Critical Reviews in Food Science and Nutrition

Thermoplastic Starch Processing and Characteristics—A Review

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Published online: 24 Feb 2014.

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Canola Council of Canada, Winnipeg, Manitoba, Canada The rising costs of nonrenewable feedstocks and environmental concerns with their industrial usage have encouraged the study and development of renewable products, including thermoplastic starch (TPS). Starch is an abundant, plant-based biodegradable material with interesting physicochemical characteristics that can be exploited, and this has received attention for development of TPS products. Starch exhibits usable thermoplastic properties when plasticizers, elevated temperatures, and shear are present. The choice of plasticizer has an effect on TPS, even when these have similar plasticization principles. Most TPS have glass transition temperature, T_g, in the range of approximately −75 to 10°C. Glassy transition of TPS is detected by differential scanning calorimeter (DSC) and thermodynamic analyzer (DMA), although DMA has been found to be more sensitive and effective. TPS has low tensile properties, typically below 6 MPa in tensile strength (TS). The addition of synthetic polymers, nanoclay, and fiber can improve TS and water-resistance ability. The moisture sorption behavior of TPS is described in GAB and BET models, from which monolayer moisture content and specific area are derived. Current studies on surface tension, gas permeability, crystallinity, and so on of the TPS are also reviewed.

Keywords Biodegradable packaging, starch-based bioplastics, biopolymers, plasticization

INTRODUCTION

Due to some well-demonstrated advantages, such as ready availability; relative low cost; excellent optical, mechanical, and barrier properties; good heat sealability; high resistance against water and grease, and so on, conventional petrochemical-based plastics have been widely used as packaging materials (Siracusa et al., 2008; Farris et al., 2009). However, petrochemical-based plastics are neither recyclable nor biodegradable, and this is a serious problem facing societies who are confronted with growing waste disposal needs and concerns of contaminated environment. In addition, the increase in nonrenewable energy is at a cost to the profitability of the plastic industry. It is becoming increasingly vital to replace petrochemical-based polymers with renewable alternatives based on biopolymers. In fact, the concept of employing biopolymers, such as polysaccharides, proteins, lipids, and derivatives, as bioplastic materials is not novel. The first patents on biodegradable packaging films used to extend the shelf life of foods were granted in the 1950s (Guilbert et al., 1996). However, low efficient performance and relatively high cost have hindered the adoption of the biopolymers as successful alternatives to petrochemical polymers. Continued interest from consumers and policymakers have encouraged scientists to continue R&D efforts toward bioplastic materials that can function well and are friendly to the environment (Peressini et al., 2003; Petersson and Stading, 2005). Thus far, four categories of the materials have been tried as alternative packaging recourses: (1) biopolymer hydrocolloids; (ii) lipids; (iii) resins; and (iv) composites. Biopolymer hydrocolloids include polysaccharides, such as cellulose (Pinotti et al., 2007), starch (Pareta and Edirisinghe, 2006; Alves et al., 2007), pectin (Fishman et al., 2000), algal gum (Veiga-Santos et al., 2005a, 2005b), and protein, such as wheat gluten (Kayserilioglu et al., 2001), soy protein, zein (Lai et al., 1997; Lai and Padua, 1997), casein (Mauer et al., 2000; Letender et al., 2002; Sohail et al., 2006), and others. Lipids include waxes (mineral oils, paraffin, beeswax, shellac, etc.), acylglycerols, and fatty acids. Resins include shellac and wood resin. Composites contain both lipid and hydrocolloid components in the form of a bilayer or an emulsion (Hernandes-Izquierdo and Krochta, 2008). Among these natural polymers, starch is considered one of the most promising candidates for the packaging materials due to its abundant availability, annual renewability, competitive price, and thermoplasticity (Lai and Padua, 1997; Mali et al., 2005a).

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Starch exhibits thermoplastic properties when plasticizers, elevated temperatures, and shear are present. The thermoplastic properties of starch are close to those of synthetic polymers, and it is possible to use processes developed for synthetic polymers for starch processing. To obtain a thermoplastic starch (TPS) material, granular starch is thermomechanically processed by kneading, extrusion, injection moulding, compression moulding, blow molding, or heating and casting in an excess water solution with the aid of plasticizers such as water, glycerol, or urea and additives such as lecithin or monoglycerides (van Soest et al., 1996). Some TPSs have been made into commercial thermoplastic polymers, 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 mainly find applications in the meat, poultry, seafood, fruit, vegetable, grain, and candy industries (Debeaufort et al., 1998). For example, Aguilar-Mendez and colleagues (2008) used gelatine-starch as a coating for avocado. They successfully delayed the respiratory climacteric pattern by three days at 20°C and extended avocado shelf-life. Mali and Grossmann (2003) applied yam starch films on storability and quality of fresh strawberries. The yam starch films significantly reduced the decay of the fruits stored at 4°C and 85% RH, and extended storage life from 14 days of the control to 21 days of the packaged fruits. However, there is a lack of comprehensive review on development of starch-based bioplastics. This review will summarize the current knowledge pertaining to starch-based thermoplastics.

BOTANIC STARCH BASICS

Starch is produced by green plants, such as barley, oats, wheat, rice corn, potato, tapioca, and pea, as an energy store occurring in highly organized structures known as starch granules, which vary in shape (round, lenticular, polygonal), granule size (1–100 μm in diameter), size distribution (uni- or bimodal), association (individual or granule cluster), and chemical composition (α-glucan, lipid, moisture, protein, and mineral content) (Tester et al., 2004; Mali et al., 2006; Zhang et al., 2008). It consists of two types of molecules: the linear and helical amylose and the branched amylopectin. Amylose is a mostly linear α-D-(1→4) glucan, whereas amylopectin is a highly branched α-D-(1→4) glucan, with α-D-(1→6) linkages at the branch points (Moates et al., 2001). In general, starch contains 20–25% amylose and 75–80% amylopectin. However, the amount of amylose or amylopectin in starch may vary depending on the plant sources. For example, the "waxy" starches contain less than 15% amylose, whereas "high" amylose starches contain greater than 40% amylose (Tester et al., 2004). In addition to amylose and amylopectin, granular starch also contains roughly 2% free fatty acids or monoglycerides, 0.6% protein, and 0.4% minerals (calcium, magnesium, phosphorus, potassium, and sodium). Its equilibrium moisture content in ambient condition ranges from

10 to 12% for cereal starch to 14 to 18% for starch from some roots and tubers.

Starch is hydrophilic. Its moisture content changes according to the variation in the relative humidity (RH) of the atmosphere in which it is stored (Tester et al., 2004). Starch granules are insoluble in cold water. When heated in water, starch granules swell and then undergo a transition process, during which amylose and amylopectin leach out until the granules break down into a mixture of polymers-in-solution. This process is known as gelatinization. The temperature at which the starch granule begins to gelatinize is called gelatinization temperature. It 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 approximately 160–170°C, whereas typical starches such as wheat starch (amylose:amylopectin is 28:72) gelatinize in the range of 52–65°C (Fang et al., 2004). A single granule gelatinizes in a narrow range of approximately 2°C, but a sample of complex starch grits or particles have a 4–10°C gelatinization range.

Native starch granules are biosynthetically assembled as semicrystalline structures, which consist of amorphous and crystalline regions. Both amylose chains and branches of amylopectin form double helices, which in turn associate and form crystalline domains (Tester et al., 2004). 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-, B-, and C-types. In an A-type crystal lattice, the double helices are packed in an antiparallel manner forming an orthorhombic unit-cell, resulting in nearly hexagonal close-packing. Cereal starches (rice, wheat, and corn) exhibit an A-type pattern. In B-type granules, the double helices also pack in an antiparallel manner but form a hexagonal unit cell with two helices per cell, leaving an open channel that is filled with water molecules. In contrast, in the A-type granule, this column of water is replaced by a double helix. Tubers, fruit, and high-amylose corn (>40%) starches exhibit a B-type pattern. The C-type granule is an intermediate structure of A- and B-types, observed for legume seed starches (Karim et al., 2000; Liu, 2005). In XRD pattern, the A-type crystal lattice shows three strong peaks at 5.8, 5.2, and 3.8 Å; B-type granules show a peak at 15.8–16.0 Å, a broad medium intensity line at approximately 5.9 Å, a strong line at 5.2 Å, and a medium-intensity double line at 4.0 and 3.7 Å; the C-type granule is identical to A-type granules except for the addition of the

Table 1 Crystallinity for native starch of various crops (from Zhang et al., 2008)

Crops	Crystallinity (%)
Maize	43–48
Wheat	36–39
Potato	23–53
Pea	17–20
Normal barley	2–24
Rice	38

medium-to-strong peak at approximately 16.0 Å (Ribotta et al., 2004). Table 1 presents the crystallinity for native starch of various crops, indicating that starch from different botanic origins possesses different crystallinity.

EXTRUSION APPROACHING A REALISTIC MANUFACTURING APPROACH FOR TPS

In the majority of studies, TPS is obtained by casting aqueous dispersions containing starch and watersoluble plasticizers into a plate. However, extrusion processing is a more realistic approach for the industrial preparation of TPS (Da Roz et al., 2006). Starch pellets or beads (also referred to as resin for plastic) are fed from the hopper along a feed screw through a barrel chamber. As starch pellets or beads travel along the barrel, it is subjected to friction, compression, and heated zones. The result is that the starch pellets homogeneously mix, melt, and further travel at the die of the screw. 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 molded into desired shapes (Thuwall et al., 2008). During the extrusion process, water contained in starch and other plasticizers destroys starch crystallinity, and starch undergoes fragmentation (Pushpadass et al., 2009a) to melt and flow like synthetic polymers.

For the extrusion process, some parameters are important to influence the final TPS products. These parameters include screw speed, moisture content of feed, barrel temperature, die diameter, energy input, pressure at the die, etc. Pushpadass and colleagues (2008) used corn starch with glycerol, stearic acid, sucrose, and urea as plasticizers to make TPS films. The ingredients were extruded at 110 and 120°C barrel temperature, respectively, at a constant screw speed of 45 rpm. They found that the film thickness decreased when barrel temperature was increasing from 110 to 120°C, whereas the results of tensile property did not show a significant difference. TPS films exhibited higher water vapor permeability (WVP) at 120 than at 110°C. It was attributed to the higher degrees of fragmentation as well as breaking of more hydrogen bonds in starch at 120°C. Lee and colleagues (2009) used a split-plot experiment to examine the effect of two screw speed levels (80 and 100 rpm, respectively) and 10 ingredients, each at two levels, on the properties of TPS foam. They concluded that an 80 rpm screw speed had a greater effect on the properties of the TPS foam than a 100 rpm screw speed due to longer retention time for ingredients to interact with starch, which is considered good for industry.

The composition of ingredients has been reported to affect the extrusion process, in which plasticizer type and amount are the most important. Approximately 25–35% liquid plasticizer, such as glycerol, is expected to extrude TPS. Higher amounts of plasticizers led to exudation, and lower amounts resulted in difficulties in processing. In addition, the ratio of amylose to amylopectin in starch affects the extrusion process. The extrusion of

Figure 1 Film blowing of hydroxypropylated starch (starch:glycerol:water = 100:22:8), at the start of blowing (left) and after some time when the bubble is stable (right; from Thunwell et al., 2008), indicating the potential of making free-standing starch film by using traditional plastic processing equipment from thermoplastic starch.

high-amylose starch can be more difficult than the processing of normal starch, partly due to the high die pressures required because of the high melt viscosity. An increase in the amylose content relative to that of normal starch is, however, interesting, because higher strength and higher toughness are expected from high-amylose materials (Mehyar and Han, 2004). Studies on the processing of high-amylose starches have hitherto been carried out (Thunwall e al., 2006a).

After extrusion, TPS can either be molded into containers or blown into films. To achieve a thin film, the starch melt has to be adjusted or shaped following passage through the extruder die. This can be done simply by pulling and squeezing the melt through calendering nips or by stretching the melt in two directions. Film blowing is a commonly used method for producing self-supporting plastic films. Thunwall and colleagues (2008) indicated that oxidized and hydroxypropylated starch could be film-blown in a satisfactory manner (Figure 1), whereas natural starch was more difficult. The difficulties include a sticky surface, insufficient tenacity, and foaming.

Besides extrusion and blowing, casting aqueous solutions or suspensions is another method to produce TPS films. Typically, a starch aqueous solution or suspension with desired formulation is cast into a well-levelled platform, and water is evaporated until the film is obtained. Usually, the first step of the casting method is heating starch in surplus water. When heated in surplus 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 et al., 2003). The second step is to dry the starchy aqueous solution. The final step is to peel the ready, dried starch film from the platform. Casting method is commonly used in the laboratory to study the gelatinization, plasticization, and glass-transition mechanisms. Koch and colleagues (2010) found longer heating times (15 min) and higher temperatures (150°C)

resulted in harsher manufacturing conditions, thereby producing fragmented films due to degradation of starch. Temperature had a greater effect on degradation of starch than did heating time. However, this degradation did not show analogous effects on the mechanical properties. Koch and colleagues (2010) postulated that there exists a critical length of the amylose chains, below which the films become fragmented.

PLASTICIZATION OF STARCH AND PLASTICIZERS

Native starch cannot be considered as a thermoplastic polymer due to strong intermolecular and intramolecular hydrogen bonding in the amylose and amylopectin macromolecular chains (Ma et al., 2007). However, in the presence of plasticizers (e.g., water, glycerine, sorbitol, etc.), at high temperatures (90–180°C), and under shear, native starch readily melts and flows, allowing for its use as an extruding, injection molding, or blowing material, similar to most conventional synthetic thermoplastic polymers (Ma et al., 2007). The role of plasticizers is to destruct granular starch by breaking the inter/intra-molecular hydrogen bonds, with an accompanying partial depolymerization of the starch backbone, and lowering the melting temperature of starch below its decomposition temperature (230°C) (Souza and Andrade, 2002; Stepto, 2003). This process of overcoming the brittleness in starch by softening the structure and by increasing the mobility of the macromolecular chains (Pushpadass et al., 2008), resulting in a lowering of processing temperature, is termed as plasticization. Some theories have been proposed to account for the mechanisms of plasticization. In the "lubricity theory", the plasticizer acts as a lubricant to facilitate movements of the macromolecules over each other, whereas "gel theory" considers the disruption of polymer–polymer interactions (hydrogen bonds and van der Waals or ionic forces). The "free volume theory" states that a plasticizer increases free volume between the polymers and lowers its glass-transition temperature (T_g). Regardless of which theory is the most appropriate, the role of a plasticizer is to interpose itself between the polymer chains and reduce the forces holding the chains together (Gioia and Guilbert, 1999).

To achieve successful plasticization, an appropriate plasticizer must meet some basic requirements. An appropriate plasticizer would be a small molecule, polar, hydrophilic, and compatible with the starch polymer. Other additional important requirements for a plasticizer are that its boiling point should be high enough to prevent its evaporation out of the material during processing and drying (Pushpadass et al., 2008), and its molecular structure and conformation should be similar to the D-glucopyranose units in the starch molecules. Commonly used plasticizers include water, glycerol, sucrose, fructose, glucose, glycols, urea, amides, and amino acids (Zhang and Han, 2006a, 2006b; Pushpadass et al., 2008). For the same source of starch, some plasticizers work more effectively than others. Traditionally, water and glycerol are considered to be the most effective plasticizers due to their small size, ease of insertion, and positioning within the three-dimensional starch networks. Some

small molecules containing -CO-NH- functional groups, such as urea, formamide, ethanolamine, and ethylene bisformamide, have also proved to be good plasticizers for TPS (Ma and Yu, 2004; Huang et al., 2006; Yang et al., 2006a, 2006b; Wang et al., 2008). They are believed to suppress retrogradation and improve the mechanical properties of TPS (Ma et al., 2005a, 2005b; Ma et al., 2006). Zullo and Iannace (2009) used a glycerol and urea/formamide mixture as plasticizer, respectively, on film blowing of TPS. They found that the urea/formamide mixture worked more effectively than glycerol in producing homogenous and robust films. Ma and Yu (2004) calculated the hydrogen bond energy between urea-starch, formamide-starch, acetamide-starch, and glycerol-starch, and found the strength order of these hydrogen bondings was as follows: urea > formamide > acetamide > polyols. Consequently, they attributed the high effectiveness of urea, formamide, and acetamide in plasticizing TPS to the stronger hydrogen bonding between the -CO-NH- groups of urea, formamide, acetamide, and HO- groups of starch. However, in view of food safety, plasticizers containing amide groups are not recommended for use in food packaging and edible films (Yu et al., 2010).

To plasticize starch successfully, a minimal amount of plasticizer is required. Pushpadass and colleagues (2008) indicated that at least 20% glycerol or any other suitable plasticizer is required to extrude flexible starch films. The starch films plasticized with 25% glycerol exhibited maximum tensile strength and an optimum modulus of elasticity. It is not feasible to extrude starch films with urea or stearic acid as the lone plasticizer at such concentrations.

Contrary to the orthodox behavior of plasticization, a plasticizer can conversely show an antiplasticization effect on TPS when it is introduced in low amounts under a critical level (generally <15%; refs. Lourdin et al., 1997; Godbillot et al., 2006; Zhang and Han, 2010). When antiplasticization occurs, the mechanical strength and Young's modulus of TPS increase, while elongation at break decreases, as shown in Figure 2. The mechanism of the antiplasticization effect of plasticizer on TPS has not been clearly understood. Further studies are needed to understand it.
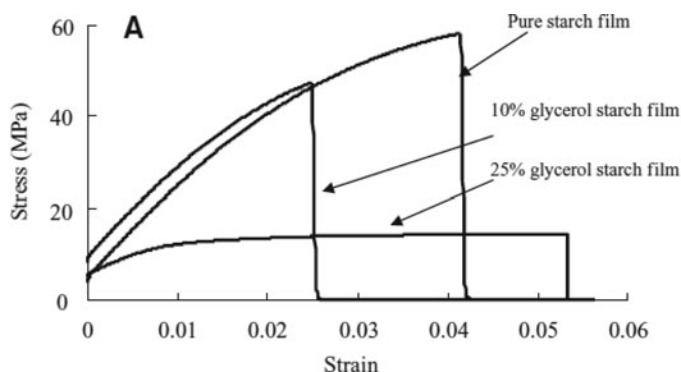

Figure 2   Strain–stress curves of pea starch film plasticized by glycerol (from Zhang and Han, 2010), indicating that strain of the starch film was reduced by adding 10% glycerol compared with pure starch film, whereas the starch film exhibited flexible when the glycerol content was up to 25%.

THERMAL AND PHYSICAL PROPERTIES OF TPS

The properties of interest in the application of TPS are mostly thermal, mechanical, barrier properties, moisture sorption behavior, retrogradation of starch, and surface tension. These properties of TPS are governed by the starch sources, additives, processing parameters, and chemical treatment of starch. Kumar and cooleagues (2011) summarized some experimental and modeling techniques to determine properties of bionanocomposites, which are also suitable for TPS products.

Glass-Transition Temperature (T_g)

Starch polymers experience multiple physical phase transitions by thermal treatment, including glass transition, gelatinization, crystallization, and melting. Figure 3 represents a diagram of changes in the physical state of starch polymer. The glass transition is one of the critical thermophysical transitions for starch-based products. Its temperature (T_g) is defined as the temperature at which the forces holding the amylose and amylopectin of the amorphous portion of starch are released to move. When the temperature rises above T_g, amylose and amylopectin obtain sufficient energy to undergo large-scale molecular motions. Conversely, when the temperature drops down below the T_g, the long-range segmental motion of the amylose and amylopectin halts. During glass transition, the polymer changes from being soft and pliable to being hard and brittle, or vice versa. Glass transition is second-order phase transition that occurs over a temperature range. As the temperature increases above T_g, many of the physical properties of the polymer sud-

denly change, among which the most important are increases in free volume, heat capacity (C_p), thermal expansion coefficient (α), dielectric coefficient (ε), and viscoelastic properties (Bhandari and Howes, 1999). Accelerated changes in these properties as a function of temperature are the basis for detecting T_g. Differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA) are common technologies to measure T_g. DSC detects changes in heat capacity (C_p) of the TPS (Ribeiro et al., 2003; Kumar et al., 2011). DMA measures the thermomechanical properties, such as storage modulus (E′), loss modulus (E″), and tanδ (E″/E′) of TPS (Zhang and Han, 2006a). In general, DMA is more sensitive to glass transition of TPS than DSC.

Predicted by the Fox and Flory relationship, native starch is determined to have T_g of 243°C (Bhandari and Howes, 1999). The addition of one or more plasticizers can dramatically reduce starch T_g. The effectiveness of plasticizer to depress starch T_g is very notable. Rodriguez-Gonzalez and colleagues (2004) depressed wheat starch T_g from 234°C to approximately −50°C by adding approximately 35% glycerol. Zhang and Han (2006a) found similar results with pea starch plasticized by glycerol, and attributed the high effectiveness of glycerol to depress the T_g to its small molecular size and high ratio of hydroxyl number to its molecular weight (3/92.09 = 0.0326). Several T_g values of TPS are listed in Table 2.

As mentioned earlier, T_g can be determined by DSC. However, most reported DSC results are not consistent and are, sometimes, controversial. This is due to the multiple phase transitions that starch undergoes during heating and the instability of water contained in starch. Frequently, researchers (Biliaderis, 1992; Chinachoti, 1996) have stated that DSC is not appropriate to
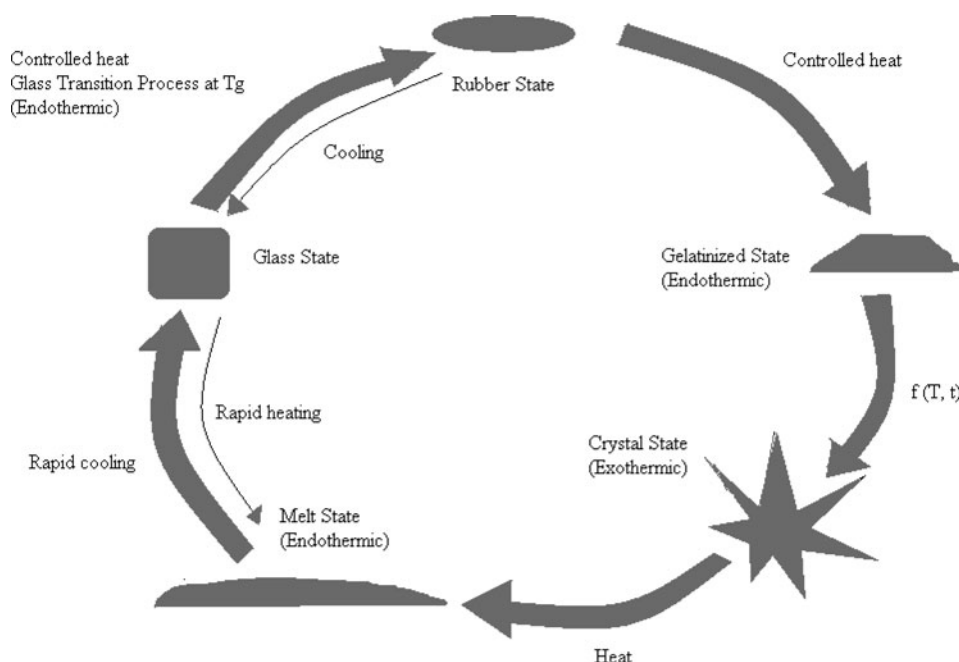

Figure 3 Change of physical state of starch polymer from glass state to melt state through rubbery, gelatinization, and crystallization (adapted and modified from Bhandari and colleagues, 1997).

Table 2   Glass-transition temperature (T_g) of several TPS

TPS product formulation	T_g (°C)	Reference
Corn starch with glycerol and triethyl citrate	20–25	Zhang et al. (2011)
Pea starch with glycerol	−66–75	Zhang and Han (2010)
Pea starch with sorbitol	−33–47	Zhang and Han (2010)
Pea starch with glucose	−26–49	Zhang and Han (2010)
Pea starch with fructose	−19–31	Zhang and Han (2010)
Wheat starch with glycerol	−56–45	Rodriguez–Gonzalez et al. (2004)
Pea starch with carboxymethyl cellulose and microcrystalline cellulose	Double T_g at −30 and 50°C, respectively	Ma et al. (2008)
Corn starch compositions	Double T_g at −60 and 110°C, respectively	Da Roz et al. (2006)
Maize starch with glycerol	−21	Sankri et al. (2010)
Corn starch with water, glycerol, and stearic acid	10.3–12.3	Pushpadass and Hanna (2009)
Wheat starch, sorbitol	∼0	Gaudin et al. (1999)

study the T_g of starch because DSC is not sensitive enough to detect the heat-flow change of starch. Recently, in order to overcome the shortcoming of DSC in testing the starch T_g, high-speed DSC (hyper DSC) has been recommended (Gramaglia et al., 2005; Katayama et al., 2008; Liu et al., 2009). DSC output is a function of the heat flow of energy per unit time. When the heating rate is increased, the heat flow or energy input per unit time increases, or the same heat flow occurs over a shorter time frame. The result of an increase in the overall sensitivity allows the measurement of glass transition that may be below the limit of detection possible by conventional DSC. Compared with a rate of 1–50°C/min of conventional DSC, high-speed DSC can scan starch samples using a heating rate of up to 500°C/min. Liu and colleagues (2009) scanned gelatinized corn starch samples containing 8.7–13.3% moisture using 20–250°C/min heating rates. They concluded that T_g of the corn starch was too weak to be detected when the heating rate was less than 50°C/min. Only when the heating rate was higher than 100°C/min was the T_g visible. Figure 4 shows conventional DSC and high-speed DSC thermograms of gelatinized corn starch containing 13.3% moisture.
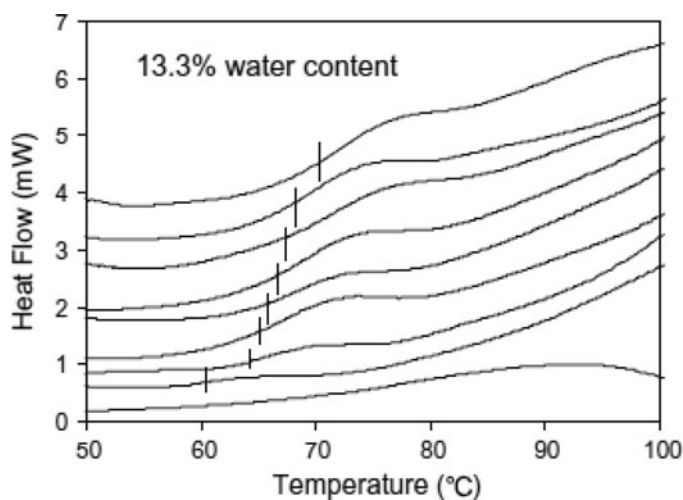

Figure 4   DSC thermogram of corn starch film containing 13.3% moisture under different heating rates: 20, 50, 100, 120, 140 160, 180, 200, and 250° C / min (from bottom to top; from Liu and colleagues, 2009). High heating rate made the heat-flow change of starch films at T_g visible.

When TPS is compounded with more than one type of plasticizer, its T_g is a nonlinear function of the T_g of individual components. The Gordon–Taylor (Equation (1)) and Couchmann and Karasz equations (Equation (2)) are commonly used mathematical relationships for predicting T_g as affected by plasticizer content in many food polymers (Bhandari and Howes, 1999; Ribeiro et al., 2003):

$$T_g = \frac{x_1 T_{g1} + (\Delta C_{P2}/\Delta C_{P1})x_2 T_{g2}}{x_1 + (\Delta C_{P2}/\Delta C_{P1})x_2} \tag{1}$$

$$T_g = \frac{\sum x_i \Delta C_{Pi} T_{gi}}{\sum x_i \Delta C_{Pi}} \tag{2}$$

where T_g is the glass-transition temperature (K) of the TPS; x_i is the weight fraction of the ith-component ($i = 1, 2, \ldots$); T_{gi} is the glass transition temperature of the ith-components; and ΔC_{Pi} is the change in heat capacity of the ith-components at T_{gi}. Values of T_g and ΔC_P for some starches and plasticizers are listed in Table 3.

Although DSC is available to make T_g measurements, by far, the most sensitive technique is DMA. Instead of heat flow, DMA measures the viscoelastic moduli, such as storage and loss modulus, damping properties, and tan delta, of materials as they are deformed under a period (sinusoidal) deformation (stress or strain) with temperature scan. After scanning the TPS sample under test, any of these viscoelastic parameters can be used to define the T_g. Figure 5 shows scans of pea starch films in tension clamps, at frequencies of 1, 5, and 10 Hz, amplitude of 10 μm,

Table 3   Glass-transition temperature (T_g) and heat-capacity change (ΔCP) for some starches and plasticizers (from Liu, 2005)

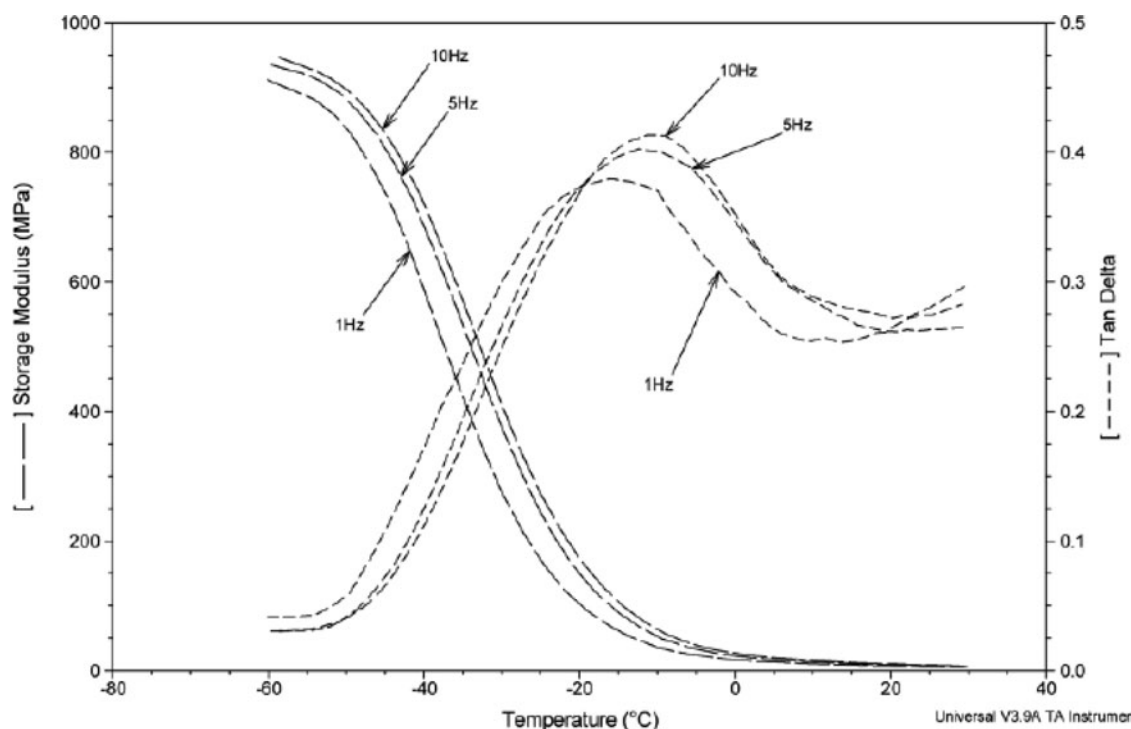| Starch and plasticizers	T_g(K)	ΔCP (J kg^{-1} K^{-1})
Pea amylose (cast 100°C)	605	265
Potato starch (cast 90°C)	589	265
Waxy maize starch (cast 90°C)	558	295
Glycerol	187	970
Water	134	1,830
Sodium lactate	246	1,960
Sorbitol	271	2,450

Figure 5   Storage modulus and tan delta thermal scans for sorbitol plasticized pea starch films (from Zhang and Han, 2006a).

and a ramp rate of $2°C/min$ (Zhang and Han, 2006a). T_g can be defined as either the mid-point between the onsets of the fall in the storage modulus or tan delta peaks.

Tensile Properties

Mechanical properties are basic properties for TPS products and often determined by tensile tests, from which mechanical properties are obtained, such as tensile strength (TS), percentage of elongation at breakage (E), percentage of elongation at yield (EY), and modulus of elasticity (EM), normally following the procedure of ASTM D882-02, Standard Test Method for Tensile Properties of Thin Plastic Sheeting. TS is the maximum tensile stress a TPS specimen can withstand before it breaks, the E value is the flexibility, and EM the stiffness (Mali et al., 2005b). The tensile properties of TPS depend on the original sources of starch, additives, glass-transition temperature (T_g), crystallinity, and ratio of amylose to amylopectin. Some studies have shown that thermoplastic amylose and amylopectin are mechanically different (Myllarinen et al., 2002; Garcia et al., 2009). Pure amylose films are stronger, whereas pure amylopectin films are more brittle. Films made of mixture of amylose and amylopectin showed that the preponderance of amylose in starch films leads to higher TS, whereas a high proportion of amylopectin leads to lower TS (Lourdin et al., 1995). This was supported by Lawton's experiments (1996), which studied several starches containing different levels of amlyose, and showed that the starch type did make a difference in the properties of

the films. Films made from high-amylose corn starch had better elongation, tensile strength, tear resistance, and impact strength, as well as higher stability at different RHs than films containing less amylose. The difference of amylose and amylopectin in the mechanical properties was presumably due to the higher degree of crystallinity in starch films containing more amylose (Liu, 2005).

The tensile properties of TPS can be adjusted by adding additives, such as plasticizers, cross-linking agents, antimicrobial agents, antioxidants, and texturizing agents. Among all of these additives, plasticizers play the most important role in TPS structure and performance, and have been widely investigated (Myllarinen et al., 2002; Zhang and Han, 2006a, 2006b). The addition of plasticizer decreases the TS and EM, and increases the E, to different extents. However, if plasticizer is overused, the E value decreases. One explanation for this phenomenon is phase-separation. As an example, if the glycerol concentration is higher than a critical level, the TPS specimen will contain two separated phases with one being the starch-rich phase, and the other being a plasticizer-rich phase, which leads to a reduced E value (Lourdin et al., 1998). Another plausible explanation is the sliding effect of the additional plasticizer molecules. When the amount of plasticizer molecules increases beyond a critical value, the interactions between starch polymers become weak, and the cohesive force of the polymer chains is reduced, resulting in a decrease in E value (Zhang and Han, 2008). In general, TPS made of native starch has TS values less than 20 MPa, indicating limited mechanical performances as shown in Table 4.

Table 4 Mechanical properties of some TPS

TPS product formulation	TS (MPa)	E (%)	EM (MPa)	References
Corn starch film with glycerol and xylitol	2.5–3.6	48–63	—	Fu et al. (2011)
Rice starch film with glycerol	1.6–11	3–60	21–533	Dias et al. (2011)
Rice starch film with sorbitol	11–22	3–4	456–1,053	Dias et al. (2011)
Cassava starch with glycerol	1.4–1.6	83–101	11–21	Muller et al. (2009a)
Corn starch with glycerol and stearic acid	0.2–2.9	46–91	3–38	Pushpadass et al. (2009a), 2009b
Amaranthus cruentus flour films wih glycerol and stearic acid	0.8–3.0	74.2–620	—	Colla et al. (2006)
Corn starch films	0.9–4.8	—	—	Da Roz et al. (2006)
Potato starch with glycerol	3	47	45	Thunwall et al. (2006a) and 2006b
Corn starch with glycerol	3	20	—	Dai et al. (2008)
Rice starch with glycerol	3.2	—	—	Mehyar and Han (2004)
Pea starch with glycerol	4.2	—	—	Mehyar and Han (2004)
Pea starch with glycerol	1.4–5.8	38–51	8–98	Zhang and Han, 2006

Gas Barrier Properties

All the polymers have been proven to be relatively permeable to small molecules such as oxygen, carbon dioxide, water vapor, organic vapors, and liquids, and provide a broad range of mass transfer characteristics, ranging from excellent to low barrier value depending on the starch resource, water hydration, plasticizer type and amount, storage temperature, and so on. Therefore, determination of the barrier properties of a TPS film is crucial for estimation of packaged product shelf-life. The gas barrier property is characterized by the gas permeability coefficient, which indicates the amount of the gas that permeates per unit of area and time through a TPS packaging film. The permeation of gas molecules usually takes place through the starch polymer amorphous phase and is generally envisaged as a combination of two processes, that is, absorption and diffusion. Gas molecules are absorbed (or dissolved) onto the TPS film surface first before they permeate through the film. The absorbed gas molecules start to diffuse into the film following Fick's first law. Gas absorption, diffusion, and permeation are typical mass transfer phenomena occurring in packaging films (Han and Scanlon, 2005). Arrhenius plots of diffusion coefficients and permeability show classical behavior that the permeability coefficient is the simple product of diffusivity (D) and solubility (S), which roughly follows an Arrhenius relation as a function of temperature.

A gas permeability coefficient for a specific TPS film is calculated by the following equation (Equation (3)):

$$P = TR \times l/\Delta p \qquad (3)$$

Where l is the thickness of the TPS film, Δp is the difference between the gas partial pressure across the film, and TR is the rate of gas transmission.

Practically, gas barrier properties for a TPS film include water vapor permeability (WVP), oxygen permeability (OP), and aroma permeability. WVP is used to describe the ability of the film to control water vapor transportation between a food system and its surrounding. Some experimental WVP data are listed in Table 5. In general, starch films have higher WVP than synthetic films due to the hydrophilic nature of starch and plasticizers. Therefore, TPS films are not considered good water vapor barriers. The poor water barrier performance of TPS films can be improved through the incorporation of lipid materials, such as neutral lipids, fatty acids, and waxes (Garcia et al., 2000a; Petersson and Stading, 2005; Han et al., 2006). Bilayer films, in which a hydrophobic lipid layer is laminated over a hydrophilic TPS 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. Plasticizer was believed to favor water vapor transmission according to reports of Zhang and Han (2006b) and Mali and colleagues (2002). Sothornvit and Krochta (2005) hypothesized that increasing the plasticizer amount reduced the cohesive forces between starch polymer chains and increased the free volume and segmental motions of starch polymers; therefore, water molecules diffused more easily and a higher WVP occurred as a result. Moreover, the addition of plasticizer increases hydrophilic nature of starch matrix resulting in easy absorption of water molecules onto the TPS surface.

Table 5 Water vapor permeability (WVP) of TPS films (adapted from Zhang et al., 2008)

TPS formulation	WVP (g mm m^{-2} h^{-1} kPa^{-1})	References
Rice starch with glycerol	16.7–31.2	Dias et al. (2011)
Rice starch with sorbitol	9.6–10.9	Dias et al. (2011)
Corn starch with glycerol	12.0–20.0	Pushpadass et al. (2009b)
Cassava starch with glycerol	2.33–10.3	Muller et al. (2009a)
Yam starch with glycerol	0.34–0.65	Mali et al. (2002)
Corn starch with glycerol	1.93–2.41	Mali et al. (2006)
Cassava starch with glycerol	1.45–2.25	Mali et al. (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 et al. (2000a)

Table 6 O$_2$ permeability (OP) of various TPS films (from Zhang et al., 2008)

Film	OP (g mm m^{-2} h^{-1} kPa^{-1})	References
Soluble starch and methyl cellulose with glycerol	3.53×10^{-5}–1.69×10^{-1}	Arvanitoyannis and Biliaderis (1999)
Soluble starch and methyl cellulose with sorbitol	3.17×10^{-4}–2.05×10^{-2}	Arvanitoyannis and Biliaderis (1999)
Soluble starch and methyl cellulose with xylose	3.56×10^{-4}–2.38×10^{-1}	Arvanitoyannis and Biliaderis (1999)
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	4.17×10^{-12}–5.00×10^{-10}	McHugh and Krochta (1994)

The oxygen barrier is another important gas barrier property for TPS film. TPS film usually has impressive O$_2$ barrier properties at low hydration conditions (Guilbert, 2000) because of its hydrophilic nature. Some O$_2$ permeabilities of TPS films are listed in Table 6. The O$_2$ permeability of PTS film is one or more order magnitudes below the synthetic polymer, such as low-density polyethylene and ethylene vinyl alcohol. Similar to WVP, the addition of plasticizer increases O$_2$ permeability by increasing the free volume and decreasing crystallinity in the starch-based matrix. Forssell and colleagues (2002) studied the effect of glycerol content on the oxygen permeability of amylopectin film at 50% relatively humidity and 20°C. It was found that the O$_2$ permeability of amylopectin film increased with increasing glycerol content to more than 10% glycerol. They also found that the O$_2$ permeability of the glycerol-plasticized starch film at constant temperature depended on the water content of the films. Below 15% water content, the film was a good oxygen barrier, but above 20%, the barrier property was lost.

The aroma barrier property is usually proposed to be the last gas barrier consideration for packaging film, because aroma compounds from the packed foodstuff are not readily absorbed into the starch matrix due to the hydrophilic nature of the starch films. Only a few studies have reported the aroma barrier properties of starch-based films including Miller and Krochta (1997). Sereno and colleagues (2009) found that the aroma permeability of hydroxypropyl maize starch films was mainly influenced by the water content in the film and the glass-to-rubber transition. Increase in film water content could result in an increase of 1 to 3 orders of magnitude for the permeability of ethanol, pyrazine, decanone, and menthone as the film's water level changed from 7.1 to 29.4% (wet basis). They also concluded that hydroxypropyl maize starch films had poor barrier behavior to aromas above its glass transition temperature. Quezada-Gallo and colleagues (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 structure of the film.

Moisture Sorption Isotherm

TPS is hydrophilic and picks up water from the environment when the environmental RH increases, or loses water while the RH decreases. Change in the moisture content leads to a change in the TPS structure and, further, leads to the change in their mechanical and thermal properties. The relationship between the water content of TPS and the environmental RH, at a constant temperature, is described by the moisture sorption isotherm (Srinivasa et al., 2003), typically shown as a sigmoidal curve. More than 200 sorption isotherm models have been developed. However, no single equation has the ability to describe accurately the relationship of equilibrium moisture content and environmental RH for various TPS over a broad range of RH and temperature. The change in the sorption isotherm is due to any modification in the composition or structure of the TPS (Sebti et al., 2003) and the fact that the water is associated with the starch matrix by different mechanisms in different water activity regions (Mali et al., 2005b). Therefore, for a specific TPS, there is a need to search for the most appropriate isotherm equation. The best-known isotherm equation is that of Guggenheim, Anderson, and de Boer (GAB), which has been widely used to describe the water sorption behavior of TPS (Mali et al., 2005b), because the model has an excellent fit for almost the entire sorption isotherm (Biliaderis et al., 1999). Except for TPS, 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 (Roy et al., 2000; Srinivasa et al., 2003). The GAB model is listed in Table 7.

In addition to the GAB model, the BET model (Table 7) is another popular model to fit sorption data (Cha et al., 2001; Srinivasa et al., 2003). The BET isotherm was originally derived by Stephen Brunauer, Paul Emmet, and Edward Teller. It is also popular in describing moisture sorption isotherm of TPS.

Table 7 Moisture sorption isotherm models

Name	Model
BET	$M = ABa_w / \{(1 - a_w)[1 + (B - 1)a_w]\}$
GAB	$M = ABCa_w / \{(1 - Ca_w)(1 + (B - 1)Caw)\}$

M, equilibrium moisture content (g water/ g dry matter); a_w, water activity; A, B, C, constants. In the 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 multilayer with respect to the bulk liquid.

However, the BET model has one shortcoming; it does not take into account water effect on structural changes in TPS as a result of water adsorption. When dissolution of TPS structure occurs at a RH greater than 70%, the BET model will not prove applicable to provide insight into the sorption process. Therefore, the BET model is usually restricted for use in the RH range of 11–55% (Mathlouthi, 2001), where film destruction does not occur. In fact, the GAB model is an extension of the BET model with a correction factor, C, for the structural changes of TPS, such that the GAB model can be used in almost the entire range of environmental RHs. Roy and colleagues (2000) claimed that the lower the C value from unity, the lower the sorption of water. At RHs greater than 85%, accuracy of moisture determination of BET falls quickly as osmotic and capillary phenomena affect water sorption due to structural changes of the films (Biliaderis et al., 1999).

One valuable information that can be evaluated from the GAB model is the value of monolayer water, parameter A in the GAB equation. The estimated monolayer concept is useful because of its relationship with the stability (physical and chemical aspects) of low- and intermediate-moisture films (Diab et al., 2001). At monolayer moisture content level, the rate of film-quality loss resulting from chemical reactions can be negligible (Zimeri and Kokini, 2002). Another important characteristic value is the specific surface area, S_o, which describes the surface characters and water-binding properties of the TPS sample. S_o is determined from the monolayer moisture content. Equation (4) is used to calculate S_o (Cassini et al., 2006; Rosa et al., 2010). The S_0 of TPS value usually increases with plasticizer content, indicating that plasticizer loosens the structure of the samples, making more surface area available for hydrophilic binding.

$$S_0 = M_m \times \frac{N_0 \times A_{H_2O}}{M_{H_2O}} = 3.5 \times 10^3 \times M_m \quad (4)$$

where S_0 is the specific surface area (m^2 g^{-1}), M_m is the monolayer moisture (parameter A in GAB model divided by 100) (water g g^{-1}, db), M_{H_2O} is the molecular weight of water (18 g mol^{-1}), N_0 is Avogadro's constant (6 × 10^{23} mol^{-1}), and A_{H_2O} is the area of one water molecule (1.06 × 10^{-19} m^2).

The sorption isotherm of TPS from different sources such as potato, pea, cassava, corn, rice, yam, and wheat have been studied extensively by Dias and colleagues (2011), Mali and colleagues (2002), Fang and Hanna (2000), Myllarinen and colleagues (2002), Biliaderis and colleagues (1999), Cha and colleagues (2001), Mali and colleagues (2005b), Zhang and Han (2008), and Zhang and colleagues (2011). Some results of the moisture sorption isotherm based on the GAB model are summarized in Table 8, indicating that the monolayer water content in the TPS samples was in the range of 3.5 to 39.0 g/100 g (d.b), and it increased with increasing plasticizer content. The glycerol-plasticized TPS contained more monolayer moisture than sorbitol- and xylose-plasticized TPS. The high MC of glycerol-plasticized TPS is probably due to the high polarity of glycerol (dielectric constant of 42.5 at 25°C; ref. Yang and

Paulson, 2000), whereas sorbitol has a dielectric constant of 33.5 at 80°C (Arvanitoyannis et al., 1997).

Retrogradation of TPS and Its Crystallinity

The amorphous phase in TPS is meta-stable and, as a result, starch retrogradates over time during storage. This process is called aging. Starch retrogradation occurs when the starch polymers in amorphous area are not in thermodynamic equilibrium, and tend to approach equilibrium with time. Mechanisms of starch retrogradation were already hypothesized by Delville and colleagues (2003), who proposed that the double helices of amylopectin short chains first form crystalline lamellae. The crystalline lamellae then gradually form a crystalline cluster. Tako and Hizukuri (2000, 2002) further proposed the mechanisms of starch retrogradation at the molecular level. They believed that 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, as well as 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 the amylopectin molecule.

The kinetics of starch retrogradation depends on several factors, among which temperature is the most important one. 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 the difference between the storage temperature and T_g (Mali et al., 2006), with increasing retrogradation rate for higher temperature, especially under the conditions of high relative humidity or high plasticizer contents (Delville et al., 2003). Conversely, when TPS is stored at temperatures below the T_g, starch polymers are in a stable glassy state, and retrogradation does not occur or is extremely slow. Indeed, T_g has been considered as a reference temperature in food industry: below T_g, the food is expected to be stable; above this temperature, the food changes in physical structures. The difference between T_g and the storage temperature T is assumed to control the rate of physical, chemical, and biologic changes. The retrogradation rate of various amorphous sugars (lactose, sucrose, sucrose, and sucrose/fructose) may be determined by using the WLF equation (Equation (5)), rather than the common Arrhenius theory (Bhandari and Howes, 1999; Ribeiro et al., 2003).

$$\log_{10}\left(\frac{t}{t_g}\right) = \frac{-C_1\left(T - T_g\right)}{C_2 + \left(T - T_g\right)} \quad (5)$$

where t is the time of crystallization, t_g the time to crystallize at T_g, C_1 and C_2 are constants (17.44 and 51.6 K, respectively), and T is the storage temperature (K). Thus far, there are no data available on the results of TPS crystallization kinetics.

Table 8 GAB model parameters values for TPS

Starch source	Plasticizer (plasticizer/ starch, w/w)	A (g of H_2O/100 g sample, d. b)	B	C	References
Pea	Glycerol (60/100)	39.0	3.21×10^{70}	0.79	Zhang and Han (2008)
Cassava	N/A	3.5	157	0.89	Mali et al. (2005b)
Cassava	Glycerol (25/100)	5.2	10.78	0.96	Mali et al. (2005b)
Cassava	Glycerol (67/100)	9.1	11.99	0.96	Mali et al. (2005b)
Cassava	Glycerol + sorbitol (1:1, w/w), (25/100)	4.3	71.93	0.97	Mali et al. (2005b)
Cassava	Glycerol + sorbitol (1:1, w/w), (67/100)	5.4	22.39	0.99	Mali et al. (2005b)
Cassava	Sorbitol (25/100)	4.3	238.00	0.97	Mali et al. (2005b)
Cassava	Sorbitol (67/100)	4.2	40.29	0.99	Mali et al. (2005b)
Rice	Glycerol (20/100)	12	1.42	0.85	Dias et al. (2011)
Rice	Glycerol (30/100)	16	1.70	0.87	Dias et al. (2011)
Rice	Sorbitol (20/100)	7	4.12	0.87	Dias et al. (2011)
Rice	Sorbitol (30/100)	11	1.31	0.82	Dias et al. (2011)
Corn starch/pea fiber or potato pulp	Glycerol + triethyl citrate (42.8/100)	16–20	-4.7×10^{61}–170	0.8	Zhang et al. (2011)
Corn starch/Pullulan blend (1:1, w/w)	N/A	7.7	20.6	0.88	Biliaderis et al. (1999)
Corn starch/Pullulan blend (1:1, w/w)	Sorbitol (11/100, sorbitol/blend)	6.0	20.3	0.99	Biliaderis et al. (1999)
Corn starch/Pullulan blend (1:1, w/w)	Sorbitol (25/100, sorbitol/blend)	7.0	6.9	1.01	Biliaderis et al. (1999)
Corn starch/Pullulan blend (1:1, w/w)	Xylose (11/100, xylose/blend)	7.8	55.0	0.97	Biliaderis et al. (1999)
Corn starch/Pullulan blend (1:1, w/w)	Xylose (25/100, xylose/blend)	9.9	20.2	0.96	Biliaderis et al. (1999)

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 multilayer with respect to the bulk liquid.

Other factors affecting the rate of starch retrogradation include environmental RH and plasticizer content. In the rubbery state, high 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 and colleagues (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 and colleagues (2000b) 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 and colleagues (2003) found that starch films without plasticizers exhibited less recrystallinity than the plasticized starch films.

Several crystal structures of starch have been reported including A-, B-, and C-types of crystallinity and V-type structures, for low- and medium-moisture starch food products, such as cakes, bread, and several extrusion-cooked starch products (Riisom et al., 1984; Chinnaswamy et al., 1989; Eliasson, 1994). van Soest and colleagues (1996) identified six crystal structures in TPS immediately after starch extrusion. These are double–helical A-, B-, and C-type structure and single helical V_H-, V_A-, or E_H-type structures. Unlike A-, B-, and C-type crystal, the V-type crystal structure is formed by amylose and has

a left-handed, single helical conformation, and has a relatively large cavity. The A-, B-, and C-type crystallinity is attributed to residual crystallinity, which is present in granular starch. The V-type single helical structures are formed during thermomechanical processing by the fast recrystallization of amylose, and are attributed to processing-induced crystallinity. In the research of van Soest and colleagues (1996), TPS composition, processing, and thermal history were reported to influence the crystal type and amount directly or indirectly.

The typical XRD patterns of TPS are characterized by sharp peaks associated with the crystalline portion area and an amorphous area (Figure 6). 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). The crystallinity of the starch films can be calculated using the following equation (Equation (6)):

$$Crystallinity = \frac{A_c}{A_c + A_a} \times 100\% \tag{6}$$

where A_c is the crystalline area on the X-ray diffractogram and A_a is the amorphous area on the X-ray diffractogram (Kalichevsky et al., 1993; Yoo and Jane, 2002).
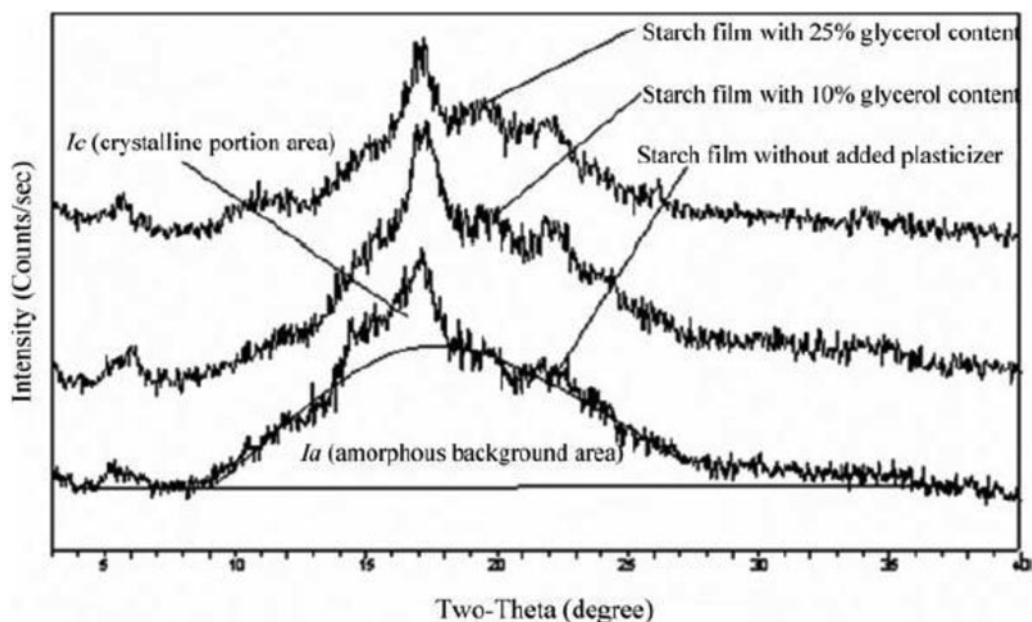
Figure 6 X-ray diffraction patterns of peas starch films plasticized by 0, 10, and 25% glycerol, respectively (from Zhang ang Han, 2010).

TPS undergoes retrogradation during aging and results in increase in crystallinity, leading to the change in the physical properties of TPS. Pushpadass and Hanna (2009) reported that the crystallinity 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, TS of TPS samples increased by 39.3–134.1%, E decreased by 48.0–81.1%, and WVP decreased by 6.1%–19.3%. Lower E value indicates TPS become stiffer, less flexible, and more difficult to handle. Therefore, these changes in mechanical properties caused adverse effects on TPS. Delville and colleagues (2003) delineated that crystallites may act as physical cross-linking points which generate internal stresses of TPS, leading to the increase in TS and decrease in E. Pushpadass and Hanna (2009) explained that the increase in crystallinity with time decreased the free volume in the TPS network and resulted in a decrease in WVP.

Surface Tension

Surface tension is technically significant for TPS capability to be printed, coated, and sealed. In food packaging, good adhesion in the seal areas is highly desirable. Without adequate adhesion, food may become contaminated with foodborne organisms or extraneous materials (Ozdemir and Floros, 2004). Surface tension is also an important parameter for wettability. High surface tension results in good spreading of a liquid on the surface. Only a few of studies are available pertaining to surface tension study for TPS, including Han and Krochta (1999), Cyras and colleagues (2008), and Zhang and colleagues (2011). Several methods can be investigated to study the surface tension, among which the Zisman method and Owens–Wendt theory are the popular ones. The Zisman method determines the so-called

critical surface free energy (γ_c), whereas the Owens–Wendt theory measures the dispersive (γ_S^d) and polar (γ_S^p) components of a surface energy. Zhang and colleagues (2011) reported starch film blended with pea fiber and potato pulp had γ_c value in the range of 30–45 mN/m, which is very comparative to those of conventional polymers. According to Zisman, liquids with surface tension lesser than 30 mN/m can wet these films successfully. The γ_c is a critical surface energy of wetting and not equal to the real surface energy of the films. The latter is larger, especially when considering the polar character of starch. Zhang and colleagues (2012) used Owens-Wendt theory to measure the surface energy of TPS film. They found TPS film made of native starch had total surface energy of nearly 80 mN/m, in which polar component of surface energy was about 70 mN/m. However, after PLA was added to native starch, surface energy of TPS film decreased significantly to 35–40 mN/m, which is comparable to conventional polymers, indicating blending PLA with starch is a potential approach to reduce the surface energy of TPS film.

Modified Starch, Nanocomposites, and Reinforcements

Because TPS made of native starch exhibits strong hydrophilic character and low mechanical properties, several approaches have been tried to mitigate these two shortcomings. Chemical modification of starch is one of approaches that has been carried out. Starch modification is generally achieved through derivatization, such as etherification, esterification, cross-linking and grafting of starch, and decomposition (acid or enzymatic hydrolysis and oxidization of starch). Such modification profoundly alters starch gelatinization, pasting, and retrogradation behavior (Singh et al., 2007). Fringant and colleagues (1998) and Gonzalez and Perez (2002) reported

that acetylation of starch hydroxyl groups reduced the tendency of starch to form strong hydrogen-bonded networks, decreased the T_g, and gelatinization temperature. During acetylation, the hydrophilic hydroxyl groups are substituted with hydrophobic acetyl groups, which can prevent the formation of hydrogen bonding between the hydroxyl groups and water molecules, leading to an increase in the water resistance of the TPS (Fringant et al., 1996; Miladinov and Hanna, 1999; Lawal and Adebowale, 2005). The other benefits of acetylation include the increase in transparency of starch films by preventing or minimizing the association of amylopectin outer branches, which cause cloudiness and syneresis in aqueous dispersions of starches. Reddy and Yang (2010) used citric acid to cross-link starch, and found cross-linked starch films have approximately 150% higher strength than non–cross-linked films. Ghanbarzadeh and colleagues (2011) reported that the WVP of the corn starch film significantly decreased 40% when citric acid content was up to 10% (w/w), and concluded 10% (w/w) was the optimum concentration of citric acid to act as a cross-linking agent in the starch matrix.

Blending starch with biodegradable polymers, such as poly (lactide), poly (caprolactone), poly (propylene carbonate), and poly (lactic acid), poly-3-hydroxybutyrate (Ke and Sun, 2000; Godbole et al., 2003; Preechawong et al., 2005; Wang et al., 2007; Wang et al., 2008), or polyester, is another approach for mitigating shortcomings related to hydrophobic characters and mechanical properties. From studies conducted on the film blowing of starch-containing biodegradable polymers, one can conclude that TPS films with good mechanical properties can be developed. For example, a blend of TPS and poly (lactic acid) in the presence of citric acid, formamide, and water as plasticizers developed a film with a very good tensile strength, which is competitive to pure PLA. In addition, the miscibility of the TPS blend and its degradation are also improved (Wang et al., 2007). In addition to biodegradable polymers, starch is also blended with synthetic polymers. Starch–polyethylene, starch–poly(vinyl alcohol) (PVA), and starch–poly(glycolic acid) co-polymers have already been prepared successfully (Pushpadass et al., 2010). All of these composite TPS were reported to have enhanced mechanical properties. However, three major issues with the composite of TPS/synthetic polymer, particularly starch/LDPE films, are still present: (i) poor adhesion and compatibility between the hydrophilic starch and the hydrophobic synthetic polymer, which results in weak functional properties; (ii) their non-biodegradability; and (iii) minor amount of starch in the total composite (≤40%; ref. Pushpadass et al., 2010).

The development of the polymer/nanofiller composites has been termed as one of the latest revolutionary steps of the polymer technology, and it has been investigated (Chen and Evans, 2005; Cyras et al., 2008; Carment et al., 2009; Wu et al., 2009; Chivrac et al., 2010). Owing to the nanometer-size particles (at least one dimension at range of 1–100 nm) dispersed in the starch polymer maxtrix, the TPS/clay nanocomposites exhibit marked improvements in properties, such as tensile strength, gas barrier, and thermal and oxidative stability. Among clay minerals, which are aluminum silicates of a layered type classified as phyllosilicates, montmorillonite (MMT) is the most commonly used layered silicates due to its environment-friendly nature and ready availability in large quantities with relatively low cost (Cyras et al., 2008). Experiments showed that the moisture content reduced significantly when 5% MMT was added to the starch, whereas the Young's modulus increased up to 500% (Cyras et al., 2008). Park and colleagues (2003) found that addition of 5% sodium montmorillonte increased the tensile strength from 2.6 to 3.3 MPa, elongation at break from 47 to 57%, and temperature at which the composite lost 50% mass from 305 to 336°C. Moreover, Huang and colleagues (2006) achieved very high tensile stress and strain, 23.7 MPa and 158.9%, respectively, for cornstarch/MMT nanocomposites with formamide and urea being plasticizers. Chung and colleagues (2010) attributed the reinforcement effect of nanoclay in TPS to the good dispersion of nanoclay in the starch molecule matrix, which results in large interface area and high interactions between the starch polymers and the nanofillers. McGlashan and Halley (2003) summarized three types of nanocomposites when nanoclays are mixed with a polymer, which are tactoid, intercalated, and exfoliated structures respectively (Figure 7). Only intercalated and exfoliated nanocomposites exhibit the most efficient improvements in physical properties, because the silicate layers are completely delaminated from each other and well-dispersed. The formation of intercalation or exfoliation depends on the type of the nanoclay and the processing conditions (Rhim and Ng, 2007). In addition to the mechanical properties, MMT was also reported to improve the gaseous barrier of the TPS. Tang and colleagues (2008) reported that the WVP of wheat starch film with MMT content of 21% was 70% lower than that of wheat starch film with no MMT. Rhim and Ng (2007) summarized nanoparticles dispersed in the starch matrix provide a tortuous path for water and gas molecules to pass through. This increases the effective path length for diffusion, thereby improving the barrier properties.

Fiber is also an approach to reinforce TPS. Commonly used fibers are cellulose nanocrystallites (Curvelo et al., 2001; Soyke-abkaew et al., 2004; Alvarez et al., 2005; Ma et al., 2005a, 2005b; Lu et al., 2006; Muller et al., 2009a, 2009b) and commercial regenerated cellulose fibers (Funke et al., 1998; Muller et al., 2009a). TPS/fiber composite has shown a great improvement in mechanical properties, gas barrier, water resistance, and thermal stability (Lu et al., 2005; Ma et al., 2005a; Panthapulakkal et al., 2006). Ma and colleagues (2005a), conducted experiments on TPS/micro-winceyette fiber composites. They found that the increase in fiber content improved the tensile strength of the composite. Later on, Ma and colleagues (2008) got similar results with pea starch/carboxymethyl cellulose (CMC) and pea starch/microcrystalline cellulose (MC) composites. Below the 9% (w/w) concentration level, CMC and MC exhibit reinforcement effect on the tensile strength (TS). This phenomenon was attributed to the remarkable intrinsic adhesion of the CMC or MC–pea starch interface caused by the chemical similarity of starch and cellulose derivatives (Ma et al., 2008). However,
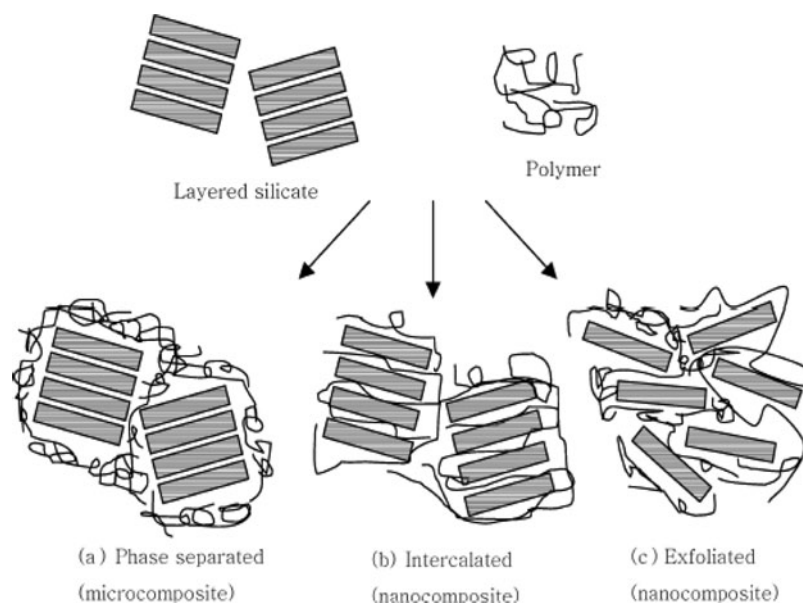
Figure 7   Three types of nanocomposite structure of polymer-layered silicate clay materials (from McGlashan and Halley, 2003).

redundant CMC or MC could induce conglomeration and reduce the tensile strength of the composite. Muller and colleagues (2009a) also found that the addition of cellulose fibers to starch-based films increased the stability of starch-based films in relation to variations in relative air humidity.

FUTURE TRENDS

TPS has been used for commercial scale to make drug-delivery capsules, golf tees, cutlery, plates, food containers, and other products (Stepto, 2003). In Europe, bioplastics account for approximately 5–10% of the current plastic market (~50,000 t; ref. Siracusa et al., 2008). More and more countries are joining this development, indicating that the TPS has promising potential for large-scale production of biodegradable packaging materials. Further applications could include food wraps, layers between food components, or being heat-sealed to form sacks, sachets, pouches, or bags to contain dry foods or preweighed ingredients (Hernandez-Izquierdo and Krochta, 2008). However, low mechanical properties, poor water vapor resistance, and retrogradation are still big challenges for the TPS. Therefore, more research is needed for TPS use and optimization. The improvement of mechanical and barrier properties of TPS products can be achieved by starch modification or working with biodegradable or synthetic polymers, nanoclay, and fiber, and would further attract interest by the industry and consumers. Extrusions, injection-molding, compress-molding, and blowing are the most important processing methods for TPS production in commercial scale. Extrusion processing conditions such as feed rates, barrel temperature profile, screw configuration, and screw speed are critical for TPS preparation. TPS transition, from glassy state to rubbery state, can be achieved by using plasticizers.

Further developments include the thermoplastic processing of modified TPS, nanocomposties, and blends of TPS with biodegradable or synthetic polymer to give the possibility of flexible TPS and materials with further improved mechanical properties, lower water sensitivity, and more stability in a variety of relative humidity. Development of instrument for industrial scale TPS manufacturing is critical. In addition, active or intelligent TPS packaging is another prospective area. Addition of antimicrobials, antioxidants, and flavors would result in a wider range of food applications (Hernandez-Izquierdo and Krochta, 2008).

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