Available online at www.sciencedirect.com

ScienceDirect

Carbohydrate Polymers 71 (2008) 269–276

Carbohydrate Polymers

www.elsevier.com/locate/carbpol

Effect of type and content of binary polyol mixtures on physical and mechanical properties of starch-based edible films

Riku A. Talja [a,*], Harry Helén [a], Yrjö H. Roos [b], Kirsi Jouppila [a]

[a] *Department of Food Technology, P.O. Box 66 (Agnes Sjöbergin katu 2), University of Helsinki, 00014 Helsinki, Finland*
[b] *Department of Food and Nutritional Sciences, University College Cork, Ireland*

Received 14 December 2006; received in revised form 21 May 2007; accepted 30 May 2007
Available online 10 June 2007

Abstract

The present study investigated effects of binary mixtures (1:1) of glycerol, xylitol and sorbitol at various concentrations on physical and mechanical properties of potato starch-based edible films stored at various relative vapor pressures (RVP). Edible films were prepared by casting using suspension of binary polyol mixtures (20–50% of solids), potato starch (50–80% of solids) and distilled water which was heated to gelatinize starch. Water sorption of films was affected by the type and content of binary polyol mixture. Water vapor permeability (WVP) of films was found to increase as the content and plasticization effect of binary polyol mixture as well as RVP gradient increased. Young's modulus of films was observed to decrease with the concurrent increase of elongation at break as the plasticization and the content of binary polyol mixture increased at RVP of 33%. Both tensile strength and elongation at break decreased when films were plasticized at the high content of binary polyol mixtures and stored at the RVP of 54% and 76%. Crystallization of polyols was not observed when binary polyol mixtures were used as plasticizers.

© 2007 Elsevier Ltd. All rights reserved.

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

1. Introduction

Edible films can be prepared from biomaterials such as polysaccharides and proteins (Kester & Fennema, 1986) and can be plasticized by low molecular weight carbohydrates, such as polyols (e.g., Mathew & Dufresne, 2002; Stading, Rindlav-Westling, & Gatenholm, 2001; Talja, Helén, Roos, & Jouppila, 2007). The main function of edible film could be to prevent mass transfer of water or other compounds, such as oxygen, carbon dioxide, oil and aroma compounds, between a product and surroundings or between different layers of a product. Function of the film could also be to act as a carrier of antimicrobial substances, aroma compounds or coloring agents or to improve mechanical handling of foods (Han, 2002) or pharmaceutical products (Krogars, Antikainen, Heinämäki, Laitinen, & Yliruusi, 2002). For many biomaterials in low moisture foods water acts as a plasticizer causing structural failures thus affecting stability and quality of such foods (Roos & Karel, 1990, 1991). Hence, it is important to control water sorption properties of low moisture foods or pharmaceutical products. Edible films can be used as barriers or retarders of water sorption of low moisture products, e.g., crackers (Bravin, Peressini, & Sensidoni, 2006). Moreover, edible films could be used to control release of drug (Tuovinen, Peltonen, & Järvinen, 2003) or active components from foods and packaging materials.

Before edible films can be applied to foods or pharmaceutical products, knowledge of water sorption, water vapor permeability (WVP) as well as mechanical properties of edible films are needed. WVP of films with good water vapor barrier properties (low or no water permeation and diffusion through film) should not increase or increase very little with increasing relative vapor pressure (RVP) (Lawton, 1996). Films should stand mechanical stress and

---

[*] Corresponding author. Tel.: +358 9 191 58301; fax: +358 9 191 58460.
E-mail address: riku.talja@helsinki.fi (R.A. Talja).

0144-8617/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.carbpol.2007.05.037

strain to such an extent that they do not break easily under a decent mechanical force. Composition of starch-based films affects such properties of films as water sorption (Bader & Göritz, 1994; Myllärinen, Partanen, Seppälä, & Forssell, 2002; Stading et al., 2001; Talja et al., 2007), WVP (e.g., Arvanitoyannis, Psomiadou, & Nakayama, 1996; Biliaderis, Lazaridou, & Arvanitoyannis, 1999; Talja et al., 2007), gas permeability (Arvanitoyannis et al., 1996; Biliaderis et al., 1999; Stading et al., 2001), crystallization of plasticizers (Krogars et al., 2003; Talja et al., 2007), glass transition temperature (T_g) (e.g., Arvanitoyannis et al., 1996; Lourdin, Coignard, Bizot, & Colonna, 1997; Myllärinen et al., 2002; Talja et al., 2007) as well as mechanical properties (e.g., Arvanitoyannis et al., 1996; Talja et al., 2007).

Phase separation and crystallization of polyol, like xylitol or sorbitol, when used as a single plasticizer at high concentrations, have been observed to occur in starch-based edible films (Krogars et al., 2003; Talja et al., 2007). Crystallization of plasticizers increased tensile strength and decreased elongation at break of starch-based edible films (Talja et al., 2007). The amount of plasticizing polyol (which is in amorphous state) decreases if crystallization of polyol occurs. Thus, Young's modulus and tensile strength of the film may increase with the concurrent decrease of elongation at break as a result of crystallization (Talja et al., 2007).

The purpose of the present study was to investigate effects of various binary mixtures (1:1) of polyols and their contents on physical and mechanical properties of potato starch-based films stored at various RVP. Binary polyol mixtures used were glycerol–xylitol (Gly–Xy), glycerol–sorbitol (Gly–S) and xylitol–sorbitol (Xy–S). Water sorption was determined and modelled to obtain water sorption isotherms for studying effects of RVP on film–water interaction. WVP was determined at various RVP gradients to study the water vapor barrier properties of films. Young's modulus, tensile strength and elongation at break were studied to describe mechanical properties of films. Glass transition temperature was studied as an indicator of plasticization of starch-based 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 to produce binary polyol 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

Edible films were prepared using suspensions of binary polyol mixtures (1:1, w/w), potato starch and distilled water. Binary polyol mixtures (20–50% of solids) were weighed and dissolved into distilled water and followed with starch addition to obtain film forming suspension, in which starch concentration (50–80% of solids) was 5% (w/w) of overall water content. Film forming suspension was heated using continuous mixing by magnetic stirrer (RH Basic, Ika Works, Inc., Wilmington, NC) and at short intervals by hand with glass rod to above 90 °C and kept at that temperature for 5 min before letting it cool down to 50 °C. Air bubbles formed during heating were removed by degassing a vacuum desiccator in which the film forming solution was kept until there was no bubble formation. Film forming solution was casted on a teflon-coated plate by a spreader with the 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 into 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 for over night. Frozen film samples in glass vials were placed into a freeze dryer (Lyovac GT 2, Amsco Finn-Aqua GmbH, Hürth, Germany) and dried for at least 48 h ($p < 0.5$ mbar). Drying of film samples was completed in a 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 vapor pressure (RVP) of 11%, 24%, 33%, 44%, 54%, 66%, 76% and 86% at 25 °C, respectively (Labuza, Kaanane, & Chen, 1985). Water contents were obtained by weighing the samples as a function of time. Three replicate samples at each RVP were analyzed. Water sorption isotherms were modelled with the Brunauer–Emmett–Teller (BET) and the 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 (=RVP/100 at equilibrium), and K and C are constants (e.g., Roos, 1995). Water activity ranges of 0.11–0.44 (Bell & Labuza, 2000) and 0.11–0.86 were used to model sorption isotherms of polyol plasticized films with the 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

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 a film sample 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 an accuracy of 0.01 mm) at six randomly selected points before the film was attached to the bowl. Bowls were placed in desiccators at RVP of 33%, 54% and 76% resulting RVP gradients of 0/33%, 0/54% and 0/76% across the film at 23.5 ± 1.5 °C. Progress of water vapor permeation was followed gravimetrically as a function of time for 7 days. Bowl was shaken horizontally after every weighing. WVP was calculated with Eq. (3) where m is weight of water permeated through the film, L is thickness of the film, A is permeation area of the film, t is time of permeation, and Δp is water vapor pressure difference at both sides of the film. Unit of WVP used is presented in brackets after Eq. (3) (ASTM, 2001). Three replicate samples were analyzed.

$$\mathrm{WVP} = \frac{m\ L}{A\ t\ \Delta p}\left[\frac{\mathrm{g\ mm}}{\mathrm{m^2 d\ kPa}}\right] \quad (3)$$

2.5. 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 force used during measurement) and elongation at break (ratio of elongation to original length of sample at break) of "dog bone" shaped film stripes length and width of which were 150 and 10 mm, respectively. Thickness of the 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 at 23.5 ± 1.5 °C were equilibrated for 7 days before testing in vacuum desiccators at RVP of 33%, 54% and 76%. At least six replicate film stripes were analyzed.

2.6. Glass transition

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 Gly–Xy, Gly–S or Xy–S at content of 40% (w/w). 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, 3–6 mg, were hermetically sealed in 40 μl aluminium pans (Mettler-27331) after equilibration at RVP of 33%, 54% and 76% at 23.5 ± 1.5 °C. DSC was used 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.

3. Results and discussion

Fresh potato starch films plasticized with binary mixtures of polyols were transparent. Elastic and flexible starch films could be prepared using binary polyol mixtures as plasticizers. Starch films plasticized with all binary mixtures of polyols at the content up to 40% were easy to handle, as they showed no stickiness. Film plasticized at Xy–S content of 50% was also easy to handle. Films were sticky at Gly–Xy and Gly–S content of 50% and, thus, difficult to handle. This could be an indication of phase separation of binary polyol plasticizer from starch matrix. Starch films plasticized with glycerol at contents of 40% or higher were found to be sticky (Talja et al., 2007) because of phase separation of glycerol from starch matrix which has been reported to occur at higher glycerol contents than 27% (w/w of solids) (Krogars et al., 2003; Lourdin et al., 1997). Moreover, phase separation of glycerol from starch film has been reported to occur above storage RVP of 60% because of crystallization of starch (van Soest, Hulleman, de Wit, & Vliegenthart, 1996). Crystallization of xylitol and sorbitol at contents of 50% and 60% (w/w of solid), respectively, when used as single plasticizers at storage RVP of 33% and 54% has been reported to occur in potato starch films (Talja et al., 2007). Similar behavior has been reported for sorbitol plasticized maize starch films at sorbitol contents over 33% at RVP of 60% (Krogars et al., 2003). Polyol crystallization in binary polyol mixtures was not observed at contents of mixtures used and under storage conditions used in the present study. Inhibition of polyol crystallization using binary polyol mixtures, as in the present study, is analogous to the confectionery products in which crystallization of sucrose could be retarded or prevented using mixture of sugars (Roos, 1995; Roos & Karel, 1991). Thickness obtained for starch-based films ranged from 33 to 74 μm.

3.1. Water sorption

Amount of sorbed water of the films increased with increasing water activity. Generally, water content of the all binary polyol plasticized films was doubled as water activity increased from 0.33 to 0.54 and further to 0.76. Steady-state water contents were reached within 48 h of storage. BET and GAB water sorption isotherms showed lower water contents for the plasticized films than for the unplasticized films under water activity of 0.6 (Fig. 1). Similar results have been reported, e.g., for starch films plasticized with single polyols (Myllärinen et al., 2002; Talja

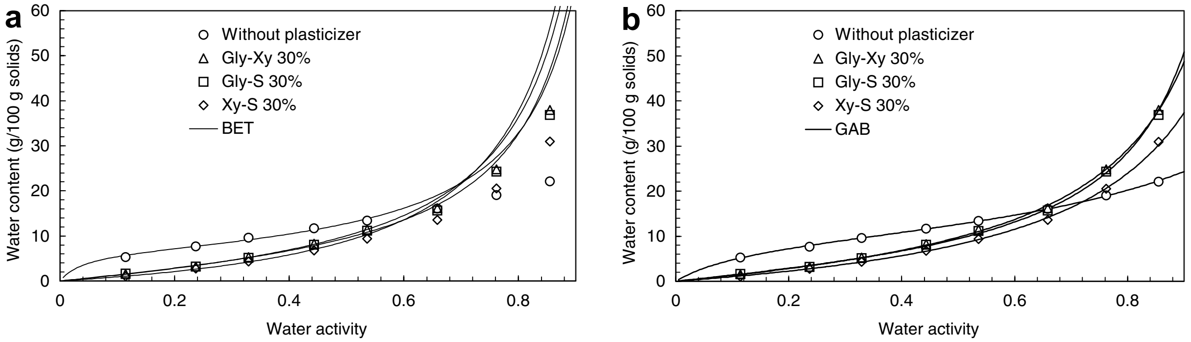

Fig. 1. Water sorption isotherms modelled with BET (a) and GAB (b) equations for potato starch-based edible films plasticized with glycerol–xylitol (Gly–Xy), glycerol–sorbitol (Gly–S) and xylitol–sorbitol (Xy–S) at content of 30% (the present study) and without plasticizer (Talja et al., 2007).

et al., 2007) and for a mixture of freeze-dried gelatinized starch and glucose (Saravacos & Stinchfield, 1965). Water activities at which water contents of plasticized and unplasticized films were equal, as modelled with the GAB equation, ranged from 0.52 to 0.79 depending on plasticizer and plasticizer content (Table 1). These water activities were similar to values reported for starch films plasticized with single polyols (Talja et al., 2007). With increasing plasticizer content of the films the water content increased, and the extent of the increase was more pronounced at high water activities (Fig. 2). Similar water sorption behavior has been reported for biopolymer films plasticized with a single polyol (Kristo & Biliaderis, 2006; Myllärinen et al., 2002; Talja et al., 2007) and for sorbitol and xylose plasticized pullulan-starch blends (Biliaderis et al., 1999). At a constant starch–plasticizer ratio with the plasticizer content of 30%, the films plasticized with Gly–Xy and Gly–S gained approximately the same water content but films plasticized with Xy–S gained apparently lower water content (Fig. 1). Similar behavior was found at all plasticizer contents used. At constant starch-plasticizer ratios films plasticized with a single lower molecular weight polyol had higher water content than films containing a higher molecular weight polyol (Talja et al., 2007). Water content corresponding to the monolayer water content for films without plasticizer and with the plasticizer content of 20% was reached at water activities of 0.39 and 0.34, respectively, independently of the plasticizer. At higher plasticizer contents (30% and 40%) monolayer water contents were reached at water activity around 0.5. Films without plasticizer and with plasticizer showed sigmoidal and almost sigmoidal sorption isotherms, respectively (Fig. 2). Polysaccharide-based products containing high contents of sugars showed long flat segment at water activities up to 0.6 followed with rapid increase in water sorption because of differences in water sorption affinities of polysaccharide and sugars (Biliaderis et al., 1999). In those polysaccharide-based products polysaccharides adsorb more water than sugar at low water activities up to 0.6, whereas polysaccharides and sugar have opposite sorption behavior at high water activities (Biliaderis et al., 1999). Lewicki (1997) suggested that water sorption behavior of mixtures of low molecular weight polar molecules and bio-

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

Plasticizer		BET		GAB			a_w
Binary polyol mixture	Content (%)	m_m	K	m_m	K	C	
Without plasticizer[a]	0	7.09	15.8	9.61	0.69	11.3	–
Gly–Xy	20	5.33	4.45	5.68	0.97	4.13	0.74
	30	8.55	1.42	9.99	0.91	1.34	0.64
	40	10.5	1.36	12.6	0.91	1.24	0.55
	50	10.2	1.49	11.4	0.96	1.37	0.53
Gly–S	20	5.39	4.56	5.70	0.96	4.36	0.75
	30	7.45	1.78	8.09	0.95	1.74	0.66
	40	9.73	1.46	11.6	0.92	1.33	0.56
	50	10.8	1.37	12.3	0.93	1.28	0.52
Xy–S	20	5.14	4.66	5.46	0.94	4.58	0.79
	30	9.85	0.82	10.5	0.87	1.03	0.73
	40	8.23	1.56	9.55	0.92	1.45	0.64
	50	13.3	0.80	14.7	0.86	0.94	0.58

Table shows also water activities (a_w) at which water contents of plasticized and unplasticized films predicted by GAB equation are equal.

[a] Data from Talja et al. (2007).

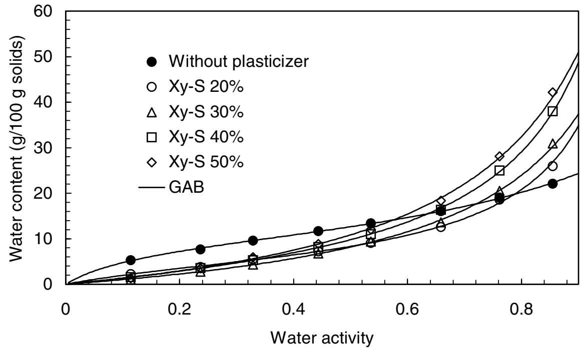

Fig. 2. Water sorption isotherms modelled with GAB equation for films plasticized with binary mixture of xylitol and sorbitol (Xy–S) at various contents ranging from 20% to 50% (the present study) and without plasticizer (Talja et al., 2007).

polymers could be predicted using water sorption isotherms of individual components. However, those predicted sorption isotherms often overestimated water contents as compared to actual ones because polar molecules probably interacted with biopolymers (Lewicki, 1997). Moreover, low water sorption of polyol plasticized biopolymer films has been observed at low water activities as was also shown in the present study. Reason for this is probably interaction between biopolymer and polyol which is creating steric hindrance against water adsorption coincidently with low affinity of polyols to bind water at low water activities (Godbillot, Dole, Joly, Rogé, & Mathlouthi, 2006; Kristo & Biliaderis, 2006; Talja et al., 2007).

3.2. Water vapor permeability

The effect of RVP on WVP of starch-based films was similar to its effect on water sorption. WVP of binary polyol plasticized films increased with increasing RVP as observed also in single polyol plasticized films (Talja et al., 2007). WVP of potato starch-based unplasticized film was generally higher than that of starch-based films plasticized with different binary polyol mixtures at all RVP gradients (Table 2). However, WVP of films plasticized at content of 50% Gly–Xy and Gly–S mixtures at the RVP gradient of 0/33% was higher than that of unplasticized film. Reason for the lower WVP of plasticized films compared to unplasticized film has been hypothesized to originate from hydrogen bonding between hydroxyl groups of polyols and starch which decreases free sorption sites for water in polyol plasticized films (Talja et al., 2007). WVP of films is dependent on both solubility coefficient and diffusion rate of water in film and they are dependent on partial pressure of water vapor (Kester & Fennema, 1986). In the present study, WVP of plasticized films increased with increasing plasticizer content as reported for biopolymer films in other studies (e.g., Chang, Cheah, & Seow, 2000; Cuq, Gontard, Aymard, & Guilbert, 1997; Talja et al., 2007). Generally, films plasticized with Gly–Xy and Xy–S mixtures at same contents had the highest and lowest WVP, respectively, at all RVP gradients. WVP of starch-based films at plasticizer content of 40% increased with decreasing T_g of film (Table 3) as observed also when single polyol plasticizers were used (Talja et al., 2007). Decrease in T_g was due to plasticization effect of binary polyol mixtures and water. WVP seemed to depend on T_g of binary polyol mixtures. WVP of films containing Gly–Xy and Gly–S was higher than that of films containing Xy–S. This could be explained by T_g of binary polyol mixtures used which was lower for mixtures containing glycerol than Xy–S. T_g values for anhydrous binary polyol mixtures (ratio of 1:1) have been reported to be −61 and −57 °C for Gly–Xy and Gly–S, respectively, and −15 °C for Xy–S (Talja, Roos, & Jouppila, 2003). Moreover, phase separation may occur in glycerol containing films resulting in slightly lowered WVP values.

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

Plasticizer		WVP (g mm d^{-1} m^{-2} kPa^{-1})		
Binary polyol mixture	Content (%)	0/33%	0/54%	0/76%
Without plasticizer[a]		1.06 ± 0.18	2.83 ± 1.44	3.00 ± 0.63
Gly–Xy	20	0.16 ± 0.01	0.50 ± 0.01	0.56 ± 0.08
	30	0.27 ± 0.06	0.54 ± 0.03	0.96 ± 0.04
	40	0.75 ± 0.11	1.29 ± 0.32	2.02 ± 0.47
	50	1.24 ± 0.14	2.21 ± 0.48	2.01 ± 0.20
Gly–S	20	0.36 ± 0.07	0.58 ± 0.06	0.78 ± 0.12
	30	0.19 ± 0.06	0.48 ± 0.13	1.15 ± 0.20
	40	0.54 ± 0.05	0.72 ± 0.09	1.41 ± 0.04
	50	1.12 ± 0.14	1.95 ± 0.05	2.07 ± 0.12
Xy–S	20	0.09 ± 0.05	0.26 ± 0.04	0.45 ± 0.04
	30	0.30 ± 0.00	0.43 ± 0.26	1.04 ± 0.73
	40	0.03 ± 0.03	0.44 ± 0.06	0.97 ± 0.22
	50	0.19 ± 0.03	0.79 ± 0.10	1.11 ± 0.12

[a] Data from Talja et al. (2007).

Table 3
Glass transition temperatures (T_g) for potato starch-based edible films plasticized with glycerol–xylitol (Gly–Xy), glycerol–sorbitol (Gly–S) and xylitol–sorbitol (Xy–S) at content of 40% (w/w of solids) at various RVP at 23.5 °C (mean value ± standard deviation from three measurements)

RVP (%)	T_g (°C)		
	Gly–Xy	Gly–S	Xy–S
33	−56.8 ± 2.2 (6.44)	−47.2 ± 2.0 (6.30)	−29.5 ± 1.2 (5.27)
54	−66.4 ± 0.8 (13.2)	−69.3 ± 1.4 (12.9)	−44.1 ± 1.0 (11.0)
76	−95.8 ± 4.0 (30.3)	−86.4 ± 2.2 (29.1)	−62.1 ± 2.0 (25.0)

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

3.3. Mechanical properties

Generally, binary polyol plasticized starch films behaved like viscoelastic materials. In the stress–strain curve obtained in the mechanical test there was first linear part (slope of which could be used in calculation of Young's modulus) followed by a curved part reaching a maximum stress (tensile strength) before or at break. Values of Young's modulus for films plasticized with binary polyol mixtures decreased with increasing plasticizer content and RVP (Fig. 3). Values of tensile strength changed concurrently with Young's modulus.

Effect of any binary polyol plasticizer at the content of 20% on elongation at break was similar at RVP of 33% and 54%. At these RVP, elongation of approximately 5% was observed for all films at plasticizer content of 20%. For all films at binary polyol content of 30%, elongation of 6–9% was observed at RVP of 33% (average water content 4.7%) (Fig. 3). Elongation of approximately 8% has been reported for corn starch films plasticized with glycerol and sorbitol at contents of around 20% and containing 5%

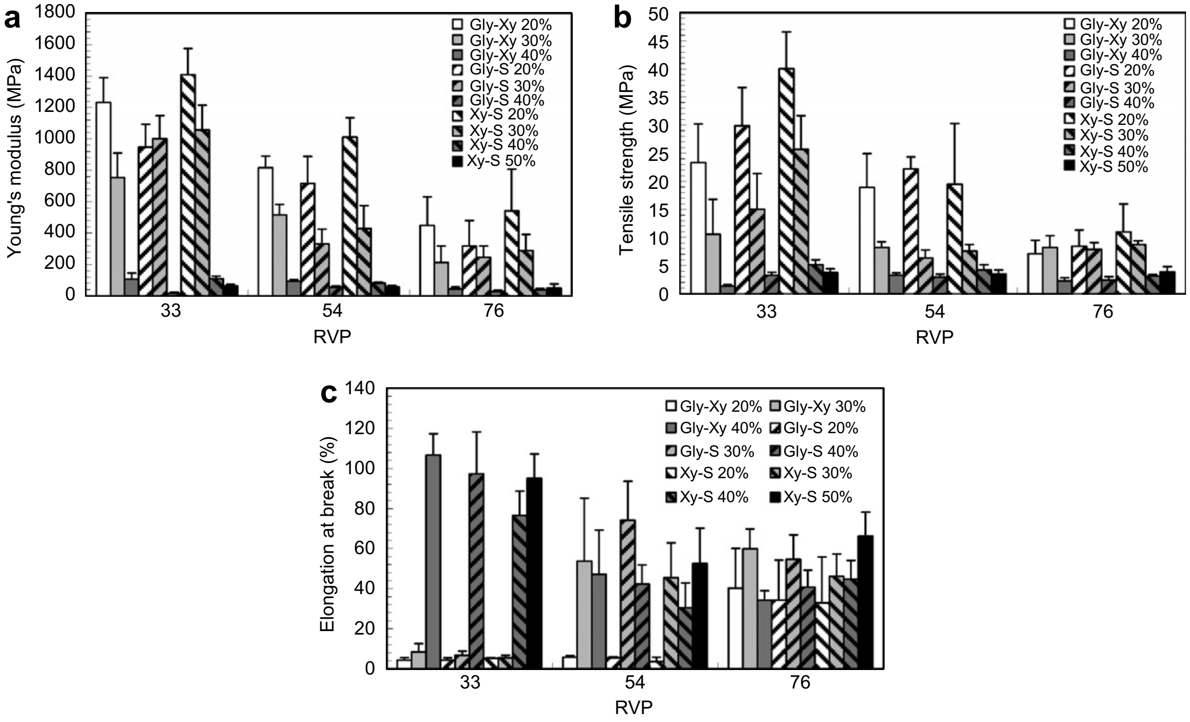

Fig. 3. Young's modulus (a), tensile strength (b) and elongation at break (c) for potato starch-based edible films plasticized with glycerol–xylitol (Gly–Xy), glycerol–sorbitol (Gly–S) and xylitol–sorbitol (Xy–S) at various contents and RVP at 23.5 °C.

water resulting in T_g of film being close to or slightly lower than storage temperature (Arvanitoyannis et al., 1996). Starch-pullulan films plasticized with sorbitol (10–20% w/w of solids) and containing water less than 9% showed maximum elongation of 4% and high Young's modulus and tensile strength values because the films were in the glassy state (ambient temperature below T_g) (Biliaderis et al., 1999). Elongation of starch-pullulan films increased remarkably as water content increased because of change from glassy to rubbery state (Biliaderis et al., 1999). In the present study, low elongation and high Young's modulus and tensile strength observed for films at plasticizer contents of 20% and 30% at RVP of 33% and for films at plasticizer content of 20% at RVP of 54% (Fig. 3) resulted most probably from low T–T_g values or glassy state of films. In all films at plasticizer contents of 20% and 30% elongation at break increased remarkably as RVP increased from 33–54% to 76% and from 33% to 54–76%, respectively, due to plasticization by water. Similar behavior has been also reported in other studies (e.g., Biliaderis et al., 1999; Mehyar & Han, 2004; Talja et al., 2007). Effect of binary polyol plasticizers on elongation at break was largest for Gly–Xy and smallest for Xy–S mixtures at fixed starch-plasticizer ratio at any RVP. Low elongation at break is characteristic for materials with brittle fracture (Cuq et al., 1997). Elongation at break value could increase even if biomaterial is in the glassy state. Brittle to ductile transition has been reported to occur in starch samples at water content of around 10% giving increased elongation at break values in mechanical testing even if starch samples were well in the glassy state (Nicholls, Appelqvist, Davies, Ingman, & Lillford, 1995). Moreover, T_g of 25 °C has been reported for amorphous amylopectin at water content of around 20% (Kalichevsky, Jaroszkiewicz, Ablett, Blanshard, & Lillford, 1992). Also, similar behavior of elongation at break has been shown for sorbitol plasticized pullulan films below their glass transition (Lazaridou, Biliaderis, & Kontogiorgos, 2003). Elongation at break of films was observed to range from 76% to 110% at plasticizer content of 40% at RVP of 33% whereas elongation ranged from 30% to 48% at RVP ranging from 54% to 76%, although elongation at break typically increases as RVP increases. Similar behavior of elongation was observed for films at the Xy–S content of 50% (Fig. 3). The reason for the structure of the film which do not stand big deformations at high RVP may be changes in interactions between starch, polyol and water. During water sorption amount of hydrogen bonds between starch–polyol and starch–starch decreased and more hydrogen bonds were formed between starch–water and polyol–water (Godbillot et al., 2006). On the other hand, decreased elongation at break could also be originated from increased starch crystallinity induced by high storage RVP as has been reported to occur in starch films (van Soest et al., 1996).

Young's moduli of films plasticized with a single polyol decreased with decreasing molecular weight of the polyol coinciding with an increase in elongation at break (Talja et al., 2007). An exception to this was film plasticized with xylitol in which crystallization of xylitol was observed to result in a concurrent increase in Young's modulus and decrease in elongation at the RVP of 54% and 76% (Talja et al., 2007). Polyol crystallization was not observed when binary polyol mixtures were used as plasticizers in starch-based films. Crystallization of sorbitol in maize starch-based films was not observed during 9 months of storage at 25 °C and RVP of 60% when used a binary polyol mixture of Gly–S (1:1) as a plasticizer at the contents of 33% and 50% (w/w, solids) (Krogars et al., 2003).

Crystallization of starch components was reported to occur during film formation resulting in increased Young's modulus and tensile strength (e.g., Rindlav-Westling, Stading, Hermansson, & Gatenholm, 1998). In the present study, endotherms probably related to melting of starch crystallites were observed in DSC thermograms recorded from the films plasticized by the binary polyol mixtures at the content of 40%. Similar melting endotherms have been reported for films prepared from blend of amylose and amylopectin (Rindlav-Westling, Stading, & Gatenholm, 2002) and potato starch-based films plasticized by polyols (Talja et al., 2007).

4. Conclusions

Elastic and flexible potato starch-based films plasticized with different binary polyol mixtures could be prepared successfully. Overall, the best properties of potato starch-based films produced in the present study were observed in Xy–S plasticized films. Such films were easy to handle and they were not sticky like Gly–Xy and Gly–S plasticized films at high plasticizer content and high water activities. Water sorption and WVP of potato starch-based edible films increased as a result of increased plasticization with binary polyol mixtures. Water sorption and WVP were lower for the films plasticized with Xy–S mixture compared to the films plasticized with Gly–Xy and Gly–S mixtures at constant plasticizer contents. Generally, the Young's modulus and tensile strength of the films decreased and elongation at break increased with increasing plasticization effect of the binary polyol mixture. However, elongation of films containing 40–50% plasticizer decreased with increasing RVP. Crystallization of polyols was not observed when binary polyol mixtures were used as plasticizers. These basic data on the effects of binary polyol mixture contents and water on the physical and mechanical properties of starch-based edible films are important in assessing applicability of starch-based edible films in food and pharmaceutical industries. Films studied in the present work are suggested to be suitable for low moisture foods and pharmaceutical products.

Acknowledgements

The study has been carried out with financial support from Tekes, the Finnish Funding Agency for Technology and Innovation, Plastiroll Ltd., Evijärven Peruna Ltd. and ABS graduate school.

References

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. In *Annual book of ASTM standards*. Philadelphia, PA: American Society for Testing and Material.

Bader, H. G., & Göritz, D. (1994). 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..

Biliaderis, C. G., Lazaridou, A., & Arvanitoyannis, I. (1999). Glass transition and physical properties of polyol-plasticised pullulan-starch blends at low moisture. *Carbohydrate Polymers, 40*(1), 29–47.

Bravin, B., Peressini, D., & Sensidoni, A. (2006). Development and application of polysaccharide–lipid edible coating to extend shelf-life of dry bakery products. *Journal of Food Engineering, 76*(3), 280–290.

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.

Cuq, B., Gontard, N., Aymard, C., & Guilbert, S. (1997). Relative humidity and temperature effects on mechanical and water vapor barrier properties of myofibrillar protein-based films. *Polymer Gels and Networks, 5*(1), 1–15.

Godbillot, L., Dole, P., Joly, C., Rogé, B., & Mathlouthi, M. (2006). Analysis of water binding in starch plasticized films. *Food Chemistry, 96*(3), 380–386.

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

Kalichevsky, M. T., Jaroszkiewicz, E. M., Ablett, S., Blanshard, J. M. V., & Lillford, P. J. (1992). The glass transition of amylopectin measured by dsc, dmta and nmr. *Carbohydrate Polymers, 18*(1), 77–88.

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

Kristo, E., & Biliaderis, C. G. (2006). Water sorption and thermo-mechanical properties of water/sorbitol-plasticized composite biopolymer films: Caseinate–pullulan bilayers and blends. *Food Hydrocolloids, 20*(7), 1057–1071.

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 composition 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.

Lawton, J. W. (1996). Effect of starch type on the properties of starch containing films. *Carbohydrate Polymers, 29*(3), 203–208.

Lewicki, P. P. (1997). Water sorption isotherms and their estimation in food model mechanical mixtures. *Journal of Food Engineering, 32*(1), 47–68.

Lazaridou, A., Biliaderis, C. G., & Kontogiorgos, V. (2003). Molecular weight effect on solution rheology of pullulan and mechanical properties of its films. *Carbohydrate Polymers, 52*(2), 151–166.

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

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

Mehyar, G. F., & Han, J. H. (2004). Physical and mechanical properties of high-amylose rice and pea starch films as affected by relative humidity and plasticizer. *Journal of Food Science, 69*(9), E449–E454.

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.

Nicholls, R. J., Appelqvist, I. A. M., Davies, A. P., Ingman, S. J., & Lillford, P. J. (1995). Glass transitions and the fracture behaviour of gluten and starches within the glassy state. *Journal of Cereal Science, 21*(1), 25–36.

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

Roos, Y., & Karel, M. (1990). Differential scanning calorimetry study of phase transitions affecting the quality of dehydrated materials. *Biotechnology Progress, 6*(2), 159–163.

Roos, Y., & Karel, M. (1991). Plasticizing effect of water on thermal behavior and crystallization of amorphous food models. *Journal of Food Science, 56*(1), 38–43.

Saravacos, G. D., & Stinchfield, R. M. (1965). Effect of temperature and pressure on the sorption of water vapor by freeze-dried food materials. *Journal of Food Science, 30*(5), 779–786.

Stading, M., Rindlav-Westling, Å., & Gatenholm, P. (2001). Humidity-induced structural transitions in amylose and amylopectin films. *Carbohydrate Polymers, 45*(3), 209–217.

Talja, R. A., Roos, Y. H., & Jouppila, K. (2003). Glass transition behavior of binary polyol mixtures. *IFT annual meeting*, July 13–16, Chicago, IL, USA. Abstract 60A-27.

Talja, R. A., Helén, H., Roos, Y. H., & Jouppila, K. (2007). Effect of various polyols and polyol contents on physical properties of potato starch-based films. *Carbohydrate Polymers, 67*(3), 288–295.

Tuovinen, L., Peltonen, S., & Järvinen, K. (2003). Drug release from starch-acetate films. *Journal of Controlled Release, 91*(3), 345–354.

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.