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INFLUENCE OF AMYLOSE-AMYLOPECTIN RATIO ON PROPERTIES OF EXTRUDED STARCH PLASTIC SHEETS

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Key Words: Amylose-Amylopectin Ratio; Bioplastic; Extrusion; Mechanical Properties; Crystallinity; Molecular Mass; Starch; Structure

ABSTRACT

Starch plastic sheets were prepared by extrusion processing of mixtures of granular high-amylopectin and high-amylose starches in the presence of glycerol and water as plasticizers. Amylose content varied between 0 and 70% (w/w). Structural characterization and determination of the mechanical properties of the sheets were performed after aging the materials between 40-65% relative humidity for 2 and 35 weeks and at 90% relative humidity for two weeks. The materials were semicrystalline and viscoelastic. The materials were described as complex heterogeneous multiphase materials. They consisted of amorphous and crystalline phases of amylose and amylopectin as well as granular structures and domains of amylose, amylopectin and amylose-amylopectin helices. Single-helical type crystallinity was formed solely by amylose directly after processing while B-type crystallinity was rapidly formed in amylose-rich materials and slowly during aging of amylopectin-rich materials.

The stress-strain and stress-relaxation properties were related to differences in amylose content, degree of crystallization and water content. The amorphous amylopectin rich materials were flexible and soft but showed an increase in stiffness and a decrease in elongation due to crystallization. Amylopectin-rich materials showed unfavorable relaxation, shrinkage and cracking during aging. The materials rich in amylopectin were sensitive to water content while the amylose-rich materials were not sensitive to water in the range of 9-13% (w/w). Stress-strain relaxation behaviors of the materials were dependent on starch structure and on experimental conditions such as strain rate and extension by which the ratio of elastic and viscous response were varied. An increase in relaxation times was found with increasing amylose content and water content for the materials with solely amylose crystallinity.

INTRODUCTION

Because of the complete biodegradation of starch to carbon dioxide and water in a relatively short time compared to most synthetic polymers [1], several researchers have studied the use of starch in plastic composites [2-4]. The goal of recent research has been to prepare consumer items trom substantially pure starch and to exclude synthetic polymers from the formulation. The starch materials contain plasticizers, such as low molecular mass alcohols, so they will melt below the decomposition temperature. Starch bioplastics can be made by conventional processing techniques used for commodity plastics such as extrusion and injection molding [2-5]. The development of products from starch makes it necessary to develop an insight into the structure-property relationships of starch plastics.

Most granular native starches are a mixture of 20-30 % amylose, a linear polymer of alpha-1,4- linked glucose units with a molecular mass in the range of 100-1,000 kg/mol, and of amylopectin, a highly branched, high molecular mass (approximately 105 kg/mol) polymer of short alpha-1,4 chains linked by alpha-1,6 bonds [6,7]. The components show features such as phase separation, aggregation and gelation in gels. The influence of the relative content in dispersions in water has been extensively studied using both native and purified amylose and amylopectin [8-18]. Upon aging, the properties of high moisture (> 50% water) materials, such as gels, are influenced by retrogradation which has been shown to be different for amylose and amylopectin [17].

The stress-strain and crystallization behavior of starch films casted from solutions have been investigated over a long period of time [18-25]. It has been shown that casted films prepared of amylose are more flexible than casted films prepared of amylopectin starch [25]. The linear amylose molecules are said to form more effective entanglements than the highly branched amylopectin molecules resulting in a better performance, such as an increase in tensile strength. Cast films are not being manufactured commercially because of the high cost of preparation from solutions. The phase changes (starch granular disruption, starch gelatinization and melting) during thermal and thermomechanical processing, such as extrusion, are influenced by low molecular mass alcohols and sugars and processing parameters [26, 27]. The degree of starch crystallite melting, 'starch conversion' or degree of starch granular disruption and starch degradation in glycerol-containing thermomechanically plasticized starch plastics differ from films cast from solutions and materials processed with only water during extrusion cooking [26, 27, 28]. It has been shown that amylose-amylopectin gels are phase-separated biphasic systems, resulting in one continuous phase entrapping the other in the cast films [8, 10, 25, 26].

Several papers have been published on the mechanical properties of starch plastics and extruded starches which were prepared from several starch sources, such as maize, wheat, potato, waxy corn and amylomaize starch [29-41]. The structural and mechanical properties of glycerol and water plasticized starch products are highly dependent on the plasticizer concentration [29-41]. Starch source has been shown to influence the properties of glycerol-containing starch plastic materials and the differences in properties were ascribed partly to the differences in amylose and amylopectin content and molecular structure [26, 30, 31, 32, 33, 35, 38, 39, 40, 41]. In contrast with the brittle amylopectin films cast from films, waxy corn extruded glycerol-containing materials were reported as highly flexible materials [33, 35, 38]. An increase in the molecular mass of amylopectin resulted in an increased elongation of glycerol-plasticized extruded plastic sheets [30, 31, 35]. It has been shown that the amounts of amylose and amylopectin effect the crystallinity present in glycerol-containing bioplastics but no direct relationships of the relative contents with properties have been reported [35, 42]. The retrogradation rate of starch has been reported to decrease with increasing glycerol content for starch gels and starch extruded sheets [41, 43].

However, little is known about the role of amylose and amylopectin and how both molecules influence the structure as well as the properties of low moisture. The purpose of this paper is to present detailed knowledge about the influence of amylose and amylopectin ratios on the properties of extruded starch materials and on starch structure and morphology. Therefore, the properties of extruded, low moisture, glycerol containing starch plastics made of reconstituted mixtures of high-amylose and amylopectin starches in the range of 0-70% amylose were characterized after aging at various storage conditions. The starch structure and morphology of the materials were assessed using X-ray diffraction, size-exclusion chromatography, light scattering, differential scanning calorimetry, polarized light microscopy and density measurements. Differences in stress-strain and stress relaxation behavior of the materials were related to the variations in starch structure and the morphology of the materials.

EXPERIMENTAL

Materials

The technical grade starches, high-amylopectin (waxy corn starch with less than 1% amylose) and high-amylose (amylomaize starch with 70% amylose), were obtained from Sigma Chemical Co. (St. Louis, USA). Amylose contents were determined by calorimetry as described below. The moisture content of the starches was 12-13%. L-α-lysophosphatidylcholine (LPC) from egg yolk (L-4129) was obtained from Sigma.

Extrusion

Samples 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 screws, which were developed for polyethylene, and a slit die. The screws had a diameter of 2 cm and a length of 30 cm. The rectangular die opening was 25 mm by 0.3 mm. The starches were premixed with glycerol to give the following composition: starch:glycerol = 100:30 (w/w). The torque was held constant at 45 ± 10 Nm by manually adjusting the amounts fed into the extruder. The screw rotation speed was 55 rpm. The temperature profile along the extruder barrel was set at 80, 140, 120, 90-100°C (from feed zone to die). The measured melt temperature in zone two was 135-145°C. The slit die melt temperature was kept below 100°C to prevent the melt from boiling and to give a bubble-free extrudate.

Conditioning

Part of each extrudate was stored at -22°C after quenching in liquid nitrogen directly atter extrusion. Other parts of each extrudate were conditioned at relative humidities (RH) between 40 and 65 ± 5% for two weeks. Other parts were stored either at 65 ± 5% RH for 2 and 35 weeks, respectively, or at 90 ± 5% RH for 2 weeks after which the materials were reconditioned at 65 ± 5% RH for two weeks before tensile measurements. All samples were conditioned at 20°C.

Moisture Determination

Because of the tendency of the starch plastics to absorb water or desorb water, special care was taken to measure the water content immediately before testing. The samples were ground under cryogenic conditions. The water content of the powder (1 g, size < 125 μm) was determined gravimetrically with an Infrared dryer (Sartorius MA40 at 95°C) or with a Gallenkamp vacuum oven (at 70°C and a pressure of less than 100 mbar).

Mechanical Properties

A Model 4301 Instron universal testing machine, operated at crosshead speeds in the range of 1-500 mm/min, was used for tensile and relaxation measurements. Dumbbell specimens were cut, according to the ISO 1184-1983 (E) standard, from the extruded ribbons immediately following extrusion and stored. Four to eight replicates of each material were averaged. The sheet thickness varied and sample dimensions were corrected individually for differences in initial thickness. The tensile stress at maximum load was calculated on the basis of the original cross-sectional area of the test specimen, by the equation: $\sigma = F/A$, where σ was the tensile stress, F was the force and A was the initial cross-sectional area. The percentage strain or elongation was calculated on the basis of the length of the narrow parallel portion, by the formula: $(l - l_l)/l_l \times 100\%$, where l was the distance between the gauge marks (in mm) and l_l, is length of the narrow parallel portion (i.e. 33 mm), which is related to the original gauge length, l_0, by $l_0/l_l = 25/33$. The elastic modulus was calculated as the initial slope of the stress-strain curve.

Stress-relaxation measurements were performed by pulling the materials at prescribed cross-head speeds until the load in the materials was in the range of 0 to 90% of the stress at the break point measured from the load-strain curves. The extension was kept constant and the change in the load was measured. The relaxation time, t, was measured as the time needed to experience a loss in the load of 30% measured from the initial load.

Molecular Mass Determination

The starch samples were dissolved in DMSO: water (90:10 (w/w); 4 mg/ml) by shaking for 48 hours or in 1 M NaOH (4 mg/ml) by stirring for 15-20 hours. Molecular masses were determined as previously described [30, 31, 35].

Differential Scanning Calorimetry (DSC)

DSC measurements were performed with a Perkin-Elmer DSC-7. The calibration was done with Indium ($\Delta H = 28.59$ J/g, onset melting point =156.60°C) and Gallium ($\Delta H = 79.91$ J/g, onset melting point = 29.78°C). An empty pan was used as a reference. Samples were weighed accurately into stainless steel pans and sealed hermetically. Gelatinization endotherms were obtained by mixing 10 mg of starch with 50-60 mg water and the melting profile of 30-40 mg of the starch samples were obtained by heating from 20 to 230°C. The glass transition temperatures were determined by heating the samples (30-40 ma) from 20 to 150°C, cooling down to -50°C followed by a rescan at a rate of 20°C/min to 200°C. Determination of the amylose content was performed on the basis of the melting enthalpy of the amylose- LPC-lipid complex [44]. LPC solutions (50 µL; 3% w/v) were added to the starch samples (10 mg accurately weighed) in the DSC pans. The samples were heated from 20°C to 140°C, cooled to 20°C (cooling rate 200°C/min), stabilized for 2 minutes at 20°C and reheated to 140°C. The amylose content was calculated on the basis of dry starch material with the following relation: (% amylose) = $(\Delta H_m)/(\Delta H_c)$ x 100%, in which $\Delta\backslash H_m$ = measured enthalpy of the melting trans-ition of the LPC-amylose complex in the second scan and ΔH_c = the enthalpy of the pure potato amylose (obtained from Avebe) complex with LPC (22.1 J/g). The amylose was essentially free of amylopectin (< 0.5%) with an average molecular mass of circa 400 kg/mol as determined with light scattering). The heating rate was 10°C/min for all samples.

Morphology

The morphology was determined with polarized light microscopy and by density measurements. The materials were sliced and viewed at a magnification of 40 times with an Axioplan universal microscope with photographs taken using the MC100 camera accessory. Density measurements were made by suspending about 10 g of the materials in paraffin oil (OPG-Farma) with a density of 0.875 kg/l and measuring the amount of displaced paraffin oil.

X-ray Diffractometry

Wide-angle X-ray diffraction patterns were measured accordingly to the methods described previously [35, 38]. The diffractograms were smoothed (points = 6; band broadening = 1.4). The area of the crystalline diffraction (A_c) was measured relative to the area of the peaks (A_t). The ratio $R(X_A) = A_c/A_t$ is related to the relative crystallinity, X. The relative B-type crystallinity was calculated by measuring the A_c/A_t ratio of the peak at 16.8 ± 0.5° (2Θ). The relative V_h-type crystallinity was calculated by measuring the A_c/JA_t ratio of the peak at 19.5 ± 0.4° (2Θ). The relative overall crystallinity, X, was expressed as the A_c/A_t ratio between 7 and 40° (2Θ).

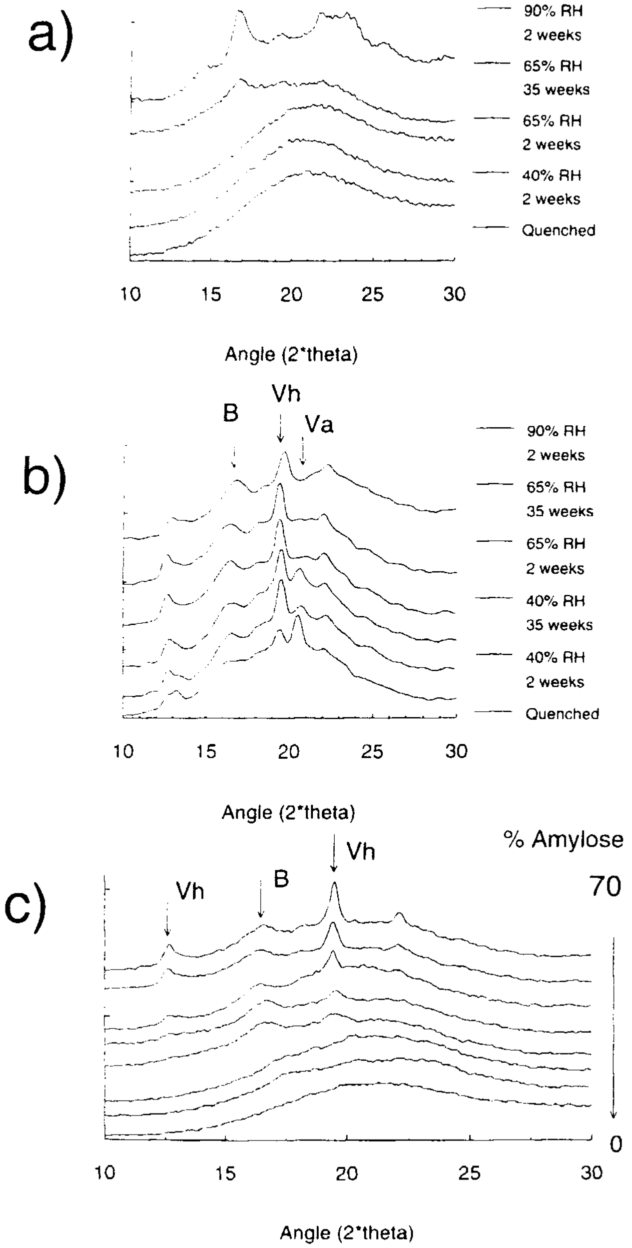
RESULTS

Structural Characterization of the Extruded Materials

During extrusion, the throughput had to be increased for materials with a higher amount (mass fraction) of amylopectin to be able to keep the torque constant during extrusion. This suggested that materials with more amylopectin had lower melt viscosities. The amount of die swell was larger for materials with less amylose. The thicknesses of the extruded ribbons were (after equilibration at 60% RH) in the range of 2-5 mm for high-amylopectin materials and 1.1-1.3 mm for the high-amylose materials. Extrudates with high amounts of amylopectin were transparent suggesting that the granular structures were completely destroyed during extrusion. The materials became less transparent with increasing amylose content. This is indicative of more inhomogeneous or crystalline materials containing possible granular structures. The density of the materials was approximately 1.46 ± 0.02 kg/1 and no significant differences between materials were observed.

With polarized light microscopy it was shown that in the materials without amylose the granular birefringence was destroyed during extrusion. With increasing amylose content granular-like structures, remnants, were in observed in the materials. The structures were irregular in shape and showed no clear birefringence. The granular-like structures were dispersed homogeneously throughout the materials. This increase in granular remnants was shown to be related to the higher melting temperature of amylomaize compared to waxy corn starch [38, 39]. With DSC, no clear endothermic transitions were observed in the materials quenched in liquid nitrogen directly after extrusion indicative of a completely or almost completely amorphous material above glass transition temperature. Several irregular, broad endothermic transitions were observed in the stored materials but the profiles were too complex for identification and quantification of the peaks. Several of these endothermic transitions observed in starch plastics have been previously assigned to both sub-glass transition endothermic events as well as to the melting of granular and recrystallized starch and amylose-lipid complexes [31, 34, 35, 37, 46].

Some typical X-ray diffractograms after extrusion are shown in Figure 1. In Figure 1a it is shown that the starch materials consisting of pure amylopectin were


a)
90% RH
2 weeks
65% RH
35 weeks
65% RH
2 weeks
40% RH
2 weeks
Quenched
10
15
20
25
30
Angle (2*theta)
b)
B
Vh
Va
90% RH
2 weeks
65% RH
35 weeks
65% RH
2 weeks
40% RH
35 weeks
40% RH
2 weeks
Quenched
10
15
20
25
30
Angle (2*theta)
c)
Vh
B
Vh
% Amylose
70
0
10
15
20
25
30
Angle (2*theta)

amorphous directly after extrusion. Slow crystallization of the amylopectin took place during aging above glass transition temperature (at 65 and 90% RH). The rate of crystallization increased with increasing RH and water content. The crystallinity is B-type, with a maximum at 16.8° (2*Θ), which was shown to be preferably formed by crystallization of the short outerchains of amylopectin in glycerol containing starch materials [27, 33, 35, 38]. In Figure 1b it is shown that starch plastics from high-amylose contained three types of crystal structures identified as the B-type, V-type (with maxima at 13.2° and 20.6°, 2*Θ) and V-type (with maxima at 12.6° and 19.4°, 2*Θ) structures. The V-type structures are formed by recrystallization of amylose during extrusion or during cooling [27, 35]. The exact role of glycerol or lipids in the formation of amylose single-helical crystallinity still remains to be shown [27, 46, 47]. The formation of the V_a-type structure is different from the E-type structure formed at low water contents in starch plastics from potato starch [27] or in extrusion cooked materials composed of amylomaize starch or normal maize starch [34, 47]. The V_a-type structure only was observed in the materials stored at low humidities and below their glass transition temperature. Above the glass transition temperature the structure converted in the V_h-type structure. The relative amount of V-type crystallinity did not increase during long-term storage. The relative abundance of these structures have been shown to be determined by composition and processing conditions and were not changed after long-term storage [27]. In Figure 1c, the diffractograms of the materials with an amylose content in the range of 0-70% are shown after storage at 65% RH for two weeks. It is shown that the relative crystallinity increased with increasing amylose content. Both the amount of B-type as well as V-type crystallinity increased. As expected the amount of V-type crystallinity was proportional to the amount of amylose. The amount of B-type crystallinity increased with increasing amylose

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Figure 1. X-ray diffractograms after extrusion and aging

a) materials consisting of pure High-amylopectin starch
b) materials consisting of pure High-amylose starch
c) materials consisting of mixtures of High-amylose and High-amylopectin starch withan amylose content in the range of 0-70% (w/w on the basis of dry starch)

The relative humidities (RH) and storage times are indicated in the Figure. The most characteristic peaks for B and V-type crystallinity are indicated by arrows. Quenched materials are those materials which were put immediately after extrusion in liquid nitrogen.

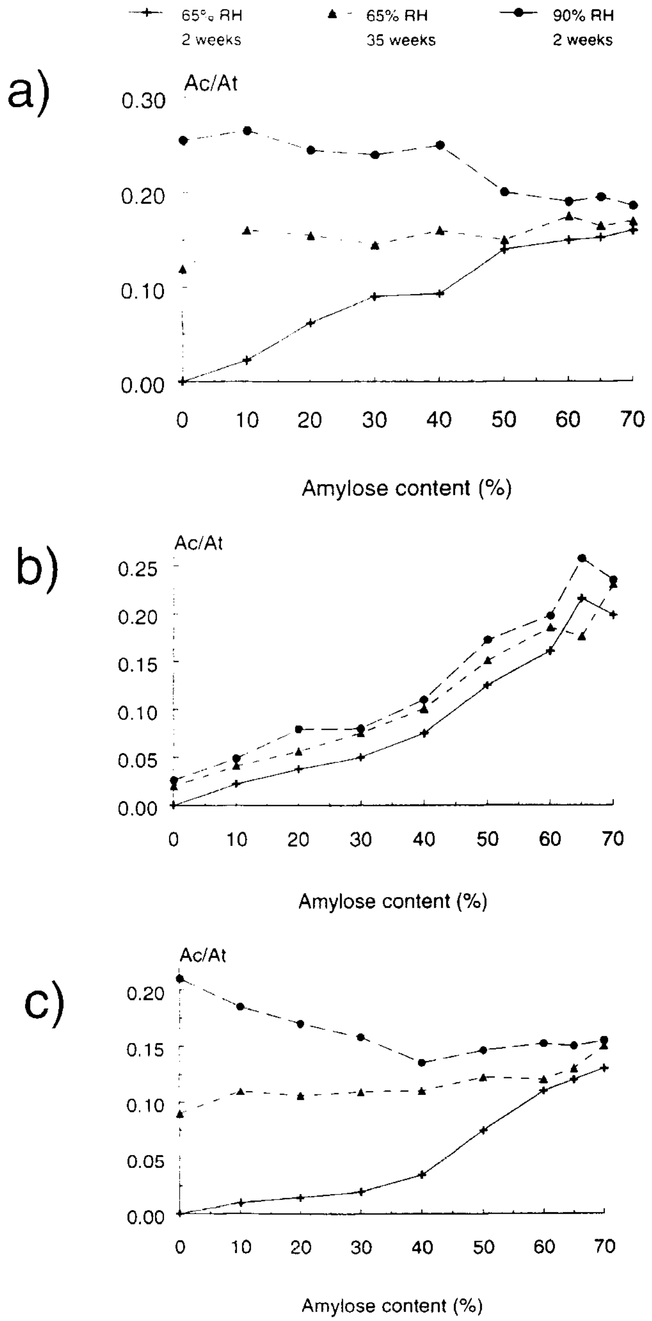

Figure 2. Relative crystallinity versus amylose content after aging

a) B-type crystallinity

b) V-type crystallinity

c) overall crystallinity

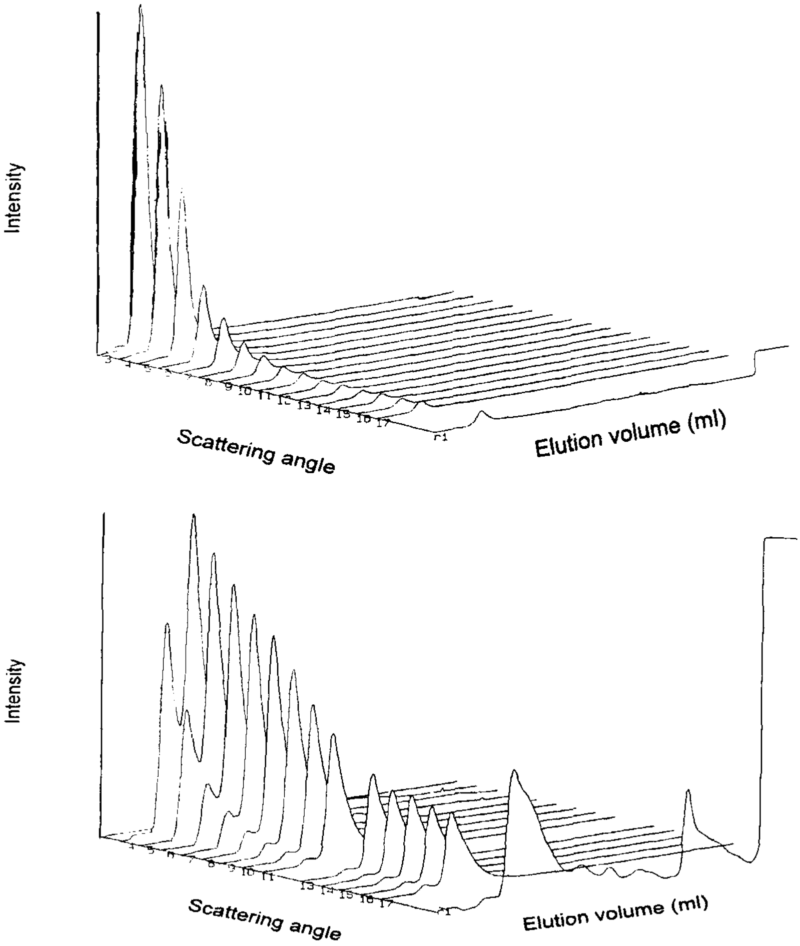

Figure 3. HPSEC-MALLS measurement of the High-amylopectin native starch (Top) and of starch sheets composed of High-amylopectin starch (Bottom); The concentration detector is indicated by *ri* and the various laser detectors by numbers.

content. This B-type crystallinity was ascribed solely to amylose. Amylopectin crystallization did not occur within two weeks at 65% RH. There are two explanations for this. Firstly, the B-type crystallinity of the high-amylose starch fraction is not completely melted during extrusion which is due to the relative low melting temperature during extrusion. The second explanation is the fast recrystallization of amorphous amylose during extrusion and cooling. Amylose is known

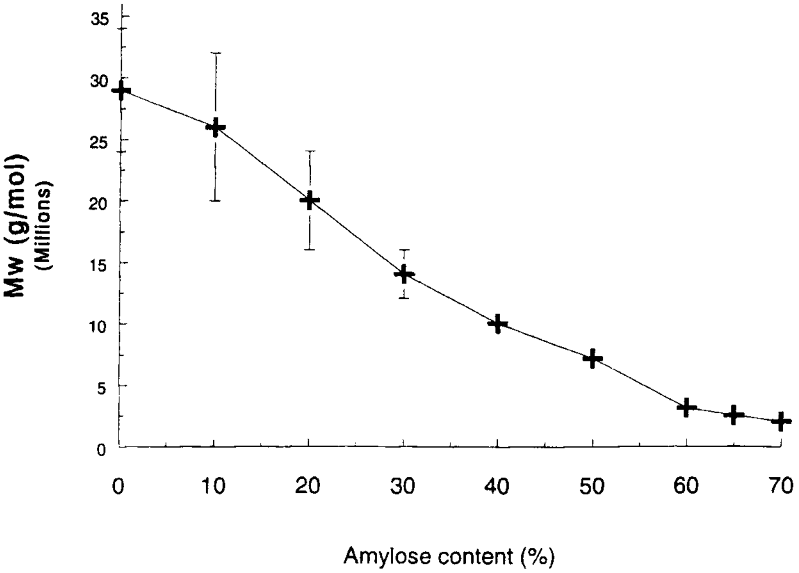

Figure 4. Average molecular mass (Mw) versus amylose content.

to crystallize into a B-type structure for high moisture starch materials rapidly compared to amylopectin [14, 17, 20, 35].

During long-term storage and high humidities the amount of B-type crystallinity increased. The rate of crystallization depended on humidity and water content. A higher water content lead to a more rapid crystallization. The formed crystallinity can be composed of both amylose and amylopectin. Another possibility is co-crystallization of amylose with the outerchains of amylopectin [8, 10]. With X-ray diffractometry no discrimination could be made between these crystals. The slow increase in B-type crystallinity was proportional to the amount of amylopectin. At least a large part of the amylopectin is involved. The relative amounts of V-type and B-type crystallinity were quantified and the total crystallinity was roughly estimated. The results are shown in Figure 2. The materials stored at 65% RH had a crystallinity of 0% for the high-amylopectin materials increasing to 10% for the high- amylose materials. The crystallinity increased for the high-amylopectin starch materials to about 20%, while the highest value for the high-amylose materials was approximately 15%.

Typical laser-light scattering signals and the chromatograms of the high-amylopectin starch before extrusion and the plastic sheet thereof after extrusion are shown in Figure 3. The calculated average molecular masses versus amylose

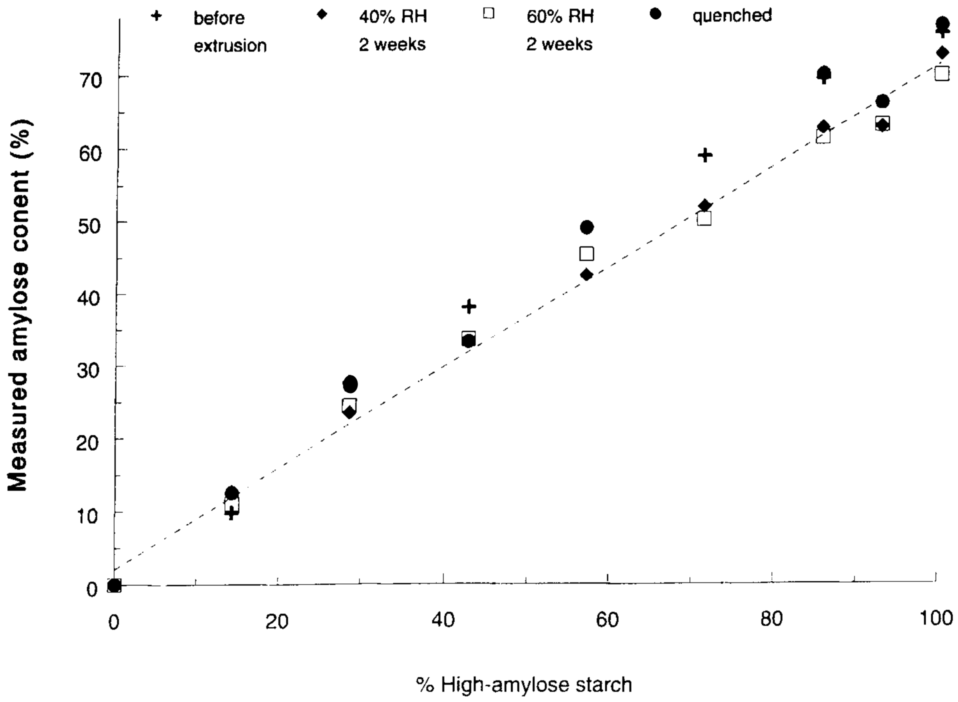

Figure 5. The amylose content of the starch mixtures before and after extrusion as determined with DSC. The results were fitted by linear regression. The slope of the curves are 1.0 to 1.1. The variances accounted for are: R_{val} is 0.981, 0.981, 0.996 and 0.994, respectively for the materials before extrusion and after storage at -22°C, 40% RH and 60% RH.

content of the materials are shown in Figure 4. The molecular mass of the high molecular mass amylopectin decreased drastically during extrusion as seen by the disappearance of the first peak at an elusion volume of 25-30 ml [26, 30, 31, 40]. This resulted in a rapid decline in average molecular mass with increasing amylose content. Because the breakdown products of the high molecular mass amylopectin overlapped with the intermediate branched amylopectin and amylose in the chromatograms, it was impossible to discriminate between the three types of molecules. Therefore, it was impossible to draw a conclusion about the breakdown of amylose taking place during extrusion. However, no significant amounts of oligosaccharides were observed in the chromatograms indicating only a breakdown of starch to a moderate level. On the basis of the fact that the amylose content of the materials after extrusion was the same as before extrusion, as shown in Figure 5, it can be said that the overall amount of long-chain linear amylose remained constant.

Mechanical Properties of the Sheet Materials

The mechanical properties of the materials were determined in time after storage at various humidities to observe the effects of variations in water content and crystallinity on the stress-strain and stress-relaxation properties.

Influence Amylose/Amylopectin Ratio and Water Content on Stress-Strain Behavior

The stress-strain properties of four batches of extruded materials were investigated after storage for two weeks between 40 and 65 ± 5% RH and 20°C. The batches differed in water content because of variations in storage humidities. The results are summarized in Table 1. The stress-strain curves were essentially linear at low extensions but curved towards the strain axis at higher extensions. The high-amylose starch materials showed a different behavior than the amylopectin starch materials. The high-amylopectin materials were weak and soft with high elongations, while the high-amylose materials were rigid-like and strong with lower elongations. The elastic modulus and tensile strength increased above an amylose content of 30%. The elongation decreased gradually with increasing amylose content as shown in Figure 6 for the materials with 12.5% water (w/w). There was a clear influence of water content on the materials with less than 50% amylose. The elastic modulus and tensile stress increased with decreasing water content. This increase has been explained for starch sheets prepared from potato starch and waxy maize with similar plasticizer (water and glycerol) content by a glass to rubber transition which occurred around 9% water (w/w) [31, 33, 35, 41]. The effect of water content was not observed for materials with more than 50% amylose. There seemed to be almost no influence on the properties of the high amylose materials within the range of 9-12.5% water.

Influence Amylose/Amylopectin Ratio on Stress-Relaxation Behavior

The results of the stress-relaxation measurements are shown in Figure 7. In Figure7a the load-relaxation curves are shown for materials measured with a drawing speed of 30 mm/min and a water content of 11% (w/w). The shapes of the load-strain curves (first part) and the relaxation time curves (second part) were related to amylose content. The influence of water content is shown in Figure 7b. The relaxation times increased with increasing water content. The relaxation times decreased with amylose content up to an amylose content of 30%. Above an amylose content of 30% the relaxation times increased. From this, it became clear that stress-relaxation measurements of the materials were complex. The materials are viscoelastic and both the viscous as well as the elastic component, which seemed

TABLE I. Results Stress-Strain Measurements before Long-Term Aging. The Materials were Stored for 2 Weeks Between 40 and 65% Rh

	E-Modulus (MPa)				Tensile stress (MPa)				Elongation (%)			
% water	12.5	11.0	10.5	9.5	12.5	11.0	10.5	9.5	12.5	11.0	10.5	9.5
% amylose												
0	7	12	4	30	0.5	0.6	0.4	1.4	453	436	453	276
10	5	13	25	43	0.4	1.1	1.5	3.3	476	312	303	135
20	3	18	16	45	0.5	1.3	0.9	3.4	442	213	309	134
30	12	14	56	61	1.2	1.6	3.8	4.4	169	165	97	98
40	9	36	16	26	1.3	3.3	2.2	3.6	142	66	101	106
50	73	60	95	39	5.4	5.4	6.6	4.4	34	38	45	80
60	51	45	79	57	5.0	5.1	6.8	6.3	36	33	37	48
65	132	-	131	-	8.3	-	8.4	-	41	-	43	-
70	101	-	107	-	8.5	-	9.1	-	53	-	51	-

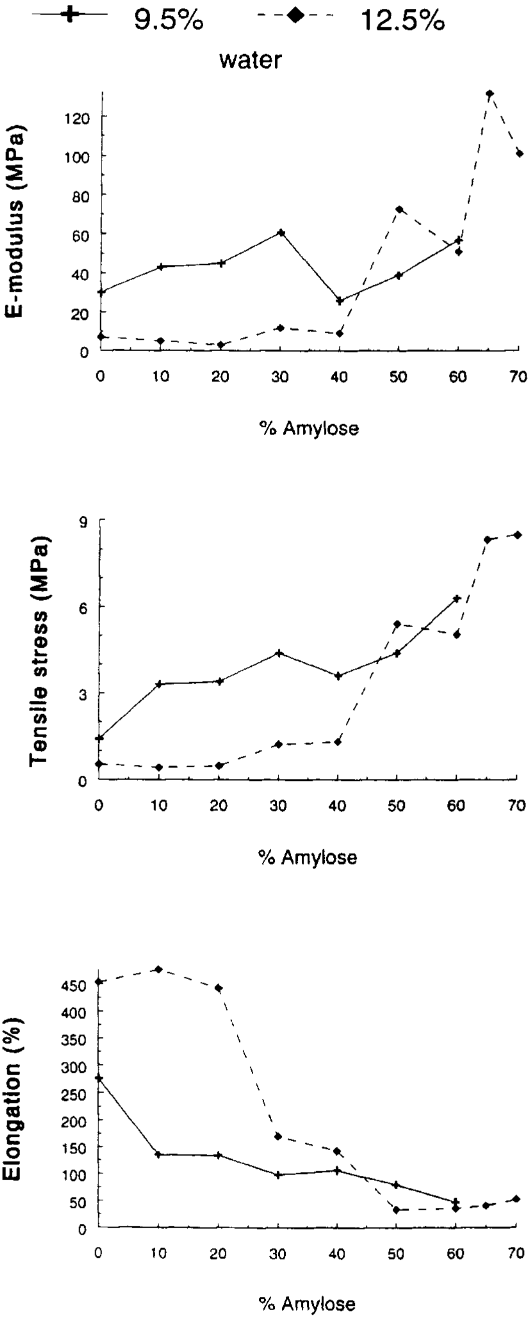

Figure 6. Elastic modulus, tensile stress and elongation versus amylose content for materials stored for 2 with a water content of 9.5 and 12.5 % (w/w), respectively.

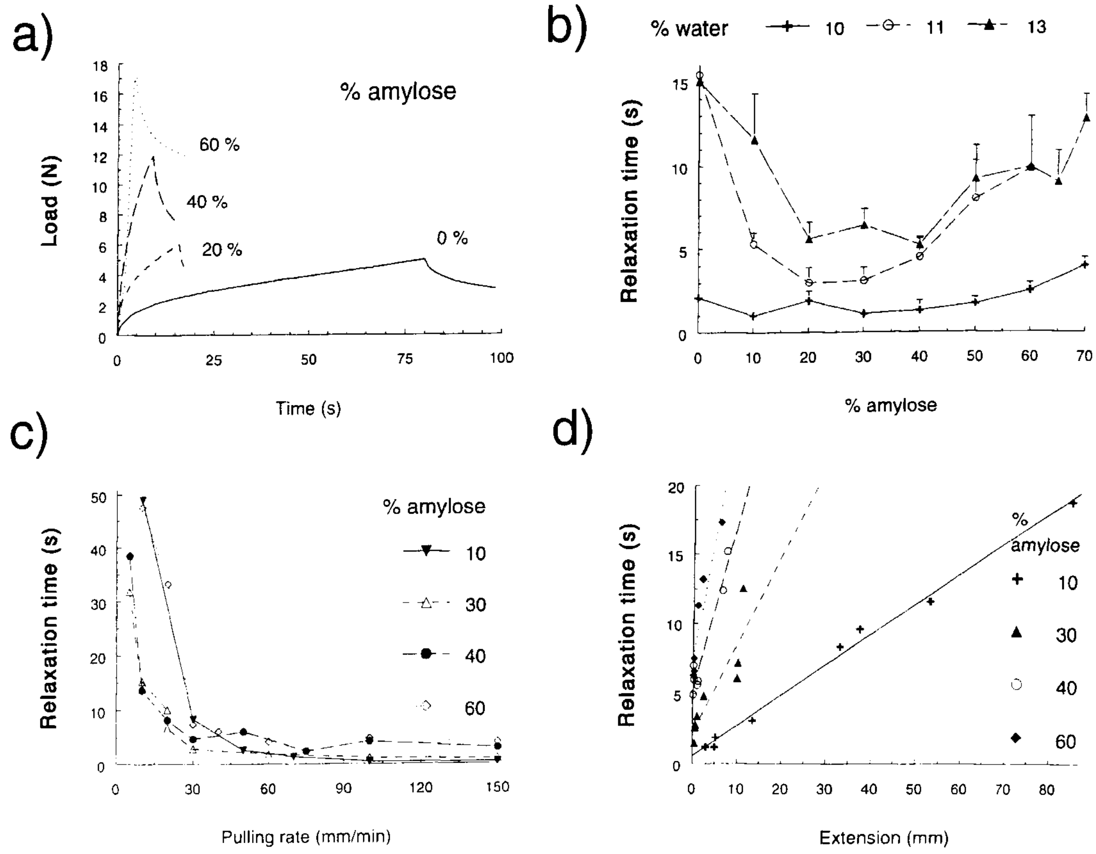

Figure 7. Stress-strain behavior of starch plastics

a) Stress-strain curves for materials containing 0, 20, 40 and 60% amylose (w/w); the pulling rate is 30 mm/min and the water content is 13% (w/w).

b) Relaxation times versus amylose content at various water contents.

c) Relaxation times for various amylose content versus pulling rate.

d) Relaxation times for various amylose content versus extension.

to be a function of amylose content, are important in the measurements. The influence of pulling rate on the relaxation time is shown in Figure 7c. The relaxation times decreased rapidly with increasing pulling rate. This change occurred at approximately 30 mm/min, but for the materials with 10 and 60% amylose, the change was more pronounced. At high pulling rates, the materials with 40 and 60%

TABLE 2. Results of Stress-Strain Measurements after Aging

	E-Modulus (MPa)			Tensile stress (MPa)			Elongation (%)		
RH (%)	65	65	90	65	65	90	65	65	90
time (weeks)	2	35	2	2	35	2	2	35	2
% amylose									
0	7	77	-	0.5	5.5	-	453	41	-
10	5	65	-	0.4	5.4	-	476	24	-
20	3	68	-	0.5	5.5	-	442	37	-
30	12	96	-	1.2	5.7	-	169	30	-
40	9	107	-	1.3	6.3	-	142	28	-
50	73	93	110	5.4	6.2	7.0	34	26	25
60	51	76	180	5.0	6.3	8.0	36	32	25
65	132	76	210	8.3	6.3	8.3	41	33	30
70	101	104	190	8.5	7.6	9.0	53	38	31

amylose relaxed more slowly than the materials with 10 and 30% amylose. In Figure 7d the influence of the extension at a pulling rate of 30 mm/min is shown. The relaxation times increased with increasing extension for the sheet materials. At high pulling rates and low extension the response of the material to the applied load was elastic and the viscous component relaxed rapidly. At high extension and low pulling rates the load-strain diagrams curved towards the strain-axis. The ratio of the viscous part and the elastic part seemed to be changed by changing both the pulling rate as well as the applied load at a pulling rate of 30 mm/min as is shown in the Figures 7c and 7d.

Influence Aging and Crystallinity in Relation with Amylose/Amylopectin Ratio on Stress-Strain Behavior

In Table 2 and Figure 8, the effects of aging and crystallization on the stress-strain properties are shown. An increase in elastic modulus and tensile stress was observed during long-term storage and during aging at high humidity for a

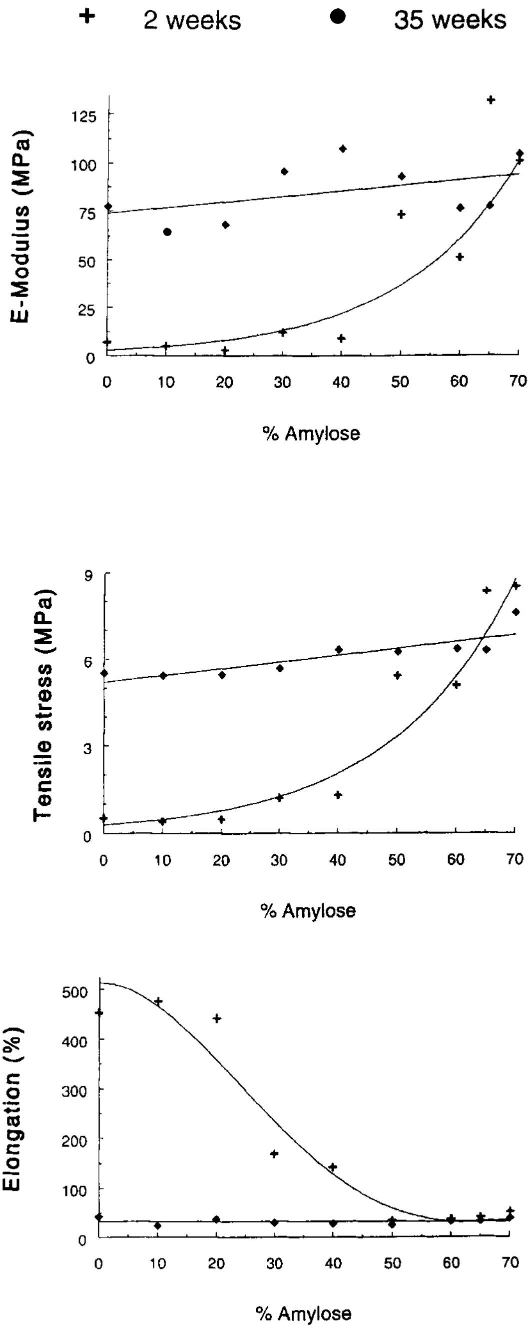

Figure 8. Elastic modulus, tensile stress and elongation versus amylose content for materials stored at 65% RH for 2 and 35 weeks, respectively.

shorter period. The strain at break decreased rapidly for the materials with high amounts of amylopectin, while the effects on the high amylose materials were less pronounced. The high-amylopectin materials formed cracks and broke after aging at 90% RH. The materials shrunk during storage at high humidities leading to a reduction in length of up to 50% of the original length. The coherency within the high amylose materials seemed to be larger as was shown by the fact that these materials did not form cracks as easy.

DISCUSSION

The starch extruded sheets are semi-crystalline materials consisting of granular remnants, an amorphous part and an ordered recrstyallized fraction. From the measurements it was not clear how the granular remnant structures affect the mechanical properties of the extruded sheets. It is most likely that if there are good interactions between the granular structures and the matrix, an increasing amount of granules with increasing amylose content would result in an increase in elastic modulus and possibly also a reinforcement of the material. On the other hand, it was shown for compression molded starch plastic materials that incomplete disruption of the native granules during processing at low plasticizer or temperature content lead to bad mechanical properties (low coherency, modulus and strength) [38, 39].

Depending on amylose content, the recrystallized ordered fraction was composed of both B-type crystals as well as V-type crystals. V-type crystallinity did not increase during long term storage while B-type crystallinity increased especially in amylopectin materials. At higher humidities this crystallization process was faster. Starch plastic materials with more amylose contained granular structures probably due to not complete disruption or gelatinization of the high amylose native granular ghosts. This is in agreement with the relative low extrusion temperature necessary for obtaining complete melting of high-amylose starch plasticized with glycerol and water [38, 39].

The materials showed viscoelastic behavior. Amylose rich materials were more elastic and solid-like while amylopectin materials behaved more viscous and gel-like. The changes in material properties with increasing amylose content were gradual and depending highly on morphology and crystallinity. The starch bioplastic materials were complex and heterogeneous consisting of a co-continous phases of amorphous and crystalline amylose and amylopectin, with differences in degree of branching, as well as granular remnants and domains enriched in amylose, amylopectin and amylose-amylopectin double helices. This is in contrast with the description of a phase separation of amylose and amylopectin in starch gels and films casted from solution, in which only one continuous phase exists [8, 10]. The occurrence of local co-crystallization of amylose and amylopectin is plausible on the basis of mechanical properties but still has to be proven by structural analysis [32, 35, 41].

The obtained stress-strain and stress-relaxation behavior depended on water content. Within the measuring range of 9-13% water (w/w) it was remarkable that no effects were observed on the stress- strain properties of the materials with high levels of amylose. There is no evidence for a difference in glass transition temperature of amylopectin or amylose for amorphous starch materials with low amounts of water and a glass transition temperature in the range of 0-20°C [48, 49]. For higher water contents (>40% water), it was shown that the glass transition temperature of amylopectin gels was even higher than of amylose gels [49].

The observations suggested that amylopectin-rich materials were more sensi-tive to water plasticization than amylose-rich materials. This was similar to the effect of glycerol on the plasticization of amylose-rich and amylopectin-rich casted films [25]. There was evidence for the presence of a rubber-like plateau in amylose containing materials compared to waxy corn starch plastics in which the decrease in elastic modulus as a function of water content was more drastic [33, 35]. An increase in helicity and crystallinity lead to a lowering of the mobility of the amorphous interphases between the physical crosslinks. Especially the increase in amylose V-type and B-type crystallinity with increasing amylose content resulted in an increase in elastic modulus due to the decrease in mobility of the amylose chains. Thus, amylose-rich materials had more entanglements by physical crosslinking and behaved more like a rubber especially a few degrees above the glass transition temperature, below the melting temperature of the crystallites. The high amylose materials were as a result less sensitive for small changes in water content. The semicrystalline nature and the tendency to form hydrogen bonds of polymers such as amylose and amylopectin retrogradation made starch plastics although a complex system. During storage the number of mobile non-bonded amylopectin outer chains decreased due to retrogradation (by formation of double helices and B-type crystallinity). This resulted in more rigid less flexible materials. For materials with similar crystallinities (see Figure 2) the properties were similar (see Figure 8). For amylose the formation of a string of hydrogen bonds and large helical structures was less limited than for, amylopectin. The chain length of the amylopectin outer chains was lower than the chain length of the amylose molecules. The linear amylose have been shown to form relatively long helical segments composed of 40 to 60 glucose units compared to the branched amylopectin molecules which forms helical segments consisting of approximately 15 glucose units [10]. Interactions and intermolecular double helices between amylose molecules would therefore be more stable [26]. This would result in lowering of the mobility and thus elastic modulus but resulted in an increase in tensile strength. During fracture, intermolecular bonds are severed between segments of different chains. An increase in the interactions between chains due to the formation of helices, in short-term stored amylose materials, would lead to an increase in tensile strength. Finally, the tensile strength increased even further by crystallization in amylose materials and long-term stored amylopectin materials. For materials after long-term aging, the amount of crystals was similar and the strength of the materials was similar.

The amorphous amylopectin materials showed a high degree of plastic flow and low fracture strength due to relatively easy slipping of the entangled chain segments [50, 51]. De-entanglement of the entangled segments, consisting of the amylopectin outer chains only, would be relatively easy because of the short chain length of the outer chains. The fracture strength was shown to depend on molecular mass of the entangled linear chain segments involved [50, 51]. The elongation was high because of the high molecular mass of the amylopectin [30, 31, 35]. The high degree of plastic flow was reflected in the stress- relaxation measurements of the amorphous materials with relatively high water content. The stress relaxation behavior of starch plastic materials was shown to be a function of pulling rate and extension, because a non-linear elastic deformation is applied [33, 35]. During applying stress to an amorphous starch plastic material at low pulling rates or high water contents, the viscous part of the material has the opportunity to relax partially and, therefore, the relaxation time would increase.

In highly crystalline materials, physical crosslinking took place therewith increasing the elastic modulus. Plastic flow would be limited and the tensile stress would increase and the elongation would decrease. This change in plastic flow or viscous flow was confirmed by the stress-relaxation measurements. The relaxation times increased with increasing amylose content at high pulling rates. At low pulling rates and high extensions, viscous flow took already place during the extension of the materials and the relaxation times increased.

CONCLUSIONS

The properties of starch plastic materials correlated with the amylose content. Starch casted films prepared by drying of a biphasic high moisture gel system, differed clearly in morphology, structure and properties compared to extruded starch plastic sheets. High amylose plastic materials showed superior strength and stiffness compared to the high amylopecth~-rich materials. The amylose-rich materials showed less deterioration of the mechanical properties due to aging than amylopectin-rich starch plastics. The amylopectin materials were very flexible, but the materials showed unfavorable relaxation and shrinkage during aging. Crystallization of amylopectin into the B-type crystal lead to shape deformation, internal stress and spontaneously cracking of the materials.

Further research is still necessary to obtain more insight in the interactions of plasticizers both during processing and during storage of the starch materials. An improved description is required of the morphological features and molecular structures in the materials in relation with properties. Even better mechanical properties of the amylose plastic materials might be obtained by an improvement of the melting process during extrusion leading to a more complete disruption of the high amylose granular structures. The most favorable crystallization seemed to be the crystallization of amylose into especially single and double helical structures which would reinforce the starch materials.

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