Synthesis and properties of starch based biomaterials
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Summary

Plastics made from fossil resources (a.o oil and gas) are very attractive materials for a broad range of applications. Examples are the use as packaging and construction materials. Its production has increased significantly since 1950, with a rate of almost 10% every year. After use, plastics may end up in the environment and cause serious environmental problems. For instance, it has a high volume to weight ratio and is generally resistant to degradation. In combination with the current high prices for petrochemical products, there is a strong need for renewable alternatives for plastics from fossil resources.

Starch-based biodegradable materials are considered interesting candidates to replace certain types of conventional plastics. Starch is relatively cheap and available from a broad range of plants. Starch is a polymer consisting of anhydroglucose (AHG) units. There are two types of polymers present in starch: amyllose and amylopectin. Amylose is essentially a linear polymer in which AHG units are predominantly connected through α-D-(1,4)-glucosidic bonds, while amylopectin is branched polymer, containing periodic branches linked with the backbones through α-D-(1,6)-glucosidic bonds. The content of amyllose and amylopectine in starch varies and largely depends on the starch source.

The use of virgin starch for packaging materials is restricted because it cannot be shaped to films with adequate mechanical properties (high percentage elongation, tensile and flexural strength). Starch is also too sensitive to water. Starch must therefore be modified before it can be applied as a biodegradable plastic. There are several starch modification methods available, such as thermoplasticization, blending with other materials, chemical modification or combinations thereof. The application of a number of prospective methods for developing starch-based biomaterials will be described in this thesis.

Chemical grafting of biodegradable polyesters on the starch backbone is expected to result in less hydrophilic and thus less water sensitive materials with improved mechanical properties. The synthesis of such grafted products by the in situ ring opening polymerization (ROP) of the monomers on the hydroxyl groups of starch is unfortunately not very straightforward. The main reasons are the water sensitivity of common catalysts and the fact that starch is poorly or even insoluble in the common organic solvents used for ROP. The application of an alternative method involving hydrophobisation of starch by the introduction of large hydrophobic SiMe₃ groups followed by a ROP with a polyester precursor and subsequent removal of the SiMe₃ groups is expected to result in higher grafting efficiencies. To gain insight in the potential of this approach, we have
initially performed research on the ROP with a simpler model system involving a simple protected mono-saccharide instead of starch.

The results for the model system involving the ROP of p-dioxanone initiated by hydroxyl groups of a protected monosaccharide (1,2;3,4-di-O-isopropylidene-α-D-galactopyranose) using Al(OiPr)_3 as the catalyst, are described in Chapter 2. The polymerizations were performed at 60-100°C, and off-white solid products with isolated yields of 30-96% were obtained. The yield of the polymers was a function of the reaction temperature and the reaction time, with higher temperatures (100°C) leading to lower yields. Average molecular weights of the products were between 970 and 6200 (7 – 58 monomer units) and were a clear function of the p-dioxanone/1,2;3,4-di-O-isopropylidene-α-D-galactopyranose ratio (at constant Al(OiPr)_3 intake), with higher ratios leading to higher molecular weights. A statistical model has been developed to quantify the effects of process variables (time, temperature and monomer: monosaccharide ratio) on the average degree of polymerization. Characterization of the products using ¹H- and ¹³C-NMR as well as MALDI-TOF mass spectrometry showed the presence of significant amounts of p-dioxanone polymers with an isopropoxide end group (20-30%).

The knowledge obtained from the model system was applied for the synthesis of starch-g-poly-ε-caprolactone using hydrophobised silylated starch. The results are described in detail in Chapter 3. The synthetic procedure may be divided into three steps: hydrophobisation of starch by the introduction of SiMe₃ groups followed by in situ ROP, and subsequent removal of the silyl groups. The silylation reaction was performed using hexamethyl disilazane (HMDS) in DMSO/toluene mixtures at 70°C. Silylated starch with a low to medium DS (0.46-0.68) was obtained. The grafting of ε-caprolactone to the silylated starch by a ring-opening polymerisation catalysed by Al(OiPr)_3 was performed in THF at 50°C. Poly-(ε)-caprolactone grafted silylated starch co-polymers with average chain length of 40-55 monomer units (molecular weight of 4500-6300) were obtained. The DS of the PCL chains was between 0.21-0.72, depending on the ε-CL to starch ratio. Considerable amounts of ε-CL homopolymers with isopropyl end-groups were also formed. The grafting efficiency for the desired reaction was 28-58%. The silyl groups of the poly-(ε)-caprolactone grafted starch co-polymers were finally successfully removed using a mild dilute hydrochloric acid treatment in THF at room temperature.

Esterification of starch with carboxylic acid derivatives is one of the oldest strategies to improve starch properties. Most of the previous starch esterification studies involved the use of short chain carboxylic acids (C1-C4), and particularly acetic acid derivatives (C2) have received considerable attention. The hydrophobicity of starch acetates is higher than virgin starch, but the products are still very brittle, even in the presence of plasticizers. The use of higher carboxylic (fatty) acid to esterify starch resulted in products with significantly improved...
mechanical properties and hydrophobicities. The synthesis of these fatty starch esters is, however, usually performed using fatty acid chlorides which are relatively expensive and rather corrosive. The use of methyl and glyceryl esters results in products with only relatively low DS. In Chapter 4-5, an alternative method for higher fatty starch esters by using fatty vinyl esters is reported.

Chapter 4 describes the results of a preliminary study on the synthesis of long fatty esters of corn starch (starch-laurate and starch-stearate) using vinyl fatty esters. The starch esters were prepared by reacting starch with vinyl laurate or vinyl stearate in the presence of basic catalysts (Na₂HPO₄, K₂CO₃, and Na-acetate) in DMSO at 110°C. The yellowish products were characterized by ¹H-, ¹³C-NMR and FT-IR. The products have a broad range of degree of substitution (DS = 0.24 - 2.96). The DS of the products was a clear function of the chain length of the fatty ester, vinyl ester to starch ratio, and the type of catalyst. For low vinyl-ester to starch ratios, an increase in the vinyl-ester concentration led to higher product DS values. At higher ratios, the DS decreased, presumably due to a reduction of the polarity of the reaction medium. K₂CO₃ and Na-acetate are superior with respect to activity when compared with Na₂HPO₄. With these catalysts, products with a DS > 2.4 could be obtained for both laurate and stearate esters.

In Chapter 5, a systematic study, including statistical modelling on the synthesis of long fatty esters of corn starch (starch-laurate and starch-stearate) using corresponding vinyl fatty esters is reported. The thermal and mechanical properties of some representative product samples are also described. The starch esters were synthesized by reacting gelatinized starch with vinyl laurate or vinyl acetate in DMSO in the presence of basic catalysts (Na₂HPO₄, K₂CO₃, and Na-acetate). Statistically adequate (R²≥0.96 and P-value of ≤10⁻⁹) second-order mathematical models correlating the effect of process variables (vinyl to AHG-starch mol ratio, reaction temperature, catalyst intake, and catalyst basicity) to the DS of the starch ester products were developed. The DS of the products is a strong function of the basicity of the catalyst. Reaction temperature and catalyst intake also affect the product DS but only to a lesser extent. The use of Na₂HPO₄ resulted in low-medium DS products (0.3-1.5 for starch laurate, 0.07-1.5 for starch stearate), while the use of K₂CO₃ and CH₃COONa catalysts resulted in medium-high DS products (2.1-2.9 for starch laurate, 1.4-3 for starch stearate). High-DS products (DS= 2.26-2.39) are totally amorphous whereas the low-DS ones (DS= 1.45-1.75) are still partially crystalline. The thermal stability of the esterified products is higher than that of native starch. Mechanical tests show that the products have tensile strength (stress at break) between 2.7-3.5 MPa, elongation at break of 3-26%, and modulus of elasticity of 46-113 MPa.

The last part of this thesis deals with reactive blending of starch and biodegradable polymers using reactive interfacial agents. In Chapter 6, the synthesis of two polycaprolactone (PCL)-based reactive interfacial agents, PCL-g-
glycidyl methacrylate (PCL-GMA) and PCL-g-diethyl maleate (PCL-g-DEM), and their use in compatibilising starch-PCL blends is described. The PCL-based compatibilisers were prepared by reacting a low molecular weight PCL (M_w 3000) with glycidyl methacrylate or diethyl maleate in the presence of benzoylperoxide initiator at 130°C. A statistically adequate model (R^2=0.957, P-value ≤10^{-9}) has been developed to quantify the effects of process variables (monomer and initiator intake, mutual solubility of the monomer into the molten polymer) on the functionalisation degree (FD) of the GMA and DEM units to the PCL backbone. Highest values of the FD (up to 45 %) were observed for PCL-g-GMA, at relatively high GMA and BPO intakes. The FD values for PCL-g-DEM were considerably lower (up to 7 %). Both of the PCL-based compatibilisers improve the interfacial adhesion between the starch particles and the PCL matrix in starch/ PCL blends. As the result, the mechanical behavior of the compatibilised blends is in general different from that of pure PCL and of the corresponding uncompatibilised blends. In particular the elastic modulus for the compatibilised blends is significantly higher (reaching up to 430 MPa) than that of uncompatibilised ones (320-340 MPa). At a fixed starch content (20 %-wt), PCL-g-DEM seems to have slightly more efficient compatibilising effect than PCL-g-GMA as shown by blends morphology and elastic modulus values. This is in contrast with chemical reactivity and amount of chemical groups along the PCL backbone (both factors favorable to GMA as compared to DEM) but it is explainable on the basis of the group distribution along the PCL backbone. The latter hypothesis is indirectly confirmed by the observation that PCL-g-GMA becomes more efficient at relatively higher starch contents in the blends.