

Effects of chemical structure of common monosaccharides
and polyols on plasticization and antiplasticization of starch
films

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BY

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A Thesis
Submitted to the Faculty of Graduate Studies
In Partial Fulfillment of the Requirements
for the Degree of

DOCTOR OF PHILOSOPHY

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University of Manitoba
Winnipeg, Manitoba

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**A Thesis/Practicum submitted to the Faculty of Graduate Studies of The University of
Manitoba in partial fulfillment of the requirement of the degree**

DOCTOR OF PHILOSOPHY

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To my parents and my family

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ABSTRACT

Monosaccharides have several hydroxyl groups and a compatible structure with starch polymers likely resulting in effective plasticization in starch films. Two groups of plasticizers (polyols and monosaccharides) were used to compare their plasticizing efficiency. Fructose, glucose, mannose, galactose, glycerol, sorbitol, ethylene glycol and maltitol were selected at 13.031 mmol per 100 g of pea starch. Edible starch films were produced after heat gelatinization and dehydration of the 3% starch dispersion. The microstructure, attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR) characteristics, thickness, moisture content, tensile strength, modulus of elasticity, elongation-at-break, water vapor permeability, and transparency of films were determined. Microstructure of the film solutions showed that some swollen starch granules and their remnants existed in the film. Compared to the FTIR spectra of pure starch films, the spectra of plasticized films showed that more hydrogen bound hydroxyl groups and more water molecules were attracted around starch polymer chains. Monosaccharide-plasticized films were comparable to the polyol-plasticized films in parameters determined from the tensile test, but were more resistant in moisture permeation than the polyol-plasticized films. It was assumed that the structural compatibility of monosaccharides with starch might result in a denser polymer-plasticizer complex, smaller size of free volume, and less segmental motions of starch chains. In conclusion, monosaccharides were identified as effective plasticizers for starch film.

Edible starch films were produced from pea starch and various plasticizers (mannose, glucose, fructose, glycerol, ethylene glycol, and sorbitol) at the ratio of 4.34, 6.50, 8.69,

and 10.87 mmol plasticizer per g of starch. After film specimens were conditioned at 50% relative humidity, mechanical properties (tensile strength, elongation, and modulus of elasticity), water vapor permeability (WVP), moisture content, and thermomechanical properties (E' and $\tan\delta$) were determined as a function of plasticizer concentration. Galactose-films appeared brittle, and maltitol-films sticky. They could not be peeled off intact from Petri dishes. Therefore, they were dropped from the experiments. The reason galactose films were brittle was probably because the galactose hygroscopicity is too low. And reason maltitol films were sticky was the maltitol amount used in the films as plasticizer was too much. At all concentration levels, monosaccharides (mannose, glucose and fructose) made the starch films stronger (higher tensile strength) and more stretchable than polyols (glycerol and sorbitol), while WVP of monosaccharide-plasticized starch films were lower than those of polyol-plasticized starch films, especially at higher plasticizer concentration level. Except for 4.34 mmol/g of mannose-plasticized film, all the other films showed similar modulus of elasticity at the same plasticizer concentration. Polyol-plasticized films had lower T_g than the monosaccharide-plasticized films. Glucose- and sorbitol-plasticized films needed more activation energy to go through their glass transition than others. Research results showed that not only the polyols but also the monosaccharides were effective in plasticizing starch films. It was concluded that the plasticizer which can provide higher ratio of hydroxyl number to its molecular weight can be considered as a better plasticizer. The best plasticizer should be water which can provide ratio of 0.056. However, water is very hard to control in the film, because it totally depends on the relative humidity (RH). The second best plasticizers should be glycerol and EG which provide ratios of 0.033 and 0.032,

respectively. Although sorbitol has ratio of 0.033, its molecular size is almost double big that of glycerol. So, sorbitol plasticization capacity is reduced. Monosaccharides have a ratio of 0.027 of hydroxyl group number to its molecular weight. However, because the structure and configuration of the monosaccharides is compatible to anhydroglucose units of the starch, they still can be competitive plasticizers to sorbitol.

Effect of plasticizer content (4.34 to 10.87 mmol per g of dry starch) and storage relative humidity (RH) (11.3% to 75.4%) on moisture content (MC), tensile strength (TS), elongation (E), modulus of elasticity (EM), and water vapor permeability (WVP) were evaluated using response surface methodology. EG was dropped, because during the experiments the EG film became brittle at low EG concentration level and low RH conditions. MC was influenced strongly by RH. Glycerol-plasticized films had the highest MC, indicating that water molecules played a more important role in plasticizing starch films. Monosaccharide-plasticized films and polyol-plasticized films had similar TS values. However, monosaccharide-plasticized films had higher E values and lower EM values than polyol-plasticized films, meaning monosaccharides had better efficiency in plasticizing starch films. Recrystallization happened in glucose- and sorbitol-plasticized films when they were stored in high RH. Sorption isotherm studies showed similar adsorption and desorption profiles for all three monosaccharide-plasticized films and hysteresis. Flory-Huggins model fitted experimental data best for starch films, while BET model fitted the data marginally.

Pea starch films were plasticized by ethylene glycol, glycerol, sorbitol, glucose, mannose, and fructose, separately. The concentration of the various plasticizers were 0%,

1%, 5%, 10%, 15%, 20%, and 25% (w/w, plasticizer/starch). Crystallinity, tensile strength (TS), elongation (E), modulus of elasticity (EM), water vapor permeability (WVP), moisture content (MC), and oxygen permeability (OP) were tested as a function of the plasticizer concentrations. After 14 ± 2 days of storage at 50 ± 2 % relative humidity, pea starch films showed increased crystallinity with increasing concentration of plasticizers from 0 to 20. Accordingly, the MC, WVP, OP, and tensile properties decreased with increasing plasticizer concentration from 0% to 20%, showing the antiplasticization effect. After 20 %, the crystallinity decreased. MC, WVP, OP increased and TS, EM decreased as plasticizer content increased. As a conclusion, addition of the plasticizers increased the crystallization of the polymer chains through the antiplasticization phenomenon at the range below 20 % (g in g of starch). Above the specific low concentration ($> 20\%$, in this case), plasticizers performed the plasticization effect. Different plasticizers had a different critical concentration range where the antiplasticization function/phenomenon was observed. Mechanism of antiplasticization had been proposed at molecular structural level. The mobility or vibration of the segments of starch polymer chains pushed aside the plasticizer molecules including water molecules. Intermolecular hydrogen bondings between O-6 of D-glucosyl residues of amylose or amylopectin molecules and OH-2 of other D-glucosyl residues of amylose or amylopectin molecules interacted to form hydrogen bonding directly.

According to the study results, the recommended plasticizer concentration for plasticization of the starch films is as follows:

Fructose is in the range of 4.34 to 10.87 mmol at almost entire RH. Mannose and glucose should be from 4.34 to 8.69 mmol at RH below 50 %. Otherwise, the crystallization

occurs. Glycerol can have a broader range. Sorbitol is like glucose. Its concentration will be below 8.69 mmol in case of crystallization occurs.

Chapter 1

Introduction

Plastics made from petroleum have been widely used through out the world. With
5 increased applications, the disposal of waste plastics has become a serious problem.
Therefore, the development of novel plastics that can be degraded by microorganisms in
soil and seawater has been emphasized. The materials that are used in developing the
novel plastics are mainly biopolymers, such as polysaccharides, proteins, lipids, and their
combination (Fang and Hanna 2000). Starch is the most commonly used natural polymer,
10 because it is inexpensive, widely available and relatively easy to handle (Guilbert and
others 1996, 1997). Recent research has shown that combining starch with synthetic
polymers does not make the synthetic fraction from the petroleum source susceptible to
biodegradation (Tanaka and others 2001; Fishman and others 2000). Therefore, the most
recent research has focused on pure starch-based materials, chemically modified starch
15 (Fringant and others 1996; 1998; Morikava and Nishinari 2000; Sitohy and Ramadan
2001), and starch/degradable polymer blend materials such as starch/cellulose, and
starch/poly vinyl alcohol (PVOH) (Arvanitoyannis and others 1998; Averous and
Fringant 2001; Wu 2003; Tanaka and others 2001). Natural starch consists of both
amylopectin and amylose. The branches of amylopectin prevent intermolecular
20 association because of the more compact configuration, lower hydrodynamic volume and
smaller radius of gyration than a linear polymer of the same molecular weight (Endres
and others 1994). Therefore, the branched amylopectin-based films are weak and brittle

whereas the linear amylose molecules can form strong and flexible films (Fang and Hanna 2000; Zobel 1988; Ke and Sun 2001). Amylose in starch is mainly responsible for
25 the film-forming capacity of starches and properties of films (Tomasik and others 1995).

Plasticizers are added into the film-forming dispersion to improve the processibility and physical properties of the films (McHugh and Krochta 1994; Debeaufort and Quezada-Gallo 1998; Guilbert and others 1996; Guilbert and others 1997). Plasticizers are
30 nonvolatile, high boiling, and non-separating substances, that change the physical and/or mechanical properties of another material when it is added (McHugh and Krochta 1994). Plasticizer plays a very important role in starch film formation, since they can strongly affect the film structures and, accordingly, their properties (Jovanovic and others 1997). The basic rationale of plasticizing is that plasticizers can attract the water molecules
35 around them, reduce the interactions between the biopolymer chains, and then increase the flexibility of films (Debeaufort and Quezada-Gallo 1998), which is analogous to the lubrication of metal parts by oil. Without plasticizers, starch films are readily broken into fragments when they are dry in ambient conditions. Some polyols, such as glycerol, sorbitol and ethylene glycol, are preferred by researchers. Their effects on starch films
40 have been extensively studied over last 20 years. The working or active parts in these plasticizer molecular structure are believed to be hydroxyl groups which are hydrophilic nature.

Study on the starch shows that both amylose and amylopectin consist of polymers of α -
45 D-glucose units in the 4C_1 conformation. In amylose these are linked $-(1\rightarrow4)-$, with the

ring oxygen atoms all on the same side, whereas in amylopectin about one residue in every twenty α -D-glucose units or so is also linked $-(1\rightarrow6)-$ forming branch-points. Glycerol plasticization on the starch film had been investigated by Godbillot and others (2006). Interactions between water, glycerol, and starch were analyzed on a stoichiometric basis in a wide range of relative humidity (RH) (0 – 80%) and of plasticizer ratios (0 – 52.6 %). A schematic representation of the different types of binding between starch, water, and glycerol is given. Mali and others (2005b), and Garcia and others (2000) found that sorbitol films had less moisture content than glycerol film. They pointed out that sorbitol can interact with starch polymer chain with higher chance than does glycerol due to the fact that sorbitol is more similar in molecular structure to glucose units than glycerol. Ryu and others (2002) found that the sorbitol films were stronger than glycerol films. Guilbert and others (1996) and Tomasik and others (1995) also pointed out that effective plasticizers must be compatible with the film-forming polymer. Sugars occur frequently in six-membered pyranose ring. Although the more strained five-membered (furanose) and seven-membered (septanose) rings occur, the amounts of these higher-energy forms are limited. Polyols are usually products from hydrogenation of the corresponding sugars. They do not exist in the ring forms. Therefore, according to the compatibility requirement, monosaccharides should be expected to act as plasticizers in starch films more effectively than, or at least comparative to, polyols, not only because of hydroxyl groups in their molecules, but also because of their similarity in structure and conformation to anhydroglucose in starch molecules. According to research published recently, the polyols are the most preferred plasticizers in starch film forming. Only a few researches regarding monosaccharides

working as plasticizers in starch films is done. The research will figure out the plasticization effect of monosaccharide on the starch films.

The presence of four different chiral centers in six-carbon aldohexose monosaccharides gives rise to 2^4 or 16 possible stereoisomeric forms of the 16 different six-carbon sugars with an aldehyde end. In our research project, only the most common monosaccharides, that is, glucose, fructose, galactose, and mannose, will be selected as plasticizers, with the reference of polyols, such as glycerol, sorbitol, maltitol, and ethylene glycol.

Preliminary studies in our lab showed that yellow field pea starch could produce films with good mechanical properties and clarity. It contains about 37 - 40 % amylose, which is much higher than other plant sources cultivated in Manitoba. Apart from favorable amylose content, yellow pea is a major crop in Canada. In 1997 - 98, Canada produced about 14 % of the world's dry peas (about 13 million tons), and most of this was exported to Europe. Saskatchewan, Alberta, and Manitoba respectively account for about 70, 20, and 10 % of the dry pea seeded area. The area cultivated has been rising for the past 20 years, especially recently, due to an expanding export market, particularly in the European Union, where peas are a traditional feed ingredient for hogs. In eastern Canada, where only 1,000 ha were seeded to peas in 1996, the crop is used mainly for on-farm livestock feed, and the prospects for peas as a new crop in areas other than the prairies seem limited (Small 1999). Opening the food wrapping or coating market to field peas would provide a boost for the crop. Therefore, the yellow field pea starch was selected for this research project.

The main objective of the research was to determine the plasticization effect of the above mentioned monosaccharides and polyols on pea starch film, and the antiplasticization mechanism of the starch film. Apart from yielding biodegradable and edible packaging products, the development of novel starch packaging materials providing potential benefit on food preservation should have a positive impact in the marketplace. The long term objective is to develop a validated method for use by food packaging industry to achieve the desired reduction of waste synthetic plastics, thereby providing enhanced food stuff sensory characteristic, providing additional nutrients contained in the starch films, and extending food shelf life by including quality enhancing agents, such as antimicrobials, antioxidants, etc.

Chapter 2

Literature Review

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2.1 GENERAL PROPERTIES AND STRUCTURE OF STARCH

Commercially important starch is obtained from corn, wheat, rice, potatoes, tapioca and peas. Starch is a polysaccharide which is produced in almost all plants by photosynthesis. Naturally occurring starch is present in the form of semicrystalline granules, which vary
110 in shape (round, lenticular, polygonal), granule size (1 - 100 μm in diameter), size distribution (uni- or bi-modal), association (individual or granule cluster), and chemical composition (α -glucan, lipid, moisture, protein and mineral content) (Tester and others 2004; Mali and others 2006). Starch consists of two components, namely amylose and amylopectin. Amylose is a mostly linear α -D-(1 \rightarrow 4) glucan, the molar mass of which is
115 several hundred thousand g/mol. Amylopectin is a highly branched α -D-(1 \rightarrow 4) glucan, with α -D-(1 \rightarrow 6) linkages at the branch points. The molar mass of amylopectin can be as large as 100 million g/mol (Moates and others 2001). The content of amylose depends on the plant source and can vary from 14 to 27 %. For example, the “waxy” starches contain less than 15% amylose, “normal” 20-35% and “high” amylose starches greater than about
120 40% (Tester and others 2004). Both amylose chains and branches of amylopectin can form double helices, which may in turn associate and form crystalline domains (Tester and others 2004). The degree of crystallinity within starch granules has been historically determined with X-ray diffraction (XRD). Maize starch granules contain 43 - 48% crystallinity; wheat, 36 - 39%; potato, 23 - 53%; pea, 17 - 20%; normal barley, 2 - 24%;

125 rice, 38% (Tester and others 2004). The application of X-ray diffraction can also reveal
the types of crystallinity due to the amylose content of starch, the starch origin, the
transformation process (thermomoulding, extrusion or casting), and the additives. Three
X-ray diffraction patterns exist in native starch granules. Cereal starches (rice, wheat, and
corn) exhibit an A-type pattern, in which the double helices pack in an anti-parallel
130 manner into an orthorhombic unit-cell (Fig. 2.1), resulting in nearly hexagonal close-
packing. Tubers, fruit, high amylose corn (> 40%) starches show a B-type pattern in
which the double helices pack also in an anti-parallel manner but into a hexagonal unit
cell with two helices per cell, leaving an open channel that is filled with water molecules
(Fig. 2.1). The C-type pattern, which is intermediate between A and B type, is observed
135 for legume seed starches (Abd-Karim and others 2000; Liu 2005; Karim and others 2000).
The A, B, and C type of X-ray diffraction patterns are shown in Fig. 2.2. Pattern A shows
three strong peaks at 5.8, 5.2, and 3.8 Å. Pattern B shows a peak at 15.8 - 16.0 Å, a broad
medium-intensity line at about 5.9 Å, a strong line at 5.2 Å and a medium-intensity
double line at 4.0 and 3.7 Å. Pattern C is the same as A except for the addition of the
140 medium-to-strong peak at about 16.0 Å (Ribotta and others 2004). Starch contains 2%
integral lipids in the form of lysophospholipids (LPL) and free fatty acids (FFA), 0.6%
protein, and 0.4% minerals (calcium, magnesium, phosphorus, potassium, and sodium).
Starch is hydrophilic. Its moisture content depends on the relative humidity (RH) of the
atmosphere in which it is stored. The moisture content of starch equilibrium in ambient
145 air ranges from 10 - 12% for cereal starch to 14 - 18% for starch from some roots and
tubers (Tester and others 2004). Starch has seen very wide applications, such as
thickening, pasting, etc. One of its advantages is renewability, since it is produced by

plants annually. Starch is also biodegradable. Its properties can be changed and adjusted to meet various purposes. Many properties of starch are close to those of synthetic
150 polymers. Therefore, it is possible to use processing of synthetic polymers, such as extrusion, injection molding, etc, for starch processing as for synthetic polymers. Starch has been used as biodegradable filler for commercial thermoplastic polymers. There has been a growing interest in obtaining thermoplastic starch containing relatively low amounts of additives. Thermoplastic starch can be used for the production of articles
155 unlikely to be recycled, such as trash and compost bags, mulch films and disposable diapers (Jovanovic and others 1997). Most recently, starch-based films for food packaging have received increasing attention from food industries and food scientists.

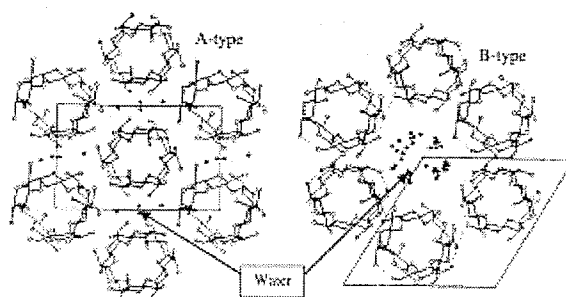
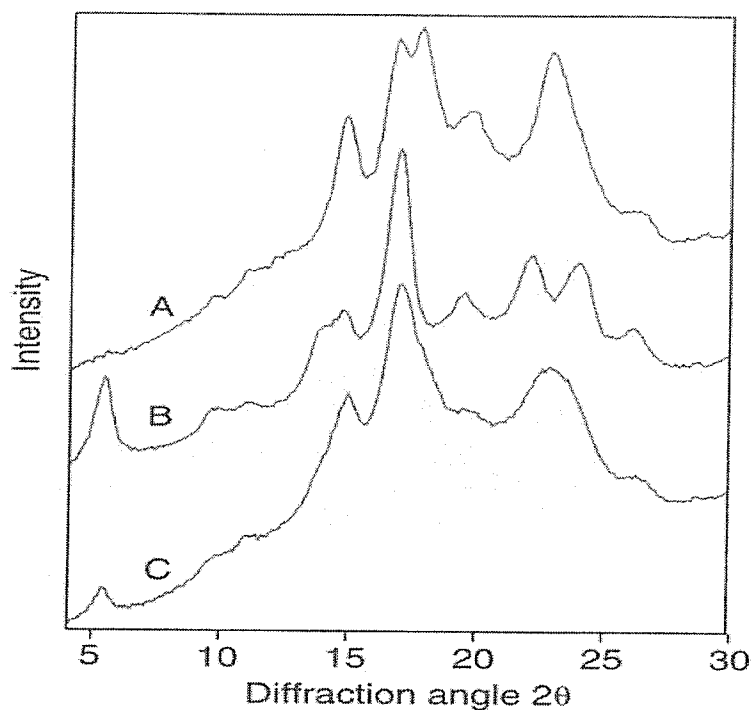


Fig. 2.1 A- and B-type polymorphs of amylose (From Wu and Sarko, 1978)



170 Fig. 2.2 X-ray diffraction spectrum for A-type (corn), B-type (potato), and C-type (pea)
starch. (from Bogracheva and others, 1999)

2.2 EDIBLE FILMS

2.2.1 History of edible films

175 Edible films and coatings were used hundreds of years ago. For example, wax was
applied to citrus fruits to delay their dehydration since the twelfth and thirteenth centuries
in China (Debeaufort and others 1998). Yuba obtained from the skin of boiled soy milk,
essentially a protein film, was used to preserve the appearance of some foodstuffs in Asia
in fifteenth century (Debeaufort and others 1998; Han and Gennadios 2005). In the
180 sixteenth century, fats were used to coat meat cuts to prevent shrinkage. Lard or wax was
used to enrobe fruit and other food stuffs in England (Miller and Krochta 1997). Later in

nineteenth century, gelatin films were used to cover meat stuffs. Also in nineteenth century, sucrose was chosen as an edible protective coating on nuts, almonds, and hazelnuts to prevent oxidation and rancidness (Debeaufort and others 1998). In the last
185 thirty years, petrochemical polymers, commonly called plastic, have been the most commonly used materials for packaging because of their high performance and low cost (Callegarin and Quezada-Gallo 1997). However, the serious environmental problems associated with non-biodegradable materials have urged scientists to search for new alternative materials (Petersson and Stading 2005; Peressini and others 2003). Thus,
190 edible or biodegradable packagings made from various biological resources and their applications have recently been investigated. Shellac and wax coatings on fruits and vegetables, zein coatings on candies, and sugar coatings on nuts are the most common commercial practices of edible coatings (Han and Gennadios 2005). Cellulose ethers (carboxymethyl cellulose, hydroxypropyl, and methylcellulose) were used as ingredients
195 in coatings for fruits, vegetables, meats, nuts, confectionery, bakery, grains, and fired products (Han and Gennadios 2005; Garcia and others 2004; Carcia and others 2002).

2.2.2 Edible film materials and their previous applications

Environmental concern about the use of synthetic plastics for food packaging has led to
200 increased interest in biodegradable and edible film research (Lai and Padua 1997; McHugh and others 1993). Both dehydration and growth of microbials in food products were delayed by using the edible and biodegradable film and coating. Moreover, the flavor, odor, and overall organoleptic characteristics were not modified. Many materials from biological resources have been used for edible or biodegradable film and coating

formulations, such as polysaccharides, proteins, lipids, or their mixtures (Debeaufort 1998). Waxes (mineral oils, paraffin, beeswax, shellac, etc.) and oils were used largely as coating on fruits, such as orange, lemon, apple, pear, etc. They are really efficient barriers to water and can prevent from weight loss of fruits. Polysaccharides used in edible or biodegradable films and coatings include cellulose (Pinotti and others 2007), starch (Alves and others 2007, Pareta and Edirisinghe 2006), pectin (Fishman and others 2000), and algae gum (Veiga-Santos and other 2005). Proteins from various plant and animal sources, including wheat gluten (Kayserilioglu and others 2001), soy protein, zein (Lai and others 1997; Lai and Padua 1997), and casein (Sohail and others 2006; Letender 2002, Mauer and others 2000), have also been used in edible films. Lipids and their derivatives are mainly used in films or coatings to improve their moisture barrier properties. The properties of edible films depend on the type of film-forming materials and especially on their structural cohesion. Additives, such as plasticizers, cross-linking agents, anti-microbial agents, anti-oxidants, and texture agents, are used to alter the functional properties of the films. Among the natural polymers, starch has been considered as one of the most promising candidates for future materials because of the attractive combination of price, availability, and thermoplasticity (Mali and others 2005a; Lai and Padua 1997). Starch-based resins have been made into compost bags, disposable food-service items (cutlery, plates, cups, etc.), packaging materials (loosefill and films), coatings, and other specialty items (Lai and others 1997). Edible films and coatings from starch mainly find applications in the meat, poultry, seafood, fruit, vegetable, grains and candies industries (Debeaufort 1998). Currently, the use of edible films is still limited in practical applications due to their hydrophilic properties. Some efforts have been made to improve

the moisture resistance and water barrier properties of the edible films by combining with synthetic polymers or lipids and biopolymers (Han and others 2006). Protein and polysaccharide edible and biodegradable films present good ratio between CO₂ and O₂ permeabilities, from 10 to 25 when those of plastic films are lower than 5. Therefore, these films can serve as modified atmosphere packaging (MAP) materials to control the ripening of the fruits and vegetables. Indeed, zein coatings were already reported to apply on tomatoes and delay their color, weight, and firmness changes. For confectionaries, edible or biodegradable films and coatings were found very efficient to reduce the lipid oxidation and permeability. Many functions of edible or biodegradable films and coatings are the same as those of synthetic packaging. But edible and biodegradable films must be chosen according to a specific application, type of food product, and its main deterioration mechanisms (Guilbert and others 2005).

2.3 STARCH FILM

2.3.1 Starch film forming mechanisms - gelatinization and recrystallization

Often, the first step to produce starch films is heating starch in water. When heated at high water content, starch is gelatinized and transformed from a semicrystalline granular material into a system containing granular remnants, or to an amorphous paste with no structure at all (Smits and others 2003). The process is termed gelatinization, which corresponds to an irreversible swelling and breakage of starch granules, and leaching of amylose and amylopectin into the solutions. The gelatinization temperature depends on the source of starch, the ratio of amylose to amylopectin, and water content. High amylose starches (amylose: amylopectin ratio 70: 30) gelatinize at around 160 - 170 °C,

whilst wheat starch (amylose: amylopectin 28: 72) gelatinizes in the range 52 - 65 °C (Fang and others 2004). A gradual dissolution of starch granules allows a further hydration up to a point where the whole structure of the starch granules is completely disintegrated (Endres and others 1994). Often, non-crystalline swollen granular remnants
 255 named ghosts remain even after a long time of gelatinization (Fig. 2.3) (Mathew and others 2006; Smits and others 2003; Zhang and Han 2006b; Mehryar and Han 2004). Studies have shown that the presence of sugars in water increases the gelatinization temperature of starch (Whistler and BeMiller 1997). Various mechanisms have been proposed, including the ability of sugar to compete for water against starch, and the
 260 ability of sugars to reduce water activity in the system, resulting in less plasticizing effect of sucrose-water solvent (Maaurf and others 2001).

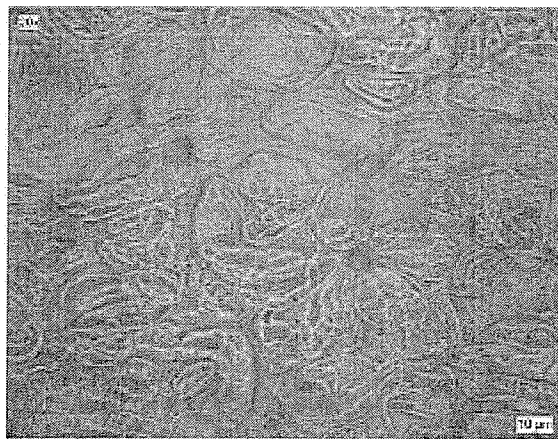


Fig. 2.3 Ghost granules on the surface of potato starch films under light microscope

(From Mathew and others, 2006)

265 T_g is defined as the temperature at which the forces holding the principal components (e.g. amylose and/or amylopectin) of an amorphous solid together are overcome, so that these components are able to undergo large-scale molecular motions. At a temperature

which is higher than the glass transition temperature (T_g), starch materials are in the
 270 rubbery state, and retrogradation (or recrystallization) occurs easily when gelatinized
 starch is stored at high relative humidity or high plasticizer contents (Delville and others
 2003). In the rubbery state, high relative humidity or high plasticizer content favors starch
 macromolecular mobility which facilitates the development of crystallinity (Delville and
 others 2003). Recently, the mechanisms of starch retrogradation have been extensively
 275 investigated. Starch retrogradation occurs as a result of intermolecular hydrogen bonding
 between O-6 of D-glucosyl residues of amylose molecules and OH-2 of D-glucosyl
 residues of short side-chains of amylopectin molecules (Fig. 2.4) (Tako and Hizukuri
 2000, 2002).

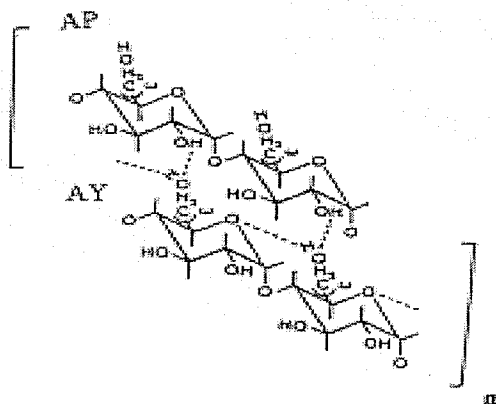
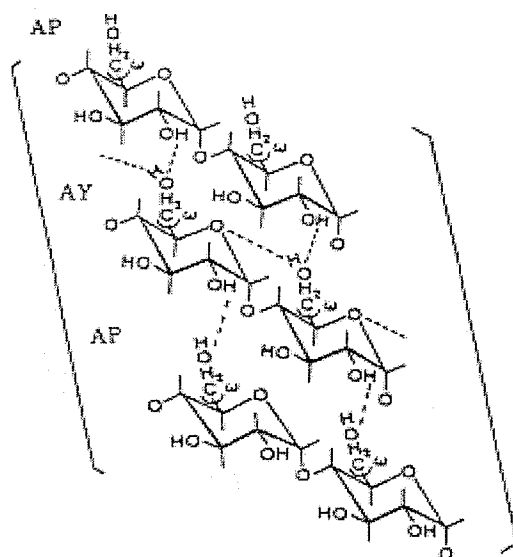


Fig. 2.4 Hydrogen bonding between amylose and amylopectin molecules (Dotted lines
 represent hydrogen bond. AY, amylose; AP, short side-chain of amylopectin molecules)

(From Tako and Hizukuri, 2002)

285 It can also be attributed to intermolecular hydrogen bonding between OH-2 of D-glucosyl residues of amylose molecules and O-6 of D-glucosyl residues of short side-chains of amylopectin molecule (Fig. 2.5).



290 Fig. 2.5 Retrogradation mechanism of starch (Dotted lines represent hydrogen bond. AY, amylose; AP, short side-chain of amylopectin molecules) (From Tako and Hizukuri, 2002)

In addition to intermolecular hydrogen bonding between amylose and amylopectin, hydrogen bonding between O-3 and OH-3 of D-glucosyl residues on different amylopectin molecules may also occur (Fig. 2.6) (Tako and Hizukuri 2000, 2002).
 295 Intramolecular association of amylopectin molecule was not suggested to exist, while intramolecular hydrogen bonding might take place between OH-6 and adjacent hemiacetal oxygen atom of the D-glucosyl residues within amylose molecules (Tako and Hizukuri 2000, 2002).

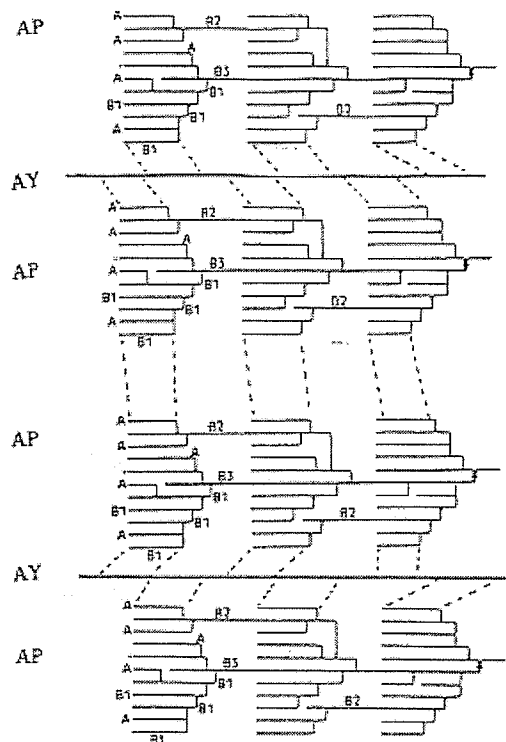
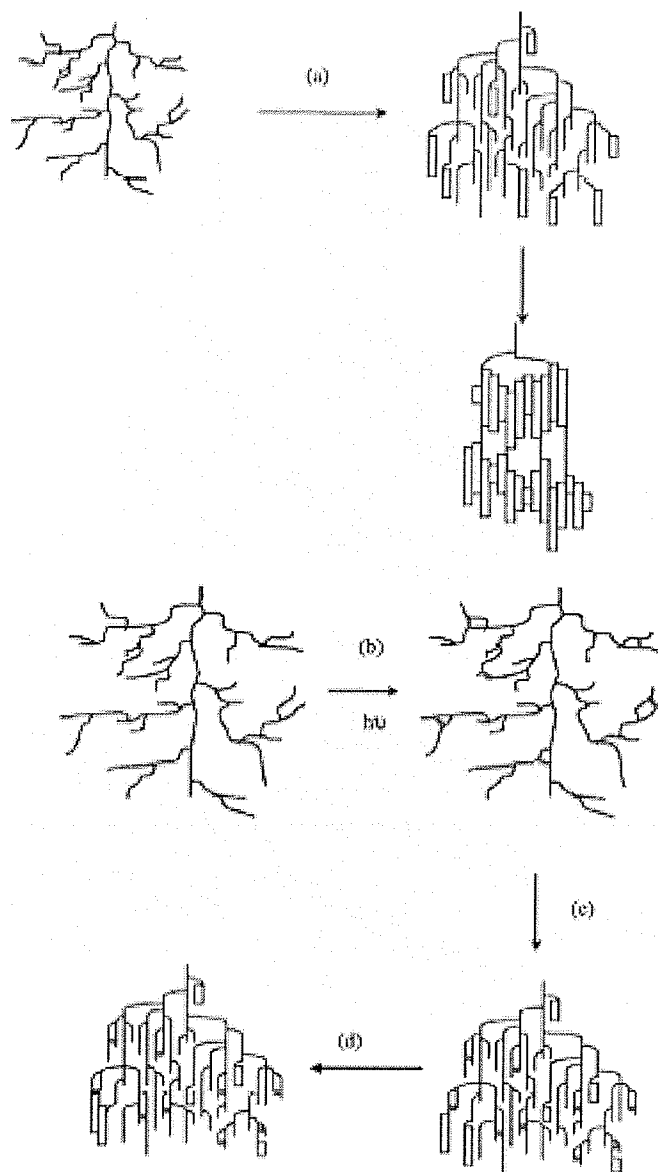


Fig. 2.6 Association between amylose and amylopectin molecules (Dotted lines, represent the hydrogen bonding sites). Two or more short-chains of amylopectin molecules may interact with one amylose molecule. Self-association within amylopectin molecules may also take place (From Tako and Hizukuri, 2002)

Mechanism of starch retrogradation is commonly hypothesized by Fig. 2.7 (Delville and others 2003). The scheme on Fig. 2.7 presents the crystalline cluster formation of amylopectin. The cluster formation begins with the formation of crystalline lamellae composed of double helices of amylopectin short chains (symbolized with rectangular boxes). Then, the packing of double helices forms crystalline clusters (Delville and others 2003).



315

Fig. 2.7 Schematics of amylopectin retrogradation at the rubbery state (amylopectin double helices are represented as rectangles). (a) uncrosslinked amylopectin (b)-(d) crosslinked amylopectin (From Delville and others, 2003)

320

The effect of various plasticizers on the crystallinity had been studied. Water content increases the degree of crystallinity and the kinetics of crystallization, while the glycerol

content slows the crystallization kinetics in starch amorphous rubbery amylopectin systems (Delville and others 2003). Crystallites may act as physical crosslinking points which generate internal stresses or cracks which lead to the damage of the starch products
325 (Delville and others 2003). Therefore, while crystallinity increases, elongation (E) decreases drastically, tensile strength (TS) and modulus of elasticity (EM) increase. Reportedly, the B-type polymorph of crystallite is developed in the aged gel of all starches irrespective of their pattern of crystallinity in the natural state. However, the type of polymorph developed in aged cereal starch gel may also depend on water content.
330 Samples containing more than 43% moisture develop the B-pattern on aging, whereas those containing less than 29% moisture give the A pattern (Karim and others 2000).

The crystallite structure of starch films is often analyzed using an X-ray diffractometer between $2\theta = 3^\circ$ and $2\theta = 40^\circ$ or 60° with a step size $2\theta = 0.02^\circ$ or 0.05° in using Cu $K_{\alpha 1}$
335 radiation ($\lambda = 0.15410$ nm) (Myllarinen and others 2002; Mali and others 2002 and 2006; Zimeri and Kokini 2002; Romero-Bastida and others 2005; Mathew and others 2006; Mizuno and others 1998). The typical X-ray diffraction patterns of starch films (Fig. 2.8) are characterized by sharp peaks associated with the crystalline diffraction and an amorphous zone. The amorphous fraction of the sample can be estimated by the area
340 between the smooth curve drawn following the scattering hump and the baseline joining the background within the low and high-angle points. The crystalline fraction can be estimated by the upper region above the smooth curve (Mali and others 2006). Therefore, the crystallinity of the starch films can be calculated using the following equation:

$$\text{Crystallinity} = \frac{A_c}{A_c + A_a} \times 100\% \quad 2.1$$

where A_c is the crystalline area on the X-ray diffractogram and A_a is the amorphous area on the X-ray diffractogram (Yoo and Jane 2002; Kalichevsky and Blanshard 1993).

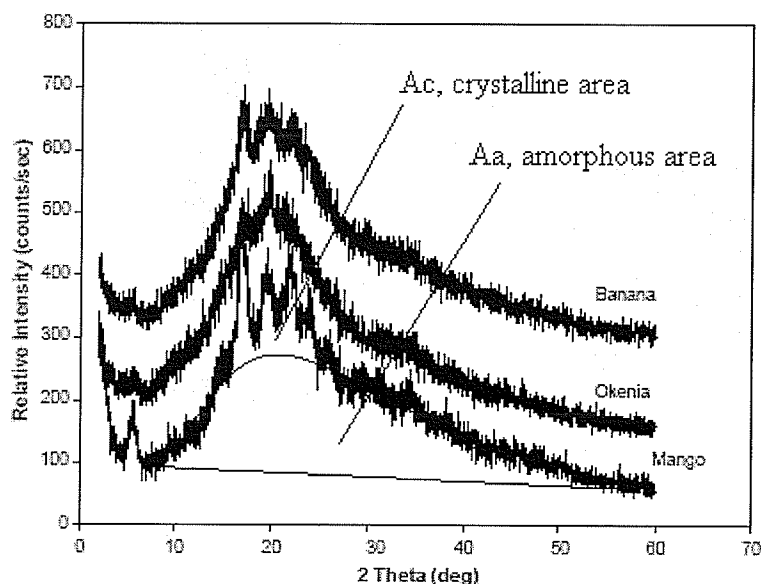


Fig. 2.8 X-ray diffraction pattern (B-type) of starch (banana, okenia, and mango, respectively) films made by thermal gelatinization at 60 days of storage at 25 °C (From Romero-Bastida and others, 2005)

The crystallinity of starch films is dependent on the processing conditions such as: the completeness of amylose dissolution in water, drying conditions (rate and temperature), plant origin of starch, moisture content of the films, and the temperature of storage (Mali and others 2002). For example, when starch films are stored at temperature below the T_g , starch polymers are in a stable glassy state, and crystallization does not occur or is

360 extremely slow. But recrystallization of starch can occur at temperatures above T_g at a rate depending on the difference between T_g and the storage temperature (Mali and others 2006). Crystallinity of starch films increased with storage time. As storage time increases, the width of X-ray diffraction peaks decrease but the peak intensity increases, showing an increase in crystallinity of starch (Mali and others 2002). Plasticizer was also found to
365 affect the crystallinity of starch. According to Mali and others (2006), glycerol limited the crystal growth and recrystallization. Glycerol could interact with the polymeric chains and interfere with polymer chain alignment due to steric hindrances. However, Garcia and others (2000) reported that plasticizers (glycerol and water) favored polymer chain mobility and allowed the development of a more stable crystalline structure during
370 shorter periods of storage. On the contrast with the conclusion of Mali and others (2006), Smits and others (2003) found that starch films without plasticizers formed less recrystallinity than the plasticized starch films. They attributed this phenomenon to the mobility of starch polymer chains. Plasticized starch polymers could easily vibrate and align up to form crystallites, while the unplasticized starch polymers interact with each
375 other strongly and lose their mobility.

2.3.2 Appearance of starch films

The appearance of starch films depends on the additives added into the starch dispersion. Pure starch films without any additives are usually colorless and transparent, but brittle.
380 Films with polyols, such as glycerol, ethylene glycol, or sorbitol, are also colorless but flexible. Films containing monosaccharides, such as fructose, mannose, and glucose, as plasticizers are yellowish. Monosaccharides are believed to cause the yellow color. The

extent the color depends on the concentration of the plasticizers used in the films (Zhang and Han 2006b)

385

When the microstructure of starch films is observed under a light microscope, starch films reveal a characteristic surface pattern with representing withered “ghost” granules (Fig. 2. 3) (Mehyar and Han 2004; Mathew and others 2006). Starch films can also be observed by scanning electron microscopy (SEM). Under SEM observation, the surface of starch films is smooth and homogeneous.

390

2.3.3 Mechanical properties of starch films

Starch films are often characterized by tensile tests, from which three mechanical properties are obtained, which are tensile strength (TS), percentage of elongation at breakage (E), and modulus of elasticity (EM). TS is a measurement of the strength of the film. It is calculated by dividing the force needed to break the film by the cross-sectional area of the initial specimen. The value of TS should not be affected by film thickness (Phan and others 2005). E value stands for the flexibility of the film. It is defined as the percentage of a change in the length of the specimen relative to the original length. EM, also named as Young’s modulus or elastic modulus, is the fundamental measurement of the film stiffness. It is calculated from the initial linear slope of the stress-strain curve (Fig. 2.9). Typical force-deformation curves are shown in Fig. 2.9. The higher the EM values the films have, the more stiff the films are (Mali and others 2005b). The test methods follow the procedure of ASTM method D882-91 (ASTM, 1991). Universal testing machine is widely chosen to test the film mechanical properties.

400

405

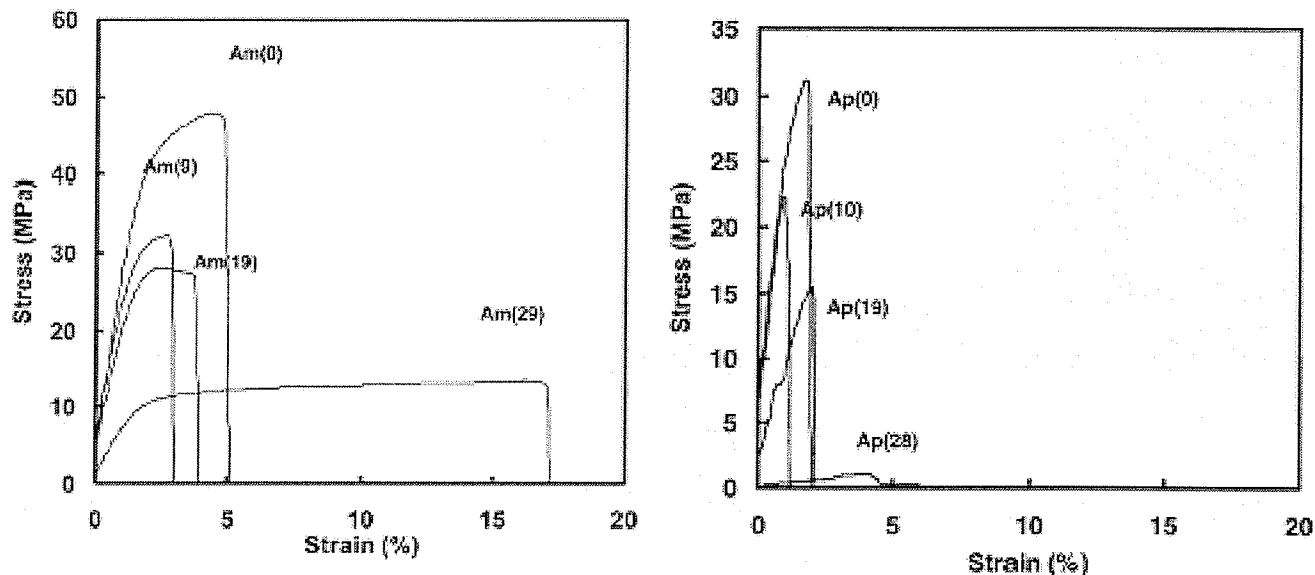


Fig. 2.9 Tensile stress-strain curves of amylose (Am) and amylopectin (Ap) films with various glycerol contents, measured at RH 50% and 20 °C (Abbreviations: Am (9)

410 denotes amylose films containing 9% glycerol; Ap (10) , amylopectin films containing 10% glycerol) (From Myllarinen and others, 2002)

Besides the original sources of starch, four factors were found to affect the mechanical
 415 properties of the films. They are plasticizer content, glass transition temperature (T_g), crystallinity, and ratio of amylose to amylopectin. During the past years, the effect of plasticizers on the mechanical properties of films prepared of starch, amylose, amylopectin and mixtures of starch and other biopolymers have been widely studied (Myllarinen and others 2002). Normally, plasticizers are used to increase E and decrease
 420 TS and EM. This is because plasticizers can increase the free volume in the amorphous

phase and reduce much more interaction between the starch polymer chains. However, anti-plasticization effect of plasticizer was found when plasticizer concentration is under a critical level (Godbillot and others 2006). When being serving at a temperature above T_g , the starch films are in the rubbery state and are flexible and extensible because more free volume is available in the starch film matrix. In contrast, when working at a temperature below T_g , the films are in the glassy state and brittle. As crystallinity increases, TS and EM of starch films increase, but E decrease, because crystallites behave like hard particles or physical cross-linkers (Liu 2005). Amylose and amylopectin films are mechanically different (Fig. 2.9) (Myllarinen and others 2002). Pure amylose films are stronger, whereas pure amylopectin films are more brittle. Films made of mixture of amylose and amylopectin were studied by Lourdin and others (1995). The results showed that the preponderance of amylose in starch films leads to higher TS, whereas the preponderance of amylopectin leads to lower TS. This is presumably due to the higher degree of crystallinity in starch films containing more amylose (Liu 2005).

2.3.4 Barrier properties of starch films

Permeation, absorption, and diffusion are typical mass transfer phenomena occurring in food packaging films (Han and Scanlon 2005). Their relationship is shown in Fig. 2.10. Therefore, three coefficients, namely permeability (P), solubility (S) and diffusion (D) coefficients are used to quantitatively characterize these three phenomena. Generally, the gas barrier property of a film is characterized by the permeability coefficient, P (Del Nobile and others, 2002), which is defined as (Han and Scanlon 2005; Roy and others 2000):

445

$$P = D \times S$$

2.2

where P is permeability coefficient, D is diffusion coefficient, and S is solubility or sorption coefficient of gas in the film. The SI units of P , D and S are $g\ mm\ m^{-2}\ h^{-1}\ kPa^{-1}$, $m^2\ s^{-1}$ and Pa^{-1} , respectively. Combining sorption and diffusion processes, P can be

450

described as follows (Han and Scanlon 2005; Arvanitoyannis and others 1997):

$$P = \frac{Q_{gas} \cdot V_{STP} \cdot L}{A \cdot t \cdot \Delta p} \quad 2.3$$

where Q_{gas} is the amount of gas diffused through the film (mol or kg), V_{STP} the volume occupied by 1 mole of the gas under standard temperature and pressure (STP) condition ($0\ ^\circ\ C$ and $1\ atm$), L the thickness of the film, A the cross-sectional diffusion area, t the time, and Δp the partial pressure difference across the package film.

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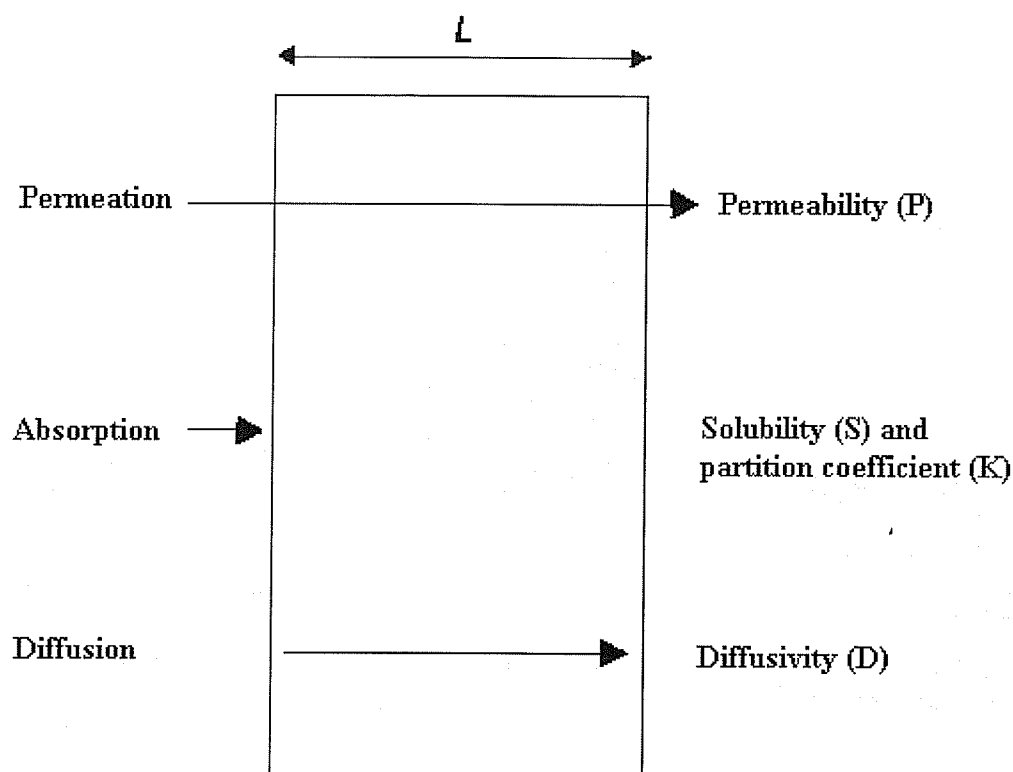


Fig. 2.10 Mass transfer phenomena and their characteristic coefficients (Adapted from Han and Scanlon, 2005)

465 Water vapor permeability (WVP) is one of the most important properties in the gas barrier performance of starch films. It indicates the ability of the films to control water vapor transportation between a food system and its surrounding. The most common method used to measure WVP is known as the “cup method”. Some variations of this method exist (Gennadios and others 1994). In this method, an acrylic cup (5 cm inside diameter, 470 1 cm depth) with a wide rim is filled with a certain amount of distilled water or desiccant and covered with a film sample to be tested. The assembly is weighed and placed in a chamber with a controlled relative humidity (RH) and temperature condition. Weight loss or gain of the cup assembly is measured periodically to determine the water vapor

transmission rate (WVTR). The WVP is calculated by multiplying WVTR by the
475 thickness of the film and dividing by the partial water vapor pressure difference inside
and outside cup (Eq. 2.3) (Zhang and Han 2006a). Experimental WVP data are listed in
Table 2.1. Generally, starch films have higher WVP than synthetic films due to the
hydrophilicity of starch. Therefore, starch films are not good water vapor barriers.

480 Theoretically, the WVP of a film should be a constant that is independent of the
difference in the partial water vapor pressure across the film. However, it does not
happen to starch films, because water molecules interact with OH groups in starch
molecules, and in turn cause plasticization leading to an increase in WVP (Del Nobile
and others 2002). Also, the thickness of the hydrophilic films affects the WVP. WVP
485 increases as the thickness increases (Gennadios and others 1994). Therefore, use of the
terms “effective permeability” or “apparent permeability” has been suggested by
researchers (Gennadios and others 1994; Roy and others 2000). The poor water barrier
performance of starch films can be improved by incorporation of lipid materials, such as
neutral lipids, fatty acids, and waxes (Han and others 2006; Petersson and Stading 2005).

490 Bilayer films in which a hydrophobic lipid layer is laminated over a hydrophilic film, and
emulsion films in which a lipid material is uniformly dispersed throughout the films have
been tested. Bilayer films have better water vapor barrier performance. However,
emulsion films possess superior mechanical properties. Starch-based films have been
considered a good candidate for modified atmosphere packaging where very high water
495 vapor permeability is required (Guilbert 2000).

Table 2. 1 Comparison of WVP values of biodegradable/edible and synthetic films

Film formulation	WVP (g mm m ⁻² h ⁻¹ kPa ⁻¹)	Reference
Yam starch with glycerol	0.34 – 0.65	Mali and others,2002
Corn starch with glycerol	1.93 – 2.41	Mali and others, 2006
Cassava starch with glycerol	1.45 – 2.25	Mali and others, 2006
Pea starch with glycerol	2.75 – 9.97	Zhang and Han, 2006a
Pea starch with sorbitol	2.61 – 6.70	Zhang and Han, 2006a
Pea starch with fructose	1.96 – 4.78	Zhang and Han, 2006a
Pea starch with mannose	2.27 – 4.63	Zhang and Han, 2006a
Corn starch with sorbitol	0.63	Garcia and others, 2000
Cellophane	0.30	Shellhammer and Krochta, 1997
Low density polyethylene	3.29×10 ⁻³	Smith, 1986
High density polyethylene	8.31×10 ⁻⁴	Smith, 1986
Nylon 6	7.52	Smith, 1986
Konjac glucomannan	4.14 – 6.91	Cheng and others, 2002
Calcium Caseinate	8.56 – 12.59	Mei and Zhao, 2003
Whey protein isolate	13.52 – 15.00	Mei and Zhao, 2003
Muscle protein of Nile Tilapia	0.60	Paschoalick and others, 2003
Wheat gluten with glycerol	0.14 – 1474.8	Roy and others, 2000
Pea protein with glycerol	4.10 – 7.41	Choi and others, 2001
Corn Zein with glycerol	1.69 – 3.20	Koh and others, 2002
Methyl cellulose with glycerol	0.58 – 1.30	Koh and others, 2002
Methyl cellulose with EG400	0.18 – 0.22	Turhan and Sahlaz, 2004

Oxygen permeability is another most important transport property of edible and
500 biodegradable films (Miller and Krochta 1997). Starch films usually have impressive O₂
barrier properties in dry conditions (Guilbert 2000) because of their hydrophilic nature.
Table 2.2 shows some O₂ permeability values of various edible films. O₂ permeability of
edible films is comparable to that of low-density polyethylene. Miller and Krochta (1997)
summarized several factors affecting the gas barrier properties of the polymer films.
505 These factors include film chemical structure, method of polymer preparation, polymer
processing conditions, free volume, crystallinity, polarity, crosslinking and grafting.
Plasticizer content (PC) and moisture content (MC) can cause large changes in starch film
structure, crystallinity. Therefore, they can substantially affect the O₂ barrier properties of
the starch films. In fact, increased PC and MC can increase the O₂ permeability by
510 increasing the free volume and decreasing crystallinity in the starch-based matrix.

Because of the hydrophilic nature of the starch films, aroma compounds from the
packed foodstuff are hard to be absorbed into the starch matrix. Therefore, the aroma
barrier property is usually proposed to be the last main barrier function of starch films.
515 The aroma barrier properties of starch films have not been thoroughly examined (Miller
and Krochta 1997). Quezada-Gallo and others (1999) studied the aroma barrier properties
of methylcellulose films, and found that the transfer rate of volatile aromatic compounds
increased with the chain length of the compounds. It was suggested that aroma molecules
interact with the methylcellulose polymer and modify the film structure.

520

Table 2. 2 O₂ permeability of various starch-based films

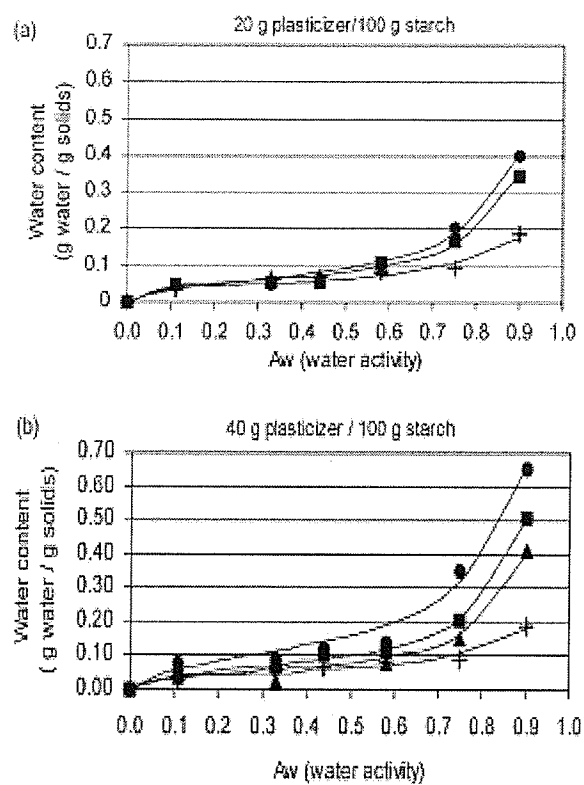
Film	OP (g mm m ⁻² h ⁻¹ kPa ⁻¹)	Reference
Soluble starch and methyl cellulose with glycerol	$3.53 \times 10^{-5} - 1.69 \times 10^{-1}$	Arvanitoyannis and Biliaderis, 1999
Soluble starch and methyl cellulose with sorbitol	$3.17 \times 10^{-4} - 2.05 \times 10^{-2}$	Arvanitoyannis and Biliaderis, 1999
Soluble starch and methyl cellulose with xylose	$3.56 \times 10^{-4} - 2.38 \times 10^{-1}$	Arvanitoyannis and Biliaderis, 1999
Whey protein film	$2.91 \times 10^{-11} - 3.17 \times 10^{-9}$	McHugh and Krochta, 1994
Rice bran film	$(1.69 - 3.70) \times 10^{-11}$	Gnanasambandam and others, 1997
LDPE	7.77×10^{-8}	McHugh and Krochta, 1994
HDPE	1.78×10^{-8}	McHugh and Krochta, 1994
Cellophane	1.05×10^{-8}	McHugh and Krochta, 1994
EVOH	$4.17 \times 10^{-12} - 5.00 \times 10^{-10}$	McHugh and Krochta, 1994

2.3.5 Sorption isotherm of starch films

525 As discussed above, starch films are very sensitive to the environmental relative humidity (RH). They absorb or lose water, leading to change in their mechanical and thermal properties. Therefore, the relationship between water content of starch films and RH has been extensively studied. This relationship, at a constant temperature, is described by the moisture sorption isotherm (Srinivasa and others 2003), typically shown as a sigmoidal

530 curve (Fig. 2.11). Moisture sorption isotherm of starch films represents the integrated hygroscopic properties of individual components. There are more than 200 sorption

isotherm models reported in the literature. However, no single equation has the ability to describe accurately the relationship of equilibrium moisture content and equilibrium RH for various starch films over a broad range of relative humidity and temperature. The change of sorption isotherm is due to any modification in the composition or structure of the films (Sebti and others 2003) and the fact that the water is associated with starch matrix by different mechanisms in different water activity regions (Mali and others 2005b). Therefore, for a specific starch film, there is a need to search for the most appropriate isotherm equation. Guggenheim, Anderson and de Boer (GAB) isotherm equation has been widely used to describe the water sorption behavior of starch films (Mali and others 2005b), since the model has an excellent fit for almost the entire sorption isotherm (Biliaderis and others 1999). Except for starch films, the GAB model was also found to be the best model in fitting the sorption isotherm data for films made from wheat gluten and chitosan-polyvinyl alcohol blend, respectively (Srinivasa and others 2003; Roy and others 2000). Beside the GAB model, the BET model, Smith model, and Flory-Huggins model are also popular models to fit sorption data (Cha and others 2001; Srinivasa and others 2003). These models are listed in Table 2.3.



560 Fig. 2.11 Effect of plasticizers on sorption isotherm for cassava starch films at 25 °C. ●: films with glycerol; ■: films with blend of glycerol and sorbitol (1:1, w:w); ▲: films with sorbitol; and +: films without plasticizer. (From Mali and others, 2005b)

570 Table 2. 3 Moisture sorption isotherm models

Name	Model
Smith	$M = A - [B \ln(1 - a_w)]$
Flory-Huggins	$M = A \exp(Ba_w)$
BET	$M = ABa_w / \{(1 - a_w)[1 + (B - 1)a_w]\}$
GAB	$M = (ABCa_w) / [(1 - Ba_w)(1 - Ba_w + BCa_w)]$

M , equilibrium moisture content (g water/ g dry matter); a_w , water activity; A , B , C , constants. In GAB model, A is the monolayer moisture content (dry basis); B is the Guggenheim constant which is a correction factor for the sorption properties of the first layer with respect to the bulk liquid; C is a correction factor for the properties of the multi layer with respect to the bulk liquid.

575

The BET isotherm was originally derived by Stephen Brunauer, Paul Emmet and Edward Teller with reference to gas adsorption on crystalline surface. Actually, the GAB model is an extension of the BET model with a correction factor, C (Table 2.3), for the structural changes of starch films. The BET model does not take into account water effect on any structural changes in the starch films as a result of water adsorption. When moisture adsorption into the film and dissolution of the film structure occur, the BET model will not prove applicable to provide insight into the sorption process. So the BET model is usually restricted to use in the RH range of 11 - 55% (Mathlouthi 2001) where film destruction does not occur. However, structural changes of starch films usually occur when the films are conditioned at a RH above 70%. Therefore, the GAB model should be used so that the parameter B can correct for the structural changes. Roy and others (2000) claimed that the lower the B value from unity, the lower the sorption of water. At RH

580

585

above 85%, accuracy of moisture determination falls quickly as osmotic and capillary
 590 phenomena affect water sorption due to structural changes of the films (Biliaderis and
 others 1999). One valuable parameter that can be roughly evaluated from the GAB and
 BET models is the value of monolayer water. The estimated monolayer concept is useful
 because of its relationship with the stability (physical and chemical aspects) of low- and
 intermediate-moisture films (Diab and others 2001). At monolayer moisture content level,
 595 the rates of film quality loss resulting from chemical reactions can be negligible (Zimeri
 and Kokini 2002).

Flory-Huggins model fits the isotherm where the interaction between adsorbate and
 adsorbent (water and starch, in case of starch films) is weaker than the interaction
 600 between adsorbate and adsorbate (water and water) (Ruthven 1984). The weak interaction
 between the adsorbate (water) and the adsorbent (starch) leads to low water uptake at low
 relative humidity. However, once a water molecule has become adsorbed at a primary
 adsorption site in starch films, the water-water interaction, which is much stronger,
 becomes the driving force of the adsorption process, resulting in accelerated water
 605 uptakes at higher relative humidity (Keller and Staudt 2005).

The goodness of fit of each model is evaluated by the mean of the relative percent
 difference between the experimental and predicted values of moisture content, also
 known as the mean relative deviation modulus, G .

$$G = (100 / n) \sum (|M_a - M_p| / M_a) \quad 2.4$$

where n is the number of observations; M_a is the moisture content experimentally determined; and M_p is the moisture content predicted by the model (Roy and others 2000).

615 A value of G lower than 5 corresponds to an extremely good fit, a predicted value between 5 and 10 shows a reasonably good prediction, and a value greater than 10 is considered a poor prediction (Roy and others 2000).

The sorption isotherm of starch films from different sources, such as corn, rice, wheat,
620 and cassava have been studied extensively (Mali and others 2002; Fang and Hanna 2000; Myllarinen and others 2002; Gaudin and others 1999; Biliaderis and others 1999; Cha and others 2001; Mali and others 2005b). As mentioned previously, the moisture sorption isotherm for starch films generally shows a sigmoidal shape and is influenced by the concentration and type of plasticizers (Mali and others 2005b). Fig. 2.11 shows the effect
625 of glycerol and sorbitol on sorption isotherm for cassava starch films at 25 °C. Higher levels of the plasticizers increase the film moisture content due to the hydrophilicity of the plasticizers. The presence of hydroxyl groups in the plasticizers facilitates moisture absorption by their interaction with water molecules through hydrogen bonding (Mail and others 2005b; Zhang and Han 2006a).

630

2.4 PLASTICIZATION OF STARCH FILMS

2.4.1 Physical chemistry of plasticization

To overcome the brittleness inherent in pure starch films, the incorporation of a plasticizer is required. Plasticizers for starch films must be compatible with the polymer

635 (starch) and be able to space out the starch molecules and reduce interaction of the polymers by interacting through hydrogen bonding with glucose chains (Nobel and Groningen 2003). As a result, the very strong inter- and intra-molecular interactions of starch polymers are loosened up, and mobility of polymer chains is increased (Romero-Bastida and others 2005). The presence of plasticizers decreases the glass transition
640 temperature, T_g , and improves the flexibility of starch films. The glass transition is a transition which happens to amorphous polymers. When the temperature drops below the T_g , the long-range segmental motion of the polymers grinds to a halt. Then the glass transition occurs, and the polymer changes from being soft and pliable to being hard and brittle from above T_g to below T_g . Therefore, T_g is one of the most important
645 characteristics of starch films. T_g values can be affected by many factors, such as the original starch sources and additives in the starch matrix. Differential scanning calorimetry (DSC) and dynamic thermal mechanical analysis (DMA) are the common technologies to measure T_g of starch films. In DSC thermograms, T_g is characterized by a step change of heat flow. The midpoint of the change in slope is identified as the T_g of the
650 starch film samples (Ribeiro and others 2003). DMA measures the thermomechanical properties, such as storage modulus (E'), loss modulus (E''), and $\tan\delta$ (E''/E') of starch films. In the glass transition zone, E' drops. T_g is defined as the mid-point between the onset and end of the fall in E' (Zhang and Han 2006a), as shown in Fig. 2.12. The drop in E' and a peak in $\tan\delta$ are denoted as α -relaxation (Lazaridou and Biliaderis 2002).
655 Normally, water acts as a plasticizer to a hydrophilic polymer and decreases its T_g . The Gordon-Taylor equation has been used to predict T_g as affected by plasticizer content in many food polymers (Ribeiro and others 2003):

$$T_g = \frac{x_1 T_{g1} + (\Delta C_{p2} / \Delta C_{p1}) x_2 T_{g2}}{x_1 + (\Delta C_{p2} / \Delta C_{p1}) x_2} \quad 2.5$$

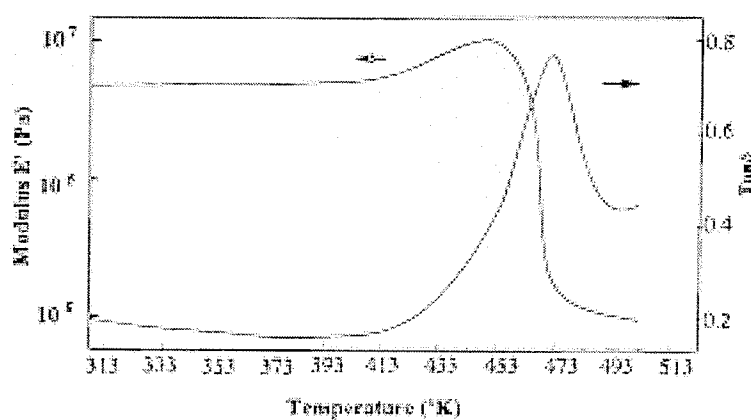
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where x_i is the weight fraction of the i th-component ($i = 1, 2, \dots$); T_{gi} is the glass transition temperature of the i th-components; and ΔC_{pi} is the change in heat capacity at T_{gi} . For a multi-component system (e.g. starch-water-glycerol), T_g can be predicted using Couchman-Karaszi equation:

665

$$T_g = \frac{\sum x_i \Delta C_{pi} T_{gi}}{\sum x_i \Delta C_{pi}} \quad 2.6$$

Values of T_g and ΔC for some starches and plasticizers are listed in Table 2.4.



670

Fig. 2.12 Typical dynamic thermal mechanical analysis (DMA) plot of dry wheat gluten proteins (From Pouplin and others, 1999)

675 Table 2. 4 The values of T_g and ΔC_{Pi} for some starches and plasticizers (Liu 2005)

	T_g (K)	ΔC_{Pi} (J kg ⁻¹ K ⁻¹)
Pea amylose (cast 100 °C)	605	265
Potato starch (cast 90 °C)	589	265
Waxy maize starch (cast 90 °C)	558	295
Glycerol	187	970
Water	134	1830
Sodium Lactate	246	1960
Sorbitol	271	2450

2.4.2 Common plasticizers and their functions in starch films

680 Plasticizers most commonly used in starch films include water, glycerol, sorbitol, and ethylene glycol (Mali and others 2005a). The plasticizer with the closest resemblance in structure to the polymers is considered the most effective plasticizer (Mali and others 2005a). The size or the shape of plasticizer molecules, the number of hydroxyl groups in the plasticizer molecules, and the compatibility of the plasticizers with the starch matrix are considered as the most important factors affecting starch plasticization (Liu 2005).

685 For example, water is the smallest among those plasticizers and provides 5.56 moles of hydroxyl groups per 100 g, compared to glycerol which provides 3.26 moles of hydroxyl groups per 100 g. It was reported that T_g of starch films containing 21% water is close to room temperature, whereas T_g of starch films containing the same amount of glycerol is

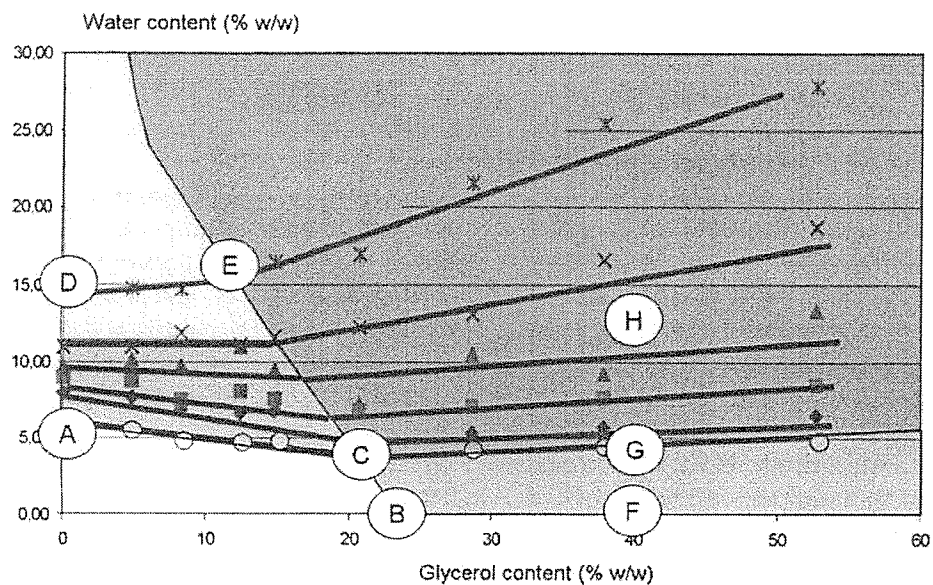
93 °C (Liu 2005). Although water is a very good plasticizer, it is easily lost by
690 dehydration at a low relative humidity (Han and Gennadio 2005). Therefore, the addition
of other chemical plasticizers to starch films is required. The non-water plasticizers fall
into two categories according to their working mechanisms:

- a. plasticizer acting as an agent that directly interacts with polymers by forming
695 hydrogen bonds so as to create some distance between polymer chains;
- b. plasticizer acting as an agent that attracts and holds a large amount of water
molecules and serving to plasticize the polymers in the films .




These two different working mechanisms are supposedly due to the physicochemical
700 properties of the plasticizer molecules. Mali and others (2005b) and Garcia others (2000)
found the same results when plasticizing cassava and corn starch films with sorbitol and
glycerol. They suggested that the chances of sorbitol molecules to interact with polymeric
starch chains are higher, since sorbitol is more similar to the molecular structure of
glucose units than glycerol. As a result, sorbitol molecules in the starch films show a
705 lower capacity to interact with water.

Recently, Godbillot and others (2006) investigated the mechanisms of water binding in
glycerol-plasticized starch films, and created a phase diagram (Fig. 2.13) containing
characteristic points distinguished by the composition, stoichiometric ratios, and type of
710 phases observed in the film. A schematic representation of the different types of
molecular interactions between starch, water, and glycerol in different phases is shown in

Fig. 2.14. It can be seen from Fig. 2.13 that below 58% RH, the increase of glycerol content up to a critical point leads to a decrease in water content, and the levels of hydration increase slightly as glycerol content increases. Above 58% RH, the level of hydration increases rapidly as RH increases. The minimum of water content at around 50% RH and 20% glycerol was considered to correspond to the saturation of starch binding sites (Godbillot and others 2006). When RH is low, the saturation of starch sites with glycerol occurs with high glycerol concentration, whereas saturation of starch sites with water occurs with low glycerol concentration. Fig. 2.14 is the schematic representation of the binding between starch, glycerol, and water. A model of starch representation involving a series of equivalent monomers of anhydro-glucose with three binding sites one of which has a stronger binding capacity (CH_2OH) was proposed, as well as models for water and glycerol. Point A corresponds to the monomolecular layer of starch primary hydration (BET layer). The calculated stoichiometric ratio at 5.5% of water is equal to 0.5 mol H_2O /mol anhydro-glucose. Point B is the point where water content in starch films is zero and glycerol is about 23%, which is equivalent to a stoichiometric ratio of 0.5 mol glycerol/mol anhydro-glucose. Point D is assumed a complete saturation of 3 hydroxyl groups in anhydro-glucose (starch) with water. Point E is considered as glycerol saturation point with multi-layer, multi-plasticizer binding. This mechanism of describing how the water, glycerol, and starch bind may be debatable. However, it gives a new method for food scientists to think about the plasticization of starch films.



735 Fig. 2.13 Phase diagram of water sorption isotherms as a function of glycerol percentage at different RH (\circ , 11%; \diamond , 33%; \blacksquare , 44%; \blacktriangle , 58%; \times , 68%; $*$, 80%) (From Godbillot and others, 2006)

schematic representation of the binding of water  glycerol  and starch 

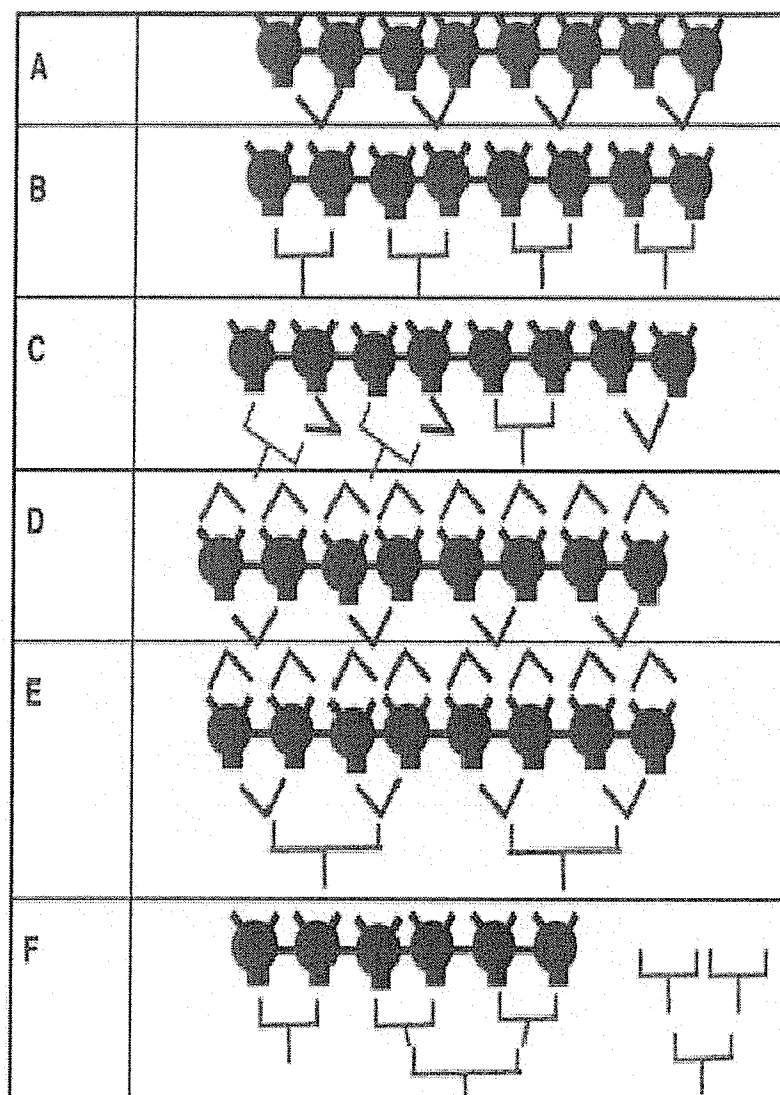


Fig. 2.14 Schematic representation of different types of binding between starch, water, and glycerol (From Godbillot and others, 2006)

2.4.3 Antiplasticization of starch films

Antiplasticization is a well-known phenomenon for synthetic polymers. This phenomenon also exists in starch films and has received increasing attention recently (Chang and others 2006). Glycerol, sorbitol, and water are the most commonly used

plasticizers in starch film production. However, these plasticizers serve as antiplasticizers when present at low concentrations. As a result, the starch films become stiffer (Chang and others 2006). Fig. 2.15 shows the EM of tapioca starch films as a function of glycerol content at different water activity (a_w) conditions. The EM of tapioca starch films in the range of a_w from 0 to 0.22 showed a maximum at a glycerol content of 2.5%. However, when a_w is greater than 0.32, increasing glycerol content results in a continuous decrease in EM. It appears, therefore, that glycerol at a low concentration in drier films can exert an antiplasticization effect on film EM (Chang and others 2006). Water also has antiplasticization effect on tapioca films. Fig. 2.16 shows TS of tapioca starch films as a function of a_w at various glycerol contents. Increasing hydration in starch films from a dry state strengthens the films until a maximum TS is reached at a critical a_w or moisture content; afterwards, further hydration weakens the films (Chang and others 2006). Different plasticizers have different antiplasticization effects on starch film, indicating differences in molecular characteristics of plasticizers and their possible dissimilar interactions with the starch polymers (Chang and others 2006).

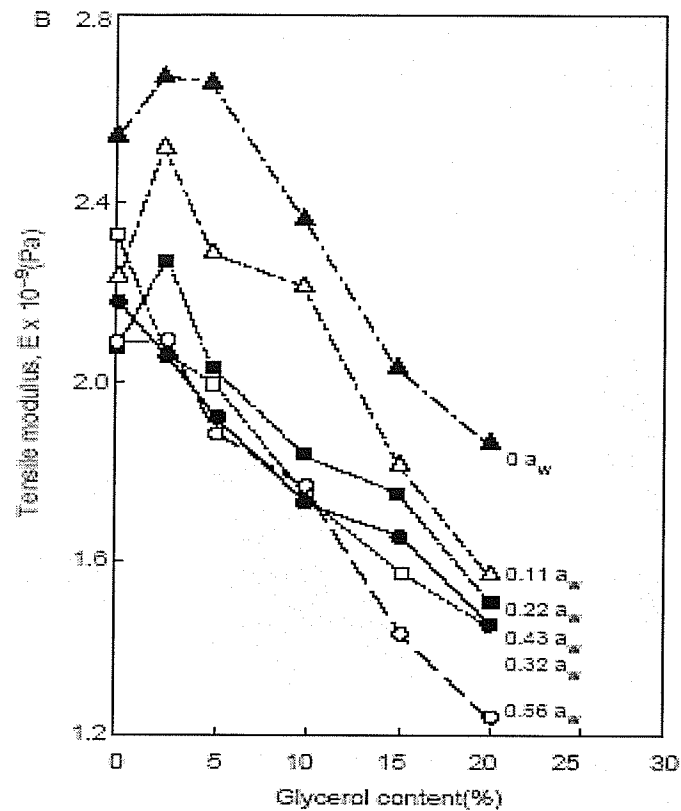


Fig. 2.15 Modulus of elasticity (EM) of tapioca starch films as a function of glycerol content (From Chang and others, 2006)

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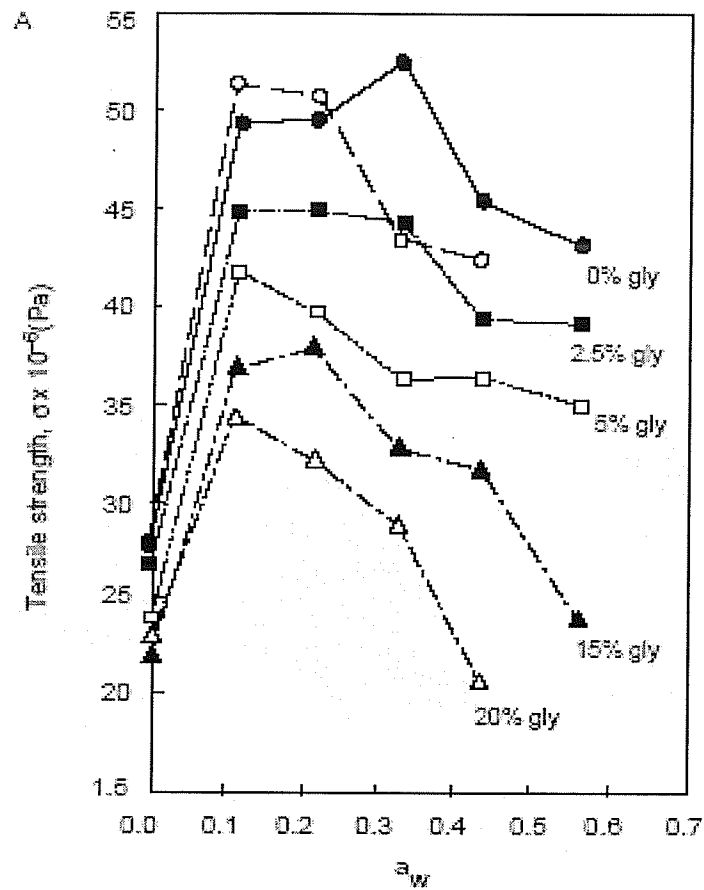


Fig. 2.16 Tensile strength of tapioca starch films as a function of water activity (a_w) with different glycerol content (From Chang and others, 2006)

Plasticization of pea starch films with monosaccharides and polyols

ABSTRACT

795 Two groups of plasticizers (polyols and monosaccharides) were used to compare their plasticizing efficiency. Fructose, glucose, mannose, galactose, glycerol, sorbitol, ethylene glycol and maltitol were selected at 4.34 mmol per g of pea starch. Edible starch films were produced after heat gelatinization and dehydration of the 3% starch dispersion. The microstructure, attenuated total reflectance-Fourier transform infrared spectroscopy
800 (ATR-FTIR) characteristics, thickness, moisture content, tensile strength, modulus of elasticity, elongation-at-break, water vapor permeability, and transparency of films were determined. Microstructure of the film solutions showed that some swollen starch granules and their remnants existed in the film. Scanning electronic microscopy (SEM) observation showed a smooth and homogeneous surface in the cross section area of the
805 films. Compared to the FTIR spectra of pure starch films, the spectra of plasticized films showed that more hydrogens bound hydroxyl groups and more water molecules were attracted around starch polymer chains. Ether linkage was probably produced in glycerol-plasticized films. Monosaccharide-plasticized films were comparable to the polyol-plasticized films in tensile test, but more resistant in moisture permeation than the polyol-
810 plasticized films. It was assumed that the structural compatibility of monosaccharides

with starch might result in denser polymer-plasticizer complex, smaller size of free volume, and less segmental motions of starch chains. In conclusion, monosaccharides were identified as effective plasticizers for starch film.

815 INTRODUCTION

Among available various biopolymers, starch is the most commonly used natural polymer, since it is inexpensive, widely available and relatively easy to handle (Guilbert and others 1996, 1997; Mali and others 2005). Plasticizers play a very important role in starch film formation affecting the film structure and, accordingly, its properties (Yang
820 and Paulson 2000). Without plasticizers, starch films are readily broken into fragments when they are dried under ambient conditions. Some polyols (especially, glycerol, sorbitol, and ethylene glycol) are considered as preferred plasticizers for starch film production (Padua and others 1995; Mali and others 2002). Generally, plasticizers must be compatible with the film-forming polymer for homogeneous distribution in the 3-
825 dimensional structure of film (Lazaridou and Biliaderis 2002; Mali and others 2002). According to the compatibility, some monosaccharides should work as plasticizers in starch films more effectively, not only because of their hydroxyl groups, but also due to their similarity in structure and conformation to anhydroglucose in starch molecules (Whistler and BeMiller 1997a). However, little scientific information dealing with the
830 monosaccharide-plasticized starch film is available. This research objective was to characterize the plasticizing efficiency of monosaccharides and polyols in high-amylose starch films. Plasticizer molecule amount, molecular size, and the number of hydroxyl groups in one plasticizer molecule are critical factors, which have significant effect on

properties of the starch film. Therefore, the same plasticizer molar ratio was considered in

the experiment.

MATERIALS AND METHODS

Materials

Commercial pea starch of Canadian yellow field peas (*Pisum sativum* L. Miranda) produced by a wet milling process, which contains 37 - 40% amylose, was supplied by Nutri-Pea Ltd (Portage-La-Prairie, Manitoba, Canada). Two different chemical groups of plasticizers were used: polyols and monosaccharides. Polyol plasticizers included glycerol, sorbitol, ethylene glycol, and maltitol. Monosaccharides used were glucose, mannose, galactose, and fructose. All the polyols and monosaccharides were purchased from Sigma Chemical Co. (St. Louis, MO, USA).

Starch Film Preparation

Aqueous dispersion of 3% (w/w) pea starch was prepared with de-ionized water. Glycerol was added to starch dispersion at 20/50 (glycerol/starch, w/w) ratio in which the glycerol molar ratio is 4.34 mmol per g of starch. All the other plasticizers were added in the same molar ratio (4.34 mmol per g of starch) instead of glycerol. The starch film-forming solutions were produced by heating the starch dispersions with agitation, maintaining the boiling temperature for 10 min to allow gelatinization, and cooling the solution temperature to 50 - 60 °C.

Starch films were cast by transferring 9 g of the film-forming solution onto a polystyrene petri dish (10 cm diameter). Solutions were spread evenly on the petri dishes and dried at room condition (22 °C) for 48 - 72 h. After drying, they were conditioned at 50 ± 2 % relative humidity (RH) for 72 h at 22 °C. The 50 ± 2 % relative humidity was obtained in a sealed chamber containing super-saturated aqueous solution of Ca(NO₃)₂. A digital RH-meter (Control Company, Friendswood, TX, USA) was placed in the chamber to monitor the change of RH inside the chamber. Dried films were peeled intact from the casting Petri dishes after RH conditioning.

Thicknesses of films were measured with an electronic digital micrometer (B. C. Ames Co., Waltham, MA, USA, 0.001 mm sensitivity) at five random positions on a film. Mean thickness values were reported for the film thickness.

Microstructure Studies of Film Solution

Starch solutions were prepared according to the method described above. After making starch solution, the starch solutions were cooled down to 50 - 60 °C. A drop of starch film-forming solution with several drops of water for dilution was dropped onto a microscope slide, and spread through evenly. After being dried at an ambient environment, the dried starch dispersion was observed under an inverted phase contrast microscope (Nikon Diaphot TMD, Kanagawa, Japan) equipped with a TV camera (Panasonic WV-1550, Matsushita Electric Industrial Co., Ltd., Osaka, Japan). The phase contrast microscopy is suitable to produce high contrast images of transparent or translucent specimens such as starch films (Liu and Han 2005). It was found that a Ph1

10× objective lens could produce clearer photomicrograph. Pictures of the starch films
880 were taken with a camera recorder (DCR-PC330, Sony Corporation, Tokyo, Japan).

ATR-FTIR Studies

Infrared spectra were recorded using a Bio-RAD ExcaliburTM FTIR spectrometer following the method of Wilhelm and others (2003). A film specimen was inserted in a
885 sample holder placed on an attenuated total reflectance (ATR) accessory (Perkin-Elmer, Inc., Boston, MA, U.S.A) at 45° angle. ATR-FTIR spectra of thin films conditioned at 50 ± 2% RH for 72 h at 22 °C were obtained by accumulation of 16 scans and a 4 cm⁻¹ resolution ranging from 400 through 4000 wave number.

Moisture Determination

The moisture content of each film was determined according to the method of Mei and Zhao (2003). The films were conditioned at 50 ± 2 % RH for 48 h at 22 °C. After conditioning, about 25 mg of the film in the form of small pieces was placed into previously dried and cooled aluminum dishes. The films along with aluminum dishes
895 were dried inside a laboratory oven (Blue M Electric Company, Blue Island, IL, USA) containing desiccants at 105 ± 2 °C for 24 h. Weights of the film samples were taken before and after drying using a digital balance (Mettler Instrument Corp., Hampton, NH, USA) with an accuracy of 0.0001 g. Moisture content (MC) was determined from the percentage of film weight loss after dehydration to original film weight before
900 dehydration. Three replications of each film were measured for moisture content values.

Tensile Tests

Tensile properties of films were determined by the method of Choi and Han (2001), which is a modified ASTM D882 method (ASTM 1991). Film specimens were cut into rectangular strips, 1 cm wide and 8 cm long, after conditioning in 50 ± 2 % relative humidity at 22 °C. Tensile strength (TS), elongation-at-break (E), and modulus of elasticity (EM) were determined from a stress-strain curve using a texture analyzing instrument (TA-XT2, Texture Technologies, Corp., Scarsdale, NY) following the procedure outlined in ASTM method D882-91 (ASTM 1991). Initial grip distance and cross-head speed were 5 cm and 0.5 mm/s, respectively. TS was calculated by dividing the peak load by the cross-sectional area (average film thickness \times 1 cm) of the initial specimen. E was defined as the percentage of change in the length (ΔL) of the specimen to the original length (L) between the grips (5 cm). EM was obtained from the initial linear slope of stress-strain curve. Each TS, E and EM was obtained from 6 replications of samples taken from the same treatment.

Water Vapor Permeability (WVP)

The modified ASTM E96-92 gravimetric method (McHugh and others 1993) was used to determine the WVP. A test film was placed on an acrylic cup containing distilled water and sealed. The whole assembly was weighed and placed in a chamber containing anhydrous calcium sulfate. The chamber was equipped with a fan and a digital RH-meter. The RH inside the chamber was kept at around 10% during the experiment. Temperature inside the chamber was about 22 °C. The fan inside the chamber was turned on during entire test period to make the RH inside the chamber even. Weight loss of cups with time

was measured periodically to obtain water vapor transmission rate (WVTR) of the films. In calculating the WVTR, linear regressions ($R^2 > 0.98$) were accomplished between weight loss and time using regression options of spreadsheet software. Three replications were conducted for the same treatment. The thicknesses of sample films were measured with an electronic digital micrometer at three random points both before and after WVTR tests. The means of these six thickness values were used to calculate WVP from WVTR results. The RH inside cup and WVP were determined using Visual Basic tools programmed by Dr. J. H. Han, and the WVP result was obtained as the mean value in $\text{g mm m}^{-2} \text{ h}^{-1} \text{ kPa}^{-1}$. The detail method can be referred by McHugh and others (1993).

Light Transmission Rate and Film Transparency

Light transmission rate and film transparency was measured at selected wavelengths from 200 to 800 nm using UV/Visible spectrophotometers (Ultraspec II, LKB Biochrom, Cambridge, UK, and 8451A, Diode Array Spectrophotometer, Hewlett Packard, Houston, TX, USA) according to the procedure reported by Shiku and others (2003), and Fang and others (2002b). Transparency of the films was calculated by the equation of Han and Floros (1997).

$$\text{Transparency} = \frac{A_{600}}{\text{Thickness}} \quad \text{or} \quad - \frac{\log T_{600}}{\text{Thickness}} \quad 3.1$$

where A_{600} and T_{600} are absorbance and transmittance at 600 nm, respectively.

Two replications were conducted for the same treatment. In order to compare optical properties, pure starch films were also tested in the same method.

950 **Scanning Electronic Microscopy (SEM) Observation**

SEM analysis was performed with a scanning electronic microscope (Stereoscan 120, Cambridge Instruments, Cambridge, UK) working under EDAX GENESIS 4000 software. Film pieces were mounted on bronze stubs using a double-sided tape and then coated with a layer of gold-Palladium (Au-Pd), allowing surface and cross-section
955 visualization.

Statistical Analysis

Data were analyzed by ANOVA using SAS (SAS Institute Inc., Cary, NC, USA) to assess the effects of plasticizers on the properties of starch films. A completely
960 randomized experimental design was used for plasticizer types. Mean values with standard deviations were compared using a Tukey mean difference test at 95% significance level with a null hypothesis of $H_0: \mu_1 = \mu_2 = \dots = \mu_n$, where μ is a mean of each treatment and n is a number of different plasticizers.

965 **RESULTS AND DISCUSSIONS**

Film Formation

After conditioning, free-standing transparent films were obtained. All the films looked clear, uniform, and smooth with a smoother undersurface that was in contact with the casting dish surface and a duller upper surface. Organoleptically, it was noticeable that

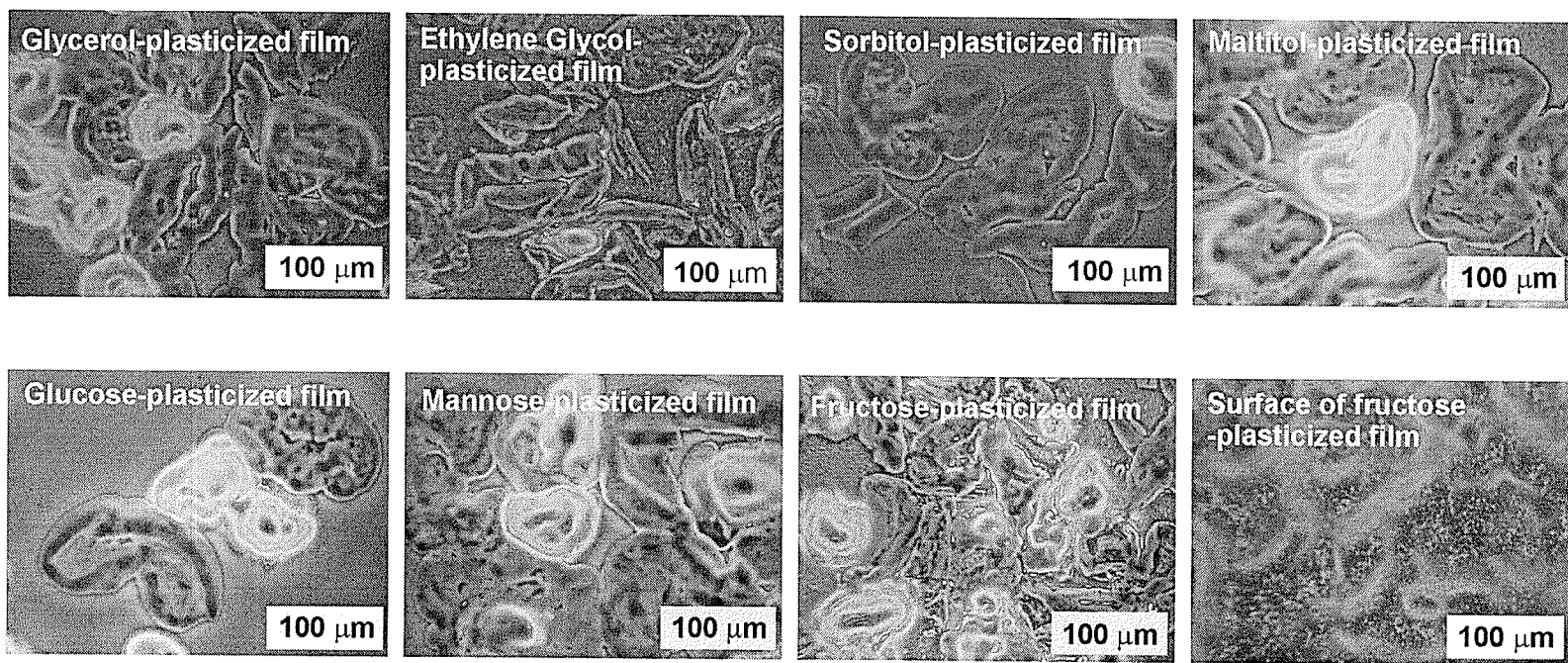
970 glucose, fructose and mannose could plasticize as effectively as the commonly used polyols did. All the films were transparent without any stain. But maltitol-plasticized films appeared slightly yellowish and thicker than other films. Visually, most polysaccharide films were reported yellowish in the literature (Garcia and others 2004; Veiga-Santos and others 2005; Villabolos and others 2005). Ethylene glycol-plasticized
975 films were slightly brittle and the thinnest. The thickness differences were mainly caused by the difference in molecular weight or mass of incorporated plasticizers in the films. Galactose-plasticized films became brittle and broken into pieces during drying due to its low hygroscopicity. Because of the brittle structure, galactose-plasticized films were not tested for mechanical and permeability properties.

980 **Starch Film Solution Microstructure**

According to the gelatinization mechanism, starch granules should be swollen and disrupted with release of amylose and amylopectin molecules into solution during heat treatment of starch dispersion. However, Fig. 3.1 shows many swollen starch granules
985 and their remnants present in the film regardless of the kinds of plasticizers contained. This means only a part of the starch polymers was solubilized, and the commonly used methods (boiling and stirring starch solution at around 100 °C) to produce starch films are not good enough to solubilize starch polymers completely. This phenomenon agrees with the results of Zobel (1984) who observed structure of starch pastes. Therefore,
990 complete solubilization of the pea starch polymers requires higher temperature than 100 °C, even with extra pressure, and a longer time. While the starch solutions were dehydrated to be films, huge number of the swollen starch granules and their remnants in

Fig. 3.1 Photomicrographs of swollen starch granules in the starch films, and microscopically messy arrangement of granules and its remnants in the surface of fructose-plasticized film

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starch solutions were randomly aggregated and compacted together to compose starch films (Liu and Han 2005). Thus, the surface of starch films with thickness being around 0.06 mm appeared microscopically a messy arrangement of starch granules and their remnants under an optical microscope. The effect of different gelatinization and pasting on the films needs further study.

ATR-FTIR spectra

The ATR-FTIR spectra of pure starch film, and plasticized films were shown in Fig. 3.2 through 3.4. Fig. 3.2 shows the spectrum of starch film without added plasticizer. Peaks at 920, 985, 1074, and 1145 cm^{-1} are attributed to C-O bonding stretch (Fang and others 2002a). The peaks at 985 and 1074 cm^{-1} are characteristic of the anhydroglucose ring O-C stretch. Peaks occurring at 1649 cm^{-1} is believed to be a feature of tightly bound water present in the starch. These results are comparable with those of earlier reports (Fang and others 2002a; Kacurakova and Wilson 2001). The peak at 2939 cm^{-1} is characteristic of C-H stretch. An extremely broad band due to hydrogen bonded hydroxyl groups appeared at its most intense 3224 cm^{-1} . This is attributed to the complex vibrational stretches associated with free, inter-, and intra-molecular bound hydroxyl groups which made up the gross structure of starch (Wu 2003; Fang and others 2002a)

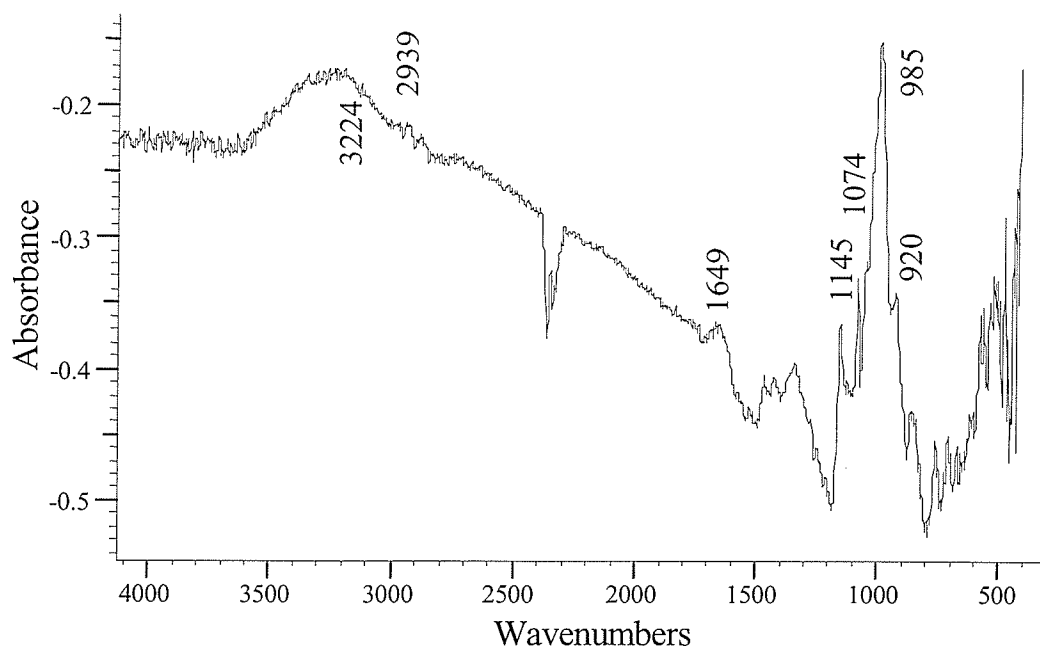


Fig. 3.2 ATR-FTIR spectrum of pure starch film

Fig. 3.3 showed the FTIR spectra of monosaccharide-plasticized films. All these three spectra had similar profiles. These similar spectroscopic profiles revealed the similar chemical components of the monosaccharide-plasticized films. Compared with Fig. 3.2, the strong bands at around 3300 cm^{-1} (hydroxyl groups) in Fig. 3.3 did not change obviously. That meant the effective amount of the hydroxyl groups existing in the films did not change significantly after the monosaccharides were applied. Therefore, it can be concluded that monosaccharides acted as plasticizers by themselves efficiently reducing the interaction between the starch polymers. The peak at 1649 cm^{-1} in Fig. 3.2 (bound water) shifted to around 1590 cm^{-1} in Fig. 3.3 indicating some water molecules were bound by monosaccharides in the plasticized-films (Smith 1999).

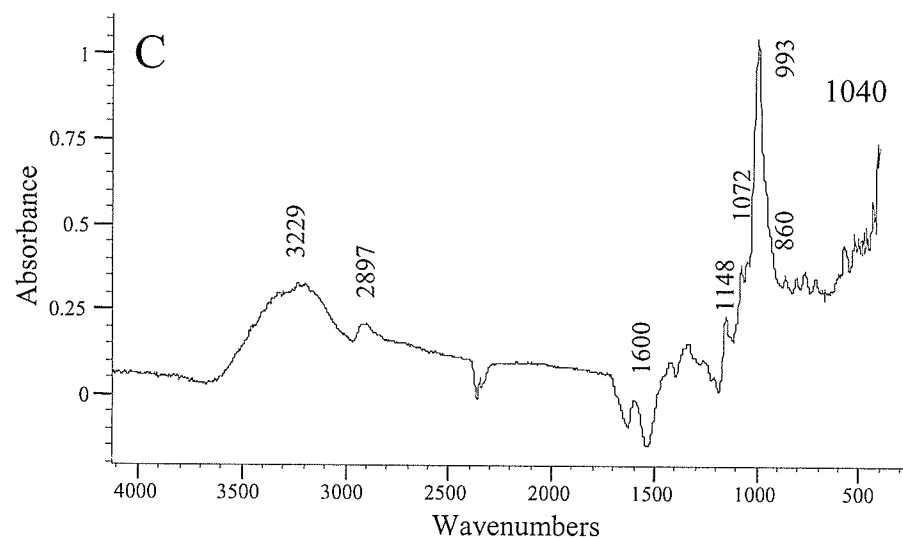
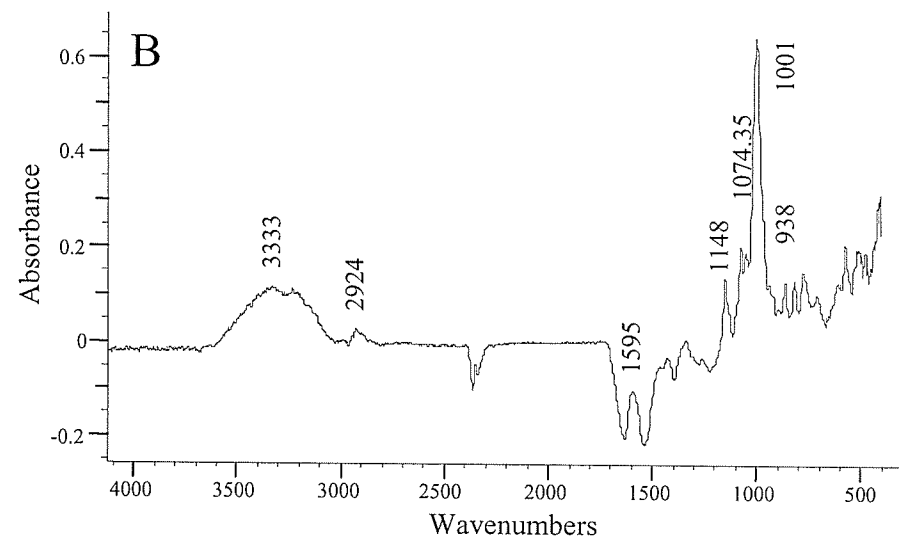
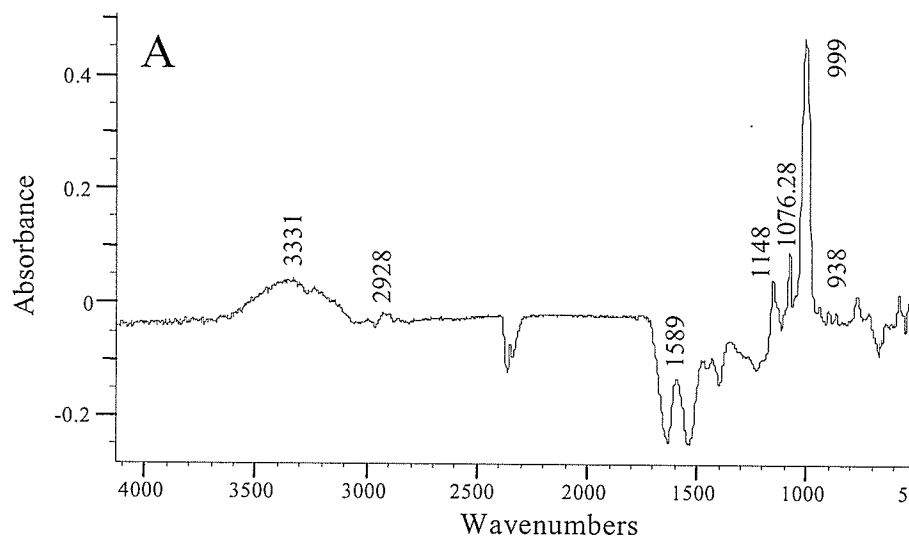


Fig. 3.3 ATR-FTIR spectra of monosaccharide-plasticized films. A: Glucose-plasticized film. B: Fructose-plasticized film. C: Mannose-plasticized film

1045

Fig. 3.4 showed the spectra of the polyol-plasticized films. Compared to the spectra of the sorbitol- and maltitol-plasticized films (Fig. 3.4 A and B) with Fig. 3.3, it is hard to find any difference. It may suggest that sorbitol and maltitol behaved as monosaccharides in starch films. Sorbitol and maltitol are hydrogenation products of glucose and maltose, respectively. Their molecules are linear in structure, but were supposed to be present similar to the ring conformations of the glucose and maltose molecules, respectively (Yang and Paulson 2000). Fig. 3.4 C and D represented the spectra of the ethylene glycol- and glycerol-plasticized films, respectively. These two profiles of spectra looked evidently different from other spectroscopic profiles, while they were similar to each other, suggesting that there would be two different plasticization mechanisms existing. 3.4 D showed peak intensity at 1145, 962 cm^{-1} increased, which is responsible for C-O stretching (Bellamy 1998). This phenomenon suggested that some etherification reactions between the starch and glycerol occurred. Fig. 3.4 C and D also showed the characteristic peak of hydroxyl groups shifted from 3224 cm^{-1} (Fig. 3.2) to around 3600 cm^{-1} and a broader band occurred, which means more hydroxyl groups of water and polyols involved in the hydrogen bonds with those of starch. Pure glycerol presents the characteristic peak at 1456 cm^{-1} (Wilhelm and others 2003). This glycerol band shifts in Fig. 3.4 D to 1477 cm^{-1} confirming that the glycerol was really attracted and bound to other chemicals, that is, water.

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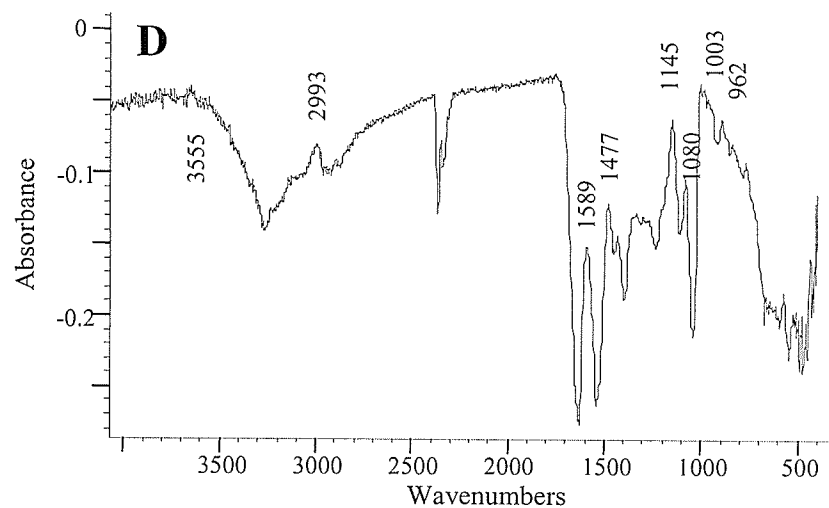
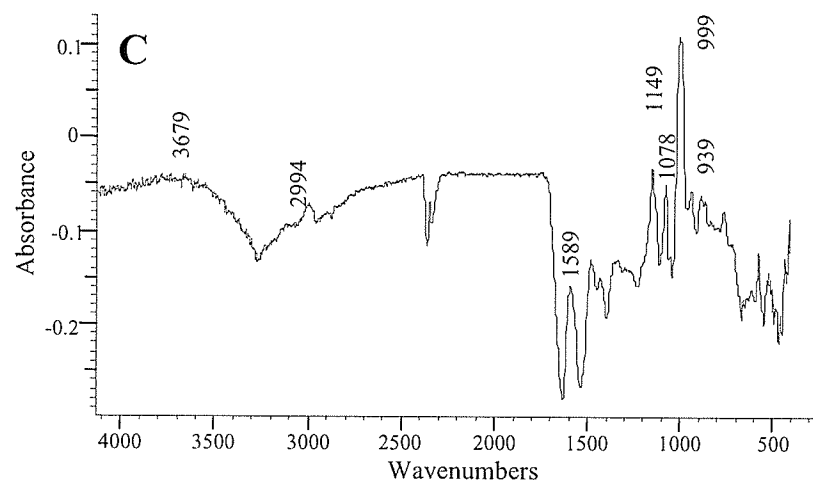
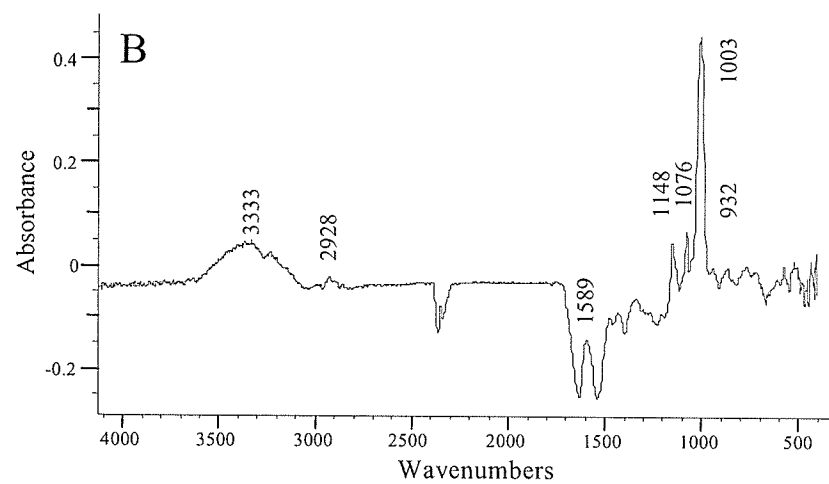
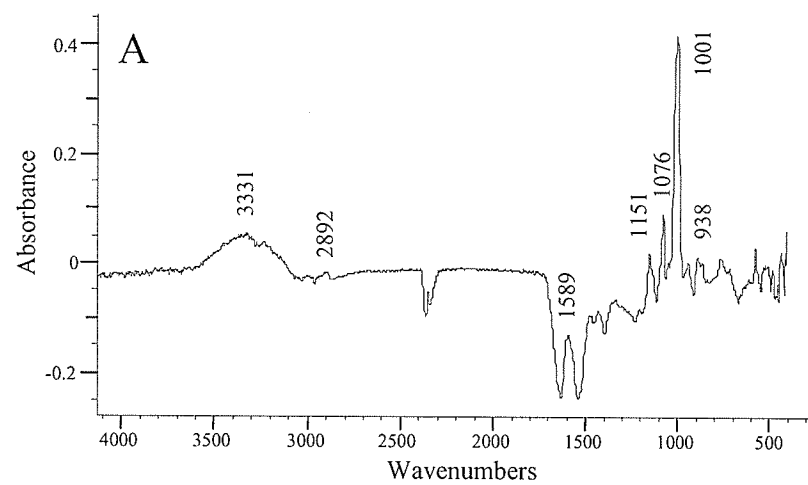


Fig. 3.4 ATR-FTIR spectra of polyol-plasticized films. A: Sorbitol-plasticized film. B: Maltitol-plasticized film. C: Ethylene Glycol-plasticized film. D: Glycerol-plasticized film

Film Thickness and Moisture Content

1070 The ethylene glycol-plasticized film was the thinnest (Table 3.1) because the amount of
the ethylene glycol added in film-forming dispersion is less than those of other
plasticizers at the same molar concentration due to its lowest molecular weight. The
thickness of ethylene glycol-plasticized film has the same thickness of non-plasticized
pure starch film. Maltitol film was one of the thickest films because the highest amount
1075 was added due to its highest molecular weight. Fructose, glucose and mannose have the
same molecular weight, therefore, the amounts of these three plasticizers were the same
in the films. However, glucose-plasticized film was significantly thinner than mannose-
plasticized films. This was related to the shortest spatial distance between starch
molecules. The chemical structures of glucose and the repeating units of starch are
1080 identical and this structural homogeneity could lead to closely packed matrix of starch
polymers, consequently reducing intermolecular distance between the polymers.

The water absorption or desorption of hydrophilic films depends on the environmental
RH change (van Soest and others 1995). Table 3.1 shows the moisture content data in the
1085 starch films after the films had been conditioned at 50 ± 2 % RH. Except for glycerol
films, the starch films plasticized by either monosaccharides or polyols have a similar
moisture content in a narrow range. Water absorption characteristic is highly related to
the polarity of the polymer (Fang and Hanna 2000). In the case of starch film, it is related
to the polarity of starch and plasticizer mixture. Since the same starch material has been
1090 used for different films, the difference in polarity of starch films is dependent on
plasticizers included. In the case of the ethylene glycol-plasticized films, the amount of

Table 3.1 Physical properties of pea starch films with the increase in plasticizer concentration

Plasticizers	Molecular Weight	Number of OH groups in one molecule	Thickness (mm)	Moisture Content (%)	Tensile Strength (MPa)	Modulus of Elasticity (MPa)	Elongation (%)
Ethylene Glycol	62.07	2	0.038±0.002 ^(d)	12.1±0.58 ^{(b)(c)(d)}	24.9±2.62 ^(a)	1584.6±149.4 ^(a)	4.2±0.56 ^(a)
Glycerol	92.09	3	0.066±0.010 ^(c)	25.3±2.30 ^(a)	5.8±0.59 ^(c)	97.5±19.5 ^{(b) (c)}	36.4±5.53 ^{(b)(c)}
Fructose	180.16	5	0.070±0.003 ^{(b)(c)}	13.9±0.18 ^(b)	8.3±0.38 ^(b)	188.6±13.9 ^(b)	30.3±5.34 ^(b)
Glucose	180.16	5	0.062±0.003 ^(c)	11.7±0.08 ^{(b)(c)(d)}	6.6±0.43 ^{(b)(c)}	110.9±16.4 ^{(b) (c)}	54.6±19.4 ^{(c)(d)}
Mannose	180.16	5	0.075±0.005 ^{(a)(b)}	12.5±0.41 ^{(b)(c)}	6.3±0.30 ^(c)	111.2±5.1 ^{(b) (c)}	70.7±13.7 ^{(c)(d)}
Sorbitol	182.17	6	0.087±0.004 ^(a)	10.8±0.21 ^{(c)(d)}	5.7±0.42 ^(c)	106.6±3.9 ^{(b) (c)}	61.2±14.2 ^{(c)(d)}
Maltitol	344	9	0.090±0.002 ^(a)	9.6±0.36 ^(d)	3.4±0.40 ^(d)	40.7±4.4 ^(c)	93.7±20.4 ^(c)
Pure starch film	0	0	0.035±0.007 ^(d)	10.6±2.02 ^{(c)(d)}	-	-	-

Values are means ± standard deviation (n = 6 for TS, EM and E values; n = 3 for thickness and water content). The values bearing different superscripts in the same column indicate significant difference at p < 0.05 using Tukey test.

water required to hydrate the film should be expected to be less than those of other films, because ethylene glycol has less hydroxyl groups compared to other plasticizers, as well as its least amount used in starch films. However, the moisture content, 12.1%, of ethylene glycol-plasticized starch films was similar to other films, except for glycerol films. This indicates that its water binding capacity is not as low as expected. Table 3.1 also shows that glycerol-plasticized film has a prominently high moisture content. It is expected that glycerol should possess different plasticizing mechanism than other monosaccharides and polyols. Glycerol may not be a plasticizer forming direct interactions with starch. Instead, it is a good water holding agent to utilize the plasticizing activity of water molecules.

Tensile Properties

Table 3.1 also shows the effect of plasticizers on the tensile properties of pea starch film. TS and EM generally decreased as the molecular weight and numbers of hydroxyl group increased, except for glycerol-plasticized film. TS and EM of ethylene glycol-plasticized films were significantly higher than those of others. In fact, the ethylene glycol-plasticized films appeared brittle and were difficult to handle during testing. Low amount and small size of ethylene glycol allowed more direct interaction between starch molecules leading to high intermolecular cohesive force and high EM. Mali and others (2002) defined that plasticizers are the materials to reduce the cohesive force of polymers. This theoretical aspect of plasticization concludes that ethylene glycol at this concentration level is not an effective plasticizer for pea starch films. Compared to ethylene glycol-plasticized films, glycerol-plasticized films showed much lower values of

TS and EM, and much higher E, although they (glycerol and ethylene glycol) have the
1120 most similarity in molecule size and structure. This difference may be attributed to higher
moisture content in glycerol-plasticized films. Fructose-, glucose-, and mannose-
plasticized films had higher or similar TS value than glycerol-, sorbitol-, and maltitol-
plasticized films, which shows that monosaccharides are good plasticizers comparable to
commonly used polyols in the same molar ratio concentration.

1125 It was meaningless to compare the effect of plasticizers on E value since film thickness
was not the same for all test films (Foulk and Bunn 2001). However, the lowest E of
monosaccharide-plasticized films compared to that of sorbitol-plasticized films indicated
that monosaccharide formed compact interaction with starch. Fructose-plasticized films
1130 showed the highest value in TS, except for the ethylene glycol-plasticized films. At this
point, it is difficult to draw an exact reason for the TS and E of monosaccharide-
plasticized films. However, the formation of strong hydrogen bond between
monosaccharide and starch molecule should be responsible for these results.

1135 The effect on reducing intermolecular interactions and the work of cohesion between
the starch chains by the plasticizers is called blocking effect (Turhan and Sahbaz 2004)
and is the main plasticization mechanism. Usually, plasticizers accomplish the blocking
effect by interfering with the direct intermolecular interactions and increasing more free
volume between the starch polymers (Mali and others 2002; Turhan and Sahbaz 2004).
1140 From Table 3.1, sorbitol-plasticized films had similar tensile properties to those of
glucose- and mannose-plasticized films. This could be attributed to similar blocking

effect resulting from the similarity of the hydrodynamic nature of sorbitol and glucose (Table 3.2), which may cause similar distance between starch molecules. Maltitol had the greatest E and lowest EM. Although maltitol's hydrodynamic radius is not available in

1145 Table 3.2, maltitol must have largest hydrodynamic radius among all the plasticizers due to its largest molecule size. Therefore, distance between starch molecules in maltitol-plasticized films would be the farthest leading to the films being more flexible.

Table 3.2 Effective hydrodynamic radii of the plasticizers

Plasticizer	Number of hydroxyl group	Effective hydrodynamic radii (nm)	Reference
Ethylene Glycol	2	0.22	Tejuca and others 2001
Glycerol	3	0.31	Schultz and Solomon 1961
Sorbitol	6	0.39	Goudet and others 1999
Maltitol	9	Not available	-
Glucose	5	0.37	Goudet and others 1999
Mannose	5	Not available	-
Fructose	5	Not available	-
Galactose	5	0.42	Schultz and Solomon 1961

1150

Water Vapor Permeability (WVP)

Table 3.3 shows the WVP of the starch films ranged from 1.90 to 2.75 g mm m⁻² h⁻¹ kPa⁻¹. It shows that monosaccharide-plasticized films had comparable WVP with the

polyol-plasticized films. Glucose- and fructose-plasticized films were more resistant to the permeation of water molecules than the glycerol- and sorbitol-plasticized starch films. The structural compatibility of monosaccharides with starch reduced the free volume and the segmental motions of starch chains. For ethylene glycol-plasticized films, the WVP was lower than other polyols films. This was due to its lowest amount in the starch films and its smallest molecular size leading to starch chains interacting directly with each other. This resulted in less free volume left in the structure of films for water molecules to transport through.

Table 3.3 Water vapor permeability (WVP) of starch films

Plasticizers	Molecular Weight	Number of hydroxyl groups in one molecule	Water vapor permeability (g mm m ⁻² h ⁻¹ kPa ⁻¹)	RH (%) gradient (up/down)
Ethylene Glycol	62.07	2	1.99±0.09 ^(b)	11.60/65.88
Glycerol	92.06	3	2.75±0.26 ^(a)	13.25/69.82
Fructose	180.16	5	1.96±0.27 ^(b)	9.00/78.81
Glucose	180.16	5	1.90±0.12 ^(b)	11.60/77.55
Mannose	180.16	5	2.27±0.18 ^{(a)(b)}	12.00/78.18
Sorbitol	182.17	6	2.61±0.15 ^(a)	13.25/76.32
Maltitol	344	9	2.28±0.16 ^{(a)(b)}	12.00/80.61

Values are means ± standard deviation (n = 3). The values bearing different superscripts in the same column indicate significant difference at p < 0.05 using Tukey test.

Table 3.3 also shows that, with total number of hydroxyl group increasing, the WVP tended to increase, except the glycerol-plasticized films. Because as the number of hydroxyl groups increased, the molecular mass of plasticizer increased, resulting in increasing hydrophilicity and widening the inter-molecular space in the starch films. The larger space promoted water vapor diffusion through the film (larger diffusivity) and accelerated the water vapor transmission (larger permeability). Glycerol-plasticized films had the highest value of WVP mostly due to its high hydrophilicity, high water holding capacity (Yang and Paulson 2000), which increased both water adsorption and diffusion.

Maltitol-plasticized films showed the same value of WVP compared to those of other films. Considering the largest molecular weight of maltitol, this result was quite exceptional. It could be explained that maltitol, which is the alcohol form of maltose (glucose-1, 4-sorbitol), possesses a glucose in its structure, and this glucose increased interactions between starch and maltitol resulting in compact structure of starch polymers giving low WVP.

With regard to other polymers, the pea starch films have WVP values slightly higher than amylose films ($1.367 \text{ g mm m}^{-2} \text{ h}^{-1} \text{ kPa}^{-1}$), much higher than cellophane films ($0.3022 \text{ g mm m}^{-2} \text{ h}^{-1} \text{ kPa}^{-1}$) and low-density polyethylene films ($0.001295 \text{ g mm m}^{-2} \text{ h}^{-1} \text{ kPa}^{-1}$) (Shellhammer and Krochta 1997). However, WVP of pea starch film was similar to or lower than wheat gluten films plasticized with glycerol ($2.518 \text{ g mm m}^{-2} \text{ hr}^{-1} \text{ kPa}^{-1}$) (Gennadios and others 1994).

Ideally, permeability of hydrophobic films is independent of the equilibrium moisture vapor pressure (or relative humidity). However, hydrophilic films exhibit a moisture vapor pressure-dependency of WVP. It had been found that wheat gluten's WVP increased by four orders of magnitude from the lowest RH condition of 0 - 11% (1.368×10⁻¹ g mm m⁻² h⁻¹ kPa⁻¹) to the highest RH condition of 75 - 84% (1.476×10³ g mm m⁻² h⁻¹ kPa⁻¹) (Roy and others 2000). For the WVP of pea starch film, although there is no research relating to the dependence of permeability on the RH condition, it is predictable that this tendency would exist. Further research is needed to identify this phenomenon.

Effect of Total Plasticizers

As mentioned above, water acts as a plasticizer. Therefore, it was necessary to compare the effect of total plasticizers, that is, water plus plasticizers, on the properties of films. Fig. 3.5 shows the effect of the total plasticizers on the physical properties (TS, EM, E and WVP) of pea starch films. From the moisture content data in Table 3.1, the amount of water was calculated. The amount of water plus the amount of the monosaccharides or polyols was used as total amount of the plasticizers. The ratio of total amount of plasticizers to the amount of starch were 23.5, 87.4, 100.8, 101.9, 103.7, 107.0, and 175.9% (w/w) for ethylene glycol-, glycerol-, sorbitol-, glucose-, mannose-, fructose-, and maltitol-plasticized starch films, respectively. Fig. 3.5 A and B show that ethylene glycol-plasticized films were the most fragile and strongest. From Fig. 3.5 A, sorbitol, glucose, mannose, and fructose-plasticized films show similar tensile properties, since their total amount of plasticizer is similar (100.8 - 107.0%, w/w). Maltitol-plasticized

films showed the least TS and EM due to the highest amount of total plasticizer (175.9%,
 1215 w/w). The highest WVP value of glycerol-plasticized films indicate that the high amount
 of water molecules in the film contribute greatly to the plasticization effect (Fig. 3.5 D).

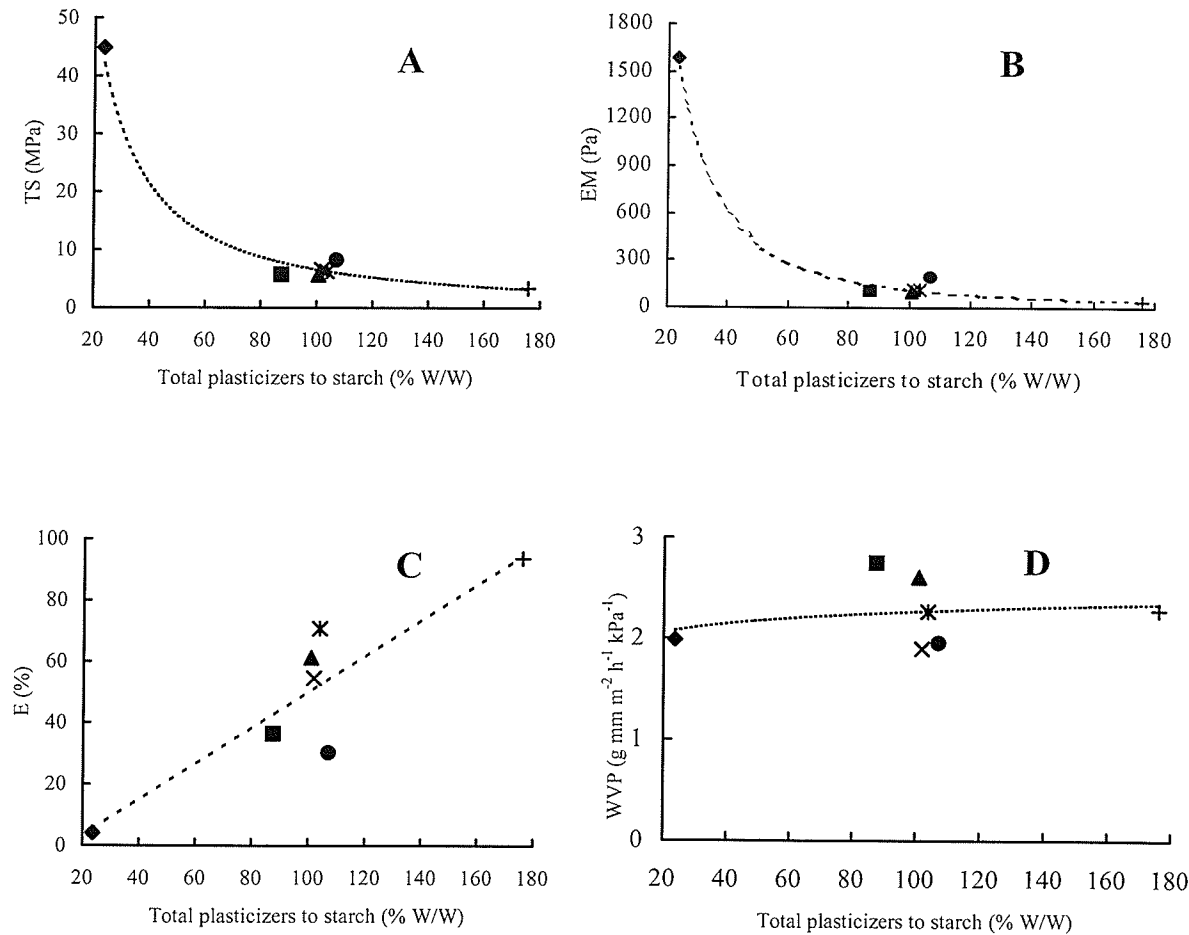


Fig. 3.5 Effects of total plasticizers (polyols or monosaccharides plus water) on
 mechanical properties and water vapor permeability (WVP) of starch films

(♦Ethylene Glycol ■Glycerol ▲Sorbitol ×Glucose *Mannose •Fructose +Maltitol)

Light transmission rate and film transparency

Starch films are ultimately used in food packaging. Therefore, the light transmission properties of the films are important to their applications. Light transmittance in UV region from 190 nm to 300 nm becomes complicated. Therefore, visible region from 300 nm to 800 nm was selected to measure the light barrier properties. Fig. 3.6 shows the light transmission rate of the films at selected wavelengths from 300 to 800 nm. Table 3.4 shows the transmission rate and transparency of starch films at 600 nm that is a commonly used wavelength for the film transparency (Han and Floros 1997; Shiku and others 2003; Fang and others 2002b).

No matter what plasticizers were used, with the wavelength increasing, the light transmission rate increases (Fig. 3.6). Shiku and others (2003), and Fang and others (2002b) reported similar results when they tested the light barrier properties with fish myofibrillar protein films and whey protein films, respectively. The transparency of the starch films are shown in Table 3.4. Fructose-plasticized films had the highest transparency followed by the maltitol-plasticized films. Sorbitol-plasticized films had the lowest values in transparency. Glycerol-, glucose-, and pure starch films had similar transparency whose values are around 1.25 - 1.27. It is hard to figure out the relationship between the transparency and compounds in films. However, comparing with pure starch films, fructose, maltitol, and ethylene glycol were helpful in improving the film transparency value. Meanwhile, glycerol, glucose, and mannose had hardly any influences on the film transparency. Sorbitol decreased the film transparency. It can be assumed that film structure and the light barrier properties of plasticizers decided the

transparency of the films. From Fig. 3.6 and Table 3.4, it could be concluded that the monosaccharide-plasticized films had comparable light barrier properties with polyol-plasticized films. Transparency values of some commonly used synthetic films were given in report by Shiku and others (2003). Low density polyethylene (LDPE), orientated polypropylene (OPP), and polyvinylchloride (PVDC) have 3.05, 1.67, and 4.58 transparency values, respectively.

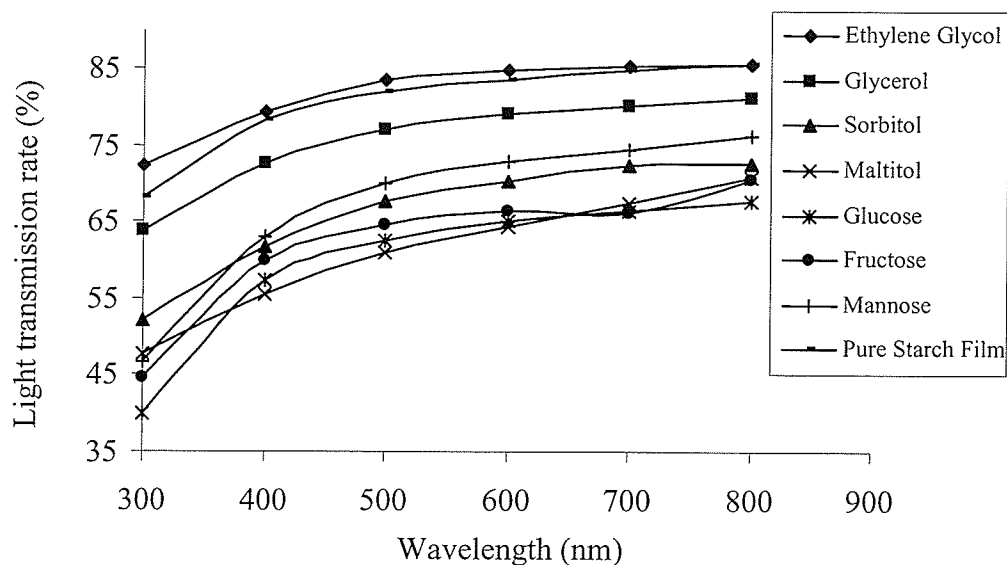


Fig. 3.6 Light transmission rate (%) of starch films at 600 nm with various plasticizers

Table 3.4 Light transmission rate (% T₆₀₀) and transparency (A₆₀₀/nm) of starch films

Transmission rate and transparency	Ethylene Glycol	Glycerol	Sorbitol	Maltitol	Glucose	Fructose	Mannose	Pure Starch Film
T ₆₀₀ , (%)	84.9±2.25	79.2±1.74	70.3±3.05	64.2±1.24	65.1±1.36	66.4±1.44	72.9±3.01	83.6±2.88
Transparency (A ₆₀₀ /nm)	1.35±0.11	1.25±0.39	1.11±0.75	1.98±0.50	1.27±0.33	2.75±0.26	1.20±0.10	1.25±0.26

Values are means±standard deviation (n=2).

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SEM Observations

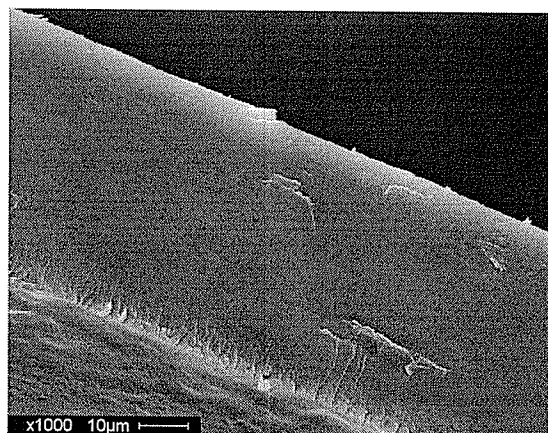
SEM observations of cross sections of films are shown in Fig. 3.7. Except for sorbitol films, all the film micrographs show relatively smooth and continuous cross sections without pores, which confirm dense and homogeneous structures. This may result from good compability of plasticizers with starch polymers. Sorbitol films show heterogeneous surface on the cross section. This may result from phase separation due to sorbitol blooming, suggesting a heterogeneous or unstable structure of sorbitol films. Transparency test had shown the sorbitol-film had the lowest values in transparency. Structural heterogeneity of the sorbitol-film shown in Fig.3.7 contributed to its low transparency. The heterogeneity of sorbitol film also contributes to its lowest transparency (Table 3.4).

CONCLUSION

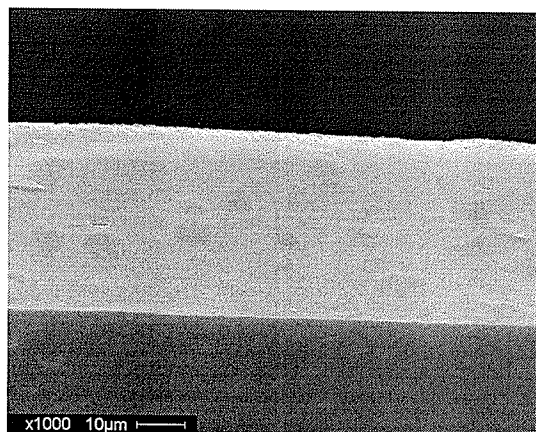
Potential use of monosaccharides in starch film as plasticizers was suggested. Microstructure studies of the starch films showed that the commonly used heating conditions of starch solution could not make all of the starch granules completely solubilized. Only a part of starch granules could be gelatinized and release the amylose and amylopectin molecules. Ethylene glycol- and glycerol-plasticized films gave different profiles of FTIR spectra from other films. More bound water and hydrogen bound hydroxyl groups existed in the films. Ether linkages were suspected to be produced in the glycerol-plasticized films. The starch films with monosaccharides (fructose, glucose, and mannose) possessed a higher moisture barrier properties compared to

polyol-plasticized starch films, except for ethylene glycol-plasticized films. All the
1295 characteristics of monosaccharide-plasticized films were comparable with polyol-
plasticized films in terms of the tensile strength, elongation, elastic modulus, and
transparency.

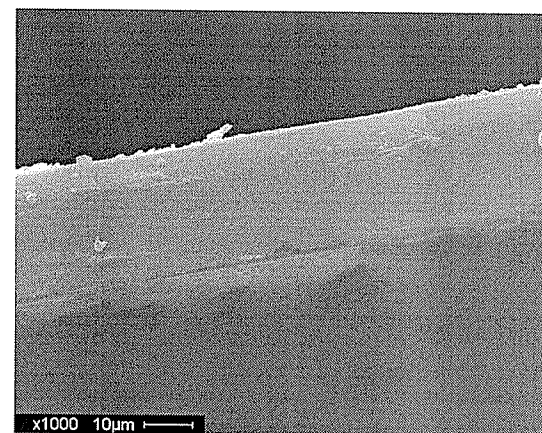
Fig. 3.7 SEM observation on the cross section of the starch films



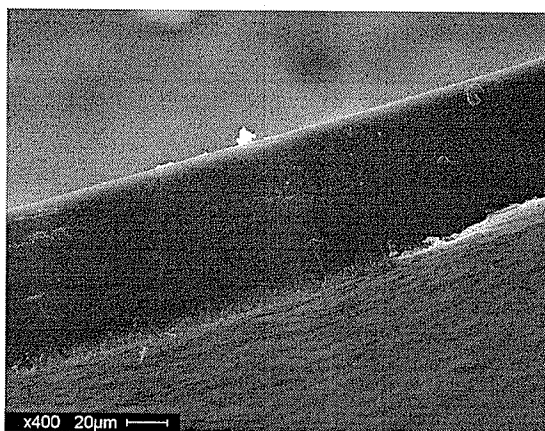
Glycerol - film



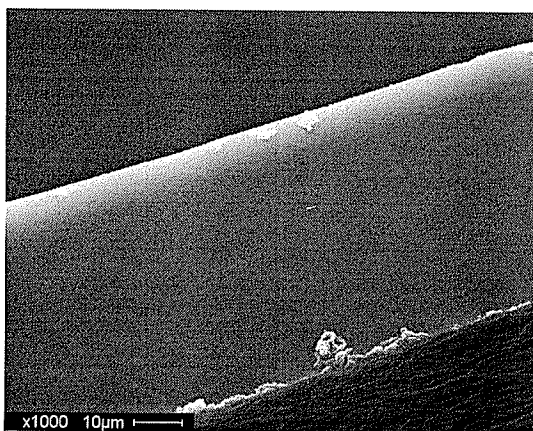
Sorbitol - film



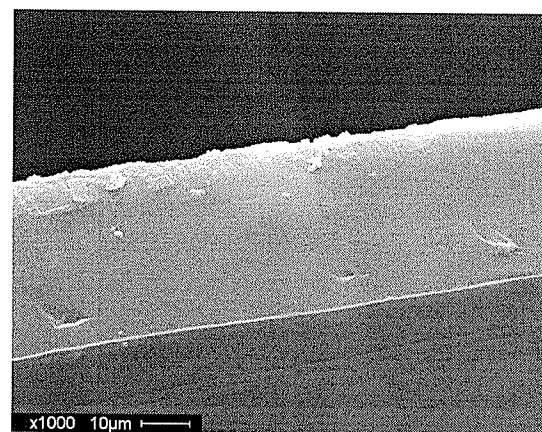
EG - film



Mannose - film



Fructose - film



Glucose - film

1300

Chapter 4

Mechanical, thermal characteristics and structure of pea starch films plasticized with monosaccharides and polyols

1305 ABSTRACT

Edible starch films were produced from pea starch and various plasticizers (mannose, glucose, fructose, galactose, glycerol, EG, sorbitol, and maltitol) at the ratio of 4.34, 6.50, 8.69, and 10.87 mmol plasticizer per g of starch. After film specimens were conditioned at 50% relative humidity (RH), mechanical properties (tensile strength, elongation, and modulus of elasticity), water vapor permeability (WVP), oxygen permeability (OP), moisture content, thermomechanical properties (E' and $\tan\delta$), and crystallinity were determined as a function of plasticizer concentration. Galactose films were too brittle, and maltitol films were too sticky. At all concentration levels, monosaccharides (mannose, glucose and fructose) made the starch films stronger (higher tensile strength) and more stretchable than polyols (glycerol and sorbitol), while WVP and OP of monosaccharide-plasticized starch films were lower than those of polyol-plasticized starch films, especially at higher plasticizer concentration level. Except for 4.34 mmol/g of mannose-plasticized film, all the other films showed similar modulus of elasticity at the same plasticizer concentration. Polyol-plasticized films had lower T_g than the monosaccharide-plasticized films. Glucose- and sorbitol-plasticized films needed more

activation energy to go through glass transition than others. After all, research results showed that not only the polyols but also the monosaccharides were effective in plasticizing starch films. Generally, the crystallinity of the films increased with the conditioning time. And high RH favored crystallization.

1325 INTRODUCTION

Plasticizer functions differently at higher concentrations. For starch films, tensile strength (TS), modulus of elasticity (ME), and glass transition temperature (T_g) were reported to decrease, while elongation (E), oxygen permeability (OP), and water vapor permeability (WVP) increase, with increase of plasticizer (Mali and others 2006; 1330 Laohakunjit and Noomhorm 2004; Paschoalick and others 2003; Thomazine and others 2005). Plasticizer was also found to slow down the crystallization process during film storage (Mali and others 2006). All these effects were due to the blocking effect of the plasticizer, that is, interaction with the polymeric chains, and interference with polymer chain alignment due to steric hindrances (Turhan and Sahbaz 2004; Mali and others 1335 2006). In Chapter 3, monosaccharides and polyols showed an effective improvement on the pea starch film properties at a relatively low concentration level. A need to characterize the effect of monosaccharide and polyol plasticizer with higher concentration levels on the properties of pea starch films is required. The objective of this study is to determine the plasticization efficiency and characteristics of monosaccharides 1340 and polyols at a series of higher concentration levels on edible starch films by mechanical, thermomechanical, gas permeability, and X-ray diffraction, for further understanding of their exact plasticizing mechanism.

MATERIALS AND METHODS

1345 **Materials**

The same pea starch resource, monosaccharides, and polyols as shown in Chapter 3 were used.

Starch Film Preparation

1350 3% (w/w, 3 g starch + 97 g water) pea starch solutions were first prepared. Plasticizers were added into aqueous dispersion of 3% (w/w) pea starch at the molar ratio of 4.34, 6.50, 8.69, and 10.87 mmol per g of starch, respectively. Then four starch solution samples with each concentration level for each plasticizer were obtained. The method to prepare the starch films was outlined in Chapter 3.

1355

Film thickness, moisture content (MC), tensile tests, and water vapor permeability (WVP) were measured by the procedures outlined in Chapter 3.

Oxygen Permeability (OP)

1360 Oxygen transmission rate (OTR) measurements were performed by using a Mocon Ox-Trans 2/20 equipped with a Coulox sensor (Modern Control, Inc., Minneapolis, MN) according to the ASTM Standard Method (ASTM, 1989) at atmospheric pressure. The machine was set at 23 °C. Starch films were placed into the oxygen test cells and exposed to pure oxygen on the upper side of the films and then flushed with inert nitrogen mixed
1365 with 2 % hydrogen on the bottom side. Nitrogen gas containing oxygen transferred

through the film was conducted to the coulometric sensor. The RH of the two gases was controlled by a humidifier to 50 %. OTR measurements were made when oxygen flux measured by the coulometric sensor was stabilized indicating that steady state was reached. Three replications were conducted for a same treatment. The thicknesses of sample films were measured with an electronic digital micrometer at three random points before OTR tests. The means of these three thickness values were used to calculate oxygen permeability (OP) from OTR results. OP was calculated according to the following equation:

$$OP = \frac{OTR \times l}{\Delta P} \quad 4.1$$

where l is the mean of film thickness. ΔP is the difference of the oxygen partial pressure. Because the gas flow was very slow in both upper and lower sides of films, ΔP value was regarded to be nearly equal to the atmosphere pressure. OP result was obtained as the mean value in $\text{cc mm m}^{-2} \text{ h}^{-1} \text{ kPa}^{-1}$.

Thermomechanical Properties

For all kinds of film samples mentioned above, dynamic mechanical analysis (DMA) was carried out with Q800 Dynamic Mechanical Analyzer (TA Instruments-Water LLC, New Castle, DE) working under Advantage Version 4.0.0 Software (TA Instruments-Water LLC) with a liquid nitrogen tank attachment. Film shape is rectangular with 25.00 mm×6.55 mm×0.15 mm ($l \times w \times t$) dimensions. A film tension clamp was used in Multi-Frequency-Stress (MFS) model, with a heating ramp rate of 2 °C min⁻¹, at 1, 5, and 10 Hz, respectively. For each analysis, the DMA stored values of storage modulus (E') and $\tan\delta$ ($\tan\delta = E''/E'$, where E'' is the loss modulus). The glass transition temperature (T_g)

was defined as the mid-point of the fall in the storage modulus. Apparent activation
1390 energy (ΔH_a) for α – relaxation was calculated and compared to each other. Samples
were run in duplicate.

X – Ray Diffraction and Crystallinity Determination

Samples were analyzed with an X-ray diffractometer (Philips PW 1710, Netherlands)
1395 between $2\theta = 3^\circ$ and $2\theta = 60^\circ$ with a step size $2\theta = 0.05^\circ$ using Cu $K_{\alpha 1}$ radiation ($\lambda =$
0.15410 nm), 40 kV and 40 mA, working under Jade 7.0 Material Data Jade XRD Pattern
Processing software (MDI Material Data Incorporated, Livermore, California). Films
(thickness around 0.05 mm) were cut into rectangular shape (5×3 cm) and clamped onto
a quartz monochromator. The diffractometer was equipped with 1° divergence slit and a
1400 0.1 mm receiving slit. The relative crystallinity (X) was carried out using the following
methods (Ribotta and others 2004, Bultosa and Taylor 2003).

$$X = \frac{I_c}{I_c + I_a} \times 100\% \quad 4.2$$

where I_c is the integrated intensity of crystalline phase, and I_a is the integrated intensity of
the amorphous phase (as shown in Fig. 2.8). Crystalline and amorphous areas were
1405 determined using Jade 7.0 software.

Statistical Analysis

Data were analyzed by a two-way ANOVA (types of plasticizers and molar ratio) using
SAS (SAS Institute, Inc., Cary, NC) to assess the effects of polyols and monosaccharides
1410 on the properties of starch films with the test null hypotheses of $H_0: s^2_{\text{plasticizer}}/s^2_{\text{error}} = 1$. A
completely randomized design was used with 6 types and 4 molar ratios of plasticizers.

Mean values with standard deviations were compared using the Tukey test at 5% significance level with a null hypothesis of $H_0: \mu_1 = \mu_2 = \dots = \mu_n$; and $H_0: \mu_1 = \mu_2 = \dots = \mu_m$, where μ is the mean of each treatment, n is the number of different types of plasticizers, and m is the number of different concentrations tested.

RESULTS AND DISCUSSIONS

After drying the film-forming solutions, except for galactose- and maltitol-films, free-standing transparent films were obtained. Galactose-films were too brittle, and maltitol-films were too sticky. They could not be peeled off intact from Petri dishes. Therefore, they are not discussed further. The glucose-plasticized films at 8.69 and 10.87 mmol/g concentration levels became brittle and opaque after conditioning (at $50 \pm 2\%$ RH for 72 h) because recrystallization of starch occurred (Fig. 4.1A). The recrystallization could get much more obvious with time resulting in inapplicability of the film. Two factors are believed to introduce the recrystallization in glucose-plasticized films. One is the molecular configuration of glucose. The glucose molecule has the exactly same structure and configuration to the anhydroglucose unit in starch molecules. Therefore, it is easy for glucose molecules to get packed into starch molecule chains. Another is the high relative humidity (RH) in which the films were conditioned. High RH increases the movement of starch chains and the glucose molecules, which facilitates the packing of the starch molecules into crystal lattices. A similar situation was also observed by Delville and others (2003) who did research on wheat starch based films. Sorbitol-plasticized films with 8.69 and 10.87 mmol sorbitol per gram starch showed the occurrence of white residues on the surface of films after 72 h conditioning at $50 \pm 2\%$ RH (Fig. 4. 1B).

1435 However, the sorbitol-plasticized film did not become brittle and opaque. The film
maintained flexibility. The white residues may have occurred from an excess amount of
sorbitol. Jangchud and Chinnan (1999), and Aulton and others (1981) assumed that when
the concentration of plasticizer was more than its compatibility limit in the polymer,
phase separation and plasticizer physical exclusion happened. All the other three kinds of
1440 film samples were intact and flexible. They appeared normal in color and texture.

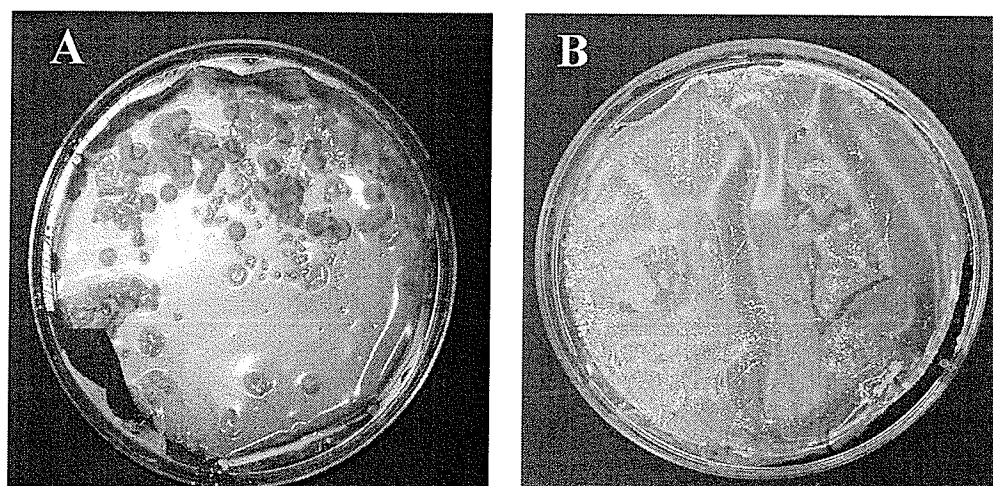


Fig. 4.1 Recrystallization of glucose-plasticized films (A) and blooming of sorbitol white
1445 residues on the sorbitol-plasticized (B) film surface

Film Thickness

Table 4.1 shows the effect of plasticizers on film thickness. The thickness of the film
increased as the amount of plasticizers increased from 4.34 to 10.87 mmol/g and as the
1450 molecular weight of plasticizer increased from 62.0 (EG) to 182.2 (sorbitol). Mannose-
plasticized starch films were thicker than others, while EG-plasticized starch films were

the thinnest. Compared to other plasticizers, EG has the smallest molecular weight. Therefore, the amount of EG is always less than other plasticizers at the same level of molar ratio to starch. It is interesting that mannose-plasticized starch films were significantly thicker than fructose- and glucose-plasticized starch films at higher concentration levels although these three monosaccharides have the same molecular weight. Therefore, mannose-plasticized starch films may have a loose structure compared to fructose- and glucose-plasticized starch films. Mannose has one different position of hydroxyl group in its structure compared to glucose structure. This implies that the geometrical configuration of monosaccharide affects the interaction with starch molecules significantly resulting in thickness difference.

1475 Table 4.1 Effects of plasticizers on the film thickness (mm) after conditioning at 50% RH

mmol per g starch	Mannose	Fructose	Glucose	Glycerol	Sorbitol	EG
4.34	0.075±0.0045 ^{cxy}	0.070±0.0030 ^{cx}	0.062±0.0026 ^{cx}	0.066±0.0100 ^{bx}	0.087±0.0037 ^{by}	0.038±0.0021 ^{cz}
6.50	0.093±0.0047 ^{bxy}	0.093±0.0020 ^{abxy}	0.078±0.0045 ^{bcx}	0.077±0.0040 ^{abx}	0.108±0.0024 ^{ay}	0.047±0.0033 ^{cz}
8.69	0.118±0.0070 ^{az}	0.086±0.0110 ^{bcx}	0.093±0.0095 ^{abxy}	0.081±0.0010 ^{abx}	0.105±0.0030 ^{ayz}	0.065±0.0042 ^{abw}
10.87	0.119±0.0053 ^{ax}	0.106±0.0035 ^{ay}	0.104±0.0069 ^{ay}	0.085±0.0014 ^{az}	0.111±0.0018 ^{axy}	0.071±0.0005 ^{aw}

Values are means±standard deviation (n=3). The values bearing different superscripts differ significantly ($p < 0.05$) using Tukey test.

a, b, c, and d are for the comparison of within columns (plasticizer concentration), and w, x, y, and z are for between columns (types of plasticizers)

1480 **Moisture Content (MC)**

Since the starch, monosaccharides and polyols are hydrophilic, water can be absorbed into the film matrix. Water acts as a plasticizer in the hydrophilic films. Water absorption and desorption of the hydrophilic films depends on the environmental relative humidity (van Soest and others 1995). Table 4.2 shows that moisture content (MC) of films after
1485 conditioning increased significantly as the plasticizer content increased, except for sorbitol-plasticized films. This result is similar to Arvanitoyannis and Biliaderis (1999) whose starch films tended to become more hydrophilic with an increase in the total plasticizer content. In starch films, plasticizers are generally more hygroscopic than starch. Thus, the difference in the water absorptivity of starch films is mostly dependent
1490 on the type and the amount of the plasticizers when the starch content remains constant. Table 4.2 shows that the MC of sorbitol-plasticized starch films were exceptionally constant with an increase of sorbitol concentration, and were the lowest MCs compared to other films. These results indicate that sorbitol does not contribute to the hydrophilic nature or hygroscopicity of starch films significantly. Previous studies provided the MC
1495 data of pure starch films ranging from 10 through 12%. The MC of sorbitol-plasticized starch films is very similar to the MC of pure starch films. Sorbitol may have similar hydrophilicity and hygroscopicity to that of pure starch, and function as a physically hindering additive between starch molecules preventing starch-starch intermolecular interaction. Glycerol-plasticized starch films contained moisture at 2 - 4.5 times that of
1500 sorbitol-plasticized starch films, and the increase in glycerol amount dramatically increase the MCs of the films. At all levels of plasticizer concentrations, glycerol-plasticized starch films contained significantly higher level of moisture in the films than

others. These results may be interpreted that glycerol acts as a water holding agent, and the higher amount of water molecules in glycerol-plasticized starch films increase plasticizing activity, while sorbitol acts as a plasticizer with a minimum contribution from water molecules. Monosaccharide-plasticized films may also have plasticizing activity from the contribution of water molecules since the increase in MC with increasing plasticizer is large (from 12 % to 22 %). The highest MC of glycerol-plasticized starch films is probably due to the high polarity of glycerol (dielectric constant of 42.5 at 25 °C) (Yang and Paulson 2000). Sorbitol has a dielectric constant of 33.5 at 80 °C (Arvanitoyannis and others 1997). Sorption isotherm behavior of starch films will be studied in Chapter 5 for further understanding of the function of water molecules in the starch film.

1525 Table 4.2 Effects of plasticizers on the moisture content (%) after conditioning at 50% RH

mmol per g starch	Mannose	Fructose	Glucose	Glycerol	Sorbitol	EG
4.34	12.4±0.41 ^{byz}	13.9±0.18 ^{by}	11.7±0.08 ^{byz}	25.3±2.30 ^{dx}	10.8±0.21 ^{az}	12.1±0.58 ^{cz}
6.50	14.6±0.76 ^{by}	22.1±0.61 ^{ax}	13.1±0.57 ^{by}	34.6±0.36 ^{cw}	9.8±0.84 ^{az}	11.6±0.30 ^{cyz}
8.69	12.7±0.52 ^{by}	15.6±0.20 ^{bx}	17.6±0.97 ^{aw}	40.5±1.19 ^{bv}	10.1±0.06 ^{az}	14.73±0.42 ^{bxy}
10.87	21.8±3.38 ^{ax}	22.8±2.85 ^{ax}	17.4±2.63 ^{ay}	52.2±2.22 ^{aw}	12.3±2.85 ^{az}	16.88±0.09 ^{ay}

Values are means±standard deviation (n=3). The values bearing different superscripts differ significantly (p < 0.05) using Tukey test.

a, b, c, and d are for the comparison of within columns (plasticizer concentration), and w, x, y, and z are for between columns (types of plasticizers).

Mechanical Properties

Fig. 4.2 shows the trends in tensile property change with respect to the type and amount of plasticizers. Detailed data with statistical analysis results are available in Appendix 4.1 – 4.3. EG-film had the highest TS in the whole plasticizer concentration range. This is due to the smallest molecular weight and least mass of EG used in the films. Starch films plasticized by monosaccharides had larger tensile strength (TS) than those plasticized by sorbitol and glycerol (Fig. 4.2A). No matter which types of plasticizers the films contained, TS decreased as the molar ratio of plasticizers increased. This tendency was generally observed by many researchers, for example, Arvanitoyannis and others (1997). They studied the films composed of potato starch and 1,4-trans-polyisoprene, and found lower TS and higher elongation when higher glycerol and sorbitol contents were in the starch blend. In the case of high amylose corn starch, Ryu and others (2002) found that the films plasticized by sorbitol were stronger than those plasticized by glycerol. They assumed that it was due to the difference in the state of the plasticizers; that is, glycerol is liquid while sorbitol is solid at room temperature. This is not in agreement with the result of pea starch films in this study.

Fig. 4.2B shows the changes in elongation (E) of starch film with respect to the plasticizer concentration. Since the thickness of the films was not accounted in calculating the E values, the comparison of E between the films is meaningful only for films having similar thickness (Foulk and Bunn 2001). Fig. 4.2B shows that EG-plasticized starch films have significantly lowest E value than other films (Appendix 4.2). This may be caused by the lowest value of thickness of EG-plasticized starch film (Table

4.1) among other films. Except for the EG-film, at 4.34 and 6.50 mmol/g concentration
1555 levels, the film thickness of other 5 different plasticized films is similar at the same
concentration of plasticizers (Table 1). Therefore, it is possible to compare the E value of
different plasticizers at 4.34 or 6.50 mmol/g concentration levels. The E values of
mannose-, fructose-, and glycerol-plasticized films significantly increased when the
plasticizer concentration increased from 4.34 to 6.50 mmol/g (Appendix 4.2), while the
1560 glycerol- and sorbitol-films did not change significantly. Similar results were obtained by
other researchers (Arvanitoyannis and Biliaderis 1999; Lazaridou and Biliaderis 2002;
Aulton and others 1981).

Fig. 4.2 C and Appendix 4.3 show that the modulus of elasticity (EM) decreased as
1565 plasticizer concentration increased. Except for EG-film which had highest EM, a slight
difference in the EM was shown among various films. Actually, at 10.87 mmol/g
concentration level, some films appeared sticky. It can be concluded that the amount of
plasticizers is a significant factor to control ductility of starch films while the type of
plasticizer is less significant.

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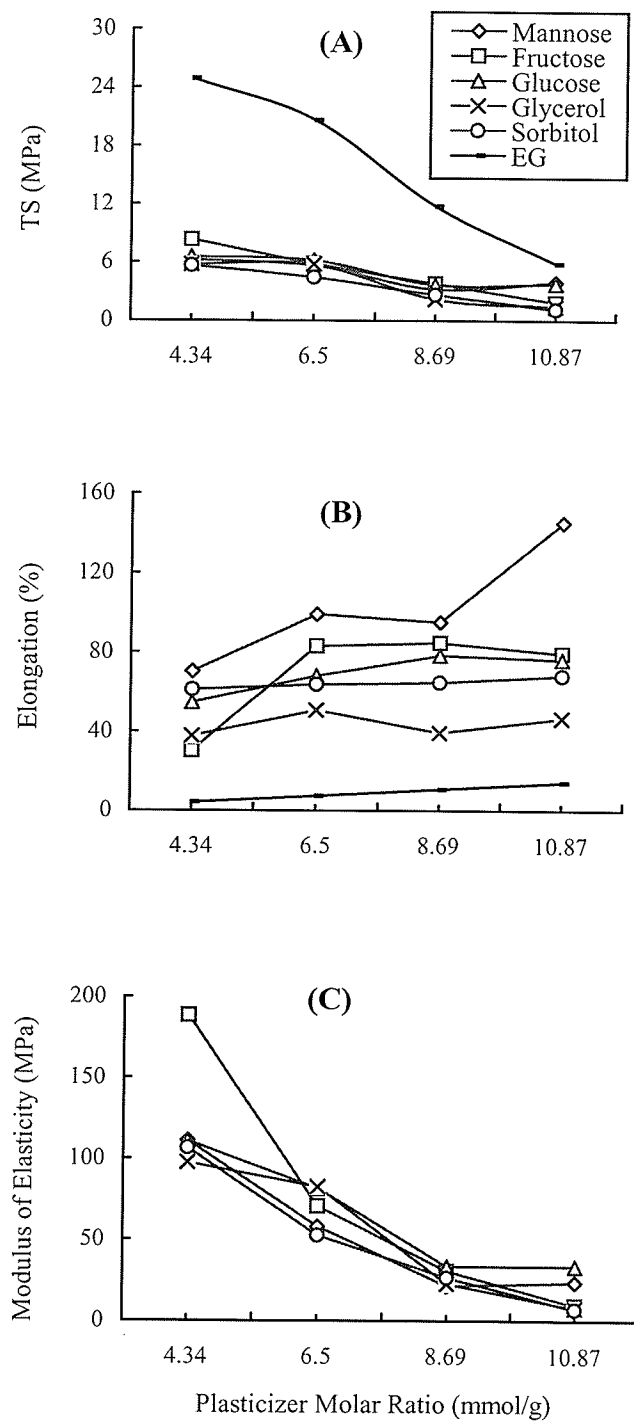


Fig. 4.2 Tensile properties of pea starch films with various plasticizers (EG-films not included in Fig. 4.2 C)

Water Vapor Permeability

1585 Water vapor permeability (WVP) of a film is an important property that greatly influences the utility of the film in food systems (Ryu and others 2002). Table 4.3 shows that WVP increased as plasticizer concentration increased. Glycerol-plasticized starch films changed their WVP more sensitively responding to the glycerol concentrations, while WVP of other starch films were changed less. Increasing plasticizer concentration
1590 reduced the cohesive forces between starch chains and increased free volume and segmental motions (Sothornvit and Krochta 2005), hence water molecules diffused more easily and higher WVP resulted. Also, the addition of a plasticizer increases hydrophilic property of starch films resulting in WVP increase (Foulk and Bunn 2001). EG-films had the lowest WVP. It was probably due to the least amount of EG added in the starch films.
1595 At 10.87 mmol/g of plasticizers in starch, the films plasticized by glycerol or sorbitol had significantly larger WVP values than those plasticized by the monosaccharides. This assumed that the structure of films plasticized by monosaccharides was more compact (that is lower diffusivity). Mali and others (2002) found that increasing glycerol concentration slightly increased the WVP of the starch films, but the differences were not
1600 significant. However, Turban and Sahbaz (2004) found that increasing polyethylene glycol content in methylcellulose-based films increased the WVP significantly. Insignificant effect of glucose concentration on WVP and the lower WVP value of glucose-plasticized starch films imply that the structural identity of glucose with starch anhydroglucose units causes compact structure and minimizes free volume and
1605 intermolecular distance.

Table 4.3 Effects of plasticizers on the water vapor permeability ($\text{g mm kPa}^{-1} \text{ h}^{-1} \text{ m}^{-2}$)

mmol per g starch	Mannose	Fructose	Glucose	Glycerol	Sorbitol	EG
4.34	$2.27 \pm 0.182^{\text{ax}}$	$1.96 \pm 0.266^{\text{ax}}$	$1.90 \pm 0.122^{\text{ax}}$	$2.75 \pm 0.263^{\text{ay}}$	$2.61 \pm 0.148^{\text{ay}}$	$1.99 \pm 0.99^{\text{ax}}$
	(12.00/78.18)	(9.00/78.81)	(11.60/77.55)	(13.25/69.82)	(13.25/76.32)	(11.00/65.88)
6.50	$2.86 \pm 0.09^{\text{bx}}$	$2.87 \pm 0.133^{\text{bx}}$	$2.84 \pm 0.073^{\text{abx}}$	$4.05 \pm 0.311^{\text{by}}$	$3.58 \pm 0.166^{\text{bxy}}$	$2.00 \pm 0.17^{\text{az}}$
	(11.40/77.16)	(11.40/77.11)	(11.00/74.45)	(11.00/63.32)	(11.00/74.56)	(11.22/67.45)
8.69	$4.51 \pm 0.37^{\text{cyz}}$	$3.17 \pm 0.175^{\text{bx}}$	$2.92 \pm 0.214^{\text{abx}}$	$5.29 \pm 0.127^{\text{cz}}$	$3.62 \pm 0.075^{\text{bxy}}$	$2.13 \pm 0.25^{\text{aw}}$
	(11.00/73.36)	(11.00/73.92)	(12.20/75.77)	(12.20/59.33)	(11.00/73.60)	(12.61/66.98)
10.87	$4.63 \pm 0.692^{\text{cx}}$	$4.78 \pm 0.905^{\text{cx}}$	$3.88 \pm 0.394^{\text{bx}}$	$9.97 \pm 0.684^{\text{dz}}$	$6.70 \pm 0.355^{\text{cy}}$	$2.57 \pm 0.36^{\text{bw}}$
	(11.50/76.70)	(11.70/75.60)	(12.40/74.03)	(12.40/62.90)	(12.10/66.10)	(11.77±69.43)

Values are means \pm standard deviation (n=3). The values bearing different superscripts differ significantly ($p < 0.05$) using Tukey test.

a, b, c, and d are for the comparison of within columns (plasticizer concentration), and w, x, y, and z are for between columns (types of plasticizers). Data in parenthesis are RH of outside/inside cups.

Oxygen Permeability

Oxygen permeability (OP) is another most important transport property of edible and biodegradable films (Miller and Krochta, 1997). Table 4.4 shows that the OP of fructose-, glycerol-, sorbitol-, and EG-films increased with increasing plasticizer concentration, while mannose- and glucose-films did not change obviously. Monosaccharide-films had much lower OP values than glycerol- and sorbitol-films, implying the structure of the monosaccharide-films was more compact than glycerol- and sorbitol-films. Sorbitol-films had the highest OP, indicating their structure was looser. Starch films had good oxygen barrier properties which can be comparable to that of low-density polyethylene (7.77×10^{-6} cc mm m^{-2} h $^{-1}$ kPa $^{-1}$). This is due to hydrophilic nature of starch. Therefore, one of the advantages of using starch films is its ability to act as an oxygen barrier.

Table 4.4 Oxygen permeability of the starch films ($\text{cc mm m}^{-2} \text{ h}^{-1} \text{ kPa}^{-1}$) $\times 10^{-6}$

mmol per g starch	Fructose	Mannose	Glucose	Glycerol	Sorbitol	EG
4.34	2.14 \pm 0.30 ^{ax}	3.07 \pm 0.41 ^{ay}	3.29 \pm 0.37 ^{ay}	11.24 \pm 1.87 ^{az}	10.00 \pm 1.01 ^{az}	2.45 \pm 0.23 ^{ax}
6.50	3.30 \pm 0.46 ^{abx}	3.00 \pm 0.60 ^{ax}	3.53 \pm 0.44 ^{ax}	14.87 \pm 2.77 ^{ay}	63.00 \pm 5.27 ^{bz}	3.78 \pm 4.15 ^{abx}
8.69	5.17 \pm 0.31 ^{bw}	3.35 \pm 0.24 ^{ax}	3.67 \pm 0.33 ^{ax}	50.14 \pm 6.18 ^{by}	71.03 \pm 6.44 ^{cz}	4.62 \pm 1.99 ^{bw}
10.87	9.52 \pm 1.75 ^{cw}	4.84 \pm 0.12 ^{bx}	3.45 \pm 0.41 ^{ax}	74.65 \pm 6.89 ^{cy}	91.63 \pm 7.42 ^{dz}	6.23 \pm 5.21 ^{cw}

1635 Values are means \pm standard deviation ($n = 2$). The values bearing different superscripts differ significantly ($p < 0.05$) using Tukey test.. a, b, and c are for the comparison of within columns (plasticizer concentration), and x, y, and z are for the between columns (types of plasticizers).

Thermomechanical Properties

EG-films, at 4.34 to 10.87 mmol concentration levels, were too brittle to be handled in this experiment. Therefore, the thermomechanical properties of EG-films are not discussed further. Table 4.5 shows the effect of plasticizers on the T_g of the films. The T_g of the films decreased with the amount of the plasticizers (from 4.34 to 10.87 mmol/g). This is in agreement with the common rule that plasticizer decreases the T_g . The reduction of T_g was about 20°C for mannose, fructose, glucose, and sorbitol-plasticized films over the plasticizer concentration range. Glycerol did not change the T_g of the film as much as the monosaccharides did. The glycerol-plasticized films had the lowest values of T_g that was around -60 °C. This indicated that the glycerol had the best effect of plasticization on the starch films. Glycerol molecules are much smaller and have higher ratio of hydroxyl number to its molecular weight ($3/92.09 = 0.0326$) than monosaccharides ($5/180.2 = 0.0277$). Although sorbitol has 0.0328 of the ratio which is similar to glycerol molecule, its plasticization efficiency was not as good as glycerol. This result could be due to the fact that sorbitol has a larger molecular size that could reduce its efficiency. Jangchud and Chinnan (1999) obtained the same conclusion when they compared glycerol to sorbitol while studying the plasticization effect of various polyols in peanut protein films. Sorbitol-plasticized films had lower T_g than the monosaccharide-plasticized films. Even though this difference in T_g was not substantial, it was significant. This situation could be explained that sorbitol molecules have higher ratio of hydroxyl group number to its molecular weight than mannose, fructose, and glucose molecules.

Table 4.5 Effects of plasticizers on the T_g ($^{\circ}\text{C}$) of starch films after conditioning at 50%RH

mmol per g starch	Mannose	Fructose	Glucose	Glycerol	Sorbitol
4.36	$2.2 \pm 0.04^{\text{aw}}$	$-6.8 \pm 0.72^{\text{ax}}$	$-8.50 \pm 0.99^{\text{ax}}$	$-53.7 \pm 5.72^{\text{ay}}$	$-14.11 \pm 2.13^{\text{az}}$
6.50	$-9.1 \pm 1.02^{\text{bw}}$	$-15.7 \pm 2.11^{\text{bx}}$	$-13.27 \pm 3.60^{\text{bx}}$	$-54.97 \pm 3.14^{\text{ay}}$	$-18.4 \pm 2.06^{\text{bxz}}$
8.69	$-16.6 \pm 2.75^{\text{cx}}$	$-18.5 \pm 1.50^{\text{bcx}}$	$-24.4 \pm 1.67^{\text{cy}}$	$-65.07 \pm 2.20^{\text{bz}}$	$-26.4 \pm 3.19^{\text{cy}}$
10.87	$-20.2 \pm 2.56^{\text{dw}}$	$-22.16 \pm 2.88^{\text{cw}}$	$-30.0 \pm 4.29^{\text{dx}}$	$-63.7 \pm 5.55^{\text{by}}$	$-34.4 \pm 3.97^{\text{dx}}$

1665 Values are means \pm standard deviation (n=2). The values bearing different superscripts differ significantly ($p < 0.05$) using Tukey test.
a, b, c, and d are for the comparison of within columns (plasticizer concentration), and w, x, y, and z are for between columns (types
of plasticizers).

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The thermomechanical behaviors of starch films in the glass transition zone was examined by DMA. The effect of plasticizer concentration on DMA traces of representative sample films, fructose-plasticized films, is demonstrated in Fig. 4.3. A drop in storage modulus E' and a peak in $\tan\delta$ are used as indicators of the glass transition (also denoted as α -relaxation) (Lazaridou and Biliaderis 2002). The $\tan\delta$ is normally found at a temperature higher than the onset or the midpoint temperature of the E' drop. The location of glass transition shifted to lower temperature direction with increase of plasticizer content due to plasticization of the starch polymers.

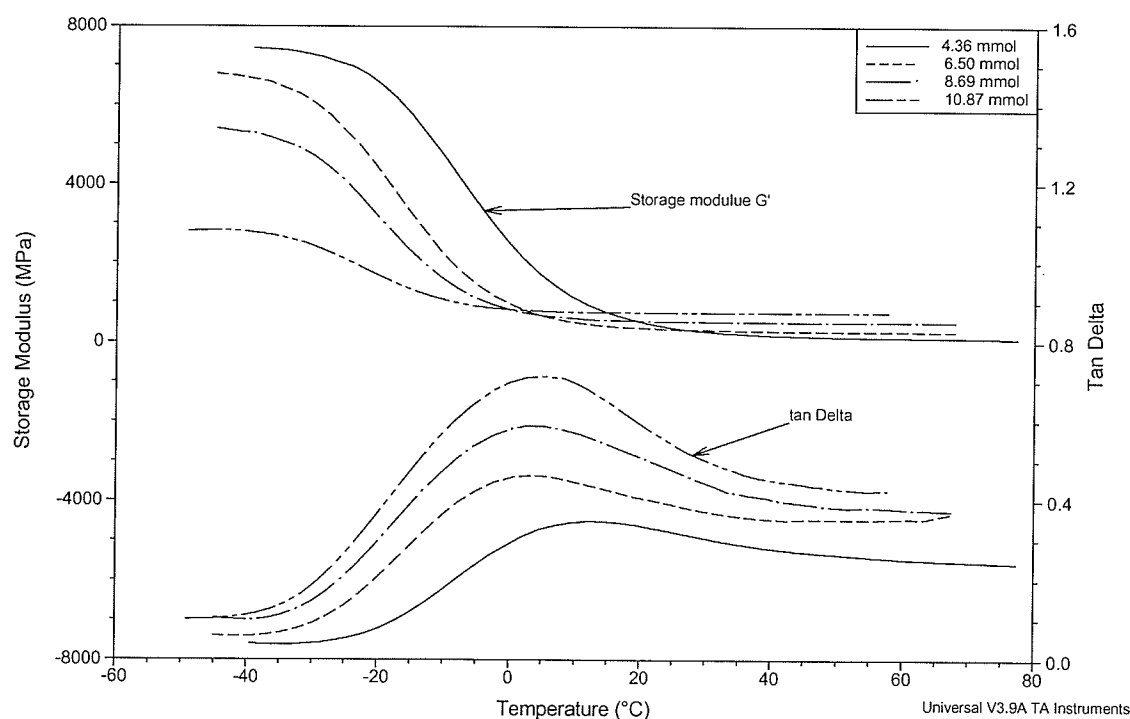


Fig. 4.3 DMA storage modulus E' and $\tan\delta$ for fructose-plasticized starch films at different plasticizer content

Increasing water content, with other plasticizer content being constant in films, increased the breadth of transition (the breadth of $\tan\delta$ peak) (Lazaridou and Biliaderis 2002; Pouplin and others 1999; Gontard and Ring 1996). This was also confirmed in our experiment. Fig. 4.4 shows the peak breadth of glycerol-plasticized films with 4.36 mmol glycerol concentration and conditioned at 24%, 43%, and 66% relative humidity environments for 72 hr. From 24% to 66%RH, the breadth of transition increased gradually. For glycerol-plasticized films, when the water content increased from 25.3% to 52.2% with glycerol content increasing from 4.36 mmol to 10.87 mmol/g, the breadth of transition of the films increased wider and wider correspondingly (Fig. 4.5). The enlargement in breadth of transition was used to suggest a lack of miscibility or microheterogeneity of the film forming polymer (Pouplin and others 1999; Gontard and Ring 1996). Many researchers also suggested that there is no phase separation between the polymer and the plasticizer in the films if there is no evidence for two individual α -relaxations occurring in $\tan\delta$ trace. In our case, no two individual α -relaxations were found in sorbitol-plasticized films (Fig. 4.6). However, the sorbitol, at 8.69 and 10.87 mmol per gram starch concentration levels, separated from the film matrix and formed the white residues on the surface of the films when we tested the thermomechanical properties of it (Fig. 4.1). Therefore, it is really debatable to prove the phase separation depending on the DMA α -relaxation trace.

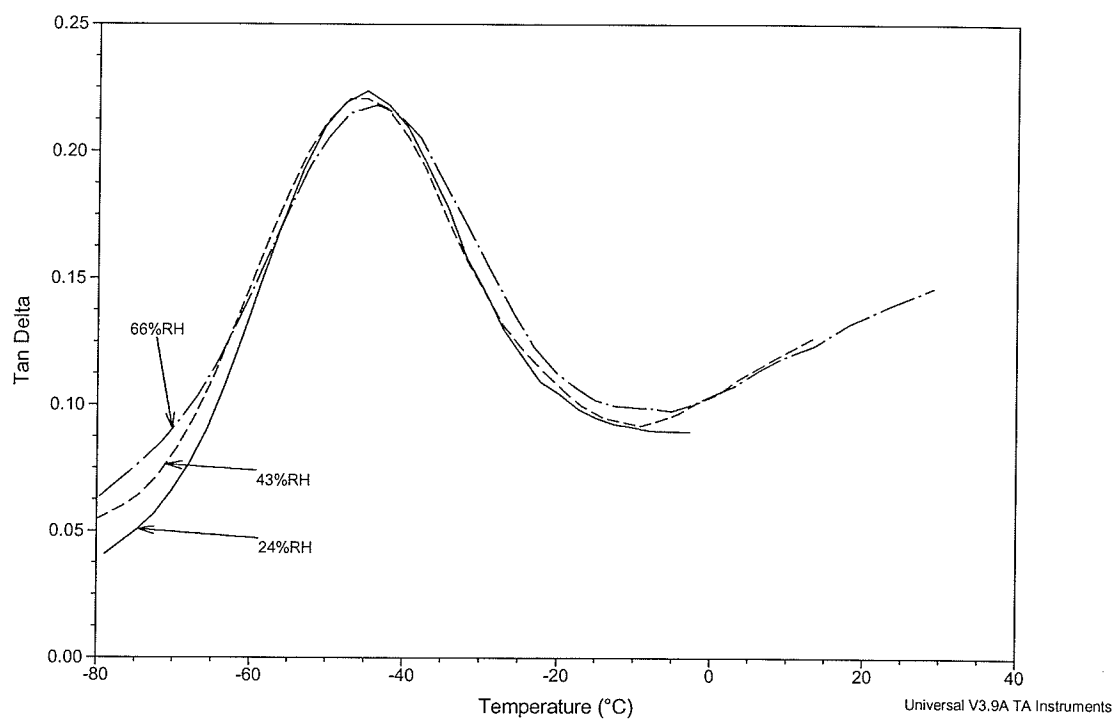


Fig. 4.4 Peak breadth of $\tan\delta$ of glycerol-plasticized films, with 4.36 mmol glycerol concentration after conditioning at 24%, 43%, and 66%RH, respectively, for 72 hr

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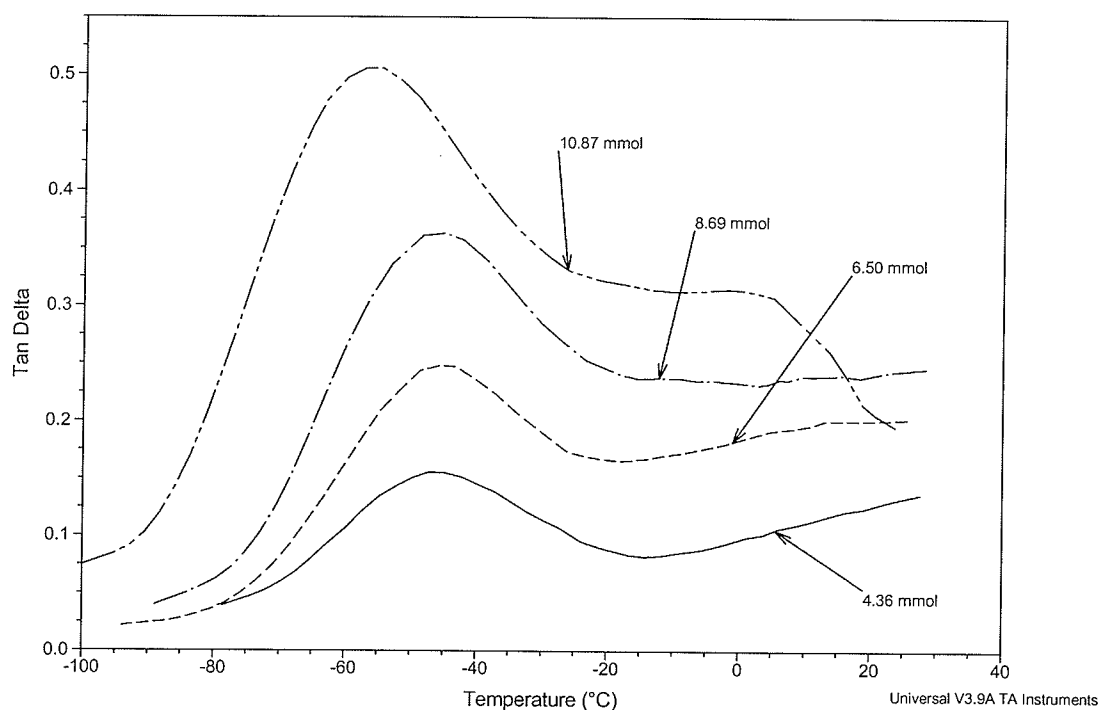


Fig. 4.5 Peak size of $\tan\delta$ of glycerol-plasticized films with various glycerol content after conditioning at $50 \pm 2\%$ RH for 72 hr

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The size of the $\tan\delta$ peak is thought to relate to the volume fraction of the material undergoing the transition (Wetton 1986). For glycerol-plasticized films, the peak size of $\tan\delta$ increased as glycerol content increased from 4.36 mmol to 10.87 mmol (Fig. 4.5). Similar results were obtained in sorbitol- and monosaccharide-plasticized films (Fig. 4.7 and Fig. 4.8), which meant the plasticization of the films was enhanced with the amount of the plasticizers. The difference in peak sizes among glycerol-plasticized films (Fig.

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4.5) was more obvious than the differences in sorbitol- (Fig. 4.7) and monosaccharide-plasticized films (Fig. 4.8). This means the transition of monosaccharide- and sorbitol-plasticized films was not as sensitive to the monosaccharide or sorbitol content in comparison to the glycerol-plasticized films. Poulin and others (1986) compared plasticization effect of water, glycerol, and sorbitol. They found that peak size of the films was much more sensitive to the water content than glycerol and sorbitol content. They suggested that glycerol and sorbitol were large molecules compared to water molecules, and when glycerol and sorbitol molecules tried to access the high-density junction zones of the polymer matrix, they were limited compared to the accessibility of smaller water molecules. Similarly, in our experiment, both monosaccharide and sorbitol are bigger than glycerol molecule. Therefore, monosaccharide and sorbitol would be more hindered by starch polymer matrix, and have less plasticization effect than glycerol.

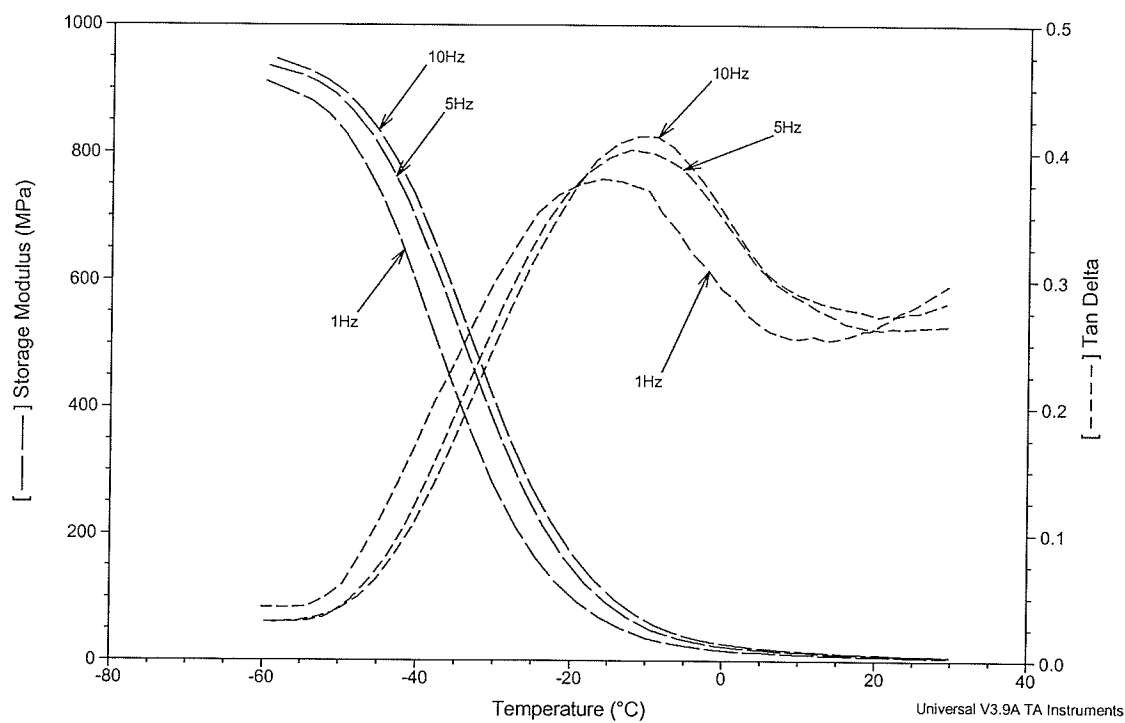


Fig. 4.6 Storage modulus E' and $\tan\delta$ thermal scans for 10.87mmol sorbitol-plasticized films

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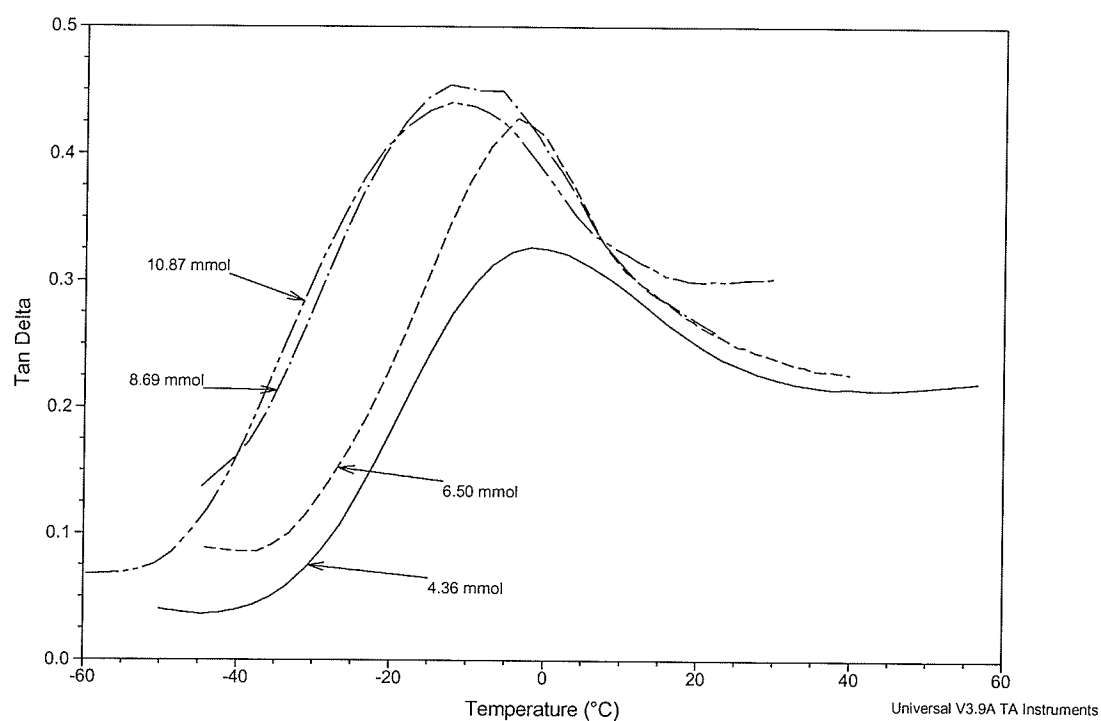


Fig. 4.7 Peak size of $\tan\delta$ of sorbitol-plasticized films with various sorbitol contents
after conditioning at 50 ± 2 %RH for 72 hr

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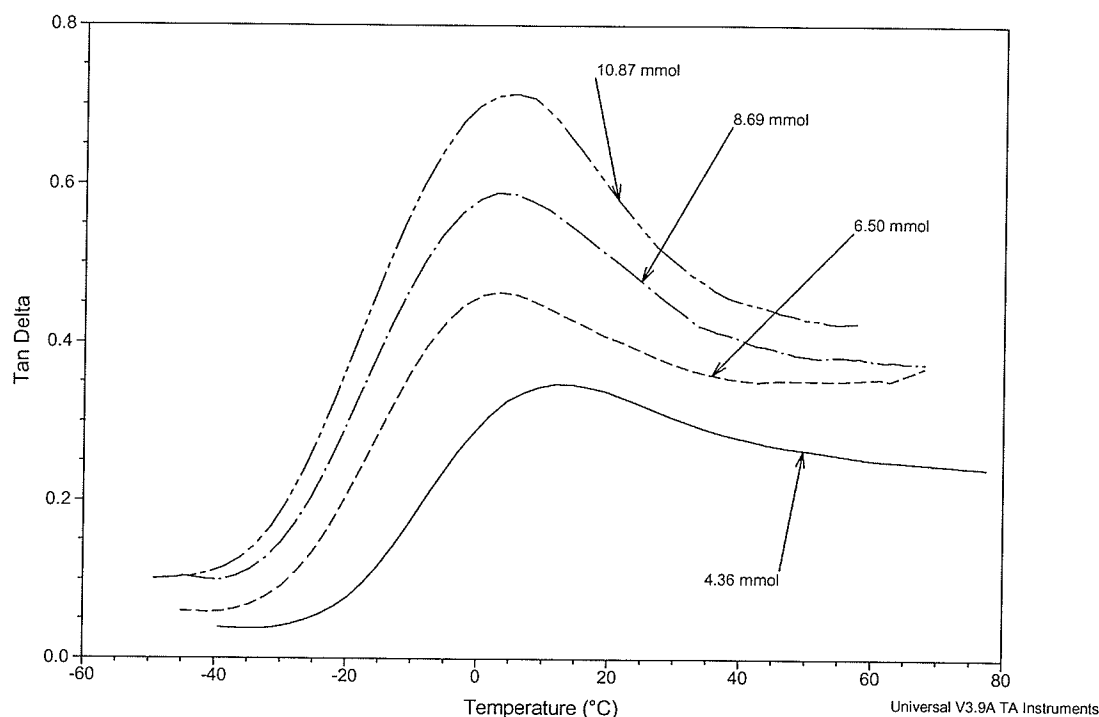


Fig. 4.8 Peak size of $\tan\delta$ of fructose-plasticized films with various fructose contents after conditioning at 50 ± 2 %RH for 72 hr

1765 With increasing frequency of mechanical oscillation, the E' and $\tan\delta$ peaks shifted to
 higher temperature (Fig. 4.6). This situation is expected for any thermally activated
 relaxation process (Lazaridou and Biliaderis 2002). Changes in $\tan\delta$ peak positions with
 frequency allow calculation of apparent activation energies (ΔH_a) for α -relaxation using
 barrier models of relaxation expressed by the Arrhenius relationship (Kalichevsky and
 1770 others 1993):

$$f = a \exp(-\Delta H_a / RT) \quad 4.3$$

where f is the frequency of mechanical oscillation, ΔH_a is the apparent activation energy, R is the universal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), T is T_g temperature (K), and a is the Arrhenius constant. Fig. 4.9 showed the variation of T_g as a function of the frequency of mechanical oscillation (1, 5, and 10 Hz) for sorbitol-plasticized films at different sorbitol content levels representing all the monosaccharide- and polyol-plasticized starch films. The regression coefficients (r^2) of Arrhenius plots for all kinds of starch films were more than 0.95. Table 4.6 showed that with increasing plasticizer content, the values of ΔH_a decreased. The ΔH_a of the examined films varied from 72.1 to 357.9 kJ mol^{-1} . The glycerol-plasticized films had the smallest ΔH_a while sorbitol-plasticized films had the highest values generally. Comparing ΔH_a between monosaccharide-plasticized films, it was apparent that these values were the same statistically implying monosaccharides had the same plasticization mechanism in starch matrix. The ΔH_a of sorbitol-film was the highest, indicating that the interaction between sorbitol and starch polymers was strong and when starch polymers went from the glassy zone through the glass transition zone to the rubbery zone, they needed more energy from environment to overcome the cohesive forces from hydrogen bonding with sorbitol molecules. The glycerol-films had less ΔH_a , indicating the linkage between starch polymers and glycerol was established through water molecules, which was much weaker. Therefore, less energy was needed for glycerol-plasticized films to go through the glass transition zone. Chitosan and starch composite films (with 0 - 30% sorbitol as plasticizer) were also reported to have 259.9 to 400.3 kJ mol^{-1} activation energies (Lazaridou and Biliaderis 2002), which are comparable with the data shown in Table 4.6. Biliaderis and others (1999) reported that corn-starch with pullulan blends plasticized with sorbitol and xylose, respectively, had 226 and 296

1795 kJ mol^{-1} of apparent activation energy. Moreover, amylopectin and gluten were estimated to have apparent activation energies of 242 and 300 kJ mol^{-1} , respectively, when they had about 10 - 13% moisture content (Kalicevsky and others 1992).

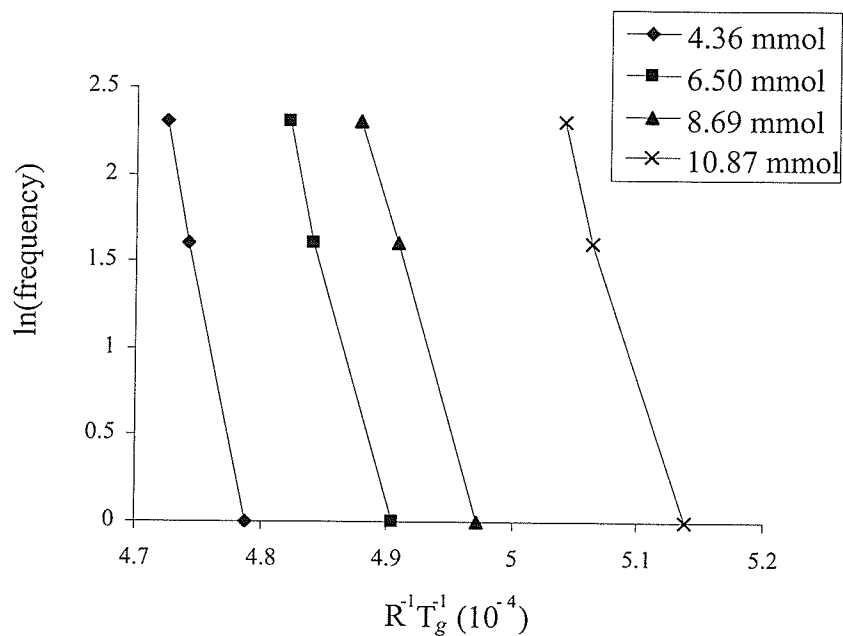


Fig. 4.9 Arrhenius plots of $\ln(\text{frequency})$ versus reciprocal T_g temperature (K^{-1}) for sorbitol-plasticized starch film at different plasticizer content

1805 Table 4.6 Apparent activation energy (ΔH_a , in kJ mol^{-1}) of the α -relaxation process for starch films plasticized by monosaccharides and polyols at different concentration levels from Arrhenius plots applied to multifrequency DMA data

mmol per g starch	Mannose	Fructose	Glucose	Glycerol	Sorbitol
4.36	200.1±12.03 ^{ay}	231.4±17.36 ^{ay}	191.5±16.79 ^{ay}	150.3±8.70 ^{az}	357.9±20.13 ^{ax}
6.50	170.4±16.32 ^{by}	166.4±14.89 ^{by}	136.1±17.41 ^{byz}	118.5±10.00 ^{bz}	274.5±16.53 ^{bx}
8.69	157.3±10.26 ^{cy}	123.0±9.99 ^{cyz}	102.5±9.10 ^{cz}	101.3±11.22 ^{bz}	246.0±12.03 ^{bx}
10.87	163.3±14.26 ^{cy}	131.5±16.25 ^{cy}	100.3±15.33 ^{cyz}	72.1±9.30 ^{cz}	232.5±16.55 ^{cx}

Values are means±standard deviation (n = 2). The values bearing different superscripts differ significantly ($p < 0.05$) using Tukey test. a, b, c, and d are for the comparison of within columns (plasticizer concentration), and w, x, y, and z are for between columns (types of plasticizers).

1810

Crystallinity and X-ray Diffraction

Table 4.7 shows the effect of plasticizers on the crystallinity of the films at 50 ± 2 %RH after 48 - 72 h condition. The crystallinity was not significantly different with increasing amount of plasticizers from 4.34 to 10.87 mmol/g. Two reasons for this phenomenon were assumed. The first is that the plasticizer is present in the films at high concentration level, which prevents crystallization from occurring. The second is that the 48 - 72 h period is not long enough for starch polymer crystalline lattices to form. Comparing the effect of different plasticizers on the film crystallinity, it is easy to find that glycerol- and EG-films have higher crystallinity. This is probably due to the small molecule size of glycerol and EG. Small glycerol and EG molecules could easily be pushed aside by the starch polymers enabling the polymers to align up. Mannose and glucose films had almost the same crystallinity which is higher than fructose films. This is because, in solution, the mannose and glucose molecules mainly exist in pyranose form which is very similar to the anhydroglucose structure composed of starch polymers, leading to the starch polymers packing up and easily forming crystals. Fructose exists in furanose ring mainly. This furanose structure does not match the anhydroglucose units composed of the starch. Sorbitol structure does not match the anhydroglucose units either. Therefore, formation of crystal became difficult and led to low crystallinity in the films.

Table 4.7 Crystallinity (%) (50 ± 2 %RH, 48 - 72 h conditioned)

mmol per g starch	Fructose	Mannose	Glucose	Glycerol	Sorbitol	EG
4.34	0.27 ± 0.03^{ax}	2.60 ± 0.50^{ay}	1.79 ± 0.73^{ay}	4.86 ± 0.87^{az}	0.42 ± 0.78^{ax}	4.23 ± 0.88^{az}
6.50	0.20 ± 0.08^{aw}	1.86 ± 0.14^{ay}	2.43 ± 0.99^{ay}	5.09 ± 0.67^{az}	0.68 ± 0.15^{ax}	3.45 ± 0.95^{az}
8.69	0.43 ± 0.17^{ax}	3.24 ± 0.98^{aw}	2.92 ± 0.47^{aw}	4.31 ± 1.19^{az}	0.41 ± 0.02^{ax}	3.60 ± 0.73^{awz}
10.87	0.23 ± 0.09^{ax}	2.17 ± 0.07^{ay}	2.40 ± 0.33^{ay}	4.33 ± 0.89^{az}	0.59 ± 0.05^{ax}	3.00 ± 1.01^{az}

Values are means \pm standard deviation ($n = 3$). The values bearing different superscripts differ significantly ($p < 0.05$) using Tukey test. a, b, and c are for the comparison of within columns (plasticizer concentration), and x, y, and z are for the between columns (types of plasticizers).

1840

Table 4.8 shows the crystallinity of the starch films after 33 days condition at 50 ± 2 %RH. After 33 days condition, glucose films, at 8.69 and 10.87 mmol/g levels, had very high crystallinity. Glucose films became opaque and brittle. They shrunk, became deformed, and lost their flexibility. Sorbitol films had white spots appearing on their surfaces. These white spots were believed to be sorbitol blooming. Mannose blooming could also be found on the mannose film surface. But it was tiny and not easy to see. The crystal morphology for sorbitol, mannose blooms, and glucose were shown in Fig. 4.10 under a light microscope. Comparing Table 4.8 to Table 4.7, all the films shows higher crystallinity after 33 days conditioning with exception of fructose films. This is in agreement with the common rule that below the melting temperature crystalline state is the only true thermodynamic equilibrium state and the polymers will spontaneously tend to approach towards the crystalline state. Fructose films looked like an exception to this rule. They did not have change in crystallinty after 33 days conditioning. It is assumed that the furanose ring of the fructose molecular structure delayed the starch polymer chains to crystallize. Water molecules played an important role in plasticizing hydrophilic starch films. Therefore, it is necessary to figure out how the environment RH affects the film structure. The effect of RH on the crystallinity was tested with two plasticizer concentration levels, e. g. 4.36 and 10.87 mmol/g, respectively. The results are shown in Table 4.9 and Table 4.10. The crystallinity increased with RH. In 73% RH environment, the crystallinities reached the highest level at either plasticizer concentration level. This is because the more water molecules in the starch films made the starch polymers more mobile facilitating more crystalline lattice to form.

Table 4.8 Crystallinity (%) (50 ± 2 % RH, 33 days conditioned)

mmol per g starch	Fructose	Mannose	Glucose	Glycerol	Sorbitol	EG
4.34	0.15 ± 0.02^{aw}	19.19 ± 2.49^{ax}	6.83 ± 5.89^{ay}	23.36 ± 1.99^{ax}	4.72 ± 2.53^{ay}	9.59 ± 3.88^{az}
6.50	0.21 ± 0.02^{av}	26.4 ± 3.71^{bw}	17.99 ± 2.65^{bx}	29.64 ± 3.91^{aw}	2.05 ± 1.66^{by}	10.80 ± 2.07^{az}
8.69	0.16 ± 0.03^{au}	30.94 ± 4.68^{cv}	54.68 ± 8.04^{cw}	22.67 ± 2.75^{ax}	3.13 ± 0.27^{by}	15.44 ± 1.44^{bz}
10.87	0.18 ± 0.01^{au}	42.55 ± 3.52^{dv}	55.82 ± 6.33^{cw}	21.61 ± 3.14^{ax}	7.56 ± 5.50^{dy}	12.96 ± 2.10^{bz}

1865 Values are means \pm standard deviation ($n = 3$). The values bearing different superscripts differ significantly ($p < 0.05$) using Tukey
test. a, b, and c are for the comparison of within columns (plasticizer concentration), and x, y, and z are for the between columns
(types of plasticizers).

1870

Table 4.9 Crystallinity (%) (at 4.36 mmol concentration, 72 h conditioned)

RH (%)	Fructose	Mannose	Glucose	Glycerol	Sorbitol	EG
23%	0.19±0.46 ^{ax}	3.95±0.86 ^{ay}	0.48±0.06 ^{ax}	0.14±0.07 ^{ax}	0.14±2.11 ^{ax}	3.96±0.72 ^{ay}
50%	0.27±0.03 ^{aw}	2.60±0.50 ^{ay}	1.79±0.43 ^{by}	4.86±0.87 ^{bz}	0.03±0.01 ^{ax}	4.23±1.23 ^{az}
73%	11.63±2.33 ^{bx}	7.98±1.20 ^{bx}	4.07±0.61 ^{cy}	20.70±3.11 ^{cz}	12.85±1.87 ^{bx}	25.66±4.62 ^{bz}

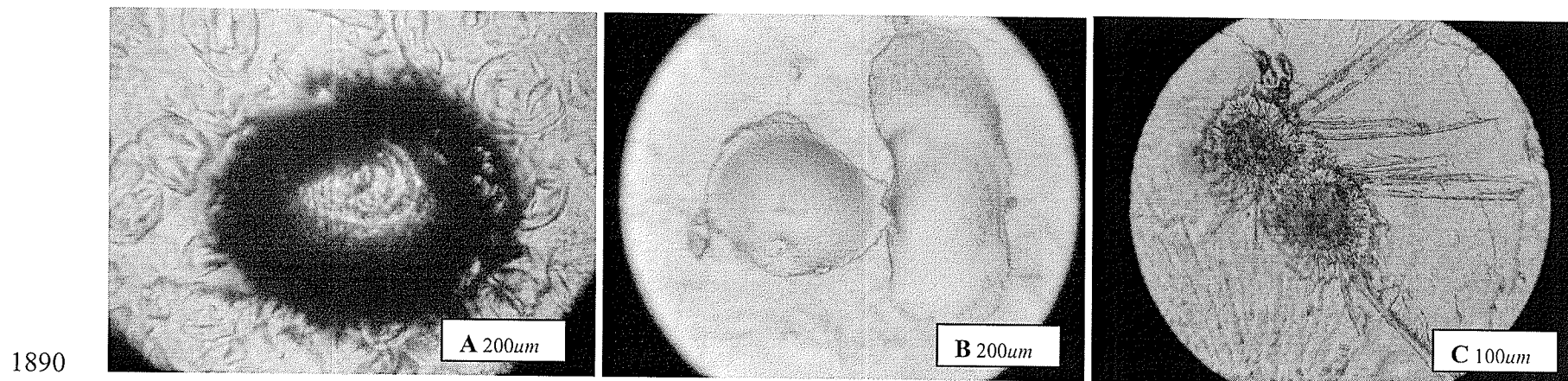
Values are means ± standard deviation (n = 3). The values bearing different superscripts differ significantly (p < 0.05) using Tukey test. a, b, and c are for the comparison of within columns (plasticizer concentration), and x, y, and z are for the between columns (types of plasticizers).

Table 4.10 Crystallinity (%) (at 10.87 mmol concentration, 72 h conditioned)

RH (%)	Fructose	Mannose	Glucose	Glycerol	Sorbitol	EG
23%	0.12±0.01 ^{ax}	0.08±0.01 ^{ax}	3.91±0.77 ^{ay}	4.13±2.45 ^{ay}	0.06±0.02 ^{ax}	3.36±0.65 ^{ay}
50%	0.23±0.09 ^{ax}	2.17±0.07 ^{by}	2.40±0.33 ^{ay}	4.33±0.89 ^{az}	0.04±0.01 ^{aw}	3.00±1.01 ^{ayz}
73%	9.12±0.57 ^{by}	1.57±0.31 ^{bx}	74.36±8.22 ^{bz}	6.98±0.94 ^{by}	1.83±0.28 ^{bx}	5.82±0.75 ^{by}

1885 Values are means ± standard deviation (n = 3). The values bearing different superscripts differ significantly (p < 0.05) using Tukey test. a, b, and c are for the comparison of within columns (plasticizer concentration), and x, y, and z are for the between columns (types of plasticizers).

Fig.4.10 Blooms and crystals of the films observed under the microscope



A: Mannose bloom on the surface of mannose-film, at 43.4 mmol/g concentration level, conditioned at 50 ± 2 %RH for 100days. B: Sorbitol blooms on the surface of sorbitol-film, at 6.50 mmol/g concentration level, conditioned at 50 ± 2 %RH for 12days. C: Crystals in glucose-films at 6.50 mmol/g concentration level, conditioned at 50 ± 2 %RH for 72 h.

1895

The X-ray diffraction pattern of starch films can be represented by a glucose-film shown in Fig. 4.11. Crystalline and amorphous zones characterize the X-ray diffractogram with peaks. Peak intensity and width are related to crystalline size and size distribution (Romero-Bastida and others 2005). The peaks observed were mainly at $2\theta = 5.6^\circ$, 16.9° , and 22.3° by which the crystal models for the starch films can be assigned to a B - type.

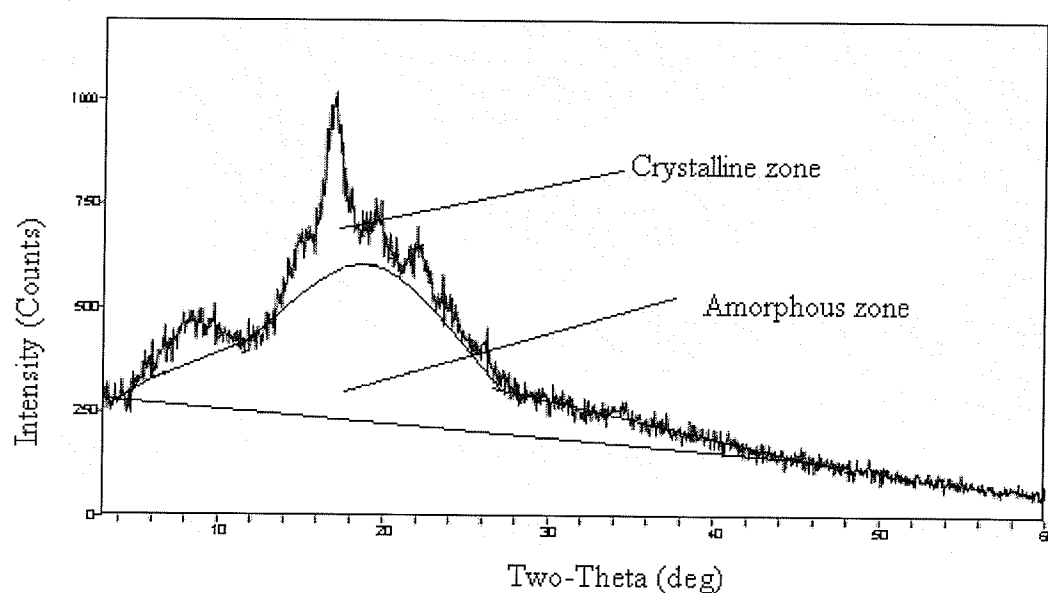


Fig.4.11 X-ray diffraction pattern for glucose-film at 6.50 mmol/g concentration level, conditioned at $50 \pm 2\%$ RH for 48 h

The discussion on plasticization mechanism of plasticizer on the properties of starch films based on molecular basis

Water and plasticizer molecules cross-link with D-glucosyl residues of starch molecules. Monosaccharides exist in pyranose or furanose rings, and polyols exist in

linear structure in solutions. Monosaccharides and polyols should have different cross-
linking mechanisms with D-glucosyl residues. Glucose is chosen as an example to
illustrate the monosaccharide plasticization mechanism. Glucose has exactly the same
structure and conformation as the anhydroglucose in starch molecules, leading to easy
and complete embedment into the starch polymers, as shown in Fig. 4. 12. Intermolecular
hydrogen bondings between OH-2 of D-anhydroglucose of starch and O-6 of a glucose
molecule occurred. The OH-2 of the glucose interacts with O-6 of D-glucosyl residue of
another starch molecule on the other side. This close and intense interaction makes the
glucose-film stronger, more compact and resistant to the gas permeation compared to
sorbitol which has the similar molecular size and weight (data shown in Table 3.1, Table
4.3 and Table 4.4). Although the structure and conformation of mannose and fructose
does not exactly match anhydroglucose of the starch polymer, they exist respectively in
pyranose and furanose ring, leading to their plasticizing the starch polymers in the similar
mechanism. Therefore, they have the similar thickness, gas barrier properties, and
apparent activation energy ((ΔH_a)) (Table 4.1, Table 4.3, and Table 4.4). Polyols exist in
linear structure. They randomly distribute in the starch matrix (Fig. 4.13, sorbitol as an
example), leading a loose structure in the films and higher thickness (Table 3.1) and
oxygen permeability (Table 4.4). As a result, the distance (d_1) between the starch
polymer chains in glucose-film is shorter than the distance (d_2) between the starch
polymer chains in sorbitol-film. Therefore, sorbitol film had low TS, large thickness, and
higher (data shown in Table 3.1 and Table 4.4).

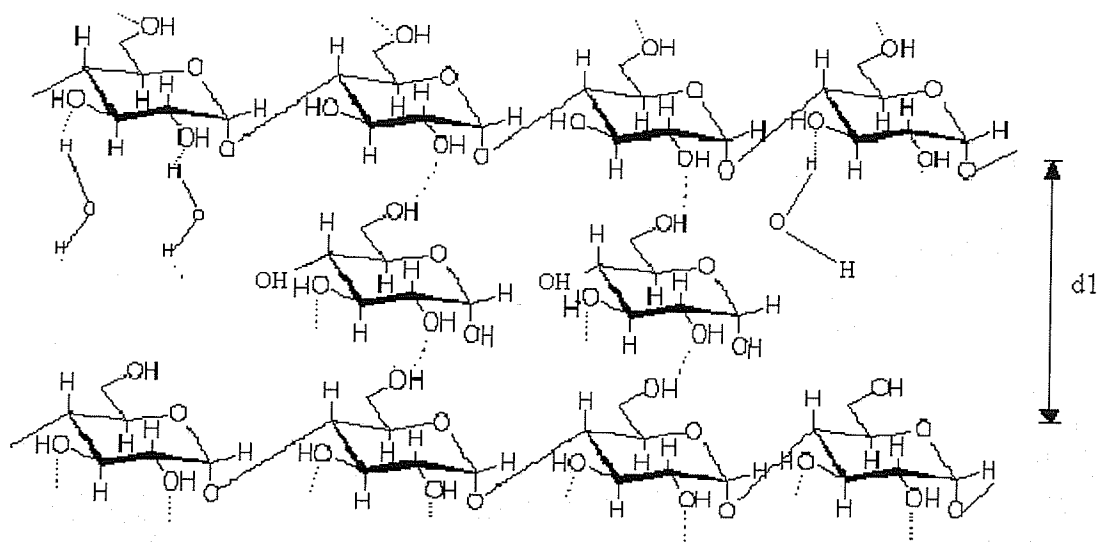


Fig. 4.12 Glucose molecule plasticization mechanism

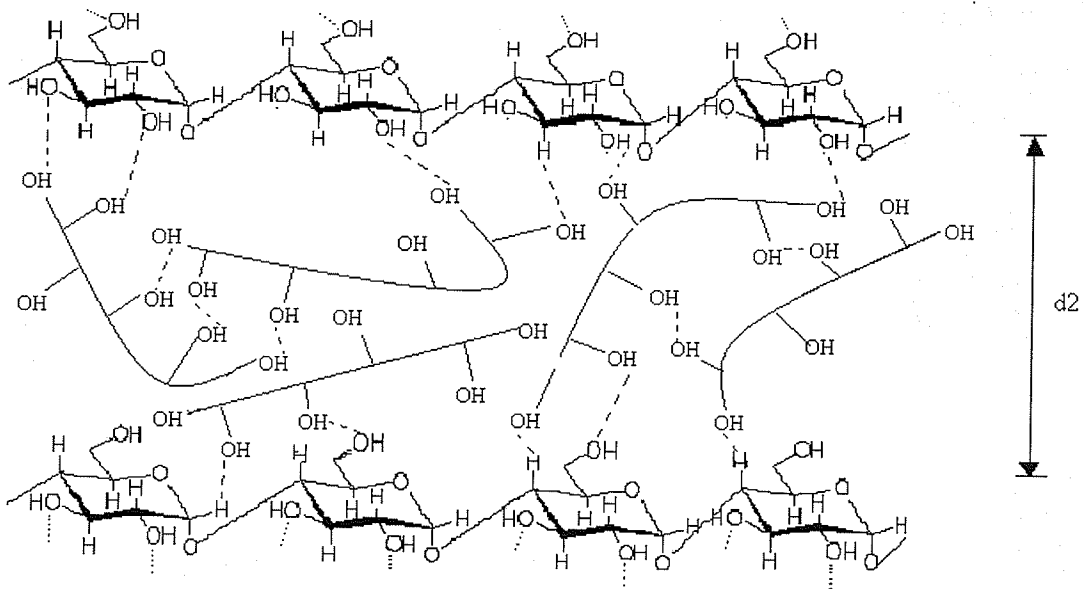


Fig. 4.13 Sorbitol molecule plasticization mechanism

CONCLUSION

1945 At ranges of 4.34 to 10.87 mmol per gram of starch, the monosaccharide-plasticized films had significantly higher tensile strength and elongation, lower water vapor permeability and oxygen permeability, and similar modulus of elasticity to polyol-plasticized films (that is glycerol- and sorbitol-plasticized films), suggesting that monosaccharide-films have denser and more compact structure compared with polyol-

1950 films. Monosaccharides can be better plasticizer in terms of physical properties. Glycerol can make the T_g and ΔH_a of the films lower than the monosaccharides. Thus glycerol can be regarded as the more effective plasticizers in terms of thermomechanical properties. Glucose molecules are identical in configuration to the anhydroglucose units of starch molecules chains. Glucose-plasticized films would have more compacted structure with

1955 less free volume. This led to more ΔH_a needed for glucose-plasticized films to go through the glass transition zone, although glucose had a good plasticization effect. Larger conditioning time and higher RH favored crystallization. Glucose facilitated the crystallization of the films due to its very identical configuration to the anhydroglucose in the starch. The plasticizer with small molecular size and high ratio of hydroxyl group

1960 number to the molecular weight increases the effectiveness of the plasticization. Molecular properties, such as hydrodynamic radius, dielectric constant, hygroscopicity, also affect the effectiveness of the plasticization.

Appendix 4.1 Effect of plasticizers on tensile strength (MPa) at 50 ± 2 % RH

mmol per g starch	Mannose	Fructose	Glucose	Glycerol	Sorbitol	EG
4.34	6.3 ± 0.29^{ayz}	8.4 ± 0.38^{ax}	6.6 ± 0.43^{ay}	5.8 ± 0.59^{az}	5.7 ± 0.42^{az}	24.9 ± 2.62^{aw}
6.50	5.7 ± 0.62^{ax}	5.9 ± 0.56^{bx}	6.2 ± 0.65^{ax}	5.8 ± 0.60^{ax}	4.4 ± 0.54^{by}	20.64 ± 3.44^{aw}
8.69	3.2 ± 0.38^{bx}	3.8 ± 0.24^{cw}	3.7 ± 0.31^{bw}	2.2 ± 0.22^{bz}	2.7 ± 0.12^{cy}	11.78 ± 2.65^{bv}
10.87	3.9 ± 0.18^{bx}	1.9 ± 0.13^{dy}	3.8 ± 0.21^{bx}	1.4 ± 0.08^{cz}	1.2 ± 0.17^{dz}	5.88 ± 1.06^{cw}

Values are means \pm standard deviation (n=6). The values bearing different superscripts differ significantly ($p < 0.05$) using Tukey test. a, b, c, and d are for the comparison of within columns (plasticizer concentration), and w, x, y, and z are for between columns (types of plasticizers).

Appendix 4.2 Effect of plasticizers on the elongation (%) at 50 ± 2 % RH

mmol per g starch	Mannose	Fructose	Glucose	Glycerol	Sorbitol	EG
4.34	70.2±14.40 ^{ax}	30.3±5.34 ^{ayz}	54.6±19.40 ^{axy}	37.6±4.47 ^{byz}	61.1±14.27 ^{ax}	4.2±0.56 ^{aw}
6.50	99.1±17.48 ^{bx}	83.0±13.64 ^{bxy}	68.0±11.69 ^{ayz}	50.6±6.49 ^{az}	63.6±8.18 ^{ayz}	7.4±0.91 ^{bw}
8.69	95.1±14.59 ^{bcx}	84.6±13.16 ^{bxy}	78.3±17.08 ^{axy}	39.3±8.25 ^{bz}	64.6±11.43 ^{ay}	10.8±1.15 ^{cw}
10.87	145.2±22.83 ^{cx}	79.3±6.68 ^{by}	76.2±7.16 ^{ay}	46.4±6.35 ^{abz}	68.0±19.87 ^{az}	14.1±4.57 ^{dw}

1970 Values are means±standard deviation (n=6). The values bearing different superscripts differ significantly ($p < 0.05$) using Tukey test. a, b, c, and d are for the comparison of within columns (plasticizer concentration), and w, x, y, and z are for between columns (types of plasticizers).

Appendix 4.3 Effect of plasticizers on the modulus of elasticity (MPa) at 50 ± 2 % RH

mmol per g starch	Mannose	Fructose	Glucose	Glycerol	Sorbitol	EG
4.34	111.2 \pm 5.07 ^{ay}	188.6 \pm 13.94 ^{ax}	110.9 \pm 16.43 ^{ay}	97.5 \pm 19.49 ^{ay}	106.6 \pm 3.88 ^{ay}	1584.6 \pm 149.40 ^{aw}
6.50	58.1 \pm 5.22 ^{by}	70.5 \pm 7.63 ^{bxy}	81.6 \pm 16.89 ^{bx}	82.6 \pm 19.49 ^{ax}	52.7 \pm 7.77 ^{by}	1140.1 \pm 10.57 ^{bw}
8.69	21.4 \pm 3.17 ^{cz}	30.8 \pm 2.99 ^{cxy}	33.4 \pm 3.54 ^{cx}	22.8 \pm 3.17 ^{bz}	26.6 \pm 2.49 ^{cyz}	660.7 \pm 10.31 ^{cw}
10.87	23.6 \pm 3.02 ^{cy}	9.4 \pm 0.53 ^{dz}	33.5 \pm 2.59 ^{cx}	7.8 \pm 0.36 ^{bz}	7.1 \pm 0.64 ^{dz}	165.3 \pm 17.83 ^{dw}

Values are means \pm standard deviation (n=6). The values bearing different superscripts differ significantly ($p < 0.05$) using Tukey test. a, b, c, and d are for the comparison of within columns (plasticizer concentration), and w, x, y, and z are for between columns (types of plasticizers).

1975

Chapter 5

Sorption isotherm and plasticization effect of moisture and plasticizers in pea starch film

1980

ABSTRACT

Pea starch films were produced with various plasticizers (glucose, fructose, mannose, sorbitol, and glycerol). Effect of plasticizer content (4.34 to 10.87 mmol per g of dry starch) and storage relative humidity (RH) (11.3% to 75.4%) on moisture content (MC), tensile strength (TS), elongation (E), modulus of elasticity (EM), and water vapor permeability (WVP) on starch films were evaluated using response surface methodology. MC of the films was influenced strongly by RH. Glycerol-plasticized films had the highest MC, indicating that water molecules played a more important role in plasticizing starch films. Monosaccharide-plasticized films and polyol-plasticized films had similar TS values. However, monosaccharide-plasticized films had higher E values and lower EM values than polyol-plasticized films, meaning monosaccharides had better efficiency in plasticizing starch films. Recrystallization happened in glucose- and sorbitol-plasticized films when they were stored at high RH. Sorption isotherm studies showed similar adsorption and desorption profiles for all three monosaccharide-plasticized films.

1995 Flory-Huggins model fitted experimental data best for starch films, while BET model fitted the data marginally.

INTRODUCTION

Water acts as a plasticizer in most hydrophilic films, and water adsorption and
2000 desorption of hydrophilic films highly depend on the environmental relative humidity
(RH) (van Soest and others 1995). The sorption isotherm of starch films, such as rice,
corn, and wheat starch films plasticized by polyols, had been previously studied by many
researchers previously (Mali and others 2002; Fang and Hanna 2000; Myllarinen and
others 2002; Gaudin and others 1999; Biliaderis and others 1999; Cha and others 2001).
2005 BET (Brunauer, Emmet, and Teller) model, GAB (Guggenheim, Anderson, and deBoer)
model, Smith model, and Flory-Huggins model were the most popular models to fit
sorption data (Srinivasa and others 2003; Cha and others 2001). Because moisture
sorption isotherm of food products represents integrated hygroscopic properties of
individual components, and is affected by any modification in the composition or
2010 structure of the food (Sebti and others 2003), no universal sorption isotherm model for
general foods. Therefore, for a specific biopolymer film, there is a need to search for the
most appropriate isotherm equation. The major objectives of the present study were to
examine the combined effects of relative humidity (RH) and plasticizer on mechanical
characteristics, water vapor barrier properties and moisture sorption isotherm of high-
2015 amylose pea starch films. Because water acts as plasticizers in hydrophilic starch films,

integrated studies involving the evaluation of mechanical and water vapor barrier properties under various RH and plasticizer content were undertaken.

MATERIALS AND METHODS

2020 **Materials**

The same pea starch resource, monosaccharides, and polyols used in Chapter 4 was chosen.

Film Preparation for Sorption Isotherm

2025 Aqueous dispersions of 3% (w/w) pea starch were prepared. Because any modification on the composition can change the sorption isotherm equations, a suitable plasticizer concentration is needed to be decided. 6.5 mmol per g pea starch, which is the intermediate concentration in our experiment is chosen. The starch dispersions were heated to 100 °C and kept boiling for about 10 min with agitation to allow gelatinization, 2030 then cooled down to 50 - 60 °C. After gelatinization, 9 g of each starch solution was transferred onto a polystyrene petri dish (10 cm diameter) and dried at 11 - 12% relative humidity (RH) at 23 °C for 3 days to form a dried starch film.

Sorption Isotherm Procedure

2035 Eight saturated salt solutions were prepared and placed in eight sealed desiccators to obtain the specific RH levels at 23 °C, which were LiCl, CH₃COOK, Mg(Cl)₂, K₂CO₃, Mg(NO₃)₂, NaNO₃, NaCl and KCl for 12, 22, 33, 43, 53, 63, 75, and 85% RH, respectively. The dried starch films were placed into the preconditioned eight desiccators

with corresponding levels of RH for 7 days. For moisture content (MC) determination,
 2040 the conditioned film samples were weighed before and after drying at 105 °C for 24 h.
 MC was calculated as the percentage of weight loss to the original weight on a dry basis.
 The a_w was measured with a hygrometer (Aw Sprint, Novasina, Swiss). Tests were
 conducted in triplicate, and average values were used. For desorption profiles, MC and a_w
 were measured after 9 g of starch film solutions on Petri dishes were placed into eight
 2045 desiccators with corresponding levels of RH and conditioned for 7 days. The moisture
 isotherm curves were created by plotting MC to a_w .

Table 2.3 shows 4 models of sorption isotherm used in this experiment. The parameters
 of these empirical models were estimated by the nonlinear regression procedure of SAS
 2050 software (SAS Institute Inc., Cary, NC). The goodness of fit of each model was evaluated
 by the mean of the relative percent difference between the experimental data and
 predicted values of the MC, which is defined as the mean relative deviation modulus (G):

$$G = (100 / n) \sum_{i=1}^n \left(\frac{|M_{ai} - M_{pi}|}{M_{ai}} \right) \quad 5.1$$

2055 where n is the number of observations, M_{ai} is experimentally determined MC of i -th data,
 and M_{pi} is predicted MC of the i -th data by models. A G value lower than 5 corresponds
 to excellent fit, a G value between 5 and 10 shows a reasonably good fit, and a G value
 greater than 10 is considered a poor fit (Roy and others 2000).

Film Characteristics with Response Surface Methodology

Experimental design

With regard to the hydrophilicity of the starch films, the plasticizer content and the storage RH of the film may be the dominant variables. Response surface methodology was conducted using a central composite rotatable design with coded values of these two variables (Diamond 2001) (Table 5.1). The effects of RH (11.3% - 75.4%) and plasticizer content (4.34 - 10.87 mmol per g starch) on the properties of starch films were evaluated by 13 treatments including five center points (43.4% RH and 7.61 mmol plasticizer per g starch) for experimental error analysis. The two-variable design codes were -1.414, -1, 0, 1, and 1.414. Corresponding actual values of RH and plasticizer content of the coded values were listed in Table 5.1. The RH of storage chambers was maintained by selected saturated solutions, which are LiCl, CH₃COOK, K₂CO₃, NaNO₂, and NaCl for 11.3, 22.9, 43.2, 65.0, and 75.4% RH, respectively, at 22 °C. These RH were approximated reasonably with the chosen RH levels of the experimental design. The following second-order polynomial model was used for regression analysis for determining the fitness of starch film properties, and estimate parameters.

$$Y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_{11} X_1^2 + \beta_{22} X_2^2 + \beta_{12} X_1 X_2 \quad 5.2$$

where β_0 , β_1 , β_2 , β_{11} , β_{22} , and β_{12} are the parameters of variables, and X_1 and X_2 are the coded independent variables for plasticizer content and RH, respectively. Design-Expert[®] Software (Version 5.0.7, Stat-Ease Corporation, Minneapolis, MN) was used to

generate the response surfaces of TS, E, EM, MC, and WVP graphically with respect to plasticizer content and RH.

2085 Table 5.1 Central composite rotatable design for the experiment

Experimental Design Points	Independent Variables	
	Plasticizer Content Level	
	(mmol per g starch)	RH (%)
1	9.92 (1)	66.0 (1)
2	9.92 (1)	20.8 (-1)
3	5.30 (-1)	66.0 (1)
4	5.30 (-1)	20.8 (-1)
5	10.87 (1.414)	43.4 (0)
6	4.34 (-1.414)	43.4 (0)
7	7.61 (0)	75.4 (1.414)
8	7.61 (0)	11.3 (-1.414)
9	7.61 (0)	43.4 (0)
10	7.61 (0)	43.4 (0)
11	7.61 (0)	43.4 (0)
12	7.61 (0)	43.4 (0)
13	7.61 (0)	43.4 (0)

Values in parentheses are codes for the independent variables.

Film-forming solutions were provided by the procedure of the sorption isotherm experiment with proper amount of plasticizers listed in Table 5.1. The film-forming solution in Petri dishes was dried at ambient condition (22 - 25 °C, 30 - 50% RH) for 48 h. The dried films in the Petri dishes were conditioned at corresponding RH (Table 5.1) for 72 h. The RH values inside chambers in the petri dishes were monitored with a digital hydrometer (Control Company, Friendswood, TX). Dried films were peeled intact from the casting dishes after conditioning. MC was determined from triplicate specimens at the corresponding plasticizer content and RH using the same procedure of sorption isotherm experiments.

Thicknesses of the films were measured at five random positions on a film with an electronic digital micrometer (B. C. Ames Co., Waltham, MA, 0.001 mm sensitivity). Average thickness values were used for calculating tensile strength (TS), modulus of elasticity (EM), and water vapor permeability (WVP) of the films.

Tensile Tests and Water Vapor Permeability

The tensile strength (TS), elongation (E), modulus of elasticity (EM), and water vapor permeability (WVP) were determined according to the methods outlined in Chapter 3.

RESULTS AND DISCUSSIONS

Sorption Isotherms

For each film that was conditioned for 72 h under the corresponding RH, the equilibrium MC was almost the same for both adsorption and desorption processing at a_w

below 0.5, and showed linearity from 0.2 up to 0.5 (Fig. 5.1). A sharp decrease for the
2115 desorption process was observed above 0.5 a_w . Linear regression analysis of MC and a_w
data for the adsorption yielded 0.88, 0.83, 0.93, 0.92, and 0.85 of R^2 values for mannose-,
glucose-, fructose-, sorbitol-, and glycerol-plasticized films, respectively. The results
were likely to obey Henry's law which states that the adsorption of atmospheric water
molecules into a starch film has a linear relationship to the partial pressure of the
2120 moisture in air (Han and Scanlon 2005). The glycerol-plasticized films adsorbed much
more moisture than other films at the same a_w (Fig. 5.1). The strong attraction of glycerol
to water was attributed to its high polarity (Zhang and Han 2006b). A hysteresis was also
shown in Fig. 5.1 for all five films between adsorption and desorption processing. From
0.9 to 0.5 of a_w in desorption process, the films lost moisture sharply. But after 0.5 of a_w ,
2125 the desorption slowed down until 0.2 of a_w . Most films showed hysteresis above 0.6 of
 a_w , while glucose-plasticized film has hysteresis above 0.5 of a_w . Fructose-plasticized
film showed the smallest difference between absorption and desorption.

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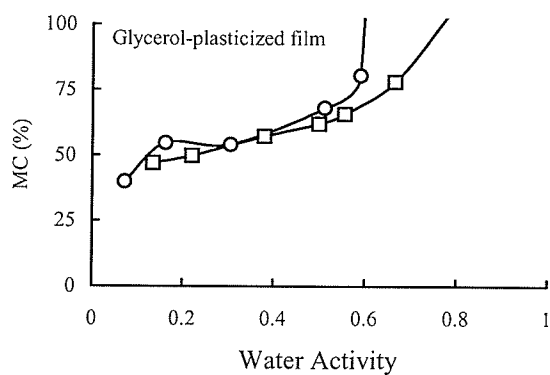
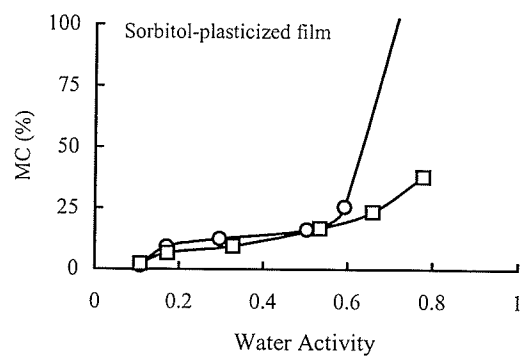
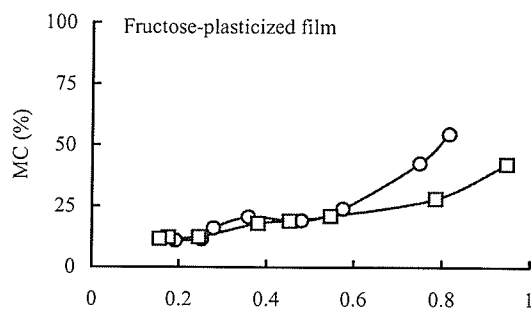
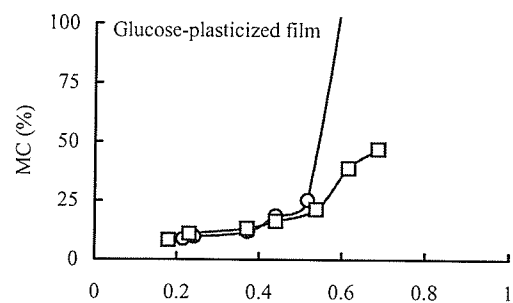
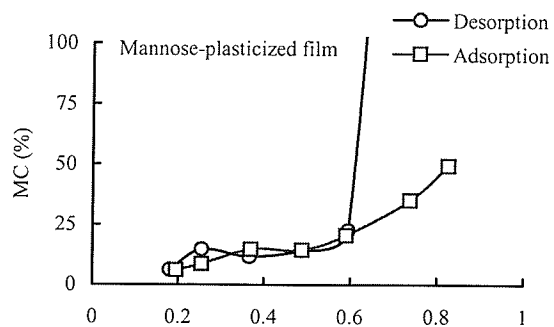


Fig. 5.1 Sorption isotherm hysteresis of starch films

Table 5.2 shows the estimated parameters and goodness of fits of adsorption models to experimental data of 72 h conditioned films. For the monosaccharide-plasticized films, Flory-Huggins models had the lowest G values which were smaller than 10, indicating that Flory-Huggins models fitted the experimental data reasonably well. For glycerol-plasticized films, all four models fitted well. For sorbitol-plasticized films, G values of all models were larger than 10. Therefore, they are not good models for sorbitol-plasticized films. In fact, GAB model fitted all kinds of films well, except for glucose- and sorbitol-plasticized films. This exception can be due to the change in the structure of the films. During preconditioning in RH above 75%, glucose- and sorbitol-plasticized films appeared recrystallized. Among the sorption isotherm models found in literatures, GAB model has received most attention in practical applications. It is regarded as reliable in modeling sorption data for many food materials for almost the entire sorption isotherm (Biliaderis and others 1999). Srinivasa and others (2003) and Roy and others (2000) found the GAB model was the best model in fitting the sorption isotherm data when they tested films made from chitosan-polyvinyl alcohol blend and wheat gluten, respectively. In our case, the Flory-Huggins equation fitted well for the three monosaccharide- and glycerol-plasticized films. Flory-Huggins model fits the isotherm in the case of weaker adsorbate-adsorbent interactions, which was water-starch matrix interactions in this case, than the adsorbate-adsorbate interaction, which was water-water interaction in this case. The weak interactions between the water and starch matrix led to low uptakes at low RH. However, once a water molecule had become adsorbed at a primary adsorption site on the surface of starch films, the water-water interaction, which was much stronger than the starch-water interaction, became the driving force of the adsorption process, resulting in

Table 5.2 Sorption isotherm model constants and G values (mean relative deviation

2170 modulus) for monosaccharide-plasticized starch films

Models ^a		A	B	C	G
Smith	Glucose	-2.82	39.94		22.68
	Fructose	10.98	10.89		4.88
	Mannose	-0.58	27.20		12.99
	Sorbitol	-0.007	23.88		13.20
	Glycerol	37.62	40.13		4.87
Flory-Huggins	Glucose	3.12	3.95		9.39
	Fructose	8.84	1.61		5.05
	Mannose	3.31	3.24		9.48
	Sorbitol	2.72	3.37		21.32
	Glycerol	34.38	1.33		7.34
BET	Glucose	19.56	1.38		16.25
	Fructose	2.75	2.97E69		63.93
	Mannose	9.06	8.40		9.27
	Sorbitol	8.96	4.91		15.33
	Glycerol	25.97	2.66E63		2.05
GAB	Glucose	10.28	5.43	1.00	17.02
	Fructose	12.89	30.07	0.73	4.25
	Mannose	10.55	4.93	0.97	7.58
	Sorbitol	9.60	3.95	0.98	14.09
	Glycerol	38.96	3.21E70	0.79	4.47

^a Mathematical models were listed in Table 1. In GAB model, A is the monolayer moisture content (fraction dry basis); B is the Guggenheim constant which is a correction factor for the sorption properties of the first layer with respect to the bulk liquid; C is a correction factor for the properties of the multi player with respect to the bulk liquid.

2175 accelerated uptakes at higher relative pressure. Therefore, it could be deduced from the
good fit of Flory-Huggins model that the interaction between water and water molecules
played a major role in the sorption isotherm. A further detailed interpretation for the
Flory-Huggins sorption isotherm behavior of the three monosaccharide- and glycerol-
plasticized films may be made as follows: the first water molecules that are absorbed
2180 loosen and swell the starch polymer structure locally (i. e., cohesion between starch
polymers), attract other water molecules in the atmosphere, and allow subsequent water
molecules to enter easily in the neighborhood of the first molecules. This means that the
absorbed water molecules effectively plasticized the starch polymer.

2185 From GAB and BET equations, the monolayer moisture in the films can be evaluated
along with its corresponding a_w . The monolayer moisture values which are A values in
GAB models range from 10.55 to 38.96 g water/100 g (d. b.) (Table 5.2). Three
monosaccharide- and sorbitol-plasticized films had similar moisture monolayer values (i.
e., around 10), which were very comparable with the A values of other biopolymers
2190 reported in the literature (Biliaderis and others 1999; Roy and others 2000). As shown in
Fig. 5.1, glycerol-plasticized films had extremely higher monolayer moisture content than
other plasticizers. Water absorption characteristic is highly related to the polarity of the
polymer (Fang and Hana 2000). The high MC of glycerol-plasticized starch films is
probably due to the high polarity of glycerol (i. e., dielectric constant 42.5 at 25 °C)
2195 (Yang and Paulson 2000). In comparison, sorbitol has a dielectric constant of 33.5 at 80
°C (Arvanitoyannis and others 1997), and EG 37.0 at 25 °C (Yang and Paulson 2000).
The dielectric values for monosaccharides are not available. They should be similar to

sorbitol's and smaller than glycerol's. Monolayer concept is useful for the preservation of foodstuff with low and intermediate MC (Diab and others 2001). For example, monolayer MC corresponds well with the critical MC at which the rates of quality loss resulting from chemical reactions in foods are negligible (Zimeri and Kokini 2002). BET model could also be used to provide the estimates of the monolayer value. However, BET model does not take into account the water effect on any structural changes in the films. When dissolution or swelling of the films have occurred, the BET model is not useful in providing insight into the sorption process. Therefore, BET model is usually restricted to the RH range of 11 - 55% (Mathlouthi 2001) where little change in film structure hardly occurs.

In BET model, B is called the BET parameter. It is expressed as follows (Keller and Staudt 2005; Gregg and Sing 1967):

$$B = \left(\frac{1}{a_{wl}} - 1 \right)^2 \quad 5.3$$

where a_{wl} is water activity necessary for monolayer water adsorbed. Table 5.3 shows the extremely high values of B (i. e., considered as infinite values) for the BET models of fructose- and glycerol-films. For fructose-films, the BET model does not fit data well because its G value is 63.93 being much bigger than 10. Therefore, it is not necessary to discuss any meaning of BET model for fructose-films. For glycerol-films, B value is 2.66×10^{63} . According to equation 5.3, a_{wl} , which is necessary for monolayer moisture, should

2220 be very small. It means that glycerol-film maintains very high moisture content due to
high hygroscopicity of glycerol even under very conditions.

In GAB model, B is also called sorption constant or Guggenheim constant. It is expressed as follows (Keller and Staudt 2005; Gregg and Sing 1967):

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$$B = B' \exp\left(\frac{H_l - H_m}{RT}\right) \quad 5.4$$

where H_l is the total heat of sorption of the monolayer water on primary sites. H_m is total heat of sorption of the multi player which differs from the heat of condensation of pure
2230 liquid water. R is the gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$). T is the temperature (K). B' is a constant. Sorption of moisture is an exothermic process. For glycerol-film, its B value for GAB model is 3.21×10^{70} indicating the exothermic heat of sorption of the monolayer water is huge compared to the exothermic heat of sorption of the multi player water.

2235 Actually, GAB model is an extension of BET model with an extra constant, C , which is a correction factor for the structural changes of starch films ranging from 0 to 1. When $C = 1$, GAB model reduces to BET model. In our case, glycerol and fructose films had lowest C values in their GAB models, meaning their film structure changed significantly during the sorption isotherm process, i. e., 72 h conditioning under corresponding RH.

2240 Meanwhile, glucose-, mannose-, and sorbitol-plasticized films had C values

approximated to 1, suggesting their structure did not change within 72 h as much as glycerol and fructose films did.

Statistical Analysis of the Regression Models for Film Characteristics

2245 Table 5.3 and 5.4 summarize the regression parameters of the second-order polynomial models (Eq. 5.2) and ANOVA results of film characteristics with respect to plasticizer content and RH. According to ANOVA, the models for TS of glucose-plasticized films, for EM of sorbitol- and glucose-plasticized films, and for E of sorbitol- and glucose-plasticized films showed significant lack of fit at $p < 1\%$ level. These models were
2250 meaningless in investigation of the relationship between variables, and their ANOVA results were not listed on Table 5.3 or 5.4. Table 5.4 showed that the regression model for MC of glucose-plasticized films was significant ($p = 0.1141$) which was very close to 10% error level. Model for E of fructose-plasticized films was significant at 5% level, and all the rest were significant at 1% level. All models, except those for MC of glucose-,
2255 E of glycerol-, and WVP of fructose-plasticized films, had R^2 values greater than 0.90. Models with R^2 over 0.9 showed a coefficient of variance below 18.03%. Thus, the models accurately agreed with experimental data and are useful for studying the effect of film forming conditions on film properties. Significant levels for the estimated coefficients of the quadratic polynomial models were also shown in Table 5.3 and 5.4.
2260 Reduced models with non-significant, or less significant, terms removed could be used to fit the film properties. The resulting models would describe the experimental data well. Further explanation of the result of statistical analysis including lack of fit will be given

separately in the following discussions with the figures of the graphical charts (i. e., response surfaces) of these models.

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Table 5.3 Statistical analysis and regression coefficients for the second-order polynomial models for mechanical properties

Coefficients	Tensile strength				Elastic modulus			Elongation		
	Gly	Sor	Fru	Man	Gly	Fru	Man	Gly	Fru	Man
β_0	2.96	3.56	3.34	4.90	31.58	37.50	31.02	39.01	59.90	120.58
β_1	-3.54 ⁽³⁾	-1.94 ⁽³⁾	-2.30 ⁽³⁾	-2.55 ⁽³⁾	-133.06 ⁽³⁾	-86.73 ⁽³⁾	-95.59 ⁽³⁾	-0.26	13.52 ⁽²⁾	22.18 ⁽³⁾
β_2	-2.18 ⁽³⁾	-3.01 ⁽³⁾	-2.22 ⁽³⁾	-2.14 ⁽³⁾	-100.91 ⁽³⁾	-101.66 ⁽³⁾	-112.34 ⁽³⁾	-2.78	3.90	9.53 ⁽²⁾
β_{11}	2.11 ⁽³⁾	0.79 ⁽²⁾	1.21 ⁽³⁾	0.61 ⁽¹⁾	78.57 ⁽³⁾	44.03 ⁽³⁾	43.00 ⁽³⁾	1.17	-6.46	-23.33 ⁽³⁾
β_{22}	0.76 ⁽³⁾	1.16 ⁽³⁾	0.39 ⁽¹⁾	-0.39	54.35 ⁽³⁾	50.75 ⁽³⁾	66.15 ⁽³⁾	-10.16 ⁽³⁾	-9.63 ⁽¹⁾	-50.27 ⁽³⁾
β_{12}	1.85 ⁽³⁾	1.35 ⁽³⁾	0.95 ⁽³⁾	0.15	98.12 ⁽³⁾	81.57 ⁽³⁾	92.60 ⁽³⁾	-10.50 ⁽³⁾	-8.60	-23.97 ⁽³⁾
Coefficient of determination (R^2)	0.99	0.97	0.98	0.95	1.00	1.00	0.99	0.85	0.74	0.95
Model significance (p)	0.0001	0.0001	0.0001	0.0002	0.0001	0.0001	0.0001	0.0088	0.0501	0.0002
Coefficient of variation (%)	11.87	15.49	11.68	16.64	8.02	11.41	16.27	17.01	23.40	18.03
Lack of fit significance (p)	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.16	0.01	0.14

Gly, Glycerol; Sor, Sorbitol; Fru, Fructose; Man, Mannose; Superscript ⁽¹⁾, ⁽²⁾, and ⁽³⁾, indicate significance at $p \leq 0.1$, $p \leq 0.05$, $p \leq 0.01$, respectively.

Model: $Y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_{11} X_1^2 + \beta_{22} X_2^2 + \beta_{12} X_1 X_2$, where X_1 and X_2 stand for plasticizer content and RH, respectively.

Table 5.4 Statistical analysis and regression coefficients for the second-order polynomial models for moisture content (MC) and water vapor permeabilites (WVP)

Coefficients	MC					WVP				
	Gly	Sor	Glu	Fru	Man	Gly	Sor	Glu	Fru	Man
β_0	40.26	11.41	12.85	18.34	15.38	4.49	2.81	2.80	3.18	2.44
β_1	7.63 ⁽³⁾	0.59	0.41	1.40 ⁽²⁾	-0.12	0.88 ⁽³⁾	0.72 ⁽³⁾	0.57 ⁽³⁾	1.19 ⁽³⁾	0.55 ⁽³⁾
β_2	3.09 ⁽³⁾	8.74 ⁽³⁾	4.28 ⁽³⁾	5.74 ⁽³⁾	4.32 ⁽³⁾	0.052	0.069	-0.26 ⁽³⁾	0.12	0.22 ⁽²⁾
β_{11}	-1.25 ⁽¹⁾	-0.76	-0.54	-2.48 ⁽³⁾	-1.60 ⁽²⁾	-0.034	0.17 ⁽²⁾	-0.038	0.48 ⁽¹⁾	0.18 ⁽²⁾
β_{22}	1.05	2.08 ⁽²⁾	-0.57	-0.45	0.22	0.062	-0.033	0.29 ⁽³⁾	0.22	0.32 ⁽³⁾
β_{12}	1.73 ⁽¹⁾	0.55	-0.13	0.40	0.025	-0.19 ⁽¹⁾	0.073	0.15	0.035	-0.062
Coefficient of determination (R^2)	0.97	0.97	0.66	0.96	0.92	0.97	0.95	0.94	0.86	0.93
Model significance (p)	0.0001	0.0001	0.1141	0.0001	0.0008	0.0001	0.0002	0.0004	0.0061	0.0006
Coefficient of variation (%)	3.74	13.36	27.52	8.52	9.63	3.78	6.13	6.48	15.03	7.17
Lack of fit significance (p)	0.02	0.53	0.18	0.01	0.03	0.18	0.10	0.01	0.10	0.27

Gly, Glycerol; Sor, Sorbitol; Glu, Glucose; Fru, Fructose; Man, Mannose; Superscript ⁽¹⁾, ⁽²⁾, and ⁽³⁾, indicate significance at $p \leq 0.1$, $p \leq 0.05$, $p \leq 0.01$, respectively.

Model: $Y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_{11} X_1^2 + \beta_{22} X_2^2 + \beta_{12} X_1 X_2$, where X_1 and X_2 stand for plasticizers content and RH, respectively.

Tensile Properties

2290 Fig.5.2 shows the TS of the starch films. Regardless of the types of plasticizer, increasing RH and plasticizer content decreased the TS of the films, indicating that both water and plasticizers (monosaccharides and polyols) plasticize the pea starch films. From Table 5.3, it was shown that the effects of both RH and plasticizer content were significant ($p < 0.01$) on the TS with negative regression parameters (i. e., β_1 and β_2). The

2295 addition of plasticizers, such as water, monosaccharides or polyols, reduces the TS of the films. This phenomenon was caused by replacing the polymer-polymer (intermolecular) hydrogen bonds (i. e., work of cohesion) with the polymer-(plasticizer)_n-polymer hydrogen bonds (Lim and others 1998). At very high RH level ($\geq 75\%$), the TS became less sensitive to the plasticizer content due to the extensive plasticization effect of the

2300 absorbed water. For glycerol-plasticized starch film, TS became insensitive to the RH change at high glycerol content level.

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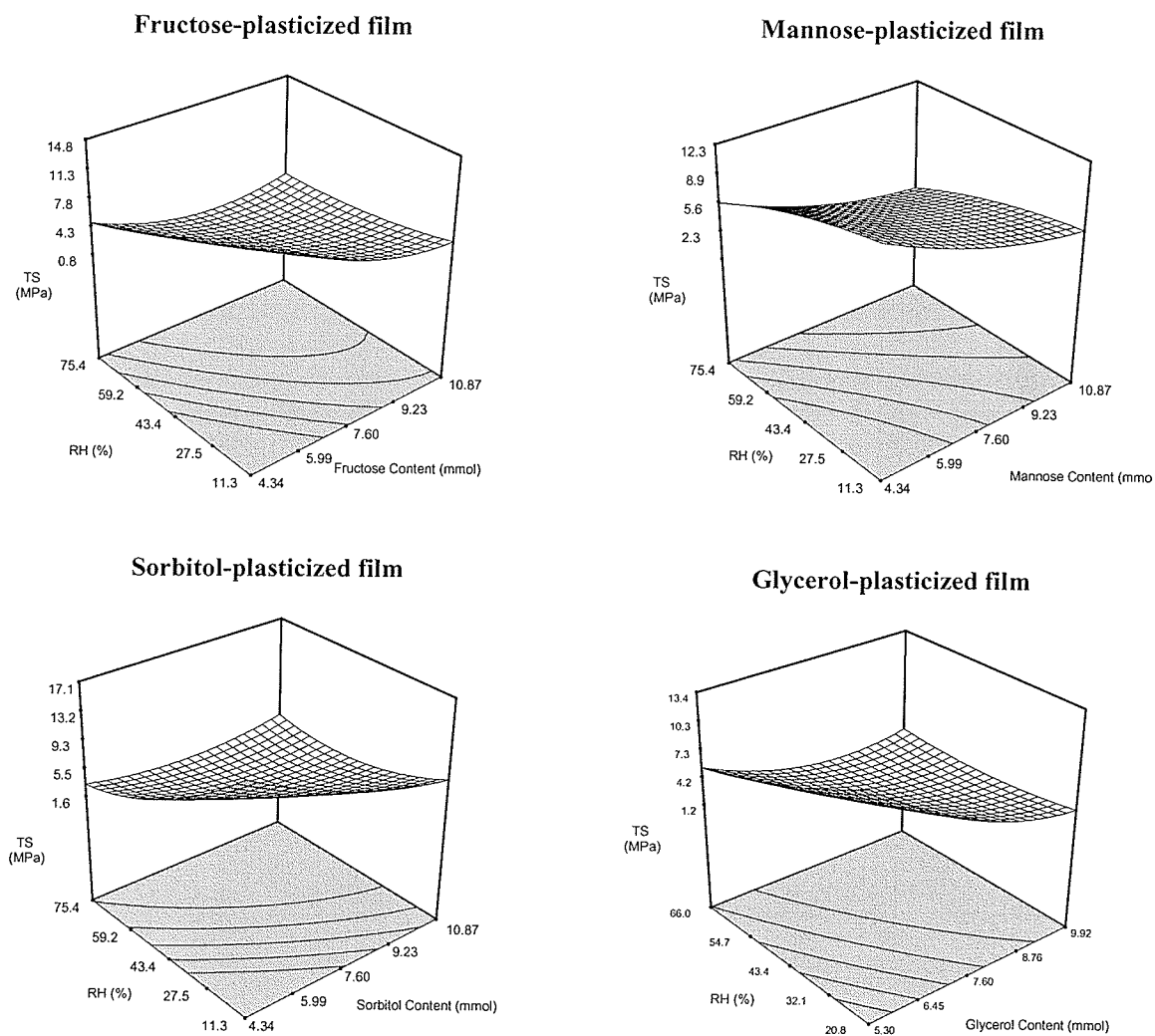
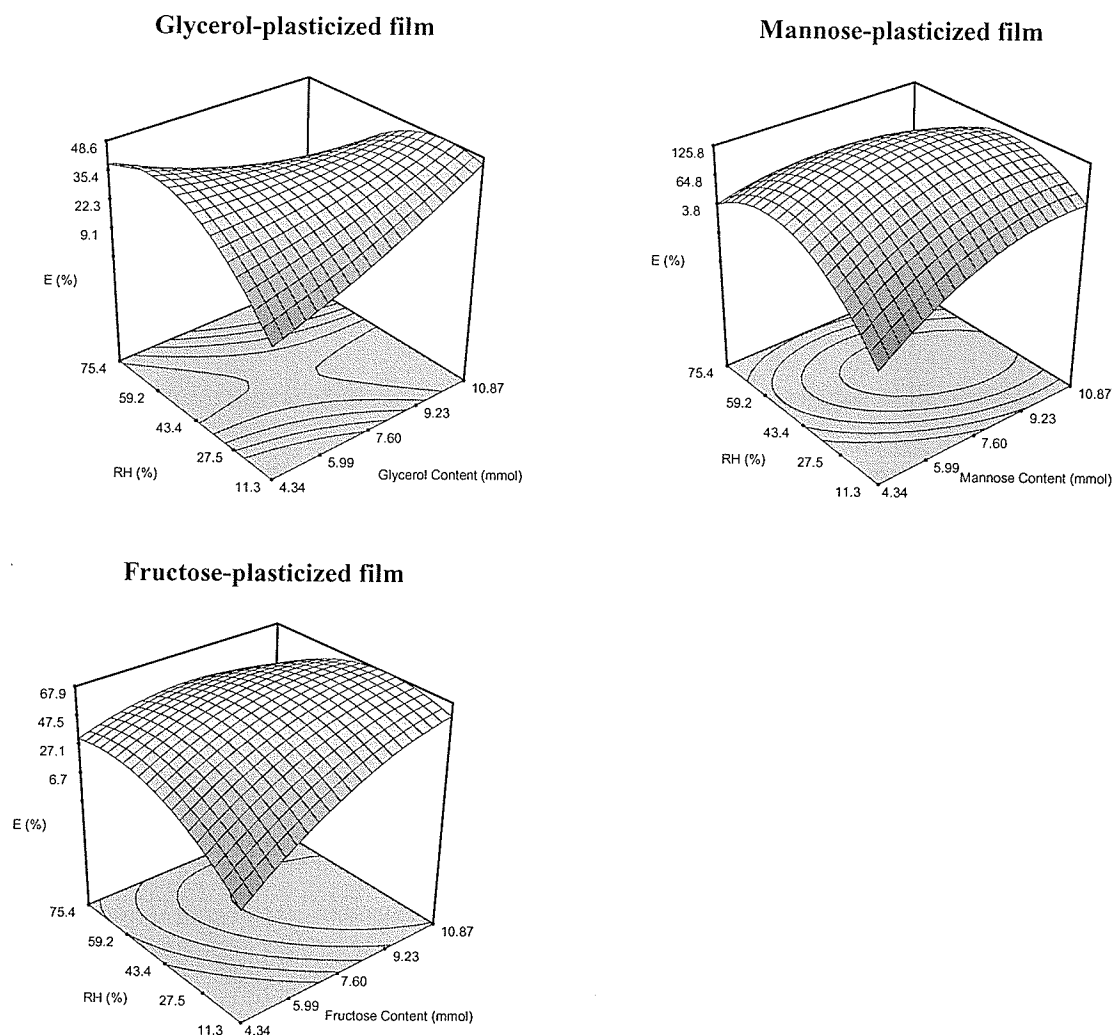


Fig. 5.2 The effect of relative humidity (RH) and plasticizer content on the tensile strength (TS) of pea starch films

Fig. 5.3 showed the elongation of the films. Below the intermediate RH ($< 43.4\%$), the E of all three films increased with increasing plasticizer content. This agreed with the general rule that a plasticizer increases the E. However, above the intermediate RH, the E of the fructose- and mannose-plasticized films did not change significantly. This result agreed with Lim and others (1998) whose films were made from transglutaminase cross-linked egg white protein. Lim and others (1998) regarded that the plasticizers, both the water and monosaccharides or polyols at low RH, acted like lubricants between the polymer chains, allowing the neighboring molecules to slide past each other more readily, thus increasing the extensibility of the polymer. At high level of RH, the E of glycerol-plasticized films decreased slightly with increasing glycerol content. It can be explained by the fact that when the RH and the monosaccharides, or the polyols, increased above a critical value, the interactions between the polymers became weak and the cohesive force of the polymer chains reduced resulting in small E at break and TS. From the Fig. 5.3, fructose-film has the maximum E value at around 11 mmole per g of starch and 40% RH, while mannose film has the maximum E value at around 9 mmole per g starch and 43% RH. The maximum E of glycerol-film may exist outside the experimental range.



2340 Fig. 5.3 The effect of relative humidity (RH) and plasticizer content on the elongation (E)
of pea starch films

2345 Fig. 5.4 shows the EM of the starch films. The three plots had similar profile that EM increased with decreasing RH and plasticizers. According to the ANOVA (Table 5.3), EM was significantly (1% level) influenced by the effects of plasticizer content (X_1 and X_1^2), RH (X_2 and X_2^2), and the interaction (X_1X_2). Decreasing the RH and plasticizer

content in the film resulted in increase in the intermolecular interactions between the starch polymers, thus starch polymer chains had higher values of cohesive force and the films became brittle. Fig. 5.4 also showed either the plasticizer content or RH could affect EM strongly when the variables were at low levels. However, when the film has high level of plasticizer content or was stored in high RH condition, the EM of films became less sensitive to the RH or plasticizer accordingly. This can be explained by the over plasticization of the polymers.

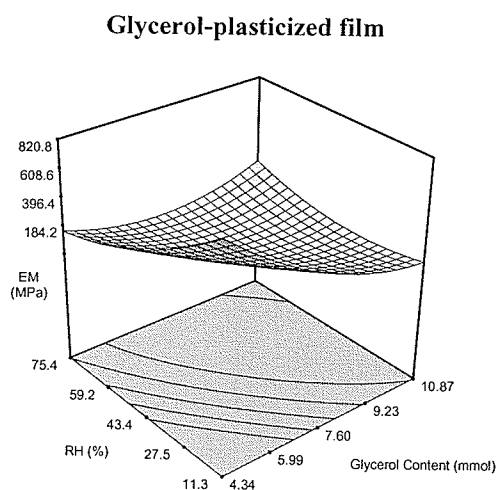
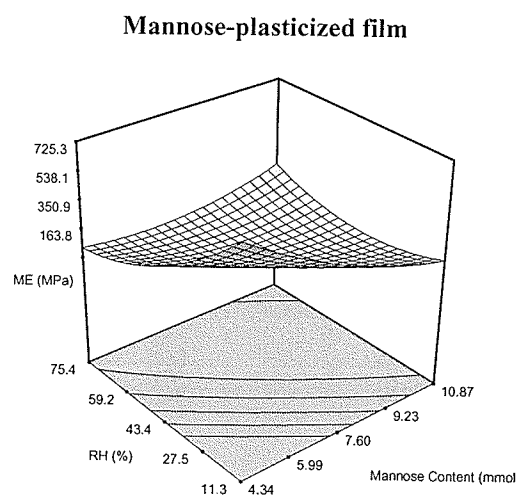
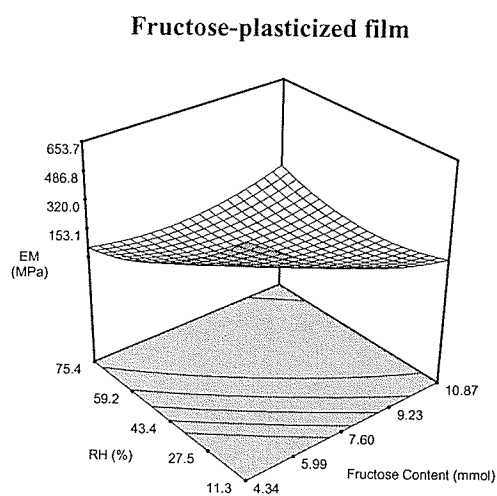


Fig. 5.4 The effect of relative humidity (RH) and plasticizer content on the elastic modulus (EM) of pea starch films

ANOVA showed that models for TS, EM, and E of glucose-plasticized film, and EM and E of sorbitol-plasticized film had significant lack of fit ($p < 0.01$) to the experiments

2375 (Table 5.3). The change in physical status of the films was supposed to be responsible for the significant lack of fit. During the experiment, glucose-plasticized films, which were conditioned at the high level RH ($\geq 66\%$), readily became rigid within several days, and turned white and opaque. Fig. 5.5 showed the glucose-plasticized film (9.92 mmol per g starch) and sorbitol-plasticized film (5.351 mmol per g starch) conditioned at 66% RH.

2380 With a phase contrast light microscope, the microstructure of recrystallized glucose-plasticized films was observed (Fig. 5.5A). Recrystallization of the glucose-plasticized film was due to the glucose molecule, which has exactly same structure, conformation, and configuration with the amylose and amylopectin glucose units. While starch polymer chains and glucose molecules vibrate, glucose molecules are easy to pack into the starch

2385 polymer chains because of its similar molecular structure and conformation. Moreover, the high RH environment favors the vibration of starch polymer chains and glucose molecules. Finally, starch and glucose became packed into a crystal lattice. Therefore, this crystalline structure may be created by retrogradation of starch as well as glucose recrystallization. This phenomenon seldom occurred when the glucose-plasticized films

2390 were conditioned at low RH ($\leq 50\%$). A similar situation was reported by Delville and others (2003) who observed that storage at high RH readily led to retrogradation and recrystallization of wheat starch films.

The sorbitol-plasticized films had different appearances from glucose-plasticized films

2395 after conditioning at high RH, which had white blooms on the surface suggesting sorbitol was recrystallized (Fig. 5.5B). This phenomenon happened in the films which were conditioned in high relative humidity only ($\geq 66\%$). It was assumed that high RH

increased the MC in the films and favored the movement of the sorbitol molecules to be separated from starch and crystallized. Inversely, low RH decreased the MC and entrapped sorbitol molecules into starch polymer matrix through the hydrogen bonds with starch, which inhibited the phase separation and recrystallization of sorbitol from starch. Crystallization was supposed to be responsible for the failure in describing the variable relationships by the ANOVA models, because crystallization changed the normal sequence of effects of variables. Mechanism of the recrystallization in the starch films needs further studies.

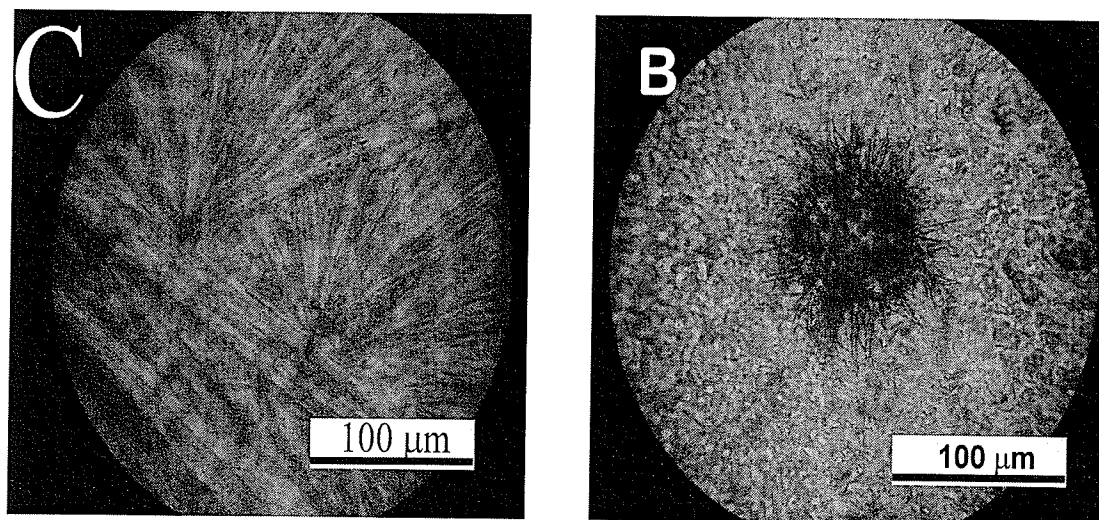


Fig. 5.5 Microstructure of the recrystallization of glucose-plasticized films (A) and sorbitol-plasticized films (B) after 6 d conditioning at 66 % RH

Film Moisture Content (MC)

Response surfaces of MC against plasticizer content and RH were presented in Fig. 5.6.

Glucose-, fructose-, and mannose-films had very similar responses. Increasing RH

2415 significantly increased the MC of the films, while changing the monosaccharide content affected the MC of the films slightly, indicating that the MC of the monosaccharide-plasticized films was mainly affected by the environmental RH. Table 5.4 showed that

the β_2 s were significant at 1% level for the MC of glucose-, fructose-, and mannose-plasticized films, respectively, while β_1 s for glucose- and mannose-plasticized films were

2420 not significant. This evidence suggested that monosaccharides had weaker attraction to water molecules than the attraction of water molecules had to water molecules, in agreement with the sorption isotherm suggestions which showed Flory-Huggins models fitted well for monosaccharide-plasticized films. For sorbitol-plasticized films, increasing RH increased the MC. However, MC was less sensitive to the sorbitol content (Fig. 5.6).

2425 Its MC response surface was very similar to those of monosaccharide-plasticized films, indicating that the sorbitol behaved like a monosaccharide in the starch film. For glycerol-plasticized films, both RH and glycerol content influenced the MC significantly.

Increasing either glycerol content or RH would increase the MC of the films greatly. In the experimental conditions, the MC values of glycerol-plasticized films ranged from

2430 27% to 58%, while other four films had only 3% to 26%. It was suggested that glycerol plasticized the starch films with a different mechanism from the other four plasticizers.

Glycerol attracted more water molecules around itself. Therefore, between the starch molecule chains and glycerol molecules, there were huge amount of water molecules trapped by the hygroscopicity of glycerol. Water molecules played a more important role

2435 of plasticization in glycerol films than in other four films. No matter what type of plasticizer was used in starch films, RH always affected the MC of the films significantly.

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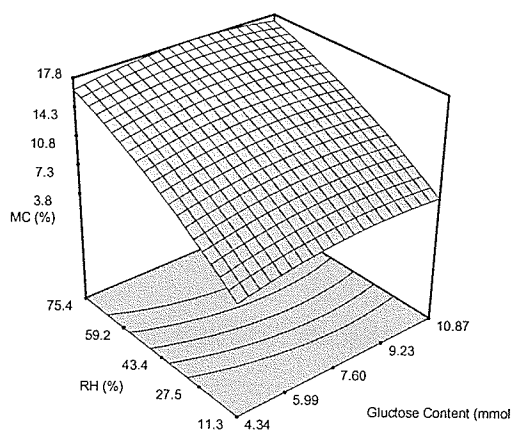
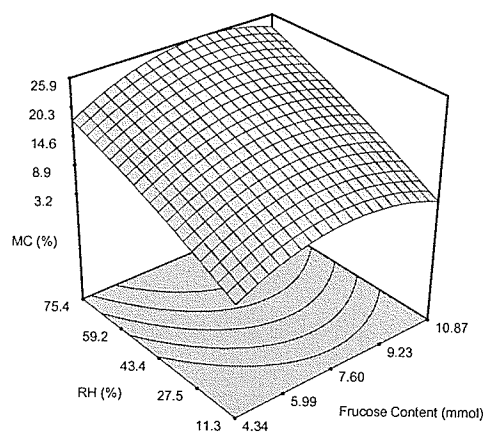
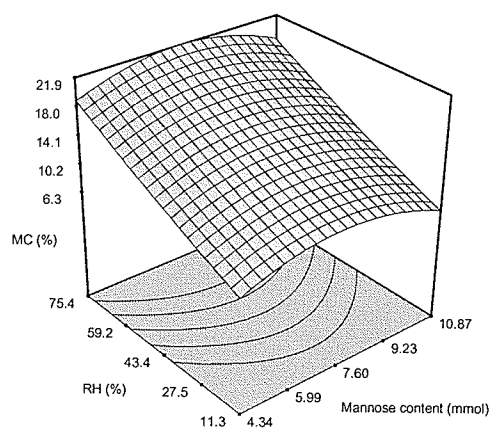
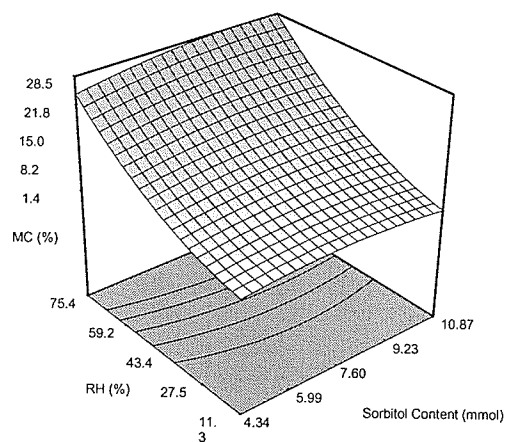
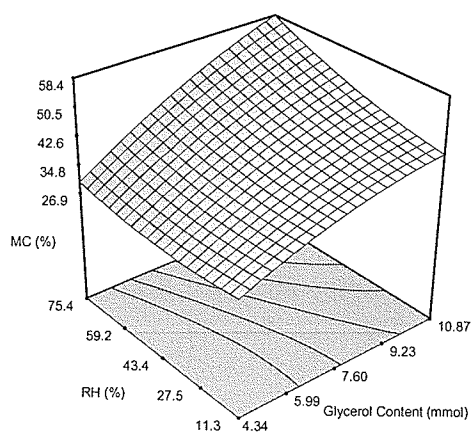
Glucose-plasticized film**Fructose-plasticized film****Mannose-plasticized film****Sorbitol-plasticized film****Glycerol-plasticized film**

Fig. 5.6 The effect of RH and plasticizer content on moisture content (MC) of pea starch film

2465 **Water Vapor Permeability (WVP)**

Fig. 5.7 showed the WVP of the films. As shown in Table 5.4, WVP of pea starch films was influenced significantly by plasticizer content (X_1). Increasing monosaccharide or polyol content resulted in increase in the WVP. This result agrees with those Mehyar and Han (2004) who got the same results with the high-amylose rice and pea starch films.

2470 Similar results were also reported on protein films by Gontard and others (1993), and Sothornvit and Krochta (2000). It is usually regarded that more plasticizer content can not only make the film less dense (Mali and others 2002), but also enhance sorption of water (Sothornvit and Krochta 2000). Thus, water molecules are more readily absorbed into the surface of the films (i.e., higher solubility), and penetrate through the film structure much
2475 more easily (i.e., higher diffusivity), resulting in an increase in permeability. However, the preceding experiments showed MC was not influenced by the plasticizer content, except for glycerol films. Therefore, we concluded that increasing WVP mainly resulted from higher diffusivity because of the lower density of the films. Increasing RH resulted in reduction of WVP in glucose films with negative β_2 value (Table 5.4). This may be
2480 caused by the retrogradation in the glucose starch films, leading to less amorphous space left in the starch films.

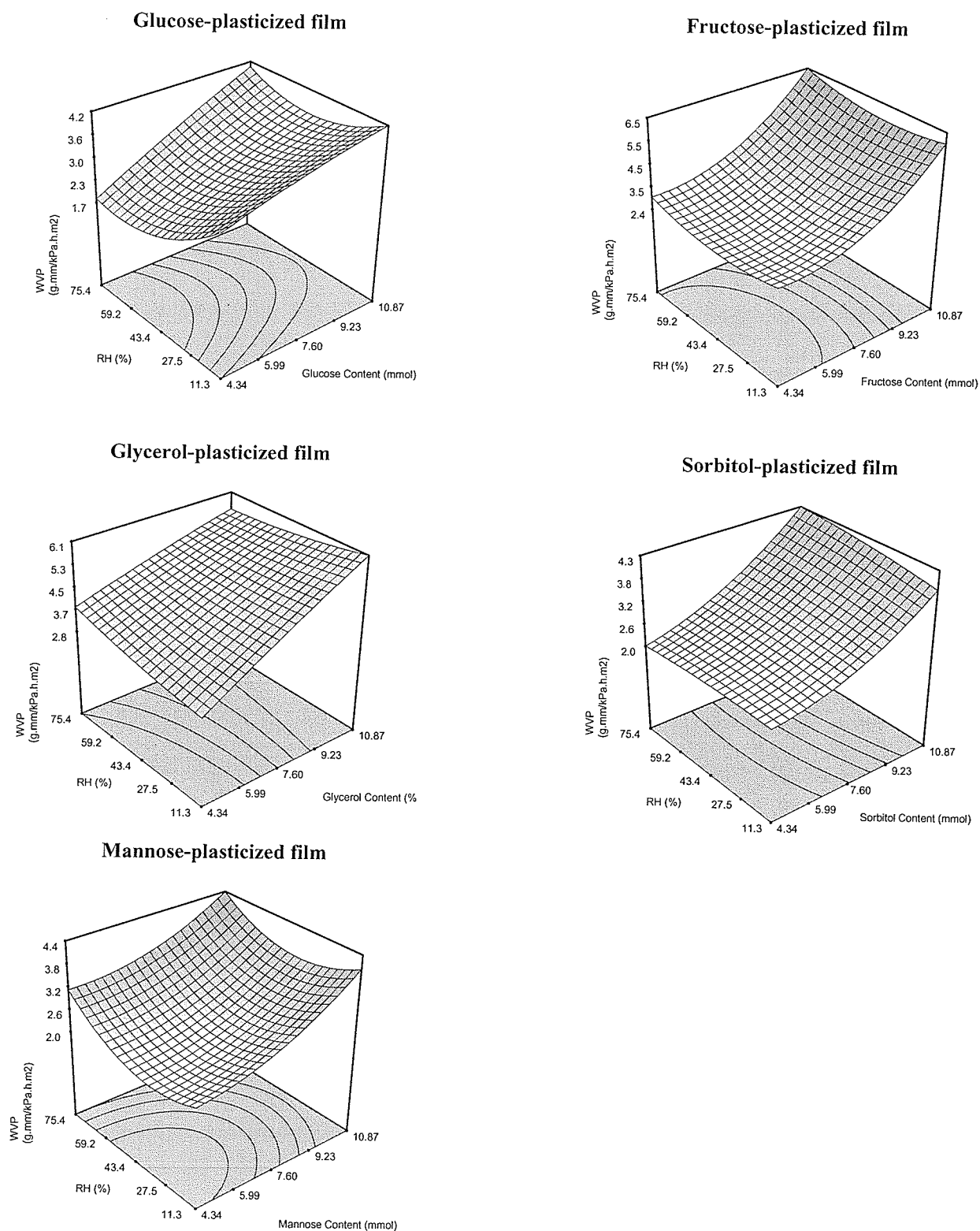


Fig. 5.7 The effect of RH and plasticizer content on water vapor permeability of pea starch films

CONCLUSION

The three common monosaccharides, glucose, fructose, and mannose, showed similar plasticizing behaviors in the pea starch films. RH significantly influenced the MC while
2490 the concentration of the monosaccharides slightly affected the MC. Glycerol-plasticized films had the highest MC, which meant water molecules played a more important role in plasticizing starch films than in other films. Flory-Huggins equation fitted sorption isotherm experimental data better than other models for the monosaccharide-plasticized films, indicating the strong molecular interaction between water molecules in the film
2495 and atmospheric water played a more important role in the sorption behavior. For tensile properties, both RH and plasticizer content had significant influences. Increasing plasticizer content and RH decreased the TS of the monosaccharide- and polyol-plasticized films. E increased with increase in RH and plasticizer content. However, when the films were over-plasticized, E decreased because of the weakness of film
2500 structure. Fructose- and mannose-plasticized films had higher values of E and lower values in EM than the glycerol-plasticized films, confirming they possessed good influence on the mechanical properties of starch films. Increasing monosaccharide or polyol content resulted in increase in WVP. Retrogradation (or recrystallization) of starch was found in glucose-plasticized films when they were stored in high RH. Sorbitol
2505 blooming was accelerated at higher RH.

Chapter 6

2510

Plasticizer-induced antiplasticization of starch film

ABSTRACT

2515 Pea starch films were plasticized by various polyols and monosaccharides at the levels of 0 % to 25 % (w/w, plasticizer/starch). After 14 days of storage at 50 % relative humidity, the crystallinity of pea starch films increased with increasing concentration of plasticizers from 0 % to 15 - 20 %. Accordingly, moisture content, water vapor permeability, oxygen permeability, and elongation decreased with increasing plasticizer concentration from 0
2520 % to 15 - 20 %, showing the antiplasticization effect. The addition of plasticizers above 20 % decreased the crystallinity of starch films, consequently showing plasticization effect. As a conclusion, the addition of the plasticizers facilitated the crystallization of the polymer chains through the antiplasticization phenomenon at the concentration range below 15 - 20 %. Above 15 - 20 %, plasticizers performed the conventional plasticization
2525 effect. Different plasticizers had different critical concentration where the antiplasticization was converted to plasticization.

INTRODUCTION

2530 Plasticizers, such as glycerol, sorbitol, and ethylene glycol, are added into starch polymers to increase flexibility of the starch films (Suyatma and others 2005, Fairley and others 1996). However, at low or intermediate range of concentration, these plasticizers do not have a plasticization effect (Chang and others 2006, Gaudin and others 1999). Controversially, tensile strength (TS) and modulus of elasticity (EM) of polymers
2535 increased, while elongation (E) and gas permeability decreased with an increase in plasticizer concentration at low concentration range. This phenomenon is named antiplasticization. The antiplasticization phenomenon of various plasticizers has been found with poly (vinyl chloride), polycarbonate, poly(methyl methacrylate), polysulfone, and polystyrene (Garcia and others 2004). The antiplasticizers should have a compatible
2540 chemical structure with the polymers and usually possess some chemical characteristics which are relatively planar and rigid. Antiplasticizers also include specific atoms such as halogen, nitrogen, oxygen, etc (Garcia and others 2004). Density study resulted in reduction of free volume and increase in density of the polymer blends when the antiplasticization occurred (Garcia and others 2004). However, some researchers doubted
2545 this explanation because the density of pure antiplasticizers is generally higher than those of pure polymer materials, and the addition of antiplasticizers, consequently, increased the density of the polymer blends (Garcia and others 2004). Gaudin and others (2000) studied the antiplasticization phenomenon with wheat starch films plasticized by sorbitol. They found that local mobility (i.e., β relaxation) of starch molecules disappeared with
2550 the addition of sorbitol up to a certain concentration, and attributed this to a strong interaction between starch and sorbitol molecules. Da Roz and others (2006) suggested

that the antiplasticization was caused by an increase in crystallinity. They advised that plasticizers have two different effects on the polymer materials, plasticization and crystallization. At low and intermediate concentration range of plasticizers, crystallization prevails more than plasticization. According to Delville and others (2003), the rationale of the crystallization by plasticizers is that the plasticizers favor starch macromolecules to have increased mobility which facilitates the starch polymers to pack into crystal lattices.

In our previous research, we found that some monosaccharides, such as glucose, fructose and mannose, could act as very efficient plasticizers in starch films when they are used at high concentration. The plasticization efficiency of monosaccharides is due to their configuration similarity to the glucan monomers of starch. The molecular structure of monosaccharides is relatively planar and rigid, and they contain oxygen atoms in their molecules. These conditions meet the requirements for the antiplasticizers suggested by Garcia and others (Garcia and others 2004). Therefore, monosaccharides may have antiplasticization activity in starch films at low and intermediate concentration. In this work, the antiplasticization effect of polyols and monosaccharides on high - amylose pea starch films was examined and the crystallinity of the pea starch films related to antiplasticization effects was investigated. The major objective of the present work is to verify that the main cause of antiplasticization is the crystallization of the starch polymers.

MATERIALS AND METHODS

2575 **Materials**

The same starch and plasticizers resources were used as in Chapter 5.

Film preparation

Aqueous dispersion (3 % w/w) of starch was prepared, and plasticizers were added into
2580 the dispersions at 0 %, 1 %, 5 %, 10 %, 15 %, 20 % and 25 % (w/w, plasticizer/starch).
The dispersions were heated and maintained at boiling temperature for 15 min with
agitation to allow complete gelatinization of the starch. After cooling the starch solution
down to 50 - 60 °C, 9 g of the starch solution was cast onto a polystyrene Petri dish (10
cm diameter), and dried at room temperature conditions over night. Before the films
2585 became fully dried, they were peeled intact from the Petri dishes, and continued to dry
under room conditions for 48 hours. After that, the translucent films were conditioned in
a chamber at 50 % relative humidity (RH) for 14 days. The 50 % RH inside sealed
chamber was obtained by saturated $\text{Ca}(\text{NO}_3)_2$ solution and an over-head fan. A digital
hydrometer (Control Company, Friendswood, TX) was placed in the RH chamber to
2590 monitor the inside RH.

The methods for measuring oxygen permeability (OP), X-ray diffraction, and
crystallinity determination were outlined in Chapter 4. The methods for measuring
moisture content (MC), tensile test, and water vapor permeability (WVP) were outlined
2595 in Chapter 3.

RESULTS AND DISCUSSION

Crystallinity

The crystallite size of the starch film was measured to be 1 - 7 nm from X-ray diffraction data. Fig. 6.1 demonstrates the X-ray diffraction patterns of 0 %, 10 %, and 25 % glycerol-films as examples. The peaks observed were mainly at $2\theta = 5.6^\circ$, 16.9° , and 22.3° by which the crystal models for the glycerol-films can be assigned to a B-type. The X-ray diffraction pattern of 10 % film had higher intensity peaks at 16.9° and 22.3° than 0 % and 25 % glycerol films, while films with 10 % glycerol film had the highest crystallinity.

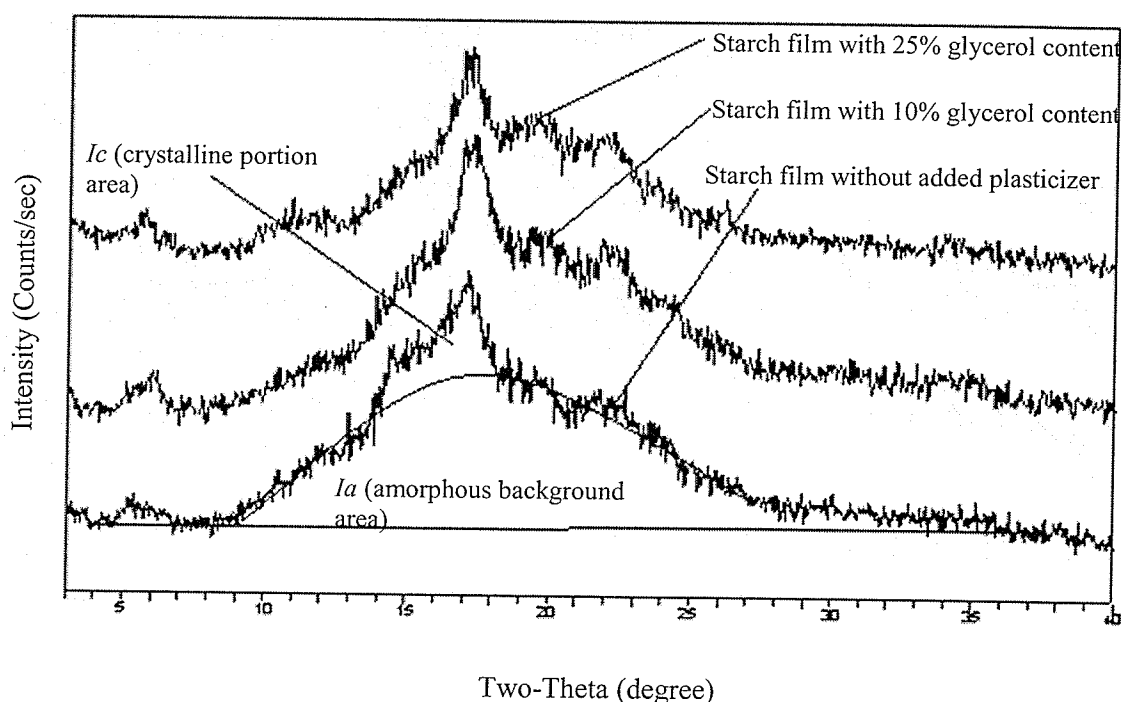


Fig. 6.1 X – ray diffraction pattern of glycerol films and film without plasticizer

Fig. 6.2 and Appendix 6.1 show the dependence of film crystallinity on the plasticizer concentration. The starch film without any plasticizer had 5.7 % crystallinity. The crystallinity of the films reached highest values when the plasticizer concentration ranged from 5 to 20 %, except ethylene glycol (EG) films. Smits and others (2003) observed similar results from wheat and potato starch plasticized by EG, glycerol and glucose. Both wheat and potato starch without any plasticizers showed lower crystallinity than those plasticized by 23.1 % plasticizers. Garcia and others (2000) reported that glycerol and water increased starch chain mobility and allowed the development of more stable crystalline structure during a short periods of storage. In the present work, it is hypothesized that the principles of recrystallization is as follows. Without plasticizer, the starch polymers interact with each other through strong hydrogen bonds. The free volume inside the starch film is lessened for the starch polymer chains to have enough mobility. After the plasticizer is added into starch, the free volume in the starch matrix increases, which enhances the mobility of starch polymer segments, leading to sliding of starch polymers. Starch polymers slide over to each other and push plasticizer molecules aside gradually. Ultimately, starch polymers interact directly and form crystallites. The plasticizer molecules are positioned outside the crystalline area. Fig. 6.3 shows the process of plasticizer extrusion from polymer crystallites. Slightly plasticized starch polymers easily vibrate and align to form crystallites, while unplasticized starch polymers interact with each other strongly through hydrogen bonds and lose mobility. Fig. 6.2 and Appendix 6.1 also show the crystallinity of the starch film decreased when the plasticizer concentration was above 20 %. This was due to the plasticizing effect of plasticizers at

high concentration. Higher concentration of plasticizer makes it difficult for starch polymers to push effectively plasticizer molecules to form a crystallite.

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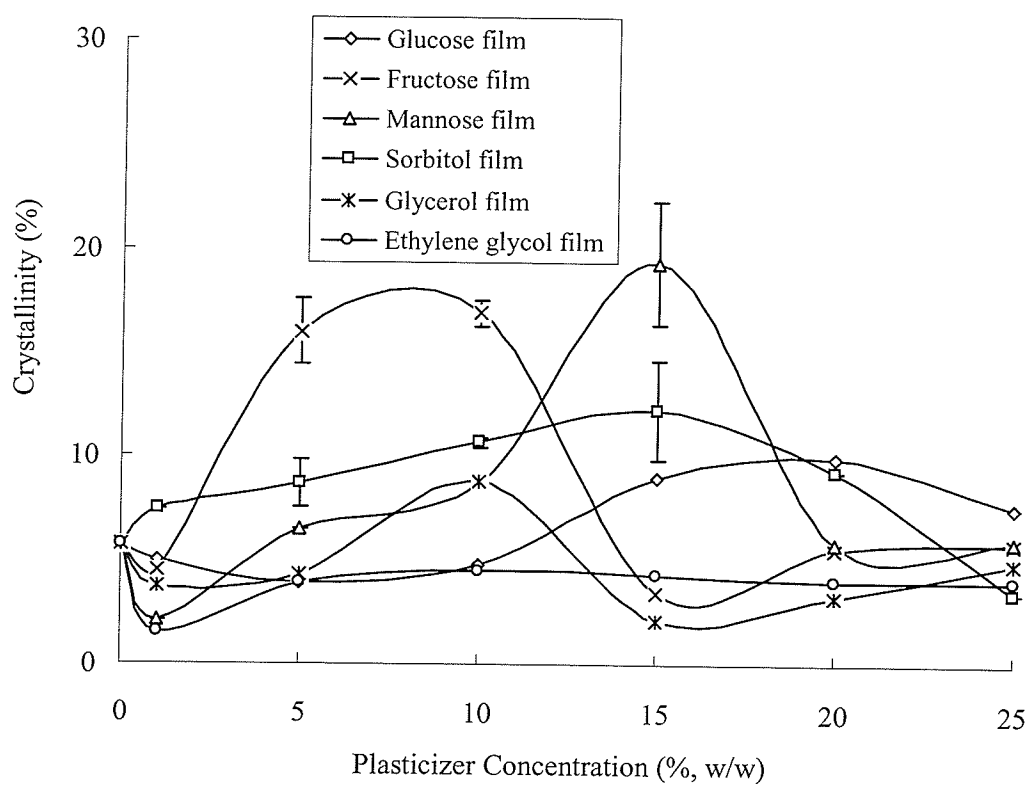


Fig. 6.2 Crystallinity of the pea starch film and the plasticizer concentration. Bars indicate mean \pm standard deviation

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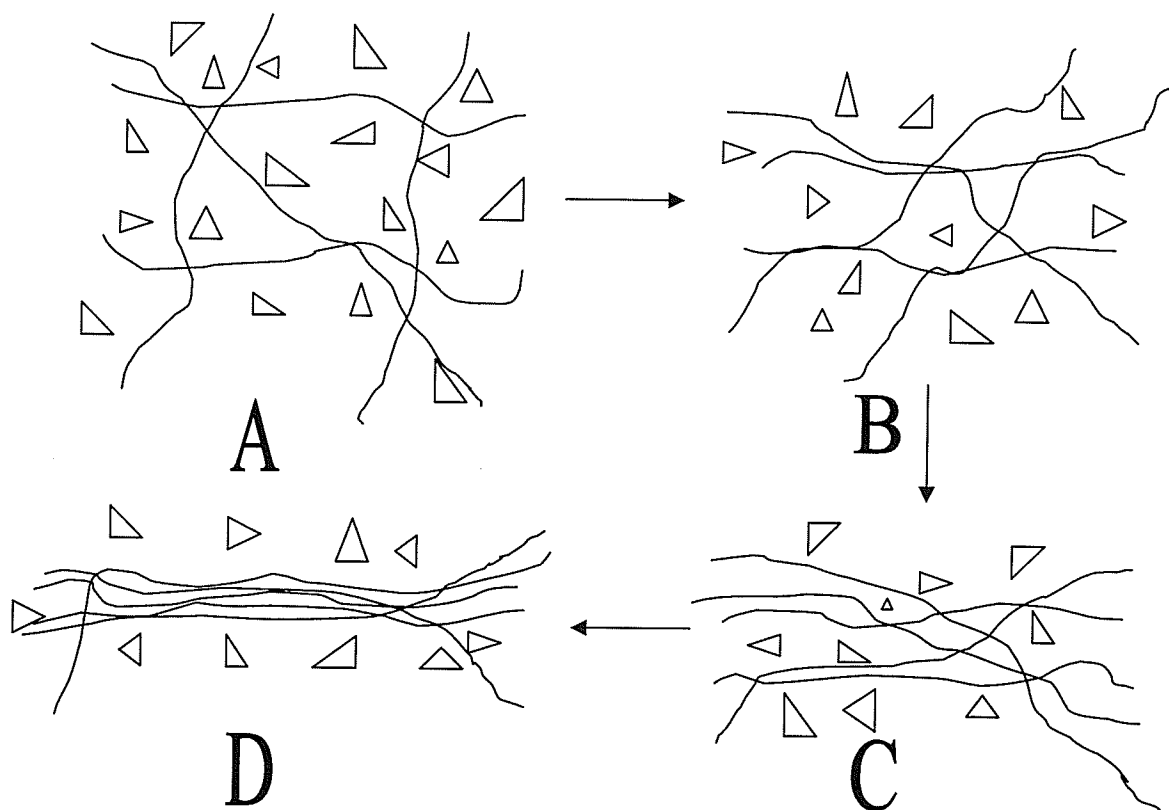


Fig. 6.3 Formation of a crystallite of starch polymers and extrusion of plasticizers. The triangles represent plasticizer molecules. A: Plasticized starch polymers with plasticizer molecules positioned between the starch polymers. B and C: Starch polymers get close to each other with some plasticizer molecules being pushed aside during dehydration. D: Starch polymers interact with each other directly leading to formation of a crystalline lattice with clusters of plasticizer molecules around the lattice.

Mass transfer of a plasticizer between the crystalline area and the amorphous area can be theoretically explained by using thermodynamic theory. When plasticizer molecules

are equilibrated in crystalline and amorphous areas, the chemical potentials of the plasticizer in the crystalline and amorphous areas are equal:

$$\mu_c^0 + RT \ln \gamma_c c_c = \mu_a^0 + RT \ln \gamma_a c_a \quad 6.1$$

2660

$$\mu_c^0 - \mu_a^0 = RT \ln \frac{\gamma_a c_a}{\gamma_c c_c} \quad 6.2$$

where, subscripts c and a stand for crystalline and amorphous areas, respectively, while μ , γ and c are standard free energy, activity coefficient and concentration of a plasticizer, respectively, R is the gas constant, and T is the absolute temperature. Because $\gamma_a c_a > \gamma_c c_c$, therefore, $\mu_c^0 - \mu_a^0 > 0$. This means the standard free energy of the plasticizer molecules decreases when they transfer from a crystalline area to an amorphous area, reflecting the preference of the plasticizer to the amorphous area of the starch films.

Moisture content

Fig. 6.4 and Appendix 6.2 show the effect of plasticizer addition on the moisture content (MC) of starch films. Generally the addition of hydrophilic plasticizers in starch films increased the MC of the films. At the concentration range of plasticizers which was tested in this study, the increase in the concentration of some plasticizers decreased the MC of the starch films. Glucose-plasticized film has 8.0 % of MC (at 1 % glucose), sorbitol-plasticized film 9.1 % (at 20 % sorbitol), glycerol-plasticized film 7.8 % (at 10 % glycerol), and ethylene glycol-plasticized film 7.8 % (at 10 % ethylene glycol), while pure starch film without any plasticizer has 11.3 % of MC. Considering the hydrophilic nature of these plasticizers, the lower MC of plasticized films than that of non-plasticized film is noticeable. Fructose and mannose did not affect the MC of starch films

significantly within the concentration range of the plasticizers from 0 to 25 % (w/w). The decrease in MC with increasing plasticizer concentration suggested that antiplasticization activity of the corresponding plasticizers may have occurred.

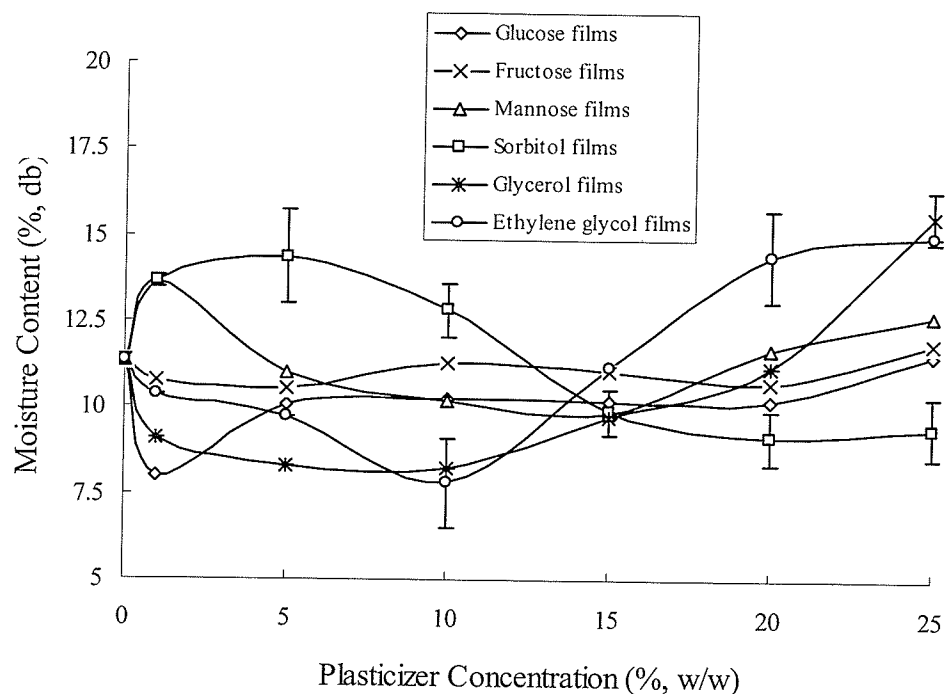


Fig. 6.4 Moisture content (MC, %, d. b) of the pea starch film and the plasticizer concentration. Bars indicate mean \pm standard deviation (Not all the error bars were added in order to clarify the figure)

Similar antiplasticization phenomenon was also found by other researchers. Gaudin and others (1999) found the MC of the wheat starch film decreased from 13.8 % to 8.6 % when sorbitol concentration increased from 0 % to around 25 %. Chang and others (2006) found the MC of tapioca starch films decreased from 10.7 % to 9.8 % when

glycerol increased from 0 % to 10 %. Myllarinen and others (2002) reported this MC reduction was caused by the replacement of water by glycerol in amylose or amylopectin films.

In our previous studies, when glycerol was present at high concentration level ($> 30\%$), glycerol-films usually showed higher MC than the films plasticized by other kinds of plasticizers, exhibiting higher affinity of glycerol to water. However, at low and intermediate glycerol concentration, glycerol-films did not show higher affinity to the water molecules, suggesting that most hydrogen bonds in glycerol molecules interacted with starch instead of water molecules.

Gas permeability

Fig. 6.5 and Appendix 6.3 show most films had their minimal OP at 10 % (w/w) plasticizer concentration, except for OP of fructose-plasticized film which has minimal OP at 5 % plasticizer. Among other plasticizers, 10 % sorbitol-plasticized film had the lowest OP value. The OP values of sorbitol pea starch film were similar to that of sorbitol wheat starch film of Gaudin and others (2000). Gaudin and others (2000) also found OP of wheat starch film decreased from $5.3 \times 10^{-7} \text{ cc mm m}^{-2} \text{ h}^{-1} \text{ kPa}^{-1}$ without sorbitol to $0.6 \times 10^{-7} \text{ cc mm m}^{-2} \text{ h}^{-1} \text{ kPa}^{-1}$ with sorbitol (10.9 % w/w). The lowest OP value for sorbitol-film is comparable to that of ethylene vinyl alcohol (EVOH, which is a common oxygen barrier plastic) which has $0.44 \times 10^{-7} \text{ cc mm m}^{-2} \text{ h}^{-1} \text{ kPa}^{-1}$ (at 0 % RH). This result makes the starch based film of potential interest for limiting oxygen transfers (Gaudin and others 2000). At the plasticizer concentration above 15 %, the OP of all films increased with an

increase in plasticizer concentration indicating 10 - 15 % is the critical transition concentration of monosaccharide and polyol plasticizers between plasticization and antiplasticization functionality.

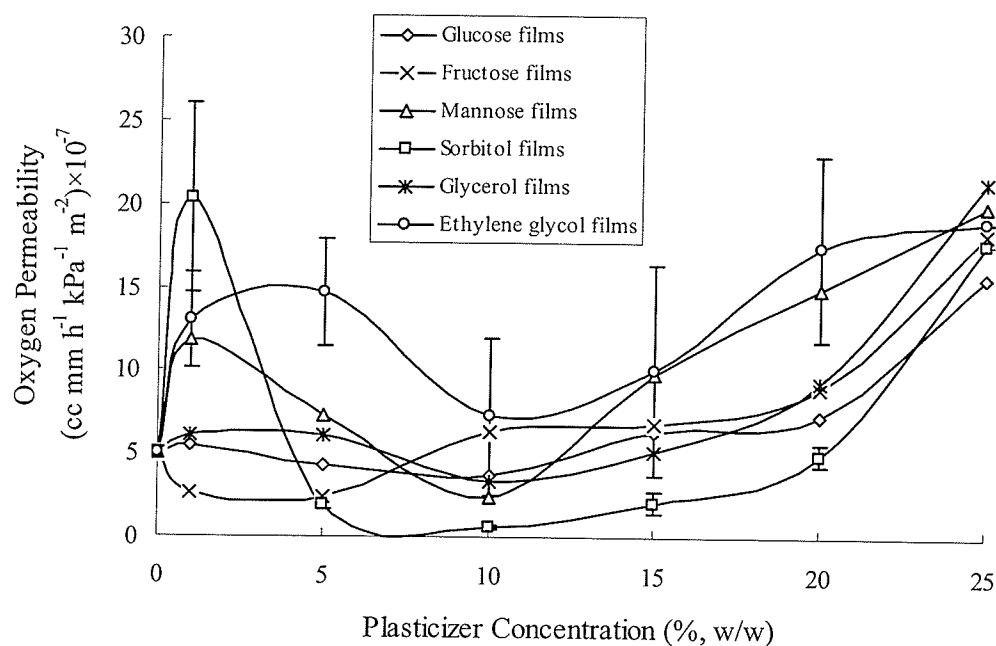


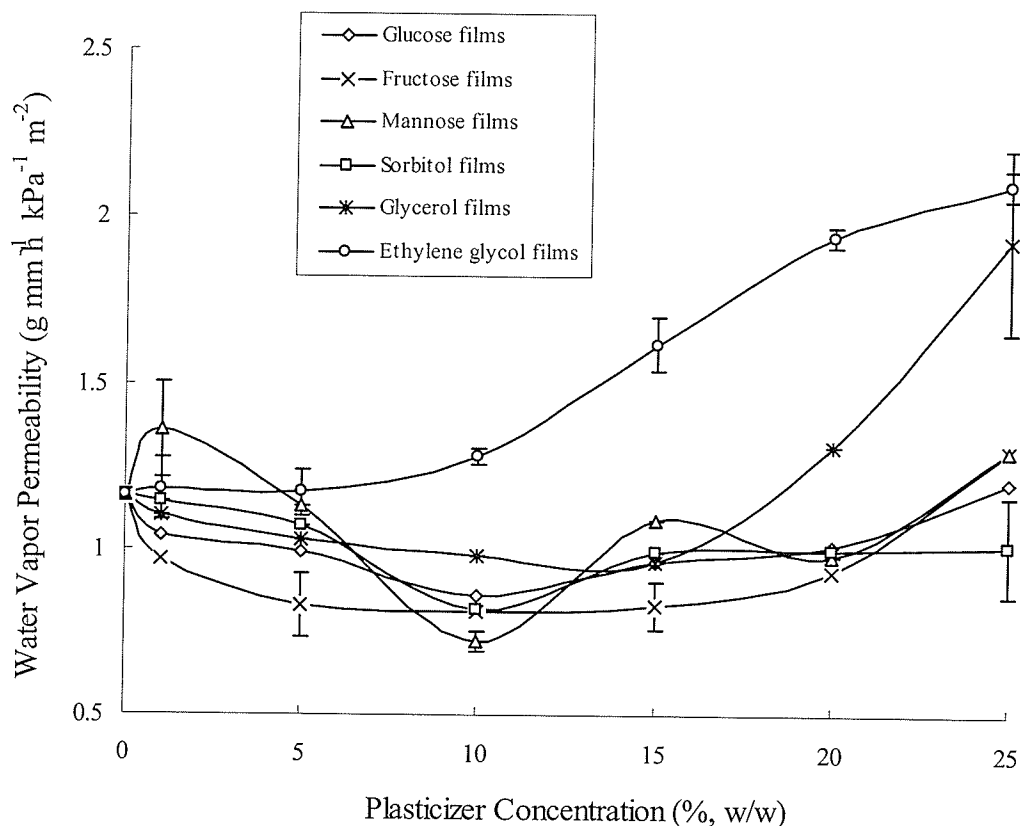
Fig. 6.5 Oxygen permeability of the pea starch film and the plasticizer concentration.

Bars indicate mean \pm standard deviation (Not all the error bars were added in order to clarify the figure)

Fig. 6.6 and Appendix 6.4 show that WVP reduced from $1.2 \text{ g mm m}^{-2} \text{ h}^{-1} \text{ kPa}^{-1}$ for the film without plasticizer to their minimal values ($0.7 - 0.9 \text{ g mm m}^{-2} \text{ h}^{-1} \text{ kPa}^{-1}$) at around 10 % plasticizer concentration. This result was found in monosaccharide- and sorbitol-plasticized films, while glycerol- and ethylene glycol-plasticized films did not change their WVP at range from 0 to 15 % concentration. Above 10 % plasticizer, WVP of all

2730 films increased with the addition of plasticizers regardless of plasticizer types. This is
very similar to the OP trend. According to Laohakunjit and Noomhorm (2004), when
glycerol concentration level is high ($\geq 30\%$), glycerol-films usually possess higher WVP
than other plasticizer-films. At low and intermediate concentration level ($< 30\%$
glycerol), glycerol-films showed similar WVP to other films. This phenomenon is in
2735 agreement with the present study. This phenomenon was probably due to the fact that
most hydrogen bonds in glycerol molecules being occupied by the starch polymer chains
when glycerol was used at low and intermediate concentration ($< 30\%$ glycerol).
Therefore, glycerol molecules lost their hygroscopicity which promotes the permeation of
water molecules (Laohakunjit and Noomhorm 2004). Maeda and Paul (1987) figured out
2740 that the gas permeability of a synthetic polymer initially decreased as plasticizers were
added to the polymer, going through a minimum and then increased with more
plasticizers.

2745



2750 Fig. 6.6 Water vapor permeability of the pea starch film and the plasticizer concentration.

Bars indicate mean \pm standard deviation (Not all the error bars were added in order to clarify the figure)

Tensile properties

2755 Fig. 6.7 and Appendices 6.5 - 6.6 show the elongation-at-break (E), tensile strength (TS) and the modulus of elasticity (EM) for pea starch films with various types and concentration of plasticizers. E of pea starch films shows a concave function with plasticizer concentration for all plasticizers. This indicates antiplasticization effects at low concentration ($< 10 - 20\%$) of monosaccharide and polyol plasticizers in pea starch

2760 films. From previous data using over $25 - 30\%$ of plasticizers, E increased when

plasticizer concentration increased. Among all plasticizers, mannose- and fructose-plasticized pea starch films have noticeable lowest E value at 10 % and 20 % concentration, respectively. These results are similar to Gaudin and others (1999), who made wheat starch films plasticized by sorbitol, and Chang and others (2006), who made
2765 tapioca starch films plasticized by glycerol. Gaudin and others (1999) found that sorbitol had antiplasticization effect on elongation when its concentration was below 27 %, while Chang and others (2006) found glycerol antiplasticization effect when it was at below 10 %. Lourdin and others (1997) also found the glycerol at around 12 % functioned antiplasticization on starch films. However, Suyatma and others (2005) found ethylene
2770 glycol had mechanical antiplasticization effect on chitosan films at 5 % concentration. This is slightly different from the present results. The reason is probably due to the difference in the starch matrix.

Fig. 6.7 does not show the antiplasticization effect of the plasticizers on TS within the
2775 experimental range of plasticizer concentration. The addition of plasticizers decreased TS due to the reduction of the interaction between the polymers. From Fig. 6.1 and Appendix 6.1, it is known that most of the starch film is amorphous. When the tensile stress was applied to the starch films, the amorphous area was deformed and extended until it was broken. The crystallite was not fractured. The more plasticizer was added into the film,
2780 the weaker interaction between the polymers in the amorphous area increased, leading to the decrease in TS of the film

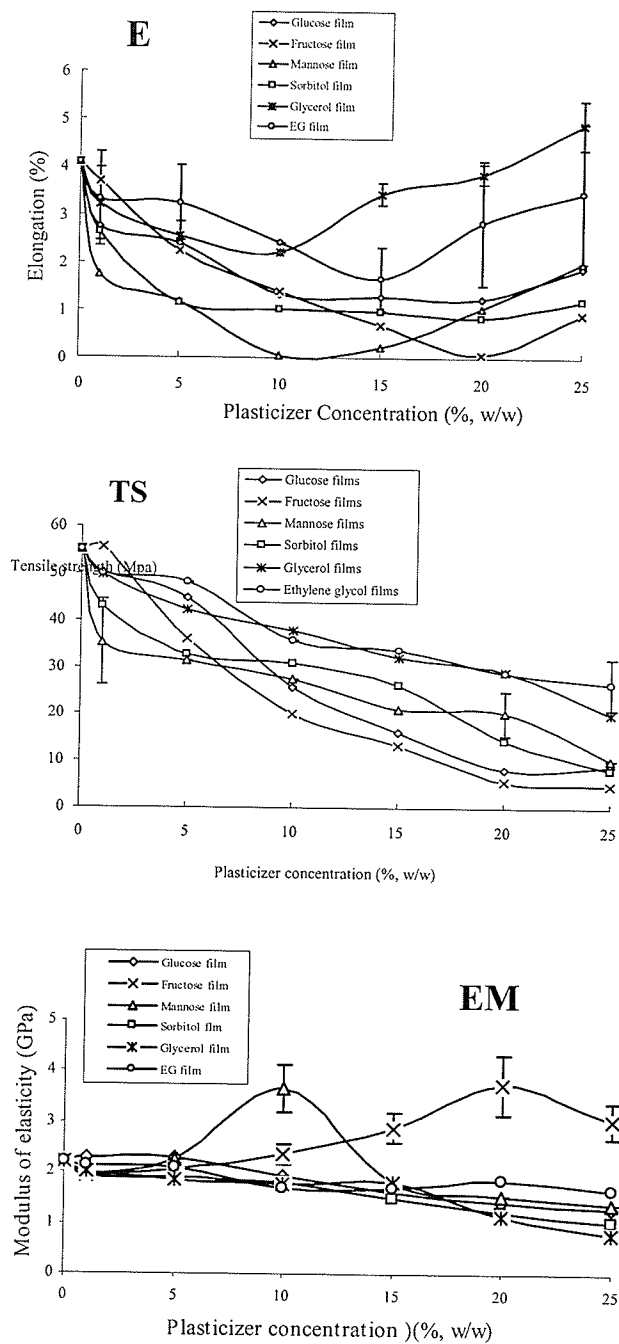


Fig. 6.7 E, TS, and EM of the pea starch film and the plasticizer concentration. Bars indicate mean \pm standard deviation (Not all the error bars were added in order to clarify the figure)

2795 Mannose- and fructose-plasticized films have the greatest EM values at 10 % and 20 %
of corresponding plasticizers. Regarding the results of E of mannose- and fructose-
plasticized films, the films show increased EM and decreased E at 10 % and 20 %
consistently, indicating antiplasticization effect at 10 % and 20 % of mannose and
fructose concentration, respectively. Besides these two plasticizers, all others show slight
2800 decrease in EM when plasticizer concentration increased.

Polyols did not have obvious antiplasticization effect on EM. Chang and others (2006)
reported that 5 % glycerol had antiplasticization effect on EM for tapioca starch film
when film a_w was bigger than 0.57.

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Effects of crystallinity changes on physical and mechanical properties

Fig. 6.8 illustrates the correlation between physical and mechanical property variables
and crystallinity of pea starch films regardless of concentrations of plasticizers. X-axis of
graphs is the crystallinity data of each film obtained from Appendix 6.1, and Y-axis is
2810 properties of corresponding films presented in Appendices 6. 2 - 6.7. To simplify the
illustration, standard deviations of variables were not displayed in Fig. 6.8. Changes in
crystallinity ranging from 2 % to 20 % did not affect MC of pea starch films. From
previous experiments (Table 4.2), the MC of 198 % (w/w) sorbitol-plasticized film was
12 %. And its film had crystallinity of 0.59 % (Table 4.7). Therefore, it is observed that

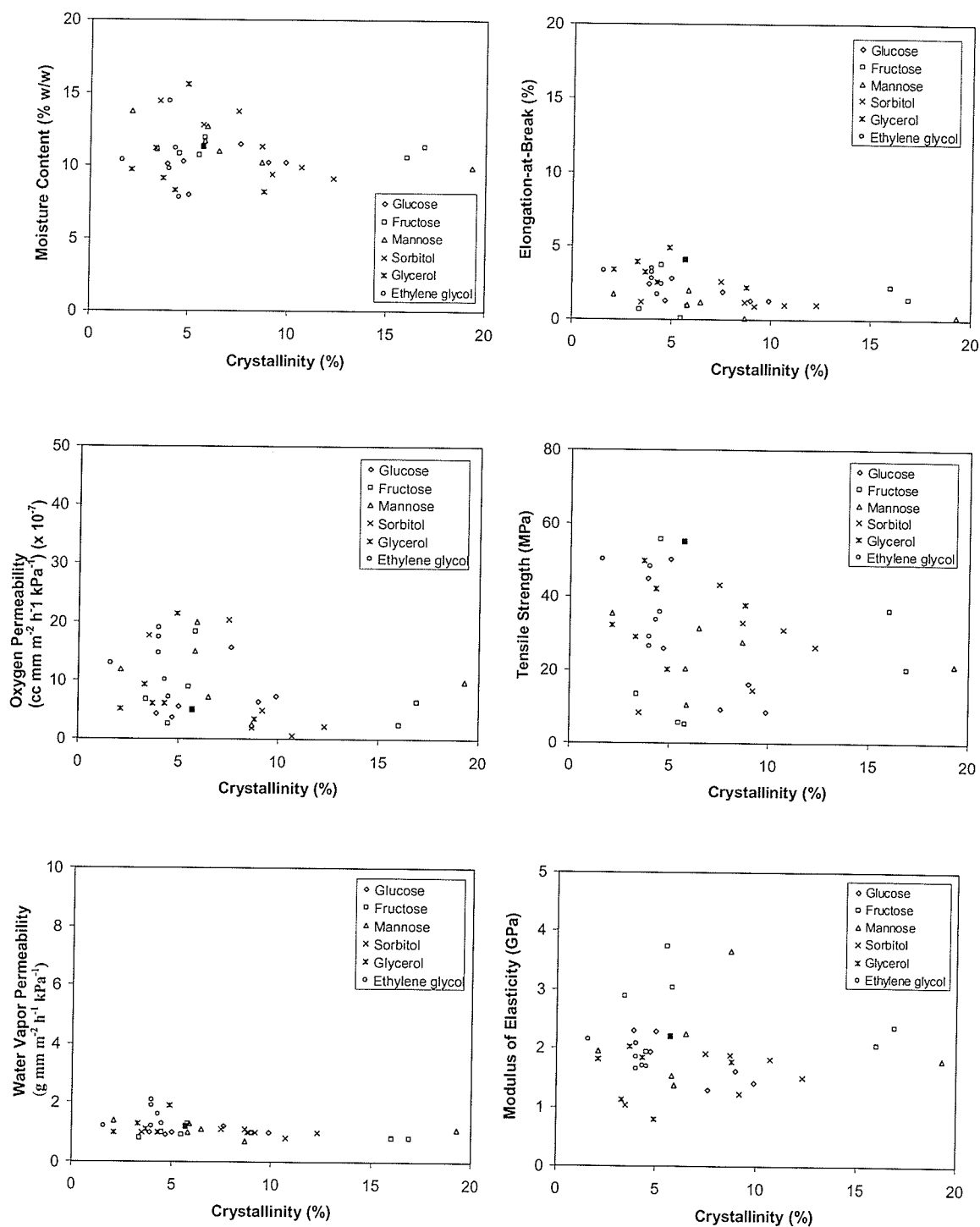


Fig. 6.8 Correlation between the physical or mechanical properties and crystallinity of the films

the MC of sorbitol-plasticized pea starch film is not sensitive to the change in crystallinity. The MC of 100 % (w/w) glycerol-film was 52.2 % (Table 4.2) which is higher than the MC of 0 - 25 % (w/w) glycerol-film. However, the glycerol-films are similar in crystallinity. It is assumed that the high MC in 100 % (w/w) glycerol-film is
2825 due to the high content of glycerol in 100 % (w/w) glycerol-film.

The change in gas barrier property in starch films is generally believed to relate to the film crystallinity. Increase in crystallites in the films made the films denser. Therefore, oxygen or water molecules diffused slower within the starch films, causing a decrease in
2830 diffusivity of the gas. Permeability is defined as the product of the coefficients of solubility and diffusion (Han and Scanlon 2005). The low diffusion of oxygen and water vapor resulted in low OP and WVP. However, the OP and WVP in Fig. 6.8 did not relate to the crystallinity of films. WVP has very small deviation ($0.7 - 1.9 \text{ g mm m}^{-2} \text{ h}^{-1} \text{ kPa}^{-1}$) with respect to the crystallinity compared to that of OP ($0.6 - 20.4 \text{ cc mm m}^{-2} \text{ h}^{-1} \text{ kPa}^{-1}$)
2835 within the experimental range of crystallinity changes. This conclusion is controversial to the theory in synthetic polymers that increase in crystallinity usually leads to a decrease in gas permeability (Forssell and others 2002). The heterogeneous nature of pea starch films and narrow range of crystallinity (2 - 20 %) would cause difficulties in identifying the permeability dependency on crystallinity compared to that of homogeneous synthetic
2840 films. Most parts of starch film are amorphous ($> 80 \%$). Therefore, the increase in crystallinity from 2 % to 20 % may not affect the mass transfer rate of gases through amorphous area. Pure starch film without any plasticizer has 5.7 % of crystallinity. From the OP result graph, it is found that at crystallinity around 5.7 %, the pure starch film has

the lowest OP value compared with OP of other plasticized films in spite of the same (5.7
2845 %) crystallinity. This result may be interpreted that the plasticizers (i.e., fructose and
mannose) facilitated oxygen transfer passage in amorphous area, and consequently OP
increases.

Elongation-at-break was not significantly affected by crystallinity in this study. Within
2850 the changing range of crystallinity in this study (i.e., 2 - 20 %), E values of pea starch
varied from 0.1 to 4.9 %. At 5.7 % of crystallinity, the pure starch film without any
plasticizer had the highest E among other films which have 5.7 % of crystallinity. The
addition of plasticizers in these films decreased the interaction between starch polymers
in the amorphous area and reduced E value. At the 5.7 % of crystallinity, the pure starch
2855 film had the greatest value of TS compared with TS of other plasticized-films which have
5.7 % of crystallinity. This result indicates that the plasticizers (i.e., fructose and
mannose) positioned in amorphous area of starch decreased interaction of starch
polymers during deformation, and reduced the force required to fracture the starch film.
Plasticizer affects the resistance of polymers to the deformation negatively.

Suggested mechanism of plasticization and retrogradation

It has been accepted that plasticization is happening when plasticizers intersperse into
starch polymer matrix and interfere with starch polymer chain alignment, leading to the
increase in the free volume of starch matrix. Starch retrogradation is caused by
2865 intermolecular hydrogen bondings between the starch polymer chains. Tako and Hizukrui
(2000, 2002) have proposed a mechanism for the retrogradation of potato starch. The

transformation from plasticization phase to retrogradation phase will be further discussed at a molecular level in the following paragraph based on Tako and Hizukrui's theory (2000, 2002). Glycerol is chosen as a representative.

2870

Among the three hydroxyl groups in a D-glucosyl residue of starch molecules, the primary hydroxyl group (CH_2OH) has a stronger binding capacity than the secondary hydroxyl groups (Godbillot and others 2006). For plasticizing model, the water and glycerol molecules cross-link with D-glucosyl residues, as shown in Fig. 6.9.

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Intermolecular hydrogen bondings between O-6 of D-glucosyl residue of amylose or amylopectin molecule and OH^- of water molecules occurred. The OH^- of the water molecules cross-linked with $\text{OH}-2$ of D-glucosyl residues of another amylose or amylopectin molecule on the other side. Glycerol molecules formed hydrogen bondings with water molecules. The assembly is like a sandwich inside which the water and

2880

glycerol molecules are squeezed. This plasticizing model can be destroyed due to the mobility of the segments of starch polymer chains. During the movement or vibration of the starch polymer chains, water and glycerol molecules were pushed aside gradually. O-6 of D-glucosyl residues of the amylose or amylopectin molecule and $\text{OH}-2$ of the D-glucosyl residues of another amylose or amylopectin molecule, which used to be

2885

separated by water or glycerol molecules, interacted to form strong hydrogen bonding, as shown in Fig. 6.10. In this situation, retrogradation of starch polymer chains is assumed to occur. The other plasticizers used in present study, i. e. EG, sorbitol, glucose, fructose, and mannose, would interact with starch polymer chains in the same way as glycerol.

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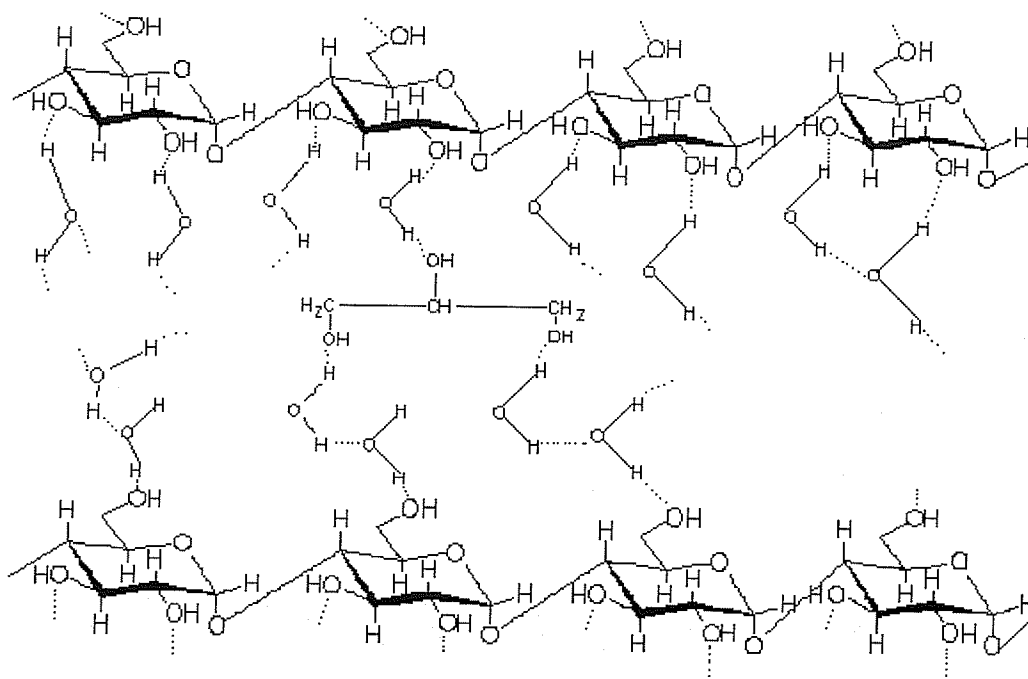
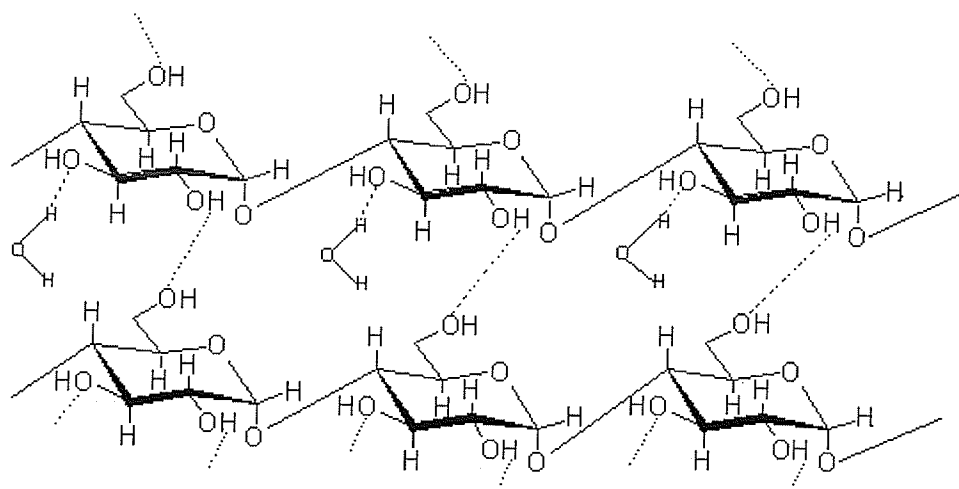


Fig. 6.9 Plasticization of pea starch film with water and glycerol. Dotted lines are hydrogen bonds.

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2900



2905 Fig. 6.10 Recrystallization of pea starch film. Dotted lines are hydrogen bonds.

According to the preceding discussions, three phase transitions, i. e. gelation, plasticization, and retrogradation, for starch polymers transforming from gel to crystal can be assumed consequently. At gelation phase, a huge amount of plasticizer molecules
 2910 intersperse between the starch polymers. The starch system appears to be a soft solid. During plasticization, most of water molecules have been evaporated. The starch system is dried out and becomes starch film. However, between the starch polymers, there are still a lot of plasticizer molecules, water and glycerol molecules, leading to a large distance and free volume between the starch polymer chains. The starch film exists in
 2915 amorphous state and has low T_g . The mobility or vibration of the segments of starch polymer chains is vigorous. Starch films are flexible. During retrogradation, the amount of plasticizer molecules between the starch polymers decreases extremely because of the

mobility or vibration of the starch polymers. The direct interaction between the starch polymers is established, leading to the reduction in the free volume in the starch film. The mobility or vibration of the starch polymers slows down or even quits. The film then has high T_g and appears brittle. These three phases are shown in Fig. 6.11.

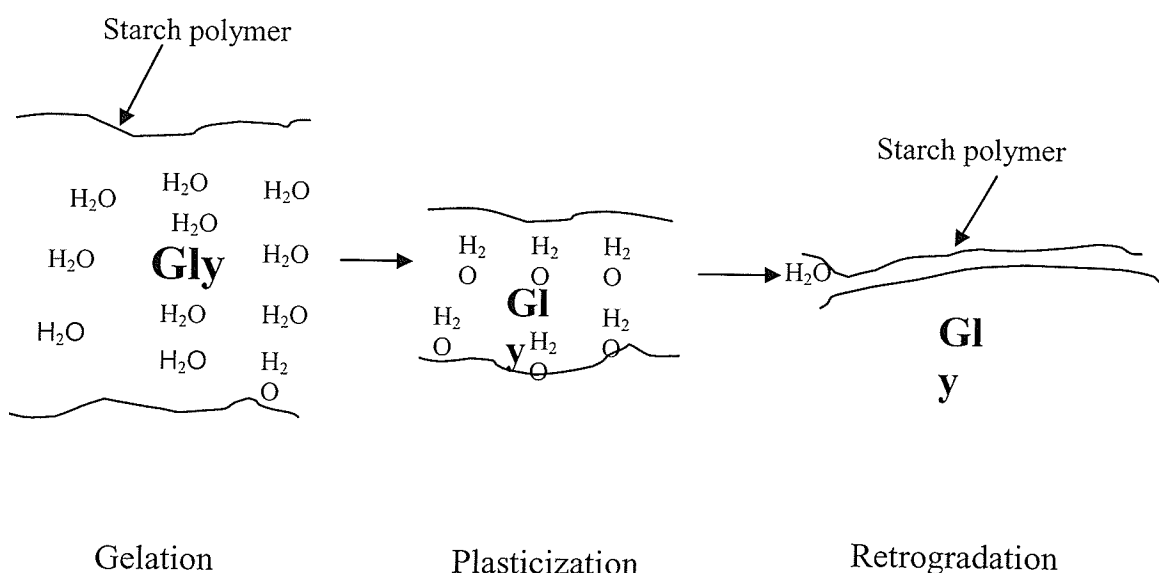


Fig. 6.11 Three phases transformations of starch films

CONCLUSION

The crystallinity of the pea starch films increased with the increase in plasticizer concentration from 1 % to 20 %. X-ray diffraction patterns showed the films with 10 - 20 % plasticizer concentration had higher crystallinity than the films with lower than 10 % or higher than 20 % plasticizer. Consequently, the MC, OP, WVP, and E decreased when the plasticizer increased from 5 to 20 %, while EM increased for the monosaccharide-films, showing the antiplasticization effect of the plasticizer at low and intermediate

concentration range. Plasticizer has plasticization or antiplasticization effect depending
2935 on its concentration. It can be finally concluded that the addition of plasticizers at the
range of low to intermediate concentration level facilitate the formation of crystallites in
the starch films, leading to the antiplasticization phenomenon.

Appendix 6.1 Crystallinity (%) of pea starch films affected by the plasticizer concentration

Plasticizer						
concentration	Glucose	Fructose	Mannose	Sorbitol	Glycerol	Ethylene glycol
% (w/w)						
0	5.7±1.73 ^{bx}	5.7±1.73 ^{cx}	5.7±1.73 ^{bx}	5.7±1.73 ^{bx}	5.7±1.73 ^{cx}	5.7±1.73 ^{dx}
1	5.00±1.41 ^{bz}	4.5±0.89 ^{byz}	2.1±0.16 ^{ax}	7.5±2.35 ^{bcz}	3.7±0.43 ^{by}	1.6±0.20 ^{aw}
5	3.9±0.23 ^{ax}	16.0±1.56 ^{dz}	6.5±0.52 ^{cy}	8.7±1.16 ^{cy}	4.3±0.73 ^{bcx}	4.0±0.30 ^{bx}
10	4.7±0.26 ^{bw}	16.9±0.61 ^{dz}	8.7±0.99 ^{dx}	10.7±0.22 ^{dy}	8.8±2.66 ^{dx}	4.5±0.38 ^{bw}
15	9.00±1.39 ^{dy}	3.4±0.94 ^{ax}	19.3±2.98 ^{ez}	12.3±2.37 ^{ey}	2.1±0.27 ^{ax}	4.3±0.32 ^{bx}
20	9.9±1.35 ^{dz}	5.5±0.37 ^{cy}	5.8±0.43 ^{by}	9.2±0.91 ^{cdz}	3.3±0.18 ^{bx}	4.0±0.75 ^{bx}
25	7.6±0.89 ^{cz}	5.8±0.24 ^{cz}	5.9±0.73 ^{bz}	3.5±0.53 ^{ax}	4.9±0.31 ^{cy}	4.0±0.56 ^{bx}

Values are means ± standard deviation (n = 3). The values bearing different superscripts differ significantly (p < 0.05) using Tukey test. a, b, and c are for the comparison of within columns (plasticizer concentration), and x, y, and z are for the between columns (types of plasticizers).

Appendix 6.2 Moisture content of pea starch films (% , d.b) affected by the plasticizer concentration

Plasticizer concentration % (w/w)	Glucose	Fructose	Mannose	Sorbitol	Glycerol	Ethylene glycol
0	11.3±1.02 ^{cx}	11.3±1.02 ^{bx}	11.3±1.02 ^{cx}	11.3±1.02 ^{bx}	11.3±1.02 ^{cx}	11.3±1.02 ^{dx}
1	8.0±0.88 ^{aw}	10.8±0.01 ^{ax}	13.7±1.30 ^{dy}	13.7±0.17 ^{dy}	9.1±0.52 ^{abwx}	10.4±0.31 ^{cx}
5	10.1±0.28 ^{bxy}	10.6±0.92 ^{axy}	11.0±1.49 ^{aby}	14.4±1.35 ^{ez}	8.3±1.28 ^{ax}	9.8±0.76 ^{bx}
10	10.3±0.43 ^{by}	11.3±0.60 ^{bz}	10.2±0.41 ^{ay}	12.8±0.78 ^{cz}	8.2±0.57 ^{ax}	7.8±2.32 ^{ax}
15	10.2±0.32 ^{by}	11.1±0.10 ^{bz}	9.9±0.89 ^{ay}	9.9±0.68 ^{aby}	9.7±0.69 ^{by}	11.2±0.90 ^{dz}
20	10.2±0.33 ^{by}	10.7±0.10 ^{ay}	11.7±0.46 ^{by}	9.1±0.78 ^{ax}	11.2±3.02 ^{cy}	14.4±1.34 ^{ez}
25	11.5±0.45 ^{cy}	11.9±0.76 ^{by}	12.7±1.05 ^{cdy}	9.4±0.89 ^{ax}	15.6±1.77 ^{dz}	15.0±2.01 ^{fz}

Values are means ± standard deviation (n = 3). The values bearing different superscripts differ significantly (p < 0.05) using Tukey test. a, b, and c are for the comparison of within columns (plasticizer concentration), and x, y, and z are for the between columns (types of plasticizers).

Appendix 6.3 Oxygen permeability ($\text{cc mm m}^{-2} \text{ h}^{-1} \text{ kPa}^{-1}$) $\times 10^{-7}$ of pea starch films affected by the plasticizer concentration

Plasticizer concentration % (w/w)	Glucose	Fructose	Mannose	Sorbitol	Glycerol	Ethylene glycol
0	5.0 \pm 2.63 ^{cx}	5.0 \pm 2.63 ^{bx}	5.0 \pm 2.63 ^{bx}	5.0 \pm 2.63 ^{cx}	5.0 \pm 2.63 ^{bx}	5.0 \pm 2.63 ^{ax}
1	5.5 \pm 0.41 ^{cx}	2.6 \pm 0.32 ^{aw}	11.9 \pm 3.42 ^{ey}	20.4 \pm 5.65 ^{dz}	6.1 \pm 2.36 ^{cx}	13.0 \pm 2.83 ^{cdy}
5	4.3 \pm 0.11 ^{bx}	2.4 \pm 0.11 ^{aw}	7.2 \pm 0.99 ^{cy}	1.9 \pm 0.29 ^{bw}	6.1 \pm 2.35 ^{cy}	14.7 \pm 3.22 ^{cdz}
10	3.7 \pm 0.32 ^{ay}	6.4 \pm 3.27 ^{cz}	2.4 \pm 0.07 ^{ax}	0.6 \pm 0.11 ^{aw}	3.4 \pm 0.30 ^{ay}	7.2 \pm 4.77 ^{abz}
15	6.3 \pm 0.77 ^{dw}	6.8 \pm 1.51 ^{cw}	9.8 \pm 1.00 ^{dy}	2.1 \pm 0.68 ^{bx}	5.1 \pm 0.37 ^{bw}	10.1 \pm 6.31 ^{bcy}
20	7.3 \pm 2.53 ^{ey}	8.9 \pm 1.77 ^{dy}	15.0 \pm 3.44 ^{fz}	4.9 \pm 0.66 ^{cx}	9.3 \pm 2.03 ^{dy}	17.4 \pm 5.54 ^{cdz}
25	15.7 \pm 3.07 ^{fx}	18.3 \pm 4.92 ^{ex}	19.9 \pm 5.60 ^{gxy}	17.7 \pm 6.71 ^{dx}	21.4 \pm 10.78 ^{ey}	19.0 \pm 2.22 ^{dxy}

Values are means \pm standard deviation ($n = 2$). The values bearing different superscripts differ significantly ($p < 0.05$) using Tukey test. a, b, and c are for the comparison of within columns (plasticizer concentration), and x, y, and z are for the between columns of plasticizers).

2950 (types

Appendix 6.4 Water vapor permeability ($\text{g mm m}^{-2} \text{ h}^{-1} \text{ kPa}^{-1}$) of pea starch films affected by the plasticizer concentration

Plasticizer concentration % (w/w)	Glucose	Fructose	Mannose	Sorbitol	Glycerol	Ethylene glycol
0	$1.2 \pm 0.13^{\text{cx}}$	$1.2 \pm 0.13^{\text{bx}}$	$1.2 \pm 0.13^{\text{cx}}$	$1.2 \pm 0.13^{\text{dx}}$	$1.2 \pm 0.13^{\text{cx}}$	$1.2 \pm 0.13^{\text{ax}}$
1	$1.0 \pm 0.11^{\text{abx}}$	$1.0 \pm 0.13^{\text{ax}}$	$1.4 \pm 0.14^{\text{dy}}$	$1.1 \pm 0.04^{\text{cdx}}$	$1.1 \pm 0.16^{\text{bx}}$	$1.2 \pm 0.09^{\text{axy}}$
5	$1.0 \pm 0.03^{\text{bx}}$	$0.8 \pm 0.10^{\text{ax}}$	$1.1 \pm 0.03^{\text{bx}}$	$1.1 \pm 0.02^{\text{bx}}$	$1.0 \pm 0.03^{\text{ax}}$	$1.2 \pm 0.07^{\text{ax}}$
10	$0.9 \pm 0.01^{\text{ax}}$	$0.8 \pm 0.04^{\text{ax}}$	$0.7 \pm 0.05^{\text{ay}}$	$0.8 \pm 0.04^{\text{ax}}$	$1.0 \pm 0.39^{\text{ax}}$	$1.3 \pm 0.03^{\text{az}}$
15	$1.0 \pm 0.06^{\text{bx}}$	$0.8 \pm 0.07^{\text{ay}}$	$1.1 \pm 0.40^{\text{bx}}$	$1.0 \pm 0.00^{\text{bx}}$	$1.0 \pm 0.21^{\text{ax}}$	$1.6 \pm 0.08^{\text{bz}}$
20	$1.0 \pm 0.10^{\text{bx}}$	$0.9 \pm 0.06^{\text{abx}}$	$1.0 \pm 0.06^{\text{bx}}$	$1.0 \pm 0.10^{\text{bx}}$	$1.3 \pm 0.00^{\text{cy}}$	$1.9 \pm 0.03^{\text{cz}}$
25	$1.2 \pm 0.12^{\text{cx}}$	$1.3 \pm 0.10^{\text{cx}}$	$1.3 \pm 0.07^{\text{cdx}}$	$1.0 \pm 0.15^{\text{by}}$	$1.9 \pm 0.28^{\text{dz}}$	$2.1 \pm 0.05^{\text{dz}}$

Values are means \pm standard deviation ($n = 3$). The values bearing different superscripts differ significantly ($p < 0.05$) using Tukey test. a, b, and c are for the comparison of within columns (plasticizer concentration), and x, y, and z are for the between columns (types of plasticizers).

2955 Appendix 6.5 Elongation at break (%) of pea starch films affected by the plasticizer concentration

Plasticizer concentration % (w/w)	Glucose	Fructose	Mannose	Sorbitol	Glycerol	Ethylene glycol
0	4.1±1.11 ^{dx}	4.1±1.11 ^{fx}	4.1±1.11 ^{ex}	4.1±1.11 ^{dx}	4.1±1.11 ^{ex}	4.1±1.11 ^{dx}
1	2.8±0.66 ^{cy}	3.7±0.81 ^{ez}	1.7±0.71 ^{cx}	2.6±1.24 ^{cy}	3.2±0.76 ^{by}	3.3±0.98 ^{cyz}
5	2.4±0.17 ^{cy}	2.2±0.06 ^{dy}	1.2±0.39 ^{bx}	1.2±0.13 ^{bx}	2.5±0.32 ^{ay}	3.2±0.78 ^{cz}
10	1.3±0.42 ^{ay}	1.4±0.41 ^{cy}	0.1±0.01 ^{ax}	1.0±0.36 ^{ay}	2.2±0.30 ^{az}	2.4±1.11 ^{bz}
15	1.3±0.55 ^{ay}	0.7±0.02 ^{bx}	0.2±0.07 ^{aw}	1.0±0.14 ^{ax}	3.4±0.23 ^{bz}	1.7±0.65 ^{ay}
20	1.3±0.10 ^{ax}	0.1±0.01 ^{aw}	1.0±0.25 ^{bx}	0.9±0.20 ^{ax}	3.9±0.22 ^{bcz}	2.8±1.31 ^{bcy}
25	1.9±0.39 ^{by}	0.9±0.28 ^{bw}	2.0±0.18 ^{dy}	1.2±0.10 ^{bx}	4.9±0.51 ^{dz}	3.5±1.46 ^{cdz}

Values are means ± standard deviation (n = 6). The values bearing different superscripts differ significantly (p < 0.05) using Tukey test. a, b, and c are for the comparison of within columns (plasticizer concentration), and x, y, and z are for the between columns (types of plasticizers).

2960 Appendix 6.6 Tensile strength (MPa) pea starch films affected by the plasticizer concentration

Plasticizer concentration % (w/w)	Glucose	Fructose	Mannose	Sorbitol	Glycerol	Ethylene glycol
0	55.0±8.70 ^{fx}	55.0±8.70 ^{ex}	55.0±8.70 ^{dx}	55.0±8.70 ^{fx}	55.0±8.70 ^{fx}	55.0±8.70 ^{efx}
1	50.2±6.20 ^{eyz}	55.7±8.57 ^{ez}	35.4±9.16 ^{cx}	43.1±12.43 ^{exy}	49.7±3.66 ^{efy}	50.1±5.64 ^{dey}
5	44.9±4.98 ^{dy}	36.1±5.33 ^{dxy}	31.4±1.76 ^{cx}	32.7±6.78 ^{dx}	42.2±7.16 ^{dexy}	48.3±4.88 ^{cdy}
10	25.9±7.78 ^{cxy}	20.1±3.17 ^{cx}	27.6±5.38 ^{bexy}	30.9±5.15 ^{cdy}	37.7±6.66 ^{cdz}	35.7±11.18 ^{bczy}
15	16.1±2.56 ^{bxy}	13.4±2.42 ^{bx}	21.1±3.41 ^{bxy}	26.3±3.47 ^{cy}	32.1±5.13 ^{bcz}	33.7±8.65 ^{bz}
20	8.4±1.77 ^{ax}	5.6±0.04 ^{aw}	20.3±4.71 ^{bz}	14.4±6.86 ^{by}	29.1±4.65 ^{bz}	28.9±9.03 ^{az}
25	9.0±2.41 ^{ax}	5.0±0.22 ^{aw}	10.3±3.75 ^{ax}	8.3±0.94 ^{ax}	20.1±1.86 ^{ay}	26.4±5.42 ^{az}

Values are means ± standard deviation (n = 6). The values bearing different superscripts differ significantly (p < 0.05) using Tukey test. a, b, and c are for the comparison of within columns (plasticizer concentration), and x, y, and z are for the between columns (types of plasticizers).

Appendix 6.7 Modulus of elasticity (MPa) of pea starch films affected by the plasticizer concentration

Plasticizer concentration % (w/w)	Glucose	Fructose	Mannose	Sorbitol	Glycerol	Ethylene glycol
0	2210±151 ^{cx}	2210±151 ^{ax}	2210±151 ^{bx}	2210±151 ^{cdx}	2210±151 ^{cx}	2210±151 ^{cx}
1	2290±116 ^{cy}	1940±420 ^{ax}	1950±171 ^{bx}	1910±206 ^{cx}	2030±31 ^{cx}	2150±100 ^{bctx}
5	2300±44 ^{cy}	2060±178 ^{ax}	2240±32 ^{by}	1880±64 ^{cx}	1840±140 ^{bx}	2090±291 ^{bx}
10	1930±352 ^{cx}	2360±200 ^{abxy}	3660±465 ^{cy}	1810±48 ^{cx}	1770±163 ^{bx}	1690±170 ^{ax}
15	1610±44 ^{bx}	2890±306 ^{by}	1800±283 ^{abx}	1500±157 ^{bx}	1820±233 ^{bcx}	1710±94 ^{ax}
20	1410±33 ^{ax}	3740±604 ^{cz}	1530±339 ^{axy}	1220±655 ^{abx}	1130±186 ^{ax}	1860±55 ^{aby}
25	1290±158 ^{ax}	3040±341 ^{bcz}	1370±500 ^{ax}	1030±323 ^{awx}	790±47 ^{aw}	1650±166 ^{ay}

Values are means ± standard deviation (n = 6). The values bearing different superscripts differ significantly (p < 0.05) using Tukey test. a, b, and c are for the comparison of within columns (plasticizer concentration), and x, y, and z are for the between columns (types of plasticizers).

General Discussion and Conclusion

From the results of chapter 3 and 4, it appears that monosaccharides behaved as good plasticizers at 4.34 to 10.87 mmol per g starch concentration range. They made starch films have higher tensile strength and elongation, lower gas permeability (WVP and OP), suggesting monosaccharide-films had dense and compact structure and be potential in practical applications. Mali and others (2005b), Garcia and others (2000), and Ryu and others (2002) found that sorbitol films had less moisture content and were stronger than glycerol film. They attributed this phenomenon to the fact that sorbitol is more similar in structure to the anhydroglucose of starch molecules than glycerol. Monosaccharide exists in pyranose or furanose ring which mostly match the structure of the anhydroglucose of the starch polymer and can easily pack into the starch polymer chains, leading to the dense and compact structure of the film. Fig.4.12 and Fig.4.13 show this two different plasticizations. As a representative of polyols, glycerol had a different plasticization mechanism. From chapter 3, 4, and 5, glycerol-films contained moisture 2 to 4.5 times those of monosaccharide- and sorbitol-films. And as glycerol content increased, the moisture content of the glycerol-film increased dramatically. This evidence meant glycerol acted as an agent that attracted and held a large amount of water molecules by hydrogen bonds. These attracted and held waters contributing to the plasticization effect in the glycerol-films. Fig.6.9 shows glycerol plasticization mechanism. Fang and Hanna (2000) pointed out that water absorption characteristic is highly related to the polarity of

the blend of plasticizer and polymer. The highest MC of glycerol-plasticized starch films is due to the high polarity of glycerol (dielectric constant of 42.5 at 25 °C) (Yang and Paulson 2000). Sorbitol has a dielectric constant of 33.5 at 80 °C (Arvanitoyannis and
2995 others 1997).

When undergoing thermomechanical test, glycerol-films had lower glass transition temperature (T_g) and less apparent activation energy (ΔH_a), indicating glycerol-films had more free volume and glycerol was an effective plasticizer. Jangchud and Chinnan
3000 (1999) attributed this high plasticization efficiency to the fact that glycerol has smaller size molecule and higher ratio of hydroxyl group number to its molecular weight (0.0326). Glucose-films had much higher ΔH_a . This was attributed to glucose's identical structure and configuration to the anhydroglucose units in the starch chains. Glucose's identical structure and configuration made it easier to pack into starch polymers and
3005 lessen the free volume in the glucose-films, leading to the limited mobility of the starch polymers.

Although glycerol acts as a better plasticizer in light of its thermal properties (has low T_g and ΔH_a), it does not mean glycerol can provide better mechanical properties to the
3010 starch film. Monosaccharides are more valuable in practice, because they make films stronger and more resistant to the gases. For application in the food packaging, the specific requirements for the food should be considered. For example, for frozen food, glycerol film is preferred because of its low T_g . Otherwise, monosaccharides should be considered as plasticizer candidates.

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Chapter 5 shows Flory-Huggins equation fitted sorption isotherm experimental data better for monosaccharide-plasticized films, indicating the molecular interaction between waters in the film was stronger than that between water and starch matrix. And this interaction between water and water played a major role in the film sorption isotherm.

3020 GAB model fitted the experimental data very well for fructose-, mannose-, and glycerol-films. The crystallization phenomenon occurred in glucose- and sorbitol films made GAB model fit badly.

Experimental data in chapter 6 shows that antiplasticization of the starch films was
3025 induced by the plasticizer in low to intermediate concentration (5 - 20 %). Crystallinity of the film, determined by X-ray diffraction, was increased with increase in plasticizer in this range. This range is similar to the findings by Smits and others (2003) who observed that potato starch with 23.1 % plasticizer (EG and glycerol) had higher crystallinity than the starch without plasticizer. As a result, MC, OP, WVP, and E decreased with increase
3030 in plasticizer content at this plasticizer range. When plasticizer content was over 20 %, plasticizer played a plasticization effect. Garcia and others (2000) assumed the mechanism of the recrystallization induced by plasticizer. The plasticizers favored the mobility or vibration of the starch polymer segments. This mobility or vibration facilitated starch polymers to push aside the plasticizer molecules positioned between the
3035 starch chains. Without the hindrance from the plasticizers, the starch chains aligned up to form crystal lattices. When plasticizer concentration was above 20 %, plasticizer could

distribute evenly in the starch matrix. It became hard for starch polymers to push aside the plasticizers completely from the space between them.

3040 Based on the principle of Tako and Hizukrui (2000, 2002), the hydrogen bondings between O-6 of D-glucosyl residue of amylose or amylopectin molecule and OH- of water molecules occurred. The OH- of the water molecules cross-linked with OH-2 of D-glucosyl residues of another amylose or amylopectin molecule on the other side. Plasticizer molecules formed hydrogen bondings with water molecules. During the
3045 movement or vibration of the starch polymer chains, water and plasticizer molecules were pushed aside gradually. O-6 of D-glucosyl residues of the amylose or amylopectin molecule and OH-2 of the D-glucosyl residues of another amylose or amylopectin molecule, which used to be separated by water or plasticizer molecules, interacted to form strong hydrogen bonding. Retrogradation of starch polymers occurred.

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Suggested mechanism of plasticizers in starch films consist of: (i) plasticizers should be distributed evenly in starch molecules and positioned between starch polymers; (ii) for the even distribution, plasticizers should be at a certain level (20 %) to prevent retrogradation; (iii) plasticizers should establish a stable interaction with starch polymers
3055 in order to prevent the phase separation of plasticizers from starch matrix; (iv) plasticizers should create certain size of free volume in starch polymers by the molecular size of plasticizers or the hydrodynamic size of hydrated plasticizers; Generally, the plasticizer which can provide higher ratio of hydroxyl number to its molecular weight can be considered as a better plasticizer. Therefore, the best plasticizer should be water which

3060 can provide ratio of 0.056. However, water is very hard to control in the film, because it
totally depends on the relative humidity (RH). The second best plasticizers should be
glycerol and EG which provide ratios of 0.033 and 0.032, respectively. Although sorbitol
has ratio of 0.033, its molecule size is almost double big that of glycerol. So, sorbitol
plasticization capacity is reduced. Monosaccharides have a ratio of 0.027 of hydroxyl
3065 group number to its molecular weight. However, because the structure and configuration
of the monosaccharides is compatible to anhydroglucose units of the starch, they still can
be competitive plasticizers to sorbitol. A plasticizer with a good plasticization effect may
not be suitable for a food packaging with specific requirements. Chapter 3 and 4 have
shown that glycerol film is weaker and less resistant to the gases than monosaccharide-
3070 films, although glycerol has a better plasticization effect. Therefore, it must be kept in
mind that the choice for a plasticizer should be based on the requirements of the food
packaging.

Further studies should focus on the mass transfer of plasticizers from crystalline area to
3075 amorphous area; the formation of starch crystal and their morphology with different
plasticizers; the effect of combination of plasticizer with additional nutrients,
antimicrobials, and antioxidants, etc, on the properties of the films; the pilot scale
production by using extrusion equipments; the applications on some foods as packaging
or coating.

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