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Effect of various polyols and polyol contents on physical and mechanical properties of potato starch-based films

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Abstract

The present study investigated effects of plasticizer (glycerol, xylitol and sorbitol) and relative humidity on physical and mechanical properties of potato starch-based edible films. Films were obtained from solutions containing gelatinized starch, polyol and water by casting and evaporating water at 35 °C. Water content of films increased with increasing relative humidity and plasticizer content. Water vapor permeability of films increased with increasing plasticizer content and storage relative humidity. Young's modulus decreased with increasing polyol content with a concurrent increase in elasticity of films. Both increased polyol and water content increased elongation at break with a decreased tensile strength. Glass transition temperatures decreased as a result of plasticization as polyol and/or water content increased. Effects of plasticizers on physical and mechanical properties of films were largest for glycerol and smallest for sorbitol. High contents of xylitol and sorbitol resulted in changes in physical and mechanical properties of films probably due to phase separation and crystallization.

Keywords: Potato starch; Edible film; Water sorption; Water vapor permeability; Mechanical properties; Glass transition temperature

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1. Introduction

There are many polysaccharide sources for edible film production, e.g., root and cereal starches, plant cell pectines, alginate and carrageenan from seaweed and cellulose (Kester & Fennema, 1986). Proteins, such as whey protein (Anker, Stading, & Hermansson, 1999) and wheat gluten (Gontard, Guilbert, & Cuq, 1992; Gennadios, Weller, & Testin, 1993), are also used to prepare edible films. Plasticizers, such as polyols, are added to improve handling of films by increasing the distance of macromolecules between each others allowing greater molecular mobility (Gaudin, Lourdin, Le Botlan, Ilari, & Colonna, 1999) resulting in flexibility of film. Water has significant role in plasticization of biomaterials (Roos, 1995), low molecular weight carbohydrates (Roos, 1993) and polyols (Talja & Roos, 2001).

Starch granules contain macromolecules, amylose and amylopectin, which form solution with hot water and gel after cooling (Miles, Morris, Orford, & Ring, 1985a; Miles, Morris, & Ring, 1985b). During gel formation amylose and amylopectin form inter- and intramolecular physical crosslinks to produce a macromolecular network (Miles et al., 1985b; Miles et al., 1985a) and film after water evaporation. Physical crosslinks in macromolecular network of starch are formed mainly by microcrystalline domains of amylose (Bader & Göritz, 1994a). The more microcrystalline domains appear in starch based-film the higher are Young's modulus and tensile strength of films (Bader & Göritz, 1994a; Rindlav-Westling, Stading, Hermansson, & Gatenholm, 1998). Starch film production under elevated temperature and low relative humidity (RH) conditions results in low degree of crystallinity of amylose and amylopectin (Rindlav, Hulleman, & Gatenholm, 1997;

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Rindlav-Westling et al., 1998). Degree of crystallinity of starch film increases with increasing amylose content of starch (García, Martino, & Zaritzky, 2000). On the other hand, plasticizer addition decreased crystallinity of corn and amylomaize starch films as compared to films without plasticizer (García et al., 2000).

Use of edible films as a barrier against gases (O_2, CO_2), water vapor or oil could extend shelf life, improve quality and handling properties of food products (Kester & Fennema, 1986; Mallikarjunan, Chinnan, Balasubramaniam, & Phillips, 1997) and pharmaceutical solids (Krogars, Antikainen, Heinämäki, Laitinen, & Yliruusi, 2002). Edible films could be used as carrier for antimicrobial substances to increase shelf life of food products (Han, 2002; Ouattara, Simard, Piette, Bégin, & Holley, 2000) as well as carrier for flavors and colouring agents (Han, 2002).

Addition of plasticizers, such as polyols, affects film properties such as water sorption, WVP, mechanical properties and glass transition temperature (T_g). Water sorbed in film acts also as a plasticizer affecting properties of starch film. Simultaneously as plasticizer content of a starch film increases, water content of the film decreases at low RH whereas water content of the film increases significantly at high RH (Gaudin et al., 1999; Lourdin, Coignard, Bizot, & Colonna, 1997b; Myllärinen, Partanen, Seppälä, & Forssell, 2002). Generally, WVP of plasticized films increases as plasticizer content of the film increases (Arvanitoyannis, Psomiadou, & Nakayama, 1996). Mechanical strength of films decreases due to plasticizer addition and water sorption resulting in decreased Young's modulus and tensile strength and increased elongation (Lourdin, Bizot, & Colonna, 1997a; Mathew & Dufresne, 2002). On the contrary, antiplasticization of polyol-plasticized starch films showing decreased elongation with increased plasticizer content has been reported at glycerol and sorbitol contents below 12 (Lourdin et al., 1997a) and 27% (w/w of solids) (Gaudin et al., 1999), respectively. Plasticizer addition decreases the glass transition temperature of the film due to weakened strength of macromolecular interactions (Gaudin et al., 1999; Lourdin et al., 1997b). Permeability of water vapor and gases through a film is greater above its glass transition temperature (Arvanitoyannis et al., 1996).

The purpose of this study was to investigate effects of various polyols and polyol contents on physical and mechanical properties of potato starch-based films. Water sorption was determined and modelled to obtain water sorption isotherms to study effects of RH on film-water interaction. Water vapor permeability was determined to study water vapor barrier properties of films. Thermal properties were determined to observe phase and state transitions occurring in films. Especially, glass transition temperature was studied as an indicator of plasticization of films. Young's modulus, tensile strength and elongation at break were studied to describe mechanical properties of films.

2. Materials and methods

2.1. Materials

Native potato starch, donated by Evijärven Peruna Ltd. (Evijärvi, Finland) was used to prepare edible films. Food grade glycerol (Dow, Stade, Germany), xylitol (Xyrofin, Kotka, Finland) and sorbitol (Cerestar, Krefeld, Germany) were used as plasticizers. Water content of starch determined gravimetrically after an oven drying at 105 °C for 4 h was 17% (w/w). Amylose content of starch determined with an enzymatic method (amylose/amylopectin assay kit, Megazyme International Ireland ltd., Bray, Ireland) was 14% (w/w of solids).

2.2. Film formation

Amount of polyol was weighed and dissolved into a distilled water and followed with starch addition to obtain film forming suspension, in which starch concentration (40% to 80% of solids) was 5% (w/w) of overall water content independently of polyol concentration (20% to 60% of solids). Film forming suspension was heated with continuous mixing over 90 °C and kept for 5 min before letting it cool down to 50 °C to obtain the film forming solution. Air bubbles formed during heating were removed by placing the film forming solution into a desiccator under vacuum until there was no bubble formation. Film forming solution was casted on a teflon-coated plate by a spreader with gap of 0.8 mm. Starch-based films were obtained by evaporating water in an oven at 35 °C for at least 4 h.

2.3. Water sorption

Pieces of films, approximately 0.5 g, were placed in to glass vials (20 ml). Glass vials were placed into a freezer at −20 °C for at least 2 h before placing them into −80 °C overnight. Frozen films in glass vials were placed into freeze dryer (Lyovac GT 2, Amsco Finn-Aqua GmbH, Hürth, Germany) and dried for at least 48 h ($p < 0.5$ mbar). Drying of films were completed in the vacuum desiccator over P_2O_5 (Merck, Darmstadt, Germany) for 7 days. Water sorption properties of various films were determined after storage of freeze-dried samples in vacuum desiccators over saturated salt solutions of LiCl, CH_3COOK, $MgCl_2$, K_2CO_3, $Mg(NO_3)_2$, $NaNO_2$, NaCl and KCl (Merck, Darmstadt, Germany) giving relative humidities (RH) of 11%, 24%, 33%, 44%, 54%, 66%, 76% and 86% at 24.8 ± 0.2 °C, respectively (Labuza, Kaanane, & Chen, 1985). Water contents were obtained by weighing samples as a function of time. Three replicate samples were analyzed. Water sorption behavior was modeled with Brunauer–Emmett–Teller (BET) and Guggenheim–Anderson–de Boer (GAB) Eqs. (1) and (2), respectively, in which m is experimental steady-state water content, m_m is monolayer water content, a_w is water activity (=RH/100 at equilibrium) and K and C are constants (e.g., Roos, 1995). Water activity ranges of

0.11 to 0.44 (Bell & Labuza, 2000) and 0.11 to 0.86 were used to model water sorption isotherms of polyol plasticized films with BET and GAB equations, respectively.

$$\frac{m}{m_m} = \frac{Ka_w}{(1-a_w)[1+(K-1)a_w]} \tag{1}$$

$$\frac{m}{m_m} = \frac{KCa_w}{(1-Ca_w)[1+(K-1)Ca_w]} \tag{2}$$

2.4. Water vapor permeability (WVP)

Granular (<6 mm) anhydrous $CaCl_2$ (J.T. Baker, Deventer, Holland), approximately 50 g, was used as a desiccant in a cylindrical bowl (height and inner diameter of 36 and 56.5 mm, respectively) which was covered with studied film attached with tape (Duct tape, Scotch, 3 M) to the bowl. Distance between surface of desiccant and film was less than 6 mm as suggested by ASTM E 96 (ASTM, 2001). Thickness of each film was measured with a micrometer (Mitutoyo, with accuracy of 0.01 mm) at six randomly selected points before the film was attached to the bowl. Bowls were placed in desiccators at RH of 33%, 54% and 76% at 23.5 ± 1.5 °C (Labuza et al., 1985) resulting in RH gradients of 0/33%, 0/54% and 0/76% across film. Progress of water vapor permeation was determined gravimetrically as a function of time for 7 days. Bowl was shaken horizontally after every weighing. Water vapor permeability was calculated with Eq. (3) where m is weight of water permeated through film, L is thickness of film, A is permeation area of film, t is time of permeation and Δp is water vapor pressure difference at both sides of film. Unit of water vapor permeability used is shown in brackets after Eq. (3). Three replicate samples were analyzed.

$$WVP = \frac{mL}{At\Delta p}\left[\frac{gmm}{m^2dkPa}\right] \tag{3}$$

2.5. Thermal properties and glass transition temperature

A differential scanning calorimeter (TA4000 DSC30, Mettler-Toledo AG, Greifensee, Switzerland) was used to determine the glass transition temperature, T_g, of the films plasticized with glycerol, xylitol or sorbitol. DSC was calibrated using melting temperatures and enthalpies of n-pentane (−129.7 °C; 116.7 J g^{-1}), n-hexane (−95 °C; 151.8 J g^{-1}), mercury (−38.8 °C; 11.4 J g^{-1}), distilled water (0.0 °C; 334.5 J g^{-1}), gallium (29.8 °C; 80.0 J g^{-1}) and indium (156.6 °C; 28.5 J g^{-1}). Film samples, 3 to 6 mg, were hermetically sealed in 40 μl aluminium pans (Mettler-27331) after equilibration over P_2O_5 and saturated salt solutions giving RH of 0%, 22%, 33%, 44%, 54%, 66%, 76%, and 86% at 23.5 ± 1.5 °C (Labuza et al., 1985), respectively. Samples were scanned from −150 to 200 °C at a heating rate of 5 °C min^{-1}. The T_g was taken from the onset temperature of step change in heat capacity. A flow of dry N_2 (50 ml min^{-1}) was used to purge the measuring cell and prevent water condensation. Three replicate samples were analyzed.

2.6. Mechanical properties

An Instron universal testing machine (model 4465, High Wycombe, England) with a 0.1 kN static load cell was used to measure Young's modulus (slope of stress-strain curve at low values of strain), tensile strength (maximum stress used during measurement) and elongation at break (ratio of elongation at break to original length of sample) of "dog bone" shaped film stripes (length of 150 mm and width of 10 mm). Thickness of film stripe was determined at six randomly selected places. Space between sample holder and crosshead was 100 mm and crosshead speed was 100 mm min^{-1}. Samples were equilibrated in vacuum desiccators over saturated salt solutions of $MgCl_2$, $Mg(NO_3)_2$ and NaCl giving RH of 33%, 54% and 76% at 23.5 ± 1.5 °C (Labuza et al., 1985), respectively, for 7 days before testing. At least five replicate film stripes were analyzed.

3. Results and discussion

Fresh potato starch film without plasticizer was transparent but it was wavy, rigid and brittle. Also, fresh potato starch films plasticized with glycerol, xylitol and sorbitol at all contents were transparent. Fresh potato starch-based films plasticized with glycerol at contents of 20% and 30% were flexible and easy to handle but at glycerol contents of 40% to 50%, even at low RH, films were flexible but sticky. Film plasticized with glycerol at content of 30% was found to become sticky when stored at RH of ⩾76%. Stickiness of glycerol plasticized films may have resulted from phase separation and diffusion of glycerol to surface of film. Phase separation of glycerol from starch matrix at higher glycerol content than 27% (w/w of solids) has been reported (Lourdin et al., 1997b). Potato starch-based films were rigid and brittle as plasticized with xylitol at content of 20% and sorbitol at contents of 20% and 30%. Similar results have been reported for wheat starch-based film at sorbitol content less than 27% (w/w of solids) (Gaudin et al., 1999). Fresh xylitol and sorbitol plasticized films were flexible at xylitol contents above 30% and at sorbitol contents above 40%. During storage xylitol and sorbitol crystallization could be observed visually from white spots appearing on the surface of films. Xylitol tended to crystallize at content of 40% at RH of 54% and at content of 50% at RH of 33% and 54%. Sorbitol crystallization was observed at content of 60% at RH of 33% and 54%. Crystallization of sorbitol when used as plasticizer at high contents has been observed to occur also in corn starch-based films (Krogars et al., 2003). Xylitol and sorbitol crystallization were not observed at RH of 76% because of dissolution of these polyols. Average thicknesses of fresh potato starch-based films plasticized with glycerol, xylitol and sorbitol were 53.5 ± 11.5, 48.9 ± 9.2 and 61.7 ± 11.3 µm, respectively.

3.1. Water sorption

Water content of all films increased with increasing RH. For all films steady-state water contents were reached within 48 h. Film without plasticizer showed clearly sigmoidal shape of water sorption isotherm and polyol plasticized films showed slightly sigmoidal shape of water sorption isotherms as modelled with BET and GAB equations (Fig. 1). Film without plasticizer had higher water content than films with plasticizer at low water activities. At constant starch-plasticizer ratios, water contents were lower in films containing a higher molecular weight plasticizer. Water activities at which water contents of plasticized and unplasticized films were equal ranged from 0.44 to 0.79 depending on plasticizer and plasticizer content (Table 1). When these water activities were exceeded water contents of plasticized films were higher than that of unplasticized film. Water content of all plasticized films increased with increasing plasticizer contents (Fig. 2). Monolayer water content of film without plasticizer was 6.6 and 9.6 g/100 g of solids as predicted by BET and GAB equations, respectively (Table 1). These values were comparable with monolayer water contents of 7.6 and 10.4 g/100 g of solids modelled with BET and GAB equations, respectively, reported for gelatinized corn starch (unpublished data in Jouppila & Roos, 1997). In most cases, monolayer water contents predicted with GAB equation were higher than those predicted with BET equation (Table 1). High monolayer water contents predicted with GAB equation for films plasticized with glycerol at contents of 40% and 50% resulted from possible phase separation of glycerol which is known to be hygroscopic. Film without plasticizer has more available sorption sites than films with plasticizer at low water activities. One glucosemonomer of starch is able to bind 0.7 to 1 molecule of water at water activity of monolayer water content (van den Berg, Kaper, Weldring, & Wolters,

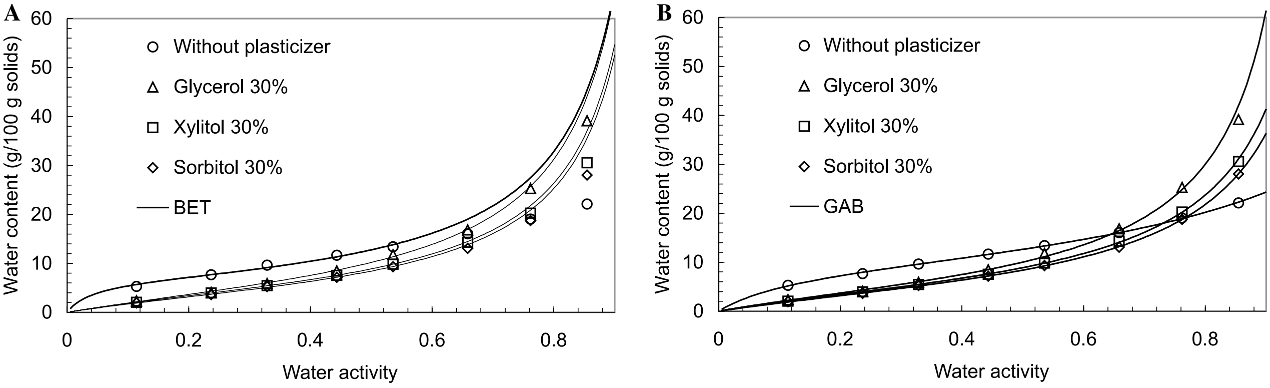

Fig. 1. Water sorption isotherms modelled with BET (A) and GAB (B) equations for potato starch-based edible films without plasticizer and plasticized with various polyols at content of 30%.

Table 1
Monolayer water contents (m_m) and constants (K and C) for potato starch films with various plasticizer and plasticizer contents calculated by BET and GAB equations (25 °C)

Plasticizer		BET		GAB			
Polyol	Content (%)	m_m	K	m_m	K	C	a_w[a]
Without plasticizer	0	7.09	15.8	9.61	0.69	11.3	–
Glycerol	20	5.95	4.42	6.19	0.98	4.25	0.68
	30	6.25	3.56	6.56	1.00	3.31	0.64
	40	12.8	0.97	18.5	0.86	0.78	0.52
	50	18.5	0.72	21.8	0.87	0.76	0.44
Xylitol	20	5.40	6.34	5.75	0.94	6.11	0.75
	30	5.63	3.72	6.13	0.95	3.45	0.73
	40	7.10	2.03	6.19	0.99	2.53	0.70
	50	3.55	7.47	3.05	1.08	10.2	0.78
Sorbitol	20	5.57	4.64	6.01	0.91	4.68	0.79
	30	5.48	3.41	6.03	0.94	3.22	0.77
	40	8.26	1.31	10.2	0.90	1.18	0.67
	50	16.2	0.48	8.57	0.97	1.23	0.65

[a] Water activities (a_w) at which water contents predicted by GAB equation of plasticized and unplasticized films are equal.

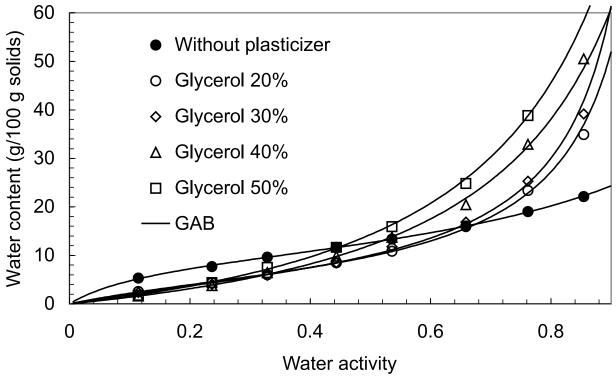

Fig. 2. Water sorption isotherms modelled with GAB equation for films without plasticizer and plasticized with glycerol at various contents.

1975). In plasticized films there are interactions between hydroxyl groups of starch and hydroxyl groups of polyol. As hydroxyl groups of polyol and glucosemonomers of starch form hydrogen bond between each others there are less sorption sites for water in glucosemonomers of starch. Hydroxyl groups located at both ends of polyol backbone are expected to be more accessible to water molecules than the other hydroxyl groups of polyol (Mathew & Dufresne, 2002). Probably these end hydroxyl groups of polyols are also more accessible to form hydrogen bonding with starch during film formation resulting in decreased amount of hydroxyl groups which could be accessible to bind water molecules at low water activities. Sorbitol was reported to decrease mobility of mobile parts of starch in wheat starch films at sorbitol contents below 27% (w/w of solids) (Gaudin et al., 1999). In anhydrous starch film, hydroxyl groups of starch and polyol interact with each other via hydrogen bonds. At low water activities, hydrogen bonds between starch and polyol are so strong that water sorption cannot break starch–polyol hydrogen bonds (Gaudin et al., 1999). Also, the present study showed that polyol plasticized starch films sorbed less water at low water activities (Table 1). Water content of unplasticized wheat starch film was greater than that of wheat starch films plasticized with sorbitol at contents of 2.5% to 39.5% (w/w of solids) when stored at RH of 57% (Gaudin et al., 1999). Lowest water content of wheat starch films were obtained at sorbitol contents of 24% to 27% (Gaudin et al., 1999). Water contents of amylose and amylopectin films without plasticizer were greater than those of films with plasticizer at low RH (Myllärinen et al., 2002) as also shown in the present study.

3.2. Water vapor permeability (WVP)

WVP of all films increased with increasing RH gradient. Similar effect of relative humidity gradient has been reported, e.g., for tapioca starch films (Chang, Cheah, & Seow, 2000). Plasticizer and plasticizer content of film affected WVP. From all plasticizers used in this study glycerol had greatest effect on the amount of water permeated through film while sorbitol had smallest effect on WVP. WVP was higher for potato starch-based film without plasticizer compared to starch-based films plasticized with polyols at all RH gradients. Exception for this was the film plasticized with 40% glycerol at all RH gradients and the film plasticized with 30% glycerol at RH gradient of 0/76% (Table 2). Visible cracks in WVP samples of film without plasticizer were not found. However, high WVP of film without plasticizer could be caused by microcracks in film. Cellulose acetate film at plasticizer content of 5% to 10% (w/w, solids) had lower WVP than film without plasticizer because of decreased molecular mobility of cellulose acetate (Guo, 1993). WVP of films is dependent on both solubility coefficient and diffusion rate of water in film which are dependent on partial pressure of water vapor (Kester & Fennema, 1986). According to water sorption data obtained in the present study water sorption of starch film decreased with plasticizer addition at low water activities as shown in Table 1. Film has probably lower capacity to transfer water through film as it contains less water. On the other hand, plasticizer probably increases diffusion rate of water in film and thus WVP increases with increasing plasticizer content. Lower WVP of polyol plasticized films as compared to WVP of film without plasticizer could result from coincident effect of both solubility coefficient and diffusion rate. At low RH, hydroxyl groups of starch form hydrogen bonds with hydroxyl groups of polyol, so polyol plasticized films do not contain as many sorption sites for water as in starch film without plasticizer.

Table 2
Water vapor permeability for potato starch-based films without and with various plasticizers and plasticizer contents (w/w of solids) at different RH gradients at 23.5 °C (mean value ± standard deviation from three measurements)

Plasticizer		WVP (g mm d^{-1} m^{-2} kPa^{-1})		
Polyol	Content (%)	0/33%	0/54%	0/76%
Without plasticizer	0	1.06 ± 0.18	2.83 ± 1.44	3.00 ± 0.63
Glycerol	20	0.48 ± 0.05	0.96 ± 0.03	1.38 ± 0.14
	30	1.25 ± 0.21	1.95 ± 0.47	3.67 ± 0.60
	40	3.29 ± 0.70	4.48 ± 0.65	6.05 ± 1.15
Xylitol	30	0.12 ± 0.01	0.45 ± 0.03	1.13 ± 0.13
	40	0.25 ± 0.05	0.88 ± 0.29	1.58 ± 0.34
Sorbitol	40	0.07 ± 0.00	0.35 ± 0.03	0.98 ± 0.10
	50	0.14 ± 0.01	0.77 ± 0.10	1.93 ± 0.07

This probably decreases diffusion rate of water molecules through film. At higher RH, hydrogen bonding between starch and polyol is disrupted by water sorption and amount of starch–water and polyol–water interactions increases resulting in swelling of film and, thus, water diffusion through film increases.

3.3. Thermal properties and glass transition temperature

Glass transition temperatures decreased as a result of plasticization as polyol and/or water content increased (Table 3). Glass transition temperatures of polyols used were −86 (Murthy, 1996), −26 and −9 °C (Talja & Roos, 2001) for glycerol, xylitol and sorbitol, respectively. In the present study, heat capacity changes of polyol plasticized films observed at glass transition regions were weak and temperature ranges between onset and endpoint of the glass transition varied from 15 to 35 °C. One glass transition was observed for films plasticized with glycerol and stored at RH of 0%. Glass transition could not be observed for films plasticized with glycerol when stored at RH of 33%, 54% and 76%. Two glass transition temperatures, plasticizer rich and polymer rich domains, have been reported for a corn starch film plasticized with glycerol (33%, w/w of solids) and stored at RH ranging from 0% to 75% (Mathew & Dufresne, 2002). One glass transition temperature was observed for films plasticized with xylitol and sorbitol (Table 3). Glass transition temperatures of 12.5 to −54.5 °C and 13 to −51.5 °C at RH 0 to 75% have been reported for corn starch film plasticized with xylitol and sorbitol (33% w/w, solids), respectively (Mathew & Dufresne, 2002). In the present study, glass transition temperature for film without plasticizer could not be determined at any storage RH used. Glass transition temperature of 90 °C has been reported for potato starch-based film without plasticizer stored at RH of 57% (Lourdin et al., 1997b).

In thermograms recorded from film at xylitol content of 50% endothermic peaks were found the maximum of which occurred at temperatures of 73, 64 and 53 °C when stored at RH of 33%, 54% and 76%, respectively. As solubility of most sugars in water increases with increasing temperature (Roos, 1995) and melting temperature of anhydrous xylitol is 93 °C (Talja & Roos, 2001) it could be concluded that these endothermic peaks were related to dissolving of xylitol crystals. We also found endothermic peaks at higher temperatures in DSC thermograms recorded from films plasticized with glycerol at content of 30% and xylitol and sorbitol at contents of 30% and 50% stored at relative humidity of 24% and over (other plasticizer contents were not studied). Onset temperatures of these endothermic peaks decreased from 170 to 94 °C and intensity of endothermic peaks increased with increasing storage RH from 24% to 86%. Endothermic peaks were not observed for films stored at RH of 0% and 11%. Such endothermic peaks may be due to melting of starch crystallites. Melting endotherms of cocrystallized amylose and amylopectin at 110 to 120 °C have been reported for films prepared from blend of amylose and amylopectin as well as from potato starch when stored at RH of 54% (Rindlav-Westling, Stading, & Gatenholm, 2002).

3.4. Mechanical properties

Values of Young's modulus decreased with increasing polyol content with a concurrent increase in elongation of films at break (Fig. 3). Both increased polyol and water content increased elongation of film at break with decreased tensile strength. Effects of plasticizers on elongation at break were largest with glycerol and smallest with sorbitol at constant starch-plasticizer ratios (Fig. 3). Increased Young's modulus and decreased elongation at break at highest xylitol and sorbitol contents in films stored at RH of 33% and 54% were probably due to polyol crystallization observed visually as white spots on the surface of films (Fig. 3). Phase separation of xylitol and sorbitol may occur in the presence of water and induce crystallization of xylitol and sorbitol when stored at RH of 33 and 54%. Polyol crystallization decreases the amount of plasticizing polyol in starch film and allows enhanced crosslink formation in starch network and thus changes in mechanical properties of the film. Crystallinity of starch film has been shown to increase with decreasing plasticizer content (García et al., 2000). More over, phase separation of starch components could be occurred simultaneously with polyol crystallization resulting in increased crystallinity of starch. Crystallization of starch components occurs during film formation (Rindlav et al., 1997; Rindlav-Westling et al., 1998) increasing Young's modulus and tensile strength (Bader & Göritz, 1994a; Rindlav-Westling et al., 1998)

Table 3
Glass transition temperatures for potato starch-based edible films plasticized with glycerol, xylitol and sorbitol (at various contents, w/w of solids) when stored at various RH at 23.5 °C (mean value ± standard deviation from three measurements)

RH (%)	Glycerol	Xylitol		Sorbitol	
	30%	30%	50%	30%	50%
0	−23.6 ± 1.8 (0)	−1.6 ± 3.0 (0)	–	38.8 ± 3.3 (0)	–
33	–	−30.7 ± 1.7 (5.47)	−32.5 ± 0.5 (4.14)	−19.8 ± 1.5 (5.25)	−25.7 ± 0.9 (4.90)
54	–	−56.7 ± 2.1 (9.85)	−47.9 ± 3.0 (6.83)	−32.2 ± 2.1 (9.31)	−48.7 ± 2.1 (9.15)
76	–	−67.6 ± 1.8 (20.3)	−77.1 ± 3.9 (10.4)	−59.8 ± 1.0 (18.8)	−57.1 ± 2.4 (26.6)

Water contents (g/100 g of solids) of films are presented after T_g value in parentheses.

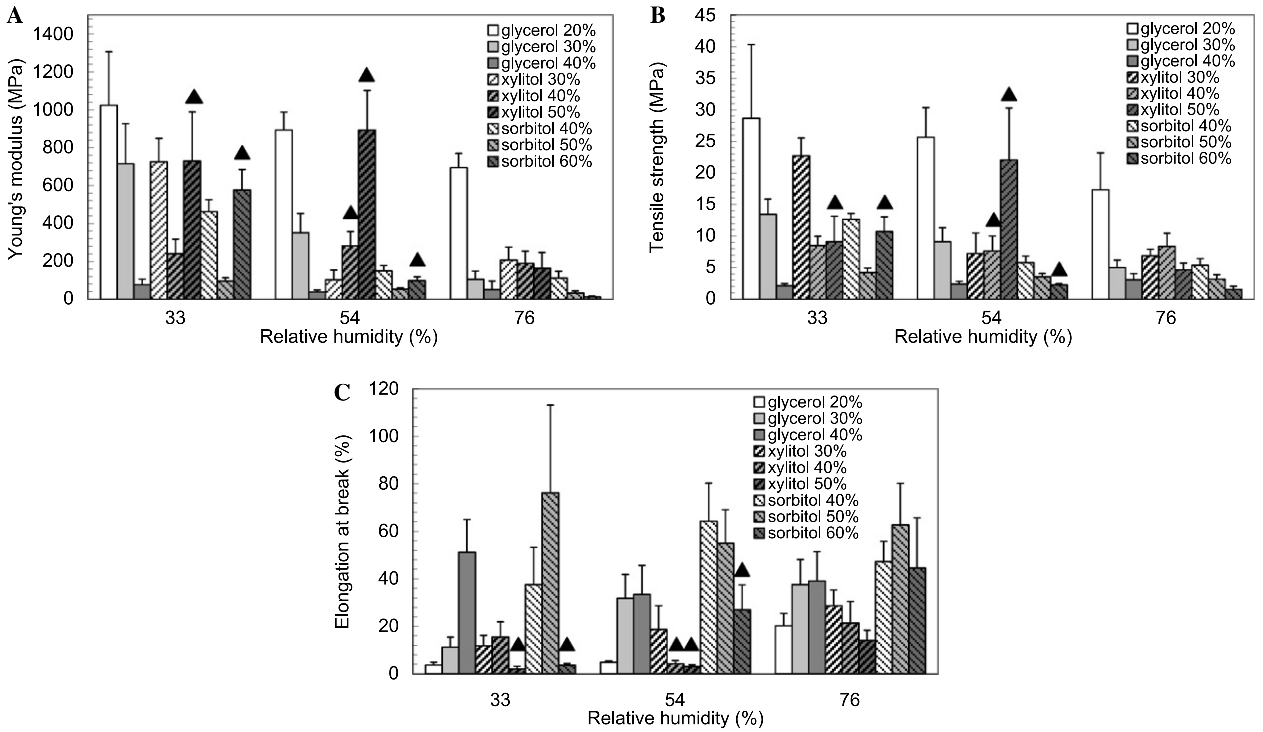

Fig. 3. Young's modulus (A), tensile strength (B) and elongation at break (C) for potato starch-based edible films with different plasticizers and plasticizer contents at various RH. Triangles are indicating possible polyol crystallization.

which could be observed from increased rigidity of starch film. Crystallinity of potato starch has been reported to increase remarkably at RH above 50%, below which low degree of crystallinity has been observed (van Soest, Hulleman, de Wit, & Vliegenthart, 1996). However, dissolution of xylitol and sorbitol crystals may occur when stored at RH of 76%. In the present study such behavior could be confirmed from the endothermic peaks observed in DSC thermograms recorded from the film containing 50% xylitol.

Water sorption in films increased with increasing water activities as discussed above. Starch films swell at high RH due to high water content of film (Bader & Göritz, 1994b). During swelling amount of hydrogen bonds between starch–polyol and starch–starch decreases and amount of hydrogen bonds between starch–water and polyol–water increases resulting in weakened structure of film which do not last big deformations. This was observed at high RH as elongation of film was found to decrease instead of increase in elongation which was expected to occur with increasing plasticizer content and RH as reviewed, e.g., by Krochta (2002). Mechanical properties of film without plasticizer could not be determined because of rigidity and brittleness of film.

4. Conclusions

Potato starch-based films plasticized with various polyols were prepared by a casting method. Plasticizer type and content were found to affect physical and mechanical properties of potato starch films. At high polyol contents, phase separation occurred resulting in a sticky surface of films plasticized with glycerol and crystallization in the films plasticized with xylitol and sorbitol. Water contents were higher at lower water activities for films without plasticizer as compared to films with plasticizer. Water contents increased with increasing plasticizer content and glycerol had the greatest and sorbitol had the smallest effect on water sorption. Water vapor permeability increased with increasing plasticizer content. Potato starch-based edible films plasticized with the same amount of glycerol, xylitol and sorbitol were permeated by water vapor to different extents in order of molecular weight of polyol. The water vapor permeability decreased with increasing molecular weight of polyol. As plasticizer content of films and storage RH increased both Young's modulus and tensile strength decreased with concurrent increase in elongation at break. Exceptions for this were films at high xylitol and sorbitol contents in which xylitol and sorbitol crystallized resulting in decreasing plasticization of films and probably increasing crystallinity of starch components.

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References

Anker, M., Stading, M., & Hermansson, A. M. (1999). Effects of pH and the gel state on the mechanical properties, moisture contents, and glass transition temperatures of whey protein films. *Journal of Agricultural and Food Chemistry, 47*(5), 1878–1886.

Arvanitoyannis, I., Psomiadou, E., & Nakayama, A. (1996). Edible films made from sodium caseinate, starches, sugars or glycerol. Part 1. *Carbohydrate Polymers, 31*(4), 179–192.

ASTM. (2001). Standard methods of test for water vapor transmission of materials in sheet form, method ASTM E 96-00. InAnnual Book of ASTM Standards. Philadelphia, PA: American Society for Testing and Material.

Bader, H. G., & Göritz, D. (1994a). Investigations on high amylose corn starch films. Part 3: stress strain behaviour. *Starch/Stärke, 46*(11), 435–439.

Bader, H. G., & Göritz, D. (1994b). Investigations on high amylose corn starch films. Part 2: water vapor sorption. *Starch/Stärke, 46*(7), 249–252.

Bell, L. N., & Labuza, T. P. (2000). *Moisture sorption: Practical aspects of isotherm measurement and use*. St. Paul, MN: American Association of Cereal Chemists, Inc.

Chang, Y. P., Cheah, P. B., & Seow, C. C. (2000). Plasticizing–antiplasticizing effects of water on physical properties of tapioca starch films in the glassy state. *Journal of Food Science, 65*(3), 445–451.

García, M. A., Martino, M. N., & Zaritzky, N. E. (2000). Microstructural characterization of plasticized starch-based films. *Starch/Stärke, 52*(4), 118–124.

Gaudin, S., Lourdin, D., Le Botlan, D., Ilari, J. L., & Colonna, P. (1999). Plasticization and mobility in starch–sorbitol films. *Journal of Cereal Science, 29*(3), 273–284.

Gennadios, A., Weller, C. L., & Testin, R. F. (1993). Modification of physical and barrier properties of edible wheat gluten-based films. *Cereal Chemistry, 70*(4), 426–429.

Gontard, N., Guilbert, S., & Cuq, J. L. (1992). Edible wheat gluten films: influence of the main process variables on film properties using response surface methodology. *Journal of Food Science, 57*(1), 190–195, 199.

Guo, J. H. (1993). Effects of plasticizers on water permeation and mechanical properties of cellulose acetate: antiplasticization in slightly plasticized polymer film. *Drug Development and Industrial Pharmacy, 19*(13), 1541–1555.

Han, J. H. (2002). Protein-based edible films and coatings carrying antimicrobial agents. In A. Gennadios (Ed.), *Protein-based films and coatings*. Boca Raton, FL: CRC press LCC.

Jouppila, K., & Roos, Y. H. (1997). The physical state of amorphous corn starch and its impact on crystallization. *Carbohydrate Polymers, 32*(2), 95–104.

Kester, J. J., & Fennema, O. R. (1986). Edible films and coatings: a review. *Food Technology, 40*(12), 47–59.

Krochta, J. M. (2002). Proteins as raw materials for films and coatings: definitions, current status, and opportunities. In A. Gennadios (Ed.), *Protein-based films and coatings*. Boca Raton, FL: CRC press LCC.

Krogars, K., Antikainen, O., Heinämäki, J., Laitinen, N., & Yliruusi, J. (2002). Tablet film-coating with amylose-rich maize starch. *European Journal of Pharmaceutical Sciences, 17*(1), 23–30.

Krogars, K., Heinämäki, J., Karjalainen, M., Niskanen, A., Leskelä, M., & Yliruusi, J. (2003). Enhanced stability of rubbery amylose-rich maize starch films plasticized with a combination of sorbitol and glycerol. *International Journal of Pharmaceutics, 251*(1-2), 205–208.

Labuza, T. P., Kaanane, A., & Chen, J. Y. (1985). Effect of temperature on the moisture sorption isotherms and water activity shift of two dehydrated foods. *Journal of Food Science, 50*(2), 385–391.

Lourdin, D., Bizot, H., & Colonna, P. (1997a). Antiplasticization in starch–glycerol films?. *Journal of Applied Polymer Science 63*(8), 1047–1053.

Lourdin, D., Coignard, L., Bizot, H., & Colonna, P. (1997b). Influence of equilibrium relative humidity and plasticizer concentration on the water content and glass transition of starch materials. *Polymer, 38*(21), 5401–5406.

Mallikarjunan, P., Chinnan, M. S., Balasubramaniam, V. M., & Phillips, R. D. (1997). Edible coatings for deep-fat frying of starchy products. *Lebensmittel-Wissenschaft & Technologie/FST, 30*(7), 709–714.

Mathew, A. P., & Dufresne, A. (2002). Plasticized waxy maize starch: effect of polyols and relative humidity on material properties. *Biomacromolecules, 3*(5), 1101–1108.

Miles, M. J., Morris, V. J., Orford, P. D., & Ring, S. G. (1985a). The roles of amylose and amylopectin in the gelation and retrogradation of starch. *Carbohydrate Research, 135*(2), 271–281.

Miles, M. J., Morris, V. J., & Ring, S. G. (1985b). Gelation of amylose. *Carbohydrate Research, 135*(2), 257–269.

Murthy, S. S. N. (1996). Experimental study of dielectric relaxation in supercooled alcohols and polyols. *Molecular Physics, 87*(3), 691–709.

Myllärinen, P., Partanen, R., Seppälä, J., & Forssell, P. (2002). Effect of glycerol on behaviour of amylose and amylopectin films. *Carbohydrate Polymers, 50*(4), 355–361.

Ouattara, B., Simard, R. E., Piette, G., Bégin, A., & Holley, R. A. (2000). Diffusion of acetic and propionic acids from chitosan-based antimicrobial packaging films. *Journal of Food Science, 65*(5), 768–773.

Rindlav, Å., Hulleman, S. H. D., & Gatenholm, P. (1997). Formation of starch films with varying crystallinity. *Carbohydrate Polymers, 34*(1-2), 25–30.

Rindlav-Westling, Å., Stading, M., & Gatenholm, P. (2002). Crystallinity and morphology in films of starch, amylose and amylopectin blends. *Biomacromolecules, 3*(1), 84–91.

Rindlav-Westling, Å., Stading, M., Hermansson, A.-M., & Gatenholm, P. (1998). Structure, mechanical and barrier properties of amylose and amylopectin films. *Carbohydrate Polymers, 36*(2-3), 217–224.

Roos, Y. (1993). Melting and glass transitions of low molecular weight carbohydrates. *Carbohydrate Research, 238*, 39–48.

Roos, Y. H. (1995). *Phase transitions in foods*. San Diego, CA: Academic Press, Inc.

Talja, R. A., & Roos, Y. H. (2001). Phase and state transition effects on dielectric, mechanical, and thermal properties of polyols. *Thermochimica Acta, 380*(2), 109–121.

van den Berg, C., Kaper, F. S., Weldring, J. A. G., & Wolters, I. (1975). Water binding by potato starch. *Journal of Food Technology, 10*(6), 589–602.

van Soest, J. J. G., Hulleman, S. H. D., de Wit, D., & Vliegenthart, J. F. G. (1996). Changes in the mechanical properties of thermoplastic potato starch in relation with changes in B-type crystallinity. *Carbohydrate Polymers, 29*(3), 225–232.