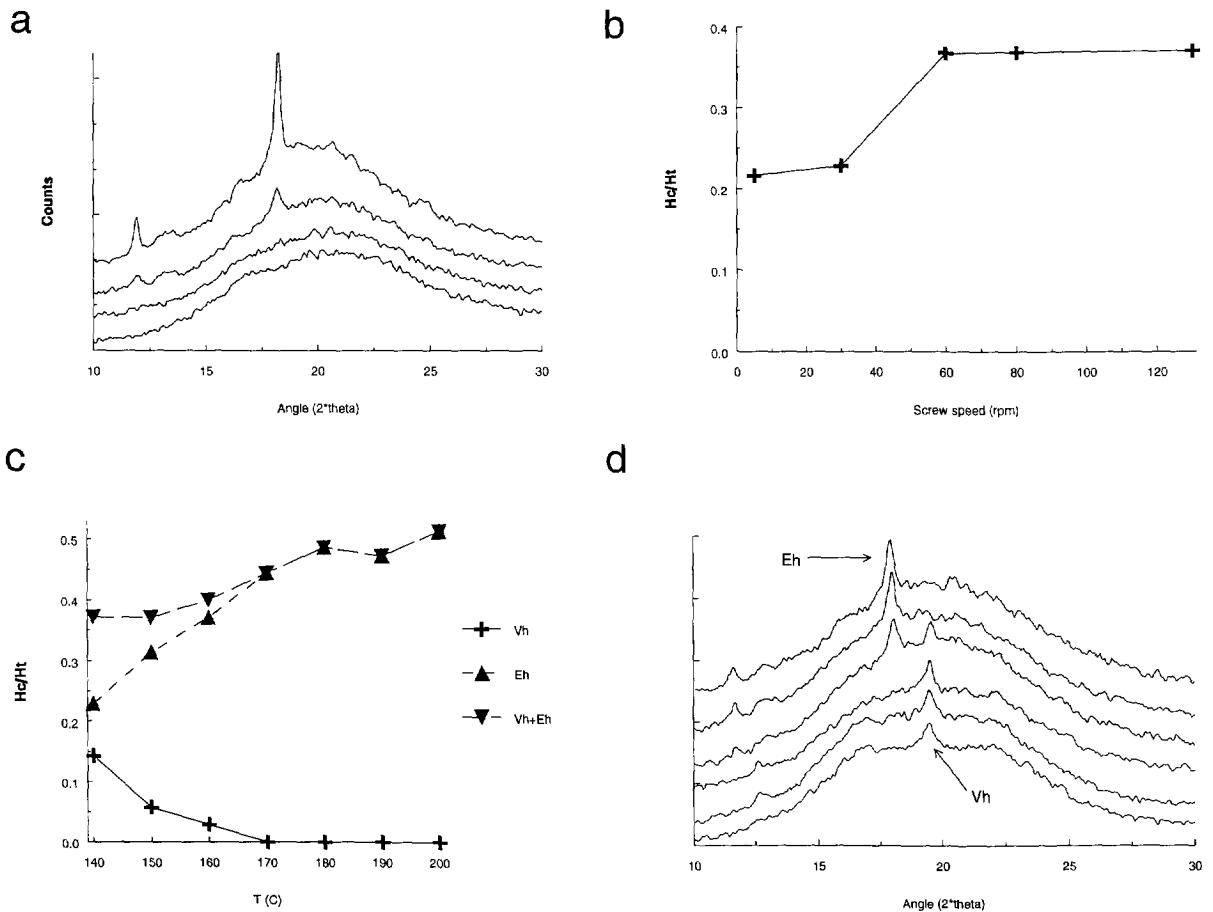


Fig. 3. The influence of processing parameters. (a) The influence of kneading time during the kneading of a potato starch–water–glycerol mixture (100:52:40 (w/w)) at 130°C. (b) The influence of screw speed during extrusion of potato starch on the amount of V_H -type crystallinity. The composition was starch–water–glycerol–lecithin–calciumstearate with a ratio of 100:22:20:3:4 (w/w). (c) The influence of melt temperature during extrusion of potato starch on the amount of V-type crystallinity. The composition was starch–water–glycerol–lecithin–calciumstearate with a ratio of 100:22:20:2:7 (w/w). (d) The diffractograms of thermoplastic starch after pressure moulding of extruded potato starch at various temperatures. The composition of the pre-extruded material was starch–water–glycerol–lecithin with a ratio of 100:22:16:3 (w/w).

amylose type crystallinity as shown in Fig. 3b for extruded materials. A variation in screw speed probably affects the amount of applied shear stress on the material resulting in a variation in single helical amylose type crystallinity.

Processing temperature: Typical examples of the influence of processing temperature on the formation of type of crystal structure and of crystallinity are shown for kneading (Fig. 2a) and compression moulding (Fig. 3d). The relation between processing temperature and amount of single helical type crystallinity is exhibited in Fig. 2a. With increasing

temperature, an increase in E_H -type crystallinity is observed, due to the liberation of amylose resulting from the increased disruption of the granular structure at higher processing temperatures. In Fig. 3d it is also shown that two types of structures are formed dependent on processing temperature. Below 180°C, the V_H structure is formed, whereas above this temperature the E_H structure is favoured.

(2) **Composition — Starch source:** Several starches from different sources have been processed with techniques such as extrusion and compression moulding. The formation of the various amylose

Table 5

The influence of starch source on the formation of amylose crystallinity. Extrusion and compression moulding have been performed with a starch to glycerol ratio of 100 to 30. The water content has been in the range of 10 to 15% (w/w) for extrusion and 10 to 35% (w/w) for compression moulding

Source	Extrusion	Compression moulding
Waxy corn	no V-type	no V-type
Amylopectin (C-AP)	no V-type	^a
Potato	E _H , V _H	E _H , V _H
Corn	E _H , V _H	E _H , V _H
Rice	V _H , V _A	^a
Wheat	E _H , V _H	E _H , V _H
Corn amylose (C-AM)	V _H , V _A	E _H , V _H

^a Not processed.

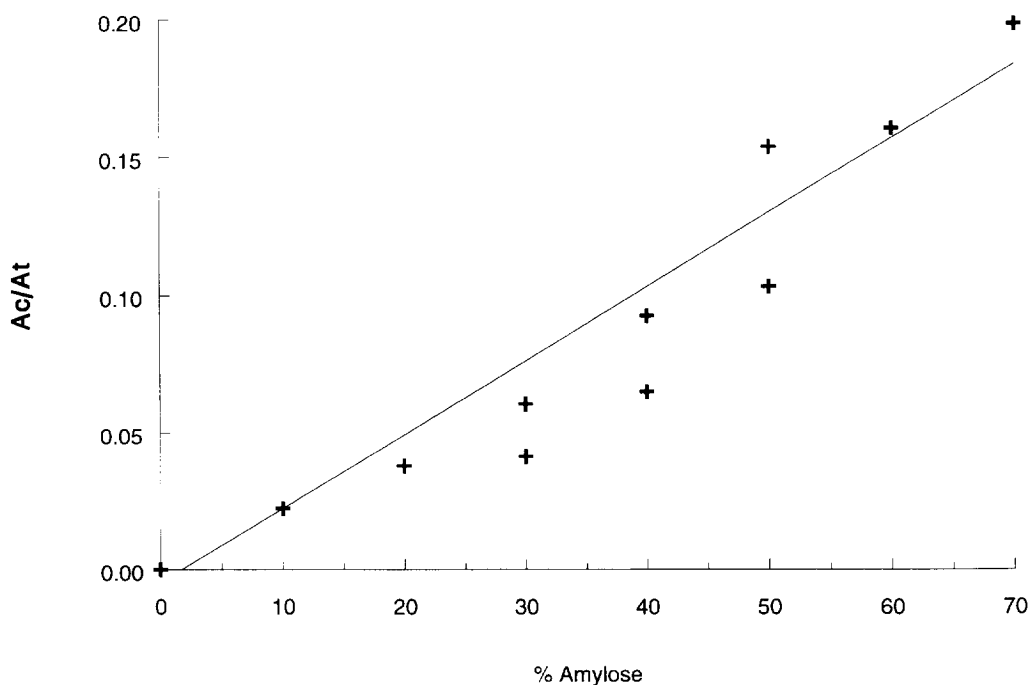


Fig. 4. The relative amount of V_H-type crystallinity in the thermoplastic starch materials vs. amylose content for extruded mixtures of the C-AM and C-AP starches. The starch–glycerol ratio was 100:30 (w/w). The relative amount of V_H-type crystallinity is expressed as the Ac/At ratio of the reflection peak at 19.5° (2θ) (bottom).

single helical crystal structures are summarized in Table 5. As expected, no V- or E-type crystallinity is observed in TPS materials, containing only amylopectin starch.

The V_H structure is found in extruded and compression moulded TPS containing more than 10% water. The formation of this structure is found in all the starches subject of this study. The E_H and V_A

structures are preferably formed in materials containing relatively little water (generally below 10% (w/w)). The V_A structure is found in extruded high amylose corn starch and rice starch containing less than 10% water after extrusion. The E_H structure is observed in extruded and compression moulded potato starch materials containing less than 10% water. The E_H structure is also found after extrusion and

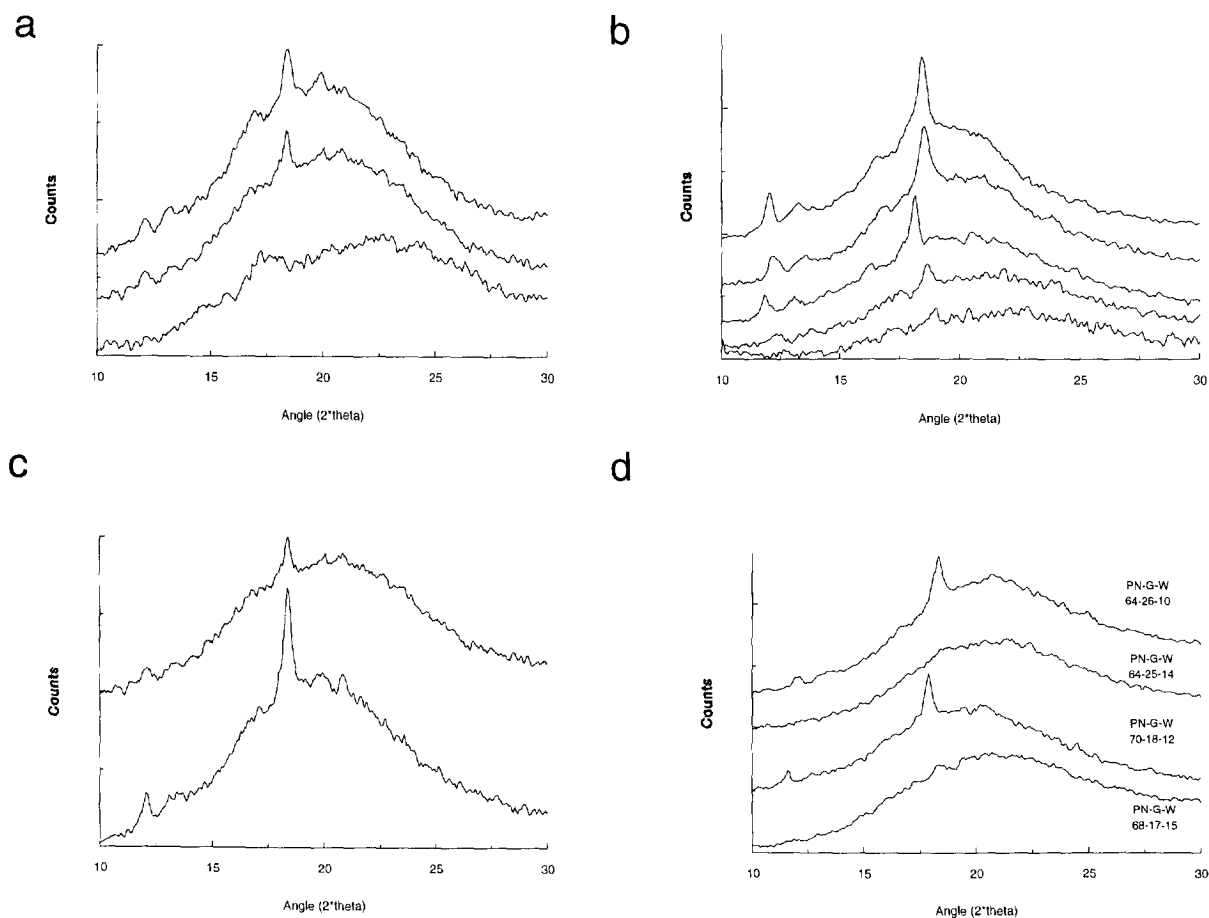


Fig. 5. (a) Diffractograms of thermoplastic potato starch after kneading with different water contents. The extra water added to the premix of starch–water–glycerol (100:21:30 (w/w)) was 0, 10 and 20%, respectively from top to bottom. The melt temperature was 110°C. (b) As (a) But with a melt temperature of 160°C. The extra water added was 0, 5, 10, 15 and 20% (w/w) respectively from top to bottom. (c) The influence of glycerol content on the diffractograms of kneaded potato starch with respectively starch–water–glycerol ratios of 100:21:21 (bottom) and 100:21:30 (top). (d) The influence of composition on the diffractograms after extrusion of potato starch. The compositions (starch–water–glycerol (w/w)) are from bottom to top 100:25:22, 100:26:17, 100:39:22 and 100:41:16 respectively.

kneading of wheat and corn starches, but not in high amylose corn starch and rice starch under similar conditions. Starch source and thereby lipid content are important factors affecting the formation of these structures although further research is needed.

Amylose content: The influence of amylose content on the formation of single helical structures is shown in Fig. 4. It is clear that the amount of amylose is proportional to the amount of crystallinity.

Plasticizer content: Some typical examples of the influence of the plasticizer content on the formation

of E_H -type crystallinity are shown in Fig. 5 for potato starch plasticized with glycerol and water. At standard processing conditions, the preferred structure in potato starch TPS materials is the E_H structure. In Fig. 5a it is shown that during kneading at 110°C with 20% extra water some B-type crystallinity is observed due to recrystallization at this relatively high water content. With decreasing amount of water the amount of E_H -type crystallinity increases. This effect is even more pronounced at higher processing temperatures (Fig. 5b). The effect of glycerol content

is shown in the Fig. 5c for kneading of potato starch and in Fig. 5d for extrusion of potato starch. It is clear that by increasing the amount of glycerol or water the amount of E_H -type crystallinity decreased. Materials with lower amounts of plasticizers like water or glycerol, probably form melts with a higher viscosity. The required higher orientation of the amylose as mentioned above is induced by the increase in shear stress forces. This results in an increase in E_H -type crystallinity with a decrease in plasticizer content.

Additives: Extrusion of calcium stearate-containing compositions with the calcium stearate content varying between 0.5 and 10% (w/w) has shown that V_H -crystallinity is formed in all materials to the same extent. At a calcium stearate content of 0.5% (w/w), only a small percentage of the total amylose is able to form a complex with calcium stearate assuming a stoichiometry of ca. 1:5. Because V_H crystallinity in the materials containing 0.5% (w/w) calcium stearate is equal to V_H crystallinity in materials containing high amounts of calcium stearate, it is assumed that calcium stearate induces the crystallization of the amylose complexes after which further crystallization occurs without participation of the complexing agent. Above 3% (w/w) incomplete complexation of calcium stearate with amylose is observed by DSC experiments by the appearance of a melting endotherm of free calcium stearate with a T_p of ca. 120°C.

4. Conclusions

Six crystal structures are observed in processed TPS, identified as native, double-helical A-, B- and C-type crystallinity and single helical V_H -, V_A - or E_H -type structures differing in helix packing. The observed native A-, B- and C-type crystallinity is attributed to residual crystallinity which is present in granular starch. The single helical structures are formed during processing. Amount and type of crystalline structure is influenced by processing parameters and composition.

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