Chapter 1

Introduction:
Production of plasticized thermoplastic starch by spray drying

Scope of the Thesis
Abstract

As introduction to this thesis, this chapter provides a general overview on starch properties, chemical and physical modification techniques and the applications of starch with emphasis on thermoplastic starch (TPS). The use of plasticizers to process starch as thermoplastic polymer and the formulation of starch with other polymers are highlighted. Traditional plastic processing techniques used for TPS will be discussed and the use of “spray-drying” as a method to produce “dry” plasticized starch will be introduced. Finally, an outline of this thesis is presented.

Content and Aim of the Thesis

The extraction of starch from agricultural products, its conversion into technical and consumer products, and the application of these products may be considered as one of the oldest branches of the chemical industry. At present, the global production of stachant and starch products is reported to be around 70 million tons/year and commercial products containing starch or starch derivatives are found in almost every chemical product sector [1].

Over the years a lot of know-how has been collected and extensive reviews covering technical and scientific aspects of stachants obtained from different resources have been issued. Reviews [2-4] and books [5-7] cover the macro-level elements related the extraction, processing and modification of the different stachants at commercial scale, the meso-level ones connected to product performance in applications, and also the micro-level aspects related to molecular structure and biosynthesis. However, well developed “resource-processing-product performance relationships” to support the development of new starch applications are still absent, with the result that new product development continues to be done on experience-based heuristics combined with trial-and-error experimentation. The work described in this thesis aims to contribute to the establishment of “resource-processing-product performance relationships” to support the development of novel product applications based on thermoplastic starch (TPS). TPS is chosen because the development of starch-based applications such as biodegradable packaging attracts a lot of research.

As an introduction for the topics discussed in this thesis, this chapter presents a summary of required background such as basic starch characteristics, pathways to modify starches and the basic processing technologies. The chapter closes with an overview of the thesis covering the contents of the different chapters.

Starch

Starch is a natural glucose-based polymer that generally is considered as a potential candidate for future biodegradable polymer products. Starch, as extracted from various plant tissues, is obtained in the form of granules with typical particle sizes between 1-100 microns [8] and the shape and size of the granules depend on the resource [9, 10]. These granules are present in the chloroplasts of green leaves and in the amyloplasts of storage organs such as seeds and tubers [11]. Granules are in fact insoluble in cold water but swell, and form a gel if the outer membrane has been broken by grinding. On the other hand, if a granule is treated in warm water, a soluble portion of the starch diffuses through the granule wall and the remainder of the granules swells to such an extent that they burst [10].
Starch is important for human nutrition. However, its nutritional value depends on its primary composition, physical structure and subsequent processing [9]. The most important sources for starches are corn, potato and cassava [12]. In 2008, the worldwide production of starch was estimated to be around 66 million tons [13]. The USA is at the top in the production of starch, Europe and Asia follow as second and third, respectively [14].

Starch is a versatile and useful polymer not only because it is low cost and obtained from natural resources, but also because its physicochemical properties can be altered through chemical or enzymatic modification. Thus, starches receive extensive attention in food research [15], as, for example, in Western Europe approximately two thirds of the production is used in the food and beverage industry. It is directly applied as thickener in sauces, custards and desserts and can, after enzymatic hydrolysis, be used as sweetener in drinks and confectionery. Starch is also important for non-food purposes as the remaining one third of total starch is used in processes like sizing of paper and board, and as adhesives in the paper, packaging and textile industries. Polyols, cyclodextrins, fructose, antibiotics and related compounds are obtained from starch via various fermentation processes [13].

**Chemical and physical properties of starch**

Starch mainly consists of two different polysaccharides: amylose and amylopectin, but the ratio of these two strongly varies depending on the starch source. Small amounts of lipids and proteins are also present in the starch granules [2].

Amylose is a predominantly linear chain of D-glucose units linked together by α-1, -4 bonds (Figure 1). The length of the amylose chain is not the same for every source; it varies among different plant species but usually ranges between $10^2$ to $10^4$ glucose units [16].

Amylopectin consists of short chains of, on the average, 20 to 30 α-1,4 linked D-glucose units which are branched by α-1,6 bonds (Figure 1). Usually it ranges to $10^4$ to $10^5$ glucose units [16].

![Figure 1](image1.png)
The relative percentage of amylose and amylopectin in most common types of cereal endosperm starches ranges between 72 and 82% amylopectin, and 18 and 28% amylose. However, some mutant genotypes of maize (Zeamays), barley (Hordeum vulgare), and rice (Oryza sativa) contain as much as 70%, amylose whereas other genotypes, called waxy, contain less than 1% (maize, barley, rice, sorghum) [17].

Starch is insoluble in cold water, but is very hygroscopic and binds water reversibly. Heating starch in water leads to loss of hydrogen bonding in the interior of the starch granule and the starch will start to gelatinize. The starch granules will rapidly swell to many times its original volume. The gelatinization temperature range can be defined as the temperature at which granular swelling begins until the temperature at which nearly 100% of the granules are gelatinized [18].

Physically, most native starches having a crystallinity of about 20-40%. They are classified as semi crystalline [19]. The amorphous regions consist of amylose and the branching points of amylopectin. The main crystalline components in granular starch are short-branched chains in the amylopectin. The crystalline regions are present in the form of double helices with a length of ~ 5 nm.

Modification of starch

Apart from the immediate use as food, native starch has a limited range of applications. This is due to its unfavorable properties like uncontrolled and high viscosity, its tendency to retrogradate, the insolubility in cold water, and the pronounced brittleness of processed materials [3, 15, 20]. As a consequence, native starches are often modified chemically or physically in order to change and improve product properties. Modification alters the starch structure and affects the hydrogen bonding in a controllable manner to enhance and extend its application. It is remarkable that many of the modifications can be executed at the molecular level, without significantly changing the superficial appearance of the granule [7]. Well-known chemical and biochemical modifications are described below and represented schematically in Figure 2.

Cross-linking

In the starch industry, cross-linking is one of the most important chemical modifications. The weak hydrogen bonding between starch chains is replaced by stronger, more permanent, covalent bonds. The majority of the glucose units in starch contain two secondary and one primary hydroxyl group, which can react easily with a wide range of compounds such as acid anhydrides, organic chloro-compounds, aldehydes, epoxy, and ethylenic compounds. Covalent bonding or cross-linking is more permanent in nature, so only a small degree is required to produce beneficial effects: typically one cross-link per 100-3000 anhydroglucose units of starch. Starch becomes more resistant to gelatinization as the number of cross-links increases. Consequently, solubility of the cross-linked starch derivatives in water is reduced and results in a higher freeze thaw stability, and a higher acid, heat, and shear stability. Also a lower tendency for retrogradation and gelatinization, and higher viscosity over their parent native starches [3, 20, 21] has been reported. The cross-linked starches have found many useful applications, especially in the food, paper, textile, and adhesive industry [3, 22].
Figure 2 Chemical and biochemical modifications of starch (reproduced with permission of the publisher) [7].

**Stabilization and Lipophilic Substitution**

Stabilization is used in conjunction with cross-linking. It is done to prevent retrogradation and to increase the tolerance of starch to temperature fluctuations such as freeze-thaw cycles. Consequently, it helps to improve the shelf life of starch products. In this modification bulky groups, such as octenylsuccinate [7], are substituted onto the starch in order to take up space and prevent dispersed, linear fragments to re-align and retrograde. The number and nature of the substituted group determines the effectiveness of stabilization. The number of substituents per 100 anhydroglucose units represents the degree of substitution (DS). Starch-starch interactions in the granule are weakened with an increase in DS level and, consequently, hydration and gelatinization is achievable at lower temperatures by cooking [7].

Native starch is hydrophilic due to the presence of polyhydroxyl groups in the polymer chain, and does not possess sufficient affinity for hydrophobic substances such as oil to be an effective emulsifier. However, through chemical modification the lipophilic functionality of starch may be improved [23]. The natural tendency of starch to interact with water can be transformed into hydrophilic-hydrophobic duality upon lipophilic substitution. This is particularly helpful to stabilize interactions between materials such as oil and water. To perform such modification, hydrophilic starch must be provided with a long hydrophobic, i.e. lipophilic, hydrocarbon chain [7]. Starch reaction with 2-(2’-octeny1)-succinic anhydride is one of the examples of such modification. It
results in the production of 2-(2’-octenyl)-succinic acid (OSA) modified starch. OSA binds covalently through esterification on starch, and provides starch with both hydrophilic and lipophilic functionalities due to the presence of carboxyl and octenyl groups, respectively. OSA modified starches are useful in food and pharmaceutical applications due to presence of dual functionalities in which the stabilization of oils exposed to an aqueous environment is desirable without the use of proteins and/or gums for medical or technological reasons [7, 23].

**Esterification**

Starch esterification is a well-known chemical modification in which some hydroxyl groups have been replaced by ester groups. The objective is to improve the gelatinization temperature and thermal stability, or to reduce the tendency for retrogradation [6, 20]. The synthesis of starch esters was already introduced 150 years ago, starting with the development of acetylated starch using acetic anhydride as the acetylating agent [24]. Different varieties of starch esters are available such as starch formates, starch nitrates, starch sulfates, starch phosphates, fatty acid starches, starch alkenyl succinates and starch xanthates [3, 24]. Acetylated starch is still an important commercial product and used in many applications. Relatively low degrees of substituted (DS) products are available on commercial level (DS 0.01-0.2). Starch acetates are divided into three different types depending on DS value [24]. Commercially available low DS products (0.01-0.2) are used as food additives and in the textile industry. Medium DS starch acetates (0.3-1) are soluble in water but high substituted starch acetate (DS of 2-3) are in organic solvents. Starch esterification with acetate groups makes the esters more hydrophobic than native starch. High DS starch acetate is useful to cast films using organic solvents. Starch acetylation is a controlled process and allows producing polymers with a range of hydrophobicities [25]. High DS starch acetates are thermoplastic materials and used as biodegradable plastics [26].

Starch esters can be made by several synthetic methods. Water is used as solvent on commercial scale with acetic anhydride as reactant and an alkaline base such as sodium hydroxide, sodium acetate, or sodium hydroxide as the catalyst [27, 28].

Fatty acid starch esters have received considerable attention in the last decade. These hydrophobic starch derivatives have a high application potential not only in the food but also in non-food industry (e.g. as reactive compound in polyurethane resins) [29] and as substitutes for oil-based polymers especially in the packaging industries [30, 31]. In the food industry, starch esters are used as binders, thickeners, and fillers. In non-alcoholic beverages it is used for the stabilization of flavor, and for frozen fruits, pies and pot pies it is used to maintain the stability at low temperature storage [6]. Starch succinates have high thickening power, freeze-thaw stability, and a low gelatinization temperature. In pharmaceutical applications [20] it is effectively used as tablet disintegrant.

**Conversions**

Chain-cleavage reactions of starch are collectively termed as conversion.

**Acid Hydrolysis**

Acid hydrolysis is an important modification to improve the physicochemical properties of starch. The acid attacks the glycosidic oxygen atom and hydrolyses the glycosidic linkage.
Consequently, the physicochemical properties of starch changes without destroying its granular structure [32]. These starches can be used at higher solid concentrations to achieve quick gelling and to provide gum or jelly with controlled texture and flexible properties [33]. It is also extensively used in textile and paper industries [34].

**Oxidation**

Starch oxidation is already applied since early 1800. A number of oxidizing agents has been used, for instance, hypochlorite, hydrogen peroxide, periodate, permanganate, dichromate, persulfate, and chlorate [35]. Oxidized starches are used in textiles, laundry finishing, building materials and food industries [32]. The main application of oxidized starch is in paper and textile industries, where it is used to improve the strength and printability of paper, and as warp sizing, respectively. Due to their low viscosity, high stability, clarity, and good binding properties, oxidized starches are widely used in the food industry, in applications such as food coating, sealing agents in confectionery or as emulsifiers. Hypochlorite oxidation is the most common method for the production of oxidized starches at industrial scale [6, 32]. During oxidation of starch with hypochlorite, cleavage of polymer chains and oxidation of hydroxyl groups to carbonyl and carboxyl groups takes place. Oxidation occurs randomly at primary hydroxyls (C-6), secondary hydroxyls (C-2, C-3, and C-4), at reducing end-groups, and at glycol groups (cleavage of C-2—C-3 bonds). The number of carboxyl and carbonyl groups on oxidized starch indicates the level of oxidation, which takes place primarily at the hydroxyl groups at C-2, C-3, and C-6 positions [20].

**Dextrinisation**

Dextrinisation, also known as pyro-conversion, is the process involving the browning of starch foods when subjected to dry heat. It is defined as the breakdown of starch into dextrin’s. It refers to two pathways of structural modification of starch. The first is partial de-polymerization achieved through addition of water. It is usually done by dry roasting the starch either alone, using the moisture contents present in the starch, or in the presence of catalytic quantities of acid. As a result, polymer fractions of varying chain length (low conversion) are obtained. The second path involves the re-polymerization in a branched manner (high conversion) and delivers products called dextrins or pyrodextrins. Depending on their properties, e.g. range of viscosity, cold-water solubility, color, reducing sugar contents and stability, they are classified as white dextrins, yellow dextrins or british gums [6].

**Enzymatic hydrolysis**

Enzymatic hydrolysis is a biochemical modification reaction. Selective enzymes are used in the hydrolysis to alter the starch structure and to achieve desired functionality. A range of chain lengths corresponding to glucose (dextrose), maltose, oligosaccharides and polysaccharides can be produced depending on the extent of hydrolysis. α-Amylase, β-amylase, glucoamylase, pullulanase, and isoamylase are the most common enzymes used for starch modification. These enzymes have been isolated from fungi, yeasts, bacteria, and plants [6]. The exact composition can be determined by dextrose equivalent (DE), which is used to define the reducing power of the product and is a measure of the degree of starch breakdown. A DE of 0 defines native starch. Dextrose equivalent
(DE) is used to define the reducing power of the product and is a measure of the degree of starch breakdown.

Starch liquefaction and saccharification are different approaches applied in enzyme hydrolysis. The liquefaction process involves the conversion of a concentrated suspension of starch granules into a solution of low viscosity by α-amylase. Saccharification involves enzymes such as glucoamylase (amyloglucosidase) to convert starch or intermediate starch hydrolysis products to D-glucose [6].

**Pregelatinisation**

Pregelatinisation is a physical modification. Certain starches need cooking to develop their required properties and the process of pregelatinisation is designed to remove the necessity for cooking. To achieve a versatile range of cold thickening starches, pregelatinisation is applied to native or modified cook-up starches [7]. The starch is pre-cooked by using one of the following processes [6]:

- Drum drying (starch suspension or starch pastes)
- Extrusion (semi-dry starch)
- Spray drying of starch suspension
- Solvent-based processing

During a spray cooking process, a starch slurry enters in a heating chamber through a special nozzle and is atomized. At the same time, hot steam is injected through a second or the same nozzle into the chamber to cook out the starch [36]. This method produces uniform gelatinized starch with minimum shear and heat damage. Spray drying is gaining popularity and offers properties that are closer to base cook-up starch [6].

Drum drying produces a cooked starch sheet from starch slurry. The starch is ground after drying to a desired particle size [37]. Slightly lower viscosities are obtained than their base starch when the drum-dried flakes are ground to the desired particle size.

Solvent-based methods produce cold water swellable starches. For example, when 20% w starch in aqueous alcohol (20 to30%w water) is heated to 160 to 175 °C for 2 to 5 min granular integrity is maintained, but birefringence is lost [38].

Pregelatinized starches are mainly used as thickening agent for pie fillings, puddings, sauces, and baby foods.

**Thermoplastic starch (TPS)**

Native starch is unsuitable for many applications due to its brittle and hydrophilic nature. Moreover, the melting point of starch is higher than the thermal decomposition temperature, which results in poor thermal process-ability [39]. Starch can be processed into a thermoplastic material only in the presence of plasticizers (water, glycerol, glycol, sorbitol, etc.) in combination with temperature and shear [39, 40]. During the last decade, numerous studies have been done on thermoplastic starch. Recently, much interest has been shown to produce biodegradable plastic items [39, 41, 42], such as trash bags, shopping bags, and dinner utensils, planting pots, diapers, and tampons.
The thermal processing of starch-based polymers involves multiple chemical and physical reactions, e.g. water diffusion, granule expansion, gelatinization, decomposition, melting and crystallization. Gelatinization is the most important phase transition, it involves all these processes and thermoplastic conversion of starch is based on it [39]. Figure 3 shows a schematic representation of the phase transitions of starch during gelatinization and retrogradation [43]. Heating in water destroys the crystalline structure of starch granules and forms amorphous amylopectin (Figure 3 a and b). Gelatinized amorphous amylopectin still contains small quantities of un-gelatinized amylopectin. Nevertheless gelatinization destroys the double-helical crystalline structure formed by the short-branched chains in amylopectin. It has been noticed that these short-branched chains form gel-balls [43], holding chains largely from the same sub-main chain (Figure 3b). Extrusion forms V-type single helix crystals (Figure 3c), having higher moduli and yield stresses for amylose-rich materials. The crystallinity of the V-type crystals increases with time (Figure 3d) [2]. Gelatinization can be done under shear and shearless conditions. In shearless gelatinization, the process mainly depends on the water content and temperature. Excess of water is required for full gelatinization of starch under shearless conditions, which Wang et al. [44] have defined as > 63%. In shear conditions, gelatinization can be achieved at low moisture contents, since the starch granules are physically torn apart by the shear forces, allowing faster transfer of water into the interior molecules [45]. Extrusion of starch is one of the examples of gelatinization under shear. In extrusion, loss of crystallinity is not caused by water penetration, but by the mechanical disruption of molecular bonds due to the intense shear fields within the extruder [46].

Figure 3 Schematic representation of the phase transitions of starch during thermal processing and aging (reproduced with permission of the publisher) [2, 20].
Furthermore, the starch decomposition temperature is higher than its pregelatinization melting temperature and consequently, starch has a high glass transition temperature \( T_g \) \[39\]. Due to free volume relaxation and retrogradation, brittleness also increases with time. To overcome these problems and to make starch more flexible and easy to use, plasticizers are blended with starch \[39, 47\]. Water plays two roles in the starch gelatinization: it breaks the structure of the native granule and acts as a plasticizer \[40\]. However, TPS containing only water has little value in practical applications because of poor mechanical properties. A second plasticizer is necessary besides water, such as poyols, urea, formamide, acetamide, and citric acid \[2\]. All have been evaluated as additional plasticizers that will allow melting phases at a temperature lower than that of starch degradation and they make starch flexible \[2, 40\]. During starch processing, the combination of shear, temperature and plasticization allows the preparation of molten thermoplastic material. The properties of plasticized starches depend very much on moisture contents. Relative humidity changes the material properties through a sorption-desorption mechanism \[40\]. Even when moisture and temperature are controlled, the properties of the material remain dynamic, changing into lower elongation at break and higher rigidness. So in order to improve the moisture impermeability of starch products, starch is formulated with renewable, natural or synthetic polymers \[2, 39, 40\].

**Thermoplastic starch/Polymer blends**

Research and development of biodegradable plastics were stimulated due to rising oil prices and further augmented by environmental concerns. The objective of intensive academic and industrial research was to develop plastics by using renewable, biodegradable resources, that fulfill market needs \[41\]. Pure starch is highly brittle, and has poor mechanical properties and stability; it is often reinforced with fibers or blended with synthetic polymers \[2\].

Blending is an important process for the modification of polymer properties. It is economical and usually does not need special equipment and techniques. From a technological point of view, a compatible blend is attained when the preferred properties are improved as a result of mixing two or more polymers. TPS is blended primarily for two reasons \[7\]; 1) to improve water resistance and mechanical performance, 2) to use TPS as modifier to make polymer blends biodegradable and economical. Since the 1970s, starch blends with polar polymers having hydroxyl groups, such as poly(vinyl alcohol) (PVA), copolymers of ethylene and partially hydrolyzed vinyl acetate (EVA) were prepared \[48-50\]. Due to the hydrophilic nature of these TPS blends, water was used as the plasticizer. Starch blends can be separated into two main categories according to \[51\];

- The source and biodegradation properties of the polymer to be blended with starch
- The processing technique for its preparation

As for the first category, the sources can be obtained directly from biodegradable biopolymers or can be synthetic polymers from either oil or renewable resources, not depending on their structure but biodegradable.

As for the second category, starch blends are prepared by two main processing techniques, i.e. melting and solution/dispersion. In melt processing, plasticization of starch granules is done in an extruder or a batch mixer to prepare the starch blend. Alternatively, two extruders are used, first a single screw extruder is used to gelatinize the starch which is fed into a twin screw extruder where other components blend with gelatinize starch \[51, 52\]. In solution or dispersion processing, casting
is frequently used to finish the product. Starch/poly(ethylene-co-acrylic acid) (EAA) cast films were the first commercial materials produced by solution or dispersion technique [48, 49]. Solution/dispersion blending is an exciting route for the production of these mixed materials, as in case of starch blends, many natural polymers and biodegradable synthetic polymers are soluble or dispersible in water. In some cases, when the polymer decomposes before melting, melting is not possible. For example using chitosan, solution blending is the only viable alternative [5].

Starch can be the continuous or the dispersed phase in TPS blends, depending on the starch/second-polymer ratio and on the processing conditions. As a consequence, the properties of the blend are determined by the interfacial interactions between starch and the other components. Numerous methods and polymers (Table 1) have been examined to improve the compatibility within these blends [5]:

1) The use of polymers with polar groups, mainly capable to form hydrogen bonds (e.g. PVA, EAA, EVOH and natural polymers like cellulose and its derivatives, gelatin and zein [4, 39, 53, 54].
2) The use of polymer mixtures, with one of them acting as a compatibilizer between starch and less hydrophilic components (e.g. PVA in TPS/polyethylene blends or a low molecular weight polymer like poly(ethylene glycol) in TPS/PLA blends) [4, 39, 54, 55].
3) The use of reactive compatibilizers, to obtain a better interface by polymer-polymer chemical interlinking (e.g. methylenediphenyl diisocyanate (MDI), pyromellitic anhydride or glycidyl methacrylate [4, 39, 56-58].
4) The development of complexes between starch and other polymers (e.g. V-type complexes) [54, 59].

Table 1
Most common polymers used in blends with thermoplastic starch [5].

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly(vinyl acetate) PVAc</td>
<td>[49, 60]</td>
</tr>
<tr>
<td>Poly(methacrylic acid-co-methyl methacrylate) MAA/MMA</td>
<td>[61]</td>
</tr>
<tr>
<td>Poly(vinyl alcohol) PVA</td>
<td>[55, 62]</td>
</tr>
<tr>
<td>Poly(acrylic acid) PAA</td>
<td>[59, 63]</td>
</tr>
<tr>
<td>Poly(ethylene-co-acrylic acid) EAA</td>
<td>[48, 49]</td>
</tr>
<tr>
<td>Poly(ethylene-co-vinyl alcohol) EVOH</td>
<td>[53, 54, 57]</td>
</tr>
<tr>
<td>Poly(□-caprolactone) PCL</td>
<td>[54, 57, 64, 65]</td>
</tr>
<tr>
<td>Poly(ethylene-vinyl acetate)</td>
<td>[66]</td>
</tr>
<tr>
<td>Polyethylene</td>
<td>[51, 52, 58, 66, 67]</td>
</tr>
<tr>
<td>Poly(ester-urethanes)</td>
<td>[68]</td>
</tr>
<tr>
<td>Poly(D.L-Lactic acid) PLA</td>
<td>[56, 69, 70]</td>
</tr>
<tr>
<td>Poly(3-hydroxybutyrylate) PHB</td>
<td>[4]</td>
</tr>
<tr>
<td>Poly(3-hydroxybutyrate-co-3-hydroxyvalerate) PHBV</td>
<td>[71]</td>
</tr>
<tr>
<td>Poly(butylene succinate adipate) PBSA</td>
<td>[72]</td>
</tr>
<tr>
<td>Polyesteramide PEA</td>
<td>[64, 73]</td>
</tr>
<tr>
<td>Zein</td>
<td>[67]</td>
</tr>
<tr>
<td>Lignin</td>
<td>[74]</td>
</tr>
<tr>
<td>Cellulose and its derivatives</td>
<td>[57]</td>
</tr>
<tr>
<td>Natural rubber</td>
<td>[63, 75, 76]</td>
</tr>
</tbody>
</table>
Blend with synthetic polymers

One of the main disadvantages of biodegradable polymers from renewable sources is their dominant hydrophilic character, fast degradation, and, in some cases, unsatisfactory mechanical properties, particularly in wet environments. In principle, the properties of natural polymers can be significantly improved by blending with synthetic polymers [41, 47, 77].

In the 1970s, many efforts have been made to produce starch-based polymers for preserving the petrochemical resources, decreasing environmental impact and searching further applications. Numerous blends of starch with various poly-olefins were developed [41, 77]. The main purpose of using starch granules in most of these cases was to increase the surface area available for attack by microorganisms. However, these blends were only partially biodegradable, and thus the advantage of using a biodegradable polysaccharide was lost. This is not acceptable from an ecological point of view [77].

Blend with biodegradable polymers

To create entirely biodegradable starch-based composites, blends have been prepared with biodegradable polymers. Starch is usually blended with components such as aliphatic polyesters, polyvinyl alcohol (PVA) and biopolymers. The common used polyesters are poly(β-hydroxyalkanoates) (PHA), poly-lactide (PLA) or poly(ε-caprolactone) (PCL). The goal of these blends is to create a completely biodegradable product at low cost while maintaining other properties at an acceptable level [77].

Plasticizer classification

Plasticizers are non-volatile low molecular weight compounds that are extensively used as additives in polymer industries [78]. The main role is to lower the glass transition temperature (Tg) to improve the flexibility and processibility of polymers. A plasticizer is defined as “a substance or material incorporated into a material (usually a plastic or elastomer) to increase its flexibility, workability, or distensibility” by IUPAC (International Union of Pure and Applied Chemistry) [47].

Plasticizers can be classified into different groups depending on their function and characteristics. In polymer science, they can be either defined as internal or external. External plasticizers interact with polymer chains, but are not chemically bonded to them by primary bonds, and can, therefore, be lost by evaporation, migration, or extraction. Internal plasticizers become part of the polymer, either are co-polymerized into the polymer structure or reacted with the original polymer [79].

Plasticizers can also be divided into primary and secondary types [80]. For a primary plasticizer, the polymer is soluble in the plasticizer at a high concentration of polymer. Plasticizer should gel the polymer quickly and should not exude from the plasticized material within the normal processing temperature range. Secondary plasticizers have low compatibility with the polymer and low gelation capacity. Secondary ones are used to lower the cost and improve product properties and are typically blended with primary plasticizers [81].
Plasticizers for TPS blends

The decomposition temperature of starch is higher than its melting temperature, so it is not possible to thermally process starch-based blends without a plasticizer or gelatinization agent [82, 83]. Many plasticizers and additives were assessed and developed to gelatinize starch during thermal processing. The preparation/processing conditions and the mechanical and thermal properties of the final material are determined by the type and quantity of plasticizer employed [5]. One of the most used plasticizers in the thermal processing of starch-based polymers is water [2, 47, 84]. However, TPS containing only water has poor mechanical properties, especially brittleness, resulting from fast retrogradation and decreases its practical applications [85, 86].

Various other plasticizers were evaluated to improve the processing properties and product performance of TPS blends e.g. glycerol [87-90], urea [91-94], formamide [92-94], sorbitol [95, 96], citric acid [97], glycol [98-101], and amino acids [102, 103]. The most common plasticizer used after water is glycerol due to its high boiling point, availability, and low cost [41]. The plasticizer- starch interaction can be very specific. The plasticizer interacts through hydrogen bonding with starch chains in a wide temperature range. The interaction increases at higher temperatures, probably due to H-bond formation. As a consequence, the material behaves like a rubber, with a rise in matrix mobility and a decrease in viscosity [47, 104]. Plasticizers containing amide groups were tested for TPS plasticization using glycerol as reference. Amide groups were effective to inhibit starch retrogradation. The mechanical properties and retrogradation of TPS blends mainly depends on the hydrogen bond-forming ability between plasticizers and starch molecules. This ability increases in the following order: urea > formamide > acetamide > polyol [93]. The moisture affinity of TPS blends depend on the plasticizer concentration and hydrophilic nature [105] e.g. during storage glycerol containing films absorb more water and at a higher rate, compared to sorbitol containing films.

Techniques used to process starch-based materials

There are various techniques that can be used for the production of bio-plastics from starch. Most common plastic processing techniques are extrusion, casting, injection molding, and compression molding [4]. All are similar to those extensively used in the processing of traditional petroleum-based plastics. However, processing of starch is more complicated and difficult to control than for conventional polymers. This is due to its unsatisfactory processing properties e.g. phase transitions, high viscosity, water evaporation, fast retrogradation, etc. However, many of these challenges can be overcome with proper formulations and suitable processing conditions. The following degrees of freedom are available to the formulator [2]:

- Plasticizers.
- Lubricants.
- Modified starches e.g. carboxylmethyl starch and hydroxypropylated starch.
- Hydrophobic polymers (e.g. PLA, PCL or cellulose) in the presence of an appropriate compatibilizer.

Traditional plastic processing techniques used for TPS modifications are described below.
Extrusion

Extrusion is the most extensively used technique for the processing of starch-based polymers. It combines numerous unit operations, including mixing, kneading, shearing, heating, cooling, shaping, and forming. The material is converted to a semi-solid mass using compression and forced to pass through a regulated opening at a pre-determined rate [6]. The residence time in the extruder is short (~10 to 60 seconds), while the temperature can be as high as 200°C [106]. Extrusion cooking is a high temperature short time process (HTST). For starch modification, it can be used as chemical reactor, such as thermo-mechanical gelatinization, liquefaction, esterification, and etherification [6].

The extrusion process can handle high viscosity polymers in the absence of solvents, can be used at a broad range of processing conditions, it offers the possibility of multiple-injection, and it allows control of both residence time (distribution) and the degree of mixing [107]. Starch extrusion has been practiced in the food industry for several decades and has recently gained increasing attention due to the interest in biodegradable TPS [108, 109]. However, some specific challenges are present in starch extrusion, including [2]:

- Different physical and chemical reactions may occur during processing that can be favorable and unfavorable.
- The rheological behavior of TPS is complex compared to conventional polymers, especially when mixed with other polymers and additives.
- The viscosity of TPS is high under regular extrusion conditions and will in many cases not lower at increasing process temperature.
- The evaporation of water can produce unwanted bubble formation in starch-based materials.

Several methods of extrusion are available. Few of them are mentioned here.

1. Two stage film/sheet extrusion
2. Extrusion film blowing
3. Multilayer co-extrusion
4. Foaming extrusion

Injection molding

Injection molding is one of the most widely used processing techniques for manufacturing plastics parts. The desired product is obtained by forcing the molten polymers under pressure into an evacuated cavity [110]. It is characterized by a high degree of automation, high productivity, and good dimensional stability of moldings. Injection molding is a cyclic process and consists of four significant processing stages i.e. filling, packing, cooling and ejection [110, 111]. The process starts with feeding hot polymer melt to the mold cavity at injection temperature. This is called the “filling stage”. Next is “post filling stage”, in which the additional molten polymer at high pressure is packed into the cavity to compensate for the expected shrinkage as the polymer solidifies. This is followed by the “cooling stage”, where cooling of the mold takes place until the part is satisfactorily rigid to be ejected. The “ejection stage” is the last step in which the mold is opened and the part is
ejected [111]. Main factors affecting molding are: materials, molding machine, model design, and process conditions [110].

### Compression molding

Compression molding has been widely applied and examined for the production of starch-based plastics. This process is investigated for manufacturing foamed containers, and usually consists of the following three steps; starch gelatinization, expanding and drying. Gelatinization and releasing the product from the mold are two important steps of compression molding, so gelatinization agents and mold releasing agents such as magnesium stearate and stearic acid are often used in formulation to prevent the sticking of starch to the mold [2].

### Film casting

Film casting has been widely used and reported in starch literature [105, 112-115]. The process consist of four main steps i.e. solution preparation, gelatinization, casting and drying. Starch solid concentrations of 3-10 % and plasticizers are directly mixed in water, transferred quantitatively to a Brabender viscograph cup, in which the solution is heated from room temperature to 95 °C. The starch plasticizer mixture is blended for 10 min. The temperature of the Brabender depends on the type of plasticizer used; for example if glycerol is added to the formulation, a higher temperature can be used. Immediately after mixing, the gelatinized suspensions are poured onto a flat Teflon or acrylic plate. Then placed in oven for ~ 24 h at about 40-75 °C and dried till constant weight [2].

Plasticizers help to ease the processing of starch and improve the mechanical properties of TPS films e.g. the flexibility of films increases by the addition of a suitable plasticizer. Glycerol and sorbitol are widely used plasticizers to make films flexible. Other chemicals such as sugars, sucrose, glucose, xylose, fructose, urea and various glycols have been investigated [100, 115, 116]. However, plasticized films lack strength and as a result, blending [25], or laminating [117] with other materials has been used to overcome this disadvantage. Aqueous blends of cellulose acetate and soluble starch has been studied intensively [76, 118-120]. Properties of such blends are suitable for a wide range of biomedical applications, from bone replacement to engineering of tissue scaffolds, to drug-delivery systems [2].

### Spray drying

Spray drying is a well know unit operation that can also be used for the preparation of starch-based materials. It is a fast drying process that produces amorphous or semi-amorphous particulates from liquid solution droplets [121]. Pre-gelatinized starch may be produced by spray drying without losing granular integrity [36, 122]. It is successfully used in pharmaceutical and food technology [123, 124]. It has been estimated that more than 15000 spray dryers of industrial size are in operation throughout the world, and approximately double that number is used in pilot plants and laboratories [123]. It is a flexible process with a lot of possibilities to improve and modify the characteristics of powders such as particle size, particle morphology, crystallinity and the amount of residual solvent [125]. It is characterized by high reliability, reproducibility and possible control of particles size. The spray drying principle is based on the nebulization of a polymer solution containing the active ingredient as solute or in suspension through a desiccating chamber. A stream of heated air is used to evaporate the solvent rapidly transforming the small droplets into solid
micro-particles [126]. Nevertheless, spray drying requires particular attention in the process control because of the high number of parameters. These limitations include problems with efficient particle collection and degradation of materials sensitive to high temperatures. Each process variable is critical and requires evaluation of parameters concerning both spray-dryer and feed formulation [127]. Feed that is to be dried is sprayed in a large cylindrical and usually vertical chamber. A large volume of hot gas is used to supply sufficient amounts of heat necessary for complete evaporation of the liquid. Heat and mass transfer takes place by the direct contact of gas and dispersed droplets. After drying the granular solid and the cooled gas are separated [128]. Classification of spray dryers can be made on the basis of several parameters, but three of them are important [129, 130].

1. Height-to-diameter ratio of the dryer chamber
2. Air-flow type
3. Atomizer type

Depending on chamber height and diameter tall and short designs are available. A height-to-diameter ratio of 5:1 is the standard for tall designs versus a 2:1 ratio for short dryers. The latter are more commonly used [129]. For airflow, three common configurations are used: co-current, countercurrent and mixed flow, describing the flow directions of air and product through the dryer chamber. Similarly three types of atomizers are available, rotary or high speed centrifugal disks, high pressure nozzles and two fluid or pneumatic atomizers [130].

Spray drying for TPS blends

A major drawback of using TPS-based material is their sensitivity to water. Slow recrystallization of starch (retrogradation) is a major problem for the use of TPS blends for the manufacturing of packaging and coating materials. The recrystallization is stimulated by the presence of water and results in the loss of mechanical properties such as flexibility and tensile properties [104].

In general all the above mentioned TPS processing methods (extrusion, film casting, injection molding) are performed in the presence of water-plasticizer combinations. The plasticizers used are mostly hydrophilic. Moreover, the extrusion process cannot be performed without the addition of water. Combinations of plasticizers and water lead to retrogradation through recombination of amylose and amylopectin and crystallization is promoted, resulting in the undesired changing of the final product properties [39].

To overcome this “disturbing” influence of water but maintaining plasticizer activity during the manufacturing process, another thermal processing route may be needed to obtain “dry” amorphous starch-plasticizer blends. For this reason spray drying TPS blends from starch water dispersions and solutions has been investigated. Spray drying processes applied to starch solutions/dispersions for the preparation of TPS blends is underdeveloped while this technology is considered as an important way to produce amorphous materials [125] or, in particular for native starches, to manufacture small amorphous particles [36].

Thesis outline

The objective of this thesis is to study the performance of thermoplastic starch films produced via compression molding of spray dried starch/plasticizer blends. Through this technique it should
be possible to obtain moisture-free amorphous starch-plasticizer blends with the potential to be used as biodegradable bio-plastics. Different plasticizers were used and the properties of TPS blends were investigated. Special focus is put on retrogradation and the degree of crystallinity of films at different humidity levels.

Chapter 2 describes the spray drying of different amylose/amylopectin blends for the purpose of subsequent processing of these materials into TPS films. Spray-drying of starch/maltodextrin formulations has been evaluated as a potential technology for the manufacture of amorphous thermoplastic starches (TPS). The properties of solution and dispersion dried TPS samples of maize starch with different amylose to amylopectin ratios were systematically studied before and after spray-drying.

Chapter 3 describes an in-depth study of the influence of malto-oligosaccharide molecular weight, i.e. dextrose equivalents (DE), on the performance of the powders and the films obtained by compression molding of spray dried powders. Maltodextrins of different molecular weights were used to evaluate whether they act as processing aid or as plasticizer.

Chapter 4 focuses on the processing of plasticized starch via classic solution casting and by compression molding of spray dried powders, respectively. Glycerol and urea were used as plasticizer, separately and in combination with maltodextrins (DE =19.1). The rate of retrogradation and crystallinity of TPS films produced by both techniques are investigated. As the production methods are not the same, differences in starch-plasticizer interactions are expected which should lead to changes in the degree of crystallinity and rate of retrogradation.

Chapter 5 aims to gain increased insight in the retrogradation of plasticized amorphous TPS films, obtained via compression molding of solution spray dried powder. Starch is plasticized by using amino acids and malic acid, all having similar molecular weights but different hydrogen bonding functionality. The samples were also co-plasticized with standard additives like glycerol, urea, and maltodextrin. Special emphasis was on the retrogradation and mechanical properties of the resulting films.

In Chapter 6, cross-linked oxidized thermoplastic potato starch (TPS) based films were prepared through ultra violet (UV) irradiation. The performance of TPS powders and films was studied. The films were formulated with malic and citric acid as plasticizers in combination with glycerol as co-plasticizer. Sodium benzoate (SB) was used as photosensitiser. Besides the effect on retrogradation, the mechanical properties of the films have been studied as a function of UV treatment and moisture exposure.

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