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Ageing of rubbery thermoplastic barley and oat starches

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Abstract

Ageing of thermoplastic barley and oat starches prepared by the extrusion technique was investigated. Glycerol-plasticized thermoplastic starches were stored in the rubbery state at 20°C and at a relative humidity of 50% for 8 months. The ageing was followed by measurements of the tensile failure stress and strain and by characterizing thermal transitions using differential scanning calorimetry, crystallization using X-ray diffraction and small-strain viscoelastic properties using dynamic mechanical thermal analysis. The initial crystal structures and the crystallization kinetics depended on the starch origin but the ultimate crystallinities and endothermic melting transitions were the same for both starches. Mechanical relaxations observed by dynamic mechanical analysis correlated well with calorimetric glass transitions. The main mechanism underlying the changes in failure properties is suggested to be slow amylopectin crystallization. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Barley starch; Oat starch; Ageing; Thermoplastic starch

1. Introduction

Most solid and semi-solid carbohydrate polymers are not at equilibrium and exhibit time-dependent changes in their structure and macroscopic properties. The glass transition of amorphous materials exerts a strong influence over the rate at which molecules explore possible configurations. Below the glass transition temperature segmental motions are limited and solid carbohydrate polymers exhibit physical ageing and enthalpy relaxation phenomena (Shogren, 1992). Additionally, small molecules such as water and permanent gases can diffuse through glassy carbohydrate polymers (Fish, 1957; Arvanitoyannis et al., 1994). Above the glass transition the scope for molecular rearrangement is much greater, polymer segments are mobile over experimental timescales and the structure of the system is able to move towards equilibrium. This work studies a system stored in a rubbery state such that the phase structure is developing from an initially amorphous state. The work underpins the development of starch as a biodegradable plastic and so concentrates on the relationship between composition, structure and material properties.

Many studies have focused on the preparation of melted or gelatinized starch by extrusion in the presence of glycerol at low moisture and at high temperatures, materials that are called thermoplastic starches (TPSs). Processing results in a material that is largely amorphous and, as a result of the glycerol and water present, the starch is plasticized to such an extent that it is close to its glass transition (Forssell et al., 1997).

Depending upon the plasticizer content and botanical origin of the starch, different mechanical properties can be produced (Shogren et al., 1992; van Soest and Essers, 1997). The hydrophilic nature of starch polymers and the glycerol plasticizer means that mechanical properties of TPSs are rather sensitive to changes of ambient humidity. Even if stored under controlled conditions mechanical properties have been observed to change, in large-strain tensile experiments the failure stress tending to increase and the failure strain to decrease. Studies of the structural changes of starch polymers during ageing have been performed by using X-ray diffraction. In a study of potato starch processed by extrusion in the presence of water and glycerol, the time-dependent changes in the product's mechanical properties were found to be correlated with changes of crystallinity (van Soest et al., 1996a). When materials were stored at a relative humidity (RH) above 60%, B-type crystals were rapidly formed during 2 weeks of storage. With increasing

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B-type crystallinity failure stress increased and failure strain decreased, and at the highest crystallinities (which resulted from storage at 90% RH) the samples cracked and spontaneously broke during storage.

The influence of glycerol and water contents on ageing of thermoplastic potato starch was recently reported (van Soest and Knooren, 1997). During the first week of storage samples above the glass transition temperature increased in strength and stiffness rapidly. Crystal formation was detected, but the overall crystallinity was low. The changes in the mechanical properties were suggested to relate with the formation of an entangled starch network and chain–chain associations. Despite the fact the many structural studies on ageing have been performed, the relationship between the mechanical and molecular structural properties remains unclear.

The present study is based upon preliminary observations of the ageing of thermoplastic barley starch plates (Forssell et al., 1996). The aim was to explain the changes in mechanical properties with the aid of structural characterization of thermoplastic materials prepared from barley and oat starches. The main variables studied are the botanical source of the starch and time.

2. Materials and methods

2.1. Materials

Barley and oat starches were from Primalco (Rajamäki, Finland). The total amylose content of barley starch was 29% and that of oat starch 27%, as determined colorimetrically according to the method of Morrison and Laignelet (1983). Measurements of lipid content based upon phosphorus determination (Morrison, 1964) (conversion factor 16.5 after Tester and Morrison, 1990) showed that the oat starch was somewhat higher in lipid than the barley starch, 1.3 and 1.0%, respectively. Glycerol was of technical grade (85%, Akzo Chemicals).

2.2. TPS processing and storage conditions

Amorphous starch–glycerol–water plates were prepared by a two-stage extrusion process. Starch and glycerol were premixed and stored overnight prior to extrusion. The glycerol content of the mixture was 30 wt% (dry weight basis) and it contained about 12 wt% water. The mixture was first processed in a twin-screw extruder (Clextral BC-21, France) followed by second extrusion step using a single-screw extruder (Brabender Plasti Corder PL 2000, Brabender, Austria) equipped with a slit die to form plates. In both extruders the barrel temperature was 170°C and the temperature at the die was 120°C. The thickness of the plates varied from 300 μm to 700 μm. TPS plates were stored at an RH of 50 ± 5% and at 20°C. After 1 week of storage the plates were analysed for the first time; these samples are termed ‘‘fresh’’ plates.

In order to analyse the effect of environmental humidity on tensile properties, oat TPSs were stored in closed chambers over saturated salt solutions at 20°C for 1 week. Salts used were LiCl, $MgCl_2$, $Mg(NO_3)_2$, NaCl and $(NH_4)_2SO_4$, providing relative humidities 11, 33, 54, 76 and 81%, respectively (Greenspan, 1977).

2.3. Moisture and glycerol contents

Moisture content was determined gravimetrically by drying small pieces of TPS plates at 105°C overnight. Glycerol content was determined enzymatically using a kit purchased from Boehringer Mannheim (No. 148270, Mannheim, Germany). TPS plates were ground to powders in a mill (Fritsch, Idar-Oberstein, Germany). Glycerol was extracted by mixing a 1% aqueous dispersion of the powder overnight at room temperature, and the glycerol content of the water was measured.

2.4. Molecular weight

Size exclusion chromatography (SEC) was used to determine mass-average molecular weight of starch before and after extrusion. μHydrogel (Millipore-Waters, Milford, MA, USA) columns 2000, 500 and 250 were used for fractionation. A dual-angle laser-light scattering detector (Precision Detectors, Amherst, MA, USA) was used to determine the absolute molecular masses. Starch was dissolved in 1 M NaOH (200 mg of starch in 10 ml of NaOH) and diluted 1:10 with 1 M NaOH. 50 mM NaOH was used as the eluent at a flow rate of 5 ml/min.

2.5. Mechanical testing

Tensile failure stress and failure strain were measured with a Texture Analyser (TA, XT.2, England) under constant storage conditions of 50% RH and 20°C in an environmentally controlled instrument room. Dumb-bell-shaped specimens, according to ISO 1184–1983 (E) standard, were cut from the extruded plates. Five replicates were tested for each material and the average value of each quantity reported.

2.6. Differential scanning calorimetry (DSC)

Differential scanning calorimetry (Mettler DSC30, Switzerland) was used to characterize the endothermic and glass transitions of the TPS plates. The sample size was about 10 mg. The sample was weighed into an aluminium pan, sealed and then analysed together with an empty reference pan. The run was performed by heating, immediate cooling and reheating again with a scanning rate of 10°C/min. Endotherms were analysed from the first heating thermograms and the glass transition temperatures (T_g) from the second heating thermograms as the midpoint of the transition. As an aid in the interpretation of the DSC scans, ‘‘dry’’ samples were run in addition to the standard ‘‘wet’’

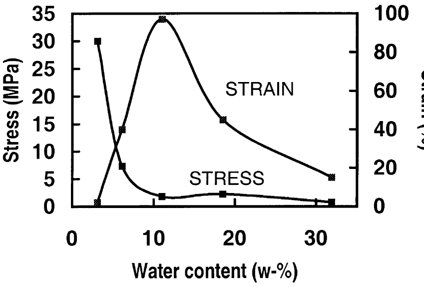

Fig. 1. The effect of water content on the tensile failure stress and failure strain (1 week old) of oat thermoplastic starch.

samples. The dry samples were prepared by drying in a vacuum desiccator with P_2O_5 at 60°C overnight.

2.7. Dynamic mechanical thermal analysis (DMTA)

Dynamic mechanical measurements were performed in the temperature range from $-$ 100°C to 80°C using a Polymer Laboratories Dynamic Mechanical Thermal Analyser (DMTA) MkII (Rheometric Scientific, Epson, UK). Samples cut from TPS plates were typically 10 mm long, 5 mm wide and 0.5 mm thick. Prior to measurement samples were conditioned over saturated $Mg(NO_3)_2$ solutions (54% RH) at 20°C for 1 week to ensure that the correct water content was maintained after transport in sealed packages between laboratories. The DMTA was used in tensile mode at a frequency of 10 Hz and a nominal peak-to-peak displacement of 16 μm. The heating rate was 2°C/min and all samples were coated with petroleum jelly (Vaseline™) to limit water evaporation during the scan. The ‘‘reducing force’’ option was used on all samples in which the constant tensile force, applied to maintain the sample in tension throughout the temperature scan, is reduced in step with the decreasing modulus of the sample.

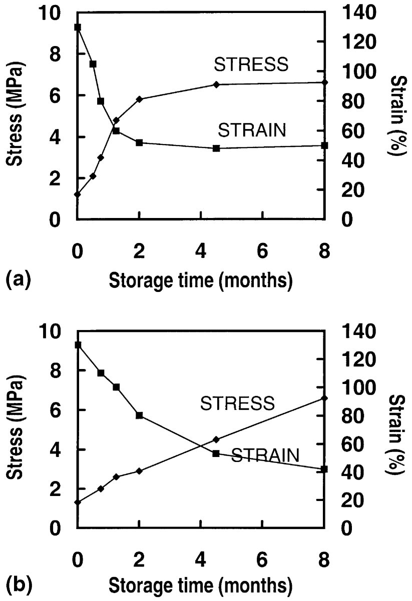

Fig. 2. The effect of ageing on the tensile failure stress and failure strain of thermoplastic starches prepared from: (a) barley starch and (b) oat starch.

2.8. X-ray diffractometry

Diffractograms were recorded from powdered samples on a Philips PC-APD diffractometer PW3710 equipped with an Anton Paar TTK temperature chamber. Diffractograms were recorded in the reflection mode in the angular range 4 to 40°(2θ). The Cu K_α radiation ($\lambda = 1.542$ Å), generated at 40 kV and 50 mA, was monochromatized with a 15 μm nickel foil. The diffractometer was equipped with a 1° divergence slit, a 15 mm beam mask, a 0.2 mm receiving slit and a 1° scatter slit. Radiation was detected by a proportional detector. Crystallinity was measured according to the method of Hermans and Weidinger (1948). Diffractograms were baseline-corrected by drawing a horizontal line through the diffraction minimum at ca. 7°(2θ). The height (H_c) of the crystalline diffraction was measured relative to the height of the peak as measured from the baseline (H_l). A crystallinity index, x_c, was calculated dividing H_c by H_l.

3. Results and discussion

3.1. Mechanical properties

Ageing of TPS plates made from barley and oat starches containing 30 wt% glycerol (dry weight basis), stored at 20°C and a relative humidity of 50%, was studied over a period of 8 to 12 months. After conditioning, the plates contained 11 ± 1% water. The glass transition temperature of the starch-rich phase of thermoplastic starches having 30% glycerol and 11% water was not detectable with a Mettler DSC30 (Forssell et al., 1997); however, recently, Lourdin et al. (1997) obtained a value of about 0°C using a Setaram DSC121. Thus the plates in this study were stored above their glass transition temperature in a rubbery state. The high temperature and shear during extrusion caused some depolymerization of the starches, but based on SEC chromatograms no differences in the extent of depolymerization were found between barley and oat starches. The mass-average molecular weight of both TPS starches was 8×10^6 g/mol.

Preliminary studies were performed on the effect of environmental humidity on the tensile properties of oat TPS plates. One-week-old plates were conditioned at different RHs. Changes in the environmental humidity greatly affected the water content of the plate, which, in turn, induced large changes in failure stress and strain (Fig. 1). When the plate was stored at low humidity ($RH < 50\%$, water content $< 11\%$) tensile failure stress increased, while at higher humidities ($RH > 50\%$, water content $> 11\%$) the plate gradually lost its mechanical strength. Tensile failure strain decreased when the humidity deviated from the

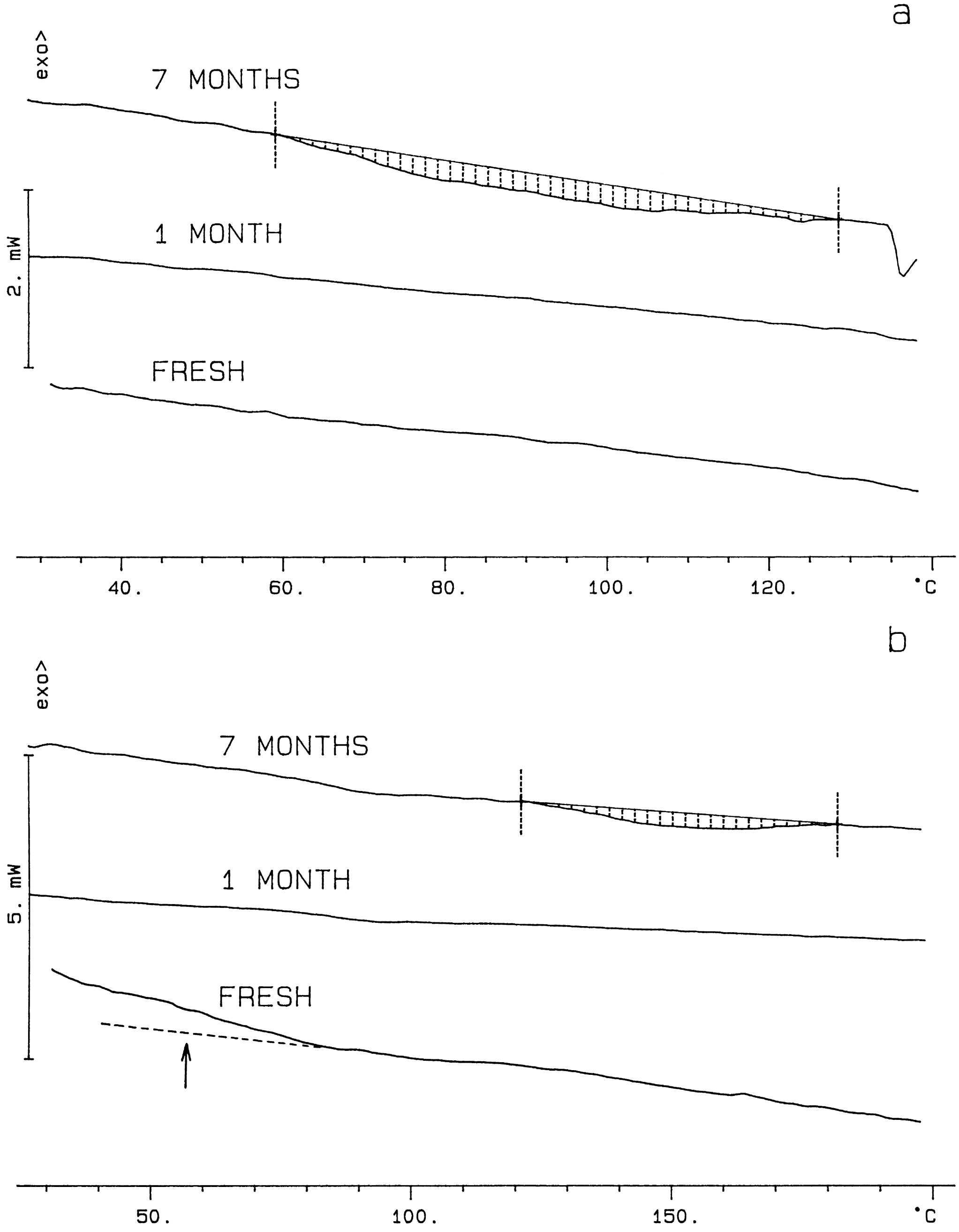

Fig. 3. The effect of ageing on the heat flow into samples of TPS prepared from barley starch: (a) the first heating DSC traces of the wet plates, (b) the first heating DSC traces of the dry plates (an arrow indicates the baseline shift of the fresh TPS) and (c) the second heating DSC traces of the dry plates.

standard storage condition (RH = 50%). Similar behaviour was recently observed when the mechanical properties of thermoplastic starches prepared from potato and waxy maize starch were investigated, and the low strength and elasticity at high water contents were explained in terms of a weakening of the interactions between the starch molecules (van Soest et al., 1996b, 1996c). Subsequent measurements were made on samples aged at 50% RH, the condition under which maximum failure strain was recorded (Fig. 1).

The fresh plates prepared from both barley and oat starches were very sticky and weak, having a tensile failure stress of 1 MPa and a failure strain of 130% (Fig. 2(a)Fig. 2(b)). Tensile failure stress increased and failure strain decreased in both plates during storage (Fig. 2). Compared with the oat TPS, the changes in the barley TPS occurred faster and after 2 months of storage the mechanical properties of barley TPS were practically constant. The changes in oat TPS continued to occur during the whole storage period, and at the age of 8 months the tensile properties of oat TPS were similar to those of barley TPS.

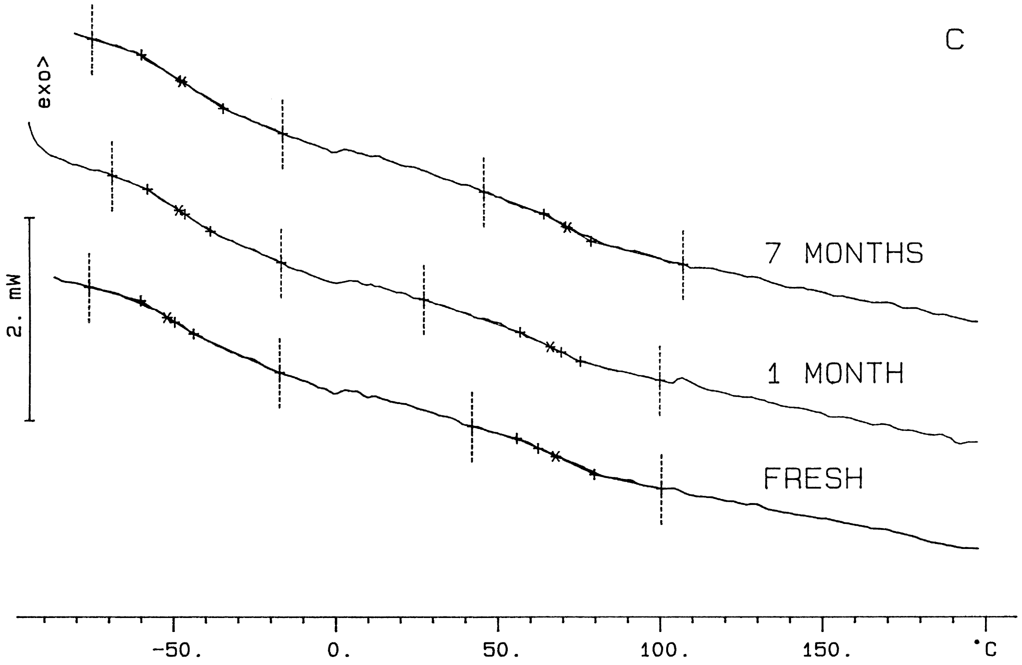

Fig. 3. Continued.

3.2. Thermal behaviour

DSC and DMTA were applied to characterize the thermal transitions of the TPS and to provide information on the physical state and structure as an aid in the interpretation of the observed time-dependent tensile properties. The calorimetric transitions of the TPS plates were analysed at a water content of 11% (conditioning at 50% RH, 20°C), termed ''wet'' samples, and at a water content of 1–2% (after vacuum drying overnight), termed ''dry'' samples. Both the first heating thermograms and the immediate reheating traces were analysed.

The overall calorimetric behaviour of barley and oat TPS was similar. Examples of the effect of storage on the first heating thermograms of wet TPSs are shown in Fig. 3(a). The first and second heating thermograms of the fresh dry TPS plates and after 1 and 7 months' storage are presented in Fig. 3(b)–(c).

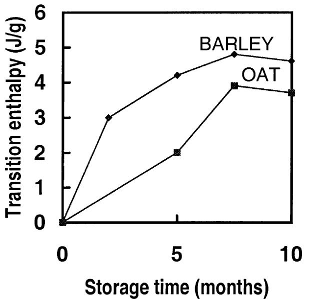

Fig. 4. The effect of ageing on the area under the endotherm for dry TPS prepared from barley and oat starches.

No transitions were observed in the first heating thermograms of the wet TPS plates when analysed as fresh (Fig. 3(a)), but the fresh and dry plates showed a broad glass transition at about +79°C (Fig. 3(b)). In the immediate reheating traces of the wet plates a glass transition at −73°C was detected (not shown in Fig. 3), whereas the reheated thermograms of the dry plates showed two transitions, at −47°C and at +71°C (Fig. 3(c)). The low-temperature transition of the dry plate was located at a higher temperature than the transition of the wet plate. The observation of two glass transitions in a starch–glycerol–water system was earlier suggested to be caused by separation of the mixture into glycerol-rich and starch-rich phases (Forssell et al., 1997). The upper glass transition temperature (+71°C) of the dry plate was located at the same temperature (+70°C) as observed earlier for the barley starch–glycerol–water powder after drying (Forssell et al., 1997).

During ageing the calorimetric thermograms changed, and gradually an endothermic peak was detected in the first heating scans (Fig. 3(a)–(b)). After 7 months' storage the thermograms of the wet plates showed a very broad, rather indistinct endotherm (Fig. 3(a)). However, for the dry plates, this endotherm was narrower and more distinct. It was present after 1 month of storage in some of the dry plates and it was easily detected in all dry plates after longer storage periods (Fig. 3(b)). The area under the endothermic peak increased with increasing storage time in both dry barley and oat TPSs but the rate of increase was faster in the case of barley TPS (Fig. 4). All endotherms disappeared when the plates were immediately reheated (Fig. 3(c)). The calorimetric behaviour indicated that the endotherms were probably caused by melting of starch crystals. In

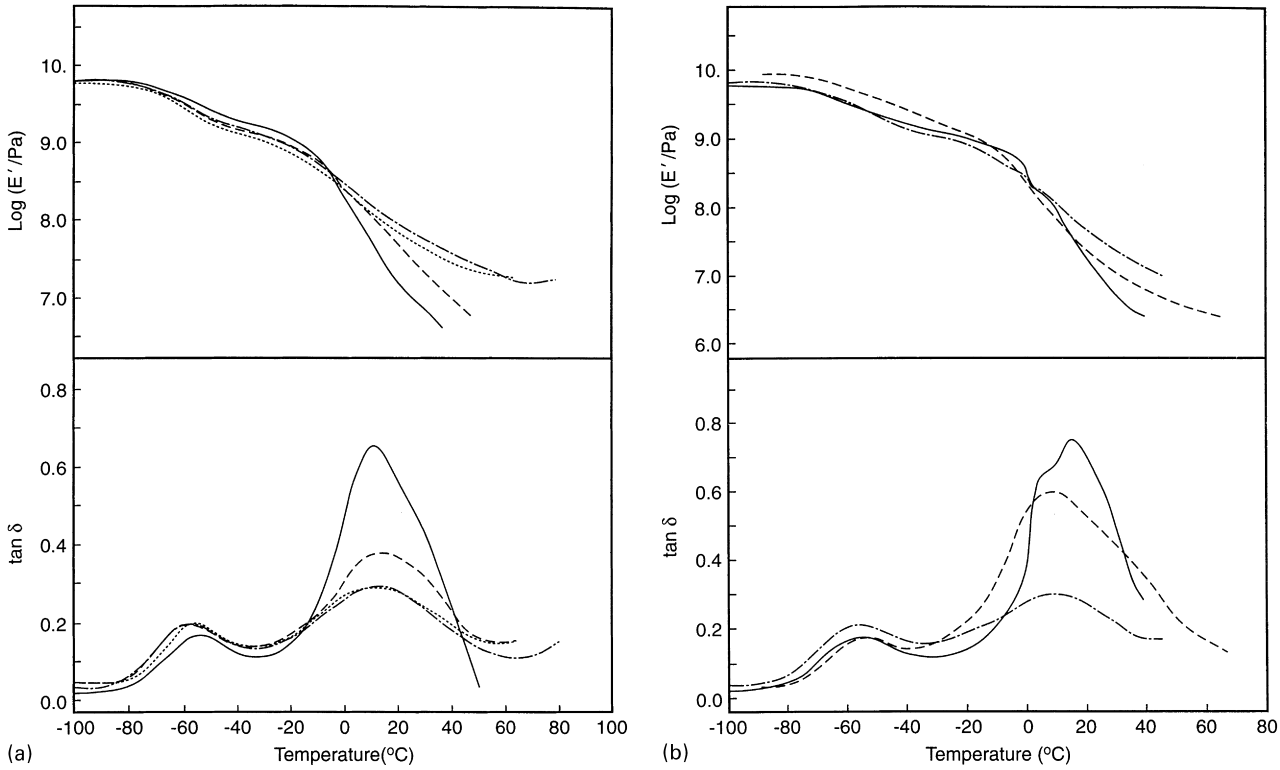

Fig. 5. The effect of ageing on the tensile modulus and tan δ of (a) barley TPS, ageing time: ———, fresh; — — —, 1 month; - - -, 4 months; — – —, 8 months and (b) oat TPS, ageing time: ———, fresh; — — —, 1 month; - - -, 4 months measured at 10 Hz.

starch–water mixtures this endotherm would be assigned to the melting of B-type recrystallized amylopectin. However, as the water content of the wet samples was 11% and that of the dry sample was 1–2%, the crystalline material contained relatively little water of hydration and so, at least in this respect, it was different from that occurring in starch–water systems. In the dry systems the amylopectin must have been dissolving in the glycerol.

Small-strain dynamic mechanical behaviour of wet TPS was analysed by means of DMTA. The effect of ageing on the tensile storage modulus and tan δ were measured as a function of temperature for barley and oat TPS (Fig. 5(a)Fig. 5(b)). Two mechanical relaxations were detected with peaks in tan δ occurring at −53 and +13°C for both starches. In the DSC a glass transition temperature was measured at −73°C, which is consistent with the lower temperature relaxation observed by DMTA. Ageing did not change the temperature nor the intensity of the lower temperature mechanical relaxation, but the higher temperature relaxation decreased in intensity with ageing as indicated by the decrease in the peak value of tan δ. The changes in intensity of the higher temperature relaxation occurred more rapidly in the barley starch than in the oat starch samples. The decrease in the magnitude of the tan δ peak was mirrored by the decrease in the fall of the storage modulus over the same temperature interval. Below the transition, at −20°C say, all the materials had similar moduli; however, above the transition (30–80°C) the storage modulus of the samples increased with ageing. Since the starch-rich phases of these materials are above their glass transitions one explanation for the increasing tensile modulus is crystallization of a starch component (Forssell et al., 1997).

A barley starch TPS plate was heated to 160°C for 7 min to investigate the effect of heat treatment on tensile properties. Before analysing the mechanical properties the plate was equilibrated at 50% RH (20°C) for 1 day. The ultimate tensile stress and strain were about the same as those of a plate after 1 month's ageing. This result indicates that the effects of ageing on tensile properties is only partially reversible by a heat–cool cycle similar to the original extrusion process. Possible explanations include: a high-melting-temperature material having crystallized in these low-water systems that is not melted at 160°C and/or rapid recrystallization having occurred during the 1 day equilibration.

3.3. Crystal structures

The oat and barley TPSs were found to contain crystalline material that would conventionally be assigned to the amylopectin (B-type) and the amylose (E_h- and V_h-types). The fresh TPSs showed single helical crystalline structures (Fig. 6(b)Fig. 6(c)), mainly E_h-type in the barley plate and V_h-type in the oat plate, which are known to be linked to amylose crystallization (Mercier et al., 1979, 1980). In addition, traces of B-type crystallinity were detected in the fresh

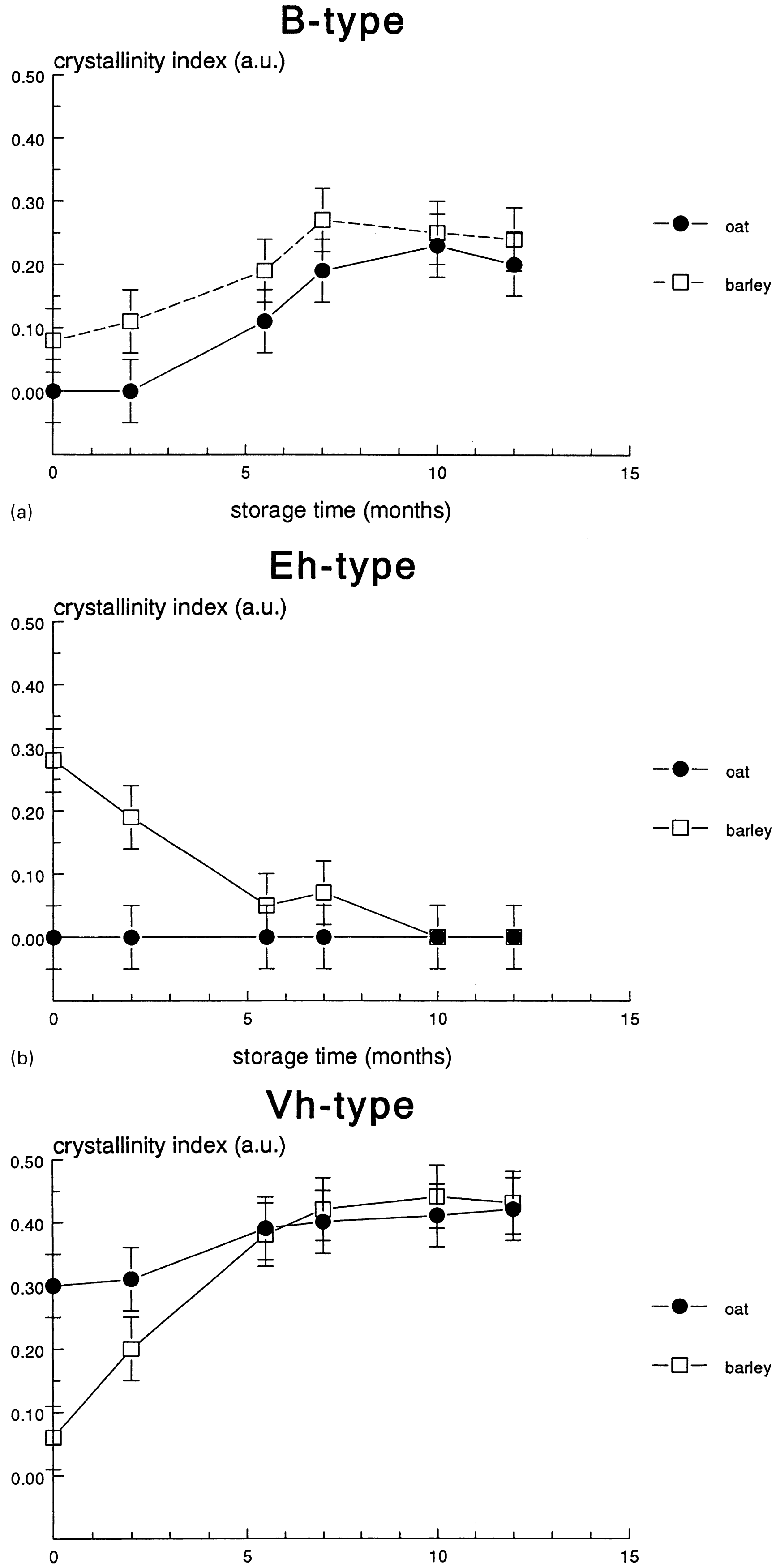

Fig. 6. The effect of ageing on the different types of crystal structure of barley and oat TPSs: (a) B-type, (b) E_h-type and (c) V_h-type crystallinities.

barley TPS (Fig. 6(a)). During the first 2 months of storage no changes were observed in the diffractogram of oat TPS, meanwhile reflections from B-type and V_h-type crystal structures of barley TPS were increasing in intensity. The small amount of B-type crystallinity present in the fresh barley TPS increased to a limited extent during the experiment (Fig. 6(a)), but the main changes occurred in the single helical structures. With increasing time the intensity due to the E_h structure in the barley TPS decreased with a corresponding increase in V_h-type structure (Fig. 6(b)Fig. 6(c)), and ultimately E_h-type structures disappeared altogether. The main change observed in the oat TPS was a gradual increase in the B-type crystallinity (Fig. 6(a)), there being relatively large amounts of V_h-type crystallinity in the fresh sample which increased to a small extent during storage. The crystal structures of barley and oat TPSs were practically the same after storage for 6 months.

3.4. Comparison of results

The ageing of TPSs, detected as an increase in failure stress and decrease in failure strain during storage, may be perhaps linked with B-type crystallization of the amylopectin. A comparison of the enthalpies of the calorimetric transitions (Fig. 4) with the B-type crystallinities measured by X-ray diffraction (Fig. 6(a)) suggests that amylopectin crystals were slowly formed in TPSs. However, the formation of the B-type crystals detected by X-ray occurred at a slower rate than the rate of formation estimated from the calorimetric endotherms, which may be due to the differences in the experimental conditions used. The calorimetric samples were analysed wet and dry, but only the endotherms of the dry samples were clear enough to calculate the kinetic data. The X-ray diffractograms were recorded only for the wet samples. If the calorimetric transitions were due to melting of amylopectin crystals, the crystallization of amylopectin may have also caused the changes in the higher temperature DMTA relaxations. The interpretation that amylopectin caused the ageing is consistent with the recently reported study of thermoplastic starches, in which the effect of amylose–amylopectin ratio on crystallinity and mechanical properties of extruded TPS sheets were investigated during ageing (van Soest and Essers, 1997). Tensile stress and elongation of TPS prepared from high-amylose amylomaize starch did not change during storage at 65% RH and at 20°C for 2 to 35 weeks, whereas the mechanical properties of TPS extrudates from waxy maize starch were changing due to the formation of B-type crystals.

Compared with the oat TPS, the initial ageing kinetics of the failure properties was faster for the barley TPS. The stiffness of starch gels is known to increase during storage for few days, which is caused by crystallization of amylopectin. Retrogradation of starch gels depends on the starch origin and can be retarded by the addition of polar lipids, but the mechanism is still unclear (Hoover, 1995). If the ageing of TPSs was solely due to formation of amylopectin crystals, the different kinetics may be explained either by different amylopectin structures or by different lipid contents of oat and barley starches (Wang and White, 1994).

Initially, small amounts of B-type crystalline structure were present in the barley TPS, which may have been caused by a rapid crystallization of amylose. The other difference between the crystallinities of oat and barley TPS was that initially the single helical structure in oat TPS was V_h-type whereas in barley TPS only E_h-type structure was observed. In studies of the structure of extruded maize grits Donald et al. (1993) found that the formation of E_h-type rather than V_h-type structures was favoured by low extrusion water content and high extrusion temperature. During the first months of storage, V_h replaced the E_h structure in the barley TPS. The change of E_h to V_h has been usually suggested to be a change of a polymorph rather than an increase in crystallinity (Mercier et al., 1979). Other studies on crystal structures of extruded TPSs have shown that, depending on starch variety and processing conditions, V_h-, V_a- or E_h-type structures are observed (van Soest et al., 1996d). The amount of V_h-type crystallinity has been shown to be linearly dependent on the amylose content of TPS. However, the effects of single helical structures on the mechanical properties of TPSs have not been demonstrated. As the change in the single helical structures is simply a change of polymorph rather than total crystallinity, this may not be important to the ageing of the material properties of oat and barley TPSs. In order to clarify this, investigations on pure amylose and amylopectin TPSs should be performed, and among other techniques DMTA should be applied.

4. Conclusion

Structural changes were analysed in order to understand the mechanical ageing of barley and oat TPS plates. The results demonstrated that the initial rate of ageing was faster for barley TPS, but the ultimate properties were similar for both TPSs. It can be concluded that crystallization and/or reorientation of amylopectin and amylose caused the ageing. Based on calorimetric transitions and on X-ray diffractograms, the major effect on failure properties may have been caused by crystallization of amylopectin. The role in ageing of the observed single helical structures of amylose remains unclear. The mechanical relaxations above 0°C and the increase in rubbery modulus detected by DMTA, which were greatly affected by ageing and also showed faster rate for barley TPS, should be investigated using pure amylose and amylopectin in order to distinguish the roles of the different starch polymers.

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