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PLASTICIZATION OF BARLEY STARCH WITH GLYCEROL AND WATER

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ABSTRACT

Barley starch was plasticized in a melt mixer using glycerol and water as plasticizers. Plasticizer concentration, time, temperature, and shear were varied, and their effects on the molecular weight of starch and the glass transition temperature and mechanical properties of the mixtures were studied. Depolymerization of amylopectin was observed in all experiments, and starch degradation proceeded further at low glycerol concentrations. The glass transition of the plasticized starch–glycerol mixtures occurred in the temperature range −50 to −100°C and was probably induced by glycerol, not by starch. The tensile strength of a starch plate containing 29 wt% glycerol was about 0.5 MPa 1 week after molding, but increased to 2–3 MPa during 5 weeks of storage at 50% relative humidity and 24°C.

INTRODUCTION

Starch is a major component of cereal foods and an abundant raw material for various industrial uses. Composed of two structurally different homopolymers of glucose, rather linear amylose and highly branched amylopectin, it appears in numerous physical states. The botanical origin determines the chain-length distribution, degree of branching, and the molecular weight of the polymers, as well as the architecture of the starch granules. The properties of starch products can, however, be varied over a wide range by processing conditions and additives. Plasticization of starch using low molecular weight alcohols in addition to water has recently been a topic of interest in attempts to produce thermoplastic starch-based products which would have the advantage of being biodegradable.

The terms thermoplastic, destructurized, or melted starch have been used in numerous patents during the past ten years to describe the changes in starch granules during processing of plastic-type materials, as reviewed by Röper and Koch [1] and Swanson et al. [2]. However, the phase changes in starch granules during thermal processing at different water levels were studied earlier. The melting of starch crystals in extrusion cooking and the accompanying changes at lower structural levels, i.e., starch degradation, have been reviewed (e.g., by Lai and Kokini [3]). The loss of starch crystallinity, "starch conversion," depends on temperature, pressure, shear, and water content. Degradation of starch molecules in extrusion has been shown to increase with increasing temperature and decreasing water content [4].

Rather little is known about the phase transitions and structural changes of starch when water is partly replaced by glycerol as a diluent in thermal processing. Glycerol has a lower dielectric constant than water and has been reported to increase the gelatinization temperature of starch [5]. Glycerol, which has a glass transition temperature of −80°C, also depresses the glass transition of amorphous starch at low water contents [6]. The broad glass transitions of polyol–starch mixtures were considered to reflect a more heterogeneous and less stable structure than that obtained with water as plasticizer [6].

The mechanical properties of plasticized starch products are largely dependent on the plasticizer concentration, and have also been shown to change during storage [7, 8]. The tensile strength decreases and the elongation increases with increasing glycerol content. Plasticized starch materials are very sensitive to humidity, and encapsulation or coating is needed to protect them from water absorption [9, 10]. If the hydrophilicity could be counterbalanced, it might be possible to achieve good gas barrier properties with plasticized starch products [11].

The aim of this work was to study the influence of plasticization conditions on the molecular weight of barley starch and on the mechanical properties of starch–glycerol blends. Improved understanding of starch conversion is needed for the development of practical applications.

MATERIALS AND METHODS

Materials

Barley starch was kindly donated by Raisio Group (Raisio, Finland). All reagents used were of analytical grade. All percentages are based on dry weight except the water content.

Plasticization and Plate Molding

Plasticization was performed in a melt mixer with co-rotating shaking screws (Brabender Plasti-Corder). Before the plasticization, starch and glycerol were mixed and stored overnight to achieve a homogeneous mixture. The plasticized material was ground under liquid nitrogen (Fritsch mill). Plates were prepared from the ground starch–glycerol blends by compression molding at 180°C, first for 10 minutes at a pressure of 20–30 kN and then for 15 minutes at 150 kN (Fontijne Table Press TP400).

Chemical and Thermal Properties

The molecular weight distribution and the average molecular weight of starch in starch–glycerol blends were analyzed by GPC techniques. μHydrogel columns 2000, 500, and 250 at 70°C were used for fractionation. Samples were dissolved in 1 M NaOH, and 50 mM NaOH was used as eluent at a flow rate of 0.5 mL/min. The mass-average molecular weight was determined by a dual angle laser-light-scattering detector (PDI 2000).

Water contents were analyzed gravimetrically after drying the samples in an oven for 1 hour at 130°C, and by Karl Fischer titration.

Hygroscopicity was analyzed by equilibrating the samples in closed chambers at different relative humidities for 1 week at 20°C. The absorbed water was analyzed gravimetrically.

Thermal properties (crystal melting, glass transition) of the samples with different moisture contents were analyzed by differential scanning calorimetry (Mettler DSC30) in closed Al-pans using a temperature scan of 0 . . . 100/150 . . . −140 . . . 100°C with a rate of 10°C/min. In the first heating the upper temperature depended on the water content of the sample. At high water contents 100°C and at low water contents 150°C were used to ensure that no water was evaporated.

Mechanical Properties

Tensile strength and elongation were measured using an Instron Universal Testing apparatus (Instron 4204) according to an ISO standard method (1184-1983 E). The molded plates were stored for at least 1 week at RH 50% and 24°C before testing. The thickness of the plates was measured with a micrometer at five different places on each plate before testing. A load of 1 kN and a speed of testing of 100 mm/min were used. Five replicates were tested for each sample.

RESULTS AND DISCUSSION

Plasticization Conditions in Melt Mixer

The effects of plasticization conditions on depolymerization of barley starch were studied by varying the glycerol and water concentrations at a constant temperature (170°C). The glycerol content varied from 14 to 57 wt% whereas the initial water content was 12 or 30 wt%. The decrease in glycerol concentration induced more depolymerization during melt mixing because of more effective shear forces (Fig. 1). The decrease in the average molecular weight was from 10^7 to 6×10^5 g/mol as the glycerol content varied from 43 to 14 wt%. Amorphous barley starch and 30 wt% water were needed to achieve plasticization at a glycerol content of 14 wt%. At higher glycerol concentrations plasticization occurred at a lower water content (12 wt%). At glycerol concentrations of 29 wt% or higher the level of depolymerization was the same at both water concentrations used (results not shown).

The effects of temperature, shear, and time on depolymerization were analyzed at a constant initial water concentration (12 wt%) and with glycerol contents of 29 and 39 wt%. In all plasticization experiments the high molecular weight amylopectin (M_w > 10^8 g/mol) depolymerized to smaller polymers. Temperature, shear, and time affected the molecular weight of starch more at a glycerol content of 29 than at 39 wt%. Temperature was varied from 110 to 190°C. A significant decrease in molecular weight occurred when the temperature was higher than 150°C (Fig. 2).

In another series of experiments, mixing time was varied from 5 to 30 minutes and shear rate from 20 to 140 rpm, whereas the temperature was constant (170°C). In this case degradation of high molecular weight amylopectin was detected as in

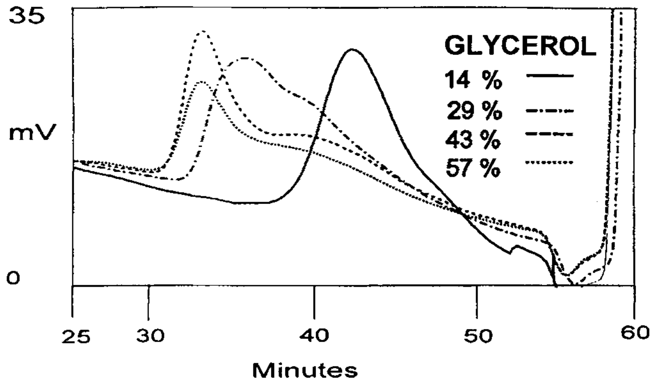

FIG. 1. Molecular weight distributions of barley starch after plasticization at 170°C for 15 minutes at different glycerol concentrations. The initial water concentration was 30 wt%.

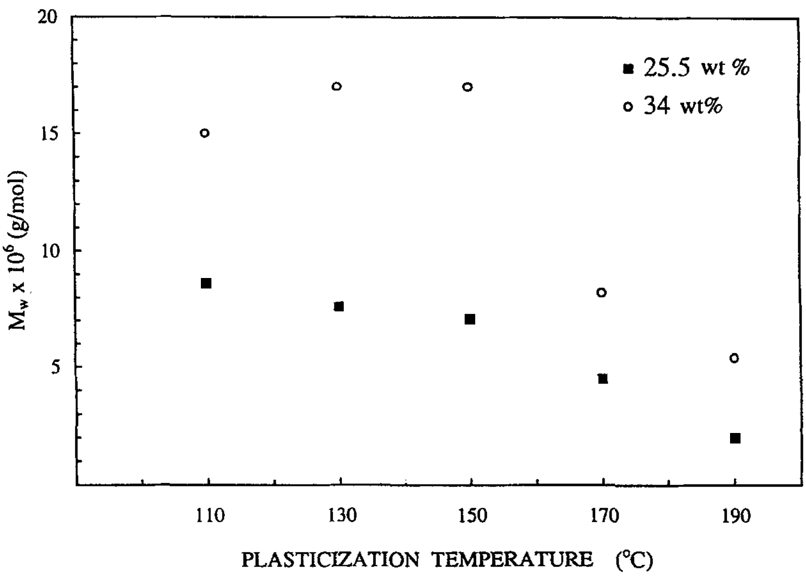

FIG. 2. Weight-average molecular masses of starch after plasticization at different temperatures (110–190°C). The glycerol contents were 25.5 and 34 wt% (29 and 39 wt% as dry weight), and the initial water content was 12 wt%.

the case of temperature changes (results not shown). A major decrease in molecular weight occurred during the first 5 minutes of mixing; thereafter depolymerization proceeded more slowly. Increasing the shear rate from 20 to 80 rpm induced starch depolymerization, whereas a further increase to 140 rpm did not cause more degradation.

Properties of the Plasticized Starch Blends

Plasticized starch with a glycerol content of 39 wt% was more hygroscopic than mixtures with lower glycerol contents (Fig. 3). At high humidity (81%) the equilibrium water content was about 30 wt%. As compared with native barley starch, the plasticized blends were less hygroscopic at low humidity. This result is in agreement with those of earlier experiments in which corn starch was plasticized with urea and glycols in an extruder [9], and indicated that glycols and urea bind strongly to starch and displace water at low and moderate humidities. Sala and Tomka [12] demonstrated a change in the sorption behavior of potato starch plasticized with glycerol as compared with native or water plasticized starch. Starch-glycerol blends were also less hygroscopic than native starch at low humidity in the present study.

The heat treatment of the equilibrated blends in DSC-pans demonstrated endothermic changes during the first heating but not during reheating. These endotherms were most probably due to melting of starch crystals because they were no longer observed during the reheating and their magnitude increased with an increase of the water content except in the case of a glycerol content of 14 wt% (Table 1).

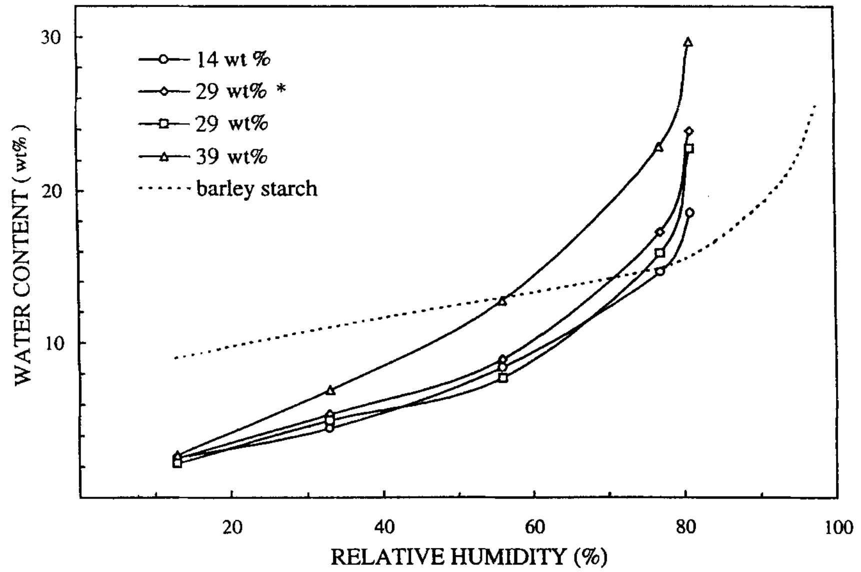

FIG. 3. Water contents of starch-glycerol blends at different relative humidities and at 20°C. Glycerol contents were 14, 29, and 39 wt%, and the initial water content was 12 wt% except in the case marked with an asterisk when it was 30 wt%. The water content of native barley starch at different relative humidities is also shown for comparison.

This blend showed endotherms only at low water content. More data are needed to explain this behavior. The molecular weight of starch in the 14 wt% glycerol blend was much lower than that in the other blends, which may also have affected crystallization.

The glass transition temperatures of the reheated starch blends were analyzed. A linear relationship between the glass transition and the water content was detected. Glass transition decreased from −53 to −105°C as the water content increased from 2 to 30% (Fig. 4). Variation in the glycerol content in the range of 14 to 39 wt% did not affect significantly the glass transition. Thus a small amount of

TABLE 1. Enthalpies of Starch-Glycerol Blend Endotherms with Different Glycerol and Moisture Contents. Enthalpies Were Calculated on the Basis of Starch Weight

Glycerol content, %	RH 33% ΔH, J/g	RH 56% ΔH, J/g	RH 77% ΔH, J/g	RH 81% ΔH, J/g
14	2.3	5.4	0	0
29*	0	0	5.9	7.5
29	0	0.9	0	6.6
39	0.9	3.9	8.4	7.8

*See Fig. 3.

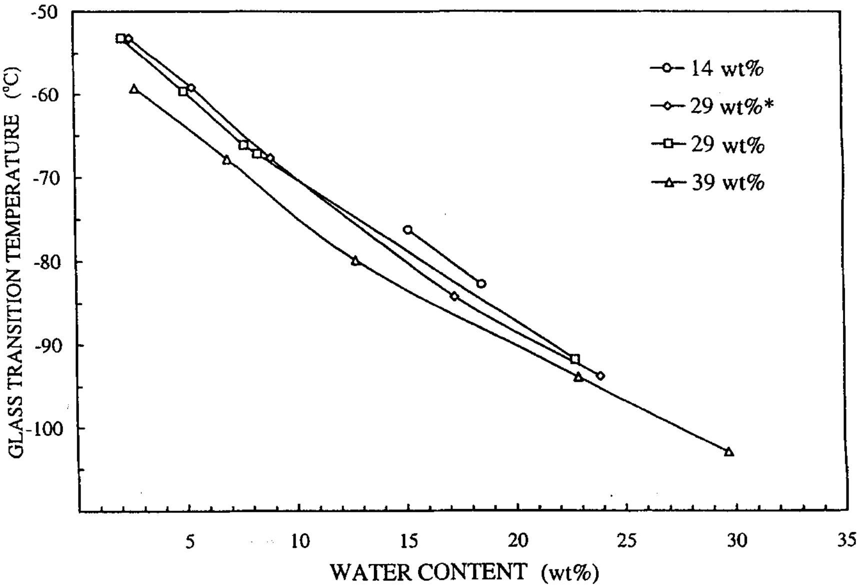

FIG. 4. Effect of water content on the glass transition temperature of starch-glycerol blends. The glycerol content varied from 14 to 39 wt%. The asterisk has the same meaning as in Fig. 3.

glycerol caused a large decrease in the glass transition of the blend, but further addition of glycerol affected only slightly the glass transition (Fig. 5). The glass transition, however, depended linearily on the water content. The results may indicate that the glass transition obtained was attributed mainly to glycerol. It remains to be studied whether the glass transition of starch can be observed at higher temperatures.

The importance of the glass transition in controlling the behavior of starch-composed foods has been widely discussed [13], but only a few studies regarding glass transition temperatures of starches plasticized with some plasticizer other than water have been reported. The extrapolated glass transition temperature of native dry starch is about 230°C, whereas at a moisture level of 20 wt% it is lowered to a value of about 20-30°C [14, 15]. According to Sala and Tomka [11], the glass transition temperature of a glycerol-plasticized starch was in the range of −40 to −50°C.

Properties of the Molded Plates

Molded plates were prepared from blends with glycerol contents of 29 and 39 wt%. The molding further depolymerized the starch polymers (Table 2). The molecular weights of the blends were five to ten times lower after the compression molding than before the procedure.

The plate with a glycerol content of 39 wt%, prepared after plasticization at 190°C, was equilibrated at different humidities in order to study its thermal behavior. The glass transition temperature depended linearly on the water content (Fig. 6). This relationship was very similar to the data of the plasticized starch blends

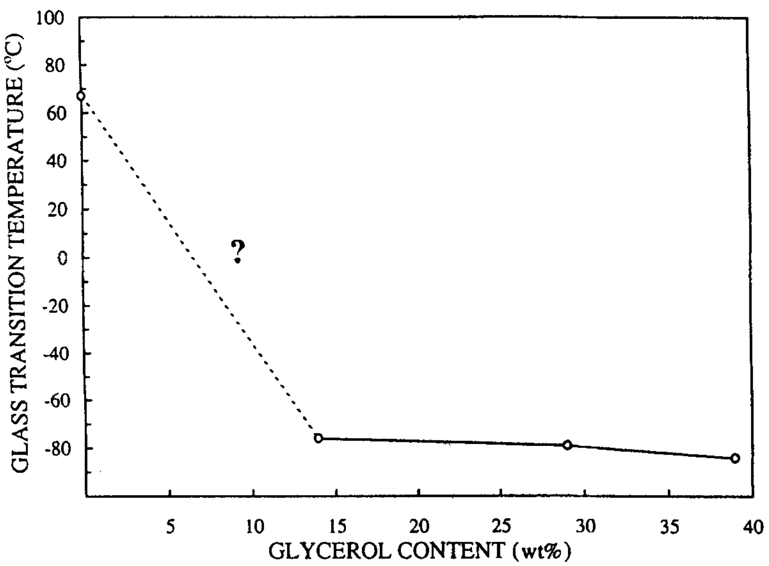

FIG. 5. Effect of glycerol content on the glass transition temperature of starch-glycerol blends. The water content was 15 wt%.

(Fig. 4), except that the absolute T_g values were higher, varying in the range of −50 to −80°C. Endothermic changes during the first heating of the plates were detected as in the case of the plasticized mixtures (Fig. 7). In addition to the endotherms at 60–80°C, smaller endotherms at 100–150°C were also detected at all water contents. None of these endotherms was observed during reheating.

The effects of the glycerol content, storage time, and plasticization temperature on tensile strength and elongation of the molded plate were studied. Stress-strain behavior during aging indicated a change from a gummy and soft to more rigid and hard material (Fig. 8). The change was especially clear in the case of the plate with a glycerol content of 29 wt%. No yield point was observed. Tensile

TABLE 2. Weight-Average Molecular Mass of Starch Before and After the Expression Molding. Plasticized Starch–Glycerol Blends Were Prepared at 130, 150, and 190°C and the Glycerol Content Was 29 or 39 wt%

Glycerol content (%) and temperature (°C)	Before expression molding $M_w \times 10^{-6}$ g/mol	After expression molding $M_w \times 10^{-6}$ g/mol
29/130	7.6	1.0
29/170	4.5	0.8
29/190	2.6	0.6
39/130	17	1.6
39/150	8.2	nd
39/190	5.4	1.0

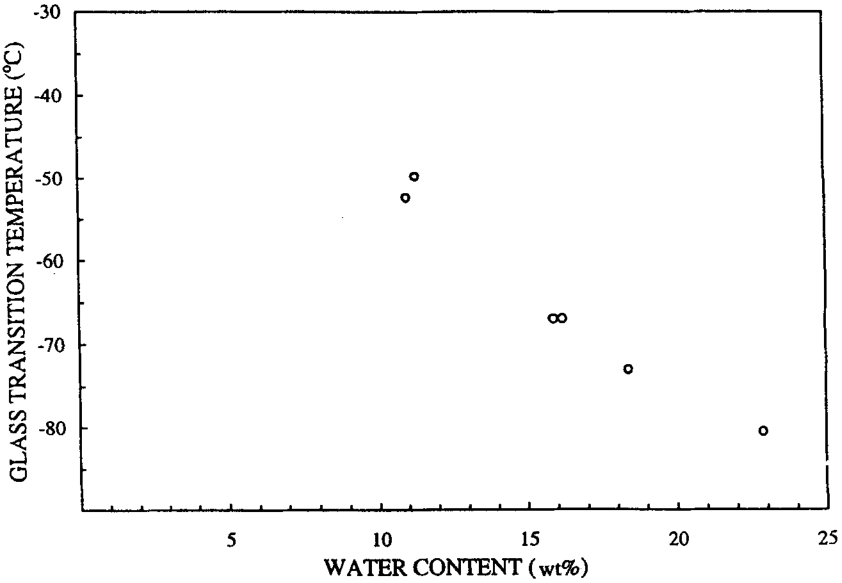

FIG. 6. Effect of the water content on the glass transition temperature of a molded plate with 39 wt% glycerol. Plasticization was performed at 190°C.

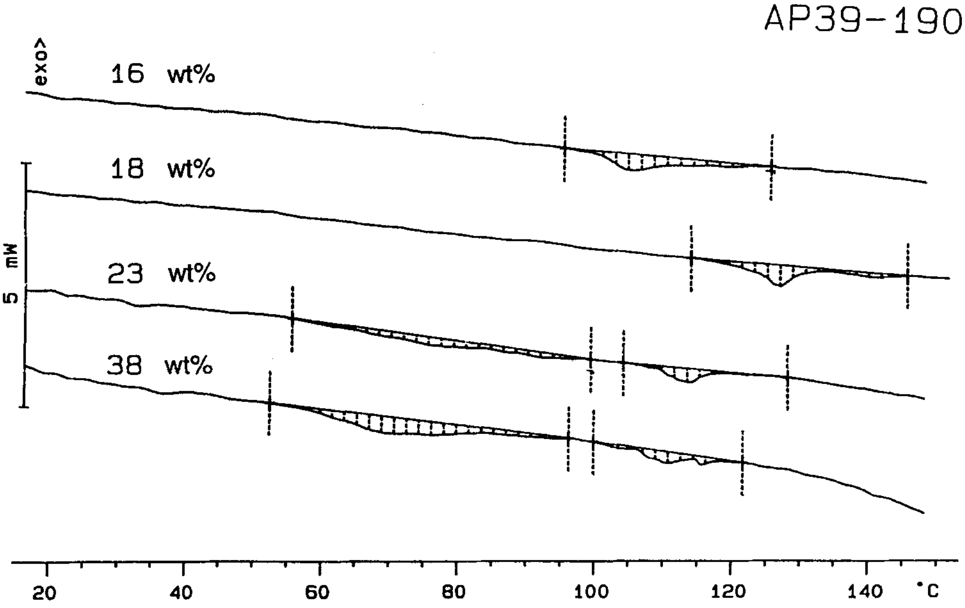

FIG. 7. DSC thermograms of the molded plates whose glass transition is shown in Fig. 6.

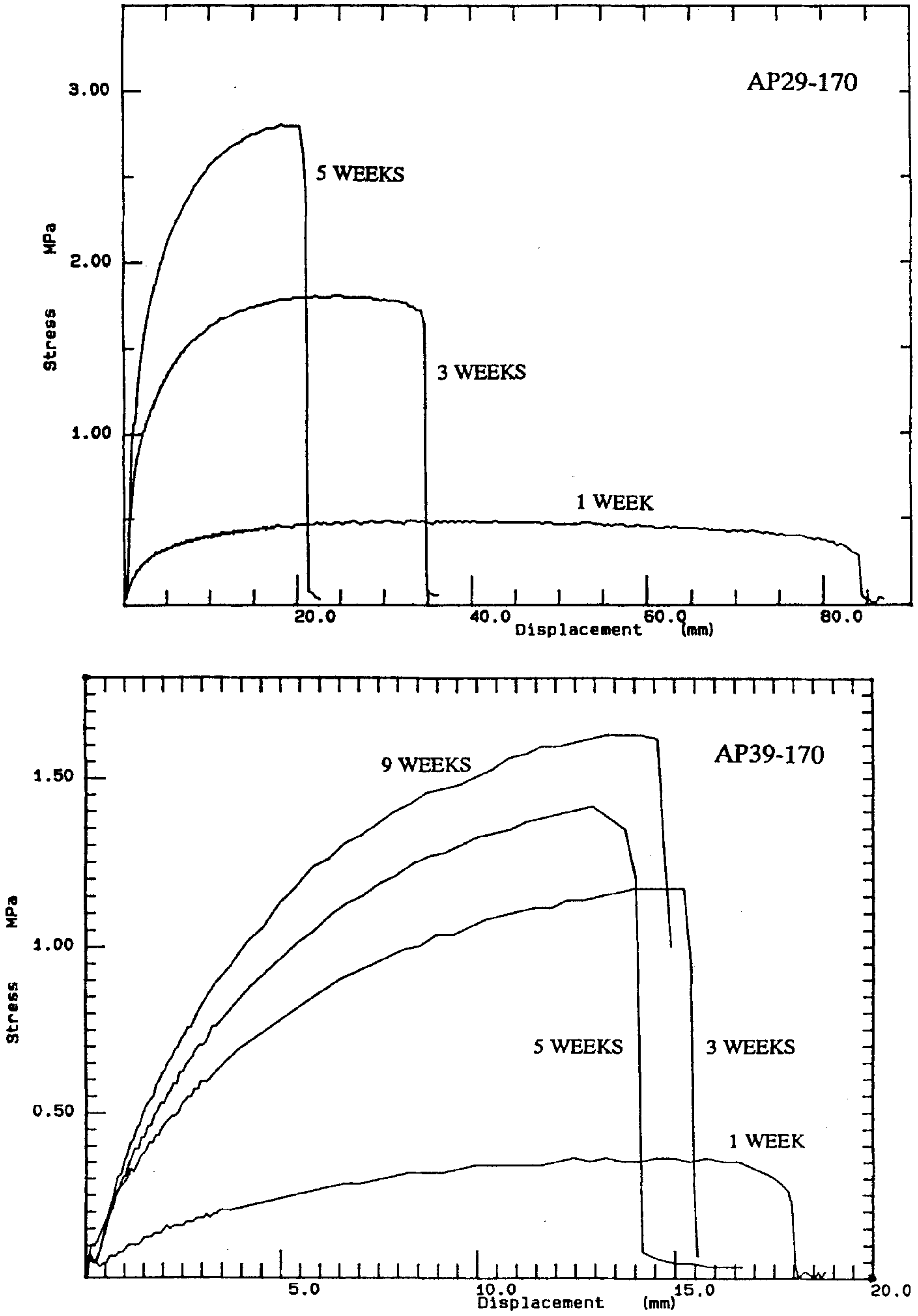

FIG. 8. Stress–strain curves for the molded plates with 29 and 39 wt% glycerol. The starch–glycerol blend was plasticized at 170°C, and the stress–strain behavior was measured during 5 or 9 weeks of aging.

strength and, surprisingly, also elongation were greater at a glycerol content of 29 wt% than at 39 wt% (Fig. 9). The plate with higher glycerol content also had a higher water content, which may have affected the mechanical properties. The water content was about 17% for the higher and 11% for the lower glycerol content. Tensile strength increased and elongation decreased during aging of the plates for 5 weeks at constant humidity. The mechanical properties of the 29 wt% glycerol plate were somewhat affected by the plastificaton temperature; tensile strength decreased and elongation increased with increasing temperature.

Evaporation of glycerol may have been the cause of the changes in tensile strength and elongation during storage, which has recently been reported to be the major problem of thermoplastic starches [1]. According to one other study, glycerol

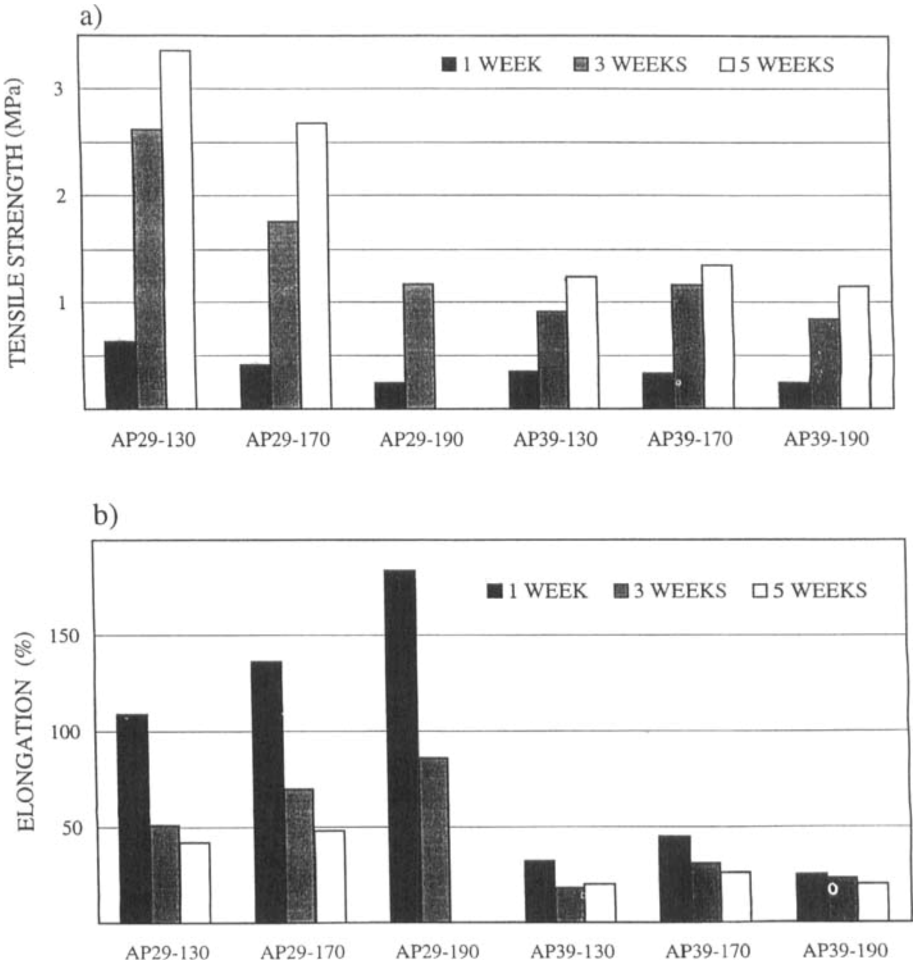

FIG. 9. Effect of storage time on tensile strength and elongation of the molded plates. The glycerol contents were 29 and 39 wt%, and the blends were plasticized at 130 to 190°C.

was considered to be tightly bound to starch because no weight losses were observed during storage of starch films [7].

The mechanical properties of corn starch plasticized with urea, glycerol, triethylene glycol (TEG), and propylene glycol (PG) were measured during aging of the ribbons at constant humidity for several months [9]. The weight ratios of glycerol to starch were 0.13/1 and 0.40/1, and at the lower glycerol content the material was too brittle to examine. The starch-glycerol blend (0.40/1) was initially rather soft and weak. Tensile strength decreased and elongation increased in the order TEG (2.4 MPa), glycerol (1.5 MPa) and PG, (too soft to analyze). Elongation tended to decrease during aging, especially in the case of the starch-glycerol ribbon as in the present study. In addition to the change in the glycerol content, crystallization of starch or an increase of entanglements in starch polymers are other causes which may have affected the change in the tensile strength during storage.

CONCLUSIONS

Under shear and at high temperature, a decrease in the glycerol concentration induced more depolymerization of barley starch because of the more effective shear forces. Crystallization during aging at 20°C depended on the water content of the plasticized starch-glycerol blend. When stored at RH 77% or at higher moisture, crystals were formed within 1 week. The glass transition temperature of the starch-glycerol blend was lower than −50°C and was greatly affected by the water content, reaching a value of −100°C at 25 wt% moisture. However, the glass transition did not necessarily reflect the mechanical behavior of starch-glycerol blends. Fresh plates prepared from starch-glycerol blends with glycerol contents of 29 or 39 wt% were rather weak, having a tensile strength of about 0.5 MPa. Tensile strength increased and elongation decreased when the 29 wt% glycerol plate was stored for 5 weeks at constant temperature and humidity.

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