

We are IntechOpen, the world's leading publisher of Open Access books Built by scientists, for scientists

6,900

Open access books available

185,000

International authors and editors

200M

Downloads

Our authors are among the

154

Countries delivered to

TOP 1%

most cited scientists

12.2%

Contributors from top 500 universities



WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com



Retrogradation and Antiplasticization of Thermoplastic Starch

Yachuan Zhang and Curtis Rempel

*Richardson Centre for Functional Foods and Nutraceuticals,
University of Manitoba, Winnipeg, MB, R3T 2N2,
Canada*

1. Introduction

Petrochemical-based plastics are widely used in modern society due to their high effective mechanical and barrier properties (Farris et al., 2009; Siracusa et al., 2008). However, petrochemical-based plastics have become an environmental concern as they are not biodegradable or recyclable. Replacing the petrochemical-based polymers with biopolymers which are renewable has become an attractive idea and necessitates research on bioplastics (Debeaufort et al., 1998). Among the biopolymers, starch is considered as one of the most promising candidates for bioplastics due to its abundant availability, annually renewability, competitive price, and potential performance, including thermoplasticity (Lai & Padua, 1997; Mali et al., 2005). Native starch does not have thermoplastic properties. However, when additional plasticizers, elevated temperatures and shear are present, native starch does exhibit thermoplastic properties. Standard techniques, such as extrusion and injection moulding, used for producing petrochemical-based plastics, can be used in thermoplastic processing of starch (Guilbert et al., 1997). Some of thermoplastic starch (TPS) has been developed into commercial products, like compost bags, packaging materials (loose fillers and films), coatings, mulch films and disposable diapers (Jovanovic et al., 1997; Lai et al., 1997). TPS film and coating are being developed for the meat, poultry, seafood, fruit, vegetable, grains and candies industry sectors (Debeaufort et al., 1998). A drawback for use of starch is that TPS products age with time during storage due to starch retrogradation, which significantly changes quality, acceptability, and shelf-life of the TPS products. This review will summarize the current knowledge of TPS pertaining to its plasticization, retrogradation, and antiplasticization.

2. Basics of starch plasticization

Native starch does not have any thermoplastic properties without addition of plasticizer(s) (e.g., water, glycerol, sorbitol, etc.). The products made from native starch are readily broken into fragments when they are dried in ambient conditions due to strong intermolecular hydrogen bonding in the amylose and amylopectin macromolecular chains (Ma et al., 2007). But in the presence of plasticizers and elevated temperatures and shear, native starch readily melts and flows, allowing for its use as an extruding, injection moulding, or blowing material, similar to most conventional synthetic thermoplastic polymers (Ma et al., 2007). The role of

plasticizers is to attract the water molecules around them, reduce the intermolecular interactions between the starch molecules, and then increase the flexibility of native starch (Ke & Sun 2001). This process of overcoming the brittleness in starch by softening the structure and by increasing the mobility of the macromolecular chains, resulting in a lowering of processing temperature, is termed as plasticization of starch. During the plasticization process, starch is transformed from a semicrystalline granular material into a system containing granular remnants, or to an amorphous paste with no structure at all (Smits et al., 2003).

Three theories have been proposed to account for the mechanisms of plasticization. These are lubricity theory, gel theory, and free volume theory. Lubricity theory proposes that the plasticizer acts as a lubricant and lubricates movements of the macromolecules over each other. Gel theory proposes that the plasticizer disrupts the interaction of starch chain bonds. Free volume theory proposes that plasticizer increases free volume between the starch chains and lowers its glass transition temperature (T_g). The commonality of these is that plasticizer is considered to interpose itself between the starch chains and reduce the forces holding the chains together (Gioia & Guilbert, 1999).

Commonly used plasticizers for TPS include water, glycerol, sucrose, fructose, glucose, glycols, urea, formamide, ethanolamine, and ethylene bisformamide, and amino acids (Huang et al., 2006; Ma & Yu, 2004; Pushpadass et al., 2008; Wang et al., 2008; Yang et al., 2006a, 2006 b; Zhang & Han, 2006a, 2006b). These chemicals are small in molecular size and are hydrophilic. Water and glycerol have traditionally been considered as the most effective plasticizers. Urea, formamide, ethanolamine, and ethylene bisformamide, which contain -CO-NH- functional groups, have recently been proven to be good plasticizers, for they are believed to suppress retrogradation and improve mechanical properties of TPS (Ma et al., 2005; Ma et al., 2006). Zullo & Iannace (2009) found that a urea/formamide mixture worked more effectively than glycerol in making homogenous and robust TPS films. Ma & Yu (2004) compared the hydrogen bond energy of the urea-starch, formamide-starch, acetamide-starch, and glycerol-starch, and concluded that urea, formamide and acetamide formed stronger hydrogen bonds with starch. Consequently urea, formamide and acetamide are more effective in plasticizing starch than polyols.

A minimum of 20% glycerol or any other suitable plasticizer is required to plasticize starch successfully (Pushpadass et al., 2008). With increasing plasticizer amount, properties of TPS, like tensile strength, Young's modulus, and glass transition temperature (T_g), decrease, while elongation and gas permeability increase. A TPS film which contains 25% glycerol is reported to exhibit maximum tensile strength and optimum modulus of elasticity (Pushpadass et al., 2008).

For industrial manufacturing of TPS, extrusion processing is a realistic approach. A typical extruder consists of a hopper, barrel, feed screw, thermocouples, and die (Fig. 1). Starch pellets or beads are fed from the hopper along the feed screw through the barrel chamber. As starch pellets or beads travels along the barrel, it is subject to friction, compression, and heated zones. The result is that the starch pellets homogeneously melt and mix as they traveled through the feed screw to the die. The die is precisely machined with a pattern opening such that the extruded starch mix takes the die pattern for its cross sectional area. TPS extrudates from the die solidify quickly. Before solidifying, TPS extrudates can be blown into films, sheets, or be moulded into desired shapes (Thunwall et al., 2006).

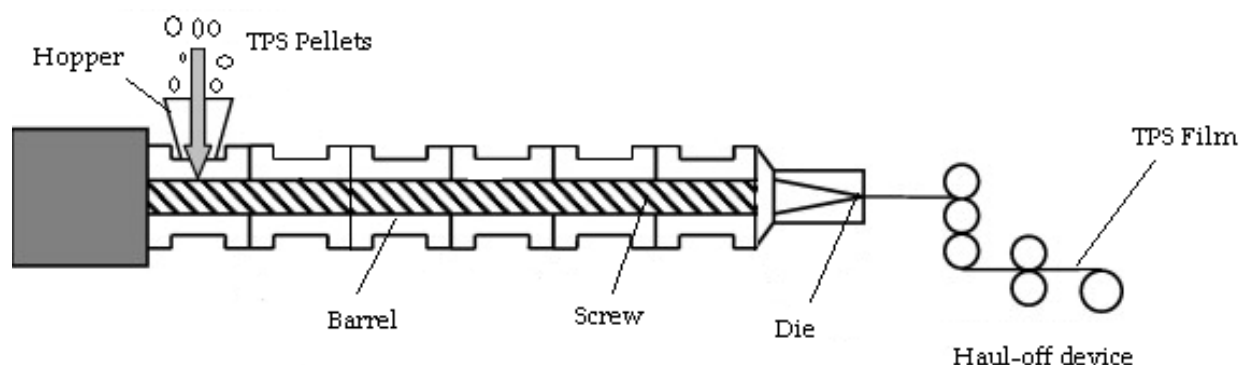


Fig. 1. A schedule of a typical extruder (Adapted from Li et al., 2011)

3. Mechanism of TPS retrogradation

Zhang & Han (2010) showed that gelatinized and plasticized TPS contains about 10% crystallinity, meaning 90% of TPS is amorphous region. Starch polymers in the amorphous region are metastable and consequently they automatically retrograde over time during storage. Mechanism of starch retrogradation has been intensively investigated. Liu & Han (2005) observed starch crystal formation of amylose and amylopectin film respectively under an inverted phase-contrast microscope. They found amylose film featured a layer of dendrites with 90-degree branching (Fig. 2a), while amylopectin film showed a network of interlinked clusters with an amorphous background (Fig. 2b). Lian et al. (2011) observed the starch retrogradation under a microscope. They found starch nuclei in 2 h and crystals in 48 h (Fig. 3a & b). Russell (1987) postulated amylose formed nuclei by congregating, and amylopectin formed crystalline lamellae by prolongating the rod-like growth of crystals. Delville et al. (2003) proposed a mechanism for formation of starch crystalline lamellae shown in Fig. 4, presenting 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 et al., 2003).

Tako & Hizukuri (2002) proposed starch retrogradation mechanisms at a molecular level, in which 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. 5). The starch retrogradation was also 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 molecules (Fig. 6). 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 also occurs (Fig. 7). The intramolecular hydrogen bonding might occur between OH-6 and adjacent hemiacetal oxygen atom of the D-glucosyl residues within an amylose molecule (Fig. 5 and 6), while the intramolecular association within an amylopectin molecule was not suggested to exist (Tako & Hizukuri, 2002).

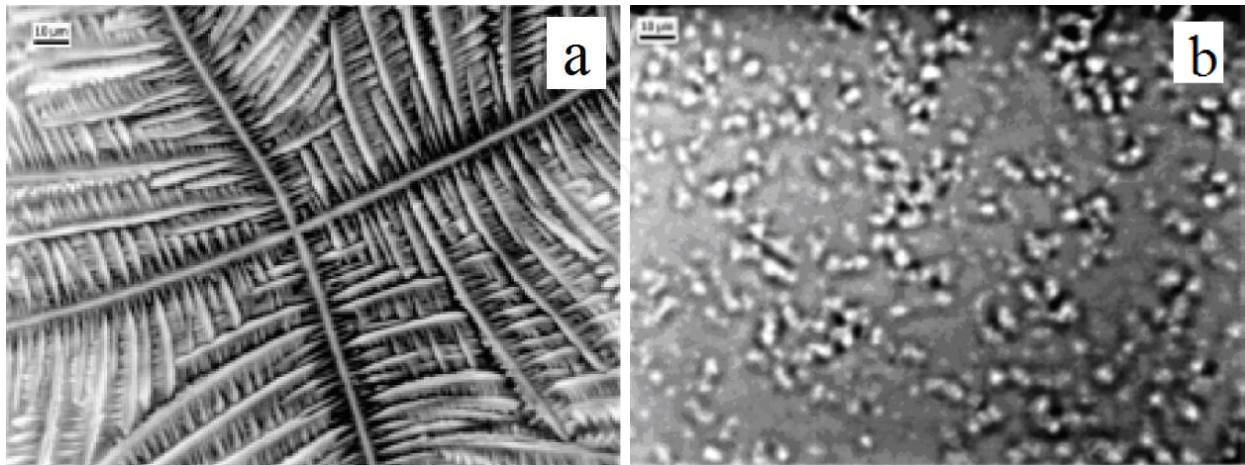


Fig. 2. Photomicrographs of amylose film (a) and amylopectin film (b). Amylose film shows a dendrite feature, while amylopectin film shows a cluster network with an amorphous background. (From Liu & Han, 2005)

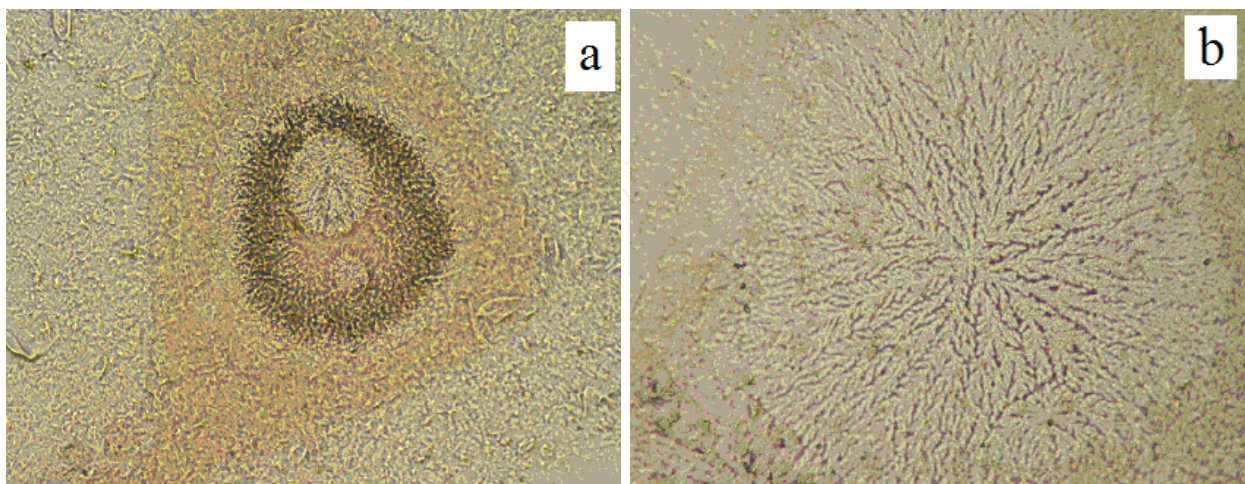


Fig. 3. Optical micrographs of retrograded starch of sweet potato aging 2 h (a) and aging 48 h (b). (From Lian et al., 2011)

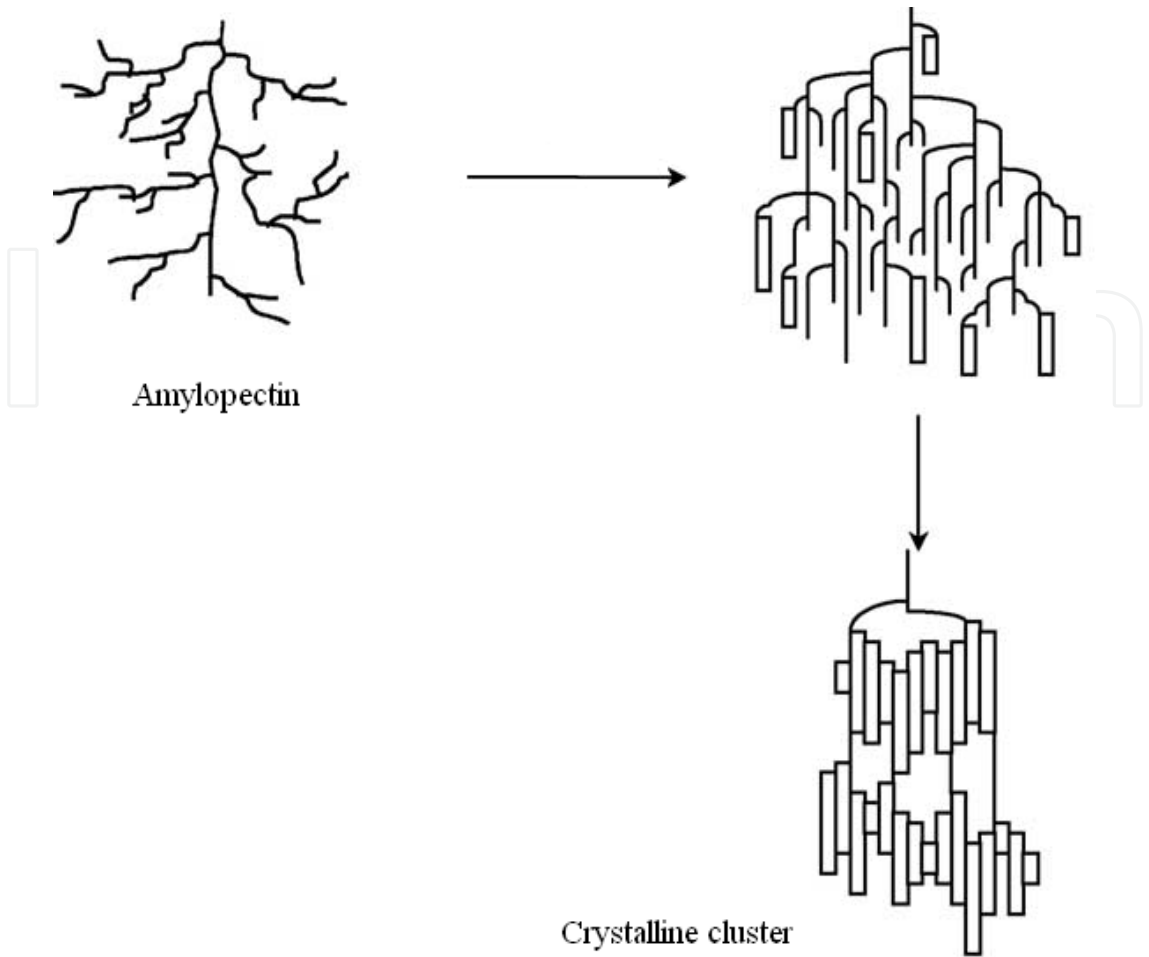


Fig. 4. Schematics of amylopectin retrogradation at the rubbery state (amylopectin double helices are represented as rectangles). (From Delville et al., 2003)

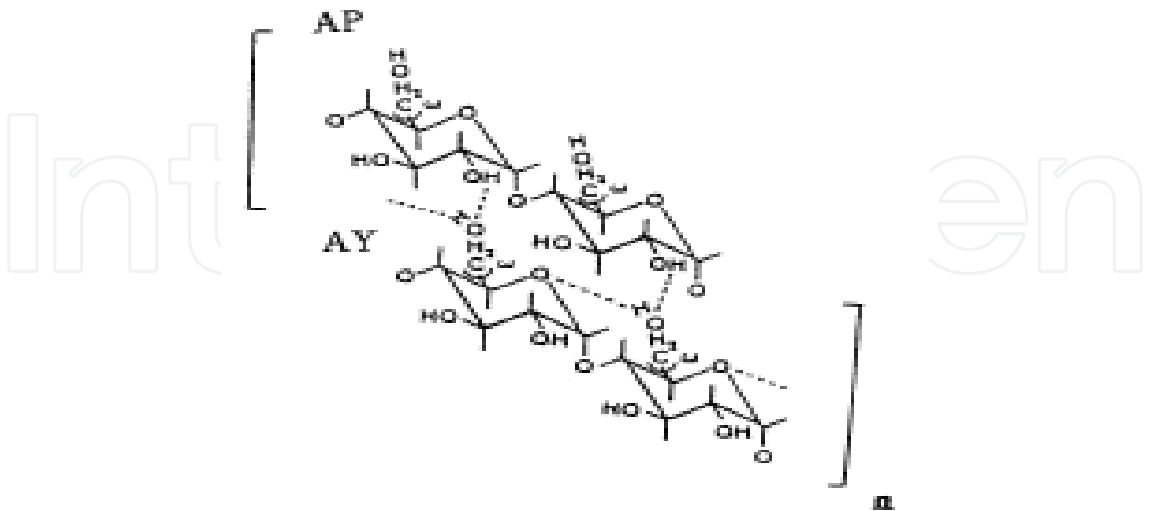


Fig. 5. Hydrogen bonding between amylose and amylopectin molecules (Dotted lines represent hydrogen bond. AY, amylose; AP, short side-chain of amylopectin molecules) (From Tako & Hizukuri, 2002)

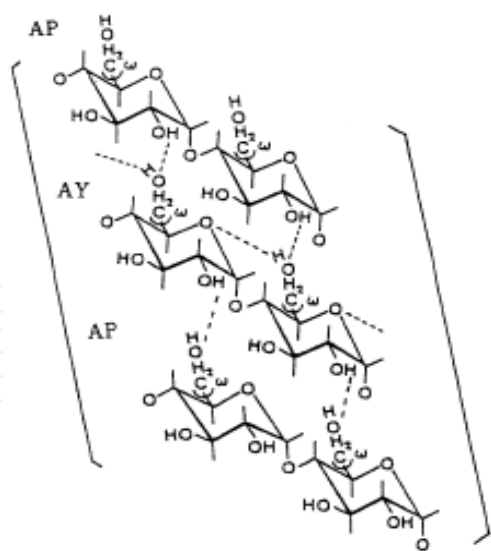


Fig. 6. Retrogradation mechanism of starch (Dotted lines represent hydrogen bond. AY, amylose; AP, short side-chain of maylopectin molecules) (From Tako & Hizukuri, 2002)

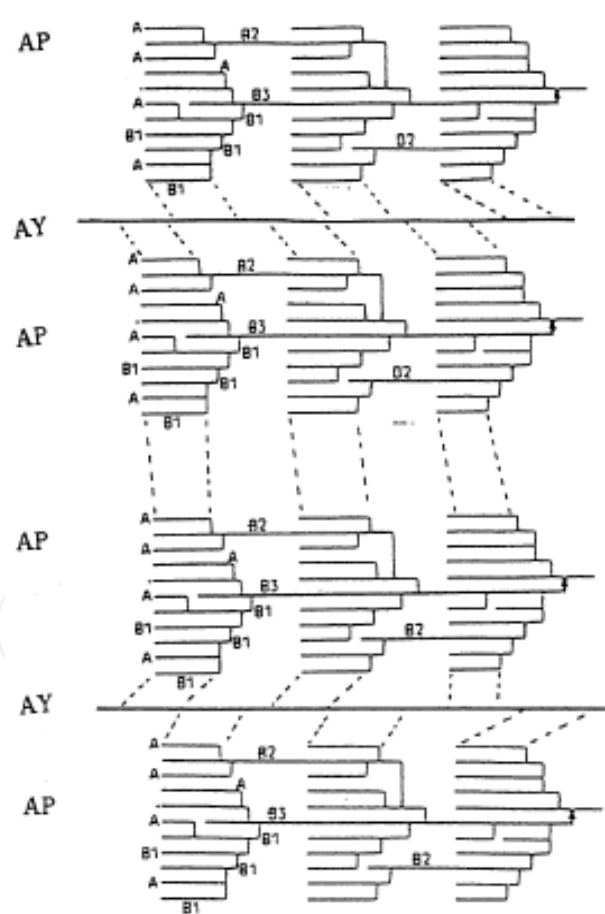


Fig. 7. Association between amylose and amylopectin molecules (Dotted lines, represent the hydrogen bonding sites). Two or more short-chains of amylopectin molecules may interact with one amylose molecule. Self-association within amylopectin molecules may also take place (From Tako & Hizukuri, 2002)

4. Effect of retrogradation on the property of thermoplastic starch

Properties of TPS products depend upon its microstructure. Zhang & Han (2010) studied the effect of crystallinity on the properties of the starch film, including moisture content, gas permeability, and tensile properties, etc. When crystallinity of glycerol-starch film increased from 6.0% to 8.0%, moisture content decreased from 11.0% to 8.0%. Similar phenomena were observed in sorbitol-, fructose-, and mannose-films. During the retrogradation process, starch chains aligned to form crystalline lamellas. Water molecules, as well as plasticizer molecules, are pushed out and evaporate resulting in reduced moisture content. Retrogradation of starch was also observed to have negative effect on gas permeability, including oxygen permeability (OP) and water vapor permeability (WVP) (Zhang and Han, 2010). Sorbitol-film had a reduction in OP from 20×10^{-7} to 0.3×10^{-7} cc mm h⁻¹ kPa⁻¹ m⁻² when its crystallinity increased from 7.0% to 12.0%, while OP in glycerol-film was reduced from 6×10^{-7} to 4×10^{-7} cc mm h⁻¹ kPa⁻¹ m⁻² when its crystallinity increased from 5.0% to 9.0%. A similar trend was also found in WVP. When crystallinity of glycerol-film increased from 6.0% to 9.0%, its WVP decreased from 1.2 to 0.9 g mm m⁻² h⁻¹ kPa⁻¹. Pushpadass & Hanna (2009) explained that the increase in crystallinity with time decreased the free volume in the TPS network and resulted in decrease in WVP. Zhang & Han (2010) proposed that crystallite in the films results in difficulty for gas molecules to diffuse within the starch films, leading to low permeability. Crystallinity also resulted in decreased elongation of the film. Elongation of mannose-film decreased from 4.0% to 0.2% when its crystallinity increased from 6.0% to 19.0%, elongation of fructose-film from 4.0% to 1.5% when its crystallinity increased from 6.0% to 18.0%. Pushpadass & Hanna (2009) reported similar findings. They reported the relative crystalline content of TPS samples increased from 3 % (after 4 h extrusion) to 7%, 14%, and 17% after 3, 30, and 120 d of storage. As a result, tensile strength of TPS samples increased by 39.3 – 134.1%, elongation decreased by 48.0 – 81.1%, and WVP decreased by 6.1 % – 19.3%. A lower E value means that TPS becomes stiffer, less flexible and more difficult to handle. Crystallites may act as physical crosslinking points which generate internal stresses of TPS, leading to the increase in tensile strength and decrease in elongation (Delville et al. 2003)

5. Technologies to study the starch retrogradation

Many analytical techniques have been developed to monitor the starch retrogradation based on the TPS property changes. These methods include differential scanning calorimetry (DSC), differential thermal analysis (DTA), X-ray diffraction (XRD), and enzymatic susceptibility, and others. Karin et al. (2000) summarized some of the methods. For TPS crystallinity study, DSC and X-ray diffraction have proven to be extremely sensitive and therefore valuable tools to quantify retrograded starches.

5.1 Differential scanning calorimetry

Differential scanning calorimetry (DSC) is a thermo-analytical technique. It measures temperatures and heat flows associated with thermal transitions in a material sample. A reference with a well-defined heat capacity over the range of temperature is identically

scanned. The difference in the heat flow between the sample and reference is detected and recorded. A plot of the differential heat flow between the reference and sample as a function of temperature is developed. When the sample undergoes a physical transformation, such as glass transition, melting, crystallization, more (or less) heat will need to flow to it than the reference to maintain both at the same temperature, resulting in a significant deviation in the difference between the two heat flows. When using DSC for starch retrogradation, the deviation between the heat flows results in a peak in the DSC curve. An example of this is illustrated in Fig. 8, using wheat starch.

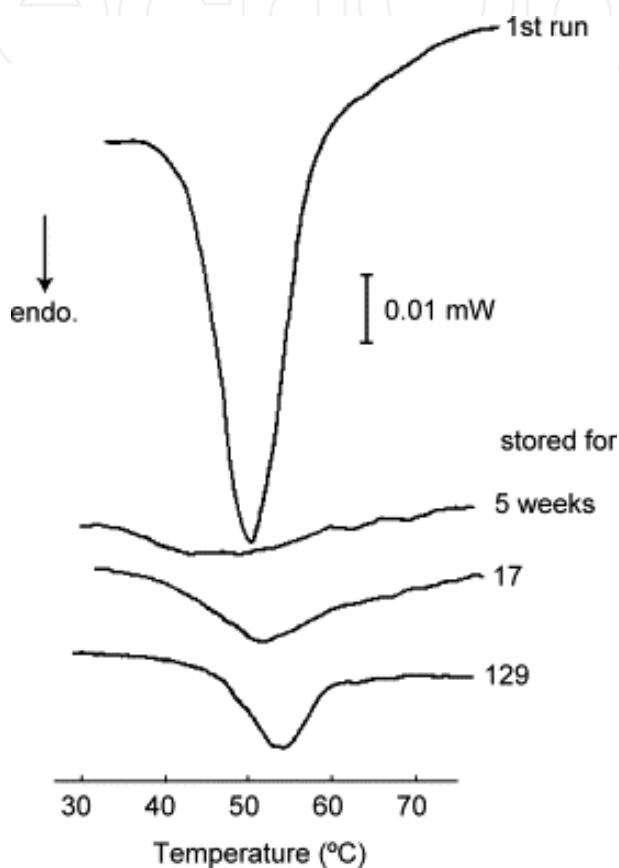


Fig. 8. Observed DSC curves for gelatinization of native wheat starch (upper) and retrograded wheat starch after storage time of 5, 17, and 129 weeks. (From Kohyama et al., 2004)

The first run in Fig. 8 represents gelatinization of wheat starch. The peaks after 5, 17, and 129 weeks were broader and shallower than that of the first run, and became deeper and more pronounced with increasing storage time.

Tian et al. (2011) used DSC to determine the retrogradation degree of rice starch by equation 1.

$$DR(t) = \frac{\Delta H_t - \Delta H_0}{\Delta H_\infty - \Delta H_0} \times 100\% \tag{1}$$

where $DR(t)$ represents the crystalline fraction (%) developed at storage time t , ΔH_0 is the enthalpy change (J/g) at storage time zero, ΔH_t is the enthalpy change at storage time t , and ΔH_∞ is the enthalpy change at unlimited time (35 days in the study). From 0 to 21 days, rice starch retrogradation went from 10% to 50%.

Application of DSC on the starch retrogradation study has a limitation. As mentioned by Biliaderis (1990), starch retrogradation consists of two processes: the rapid gelation of amylose solubilized during gelatinization and the slower recrystallization of amylopectin. DSC is only used to determine the latter phenomenon, since the re-organized region in amylopectin melts while the re-organized region in amylose does not (Gidley & Bulpin, 1987; Russell, 1987).

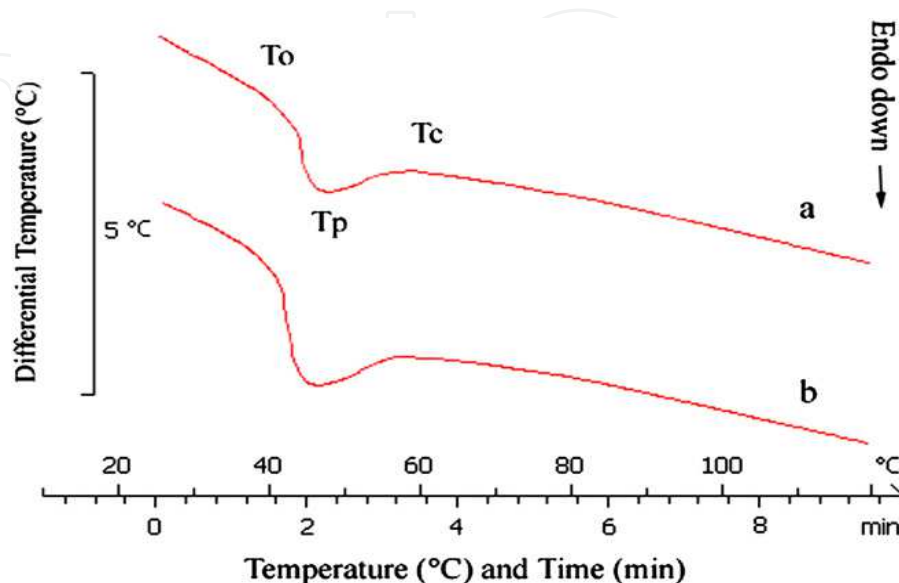


Fig. 9. DTA curves for (a) the gelatinized and (b) the 35-day retrograded rice starch containing 1.9% amylose. T_o is the onset temperature, T_p the peak temperature, and T_c the conclusion temperature, respectively. (From Tian et al., 2011)

5.2 Differential thermal analysis

An alternative technique, which shares much in common with DSC, is differential thermal analysis (DTA). In this technique it is the heat flow to the sample and reference that remains the same rather than the temperature. When the sample and reference are heated identically, phase changes and other thermal processes cause a difference in temperature between the sample and reference. The differential temperature is then plotted against temperature or against time as a DTA curve that provides data on the physical and chemical transformations, such as crystallization, gelatinization (Wada et al., 1979), melting, and sublimation (Morita, 1956). Fig. 9 shows a DTA curve for retrogradation of rice starch. Tian et al. (2011) used DAT technology to study rice starch retrogradation, which contained 29.3%, 13.5%, and 1.9% amylose. They found the storage time from 0 to 35 days slightly decreased the onset temperature (T_o), the peak temperature (T_p), and the conclusion temperature (T_c) for the retrograded starch. This was attributed to the fact that the number of the perfect crystal nuclei was reduced with storage time and the imperfect crystalline nuclei were increased during the retrogradation. By using equation 2, crystalline fraction of the retrograded starch was calculated.

$$DR(t) = \left(\frac{\Delta T_t - \Delta T_0}{\Delta T_\infty - \Delta T_0} \right) \times 100\% \quad (2)$$

where $DR(t)$ is the crystalline fraction (%) formed at storage time t , ΔT_t is the maximum differential temperature for the t day retrograded starch, ΔT_0 is the maximum differential temperature for the gelatinized starch, and ΔT_∞ is the maximum differential temperature for the long-term, for example 35 days, retrograded starch. With equation 2, Tian et al. (2011) calculated the rice starch crystallized from around 10% to 50~60% with increasing of the storage time from 0 to 21 days. The DR data obtained from DTA was slightly higher than that evaluated from the DSC, but no significant difference between the two data was found.

5.3 X-ray diffraction

The application of X-ray diffraction (XRD) on the study of starch crystallinity has shown that three X-ray diffraction crystal patterns exist in native starch granules, namely A-type, B-type, and C-type. The typical XRD patterns of TPS are characterized by sharp peaks associated with the crystalline portion area and an amorphous area (Fig. 10). The amorphous fraction of the sample can be estimated by the area 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 et al., 2006). Equation 3 was used to estimate crystallinity of the TPS.

$$DR = \frac{I_c}{I_c + I_a} \times 100\% \quad (3)$$

where DR is the crystalline fraction (%), I_c is the crystalline area on the X-ray diffractogram and I_a is the amorphous area on the X-ray diffractogram (Kalichevsky et al., 1993; Yoo & Jane, 2002). With the X-ray method, Zhang & Han (2010) studied the anti-plasticization of pea starch film. They announced that native pea starch film contained about 6.0% crystalline structure, and the crystallinity increased with plasticizer content increasing until 25%. The X-ray method is one of most popular methods for studying TPS structure and its application has been widely studied (Garcia et al., 2000; Smith et al., 2003; Zhang & Han, 2010).

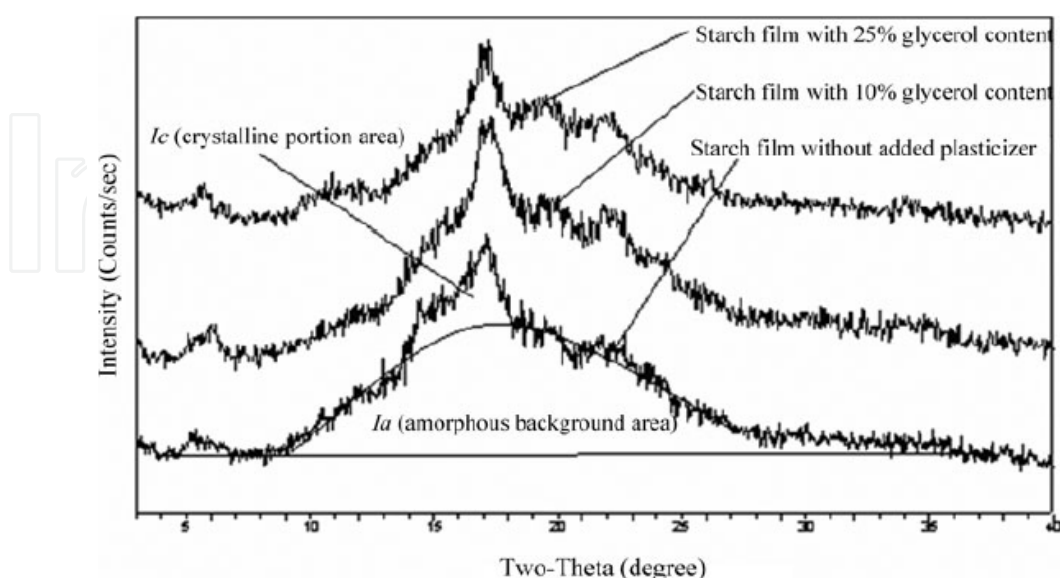


Fig. 10. X-ray diffraction patterns of peas starch films plasticized by 0, 10, and 25 % glycerol, respectively. (From Zhang & Han, 2010)

5.4 Enzymatic susceptibility

As a result of retrogradation, starch forms resistant starch which is resistant to the enzyme hydrolysis. Enzymatic method has been developed which is based on measuring the resistant starch level to determine the starch retrogradation degree. Tsuge et al. (1990) gave a detailed procedure on how to conduct enzymatic measurement on the retrograded starch. Tian et al. (2010) repeated it with rice starch and α -amylase from *Bacillus subtilis*. Equation 4 was used to estimate the retrogradation degree.

$$DR = 100 \times (b - c) / (a - c) \quad (4)$$

where DR is the crystalline fraction (%), a represents absorbance read of total starch fraction in a spectrophotometer, b the absorbance of starch fraction to be tested, and c the absorbance of the complete digestion of starch. Wave length of 625 nm was selected for the absorbance measurement. Tian et al. (2010) measured rice starch retrogradation and found 7 – 28% crystallinity during storage of 1 – 14 hours.

5.5 Size-exclusion high performance liquid chromatography

Size-exclusion high performance liquid chromatography (SE-HPLC) is usually used to determine the molecular weight (M_w) of starch components, according to the different retention time (T_R) for its components. Tian et al. (2010) used it to estimate amylose retrogradation in rice starch and compared the results with that of enzymatic measurement and DSC. Equation 5 was used to calculate the amylose recrystalline fraction in the rice starch.

$$DR(t) = A \times (T_t - T_0) / (T_\infty - T_0) \times 100\% \quad (5)$$

Where $DR(t)$ represents the recrystalline fraction of amylose (%) developed at time t , T_t is retention time of the sample stored for t hours, T_0 is the retention time of the gelatinized sample, T_∞ is limiting retention time of 24 h storage sample, and A is the amylose area (%) occupied of the peak (Tain et al., 2010).

Tian et al. (2010) found two peaks in SE-HPLC plot with retention time 13.2 min and 16.0 min respectively. The first peak was ascribed to the amylopectin retrogradation and the second one amylose retrogradation. Analysis on retrogradation degree of rice starch showed 7 – 25% crystallinity during storage of 1 – 14 hours. This data corroborated that obtained by enzymatic measurement, but not with DSC data. DSC is reported to be suitable for amylopectin retrogradation study, not for amylose crystallization. Tian et al. (2010) further concluded that SE-HPLC is an effective method to measure the amylose retrogradation during short-term storage time, i.e. 0 – 24 h.

6. Factors which can affect the retrogradation of starch

While many factors may affect the retrogradation of starch, the botanical source is the most important one. Different botanical sources produce starches which are different with respect to properties such as amylose/amylopectin ratio (Gudmundsson & Eliasson, 1990; Klucinec

& Thompson, 2002), lipid content (Gudmundsson & Eliasson, 1990), and amylopectin fine structure (Kalichevsky et al., 1990). These properties will strongly influence the starch retrogradation kinetics. Ottenhof et al. (2005) stated that potato TPS ($34 \pm 1\%$ water content, w/w) showed the highest rate of retrogradation ($\sim 0.17 \text{ h}^{-1}$) followed by waxy maize ($\sim 0.12 \text{ h}^{-1}$), while wheat TPS was the slowest ($\sim 0.05 \text{ h}^{-1}$). In addition of the botanical source, factors such as storage time, environmental temperature, and TPS moisture and plasticizer content, influence starch retrogradation also (Mali et al., 2002).

6.1 Storage temperature

At a temperature which is higher than the T_g , TPS is in the rubbery state and its starch molecule retrogradation (or recrystallization) in the amorphous phase occurs easily. The rate of starch retrogradation depends on difference between the storage temperature and T_g (Mali et al., 2006), with increasing retrogradation rate for higher temperature, especially under the conditions when TPS being stored at high relative humidity or high plasticizer contents (Delville et al., 2003). Conversely, when TPS is stored at temperature below the T_g , starch polymers are in a stable glassy state, and retrogradation does not occur or is extremely slow (Baik et al., 1997). Williams-Ferry-Landel (WLF) equation was commonly used to study the kinetic of the retrogradation process (Baik et al., 1997) at different temperature value.

$$\log_{10}\left(\frac{t}{t_g}\right) = \frac{-C_1(T - T_g)}{C_2 + (T - T_g)} \tag{6}$$

where t is the time of crystallisation, t_g the time to crystallise at T_g , C_1 and C_2 are constants (17.44 and 51.6K, respectively), and T is the temperature (K). Currently, there are numerous studies available on native starch, but limited studies are available on TPS retrogradation rate results at different storage temperatures.

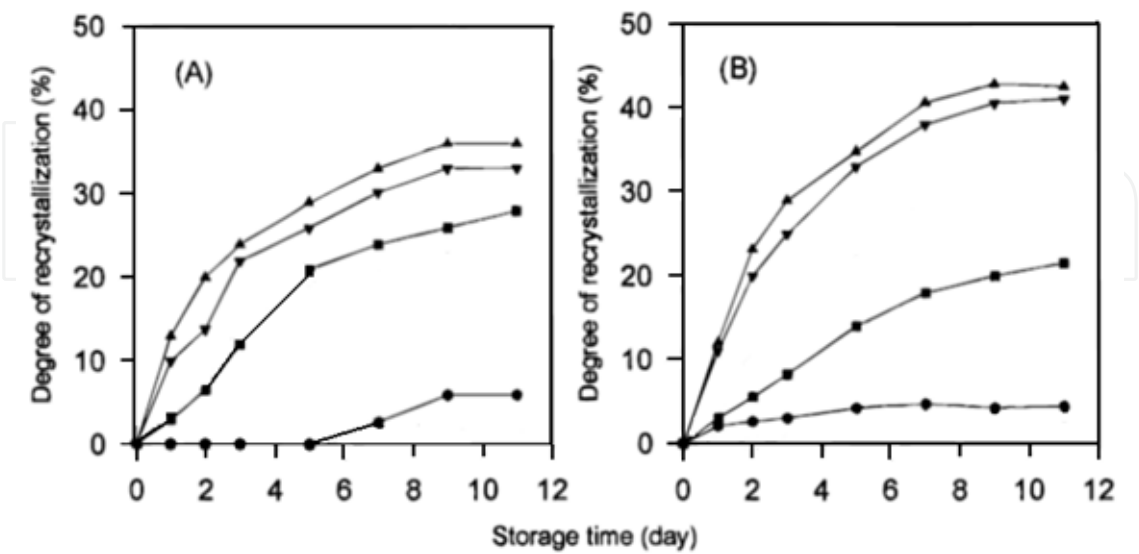


Fig. 11. Changes in degree of retrogradation of nonwaxy (A) and waxy (B) rice starch gels during storage at various temperatures; ●, 30; ■, 20; ▲, 4; ▼, 0 °C. (Adapted from Baik et al., 1997)

6.2 Storage time

Storage time increases starch retrogradation. Fig. 11 shows the relationship between degree of retrogradation of waxy rice starch gels with storage time. Rice starch becomes increasingly retrogradated with storage time, until the 9th day when it levels off (Baik et al., 1997). Mali et al. (2002) found as storage time increased, the width of the X-ray diffraction peak of starch samples decreased but its peak intensity increased, showing an increase in crystallinity of starch.

6.3 Storage relative humidity and plasticizer content

In the rubbery state, high relative humidity (RH) favors starch macromolecular mobility which in turn facilitates the development of retrogradation (Delville et al., 2003). Glycerol content slows the crystallization kinetics in starch (Delville et al., 2003). According to Mali et al. (2006), glycerol limited the crystal growth and recrystallization by interacting with the polymeric chains and interfering with polymer chain alignment due to steric hindrances. Controversially, Garcia et al. (2000) reported that plasticizers (including glycerol and water) favored polymer chain mobility and allowed the development of a more stable crystalline structure during shorter periods of storage. Similarly, Smits et al. (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, because plasticized starch polymers could easily vibrate and align up to form crystallites, while the unplasticized starch polymers interact with each other strongly and lose their mobility. Zhang & Han (2010) found that plasticizer concentration plays a critical role in starch retrogradation. When plasticizer content is greater than 25%, the plasticizer limits the starch polymer retrogradation. Otherwise, the plasticizer will favour the crystallization of the starch chains. Fig. 12 shows the relationship of starch film crystallinity and the plasticizer concentration.

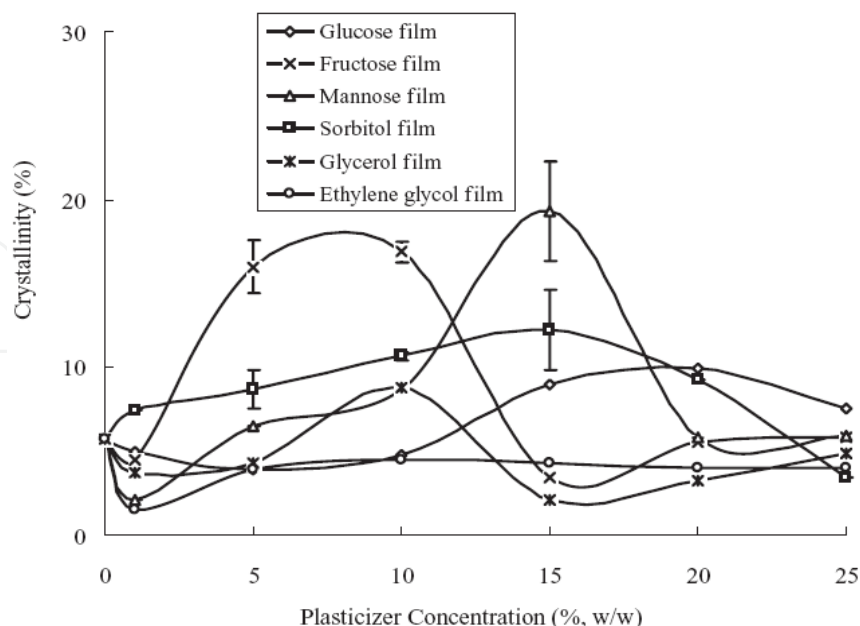


Fig. 12. Relationship of crystallinity of pea starch film and the plasticizer concentration. Crystallinity of the starch films increases with plasticizer concentration increasing until 25%. Bars indicate mean \pm standard deviation. (From Zhang & Han, 2010)

7. TPS antiplasticization and its explanation

Antiplasticization is a well-known phenomenon for synthetic polymers. This phenomenon also exists in TPS and has been receiving increasing attention recently (Chang et al., 2006). Contrary to the orthodox behaviour of plasticization, plasticizer can reduce elongation and gas permeability, and increase tensile strength and modulus of elasticity of TPS when it is introduced in low amount under a critical level (generally <25%) (Godbillot et al., 2006; Lourdin et al., 1997; Zhang & Han, 2010). Fig. 13 shows strain–stress curves of pea starch films plasticized by glycerol and mannose respectively, indicating the starch films plasticized by glycerol and mannose had less stress and strain than the film without any plasticizers.

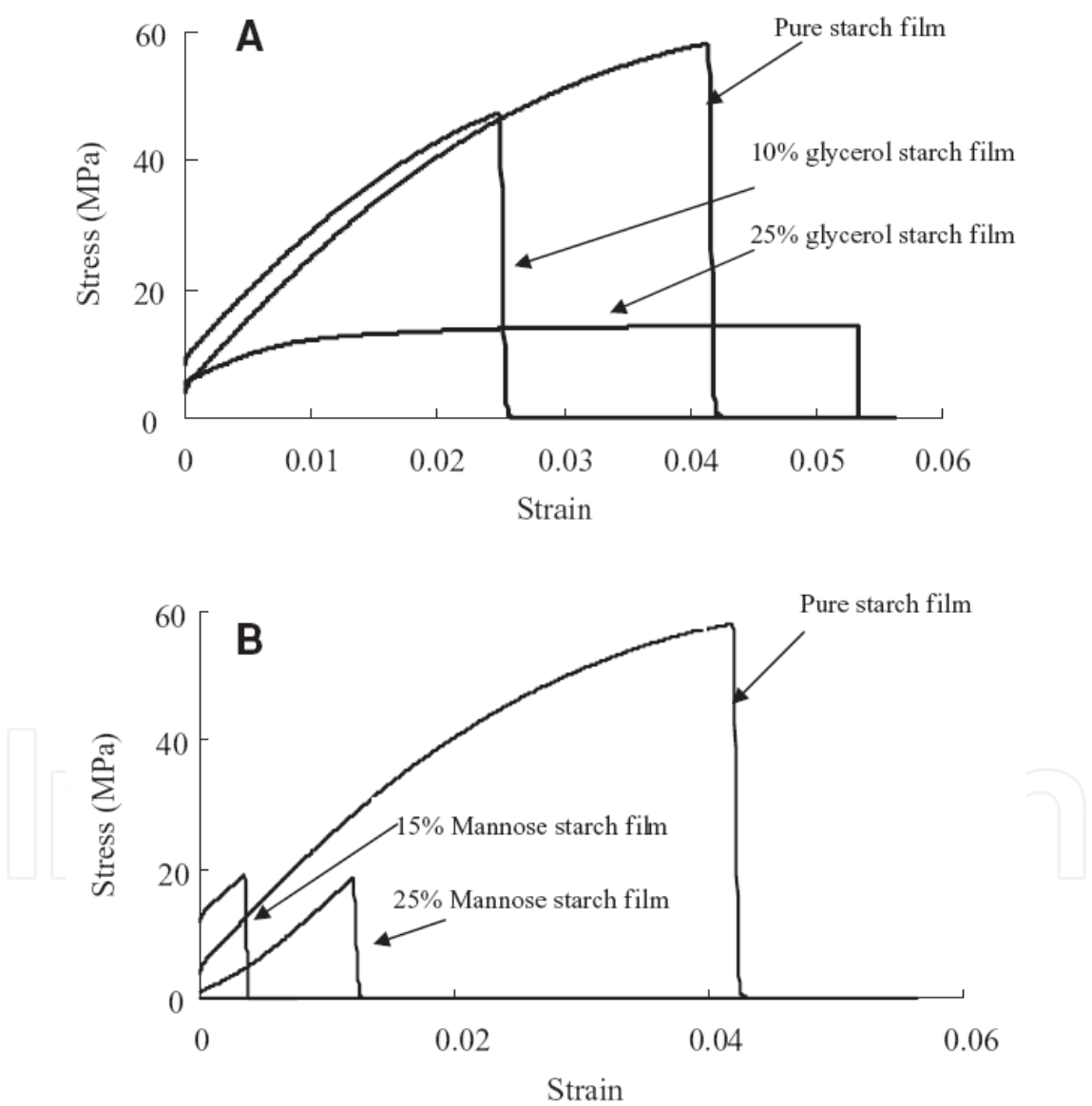


Fig. 13. Strain–stress curves of pea starch films plasticized by glycerol and mannose respectively, indicating the starch films plasticized by glycerol and mannose had less stress and strain than the film without any plasticizers. (From Zhang & Han, 2010)

Mechanism of anti-plasticization effect of plasticizer on TPS has not been clearly understood, but some efforts have been made to elucidate its mechanism. Zhang & Han (2010) found that starch retrogradation results in antiplasticization phenomena. The crystallinity of the pea starch films increased with plasticizer content increasing from 1% to 20%, leading to decrease in MC, OP, WVP, and E, and increase in EM. Plasticizer performs plasticization or antiplasticization depending on its concentration. Addition of plasticizers at the range of low to intermediate concentration level (1% to 25%) facilitates the formation of crystallites in the starch films, leading to the antiplasticization. Zhang & Han (2010) further proposed an anti-plasticization model. Due to the movement or vibration of the starch polymer chains, water and plasticizer molecules were pushed aside gradually from starch polymers. D-glucosyl residues of the amylose or amylopectin, which used to be separated by water or plasticizers molecules, interacted to form strong hydrogen bonds causing retrogradation or recrystallization. However, when starch polymer was plasticized by high content plasticizer (>25%), the plasticizer molecules could not be pushed aside completely from the starch polymers. Then, the plasticizers performed their plasticization effect, which was to interrupt interaction between the hydrogen bondings of starch polymers, increase the TPS elongation, reduce its T_g , and prevent retrogradation of starch chains.

8. Summary

Thermoplastic starch (TPS) has attained more attention for its potential to replace the conventional polymers. Retrogradation occurs in TPS with time and affects its properties and applications. TPS contains normally 10% crystallinity, but this value changes with storage time, temperature, atmosphere relative humidity, and plasticizer content. Starch retrogradation mechanisms are discussed at molecular level. Methods to measure the retrogradation degree, such as differential scanning calorimetry, differential thermal analysis, X-ray, etc. are also reviewed. Changes in TPS property, such as tensile strength, elongation, gas permeability, are due to the retrogradation of starch polymers and these are described.

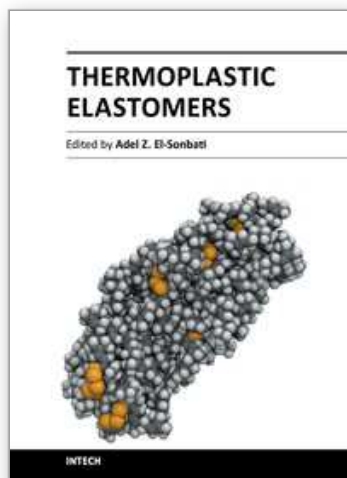
9. References

- Baik, M.Y., Kim, K.J., Cheon, K.C., Ha, Y.C., Kim, W.S. (1997). Recrystallization kinetics and glass transition of rice starch gel system. *Journal of Agricultural and Food Chemistry*, 45, pp. 4242-4248.
- Biliaderis, C. G. (1990). Thermal analysis of food carbohydrates. In: *Thermal Analysis of Foods*, Harwalkar, V.R. and Ma, C.Y. pp. 120-134. Elsevier Applied Science, ISBN: 9781851664368, London.
- Chang, Y.P., Abd Karim, A., Seow, C.C. (2006). Interactive plasticizing-antiplasticizing effects of water and glycerol on the tensile properties of tapioca starch films. *Starch*, 55, pp.304-312.
- Debeaufort, F., Quezada-Gallo, J.A., Voilley, A. (1998). Edible films and coatings: tomorrow's packagings: a review. *Critical Reviews in Food Science and Nutrition*. 38, pp.299-313.
- Delville, J., Joly, C., Dole, P., Bliard, C. (2003). Influence of photocrosslinking on the retrogradation of wheat starch based films. *Carbohydrate Polymers*, 53, pp.373-381.
- Farris, S., Schaich, K.M., Liu, L.S., Piergiovanni, L., Yam, K.L. (2009). Development of polyion-complex hydrogels as an alternative approach for the production of bio-

- based polymers for food packaging applications: a review. *Trends in Food Science & Technology*, 20, pp.316-332.
- Garcia, M.A., Martino, M.N., Zaritzky, N.E., Plata, L. (2000). Microstructural characterization of plasticized starch based films. *Starch*, 52, pp.118-124.
- Gidley, M.J., Bulpin, P.V. (1987). Crystallization of malto-oligosaccharides as models of the crystalline of starch: minimum chain-length requirement for the formation of double helices. *Carbohydrate Research*, 161, pp.291-300.
- Gioia, L.D., Guilbert, S. (1999). Corn Protein-Based Thermoplastic resins: effect of some polar and amphiphilic plasticizers. *Journal of Agricultural and Food Chemistry*, 47, pp.1254-1261.
- Godbillot, L., Dole, P., Joly, C., Roge, B., Mathlouthi, M. (2006). Analysis of water binding in starch plasticized films. *Food Chemistry*, 96, pp.380-386.
- Gudmundsson, M.; Eliasson, A.C. (1990). Retrogradation of amylopectin and the effects of amylose and added surfactants/emulsifiers. *Carbohydrate Polymers*, 13, pp.295-315.
- Guilbert, S.; Cuq, B.; Gontard, N. (1997). Recent innovations in edible and/or biodegradable packaging materials. *Food Additives and Contaminants*, 14, 6, pp.741-751.
- Huang, M., Yu, J., Ma, X. (2006). High mechanical performance MMT-urea and formamide-plasticized thermoplastic cornstarch biodegradable nanocomposites. *Carbohydrate Polymers*, 63, pp. 393-399.
- Jovanovic, S., Jeremic, K., Jovanovic, R., Donlagic, J., Dunjic, B. (1997). Preparation of thermoplastic starch. *Journal of the Serbian Chemical Society*, 62, pp. 623-629.
- Kalichevsky, M.T., Blanshard, J.M. V., and Marsh, R.D.L. (1993). Applications of mechanical spectroscopy to the study of glassy biopolymers and related systems. In: *The glassy state in foods*. Blanshard, J. and Lillford, P.J., pp. 133-156, Nottingham University Press, ISBN: 9781897676202, Leicestershire, UK.
- Kalichevsky, M.T.; Orford, P.D.; Ring, S.G. (1990). The retrogradation and gelation of amylopectin from various botanical sources. *Carbohydrate Research*, 198, pp. 49-55.
- Karin, A.A., Norziah, M.H., Seow, C.C. (2000). Methods for the study of starch retrogradation. *Food Chemistry*, 71, pp. 9-36.
- Ke, T.; Sun, X. (2001). Thermal and mechanical properties of poly (lactic acid) and starch blends with various plasticizers. *Transactions of the American Society*, 44, pp. 945-953.
- Klucinec, J.D.; Thompson, D.B. (2002). Amylopectin nature and amylose-to-amylopectin ratio as influences on the behavior of gels of dispersed starch. *Cereal Chemistry*, 79, pp. 24-35.
- Kohyama, K., Matsuki, J., Yasui, T., Sasaki, T. (2004). A different thermal analysis of the gelatinization and retrogradation of wheat starches with different amylose chain lengths. *Carbohydrate Polymers*, 58, pp. 71-77.
- Lai, H.M., Padua, G.W. (1997). Properties and microstructure of plasticized zein films. *Cereal Chemistry*, 74, pp. 771-775.
- Lai, H.M., Padua, G.W., Wei, L.S. (1997). Properties and microstructure of zein sheets plasticized with palmitic and stearic acids. *Cereal Chemistry*, 74, pp. 83-90.
- Li, M., Liu, P., Zou, W., Yu, L., Xie, F., Pu, H., Liu, H., Chen, L. (2011). Extrusion processing and characterization of edible starch films with different amylose contents. *Journal of Food Engineering*, 106, pp. 95-101.

- Lian, X., Zhao, S., Liu, Q., Zhang, X. (2011). A photographic approach to the possible mechanism of retrogradation of sweet potato starch. *International journal of biological macromolecules*, 48, pp. 125-128.
- Liu, Z., Han, J.H. (2005). Film-forming characteristics of starches. *Journal of Food Science*, 70, pp. E31-E36.
- Lourdin, D., Bizot, H., Colonna, P. (1997). "Antiplasticization" in starch-glycerol films? *Journal of Applied Polymer Science*, 63, pp. 1047-1053.
- Ma, X.F., Yu, J.G. (2004). The plasticized containing amide groups for thermoplastic starch. *Carbohydrate Polymers*, 57, pp. 197-203.
- Ma, X.F., Yu, J.G., Ma, Y.B. (2005). Urea and formamide as a mixed plasticizer for thermoplastic wheat flour. *Carbohydrate Polymers*, 60, pp. 111-116.
- Ma, X.F., Yu, J.G., Wan, J.J. (2006). Urea and ethanolamine as a mixed plasticizer for thermoplastic starch. *Carbohydrate Polymers*, 64, pp. 267-273.
- Ma, X.F., Yu, J.G., Wang, N. (2007). Fly ash reinforced thermoplastic starch composites. *Carbohydrate Polymers*, 67, pp. 32-39.
- Mali, S., Grossmann, M.V.E., Garcia, M.A., Martino, M.N., Zaritzky, N.E. (2002). Microstructural characterization of yam starch films. *Carbohydrate Polymers*, 50, pp. 379-386.
- Mali, S., Grossmann, M.V.E., Garcia, M.A., Martino, M.N., Zaritzky, N.Z. (2005). Mechanical and thermal properties of yam starch films. *Food Hydrocolloids*, 19, pp. 157-164.
- Mali, S., Grossmann, M.V.E., Garcia, M.A., Martino, M.N., Zaritzky, N.E. (2006). Effects of controlled storage on thermal, mechanical and barrier properties of plasticized films from different starch sources. *J Food Engineering*, 75, pp. 453-460.
- Morita, H. (1956). Characterization of starch and related polysaccharides by differential thermal analysis. *Analytical Chemistry*, 28, pp. 64-67.
- Ottenhof, M.A., Hill, S.E., Farhat, I.A. (2005). Comparative study of the retrogradation of intermediate water content waxy maize, wheat, and potato starches. *Journal of Agricultural and Food Chemistry*, 53, pp. 631-638.
- Pushpadass, H.A., Hanna, M.A. (2009). Age-induced changes in the microstructure and selected properties of extruded starch films plasticized with glycerol and stearic acid. *Industrial & Engineering Chemistry Research*, 48, pp. 8457-8463.
- Pushpadass, H.A., Marx, D.B., Hanna, M.A. (2008). Effect of extrusion temperature and plasticizers on the physical and functional properties of starch films. *Starch*, 60, pp. 527-538.
- Ressull, P.L. (1987). The aging of gels from starches of different amylose/amylopectin content studied by differential scanning calorimetry. *Journal of Cereal Science*, 6, pp. 147-158.
- Siracusa, V., Rocculi, P., Romani, S., Rosa, M.D. (2008). Biodegradable polymers for food packaging: a review. *Trends on Food Science & Technology*, 19, pp. 634-643.
- Smits, A.L.M., Kruiskamp, P.H., van Soes, J.J.G., Vliegenthart J.F.G. (2003). The influence of various small plasticizers and malto-oligosaccharides on the retrogradation of (partly) gelatinized starch. *Carbohydrate Polymers*, 51, pp. 417-427.
- Tako, M., Hizukuri, S. (2002). Gelatinization mechanism of potato starch. *Carbohydrate Polymers*, 48, pp. 397-401.
- Tian, Y., Li, Y., Xu, X., Jin, Z. (2011). Starch retrogradation studies by thermogravimetric analysis (TGA). *Carbohydrate Polymers*, 84, pp. 1165-1168.

- Tian, Y., Li, Y., Xu, X., Jin, Z., Jiao, A., Wang, J., and Yu, B. (2010). A novel size-exclusion high performance liquid chromatography (SE-HPLC) method for measuring degree of amylose retrogradation in rice starch. *Food Chemistry*, 118, pp. 445-448.
- Thunwall, M., Boldizar, A., Rigdahl, M. (2006). Extrusion processing of high amylose potato starch materials. *Carbohydrate Polymers*, 65, pp. 441-446.
- Tsuge, H., Hishida, M., Iwasaki, H., Watanabe, S., Goshima, G. (1990). Enzymatic evaluation for the degree of starch retrogradation in foods and foodstuffs. *Starch*, 42, pp. 213-216.
- Wada, K., Takahashi, K., Shirai, K., Kawamura, A. (1979). Differential thermal analysis (DTA) applied to examining gelatinization of starches in foods. *Journal of Food Science*, 44, pp. 1366-1372.
- Wang, N., Yu, J., Chang, P.R., Ma, X. (2008). Influence of formamide and water on the properties of thermoplastic starch/poly(lactic acid) blends. *Carbohydrate Polymers*, 71, pp. 109-118.
- Yang, J.H., Yu, J.G., Ma, X.F. (2006a). Study on the properties of ethylenebisformamide and sorbitol plasticized corn starch (ESPTPS). *Carbohydrate Polymers*, 66, pp. 110-116.
- Yang, J.H., Yu, J.G., Ma, X.F. (2006b). Preparation and properties of ethylenebisformamide plasticized potato starch (EPTPS). *Carbohydrate Polymers*, 63, pp. 218-223.
- Yoo, S.H., Jane, J.L. (2002). Structural and physical characteristics of waxy and other wheat starches. *Carbohydrate Polymers*, 49, pp. 297-305.
- Zhang, Y., Han, J.H. (2006a). Mechanical and thermal characteristics of pea starch films plasticized with monosaccharides and polyols. *Journal of Food Science*, 71, pp. E109-E118.
- Zhang, Y., Han, J.H. (2006b). Plasticization of pea starch films with monosaccharides and polyols. *Journal of Food Science*, 71, pp. E253-E261.
- Zhang, Y., Han, J.H. (2010). Crystallization of high-amylose starch by the addition of plasticizers at low and intermediate concentrations. *Journal of Food Science*, 75, pp. N8-N16.
- Zullo, R., Iannace, S. (2009). The effects of different starch sources and plasticizers on film blowing of thermoplastic starch: Correlation among process, elongational properties and macromolecular structure. *Carbohydrate Polymers*, 77, pp. 376-383.



Thermoplastic Elastomers

Edited by Prof. Adel El-Sonbati

ISBN 978-953-51-0346-2

Hard cover, 416 pages

Publisher InTech

Published online 28, March, 2012

Published in print edition March, 2012

Thermoplastics can be used for various applications, which range from household articles to the aeronautic sector. This book, "Thermoplastic Elastomers", is comprised of nineteen chapters, written by specialized scientists dealing with physical and/or chemical modifications of thermoplastics and thermoplastic starch. Such studies will provide a great benefit to specialists in food, electric, telecommunication devices, and plastic industries. Each chapter provides a comprehensive introduction to a specific topic, with a survey of developments to date.

How to reference

In order to correctly reference this scholarly work, feel free to copy and paste the following:

Yachuan Zhang and Curtis Rempel (2012). Retrogradation and Antiplasticization of Thermoplastic Starch, Thermoplastic Elastomers, Prof. Adel El-Sonbati (Ed.), ISBN: 978-953-51-0346-2, InTech, Available from: <http://www.intechopen.com/books/thermoplastic-elastomers/retrogradation-and-antiplasticization-of-thermoplastic-starch>

INTECH
open science | open minds

InTech Europe

University Campus STeP Ri
Slavka Krautzeka 83/A
51000 Rijeka, Croatia
Phone: +385 (51) 770 447
Fax: +385 (51) 686 166
www.intechopen.com

InTech China

Unit 405, Office Block, Hotel Equatorial Shanghai
No.65, Yan An Road (West), Shanghai, 200040, China
中国上海市延安西路65号上海国际贵都大饭店办公楼405单元
Phone: +86-21-62489820
Fax: +86-21-62489821

© 2012 The Author(s). Licensee IntechOpen. This is an open access article distributed under the terms of the [Creative Commons Attribution 3.0 License](https://creativecommons.org/licenses/by/3.0/), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

IntechOpen

IntechOpen