

Structure and Properties of Compression-Molded Thermoplastic Starch Materials from Normal and High-Amylose Maize Starches

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ABSTRACT: The structural and mechanical properties of compression-molded normal and high-amylose maize starches were studied as a function of processing water content and ageing time. Rubbery thermoplastic starches were produced by compression molding of four maize starches with differences in amylose content and amylopectin structure. Glycerol (30% on the basis of dry starch) and water (between 10 and 35% on the basis of total mass) were used as plasticizers. After processing, the amorphous thermoplastic starch materials crystallized during ageing. The semicrystalline materials contained both E-type and V-type, as well as B-type crystallinity. The properties of the thermoplastic starch materials are dependent on water content during processing, starch source, and ageing time. The normal maize starch materials are highly flexible with elongations between 56 and 104%. The elongations of the high-amylose maize starch materials were between 5–35%. The tensile stress and *E*-modulus of the normal maize starch materials were in the range of 3.9–6.7 and 27–131 MPa, respectively. The tensile stress and *E*-modulus of the high-amylose maize starch materials increased from approximately 0.5 to 23 and 5 to 700 MPa, respectively, with increasing water content during processing from 10 to 35%. The differences in mechanical properties of the normal and high-amylose materials were explained by differences in the structure of the amylose and amylopectin structure. It was concluded that both lead to differences in the starch network. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **64**: 631–644, 1997

Key words: amylose–amylopectin ratio; thermoplastic starch; mechanical properties; crystallinity; molecular mass

INTRODUCTION

In the last decade, several researchers have shown the possibility to make completely biodegradable¹ consumer items from substantially pure starch and to exclude synthetic polymers from the formulation.^{2–5} These starch materials contain plasticizers so that the native starch gran-

ules melt below the decomposition temperature and yield products in which starch forms a continuous polymeric phase. This type of starch, made by processing techniques such as extrusion and injection molding, is referred to as thermoplastic starch (TPS).⁵ To be able to broaden the usage and improve the quality of products from TPS makes it necessary to get insight in the structure–property relationships of TPS.

Native starches are usually a mixture of 20–30% amylose, an essentially linear glucose polymer with a molecular mass in the range of 100,000 to 1,000,000 g/mol, and of 70–80% of the highly

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branched amylopectin with a molecular mass of approximately 10^8 g/mol.^{6,7} Gels and dispersions from both native as well as purified amylose and amylopectin starches show differences in properties such as phase separation, gelation, aggregation, and crystallization.^{8–18} Starch crystallization in starch films cast from solutions and their mechanical properties have been investigated previously.^{18–25} It has been shown that cast films prepared of amylose are more flexible than films prepared of amylopectin.²⁵ The linear amylose molecules have been said to form more effective entanglements than the highly branched amylopectin molecules, resulting in an increase in tensile strength.

A major disadvantage of cast films is the high cost of preparation from solutions. Therefore, thermomechanical processing techniques such as extrusion, compression molding, and injection molding are used for preparing starch products nowadays. The melting of the starch granule and starch gelation have been shown to be different from the process during film casting.²⁶ Several articles have been published on the mechanical properties of TPS and extruded starches prepared from several starch sources, such as maize, wheat, potato, waxy maize, and amylo maize starch.^{27–35} It has been shown that the amount of amylose and amylopectin affects the crystallinity present in glycerol-containing TPS plastics, but no relationships with properties have been reported.^{35,36} Little is known about the role of amylose and amylopectin in granular starches and how both molecules influence the structure as well as the properties of low-moisture, glycerol-containing starch plastics.

The scope of this article is to acquire detailed knowledge about the influence of amylose and amylopectin in various granular starches on the properties of TPS materials but also on starch structure and morphology. Therefore, the properties of compression-molded glycerol-containing TPS made of normal and high-amylose granular starches have been characterized. The starch structure and morphology of the TPS materials are assessed using X-ray diffraction (XRD), size-exclusion chromatography (SEC), laser light scattering (LLS), differential scanning calorimetry (DSC), and polarized light microscopy (PM). Differences in stress-strain and stress-relaxation behavior of the materials have been related to the variations in starch structure and the morphology of the materials.

MATERIALS AND METHODS

Materials

High-amylose maize starch (maize amylose with 70% amylose labelled as CN70, with CN = corn native), technical grade, was obtained from Sigma Chemical Co. (St. Louis, Minnesota). Amylo maize starches, Gelose 50 (55–56% amylose, denoted as CN48) and Gelose 80 (87% amylose, denoted as CN63), and a normal maize starch (25–27% amylose, labelled as CN30) were obtained from Starch Australasia Limited, Lane Cove, Australia. The indicated amylose contents (w/w on the basis of dry starch) were determined by a spectrophotometric procedure. The water contents of the starches were 11–13% (w/w). *L*- α -lysophosphatidylcholine (LPC) from egg yolk (L-4129) was also obtained from Sigma. Glycerol (density 1.26 g/mL) was from Chemproha Chemical Distributors, The Netherlands.

Compression Molding

Starches were mixed with a constant amount of glycerol to give the following composition: starch : glycerol = 100 : 30 (w/w on the basis of dry starch). These premixes were further mixed with water to obtain mixtures with water contents in the range of 8–35% (w/w on the basis of total mass). The compositions were expressed as w/w ratios of starch (dry matter) : glycerol : water on the basis of total mass. To obtain the TPS materials, 45 g of the starch-glycerol-water mixtures were applied to a mold with the inner dimensions of $100 \times 150 \times 2$ mm ($1 \times w \times h$). The outer dimensions of the mold were 300×350 mm. The samples were covered with positron emission photography (PET) foil at both sides to facilitate mold release. The mold was placed in a hydraulic PHI press (City of Industry, California). An initial pressure of 3–4 tonnes was applied. The mold was then heated to 100°C at a rate of 10°C/min. At 100°C, a pressure of 40 tonnes was applied, and the temperature was raised at 10°C/min to finally reach a temperature of 160°C, which was kept for another 5 min. Subsequently, the mold was cooled to room temperature at 10–15°C/min, and the material was released from the mold. The materials were conditioned at a relative humidity (RH) of $60 \pm 5\%$ RH during three weeks at a temperature of 20°C.

Moisture Determination

Because of the tendency of TPS to absorb or desorb water, special care was taken to measure the water content immediately at the time of testing. The samples were ground under cryogenic conditions. The water content of the powder (1 g, size < 125 μm) was determined gravimetrically either with an infrared (IR) dryer (Sartorius MA40) at 95°C or with a Gallenkamp vacuum oven at 70°C at a pressure of less than 100 mBar overnight. The volatility of the glycerol meant that the measurements of the IR dryer should not exceed 5 min to minimize the loss of glycerol during measurements.

Mechanical Testing

A Model 4301 Instron Universal Testing Machine, operated at a grip length of 80 mm and a cross-head speed of 10 mm/min was used for tensile and relaxation measurements. Dumbbell specimens according to the ISO 1184-1983 (E) standard were cut from the sheets. Five replicates were averaged for each material. The sheet thickness varied, and sample dimensions were corrected individually for the 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 following 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 following 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), which is related to the original gauge length, l_0 by $l_0/l_1 = 25/33$. The elastic modulus was calculated from the initial slope of the stress-strain curve.

Molecular Mass Determination

The starch samples were dissolved in 1M sodium hydroxide (4 mg/mL) by stirring for 15–20 h. Molecular masses were determined as described previously.^{30,31}

Differential Scanning Calorimetry

DSC measurements were performed with a Perkin-Elmer DSC-7. The gelatinization and melting

Table I Amylose Contents of the Various Native Starches

Starch Type	Amylose Content (+SD) ^a		
	DSC Method	Standard Deviation	Spectrophotometry
CN25	30	± 5	26 ± 1
CN50	48	± 4	55 ± 1
CN70	70	± 3	70 ± 3
CN87	63	± 5	90 ± 5

^a SD = standard deviation.

endotherms, glass transition temperatures, and amylose contents were obtained as described previously.^{31,32}

Morphology, Density, and X-ray Diffractometry

The morphology (PM), density, and crystallinity were determined as described previously.^{31,32}

RESULTS AND DISCUSSION

Characterization of Starches Before Processing

The normal maize starch (CN30) shows an A-type diffractogram, while the high-amylose starches (CN48, CN63, and CN70) show a B-type diffractogram. The normal maize starch consists of birefringent granules with PM. The high-amylose starch are composed of less regular shaped, smaller granules. The granules show no bright birefringence Maltese crosses. The amylose contents, as determined by the complex formation with lyso-lecithin, deviate from the values obtained by iodine binding and ultraviolet spectrophotometry, as is shown in Table I. These differences probably arise from the differences in the degree of branching of amylose and amylopectin. With SEC and LLS, it is shown that mass average molecular mass decreases for the series: CN30 ($60,000 \pm 10,000$ kg/mol), CN48 ($20,000 \pm 4,000$ kg/mol), CN63 ($12,000 \pm 4,000$ kg/mol), and CN70 ($10,000 \pm 5,000$ kg/mol). This decrease is only partly due to the differences in amylose content and the large differences in molecular mass of amylose and the highly branched amylopectin; but, also, the molecular mass of the branched amylopectin molecules decreases. This is indicative of the presence of intermediately branched or

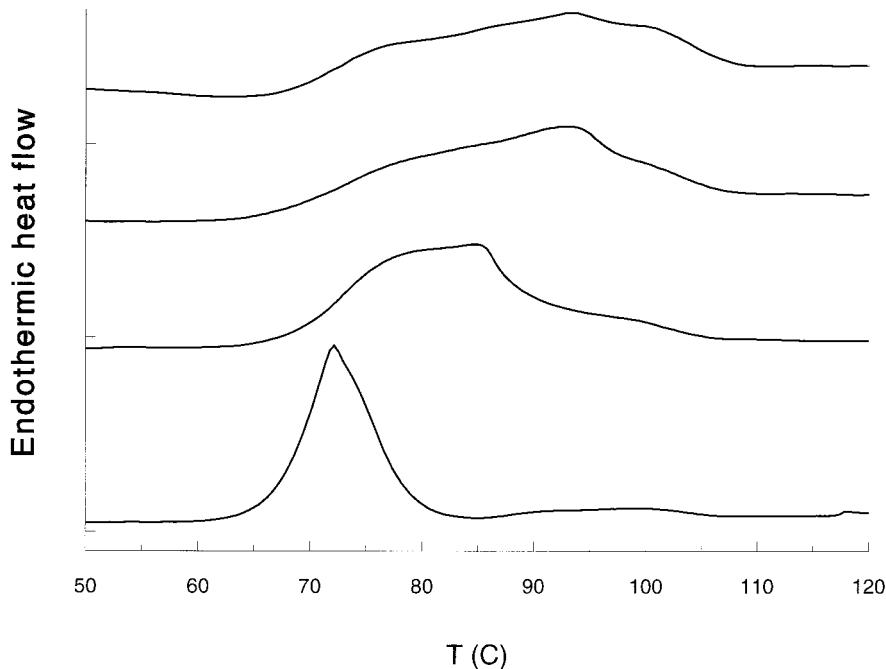


Figure 1 The gelatinization endotherms of the CN30, CN48, CN63, and CN70 granular starches, respectively, from bottom to top.

low-molecular-mass amylopectin-type molecules, as observed previously in amylomaizes.⁷

The gelatinization endotherms of the native starches are shown in Figure 1. The normal maize starch shows two peaks: one with an onset temperature of 65°C and a peak temperature of 71°C, and one with an onset temperature of 90°C and a peak temperature of 95°C, respectively. The peaks are attributed to melting of the amylopectin crystallinity during gelatinization and to melting of the amylose-lipid complexes. A broadening of the gelatinization endotherm is observed for the high-amylose starches. The onset temperature remains at approximately 65°C, but the peak and conclusion temperatures are shifted to higher values. The broadening increases in the series CN30, CN48, CN63, and CN70. This shift in melting range has been explained by the difference in average chain length of the outer chains of amylopectin and the presence of the intermediately branched, amylopectin-like molecules. Hence, the crystallite sizes increases.³⁷ To determine temperature ranges and moisture contents for compression molding of the four starches with 30% glycerol, DSC measurements have been performed. The melting profiles of the starch premixes with glycerol and water at various water contents are shown in Figure 2. A similar peak broadening is

observed, as is seen in Figure 1. At water contents in the range of 8–10%, incomplete melting takes place. At water contents above 20%, the melting endotherms are in the range of 65 to 150°C. This suggests that complete granular crystallite melting can take place at 160°C, which is the temperature used during compression molding.

Structural Characterization of the Compression-Molded Materials

In Figure 3, some typical PM photographs are shown of the influence of water content on the melting of the starch granules during compression molding of CN48. In Figure 3(a), the native granules are shown before molding. It is shown that, at water contents in the range of 10–20%, several granular birefringent structures are still present [Fig. 3(b)]. At water contents above 20%, the TPS materials are almost without granular rest structures, although some granular ghosts are found [Fig. 3(c)]. A decrease in the amount of birefringent granules and ghosts with increasing processing water content is also observed for the CN30, CN63, and CN70 materials. For materials molded at low water contents (<20%), granules can be easily loosened from the surface upon immersion in water, which is indicative of limited

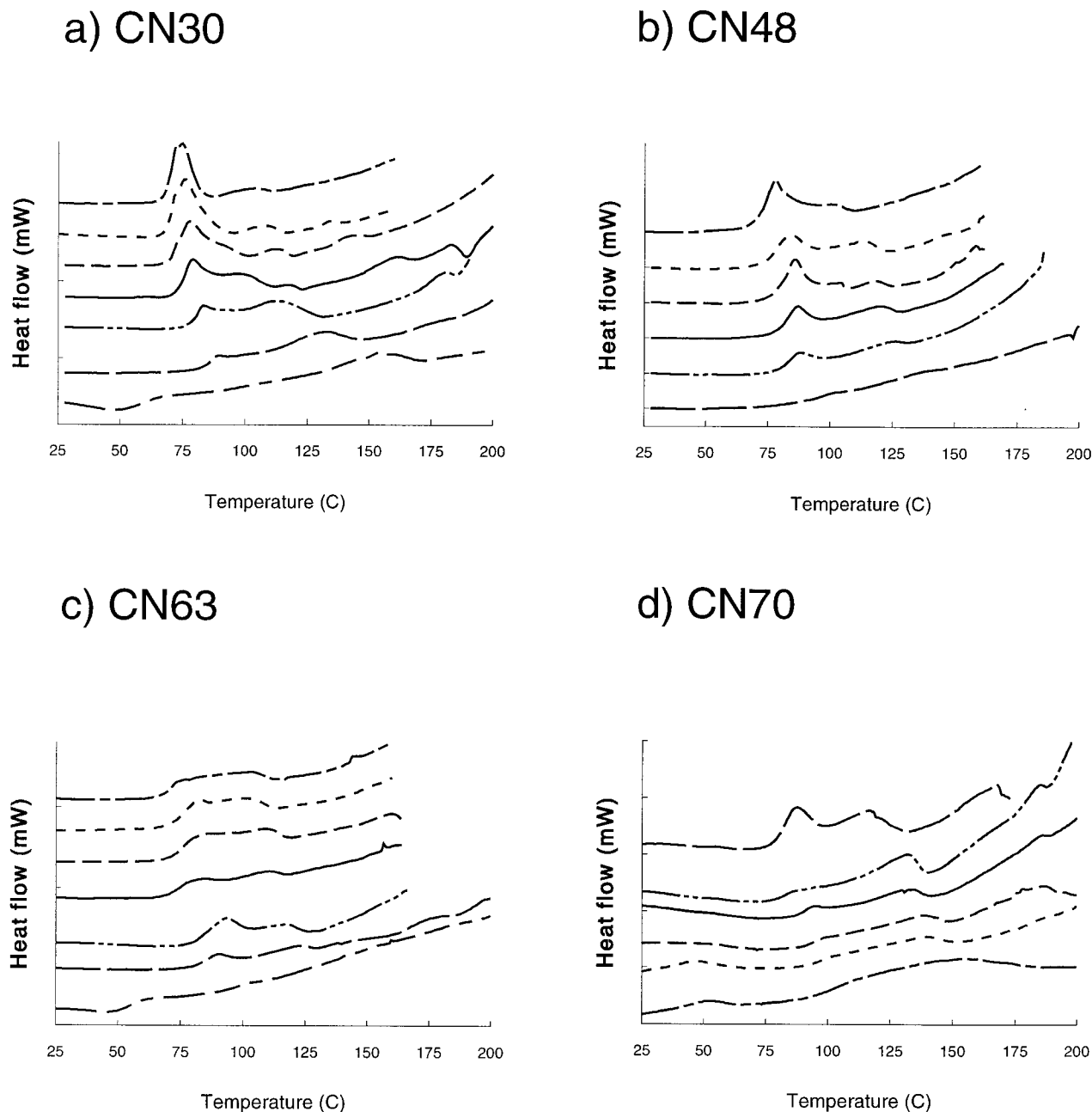


Figure 2 The melting profiles of the premixes with 30% glycerol as a function of water content for the four starches. The water is in range of 10 to 70% (w/w on the basis of total mass) from bottom to top: (a) CN30, (b) CN48, (c) CN63, and (d) CN70.

coherency and intergranular association. For the starches molded at higher water contents, the TPS materials remain intact, although swelling is observed upon immersion in water. No changes were observed with PM during ageing. No significant differences in density have been observed for the various materials at identical water contents.

Typical XRD patterns after compression molding are shown in Figure 4. Two types of crystallinity are observed in the materials, identified as the B-type (with a maximum at 16.8 degrees, $2^*\theta$), and the V_h -type (with maxima at 12.6 and 19.4 degrees, $2^*\theta$) structures.^{35,36} In TPS samples, which have been quenched in liquid nitrogen

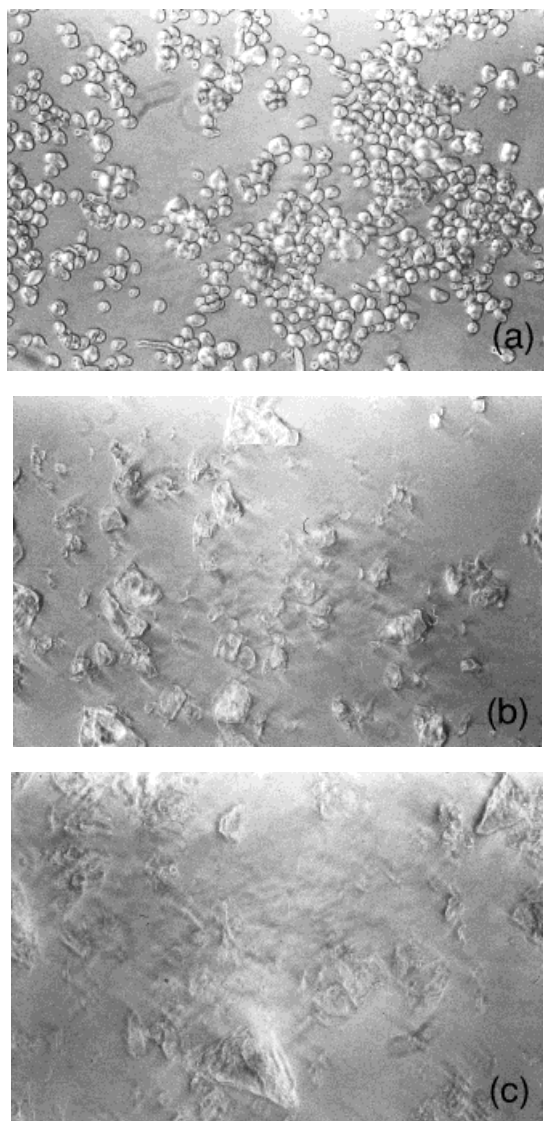


Figure 3 (a) Polarized light microscopy of the granular structure of CN48. (b) Polarized light microscopy of the CN48 TPS materials processed with 10% water. (c) Polarized light microscopy of the CN48 TPS materials processed with 35% water.

directly after compression molding, only V_h -type crystallinity has been observed, indicative of the rapid formation of this amylose type crystallinity in glycerol-containing TPS materials.^{35,36} Quenched materials show no residual A- or B-type crystallinity. During ageing for three weeks, no significant changes have been observed in V-type crystallinity, as is shown in Figure 4(a) for CN48. Also, no differences are observed in V-type crystallinity versus processing water contents [Fig. 4(a)] or due to the selected starch source [Figs.

4(c) and (d)]. At lower processing water contents, no changes are observed in B-type crystallinity after one day of storage at 60% RH [Fig. 4(b)]. The amount of B-type crystallinity increases for materials processed with more than 10% water. The materials which have been processed with 35% water show the highest amount of B-type crystallinity. The increase in B-type crystallinity is observed especially during the first few days. The amount of B-type crystallinity is only slightly influenced by starch source, as is seen in Figures 4(c) and (d). B-type crystallinity is formed in the TPS materials with more amylose to a higher degree over a period of three weeks. This indicates, especially, that amylose is responsible for the rapid formation of B-type crystallinity during short-term storage at relatively low humidities.^{32,33,35,36} Remarkable is the fact that in these glycerol TPS materials, B-type crystallinity is favored over A-type crystallinity, as is formed during retrogradation in extruded maize and amylo-maize starch with only water added as a plasticizer.³⁴

During DSC experiments of the TPS materials after two weeks ageing at 60% RH, no glass transition or melting transitions have been observed in the range of temperatures between -10 to 150°C . The materials, with a water content of approximately 11–13% (w/w), are still very flexible at room temperature. The expected glass transition is therefore below 20°C and is usually difficult to detect with DSC. To be able to melt retrograded helical structures or crystalline structures in the TPS materials, excess water (70% w/w) has been added before DSC experiments. Some representative DSC thermograms are shown in Figure 5. Two types of transitions are found with onset temperatures of approximately $40 \pm 5^\circ\text{C}$ and $110 \pm 5^\circ\text{C}$. A third endothermic transition, with an onset temperature of $90 \pm 5^\circ\text{C}$, is found after rapid cooling after the first scan and reheating during a second of the materials with excess water [Fig. 5(d)]. The third endothermic transition is ascribed to the rapid recrystallization of amylose-lipid complexes, usually referred to as type I complexes³⁸ consisting of helical chain segments with little long-range ordering. The endothermic transition at approximately 110°C is due to the slower recrystallization of amylose-lipid complexes at higher temperatures, usually denoted as type II complexes,³⁸ during slower cooling processes, such as during compression molding. No significant changes are observed in the relative amount

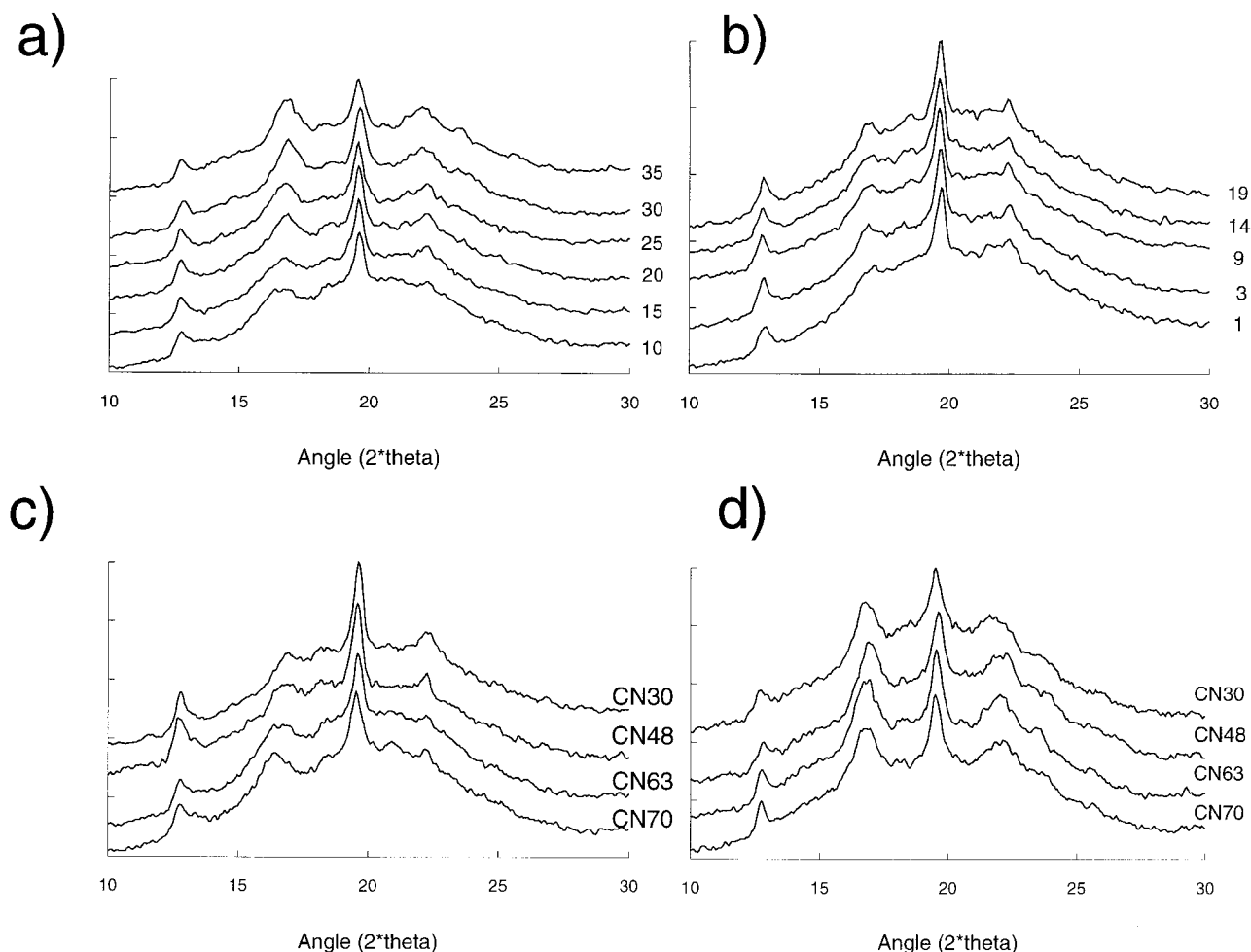


Figure 4 Typical X-ray diffractograms of the TPS materials after processing: (a) influence of water content during processing after 19 days of ageing of the CN48 TPS material (the amount water during compression molding (% water) is indicated); (b) influence of ageing time on the crystallinity of the CN30 TPS materials (ageing time is indicated in days); (c) influence of starch source on crystallinity of the TPS materials processed with 10% water after 19 days of ageing; (d) influence of starch source on crystallinity of the TPS materials processed with 35% water after 19 days of ageing.

of these complexes for the various starch sources, probably because of the presence of similar amounts of lipids in these starches. A clear difference in the first endothermic transitions with an onset temperature of 40°C is found for the three starch sources (CN30, CN48, and CN63). This transition is ascribed to recrystallized amylopectin or amylopectin-like structures, such as are found in amylomaizes. A sharp transition is found between 40 and 60°C with a peak temperature of approximately 50°C for the CN30 TPS materials. The enthalpy of this transition increases with increasing processing water content from 4.0 to 7.0

± 0.5 J/g dry starch material. The transitions found for the CN48 and CN63 TPS materials are very broad or even seem to be completely absent for the CN63 TPS materials. The transitions are too irregular to give reliable data on differences in the enthalpy (approximately 1–5 J/g dry starch materials) in relation with water content during processing. The occurrence of higher melting temperatures in recrystallized B-type potato starch compared to recrystallized B-type waxy maize starch have been ascribed to the longer chain length of the potato starch amylopectin outer chains in comparison with waxy maize starch²⁶

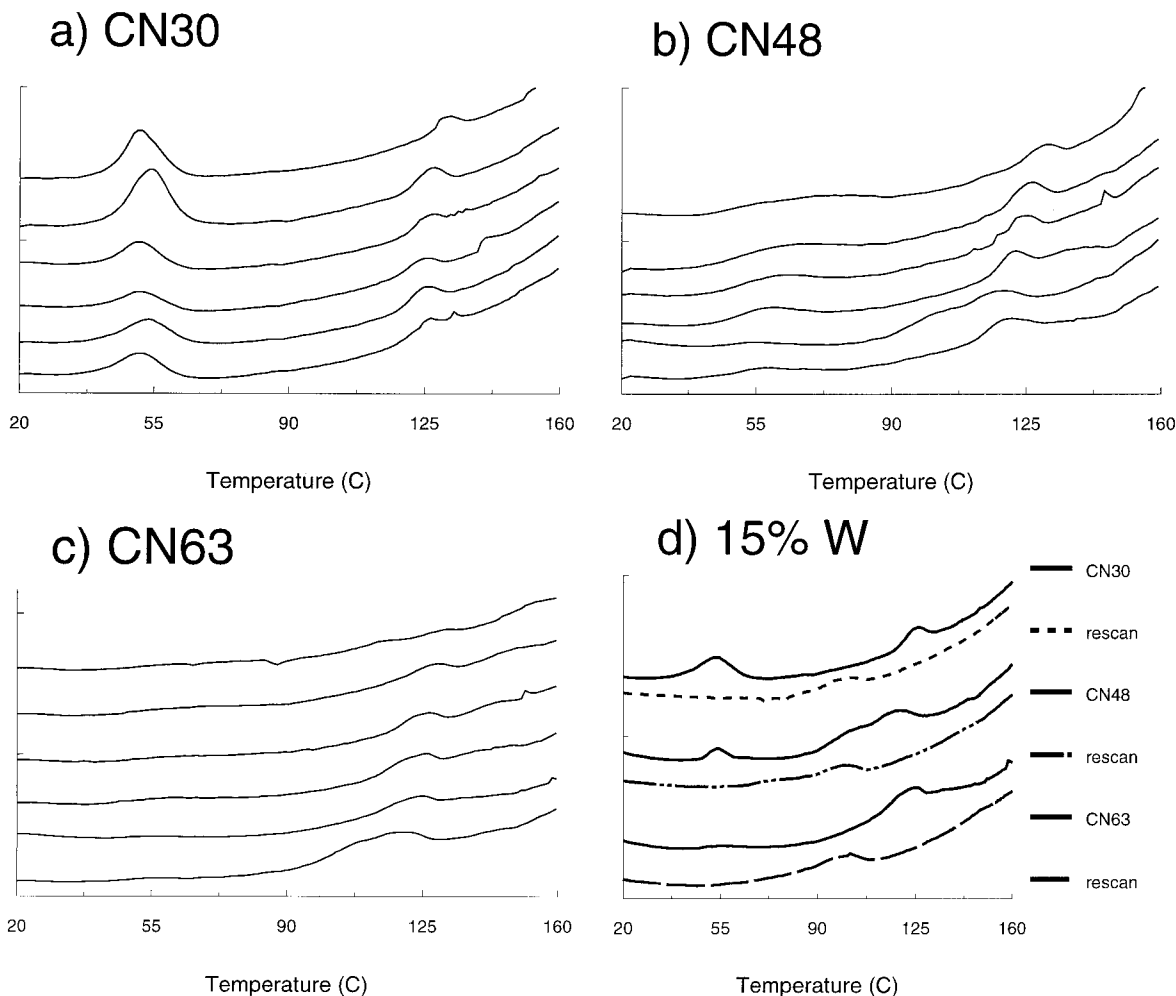


Figure 5 Typical DSC thermograms of the TPS materials after processing and ageing for 19 days: (a) CN30, (b) CN48, and (c) CN63. The water content during processing has been 10, 15, 20, 25, 30, and 35% from bottom to the top. (d) The differences of the three starches processed with 15% water with the second rescans added.

and is in also in agreement with the melting of the normal maize starch and the high-amylose starches described previously³⁷ (see Figs. 1 and 2). This seems to support the idea of the presence of the amylopectin-like, intermediately branched molecules with long outer chains forming B-type crystallinity in the high-amylose TPS materials. Melting of highly crystalline recrystallized B-type amylose occurs at temperatures above 160°C overlapping with the depolymerization of starch. Therefore, it is difficult to obtain reliable data on transitions above 160°C, and no attempt has been made, although endothermic transitions have been observed above 160°C in the TPS materials.

Mechanical Properties of the TPS Materials: Influence of Starch Source on Stress–Strain Behavior

A typical example of the change in water content during ageing is shown in Figure 6 for the TPS materials of CN48. It is shown that during the first day of ageing, the changes in water content are rapid. After six days, the equilibrium water content for all the materials is at 60% RH approximately $12 \pm 1\%$ (w/w). The variations in water content are still present due to the deviations in RH ($\pm 5\%$). The mechanical properties of the TPS materials prepared by compression molding of the four native starches are

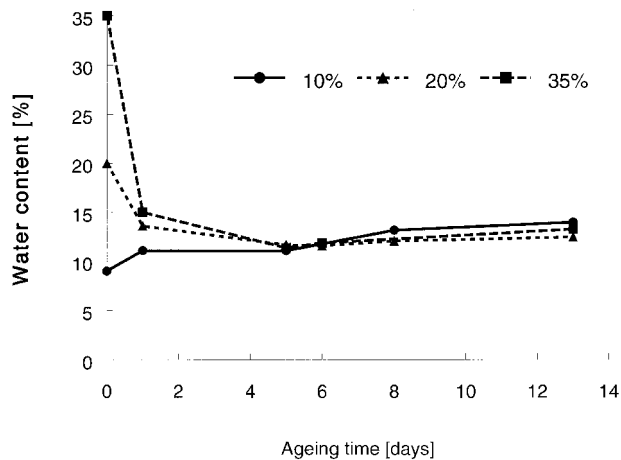


Figure 6 An example of the changes in water content during ageing of the CN48 TPS materials; the water content during processing is indicated in the figure.

shown in Figure 7 in relation with processing water content. The TPS materials have been stored for 19 days before mechanical analysis. A clear difference is found between the normal maize materials and the high-amylose TPS materials. For the normal maize (CN30) TPS materials, the elongation is decreasing from about 104 to 56% with increasing processing water content. The E -modulus and the stress at peak increase slightly with increasing processing water content from 27 to 131 and 3.9 to 6.7 MPa, respectively. For the high-amylose materials, the mechanical properties are clearly different compared to the normal maize TPS materials. The elongation is in the order of magnitude of 5–35% with a maximum at approximately 20–25% processing water content. At a processing water content below 20%, the E -moduli and the stresses at peak are around 0–200 and 0–6 MPa, respectively. The E -moduli and stresses at peak increase to approximately 550–700 and 16–23 MPa, respectively, at a processing water content of 30–35% (w/w).

Mechanical Properties of the TPS Materials: Influence of Ageing on Stress–Strain Behavior

The time-dependent properties of the TPS materials after compression molding of the starches denoted as CN30, CN48, and CN63 are shown in Figure 8. Three different water contents (10, 20, and 35%) during molding have been investigated. For the TPS materials (CN48 and CN63), com-

pression-molded with a water content of 10% (w/w), no significant changes in mechanical properties (elongation, stress at peak, and E -modulus) are found during ageing. For the CN30 TPS materials, a slight increase in stress and E -modulus and a slight decrease in elongation is found. For materials obtained by compression molding with 20 or 35% (w/w), the effect of ageing is clearly shown for the TPS materials prepared from CN30, CN48, and CN63. The elongation decreases, while the stress at peak and the E -modulus increases. The increases in stress at peak and the E -modulus are more pronounced for the materials that have been processed with 35% water than with 20% water. Remarkable are the changes in elongation of the high-amylose TPS materials. The elongation of materials processed at 35% water are lower than those materials that have been processed with 20% water. This is in agreement with the maximum observed in elongation versus processing water content (see Fig. 7). Because of the high water content during the first days of ageing, the degree of retrogradation (and, thus, more crystallinity) is higher for the materials processed with 35% water. These increases in stress and modulus and this decrease in elongation during storage of TPS materials above glass transition temperatures are in accordance with previously published results.³²

Discussion

It is clearly seen that the stress–strain properties are completely different for the normal maize starch and the high-amylose maize starch TPS materials. The mechanical properties are also dependent on processing water content. The melting of the starch granular structure and starch mobility depend on water content. The normal maize starch already forms materials with a high degree of coherency at relatively low water contents during processing. The formation of intergranular interactions and an amorphous starch network are regulated by processing water content. The amylo maize starches melt at higher water contents, and the formation of the starch network is only established above a water content of 20–25%. The amount of amylose and the structure of the amylopectin molecules of the various starch sources play an important role in the strength, stiffness, and flexibility of the formed network. At water contents above 20%, the high-amylose TPS materi-

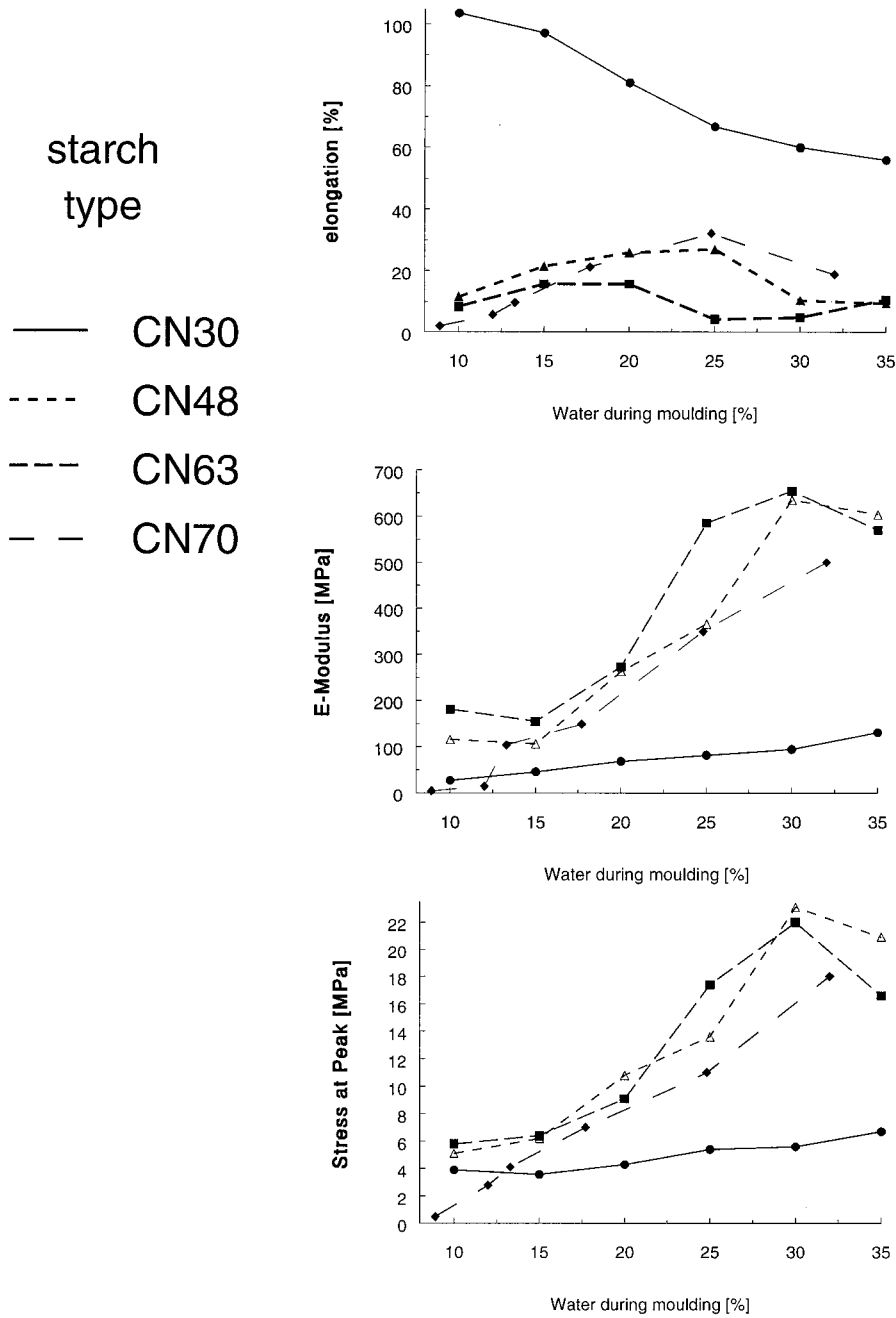


Figure 7 The mechanical properties of the TPS materials after 19 days of ageing. The elongation, *E*-modulus, and stress at peak versus processing water content are shown from top to bottom.

als are tough, while the normal maize starch materials are soft. Amylose and the intermediately branched amylopectin molecules give a higher degree of chain-chain (polymer-polymer) associations and more entangled starch

matrix. These entanglements are likely to consist of double helical structures of amylose and the outer chains of amylopectin. The higher degree of polymer-polymer interactions is confirmed by the DSC and X-ray analyses. The in-

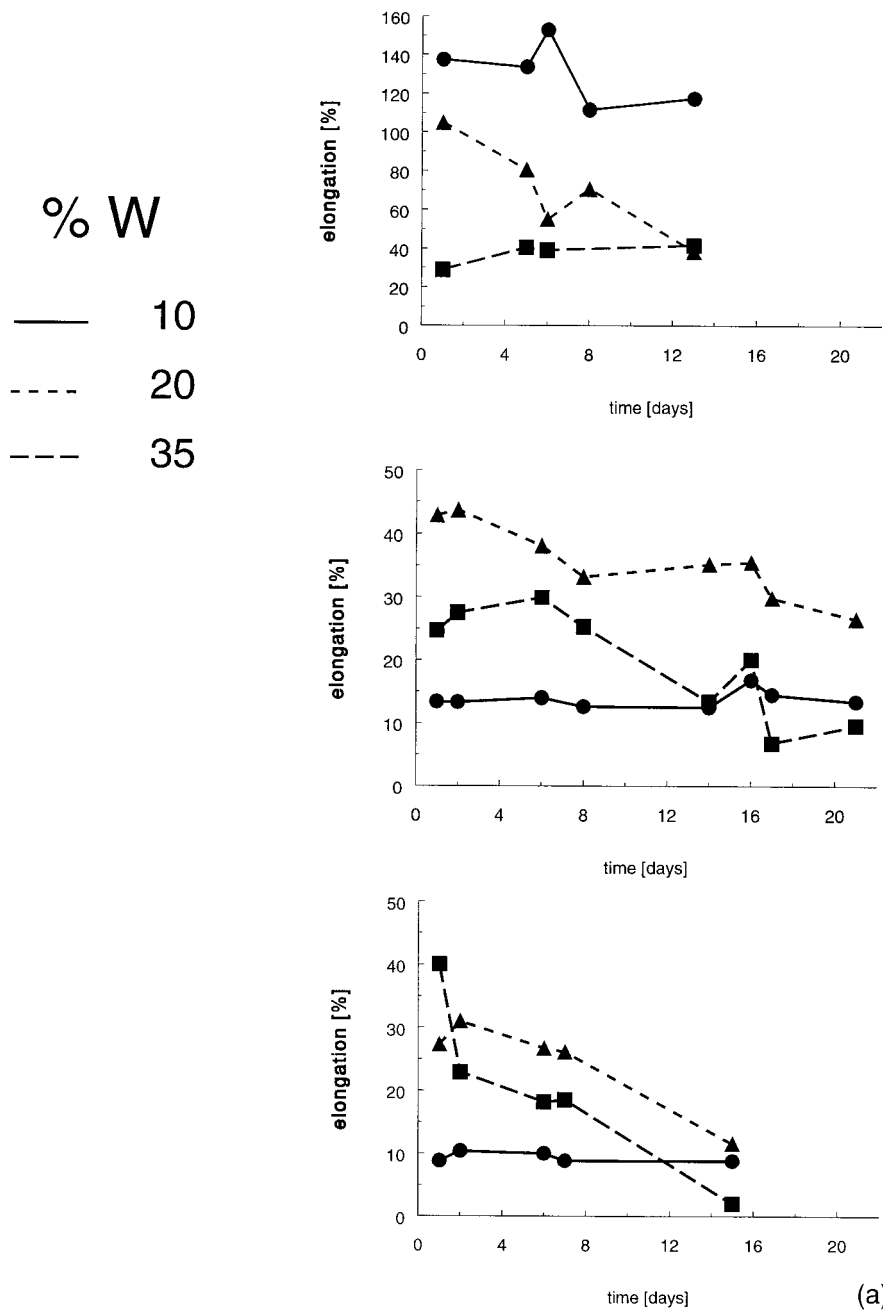


Figure 8 The changes in mechanical properties during ageing of the TPS materials processed with 10, 20, and 35% water, respectively: (a) elongation versus ageing time; (b) *E*-modulus versus ageing time; (c) stress at peak versus ageing time. The CN30, CN48, and CN63 TPS materials are shown from top to bottom.

fluence of the formation of double helices and the formation of crystalline structures is seen by the effects of ageing on the material properties. An increase in B-type crystallinity leads

to an decrease in elongation and a increase in tensile strength. The amount of interactions is larger for the high-amylose materials, which also contain a higher degree of crystallinity.

% W

— 10
 - - - 20
 - - - 35

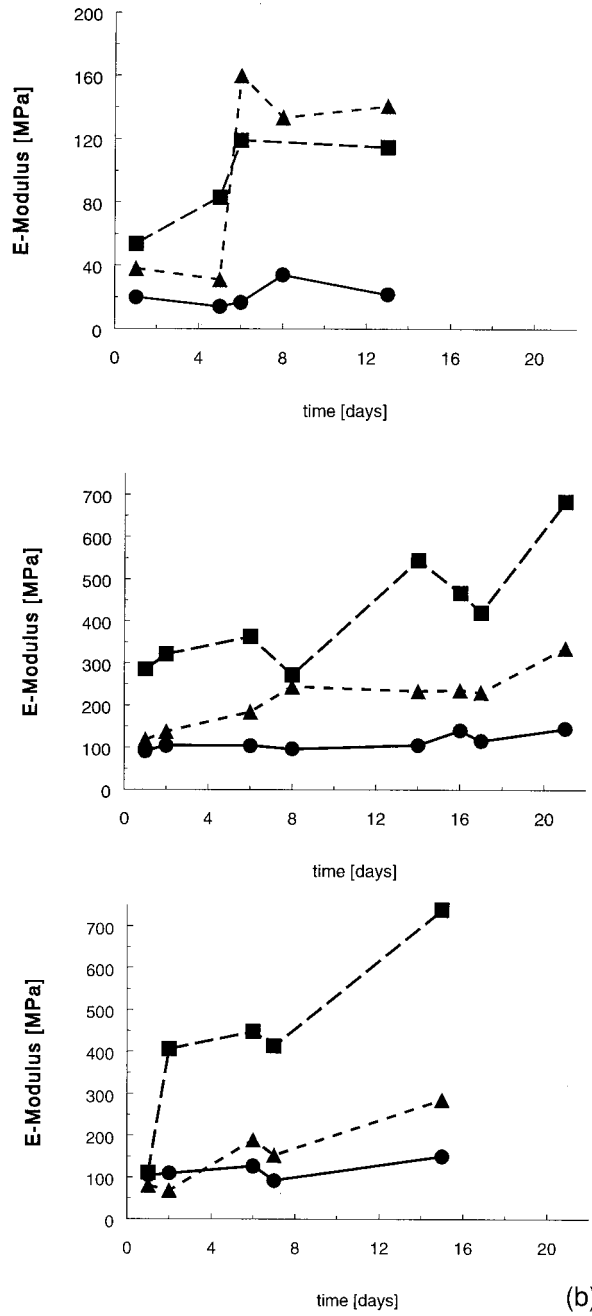


Figure 8 (Continued from the previous page)

CONCLUSIONS

The properties of compression-molded thermoplastic maize starches are highly dependent on water content during processing. The water content is an important factor in the formation of a starch net-

work during processing. The materials from high-amylose maize starches are tough with higher strength and with low elongations compared to the normal maize starch materials. The differences in mechanical properties are attributed to variations in amylose content, as well as the differences in amylo-

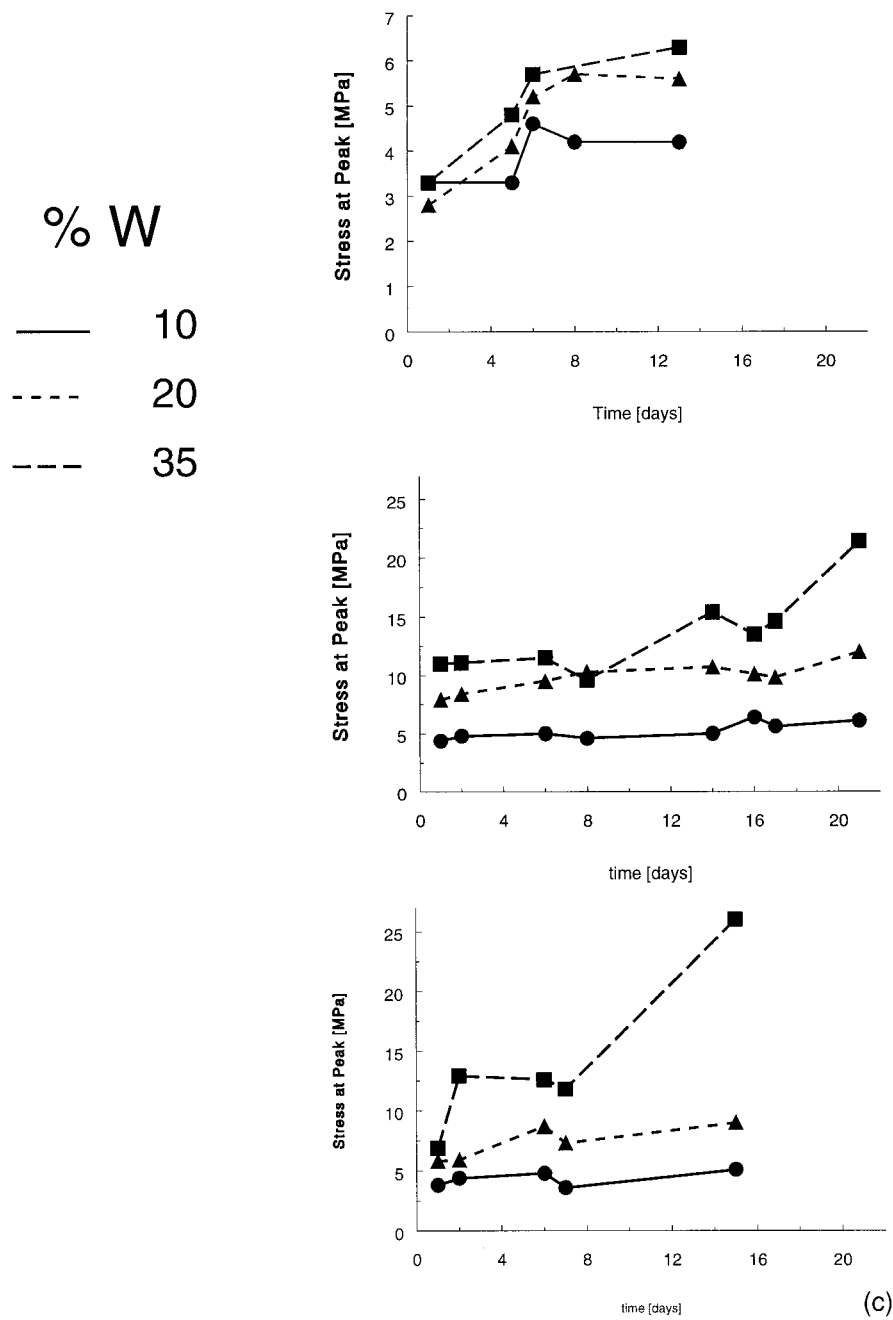


Figure 8 (Continued from the previous page)

pectin degree of branching. The high-amylose starch materials form a more ordered and entangled starch network.

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