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The role of water during plasticization of native starches

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Flexible, starch-based plastics of native corn, potato, waxy corn and wheat starch were produced by compression moulding mixtures of native starch and glycerol in the weight ratio 0.30 ($W_{\mathrm{glycerol}}/W_{\mathrm{dry\ starch}}$). In these premixes, the weight ratio water/dry starch was varied between 0.112 and 0.422. The mechanical properties of these compression moulded starches, with a glass–rubber transition temperature below room temperature, were strongly dependent on the water content of the premix. Varying the water content in the premixes led to large changes in strain and stress at break. This effect could be explained by a dependence of the polysaccharide mobility on the water content in the premix. The mechanical properties of the materials were also dependent on starch source, and hence on the composition of the native starch and the structure of the constituting polysaccharides. From the results it could be concluded that both amylose and amylopectin formed chain interactions or entanglements in the materials. © 1998 Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

The development and production of biodegradable thermoplastic starch is considered important for reducing the total amount of plastic waste. In the literature, a wide range of studies on the processing of starch[1–17] yield a broad description of the starch system, although direct relations between structure, processing and properties of the produced materials still are not very clear and likewise extremely complex.

Polymer-chemistry aspects, indispensable for the knowledge of, and hence the development of thermoplastic starches for industrial applications, have to be incorporated in the processing of these materials. From a polymer-chemistry perspective, several known concepts have shown to be applicable to starch[18,19]. The effects of the amount of water and other plasticizers on the mechanical properties of thermoplastic starches have been determined by several researchers[2,12]. The polymer-chemistry concept, that an increase in plasticizer content causes a decrease of the glass–rubber transition temperature (T_g), can be applied to thermoplastic starch[18,20]. Furthermore, polymer recrystallization at temperatures above T_g is observed[21]. At sub-T_g conditions, relaxation phenomena such as free volume relaxation is thought to cause a physical ageing of the material, resulting in embrittlement[20,22].

Differences between starch and synthetic polymers are the native, granular structure of starch and the presence of two different polysaccharides; the linear ($1 \rightarrow 4$)-linked α-D-glucan amylose and the high molecular weight, highly ($1 \rightarrow 6$)-branched α-D-glucan amylopectin ($= 10^6$–$10^8\ \mathrm{g\ mol^{-1}}$)[23]. The granular structure gives rise to the characteristic gelatinization behaviour of starches in excess [> 70% (w/w)] water. In these starch gels, residual granular structures, mainly consisting of amorphous amylopectin, embedded in an entangled matrix of leached amylose, remain present[24,25]. This morphology strongly influences the rheological behaviour of starch gels[26]. In thermoplastic starch, destructurization of the starch granules is performed at relatively high temperatures, high-shear conditions, and with limited amounts of water, the latter hindering both granule swelling and disintegration[27–29], yielding a microscopically homogeneous material. Although often considered microscopically homogeneous[15], remnants of starch granules can still be present in the processed materials.

As in synthetic polymers, the development of an optimally entangled or highly interacting polymer system is expected to be necessary for obtaining materials with good mechanical properties. As polymer mobility will determine the formation of polymer chain–chain interactions and entanglements, processing parameters such as temperature, shear and pressure, and composition of the premix, such as plasticizer content and starch source, are thought to influence the resulting mechanical properties of plasticized starches. Although very little is known on its specific function in low-moisture, high-temperature processed starches, water is thought to influence polysaccharide mobility and hence the formation of chain–chain interactions or entanglements. In this study, research is focused on the relation between water content during the compression moulding of relatively low-water systems [< 25% (w/w)] and the resulting mechanical properties of the produced material. A constant amount of glycerol will be added to decrease the T_g to temperatures below room temperature and the amount of water will be varied in the mixtures. After reconditioning to equal water contents, the influence of the amount of water present during processing can be evaluated, as all other parameters, such as T_g and crystallinity, will be constant in the reconditioned materials. Corn, potato and wheat starches [amylose content 20–30% (w/w)[30,31]], and

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amylose-free waxy corn starch will be used throughout the study.

EXPERIMENTAL

Preparation of starch–glycerol–water mixtures

Water contents of corn starch (Meritena A, Amylum/ZBB), dried potato starch (Perfectamyl D6, AVEBE), waxy corn starch (Cerestar SF 04211, Gruppo Ferruzi) and wheat starch (Doittau Emuldo) were determined using a Sartorius MA40 infrared dryer by measuring the weight loss 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 and Co., Denmark). After equilibration for at least 24 h, calculated volumes of water were added to parts of this mixture and mixed for 5 min using a Hobart N-50 mixer (Hobart, Canada). Samples were equilibrated for at least 24 h before use. Depending on the initial water content of the starch, the weight ratio between starch (dry matter) and water of the resulting starch–glycerol–water mixtures varied between 100:11.2 and 100:42.2 (w:w). This starch:water ratio is further referred to as W, with W being 100 times the ratio between the total weight of water divided by the total weight of starch expressed as dry matter ($W = 100 \times W_{\text{water}}/W_{\text{dry starch}}$, with $11.2 < W < 42.2$). The value of W was limited to values lower than 40–45, as at higher W the materials were too weak to release from the mould undamaged.

Preparation of compression moulded tensile bars

Forty-five grams of starch–glycerol–water mixture were applied to a mould of inner dimensions 100 × 150 × 2 mm (l × w × h). The outer cross-sectional area of the mould was 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 (300 × 350 mm), an initial pressure of 3–4 tonnes was applied. The mould was then heated to 100°C at 10°C min^{-1}. At 100°C, 40 tonnes were applied to the mould and the temperature was raised at 10°C min^{-1} to 160°C, which was maintained for 5 min. The mould was cooled to room temperature at a rate of 10–15°C min^{-1} and the mould content was released. 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. The materials were equilibrated for 12–14 days at 20°C and 55% relative humidity (r.h.).

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 to a gauge length of 34 mm. The thickness of each tensile bar was measured in triplicate before mechanical testing. The width of the tensile bars was 15 mm. For each material, four to five tensile bars were tested. After mechanical analysis, about 20 g of material were placed in a KCH A10 analytical mill (Kinematica, Switzerland) and cooled with liquid nitrogen. The sample was milled for 5–10 s and quickly transferred to a closed vessel to prevent water absorption.

Polarized light microscopy

The morphology of a sample was analysed by examination of a thin slice (50–100 μm) of the moulded material with a Zeiss Axioplan microscope with crossed polaroids.

Wide angle X-ray scattering

Diffractograms of powdered samples were recorded on a Philips PC-APD diffractometer, consisting of a PW1830 generator, a PW3710 mpd control and a PW3020 goniometer. Diffractograms were recorded in the reflection geometry. The CuK radiation, generated at 40 kV and 50 mA, was monochromatized using a 15 μm nickel foil ($\lambda_{\alpha 1,2} = 0.1542$ nm). 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. Scattered radiation was detected in the angular range 5–40° (2θ) using a proportional detector.

Moisture determination

About 1 g of accurately weighed, powdered sample was placed in a Gallenkamp vacuum oven at 70°C. The oven was evacuated to < 50 mbar. After 20 h, the weight loss of the sample was determined, from which the water content was calculated. At these conditions, evaporation of glycerol was negligible.

RESULTS AND DISCUSSION

The mechanical properties of the compression moulded starch–glycerol–water mixtures showed a strong dependency on both water content in the premix W and starch source. The stress–strain curves, of which several examples are shown in *Figure 1*, shows visco-elastic behaviour for all starches, although significant differences in mechanical properties can be observed between starch sources. Glycerol is known to act as a plasticizer for starch and, at the proportion of glycerol used, the T_gs of the conditioned samples were below room temperature (weight ratio of dry starch:glycerol:water = 100:30:18–21). Therefore, the conditioned materials all showed relatively high ϵ_b and low σ_b and E-modulus. For all starch samples, ϵ_b and σ_b *versus* water content at compression moulding W are depicted in *Figure 2*. Initially, a strong increase in ϵ_b with

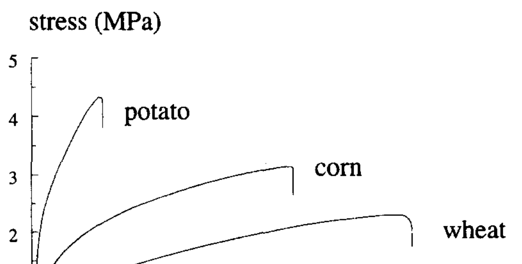

Figure 1 Stress–strain curves of potato, corn, wheat and waxy corn starch compression moulded materials at $W \approx 20$

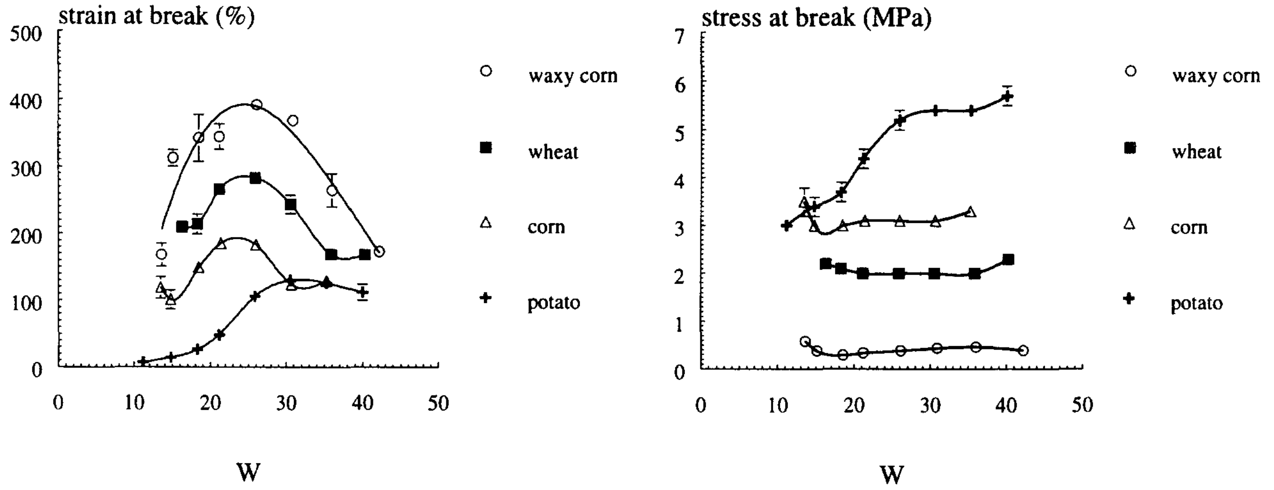

Figure 2 Strain at break (ϵ_b) and nominal stress at break (σ_b) *versus* water content during compression moulding (W) for potato, corn, wheat and waxy corn starch. Where no error bars are given, the standard deviation is smaller than the marker used. For clarity, no smaller markers were used

increasing water content W was observed for each starch source. For potato starch, a maximum in ϵ_b was found at $W = 30$–35, whereas for the other starches, this maximum was observed at $W = 20$–25. For potato starch, σ_b also increased with increasing W. Although for corn, waxy corn and wheat starches, nominal σ_b does not change with W, true σ_b in the materials is increasing with W increasing from 10 to 25, as at increasing elongation, contraction of the tested area occurred. For the same reason, true σ_b in potato starch will be higher than that depicted in *Figure 2*. In these moulded, glycerol-plasticized materials, the initial increase of ϵ_b and true σ_b with increasing W suggests a facilitated interaction between the constituting polysaccharides (via chain–chain interactions or entanglements) with increasing W, which leads to more coherent materials.

The E-moduli of compression moulded potato, corn, wheat and waxy corn starches showed no significant relationship with W. For potato, corn, wheat and waxy corn starch, the E-moduli remained constant between 80–120 (± 10) MPa, 20–25 (± 3) MPa, 12–20 (± 3) MPa and 2–4 (± 1) MPa, respectively. The average standard deviation is given in parentheses.

To be able to compare and interpret the mechanical properties of the produced materials, their water contents were determined. The equilibrium water content of the tensile bars, measured directly after mechanical testing, was 12.1–14.3% (%w/w). There was no significant relation between measured water content after conditioning and water content in the premix W or starch source. For materials containing starch and glycerol in the weight ratio 100:30, a transition from the rubbery to the glassy state is expected at a water content of approximately 9% (w/w) at the storage temperature (20°C). As the water content, and therefore T_g, is a constant for all these starches, comparison of the mechanical properties of these moulded starches will give information on the effect of W on polymer mobility.

For several materials, compression moulded at $W \approx 20$, diffractograms are presented in *Figure 3*. The diffractograms of moulded corn and wheat starch revealed the presence of a small amount of V_H-type crystallinity [$d \approx 0.455$ nm/diffraction angle $\approx 19.5°$ (2θ)][32,33], caused by crystallization of amylose with either fatty acids or lysophospholipids or both which are present in small amounts in native wheat and corn starch[30,34,35]. In a corn sample which was quenched in liquid nitrogen directly after compression moulding, V_H-type crystallinity was also observed, indicating a rapid formation of this type of crystallinity. A slight decrease in V_H-type crystallinity with increasing W was observed, suggesting a favoured formation of V_H-type crystallinity at low W. Furthermore, in compression moulded potato, corn and wheat starch, low amounts of presumably B-type crystallinity were observed [$d \approx 0.522$ nm/diffraction angle $\approx 17°$ (2θ)]. Quenched samples of moulded corn and potato starch did not show any (residual) A- or B-type crystallinity. As the formation of B-type crystallinity is favoured over A-type crystallinity at these conditions, the observed crystallinity was related to the recrystallization of amylose or the outer chains of amylopectin or both into the B-type lattice[22,36,37]. Moulded waxy corn starch was amorphous after conditioning. This is possibly due to the absence of amylose and the relatively short outer chains of amylopectin which lead to a lower rate of recrystallization as was studied before in starch gels[38]. It was concluded that the observed variations in crystallinity and crystal type within each series were insignificant. It can therefore be concluded that, within each series, the observed initial increase of ϵ_b and (true) σ_b with increasing W, as can be observed in *Figure 2* for all starch sources, is entirely due to the variation of water content in the premix W.

As σ_b and ϵ_b initially increased with increasing W, it can be concluded that, with increasing W, polysaccharides increasingly migrate or leach out of the granules, forming (glycerol- or water-mediated) chain–chain contacts via hydrogen bridges or entanglements. Due to this larger fraction of non-granular, interacting polysaccharides, the materials become more deformable without losing coherence. Interestingly, in contrast to ϵ_b and σ_b, the E-modulus of the materials was independent of W. Apparently, the E-modulus is not dependent on the amount of destructurized or non-granular material, which suggests that the total amount of interactions or entanglements in the materials does not increase when transforming (a fraction of) the native, granular organization into a non-granular polysaccharide system. The specific mobility of the constituting polysaccharides amylose and amylopectin will play an important role in determining the formation of (hydrogen-bridged) chain–chain contacts or entanglements.

Support for the abovementioned explanation is given by polarized light microscopy, as shown in *Figure 4* for potato starch, moulded at different values of W. A decrease in birefringent granules with increasing W occurred. For potato starch moulded at low Ws, it was also observed that, upon

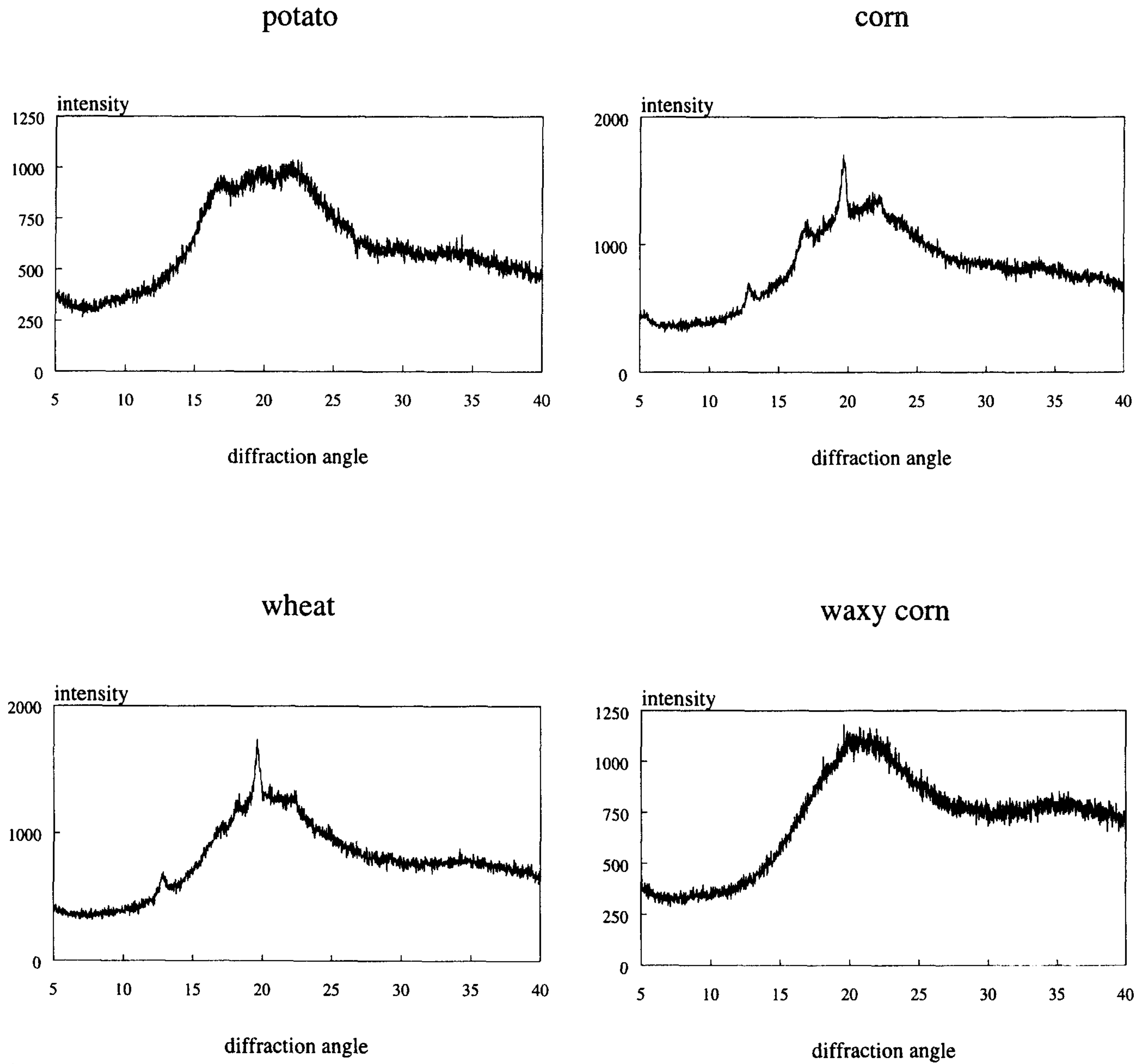

Figure 3 Diffractograms of compression moulded starches from different sources. The starches were compression moulded at $W \approx 20$

immersion in water, (deformed) granules were loosened from the material, indicative of a limited intergranular association. At higher W, tensile bars remained intact upon immersion in water, although swelling of the materials was observed. As, at the water contents used ($11.2 < W < 42.2$), all intrinsic or added water is incorporated in the starch granules[39], it can be assumed that, in the starch–glycerol–water mixture before compression moulding, the total volume is filled with starch granules, with no significant amount of interstitial water present. Therefore, swelling of the granules during compression moulding will be limited. The results from microscopy and the water stability of the tensile bars showed that the coherence in the moulded materials strongly correlates with the extent of disintegration of the granular structures and hence the ability of the polysaccharides to migrate and form entangled or interacting regions in the starch matrix. As this behaviour is closely associated with polymer mobility and therewith W, it confirms the abovementioned explanation.

For compression moulded potato starch, a decrease in ϵ_b with $W > 30$–35 was observed in *Figure 2*. Obviously, at these values of W, the polymer matrix is not able to deform to higher elongations, suggesting that, under these conditions, the polysaccharides show maximum interaction. No birefringent granular structure could be observed in these materials (*Figure 4*). For moulded corn, waxy corn and wheat starch, the decreases of ϵ_b at $W > 20$–25 suggest that the interaction or entanglement of the polysaccharides apparently is limited at relatively high W. Above these values of W, the formation of an even more coherent polysaccharide system is obviously hindered, possibly due to the formation of inter- and intramolecular contacts within (partially disrupted) granules or granule remnants instead of the formation of a non-granular, homogeneous polysaccharide network.

The observed differences in crystallinity and crystal type in the series potato, corn, waxy corn and wheat will be (partially) responsible for the differences in mechanical properties between the starch sources. The formation of small amounts of B-type crystallinity is known to increase stiffness and stress at break and decrease strain at break in these starches[40]. Hence, the decrease of the E-modulus and

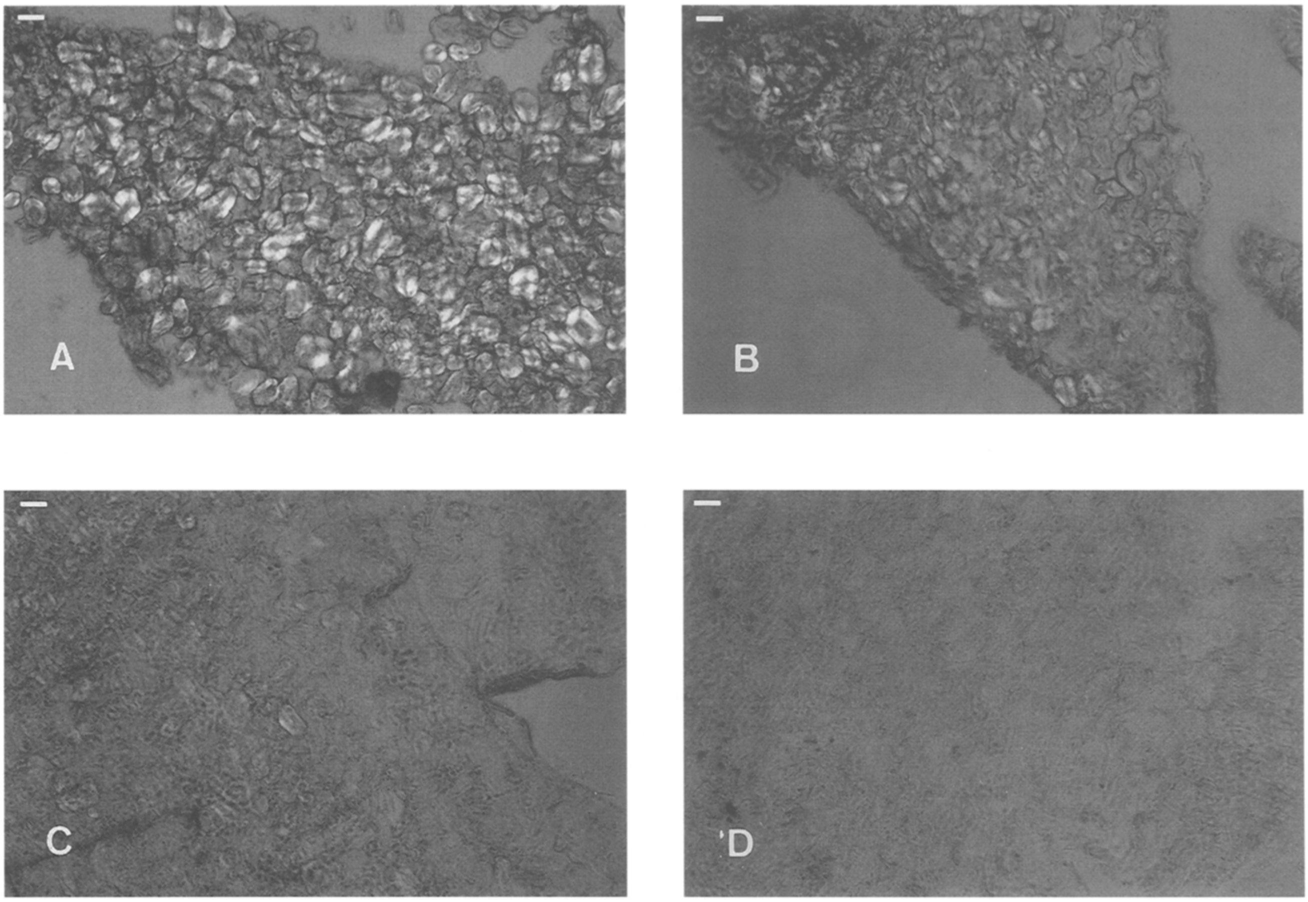

Figure 4 Morphology of compression moulded potato starch at A, $W = 11.2$; B, $W = 18.3$; C, $W = 25.9$; and D, $W = 40.0$, as observed with crossed polaroids. The bar corresponds to 50 μm

stress at break and the increase of strain at break in the series potato–corn– wheat–waxy corn seems to be (partially) related to a (polysaccharide composition-related) decrease in B-type crystallinity in this series, as can be observed in *Figure 3* by a small decrease of the height at the diffraction angle of 17° (2θ).

The dependency of the mechanical properties on W for corn, potato and wheat starch could suggest that amylose mobility determined the properties of the materials. As amylose from potato starch has a higher degree of polymerization and therewith a lower mobility than amylose from corn and wheat[41,42], it could be assumed that this explains the observed differences in W at which a maximum in ϵ_b was observed. However, waxy corn starch (containing no amylose) showed the same dependency as corn and wheat, which suggests that at the conditions used, not only amylose but also amylopectin is involved in the formation of an interacting polysaccharide network in these materials.

Based upon the obtained results, the capacity of both amylose and amylopectin to form chain-associated or entangled systems at relatively low-water and high-temperature conditions is considered to be an important factor in determining the mechanical properties of moulded starches above T_g. During the processing of starches, attention should be paid to the mobility of the polysaccharides by optimizing the water content during processing, in order to ensure the formation of a coherent polymer system.

CONCLUSIONS

The mechanical properties above T_g of compression moulded corn, potato, waxy corn and wheat starch were highly dependent on both water content during compression moulding and starch type.

It was concluded that an increase in W enhanced the formation of entangled or glycerol- or water-mediated chain–chain associated polysaccharides in these systems. This suggested that, at the conditions used, polymer mobility during processing is an important parameter determining the mechanical properties in compression moulded starch.

Differences in mechanical properties between materials from different starch types cannot be attributed to a variation in B-type crystallinity or content and degree of polymerization of amylose solely. Amylopectin also seems to influence the mechanical properties in these systems.

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