Influence of Glycerol and Water Content on the Structure and Properties of Extruded Starch Plastic Sheets during Aging

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ABSTRACT: The properties of starch plastic sheets were investigated by stress–strain measurements in relation with starch crystallinity. Granular potato starch was plasticized with different amounts of glycerol and water by extrusion. The materials were amorphous directly after processing. During aging above the glass transition temperature at various humidities single helical (V and E-type) and double helical (B-type) crystallinity was formed. The rate of crystallization is a function of water and glycerol content. The amorphous rubbery materials were soft and weak with high elongations. During aging the materials became less flexible with higher elastic modulus and tensile stress. The changes are related to changes in water content and glass transition temperature and to changes in B-type crystallinity. The changes in stress–strain properties are explained by the formation of helical structures and crystals, which results in a reinforcement of the starch network by physical crosslinking. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **64:** 1411–1422, 1997

Key words: potato starch; bioplastic; extrusion; mechanical properties; crystallinity

INTRODUCTION

Several materials were developed on the basis of starch and natural additives such as water, glycerol, and lecithin.[1–7] Starch bioplastics are obtained by processing of granular starch by techniques such as extrusion, kneading, compression molding, and injection molding. The materials are susceptible to aging and starch crystallization. Products are exposed to various humidities and temperatures during usage and storage. This leads to differences in water content and to differences in properties such as crystallization behavior.[8–13] Various articles have been published in the field of structure–property relationships of starch–polymer blends or composites.[14–18] A beginning has been made of the description of pure starch bioplastics, but the relations between aging and crystallization and material properties are still not very clear because of the complexity.

In contrast with high-moisture and intermediate-moisture materials such as gels, cakes, and breads, starch bioplastics contains only a limited amount of water (less than 20% w/w) both during processing and after processing. Most research was focussed on the crystallization and retrogradation of high-moisture (>50% w/w) and intermediate-moisture (20–50% w/w) materials.[19–24] Glycerol containing starch plastics were shown to recrystallize into various crystal structures depending on processing as well as storage conditions.[8] Amylose was shown to crystallize into several single helical crystal structures and the B-type double helical crystal structure.[8] Crystallization of amylopectin into the B-type crystal structure is slow compared to amylose crystallization in starch bioplastics.[10] B-Type crystallinity was shown to affect the mechanical properties of

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rubbery starch materials during long-term storage for more than 2 weeks.[9] No detailed information is still available about the effects of aging and crystallization during short-term storage of rubbery starch plastics. Glycerol was shown to decrease the retrogradation rate of waxy maize starch in a gel.[25] No data was reported until now about the influence of glycerol content on starch crystallization in relation with mechanical properties.

This study was focussed on the influence of crystallization on the mechanical properties of glycerol containing potato starch plastic sheets. The sheets were made by extrusion processing with differences in plasticizer content, i.e. water and glycerol. The structure and properties of the materials were followed directly after processing.

EXPERIMENTAL

Materials and Extrusion

Potato starch (PN) was obtained from Avebe, Foxhol, The Netherlands. Thermoplastic starch materials were prepared by extruding narrow sheets using a Haake Rheocord 90 system equipped with a laboratory-scale Rheomex TW 100 counterrotating twin screw extruder fitted with a slit die. The dimensions of the die were: width = 25 mm and thickness = 0.3 mm. The starches were premixed with glycerol to give the following compositions: starch (PN) : glycerol (G) : water (W) = 100 : 26 : 17, 100 : 25 : 22, 100 : 39 : 22, and 100 : 41 : 16 (w/w/w), denoted as the materials PN26G17W, PN25G22W, PN39G22W, and PN41G16W, respectively. The compositions on the basis of total mass were starch (PN):glycerol (G) : water (W) = 70 : 18 : 12, 68 : 17 : 15, 61 : 25 : 14, and 64 : 26 : 10% (w/w/w) for the materials PN26G17W, PN25G22W, PN39G22W, and PN41G16W, respectively. The mixtures were manually fed into the extruder with a constant throughput. The torque was held at a constant level but dependent on composition. The average torques were 60, 56, 33, and 25 for the materials PN26G17W, PN25G22W, PN39G22W, and PN41G16W, respectively. The screw rotation speed was 55 r.p.m.. The temperature profile along the extruder barrel was set at 90, 150, 130, 90–100°C (from feed zone to die). The measured melt temperature in zone two was 150–160°C. The slit die melt temperature was kept below 100°C to prevent the
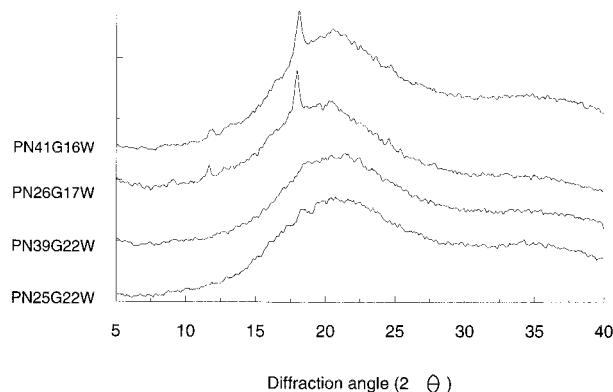

Figure 1 X-ray diffractograms of the sheets after 1 day of aging. From the top to bottom are shown the materials denoted as PN41G16W, PN26G17W, PN39G22W, and PN25G22W.

melt from boiling and to give a bubble-free extrudate.

Conditioning

Part of the extruded sheets was stored at −22°C after quenching in liquid nitrogen directly after extrusion. Part of the materials was conditioned at a relative humidity (RH) of approximately 61 ± 3% for several weeks at a temperature of 20°C. The PN25G22W sheets were also stored at ambient humidity and temperature (between 20 and 25°C) to simulate normal storage conditions. The relative humidities of the two experiments performed were approximately 61 ± 5% RH and 54 ± 5% RH, respectively. The water content, structure, and mechanical properties of the materials were measured directly from the first day after extrusion processing.

Moisture Determination

Because of the tendency of starch plastics to absorb or desorb water special care was taken to measure the water content immediately at the time of testing. The samples were grounded under cryogenic conditions. The water content of the powder (1 g, size < 125 μm) was determined gravimetrically with a Gallenkamp vacuum oven at 70°C at a pressure of less than 100 mBar overnight.

Mechanical Properties

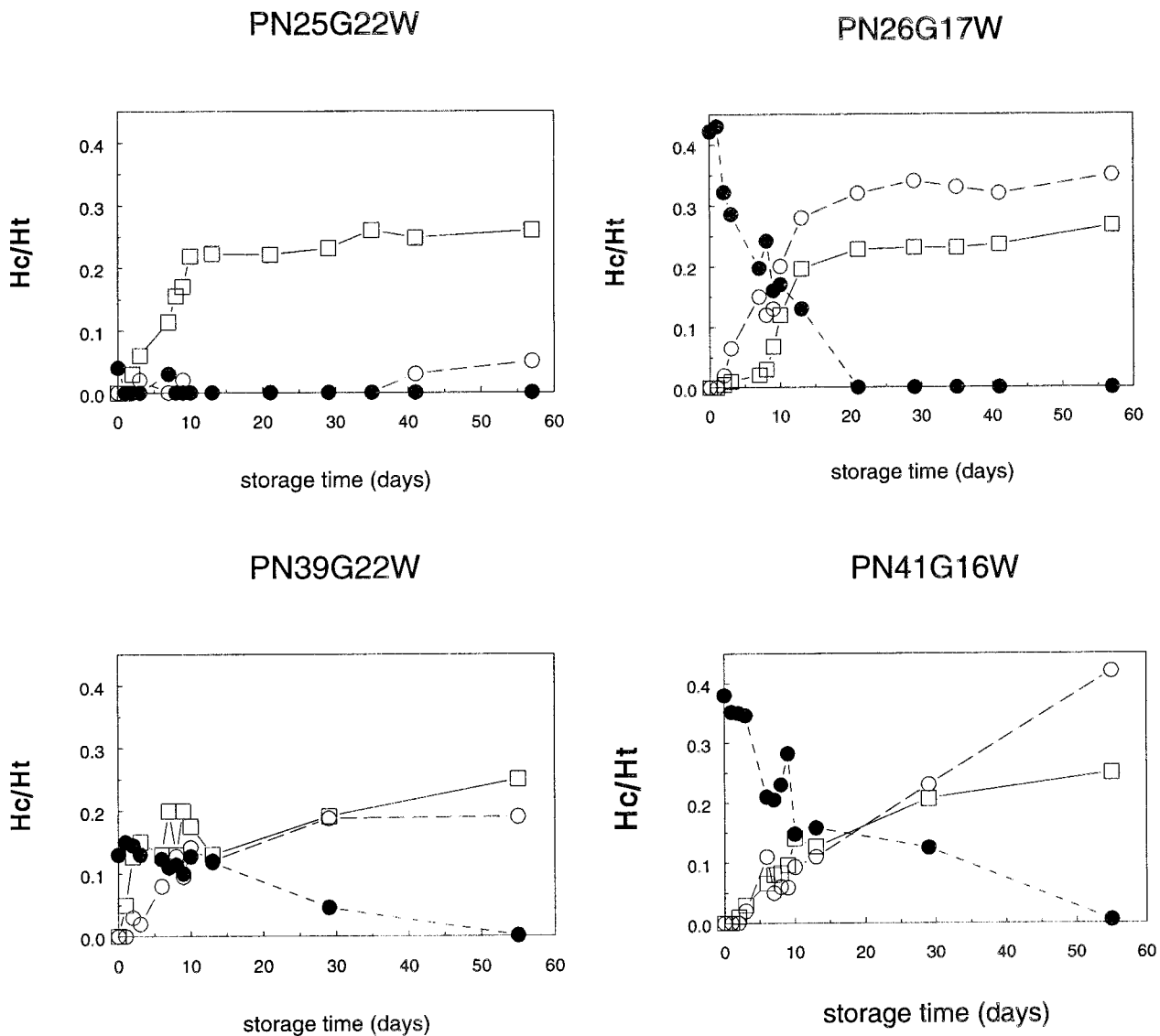Tensile measurements were performed on a Model 4301 Instron Universal Testing Machine

PN25G22W

PN26G17W

PN39G22W

PN41G16W

Figure 2 The changes in E_h-, V_h- and B-type crystallinity expressed as H_c/H_t ratio as a function of aging or storage time at a relative humidity of 60%. ● E_h-type, ○ V_h-type, □ B-type.

as described previously.[10] A crosshead speed of 10 mm/min was used for all samples.

Differential Scanning Calorimetry (DSC)

DSC measurements were performed with a Perkin−Elmer DSC-7. Calibration was done with Indium (ΔH = 28.59 J/g, onset melting point = 156.60°C) and Gallium (ΔH = 79.91 J/g, onset melting point = 29.78°C). An empty pan was used as a reference. Samples (30−40 mg) were weighed accurately into stainless steel pans, sealed hermetically, and heated from −10 to 200°C or to

100°C, after which the materials were cooled rapidly and reheated again from −10 to 200°C. The scan rate was 10°C/min.

Polarized Light Microscopy

The morphology was determined with polarized light microscopy. The materials were sliced and viewed at a magnification of 40 times with a Axioplan Universal Microscope with photographs taken using the MC100 camera accessory.

X-Ray Diffractometry

Wide-angle x-ray diffraction patterns were measured according to the methods described previously.[8,10] The height of the crystalline diffraction (H_c) was measured relative to the height of the peaks (H_t). The relative B-type crystallinity was expressed by the H_c/H_t ratio of the peak at 16.8° (2Θ). The ratio $R(X_H) = H_c/H_t$ was shown to be proportional to the relative crystallinity, X, compared to native potato starch. The relative V_h-type and E_h-type crystallinity were expressed as the H_c/H_t ratio of the peaks at 19.5° and 18.0° (2Θ), respectively. The overall crystallinity, %X, was expressed as the A_c/A_t ratio (×100%) between 7 and 40° (2Θ).

RESULTS AND DISCUSSION

Structural Characterization

Polarized light microscopy showed that the sheets contained only a limited amount, less than a few percent, of granular birefringent and nonbirefrigent structures. The sheets were translucent, which also suggested that the granular structures were destroyed during processing. Due to the high shear and temperatures during extrusion most granules were torn apart and melted. The materials showed no melting transitions below 160°C directly after extrusion (quenched) as determined by DSC. This is typical of a starch material containing no granular crystallinity.[8-10] Some typical x-ray diffractograms are shown in Figure 1 of the quenched materials. No residual B-type crystallinity was observed. The materials with 22% water were completely amorphous. The materials with the lower water contents, denoted as PN41G16W and PN26G17W, contained some recrystallized amylose with the E_h-type crystal structure, which is commonly observed in glycerol containing starch plastics.[8] The E_h-type crystal structure was not stable during aging at room temperature and humidities above 55% and rearranged into the V_h-type crystal structure.[8] During aging the B-type crystal structure was formed in the extruded sheets. The relative amounts of V-type, E-type and B-type crystallinity as a function of storage time are shown in Figure 2, for the controlled storage humidities, and 3, for the ambient storage humidities. In material PN25G22W, with 15% water (on the basis of total mass), almost no E-type and V-type crystallinity occurred. The total amount of E-type and V-type increased with decreasing water
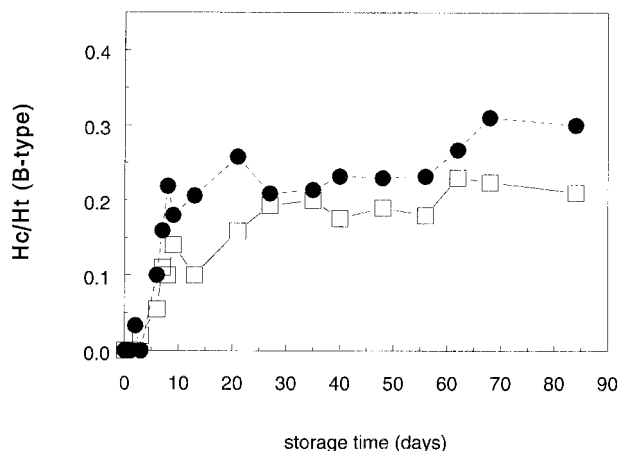

Figure 3 The changes in B-type crystallinity for material PN25G22W expressed as H_c/H_t ratio as a function of aging or storage time at 54% (□) and 61% (●) RH, respectively.

content (on the basis of total mass) during processing. During aging E-type crystallinity decreased and V-type crystallinity increased. Also, B-type crystallinity was formed in the materials during aging. The overall crystallinity of the materials was low, %X < 10%, even after long-term aging.

Changes in Water Content

The changes in water content and the mechanical properties during aging of the sheets are shown in the Figures 4–7 for the materials with differences in plasticizer content during processing stored at a controlled humidity of approximately 61% RH. For the materials with the lower glycerol content the equilibrium water content was approximately 14% (w/w on the basis of total mass) for the materials stored at 61% RH. Material PN39G2W reached equilibrium at a water content of approximately 18–20%. Equilibrium was obtained after about 10 days except for the materials denoted as PN41G16W. The uptake of water took a longer time for this material compared with the PN39G22W materials due to the lower starting water content. The equilibrium/water content was higher for the materials with the higher glycerol content due to the hygroscopic character of glycerol.

In Figure 8 the changes in water content and the properties are shown for the PN25G22W materials stored at ambient RH and temperature. For these materials the water content of the materials stored at approximately 61% RH was higher than of the materials stored at approximately 54%
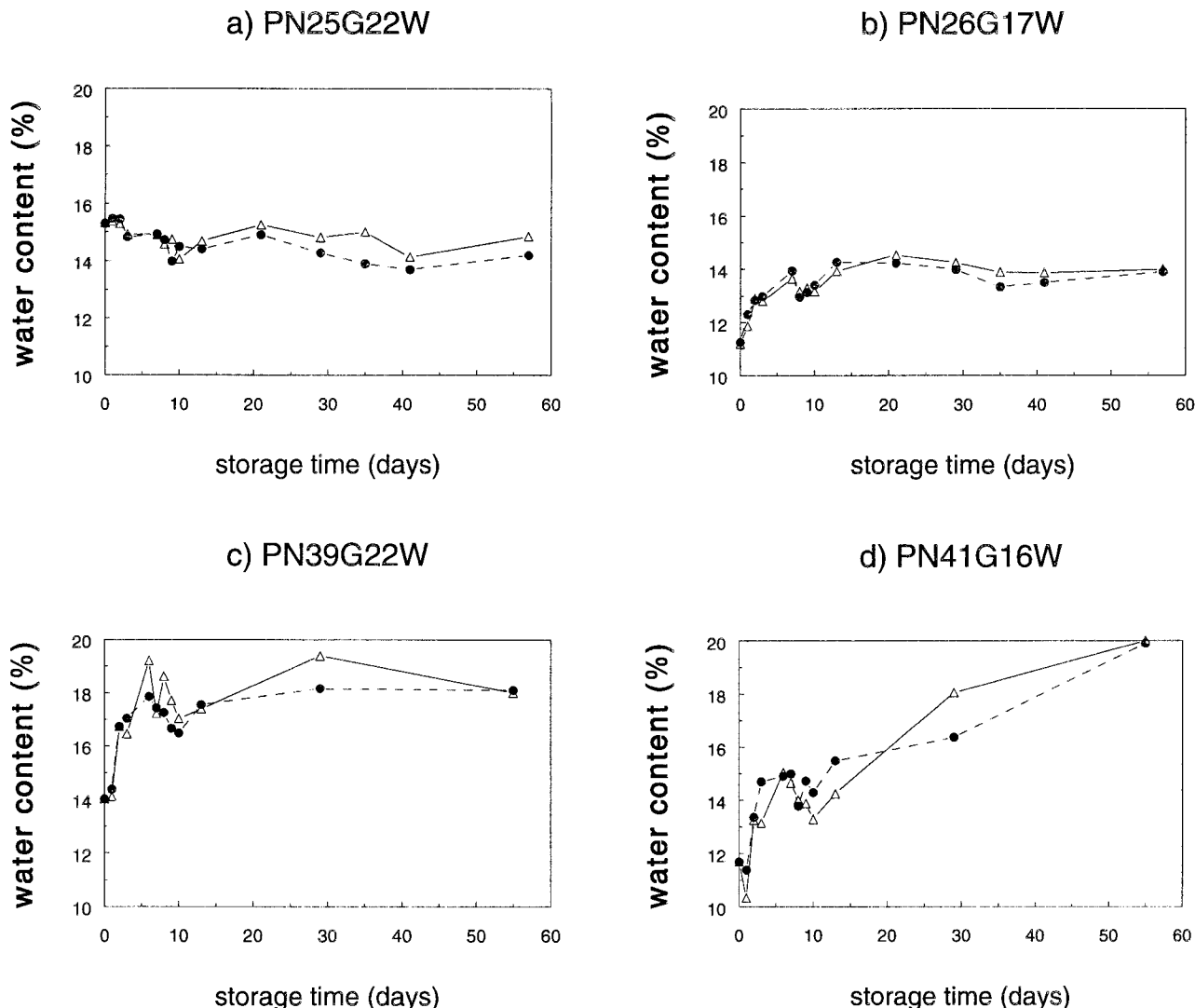
a) PN25G22W

b) PN26G17W

c) PN39G22W

d) PN41G16W

Figure 4 The changes in water content during aging. The materials were prepared in duplo. (a) PN25G22W, (b) PN26G17W, (c) PN39G22W, and (d) PN41G16W.

RH. The water content of the materials stored at 61% RH remained approximately 13–15%, while the materials stored at 54% RH became more dry with a water content finally of approximately 11–12%. At these storage conditions the water content of the materials are different, which reflected in completely different material properties, as is shown below.

Stress–Strain Properties

Some typical load–strain curves are shown in Figure 9 at different stages during aging. The load–strain diagrams of the materials showed the typical pattern of rubbery starch plastic materials re-

ported previously.[9,10,26] The plots were essentially linear at low strain and curved towards the strain axis at higher strains. At high plasticizer content the fracturing process was slow (tearing). At a water content of approximately 10–12% (w/w) the PN25G22W and the PN26G17W materials showed a ductile region with a yield point after which the stress decreased with increasing strain (stress softening). The materials were tough and rubbery. The PN39G17W and PN41G16W materials with the higher glycerol content showed no yielding behavior.

In Figure 5 it is clearly shown that the elongation decreased rapidly in time during the first week for the materials denoted as PN25G22W,
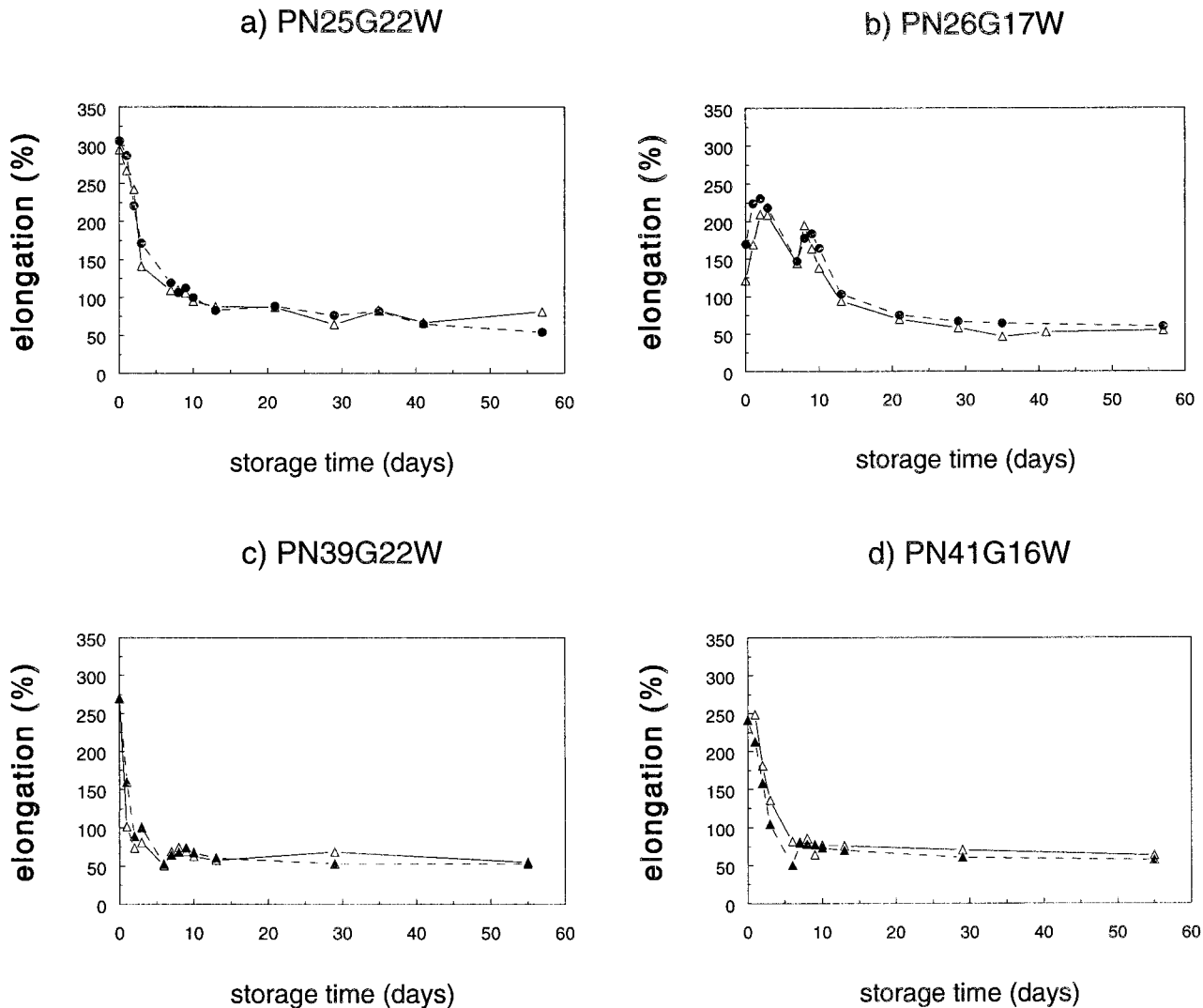
a) PN25G22W

b) PN26G17W

c) PN39G22W

d) PN41G16W

Figure 5 The changes in elongation during aging. The materials were prepared in duplo. (a) PN25G22W, (b) PN26G17W, (c) PN39G22W, and (d) PN41G16W.

PN39G22W, and PN41G16W, respectively. The E-modulus and the tensile stress increased in time (see Figs. 6 and 7). These materials were rubbery and the glass transition temperature was below storage temperature ($<20°C$). For material PN26G17W the elongation increased from approximately 150 to 225% during the first days of aging. The tensile stress and E-modulus decreased over this period. The PN26G17W materials were glassy directly after extrusion with a water content of approximately 11%. A glass transition temperature is observed at approximately 40°C, as is shown in Figure 10. The PN26G17W materials also showed the endothermic transition described previously in terms of specific water–carbohydrate interactions or polymer–polymer

interactions, which occur below the glass transition temperature.[27–28]

During storage for over 1 week, only slight changes in elongation were observed. The E-modulus of the materials with the higher glycerol content showed almost no increase in after the first week of storage. The E-modulus reached a level of approximately 10–20 MPa. The materials with the lower amount of glycerol showed a strong increase in E-modulus during further aging upto a level of 70 MPa for materials with approximately 14% water and even upto 270 MPa for the materials stored at ambient conditions with a water content of approximately 11%. The E-modulus was clearly sensitive to the amount of plasticizer and especially water content. The tensile stress also
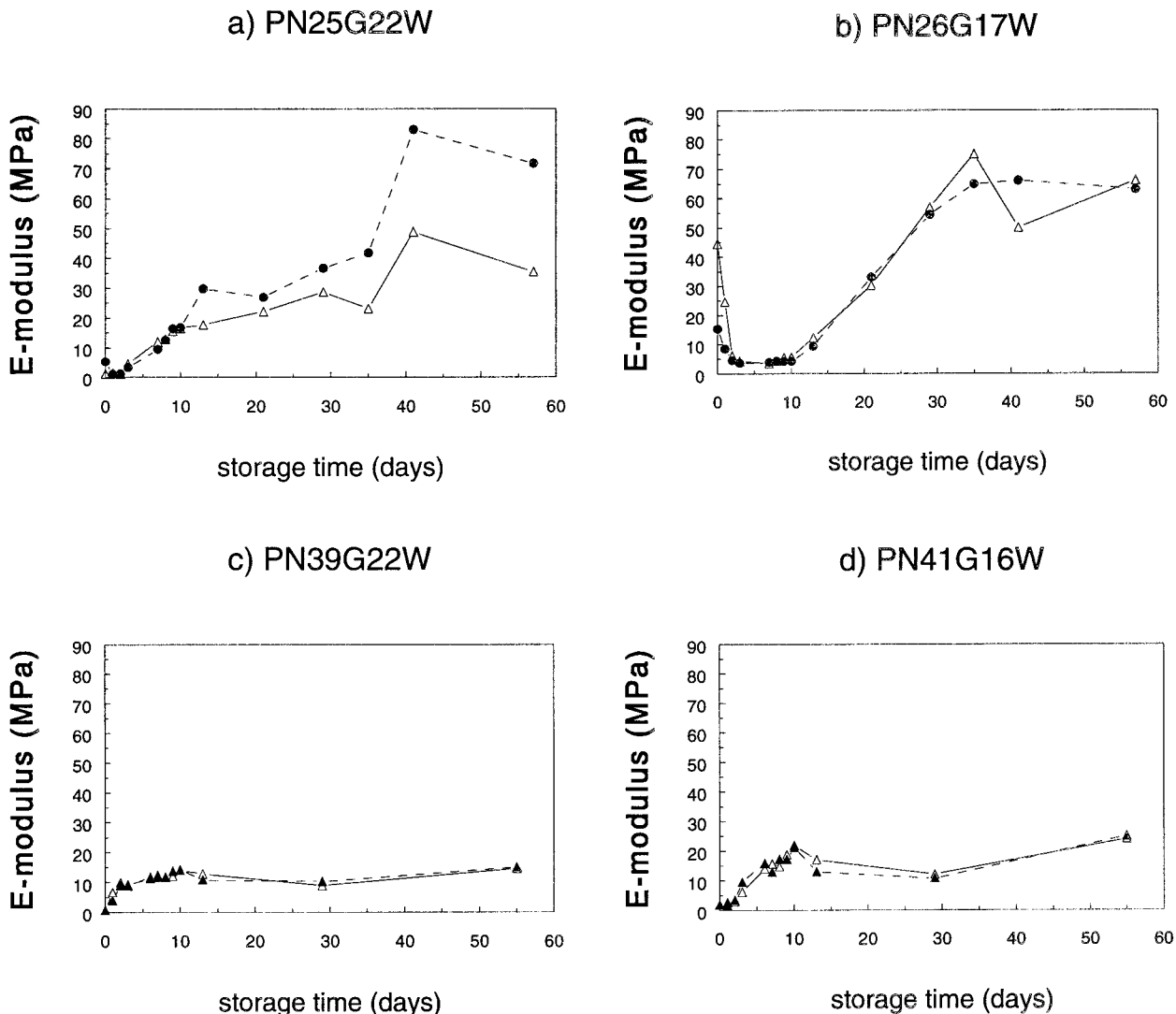
a) PN25G22W

b) PN26G17W

c) PN39G22W

d) PN41G16W

Figure 6 The changes in E-modulus during aging. The materials were prepared in duplo. (a) PN25G22W, (b) PN26G17W, (c) PN39G22W, and (d) PN41G16W.

showed a further increase in time upto about 10 MPa after 57 days storage. Noticeable is the fact that the tensile stress is less sensitive to the amount of plasticizer compared with the E-modulus.

DISCUSSION

The amount of single helical crystallinity (E_h and V_h) seems to depend more on the amount of water during processing than on the amount of total plasticizer (glycerol and water). The rate of rearrangement of E-type crystallinity in the V-type crystallinity is determined by the amount of water in the materials. The overall amount of amylose–

single helical crystallinity does not during aging and, therefore, changes in properties during aging are not related to single helical crystallinity.

The rate of formation of the double helical B-type crystallinity is also determined by the amount of plasticizer in the materials. The crystallization rate increases with increasing plasticizer content, both water as well as glycerol. In a gel system the retrogradation rate of amylopectin has been shown to decrease by the replacement of water by glycerol.[25] In the extruded materials with higher glycerol levels the fast uptake of water and the higher water content in the materials leads to an increase in crystallization rate. By comparison of the materials PN25G22W and PN41G16W it is seen that the material with the
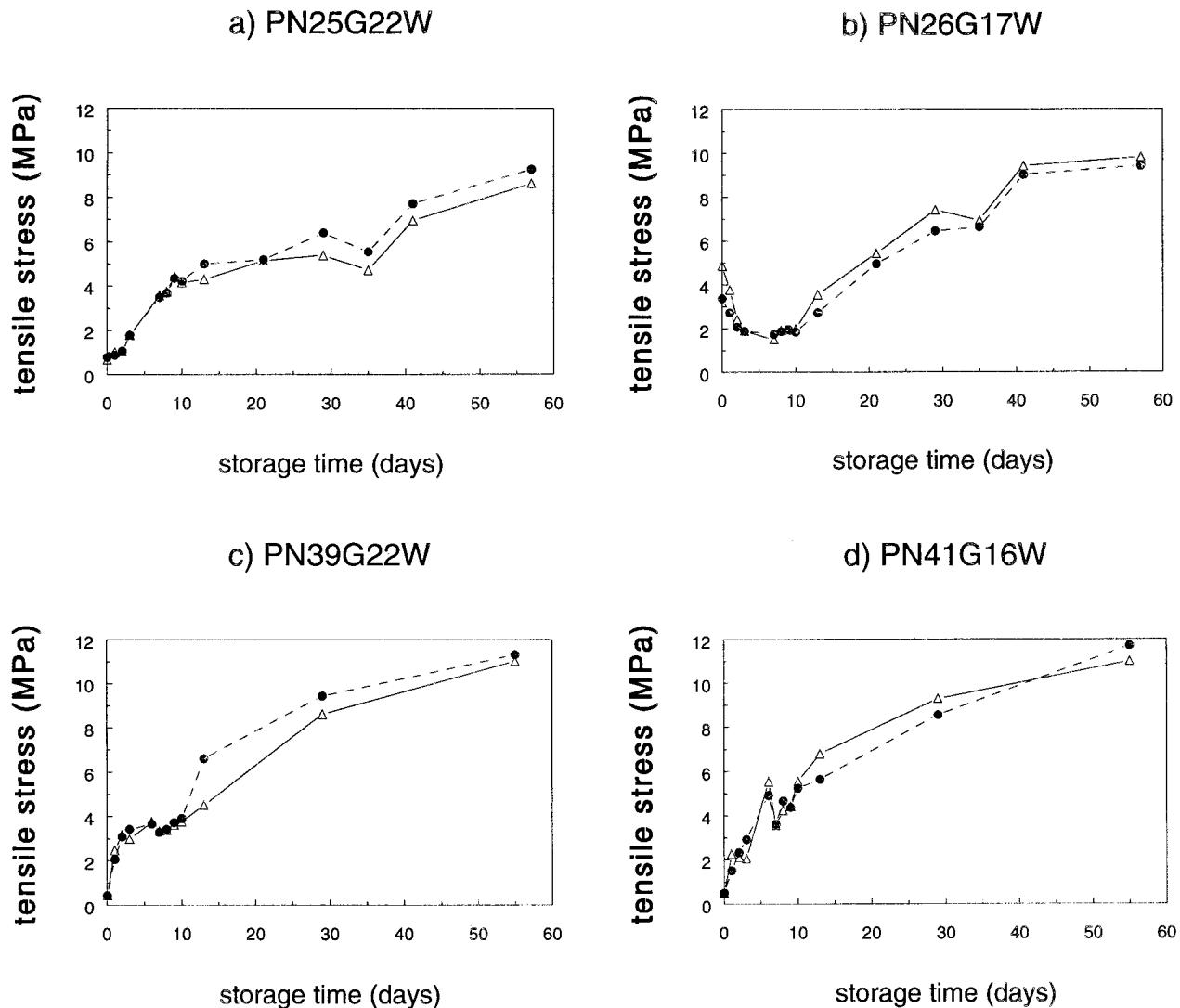
a) PN25G22W

b) PN26G17W

c) PN39G22W

d) PN41G16W

Figure 7   The changes in tensile stress during aging. The materials were prepared in duplo. (a) PN25G22W, (b) PN26G17W, (c) PN39G22W, and (d) PN41G16W.

higher amount of water crystallizes more rapid than the material with the higher overall plasticizer content. This can be explained by the fact that water is a better plasticizer than glycerol.[29] In material PN25G17W there is a delay in crystallization of approximately 7 days due to the fact that these materials are below their glassy transition temperature directly after extrusion. The crystallization rate of the PN39G22W materials is the highest due to the high initial water and glycerol content and the rapid uptake of water during storage. The crystallization rate of the materials is, thus, a function of initial water content, of initial glycerol content, and of the changes in water content during aging.

The changes in water content and crystallinity

are affecting the stress–strain properties. During the first week of aging the changes in elongation are very pronounced. The changes in elongation are clearly related to the changes in starch structure and B-type crystallinity. The decreases in elongation are more pronounced for the materials that crystallize more rapidly. However, the elongation of starch plastic sheets is also influenced by water content as described previously.[9] A maximum is observed at a rather discrete water content.[9] It is clear that the elongation of the sheet materials with the higher glycerol content drops more rapidly during aging. This decrease in elongation is enhanced by the rapid uptake of water during aging. The degree of crystallinity is still low during the first week of aging. The changes
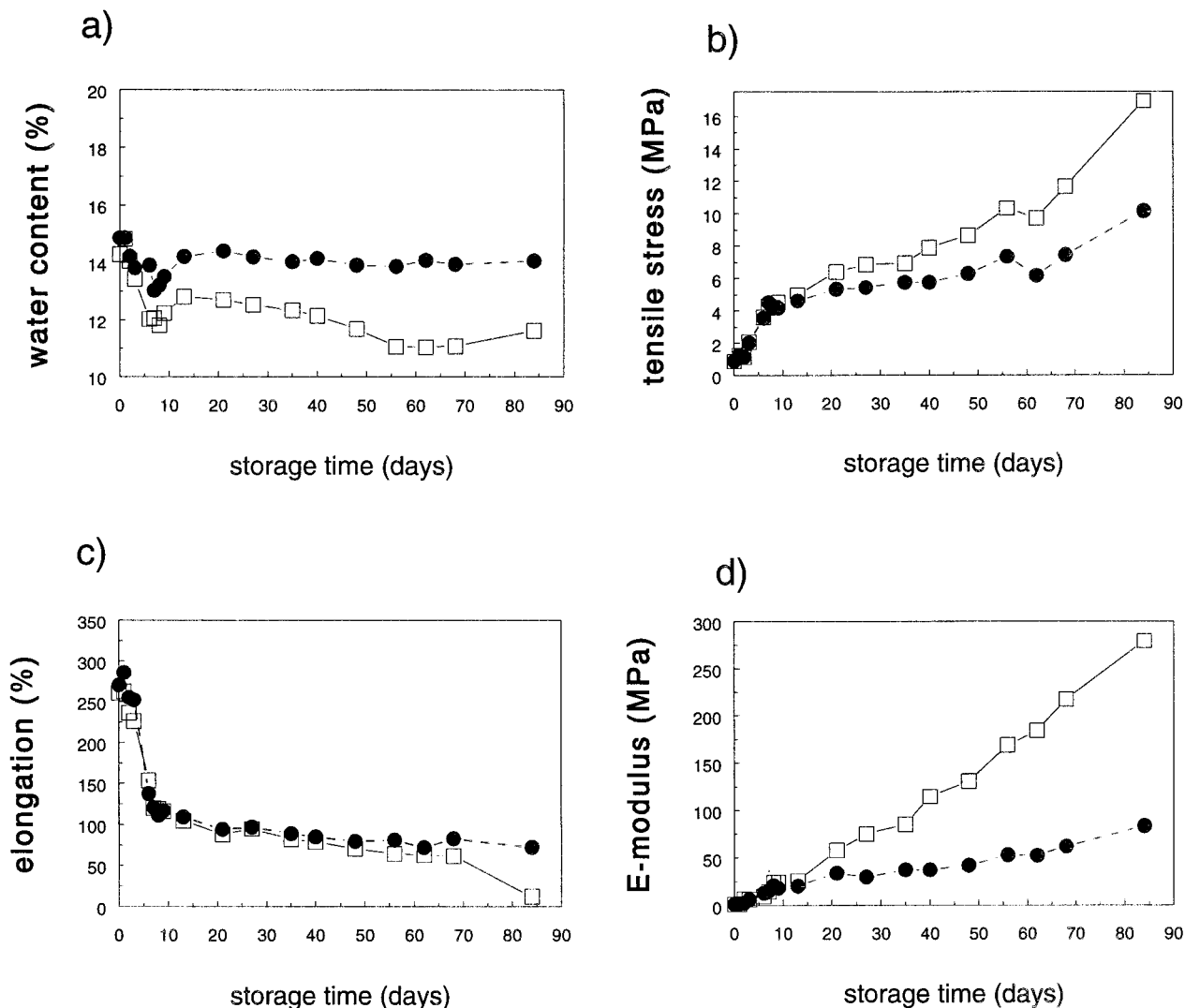
a)

b)

c)

d)

Figure 8 The changes in water content (a), tensile stress (b), elongation (c) and E-modulus (d) for material PN25G22W as a function of aging or storage time at 54% (□) and 61% (●) RH, respectively.

in stress–strain properties are, therefore, probably not only related to the formation of long-range ordering (crystallinity) but also by the formation of short-range ordering (the formation of helicity) and the relaxation of especially the large amylopectin molecules. It is still not clear in what extent the formation of double helices plays a role in the changes in properties. The rate of formation of ordering and relaxation will be increased with increasing plasticizer content due to the higher mobility of the molecules.

The tensile stress was shown to increase with increasing B-type crystallinity. The formed crystals act as physical crosslinks increasing the strength of the extruded sheets. The influence of

water on the tensile stress was only observed for those materials that were only slightly above their glass transition temperature. This accounts for the PN26G17W materials during the first week of storage and the materials PN25G22W with decreasing water content (Fig. 8). The materials with a water content of approximately 12% (w/w on the basis of total mass) and a glycerol content of approximately 25–26% (w/w on the basis of dry starch) were glassy.

The changes in E-modulus are related to both water content as well as crystallinity. The materials with 39 and 41% glycerol were directly after extrusion gel-like materials. After the first week of aging the E-modulus increased and the materi-
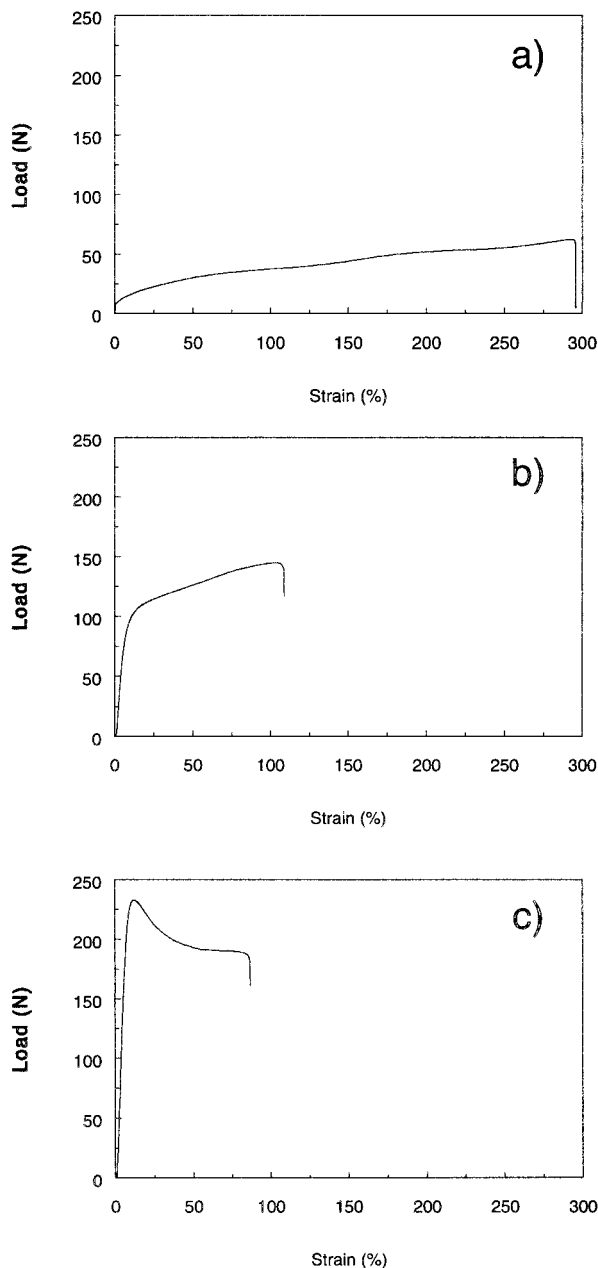
Figure 9 Typical load–strain curves of the starch materials (PN25G22W) during aging. (a) The materials after 1 day of aging. (b) The materials after 9 days of aging. (c) The materials after 35 days of aging.

als became more rubbery. This change in behavior is probably due to the increase in chain associations, such as the formation of double helices, of both amylose as well as amylopectin. The coherency in the materials increases as a result. The materials with the high amounts of total plasticizer have low E-moduli as expected because of the plasticizing effect of water and glycerol. The

materials with the higher amounts of glycerol show almost no effect of increased crystallization after the first week of aging while the materials with the lower glycerol contents show a further increase in E-moduli. It seems that the height of the rubber plateau is increased during aging. Especially the PN25G22W materials stored at 54% RH showed an increase in E-modulus although the crystallization rate was lower. These materials became more glassy during storage. The effects due to loss of plasticizer was more pronounced than the increases in crystallinity.

The effects of aging on starch structure and the stress–strain properties can be explained by the previously proposed models of starch structure in starch plastics[30,31] and retrograded starch.[32] In these models the amylose and amylopectin forms a network composed of amorphous amylose and amylopectin containing granular rest structures (amylopectin ghosts). During aging amylose forms partly single-helical structures that can crystallize into several crystal structures.[8] Double-helical structures are formed by amylose and amylopectin above glass transition temperature. The double helices can be formed by (a) two unit chains of amylopectin in the same molecule, (b) a chain of amylose within the same molecule by chain folding (c) two unit chains of two different amylose molecules, (d) one amylose chain with an amylopectin outer chain, (e) two outer chains of different amylopectin molecules. The double helices can form aggregates and crystallize into the B-type crystalline structures consisting of pure amylose, of pure amylopectin and of amylose–amylopectin cocrystals. The formation of helicity is regarded as a fast process preceding crystallization.[25] The formation of amylose crystallinity is shown to be a relatively fast process compared to the crystallization of the amylopectin outer chains.[10,25] The formation of helicity and crystallinity can be seen as the formation of a physically crosslinked starch network. This results in a strengthening and a stiffening of the materials. The materials directly after extrusion are mainly consisting of amorphous starch with a high molecular weight. Plastic flow in the materials with high plasticizer content is a relatively easy process leading to very high elongations. The effects of aging become very clearly visible during the first week after extrusion, suggesting that starch helicity is important for the properties of starch-based plastics. The formation of intramolecular amylopectin crystallinity does not play a significant role in the materials that were investigated
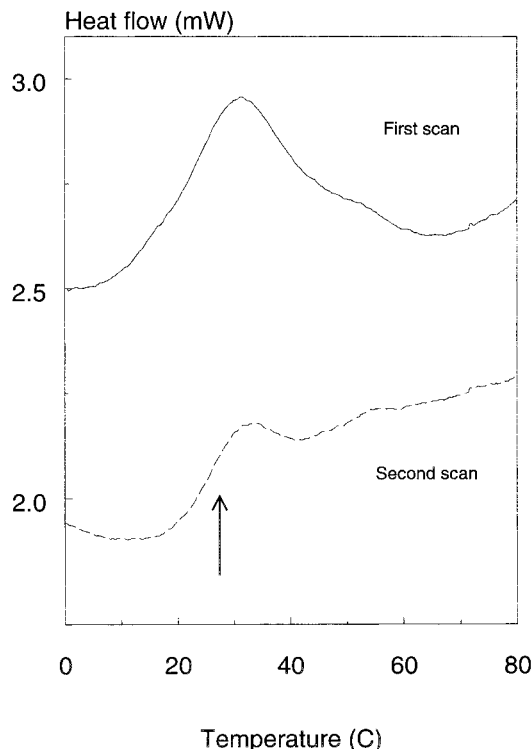
Figure 10 DSC thermogram of material PN26G17W 1 day after extrusion processing. The position of the glass transition (27°C; $0.1 \pm 0.05 \; \text{J} \cdot \text{g}^{-1} \cdot \text{K}^{-1}$) is indicated by the arrow.

changes in properties of starch-based plastics in the rubbery state put an important constraint on the development of rubbery products from starch. It is not only important to control the long-term aging processes taking place in starch plastic materials but also the aging processes over a shorter period.

in this article. Intramolecular amylopectin crystallization, in waxy corn starch plastics, has been found to be a relatively slow process leading to spontaneously formed cracks.[10] The level of crystallinity is still low, and probably a large part of the crystals consists of amylose and amylose–amylopectin intermolecular crystallinity.

CONCLUSIONS

The changes in crystallinity in starch plastic sheets are clearly related to the initial amount of plasticizer and the changes in water content during aging. The changes reflected in the stress–strain properties of the materials. The materials above their glass transition temperature were soft, almost behaving as a gel, directly after extrusion. The strength and stiffness increased rapidly during the first week of storage.

The differences in material properties were attributed to the formation of an entangled starch matrix and by starch chain–chain associations that are related to plasticizer content. The rapid

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