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Thermoplastic Starch

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1. Introduction

Thermoplastics are polymers that can flow when heated above a melting or vitrification temperature. They undergo plastic deformation, meaning viscous flow with often-complex rheology due to their large molar mass, entanglements, interactions and chain branches. Starch is a natural polymer with complex levels of structure that impinge upon thermoplastic deformation. Natural polymers are no different to synthetic polymers once some added levels of structural complexity are understood (Wunderlich, 2011). Starch is a semi-crystalline polymer that does not melt in the traditional sense to form a liquid. Starch melting does mean loss of crystallinity due to disruption of hydrogen bonds, however melting occurs in the presence of a moderate (10-30 % w/w) water content. Starch crystals contain about 9-10 % w/w of bound water, where bound water means water that does not freeze when cooled below 0 °C. Additional water is required for melting of starch at convenient temperatures below the boiling temperature of water and the degradation temperature of the starch.

Starches are applicable to thermoplastic processing, unlike other polysaccharides such as cellulose and various gums. Cellulose is a natural structural polymer designed for regularity of packing, chain stiffening and strong cohesion via hydrogen bonding. Cellulose is a structural polymer forming cell walls in plants and it cannot be melted at moderate temperatures when only water is present. Cellulose has interesting solution properties of practical importance since solution processing is the method for transforming cellulose into fibres and films. Starch is an energy storage polymer designed for reversible chain propagation and reversible structure formation to allow access to enzymes for its energy forming degradation. Starch is a biopolymer that is biodegradable, suitable for green packaging materials providing that it can be formulated and readily processed into usable forms. Traditional processing equipment such as extrusion and thermoforming can be used with adaption for the specific characteristics of starch.

Thermal processing of starch has been reviewed as to changes in microstructure, phase transitions and rheology as a consequence of processing technique, conditions and formulations (Liu, Xie, Yu, Chen, Li, 2009). Starch has a unique microstructure that contributes multiphase transitions during thermal processing that provides an illustrative model to demonstrate conceptual approaches to understanding structure-processing-property relationships in all polymers. A unique characteristic of starches is their thermal processing properties that are considerably more complex than those of conventional

polymers, because multiple chemical and physical reactions take place during processing. Examples of phenomena taking place during processing are: water diffusion, granular expansion, gelatinization, decomposition, melting and crystallization. Of the phase transitions, gelatinization is of most importance because it is the means of conversion of starch to a thermoplastic. The starch decomposition temperature is higher than its pre-gelatinization melting temperature. Conventional processing techniques such as extrusion, injection molding, compression molding, thermoforming and reactive extrusion, have been adapted for processing thermoplastic starch.

Starch is a versatile biopolymer obtained from renewable plant resources such as maize, wheat and potato harvests. Starch consists of two component polymers, amylose (AM) and amylopectin (AP). Amylose is the linear polysaccharide, poly(α -1,4-glucopyranosyl). Amylopectin is poly(α -1,4-glucopyranosyl) with many α -1,6-glucopyranosyl branches. The molar mass of AM is large, $>10^6$ g/mol, while AP is $>10^7$ g/mol. There are various crystal forms of starch, due to double helix formation of linear regions of AP. The crystalline and amorphous regions assemble in layered formations to ultimately constitute the starch granules. Starch is economically competitive with polymers derived from petroleum for manufacture of packaging materials. Starch based materials are biodegradable.

Thermoplastic starch (TPS) has attracted much attention due to its thermoplastic-like processability with temperature and shear, though the structures being disrupted are more complex than those of synthetic thermoplastics. However, TPS is no different to any other polymer with respect to linear and branched structures, molar mass, glass transition temperature, plasticiser modification, crystallinity and melting temperature. Starch is a stereo-regular polymer with chirality, directionality of the chains, branching and a high density of hydrogen bonding. Polymerisation of glucose into starch not only builds the primary chains, but forms the secondary regular packing of chains into crystals and the clustering of crystals into tertiary cell structures.

The aim of this review is to provide a framework for the transition from native starch, from its primary molecular structure, secondary structure and tertiary granules to thermoplastic starch with its properties that parallel and contrast with synthesis thermoplastics. Objectives will be to interpret chemical structure changes in forming thermoplastic starch and additives that will assist with native structure dissociation, processing and the properties of materials formed from starch compositions.

2. Structure and chemistry of starch

The structure of starch considered from a top down approach begins with visual features and mines toward chemical bonding: starch consists of granules, and the granules have cell walls separating them. Within each cell are crystal bundles interspersed with amorphous starch, lipids and waxes and then the individual crystalline regions (Shogren, 2009). Several crystal structures are formed depending on the source of the starch: A (cereal starch), B (tuber starch), C (a combination of A and B crystals), V (retrograded starch) type. Starches consist of amylose and amylopectin at the molecular level in helical coils. Figure 1 shows a schematic of various levels of starch morphology and chemical structures for amylopectin, with amylose amorphous regions omitted. The primary structure of starch is the linking of glucose units into a continuous chain of amylose and with branches in amylopectin.

Adjacent amylopectin branches form a double helical secondary structure that is the basis of crystallinity in starch granules. The double helical structures then associate into a tertiary structure of a superhelix of the secondary double helical configuration. Further superstructures form combined with inter-crystalline amylose and associated lipids. Figure 2 shows a starch tetramer to illustrate a stereochemical view of the primary starch structure, representative of an amylose starch chain without branching.

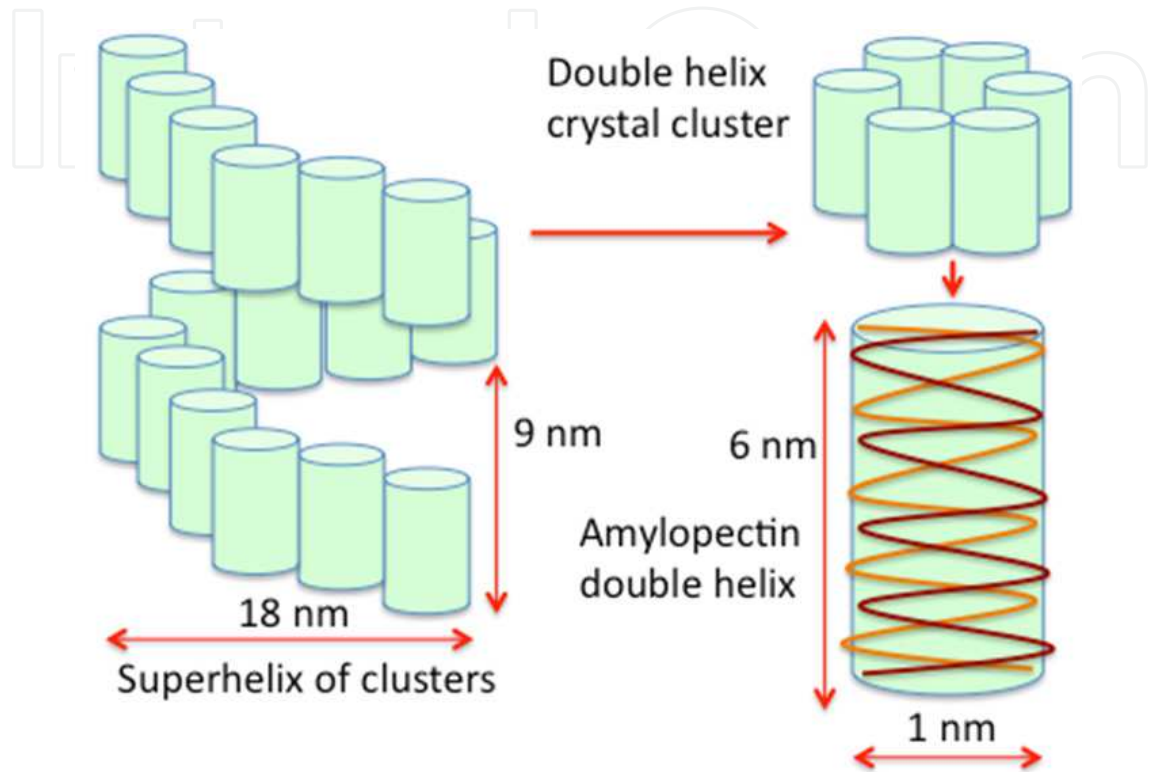


Fig. 1. Diagram of starch amylopectin superstructures

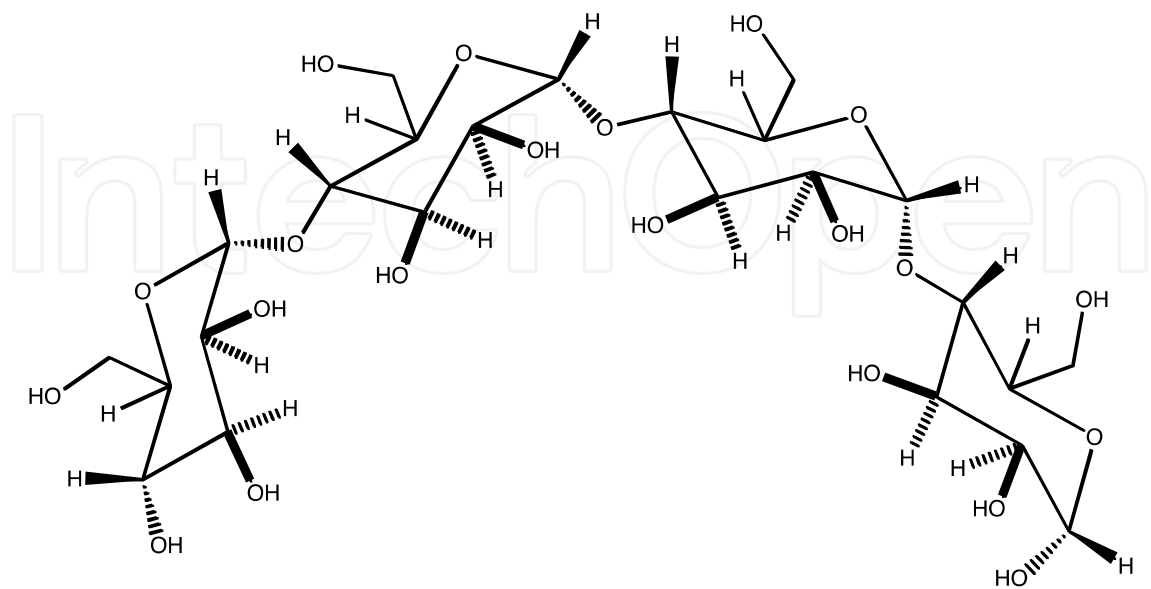


Fig. 2. Chemical structure of a starch tetramer showing conformation of glucose and stereochemistry of hydroxyl substituents and the α -1,4-glycosidic linkages

The glucose monomer units in starch have all hydroxyl groups in the plane of the six-membered ring. Asymmetry is introduced by the out-of-plane alpha-1-link to carbon 4 of an adjacent glucose. The asymmetry of the alpha-1,4-link causes starch to form a helical structure in contrast to the planar beta-1,4-link of cellulose that makes a planar cellulose structure. Biomolecules are characterised by the stereochemistry of their monomers that translates through into the morphology of their secondary and tertiary structures. Thus starch structures are all controlled from a bottom-up approach. Amylopectin is the same as amylose except that it contains alpha-1,6-links at chain branches as well as alpha-1,4 links. The chain links and branches are directional with only one chain end in a hemi-acetal form that is the end hydroxyl group is attached to a C1. All other chain ends, including those of the branches end with a C4 hydroxyl group. An idealized amylopectin branched molecule is shown in Figure 3. After each branch point the branching chains can coil together as a double helix.

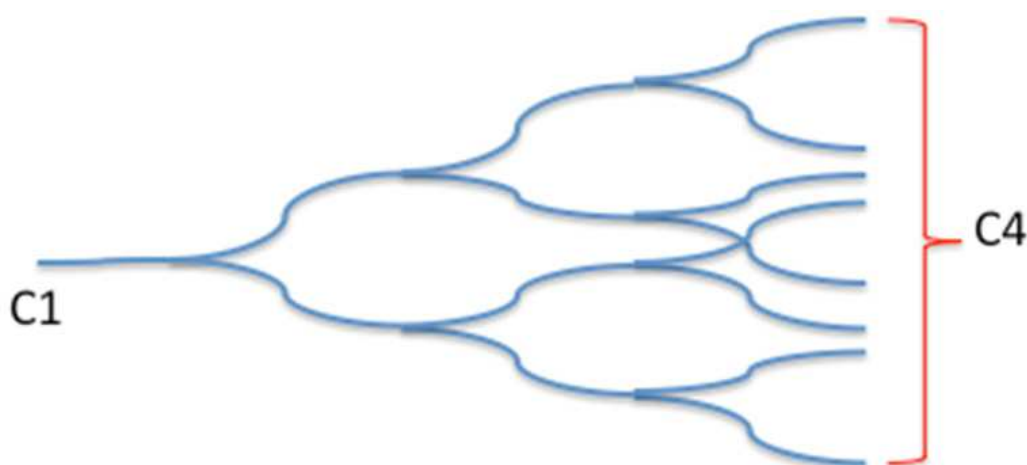


Fig. 3. Schematic of amylopectin with one C1 hemi-acetal end group

In contrast to synthetic thermoplastics such as polyethylenes, it is the branched starch molecules, amylopectin, that crystallise as double helices in the native starch granules. With polyethylene the linear chain or linear chain segments crystallize and branches are excluded from the crystals. The linear amylose resides in amorphous regions between the crystals. Amylose is therefore more water-soluble because it can be extracted from amorphous regions. Similar to synthetic thermoplastics, high amylose starches have more suitable rheology for processing by extrusion. Linear molecules can flow better than branched molecules and amylose has a lower molar mass though it can be in the range of 1000 kg mol^{-1} , while amylopectin is many times larger. Starch is like a polar, hydrogen bonded form of polyethylene, with linear and branched (or low density) type molecular architectures. There are few synthetic polymers that can be considered as analogues of starch. Poly(vinyl alcohol) is a linear synthetic polymer with a hydroxyl group on each monomer residue. Of synthetic polymers poly(vinyl alcohol) is most like amylose, and it is one of the few synthetic polymers to be reasonably rapidly biodegradable. This may be why poly(vinyl alcohol) has often been used as a blending polymer for starch. Poly(vinyl alcohol) is crystallisable, however it does not have branches, at least not to the extent of amylopectin for which there is no synthetic polymer analogue. While in the starch granule it is

amylopectin that crystallises, after formation of amorphous starch it is the linear amylose that crystallises. This implies that the linear polymer, amylose, forms the more kinetically and thermodynamically stable crystals.

3. Thermoplastic starch

Formation of soluble starch or thermoplastic starch requires disruption of starch granules and their supramolecular structures, dissociation of complexes with lipids and melting of crystals with the assistance of added water. Figure 4 shows an environmental scanning electron microscope (SEM) image of corn starch granules. Though there is bound water within starch that varies with ambient humidity, water is typically added. A water concentration of 25 % w/w will give a gelatinisation temperature with a range of 60-70 °C. Gelatinisation is assisted by shear. An extruder, either a twin-screw or single-screw, is suitable for continuous shear processing. Alternatively batch mixers with a wiping action can be used.

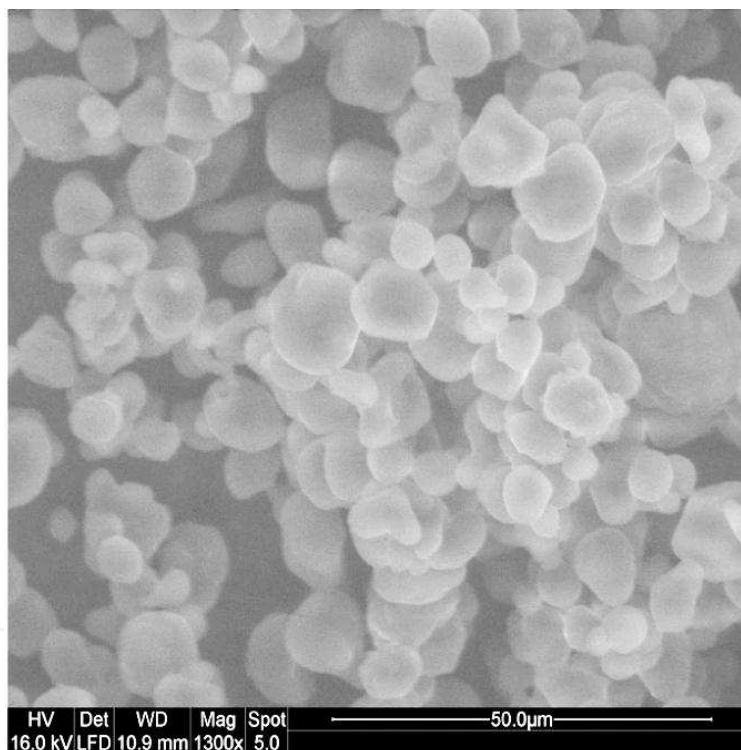


Fig. 4. Environmental SEM of corn starch granules

A starch solution can be formed by thoroughly mixing starch with cold water to form a uniform suspension. The suspension will be a milky colour with a relatively high viscosity. The suspension can then be heated without coagulation. Gradual heating produces a clear solution of increased viscosity. If the solution is stored for several days it will gradually become opalescent through to milky. Starch solutions are not stable because hydrogen bonds within and between starch molecules are more stable than the hydrogen bonds with water that keep the starch in solution. Formation of starch-starch hydrogen bonds accompany ordering of starch molecules into crystalline structures different from the original starch granules. The ordering can be considered as a lyophilic liquid crystalline

behaviour. Excessive heating of a starch in water solution will cause the starch to flocculate. This will be experienced as a continuous increase in viscosity until gelation and then formation of a strengthening gel structure. This gelation is consistent with lower critical solution temperature (LCST) behaviour. LCST behaviour is observed with solutions/solubility of other highly hydrogen bonding polymers in water, such as poly(methacrylic acid).

Conversion of starch into a packaging material requires disruption of the starch granules and their constitutive crystals into a flowable thermoplastic. High AM content is preferred for preparation of thermoformable starch due to the better flow properties of the linear polymer and its decreased tendency to crystallise. High amylose corn starch is the major source of amylose-rich starch and it can have amylose contents of up to 80 %. Typically high AM starch can be processed in an extruder if it is first equilibrated with water and any other plasticisers, normally alcohols such as glycerol. Water must diffuse into the granules and hydrogen bond with the starch. Upon heating the granules undergo destructure and the crystals melt to form a uniform viscous starch fluid. Processing, strength and stability of the starch is assisted by addition of a hydrophilic polymer such as poly(vinyl alcohol), poly(oxyethylene), poly(caprolactam) or poly(vinylpyrrolidone). After formation of a starch film the added polymer stabilises the amorphous structure by hydrogen bonding with the starch. This prevents recrystallization of the starch to form V-type crystals in a process called retrogradation. Another way to limit retrogradation is to use substituted starch such as hydroxyethyl, hydroxypropyl or acetoxy starches. The substituents interrupt the structural regularity of the starch and thereby restrict crystallization.

The viscosity increases considerably as the molecules are freed from their ordered superstructures and the gelatinous mass becomes transparent. The gelatinised starch is amorphous and referred to as thermoplastic starch (TPS) since it can be reprocessed so long as water content is retained or replenished. The glass transition temperature of starch is uncertain, but likely to be about -50 to -10 °C with the water content suitable for gelatinisation and subsequent processing. TPS has properties expected of any thermoplastic though water content is required for them to be revealed. TPS has a glass transition temperature, it can flow under shear when heated and it can slowly crystallise. TPS sheets are transparent, though depending on the extent of shear mixing there can be traces of starch granules recognisable as faint outlines. These are called ghost granules and they disturb the clarity of sheets and films of TPS, which is a problem for some packaging applications.

Disruption of the ordered structures within starch is necessary to prepare thermoplastic starch. Heat is required along with shear to disrupt native starch structures to form a homogeneous thermoplastic starch that can flow or form into shapes. Water content, shear degradation by chain cleavage and thermal degradation by dehydration or bond rupture are limitations in the processing of TPS. Residual crystallinity and re-crystallisation formed by the retrogradation process causes loss of film clarity and embrittlement. After processing amylopectin enhances the properties of TPS and retards retrogradation in TPS. Retrogradation involves the more thermodynamically and kinetically favourable crystallisation of the linear amylose to form V-type crystals that are distinct from native starch crystals.

Gelatinisation of cassava and potato starches at low water levels ($>20\%$ w/w) in the presence of sodium chloride caused a decrease in gelatinisation temperature (Farahnaky, Farhat, Mitchell, Hill, 2009). A range of moisture contents was studied and the decrease in gelatinisation temperatures was $30\text{ }^{\circ}\text{C}$ at a water content of 11% w/w for example.

Retrogradation of waxy corn starch has been studied using differential scanning calorimetry (DSC) and it was found that an endotherm developed after 2-5 h and increased with time (Liu, Yu, Tong, Chen, 2010). Two-phase transitions were identified; the Gr transition was due to helix-helix dissociation while the M1r transition was due to a helix-coil transition. This indicated reformation of mainly the amylopectin molecules due to an original structural memory. The retrogradation in this high amylopectin starch was due to reforming of the amylopectin double helix. The process was inhibited by increased amylose content. Cassava starch retrogradation has been studied using X-ray diffraction and DSC and it was found that with this starch the gelatinisation procedure has no significant effect on the melting enthalpy upon retrogradation, while the storage temperature was a factor (Rodriguez-Sandoval, Fernandez-Quintero, Cuvelier, Relkin, Bello-Perez, 2008).

Starch with about $15\text{--}25\%$ w/w water shows a gelatinisation peak in differential scanning calorimetry (DSC) at $60\text{--}70\text{ }^{\circ}\text{C}$. This endotherm is a double peak with this lower temperature peak being due to disruption of starch-lipid complexes and the high temperature peak being due to melting of starch crystals. The endotherm has a relatively small area, heat of fusion. The term melting is used to describe disruption of crystals in starch, though it does not mean melting in the sense of crystals becoming a flowable melted liquid. The gelatinised starch is a fluid that can flow under shear because of the presence of water, so it could be described as a concentrated starch-water solution.

There is uncertainty in the position of the glass transition temperature. When T_g is plotted against T_m for many synthetic polymers a trend is observed that $T_g \sim 2/3 \cdot T_m$ (temperatures in Kelvin). Therefore T_g of starch should be below $0\text{ }^{\circ}\text{C}$. Some careful DSC and dynamic mechanical analysis (DMA) measurements have shown T_g to be in a range -10 to 0°C . In this range T_g can be obscured or uncertain due to the large melting endotherm of free water in the processing of starch. The glass transition of waxy maize starch and water ($1:2$ w/w) has been studied using DSC after different degrees of gelatinisation (Sang, Alavi, Shi, 2009). A three-phase model with an amorphous phase, a rigid amorphous phase and a crystalline phase was proposed to interpret the data. Gelatinisation had an onset of $61.5\text{ }^{\circ}\text{C}$ with a maximum of $70.3\text{ }^{\circ}\text{C}$ and an end temperature of $81.7\text{ }^{\circ}\text{C}$. The T_g temperature and detection depended upon prior thermal history and gelatinisation, however a distinct subzero T_g of annealed native starch granules was observed after annealing at $-7\text{ }^{\circ}\text{C}$.

3.1 Plasticisers

Water is the main plasticiser, however it is too transient to be used as the sole plasticiser for TPS. Other less volatile plasticisers are glycerol, pentaerythritol, polyols, sugar alcohols, poly(oxyethylene)s, poly(oxypropylene)s, non-ionic and anionic surfactants. Hydrogen bonding polar liquids are most suitable. Plasticisers with a high affinity for water, such as glycerol, can exhibit anti-plasticisation at particular concentrations, typically low concentrations depending on water content. Anti-plasticiser activity has been found, for different reasons in dioctyl phthalate plasticised poly(vinyl chloride). Anti-plasticisation may

occur when the plasticiser has a higher affinity for water than does starch, thus the plasticiser–water coupling lowers the total plasticiser available to hydrogen bond with starch. This causes an increase in the T_g , gelatinisation temperature and increased brittleness.

Plasticiser activity has been related to water sorption isotherms that give molar sorption enthalpies of starch–plasticiser systems. Competitive plasticisation has been assessed using glass transition temperature models. The study validated the anti-plasticization limit for glycerol to be ~10–15 % w/w, however for xylitol, its anti-plasticization limit did not manifest until 20 % w/w (Liu, Chaudhary, Ingram, John, 2011). A new hydrogen bonding highly polar plasticizer, N,N-bis(2-hydroxyethyl)formamide, has been synthesized and used to prepare TPS from corn starch (Dai, Chang, Yu, Ma, 2008). Hydrogen bonding between the plasticizer and starch was confirmed using Fourier transform infrared (FTIR) spectroscopy and SEM showed granules to be completely disrupted after gelatinization with the new plasticizer. Comparison of the plasticizer with glycerol was made and at low relative humidity, modulus was higher while at high relative humidity extension at break was higher when the new plasticizer was included compared with glycerol.

Wheat starch plasticization in the water–glycerol combination was used to study the time–temperature regime for melt processing of TPS using excess plasticizers (Li, Sarazin, Favis, 2008). Gelatinization occurred between 1 min and 3 min with an excess of plasticizers with a rapid reduction of granule phase size.

Plasticisers for starch function the same as plasticiser in synthetic polymers. An additional function of starch plasticisers is that they form a complex via hydrogen bonding with the starch and prevent retrogradation, which will cause embrittlement due to gradual recrystallization. Where the plasticiser is a polymer the correct term is an allomer, which then is a polymer blend as treated in the next section. Retrogradation is more severe in high amylose starch since it is the amylose that forms the V-type crystals. However high amylose starch is the most suitable for processing to form TPS. Additives are required to stabilise TPS against retrogradation to ensure reliable properties over time.

Fatty acids such as stearic acid are mostly hydrophobic, however the hydrophobic chain preferentially resides inside of starch helical coils forming a complex. A similar complex is formed with iodine giving a red to blue colour depending on the length of the coil and the number of iodine molecules aligned inside the coil. The interior of starch coils is more hydrophobic than the exterior due to the stereo-aligned pendant hydroxyl groups. The iodine complexes with glycans have been used to elucidate the structure of dispersed starch molecules, where iodine can bind with corn starch with only 8 % w/w water content. Complexes with iodine and different starches (corn and potato) of varying water content were compared and potato starch where amylose was more closely involved with crystal structures, was found to form more effective complexes based upon formation of a more intense colour (Saibene D, Zobel H F, Thompson D B, Seetharaman K, 2008). Layered films based on lipophilic starch and gelatin were formed with varying amounts of fatty acids (palmitic, lauric, myristic, capric, caproic and caprylic) and sorbitol plasticizer (Fakhouri, Fontes, Innocentini-Mei, Collares-Queiroz, 2009). The addition of fatty acids decreased opacity and elongation while decreasing tensile strength and water vapor permeability.

Native corn starch was plasticized with water, glycerol and stearic acid and gelatinized in a twin-screw extruder (Pushpadass, Kumar, Jackson, Wehling, Dumais, Hanna, 2009).

Gelatinization temperature range depended on glycerol content and lipid-amylose complexes were formed depending on stearic acid and moisture content. Extrusion caused fragmentation of the starch that was detected by size exclusion chromatography and cross-polarisation magic angle spinning nuclear magnetic resonance spectroscopy.

3.2 Starch–Polymer blends

Substituted starch can be extrusion gelatinised in the presence of added hydrophilic polymer with water as the only plasticizer. Without addition of glycerol, or other alcohol, the gelation and plasticity of the starch is only dependent on water content. The subsequent equilibrium water content controls the flexibility, tensile strength and elongation. The added hydrophilic polymer contributes to the strength, and together with the substituted groups, restricts retrogradation. In addition to the chemical processes contributing to gelation, the extrusion conditions including shear, residence time and temperature physically provide gelation and homogenisation. Polymers that have been blended with TPU are poly(vinyl alcohol) pure or with some residual acetate, biopolyesters such as poly(lactic acid), poly(hydroxyl alkanoate)s; poly(butylene succinate) and poly(butylene adipate). Other polar thermoplastics, such as poly(N-vinylpyrrolidone) and poly(caprolactam), are suitable though biopolymers are preferred to maintain overall biodegradability.

Starch-poly(caprolactone) (PCL) blends have been produced by extrusion with an in-line rheometer slit die (Belard, Dole, Averous, 2009). A multilayer structure could be generated with a PCL outer skin that was formed depending on the molar mass of the PCL. The phase separation between starch and PCL showed that the polymers were not miscible in the blend, yet they were expected to be compatible. Starch-poly(lactic acid) (PLA) blends have been filled with nano-clay (Cloisite 30B) to form nano-composite blends (Lee, Hanna, 2009). The clay was found to be present as tactoids that influenced melting temperature, onset degradation temperature, radial expansion ratio, density, bulk compressibility and bulk spring index.

TPS requires that starch be a continuous phase and exhibit flow and processability. In some starch blends the starch is dispersed like filler in a continuous phase of a second polymer. This is the case with starch-polyethylene blends where starch is dispersed in the polyethylene, usually with compatibilisation via a maleic anhydride grafted polyethylene or use of a substituted starch. Such starch blends enhance biodegradability of the matrix polymer through degradation of the starch leaving a porous framework of synthetic polymer that then slowly degrades. Degradation is usually too slow to be classified as biodegradable according to international standard definition.

3.3 Composites

Composites of TPS are prepared for the same advantages as for synthetic thermoplastics. Typical mineral fillers include talc, clays, silica and cellulose fibres particularly microcrystalline cellulose and cellulose nano-fibres. The filler can be dispersed in starch during the gelatinisation extrusion process. It is advantageous if a twin-screw extruder with multiple inlet ports is used so that gelatinisation, plasticiser and filler addition can be separated processing steps within the one extrusion cycle.

Composites are used to reinforce, limit properties dependence on moisture or humidity, as well as restrain retrogradation. Composites tend to be more brittle, which is a problem for TPS sheets. Combinations of composites with plasticiser are used to arrive at optimum properties where inert fillers assist with reduction of problems associated with the starch phase.

A starch film with poly(vinyl alcohol) and nano-silica was prepared (Huali-Tang, Shangwen-Tang, Peng-Zou, 2009). The nano-silica was found to be evenly distributed and the films exhibited improved mechanical properties, water resistance and optical clarity when nano-silica was present. A nano-composite was prepared from starch and unmodified montmorillonite and it was found that water resistance and water vapour permeability decreased when only small amounts of the clay were added. (Maksimov, Lagzdins, Lilichenko, Plume, 2009). The permeability of water determined as a function of orientation of the platelet clay layers calculated by a method of orientation averaging of permeability characteristics of separated structural elements with planar orientation of lamellar filler particles. A comparison of nano-composites prepared from three modified montmorillonite clays (Cloisite Na⁺, Cloisite 30B and Cloisite 10A) was made under 60 % and 90 % relative humidity (Perez, Alvarez, Mondragun, Vazquez, 2008). The nano-composite matrix consisted of a blend of starch and PCL. Each of the nanocomposites showed decreased water diffusion coefficient considered to be due to a tortuous path for diffusion. Elongation at break increased though in general mechanical properties decreased upon exposure to water.

TPS materials blended with poly(vinyl alcohol) and reinforced with sodium montmorillonite were prepared and found to have highly exfoliated clay structures (Dean K M, Do M D, Petinakis E, Yu, 2008). PVALc was found to be important for expanding inter-gallery spaces in the clay. Composites containing both PVALc and clay were found to have superior increases in tensile modulus and strength, due to both enhanced interfacial interactions and retardation of retrogradation.

Layered clays like monmorillonite have been much studied in starch composites. As described above Cloisite clays are featured in the literature. Swelling of clays with water involves migration of the small water molecules into clay galleries where the water solvate intergallery sodium ions and the silicate anions on surfaces. Solvation causes the layer spacing to increase against the ionic attractions, with stabilisation due to the solvation, though with loss of entropy by the water molecules. Swelling occurs similarly with many polar organic molecules such as alcohols, amines, carbonyls and ethers. Swelling occurs with polar polymers such as poly(oxyethylene) (POE). POE ether groups solvate sodium ions and through hydroxy end-groups the surface silicate anions are solvated. Migration of the larger POE into galleries will be slower and solvation will be less strong than with water, but the loss of entropy is less for polymer adsorption onto a surface than it is with water. A special case of POE is crown ethers where the cyclic structure has a cavity surrounded by ether groups that is the correct size to accommodate a sodium ion. Ion-exchange of inter-gallery sodium ions with alkylammonium ions is an efficient way to retain the ionic balance while introducing hydrophobic groups into the galleries. The hydrophobic groups reduce the interlayer adhesion of the clay and when clay layers separate the surface energy of the layers is reduced to that of hydrocarbons. Rheological properties of clays are twofold. The first is due to absorption of water, or other polar molecules, from the liquid phase and binding them by solvation. Solvated clay is suspended as colloidal particles that flocculate to form high viscosity and under shear separate to form reduced viscosity. Clay particles are

thus shear thinning and due to the time required for flocculation, they are thixotropic. A second mechanism is where the solvated clay layers exfoliate providing greatly increased surfaces for solvation and associated rheological behavior. Clay with inter-gallery sodium ions, or other alkali metals ions, can exfoliate under high shear force, though the resulting surface energy increase is unfavorable. Ion exchange with alkylammonium ions creates hydrophobic clay gallery surfaces that are exfoliated with lower shear and the lower surface energy of the layers provides a more stable system. After shearing has stopped, the layers can associate through ionic end groups or through hydrophobic interactions between surfaces. The alkylammonium treated clays are shear thinning and thixotropic agents, and can further be describes as hydrophobic thickening agents.

Clay is swelled in water and other polar media by intercalation due to solvation of the gallery sodium ions and the anionic silicate surfaces. The binding of the clay layers by the gallery sodium ions is overcome by the solvation energy gained minus the entropy lost by the solvating molecules. Exfoliation of the clay increases surface energy extensively due to the huge surface area of the many exfoliated clay layers. Thin layers are an unstable state because their mass is nearly all surface. If the layer were fluid, they would contract into spherical beads. The clay layers are of sub-nanometre thickness making the surface to volume extremely high. This huge surface area must be reduced by solvation if the exfoliated state is to be thermodynamically supported. Shear can provide energy for exfoliation, but after the shearing to process the layers must be stabilized by solvation or recombination. Starch is hydrophilic and able to adsorb to the layers and assist with stabilization with less loss of entropy than required by many water molecules. Thus, exfoliated sodium montmorillonite is unstable even with polar molecules or macromolecules adsorbed onto the surfaces.

An alternative is where the gallery sodium ions have been exchanged by alkylammonium ions. Ionic neutrality is maintained but the clay layers are separated by alkyl chains and bound by dispersive forces from the alkyl chains. The shear force required to separate the layers is low and the exfoliated sheets have relatively low hydrocarbon surface energy. The surface energy required to be supported for stabilization of the clay layers is low and their tendency to recombine is low. Solvation by water or polar molecules can occur along the layer edges where polar silicates are exposed. The clay layers are analogous to layered surfactants with both polar and non-polar regions. Starch has hydrophobic as well as hydrophilic functionality. The starch hydrophobic groups can stabilize the low surface generated by exfoliation of treated clay with minimal loss of entropy compared with solvation by many small molecules. Creation of thin layers of any material requires an accompanying mechanism for reduction of surface energy with minimal entropy loss to the system. Reinforcement, diffusion reduction and rheological action of clays will be enhanced by hydrophobic modification, even in aqueous or polar environments.

All-starch nano-composites have been formed from cassava starch reinforced with waxy starch nano-crystals with glycerol plasticizer (Garcia, Ribba, Dufresne, Aranguren, Goyanes, 2009). A reinforcing effect was found in the composites, along with increased equilibrium water content. The reinforcement was interpreted as due to strong hydrogen bonding interactions between filler and matrix, and the nano-crystals were well dispersed, which provided decreased permeability. Similarly, nano-composites have been formed by

reinforcing waxy starch films with starch nanocrystals, using sorbitol as plasticizer by formation from solution by casting and evaporation to form films (Viguie, Molina-Boisseau, Dufresne, 2007). Thermal and mechanical characterization was performed after conditioning in moist atmospheres.

Advanced nano-composites of TPS have been formed with multi-walled carbon nano-tubes (MWCNT) with glycerol plasticizer for potential application as electroactive polymers (Ma, Yu, Wang, 2008). The composites displayed restrained retrogradation, increased modulus and tensile strength, with decreased toughness. The composites were conductive though conductivity was sensitive to water content. The percolation threshold for conductivity occurred at a MWCNT content of 3.8 % w/w.

TPS biocomposites have been formed by blending with PLA and reinforcement with coir cellulose fibres with maleic anhydride as compatibiliser or coupling agent (Lovino, Zullo, Rao, Cassar, Gianfreda, 2008). The composites showed a high degree of biodegradability as determined by carbon dioxide production upon composting. SEM showed crazing patterns on the surface and the growth of bacteria on the surfaces was observed using optical microscopy. Hybrid composites of TPS blends with PVAIc plasticized with glycerol and reinforced with layered clay and jute fabric (Ray, Sengupta, Sengupta, Mohanty, Misra, 2007). The hybrid composites were prepared by a solution casting method. The combined filler of clay and jute are of vastly differing dimension scales. The mechanical properties were superior and fracture surfaces demonstrated strong bonding between the matrix and jute. The clay filled matrix did not display plastic deformation.

3.4 Stabilisers

Starch is readily biodegradable and a natural energy storage substance in plants. It is a nutrient source for microorganisms and this makes starch materials a target for various fungal and bacterial growths. Biodegradability may begin before the required end-of-life. Additives may be included to prevent premature biodegradation though the additive level must not prevent ultimate biodegradation, nor be toxic to packaging contents and hence users.

An important area of investigation is to develop additives that decrease the susceptibility of starch materials to moisture and cyclic humidity conditions. Stabilisation against retrogradation is important, though this is usually a function of the plasticisers and filler. Thermal degradation of starch occurs by loss of water. First free water is lost, followed by weakly bound water, then bound water and the TPS no longer has the plasticizing effect of the water. During degradation water formed from dehydration reactions of the starch is eliminated and the starch degrades forming a carbonaceous residue. Figure 5 shows degradation of starch studied using thermogravimetry with water evolved from the start of the scan until about 120 °C. A sharp degradation mass loss begins at about 300 °C under the scanning conditions of 20 °C min⁻¹ under nitrogen with switch to air at 810 °C. After the rapid degradation, a broad temperature range degradation occurred from 350 °C as the residual organic species degraded to form a carbonaceous residue that was oxidized in air after 810 °C. Comparison is made with a starch-calcium carbonate composite that contained less water and degraded at higher temperature. The calcium carbonate decomposed to calcium oxide with elimination of carbon dioxide above 700 °C.

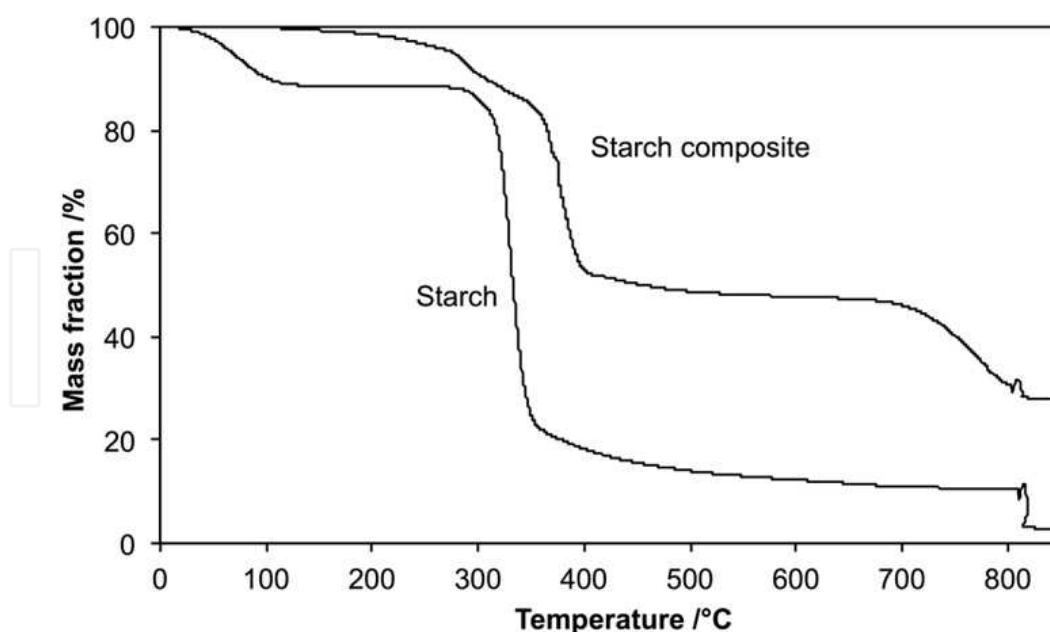


Fig. 5. Thermogravimetry of TPS and a TPS-calcium carbonate composite

3.5 Starch derivatives

Starch is a potentially great biomaterial resource due to its natural abundance and biodegradability. However, some serious problems also exist in starch-based materials, such as poor long-term stability caused by water absorption, high hydrophilicity, poor mechanical properties and poor processability. To improve the properties of starch-based materials, extensive studies have been focused on chemical modification of starch.

Many reactions have been used to derivatize starch due to available hydroxyl groups. The hydroxyl groups on starch are slightly more acidic than typical alcohol hydroxyl groups. This is why base catalysis is effective for most of the reactions summarized in this section. Carboxylic anhydrides, such as maleic anhydride are used for vinyl functionalization. Acyl halide via a Schotten-Bowmann reaction using base catalysis, or sulfonyl chloride. Reaction with aldehyde for acetal formation, such as crosslinking with glutaraldehyde. Vinylsulfone reaction via a Michael reaction is used for adding an ethyl sulfone derivative. Azinyl chloride (cyanuryl trichloride) can be used to link reactive dyes or with an alkyl group. Epoxy ring opening is used to form 2-hydroxypropyl starch or in general 2-hydroxylalkyl starch. Lactone ester ring opening such as caprolactone has been used to form polycaprolactone grafts. Oxazoline (ring opening) has been used to form a convenient linking group. Etherification is used to form methylated starch, such as with iodomethane or dimethyl sulfate. Carboxylation using chloroacetic acid has been used to form carboxymethyl starch. Isocyanate reaction has been used to form a urethane link to starch, however isocyanate is toxic though it will be likely react to completion.

Maleated TPS has been used in reactive extrusion melt blending with poly(butylene adipate-co-terephthalate) (PBAT) for blown-film application (Raquez, Nabar, Narayan, Dubois, 2008). Maleated TPS was formed by reaction of maleic anhydride and corn starch with glycerol plasticizer in an extruder, followed by addition of PBAT further along the extruder screw to form the complete reaction compatibilized blend in a single step. Grafting was via

transesterification via the maleic anhydride functionality of the TPS. Confirmation of successful grafting was obtained from soxhlet extraction and infrared spectroscopy. Some blends contained 70 % w/w PBAT therefore it is likely that PBAT was the continuous phase with dispersed TPS, though the interfacial area was high due to a fine phase morphology.

If a functional group reaction is to be used for reactive processing it must be capable of complete reaction within the residence time in the extruder and the by-products must be suited to remaining in the final product. Few organic functional groups can react fast without forming an equilibrium, which is why step growth polymerization is limited to few reactions. The more reactive substances tend to be toxic and not stable in water. The reactions summarized are suitable for batch reaction in solution.

Radical initiated derivatization of starch is another alternative. Ceric ion, hydrogen peroxide to form an alkoxy radical on starch can be used for reaction with an additive monomer. A thermal peroxide reaction such as with t-butyl peroxide is less selective for grafting than a redox system. The reactant needs not be a polymer, grafting can occur between starch and another polymer; if in an emulsion, the other polymer could be hydrophobic. Radical reactions are generally faster than functional group reactions, but residual monomer will remain unless oligomer or polymers are used as the graft. Crosslinking (gel formation) will be a problem and require a low radical concentration.

Sol-gel reactions using tetraethoxysilane (TEOS), or tetrabutyltitanate (TBTi), provide in-situ formation of the corresponding oxides, silica and titanium dioxide, gives high dispersion and bonding with starch. Borate or boric acid precursors such as borate ester form complexes that can crosslink starch. Any residual sol compound will continue to react with water in the starch until complete conversion. These composites are likely to have interlinked chains making them difficult to process, though some may be thixotropic enabling both processing and subsequent strength development.

Complexation or adsorption of starch onto surfaces can be used to modify starch. For example, alumina with a positive zeta potential, or silica such as precipitated or fumed silica with a negative zeta potential, and surface-active clays or minerals that have hydrophilic edges and hydrophobic faces such as montmorillonite, kaolin and talc can strongly adsorb starch. No reaction is required; dispersion is required and while this may result in high viscosity or gelation; the fluid dispersion is likely to be shear thinning or thixotropic.

3.6 Oxidised starch

Starch is chemically modified in various ways with oxidation being a common process. Starch has been oxidised using hypochlorite resulting in an increase in carboxylic acid and carbonyl groups (Sangseethong, Lertphanich, Sriroth, 2009). Oxidation rate depended on the alkalinity of the reaction medium and this influenced the viscosity of the oxidised starch solution, decreased the gelatinisation temperature though retrogradation was slightly increased. The light transmission was less changed with oxidised starch. Banana starch was oxidised and acetylated, then the product was used to form TPS films (Baruk, Zamudio-Flores, Bautista-Baoos, Salgado-Delgado, Arturo, Bello-Perez, 2009). Oxidation increased solubility while acetylation decreased solubility. The oxidised starch showed a high modulus and lower elongation at break that was not significantly changed by acetylation, though acetylation reduced the barrier properties.

4. Processing

Shear for disruption of super-structures can take place in a batch internal mixer for small-scale preparations. Extrusion is more practical for pilot scale or commercial production. After formation of TPS sheets or films final shaping may be by thermoforming. Extrusion of starch is best performed in a twin-screw extruder where custom combinations of rheological elements can be assembled along the screw. Zone of high shear will assist with disruption of granules while uncoiling of molecules can take place in less shear intensive zones. Formulations often require inlets for plasticiser, filler or other additives along the extruder barrel. Escape of volatiles such as steam will be required, without loss of other materials. At the extruder die the TPS will emerge with a higher moisture content than the equilibrium moisture content of TPS sheet or film. A drying zone will be needed before the product TPS is wound into a coil for storage, transport or prior to further shaping.

Extrusion or high shear is required to disrupt the native starch structure and produce a uniform composition with other components. The extrudate must be a uniform continuous stream with rheology suitable for shaping. The process is more complex than extrusion of typical thermoplastics but the outcome is similar.

Starch foams can be produced using partial vaporisation of entrained water to form a cellular structure. The foams can be in the form of continuous extrudates or popcorn type granules that are used as protective inserts in packaging.

5. Properties

Starch crystal structures are characterised using wide-angle X-ray scattering (WAXS). A Kratzky powder camera is used on starch specimens that have been cryo-ground into powder. Figure 6 shows a WAXS pattern for waxy potato starch with diffraction peaks characteristic of B type crystals; camera type: powder, source 0.154 nm, power 4.0 kW, aperture 200 μm , range 5-35°, count time 10 s⁻¹, interval 0.05 data/°. Figure 7 shows a WAXS pattern for corn starch captured under the same conditions shown above. Figure 8 shows a WAXS pattern for TPS, that is gelatinised starch where the lower curve has been aged, compared with the upper curve, and small peaks indicating onset of retrogradation crystallisation are beginning to emerge.

The modulus of TPS compositions is typically high compared with synthetic thermoplastics. Elastic properties at low strain are measurable however TPS has low, moisture dependant, elongation at break. The high modulus of TPS has dependence upon moisture, other plasticisers, fillers and recrystallization. TPS has high strength, that is break stress for brittle materials or yield stress for ductile materials, due to inter- and intra-molecular hydrogen bonding, and strong adhesion to blended polymers and fillers. Fracture of starch materials tend to be brittle and increasingly brittle with time due to moisture and recrystallization.

Dynamic mechanical properties (modulated force thermomechanometry (mf-TM)) is used for detection of damping peaks, elastic and loss modulus changes with temperature. Mf-TM was performed using a Perkin-Elmer Diamond DMA in tensile mode. A synthetic frequency consisting of 0.5, 1, 2, 10, 20 Hz was applied with constant amplitude of 10 μm . Fourier

analysis deconvoluted the data into the five constituent frequencies. A $\tan(\delta)$ curve is shown for each heating rate scan since these curves showing the best resolution. Examples of storage and loss curves are shown for heating at $10\text{ }^{\circ}\text{C min}^{-1}$. The specimen was coated with paraffin oil and a higher heating rate than normally used for mf-TM (typically $2\text{ }^{\circ}\text{C min}^{-1}$ used) to minimise moisture loss during the scan. The damping curves in Figure 6 show a phase change at about $90\text{ }^{\circ}\text{C}$ interpreted to be due to melting of crystals formed by retrogradation.

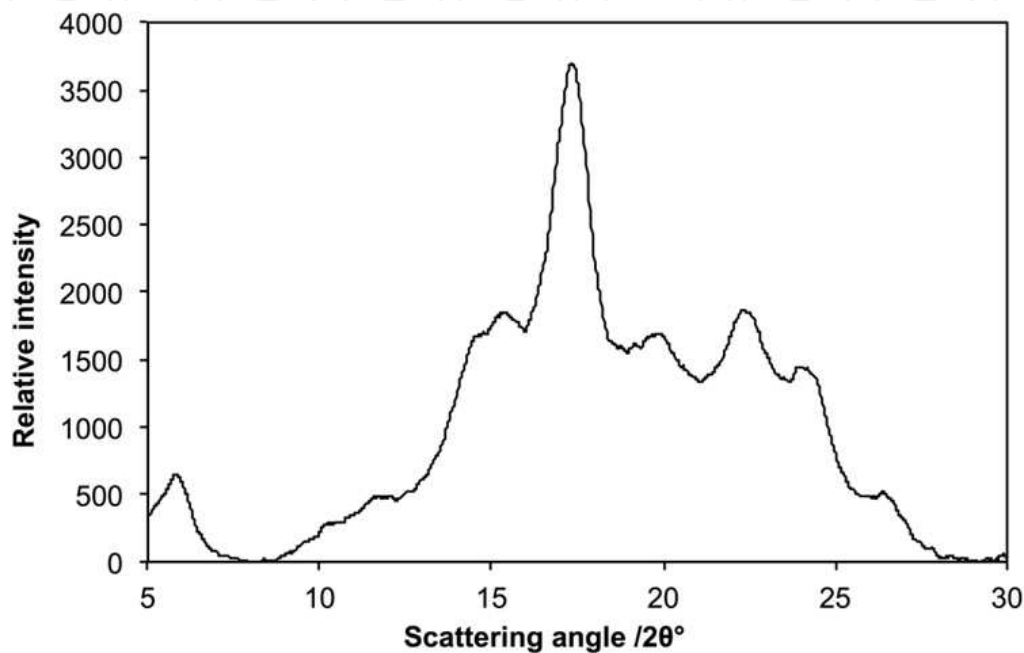


Fig. 6. WAXS pattern for waxy potato starch (B type crystals)

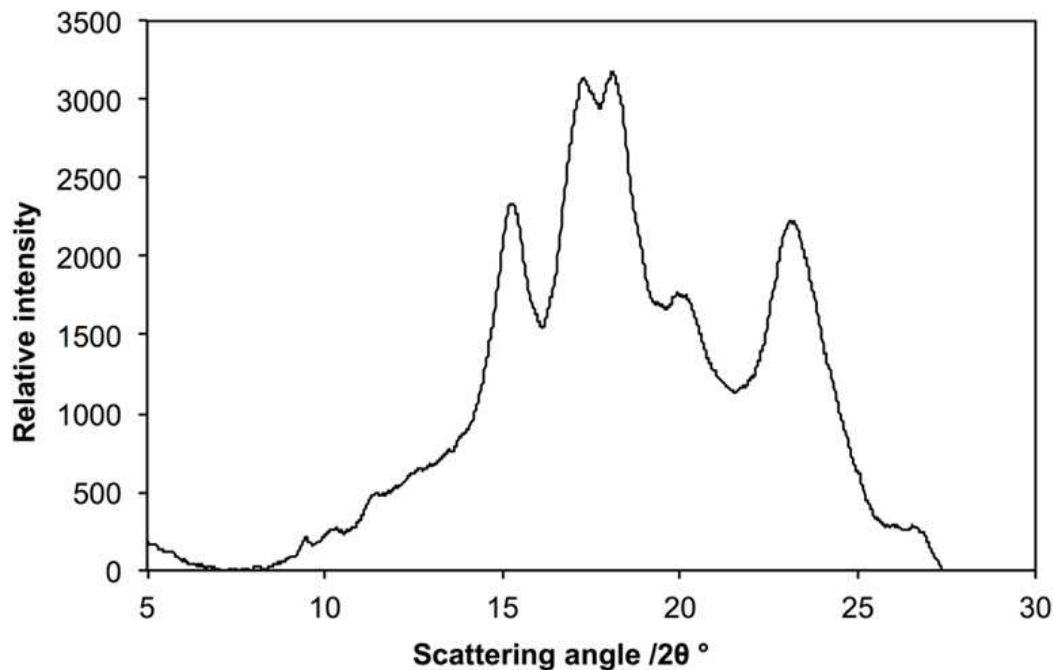


Fig. 7. WAXS pattern for corn starch (A type crystals)

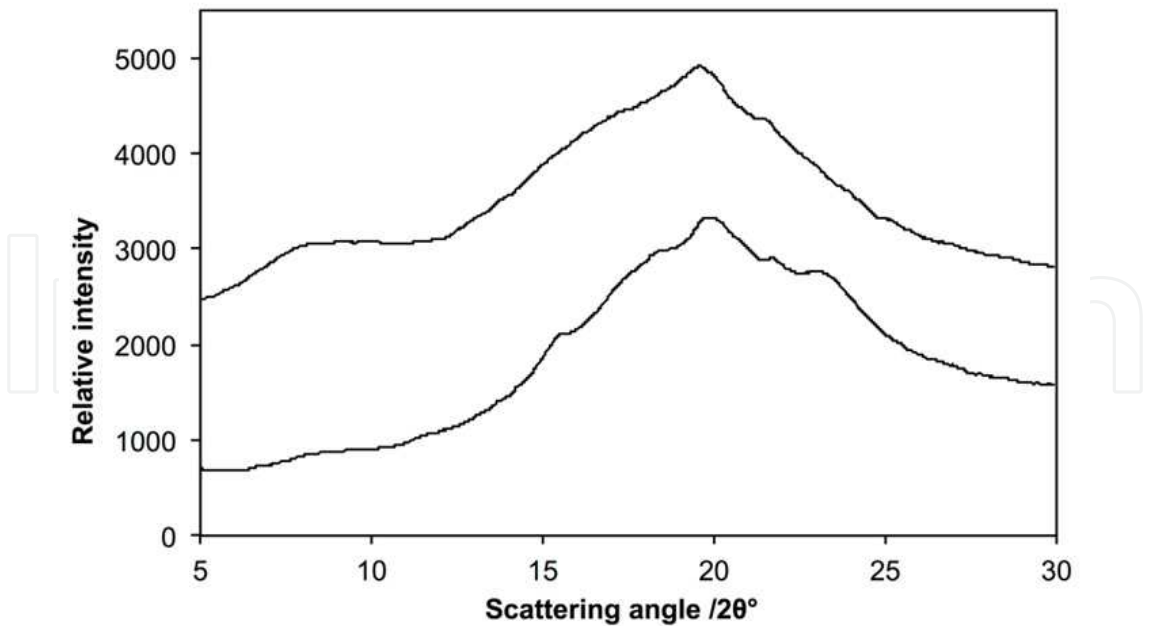


Fig. 8. WAXS patterns for TPS where the lower curve has been aged compared with the upper curve

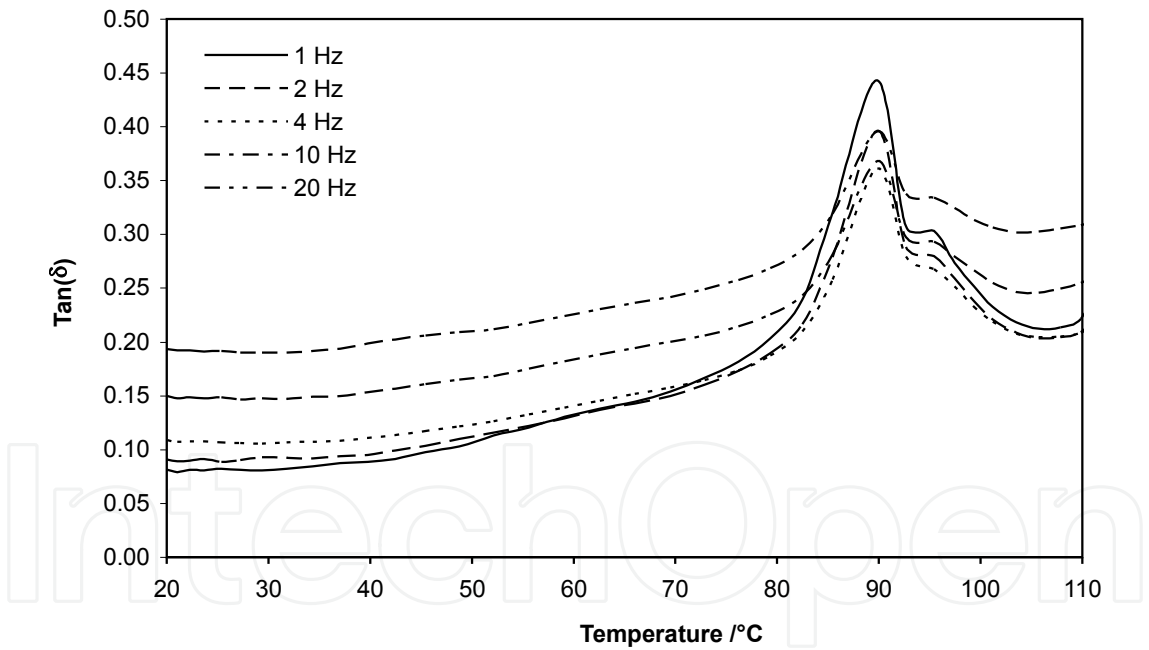


Fig. 9. Thermoplastic starch sheet, mf-TM tensile mode at 10 °C min⁻¹

TPS sheets are often brittle and mf-TM is performed better using single cantilever bend mode instead of tensile mode. Figure 10 shows such an analysis performed using a TA Instruments Q800 DMA with 0.2 % strain, 1 Hz frequency and heating at 2 °C min⁻¹. The specimen was coated with paraffin oil prior to clamping in the instrument to minimize moisture loss during the scan. The glass transition denoted by the peak of loss modulus or damping factor is at a higher temperature than that shown in Figure 9 since at the slower scan rate loss of moisture during the scan made the specimen more brittle with higher glass

transition temperature. Scans were performed at 1, 2, 5 and 10 °C min⁻¹ and 10 °C gave the best scan though with highest thermal lag. Thermomechanical analysis requires a compromise between moisture loss and thermal lag of the instrument.

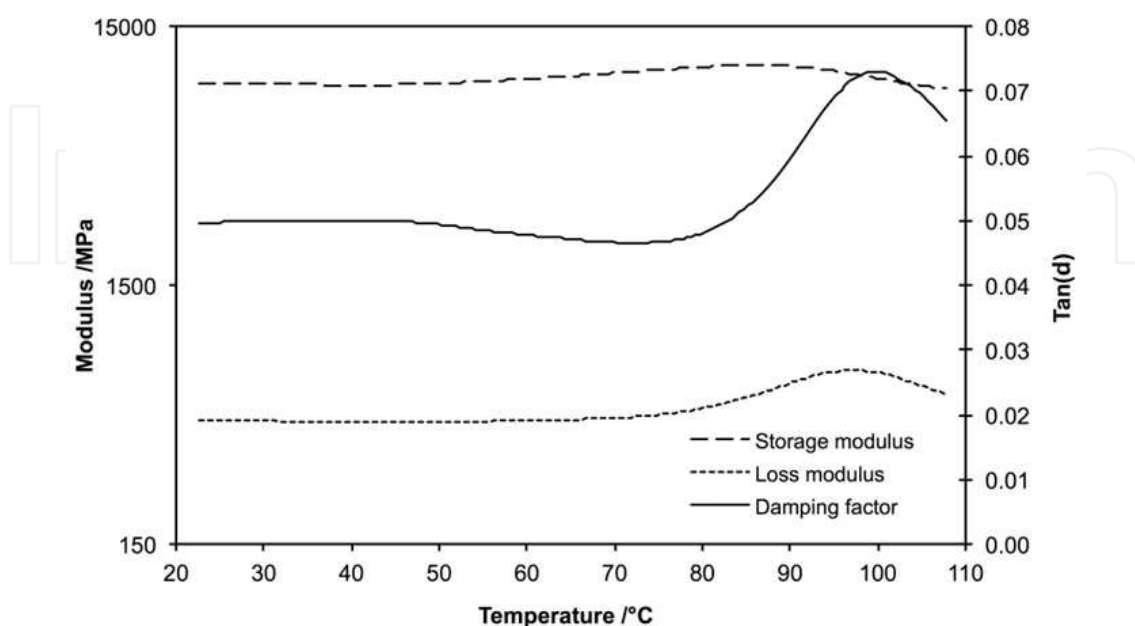


Fig. 10. Thermoplastic starch sheet, mf-TM single cantilever bend mode at 2 °C min⁻¹

Dielectric properties of TPS are sensitive to changes in structure due to the density of polar groups and water content. Thermally stimulated depolarization current (TSDC) has been used to study the dielectric relaxations in cassava starch on semi-crystalline and amorphous variations (Laredo, Newman, Bello, Muller, 2009). Three secondary relaxation modes were detected and interpreted as due to short-range orientations of polar groups or to main chain restricted motion. Moisture plasticization contributed to relaxation Vogel-Tammann-Fulcher parameters that confirmed cooperative relaxation. A heterogeneous amorphous phase resulted in a bimodal distribution of relaxation times.

Vapour transmission – oxygen, moisture, other volatiles, tends to be low compared with other polymers due to density of hydrogen bonds and polarity to restrain diffusion of small molecules. Vapour transmission is dependant upon moisture content and any crystal structures remaining or formed. Moisture sorption is a problem, however moisture does not readily pass through TPS sheets.

5.1 Property changes with time

Thermoplastic starch structure changes with time, temperature and humidity. These changes are the greatest limitation for adoption of TPS in commercial applications. TPS is hydrophilic and during ambient humidity changes the water content of the starch varies. There is a water content hysteresis depending upon whether the humidity is increasing or decreasing because desorption of hydrogen bonded water is delayed compared with adsorption of water. Moisture and other TPS components exchange with packaging contents, either water is absorbed into the TPS, softening it, while drying the package contents or water is absorbed into the package contents drying and embrittling the TPS package.

Similar to moisture content other plasticisers in TPS can bleed or become leached or extracted. Small molecule plasticisers such as glycerol are relatively involatile though they may migrate to the surface with water transfer or become extracted by adjacent materials such as packaging contents. Other plasticisers may separate depending upon changes in water content or due to their compatibility with TPS. Combinations of plasticisers create complex phase diagrams that may involve crystallinity and mutual attractions.

Humidity responsive starch-poly(methyl acrylate) films were formed as graft copolymers that were plasticized with water and urea (Willett, 2008). The films display significant shrinkage that was composition independent in relative humidities greater than 50 % and in relative humidities above 75 % shrinkage was correlated with the urea:starch weight ratio that determines the equilibrium moisture content of the films. A master curve was constructed by shifting shrinkage data with respect to a reference relative humidity, demonstrating that relaxation processes in the starch phase control film shrinkage that was accompanied by loss of orientation within the starch. While moisture sensitivity is to be avoided in typical TPS applications and it is an undesired property, it can be exploited in materials that are sensors to humidity when controlled shrinkages are designed into the structure.

A severe property change is retrogradation caused by re-crystallisation of amylopectin or crystallisation of amylose to form new V-type crystals. Retrogradation causes embrittlement of TPS and loss of optical clarity often accompanies this. Retrogradation is usually more rapid in high amylose starches, since the linear chains are most mobile to form single helix V-type crystals. Re-crystallisation of amylopectin occurs by reforming double helical crystals by inter-coiling of adjacent chain branches.

Further changes in TPS with time can arise from mould growth due to presence of combined moisture and nutrients, however this form of change is specific to the next section.

6. Biodegradation

Starch is a nutrient for many organisms and since water is present in the final structure the starch is readily biodegraded. Water can easily be absorbed by starch resulting in disintegration of the material by partial solubility. Partially solubilised starch is even more readily biodegraded by enzymes principally from microorganisms. Starch-poly(vinyl alcohol) blends were plasticised with glycerol and reinforced with unripe coconut fibres to form fully biodegradable composites (Rosa, Chiou, Medeiros, Wood, Mattoso, Syed, Inam, 2009)). Degradation rate slowed when fibre content increased, though crystallinity was not changed in the composites. The blend and composites degraded slower in composite than the pure TPS.

7. Applications

Commercialisation of thermoplastic starch and starch-based polymers has been progressing. Due to the inherent biodegradability of starch materials they are allied mostly to packaging as films or sheet that can be subsequently shaped by thermoforming into custom packaging requirements. Starch is most suited for packaging of dry products, otherwise there will be a diffusion transfer and equilibrium established between the TPS package and its contents. TPS foams are suited for damping impacts to protect fragile products. TPS solve the issue of disposal of packaging materials because they are biodegradable into environmentally friendly fragments, depending on the nature of non-starch components of TPS compositions.

8. Future directions

Improved processing techniques due to equipment design (screw element design, feed stages, steam release and plasticiser addition) to accommodate retention of water content. Plasticiser structures that are specific to starch and can be used with starch-filler composites, while limiting moisture susceptibility are required. Where plasticisers are not able to enhance properties, polymer blends may be more suited due to the large size of polymer molecules compared with plasticisers. The primary limitations to TPS are moisture variation and retrogradation causing embrittlement during storage that is not desired for packaging materials. A challenge is for starch with more specific initial properties to be available. The structure of synthetic properties can be controlled better than that of biopolymers causing a major set-back for materials from natural resources where properties may change with source, season or plant variant. This makes preparation of commercial products with precise tolerances difficult.

9. Conclusion

Native starch has complex supra-molecular structures that must be disrupted and dissociated to form amorphous thermoplastic starch. Water, other plasticisers, temperature and shear are important in gelatinising starch to form TPS. TPS is processed using extrusion then formed using injection moulding or thermoforming, the same as synthetic thermoplastics. TPS can be combined with other polymers in blends and fillers to form composites. Problems with TPS are water sorption and retrogradation, causing properties to change over time and under prevailing ambient conditions. There are many varieties of starch with differing composition, processing behaviour and properties. This makes development of TPS materials highly specific to particular starch types during development and application. Starch has interesting theoretical properties as a polymer. There is not theoretical distinction between synthetic and natural polymers, except for the complex intermolecular interactions resulting from polarity and hydrogen bond formation and the multileveled hierarchy of ordered structures that form. Starch presents many characteristics, found in synthetic polymers, in the one polymer: linear chains with a single repeat unit, branching, hydrogen bonding, crystallinity, gelatinisation, melting and glass transition phenomena, liquid crystalline characteristics, retrogradation, upper critical solution temperature behaviour, solubility, gelation all combined to form the technology of thermoplastic starch production.

10. Appendix

10.1 Abbreviations

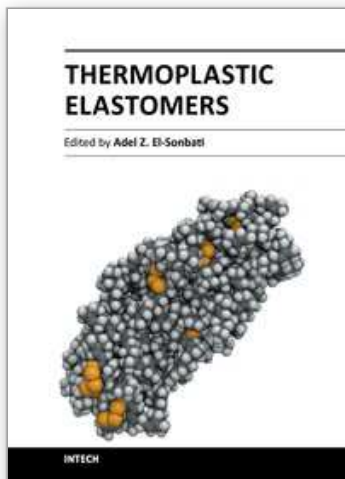
DMA	dynamic mechanical analysis
DSC	differential scanning calorimetry
FTIR	Fourier transform infrared
LCST	lower critical solution temperature
mf-TM	modulated force thermomechanometry
MWCNT	multi-wall carbon nano-tube
PBAT	poly(butylene adipate-co-terephthalate)
PCL	poly(caprolactone)
PLA	poly(lactic acid)

PVAIc	poly(vinyl alcohol)
SEM	scanning electron microscope
TBuTi	tetrabutyltitanate
TEOS	tetraethoxysilane
T_g	glass transition temperature
T_m	melting temperature
TPS	thermoplastic starch
TSDC	thermally stimulated depolarization current technique
WAXS	wide-angle X-ray scattering

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Thermoplastic Elastomers

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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.

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