

Changes in the mechanical properties of thermoplastic potato starch in relation with changes in B-type crystallinity

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The influence of crystallization on the stress-strain behaviour of thermoplastic potato starch has been monitored. Potato starch has been processed by extrusion with glycerol and water added as plasticizers. The thermoplastic starch consists of a molecular network of semicrystalline amylose and amylopectin with some granular fragments. A rapid increase in B-type crystallinity and a change in mechanical properties is observed within 2 weeks at 70 and 90% relative humidities. An increase in B-type crystallinity from 5 to 30% compared to native potato starch leads to an increased elastic modulus (from 10 to 70 MPa) and tensile stress (from 3 to 7 MPa) for thermoplastic starch materials with a water content of circa 15%. The elongation is decreased from 105 to 55%. For materials with more than 30% B-type crystallinity relative to native potato starch, a sharp decrease in elongation is observed and the materials form cracks. The effects are explained by an increase in physical cross-links by amylose and amylopectin intermolecular double helix formation and crystallization resulting in a reinforced network. A further intramolecular crystallization of the amorphous amylopectin reduces the intermolecular interactions of amylopectin and induces internal stress within the network of semicrystalline amylose and amylopectin. The increased internal stress at the highly crystalline amylopectin sites finally leads to cracking of the materials. Copyright © 1996 Elsevier Science Limited.

INTRODUCTION

In the past decades, several new products based on thermoplastic starch (TPS) have been developed (Wittwer & Tomka, 1987; Lay *et al.*, 1992; Stepto *et al.*, 1988; Röper & Koeh, 1990; Lai & Kokini, 1991; Wiedmann & Strobel, 1991; Chinnaswamy & Hanna, 1991; Stepto & Tomka, 1987; Bastioli *et al.*, 1992). Several of these materials are blends of TPS and various petrochemical plastics, such as polyethylene. More recently, products have been prepared solely on the basis of thermoplastic starch (De Brock *et al.*, 1993). These materials are susceptible to starch retrogradation and crystallization. Most materials are exposed to various humidities during storage and usage, which leads to variations in water content and to differences in properties caused by starch crystallization (Kirby *et al.*, 1993; Ollett *et al.*, 1991; Dell & Kohlman, 1994; van Soest *et al.*, 1995).

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Most research on the crystallization behaviour of starch has been focused on high (>66% w/w) and intermediate (ca. 50% w/w) moisture materials such as gels, cakes and bread (Miles *et al.*, 1985; Orford *et al.*, 1987; Ring *et al.*, 1987; Russell, 1987). Starch gels are considered as composites consisting of swollen granules filling an interpenetrating amylose and amylopectin network. The residual swollen granules increase the stiffness of the gel (Biliaderis & Zawistowski, 1990). Upon storage the stiffness of the starch gel slowly increases. The stiffening of starch gels is accompanied by the formation of crystals (Miles *et al.*, 1985; Orford *et al.*, 1987; Ring *et al.*, 1987; Russell, 1987; Morris, 1990; Biliaderis & Zawistowski, 1990). In casted films, the formation of these crystal structures depends on processing conditions, such as drying temperature, and on composition, which is related to starch source and additives (Bader & Göritz, 1994). Gelatinization of starch usually takes place at high water content (>66%) and relatively low temperatures (50–80°C). To make thermoplastic starch, granular starches are plasticized with the aid of relatively low amounts of plasticizers

like water and glycerol. During the processing of thermoplastic starch by extrusion, compression moulding or injection moulding, the temperature and shear stress are high compared to the gelatinization of starch. The water content in most cases is lower than 20% both during processing and usage. Glycerol is already known to influence the crystallization kinetics of amylopectin (van Soest *et al.*, 1994). Processing of a thermoplastic starch leads to differences in starch melting due to the low water content, a different morphology of the materials and to differences in aggregation and crystallization behaviour of the amylose and amylopectin compared to gels or high moisture materials.

The purpose of this study is to get insight into the influence of storage humidity on the formation of B-type crystallinity and on the stress-strain behaviour of thermoplastic potato starch materials. The glycerol-containing TPS materials will be made by extrusion processing with relatively low amounts of plasticizers, at high shear stresses and at high temperatures. An increase in crystallinity will be established by aging of the TPS materials at various humidities.

MATERIALS AND METHODS

Extrusion

Potato starch was obtained from Avebe, Foxhol, The Netherlands. TPS materials were prepared by extruding narrow sheets using a Haake Rheocord 90 system equipped with a laboratory-scale Rheomex TW 100 counter-rotating twin screw extruder fitted with a slit die. The die had a width of 25 mm and height of 0.4 mm. The native starches were mixed with glycerol and water in the ratios: starch:water:glycerol is 66:14:20 (w/w/w). The mixtures were manually fed into the extruder. The torque was held between 35–65 N·m. The screw rotation speed was 50 rpm. The temperature profile along the extruder barrel was 70, 140, 120, 80–100°C (from feed zone to die). The measured melt temperature in zone two was 140°C.

Conditioning

Part of the materials was stored at –22°C after quenching in liquid nitrogen directly after extrusion. The rest was stored for an initial storage period of two weeks at 60% RH and 20°C. After this initial period, part of the material was stored for two weeks at various relative humidities (RH) in the range of 0–100% to obtain information about the dependence of the properties on storage humidity. The changes in crystallinity and the time dependencies of the mechanical properties were also investigated at 60, 70 and 90% RH after the initial storage period of two weeks at 60% RH. Subsequently, all the materials were reconditioned at 60±5%

Table 1. The differences in storage before mechanical testing and X-ray measurements

number	Conditioning period (RH/time)		
	1	2	3
1	60%/2 weeks	60%/variable	60%/2 weeks
2	60%/2 weeks	70%/variable	60%/2 weeks
3	60%/2 weeks	90%/variable	60%/2 weeks
4	60%/2 weeks	0–100%/2 weeks	60%/2 weeks

RH for two weeks, to level out the differences in water content after storage at the various RH, after which mechanical testing and X-ray diffraction measurements were performed. The water content after reconditioning was 15±1% (w/w). The differences in conditioning are summarized in Table 1.

Moisture determination

Because of the tendency of TPS to adsorb or desorb water, special care was taken to measure the water content immediately at the time of testing. The samples were milled under cryogenic conditions. The water content of the powder (1 g, size < 125 µm) was determined gravimetrically with a Gallenkamp oven at 70°C at a pressure of less than 100 mBar overnight. Due to the volatility of glycerol, the measurements did not exceed 24 h to minimize the loss of glycerol.

Mechanical testing

Dumb-bell specimens according to the ISO 1184-1983 (E) standard were cut from the extruded ribbons directly after extrusion and storing. The sheet thickness varied and corrections were made for the differences in thickness before measurements. A Model 4301 Instron Universal Testing Machine operated at a grip length of 80 mm and a crosshead speed of 10 mm/min was used for tensile testing. The tensile stress at maximal load was calculated on the basis of the original cross-sectional area of the test specimen, by the equation: $\sigma = F/A$, where σ is the tensile stress, F is the force and A is the initial cross-sectional area. The percentage of strain or elongation was calculated on the basis of the length of the narrow parallel portion, by the formula: $(l - l_1)/l_1 \times 100\%$, where l is the distance between the gauge marks (in mm) and l_1 is length of the narrow parallel portion (i.e. 33 mm). The elastic modulus (E-modulus) was calculated from the initial slope of the stress-strain curve. The data were averages of 4 to 8 tensile bars.

DSC

DSC 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 ($\Delta H_{\text{fusion}} = 79.91$ 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. Glass transition temperatures were determined by heating the samples (30–40 mg) from 20 to 150°C at a rate of $10^\circ\text{C}/\text{min}$, cooling down to -50°C at a rate of $200^\circ\text{C}/\text{min}$, followed by a rescan at a rate of $20^\circ\text{C}/\text{min}$ to 200°C .

Polarized light microscopy

The materials were cut into thin slices and inspected at a magnification of 40 times with an Axioplan Universal Microscope with photographs taken using a MC100 camera accessory.

X-ray diffractometry

Wide-angle X-ray diffraction patterns were recorded using a Philips powder diffractometer (Model PW 3710) operated at the $\text{CuK}\alpha$ wavelength of 1.542 \AA . The radiation from the anode, operating at 40 kV and 50mA, was monochromized using a $15 \mu\text{m}$ Ni foil. The scattered radiation was detected using a proportional detector. Measurements of diffracted intensities were made over the angular range of $5\text{--}40^\circ$ (2θ) at ambient temperature. Crystallinity was measured according to the methods of Hermans & Weidinger (1949). Diffractograms were smoothed (Savitsky–Golay, polynome = 2, points = 15) and baseline corrected by drawing a straight line at a diffraction angle of 7° (2θ). The height (H_c) of the crystalline diffraction, characteristic of B-type crystallinity, at an angle of $16.8\text{--}17.2^\circ$ (2θ) was measured relatively to the height (H_t) of the peak measured from the horizontal baseline. The ratio $R(X_H) = H_c/H_t$ is related to %X by the relation: $\%X_{\text{XRD}} = [R(X_H) - 0.095]/0.0055$ (van Soest *et al.*, 1995a). %X is defined as the relative B-type crystallinity compared to native potato starch (for which %X = 100%).

RESULTS AND DISCUSSION

The extruded thermoplastic potato starch materials show a considerable amount of extrudate-swell (up to 10 times the die height) due to relaxation of the shear-induced orientation (stretching) of the high molecular weight starch. The morphology of the extruded TPS materials has been investigated with polarized light microscopy. It is shown that less than a few percent of residual granular structure is present in the materials. Due to the high shear conditions the granules are molten or physically broken up into small fragments and therefore no birefringence of intact granules is observed. Some typical X-ray diffractograms of the extruded TPS materials are shown in Fig. 1. The X-ray diffraction patterns of the TPS materials, which have

been rapidly cooled in liquid nitrogen directly after extrusion, show no distinct reflections. All crystallinity in the native granule is melted during extrusion and therefore crystallinity observed during storage is ascribed to recrystallization.

Recrystallization into single-helical amylose crystals

Directly, within a few hours after extrusion of potato starch, a small amount of E_h type crystallinity is formed in the glycerol containing TPS materials (Fig. 1). This crystal lattice is metastable and rearranges, during storage for more than several days at 60% RH, into a six-fold helical crystal structure, labelled as V_h ($h = \text{hydrated}$) (Fig. 2) (Mercier *et al.*, 1980). The total amount of V_h -crystallinity is not changed any further by increasing the water content and thereby facilitating starch reorganization by lowering the glass transition temperature of the TPS materials. These types of structures are formed by the crystallization of amylose. The organization of the crystal lattice and the abundance of the various single helical crystal structures is dependent on processing conditions like shear and temperature, and composition, i.e. starch type as well as plasticizer content (van Soest *et al.*, 1995a). Due to the high temperatures and high shear conditions, single helical structures can be formed which crystallize rapidly on cooling.

Recrystallization into B-type crystals

For TPS material stored at 55% RH, the water content is lowered to about 10–12%. The glass transition temperature of these materials is $35 \pm 5^\circ\text{C}$ which is above storage temperature. No B-type crystallinity is observed in these materials. Materials stored at 60% RH and 20°C are shown to crystallize for a small part during the first two weeks in a B-type crystallinity. In gels, this initial crystal-

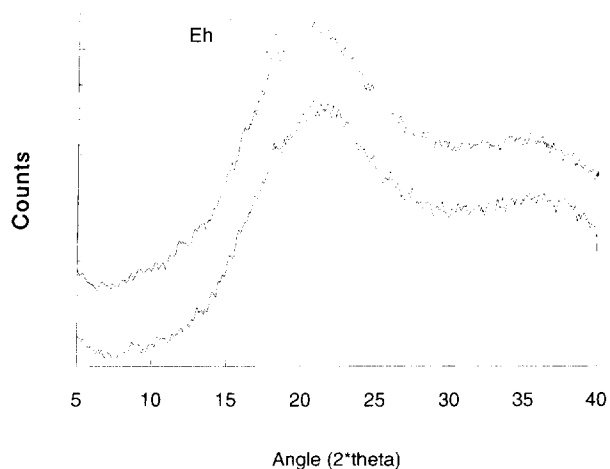


Fig. 1. The diffractograms of amorphous TPS directly after extrusion (bottom) and after a few hours of storage at 60% RH and 20°C (top).

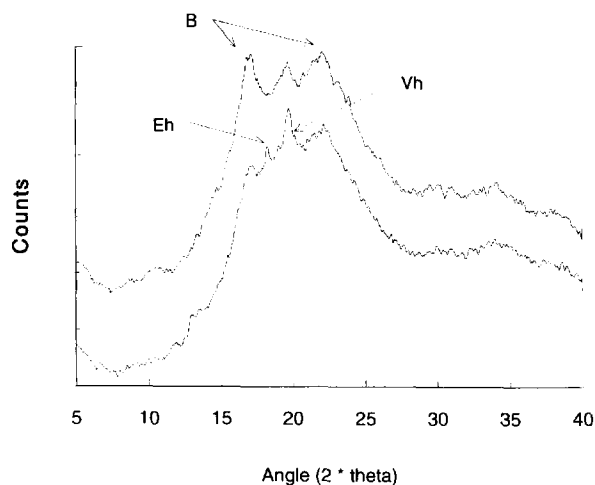


Fig. 2. The diffractograms of TPS materials stored at 60% RH (bottom) and 90% RH (top) for two weeks.

linity is explained by the fast crystallization of double helices of amylose (Morris, 1990). Directly after extrusion the warm polymer melt takes up some water. The water content then is usually about 16%. During a period of two weeks the water content is lowered slightly and stabilized at $15 \pm 1\%$. The amount of B-type crystallinity is then circa 5% relative to native potato starch. A very broad glass to rubber transition of the materials stored at 60% RH (containing 14% water) was observed with differential scanning calorimetry in the range of 0–15°C. Apparently, crystallization is slow at storage temperatures a few degrees above the glass transition temperature. After the initial storage period of two weeks at 60%, 70 and 90% RH, the materials have been conditioned at 60, 70 and 90% RH, respectively. The relative amount of B-type crystallinity as a function of storage time at 60%, 70% and 90% RH, respectively, is shown in Fig. 3. During prolonged storage at 60% RH, the increase in B-type crystallinity is approximately 5% over a period of two weeks. During storage at 70% RH, the rate of crystallization is slightly higher, especially during the first few days. During storage at 90% RH, the amount of B-type crystallinity is increased even more rapidly and ultimately reaches a higher level. The water content in the materials increases during storage at 90% RH to 25–30% during the first day of storage. This increase in water content lowers the glass transition temperature below 0°C, thereby increasing the crystallization rate of the starch. Thus, a clear difference in crystallization rate and crystallinity is observed for materials stored at various humidities. The long-term formation of B-type crystallinity is probably mainly due to the relative slow crystallization of amylopectin, while the fast formed B-type crystals will consist mainly of amylose as reported for gels (Morris, 1990). It is likely that amylose and amylopectin can form intermolecular double helices. Therefore, co-crystallization of amylose with amylopectin is probably also important and cannot be discarded on the basis of

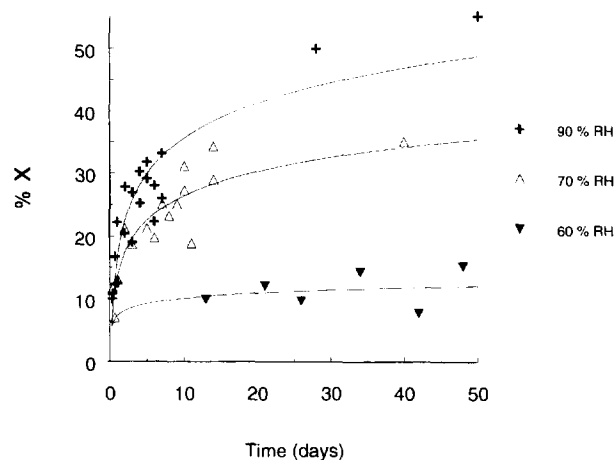


Fig. 3. The relative B-type crystallinity (%X) vs. storage time at 60, 70 and 90% RH, respectively, after an initial aging period of 2 weeks at 60% RH.

these results. This type of crystallization, which will consist of similar double helical aggregates, cannot be distinguished by X-ray measurements because it also will lead to a B-type crystal structure.

Stress-strain properties

After conditioning at various RH, the materials have been reconditioned at 60% RH for two weeks during which a water content is reached in the range of 14–16%. Thus, the materials obtained after storage at variable RH, may differ slightly in water content, before the mechanical properties have been determined due to the variation in reconditioning RH. Typical load-strain curves of the materials with different amounts of B-type crystallinity as a result of storage at variable humidities are shown in Fig. 4. The materials with low amount of crystallinity ($X = 5\%$) are soft, while the materials with $X = 20\%$ are tougher with lower elongation. A yield point is even observed for materials with X ca. 25%.

Effect of storage time

The materials stored at 60% RH show only a slight increase in B-type crystallinity after the initial storage period of two weeks. The changes in mechanical properties are only small. The E-modulus is slightly increased and the elongation decreases only slightly from about 100 to 80% during an additional aging of 15 days. For the TPS materials which have been stored at 70% RH after the initial storage period of two weeks at 60% RH, the results of the stress-strain measurements are shown in Fig. 5. The properties change drastically during the first period of storage at 70% RH. The tensile stress and the E-modulus for both materials increase with an increase in B-type crystallinity, whereas the strain at break decreases strongly with increasing crystallinity between 0 and 20%.

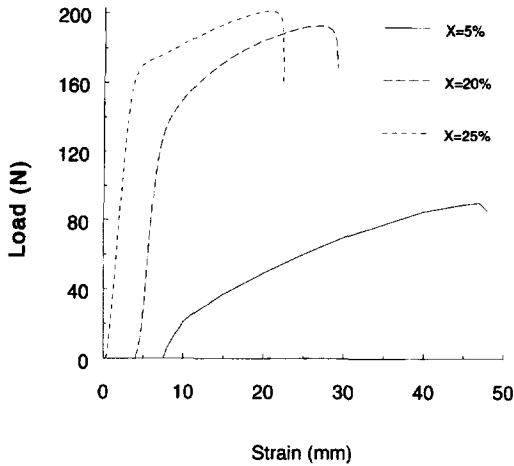


Fig. 4. The stress-strain curves of a TPS material with 5% (offset on x -axis is 7 mm), 20 (offset on x -axis is 4 mm) and 25% B-type crystallinity, respectively.

The results for the materials stored at 90% RH for various periods after initial storage at 60% RH are

shown in Fig. 6. The tensile stress and the E-modulus are increased and the strain at break is decreased, during the first seven days at 90% RH, with an increase in crystallinity from approximately 5 to 35% (Fig. 6). The number of cracks in the tensile bars increases in time with an increase in B-type crystallinity. For materials conditioned at 90% RH for more than seven days, X exceeds 40%. These materials show a considerable number of cracks and mechanical testing is not possible. The changes in properties are even more pronounced during the first days of storage than for materials stored at 70% RH. The uptake of water at 90% RH is more rapid which causes faster crystallization and a higher crystallinity.

Effect of storage humidity

The E-modulus and the tensile stress or the tensile strength, increases with an increase in B-type crystallinity as shown in Fig. 7 for material stored at various RH for an additional period of two weeks. For materi-

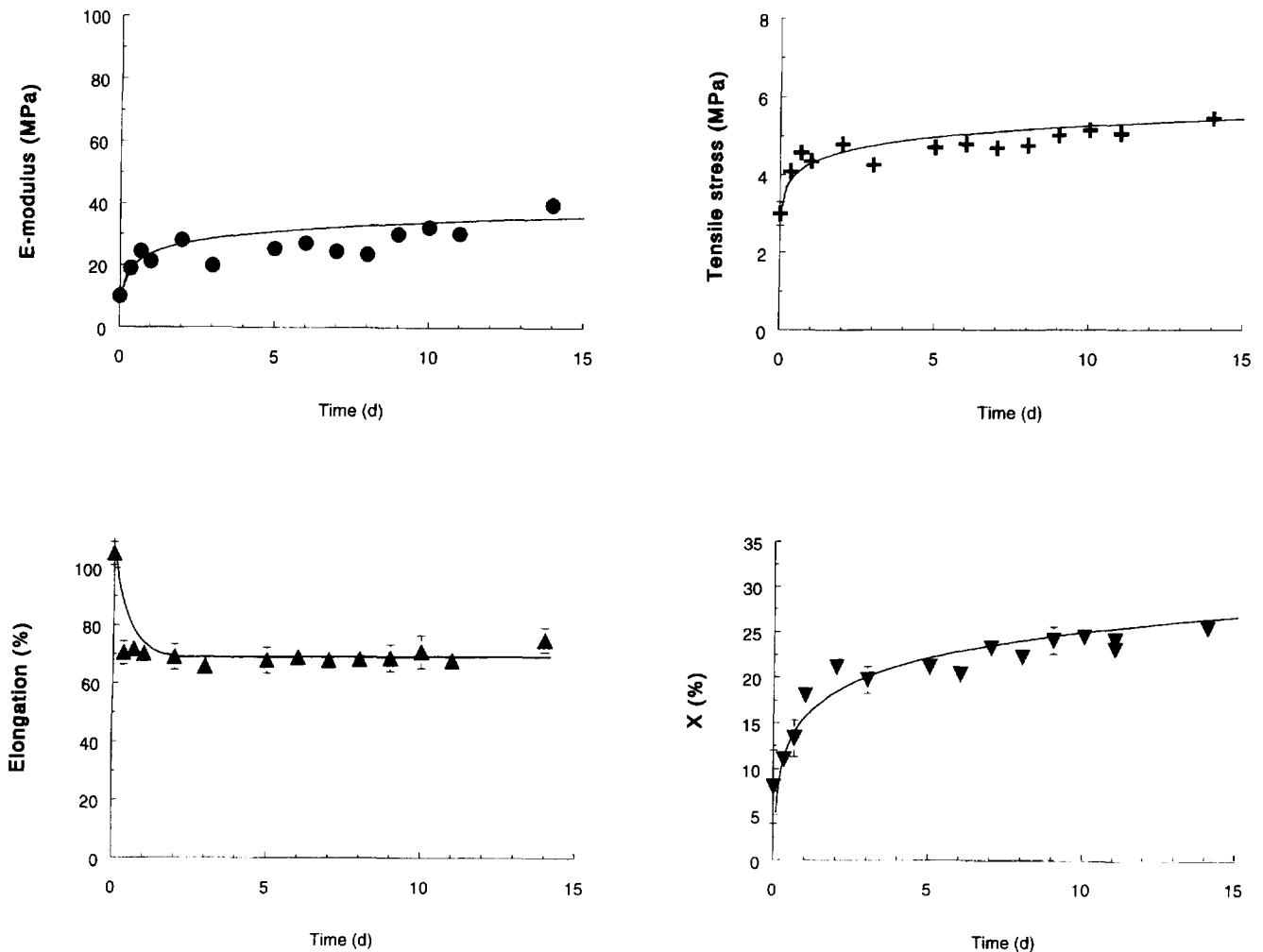


Fig. 5. The mechanical properties and relative crystallinity vs. storage time of TPS aged at 70% RH. (Upper left) E-modulus vs. storage time. (Upper right) Tensile stress of batch 3 vs. storage time. (Lower left) Elongation vs. storage time. (Lower right) % X vs. storage time.

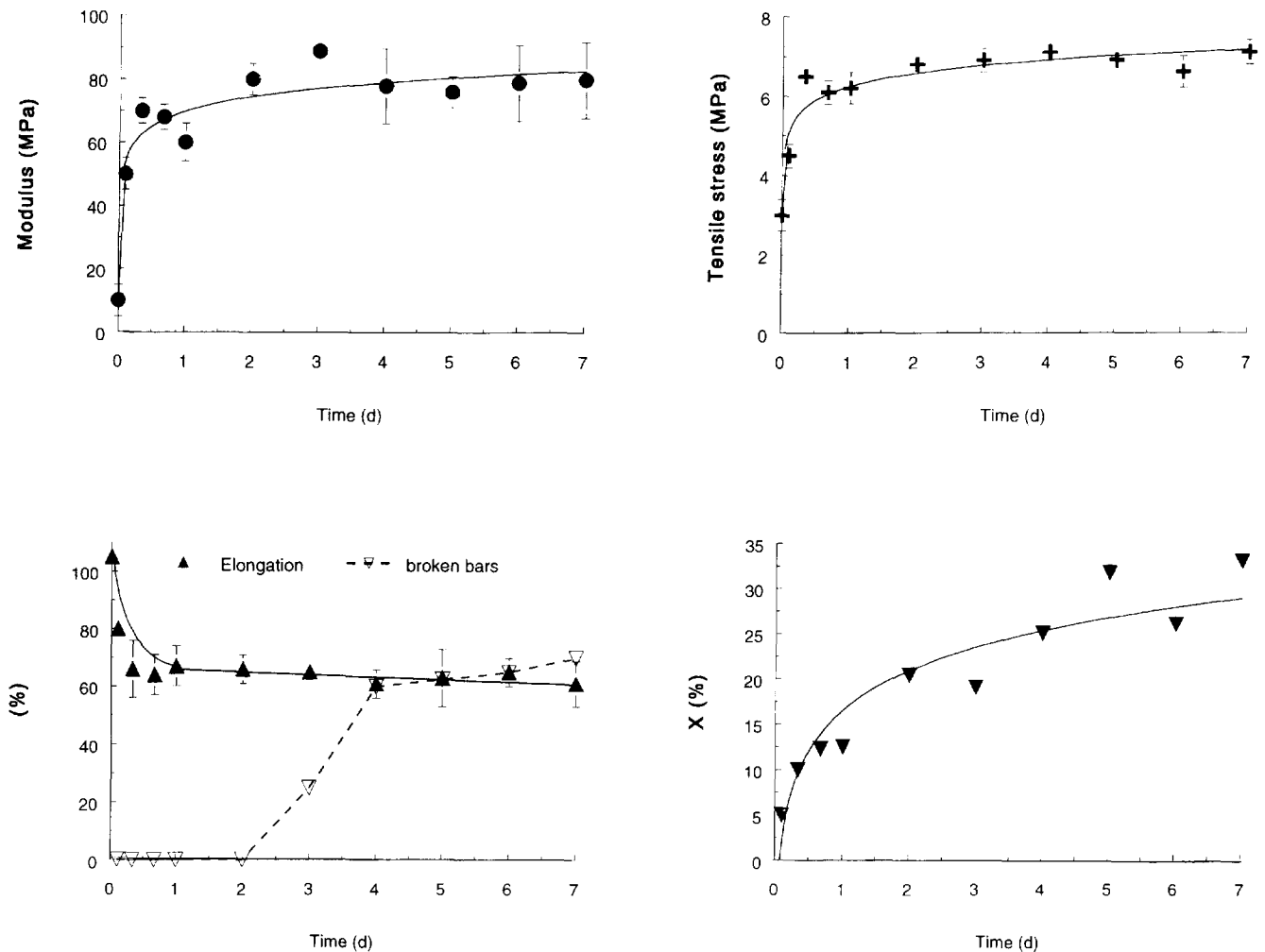


Fig. 6. The mechanical properties and relative crystallinity vs. storage time of TPS aged at 90% RH. (Upper left) E-modulus vs. storage time. (Upper right) Tensile stress of batch 3 vs. storage time. (Lower left) Elongation and % broken bars vs. storage time. (Lower right) %X vs. storage time.

als stored at humidities below 50% almost no B-type crystallinity is observed. For materials stored at higher humidities, the crystallinity is increased from 0 to 40% relative to native potato starch. Most materials show cracks and several samples break spontaneously. For materials with B-type crystallinity above 5% the tensile stress and the E-modulus are increased from approximately 5.5 to 7 and 40 to 60 MPa, respectively. The strain at break is decreased from 90 to 55%. The amount of broken samples increases to 100% at high humidities (90% RH). The slight differences in absolute values of the stress-strain properties in comparison with the results presented in Figs 5 and 6 are due to variations in storage conditions and water content directly before stress-strain measurements.

Description of TPS in terms of a molecular network

It is shown that the changes in storage humidity affect the amount of B-type crystallinity in TPS (Figs 5–7).

The change in crystallinity influences the stress-strain behaviour of thermoplastic potato starch especially at lower crystallinity ($X < 20\%$). During extrusion the native granular structure is disrupted and the crystalline structure of the amylopectin melts. It is assumed that a complex network is formed consisting of amorphous amylose and amylopectin with some residual fragments of granular structures. The amylose molecules in TPS form V-type and B-type crystalline structures. During storage above glass transition temperatures, B-type crystallinity is formed in TPS materials by amylose as well as amylopectin. The amount of V-type amylose crystals is not changed after the initial storage period and therefore changes in mechanical properties after this period will be due to changes in B-type crystallinity.

The formation of B-type crystallinity and the influence on the mechanical properties of TPS is explained by the following mechanisms. Amorphous amylose and amylopectin form double helical structures which

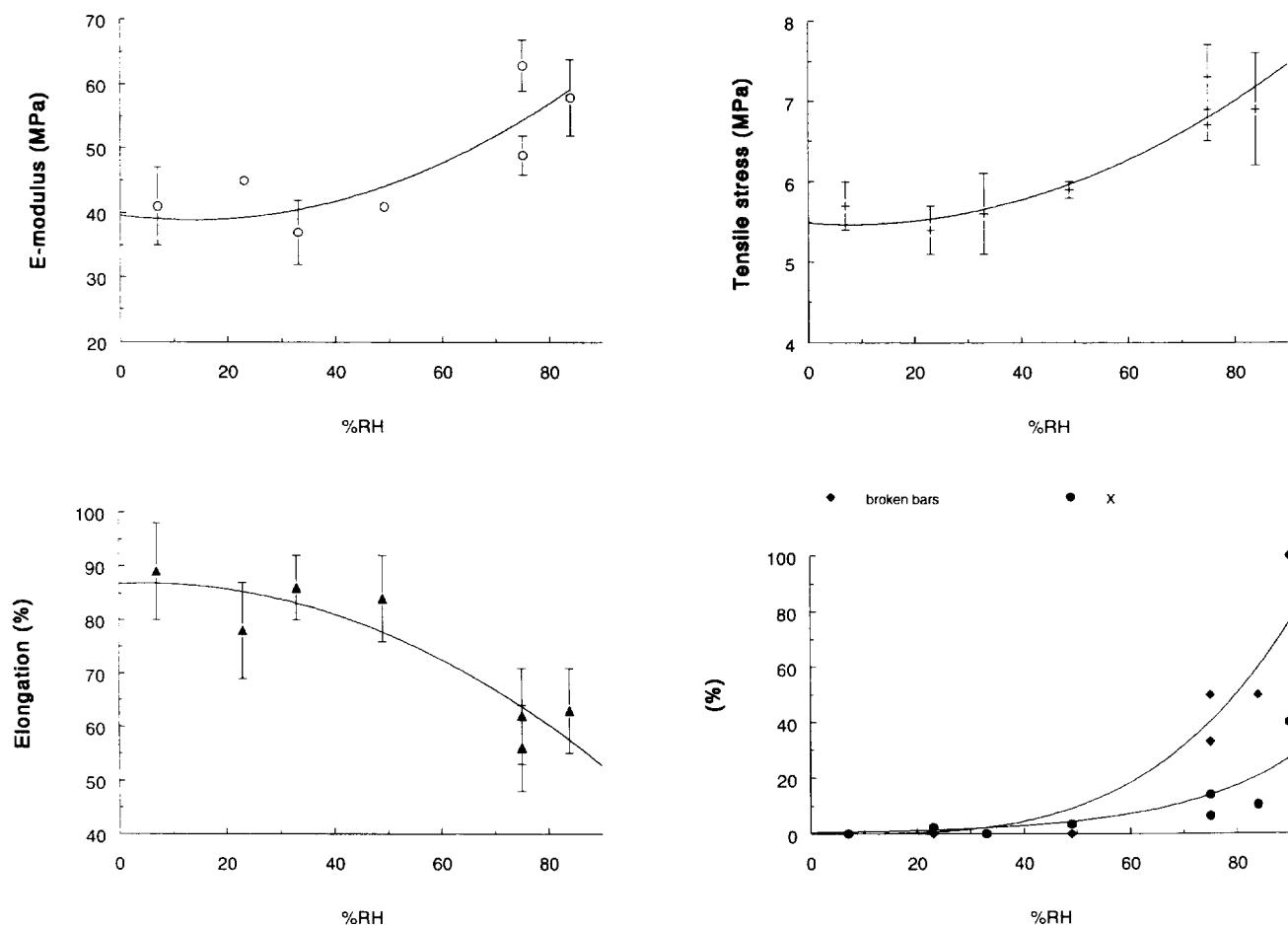


Fig. 7. The mechanical properties and relative crystallinity vs. relative humidity of TPS aged at various RH for two weeks. (Upper left) E-modulus vs. %RH. (Upper right) Tensile stress vs. %RH. (Lower left) Elongation vs. %RH. (Lower right) %X and number of broken bars vs. %RH.

aggregate into a B-type crystalline structure. The crystallinity reinforces the starch network by physical crosslinking and an increase in E-modulus and tensile stress is observed. As in gels (Morris, 1990), amorphous amylopectin is assumed to form double helices which crystallize in a B-type crystallinity at a lower rate than amylose, but to what extent amylose and amylopectin participate each in the observed B-type crystallinity in TPS is not clear. The formation of double helices between amylopectin and amylose, which possibly may participate in the formation of the B-type structure, also can lead to a strengthening of the starch network. This hypothesis remains to be confirmed as it is impossible yet to distinguish co-crystals from pure amylose or amylopectin crystals. The slow crystallization leads to a further increase in E-modulus and in tensile strength. The changes in properties are comparable to the observed stiffening of starch gels, composed of amylose and amylopectin, accompanied by the formation of B-type crystallinity (Morris, 1990). The increase in E-modulus and tensile stress can also be the result of a change in water and glycerol content of the amorphous

part of the TPS. B-type crystals contain ca. 27% water and no glycerol. The amount of plasticizer content in the amorphous regions therefore can be a function of crystallinity, therewith changing the glass transition temperature of the amorphous regions. The magnitude of this change in plasticizer content is still very low (<1%) at crystallinities up to 35%. The change in crystallinity in TPS leads to a change in stress-strain behaviour (Fig. 4). At low crystallinity the curves are smooth and no yielding is observed. At higher crystallinity the curves are not smooth and a discontinuity is observed. The strain at break is only slightly decreased by an increase in relative crystallinity up to approximately 30%. The amorphous part of the material is thus even at relatively high crystallinity still the main part of the TPS materials (more than 90% w/w). The strain is likely to be highly determined by plastic flow of the amorphous part of the starch in the TPS materials which occurs above glass transition temperature.

The interactions in the amorphous matrix can be mainly attributed to hydrogen bridging (van Soest *et al.*, 1995b). A large part of the outer chains of the

amylopectin molecules have interactions with neighbouring amylose and amylopectin molecules. Amorphous amylopectin TPS materials are shown to form a highly coherent network with high elongations up to 500% (van Soest *et al.*, 1995c), while partial acid hydrolysis of starch leads to a reduction of the elongation (van Soest *et al.*, 1995d). The elongation of these TPS materials is declining after crystallization of part of the amylopectin. Above 30% crystallinity, the number of interactions between different amylopectin molecules is assumed to decrease by the formation of intramolecular crystallinity of amylopectin. A crystalline amylopectin molecule has only limited interactions by hydrogen bridging with amylose and amylopectin molecules within the amorphous regions. Amorphous amylopectin molecules are highly stretched by the shear stress forces during extrusion as is seen by the extrudate swell and the shrinking of the rubbery materials after storage at high humidities (van Soest *et al.*, 1995c). The amylopectin molecules tend to form the more compact cluster structure, as proposed by Hizukuri (1986), during aging and crystallization which results in an increased internal stress in the TPS materials. At the crystalline junction zones spontaneous cracks are formed. An abrupt decrease in elongation is observed when the aggregates of double helices within one amylopectin molecule have become large enough forming an intramolecular B-type crystal.

CONCLUSIONS

By extrusion of native potato starch with glycerol, an amorphous thermoplastic material is obtained. The formation of intermolecular double helical structures of amylose and amylopectin and an increase in amylose and amylopectin B-type crystallinity stiffens and strengthens the materials. This change in properties is explained by the formation of physical cross-links in a complex network of amorphous amylose and amylopectin. A further increase in intramolecular amylopectin crystallization reduces the interactions of the amorphous part of the materials. This results in a lowering of the elongation and formation of cracks.

A slight increase in crystallinity improves the stiffness and strength of these glycerol-containing TPS materials. However, the mechanical properties are rapidly declining after storage for several days at 70 and 90% RH. This makes the use of these type of glycerol containing TPS materials limited at high storage humidities.

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REFERENCES

- Bader, H.G. & Göritz, D. (1994). *Starch/Staerke*, **46**, 435.
- Bastioli, C., Bellotti, V. & Montino, A. (1992). *Italy PCT Int. Appl.*, 9,214,782.
- Biliaderis, C.G. & Zawistowski, J. (1990). *Cereal Chem.*, **67**, 240.
- Chinnaswamy, R. & Hanna, M.A. (1991). *Starch/Staerke*, **43**, 396.
- De Brock, I.L.H.A., Van den Broecke, P.M.R. & Bahr, K.-H. (1993). *EP Appl.*, **599**, 535.
- Dell, P.A. & Kohlman, W.G. (1994). *J. Appl. Polym. Sci.*, **52**, 353.
- Hermans, P.H. & Weidinger, A. (1949). *J. Polym. Sci.*, **4**, 135.
- Hizukuri, S. (1986). *Carbohydr. Res.*, **147**, 342.
- Kirby, A.R., Clark, S.A., Parker, R. & Smith, A.C. (1993). *J. Materials Sci.*, **28**, 5937.
- Lai, L.S. & Kokini, J.L. (1991). *Biotechnol. Prog.*, **7**, 251.
- Lay, L.S., Rehm, J., Stepto, R.F., Thoma, M., Sachetto, J.P., Lentz, D.J. & Silbiger, J. (1992). US Patent 5,095,054.
- Mercier, C., Charbonnier, R., Grebaut, J. & de la Gueriviere, J.F. (1980). *Cereal Chem.*, **57**, 4.
- Miles, M.J., Morris, V.J., Orford, P.D. & Ring, S.G. (1985). *Carbohydrate Res.*, **135**, 271.
- Morris, V.J. (1990). *Trends Food Sci. Technol.*, **1**, 2.
- Ollett, A.-L., Parker, R. & Smith, A.C. (1991). *J. Materials Sci.*, **26**, 1351.
- Orford, P.D., Ring, S.G., Carroll, V., Miles, M.J. & Morris, V.J. (1987). *J. Sci. Food Agric.*, **39**, 169.
- Ring, S.G., Colonna, P., l'Anson, K.J., Kalichevsky, M.T., Miles, M.J., Morris, V.J. & Orford, P.D. (1987). *Carbohydr. Res.*, **162**, 277.
- Röper, H. & Koeh, H. (1990). *Starch/Staerke*, **42**, 123.
- Russell, P.L. (1987). *J. Cereal Sci.*, **6**, 147.
- Soest, J.J.G. van, Tournois, H., de Wit, D. & Vliegthart, J.F.G. (1994). *Polymer*, **35**, 4721.
- Soest, J.J.G. van, Hulleman, S.H.D., de Wit, D., Vliegthart, J.F.G. (1995a). *Ind. Crops Prod.*, **5**, 11.
- Soest, J.J.G. van, Tournois, H., de Wit, D. & Vliegthart, J.F.G. (1995b). *Carbohydr. Res.*, **279**, 201.
- Soest, J.J.G. van, de Wit, D. & Vliegthart, J.F.G. (1995c). *J. Appl. Polym. Sci.*, accepted.
- Soest, J.J.G. van, Benes, K. & de Wit, D. (1995d). *Starch/Staerke*, **47**, 429.
- Stepto, R. & Tomka, I. (1987). *Chimia*, **41**, 76.
- Stepto, R.F.T., Tomka, I. & Thoma, M. (1988). *EP Appl.*, **304**, 401.
- Wiedmann, W. & Strobel, E. (1991). *Starch/Staerke*, **43**, 138.
- Wittwer, F. & Tomka, I. (1987). US Patent 4,673,438.