Preparation and characterization of potato starch films plasticized with polyols

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ACADEMIC DISSERTATION

To be presented, with the permission of the Faculty of Agriculture and Forestry of the University of Helsinki, for public criticism in the lecture room B2, Viikki, Helsinki on December 5th, 2007, at 12 o'clock noon.

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Abstract

The present study investigated the potato starches and polyols which were used to prepare edible films. The amylose content and the gelatinization properties of various potato starches extracted from different potato cultivars were determined. The amylose content of potato starches varied between 11.9 and 20.1%. Onset temperatures of gelatinization of potato starches in excess water varied independently of the amylose content from 58 to 61°C determined using differential scanning calorimetry (DSC). The crystallinity of selected native starches with low, medium and high amylose content was determined by X-ray diffraction. The relative crystallinity was found to be around 10–13% in selected native potato starches containing 13–17% water. The glass transition temperature, crystallization melting behavior and relaxations of polyols, erythritol, sorbitol and xylitol, were determined using (DSC), dielectric analysis (DEA) and dynamic mechanical analysis (DMA). The glass transition temperatures of xylitol and sorbitol decreased as a result of water plasticization. Anhydrous amorphous erythritol crystallized rapidly. Edible films were obtained from solutions containing gelatinized starch, plasticizer (polyol or binary polyol mixture) and water by casting and evaporating water at 35°C. The present study investigated effects of plasticizer type and content on physical and mechanical properties of edible films stored at various relative water vapor pressures (RVP). The crystallinity of edible films with low, medium and high amylose content was determined by X-ray diffraction and they were found to be practically amorphous. Water sorption and water vapor permeability (WVP) of films was affected by the type and content of plasticizer. Water vapor permeability of films increased with increasing plasticizer content and storage RVP. Generally, Young's modulus and tensile strength decreased with increasing plasticizer and water content with a concurrent increase in elongation at break of films. High contents of xylitol and sorbitol resulted in changes in physical and mechanical properties of films probably due to phase separation and crystallization of xylitol and sorbitol which was not observed when binary polyol mixtures were used as plasticizers. The mechanical properties and the water vapor permeability (WVP) of the films were found to be independent of the amylose content.

Preface

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Helsinki, November 2007

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Contents

List of original publications

This thesis is based on the following original publications, which are referred to by their Roman numbers I–IV:

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

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

III Talja R.A., Helén H., Roos Y.H. and Jouppila K. (2007). Effects of type and content of binary polyol mixtures on physical and mechanical properties of starch-based edible films. *Carbohydrate Polymers.* In press. doi: 10.1016/j.carbpol.2007.05.037

IV Talja R.A., Peura M., Serimaa R. and Jouppila K. (2007). Effects of amylose content on physical and mechanical properties of starch-based edible films. *Biomacromolecules.* Accepted.

Abbreviations

ANOVA	analysis of variance
a_w	water activity
B1	Bulk 2002 (potato cultivar and year grown)
BET	Brunauer-Emmett-Teller
Con A	concanavalin A
DEA	dielectric analysis
ΔH	melting or gelatinization enthalpy
DMA	dynamic mechanical analysis
DMSO	dimethyl sulphoxide
DSC	differential scanning calorimetry
ε'	permittivity
ε''	loss factor
E'	storage modulus
E''	loss modulus
GAB	Guggenheim-Anderson-de Boer
Gly-Xyl	binary mixture of glycerol and xylitol
Gly-Sor	binary mixture of glycerol and sorbitol
GP	gas permeability
K1	Kardal 2002 (potato cultivar and year grown)
K2	Kardal 2003 (potato cultivar and year grown)
m_m	monolayer water content
P1	Posmo 2002 (potato cultivar and year grown)
P2	Posmo 2003 (potato cultivar and year grown)
RVP	relative vapor pressure
Sa1	Saturna 2002 (potato cultivar and year grown)
Sa2	Saturna 2003 (potato cultivar and year grown)
Se1	Seresta 2003 (potato cultivar and year grown)
$tan\delta$	ratio of ε'' to ε' or E'' to E'
T_g	glass transition temperature
T_c	crystallization temperature
T_m	melting temperature
V1	Van Gogh 2002 (potato cultivar and year grown)
WVP	water vapor permeability
XRD	X-ray diffractometry
Xyl-Sor	binary mixture of xylitol and sorbitol

1 INTRODUCTION

The need for new environmentally friendly packaging materials increases constantly. Thus the suitability of biomaterials, especially biopolymers, for film production has been intensively studied. Biomaterial films can be edible or inedible depending on the raw materials, preparation process and end use. Typical biopolymers used to prepare edible films are cereal proteins and polysaccharides including starch, milk proteins, root and tuber starches. An advantage of biopolymer films is that they are generally biodegradable and also renewable, thus they could reduce environmental load. However, synthetic packaging materials can not be replaced fully by biomaterials because they the former better mechanical properties.

A function of food packaging is to preserve food through transportation from the production plant to the market and the consumer. To achieve this it should protect the contents from outside environmental effects. Physical damage to the food could result from dropping or compression in the warehouse, during transportation or in the home (Robertson, 1993). Food products could be damaged due to ambient environmental effects such as water, gases, light, odor or micro-organisms unless appropriate packaging is used (Robertson, 1993). Biopolymer based packaging is not able to protect food products from all outside environmental effects because of relatively poor mechanical properties and high hydrophilicity. It is able to protect from some of the environmental effects when used together with other packaging materials, *e.g.*, by coating cardboard with biopolymers, gas barrier properties of cardboard-based package can be enhanced.

Many food products are sensitive to ambient environmental effects which may dramatically decrease quality and shelf-life. It may be possible to improve food quality and shelf-life by coating low moisture food products with biomaterial based coatings. These coatings prevent or retard water transfer from surrounding atmosphere to the food products. This is important because water may initiate deteriorative changes in foods, like crystallization of amorphous materials, collapse or stickiness of low moisture food components and increase micro-organism activity (Roos, 1995). Edible films can be used as barriers or retarders of water sorption of low moisture products, *e.g.*, crackers (Bravin *et al.*, 2006). Biomaterial film may be used to separate layers having different water activities retarding water transfer from one layer to the other (Guillard *et al.*, 2003). For example, a crispy layer with a low moisture content can adsorb water from moist layer resulting in loss of crispness. This same technique could be used to prevent oil transfer between different layers. Film coatings may be a barrier for oxygen decreasing oil or fat oxidation in the food products. Film coatings may also be used as a barrier for oil uptake in deep fat frying (Holownia *et al.*, 2000) and, thus, contribute to combating obesity.

Edible films may also be used as a carrying agent for antimicrobial or functional substances, such as additives, aroma compounds or coloring agents (Han, 2002). Edible film coating with encapsulated antimicrobial substances can retard growth of micro-organisms on the surface of food product (Ko *et al.*, 2001). For example, one commercially available application of edible films is as breath freshening film stripes. Aroma compounds are added into these film stripes and they are released as they get moisture from the mouth thus freshening breath.

Edible films have also an important role in pharmaceutical applications. Film coatings are used to enhance mechanical handling properties of pharmaceutical solids preventing disintegration. Differently dyed films may be used to improve identification of pharmaceutical solids and colorless films could be used to increase gloss of pharmaceutical solids. It also possible to mask the taste of a pharmaceutical by film coating. This kind of film or coating may be used with or without aroma compounds. Edible films can be used to control drug release (Tuovinen *et al.*, 2003).

The properties of biomaterial films are studied with various techniques to obtain information which may be used to predict quality and stability of food products and pharmaceutical solids. Water sorption and water vapor permeability are studied to model interactions between biomaterial films and water. Information about mechanical properties of biomaterial films is needed especially if they are used to improve mechanical handling properties of solid food and pharmaceutical products. Knowledge of the structure of the films can help understand the changes occurring in films.

The literature review in the present study discusses the materials used to prepare edible films and the properties usually measured to characterize the edible films.

2 LITERATURE REVIEW

2.1 Film forming materials

Film forming materials, such as starches, proteins and polyols, are used for different purposes in a biomaterial and/or edible film preparation process. Biopolymers like starches and proteins create the basic network structure of the film. However, films prepared from biopolymers are often too fragile to stand handling, *e.g.*, bending or stretching. Thus, they have to be plasticized using low molecular weight substances, such as polyols, which decrease interactions between the biopolymer chains. Due to plasticization better handling properties may be obtained whereas other properties, such as water sorption, gas permeability and mechanical properties, may weaken.

Biopolymers used in film preparation are often carbohydrates or proteins extracted or separated from plants, animal tissues or animal products. The storage carbohydrate in plants is starch. Depending on the plant the starch is formed in different parts of the plant, *e.g.*, grain, tuber or root (Banks and Greenwood, 1975). Other carbohydrates found in the plants *e.g.* the cell wall include cellulose and pectin (MacDougall and Ring, 2004). Some carbohydrates, such as alginate and carrageenan, are found in seaweeds (Ramsden, 2004). Cereal grains contain, in addition to starch, protein, such as gluten (wheat) and zein (maize) (Bergthaller, 2004). Biopolymers extracted from animal products or parts are also used in edible film manufacturing. Casein and whey proteins are separated from milk and they are often used to prepare films (McHugh and Krochta, 1994a). Gelatin is a derivative of collagen a protein which can be extracted from animal skin or bones (Arvanitoyannis, 2002). Gelatin may be used to produce edible film, *e.g.*, for food preservation and pharmaceutical capsules (Arvanitoyannis, 2002).

Out of all of the film forming materials mentioned in this section, this literature review focuses mainly on the starch and polyols. Water is not discussed directly as a plasticizer in this thesis since plasticizing effect of water is not as simple as it is for polyols. The content of polyol in starch is easy to control but the water content in the film changes with RVP and thus is not as easy to control.

2.1.1 Starch

Native starch, which occurs in a granular form, is one of the main carbohydrate resources found in cereal and tuber plants, such as maize and potato, respectively. The main components of starch are linear amylose and highly branched amylopectin composed of glucose units via α-1,4 bonds (Blanshard, 1987). Amylopectin contains
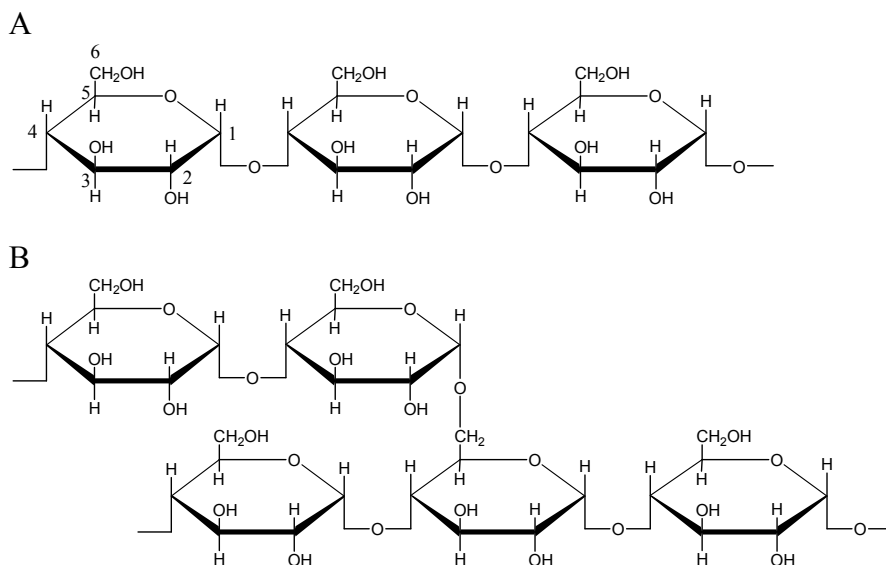
A

B

Figure 1. Molecular structures of the amylose (A) and the amylopectin (B). Numbers (1–6) in the first glucose unit of the amylose show numbering of carbon atoms in glucose molecule.

also 2–4% branching points (Wang *et al.*, 1998) formed by α-1,6 bonds on the main backbone and other branches (Blanshard, 1987) (**Figure 1**). The molecular weight of amylose and amylopectin varies between botanical sources of starch. For example, weight average molecular weights of 2×10^6 g mol^{-1} and 20×10^6 g mol^{-1} determined by light scattering have been reported to amylose extracted from maize and potato, respectively and correspondingly, values of 112×10^6 g mol^{-1} and 61×10^6 g mol^{-1} have been reported to amylopectin of maize and potato, respectively (Aberle *et al.*, 1994).

The way amylose and amylopectin are arranged in the starch granule has been studied and reviewed by several authors. Starch granules contain growth rings composed of semi-crystalline and amorphous zones (Jobling, 2004). In semi-crystalline zones amylopectin forms lamellar structure consisting of crystalline, ordered double helical structures and rigid amorphous branching zones (Gallant *et al.*, 1997). Some of the amylose may be a part of these amylopectin double helices (Jenkins and Donald, 1995). Amorphous zones in starch granules are composed of random ordered amylose and amylopectin (Jobling, 2004). However, it has been shown that amylose molecules can form a double helical structure in maize starch containing high amount of amylose (Tester *et al.*, 2000). The native starch has three crystalline polymorphs A, B or C-type depending on the origin of starch. A-type polymorph appears in cereal starches whereas B-type polymorph appears mostly in potato and other tuber starches (Banks and Greenwood, 1975). For example, C-type polymorph appears in the pea starch, which contains both A- and B-type polymorphs in the same native starch granule (Bogracheva *et al.*, 1998). A- and B-type polymorphs differ from each other by packing of double

helical structures where more dense packed double helices form A-type polymorphs and less dense packed double helices form B-type polymorphs (Blanshard, 1987).

The ratio of amylose and amylopectin in the starch may affect starch behavior in processing and properties of the end product. Starch gelatinization properties and swelling of granules (Biliaderis *et al.*, 1986; Cottrell *et al.*, 1995) as well as pasting properties (Cottrell *et al.*, 1995; Jane *et al.*, 1999) have been shown to be affected by amylose content. According to Jane (2004) the temperature range at which starch granules lose their ordered structure in the presence of excess water is the gelatinization temperature. On heating above this temperature viscosity develops a process which is called pasting. Crystallinity in native starch has been shown to correlate with amylose content an increase of which decreases crystallinity of native starch (Cheetham and Tao, 1998). The amylose and amylopectin ratio in the starch may affect the properties of starch-based products. A high amylose content of starch may increase crystallinity of starch-based products, which is seen as firming of texture. Moreover, texture of starch-based products is hardened by fast crystallization of amylose during cooling and slow crystallization of amylopectin during storage as reviewed by Biliaderis (1992).

There are also small quantities of other components in starch, such as minerals, proteins and lipids, which generally have minor effect on starch properties (Tester *et al.*, 2004). One exception to this is phosphorous and its derivatives found in starches, especially in potato starch. Increasing phosphorous content increases the peak viscosity of starch water mixtures but decreases final viscosity (Liu *et al.*, 2003b; Jane, 2004). Moreover, the phosphorous increases water uptake of starch as reviewed by Blennow *et al.* (2002). Potato starch contains higher amounts of phosphorous than other starches (Jane, 2004). The majority of the phosphorous is bound to amorphous zone of amylopectin after every 100 glucose units either carbon 3 or 6 (Blennow *et al.*, 1998, 2000).

Starch granules are insoluble in cold water. When heated in excess water starch granules swell and the ordered structure is disrupted at gelatinization temperature range resulting in an increase in viscosity (Biliaderis *et al.*, 1980). Bogracheva *et al.* (2006) have shown using the light microscopy that the swelling and disruption of starch granule start from the hilum area, which is the less ordered area near the center, of the granule. Swelling of the granule results from water adsorption in the amorphous region of the starch granule (Bogracheva *et al.*, 2002). During the swelling of the granule more amorphous regions come available for water adsorption increasing the swelling followed by disruption of ordered structures. On heating crystalline areas are melted the melting temepature depending on the water content (Biliaderis *et al.*, 1980). In excess water the crystalline structure of the potato starch has shown to disappear completely during the gelatinization process (Liu *et al.*, 2003a; Vermeylen *et al.*, 2006). In the gelatinization process agitation or mixing is needed to maximize amylose and amylopectin leaching into water. The reason for this is that water adsorption is interrupted into the granule

because granules become surrounded by concentrated regions of leached amylose (Bogracheva *et al.*, 2006). This also prevents amylose and amylopectin diffusion from granule into water phase resulting in partly gelatinized granules (Bogracheva *et al.*, 2006). Starch gelatinization is needed to obtain the starch gel, macromolecular network structure, which is formed during cooling of gelatinized starch.

In starch systems with a high water content crystallization, often called retrogradation, takes place during storage (Lionetto *et al.*, 2005). The retrogradation involves two processes: firstly rapid formation of the double helical chain segments of amylose which form helix-helix aggregates, crystallites and secondly slow amylopectin crystallization which may take weeks (Miles *et al.*, 1985b). Miles *et al.* (1985a) have reported that increasing amylose concentration increases the crystallinity of the amylose gel. Moreover, Miles *et al.* (1985a) reported that crystallization rate increases with amylose concentration in amylose gels. The network structure in amylose gels developed more rapidly than the crystallinity (Miles *et al.*, 1985a).

2.1.2 Polyol

Polyols (polyalcohols) are low molecular weight carbohydrates which are used in food, non-food, health care and pharmaceutical applications. They are increasingly used to provide the sweetness of various products or replace sucrose in confectionery. Polyols are used in chewing gum, because they do not contribute to development of dental caries and they neutralize pH in the mouth. Moreover, polyols are also used as plasticizers in the edible films.

Commonly, polyols are produced by the hydrogenation process in which hydrogen is added to the carbonyl group of saccharides (Whistler and BeMiller, 1997). Depending on the starting materials of the hydrogenation process polyols are divided into three categories which are hydrogenated monosaccharides, hydrogenated disaccharides and mixtures of hydrogenated polysaccharides (Embuscado, 2006). The hydrogenation process of monosaccharides, such as D-glycerose, D-xylose, D-glucose and D-mannose, yields glycerol, xylitol, D-glucitol (sorbitol) and mannitol, respectively, and correspondingly the hydrogenation process of disaccharides, such as maltose or lactose, yields maltitol and lactitol, respectively (Whistler and BeMiller, 1997). Erythritol is the first polyol to be produced by an entirely biotechnological process (Goossens and Gonze, 2000). In this process glucose obtained by enzymatic hydrolysis from starch or sugar is biochemically fermented to produce erythritol using yeast or fungus (Goossens and Gonze, 2000).

Table 1. Characteristic properties of various monosaccharide- and disaccharide-based polyols: molecular weight (M_w, g mol^{-1}), onset of the glass transition (T_g, °C) and melting (T_m, °C) temperatures, T_m/T_g ratio and melting enthalpy (ΔH, J g^{-1}).

Polyol	M_w[a]	T_g	T_m	T_m/T_g[b]	ΔH	Reference
Monosaccharide-based						
Glycerol	92	–86	-	-	-	Murthy (1996)
Erythritol	122	–45[c]	118	1.71	323	Barone et al. (1990)
Xylitol	152	–29	95	1.51	226	Roos (1993)
Sorbitol	182	–9	99	1.41	154	Roos (1993)
Mannitol	182	11[d]	167–170	1.53	-	Yu et al. (1998)
Disaccharide-based						
Maltitol	344	39	149	1.35	147	Roos (1993)
Lactitol	344	50	-	-	-	Jouppila et al. (2007)

[a] Calculated from molecular structures presented in Whistler and BeMiller (1997).
[b] Calculated in Kelvins.
[c] The T_g from the present study (I).
[d] Extrapolated value by Yu et al. (1998).

Most of the polyols, such as erythritol, xylitol and sorbitol, appear as crystalline powders which have their characteristic melting temperatures, whereas glycerol is a melt. When polyols, such as xylitol and sorbitol, are heated above their melting temperature (T_m) and quench cooled, amorphous melts are obtained (Roos, 1993). The glass transition temperature (T_g) may be determined for these anhydrous amorphous polyol melts. The glass transition occurs over the glass-rubber transition region and results in dramatic drop of modulus and change in molecular mobility (Roos, 1995). Onset, midpoint or endset temperature of temperature range over which glass transition

occurs can be taken as T_g. A characteristic of monosaccharide-based polyols is that their T_g are below room temperature, whereas T_g of disaccharide-based polyols are generally above room temperature (**Table 1**). Moreover, polyols could be plasticized by water or another low molecular weight carbohydrate resulting in a decreased T_g (Slade and Levine, 1991; Roos, 1993).

The tendency of polyols to crystallize can be estimated by the ratio of T_m and T_g (T_m/T_g). Generally, polyols with a high T_m/T_g ratios are readily crystallizable (Slade and Levine, 1991). Amorphous polyols having a high tendency to crystallize may be mixed with other polyols or low weight carbohydrates to retard or even inhibit crystallization. In confectionery products mixture of sugars may be used to retard or prevent the crystallization of sucrose (Roos and Karel, 1991a; Roos, 1995).

Monosaccharide-based polyols, such as glycerol and sorbitol, are widely used as plasticizers in edible film applications because of their plasticization ability due to their low molecular weights. Plasticizer is added to the film to give better handling properties

like flexibility and elasticity. Plasticizer decreases interactions between biopolymer chains, such as amylose and amylopectin, thus preventing their close packing which results in lower degree of crystallinity in the film (García *et al.*, 2000). Pores and cracks in the film could be also prevented by using plasticizers (García *et al.*, 2000). Polyols are good plasticizers because of their low molecular weight and T_g. Generally, the lower the T_g of the plasticizer the less it will be needed to obtain plasticized film. This is fairly important because at the high plasticizer content phase separation of the plasticizer may occur.

2.2 Biopolymer films

2.2.1 Film formation processes

Most biopolymers are hydrophilic and, thus, water is the solvent used most often to dissolve biopolymers to obtain film forming solutions. Instead of water some other solvents with or without water can be used to dissolve biopolymers. Usually, heating with solvent is needed to disrupt the native structure of the biopolymer to obtain a film forming solution. Plasticizer is added to the film forming solution at a convenient stage of the process to obtain flexible and elastic films which are often desired.

There are various biomaterial film forming processes such as casting, spraying, extrusion and thermo-molding. The most common process to produce films on a laboratory scale is casting, which is used to produce free films for testing. In this process, a film forming solution is cast on a non-adhesive surface. Water or solvent is evaporated from the solution in order to form the film (*e.g.*, Anker *et al.*, 2001; Lazaridou and Biliaderis, 2002; Rindlav-Westling *et al.*, 2002). As a result of solvent evaporation, biopolymer inceases with the result that hydrogen bonds are formed and basic film structure is created. Environmental properties, such as temperature and air relative humidity, during the evaporation stage could be used to control some of the film properties (Rindlav *et al.*, 1997; Rindlav-Westling *et al.*, 1998; Kawahara *et al.*, 2003). One application of casting is dipping, in which a product is dipped into the film forming solution to obtain a coating (Holownia *et al.*, 2000; Cisneros-Zevallos and Krochta, 2003). In the spraying process a film forming solution is sprayed onto a surface of product on which droplets formed by a sprayer form uniform films. In spraying, solvent evaporates to some extent after leaving the nozzle of the sprayer allowing a shorter drying time for coating. Even if film formation occurs in a different way in casting and spraying processes the same starch-based film forming solution could be used in casting (Krogars *et al.*, 2003c) and spraying (Krogars *et al.*, 2003a). Continuous film forming can be carried out using extrusion which is widely used to produce synthetic polymer films. Extrusion has been used to produce films or sheets from starch (van Soest and

Knooren, 1997), wheat gluten (Hochstetter *et al.*, 2006) and mixtures of proteins and carbohydrates (Talja *et al.*, 2007). In thermo-molding film forming materials, which are mixed with blender or extruder, are pressed between two heated plates to obtain films (Arvanitoyannis *et al.*, 1998; Thunwall *et al.*, 2006).

A starch film forming solution is prepared by heating to gelatinize starch in excess water in which plasticizer is added before gelatinization (Mathew and Dufresne, 2002; Mehyar and Han, 2004) or after gelatinization into the hot solution (95°C) (Krogars *et al.*, 2002). In some studies film forming suspension containing native starch, amylose, amylopectin or mixture of amylose and amylopectin is heated in a pressurized vessel to complete amylose and amylopectin leaching into the solution (Rindlav-Westling *et al.*, 2002; Mathew and Dufresne, 2002; Myllärinen *et al.*, 2002a). After gelatinization, the film forming solution is poured onto a non-adhesive plate, such as polytetrafluoroethylene (teflon®). Water is evaporated from the film forming solution to obtain films at various conditions, *e.g.*, at the room temperature at the controlled RVP conditions (Rindlav-Westling *et al.*, 2003; Mehyar and Han, 2004) or in an oven at elevated temperatures (Mathew and Dufresne, 2002; Myllärinen *et al.*, 2002a; Mali *et al.*, 2006). These different drying conditions affect film properties because of different settling times of biopolymers. The longer the film formation takes the longer time there is for a film component to phase separate and crystallize. Rindlav-Westling *et al.* (2003) have reported small and less aggregated amylose phases in the starch film for shorter drying times. Films prepared from starch or starch with added amylopectin resulted in a phase separated structure in the film (Rindlav-Westling *et al.*, 2002). Moreover, structure of film prepared using starch with added amylose was more homogeneous, but crystallinity of films was higher than that of film produced from starch only (Rindlav-Westling *et al.*, 2002).

2.2.2 Water sorption

Water sorption may be either adsorption or desorption (Roos, 1995). Water adsorption of the hydroscopic material can occur when the vapor pressure of water in the atmosphere is higher than vapor pressure of water in the material and oppositely as water desorption occurs (Roos, 1995). Water sorption of the material can be modeled using sorption isotherm (**Figure 2**), which shows the amount of sorbed water as a function of RVP at a constant temperature (*e.g.*, Roos, 1995). Water activity (a_w), which is, *e.g.*, a property of aqueous solutions, is defined as the ratio of the vapor pressures of pure water (p_w) and solution (p_s) ($a_w = p_s/p_w$) (deMan, 1999). Moreover, the relationship
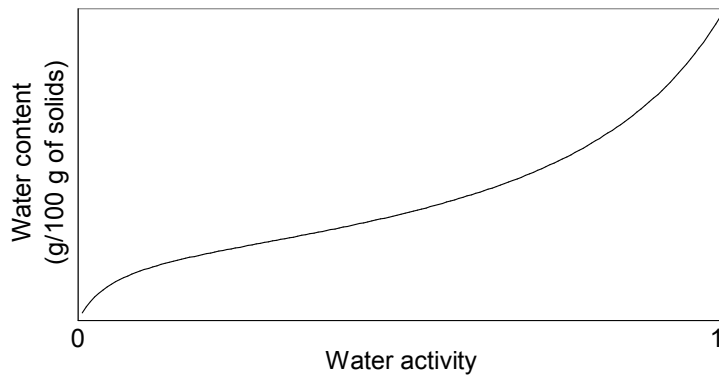
Figure 2. Typical, sigmoid sorption isotherm of a food system and biomaterial film.

between a_w and relative vapor pressure (RVP) at equilibrium can be presented as follows a_w=RVP/100 (Bell and Labuza, 2000). The water sorption of the material increases with increasing a_w or RVP. Water sorption isotherm of most foods (Bell and Labuza, 2000) and biomaterial films (*e.g.*, Myllärinen *et al.*, 2002b; Kristo and Biliaderis, 2006) is a sigmoid curve as shown in **Figure 2**. Two bends are noted in this type of isotherm: one around an a_w of 0.2–0.4 and another at 0.65–0.75, which result from changes in the magnitude of the separate physical chemical effects (Bell and Labuza, 2000). deMan (1999) has suggested the rough division of the dominating events in water sorption isotherm separated by the two bends observed: the first part before the first bend describes the adsorption of the monolayer of the water; the second flatter part before the second bend corresponds to adsorption of additional layer of water; in the third part after the second bend condensation of water in capillaries and pores of the material dominates.

Water sorption is a characteristic property of material, *e.g.*, food system or biomaterial film, depending on material composition. Water may affect the physical state and stability of the material (Roos, 1995) and, thus, knowledge of water sorption is essential. Amorphous materials may be plasticized by water resulting in increased molecular mobility and loss of their stability. For example, crystallization of lactose in amorphous milk powders occurs during storage at RVP of 44% or above, which may be observed from the loss of adsorbed water (Jouppila and Roos, 1994). This may be explained by the fact that crystalline materials, such as sugars, adsorb water only at crystallite surface (Bell and Labuza, 2000). At very high RVP, crystals can be dissolved by adsorbed water, which is seen as a steep increase in the sorption isotherm. In the presence of biopolymers, soluble amorphous low molecular weight solids, such as sugars and minerals, have been reported to adsorb very little water at low RVP, whereas biopolymers are mainly responsible for water sorption (Saravacos and Stinchfield, 1965).

Usually, biopolymers are hydrophilic and they are plasticized with hydrophilic low molecular weight carbohydrates, such as polyols. Polyols have a different tendency to adsorb water which depends on the molecular weight and number of hydroxyl groups present (Mathew and Dufresne, 2002). Moreover, it has been proposed that the end hydroxyl groups of the backbone of polyols are the most accessible to bind water and also interact with starch molecules (Mathew and Dufresne, 2002). For example glycerol, xylitol and sorbitol has three, five and six carbon atoms on their backbone, respectively, and one hydroxyl group attached on each carbon. This leads to the fact that there are two end hydroxyl groups from all of the three, five and six hydroxyl groups of the glycerol, xylitol and sorbitol, respectively. According to this glycerol binds the highest amount of water as corresponding weight portions of these polyols are stored at the same conditions. One glucose monomer of starch is able to bind 0.7 to 1 molecule of water at the water activity corresponding to the monolayer water content (van den Berg *et al.*, 1975). One could assume that water sorption of polyol plasticized starch film is the sum of water sorption of the individual components. However, the starch films plasticized with polyols have been shown to adsorb less water than films without plasticizer up to water activities around 0.6 (Myllärinen *et al.*, 2002a; Kristo and Biliaderis, 2006). Polyol plasticized materials show a steep increase in water sorption at water activities around 0.6 because water sorption affinity of polyol increases (Biliaderis *et al.*, 1999). Lewicki (1997) suggested that water sorption behavior of mixtures of low molecular weight polar molecules and biopolymers 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; Enrione et al., 2007a). The 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 *et al.*, 2006; Kristo and Biliaderis, 2006). Hartley et al. (1995) have stated that prediction of water partitioning in a sample can not be estimated directly from sorption isotherms of the pure components.

2.2.3 Thermal properties

Depending on the physical state of the material, either glassy or rubbery state, its properties may be significantly different (Roos, 1987; Roos and Karel, 1991a). The glass transition of the material is a change, in which the material turns from the glassy to rubbery state gradually during heating. The glass transition of the material could be decreased by adding plasticizer. The glassy film is brittle, *i.e.,* it breaks at small deformations. In contrast in the rubbery state the film is elastic and better able to stand handling, such as bending and stretching.

Table 2. The glass transition temperature (T_g; °C) for various biomaterial films with varying biopolymer/plasticizer ratio and water content determined using DSC or DMA techniques.

Composition of the film			Water	T_g	Tech.	Reference
Biopolymer	Plasticizer	Ratio				
Polysaccharide						
Tapioca starch	Without	100/0	12.1	165	DSC	Chang *et al.* (2000)
Corn starch	Glycerol	83/17	10.9	35	DSC	Mali *et al.* (2006)
Corn starch	Glycerol	80/20	5	3	DMA[a]	Arvanitoyannis *et al.* (1996)
Waxy maize starch	Glycerol	67/33	7.7	–48, 27	DSC	Mathew and Dufresne (2002)
Cassava starch	Glycerol	67/33	33	–62, –30	DMA[a]	Famá *et al.* (2007)
Waxy maize starch	Xylitol	67/33	7.7	–40	DSC	Mathew and Dufresne (2002)
Corn starch	Sorbitol	71/29	5	–19	DMA[a]	Arvanitoyannis *et al.* (1996)
Waxy maize starch	Sorbitol	67/33	7.7	–7	DSC	Mathew and Dufresne (2002)
Galactomannan	Glycerol	60/40	11.5	–61	DMA[b]	Mikkonen *et al.* (2007)
Galactomannan	Sorbitol	60/40	10.6	–13	DMA[b]	Mikkonen *et al.* (2007)
Protein						
Gluten	Glycerol	73/27	18.7	–62, –5	DMA[a]	Cherian *et al.* (1995)
Whey protein isolate	Glycerol	68/32	22	–56	DMA[a]	Anker *et al.* (2001)
Whey protein isolate	Glycerol	67/33	39	–82	DSC	Shaw *et al.* (2002)
Whey protein isolate	Xylitol	67/33	20	–49	DSC	Shaw *et al.* (2002)
Whey protein isolate	Sorbitol	67/33	21	–38	DSC	Shaw *et al.* (2002)
Whey protein isolate	Sorbitol	55/45	9.1	–14	DMA[a]	Anker *et al.* (2001)
Whey protein isolate	Glycerol	80/20	5	60	DSC	Lawton (2004)
Whey protein isolate	Glycerol	60/40	5	50	DSC	Lawton (2004)
Polysaccharide/Protein						
Chitosan/Corn starch	Sorbitol	35/35/30	11.2	20	DMA[a]	Lazaridou and Biliaderis (2002)

[a] taken from the maximum of *tanδ* peak at 1 Hz;
[b] taken from the maximum of *E″* peak at 1 Hz;

The T_g of the film can be determined by the composition of the film. An increasing molecular weight of the molecule increases the T_g (Sperling, 1992). Increasing portions of the low molecular weight carbohydrate plasticize the blend consequently decreasing the T_g, which can be modeled using the Gordon-Taylor equation (**Equation 1** see chapter 4.3.2) (Gordon and Taylor, 1952). Generally, the T_g of the blend is dependent on the T_g of the biopolymer and the low weight carbohydrate. The T_g of the blend may be somewhere between the glass transition temperatures of the biopolymer and low molecular weight carbohydrate depending on their proportions. The T_g of anhydrous amorphous starch has been reported to be around 240°C (Biliaderis *et al.*, 1986; Roos and Karel, 1991b) whereas polyols have significantly lower T_g values, for the most of them below room temperature as presented in **Table 1**. One T_g should be obtained for the homogeneous blend whereas the blend with phase separated fractions may show own T_g for the fractions.

Table 2 shows some T_g values of biopolymer films plasticized by polyols. Generally, films plasticized with glycerol have markedly lower T_g than that of films plasticized with sorbitol or xylitol. Moreover, increasing plasticizer content in the films decreased the T_g (**Table 2**). The T_g of the hydrophilic film is also affected by water the T_g of which was −135°C as reported by Johari *et al.* (1987). Plasticizing effect of water on the biopolymer films can also be seen in **Table 2** in which T_g values of films with the same plasticizer with higher water content are lower than films with lower water content. Measuring technique affects the T_g value obtained. In the DSC measurement a gradual baseline shift is observed between the onset and endset of the glass transition. The DMA analysis is carried out using various frequencies and α-relaxation is observed around the T_g determined by DSC. Two T_g values were reported for some films due to phase separation of polyol from biopolymer matrix resulting in polyol-rich and -poor phases (**Table 2**). Especially, phase separation of glycerol has been reported to occur in films which can be seen from two separate transitions in the DSC thermograms (Mathew and Dufresne, 2002) or mechanical spectra (Lourdin *et al.*, 1997a; Moates *et al.*, 2001). Increasing water content of film may promote phase separation due to decreasing T_g and increasing diffusion rate of the polyol. Moreover, phase separation of sorbitol and its crystallization have been reported for starch film plasticized with sorbitol (Krogars *et al.*, 2003b). This is in accordance with the fact that increasing water activity increases tendency of low molecular weight carbohydrates to crystallize due to their decreased T_g (Roos and Karel, 1991a).

2.2.4 Permeability properties

The permeability properties of the biomaterial films are important because the films may be used as a packaging or coating to protect products against water vapor or gases, such as O_2, N_2 and CO_2. In food packaging applications low water vapor permeability (WVP) and gas permeability (GP) are often desired (Robertson, 1993). Thus, the films must be even, because any pores or cracks increase significantly the WVP and GP. When there are pores or cracks in the film permeating molecules can penetrate through the film without any resistance.

Permeability (P) is dependent on the solubility (S) of permeating molecule into the film and its diffusion (D) through the film and permeability can be presented as follows P=S·D (Arvanitoyannis *et al.*, 1994; McHugh and Krochta, 1994b). The driving force of the permeation process is pressure (concentration) difference of permeating molecules on the both sides of the film. The direction of permeation is from the higher pressure to the lower one. In **Figure 3** permeation of the molecules (water or gas) through the film is schemtaically illustrated. First, permeating molecule must condensate on the surface
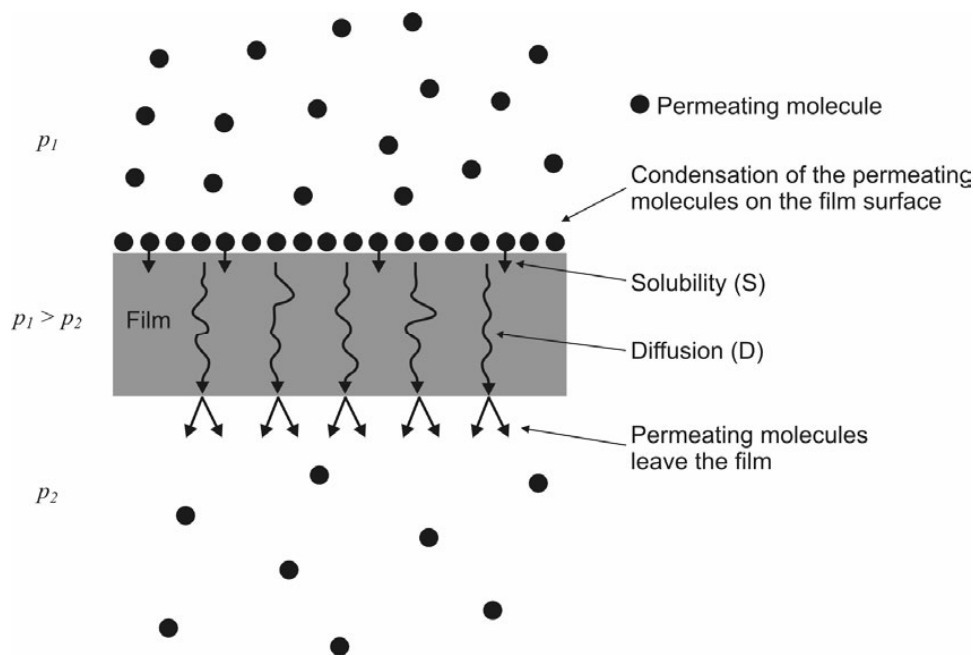
Figure 3. Permeability (P) of molecules from higher pressure (p_1) to lower pressure (p_2) through the film (redrawn according to Harry Helén's lecture notes).

of the film where the permeating molecule solubilizes into the film. This is followed by diffusion in which the permeating molecule have to find its way through the film. Finally, the permeating molecule must leave the film after it has diffused through the film.

Hydrophilic films, such as starch films, are good barriers to O_2, CO_2 and oil but poor to water (Biliaderis *et al.*, 1999). Moreover, starch films are better barriers to O_2 than CO_2 and they may act as selective barriers (García *et al.*, 2000). Generally, the WVP and GP of the film are changed by the type and content of the plasticizer. Addition of plasticizer decreases the T_g due to increased molecular mobility in the film increasing simultaneously diffusivity of the permeating molecules and thus permeability increases (Arvanitoyannis *et al.*, 1994, 1996; Biliaderis *et al.*, 1999). GP of film changes at the T_g which can be predicted from the permeability data determined at various temperatures (Arvanitoyannis *et al.*, 1994, 1996; Biliaderis *et al.*, 1999). Moreover, the GP (Arvanitoyannis *et al.*, 1994, 1996; Biliaderis *et al.*, 1999) and WVP (Kester and Fennema, 1989) of the films increase with increasing temperature.

The WVP properties of the films alter as comparable portions of various types of plasticizers are used (**Table 3**). For example, glycerol decreases more the barrier ability of the starch (Arvanitoyannis *et al.*, 1996) and whey protein (Shaw *et al.*, 2002) films against water vapor than sorbitol. This can be explained by the fact that glycerol

Table 3. Water vapor permeabilities (WVP; g mm m^{-2} d^{-1} kPa^{-1}) presented in the literature to different biomaterial films. Biopolymer/plasticizer composition of the films is presented in w/w of the solids. The first and second values in the RVP-gradient is RVP inside and outside of permeation cell, respectively, at given temperature (*T*; °C) (nr equals not reported).

Composition of the film			RVP-gradient	*T*	WVP	Reference
Biopolymer	Plasticizer	Ratio				
Polysaccharide						
Corn starch	Without	100/0	0/75	25	72[a]	Mali *et al.* (2006)
Potato starch	Without	100/0	74/50	23	118[a]	Petersson and Stading (2005)
Tapioca starch	Without	100/0	0/30	30	29[a]	Chang *et al.* (2000)
Tapioca starch	Without	100/0	0/80	30	45[a]	Chang *et al.* (2000)
Cassava starch	Glycerol	85/15	22/57	25	5[a]	Phan *et al.* (2005)
Cassava starch	Glycerol	85/15	22/99	25	10[a]	Phan *et al.* (2005)
Corn starch	Glycerol	83/17	0/75	25	46[a]	Mali *et al.* (2006)
Corn starch	Glycerol	71/29	0/75	25	58[a]	Mali *et al.* (2006)
Amylose	Glycerol	71/29	100/50	nr	103	Rindlav-Westling *et al.* (1998)
Amylopectin	Glycerol	71/29	100/50	nr	124	Rindlav-Westling *et al.* (1998)
Protein						
Whey protein isolate	Glycerol	67/33	100/50	23	120	Shaw *et al.* (2002)
Whey protein isolate	Xylitol	67/33	100/50	23	85	Shaw *et al.* (2002)
Whey protein isolate	Sorbitol	63/37	77/0	25	64	McHugh *et al.* (1994)
Whey protein isolate	Sorbitol	67/33	100/50	23	78	Shaw *et al.* (2002)
Gelatin	Glycerol	80/20	0/100	25	16.9	Thomazine *et al.* (2005)
Gelatin	Glycerol	65/35	0/100	25	22.9	Thomazine *et al.* (2005)
Gelatin	Sorbitol	80/20	0/100	25	12.9	Thomazine *et al.* (2005)
Gelatin	Sorbitol	65/35	0/100	25	15.9	Thomazine *et al.* (2005)

[a] Converted to the present unit by author.

decreases T_g more effectively than sorbitol. The starch film without plasticizer has higher WVP than the films plasticized with glycerol at low content (Mali *et al.*, 2004) even if the film without plasticizer have a higher T_g (Mali *et al.* 2006). This was probably due to pores and cracks in the film without plasticizer, which were filled up by plasticizer addition resulting in decreased WVP (Mali *et al.*, 2004). Similarly, high permeability of CO_2 was reported for the starch film without plasticizer because of pores (García *et al.*, 2000).

The WVP may be changed significantly depending on the, difference in the water vapor pressures, across the film (RVP gradient) (**Table 3**). The RVP gradient is obtained using lower and higher RVP across the film mounted in the permeation cell. Usually, the lower RVP is kept constant and the higher RVP is increased. WVP increases with increasing RVP because of increasing water plasticization of the film (Chang *et al.*, 2000). When the higher RVP is kept constant and the lower RVP is increased the WVP increases markedly because of water plasticization which is decreasing integrity of the film structure (Kester and Fennema, 1989). The film may also swell due to water plasticization increasing the WVP due to less dense biopolymer structure in the film. The accuracy of the WVP measurements of the hydrophilic film may vary because of

varying amounts of water in different regions of the film (Biliaderis *et al.*, 1999). Thickness of the film has been reported to be inversely proportional to the WVP (McHugh *et al.*, 1993; Longares *et al.*, 2004; Bravin *et al.*, 2006). This phenomenon is explained to be originated from increased resistance of the film to mass transfer because of increased water vapor pressure on the film surface (McHugh *et al.*, 1993).

The WVP of the corn, yam and cassava starch films without plasticizer decreases due to increasing crystallinity in the films (Mali *et al.*, 2006). WVP decreases with increasing crystalline zones because permeation occurs through amorphous zones in the film (Mali *et al.*, 2006). Plasticizer addition has been shown to retard starch crystallization which was the reason why WVP of the films with plasticizer did not change during storage (Mali *et al.*, 2006). The density of the starch film structure without plasticizer increases due to enthalpy relaxation resulting from the increase in the density of the film simultaneously decreasing diffusion of water molecules resulting in reduced WVP (Kim *et al.*, 2003).

2.2.5 Mechanical properties

Usually, in the mechanical testing of the film a stress-strain experiment is carried out where a film sample is stretched at a constant rate until it breaks. The stress-strain curve (**Figure 4**) obtained can be used to determine Young's modulus, tensile strength and elongation at break. Hook's law assumes perfect elasticity of material (Sperling, 1992), this can be seen as a linear part at the beginning of stress-strain curve. Perfect elasticity of a sample can be seen as immediate recovery to its original length, after the deformation force is released in the linear region. This linear region is used to calculate Young's modulus which is a measure of material stiffness (Sperling, 1992). Generally, materials are assumed to obey Hook's law at low strain values. Tensile strength is defined as maximum force (stress) used during stress-strain experiment or force obtained at the break point of sample. The terms "maximum tensile strength" and "tensile strength at break" can be used to distinguish between these two terms. In the present study, only maximum tensile strength is reported and the term of "tensile strength" is used for it. Elongation at break is the increase of the sample length from its original length in the stress-strain experiment at the break point. The break point is seen in **Figure 4** as a vertical drop in the stress-strain curve.

The desired properties are dependent on the application for which the films are made. For example, in one application more brittle films are desired whereas in another application more elastic and flexible films are desired. By this mean, *e.g.*, the terms good and poor mechanical properties should be considered with caution. Usually, brittle
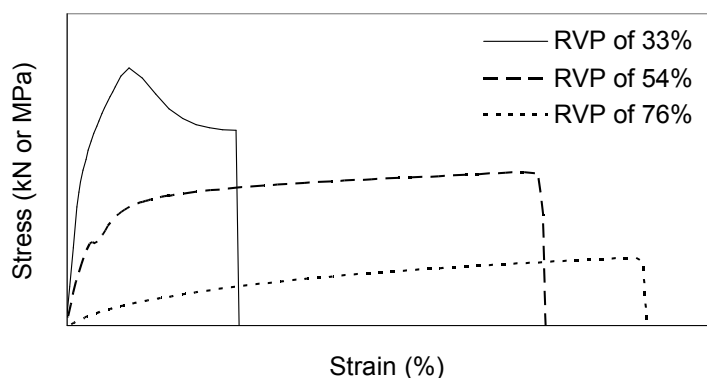
Figure 4. Effect of the relative vapor pressure (RVP) on the stress-strain curve.

film have good barrier properties against water and gases, if the film is even and undamaged. Such films do not have necessarily good mechanical properties with good handling properties allowing bending and stand stretching. Thus, the films have to be plasticized to obtain more flexible and elastic films when barrier properties are weakened.

Elongation at break for brittle plastic samples is usually 1–2% of their original length and stress increases linearly with strain until break (Sperling, 1992). For brittle/glassy biopolymer films reported values of elongation at break vary from 3 to 9%. These films have a high Young's modulus and tensile strength (Biliaderis *et al.*, 1999). Anyhow, slightly increased elongation at break has been observed for biopolymer films which were in the glassy state without plasticizer (Lazaridou and Biliaderis, 2002; Lazaridou *et al.*, 2003; Chang *et al.*, 2000). In these films water content varied approximately from 5 to 15% and they still remained in the glassy state in which brittle to ductile transition was observed (Chang *et al.*, 2000; Lazaridou and Biliaderis, 2002; Lazaridou *et al.*, 2003). Similar brittle to ductile transition induced by water have been reported for the gelatinized starch in the glassy state (Nicholls *et al.*, 1995). Lazaridou and Biliaderis (2002) have stated that plasticizer addition also induces the brittle to ductile transition in the glassy state.

In the mechanical testing of the films, which are in the rubbery state, above T_g, different mechanical properties of the films are obtained as compared to those of the glassy films. Clearly lower values of Young's modulus and tensile strength and higher values of elongation at break of the biopolymer films have been reported for the rubbery films than for the glassy ones (Biliaderis *et al.*, 1999; Lazaridou *et al.*, 2003; Mali *et al.*, 2006). Lazaridou *et al.* (2003) have shown for films made of pullulan and sorbitol that significantly increased values of elongation at break when the films turned gradually from brittle to rubbery state due to increasing water content. The values of Young's modulus and tensile strength of the pullulan sorbitol film decreased simultaneously

when elongation at break increased due to water or/and polyol plasticization (Singh *et al.*, 2003). Similar trends in mechanical properties have been reported for the polyol plasticized films prepared from starch (Mehyar and Han, 2004; Alves *et al.*, 2007), other polysaccharides (Debeaufort and Voilley, 1997) and proteins (Anker *et al.*, 1999; Lawton, 2004). Effect of water plasticization on the stress-strain curve of starch-based film is shown in **Figure 4**. At the beginning the slope (Young's modulus) and height (tensile strength) of the curves decrease and length (elongation at break) increases with increasing water content.

The effect of amylose content on the starch-based films has been studied previously. In these studies, films have often been prepared from physical blend of amylose and amylopectin which is plasticized with various polyols. The amylose content affects the crystallinity of the starch film, which is often linked to the mechanical properties (Rindlav-Westling *et al.*, 1998). The increasing crystallinity of amylose and amylopectin in the film increases Young's modulus and tensile strength simultaneously decreasing elongation at break (van Soest *et al.*, 1996b).

3 OBJECTIVES OF THE PRESENT STUDY

The biomaterial films may be used to enhance quality and stability of food and pharmaceutical solids. The ultimate goal of the present thesis was to investigate preparation of biomaterial films based on potato starch combined with polyols and characterize properties of the films with varying composition at controlled environmental conditions.

The specific objectives of the present study were:

1) to study thermal properties of low molecular weight carbohydrates used as a plasticizer in potato starch-based films,
2) to prepare potato starch-based films plasticized by polyols,
3) to investigate effect of plasticizer type and content on physical and mechanical properties of potato starch-based films and
4) to investigate effect of amylose content on physical and mechanical properties of potato starch-based films.

4 MATERIALS AND METHODS

4.1 Materials

Food grade erythritol (Cerestar, Neuilly-sur-Seine, France) (I), glycerol (Dow, Stade, Germany) (II–III), sorbitol (Roquette Fréres, Lestrem, France (I) and Cerestar, Krefeld, Germany (II–IV)) and xylitol (Roquette Fréres, Lestrem, France (I) and Xyrofin, Kotka, Finland (II–IV)) were used in the present study. Native potato starches, donated by Evijärven Peruna Ltd. (Evijärvi, Finland) were characterized (IV) and used in the preparation of edible films (II–IV).

4.2 Characterization of starches (IV)

4.2.1 Amylose content

Amylose content of potato starches was analyzed by an enzymatic method (Megazyme International Ireland Ltd., Bray, Ireland). Potato starch sample was dissolved with dimethyl sulphoxide (DMSO). Dissolved starch sample was divided into two parts to determine amylose and total starch contents. Amylopectin was precipitated with concanavalin A (Con A) to produce amylopectin-free amylose solution. Carbohydrates in these solutions were hydrolyzed enzymatically into glucose molecules with a mixture of amyloglucosidase and α-amylase enzymes. Glucose molecules in a solution were oxidized with glucose oxidase/peroxidase reagent resulting in color change of the solution. Absorbance at wavelength of 510 nm for oxidized glucose solutions from amylose and total starch was determined with a spectrophotometer (Perkin Elmer, UV/VIS, Spectrometer Lambda 2, Überlingen, Germany). Absorbances of the solutions were used to calculate amylose and total starch contents, which could be used to calculate amylopectin content.

4.2.2 Gelatinization properties

A differential scanning calorimeter (TA4000 DSC30, Mettler-Toledo AG, Greifensee, Switzerland) was used to determine onset, peak and endset temperatures and enthalpy of starch gelatinization (IV). Starch samples were mixed with water to obtain a solid content of 5% (w/w) and the mixtures were hermetically sealed in 40-μl aluminium pans (Mettler-27331). DSC calibration is described in the original publication I. Starch

samples were scanned from 15 to 90°C at a heating rate of 5°C min^{-1} and the measuring cell was purged with a flow of N$_2$ at 50 ml min^{-1}.

4.2.3 Crystallinity

Starches containing low, medium and high amylose contents were selected for X-ray diffraction (XRD) measurements. Starch tablets, diameter 15 mm and thickness 0.6–0.7 mm, for XRD measurements were prepared by compressing using a pressing cylinder and a piston. The XRD measurement was carried out using the symmetrical transmission geometry with CuK$_{\alpha 1}$ radiation from a sealed X-ray tube monochromatized using a Ge(111) monochromator in the incident beam. The intensities were measured with NaI(Tl) detector (Quartz&Silice, France) at the scattering angles (2θ) from 10 to 50°.

4.3 Characterization of polyols (I)

4.3.1 Sample preparation

Thermal properties of polyols (erythritol, sorbitol and xylitol) were analyzed using various thermoanalytical techniques (I). Amorphous anhydrous samples were prepared by heating crystalline polyols above their melting temperatures followed by quench cooling. Xylitol and sorbitol samples with different water contents (10, 20, 30 and 40%) were produced by adding the corresponding amount of distilled water to the crystalline polyol followed by gentle heating with mixing. The exact water contents of the polyol samples were determined gravimetrically after they were cooled down to room temperature. Mixtures of amorphous and crystalline xylitol were prepared by adding 1% (w/w) of crystalline xylitol at room temperature into the amorphous anhydrous xylitol melt.

4.3.2 Differential scanning calorimeter (DSC)

A differential scanning calorimeter (TA4000 DSC30, Mettler-Toledo AG, Greifensee, Switzerland) was used to determine the glass transition (T_g), crystallization (T_c) and melting (T_m) temperatures of the polyol samples sealed in 40-µl aluminium pans (Mettler-27331). DSC calibration is described in the original publication I. DSC was used at a heating rate of 5°C min^{-1} and the measuring cell was purged with a flow of N$_2$

at 50 ml min^{-1}. Temperature range altered depending on polyol, but as a guideline measurement was started from at least 30°C below and continued to 20°C above the transition. The T_g, T_c and T_m were taken from the onset temperatures of endothermic step change, exothermic peak and endothermic peak, respectively.

The decrease of T_g of xylitol and sorbitol due to water plasticization was modeled using the Gordon-Taylor **Equation 1** (Gordon and Taylor, 1952) where T_{g1} and T_{g2} are glass transition temperatures and w_1 and w_2 are weight fractions of polyol and water, respectively, and k is a constant derived from experimental data.

$$T_g = \frac{w_1 T_{g1} + k w_2 T_{g2}}{w_1 + k w_2} \qquad (1)$$

4.3.3 Dielectric analysis (DEA)

A dielectric analyzer (DEA2970, TA Instruments, New Castle, Delaware, USA) was used to study α-relaxation of polyol samples at a parallel plate mode. DEA was used at a heating rate of 2°C min^{-1} from −150 to 140°C and the measuring cell was purged with a flow of N_2 at 250 ml min^{-1}. Permittivity (ε') and loss factor (ε'') data were collected using frequencies of 0.1, 0.5, 1, 5, 10, 100 and 1000 Hz. Dissipation factor (*tanδ*), ratio of ε'' to ε', was calculated and a maximum of *tanδ* peak at frequency of 0.1 Hz was taken as T_g.

4.3.4 Dynamic mechanical analysis (DMA)

A dynamic mechanical analyzer (DMA 242, Netzsch-Gerätenbau GmbH, Selb, Germany) was used to study α-relaxation of polyol samples using a disk-bending sample holder, which consisted three stainless steel sheets with holes. Polyol samples were placed in the disk-bending sample holder between two PET-films (**Figure 5**). DMA was used at a heating rate of 2°C min^{-1} using frequencies of 1, 2.5, 5, 10 and 20 Hz. Storage modulus (E') and loss modulus (E'') data were collected and a maximum of E'' peak at frequency of 1 Hz was taken as T_g.
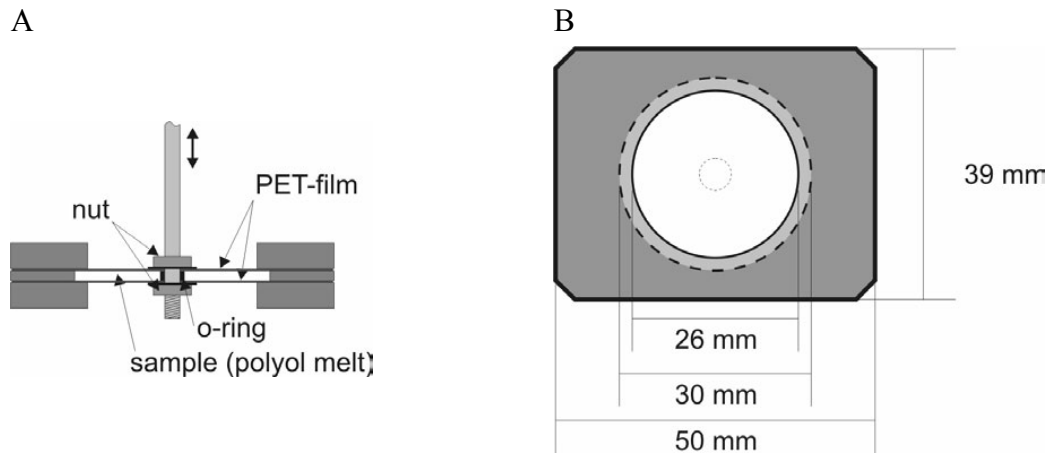
A

B

Figure 5. Schematic drawing of the disk-bending sample holder used to analyze polyol melts. The cross-section (A) and from the top (B) of sample holder. Sample was located between two thin (0.5 mm) polyethylene terephtalate (PET) films. Double headed arrow describes the direction of oscillating dynamic force. The sample holder was adapted from MacInnes (1993).

4.4 Film formation (II–IV)

Starch-based films were prepared by casting because it is the commonly used technique to prepare edible films on a laboratory scale. Polyols, which were used to plasticize films, were selected on the basis of the study carried out with single polyols (I). Anhydrous xylitol and sorbitol melts remained well in an amorphous state whereas erythritol tended to crystallize easily which was the reason not to use erythritol as a plasticizer in films. Moreover, glycerol was selected because it is commonly used as a plasticizer in biopolymer films.

Edible films were prepared (**Figure 6**) using suspensions of plasticizer, potato starch and distilled water. Polyols (glycerol, xylitol and sorbitol) were used as a single polyol (II) or binary polyol mixture at a ratio of 1 to 1 (III). Amount of plasticizers (20–60% of solids, w/w) was weighed and dissolved into distilled water and followed with addition of starch to obtain film forming suspension, in which starch concentration was 5% (w/w) of overall water content independently of plasticizer concentration. Starches with varying amylose contents were also used to prepare films plasticized with the binary mixture of xylitol and sorbitol at content of 30% (IV). Film forming suspension was heated with continuous mixing by a magnetic stirrer (RH Basic, Ika Works, Inc., Wilmington, NC, USA) and at short intervals by hand with a glass rod to above 90°C to obtain film forming solution. The solution was kept at 90°C for 5 minutes before letting
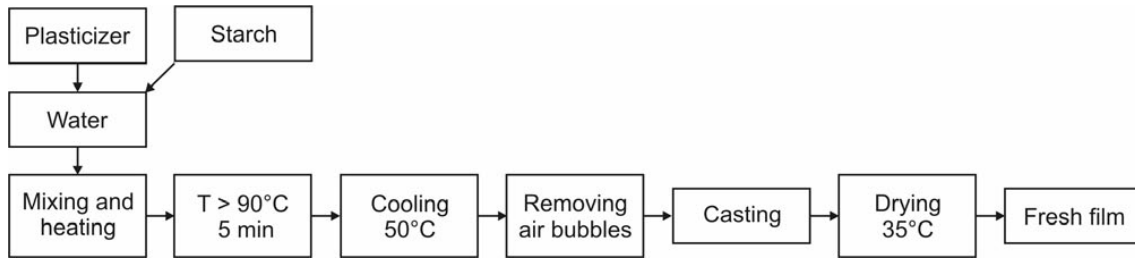
Figure 6. The film formation process.

it cool down to 50°C. Air bubbles formed during heating were removed from the film forming solution before it was casted on a teflon®-coated plate. Starch-based films were obtained by evaporating water in an oven at 35°C.

4.5 Characterization of films

4.5.1 Water sorption (II–IV)

Pieces of films were placed into glass vials, which were placed into a freezer at –20°C for at least two hours before placing them into –80°C for 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 hours ($p < 0.5$ mbar). Drying of films was completed in a vacuum desiccator over P_2O_5 for 7 days. Water sorption properties of various films were determined after storage of freeze-dried samples in vacuum desiccators over saturated salt solutions giving relative vapour pressures (RVP) ranging from 11 to 86% at 25°C. Water contents of the films were followed gravimetrically as a function of time. Water sorption behavior was modeled with Brunauer-Emmett-Teller (BET) **Equation 2** and Guggenheim-Anderson-de Boer (GAB) **Equation 3** using water activity range of 0.11–0.44 and 0.11–0.86, respectively. In those equations m is the 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).

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

$$\frac{m}{m_m} = \frac{KCa_w}{(1-Ca_w)[1+(K-1)Ca_w]} \tag{3}$$

4.5.2 Water vapor permeability (WVP) (II–IV)

WVP properties of the films were studied gravimetrically using modified ASTM E 96 (2001) method. Anhydrous $CaCl_2$ (J.T. Baker, Deventer, Holland) was used as a desiccant in a cup which was covered with studied film. Thickness of each film was measured with a micrometer (Mitutoyo, Japan, with accuracy of 0.01 mm) at six randomly selected points after which the film was attached to the cup. The cup was placed in desiccators at RVP of 33, 54 and 76% resulting in RVP gradients of 0/33 (II–III), 0/54 (II–IV) and 0/76% (II–III) across the film at 23.5±1.5°C. Progress of water vapor permeation was determined gravimetrically as a function of time for 7 days. The cup was shaken horizontally after every weighing. Water vapor permeability was calculated with **Equation 4** where m is the weight of water permeated through film, L is the thickness of film, A is the permeation area of the film, t is time of permeation and Δp is water vapor pressure difference at both sides of the film.

$$WVP = \frac{m\,L}{A\,t\,\Delta p} \tag{4}$$

4.5.3 Thermal properties (II–III)

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 single polyols (II) and binary mixture of polyols (III). Film samples were hermetically sealed in 40-µl aluminium pans after equilibration at RVP of 0, 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} and the measuring cell was purged with a flow of N_2 at 50 ml min^{-1}. The glass transition temperature was taken from the onset temperature of step change in heat capacity.

4.5.4 Mechanical properties (II–IV)

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) of "dog bone" shaped film stripes length and width of which were 150 mm and 10 mm, respectively. 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 at RVP of 33, 54 and 76% at 23.5±1.5°C for 7 days prior to testing.

4.5.5 Crystallinity (IV)

Films containing low, medium and high amylose contents were selected for XRD measurements. Film samples were stored at RVP of 54% at 21°C for one week prior to the measurements. The scattering pattern of the films was measured using perpendicular transmission mode. The setup consisted of a rotating anode X-ray tube (Rigaku, Japan), a totally reflecting focusing mirror, a bent Si(111) crystal monochromator and MAR345 image plate detector (Mar Research, Germany), in which the CuK$_{\alpha1}$ radiation beam was focused through semi-transparent beamstop. The measured scattering patterns were isotropic and the intensity curves at the scattering angles (2θ) from 4 to 55° were obtained by integration over the azimuth angle.

4.5.6 Statistical data analysis and experimental plan

Data of starches with varying amylose contents and the films based on them were statistically analyzed using the analysis of variance (ANOVA) followed by Tukey test (Statsgraphics Plus for Windows v4.0) (IV).

The present study consists of four different experimental parts, which were published as individual original publications referred by Roman numbers. The structure of the experimental plan and the way how the different experimental parts are joined together in the present study are shown in **Figure 7**.
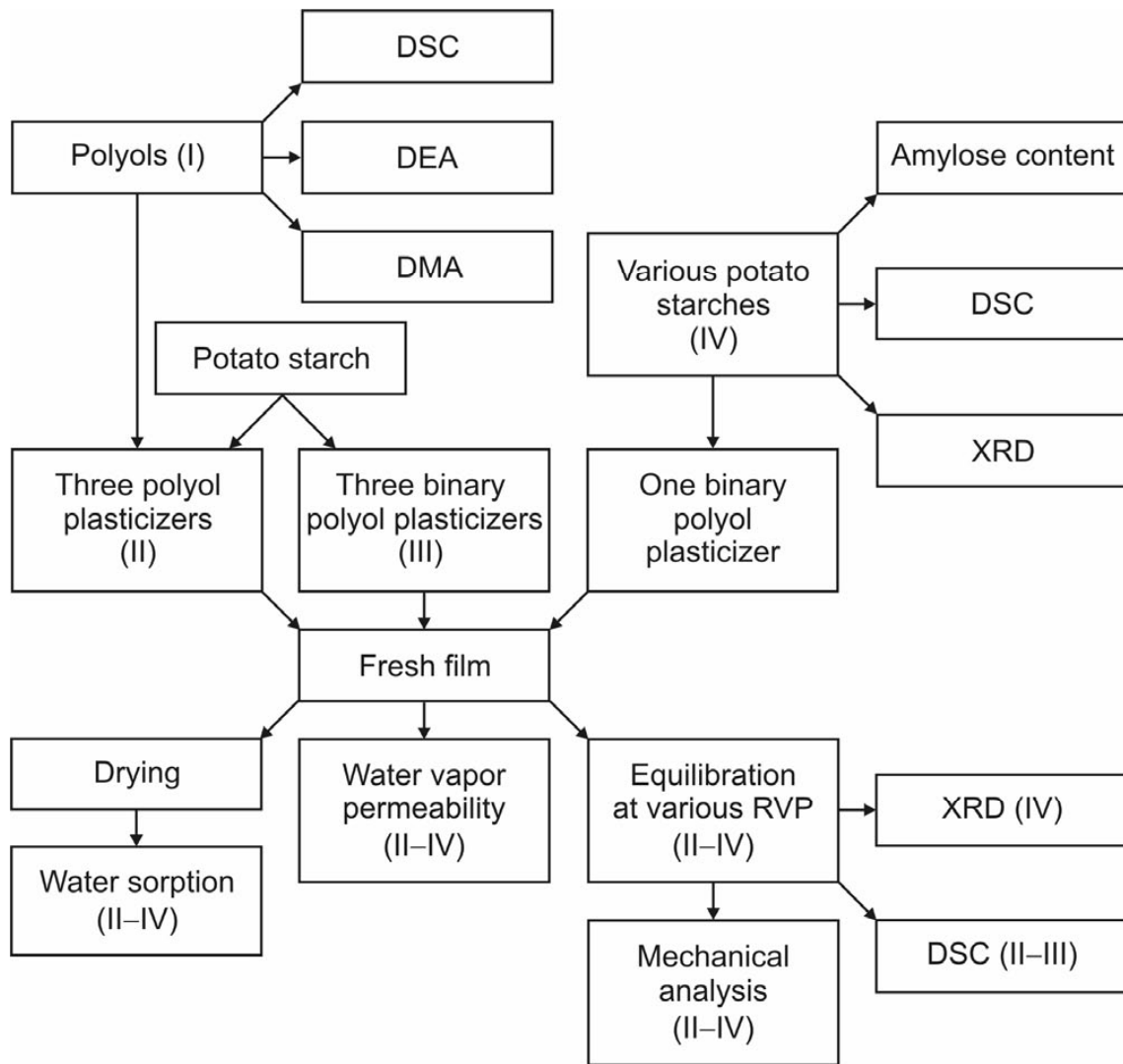
Figure 7. The experimental plan of the present study. Roman number refers to the original publications.

5 RESULTS

5.1 Characterization of potato starch (IV)

5.1.1 Amylose content

The amylose content the of total starch was determined from the native potato starches extracted from various potato cultivars by using enzymatic method. The amylose content of potato starches varied between 11.9 and 20.1% (see Table 1 in IV) and the rest of the starch sample was amylopectin. Moreover, there were three potato cultivars grown in both 2002 and 2003 used to extract potato starch (Kardal 2002, K1; Kardal 2003, K2; Posmo 2002, P1; Posmo 2003, P2; Saturna 2002, Sa1; Saturna 2003, Sa2). Potato starch extracted from cultivars K1 and P1 grown in year 2002 and Sa2 grown in 2003 had higher amylose content than the same cultivars K2 and P2 grown in 2003 and Sa1 grown in 2002.

5.1.2 Gelatinization

Starch gelatinization, disruption of the native structure of the starch granule, was studied for starches with various amylose contents in excess water under heating by DSC. Thermograms recorded with DSC from starch-water mixtures showed one endothermic peak, the gelatinization endotherm, at temperatures ranging from 58 to 69°C varying only little indicating that the amylose content did not affect gelatinization (see Table 1 in IV). Moreover, the gelatinization endotherm was not observed during the second heating which was carried out immediately after the first heating.

5.1.3 Crystallinity

XRD measurements were carried out for selected potato starches with a low (Posmo 2003, P2), medium (Bulk 2002, B1; Van Gogh, V1) and high (Seresta 2003, Se1) amylose content. The X-ray diffraction patterns obtained for various starches showed strong peaks at scattering angles of 17 and 22° and weaker peaks at scattering angles of 15, 19 and 24° (**Figure 8**). The relative crystallinities of the native potato starches were almost equal, 10–13%, independently of the amylose content (see Table 1 in IV).
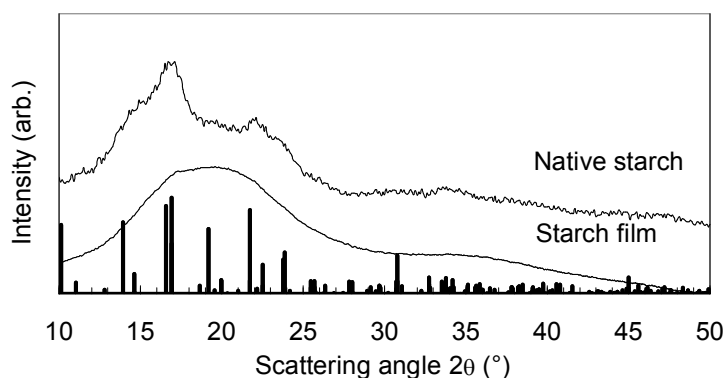
Figure 8. The X-ray diffraction patterns for native potato starch (Bulk 2002) and film prepared from it and plasticized using binary mixture of xylitol and sorbitol at the content of 30% of solids and stored at RVP of 54% at 21°C. The positions and relative intensities of the reflections of the B-type starch structure calculated according to Imberty and Perez (1988) are presented by vertical lines.

5.2 Characterization of polyols (I)

In the present study, amorphous melts from crystalline sorbitol and xylitol could be obtained by heating and they showed T_g and T_m at their characteristic temperatures. However, erythritol was found to crystallize rapidly after the erythritol melt was obtained. A cooling rate of 5°C min^{-1} used in DSC was found to allow complete crystallization of erythritol and no T_g was apparent in a subsequent reheating scan. However, erythritol samples quench cooled using the highest applicable cooling rate (approximately 50°C min^{-1}) gave T_g of –45°C in an immediate rescan. The T_g was followed by a crystallization exotherm occurring over a temperature range from –10 to 5°C. Amorphous xylitol and sorbitol melts were found to have a T_g with onset temperature at –24 and –6°C, respectively. The T_g of xylitol and sorbitol solutions decreased with increasing water content (10, 20, 30 and 40%). However, the xylitol and sorbitol samples containing 40% of water showed devitrification (ice formation) exotherm followed by an ice melting endotherm. At higher water contents (> 40%) xylitol and sorbitol tended to form crystalline layer on top of the solution when it was attempted to prepare. The T_g of amorphous xylitol and sorbitol and their water solutions determined using DEA and DMA at low measurement frequencies were slightly different when obtained using different techniques and from those T_g values determined by DSC. Moreover, the T_g of xylitol and sorbitol determined by both DEA and DMA was found to increase with increasing measurement frequency.

The onset temperature of the endothermic melting of the crystalline erythritol, xylitol and sorbitol were found at 118, 93 and 95°C, respectively, as determined by DSC. Corresponding melting temperature of the polyols could be also seen in DEA spectra as a steep increase in the permittivity and the loss factor data. The temperature ratio

between the melting and the glass transition temperatures (T_m/T_g) was calculated for polyols. The T_m/T_g ratio for erythritol (1.71) was clearly higher than those of xylitol (1.48) and sorbitol (1.38) indicating higher tendency of erythritol to crystallize.

The DSC thermogram for an anhydrous mixture of crystalline (1% w/w) and amorphous xylitol showed the T_g at the same temperature (onset –24°C) as the T_g of anhydrous, amorphous xylitol. The T_g was followed by a crystallization exotherm with onset at 37°C and peak maximum at 59°C. The melting endotherm of the crystals had an onset at 90°C. The same material showed an α-relaxation at a frequency dependent temperature in the both DEA and DMA measurements. Frequency independent changes in the DEA measurement were observed at around 40 and 94°C corresponding to crystallization and melting transitions of xylitol, respectively. Similar frequency independent change in the DMA measurement indicating xylitol crystallization was seen at around 40°C.

5.3 Characterization of the potato starch-based film

5.3.1 Appearance of the fresh and stored films (II–IV)

Films prepared without or with plasticizer, which were obtained after oven drying, are called in this thesis fresh films. Film samples for various analyses were prepared from these fresh films by storing them at various RVP prior to testing. Appearance of fresh and stored films is described in **Table 4**. Fresh potato starch film without plasticizer was transparent but it was wavy, rigid and brittle and as a consequence of that it was difficult to handle (II). All fresh potato starch films plasticized with single polyol or binary polyol mixtures were transparent independently of plasticizer content (II–III). At low plasticizer content the fresh films were brittle whereas at high plasticizer content they were elastic and flexible. Moreover, fresh films plasticized with glycerol at a content of 50% were found to be sticky.

During one-week storage under various RVP conditions at 25°C appearance of the films changed depending on the type and content of the plasticizer (**Table 4**) (II–III). Films without plasticizer remained brittle at all RVP. Due to water plasticization the most of the films turned to flexible and elastic even if few films remained brittle at RVP of 33 or/and 54%. In the films plasticized with glycerol surface stickiness was observed under all RVP conditions but the films at glycerol contents of 20 and 30% as stored at RVP of 33–76 and 33–54%, respectively, were not sticky (II). In contrast to this, in the films plasticized with the other plasticizers at high contents surface stickiness of film was observed only at RVP of 76% (II–III). During storage at RVP of 33 and 54% xylitol and

Table 4. Appearance of films with various plasticizer type and contents (w/w of solids) as fresh and after storage at various relative vapor pressures (RVP) at 25°C. Appearance is described with the following terms and abbreviations: transparent (T), brittle and fragile (B), flexible and elastic (F), sticky (S) and polyol crystallization (C).

Plasticizer			RVP (%)		
Type	Content (%)	Fresh	33	54	76
Without	0	T, B	T, B	T, B	T, B
Glycerol	20	T, B	T, B	T, F	T, F
	30	T, B	T, F	T, F	T, F, S
	40	T, F	T, F, S	T, F, S	T, F, S
	50	T, F, S	T, F, S	T, F, S	T, F, S
Xylitol	20	T, B	T, B	T, B	T, F
	30	T, B	T, B	T, F	T, F
	40	T, B	T, F	T, B, C	T, F, S
	50	T, F	T, B,C	B, C	T, F, S
Sorbitol	20	T, B	T, B	T, B	T, F
	30	T, B	T, B	T, F	T, F
	40	T, B	T, F	T, F	T, F
	50	T, F	T, F	T, F	T, F, S
	60	T, F	T, B, C	F, C	T, F, S
Gly-Xyl	20	T, B	T, B	T, B	T, F
	30	T, B	T, B	T, F	T, F
	40	T, F	T, F	T, F	T, F, S
	50	T, F	T, F	T, F	T, F, S
Gly-Sor	20	T, B	T, B	T, B	T, F
	30	T, B	T, B	T, F	T, F
	40	T, F	T, F	T, F	T, F, S
	50	T, F	T, F	T, F	T, F, S
Xyl-Sor	20	T, B	T, B	T, B	T, F
	30	T, B	T, B	T, F	T, F
	40	T, B	T, F	T, F	T, F
	50	T, F	T, F	T, F	T, F, S

sorbitol crystallization could be observed visually from white spots appearing on the surface of films, still remaining mostly transparent. However, at higher xylitol and sorbitol content or RVP the films turned white being opaque with only a few transparent regions due to polyol crystallization (II). The films, in which polyol crystallization was observed, became sticky when stored at RVP of 76% due to dissolution of crystalline polyol (II). As the binary polyol plasticizer was used in the films the films were found to be less sticky and polyol crystallization could not be observed (III). All the films prepared using starches with varying amylose content and the binary mixture of Xyl-Sor at the content of 30% had equal appearance (**Table 4**) (IV).

5.3.2 Water sorption (II–III)

Water content of all films increased with increasing RVP. For all films steady-state water contents were reached within 48 hours. Films without plasticizer (II) showed clearly sigmoidal shape of water sorption isotherm and single polyol (II) and binary polyol mixture (III) plasticized films showed slightly sigmoidal shape of water sorption isotherms as modeled with BET and GAB equations. 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 (II). Similarly, at the corresponding plasticizer content, the films plasticized with Gly-Xyl and Gly-Sor gained approximately the same water content but the films plasticized with Xyl-Sor gained apparently lower water content (III). 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 (II–III). When these water activities were exceeded the water contents of the plasticized films were higher than that of unplasticized film. Water content of all plasticized films increased with increasing plasticizer contents. In most cases, monolayer water contents predicted with GAB equation were higher than those predicted with BET equation (see Table 1 in both II and III). Monolayer water contents were found to be significantly higher as predicted with GAB and BET equations for films plasticized with glycerol at contents of 40 and 50%. Low monolayer water content was predicted for film plasticized with xylitol at content of 50% due to xylitol crystallization in the film.

5.3.3 Thermal properties (II–III)

In the present study, heat capacity changes of polyol plasticized films observed at glass transition temperature range were weak and temperature ranges between onset and endpoint of the glass transition varied from 15 to 35°C. Glass transition temperatures decreased as a result of plasticization as the content of polyol, binary polyol mixture and/or water increased (II–III). The glass transition was observed for films plasticized with glycerol and stored at RVP of 0% whereas the T_g could not be observed as stored at RVP of 33, 54 and 76%. The glass transition temperature for films without plasticizer could not be determined at any storage RVP used (II). One glass transition temperature was observed for films plasticized with all polyols and binary polyol mixtures indicating that phase separation had not occurred (II–III).

In thermograms recorded from film at xylitol content of 50% it was found endothermic peaks with the maximum at temperatures of 73, 64 and 53°C when stored at RVP of 33, 54 and 76%, respectively, and they were concluded to relate to dissolving of xylitol

crystals (II). Endothermic peaks were also found 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 RVP of 24% and over (other plasticizer contents were not studied). Onset temperatures of these endothermic peaks decreased from 170 to 94°C and enthalpy of endothermic change increased with increasing storage RVP from 24 to 86%. Endothermic peaks were not observed for films stored at RVP of 0 and 11%. Those endothermic peaks were supposed to result from melting of starch crystallites in the films.

5.3.4 Crystallinity (IV)

Films made of starches with a low (Posmo 2003, P2), medium (Bulk 2002, B1; Van Gogh, V1) and high (Seresta 2003, Se1) amylose content were studied by XRD. These films were stored at RVP of 54% for one week prior to XRD measurements. For films prepared from P2, V1 and Se1 a weak peak at the scattering angle of 17° (**Figure 8**) was observed, indicating that the films were mostly amorphous but contained a small amount of crystallites (0–4%).

5.3.5 Water vapor permeability (WVP) (II–IV)

WVP of film without plasticizer and plasticized films increased with increasing RVP gradient. Generally, films without plasticizer, in which visible cracks were not found, had higher WVP than plasticized films (II–III) (**Figure 9**). Exceptions for this were the films containing glycerol: the film plasticized at glycerol content of 40% at all RVP gradients, the film plasticized at glycerol content of 30% at RVP gradient of 0/76% (II) and the films plasticized at Gly-Xyl and Gly-Sor content of 50% at RVP gradient of 0/33% (III). Plasticizer type and content affected WVP of film. From all plasticizers used in this study glycerol had the greatest effect on the amount of water permeated through the film. The films plasticized with other plasticizers, xylitol, sorbitol and all binary polyol mixtures, had apparently lower WVP than films plasticized with corresponding content of glycerol at all RVP gradients (II–III). Generally, the films plasticized with binary mixture of Xyl-Sor had the lowest WVP of the all films studied (III). Varying amylose contents in the films were not found to affect WVP properties (IV).
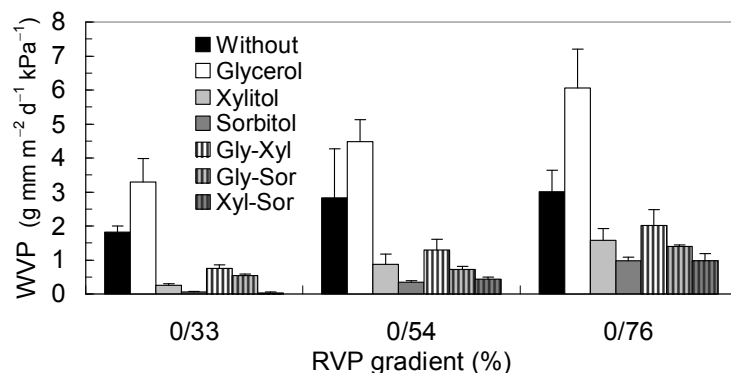
Figure 9. WVP of the potato starch films without and with various plasticizers at the content of 40%.

5.3.6 Mechanical properties (II–IV)

Generally, all starch films plasticized with polyol and binary polyol mixture behaved like viscoelastic materials. In the stress-strain curve obtained in the mechanical test there was first a linear part followed by a curved part reaching a maximum stress before or at break as shown in **Figure 4**. Generally, the values of Young's modulus for the films plasticized with polyol and binary polyol mixtures decreased with increasing plasticizer content and RVP. The values of tensile strength changed concurrently with the values of Young's modulus. Generally, both increased plasticizer content and increased water content increased the elongation of a film at break (II–III). Elongation at break value of 5% was obtained for the films with the plasticizer content of 20% and stored at RVP of 33 and 54% (II–III). For all films plasticized with any plasticizer at content of 30%, elongation of 6–11% was observed at RVP of 33%. Such films with low values of elongation at break high values of Young's modulus and tensile strength were observed. The films in which polyol crystallization took place (**Table 4**) showed high values of Young's modulus and tensile strength and low value of elongation at break (II). **Figure 10** shows high value of Young's modulus and low value of elongation at break at RVP of 54% for the film plasticized with xylitol in which polyol crystallization occurs. A slightly increasing trend in the Young's modulus and the tensile strength as a function of the amylose content was observed, but the differences were found to be statistically insignificant (IV). The values of elongation at break were found to be similarly independent of amylose content.
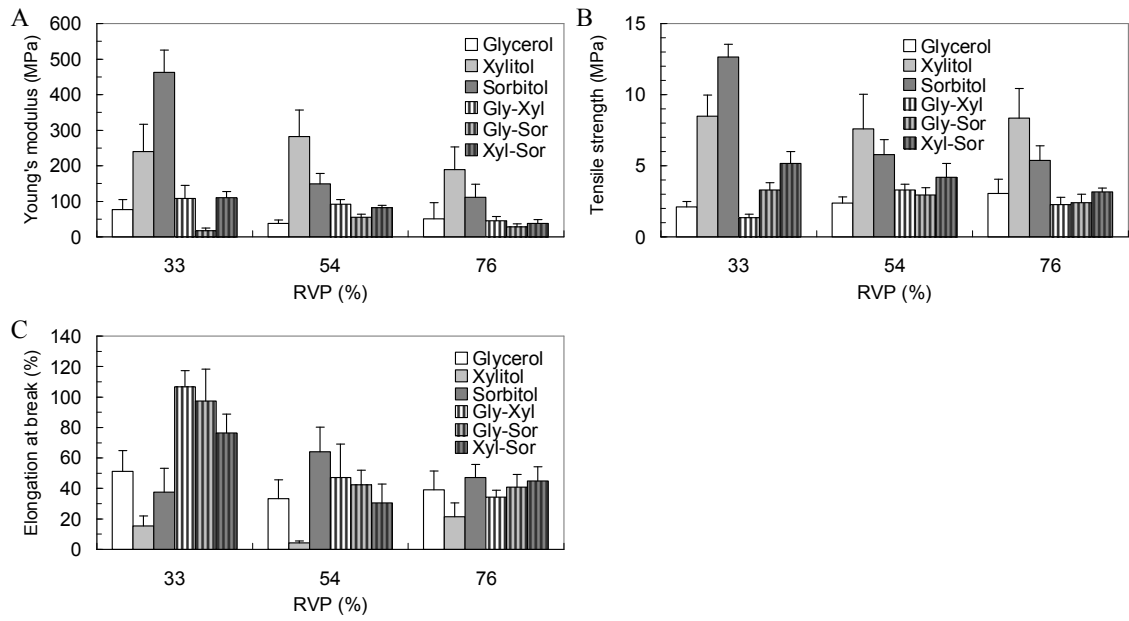
Figure 10. Young's modulus (A), tensile strength (B) and elongation at break (C) for potato starch based films plasticized at various plasticizers at content of 40%.

6 DISCUSSION

6.1 Characterization of potato starch (IV)

6.1.1 Amylose content

The amylose content varied between different starches extracted from various potato cultivars 17% (Rosin *et al.*, 2002), 18% (Svegmark *et al.*, 2002) and 19–24% (Vasanthan *et al.*, 1999) as was also shown in the present study. However, in the present study bigger differences (11.9–20.1%) between various potato starches was found. Differences in the amylose content can be attributed to different growing conditions, *e.g.*, temperature and location, which have been reported to affect the amylose content of potato starch (Cottrell *et al.*, 1995; Svegmark *et al.*, 2002). Moreover, amylose content has been shown to vary for starches from other botanical sources, *e.g.*, oat (20–25%) (Hoover *et al.*, 2003) and rice (2–31%) (Biliaderis *et al.*, 1986).

6.1.2 Gelatinization

At the gelatinization temperature range of starch, one or more peaks may be obtained depending on the water content present. A single symmetrical endotherm at the gelatinization temperature range has been reported for rice starch-water mixtures containing more than 60% water and more than one peak at lower water contents (Biliaderis *et al.*, 1986). In the present study, high water content was used and one peak in the gelatinization temperature range was observed. The gelatinization temperatures determined in the present study were similar to those reported for different potato starches with varying amylose contents (Cottrell *et al.*, 1995; Jane *et al.*, 1999). Variation in the gelatinization enthalpy between the different starches was found but it was not dependent on the amylose content. At high water contents, the gelatinization enthalpy of starch can account for swelling of the starch granules, melting of the crystallites and extensive hydration of the starch molecules (Biliaderis *et al.*, 1980). In the present study, the granule size distribution of the starches was not investigated but it may also be one explanation to the variation in the gelatinization enthalpies. Increased granule sizes of potato starch have been reported to increase the gelatinization enthalpy (Kaur *et al.*, 2002; Bogracheva *et al.*, 2006). Moreover, the crystallinity of native starch granules has shown to affect the gelatinization enthalpy (Singh *et al.*, 2003).

6.1.3 Crystallinity

The X-ray diffraction patterns obtained for P2, V1, Se1 and B1 starches showed strong peaks at scattering angles of 17 and 22° and weaker peaks at scattering angles of 15, 19 and 24°. The peaks observed at these scattering angles are typical of native potato starch which has B-type crystal structure (Imberty and Perez, 1988; van Soest *et al.*, 1996a). The positions and relative intensities of the reflections of B-type structure based on the atomic coordinates by Imberty and Perez (1988) calculated by the program PowderCell (Kraus and Nolze, 1996) were found to correlate with the X-ray diffraction patterns obtained in the present study. In the present study, the relative crystallinity of the native potato starches was almost equal, 10–13%, independently of the amylose content (see Table 1 in IV). The results are in accordance with those of the previous study (Väänänen *et al.*, 2003) where crystallinities between 12 and 16% were obtained for starch samples with water contents between 7 and 13%. Cheetham and Tao (1998) have shown linearly decreasing crystallinity of A-type maize starch with increasing amylose content. They showed also that amylose was less effective in reducing the crystallinity of B-type maize starch, as compared to A-type maize starch. This could be one reason for the fact that differences between potato starches were not found in the present study.

6.2 Characterization of polyols (I)

In the present study, the glass transition temperatures of –24 and –6°C for anhydrous amorphous xylitol and sorbitol, respectively, could be successfully determined using DSC. These temperatures differed to some extent from those reported for xylitol (–19°C) by Orford *et al.* (1990) and for sorbitol (–5°C) by Murthy (1996). α-Relaxation, occurring in the glass transition region, was determined for xylitol and sorbitol using DEA and DMA at various frequencies. Moreover, in the both techniques, DEA and DMA, the α-relaxations at different frequencies followed linearly the Arrhenius relationship (see Eq. 1 in I). α-Relaxation temperatures of xylitol and sorbitol obtained at DEA and DMA at frequencies of 0.1 and 1 Hz, respectively, correlated with T_g values determined by DSC. Noel *et al.* (1992) reported α-relaxation values of –14°C for xylitol and 11°C for sorbitol as measured by DEA using frequency of 1 kHz and a heating rate of 1°C min^{-1}. In the present study, DEA results gave the α-relaxation values of –6°C for xylitol and 13°C for sorbitol at 1 kHz frequency and a heating rate of 2°C min^{-1}. The difference in the α-relaxation values of Noel *et al.* (1992) and those of the present study may reflect the difference in the dynamic heating rates, as the slower heating rate may be expected to be more sensitive for detecting changes in the α-relaxation and to shift the observed relaxation peak to a lower temperature. α-

Relaxation temperatures of xylitol and sorbitol determined using DMA was not found from literature.

The T_g of sorbitol and xylitol decreased with increasing water content. The observed water plasticization resulted from an increase in the free volume of the material allowing a higher molecular mobility for the polyol molecules. As a consequence, the T_g decreased to a lower temperature (Roos, 1995). As water plasticization of xylitol and sorbitol was modeled with Gordon-Taylor equation (Gordon and Taylor, 1952) (**Equation 1**) using T_g value of −135°C for water (Johari *et al.*, 1987) and T_g of anhydrous amorphous xylitol and sorbitol a good fit was found for all techniques used. There was a slight difference between different techniques which could be resulted from the fact that the glass transition is a relaxation process and the DMA and DEA results are highly dependent on the measurement frequencies. Therefore, various methods of measurement do not represent similar observation times and the results may not be comparable.

The glass transition temperature of erythritol was difficult to determine because erythritol was found to crystallize rapidly from an erythritol melt. Prior to the T_g determination, the maximum cooling rate was used in the DSC to avoid crystal formation. The T_g of anhydrous amorphous erythritol was found to be −45°C. In the present study, DEA and DMA techniques could not be used to determine α-relaxation behavior of the amorphous erythritol due to its rapid crystallization.

The melting temperatures of 118, 93 and 95°C were determined using DSC for erythritol, xylitol and sorbitol, respectively. Moreover, similar melting temperatures of 118, 92 and 97°C were obtained by DEA for erythritol, xylitol and sorbitol, respectivley. Barone *et al.* (1990) have reported melting temperatures of 118, 93 and 93°C for erythritol, xylitol and sorbitol crystals, respectively, determined by DSC. The temperature ratio between the melting and glass transition temperatures (T_m/T_g) was calculated to estimate crystallization tendency of polyols. Generally, carbohydrates with high T_m/T_g ratios are readily crystallizable (Slade and Levine, 1991) and have a high heat of fusion (Raemy and Schweizer, 1983). The data in the present study showed that the temperature difference between the T_g and T_m of erythritol was large being 163°C and giving a T_m/T_g ratio of 1.71, whereas corresponding values of 117 and 101°C and 1.48 and 1.38 were obtained to xylitol and sorbitol, respectively. The T_m/T_g ratio of erythritol is apparently higher than that of xylitol and sorbitol and agrees with the observed high tendency of erythritol to crystallize from the amorphous state. Roos (1993) found that the T_m/T_g ratios were 1.48 for xylitol and 1.36 for sorbitol and within the range 1.33–1.37 for the most sugars. High tendency to crystallization was the reason why erythritol was not used as a plasticizer in the films.

6.3 Characterization of the potato starch-based film

6.3.1 Appearance of the fresh and stored films (II–IV)

Fresh potato starch films at low plasticizer content were found to be brittle and rigid (II–III). These films had low water content after an oven drying and they were most probably in the glassy state. The previous studies have shown that amylopectin (Kalichevsky *et al.*, 1992) and amylopectin plasticized with fructose (Kalichevsky and Blanshard, 1993) containing low water content were in the glassy state at room temperature showing brittle behavior. Water plasticizes biomaterials effectively decreasing their glass transition temperature as showed, *e.g.*, for blend of pullulan and starch (Biliaderis *et al.*, 1999). The films equilibrated at various RVP showed brittle or elastic behavior depending on plasticizer content and RVP (**Table 4**). The brittle films were obtained because films could not be plasticized sufficiently due to low plasticizer contents. Gaudin *et al.* (1999) have reported brittle behavior for films plasticized at a sorbitol content less than 27% of solids. The films with sticky surfaces were obtained at the high plasticizer content and RVP. The stickiness may have resulted from phase separation and diffusion of polyol, especially glycerol, onto the surface of the film. Moreover, in the film with high xylitol and sorbitol contents, phase separation was observed on the surface of the film as a white appearance, polyol crystallites, which were dissolved at high RVP causing sticky surface. Phase separation of glycerol from starch matrix at higher glycerol content than 27% (w/w of solids) has been reported (Lourdin *et al.*, 1997b). 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 *et al.*, 1996b). Crystallization of sorbitol when used as a plasticizer at high contents has been observed to occur also in corn starch-based films (Krogars *et al.*, 2003b). Moreover, stability of erythritol plasticized starch films decreased due to crystallization of the erythritol (Fernández Cervera *et al.*, 2004). Increasing water content in the film decreases hydrogen bonding between starch and polyol increasing polyol diffusivity and, thus, phase separation may occur (Godbillot *et al.*, 2006). Polyol crystallization in binary polyol mixtures was not observed at contents of mixtures used and under storage conditions used in the present study (III). Krogars *et al.* (2003b) have used in the starch film a binary mixture of glycerol and sorbitol as plasticizer by which sorbitol crystallization could be prevented. Inhibition of polyol crystallization using binary polyol mixtures is analogous to the confectionery products in which crystallization of sucrose could be retarded or prevented using mixture of sugars (Roos and Karel, 1991a; Arvanitoyannis and Blanshard, 1994). Roos and Karel (1991a) have reported delayed sucrose crystallization above its T_g due to fructose addition resulting in increased viscosity.

6.3.2 Water sorption (II–IV)

Water content of all films increased with increasing RVP and steady-state water contents were reached within 48 h. Water sorption isotherms of the plasticized films modeled using GAB model (**Equation 3**) were similar in the shape whereas the film without plasticizer showed different shape (II–III, see Fig. 1–2). Correspondingly, water sorption isotherms modeled using BET model (**Equation 2**) did not show as a good fit with the data as GAB model. This resulted most probably from the fact that water activity values of 0–0.44 were used in BET modeling. Bell and Labuza (2000) have stated that the BET model is applicable only in water activity range up to 0.5.

The film without plasticizer had a higher water content than the films with any plasticizer type and content at low water activity. Moreover, the water content of the films increased with increasing plasticizer content and the extent of the increase was more pronounced at high water activities (II–III). Similar water sorption behavior has been reported for amylose and amylopectin films plasticized with glycerol (Myllärinen *et al.*, 2002b), waxy maize starch glycerol blends (Enrione *et al.*, 2007b), caseinate-pullulan films plasticized with sorbitol (Kristo and Biliaderis, 2006), pullulan starch blends plasticized with sorbitol and xylose (Biliaderis *et al.*, 1999) and mixture of freeze-dried gelatinized starch and glucose (Saravacos and Stinchfield, 1965). Films without plasticizer has more available sorption sites than films with plasticizer at low water activities. One glucose monomer of starch is able to bind 0.7 to 1 molecule of water at water activity of monolayer water content (van den Berg *et al.*, 1975) and the first water molecules are bound tightly in the starch at water activities below 0.2 (Bader and Göritz, 1994a).

In plasticized films there are interactions between hydroxyl groups of starch and hydroxyl groups of polyol. As hydroxyl groups of polyol and glucose monomers of starch form hydrogen bond between each others there are less sorption sites available for water in glucose monomers of starch. Hydroxyl groups located at both ends of polyol backbone were expected to be more accessible to water molecules than the other hydroxyl groups of polyol (Mathew and 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. Polysaccharide-based products containing high contents of sugars showed long flat segments in the sorption isotherm at water activities up to 0.6 followed with rapid increase in water sorption because of differences in water sorption affinities of polysaccharides and sugars (Biliaderis *et al.*, 1999). In those polysaccharide-based products, polysaccharides adsorbed more water than sugars at low water activities up to 0.6, whereas polysaccharides and sugars have opposite sorption behavior at high water activities (Biliaderis *et al.*, 1999). 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 were so strong that water sorption cannot break starch-polyol hydrogen bonds (Gaudin *et al.*, 1999). This is in agreement with results in the present study, which showed also that polyol plasticized starch films sorbed less water at low water activities independently of plasticizer type and content.

In the present study amylose content was not observed to affect water sorption behavior of the films plasticized by the binary mixture of xylitol and sorbitol (IV). The water content of films prepared from amylose and amylopectin blends was reported to increase with increasing amylose content (Rindlav-Westling *et al.*, 2002). The increasing water content of starch films is related to the increase in crystallinity in film because water incorporates with B-type crystalline structure (Rindlav *et al.*, 1997). In the present study, difference between the lowest and highest amylose contents from total starch was about 10%. This difference was probably too small, so that the effect of the amylose content on the properties of the film could be found out.

6.3.3 Thermal properties (II–III)

The T_g of polyols used were –86 (Murthy, 1996), –26 and –6°C (I) for glycerol, xylitol and sorbitol, respectively. Moreover, the T_g values for anhydrous binary polyol mixtures (ratio of 1:1) have been reported to be –61 and –57°C for Gly-Xyl and Gly-Sor, respectively, and –15°C for Xyl-Sor (Talja *et al.*, 2003). In the present study, one T_g was obtained for the films plasticized with all polyols and binary polyol mixtures and T_g of the films decreased with increasing RVP. The T_g of the films were in accordance with the T_g of the anhydrous amorphous polyols and binary polyol mixtures (II–III). The T_g of the film plasticized at glycerol content of 30% and stored at RVP of 0% could be determined whereas the T_g of the films plasticized with xylitol and sorbitol at contents of 30 and 50% could be determined when stored at RVP ranging from 0 to 76% (II). Two T_g values, plasticizer rich and polymer rich domains, have been reported for a corn starch film plasticized at glycerol content of 33% of solids and stored at RVP ranging from 0 to 75% (Mathew and Dufresne, 2002). The T_g of corn starch films plasticized with xylitol (33% w/w, solids) varied from 13 to –55°C and the T_g of films plasticized with sorbitol (33% w/w, solids) varied from 13 to –52°C at RVP ranging from 0 to 75% (Mathew and Dufresne, 2002). The T_g of 90°C has been reported for potato starch-based film without plasticizer stored at RVP of 57% (Lourdin *et al.*, 1997b).

Temperatures of endothermic peaks decreased from 73 to 53°C for the film plasticized at xylitol content of 50% when stored at RVP ranging from 33 to 76%. These endothermic peaks were related to dissolving of xylitol crystals which could be suggested from by the facts that solubility of most sugars in water increases with increasing temperature (Roos, 1995) and melting temperature of anhydrous xylitol is 93°C (I). Moreover, endothermic peaks at higher temperature (94–170°C) were found in the DSC thermograms recorded from the films plasticized with glycerol at content of 30% and xylitol and sorbitol at contents of 30 and 50% stored at various RVP (II). Such endothermic peaks may be due to melting of starch crystallites. Melting endotherms of cocrystallized amylose and amylopectin at 110–120°C have been reported for films prepared from blend of amylose and amylopectin as well as from potato starch when stored at RVP of 54% (Rindlav-Westling *et al.*, 2002).

6.3.4 Crystallinity (IV)

For films prepared from P2, V1 and Se1, a small peak at the scattering angle of 17° was observed, indicating that the films were mostly amorphous but contained a small amount of crystallites. One reason for the low crystallinity could be the rapid drying of films in an oven with air circulation, which removed the evaporated water from the film surface effectively. In the case of starch gel it has been shown that crystallinity increased over several days when there was water present all the time (Miles *et al.*, 1985b). But this is not the case in film formation, in which water is removed and there is not time enough to form crystallinity in the film. Anyhow, water plasticizes the starch macromolecules in the film forming suspension, allowing higher molecular mobility and crystallization (Rindlav-Westling *et al.*, 1998). Increasing RVP during the starch film formation has been reported to extend the formation time and simultaneously to increase the crystallinity, whereas an elevated temperature has been reported to reduce the crystallinity (Rindlav *et al.*, 1997). In the present study, another explanation for the low crystallinity observed in starch films could be the binary polyol plasticizer and its tendency to retard crystallization in starch. The use of a plasticizer has been reported to decrease the crystallinity of starch-based films because the plasticizer hindered the packing of starch macromolecules (García *et al.*, 2000; Mali *et al.*, 2006; Shi *et al.*, 2007). Starch films plasticized at glycerol content of 20% of solids were reported to be amorphous after 24 hours of storage at RVP of 57% (Lourdin *et al.*, 1995). The storage conditions used in the present study is close to those conditions under which the crystallinity in a glycerol-plasticized (23.3% of solids) starch film did not increase during the storage (van Soest *et al.*, 1996b). The crystallinity in potato starch films has been shown to increase significantly during two weeks of storage as the relative humidity increased from 60 to 70% (van Soest *et al.*, 1996b).

6.3.5 Water vapor permeability (II–IV)

In the present study WVP properties of the all films could be determined successfully. A constant weight increase as a function of time was observed and WVP of all films increased with increasing RVP gradient (II–III). Similar effect of RVP gradient has been reported, *e.g.*, for tapioca starch films (Chang *et al.*, 2000). The film has a lower capacity to transfer water through its structure when it contains less water. On the other hand, the film plasticization probably increases diffusion rate of water in film and, thus, WVP increases with increasing plasticizer content. 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 and Fennema, 1986). In the present study, WVP of plasticized films increased with increasing plasticizer content as reported for biopolymer films in the other studies (*e.g.*, Cuq *et al.*, 1997; Chang *et al.*, 2000). At low RVP, 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. This probably decreases diffusion rate of water molecules through the plasticized film. Guo (1993) has shown for cellulose acetate film at plasticizer contents of 5–10% (w/w, solids) lower WVP values than for film without plasticizer because of decreased molecular mobility of cellulose acetate due to biopolymer plasticizer interactions. At higher RVP, 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. On the contrary, the cracks and pores have been reported to increase WVP of the films without plasticizer (Mali *et al.*, 2004).

WVP seemed to be dependent on plasticizer content and type in the films. The T_g of the polyols (I) and binary polyol mixtures (Talja *et al.*, 2003) were found to affect T_g of the film and WVP. WVP of films containing glycerol was higher than that of films containing other plasticizers used in the present study. Decrease in T_g was due to plasticization effect of the polyols and binary polyol mixtures as well as water. Moreover, phase separation may occur in glycerol containing films resulting in slightly lowered WVP values.

In the present study WVP of the films was not found to depend on the amylose content. Amylose content did not affect crystallinity in the films. Crystallinity in the starch film has been reported to affect WVP due to decreased diffusivity of water molecules (Mali et al., 2006). Moreover, WVP of films prepared from blends of cassava starch and amylose has been reported to increase with increasing amylose content due to an increased number of free hydroxyl groups (Alves *et al.*, 2007). The differences found in the present study in WVP probably originated from the difference in film thicknesses. Generally, WVP increased slightly with increasing thickness, although the thickness values were already used in the calculation of WVP. An increase of WVP with

increasing thickness has been reported for protein films (McHugh *et al.*, 1993; Longares *et al.*, 2004).

6.3.6 Mechanical properties (II–IV)

Generally, Young's modulus and tensile strength of films plasticized with single polyols and binary polyols mixtures decreased with decreasing T_g of the single polyol (I) and binary polyol plasticizers (Talja *et al.*, 2003) coinciding with an increase in elongation at break (II–III). Moreover, the films were plasticized by water (II–III). In the present study, low values of elongation at break were observed for films with low plasticizer contents (II–III). 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 *et al.*, 1995). Elongation at break of approximately 8% was reported for corn starch films plasticized with glycerol and sorbitol at contents of around 20% of solids and containing 5% 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% to 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 in all films at plasticizer contents of 20% and 30% values of 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 (II–III). Similar behavior has been also reported in other studies (*e.g.*, Biliaderis *et al.*, 1999; Mehyar and Han, 2004). Starch films swelled at high RVP due to high water content of film (Bader and Göritz, 1994a). 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 the film which do not last big deformations. This was observed at high RVP as elongation of film was found to decrease instead of increase which was expected to occur with increasing plasticizer content and RVP as reviewed, *e.g.*, by Krochta (2002).

In the present study xylitol and sorbitol crystallization in the films was observed resulting in increased values of Young's modulus and tensile strength (II). Such change in the mechanical properties was most probably resulted from decreased amount of plasticizing polyol in the film allowing enhanced interactions between starch molecules.

Crystallinity in starch film has been shown to increase with decreasing plasticizer content (García *et al.*, 2000). Moreover, phase separation of starch components could occur simultaneously with polyol crystallization resulting in increased crystallinity of starch. Polyol crystallization was not observed when binary polyol mixtures were used as plasticizers in starch-based films (III). Crystallization of sorbitol in maize starch-based films was not observed during 9 months of storage at 25°C and RVP of 60% when a binary polyol mixture of Gly-Sor (1:1) was used as a plasticizer at the contents of 33% and 50% (w/w, solids) (Krogars *et al.*, 2003b).

In the present study low crystallinity of starch was observed in the films varying amylose contents plasticized with Xyl-Sor at content of 30% at RVP of 54%. Mechanical properties of such films seemed to be independent of amylose content (IV). Low crystallinity in potato starch film observed at RVP below 50%, but crystallinity in film increased remarkably at RVP above 50% (van Soest *et al.*, 1996b). Decreased values of elongation at break were originated from increased starch crystallinity induced by high storage RVP as it has been reported to occur in starch films (van Soest *et al.*, 1996b). Moreover, the Young's modulus and the tensile strength of glycerol plasticized potato starch films increased with increasing crystallinity during the storage time (van Soest *et al.*, 1996b). Crystallization of starch components occurred during film formation (Rindlav *et al.*, 1997; Rindlav-Westling *et al.*, 1998) increasing Young's modulus and tensile strength (Rindlav-Westling *et al.*, 1998; Bader and Göritz, 1994b) which could be observed from increased rigidity of the starch film. The Young's modulus and the tensile strength of glycerol plasticized cassava starch films have been reported to increase with increasing amount of added amylose due to a denser polymer network (Alves *et al.*, 2007).

7 SUMMARY AND CONCLUSIONS

The amylose content of the potato starches was found to vary from 11.9 to 20.1% and there were differences in the amylose content of starches extracted from the same potato cultivars grown during different years. The gelatinization properties and the crystallinity (10–13%) of various native potato starches were found to be independent of the amylose content. The glass transition temperatures (T_g) of the polyols were well below room temperature being for erythritol, xylitol and sorbitol –45, –29 and –6°C, respectively, as determined by differential scanning calorimeter (DSC). Similar T_g, taken from α-relaxation, was obtained for xylitol and sorbitol as dielectric analysis (DEA) and dynamic mechanical analysis (DMA) were used. The T_g values of polyols decreased with increasing water content due to water plasticization. Similar plasticization behavior was observed from complementary detection of changes in dielectric, mechanical and thermal properties occurring over the glass transition. In the present study the polyols selected to plasticize the starch films were glycerol, xylitol and sorbitol and their binary mixtures. Glycerol was selected because it is well known and widely used as a plasticizer in the biomaterial films. Erythritol was not used as a plasticizer in the films because of its high tendency to crystallize. The polyols and binary polyol mixtures could be used as plasticizer in the films prepared by casting to obtain flexible and elastic films which were easy to handle. Brittle films were obtained as low plasticizer contents were used. In the films plasticized at high contents of glycerol, xylitol and sorbitol, phase separation took place resulting in sticky surface on the films plasticized by glycerol, whereas crystallites appeared on the films plasticized by xylitol and sorbitol. Moreover, crystallites observed on the surface of the film dissolved at high RVP resulting in sticky surface of the film. The crystallization of xylitol and sorbitol could be prevented as the binary mixtures of polyols were used to plasticize films. The storage RVP affected the film properties in addition with polyol and binary polyol plasticizer. Plasticizer type and content were found to affect physical and mechanical properties of potato starch films. Water sorption and WVP of films increased as a result of increased plasticization with polyols and binary polyol mixtures. As plasticizer content of films and storage RVP 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. In films starch was found to be amorphous, which may be due to the fast drying process and the presence of plasticizer. Difference in amylose content of native potato starches did not have remarkable effect on potato starch films properties. This indicates that adjustment of the film forming process is not needed when the starch batch is changed. The effect of amylose content of native starch on the film properties seemed to be less important in the present study than what has been observed in films prepared from a blend of native starch and amylose (Alves *et al.*,

2007) or a blend of amylose and amylopectin (Lourdin *et al.*, 1995). Overall, the best properties, if good barrier and mechanical handling properties are desired, of potato starch-based films produced in the present study were observed in Xyl-Sor plasticized films. The basic data obtained in the present study on the effects of plasticizer type and content as well as water on the physical and mechanical properties of films are important in assessing applicability of films in food and pharmaceutical industries. Films studied in the present work are suggested to be suitable for low moisture foods and pharmaceutical products.

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