Synthesis and properties of starch based biomaterials
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Chapter 1
Introduction

Abstract
A general overview of starch properties will be given and the potential use of starch as a starting material for a wide range of green biomaterials will be reviewed and discussed. Different routes to modify starch to improve the product properties and to extend the application range will be provided. Finally, an outline of this thesis is given.
1.1. Starch

75% of all organic material on earth is present in the form of polysaccharides [1]. An important polysaccharide is starch. Plants synthesize and store starch in their structure as an energy reserve. It is generally deposited in the form of small granules or cells with diameters between 1-100 µm [2]. Starch is found in seeds (i.e. corn, maize, wheat, rice, sorghum, barley, or peas) and in tubers or roots (i.e. potato or cassava) of the plants [2-3]. Most of the starch produced worldwide is derived from corn, but other types of starch such as cassava, sweet potato, potato, and wheat starch are also produced in large amounts [2, 4-5]. Most starch crops are very productive. Potato accumulates starch to approximately 75% of the dry weight in the tubers with a yield up to 21 ton starch per hectare, while corn seeds consist of 65-80% starch by weight, with an average yield of 4.9 ton starch per hectare [6].

The worldwide production of starch in 2008 is estimated to be around 66 million tons [7]. Most of the starch is produced in the USA. The second and third starch producer regions are Europe and Asia [4-5]. Past, current and future estimations of worldwide starch production are given in Figure 1.1. [7]. The current price of corn starch is around $0.45 (estimated from the total volume and value of the US corn starch export [8]).

![Figure 1.1](image-url)
1.1.1. Starch production processes

Starch is generally extracted from the plant by wet milling processes [9-10]. The plant material is grounded in water, the debris is filtered from the slurry, and starch granules are obtained after centrifugation from the suspension. As an example, a typical corn starch production process is given in Figure 1.2.a. The starch is present in the endosperms (floury and horny), and is embedded in a proteinaceous cellular matrix as is shown in Figure 1.2.b. After initial cleaning to remove cob, sand, and other foreign materials, the corn kernel is softened by steeping in warm water containing SO₂ until the volume of the kernel increases with 55-65%. After a coarse milling, the mixture is fed to a hydrocyclone to separate the germ and the rest of the kernel, which is again fed to a second milling process. The resulting suspension from the mills contains fiber, gluten, and starch. The fiber is removed using washing screens. The low density gluten is separated from the starch suspension by centrifugation. The resulting starch is further washed in a cyclone and finally dried.

Figure 1.2. Corn starch production [9]
a. Typical corn-milling operation
b. Cross-sectional view of a corn kernel
1.1.2. Structure and properties of starch

Starch is a polymer consisting of anhydroglucose (AHG) units (see Figure 1.3.a.) [2]. Two types of AHG polymers are usually present in starch: amylose and amylopectin [2-3, 6]. Amylose is essentially a linear polymer in which AHG units are predominantly connected through \( \alpha-D-(1,4) \)-glucosidic bonds. The molecular weight of amylose is a function of the plant source and processing method, but usually in the range of 1.6-7 \( \times \) 10\(^5\) Da [9]. Amylopectin is a branched polymer, containing periodic branches linked with the backbones through \( \alpha-D-(1,6) \)-glucosidic bonds [2]. Each branch contains about 20-30 anhydroglucose units. The molecular weight of amylopectin is higher than that of amylose and is typically 4-5 \( \times \) 10\(^8\) Da [9]. The content of amylose and amylopectine in starch varies and largely depends on the starch source. Typically, the amylose content is between 18-28% [2]. The amylose content of several common starches is given in Table 1.1. [3].

![Chemical Structure of Starch](image)

**Figure 1.3.** Chemical Structure of Starch
a. Anhydroglucose (AHG) unit
b. Amylose
c. Amylopectin

Starch is insoluble in cold water, but it is very hygroscopic and binds water reversibly. Heating a starch solution leads to loss of hydrogen bonding in the interior of the starch granule and the starch will start to gelatinize. The starch granules will swell rapidly to many times of its original volume. The linear
amylose molecules leach out of the granules into the solution. The resulting suspension contains a mixture of linear amylose molecules, swollen granules, and granule fragments, and, depending on the amount of water present, will form a thick paste or gel. The gelatinization temperature range can be defined as the temperature at which granular swelling begins until the temperature when nearly 100% of the granules are gelatinized [9]. The gelatinization temperature range of various starch sources is given in Table 1.2.

Table 1.1. Amylose content of common starches [3]

<table>
<thead>
<tr>
<th>Starch</th>
<th>Amylose (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arrowroot</td>
<td>20.5</td>
</tr>
<tr>
<td>Corn</td>
<td>28</td>
</tr>
<tr>
<td>Hybrid amylo maize V</td>
<td>52</td>
</tr>
<tr>
<td>Hybrid amylo maize VII</td>
<td>70-75</td>
</tr>
<tr>
<td>Oat</td>
<td>27</td>
</tr>
<tr>
<td>Manioc</td>
<td>15.7</td>
</tr>
<tr>
<td>Potato</td>
<td>20</td>
</tr>
<tr>
<td>Rice</td>
<td>18.5</td>
</tr>
<tr>
<td>Sago</td>
<td>25.8</td>
</tr>
<tr>
<td>Sweet potato</td>
<td>17.8</td>
</tr>
<tr>
<td>Tapioca</td>
<td>16.7</td>
</tr>
<tr>
<td>Wheat</td>
<td>26</td>
</tr>
</tbody>
</table>

Table 1.2. Starch gelatinization temperature range [9]

<table>
<thead>
<tr>
<th>Starch</th>
<th>Gelatinization Temperature Range [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Potato</td>
<td>59-68</td>
</tr>
<tr>
<td>Tapioca</td>
<td>58.5-70</td>
</tr>
<tr>
<td>Corn</td>
<td>62-72</td>
</tr>
<tr>
<td>Waxy corn</td>
<td>63-72</td>
</tr>
<tr>
<td>Wheat</td>
<td>58-64</td>
</tr>
</tbody>
</table>

1.2. Biomaterials from starch

1.2.1. Plastic Applications and Waste Issues

Plastic is the general term for a wide range of synthetic or semisynthetic polymerisation products. Plastics are used in a wide range of applications and the demand is still increasing every year [11]. The first generation of commercial plastics was derived from cellulose nitrate and is known as celluloid [12-14]. Cellulose nitrate was first prepared by A. Parker in 1838, and celluloid was
patented by J. Hyatt in 1870 [13]. While celluloid is derived from a natural polymer (cellulose), the oldest purely synthetic plastic is Bakelite, discovered by Baekeland in 1907 [12, 15]. A dramatic increase in demand for plastics began after World War II, when polyethylene (PE) was invented. PE is a very versatile plastic because it can be shaped easily into various forms, for instance to be used in packaging and paper coatings [13].

Plastics are very attractive materials. They have a low density and can be shaped in thin films while maintaining good properties. The latter is important when using the material for packaging purposes to save weight, space, and energy during transportation of goods. Plastics have lower melting temperatures compared to glass and metals, and therefore need less energy to shape it into useful materials [13]. The production and consumption of plastics has increased significantly with a rate of almost 10% every year since 1950. In 2006, the worldwide plastics production has reached 245 million ton per annum [11] (see Figure 1.4.). The largest application of plastics is for packaging purposes. About 29% of the total plastics produced in the USA [1], and 37% of the total plastics demand in EU [11] is used as packaging materials. Important polymers used for packaging are polyethylene (HDPE and LDPE), polypropylene (PP), polystyrene (PS), polyvinyl chloride (PVC), polyethylene terephthalate (PET), and polycarbonates (PC). Plastics are also used for building materials and automotive, electrical, and consumer products (see Figure 1.5.)

**Figure 1.4.** Worldwide Plastics Production (1950-2006) [11]
Plastic waste, however, is causing serious environmental problems. It has a high volume to weight ratio and is resistant to degradation. Plastics have been polluting sea [1, 16], soil, rivers, and lakes, threatening fishery, ship navigation, hydropower plants operation, irrigation, and other public works [17]. Plastic litter is hazardous to wildlife [1, 6], and accumulation of its residues in soil cause significant reductions in agricultural yields.

The disposal of plastics materials in municipal solid waste (MSW) is a serious issue in many parts in the world. In the USA, the amount of plastics in MSW increased from less than 1% in the 1960 to 11.7% in 2006 [18]. The volume fraction of plastic in MSW is much larger due to the low density of plastics, and may be more than twice the weight fraction [13]. In 1996, plastics waste was ranked as the second major source of MSW after paper and paperboard, consisting of 25%-v of the total waste [13]. Recycling (part of) the plastics to reduce the amount of MSW also has limitations. It is not applicable for thermoset resins [19], and is only effective for single plastic sources or simple plastic formulations. Co-mingled plastics, which are usually found in waste streams, are not easy to recycle [19]. In Europe (2006), only 20% of the plastic is recycled. Most of the waste is still disposed (50%) by landfill or incinerated to recover the energy (30%) [11].

![Figure 1.5. Plastic applications and waste treatment in Europe [11]](image)

1.2.2. The potential of biodegradable plastics

The application of biodegradable plastics could be an attractive solution for the problems related to the use of conventional plastics (vide infra). Biodegradable plastics are polymeric materials capable of decomposing when given an
appropriate environment and sufficient amount of time [15]. Biodegradable plastics have gained considerable interest since the 1980s. Nowadays new types of biodegradable plastics with improved properties and lower costs have been developed [13]. Biodegradable plastic waste may be treated in composting facilities, together with food and yard waste as well as paper. It may also be treated in sewage sludge water treatment plants or buried in the soil [20-21]. The considerable growth of interest in composting as a means to replace landfill due to the decreasing disposal spaces (especially in Europe) may also help the progress of biodegradable plastics development [13].

Several authorities have provided definitions for biodegradable plastics [22], and these are shown below:

ISO 472: 1998 - A plastic designed to undergo a significant change in its chemical structure under specific environmental conditions resulting in a loss of some properties that may vary as measured by standard test methods appropriate to the plastics and application in a period of time that determines its classification. The change in chemical structure results from the action of naturally occurring microorganisms.

ASTM sub-committee D20.96 proposal - Degradable plastics are plastic materials that undergo bond scission in the backbone of a polymer through chemical, biological and/or physical forces in the environment at a rate which leads to fragmentation or disintegration of the plastics.

Japanese Biodegradable Plastic Society draft proposal - Biodegradable plastics are polymeric materials which are changed into lower molecular weight compounds where at least one step in the degradation process is through metabolism in the presence of naturally occurring organisms.

DIN 103.2 working group on biodegradable polymers - Biodegradation of a plastic material is a process leading to naturally occurring metabolic end products.

Biodegradable plastics may be classified into two general groups, biopolymers from nature (from plants, animals, and microorganisms) and biodegradable synthetic polymers [1]. Common natural biopolymers are carbohydrates, proteins (present abundantly in plants and animals), and polyesters from micro-organisms [1]. Biopolymers are inherently biodegradable, because they take part in nature’s cycle of renewal.

The market price of biodegradable plastics (mainly from starch and PLA) has decreased the last years, and since 2000 they have become competitive with traditional materials in some applications [20-21]. The price of these biodegradable plastics is expected to be reduced considerably in the next decade [23]. For instance, the price of PLA based plastics in 2010 is estimated to be around € 1.5/
kg, half of its price in 2003 (around 3 Euro/kg). The price of starch-based biodegradable plastics (€ 1.50-4.50/ kg in 2005) is also expected to be lower in the future due to considerable reduction in modification costs [23]. Biodegradable plastics are especially very useful for single-use applications, when recycling is not practical or uneconomical [20-21], or when environmental impacts have to be minimized. Examples are the use as packaging material for carrier bags, consumer products and food products. Biodegradable plastics are also used for food servicewares [20], towels, utensils [15], agricultural products (mulch films, pots), hygienic materials (diapers, napkins) [24], breathable fabrics, biofillers for tires, and chewable items for pets [1, 20].

1.2.3. Biodegradable Plastics from Starch

Starch is a very attractive source for the development of biodegradable plastics [6]. The price of starch in 2007 was about $ 0.45 per kg [8]. This price is much lower than conventional plastics derived from oil, such as polyethylene (PE, € 1.2-1.4 or $ 1.8- 2.4 per kg in 2007-2008 [25]). Starch may become an attractive raw material for plastics in the future, because the price of oil based polymers may still increase due to the rise in the crude oil prices [25]. Bastioli [20-21] showed that nearly all biodegradable plastics available in the market are derived from starch, either from starch-based materials (slightly modified starch, alone or complexed with natural or synthetic biodegradable polymers) or from polylactic acid which originates from the fermentation of a starch feedstock. The global production capacity of starch-based bioplastics in 2010 is estimated to increase to 200-300 kiloton per year from 77-200 kiloton in 2003 [23].

Virgin starch is not suitable as a packaging material. It cannot be shaped in films with adequate mechanical properties (high percentage elongation, tensile and flexural strength) and is too sensitive to water [26-27]. Consequently, starch must be modified, either by plasticization, blending with other materials, chemical modification or combinations of them [26], before they can be applied as biodegradable plastics.

1.3. Starch modifications to improve product properties

Several techniques may be applied to develop starch based biomaterials with improved properties. These are summarized briefly in the next sections.
1.3.1. Thermoplasticized starch

Virgin starch is brittle and difficult to be processed into articles due to its relatively high glass transition temperature ($T_g$, approximately 230 °C) [28], which is even above the thermal degradation temperature. [29]. The brittleness is known to increase in time due to free volume relaxation and retrogradation. This problem is mainly caused by the presence of strong inter- and intra-molecular hydrogen bonds between the starch macromolecules [28, 30].

Starch can be modified to obtain materials which melt below the decomposition temperature [31], and therefore are processable by conventional polymer processing techniques such as injection, extrusion, and blow moulding [28, 30, 32-36]. The modified products are known as thermoplastic, destructed, plasticized, or melted starch [29, 33]. The modification involves break down of the starch granular structure by the use of plasticizers at high temperatures (90-180 °C) and shear, which will result in a continuous phase in the form of a viscous melt [29-30, 32, 37]. The thermoplasticization process will decrease the interactions of the molecular chain and destruct the structure of the starch [38]. As the result, the semicrystalline structure of starch and its granular form are lost and the starch polymers are partially depolymerized, resulted in the formation of an amorphous mass [35, 39].

There are several substances used as plasticizer for the preparation of thermoplastic starch (TPS), such as water and polyols (glycerol, glycol, sorbitol, sugars) [30, 40]. The use of water as a plasticizer is not preferable, because the resulting product will be brittle when equilibrated with ambient humidity [35]. The use of other plasticizers (for example glycerol) results in a rubbery material, with better properties than virgin starch in various applications.

Yu, et al [28] discovered that the elongation of break of the thermoplastic starch is significantly improved by plasticization with glycol, glycerol, and hexylene glycol. The plasticized starch properties may be tuned by changing the temperature of processing, water content, and the properties and amount of plasticizers. For instance, the thermal properties of glycerol-plasticized starch are a function of water content [31, 35, 40]. At intermediate water levels, phase separation may still occur. A biodegradation study according to ISO/CEN 14852 and ASTM D5209-92 standards [41] on films made from starch–glycerol–water mixtures confirmed that the films are easily biodegradable.

Although thermoplasticization seems to be a promising method, TPS synthesized from polylol and sugar plasticizers have the tendency to re-crystallize (retrogradation) after being stored for a period of time, which results in embrittlement. Another issue is the poor water resistance and low strength, which still limits their use. The plasticizers are also usually hydrophilic and can be
washed out by water [29]. Solutions to improve the properties of TPS are blending, or coating with hydrophobic polymers [33, 39].

1.3.2. Cross-linked starch

An anhydroglucose molecule of starch contains two secondary and one primary hydroxyl group. These hydroxyls can react easily with a wide range of compounds such as acid anhydrides, organic chloro-compounds, aldehydes, epoxy, and ethylenic compounds. Chemicals of these classes having two or more of the reactive groups may react with two or more hydroxyls of the starch molecules. The products are called cross-linked starches. Cross-linking results in a reduction of the solubility in water and to thickening, leading to higher viscosities [42-43]. The cross-linked starches have found many applications, especially in the food, paper, textile, and adhesive industry.

Silva, et al [43] studied the mechanical properties of films from maize starch cross-linked by sodium trimetaphosphate (SMTP). Higher processing temperatures generally led to higher cross-linking levels, resulting in an increase of the Young’s modulus and tensile strength of the products and a decrease in elongation at break. The cross-linked products are therefore more rigid (and less elastic) materials than virgin starch [43].

1.3.3. Starch Esters

The development of starch esters started in the mid 19th century [44, 46]. Already in 1865, Schuetzenberger acetylated starch with acetic anhydride [44]. Most studies dealt with the synthesis of starch esters of C1-C4 carboxylic acids, and particularly with acetic acid [45].

The simplest starch ester is starch formate (C1), synthesized by direct addition of formic acid to starch at room temperature. The esterification reaction is catalyzed by H+ and proceeds with the formation of water [46]. Breakdown of the starch and the formation of low molecular weight products occur to a significant extent [47]. As a result, the use of formyl esters of starch is much lower than that of acetate esters.

The most popular starch ester is starch acetate [46]. Three different types of starch acetates may be distinguished, differing in Degree of Substitution (DS). The DS is defined as the moles of substituents per mole of AHG units [48]. Low DS products (0.01-0.2) are commercially available and used as food additives and in the textile industry. Medium DS starch acetates (0.3-1) are still soluble in water, while highly substituted starch acetate (DS of 2-3) are soluble in organic solvents. Substitution of the hydroxyl groups of starch with acetate groups makes the esters more hydrophobic than native starch. High DS starch acetate can be easily casted
into films using organic solvents. The degree of acetylation of starch acetates can be easily controlled, allowing the polymer to be produced with a range of hydrophobicities [22]. High DS starch acetates are thermoplastic materials suitable to be used as biodegradable plastics [45].

Several synthetic routes have been developed for starch esters. Esterification may be performed using acid anhydrides in aqueous media or organic solvents (pyridine, DMSO, xylene, DMF, or isopropanol) with acidic (hydrochloric or sulfuric acid) or alkaline (NaOH or triethylamine) catalysts [26]. Starch triacetate has been successfully synthesized using acetic anhydride in combination with pyridine-gelatinized starch [44]. Starch esters have also been synthesized using alkanoyl chlorides [49-53]. Another attractive route involves the use of vinyl esters as reagents [54]. The kinetics of the reaction between gelatinized aqueous potato starch and vinyl acetate was studied by De Graaf, et al [55-56], and is shown in Scheme 1.1. Acetylation of starch in water and DMSO using vinyl acetate has been studied lately by Mormann and Al-Higari [57] as well as Dicke [58]. Neutral and weak acid/alkaline catalysts result in regioselective substitution at the C2 hydroxyl groups of starch, while alkaline catalysts (such as carbonate, hydrogen carbonate, acetate, and phosphate) will result in C-2, but also C-6 and C-3 substitution [58].

![Scheme 1.1. Mechanism of starch acetylation using vinyl acetate](image-url)
The synthesis of long chain fatty acid ester of starch has attracted much interest lately. The introduction of longer acid chain is expected to reduce the brittleness of virgin starch and to increase its hydrophobicity [48]. Fatty-acid starch esters have been synthesized using fatty acid (octanoyl, dodecanoyl, octadecanoyl) chlorides [49-53]. The fatty acid chloride reactants are, however, relatively expensive and rather corrosive. The use of methyl and glyceryl esters of fatty acid (in the absence of solvent) to synthesize starch fatty acid esters has also been studied [59], but only relatively low-DS (0.34-0.61) products could be obtained using this approach.

1.3.4. Starch - Biopolymer Blends and Graft Co-Polymers

Blending of different polymers is an established method to obtain products with improved properties. However, polymers are rarely miscible with each other [60] so that, in the simplest case of a binary blend, one component will be dispersed into the other. The degree of adhesion (binding) between the dispersed phase and the matrix is dependent on the molecular interactions between the two components and represents a crucial factor in determining the morphology of the blends and eventually the product performance [60]. Two main methodologies are applied for the production of polymer blends. The first involves simple melt mixing of the two components for example by extrusion. By working at temperatures above the melting point or glass transition temperature of the two components, the latter are mixed together. If the right combination of chemical groups on the two components is present along the polymers backbone, a chemical reaction might take place upon processing (reactive extrusion). The second methodology for producing polymer blends involves the in situ polymerization of one component (thus originally present in the blend in monomeric form) in the presence of the second one. The classical example of such process is represented by the production of High Impact Poystyrene (HIPS) obtained by styrene polymerization in the presence of polybutadiene [61]. Although the in situ polymerization process is not as technologically straightforward and economically convenient as melt-mixing, it is frequently used in order to chemically graft the polymerized component on the other one (polystyrene on polybutadiene in our example above [61]). As a result, the two components are chemically linked to each other, which in turn provide a very strong adhesion at the molecular level between the dispersed phase and the matrix. Despite this advantage, melt-mixing remains the preferred route to polymer blends mainly because of very practical reasons: low costs, availability of mixing equipment and no necessity to use any organic solvent (often employed for the in situ polymerization). However, in order to achieve also a good molecular adhesion between the phases by melt mixing, interfacial agents (e.g. compatibilizers) might be used. Their role is comparable to the one of a surfactant in emulsion formation [61], i.e. they locate themselves at the interface between the
two components stabilizing the dispersion (most probably by a steric repulsion mechanism [62]) and providing an improved adhesion at the interface. A suitable interfacial agent for the blends of two polymeric materials is a block copolymer for which the chemical structure of every block is the same (or very similar) to the one of the individual components to be blended [63] (illustrated in Figure 1.6.). Interfacial agents already available on the market can be used as such or can be produced upon mixing (in situ) by chemical reaction of the two components.

In the past, there have been efforts to blend as well as to graft synthetic polymers onto starch. The synthesis of compatibilizer and its use for starch/synthetic polymer blending has also been studied. The products have been synthesized in the lab as well as on industrial scale [32, 39, 64-98]. The blending and grafting of starch with synthetic polymers is usually performed to achieve higher hydrophobicity and to improve the mechanical and thermal properties as well as to obtain cheaper and more biodegradable products.

![Figure 1.6.](image)

**Figure 1.6.** Illustration of the role of interfacial agent in compatibilizing blends

### 1.3.4.1. Starch-based blends by melt mixing

Starch-synthetic polymer blending has been studied as early as in 1973 [64-65]. The most often used synthetic polymer for blending with starch is polyethylene [27, 66-81]. The starch/polyethylene blends are used for agricultural mulch [27, 80-81] or food packaging [78]. The uncompatibilized blends of starch and
polyethylene show a coarse phase separation due to differences in polarity of starch (hydrophilic) and polyethylene (hydrophobic). The mechanical properties of these blends (tensile strength and elongation at break) decrease at higher starch content. Polyethylene-g-maleic anhydride (PE-g-MA) and polyethylene-g-glycidyl methacrylate (PE-g-GMA) have been used as reactive compatibilizer for starch/PE blends. PE-g-MA contains reactive anhydride sites, while PE-g-GMA possesses epoxide groups, which both can react in situ with the hydroxyl groups of starch [70, 72-73]. As a result a graft copolymer (PE-g-Starch), i.e. the compatibilizer, is formed upon mixing, thus improving the dispersion of starch in the PE matrix. The mechanical properties of the blend are also improved. The tensile strength of the uncompatibilized blends is drastically reduced when starch content is increased, while the tensile strength of the compatibilized ones decreases only slightly with the starch content.

The use of conventional synthetic polymer such as PE for blending with starch will only result in a partially biodegradable material, since the conventional synthetic polymers are usually poorly or non-biodegradable. To obtain completely biodegradable products, synthetic biodegradable polymers have been applied, among which synthetic polyesters are considered very promising materials [82]. Examples of these biodegradable polyesters are poly-glycolide, poly-dioxanone, poly-lactides, and poly-lactones (such as poly-butyrolactone, poly-valerolactone, and poly-caprolactone). The ester bonds of these polymers are susceptible to attack by water and this leads to enhanced biodegradability. These biodegradable polyesters will finally decompose into non-toxic products [73]. Some of these polyesters also have very good mechanical, thermal and water/gas permeability properties that are even comparable to bulk non-biodegradable polymers such as PE and PP, and EVOH [26].

Polycaprolactone (PCL) is a well-known synthetic biodegradable polyester, which combines excellent biodegradability with acceptable mechanical properties. Studies on the blending of starch with PCL have been already described [32, 39, 84-98]. As is the case of blends with PE, the uncompatibilized blends of starch with PCL give coarse phase separation and a reduction in the mechanical properties when the starch content is increased. The use of reactive compatibilizer precursors PCL-g-glycidyl methacrylate (PCL-g-GMA) [89-90], PCL-g-pyromellitic anhydride [94-95], PCL-g-maleic anhydride (PCL-g-MA) [91, 96], dextran-g-PCL [92], and of a premade starch-g-PCL [93] for starch/PCL blends resulted in a better dispersion between the phases and in turn in improved mechanical properties compared to the uncompatibilized blends. Despite these good results, systematic studies on the compatibilizer precursor synthesis as well as on the influence of the chain topology and chemical reactivity (for the in situ compatibilizer formation) have not yet been reported.
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1.3.4.2. Starch-based blends by in situ polymerization

The synthesis of starch based graft copolymers by in situ polymerization represents not only an alternative route to melt blending (vide supra) for the production of novel biomaterials, but it can also provide an efficient synthetic methodology for the production of a compatibilizer to be used for melt blending of starch with a biopolymer [93].

In the past, starch-g-PCL has been synthesized using toxic materials such as isocyanates [93]. Another approach consists of the Ring Opening Polymerization (ROP) of ε-caprolactone monomer in the presence of starch. In this reaction, the hydroxyl groups of starch are supposed to function as initiating sites. Previous studies showed that common ROP catalysts such as tin octoate or aluminium isopropoxide gave low (0-14%) grafting efficiencies (GE, defined as the percentage of grafted polyester to starch compared to the total amount of homopolymer and grafted polyester) [97]. Starch is a very hydrophilic material that always contains moisture. The water in starch granules competes with the hydroxyl groups of starch in the initiation step of the polymerization reaction, leading to formation of PCL homopolymers rather than starch-g-PCL, thus resulting eventually in low GE values [97]. Another possible cause for the low GE values is the heterogenous nature of the reaction. Starch is insoluble in the typical organic solvents used for ROP (such as toluene or THF), and the presence of liquid-solid reaction system leads to reduced reaction rates between starch and ε-caprolactone. The highest GE value (up to 90%) has been achieved when using triethylaluminium as catalyst [97-98], which however is extremely air- and water-sensitive, and difficult to handle since it releases ethane, a very flammable by-product, during the reaction.

A new strategy for the in situ ROP of ε-caprolactone on starch with the use of common ROP catalyst is therefore highly desirable.

1.4. Thesis Outline

The objective of this thesis is to study synthetic pathways to obtain starch derivatives with the potential to be used as bioplastic. Three routes have been studied in detail: starch esterification, starch/ biopolymer blending, and starch-g-biopolymer formation.

Chapter 2 describes the ROP of p-dioxanone initiated by a protected monosaccharide (1,2;3,4-di-O-isopropylidene-α-D-galactopyranose) using Al(OiPr)₃ as the catalyst. The results of this study have been used as input for the synthesis of the starch-g-PCL.

In Chapter 3, the synthesis of starch-g-PCL is reported. The method applied basically consists of three steps (temporary partial protection of starch-hydroxyl
by trimethylsilyl groups, ROP of ε-CL on the remaining starch-hydroxyl groups, and removal of the silyl groups).

A preliminary study on the effect of several process variables (reactant ratio, addition of co-solvent, and application of different catalysts) on starch esterification using vinyl fatty esters (vinyl laurate and vinyl stearate) is provided in Chapter 4.

Based on these preliminary results, a systematic experimental study on the effect of the process variables on the starch ester DS has been performed. The results were quantified using a statistical model. The model, together with the mechanical and thermal properties of the synthesized starch esters are reported in Chapter 5.

The synthesis of two interesting compatibilizers (PCL-g-GMA and PCL-g-DEM) for starch/PCL blends is discussed in Chapter 6. The use of these compatibilizers in starch/PCL blends, including the mechanical and thermal properties, are also reported.

1.5. References


Chapter 1


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Chapter 1


