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Effect of glycerol on behaviour of amylose and amylopectin films

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Abstract

The effect of water and glycerol on sorption and calorimetric T_gs of amylose and amylopectin films were examined. The mechanical properties of the films were also analysed under varying glycerol content at constant RH and temperature. Based on changes observed in sorption and tensile failure behaviour glycerol was strongly interacted with both starch polymers. Even though water was observed to be more efficient plasticiser than glycerol, glycerol also affected the T_g. But in spite of the observed decrease in T_g under low glycerol contents brittleness of the films increased based on changes in elongation. The increase in brittleness of both polymers was also in agreement with their actual behaviour. At around 20% glycerol great change in the rheological properties occurred. Above 20% glycerol amylose film showed much larger elongation than the low glycerol content films and was still strong but the amylopectin produced a very week and non-flexible film. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Plasticisation; Water sorption; Glass transition temperature; Stress; Strain

1. Introduction

Many studies have focused on the preparation of melted starch by extrusion in the presence of glycerol, materials that are called thermoplastic starches (TPSs). Depending upon the glycerol content and botanical origin of starch, materials with different mechanical properties can be produced (Della Valle, Buleon, Carreau, Lavoie, & Vergnes, 1998; Hulleman, Janssen, & Feil, 1998; van Soest & Essers, 1997). The hydrophilic nature of starchy polymers makes them sensitive to the environmental humidity and the presence of high level of glycerol strengthens this behaviour. It has also been pointed out that during storage, TPSs made of potato starch have a tendency to change their structures to become more brittle (van Soest, Hulleman, de Wit, & Vliegenthart, 1996a). Even though occurring during longer storage times the changes observed in TPSs are very similar to retrogradation of normal starch gels indicating that this process may be linked with crystallisation of amylopectin (Forssell, Hulleman, Myllärinen, Moates, & Parker, 1999).

Early investigations on melted or dissolved starch were focused on film formation properties of starch polymers. A solvent-casting procedure was applied, in which starch was dissolved at low concentration in water or in other solvents and a film was produced by evaporating the solvent (Wolff, Davis, Cluskey, Gundrum, & Rist, 1951; Langlois & Wagoner, 1967). Especially amylose was observed to be an excellent film former, and claimed to have equivalent properties to cellulose films. Recent studies on starch films prepared by water casting and plasticised by glycerol have tried to elucidate in more detail the effects of starch structure on plasticisation and properties (Lourdin, Della Valle, & Colonna, 1995; Rindlav-Westling, Stading, & Hermansson, Gatenholm, 1998). The structures of the films were reported to vary, and were observed to be wholly amorphous (Lourdin et al., 1995), or amylose films were crystalline and the structure of amylopectin films depended on the preparation conditions (Rindlav-Westling et al., 1998). It was concluded that amylopectin was more sensitive than amylose to plasticisation caused by glycerol. Amylose was also detected to form mechanically stronger films.

Glass transition temperature (T_g) is the most important parameter in determining the mechanical properties of amorphous polymers and in controlling the kinetics of crystallisation of amorphous materials (Biliaderis, Page, Maurice, & Juliano, 1986; Levine & Slade, 1986; Orford, Parker, Ring, & Smith, 1989; Schenz, 1995). For dry amylose and amylopectin the T_g has been estimated to be at 227 °C, and the presence of 13% water has been observed to decrease the T_g to 56 °C (Orford et al., 1989). The T_g of gelatinised wheat starch was detected to be at room temperature

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when containing 22% water (Zeleznak & Hoseney, 1987). Many other studies have demonstrated the plasticisation effect of water on starches and also the various techniques for analysing of T_g has been compared. When examing different techniques, the most often used DSC was observed to give 10–30 °C higher T_gs than pulsed NMR (Kalichevsky, Jaroszkiewicz, Ablett, Blanshard, & Lillford, 1992). Effect of water on T_gs of amylose and amylopectin was recently analysed using DSC (Bizot, Le Bail, Leroux, Davy, Parker, & Buleon, 1997). The very branched amylopectin had somewhat lower T_g than the amylose polymer. Based on the reported studies and practical observations, starches are in the glassy state and are brittle materials under ambient conditions in the presence of water only.

The ternary system obtained by plasticising starch with water and glycerol has appeared to behave in a rather complicated way. The effect of glycerol and other plasticisers on T_g of potato starch was analysed and glycerol was observed to plasticise starch following relatively well Couchman's model for monophasic polymer-solvent system (Lourdin, Coignard, Bizot, & Colonna, 1997a; Lourdin, Bizot, & Colonna, 1997b). The other study, in which plasticisation of barley starch by a combination of water and glycerol was investigated, indicated a phase separation behaviour based on two calorimetric glass transition temperatures (Forssell, Mikkilä, Moates, & Parker, 1997). Furthermore, an investigation in which amylose and maltose were plasticised by glycerol also pointed out a complex phase separation above 25% glycerol based on dielectric mechanical analysis (Lourdin, Ring, & Colonna, 1998). Recently dynamic mechanical, dielectric and calorimetric behaviour of a binary amylose–glycerol system indicated that the system was composed of amylose- rich and glycerol-rich phases (Moates, Noel, Parker, & Ring, 2001).

This work builds on earlier studies, which reported phase and glass transition behaviour and aging of TPSs processed by extrusion (Forssell et al., 1997, 1999), and this study is an attempt to understand better the plasticisation of starch polymers by investigating thin amylose and amylopectin films prepared by a casting technique.

2. Materials and experimental

2.1. Materials

Amylose was obtained from Sigma (A-0512, isolated from potato) and amylopectin was granular waxy maize starch (National Starch, Amioca Powder TF, with 98% of amylopectin from dw.). Glycerol was from Merck (98–99% purity, analytical grade).

2.2. Film preparation

Amylose and amylopectin were first treated with a small amount of ethanol (1 ml/10 g starch), then 10, 15, 20 or 30% (total dry basis) of glycerol and lately water was added. Heating of the solution was performed in a special pressure vessel (500 ml total volume) equipped with a stirrer (VTT Automation, Espoo, Finland). For dissolution of the polymers 1 or 2% of starch concentration was used, and the temperature was increased up to 140 °C and kept constant for 30 min. Before opening the chamber the hot solution was cooled to 100 °C, and poured on a prewarmed (70 °C) teflon mould (11 × 3 cm) and weighed (10 g of solution). Water was evaporated from the moulds in a ventilated oven at 70 °C for 3–4 h. Dry films were put in open polyethylene bags and stored at 20 °C and at RH 50% for one week before the measurements were performed.

Both amylose and amylopectin films were transparent and their thicknesses varied from 20 to 30 μm. Amylopectin film was more brittle in structure, especially the film with 10% glycerol and the highly plasticised film had some gumminess. Amylose films were more easily handled, both for the low glycerol and the high glycerol sample.

2.3. Water sorption

For the sorption experiment, the films were cryomilled using a sieve mesh with the opening of 500 μm (Fritsch Pulverisette Mill, Manufactures of Laboratory Instruments, Idar-Oberstein, Germany). The fine powder (200 mg) was weighed into ceramic dishes (previously dried over P_2O_5 at 50 °C) and put in glass chambers with constant humidity. The humidity was controlled using saturated salt solutions. The percentages of RHs and the salts were: 11 (LiCl), 33 ($MgCl_2$), 54 ($Mg(NO_3)_2$), 81 ($(NH_4)_2SO_4$) and 91 (KNO_3). The samples were kept in RH chambers at 20 °C for seven days. The water content was calculated based on the weight change and on the initial water content of the powder, which was measured by Karl Fischer titration (Mettler DL18).

2.4. Glass transition

Glass transition temperatures of the films were measured with Mettler Toledo DSC (TA 4000 system, Switzerland). Sealed pressure pans (Mettler, ME26929) were used with empty pans as the reference. The scanning rate was 10 °C min^{minus1}, and the scan was performed from 20 to 170 followed by (−150)–170 °C. The glass transition temperature was taken as the midpoint of the change in heat capacity observed in the second heating scan. The changes in heat capacities (Δc_p) were evaluated by the Mettler system.

2.5. Tensile analysis

Mechanical properties of the films (20 × 80 mm) were measured by Texture Analyser (TA. XT2, Surrey, England) with a standard method of ISO 1184-1983. The experiments were performed under controlled conditions, at 20 °C and RH 50%. Before the testing thicknesses of the films were measured with a microtom (Mitoyo, Japan). Five measurements were run of each test sample, and the variations

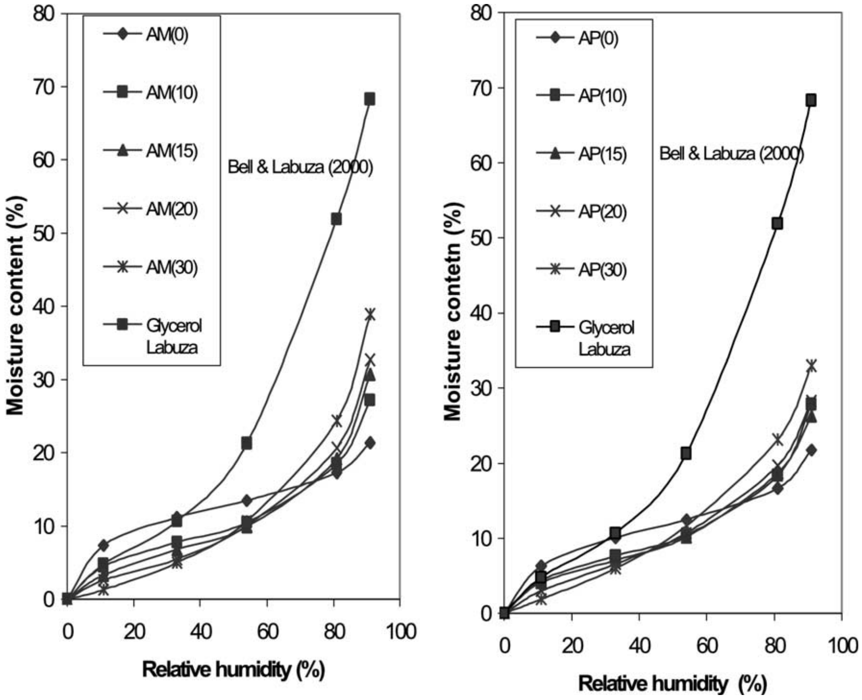

Fig. 1. Effect of glycerol on the water sorption isotherm of amylose (AM) and amylopectin (AP) at 20 °C.

were ±0.4–7 MPa and ±0.3–6% for stress and strain, respectively.

3. Results and discussion

3.1. Water sorption at 20 °C

Sorption isotherms were determined primarily in order to know the water contents of the films under glass transition and tensile experiments. When investigating the starch powders without glycerol (Fig. 1a and b), the amylopectin was found to have sorbed somewhat less water, which is in agreement with earlier work of Bizot et al. (1997). The overall effect of glycerol on water sorption was very similar for both amylopectin and amylose, which was reported for the first time by Sala and Tomka (1992). In Fig. 1 the sorption isotherm of pure glycerol is also shown (Bell & Labuza, 2000), which demonstrates, that the effect of glycerol is not a simple superimposition.

At low humidities below RH 50% the equilibrium water content for both amylopectin and amylose was lower in the presence of glycerol than without glycerol, and the effect increased with increasing glycerol content (Fig. 1a and b). This phenomenon could perhaps be explained by a replacement of the very strongly immobilised structural water with glycerol (van den Berg, 1981). Similar observation was recently reported of sorbitol plasticised starch films, which were stored at RH 57% (Gaudin, Lourdin, Le Botlan, Ilari, & Colonna, 1999). The water contents of the films were 14 and 9% without sorbitol and with 25% sorbitol, respectively. One of the conclusions in that study was that sorbitol may be strongly bound with starch under low sorbitol contents. Biliaderis, Lazaridou, & Arvanitoyannis, (1999) also demonstrated the same type of behaviour for sorbitol and xylose-plasticised pullulan-starch mixture, but the effect was not really significant.

At RH 50% the isotherms of the glycerol plasticised films crossed each other and contained at that point about 10% of water. Above RH 50% the highest glycerol content showed the highest water content. Furthermore, above RH 70% the equilibrium water contents of the glycerol-plasticised powders were higher than the powders without glycerol. Could this be linked with the phase separation, which will be discussed together with the glass transition results?

Even though the main sorption behaviour was similar for both starchy polymers, one difference was detected at the highest RH; the amylose sorbed more water than the corresponding amylopectin powder (Fig. 1a and b). Crystallisation is known to decrease water sorption of hydrophilic polymers, and crystal formation of glycerol-plasticised starches was earlier observed to occur within one week at 20 °C in the presence of a high concentration of glycerol during storage under high humidity (Forssell et al., 1999). Thus the lower water content in the amylopectin may be explained by amylopectin crystallisation.

3.2. Glass transition temperature

Calorimetric glass transitions of both amylose and amylopectin powders were not easy to detect especially for amylose. The starch polymers did not differ in their

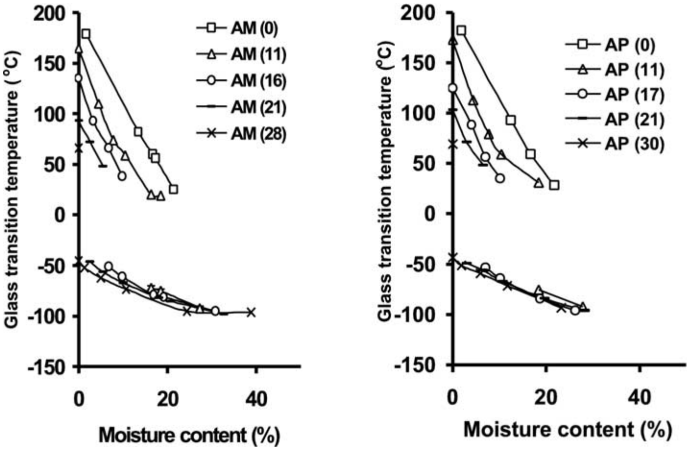

Fig. 2. Dependence of the calorimetric glass transition temperature on water and glycerol contents, for amylose (AM) and for amylopectin (AP).

behaviour (Fig. 2). Depending upon film compositions the DSC-thermograms showed either 'upper' or 'lower' temperature transitions or both, which was very similar behaviour to that observed earlier for extruded barley starch (Forssell et al., 1997). The upper and lower transitions (Δc_ps) were observed in most cases in systems with glycerol contents below 30%. This behaviour was earlier suggested to be related to starch-rich and starch-poor regions caused by partially separated phases. The upper and lower transitions seem to be a property of glycerol-plasticised starches, and are independent of processing methods.

As suggested by the earlier observations in the absence of glycerol both amylose and amylopectin showed only the upper glass transition. Orford et al. (1989) approximated that the T_gs of dry amylose and amylopectin are at 227 °C and based on extrapolations performed by Bizot et al. (1997) dry starch transition is at 332 °C. Furthermore, to decrease T_g of amylose or potato starch close to room temperature 0.21 g of water per one gram of starch was needed (Bizot et al., 1997). Earlier Zeleznak and Hoseney (1987) concluded that, the glass transition temperature of wheat starch was extremely sensitive to moisture, and concluded that at moistures above 22% T_g is below room temperature.

In the present study the T_g was also equal to room temperature when the water content was 21%, but with the same concentration of glycerol T_g was as high as 93 °C. Thus as a plasticiser glycerol was less effective than water, and based on calculations about 35% glycerol would be needed to decrease T_g to room temperature. Except in the dry amylose no upper transition could be seen in the highly (30%) plasticised powders. Based on earlier results (Lourdin et al., 1998) T_g of amylose is at room temperature when containing 14% water and 25% of glycerol.

In a more basic investigation performed by Lourdin et al. (1998) primary and secondary relaxations of an amylose–glycerol–water system were examined using dielectric analysis. A depressive effect on T_g was observed using glycerol quantities from 0 to 25%, but at higher glycerol contents discontinuities in relaxation temperatures and activation energies were detected. This was concluded to be due to phase separation, probably due to the existence of glycerol-rich microdomains. Very recently dielectric method, dynamic mechanical and calorimetric techniques were applied to study phase behaviour of dry amylose–glycerol system (Moates et al., 2001). The observed relaxations were influenced by both amylose-rich and glycerol-rich phases, which produced a postulation about partial miscibility of amylose and glycerol.

The overall observations concerning T_gs were very similar for both amylopectin and amylose, except a small difference was detected in systems having only the lower transition. For both polymers the transition temperature decreased with increasing water content, but in the case of amylose the glycerol content also affected somewhat the location of the transition. The water effect was lost at the highest water content in the amylose powder because part of the water was bulk water, and thus freezing below 0 °C.

The heat capacity changes (Δc_p) of the upper transitions for both polymers were difficult to determine, and the calculated values were small varying from 0.04 to 0.16 J $g^{-1}K^{-1}$. The lower Δc_ps were larger and more easily evaluated especially for the highly plasticised amylopectin, varying from 0.1 to 0.4 J $g^{-1}K^{-1}$. Bizot et al. (1997) used a more sensitive DSC apparatus than applied in the present work and obtained Δc_p values for amylopectin with 10% water and for dry amylose, of 0.27 and 0.265 J $g^{-1}K^{-1}$, respectively.

3.3. Tensile failure properties

Mechanically amylose and amylopectin films behaved differently, which was easily seen when looking at the primary tensile results (Figs. 3 and 4). The tensile failure stress–strain curves showed the more brittle character of the films prepared of amylopectin, which was also observed when handling the films. For the amylopectin film with 10% glycerol the measurement was extremely difficult to perform. The tensile experiments were conducted at RH 50% and 20 °C. Under this condition the water content of

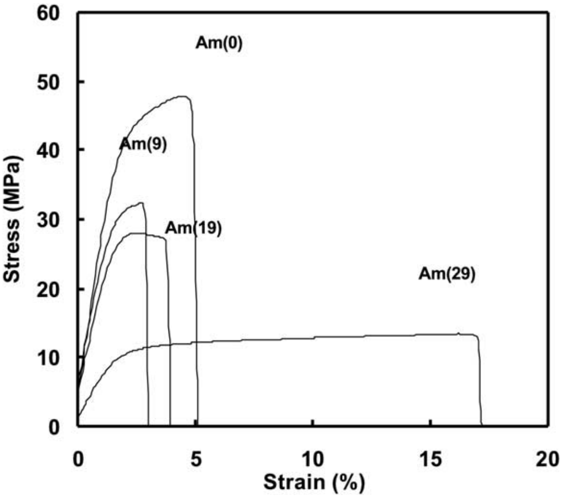

Fig. 3. Stress–strain curves of the amylose films with varying glycerol contents and measured at RH 50% and at 20 °C.

all films were about 10% based on sorption isotherms (Fig 1a and b), and this means that the glycerol was the only variable. Even though mechanically the polymer films differed, glycerol affected similarly the overall behaviour of both films. Under low glycerol contents both strain and stress decreased, but above 20% glycerol elongation reached larger values.

When investigating the effect of glycerol on amylose and amylopectin films in more detail, a clear difference was, however, observed (Fig. 5). The highly plastised amylose film (30% glycerol) was rather strong showing a tensile stress of 10 MPa (as strong as a polyethylene film), but the corresponding amylopectin film had lost its strength entirely. Addition of more than 30% glycerol to amylopectin resulted in a liquid-like behaviour being observed. On the other hand, from the amylose–glycerol–water mixture a film was formed even if as high as 70% of glycerol was used. This may indicate the crucial role of polymer network in formation of the film structure in the presence of high amount of plasticiser. Strains were overall small, ranging from close to zero to 5%, except in the highly plasticised amylose film that showed about 15% elongation.

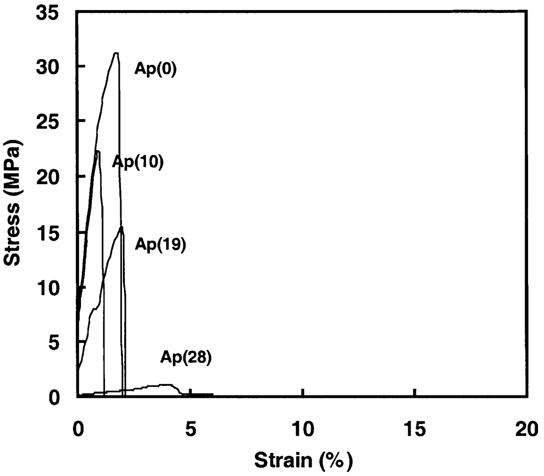

Fig. 4. Stress–strain curves of the amylopectin films with varying glycerol contents and measured at RH 50% and at 20 °C.

During the last decade the effects of plasticisers on the mechanical properties of films prepared of starch, amylose, amylopectin and mixtures of starch and other biopolymers have been widely studied. Investigations about the role of water on films made of Hylon V (maize starch with 50% amylose) by a water casting technique were performed at 20 °C (Bader and Göritz, 1994). A dry Hylon film was found to be very strong (90 MPa) and brittle. Softening was observed to start at a water content of 7–10% because of the presence of less tightly bound water. Defatting of corn starch increased elongation under high RH.

When mixing different ratios of amylose and amylopectin with 20% of glycerol the amylose rich films were observed to be slightly stronger than the amylopectin films, but amylopectin films were not mentioned to be brittle (Lourdin et al., 1995). van Soest, de Wit, and Vliegenthart (1996b) detected a sharp fall in mechanical properties in extruded amylopectin materials with 10% water, and this was concluded to be due to a change from the glassy to rubbery state. Larger stress and strain values than observed in the present study were found for highly plasticised films prepared of amylose and amylopectin (Rindlav-Westling et al., 1998). The larger strains could be due to thicker films, and the higher stresses perhaps due to increased crystalline phase. The tensile behaviour of amylose film in the present study could perhaps be related to the glycerol-rich microdomains, which were suggested to exist above 25% glycerol (Lourdin et al., 1998). And if so, what does this mean with regard to plasticisation mechanism? The very recent assumption about the existence of phase separation in dry amylose–glycerol mixtures makes things even more difficult to explain.

The mechanism of plasticisation of wheat starch by sorbitol was recently examined using DMTA and NMR (Gaudin et al., 1999). Based on low resolution NMR, below 27% sorbitol, starch and sorbitol were strongly interacted with each other, which resulted in decreasing the mobility of the system, whereas above 27% sorbitol, water perhaps interacted with sorbitol. At low sorbitol contents films were observed to be rigid and brittle. It was concluded that at high concentration (above 27%) sorbitol acted as a plasticiser. Similar antiplasticisation was earlier observed for glycerol plasticised potato starch, in which study mechanical properties exhibited minimum elongation at 12% glycerol (Lourdin et al., 1997b).

Coffin and Fishman (1993) planned to examine mechanical properties of cast films prepared of high amylose (70%) and waxy maize starches mixed with pectins. However, all attempts to use waxy maize starch failed because the products were too brittle. Strong films were produced from mixtures of high amylose starch and pectins, and glycerol was observed to be a good plasticiser making the

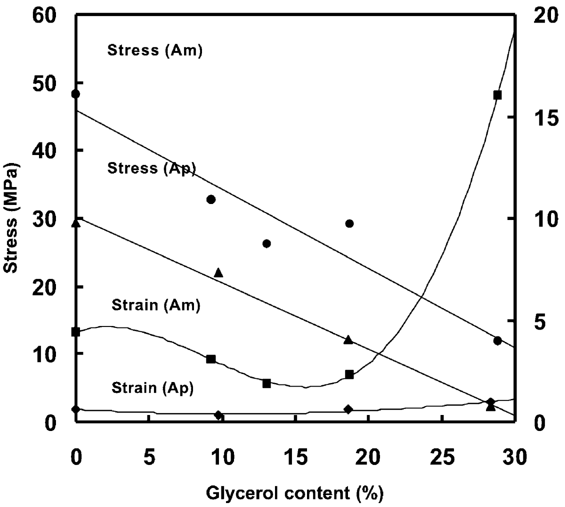

Fig. 5. Tensile stress and strain from Figs. 3 and 4, expressed as a function of the glycerol content for amylose (AM) and amylopectin (AP) films.

films less brittle. Even though starch had a negative effect on the mechanical properties it reduced the stickiness of the films. Coffin and Fishman (1994) went on with their studies on high amylose maize starch–pectin films and concluded that the plasticisation mechanism involves both bound and unbound glycerol, the former influencing the physical properties and latter acting as a solvent. The pectin–starch films were stronger but less flexible than the amylose films studied in the present work, but in both studies very high glycerol contents could be used.

4. Conclusions

As compared with the amylose films stress–strain curves of the amylopectin films indicated more brittle character, which was in agreement with the actual behaviour of the films. Glycerol and starch polymers strongly interacted, and at low glycerol contents this interaction resulted in more brittle structure for both polymer networks. Especially the amylopectin film with 10% glycerol was extremely difficult to handle and perform the tensile analysis due to its brittleness. Increase in elongation was observed when more than 20% of glycerol was added to amylose, which is a system, has earlier suggested to be phase-separated. At higher glycerol concentrations amylose could form films up to 70% glycerol, but from amylopectin only fluid-like material was produced above 30% glycerol. This indicated that the polymer network primarily defined the material property of the highly plasticised starch films.

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