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Synthesis and application of hydrophobized waxy potato starch

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Synthesis and application of hydrophobized waxy potato starch

Jan Willem Johannes Miel

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To:

my parents and sister

List of contents

Chapter 1	Introduction	9
Chapter 2	Properties of benzylated native and oxidized waxy potato starch	31
Chapter 3	Replacement of SBR latex by hydrophobic starch in paper coatings	53
Chapter 4	The effect of oxidation and 1-butoxy-2-hydroxypropylation on the properties of waxy potato starch	75
Chapter 5	The use of oxidized and 1-butoxy-2-hydroxypropylated waxy potato starch in paper coatings	95
Chapter 6	Overview, evaluation, reflection and outlook	113
	Appendix A: The DIXON lab-coating machine	133
	Summary	135
	Acknowledgemets	143

Chapter 1

Introduction

Increasing resource prices, environmental awareness and economic opportunities are driving forces to develop renewable, often bio-based, materials [1]. The development of products like packaging materials, coatings, construction materials, etc., based on renewable resources receives much attention. As such, carbohydrates constitute an interesting class of bio-molecules because of their abundance in nature and their diverse chemical and physical properties.

This thesis describes the research aimed at the introduction of waxy potato starch derivatives as replacement for styrene butadiene rubber (SBR) latex as the binding ingredient in paper coatings. The central hypothesis is that hydrophobic groups on the starch backbone are required to achieve coating properties similar to latex-based coatings. This includes performance during the application process as well as the printing process. Chemical product engineering distinguishes between base-material properties, intrinsic properties of reaction products, formulation properties, application behavior and end-use properties. All these stages are inter connected; changes in the reaction conditions of the base-materials can lead to different properties, which will affect the formulation- and applications behavior and, ultimately, the end-product. On the other hand, if a change of end-use property is required; this could be achieved by changes in the application-process, the formulation and the reaction conditions or in the base materials. This interconnectivity makes chemical product engineering both complex and challenging.

Starch

After cellulose, starch is the most abundant carbohydrate in nature. It is formed in seeds, roots or tubers of higher plants for energy storage [2]. For many years, starch has been utilized in a large variety of applications. Already in 800 BC [3], starch was applied in cosmetics. Current uses range from nutritional to industrial applications like soups, sauces, concrete, drilling fluids, adhesives, textile, paper making and many more [4,5]. For many of these applications, some kind of (chemical) modification of native starch is required in order to perform as required. The functionality of starch

may vary from adhesion, rheology, film forming, water binding capacity, flocculation or a combination of these properties [5]. The total starch production in the EU in 2012 amounted 10 million tons vs. 75 million tons worldwide [6], see Figure 1. The total annual turnover for starch companies in the EU was € 7.7 billion in 2010 [7].

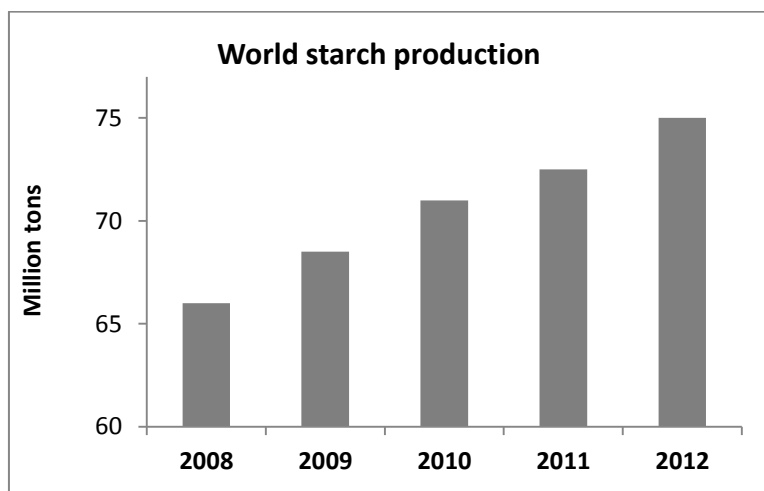


Figure 1: total world production of starch in million tons [6].

Form and structure of starch

Starch is a poly-saccharide composed of α -D glucose monomers, see Figure 2. After polymerization, in which water is eliminated, the repeating units are often referred to as anhydroglucose-units (AGU). Two major forms of starch are formed; the first is amylose, a mainly linear chain of α (1-4) linked AGU, with a degree of polymerization (DP) up to 3000. The second is amylopectine, which is a branched molecule. The branching points are α (1-6) links. The total DP of amylopectine is estimated to exceed 10^6 . Amylose contains approximately 0.5% α (1-6) linkages and amylopectine around 5% which makes it a highly branched polymer [8].

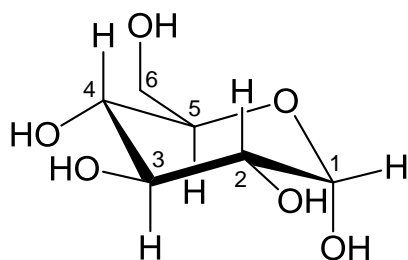


Figure 2: α -D Glucose molecule.

The structure of amylose and amylopectine is extensively described in the literature [2,5]. Perez and Bertoft [9] published a review about the starch granule architecture, from the AGU monomers all the way up to the granule macro structure. The branching points and linear sections of amylopectine form alternating amorphous and crystalline lamellae within the starch granule. The model of the amylopectin molecule took many years to develop and is still subject of debate [10]. The cluster-model, shown in Figure 3, divides the amylopectine molecule into clusters. Each cluster contains so-called A- and B chains. A-chains are located in only one cluster and do not have side-chains. B-chains do contain side chains, but can be located in 1 cluster (B1-chain), 2 clusters (B2 chain) or more (\geq B3-chain). The C-chain is the chain that contains the reducing end.

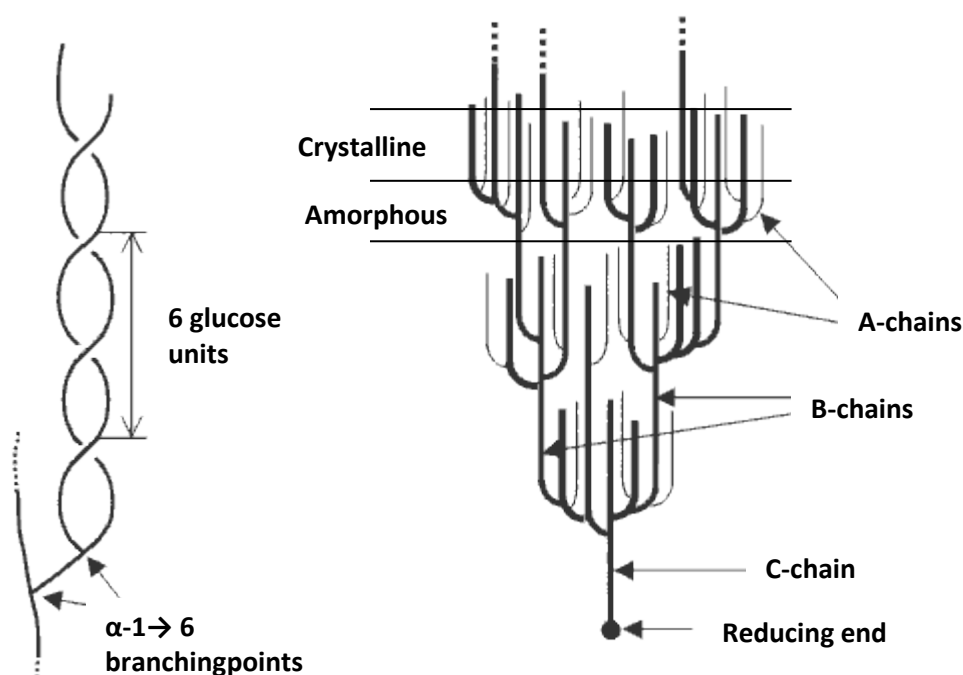


Figure 3: amylopectin skeleton structure, schematic (adapted from [11], with permission).

Botanic origin and growing conditions highly influence the characteristics of different types of starch. They determine the shape and size distribution of the granules [12] and thereby the powder-handling properties. Typical variations in the molecular composition are the ratio of amylose and amylopectine as well as the fine- structure of the amylopectine skeleton and side-chain length [13]. The fine- structure of amylopectine is linked to the gelatinization behavior of starch granules [14]. Some characteristics of different starch types are summarized in Table 1.

Granule property	Potato	Maize	Wheat	Tapioca
Diameter				
Range (μm)	5-100	3-26	1-40	4-35
Mean	30	15	10	20
Amylopectin (%W)	21	28	28	17
DP				
Amylose	3000	800	800	3000
Amylopectin ($\times 10^6$)	2	2	2	2
A-chain	16 ^a	13 ^b	12 ^b	12 ^a
B1-Chain	24 ^a	25 ^b	25 ^b	21 ^a
Pasting temp ($^{\circ}\text{C}$)	60-65	75-80	80-85	65-70

Table 1: some characteristics of starch from different sources [12].

^a) From Hizukuri et al. [15].

^b) From Hanashiro et al. [13].

Gelatinization and retrogradation of starch

For most applications, the starch granular structure is disrupted in a process called gelatinization. Gelatinization in water involves a series of subsequent steps. In Figure 4, the gelatinization process described above is displayed in a viscogram.

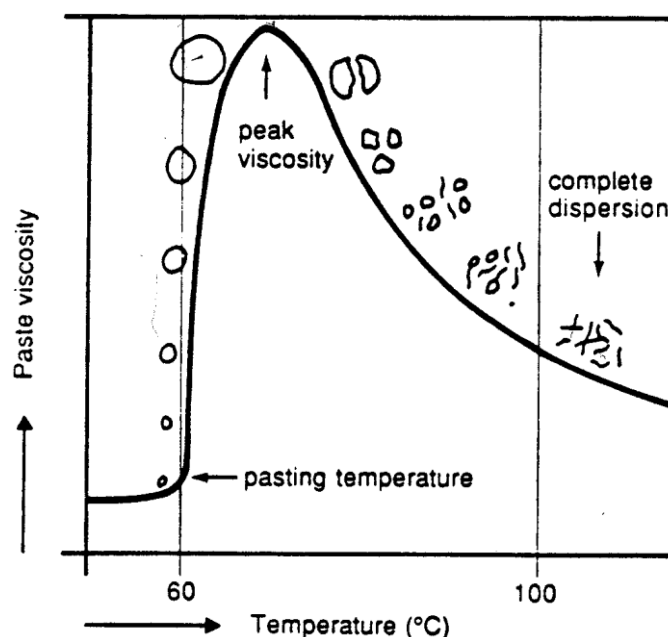


Figure 4: illustration of the gelatinization process by a rapid visco analysis diagram.

Gelatinization is described by Gudmundsson [16] as 'a term used for the changes that occur in gelatinized starch from an initially amorphous state to a more ordered or crystalline state'. At the pasting temperature, or on-set temperature, starch granules start to swell, thereby taking up water.

Due to granular swelling, the viscosity of a granular suspension starts to increase. If amylose is present in the starch granules, it leaches out of the granules into solution. At the so called 'peak temperature', the viscosity is at its maximum and granular disruption occurs. The double helical structure of the amylopectine dissociates [17] and the crystalline structure is lost. The process of gelatinization is irreversible. The characteristic features of the gelatinization process are related to granular size and structure, amylose-amylopectine ratio, presence of lipids, proteins or phosphate groups, the amylopectine fine-structure, crystalline organization of amylopectine (A-, B- or C type) and chemical modification [5]. The subsequent steps of gelatinization can be visualized by means of rapid visco analysis (RVA) in which a starch suspension is heated while the viscosity is recorded.

In general, amylose retrogradates more easily than amylopectine and in addition, amylose may co-crystallize with amylopectine. A high amylopectine content is favorable in applications that require for example a stable viscosity. The rate of retrogradation depends on the amount of amylose present, temperature, moisture content (in case of solid), concentration (in case of solution) and the type and level of modification [5,17]. Retrogradation can be detected by measuring the starch viscosity, Differential Scanning Calorimetry (DSC), X-ray diffraction (XRD) and other methods [5]. Figure 5 displays a schematic representation of the retrogradation of amylose.

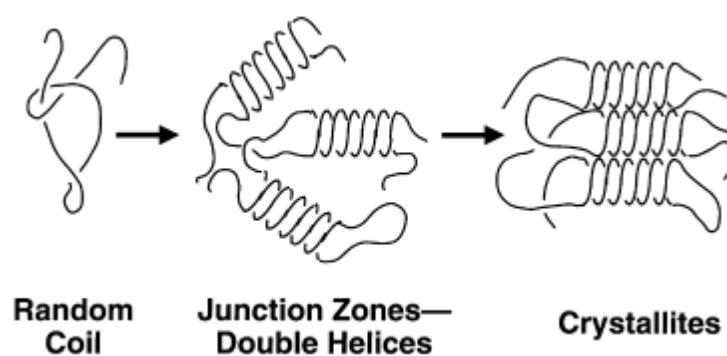


Figure 5: schematic representation of amylose retrogradation, adapted from [18], with permission.

Chemical modification of starch

Native starch is modified either chemically, physically or enzymatically for almost all applications. By modification, the properties of starch are tailored to the demands of a specific application. Chemically, starch is a poly-alcohol. The OH at C-6 is a primary alcohol and the OH at C2 and C3 are secondary alcohols. In general, primary alcohols are most reactive. However, due to the anomeric

centre at C1, the reactivity of the starch OH-groups becomes, in decreasing order: C2 > C6 > C3 [19]. Tomasik [20] extensively reviewed chemical modification of starch, which can be divided into different categories, schematically summarized in Table 2.

<i>Modification</i>	
Degradation	Mw ↓
Oxidation	St → St=O, St-COOH
Crosslinking	St – O – X – O – St
Esterification	St – O – CO – R
Etherification	St – O – R
Grafting	St – g – R

Table 2: categories of chemical modifications of starch.

Degradation of starch is generally performed by acids or enzymes. The starch molecules are hydrolyzed, thereby leading to a lowering of the molecular weight. Generally, this method is used to produce dextrans or glucose syrups. Oxidation is usually performed by the reaction of starch with sodium hypochlorite [21] under basic conditions. Sodium periodate or hydrogen peroxide may also be used [5]. During the hypochlorite oxidation the starch is degraded to some extent, causing decreased solution viscosity at increasing level of oxidation. An important difference with acid degradation is the introduction of negatively charged carbonyl- and carboxyl groups in case of oxidation. These groups enhance the solubility of the starch and decrease retrogradation of the starch solution due to repulsion of the negative charges.

A cross-linking reaction connects the hydroxyl groups of two starch molecules and thus increases the average molecular weight. A typical example is cross-linking by epichlorohydrin [20]. Esterification and etherification are substitution reactions in which a molecule is substituted on one of the hydroxyl groups on the anhydroglucose monomer, thereby forming an ether or an ester. Grafting is usually referred to as the polymerization of a substance on the starch backbone. Polymerization can be initiated on a hydroxyl group or by radical polymerization in which a radical is first formed on the starch backbone from which polymerization is initiated. Examples are the polymerization of styrene or acrylic acid on starch [20].

Modification techniques

Modification of starch can be performed by several techniques. In general, reactions can be performed in (aqueous) suspension, solution or under (semi) dry conditions [5,20]. The advantage of reactions in aqueous suspension is the potentially high starch concentration in water during the

reaction. Industrial starch chemistry is preferably performed in aqueous suspension [19]. After the reaction, the starch granules can easily be washed and dried. Solution-reactions can be performed when starch is solubilized in water, DMSO, pyridine or another solvent. For other than academic research, mostly water is used as a solubilizing agent. Primarily, reactions which require a high temperature are performed in this way or if a cold-water soluble product is desired. The disadvantage of this method is the large amount of water that needs to be evaporated (Starch suspensions have a maximum concentration of about 40 %W of dry solids and thus 60 %W of the total mixture will be water). Reactive extrusion is a process where starch is plasticized at 25 – 30 %W moisture content yielding cold water soluble products [22]. Semi-dry reactions take place in the starch granule at 20 – 25 %W moisture content and yield a product that still needs to be cooked [5]. The general advantage of semi-dry methods is the absence of a drying step. Both solution- and extrusion reactions are typically performed if very high conversions can be obtained so less residuals remain in the product or when the by products are allowed in the final product [19]. The absence of a purification step means that these types of reactions cannot be used if the by-products are not allowed in the end-product.

Paper and paper coatings

The global paper and paper board production in 2011 was 407 million tons of which 35% was for printing and writing [23]. To improve the printing quality of paper, a coating can be applied which results in decreased surface roughness, better ink holdout and increased image sharpness [24,25]. The coated paper may be used for glossy magazines, posters, catalogues, etc. The reduction of surface roughness reduces light scattering, which results in sharper print images as can be seen in Figure 6. Paper coating is primarily applied to increase the aesthetic value of paper [26].

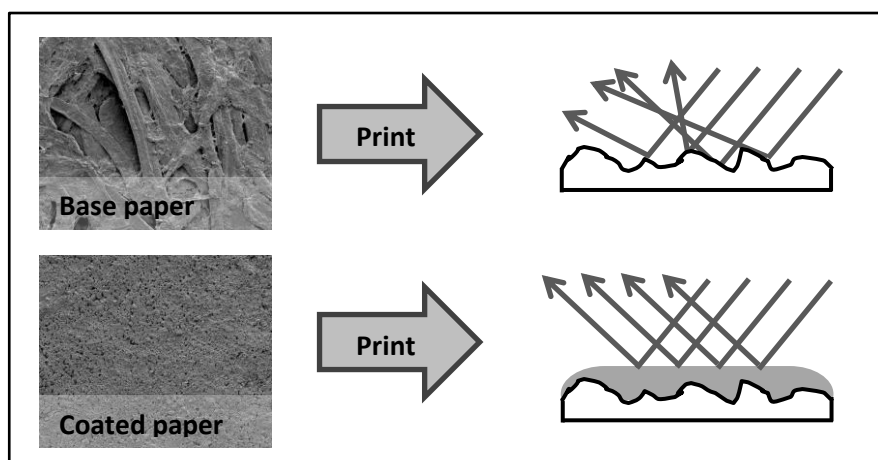


Figure 6: reduced surface roughness reduces light scattering, redrawn from [27].

For high-quality paper products, three layers of coating are usually applied. The first two layers serve to level the paper surface, while the third layer, the so-called “top-coat”, gives the paper its desired functionality and appearance [26].

Application analysis

The next section is dedicated to analyzing and understanding the paper coating- and printing process in order to understand the challenge of replacing SBR latex by starch. Requirements regarding e.g. rheological behavior and surface energy in relation to the application process of the coating will be used to formulate the research hypothesis.

General requirements

During the printing process, the ink must be allowed to form a uniform layer without deficiencies. The printing quality is influenced by the printing process as well as the coating properties. The top-coat should be a uniform, porous, layer that adheres well to its substrate and is able to resist the forces during processing and use. During the coating process itself, the rheological behavior of the formulation is very critical [25,26]. These requirements will be further described and clarified below.

Coating composition

A typical top-coating composition is displayed in Table 3. The main ingredient of the coating formulation, and largely responsible for its appearance is the pigment; clay (Kaolin), Calcium carbonate (ground or precipitated), talc or titanium dioxide. A binding agent is added to the pigment suspension to adhere pigment particles to each other and to the substrate. Many different binders are available; synthetic binders like SBR- or poly-(vinyl-acetate) latexes, and natural binders such as (modified) starch, carboxymethyl-cellulose, casein or other proteins. The formulation is adjusted to pH 8,5 – 9 with NaOH to minimize formulation viscosity [26]. Other additives, like optical whiteners, de-foaming agents, biocides, etc., can be added to optimize processing- and end-use properties [26]. The total solids content is predominantly determined by the solids content of the pigment (75-78 %W) and the binder (starch \leq 35 %W, latex \sim 50 %W). Latex-based coatings generally have a higher solids content. Preferably, the total solids content is >65 %W to minimize drying costs. Therefore, the solids content of the binder (starch) should not be much lower than 35 %W. A latex-based coating,

prepared according to Table 3 has a solids content of around 71 %W while a starch-based coating would be 67 %W solids at maximum due to the lower solids content of the starch solution compared to the latex. When starch is used, sometimes the formulation has to be diluted somewhat to achieve target viscosity. If other additives are also taken into account, the solids content of a top-coat formulation has a typical solids content between 62 and 67 %W [28].

<i>Component</i>	<i>Parts (Dry Solids)</i>	<i>Compound solids content (%W)</i>
Pigment	100	75 – 78
Binder	<i>Latex</i> 5 – 15 (12) ^a	50
	<i>Starch</i> 5 – 15 (12) ^a	≤ 40
NaOH	< 0.1	5 – 10
Optical whitener	0.5 – 0.8	-
Other additives	0.5	-
Defoaming agents	< 0.1	-
Biocides	< 0.1	-

Table 3: simplified recipe of a top-coating formulation [26].

^{a)} 12 parts of binder is commonly used

SBR latex coating binder

The final coating properties are strongly influenced by the binder, since it is the second major component and surrounds the pigment particles. The presence of a binder prevents detachment of the pigment particles when stress is applied, for example during printing. Currently, latex binders outperform starch in top-coatings both during application and the printing process. SBR latex is composed of styrene and butadiene monomers which are polymerized in emulsion. Acrylate groups may be co-polymerized for stabilization or tuning the hydrophobicity. Typically, a latex formulation has a solids content of 50 %W, a viscosity of around 400 mPa.s and an average particle size of around 140 nm. During coating deposition, the viscosity is very low and, because of its high solids content, the total amount of water of the coating formulation is low which reduces drying costs. After drying, the coating forms a uniform porous layer, which is beneficial for the printing process [26,29,30]. In addition, SBR is hydrophobic which enhances the ink receptivity of the coated paper. A disadvantage of latex is its low water binding capacity. During application, the formulation undergoes a pressure peak upon passing the blade, driving water into the base-layer; see Figure 7. Moreover, the viscosity of a latex-based coating is generally too low; < 900 mPa.s while around 1200 mPa.s is required for good machine runability. Both issues can be solved by adding a hygroscopic rheology modifier, for example Carboxy Methyl Cellulose (CMC).

Coating application process

The application technique for the coating layer, focused on in this thesis, is blade-coating; a common technique for the deposition of top-coatings [25,31]. After the coating formulation has been applied on the paper, it is adjusted to the desired thickness by means of a blade [24] as schematically shown in Figure 7. Typically, the layer thickness ranges from 10 – 20 μm at a speed of 1500 - 2000 m/min [24]. These conditions result in a shear rate in the order of magnitude of 10^7 s^{-1} [28] for a period of roughly 30-40 μs . The coating temperature during application is commonly around 30°C. Latex based coatings typically have a viscosity around 50 mPa.s under these conditions. After application, the paper web proceeds into a drying section. Here, the coating will develop its final properties. The whole process takes 5 – 10 seconds to complete. In this time, all properties should develop as desired.

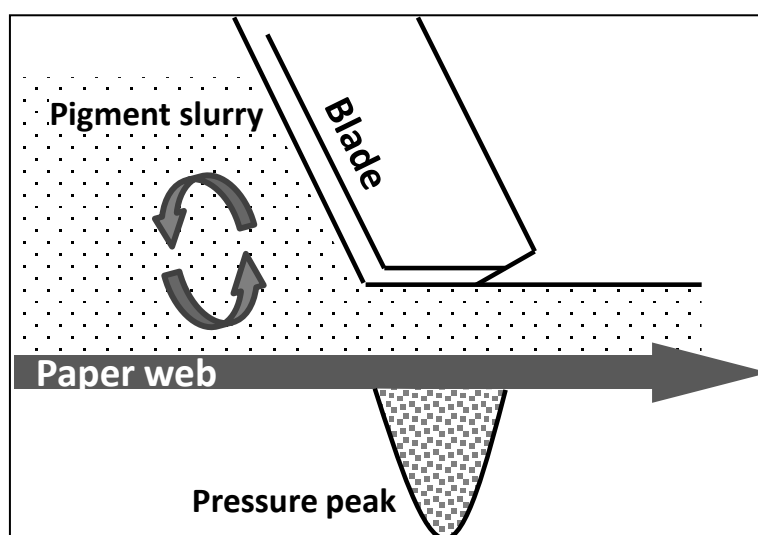


Figure 7: schematic, simplified representation of the blade-coating process, redrawn from [32].

Dewatering behavior

During the coating process some water is driven out of the formulation into the substrate (paper, pre- or mid coat) due to the pressure peak under the blade [26]. In addition, water can migrate to the substrate by capillary transport prior to drying. The process of water moving from the formulation into the substrate is referred to as ‘water retention’ or ‘dewatering behavior’ [26], the latter being used in this thesis. Dewatering of latex-based coatings is relatively high since polymer spheres do not bind the water. Accordingly, dissolved polymers like starch or CMC display little dewatering [33].

Consolidation process

The coating consolidation process of latex-based coatings is characterized by a sequence of events, described by Watanabe and Lepoutre [29,34]. Zang et al [35] proposed an extension to the model of the latter. Four stages in coating consolidation are identified: the “liquid stage”, “liquid-gel transition stage”, “gel-drying stage” and finally the “solid stage”. These stages are distinguished by changes in gloss and reflectance, which is illustrated in Figure 8. In the liquid stage, <50V% solids [34], water can move freely to the coating surface to evaporate. Shrinkage due to water loss is completely equal to the volume of evaporated water. The distance between particles decreases, but they are not deformed. At still increasing solids content, the first critical concentration (FCC) is reached, which is marked by a sudden drop in coating gloss [34]. At this solids content, a gel-like filter cake starts to form at the coating-air interface while the bulk of the coating remains in the liquid stage. Water moves from the bulk through the filter cake to the coating surface by capillary transport. This stage is also referred to as the liquid-gel transition phase [35]. As drying continues, the liquid-phase layer becomes thinner as more water evaporates until the whole coating layer is a homogeneous gel. This solids content is defined as the latex coalescence concentration (LCC) [35]. The remaining water is held within the coating capillaries. Since the pigment particles are rigid, shrinkage at increasing solids content in this stage is due to latex particle deformation. Maximum latex particle deformation is reached at the second critical concentration (SCC).

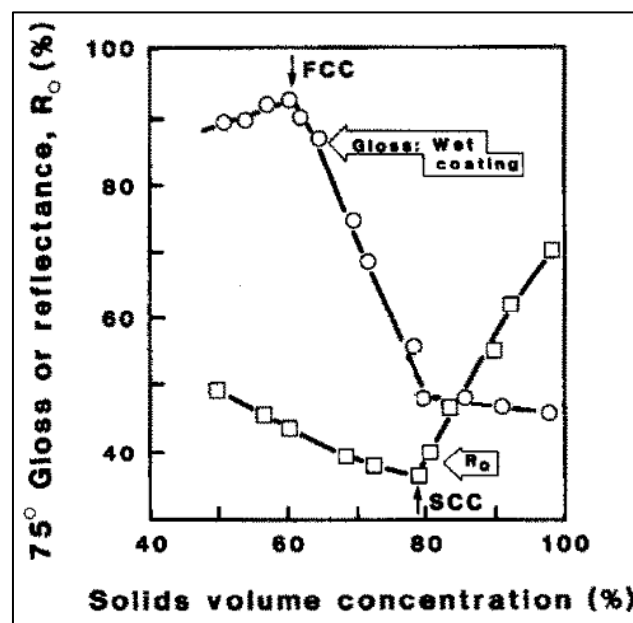


Figure 8: FCC and SCC as described by Watanabe and Lepoutre [29,34].

The SCC is marked by a sudden increase in reflectance. Up to the SCC, the water-air interface has remained at the coating-air interface but now starts to move into the coating layer [29,34,35]. The

solid-stage is the final drying stage. Shrinkage in this stage is practically zero and is independent of the water content of the coating. At the solid stage, all coating components are fixed and can/will not deform or displace anymore. The process is schematically represented in Figure 9.

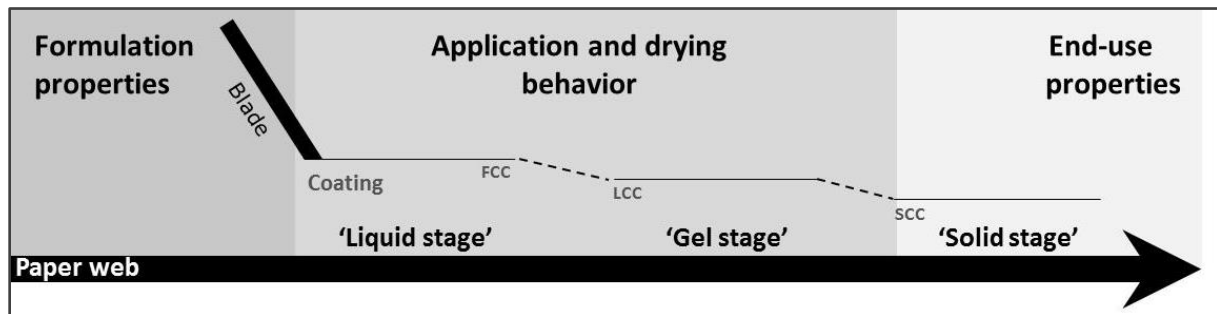


Figure 9: schematic representation of the coating and drying process.

Much work has been performed to predict the drying behavior of paper coatings [36-39]. Extensive modeling and experiments have indicated that many parameters influence the coating consolidation process: rheological behavior of the coating [40], surface tension of the liquid phase, drying speed and temperature, Brownian motion, coating layer thickness, particle size distributions of pigment and binder [41], electrostatic and van de Waals interactions [36], liquid density, capillary size, salinity, presence of dissolved polymers [33] and many other factors. Most research is focused on latex-based coatings. Figure 10 displays a SEM image of a latex-based paper coating from a typical pilot coater experiment. The coating recipe was according to Table 3, with 12 parts of latex. Note the porous structure and arrangement of fine- and course particles.

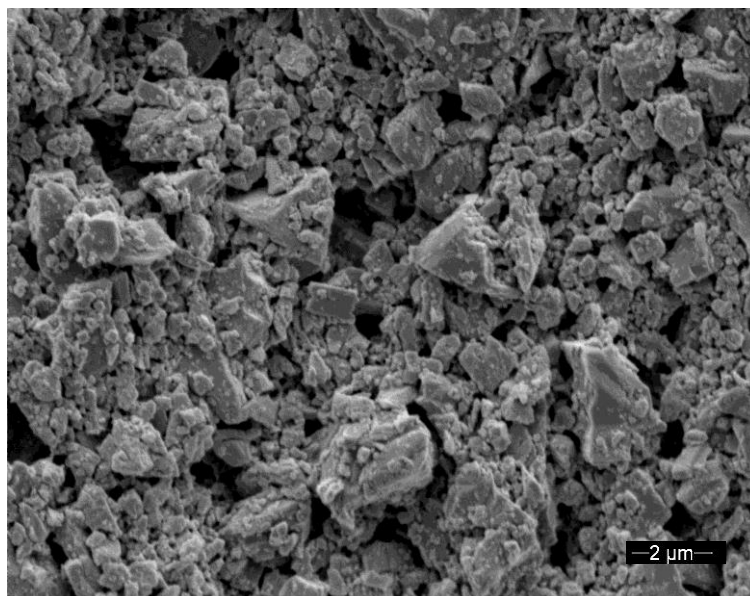


Figure 10: SEM image of all-latex coating from pilot coater trial, further discussion in chapters 3 and 5.

Printing process

Offset printing techniques cover 60 % of the market [26] and are therefore assumed to be the standard in this thesis. The ink is transferred over a system of rolls onto the substrate, as illustrated in Figure 11.

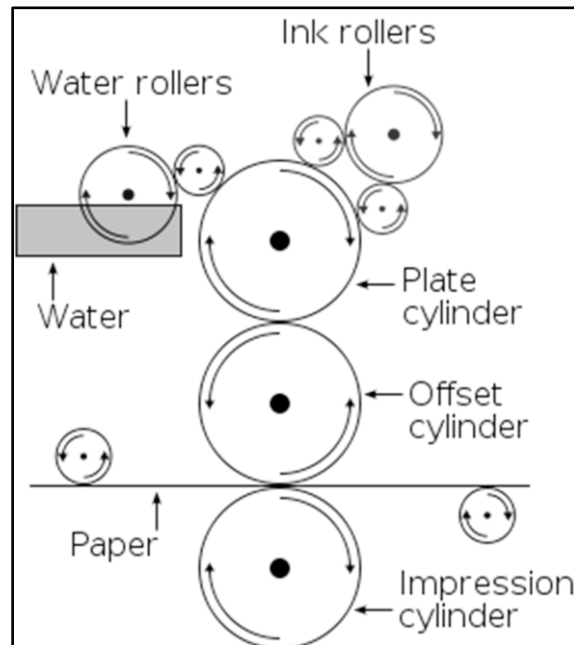


Figure 11: schematic overview of off-set printing process reprinted from [42], with permission.

The carrier liquid of the ink contains C12-C20 alkanes [43] which have a surface tension of around 20 mN/m. Water, also referred to as 'fountain solution', is used to cover the area of the rolls where no ink should be, to obtain the desired images. Usually, four colors are applied; black, blue, yellow and magenta. Some water is transferred to the substrate at application of each color, also in places where the next color will be deposited; in some cases up to four times. Oil and water both need to be absorbed by the coating layer. Optimal printing conditions are a complex compromise of many different properties, however, from the above it is clear that pore structure and surface tension of the coating surface should be sufficient and uniform [26]. An exact number for pore size distribution is hard to define since it is case-sensitive; too small pores cause slow oil transport and too large pores result in uneven ink distribution [26]. The same applies for surface tension since both oil- and water wettability should be sufficient. If the applied latex is too hydrophilic, however, printability decreases [26]. The ink setting mechanism can be regarded as a filtration process, similar to the coating process [44].

Replacing SBR by starch

Up to this point, the coating process has been discussed for latex-based formulations. If latex is replaced by starch, many changes are introduced into a complex system in which many properties are connected. If starch is used, the ratio between the dispersed- and continuous phase in the formulation changes, as well as the composition and nature of the continuous phase. The presence of starch causes changes in the consolidation mechanism. It is well-accepted that starch migrates to the coating interfaces during drying and may cause irregularities in the ink-coverage, also known as mottling.

A standard coating formulation, based on SBR latex, has a solids content of around 73 %W whereas if the total mass of latex is replaced by starch, the maximum solids content is a little less than 69 %W. Since latex is dispersed and starch is dissolved and therefore has become part of the continuous (aqueous) phase, the free space between the pigment particles increases. This is illustrated in Figure 12, where three cases are considered, based on the recipe from Table 3: 1) all latex with 50 %W solids, 2) all starch at 35 %W solids and 3) all starch based on 73 %W solids content. It is assumed that the density of the pigment particles is 2700 kg/m^3 , latex particles 1000 kg/m^3 and starch 1600 kg/m^3 (calculated from [45]).

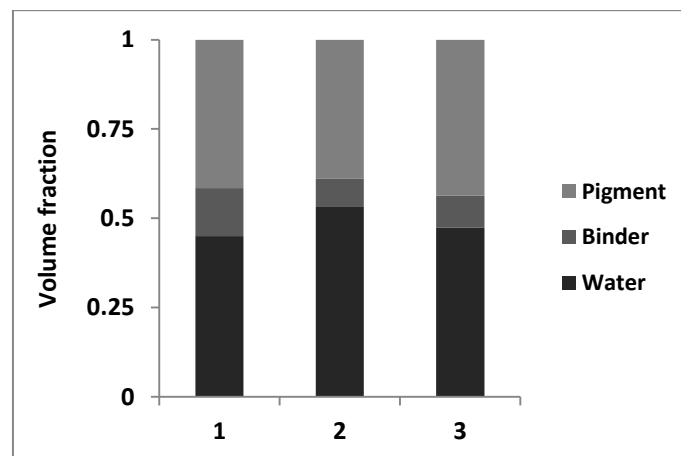


Figure 12: relative fraction of coating compounds for 1: latex (50 %W), 2: starch (35 %W), 3: starch (73 %W).

Figure 12 shows that even if the total water content of the formulation is the same for latex and starch, the total volume of the continuous phase is still larger in the case of starch. This means that the immobilization at the LCC is postponed and that the pigment particles have a higher mobility.

The replacement of latex by starch also changes the behavior of the continuous water phase. Starch is dissolved whereas latex is dispersed. This implies a viscosity increase of the water phase. In general, the viscosity of dispersions can be described by the Einstein equation [46]:

$$\mu_f = \mu_0(1 + [\mu]\Phi) \quad (\text{Equation 1})$$

Here, μ_f is the measured viscosity of the formulation, μ_0 is the viscosity of the continuous phase, $[\mu]$ is the intrinsic viscosity of the dispersed particles (2.5 for spherical particles) and Φ is the volume fraction of spheres in the continuous phase. For calcium carbonate, intrinsic viscosities of 2.8 and 4.6 mPa.s were reported [47,48]. This equation only applies for low volume fractions of solids ($\phi < 0.2$), but illustrates the effect of the viscosity of the continuous phase on the total formulation viscosity. In addition, increasing the molecular weight of latexes does not affect the rheological behavior at similar particle size and volume fraction. If the molecules are dissolved, however, there is a strong relation between viscosity and molecular weight [46]:

$$\mu \approx K * M_w^{3.4} \quad (\text{Equation 2})$$

μ resembles the solution viscosity, M_w is the average molecular weight of the dissolved component. K is a correction factor. Decreasing the molecular weight by 1 order of magnitude decreases the viscosity by >3 orders of magnitude. To decrease the coating viscosity, degraded (oxidized) starches are applied today [5,21]. By oxidation, the viscosity of starch can be tailored to the required value. If the starch viscosity becomes too low, however, binder migration is more likely to occur. In addition, due to the decreased molecular weight, the binding strength will decrease. It is the combination of decreasing the molecular weight and the introduction of carbonyl- and carboxyl groups that makes oxidized starch suitable for paper coatings. The introduction of these groups results in a stable starch solution. If, for example, the viscosity of the starch solution would be reduced by acid degradation, the starch solution would retrograde more quickly due to the absence of the negatively charged (repelling) groups which would result in increased coating formulation viscosity [49].

Binder migration

Binder components in the coating formulation can migrate with the aqueous phase, which is absorbed by the substrate and evaporated at the coating-air interface during the coating process [33,50,51]. Binder migration is not per se undesired [33]. Excessive migration to the substrate may

cause decreased adhesion strength, due to decreased binder content in the coating [33]. Printing problems occur if the binder distribution at the coating surface is non-uniform [26,52].

Both dissolved and dispersed binders show migration [53]. It was established that latex migrates before the FCC is reached [34]. Latex particles move by Brownian motion and get trapped at the surface where they accumulate. Latex migration is influenced by coating viscosity [54], presence of soluble polymers, [33], latex-pigment particle size ratio [41], substrate absorbency, application process, coating weight, drying conditions and more [50]. Above FCC, the capillary structure prevents latex particles from migration. Capillary pressure now is the driving force for water transport to the surface. Dissolved binders, i.e. starch or CMC, are transported with the aqueous phase [51]. Below FCC, starch levels remain relatively uniform due to diffusion [38]. Migration of dissolved compounds is a function of the viscosity and the surface tension of the aqueous phase, diffusivity of the dissolved compound. Above SCC, no migration occurs anymore [29,34]. Pan et. al. [38] described binder migration as a function of a capillary number, and a Peclet number. The capillary number balances capillary- and viscous forces.

$$Ca = \frac{\mu WL}{\gamma \rho r_p} \quad (\text{Equation 3})$$

Where μ is the liquid viscosity, W is the initial drying rate at the coating surface, L is the layer thickness, γ is the liquid surface tension, ρ is the liquid density, r_p is the pore-size radius. At $Ca > 1$ viscous flow dominates and at $Ca < 1$ the capillary forces. The Peclet number (Pe) balances convection and diffusion of dissolved compounds; D is the diffusivity of starch, the subscript 'b' and 'l' represent 'binder' and 'liquid'.

$$Pe = \frac{WL}{\rho_l D_b} \quad (\text{Equation 4})$$

These equations exemplify that concentration and molar weight as well as the surface tension of the dissolved component affects migration behavior. To prevent migration of starch, the capillary pressure, and as a consequence the liquid surface tension, should be low. The viscosity should be relatively high. Layer thickness, liquid density, initial drying rate and pore size are system-specific, but high drying rates and thicker layers promote migration. High viscosity suppresses migration, but as mentioned earlier, the viscosity of the coating formulation during the coating process at a shear rate of 10^6 s^{-1} should be $\leq 50 \text{ mPa.s}$. This makes the rheological behavior of the coating formulation a critical parameter.

Migration of starch may also occur upon re-wetting and subsequent drying of the coating layers. This may occur either during the application of subsequent coating layers or during the printing

process when water (fountain solution) is transferred to the coating layer, as described above. It was shown by Dobler et al. [55] that starch migrates from the pre- and mid coating layer to the top-coat upon application, thereby causing a printing defect called 'mottling'.

Mottling

Mottling is a common printing deficiency. It is the result of an uneven ink density distribution, visible as darker and lighter spots. The causes and mechanisms of mottling of starch containing coatings were extensively reviewed by Ragnarsson in his PhD-thesis [56]. Mottling is either caused by bad printer configuration or by the substrate quality. In this case, only the latter will be discussed. Two types of mottling result from substrate quality. The first is uneven drying/absorption pattern of the ink, called back-trap mottle. The second is water-interference mottle: uneven absorption of fountain-solution by which the ink is repelled, resulting in uneven ink distribution at the coating surface. Substrate quality in this case includes local variations in porosity and oil wettability due to uneven binder migration. Causes of uneven binder migration are variations in coating weight, drying speed, coating shrinkage and reduced coating porosity by calendering. Calendering results in a higher gloss but at the cost of decreased porosity and thus the chance of mottling. Blade coating itself results in uneven coat-weight distribution, because all the voids in the base-paper will be filled with coating formulation. Drying speed is translated to the transport of the continuous phase to the coating surface to evaporate. Increased drying speed means increased transport. In addition, during drying there is some starch diffusion from the surface to the bulk, which is less significant at high drying speed. Shrinkage occurs due to capillary forces. Latex particles are deformed by these, but they are immobilized above LCC. Starch, however is mobile until SCC. The capillary forces promote migration and drive the pigment particles closer together. Calendering increases gloss by smoothening the coating surface, affecting the porosity at the coating-air interface.

Research hypothesis

The above suggests that the performance of starch containing coatings could improve if the starch molecule would have increased hydrophobicity. The capillary forces in the coating formulation during the drying process would be decreased which should result in a decrease of starch migration and thus a lower surface starch content. On the other hand, increased starch dry film hydrophobicity should improve the interaction with ink and hence the printing behavior.

Research strategy

The supposed advantages of increased hydrophobicity of the starch molecule by a chemical reaction are related to application- and end use properties. In between are the intrinsic starch properties and the coating formulation properties. Therefore, first starches with hydrophobic substituents were produced and characterized. Subsequently, the formulation-, application- and end-use properties were evaluated to obtain an overview of the consequences of the increased hydrophobicity. In addition, for this research waxy potato starch (>99 % amylopectine) was used as well as some oxidized derivatives of waxy potato starch, to control starch solution viscosity. The advantages of waxy potato starch are: 1) increased solution stability due to the absence of amylose, 2) the presence of only one type of molecule (amylopectine) instead of two and 3) potato starch contains only minor amounts of protein and fat. For the production and characterization of the hydrophobized starches, standard laboratory techniques were applied including NMR, FTIR, GC, UV-vis, rheometer, Rapid Visco Analysis (RVA) and contact angle measurement. Coatings were tested on dewatering and rheological behavior with various techniques and subsequently applied to the paper by a laboratory blade-coating device, called a DIXON coater, of which a detailed description is added in Appendix A. Coating surface properties were determined by specific equipment for mottling, bonding (or pick) strength and porosity. The surface starch content was determined by means of FTIR. SEM imaging was used to study the coating surface morphology in more detail.

Thesis outline

Chapter 1, the introduction, aims to introduce the reader to starch and paper coating in general, the specific challenges arising from replacing SBR by starch and the research strategy. These aspects provide a background and justification with respect to the performed experiments in the following chapters. **Chapter 2** describes the production and characterization of benzylated derivatives of (oxidized) waxy potato starch. Reactions were performed according to known literature. The effect of the degree of substitution (DS) of benzyl groups in combination with the level of oxidation on the pasting behavior, solution viscosity and surface tension are studied. **Chapter 3** describes the formulation- and end-use properties of the benzylated starches, prepared and characterized in Chapter 2. The dewatering behavior as well as the viscosity of coating formulations was studied. In addition, important end-use properties of coated paper samples were evaluated, such as binding strength and ink mottle. **Chapter 4** describes the hydrophobic modification of (oxidized) waxy potato starch using butyl-glycidyl ether, an epoxide. The reaction was performed similar to the benzylation

reaction, at somewhat milder reaction conditions. The products were characterized in a similar way as in Chapter 2. In **Chapter 5**, the formulation- and end-use properties of the starches, prepared in Chapter 4, are evaluated in a similar way as in chapter 3. Finally, in **Chapter 6**, an overview and analysis of the results from Chapters 2 – 5 is presented. This includes a comparison between the two hydrophobic modifications performed in this thesis, lessons that can be drawn from these results and suggestions for further research activities. This thesis also contains an appendix on the DIXON lab-coating device and a summary.

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Chapter 2

Properties of benzylated native and oxidized waxy potato starch

Abstract

New benzylated products based on waxy potato starch and oxidized waxy potato starch were prepared and characterized. Characterization was performed on properties relevant for the replacement of styrene butadiene rubber (SBR) latex in high quality paper coatings. Waxy potato starch does not contain amylose, which may result in different product behavior than reported for normal potato starch or corn starch. The reaction was pseudo-zero order in benzyl chloride. The reaction efficiency was similar to values reported for normal potato- and corn starch. Both in case of native classic- as well as waxy potato starch, a dispersion was obtained upon cooking their benzylated products. The oxidized derivatives, however, showed a dramatic increase in the viscosity at a degree of substitution (DS) >0.3 . Native waxy potato starch becomes insoluble at a DS of 0.375. The increased viscosity could be tuned by changing the level of oxidation. The pasting-peak of benzylated oxidized starches increased, while the onset temperature decreased. The surface tension of the dry starch films dropped from 57 to 43 mN/m after benzylation. The relative contribution of polar forces to the surface tension decreased. It was calculated that the work of adhesion between all benzylated starch products and cellulose decreases at increasing DS, which may be a drawback. Overall, increased hydrophobicity is assumed to be beneficial for the application in paper coatings.

Key words: *waxy potato starch, hydrophobic modification, benzylation, viscosity, surface tension*

Introduction

Starch from different sources are used as functional ingredients in many applications and provide viscosity, texture, adhesion, appearance, etc., or a combination [1] of these features. For most applications (chemical) modification of the native types is required to some extent [2] to tailor

properties to specific product demands. Added functionality by modification may allow starch to be used as a renewable resource to replace functional, oil based polymers in a cost efficient way. One example is the paper industry, where cationic starch is an important ingredient in wet-end applications and oxidized starches are used in increasing amounts in coatings [3].

High quality paper coatings are applied for improved printing quality. Typically, such a coating is composed of a pigment, a binder and minor amounts of other additives [4]. The binder provides adhesion between the substrate and the coating components. Synthetic binders like (styrene butadiene rubber) SBR latex or natural binders such as starch are applied either solely or in a co-binder system [4].

SBR latex is a stable colloidal dispersion which is mainly composed of two hydrophobic monomers; styrene and butadiene [5]. The viscosity of latex is around 300 mPa.s at 50 %W solids content and displays shear thinning behavior. These are desirable properties for a common coating technique such as blade coating [6], which is operated at a speed of around 2000 m/min with shear rates exceeding 10^7 s^{-1} . For economic reasons, a total formulation solids content of about 70% is required at a viscosity of around 1000 mPa.s for good machine runability. After application, the coating formulation is dried at high temperature, close to the boiling point of water [7]. The whole process typically occurs in less than 5 seconds in which SBR latex is capable of forming a uniform, well adhering, porous surface in the form of a water resistant, flexible film with a low surface energy. This surface provides proper wettability for the oil, present in the ink used for off-set printing [8,9].

Starches on the other hand, are hydrophilic bio-macromolecules forming viscous gels in water after gelatinization and cooking, exceeding 300 mPa.s at a solids content of 5 %W. Starch films are expected to be more rigid, recrystallize over time (retrogradation) and have a higher surface energy than SBR latex due to the abundant presence of hydroxyl groups. Currently, oxidized starches are already applied in base- and mid-coatings. Sufficiently low paste viscosity at concentrations of at least 30 %W is realized by oxidation of classic native potato starch (PS) [10]. Replacement of synthetic binders by starch in paper coating formulations was found to have an effect on the entire downstream processing chain. The drying behavior changes [11] and, more importantly, the presence of starch has been linked to a common printing deficiency called mottling [12,13]. Migration of starch to the coating surface may occur during the drying process or as a result of subsequent wetting and drying either by application of new coating layers or during offset printing. Viscosity, surface tension and drying speed were used to model and describe the migration process [10,14-17].

Besides hypochlorite oxidation, benzylation of corn- and potato starch is reported in the patent literature for the replacement of SBR latex [19]. Benzylated starches yield a stable, latex-like, starch-based dispersion upon cooking with sub-micron particle size and decreased viscosity compared to native starch. Moreover, the formation of a water resistant, well adhering starch film was achieved. These properties were reported to be beneficial for the application of starch in paper coating formulations [18,19]. Many reports on hydrophobic modification of starch in general exist in the literature [20-24], however, none was investigated as thoroughly as benzylation. Gomberg and Buchler [25] first reported on benzylated carbohydrates in 1921 and since then optimization of the production process [19,26-28], kinetics [23,29] and substitution pattern [30] have been investigated. The viscosity of cooked pastes of benzylated starches is still too high for application in paper coatings, which can be concluded from the viscosities reported by Bohrisch et. al [27]. The decreased viscosity of benzylated starches may be the result of the formation of a dispersion. Part of the total starch solids content is held by the dispersed particles leaving less dissolved starch to contribute to the 'dispersion' viscosity. In the literature, however, it is also reported that the introduction of hydrophobic properties on a hydrophilic polymer increases the viscosity and may introduce a lower critical solution temperature (LCST) [31].

Waxy potato starch is a relatively new product [32,33]. Due to the absence of amylose, solutions based on waxy starch have increased stability and may form amorphous dry films. As far as the authors are aware, no reports on benzylation of waxy potato starch, or oxidized potato starches exist in the literature. This article reports on the investigation of the hypothesis that a combination of oxidation and hydrophobic modification by benzylation provides properties which should improve the performance of waxy potato starch in paper coating. This includes a sufficiently low solution viscosity, reduced water sensitivity to limit migration and a decreased film surface energy to improve oil wettability during off-set printing. Waxy potato starch (>99% amylopectine) and three grades of commercially available oxidized grades of waxy potato starch and native potato starch (20% amylose) were used as starting materials.

Experimental

Materials

Native potato starch, native waxy potato starch (>99% amylopectine) and oxidized waxy potato starches (Perfectafilm X115, X85 and X55) were kindly supplied by AVEBE Foxhol, The Netherlands, and were used as received. DMSO chromasolv-plus for HPLC >99.7% (Sigma) with 5 g/l LiBr (Sigma)

was used for GPC measurements to determine the starch molecular weight. Sodium hydroxide (Merck), benzyl chloride (Sigma), sodium sulfate (Sigma) and HCl (Merck) were used as received. For chemical analysis: Methanol (100%, Sigma) and Acetic acid (100%, Merck) were used as received. For contact angle measurement water, formamide (Sigma), diiodomethane (Sigma) and ethylene glycol (0% water, Sigma) were used as received.

Synthesis

The synthesis of benzylated starch was performed according to Berkhout and Guns [19], with modifications. Starch was suspended in water containing 350 g/l of sodium sulfate at 35 °C and fed into a jacketed, stirred glass reactor in a 38 W% suspension, based on dry mass starch in water. 3 Grams of NaOH per mole anhydroglucose (AGU) was added drop wise as a 5 W% in water solution while vigorously stirring. The temperature was raised to 50°C. The required amount of benzyl chloride to obtain the desired (or theoretical maximum) degree of substitution (DS_{th}) was added. DS will be used here to indicate the ratio between the moles benzyl chloride added per mole of AGU. An AGU unit has three hydroxyl groups available for substitution. By definition, the maximum DS is therefore 3. NaOH (5 W%) was added drop wise over 48h to a total of 1.05 mol NaOH per mole benzyl chloride. The reaction was allowed to proceed for a total of 72h after addition of benzyl chloride. Prior to washing, the reactor content was neutralized to pH 5-6 with 6 N HCl. The product was washed three times with demi water and three times with acetone to remove any residuals. Products were dried for at least 48h at 35°C and ground before storing.

Chemical characterization

The DS was determined by UV-absorption according to Marsman et al. [34], with modifications. 5 gram of starch sample was washed with 50 ml methanol for 1 hour, decanted and dried at 105°C. The samples were dissolved in 50 ml of a 50/50- V/V mixture of 100% acetic acid and 0.2 M HCl at 95°C for 15 minutes while stirring. After cooling, the UV absorption was measured on a PE UV/Vis Lambda 12 spectrometer. The spectrometer was calibrated with benzyl-alcohol [35]. The reaction efficiency was calculated from the ratio $DS_{UV} : DS_{th}$.

Gelatinization behavior

Gelatinization behavior of the products was recorded on a Newport Scientific Pty Ltd, Australia RVA-super4 Rapid Visco Analyzer. The samples were prepared at 20 W% dry solids of starch; the

native starch products were prepared at 5 W%. The heating and cooling cycle, also used by others [36], comprised of rapid stirring at 960 rpm for 10 seconds and subsequently 160 rpm for the remaining run time. Before heating, the sample was stirred for 2 minutes at 30°C. Next, the temperature profile was set to increase from 30 to 90 °C at 15°C/min. After a holding time of 4 minutes at 90°C, the sample was cooled back to 30 °C at 15°C/min. The measurement was allowed to proceed for 8 more minutes at 30°C.

Solution preparation

Solutions of starch were prepared by stirring a 15 %W (native) or 35 %W (oxidized) suspension, based on starch dry solids, in a hot-water-bath at 95°C for 30 minutes at 600 rpm with a six-hole lab-stirrer. Dilutions were prepared by adding warm demi water (>50°C). In some cases, the starch solution would foam upon cooking. The stirrer speed was adjusted in these cases.

Solution viscosity: concentration and temperature dependence

The viscosity of starch solutions was determined on a Haacke III rheometer using a cone – plate configuration at 20°C. The gap distance (d) was 0.105 mm, the cone diameter 60 mm and the angle 2°. Two ml of a starch solution was used and measured at 10 s⁻¹ shear rate. The viscosity as a function of temperature was determined between 20 and 70°C at a constant shear rate of 10 s⁻¹. The viscosity was averaged over 5 seconds after 30 seconds of stabilizing.

UV-emission spectroscopy

The UV emission spectrum of pyrene in starch solutions was recorded on Fluorolog3-22 fluorescence spectrometer according to known literature [37]. The excitation wavelength was 334 nm at a slit width of 8 nm and the spectrum was recorded from 350-420 nm at a slit width of 2 nm. The ratio between the emission peak at 373 nm (I₁) and 384 nm (I₃) was calculated. A concentration of 2 µM pyrene was obtained by adding 8*10⁻³ W% pyrene in methanol to the samples.

Molecular weight

The molecular weight was determined on an Agilent Technologies 1260 infinity GPC-SEC system with DMSO containing 5 g/l LiBr to enhance gelatinization, according to Ciric et. al. [38]. The concentration of starch was set to 2 mg/ml. Starch samples were gelatinized in water and freeze-

dried after which the sample was stirred overnight in DMSO at room temperature, heated and stirred at 95°C for 2 hours and filtered over a 0.45 µm filter. The GPC system was equipped with a PFG guard-column and a G1362A 1260 RID Agilent Technologies RI detector. Samples were injected twice (1 µl) at a flowrate of 0.5 ml/min. The system was calibrated with Pullulan 800.

Contact angle measurement

Starch films for contact angle measurement were prepared from a 3 W% solution. The solutions were dropped onto a 2 x 5 cm (b x l) glass plate and dried at ambient conditions for more than 48h. The surface energy was determined on a Dataphysics OCA 15 machine according to the method of Owens and Wendt [39]. Three liquids were applied; water, formamide and diiodomethane. The contact angle was averaged over 2 seconds at stable contact angle. In some cases, ethylene glycol was used to replace water if the contact angle would not stabilize. Five repetitions per liquid per sample were made. Samples were prepared in two fold. The surface tension of the starch products was used to predict the work of adhesion and the sensitivity to separation upon wetting [40]. The work of adhesion can be estimated by the Dupré relation (Equation 1):

$$W_{adh} = \gamma_{S_1} + \gamma_{S_2} - \gamma_{S_1S_2} \approx 2 \left[(\gamma_{S_1}^d \gamma_{S_2}^d)^{1/2} + (\gamma_{S_1}^p \gamma_{S_2}^p)^{1/2} \right] \quad (\text{Equation 1})$$

W_{adh} is the work required to separate surface 1 and 2, γ_i is the surface tension, S_1 is solid 1 (in this case starch) and S_2 is solid 2 (cellulose or CaCO_3). Superscripts d and p represent the contribution of disperse- and polar forces to the total surface tension. For $W_{adh} > 0$, adhesion takes place and a higher value means that more energy is required to separate compounds 1 and 2. Equation 1 can be applied to indicate spontaneous separation of a polymer if submerged in a liquid. For S_1 and S_2 the interactions between the solid and the liquid (S_1L and S_2L) are substituted, leading to Equation 2:

$$W_{adh} = \gamma_{S_1L} + \gamma_{S_2L} - \gamma_{S_1S_2} \quad (\text{Equation 2})$$

Here, γ_{S_1L} is the solid1-liquid interaction. Separation occurs if $\gamma_{S_1S_2} > \gamma_{S_1L} + \gamma_{S_2L}$. γ_{S_1L} was calculated from the contact angle results and by using Equation 3:

$$\gamma_{1,2} = \gamma_1 + \gamma_2 - \left[2(\gamma_1^d \gamma_2^d)^{1/2} + 2(\gamma_1^p \gamma_2^p)^{1/2} \right] \quad (\text{Equation 3})$$

Equation 3 is a general equation. In fact, the subscripts 1 and 2 may represent any compound, either a gas, solid or liquid.

Results and discussion

Benzylated waxy potato starch derivatives were synthesized from starting materials with varying level of oxidation. The molecular weight of the starting materials is shown in Table 1. After washing and drying the product, chemical characterization by UV spectrometry was performed to determine the reaction efficiency. The pasting profile was recorded and the viscosity as a function of concentration and temperature was determined. Contact angle measurements provided data to calculate the surface tension including the polar and disperse contributions.

Starch ^a	M _w (10 ⁶)
Waxy potato (native)-0	30.2
X115-0	6.30
X85-0	2.60
X55-0	0.77

Table 1: molecular weight of starting materials.

a) “-0” indicates that the reported value is a property of the starting material, as received.

Reaction

Unlike normal potato starch, native waxy potato starch did not turn yellow upon addition of NaOH, due to the lower amount of reducing ends in the waxy starch [41]. Oxidized waxy potato starches showed yellow-coloring; at increasing DS and level of oxidation, coloring increased. Upon neutralization, coloring decreased and most color was washed out. The products were all slightly yellow. After 24-48 hours, minor coagulation of granules occurred at the highest DS (0.3 and higher). A small fraction of the starch seemed to dissolve during the washing procedure since foam formation was observed, which was also reported in the literature [23]. At the last water-washing step, the products at a DS > 0.2 showed decreased filterability. Minor swelling of granules based on oxidized starch was observed upon the addition of acetone at the first wash. This effect may be explained by the increased solubility of benzylated starch towards organic liquids as reported by Hamilton and Yanovsky [42]. Up to a DS of 0.375, the granules of the oxidized and benzylated starches showed minor damage and occasional swelling or gelatinization, but did not lose their crystallinity as a consequence of the rather severe reaction conditions. In Figure 1 the difference between X85-0 and X85-0.375 (X85 with a DS of 0.375) is shown. The Maltese cross was observed with cross-polarized light under the microscope for all products listed in Table 2.

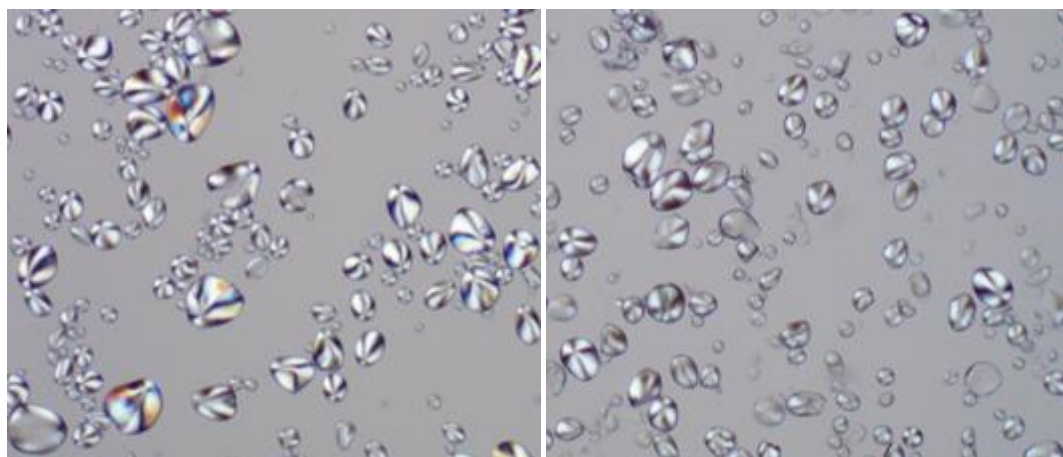


Figure 1: microscope images X85-0 (left) and X85-0.375 Bn (right) under polarized light; 100X

The DS and reaction efficiencies of all starches are displayed in Table 2. Only for DS-0.375 a reaction time of 96h was applied, the other reactions were finished after 72h.

Sample	DS ^a _{th}	DS _{UV}	Efficiency (%)
W^b-0.125	0.125	0.10 ± 0.002	84
W-0.25	0.25	0.20 ± 0.004	81
W-0.375	0.375	0.29 ± 0.051	76
PS-0.25	0.25	0.22	88
X115-0.375	0.375	0.28	74
X85-0.0027	0.027	0.023	85
X85-0.125	0.125	0.09 ± 0.004	73
X85-0.25	0.25	0.19 ± 0.021	75
X85-0.375^c	0.375	0.25 ± 0.02	67
X55-0.2	0.2	0.16	79
X55-0.3^c	0.3	0.22	73

Table 2: reaction efficiency of benzylation of waxy potato starches.

^{a)} Theoretical DS: moles benzyl chloride added per mole AGU.

^{b)} Native waxy potato starch is indicated as 'W' and native 'regular' potato starch as 'PS'.

^{c)} Some of the product dissolved during washing.

The reaction efficiencies are similar to values found in the literature [19,27], so the level of oxidation does not influence the efficiency of the benzylation reaction. During the reaction, samples were taken every 24 hours. The work-up procedure of these samples was similar as described above. Figure 2 shows typical DS build-in curves; both for native and oxidized base materials the progress was similar.

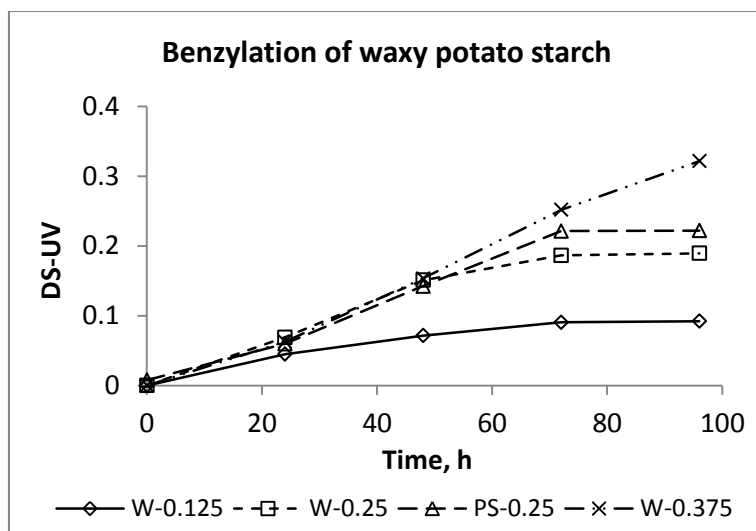


Figure 2: typical DS curve of different Benzylated starches.

The reaction kinetics appears pseudo-zero-order in benzyl chloride, which has limited solubility in water [23]. Cho & Lim [28] showed that the reaction rate depends on the NaOH concentration. During the reaction of DS = 0.125, $[\text{OH}^-]$ is lower compared to reactions with a higher DS. Therefore, the reaction rate is lower. The other reactions proceed at a increasing $[\text{OH}^-]$, but in both the DS = 0.25 and 0.375 reaction, the total reaction rate is almost equal for 48h. So the total rate of reaction appears to be limited by the concentration of benzyl chloride in the continuous phase. Both effects can be observed in Figure 2.

Rapid visco analysis

An RVA-profile reveals the pasting behavior of starch granules in suspension upon heating [43]. The granules will start swelling at the onset temperature, thereby increasing the viscosity of the suspension. At the peak viscosity, starch granules start to disintegrate and the starch will dissolve into the water phase. Although the starch granules may not completely disintegrate during an RVA measurement, due to lack of shear- and thermal input, an RVA profile provides useful information regarding the behavior of the product upon thermomechanical processing. The viscosity peak height may indicate possible processing problems upon cooking. The hot paste temperature is a measure for the starch solution viscosity just after processing and the set-back shows the increase of the solution viscosity when the paste cools down.

The results of the RVA measurements of all products are listed in Table 3. Native waxy potato starches show a decrease in the peak viscosity at increasing DS. The higher final viscosity of W-0.25 (625 mPa.s) compared to PS-0.25 (81 mPa.s), is explained by the absence of amylose, which has a lower molecular weight and thus a lower viscosity. The RVA profile of W-0.25 is very different from the oxidized starches, as can be seen in Figure 3. The decreased viscosity is explained by the formation of a dispersion [19,27]. Gelatinization proceeds slow and the viscosity increases well into the steady temperature period of 90 °C. The granules of W-0.375 Bn did not dissolve at all: merely deformed, amorphous (no Maltese cross under cross-polarized light), but distinct structures were observed. From Table 3 it can be observed that all derivatives from W-0 except W-0.375 have a decreased pasting-onset temperature compared to W-0, which is common for modified starches in general [44-46]: compare the onset temperatures of W-0 (72.8°C), X115-0, X85-0 and X55-0 (60.8 °C).

Sample	DS-th	P-onset (°C)	P-temp (°C)	Viscosity (mPa.s)				
				Peak	Hot paste	Final paste	Breakdown	Setback
W^a	0	72.8	83.6	2863	1350	1518	1513	168
W^a	0.125	71.4	59.9	1506	1468	1856	38	388
W^a	0.25	70.8	90.0	311	358	625	-47	267
W^a	0.375	79.6	90.0	20	11	6	9	-5
PS^a	0.25	72.1	90.0	32	52	81	-20	29
X115	0	70.0	78.7	2250	197	920	2053	723
X115	0.375	64.9	83.7	2660	215	17468	2445	17253
X85	0	65.6	72.5	602	65	256	537	191
X85	Control	62.3	74.1	787	40	164	747	124
X85	0.125	62.6	71.4	1410	47	173	1363	126
X85	0.25	61.2	72.1	1677	61	561	1616	500
X85	0.375	65.6	79.7	1250	78	5161	1172	5083
X55	0	60.8	66.1	211	26	84	185	58
X55	0.2	62.2	68.0	1152	28	168	1124	140
X55	0.3	52.8	75.4	435	33	733	402	700

Table 3: RVA results

^{a)} The RVA profile of waxy potato starches were recorded at 5W%.

At increasing degree of benzylation, the decrease of the onset temperature is further enhanced in most cases, for example X85-0 (65.6 °C) vs. X85-0.25 (61.2 °C). However, if the hydrophobic content increases, for example for X85-0.375, the onset temperature increases again, which indicates a decreased tendency of the granules to dissolve. All measured onset temperatures were well above the reaction temperature. Moreover, oxidized and benzylated starches show a considerable increase

in the peak viscosity. To verify if the increase in peak viscosity was the result of hydrophobic content, a control experiment (without benzyl chloride) was performed with X85-0 as a starting material. As can be observed from Table 3, the RVA profile of X85-blanco does not show the increased peak viscosity, which gives reason to assume that the increased peak viscosity of benzylated and oxidized starches is caused by the benzyl-groups.

At $DS_{th} > 0.3$, the oxidized starches show a considerable increase in end-viscosity compared to their starting materials. The end-viscosity of these products was a function of the level of oxidation: a higher level of oxidation yielded a lower end-viscosity, as is illustrated in Figure 3.

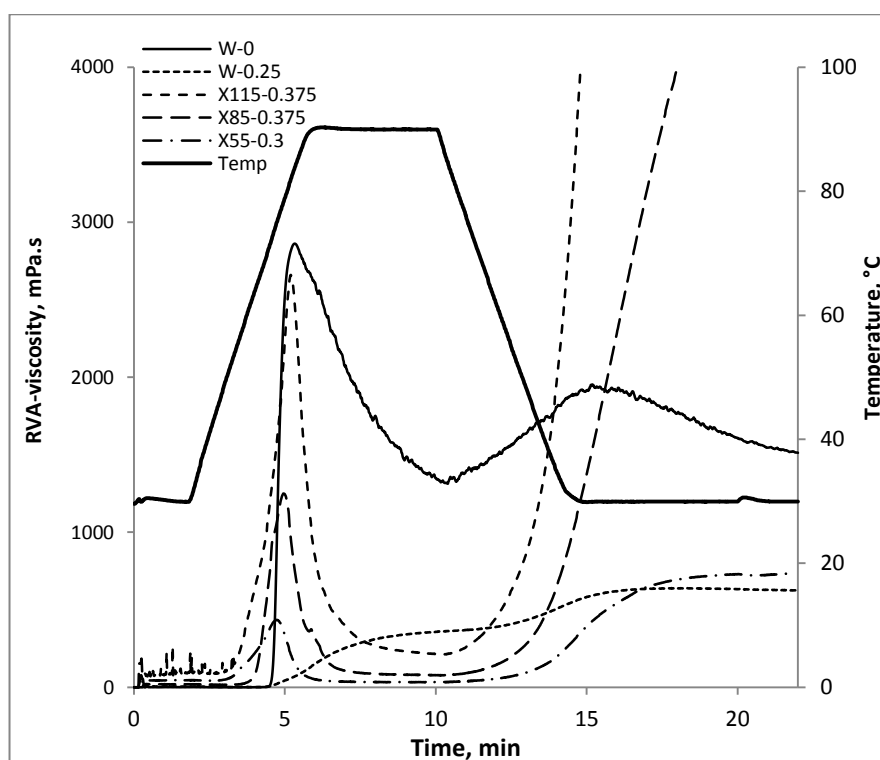


Figure 3: RVA recordings of benzylated starches.

Normally, such an increase is ascribed to retrogradation, a recrystallization process which causes a viscosity increase. Huijbrechts et. al [36], who modified native corn starch with Allyl Glycidyl Ether (AGE), observed a similar increase in final paste viscosity even without using degraded starch, and explained it by retrogradation. The cooked pastes of benzylated oxidized waxy potato starches, however, remained liquid, so apparently retrogradation was not believed to take place in this case. It is remarkable that for example X115-0.375 shows an enormous increase of the end-viscosity while the granules of W-0.375 do not disintegrate at all. This suggests that W-0.375 may be dissolved, but the viscosity difference between the starch gel-granule and the water is too large for complete

granular disruption. Another possibility is that the presence of carbonyl- and carboxyl groups from the oxidation process enhances solubilization.

Cooked starch paste viscosity

Figure 4-a shows the viscosity profiles of benzylated waxy- and normal potato starch. The solution texture of native waxy potato starch suggested incomplete granular disruption. Increased cooking time to 60 minutes did not change the profile. A DSC study by Thiewes and Steeneken [47] showed that at temperatures well above 100°C structural changes still occur. Other cooking methods, such as jet-cooking, improve gelatinization [18,27,48] but were not applied here. The viscosity of sample W-0.25 exceeded the viscosity of W-0 solution above a concentration of 8 W%, so the apparent decrease in viscosity suggested by the RVA measurement is only partly true. A sub-micron dispersion was formed by W-0.25, similar to PS-0.25, which is in agreement with known literature [18,19,27]. Due to the increased viscosity at increasing concentration and the presence of dispersed particles, it seems that at least part of the starch still dissolves, and that part also had a higher viscosity than native starch. Similar to the observations made during RVA measurements, the granules W-0.375 did not dissolve, despite a higher concentration (15 vs. 5 %W), longer cooking time and increased stirrer speed. Therefore, this product is not further taken into account.

The use of oxidized waxy potato starches as a base material for the benzylation reaction resulted in increased solubility of the products. The pastes obtained by cooking were not 'milky', but yellowish and slightly opaque. Unlike what was reported about degraded maize starch in the literature [27], no sub-micron dispersion was obtained, except occasional undissolved granule fractions were detected by light microscope. Figure 4 b-d show the viscosity profiles of oxidized and benzylated waxy potato starch products. The starting materials have decreased viscosity compared to W-0, due to degradation by the oxidation process. Decreased viscosity of the starting-material results in a decreased viscosity at a similar DS: X85-0.375 has a lower viscosity than X115-0.375. If the starting material is the same, however, the viscosity of the cooked starch dispersion depends strongly on the DS, as well as the concentration. This is best shown in Figure 4-b, where the viscosity of X115-0.375 exceeds the viscosity of X115-0 above 15 %W. Only X85-0.125 is lower than X85-0 over the whole measured concentration range. The other exception is X55-0.2 has a higher viscosity than X55-0 in the dilute region, but also the strong increase above 15 %W. This observation is left unexplained. All cooked benzylated starch products were stable at all concentrations, i.e. the

viscosity did not change over 24h, so no retrogradation occurred. The increase in viscosity is most pronounced at DS-th of 0.3 – 0.375. At high concentrations, the increase in viscosity sometimes exceeds 2 orders of magnitude compared to the starting material while at low concentrations the viscosity is lower. For example, the viscosity of X115-0 increases from 100 mPa.s. at 10 %W to approximately 3000 mPa.s at 25 %W while X115-0.375 increases from 13 to 200.000 mPa.s over the same range.

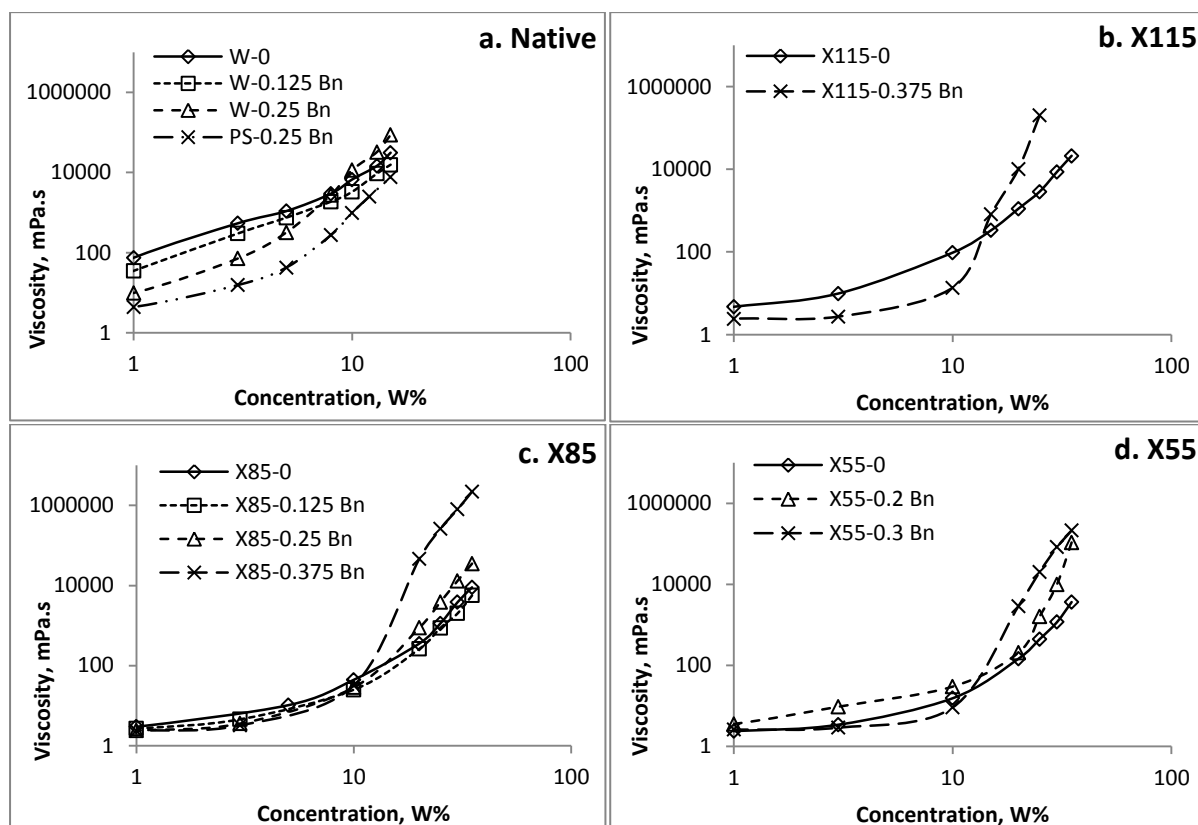


Figure 4: typical examples of concentration-viscosity behavior of benzylated starches ^{a)}.

^{a)} X115-0.375 at 25% was extrapolated; at 2 s^{-1} the rheometer was operating at maximum torque.

The large viscosity increase may be explained by hydrophobic interactions of the benzyl groups. It is known that hydrophobic groups, substituted on a water soluble polymer, introduce new rheological properties to the product; one of the possibilities being increased viscosity [31,49]. The new rheological behavior is a function of the substitution pattern on the polymer backbone; random or block-wise. Block-size and relative hydrophobicity of the substituent contributes to the magnitude of hydrophobic interaction. In the dilute regime, hydrophobic blocks cause aggregates, which decrease the hydrodynamic volume of the molecules and hence the viscosity. Above a critical concentration the aggregates become interconnected and a three dimensional network is formed,

resulting in a large viscosity increase [50,51]. In starch chemistry it is well accepted that reaction takes place in the amorphous parts of the starch granules (i.e. near 1-6 linkages) [52], which suggests that a 'block like'- rather than a random substitution pattern of benzyl groups seems more likely to have formed during the reaction. Moreover, it seems logical to assume that the viscosity increase of oxidized starches also occurs for native starches. It is strange, therefore, that both normal and waxy potato starch with DS-th = 0.25 form a dispersion and not a 'very high' viscous gel, as observed by Huijbrechts et al. [53] who substituted allyl glycidyl ether on corn starch.

Pyrene UV emission measurements revealed hydrophobic interactions between the benzyl groups in the starch solutions. In addition, the molecular weight distribution, determined by GPC measurements, show that the changes in viscosity are too large to be accounted for by the increase of molecular weight due to addition of benzyl groups alone, see Table 4. It can be observed that the molecular weight of the control experiment products decreases by about 20%. After benzylation, the decrease is less. In fact, only at a DS-th of 0.375 the molecular weight of X85 increases by 11% while it should have increased by about 20% if no degradation would take place. Another explanation of the increased viscosity could be the formation of amylose-lipid complexes, which may also be formed by potato starch amylopectine due to its fine-structure [54-56], but these were not determined here.

Starch	M _w (10 ⁶)
X85-0	2.60 ± 0.17
X85-BI-R	2.09 ± 0.02
X85-0.125	2.52 ± 0.08
X85-0.25	2.13 ± 0.09
X85-0.375	2.89 ± 0.11

Table 4: molecular weight distribution of Benzylated X85 products

Effect temperature

To the best of our knowledge, the viscosity as a function of temperature of benzylated starches has not been reported in the literature before. Amphiphilic polymers are known to display peculiar thermo responsive rheological behavior due to a shift in the balance between polar and disperse forces [31,57]. This may result in the introduction of an upper- or lower critical solution temperature (UCST/LCST), which results in a sudden change in viscosity at increasing temperature. Usually, a liquid or solution shows a gradual decrease in viscosity if the temperature increases. Figure 5 shows the viscosity as a function of temperature for the products based on X85. Other products showed similar thermal behavior, except for W-0 and W0.125 which showed little temperature dependence.

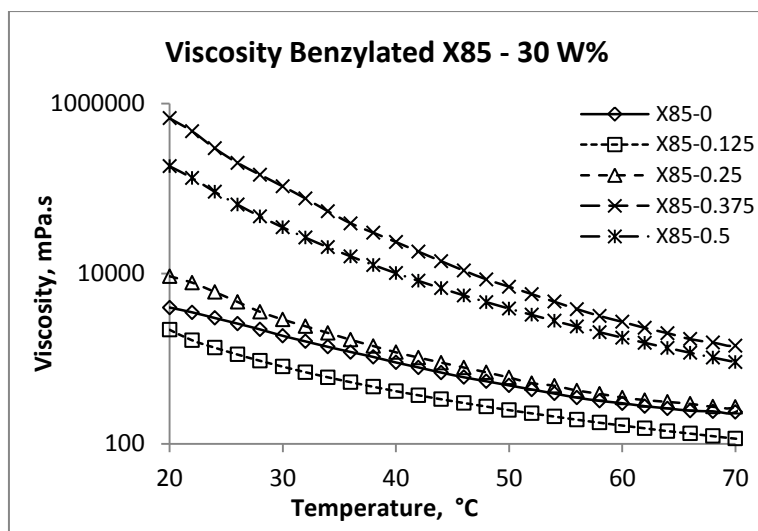


Figure 5: typical temperature profiles of benzylated waxy potato starch products.

All temperature profiles could be modeled by the Andrade relation (Equation 4), which is basically an Arrhenius type equation [58].

$$\log(\eta) = A + \frac{B}{T} \quad (\text{Equation 4})$$

Here, T is the absolute temperature, in K. The term B represents the activation energy; the force needed to increase Brownian motion of molecules. A is a pre-exponential factor.

Starch	DS _{Bn}	η - 30 % ^a mPa.s (10 ³)	-A	B	R ²
Waxy	0	31.3 ^b	-1.04	880	0.998
Waxy	0.125	15.7 ^b	-1.05	840	0.994
Waxy	0.25	32.7 ^b	8.44	3790	0.984
Potato	0,25	2.5	2.45	1650	0.990
X115	0	8.6	3.56	2310	0.999
X115	0.375	10.2 ^c	6.54	2840	0.987
X85	0	3.8	5.93	2790	0.999
X85	0.125	2.0	4.38	2240	0.998
X85	0.25	13.0	8.32	3570	0.996
X85	0.375	717.3	13.41	5590	0.999
X85	0.5	175.9	8.78	3790	0.962
X55	0	1.2	6.55	2800	0.997
X55	0.2	10.0	9.28	3950	0.999
X55	0.3	82.7	12.45	5030	0.994

Table 5: Andrade coefficients of starch solutions and viscosity at 30W%

^{a)} Viscosity at 20°C

^{b)} Viscosity at 13 %W

^{c)} Viscosity at 20 %W

The profiles of all products could be fitted by the Andrade model. This suggests the starch dispersions show normal thermo-rheological behavior and that in the reported range the nature of the dispersion is unchanged; i.e. the amount of dissolved material remains the same. Table 5 shows the Andrade parameters of the measured starch dispersions; only 30 %W concentrations are displayed. W-0, W-0.125 and X115-0 deviate from the general correlation between A and B [58] but showed a reasonable fit. Based on the above, it was concluded that the benzylated starch solutions did not show thermo responsive behavior. Instead, normal behavior for dissolved polymers was observed.

Dry starch film surface tension

The film surface tension of W-0 was determined as 56.9 mN/m, which is in agreement to the values found in the literature. Bengtsson et. al. reported a surface tension of around 50 mN/m for normal potato starch. A value of around 60 mN/m was reported for maize starch by Angellier et. al. [59] and by Thielemans et. al. [60]. The surface tension values, the work of adhesion and the work of separation in water are listed in Table 6 for all products.

Although the surface tension of oxidized starches remains approximately 56 mN/m, the contribution of polar forces to the surface tension seems to increase at increased degree of oxidation, but the X55-0 deviates from this trend. Upon benzylation, the total surface tension of the films of all products decreases and the relative contribution of dispersive forces increased, especially for the native starch products. W-0 had a contribution of polar forces of 31.7 mN/m which dropped to 9.2 mN/m for W-0.25. In addition, the film surface tension of the products approaches 45 mN/m upon benzylation. This value approaches 43.1 mN/m, which is the surface tension measured for Styronal D517, a commercially available SBR latex from BASF applied in paper coatings by the paper industry, here used as a reference. At similar DS, but different levels of oxidation (molecular weight), the surface tension of starch films are comparable which is in agreement with the literature [40]. If W_{adh} is calculated according to Equation 1 for starch-cellulose as well as starch- $CaCO_3$, it is found that the interaction reduces as DS increases. This means that it will take less energy to separate the two compounds. Furthermore, Equation 2 was used to calculate W_{adh} in case of submerging the composite in water. The calculation shows that spontaneous separation will occur in all cases ($W_{adh} < 0$), however, the water sensitivity decreases considerably as DS-Bn increases. Note that some starches, with respect to surface properties, show very similar results compared to Styronal D517.

Low water sensitivity is important since water is used to cover areas not to be covered by ink during off-set printing. Repeated contact with water may cause migration of starch, which is undesirable.

Starch-sample	γ^D	γ^P	γ^T	R^2	St-Cell ^b	St-CaCO ₃	Cell.sep	CaCO ₃ sep
W-0	25.3	31.7	56.9	0.998	112.5	213.7	-99.5	-176.6
W-0.125	31.0	16.1	47.1	0.850	105.2	181.6	-84.1	-136.2
W-0.25	36.1	9.2	45.3	0.957	102.3	163.8	-73.0	-110.3
A-0.25	37.9	7.0	44.9	0.912	100.8	156.4	-67.8	-99.1
X115-0	24.8	31.8	56.0	0.990	111.9	213.2	-99.6	-176.6
X115-0.375	27.7	17.3	45.0	0.976	102.6	180.7	-82.8	-136.6
X85-0	21.7	35.1	56.8	0.999	110.3	215.5	-98.2	-179.2
X85-0.125	31.4	16.9	48.3	0.908	106.5	184.6	-85.9	-139.6
X85-0.25	29.2	17.2	46.4	0.902	104.3	182.5	-84.2	-138.2
X85-0.375	30.3	14.7	45.0	0.944	102.9	176.2	-80.6	-129.7
X55-0	26.7	24.4	51.1	0.943	108.2	198.7	-92.5	-158.7
X55-0.2	30.9	13.0	44.9	0.886	101.6	171.4	-76.7	-122.2
X55-0.3	29.6	15.0	44.5	0.912	102.4	176.3	-80.6	-130.2
Styronal D517	23.0	20.1	43.1	0.950	99.5	181.9	-81.9	-139.9

Table 6: surface tension components of benzylated waxy potato starch products and calculated W_{adh} for various systems.

a) The surface tension is reported in mN/m for all values.

b) St-Cell and St-CaCO₃ represent W_{adh} for starch-cellulose and starch-CaCO₃. Cell-sep and CaCO₃-sep represent the work of separation in water for these systems. Values for the surface tension of cellulose, CaCO₃ and water were obtained from the literature for disperse (d), polar (p) and total (t). Cellulose (40, 18.8, 58.8 mN/m) from [61,62], CaCO₃ (54.5, 153.4, 207.9 mN/m) from [63] and water (21.8, 51, 72.8 mN/m) from [40].

Conclusion

A range of benzylated potato starches based on waxy potato starch was prepared and characterized. The effect of the level of oxidation and DS on starch properties upon benzylation was studied. Industrial grades of oxidized waxy potato starch were used for this purpose. The reaction efficiency of benzylation was not influenced by the degree of oxidation and was comparable to values found in the literature with respect to normal potato starch and corn starch. An increase of RVA peak viscosity was observed which was assigned to the presence of hydrophobic groups. Native, benzylated waxy potato starch behaved similar to what was described in the literature regarding benzylated normal potato starch; it only had a higher viscosity. A significant viscosity increase was found for oxidized starches at DS > 0.3. By varying the degree of oxidation and DS-Bn, the viscosity and hydrophobic content of the starch solution can be tuned, which could be beneficial for the

paper coating process. Benzylated oxidized starches did not form dispersions like the native benzylated starches upon cooking. This can be explained by either the decreased molecular weight of oxidized starches or by the presence of carbonyl- and carboxyl groups in oxidized starch. The relatively small increase of the molecular weight, determined by GPC, and the peak shift in the pyrene emission spectrum indicated that the increased viscosity is most likely the result of hydrophobic interactions. Amylose-lipid complex formation was not measured but may also contribute to the total viscosity. No thermosresponsive rheological effects were detected. The starch film surface tension decreased at increasing DS and the contribution of polar forces to the total surface tension decreased as expected. It was calculated that the water sensitivity decreased as well. The results suggest that benzylated starches based on oxidized waxy potato starches should, at least partly, be able to replace SBR in paper coatings. Further research will focus on this subject.

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Chapter 3

Replacement of SBR latex by hydrophobic starch in paper coatings

Abstract

Waxy potato starch was oxidized and benzylated and applied in paper coatings to study the effect on the coating formulations and end-use properties. The rheological behavior of the formulations was investigated and the coatings were applied on paper to evaluate product performance. Standard techniques for paper coating characterization were used. Migration of starch to the coating surface during the drying process was studied by FTIR spectroscopy. It was found that oxidation and benzylation reduce the amount of starch at the surface, implying a more uniform distribution over the coating layer. The porosity of coatings increases at increasing degree of substitution (DS). The binding strength decreased. SEM images suggest that the morphology of the coatings relates to starch rheology.

Key words: *waxy potato starch, oxidized, benzylation, paper coating, rheology, surface properties, migration.*

Introduction

Starch is a hydrophilic, water soluble biopolymer with a high molecular weight and is formed in roots, tubers and seeds. Starch can appear in a mainly linear form, called amylose, and in a highly branched form: amylopectine. Both varieties are polymers of α (1-4) linked D glucose monomers, also referred to as anhydro glucose units (AGU). The fine-structure of amylose and amylopectine depends on the botanical origin and growing conditions of the plant [1-3]. Starch is applied for nutritional- and (industrial) functional purposes and may provide energy, texture, adhesion and viscosity. Examples of applications are: adhesives, textile yarn sizing, soups, sauces, paper and paper coatings. In most cases, native starch must be (chemically) modified to make it suitable for a specific application. Increasing efforts are made to replace products based on fossil resources by, amongst

others, starch. This is due to high oil prices and environmental awareness which caused a global trend towards an economic model based on renewable materials [4,5]. Modification of starch is essential for replacing oil-based products, which are often tailor-made for specific applications. A large variety of different modifications have been performed in the past [6]. Many modifications, like esterification, etherification or cross-linking make use of the reactivity of one of the three hydroxyl groups of the AGU monomer, allowing for a maximum degree of substitution (DS) of 3.

In the current paper, we report on work done on the replacement of styrene butadiene rubber (SBR) latex as a binding agent in high-quality paper coatings by oxidized and benzylated waxy potato starch (> 99% amylopectin). A paper coating is a composite of a pigment (such as CaCO_3 or clay) and a binder (latex or starch), applied to enhance the appearance and printing quality of base paper in glossy magazines, posters, catalogs, etcetera [7]. Such coatings are usually applied in three layers, a pre-, mid- and a top-coating [8]. Coated paper is often printed by offset printing [7,8], a common technique in which oil-based ink is used. A balanced set of properties in both the formulation and the final product, required for top-coatings, is currently only achieved by using latex as the main binding agent [8]. SBR latex is a (colloidal) dispersion with an average particle size of around 120-140 nm [9]. The solids content of an SBR latex is typically around 50 %W with a viscosity (Brookfield) of 300-400 mPa.s. These properties allow for high speed application, up to 2000 m/min, by blade coating [10] at high formulation solids content and a reasonably low viscosity to ensure good machine runability [7,8]. SBR for paper coatings has a high molecular weight (MW) providing strength and copolymerized acrylic acid groups for stabilization of the dispersion and to balance the hydrophilic and hydrophobic content [8].

Today, the high viscosity of native starch is reduced by oxidation [11], which allows starch to be used in pre- and mid coatings. Oxidation by hypochlorite [11] causes a decrease of the molecular weight and also introduces carbonyl- and carboxyl groups to the starch which reduce retrogradation [12,13]. Full replacement of SBR in top-coatings has not been reported yet. Replacement of SBR latex by starch leads to a complex series of interconnected phenomena. The consolidation mechanism of the formulation is a capillary process [14-16] and is therefore strongly affected by the rheology and surface tension of the continuous phase of the formulation [17-21]. The consolidation mechanism affects the coating structure regarding surface roughness and porosity. In addition, the surface tension of the starch film is higher and more hydrophilic than that of SBR as can be deduced from the chemical structure of the two compounds, displayed in Figure 1.

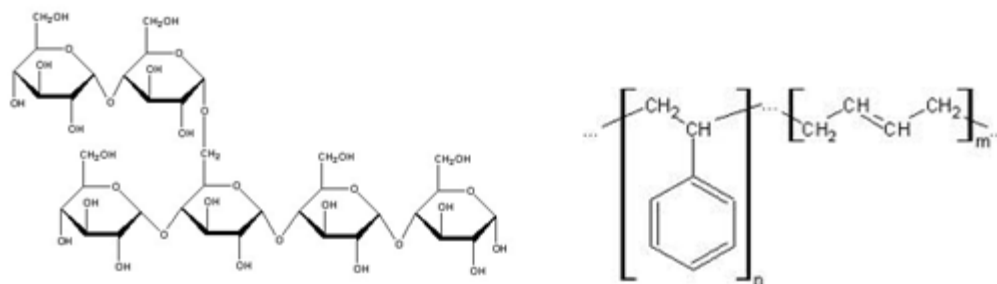


Figure 1: simplified chemical structures of starch (left) and SBR (right).

All these phenomena affect the general coating performance. Uneven binder distribution may cause adhesion problems and a common printing deficiency called print mottle [8,12,22], caused by uneven ink-setting leading to lighter and darker spots. It is recognized that starch is more likely to cause print mottle than SBR latex [23], however, the coating processing- and drying conditions strongly influence coating consolidation behavior and binder distribution, as was thoroughly reviewed by Ragnarsson [22]. Starch has been reported to migrate to the coating surface [18,24]. Latex-based top coatings have also been reported to contain starch which migrated from the pre- and mid coating during the application process [25].

The research reported in this paper is based on the hypothesis that hydrophobic groups provide properties to the starch that enables successful replacement of SBR. Experiments in Chapter 2 showed that the viscosity of the starch solutions and the starch dry film surface tension can be controlled by changing the level of oxidation and the degree of substitution of benzyl-groups (in short, DS). Structure-function relationships of benzylated starches with respect to blade coating were reported, including the dewatering behavior and the coating formulation viscosity as well as binding strength, porosity and print mottle were evaluated of coated paper samples. The surface starch content of the coatings was evaluated qualitatively by FTIR spectroscopy. SEM-images were taken to evaluate the surface structure of the coated paper samples.

Experimental

Materials

Native potato starch, waxy potato starch and two commercial grades of oxidized waxy potato starches; Perfectafilm X85 and X55 were kindly supplied by AVEBE Foxhol, The Netherlands.

Preparation and characterization of benzylated starches was performed as in Chapter 2. Table 1 provides an overview of the starches and their properties, used for this research. Hydrocarb 60, a ground calcium carbonate coating pigment (GCC, 60 % < 2 μm), was obtained from Omya (Oftringen, Switzerland) and was homogenized before use. Sodium hydroxide (Sigma) was used in a 10% solution. Coating base paper of 82 g/m² was obtained from Burgo Ardennes (Virton, Belgium).

Starch	DS	$\eta_{\text{starch}} - 30\%$ 10 ³ mPa.s	$\sigma^{\text{d}}_{\text{film}}$ mN/m	$\sigma^{\text{p}}_{\text{film}}$ mN/m	$\sigma_{\text{total, film}}$ mN/m
W^a	0.25	32.7 ^b	36.1	9.2	45.3
PS^a	0.25	2.5 ^b	37.9	7.0	44.9
X85	0	3.8	21.7	35.1	56.8
X85	0.125	2.0	31.4	16.9	48.3
X85	0.25	13.0	29.2	17.2	46.4
X85	0.375	717.3	30.3	14.7	45.0
X55	0	1.2	26.7	24.4	51.1
X55	0.2	10.0	30.9	13.0	44.9
X55	0.3	82.7	29.6	15.0	44.5
Carbital 60		0.5 ^c	-	-	-

Table 1: used starches and their viscosity and surface tension according to Chapter 2.

^{a)} 'W' represents native waxy potato starch as starting material, 'PS' the regular potato starch.

^{b)} 13 %W in water

^{c)} ± 78 %W in water

Starch paste preparation

Starch pastes based on oxidized starch products were prepared at 35-38 W% aqueous dispersions; pastes based on native starches were prepared at 12-15 W%. Cooked starch pastes were prepared as follows: water was added to 1050 g of dry solids starch to obtain a total of 3 kg suspension. The suspension was mixed and fed to a mini jet-cooker at approximately 1 kg/min and cooked at 5 bar steam pressure at 140°C. The holding-time was 30 seconds. The starch concentration was determined on an ATAGO-RX 5000cx refractometer at a sample temperature between 25 and 30 °C.

Coating formulation preparation

To 100 parts (1.5 kg) dry solids of Hydrocarb 60, 78 %W aqueous dispersion, 12 parts dry solids of starch was added as a paste while mixing vigorously with a Pendraulic mixer. The pH was adjusted to 8.5 – 9.0 with a 10 %W NaOH solution. Water was added and mixed similarly to adjust the coating viscosity and/or solids content. The coating formulation was cooled to 30 °C prior to further

characterization. The total solids content of the coating formulation was determined gravimetrically by a CEM Labwave 9000 microwave.

Viscosity

Formulation viscosity at low shear rate was determined on a Brookfield viscometer at 100 rpm. The viscometer was allowed to stabilize for 15 seconds before reading the value. The high shear viscosity was measured on a Hercules DV-10 Hi Shear viscometer. A spindle type A was used. The shear rate was increased from 0 – 4500 s⁻¹ and back to 0 s⁻¹ in 20 seconds. 45 grams of the formulation was used per measurement.

Dewatering

Dewatering behavior of the coating formulations was determined on a AA-GWR water retention meter. Dewatering was determined gravimetrically by air-pressing 8 ml of coating formulation at 1,5 bar for 15 seconds through a polyester membrane with a 5 µm pore size from GE water- & process technologies onto a filter paper. The radius of the sample compartment was 3.192 cm; the mass of water passed through the membrane was multiplied by 1250 to obtain the dewatering in g/m².

Coating application

The coatings were applied single-sided to base-paper by means of a DIXON lab-blade-coating machine. The viscosity of the coating formulation was adjusted with water to a Brookfield viscosity of 1200 – 2000 mPa.s. The paper-web speed of the DIXON machine was 50 m/min. Four blade pressures, ranging from 0.5 – 4 bar were applied to each coating to obtain a series of similar coating-weight. The dryer was operated at 125°C at 3 bar steam. Moisture content of the coated paper after drying was approximately 6%. After application and drying, the paper samples were allowed to equilibrate at 23 ± 1 °C and 50 % RH (ISO-187) for at least 48 h prior to further measurement. The applied coating weight was determined gravimetrically according to ISO-536. The coating weight was calculated by Equation 1:

$$W = \frac{m_{blank} - m_{coated}}{A_{A4} * n} \quad \text{(Equation 1)}$$

Here, W is the amount of coating in g/m^2 , m_i is the mass of n sheets of paper; A is the surface area in m^2 of 1 A4 sheet and n is the number of sheets, in this case $n = 10$

IGT dry pick - bonding strength

IGT dry pick, or binding strength, of the coatings was determined according to ISO-3738 on an IGT-AIC2-5 machine. IGT pick test oil of standard viscosity was used. The oil viscosity was 520 mPa.s (Newtonian behavior) at standard conditions ($23 \pm 1^\circ\text{C}$). A layer thickness of 8 μm was rolled over the coated paper at increasing speed, maximum 4 m/s. The speed at which pick occurred was determined visually. The distance at which dry pick occurs relates to the roller speed at dry pick. The speed at pick, multiplied by the viscosity of the test oil at this speed yields the 'viscosity-velocity-product (VVP)'. A high VVP value indicates a high bonding strength. The reported value is the average of 5 measurements.

Curley porosity

The Curley porosity of coated papers was determined on a Lorenten & Weltre Densometer according to ISO-5636-5. The time required to pass 100 ml of air through the coated paper is a measure for its porosity. This measurement only gives an indication of total free flow area, not about pore size; an increased time to pass 100 ml means a decreased free flow area. The reported value is the average of 5 measurements.

Print mottle

Print mottle tests were performed on a Prüfbau MZ-II machine. Huber Proofing and Mottling test ink type 408010 was used. 200 mm^3 of ink was homogenized on the machine's roll system for 30 seconds. Then the ink was transferred to a test roller, which transfers the ink to the paper, for 15 seconds. The ink was transferred to the paper at 0.5 m/s and rolled over by clean ink rollers; 1 immediately and subsequently 3 times at 10 second intervals. The samples were assessed visually for mottling.

Binder migration by FTIR

To establish an indication of binder migration, FTIR spectra of the coated papers were recorded on a Bruker Tensor 27, equipped with a platinum ATR. Therefore, the intensities of the starch peak at 1080 cm^{-1} (from 1070 to 1090 cm^{-1}) and CaCO_3 (pigment) peak from 855 to 890 cm^{-1} were determined by direct peak integration. The ratio of the integrated starch- and CaCO_3 peaks was used to indicate changes in the coating surface starch content. All coated papers were measured ten times per sample; samples were measured in two-fold.

SEM imaging

Scanning Electron Microscope (SEM) images for coated paper samples were recorded on a Philips/Fei (XL30) ESEM instrument operating at 3 kV acceleration voltage. A small amount of sample was deposited on a double adhesive carbon tab and then coated with 1-2 nm gold to prevent charging. Images were acquired using a secondary electron detector under high vacuum conditions (5×10^{-6} mbar).

Results and discussion

Benzylated starches, based on normal potato starch, waxy potato starch and two grades of oxidized waxy potato starch were pasted in a jet-cooker and added to a standard pigment formulation used in top-coatings. Standard tests were performed to evaluate formulation- and end use properties of the coated paper samples. FTIR measurements were performed to investigate the surface composition and the surface structure was evaluated by SEM imaging.

Formulation viscosity

Figure 2 displays the Brookfield viscosity profiles of coating formulations based on PS-0.25, W-0.25 and X85-0, 0.125, 0.25 and 0.375. The viscosities of these formulations depend strongly on the viscosity of the used starch solutions, summarized in Table 1. The coatings based on PS-0.25 and W-0.25 have a fairly low viscosity, however, the solids content is low for industrial application [8]. Increasing the total formulation solids content requires increased starch-solution concentration, which was not possible for these starches because the viscosity peak during jet-cooking would be too

high to process them. This illustrates the logic of using oxidized starch as a starting material, which can be cooked in a concentration up to 35 %W. Benzylated starches based on X85 produce coating formulations with a viscosity too high for the blade-coating process and have to be diluted to achieve the target viscosity for application. The high formulation viscosity with X85-0.375 is caused the high paste viscosity of this derivative. Formulations based on benzylated X55 needed much less dilution to achieve target viscosity for application, as can be seen in Table 2. A typical latex based coating formulation has a solids content of around 70 %W at a viscosity of 700 mPa.s which has to be increased using carboxy methyl cellulose to achieve a target viscosity of 1200 mPa.s for good machine runnability.

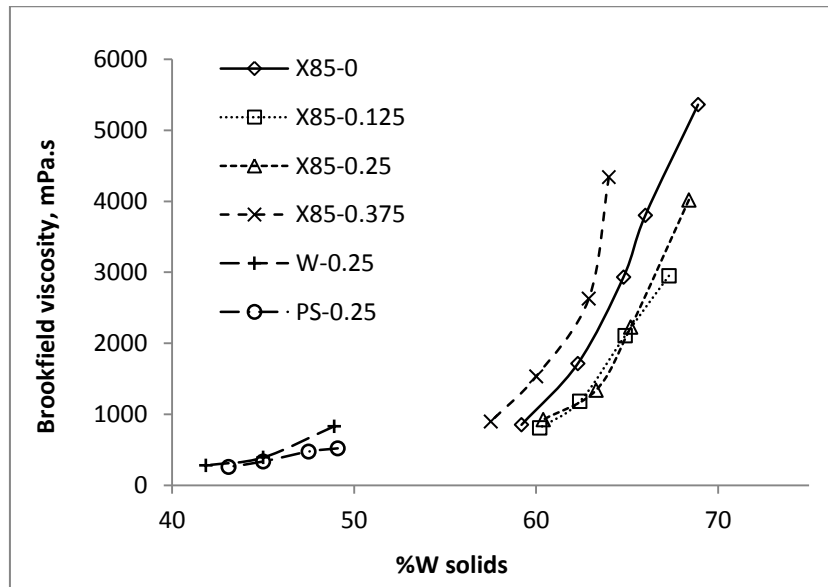


Figure 2: viscosity of coating formulations with 12 parts native potato starch and X85

The coating formulation viscosity is heavily influenced by the viscosity of the starch solution. The viscosity of Hydrocarb 60 is around 300-400 mPa.s at 78 %W solids content. Normally, the viscosity of a dispersion can be predicted by the Einstein equation; Equation 2. Here, (η) is the dispersion viscosity, (η_0) is the viscosity of the medium, in this case a starch solution, [η] is the intrinsic viscosity of the dispersed particles and ϕ (phi) represents the volume fraction of solids in suspension.

$$\eta = \eta_0(1 - [\eta]\Phi) \quad (\text{Equation 2})$$

However, the Einstein equation is only valid for very low values of ϕ (<0.2). The Krieger-Dougherty equation (Equation 3 [26]), which is a semi-empirical relation, is therefore often used for dispersions at higher solids contents and accounts for the maximum packing (ϕ_{\max}):

$$\eta = \eta_0 \left(1 - \frac{\Phi}{\Phi_{\max}}\right)^{-[\eta]\Phi_{\max}} \quad (\text{Equation 3})$$

Both equations illustrate the impact of the viscosity of the continuous phase, η_0 , on the total suspension viscosity: η . Water has a viscosity of 1 mPa.s and is also a Newtonian liquid. For latex based formulations, these equations apply reasonably well. Starch solutions are more viscous which results in an increased formulation viscosity compared to latexes. Since η_0 is a function of the starch concentration, which increases during the drying process, it is difficult to apply Equation 3 without introducing large errors. In addition, Hone & Howe [27] showed that suspensions in aqueous gelatin could not accurately be modeled by the Krieger-Dougherty equation.

The viscosity as a function of the shear rate of coating formulations based on benzylated X85 at 62 - 63 %W solids content is presented in Figure 3. In general, the differences in viscosity between the coatings, e.g. X85-0 vs. X85-0.375, are comparable to those measured at low shear rate. The formulation based on X85-0.375 shows enhanced shear thinning behavior, which is common behavior for associative polymers [28]. Moreover, the coating based on X85-0.375 regains more of its starting viscosity at decreasing shear rate, compared to the other formulations. This is an indication of associative behavior of the starch. Based on work by Pan et al. and Sand et al. [19,29], it may be expected that the changed rheological behavior affects the consolidation process of the coating. On the other hand, the test reported here was performed at very different time scale than the production process; 20 seconds vs. 30 μ s, so it may be unlikely that recovery of the viscosity will occur before the coating is dry.

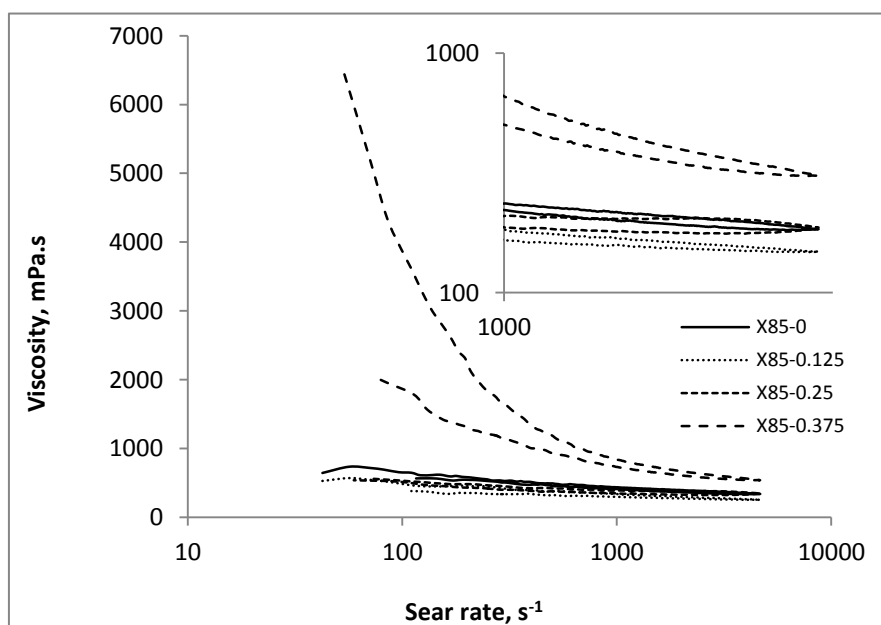


Figure 3: high shear viscosities of oxidized benzylated waxy potato starch X85.

Dewatering

The dewatering behavior of a formulation relates to the machine runability of a formulation as well as the binder penetration into the substrate. During application, the formulation is subjected to a pressure peak while passing the coating blade. The substrate effectively becomes a filter on which the formulation is filtered. Low dewatering is desired for good coating leveling after application and too much water in the paper web may compromise the web strength. Moreover, excessive dewatering may cause irregularities in the coating structure due to premature coagulation of pigment particles [8].

Typically, dewatering values of latex based coatings easily exceed 80 g/m^2 [30]; dispersed particles do not bind water as effectively as a dissolved, hydrophilic, polymer such as starch or carboxy methyl cellulose. Dewatering behavior has been measured for all formulations and is reported in Table 2. The dewatering was constant over a wide range of solids contents (50-67 %W). Sandas et. al. [30] showed that the presence of a dissolved polymer in a latex based coating formulation decreases dewatering considerably, which is observed here as well. The low dewatering values also supports the conclusion from Chapter 2 that benzylated starch behaves like a dissolved polymer rather than a latex, as was suggested in the literature [31-33]. The dewatering of X85-0.375 and X55-0.3 increases by almost a factor 2 compared to the other starch-formulations, see Table 2. This effect is large compared to the other values, but still low compared to latex-based coatings [8].

Starch	DS-Bn	solids %W	$\eta_{\text{BrF}}^{\text{a}}$ mPa.s	$\eta_{\text{Hercules}}^{\text{b}}$ mPa.s	Dewatering g/m ²
W	0.25	50.8	940	153	7.8
PS	0.25	51.9	920	243	6.6
X85	0	62.7	1320	481	6.5
X85	0.125	64.4	1560	395	6.2
X85	0.25	63.8	1640	640	6.2
X85	0.375	60.4	1860	330	13.8
X55	0	67.4	1700	443	5
X55	0.2	66.6	1000	228	4.5
X55	0.3	62.5	1820	603	8.8

Table 2: characteristics of coating formulations as applied to paper.

^{a)} Measured at 100 rpm.

^{b)} Viscosity at 1000 rpm, 4500 s^{-1} .

Dixon application

Nine different formulations were prepared for application on coating base paper with a DIXON laboratory blade-coating machine. The formulations were prepared at a solid-content as high as possible, with a Brookfield viscosity (100 rpm) of 1200 - 2000 mPa.s. All measured characteristics are reported in Table 2. The low viscosity and solids content of the formulations based on WP-0.25 and PS-0.25 is due to the maximum solids content of 15 %W of the starch suspensions prior to pasting.

Coating properties

After application, A4 sized coated paper samples were cut from the roll and allowed to reach equilibrium moisture content at standard conditions (23 ± 1 °C, 50 %RH) for a minimum of 48 h. A series of standard tests was performed to compare the surface properties of the coated papers. The results are presented in Table 3.

Starch	DS-th	Coat weight g/m ²	VVP mN/m	Porosity s
Base paper	-	0	761 ± 22	32 ± 1
WP	0.25	11.6	971 ± 38	310 ± 9
PS	0.25	12.6	1164 ± 73	633 ± 14
X85	0	12.7	1122 ± 26	723 ± 41
X85	0.125	12.5	1124 ± 54	1083 ± 39
X85	0.25	13.5	1130 ± 35	814 ± 44
X85	0.375	12.0	1046 ± 34	358 ± 12
X55	0	13.3	1147 ± 61	805 ± 62
X55	0.2	12.3	1087 ± 30	680 ± 38
X55	0.3	12.8	956 ± 36	379 ± 18

Table 3: coating weight, IGT dry pick and porosity of applied coatings.

An applied coating weight of 12.6 ± 0.6 was realized for all formulations. The results show that the strength of the paper surface is enhanced by the coating; IGT dry-pick (VVP) increased in all cases compared to non-coated base-paper. The DS and the level of oxidation of the starting materials do not seem to be of much influence; only X85-0.375 and X55-0.3 show a decrease of dry-pick resistance. Overall, the total variation in dry-pick differs only about 17% (950 – 1160) with an average error of 4 – 5 % which leaves little room to correlate these data to other phenomena like differences in picking-oil penetration due to porosity differences, formulation viscosity or differences in the dewatering behavior which may enhance mechanical interlocking of the binding agent with the

substrate [34]. It is not clear what causes the relatively large difference between normal and waxy potato starch. Perhaps the differences originate from the presence of amylose.

Differences in the coating porosity are more pronounced than differences in binding strength. However, no significant correlation was found between porosity and formulation viscosity. During the drying process, capillary forces cause the coating layer to shrink after the gel-point, i.e. the second stage of drying [16]. It appears therefore plausible that the differences in porosity are due to changed drying behavior, which in turn is caused by the presence of benzyl groups on the starch backbone. The coating porosity and the binding strength show a weak relation, as is displayed in Figure 4. Decreased contact area at increased porosity may explain reduced binding strength, since the force at which picking starts to occur should be proportional to the contact area. For the samples X55-0 and X85-0 and their benzylated derivatives at DS-0.3 and 0.375, it was calculated in Chapter 2 that the work of adhesion between the starch and the cellulose decreases about 5% due to benzylation. In addition, the porosity roughly increases by 50% while the bonding strength only decreases about 10%. Since the increase in porosity is much larger than the decrease in binding strength, mechanical interlocking of the compounds by starch seems at least partly responsible for the expressed binding strength [34], besides the direct interaction between starch and the other compounds.

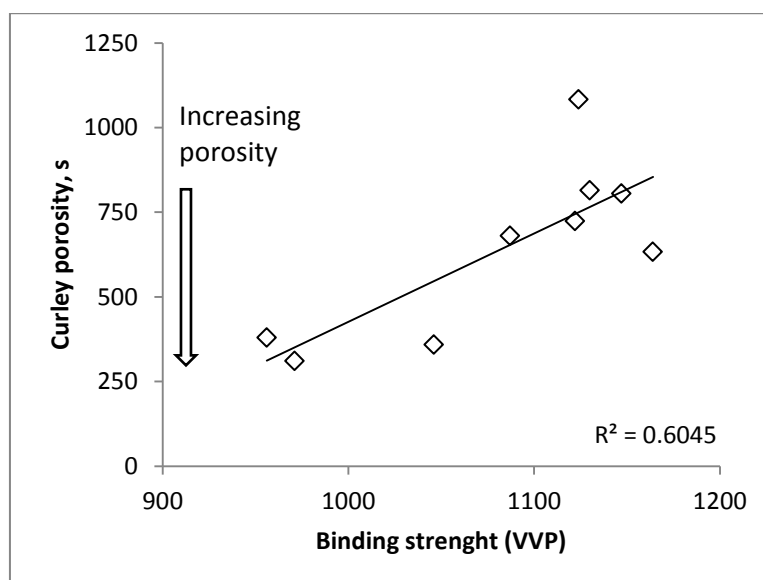


Figure 4: correlation between porosity and surface strength.

Mottling tests

Print mottle is caused by the combination of the surface structure (porosity) and surface energy of the printed substrate [22,23,35-40], i.e.: a coating having surface energy that allows for ink wetting and a non-porous surface structure will show mottling and vice versa. Pictures, taken from the mottling tests are displayed in Figure 5. The coatings based on X85-0 and X55-0 show mottling, as do coatings based on X85-0.125 (not shown), X85-0.25 and X55-0.2. The coatings with X85-0.375 and X55-0.3 show a more even ink distribution. The white spots observed at the X85-0.375 coating give the impression of mottling but are in fact spots on which no ink is deposited, probably due to the high porosity. Note that the surface tension of X55-0.2 and X55-0.3 (44.9 vs. 44.5 mN/m, both with a disperse component of 30 mN/m) cannot explain the difference in print mottle. In addition, print mottle decreases for X55-0.2 compared to X55-0, but improves further for X55-0.3.

The same can be stated for the native starches: PS-0.25 coating shows a fairly uniform ink distribution and W-0.25 does not while both starch films have a similar surface tension with a very small contribution of polar forces. In addition, it can be observed that PS-0.25 displays low/no mottling while X85-0.25 and X55-0.2 perform poorly. Moreover, the difference in total surface tension between PS-0.25 and X55-0.3 is low, but the contribution of polar forces is large. This observation suggests that the surface energy, DS, but also the total formulation solids content (solids PS-0.25 << X55-0.3) are not the dominant parameters that determine print mottle in this case. Moreover, oxidation is not required to obtain better print-behavior, but is nevertheless necessary for economic reasons. The biggest difference between the coatings is the rheological behavior of the starches. If the first statement of this paragraph is true, differences in surface structure should explain differences in print mottle.

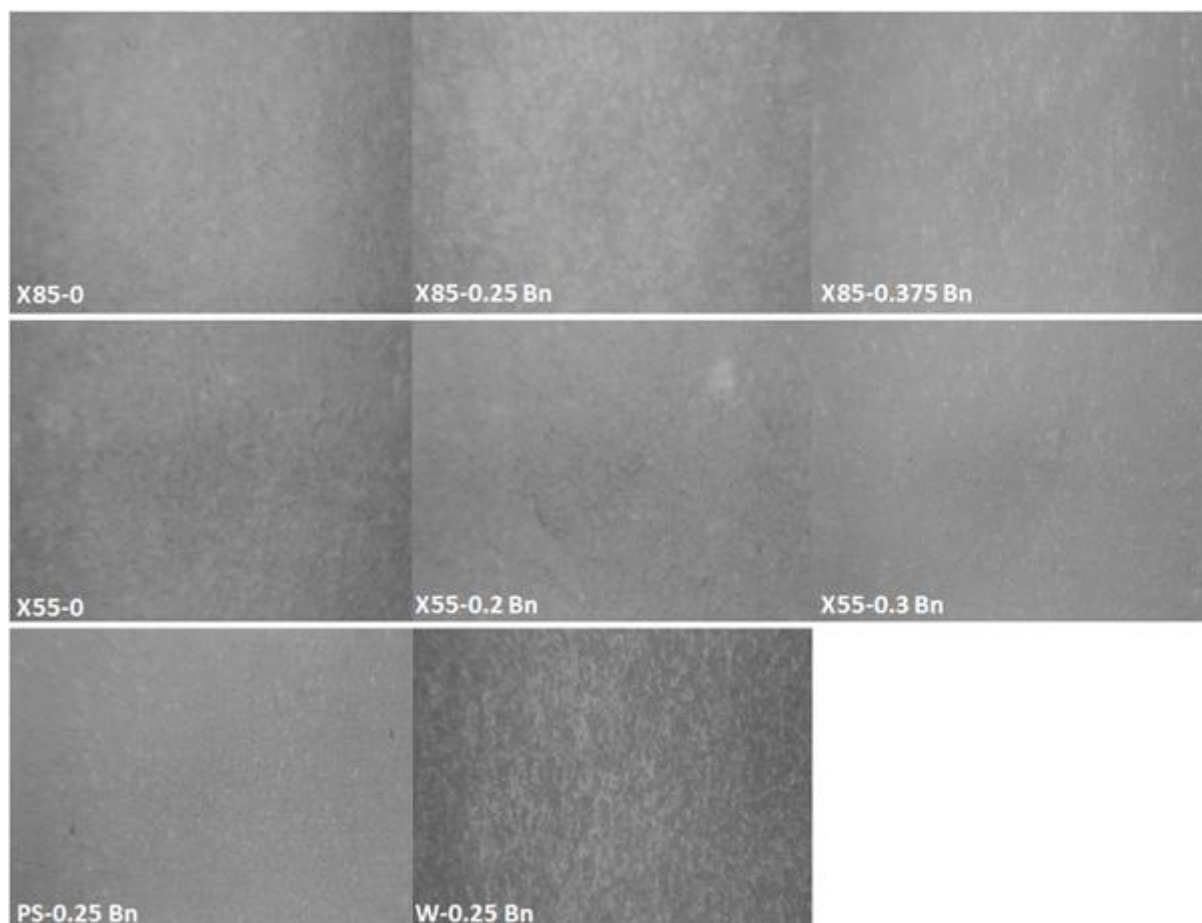


Figure 5: mottling tests of coatings based on benzylated starches, magnification 5x.

SEM

SEM images were produced to investigate the surface structure of the coatings. In Figure 6, the coatings in which benzylated X85 and X55 was used are shown at 5000X magnification. The coating with X85-0 is taken as a reference here. The course particles have a size of around 2 μm and the space between them is filled with fine particles. Some relief is visible; the surface is not completely flat. X85-0.25 shows an increase of fine particles compared to the reference coating with X85-0 and a decrease of cavities, which is in accordance to the detected porosity decrease. X85-0.375 is clearly more porous, which is also in agreement with the porosity measurement and has also less fine particles at the surface. The coating shows less relief in comparison to X85-0 and X85-0.25; fine and course particles are at the same level. This may be the result of fast immobilization or by reduced shrinkage of the coating during the drying process, normally caused by capillary forces [14,16], due to the high viscosity of the X85-0.375 solution. If this is true, the fine particles at the surface of X85-0 and X85-0.25 are the result of transport during the drying process and/or particle settling.

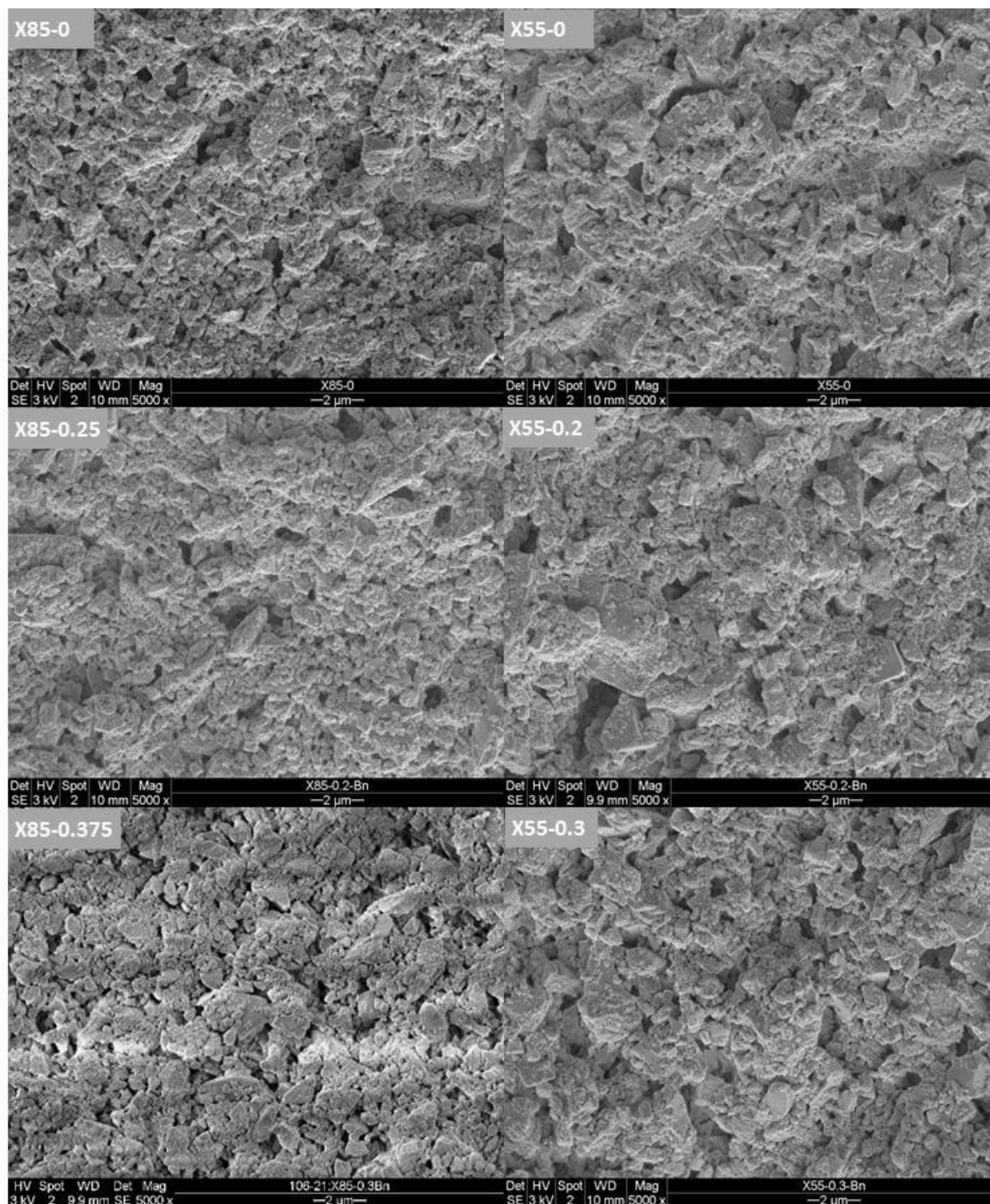


Figure 6: SEM images of coated papers using benzylated starches; magnification 5000X, bar = 2 µm.

If the coatings of the X55-series are compared to X85-0, then it can be seen that X55-0 has a lower porosity. X55-0.2 looks less porous but is in fact more porous than X85-0 according to the porosity measurement. The amount of visible fine particles for both X55-0 and X55-0.2 is higher compared to the X85-0 coating which could be explained by the low viscosity and subsequent postponed immobilization. Finally, if the X55-0.3 coating is observed, it can be seen that the porosity is higher

(as measured), but not as high as the X85-0.375 coating, there are not as much fine particles at the surface and the surface seems to have more height-differences. The difference in porosity of the coatings with PS-0.25 and W-0.25 was visible from the SEM-images, but is not shown here.

The observed structural differences may explain some results of the mottling tests. In the case of X55-0.3, the viscosity was lower than X85-0.375, which probably allowed the coating to settle/shrink somewhat. On the other hand, the also fast increasing viscosity at increasing concentration of this derivative may have resulted in increased porosity and permit improved ink reception. In addition, the difference in surface structure between X55-0.2 and X55-0.3 suggest that some roughness is needed for good printability, which is supported by known literature [37], and supports the statement that the surface energy or DS in this case is less important than rheological behavior. Finally, notice that there is no indication of 'sealing' by a starch film, but there are differences in the amount of fine particles that determine the coating porosity.

FTIR

The presence of starch has been linked to print mottle [25]. Therefore, the amount of starch at the coating interface was qualitatively determined using FTIR by comparing the ratios of the starch- and CaCO_3 peaks of coatings based on different starches. Consolidation and drying of coating formulations based on latex is described extensively in the literature [8,14-16,19,41]. Pan et. al [29] described transport of the aqueous phase and binder migration by defining a capillary number, Ca , see Equation 4:

$$Ca = \frac{W L \mu}{\gamma_l \rho R} \quad (\text{Equation 4})$$

Here, W is the initial drying rate, L is the characteristic length (coating thickness), μ is the viscosity, γ_l the surface tension of the aqueous phase, ρ the liquid phase density and R is a relative particle-pore-size ratio. The drying rate, coating layer thickness and pigment composition (R) were kept constant during this research to limit the number of variables. As stated earlier, it is hard to model starch based formulations due to continuous variation in temperature, solids content and viscosity of the continuous phase during the drying process. Nevertheless, according to Equation 4, migration should decrease when the Ca number increases, hence at increasing viscosity or decreasing liquid surface tension. The calculated ratios of the integrated starch- and CaCO_3 peaks are presented in Figure 7.

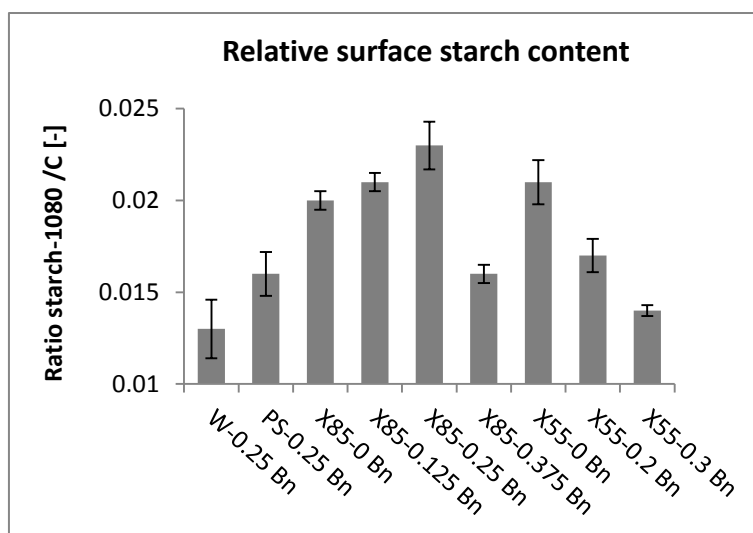


Figure 7: ratios of the peaks of CaCO_3 (700 cm^{-1}) and starch (1080 cm^{-1}) for various coatings

The most general observation from Figure 7 is that a higher starch viscosity leads to a lower starch- CaCO_3 peak ratio, which is in agreement with the prediction by the capillary number, Ca . For example: the viscosity of $\text{PS-0.25} < \text{W-0.25}$ and $\text{X85-0} < \text{X85-0.375}$ and $\text{X55-0} < \text{X55-0.3}$. According to the literature [18,29,42], a decreased viscosity should enhance migration while a decreased surface tension of the continuous phase decreases migration due to decreased capillary transport. Unfortunately, the surface tension of the starch solutions was not studied at drying conditions and any further modeling was unsuccessful. Attempts to relate the surface starch content (SSC) to different parameters did not yield reliable/significant correlations: SSC-log_η ($R^2 = 0.3$), $\text{SSC-film surface tension}$ ($R^2 = 0.29$), SSC-IGT dry pick ($R^2 = 0.57$) and SCC-porosity ($R^2 = 0.74$). Interestingly, for the latter correlation, SCC was proportional to the porosity: at a low porosity, SCC was low and vice versa, shown in Figure 8.

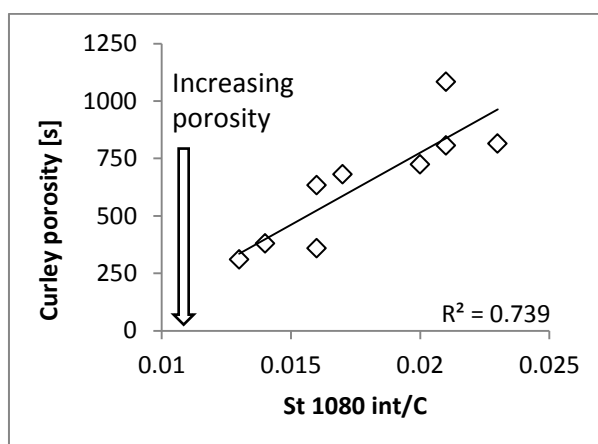


Figure 8: relation of surface starch content to coating porosity.

This effect could not clearly be explained, but it was established by SEM imaging that more fine particles are present at the surface at decreasing porosity while no starch could be observed. This either means that starch is poorly visible by SEM or that the FTIR measurement is influenced by the surface porosity. On the other hand, if a uniform starch-film is formed around every pigment particle, this implies that the amount of starch at the surface is determined by the number of particles at the surface, which is higher at lower porosity.

Unfortunately, the FTIR method is not (yet) quantitative, but illustrates a relative amount of starch at the coating surface between 0.5 and 2 μm , depending on the IR wavelength and material. The decreased surface starch content is most likely due to increased viscosity.

Conclusion

Nine paper coating formulations were prepared, using oxidized and benzylated waxy potato starch derivatives. They were applied on paper to investigate the hypothesis that hydrophobic substitution of starch is necessary to successfully replace SBR latex as a binding agent in paper coatings. Formulation- and final product properties were characterized. Dewatering of the formulations did not exceed 15 g/m^2 which is considered low compared to 80 g/m^2 for latex based coatings. Reduced dewatering alone implies that less starch from underlying layers would migrate during application of the top-layer due to a lower amount of water present. The formulation viscosity is largely determined by the starch solutions viscosity which is in turn controlled by hydrophobic content and the level of oxidation. Standard models to predict the suspension viscosity as a function of solids content could not be applied since the solution viscosity is a function of the starch concentration. The consolidation process is a capillary process and is thus governed by the viscosity and the surface tension of the aqueous phase. Increased viscosity at increasing starch concentrations seems to be beneficial, within limits, for the development of a well performing coating structure; increased porosity and decreased amount of fine particles at the coating surface. Insufficient information about the starch liquid surface tension at application conditions hinders modeling of the drying behavior by the capillary number.

The properties of the coating surfaces were studied with a variety of techniques. This yielded valuable information about the coating structure and print mottle, but it proved difficult to describe coating performance as a function of oxidation and benzylation of waxy potato starch. The differences between the starches result in a variety of phenomena which do not directly correlate. The rheological behavior of the starch solutions seems to be the best indication of the development

of the coating structure. The relation between starch film surface tension and print mottle could not be established due to structural differences of the coating surfaces. On the other hand, the starches of the coatings that performed best (PS-0.25, X55-0.3 and X85-0.375) did have a total surface tension close to that of a commercial latex (43 mN/m) used by the paper industry. In addition, these coatings had in common that (a) the amount of fine particles at the coating surface was low (SEM images), (b) the porosity was high and (c) the surface starch content was relatively low (FTIR). However, from these experiments it cannot be concluded that the coating performance would improve if a non-hydrophobized starch product could somehow generate a similar coating morphology. On the other hand, the improved mottling behavior and good bonding strength suggest that optimization of the degree of oxidation and benzylolation may very well lead to a well-tuned set of properties favoring starch over latex as a coating binder. Besides benzylolation, it would be interesting to evaluate the effect of other hydrophobic substituents on the behavior of oxidized starches.

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Chapter 4

The effect of oxidation and 1-butoxy-2-hydroxypropylation on the properties of waxy potato starch

Abstract

Native and oxidized waxy potato starch was hydrophobized using butyl glycidyl ether (BGE), forming 1-butoxy-2-hydroxypropyl (BHP) derivatives. The aim was to produce starch derivatives suitable for replacing styrene butadiene rubber (SBR) latex in paper coatings. The products were characterized on molar substitution (MS), pasting behavior, solution viscosity as a function of concentration and temperature and dry film surface tension. The reaction efficiency was 70 % on average, which is similar to the same reaction with acid degraded corn starch, reported in the literature. The RVA peak-viscosity increased ten to twenty times due to the introduction of BHP groups. The RVA end-viscosity of native waxy potato starch, hydrophobized with BHP groups, increased almost four times. However, for oxidized products with BHP groups, the viscosity was similar to the starting materials. Starch solutions prepared by more severe and prolonged mixing for a longer time at higher temperature than RVA, showed a decrease of the viscosity compared to the RVA end-viscosity. The molecular weight of the samples did not show significant changes. No thermo responsive rheological behavior was detected, in contradiction to what was expected from literature reports on BHP starch and despite the fact that hydrophobic interactions were detected. It was concluded that hydrophobic waxy potato starch derivatives may be used in paper coatings.

Keywords: *waxy potato starch, hydrophobic modification, butyl hydroxypropyl, viscosity, surface tension*

Introduction

Bio-based products may provide economically favorable opportunities to replace oil based products by renewable resources. Starch is the subject of numerous research projects in pursuit of

this goal since it is available in large quantities at low cost. Starch is a polysaccharide composed of α (1-4) and α (1-6) linked D-glucose monomers, also referred to as anhydro glucose monomers (AGU). Starch molecules which are predominantly linear and have mainly α (1-4) bonds are called amylose while the branched type, with about 5 % α (1-6) linkages, is called amylopectine.

The aim of this research was to prepare hydrophobic starch derivatives to replace SBR latex in paper coatings. High quality paper coatings are applied to improve the visual quality of paper for posters and glossy magazines. By means of a process called blade-coating, three subsequent layers are applied: a pre-, mid- and top coat. The thickness of each layer is around 10 μm and is applied at 2000 m/min or more which makes the formulation rheology an important property. In addition, the solids content of the coating formulation should be as high as possible to cut drying costs. During the drying process, the final coating properties are developed [1-4]. For the printing-process, often web-offset printing for this paper quality, the interaction between the coating and the ink is important. Replacement of SBR latex by oxidized starches can be achieved already in the pre- and mid coat; however, for the top-coat printability problems have been related to starch and its hydrophilic character in particular [5-10]. Therefore, hydrophobic modification was applied in an attempt to overcome these problems.

In earlier research, benzylation of waxy potato starch was performed by our group, which yielded hydrophobized waxy potato starch derivatives with improved coating properties, see Chapter 2 and Chapter 3. Unfortunately, benzyl chloride is suspected to be carcinogenic [11]. Moreover, up to 30% of the benzyl chloride is converted to benzyl alcohol and a minor amount of dibenzyl ether in side-reactions [12-14]. Furthermore, a high degree of benzylation in combination with high level of oxidation yielded products that were sometimes badly filterable, see Chapter 2. The use of a different reagent might overcome some of these drawbacks.

Other hydrophobic substituents are reported in the literature [15-21]. Alkyl halide reagents produce HCl during the reaction, which must to be neutralized to allow the reaction to proceed to completion. In addition, a starch ester could degrade during the application process; a typical coating formulation has a pH of 8.5 – 9 [22] and thus saponification might occur. Hydrophobic starch ethers are therefore preferred. Epoxide reagents have the advantage that the deprotonating agent which activates the starch is a catalyst so no additional sodium hydroxide needs to be added during the reaction. Reports of reactions with starch and epoxides up to C18 exist in the literature [15,16,21,23-25]. The general reaction scheme of starch with an epoxide is shown in Figure 1.

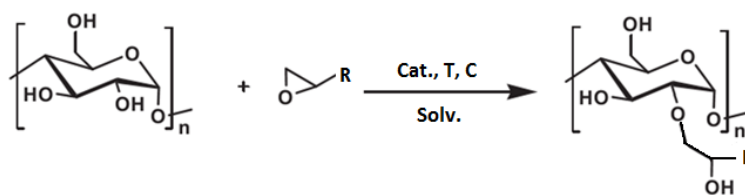


Figure 1: schematic reaction scheme of starch with an epoxide.

Especially reactions with long carbon chain epoxide reagents were performed using quite rigorous conditions (about 140 °C) [21], resulting in granule disruption and complex, expensive product work-up procedures when the by-products of the reaction are not allowed in the end product. Slurry reactions in water are therefore preferred by the industry [26]. Huijbrechts et. al. [23,27] prepared hydrophobic maize starch in a slurry reaction using allyl glycidyl ether (AGE) to form allyl-hydroxypropyl (AHP) starch while leaving the starch granules intact. The viscosity of AHP starch increased. Starch hydrophobized with Octenyl Succinic Anhydride (OSA) [28,29] also showed increased viscosity. Benzylated native starches showed a decreased viscosity [30], but formed a dispersion which was not reported for AHP and OSA starches. Generally, increased hydrophobic content of water soluble polymers results in a viscosity increase [31]. An interesting report was found on a starch ether similar to AHP-starch; butyl hydroxypropyl (BHP) starch [32]. It was reported that the BHP groups introduced a lower critical solution temperature (LCST) to the starch, which may be an interesting property within the context of this paper coating focused research. LCST was not reported for benzylated starches or the AHP starch.

In the current research, BHP-starches were prepared by reacting Butyl Glycidyl Ether (BGE) with native waxy potato starch and two grades of commercially available oxidized waxy potato starch, i.e. Perfectafilm X85 and X55, to yield a granular product. The reaction efficiency was determined by GC analysis of isopropyl iodide after destruction in hydrogen iodide and in situ extraction in p-xylene. NMR and FTIR spectroscopy were used to establish that the new product was indeed formed. Pasting behavior was studied by Rapid Visco Analysis (RVA). Viscosity as a function of degree of oxidation, MS, concentration and temperature was measured. The surface tension of cast and dried starch films was measured by contact angle measurement.

Materials and methods

Materials used

Native waxy potato starch and two grades of commercially available oxidized waxy potato starch, Perfectafilm X85 and -X55, were kindly supplied by AVEBE Foxhol, The Netherlands, and used as received. Butyl glycidyl ether (BGE), 95%, was obtained from Sigma and used as received. Sodium hydroxide and sodium sulphate were obtained from Sigma. Adipic acid (analytical grade, Sigma), HI 57%, stabilized (Sigma) and p-Xylene pro analysis (Sigma) were used. 2-iodopropane (pro analysis, Sigma) was used for calibration.

Synthesis

Reactions were performed according to Berkhout and Guns [30], with some modifications. Starch (100 g dry at 15 %W moisture) was suspended in 200 g/l sodium sulphate solution to obtain a 38 %W suspension, based on starch dry solids in water. Three grams of sodium hydroxide (1,1 M) per mole AGU was added drop-wise to the suspension (35°C) while vigorously stirring. BGE (for MS 0.2 or 0.3) was added and the mixture was heated to 50°C. MS is the molar substitution, or the moles of substituent per mole AGU. Theoretically, MS can be higher than 3 since the product introduces a new hydroxyl group. The reaction was allowed to continue for 48h. After 48h the reaction mixture was neutralized to pH 5-6 with 1M HCl. The suspension was filtered over a size 3 Duran glass filter and re-suspended 3 times in 200 ml of water and filtered and 3 times with 200 ml of acetone. The obtained product was allowed to dry at 50°C for a minimum of 24 hours. Samples, taken to monitor the reaction were treated likewise. Samples were named after their starting material, Waxy (W), X85 or X55 and the MS: 0.2 or 0.3, for example W-0.2.

Molar substitution

The MS of BHP groups was determined according to Hodges [33], Morgan [34] and Lortz [35]. Ether bonds are cleaved and iodated, releasing 2-iodopropane from the propyl group of the BHP substituent and is extracted in situ in p-xylene. Starch, 40 – 50 mg, was weighed accurately into a 4 ml Thermo Scientific Reacti-Vial with an appropriate septum, together with 120 mg of adipic acid, 2 ml of hydrogen iodide, 57 %W, and 2,00 ml p-xylene pro analysis. The vial was placed in a heating mantle at 150 °C for 2h and stirred with a magnet stirrer at 900 rpm. After the reaction, the vials

were allowed to cool to room temperature and the organic phase was filtered over a 0.45 μm PTFE filter into a GC-vial. The GC spectrum was recorded on an Agilent 6890 series, equipped with a HP1 methylsiloxane column, type HP1909Z-433 and FID detector. The injection volume was 1 μl , the injection temperature was 250 °C and the starting temperature of the column was 40°C for 2 minutes. The temperature was increased at 1°C/min until 65°C after which the temperature was raised to 250°C. The carrier gas was helium; the split flow ratio was 100:1. The flow rate of the carrier gas was 0.8 ml/min. The system was calibrated using 2-iodopropane, 99% pure, in p-xylene ($R^2 > 0.999$). The retention time of 2-iodopropane was 4.47 minutes.

NMR

^1H -NMR spectra were recorded in D_2O on a AS400 MHz NMR spectrometer. BHP starch, 20 mg, was hydrolyzed in 1 ml 0,1 M HCl for 2 hours and subsequently freeze-dried and re-dissolved in D_2O and freeze-dried two more times. Finally, 1 ml of D_2O was added and the sample was transferred into an NMR tube. Spectra were recorded with 128 repetitions and a relaxation delay of 1 second.

FTIR

FTIR spectra of the starch products were recorded in KBr on a Bruker tensor 27 machine. The spectra were recorded from 400 – 3500 cm^{-1} with a resolution of 4 cm^{-1} and 16 repetitions.

Pasting properties

Gelatinization behavior of the products was recorded on a Newport Scientific Pty Ltd, Australia RVA-super4 Rapid Visco Analyzer. The samples were prepared at 20 W% dry solids of starch; the native starch products were prepared at 5 W%. The heating and cooling cycle, also used by others [27], comprised of rapid stirring at 960 rpm for 10 seconds and subsequently 160 rpm for the remaining run time. Before heating, the sample was stirred for 2 minutes at 30°C. Next, the temperature profile was set to increase from 30 to 90 °C at 15°C/min. After a holding time of 4 minutes at 90°C, the sample was cooled back to 30 °C at 15°C/min. The measurement was allowed to proceed for 8 more minutes at 30°C.

Solution preparation

Solutions of starch were prepared by stirring 100 grams of a 15 %W (native) or 35 %W (oxidezed) starch suspension in a hot-water-bath at 95°C for 30 minutes at 600 rpm with a six-hole lab-stirrer. Dilutions were prepared by adding warm demi water (>50°C) followed by homogenization. In case of foaming of the starch solution the stirrer speed and cooking time were adjusted if necessary. Samples above 10 %W were stored at 50 °C until measurement (within 2 hours) to prevent retrogradation.

Solution viscosity: effect of concentration and temperature

The viscosity of starch solutions was determined on a Haacke III rheometer using a cone – plate configuration at 20°C. The gap distance (d) was 0.105 mm. The cone diameter was 60.000 mm and the angle was 2°. Two ml of a starch solution was used and measured at 10 s⁻¹ shear rate. The viscosity as a function of temperature was determined between 20 and 70°C at a constant shear rate of 10 s⁻¹. After a temperature increase, the viscosity was averaged over 5 seconds after 30 seconds of stabilizing.

Molecular weight

The molecular weight was determined on an Agilent Technologies 1260 infinity GPC-SEC system with DMSO containing 5 g/l LiBr to enhance gelatinization, according to Ciric et. al. [36]. The concentration of starch was set to 2 mg/ml. First, the starch was gelatinized in water and freeze-dried after which the sample was stirred in DMSO at room temperature overnight, heated and stirred at 95°C for 2 hours and filtered over a 0.45 µm filter. The GPC system was equipped with a PFG guard-column and a G1362A 1260 RID Agilent Technologies RI detector. Samples were injected twice (1 µl) at a flowrate of 0.5 ml/min. The system was calibrated with pullulan 800.

UV-emission spectroscopy

The UV emission spectrum of pyrene in starch solutions was recorded on a Fluorolog 3-22 fluorescence machine according to known literature [37]. The excitation wavelength was 334 nm at a slit width of 8 nm and the spectrum was recorded from 350-420 nm at a slit width of 2 nm. The ratio

between peak 1 (373 nm) and 3 (384 nm) was calculated. A concentration of 2 μM pyrene was realized by adding $8 \cdot 10^{-3}$ W% pyrene in methanol to the samples.

Contact angle measurement

Starch films for contact angle measurement were prepared from a 3 W% solution. The solutions were dropped onto a 2 * 5 cm (L*B) glass plate and dried at ambient conditions for more than 48h. The surface energy was determined on a Dataphysics OCA 15 machine according to the method of Owens and Wendt [38]. Three liquids were applied; water, formamide (Sigma) and diiodomethane (Sigma). The contact angle was averaged over 2 seconds at stable contact angle. In some cases, ethylene glycol was used to replace water if the contact angle would not stabilize. Ten repetitions per liquid per starch film were made over two samples (so 2 * 5 = 10 repetitions).

Results and discussion

Waxy potato starch and two grades of commercially available grades of oxidized waxy potato starch, Perfectafilm X85 and X55, were reacted with BGE under mild reaction conditions. The reaction scheme is displayed in Figure 2. A granular product was obtained and characterized on reaction efficiency, pasting behavior, viscosity, hydrophobic interactions and dry film surface tension.

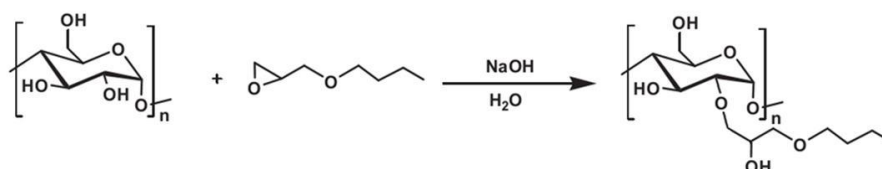


Figure 2: reaction scheme of BGE with starch.

Synthesis, efficiency and molecular composition

The reaction proceeded without mixing problems; no coagulation was observed. The color of the reaction mixture with oxidized starches was yellow towards the end of the reaction. Upon neutralization, coloring would decrease almost completely upon washing with water and acetone. Native waxy potato starch and X85 at $MS_{\text{max}} = 0.2$ showed no filtration difficulties. Starch granules from the other products seemed to swell somewhat during the washing process and formed a gel-

like substance. However, all products were filterable and yielded white to slightly yellow powders at increasing degree of oxidation. The reaction of starch with BGE proceeded as a pseudo zero-order. At increased BGE concentration, the reaction rate would still be the same, indicating that the reaction rate is limited by the solubility of BGE in water. Some typical reaction profiles are shown in Figure 3. Table 1 shows the efficiencies of all reactions, which were all in the range of 63 - 77%, which is generally less than reported in the literature for long chain epoxides [21], but comparable to values reported by Ju et. al. [32]. At the highest degree of oxidation (X55), the reaction efficiency was lowest. It is not clear if in this case the efficiency decrease is due to the degree of oxidation or maybe wash-out of product; some foaming was observed during the washing process. The reaction reached the maximum MS between 24-48 hours, depending on the MS_{max} .

Sample	MS_{max} -BHP	MS-GC	Efficiency, %
W-0.2	0.2	0.15	74.9
X85-0.2	0.2	0.15	73.7
X85-0.3	0.3	0.23	76.8
X55-0.2	0.2	0.13	63.8
X55-0.3	0.3	0.19	63.7

Table 1: reaction efficiencies of BHP starch products.

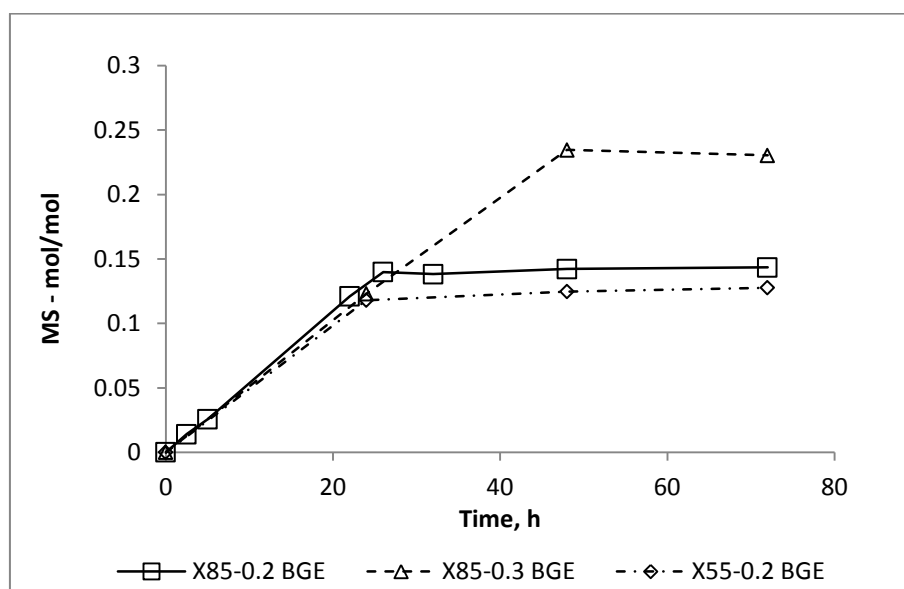


Figure 3: typical MS-build-in curves of BGE.

In the NMR spectrum, shown in Figure 4, the peaks of the starch-ring protons appear between 3 and 4 ppm. The anomeric protons are the doublets at 4.5 and 5.1 ppm (α - and β anomers, respectively) [39]; the acid hydrolysis allows ring-opening and -closing of the glucose monomer.

Therefore, the anomeric protons can assume both α - and β configuration. The small peak at approx. 5.3 ppm may either be a shifted anomer due to BHP substitution at C2 [40] or an anomer at an AGU with an α (1-6) glycosidic link that was stabilized by the presence of a BHP group [41]. The CH_3 of the butyl group shows a triplet at 0.75 ppm, the two CH_2 groups appear as sextets and the CH_2 next to the oxygen lies at 3 ppm but the intensity is much lower. The protons of the glycidyl-part overlap with the ring-protons of the starch and are therefore not visible in the spectrum. The emerging small peak at 3.8 ppm could not be assigned. To confirm that a reaction took place, starch was mixed with BGE and brought to reaction conditions without NaOH as a catalyst. The mixture was worked-up in a similar manner as before and an NMR spectrum was recorded. The BHP peaks were not visible in this spectrum and therefore it is concluded that a new product was indeed formed in the cases where the catalyst was added.

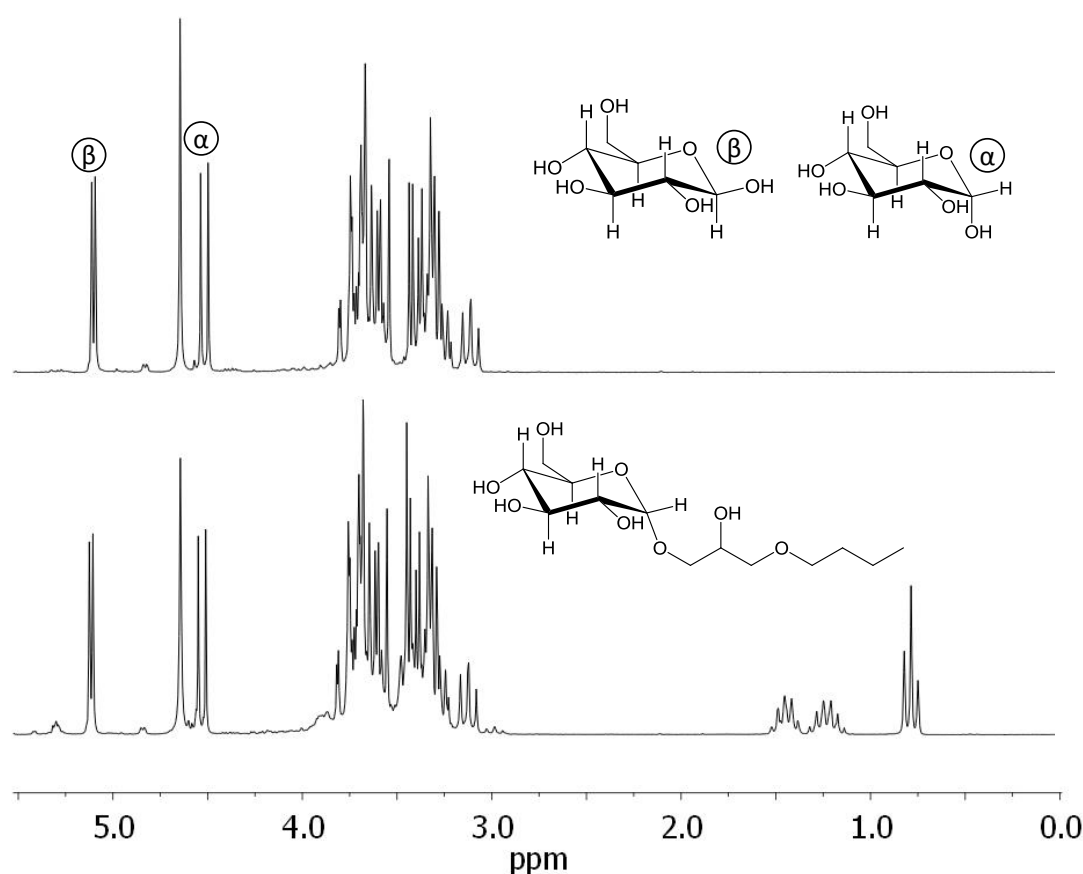


Figure 4: NMR spectrum of X85-0 (upper) and X85-0.3 BHP (lower).

FTIR

The FTIR spectrum in Figure 5 shows an increased absorbance from 2800-3000 cm^{-1} . These wavelengths are associated with CH_2 and CH_3 stretch-vibrations, which is ascribed to the BHP-group.

The increased peak intensity indicates that the amount of alkane-like material in the sample increases; another indication that a new product was indeed formed during the reaction. In addition, the increased intensity of the peak at 1016 cm^{-1} indicates increased ether C-O stretch vibrations. Per BHP unit, two ether bonds are added to the structure; one is formed by the reaction at the AGU and one from the BHP unit itself (see Figure 2).

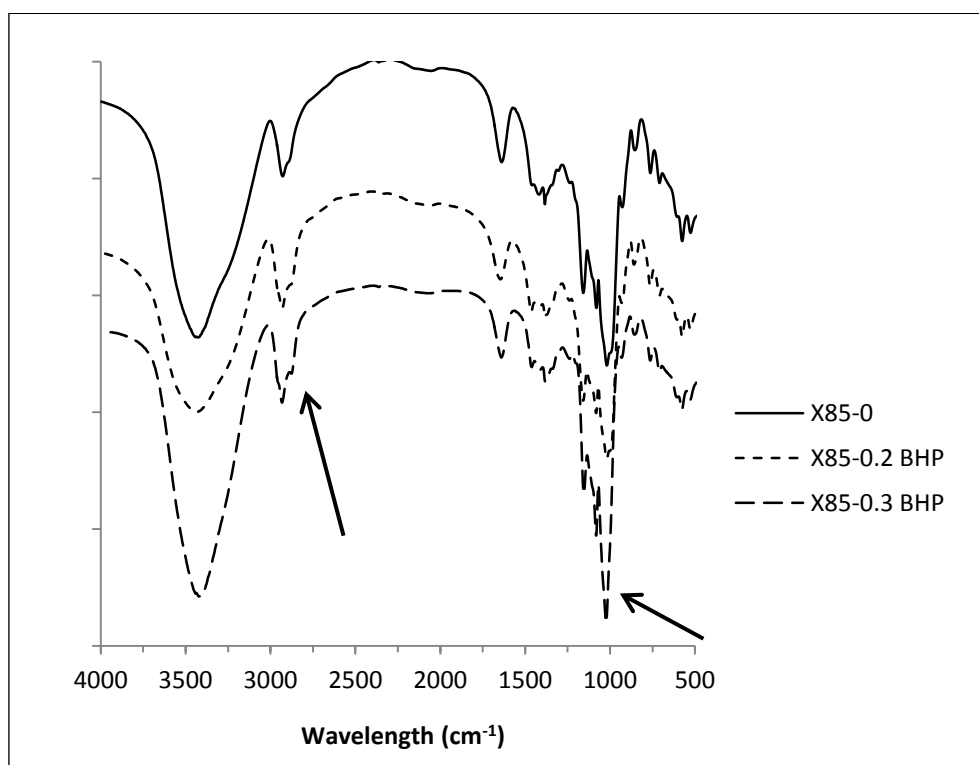


Figure 5: FTIR spectra of X85-0 and its BHP starches.

Pasting behavior

The pasting behavior of starch is an important characteristic, especially in relation to industrial processing. For most applications starch is used in an aqueous 'solution': it is first dispersed in water and then cooked under appropriate conditions. The pasting behavior gives an indication for the requirements of the cooking conditions and -equipment. The pasting process of starch is initiated by gelatinization of the starch granules and granular swelling by water up take. Swelling of the starch granules causes the viscosity to increase fast and starts decreasing when the granules start to disintegrate. Upon cooling the viscosity increases again. Changes in the pasting behavior indicate changes in the molecular structure of (modified) starch.

The BHP starches display different in pasting behavior compared to the starting materials, as can be seen in Table 2 and Figure 6. To validate the effect of the reaction conditions to the pasting

behavior of the starting material, a control-reaction was performed, without the addition of BGE. As can be observed from Table 2, this product, X85-control, had a peak viscosity comparable to the starting material, X85-0 (787 vs. 600 mPa.s). After modification, the viscosity peak of all starting materials increased considerably. For example X85-0.2 has a peak viscosity of 6500 mPa.s, which is ten times as high as X85-0. The viscosity of native waxy potato starch after modification was higher in all stages after gelatinization started. Products based on oxidized starches showed no major changes in the hot paste- and end-viscosity. Buwalda et al. [42] suggested that hydrophobic chains shorter than ten carbon atoms substituted on a starch molecule are too short to cause a viscosity increase due to carbon chain interaction.

Sample	MS-th	P-onset (°C)	P-temp (°C)	Viscosity (mPa.s)				
				Peak	Hot paste	Final paste	Breakdown	Setback
Waxy^a	0	70.0	83.2	2860	1340	1510	1520	170
Waxy^a	0.2	71.6	79.4	20280	4650	5400	15630	750
X85	0	65.6	72.5	600	65	260	535	195
X85	Control	62.3	74.1	787	40	164	747	124
X85	0.2	63.5	74.8	6500	48	200	6452	152
X85	0.3	66.8	75.5	6520	82	290	6438	208
X55	0	60.8	66.1	210	26	84	184	58
X55	0.2	60.2	69.5	5100	22	64	5078	42
X55	0.3	60.1	71.3	4550	28	80	4522	52

Table 2: RVA characteristics of BHP starch products.

^{a)} Waxy starch products were pasted at 5 %W starch content, oxidized products at 20 %W.

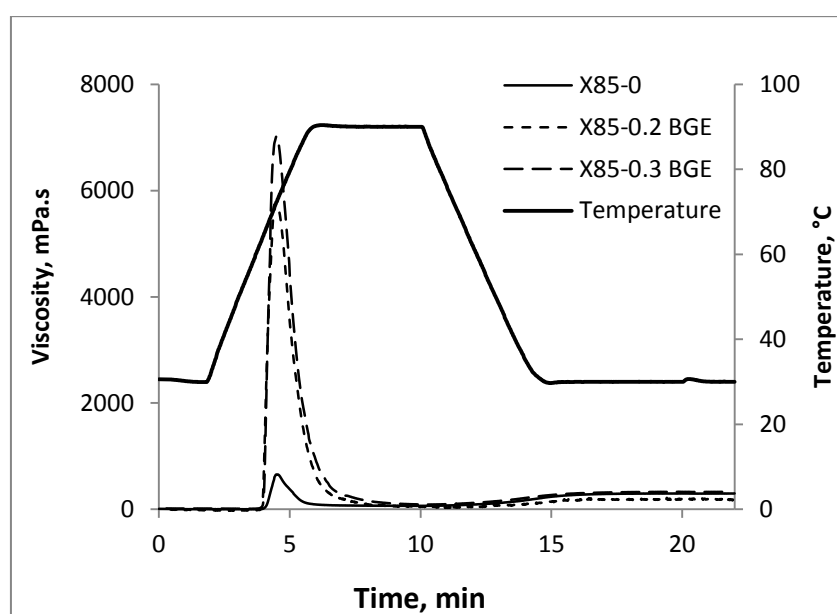


Figure 6: typical RVA profiles of BHP starch samples.

Solution viscosity: concentration and temperature dependence

The cooked starch pastes were diluted in a series from 35 %W – 1 %W (waxy starch 15 – 1 %W) to determine the effect of concentration and temperature on the viscosity. Figure 7 shows that the viscosity of oxidized starches decrease at increasing MS- BHP, in contrast to what was observed from the RVA measurements. In addition, the viscosity of Waxy potato starch with MS = 0.2, not shown, did not change at all compared to W-0, while a major increase was observed from the RVA.

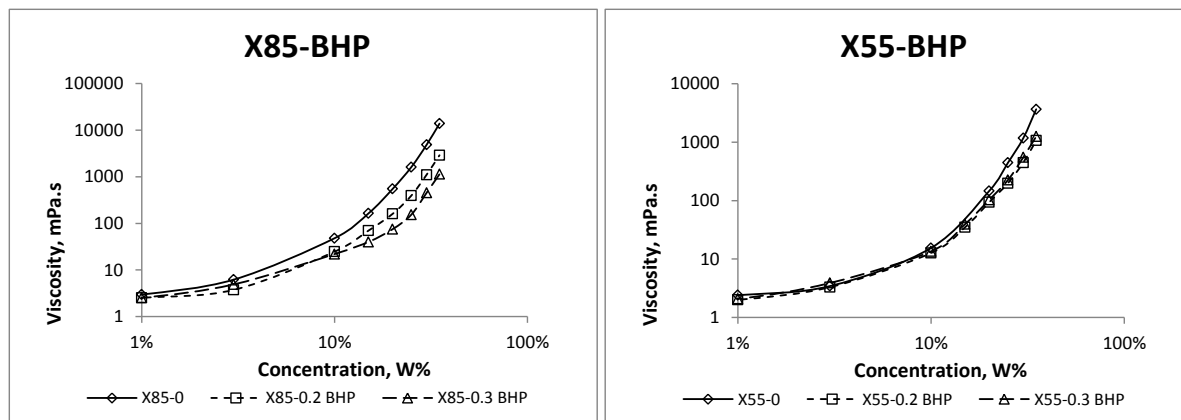


Figure 7: viscosity profiles of BHP derivatives based on oxidized waxy potato starch.

The difference may be explained by the difference in cooking methods [43]. RVA measurements were performed at 20 %W starch solids content, while here the concentration was 35 %W. The increased solids content causes increased shear between the starch granules, enhancing the pasting process. Moreover, the energy input from stirring in this case was higher compared to the RVA measurement. In Chapter 2, it was shown that benzyl groups at a degree of substitution (DS) = 0.375 increased the viscosity of X85 to over 1 million mPa.s at 35 %W. In addition, the solution of W-0.2 BHP was clear while benzylated native waxy potato starch yielded a dispersion.

Ju et al. [32] reported an LCST at 33 °C for acid degraded corn starch at $MS_{BHP} = 0.3$. The (oxidized) waxy potato starch derivatives prepared for this research, however, did not show such behavior. The solution remained clear over the whole temperature range. Waxy potato starch and X55 behaved similarly to the samples of X85, shown in Figure 8 and are not discussed further. The differences in behavior between the products here and those reported by Ju et. al. may be partly explained by the difference in the starch starting material: oxidized waxy potato starch vs. acid degraded corn starch. The introduction of carbonyl- and carboxyl groups by the hypochlorite oxidation process gives the starch different properties than acid degraded starch, the latter retrogradates much faster. In addition, the composition of corn starch is different from potato starch, for instance, the latter does

not contain fat or protein. Another explanation may be the preparation method: aqueous slurry reaction for waxy potato vs. solution reaction in DMSO for corn starch. Finally, in this research the MS was max. 0.3 while Ju et al. prepared starches at MS > 0.3. According to Buwalda et al. [42] aggregation due to hydrophobic interaction of a substituent on the starch backbone does not take place up to a carbon chain length of ten carbon atoms, but that does not explain the effect detected by Ju et al.

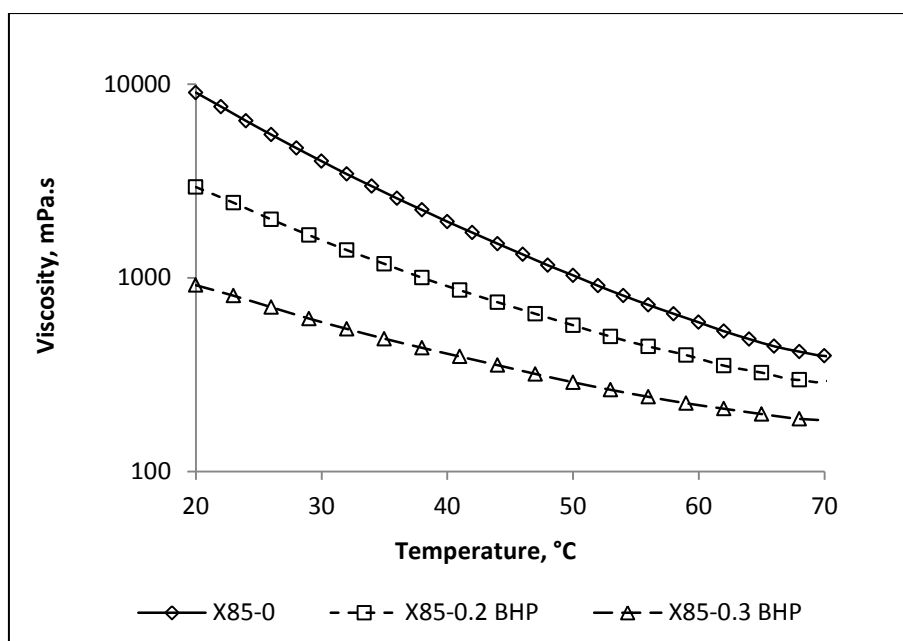


Figure 8: viscosity of BHP derivatives of X85 as a function of temperature at 35 %W.

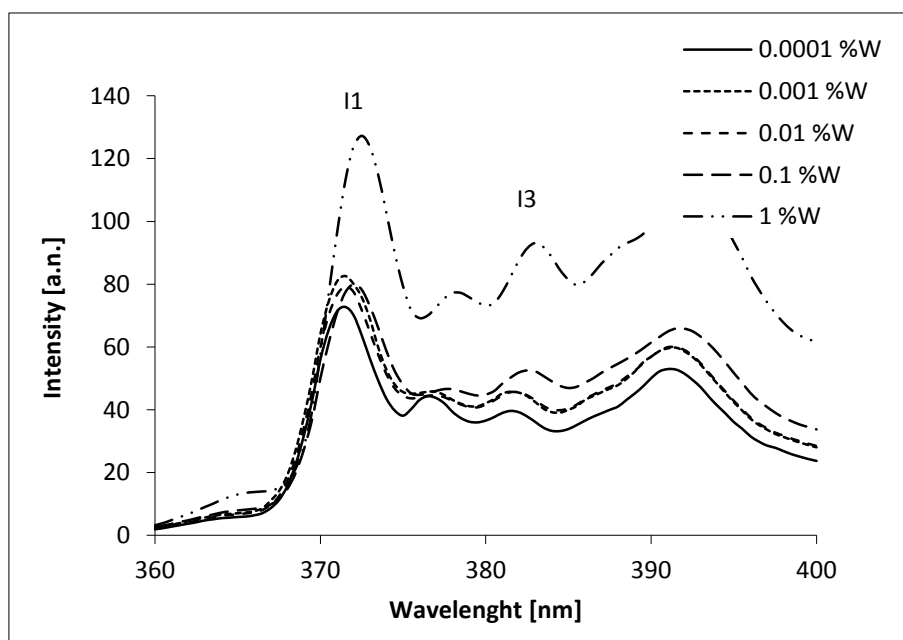


Figure 9: UV emission spectrum of pyrene with X85-0.3 BHP, arbitrary numbers

Hydrophobic interactions were detected by UV emission-spectrometry using pyrene as a hydrophobic probe. The emission spectrum of pyrene changes when its hydrophobic environment changes and the ratio of the intensity of peak 1 and 3 is used to indicate this change [37]. Figure 9 shows the pyrene emission spectrum with X85-0.3.

The ratio I₁/I₃ for X85-0.3 shifted from 1.85 to 1.35 between 0.001 and 0.1 %W, which indicates hydrophobic interaction. The spectrum of X85-0 did not show this trend. Concentrations higher than 1 %W were not taken into account since the solution viscosity increased and the clarity decreased somewhat which may compromise proper measurement. In addition, the molecular weight of the modified starch products, determined by GPC-SEC, did not change significantly at increasing MS-BHP. At MS = 0.2 it was a few percent lower than the starting material and at MS = 0.3 it was somewhat higher. It was concluded that the measured decreasing viscosity at increasing MS-BHP, for example for the series X85-0, X85-0.2 and X85-0.3, could not be accounted for by the molecular weight distribution or by hydrophobic interactions.

Surface tension

The surface tension of the starch films was determined in order to evaluate the effect of BHP groups on the surface properties. From Figure 10 it can be observed that the surface tension drops considerably at the lowest MS-BHP and the relative contribution of disperse forces increases, compared to the starting materials. However, at increasing MS these trends do not continue. The surface tension of the W-0.2 is slightly lower than the other BHP starches with a high disperse contribution. More importantly, the film surface tension of the oxidized derivatives matches with that of a film of commercial SBR latex, Styronal D517, which was prepared for comparison. The surface tension of a substance can be used to indicate the work of adhesion, W_{adh} , between two materials by means of the Dupré-equation, see Equation 1.

$$W_{adh} = \gamma_{S_1} + \gamma_{S_2} - \gamma_{S_1 S_2} \approx 2 \left[\left(\gamma_{S_1}^d \gamma_{S_2}^d \right)^{1/2} + \left(\gamma_{S_1}^p \gamma_{S_2}^p \right)^{1/2} \right] \quad (\text{Equation 1})$$

W_{adh} is the work required to separate surface S_1 and S_2 , γ is the surface tension, the superscripts 'd' and 'p' represent the disperse and polar contributions to the total surface tension. At $W_{adh} > 0$ adhesion takes place. In fact, the surfaces do not necessarily need to be two solids, but may be any combination: solid-solid, solid-liquid, solid-gas, liquid-liquid, etcetera [44]. Literature values for the surface tension, disperse (D), polar (P) and total (T=D+P) of cellulose (40^D, 18.8^P, 58.8^T mN/m; [45,46]), CaCO₃ (54.5^D, 153.4^P, 207.9^T mN/m; [47]) and water (21.8^D, 51^P, 72.8^T mN/m; [44]) were used to calculate the change in W_{adh} for starch-cellulose, starch-CaCO₃ and the energy of separation

upon submerging in water according to van Krevelen [44]. The calculations showed a decrease in W_{adh} between the hydrophobized starches towards both cellulose and $CaCO_3$. In addition, a lower water sensitivity was predicted which means that the starch should show a decreased tendency to migrate during coating application or during printing by, for example, wet offset printing [22] in which water is used to distinguish between areas with and without ink.

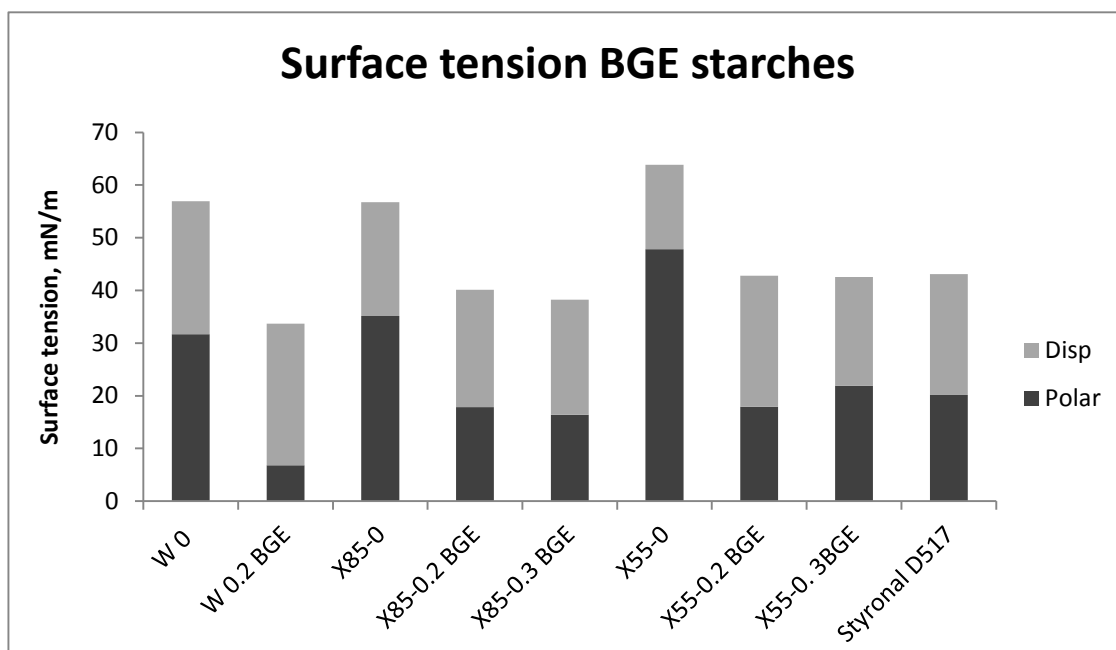


Figure 10: surface tension of BHP starches according to OWRK.

Conclusion

Eight different products based on waxy potato starch were prepared and characterized to evaluate the applicability in paper coatings for latex replacement. The reaction was pseudo zero-order in BGE. The RVA diagram of W-0.2 showed a clear increase of the peak- and end viscosity compared to native waxy potato starch. Hydrophobized derivatives based on oxidized waxy potato starch showed the increased peak viscosity after reaction with BGE, but no change in the end viscosity. The solution viscosity of all products, prepared by cooking at higher temperature for a longer period, higher concentration and higher mechanical input from stirring, was lower than expected, based on RVA measurements. The decreased viscosity could not be explained by the molecular weight distribution or by the presence of hydrophobic interactions, which was established by UV spectroscopy. Thermo responsive behavior was not observed for these products and also in the literature, some contradiction was found regarding this subject. The surface tension of the dry films of BHP starches dropped considerably to a value comparable to that of a film prepared from commercially available latex. Despite the fact that the decreased viscosity cannot satisfactory be

explained the prepared products provide an interesting opportunity to investigate the effects of their properties on the paper coating process.

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Chapter 5

The use of oxidized and 1-butoxy-2-hydroxypropylated waxy potato starch in paper coating.

Abstract

Waxy potato starches with a varying level of oxidation and 1-butoxy-2-hydroxypropyl (BHP) substitution were used as replacements for styrene butadiene rubber (SBR) latex in paper coatings. The formulation rheology was measured using three different techniques to investigate the viscosity in a 30 to 10^6 s^{-1} range of shear rates. The viscosity of BHP starches decreased compared to the starting materials, but the shear thinning behavior was unaffected. Formulations were applied on paper by means of a lab-scale blade-coating machine. A series of standard paper tests were carried out to evaluate the effect of hydrophobic groups on product performance. The ink distribution became more regular by the introduction of BHP groups and resembled that of a latex based coating. In addition, it was shown by using FTIR that the starch content in the coating surface is decreased when hydrophobic starch is used. SEM imaging revealed that a combination of oxidation and hydrophobic modification with BHP groups of waxy potato starch results in a coating structure more similar to a latex based coating than that of starches without BHP groups. The porosity of the coating seems to be less important than the surface structure.

Keywords: *waxy potato starch, oxidized, butyl hydroxypropyl, paper coating, rheology, surface properties, migration*

Introduction

Replacement of polymers based on fossil oil by materials from renewable resources like starch has gained interest from the industry due to rising raw material (oil) prices and increased consumer awareness about environmental issues. Simply replacing an oil based material directly by a natural product is often impossible due to differences in material properties, unfavorable economics or

both. Added functionality, however, may increase the economic value of materials from renewable resources.

In Chapter 2 and Chapter 4 the functionalization of waxy potato starch was reported. A combination of oxidation and subsequent addition of benzyl- (Bn) or butyl hydroxypropyl (BHP) groups allowed the manipulation of the original properties of the starch. The viscosity and dry film surface tension of these products were determined to evaluate the applicability of these starches in high quality paper coatings with the aim to replace styrene butadiene rubber (SBR) latex as a binding agent.

The application of such a coating usually occurs by a technique called blade coating [1], a high-tech process in which the coating formulation is applied at a shear rate of about 10^7 s^{-1} followed by drying. During this process, a uniform coating layer should develop in such a way that the visual appearance of the paper is enhanced and allows for web-offset printing [2]. Currently, the rheological behavior of starch can be tuned by hypochlorite oxidation [2-4] to perform well during the coating process. If latex is replaced by starch, however, a common printing deficiency called print mottle is often observed. Print mottle is influenced by base paper quality, the coating-binder system, dewatering of the formulation, drying strategy, coating structure, surface tension and binder migration [2,5,6]. This complexity makes it extremely difficult to predict mottling. The substitution of benzyl groups on the starch backbone caused an increased starch viscosity. The surface of the coating using benzylated starch that showed the lowest mottling also showed increased relief, shown by SEM, compared to the non benzylated product discussed in Chapter 3. Both benzylated and BHP functionalized starches showed decreased starch film surface tension, comparable to benzylated starches and an SBR latex film. In contradiction to the benzylated products, BHP starches had a lower viscosity than the starting material, shown in Chapter 4, which opens an opportunity to investigate the influence of formulation viscosity in combination with decreased starch film surface tension on coating properties. A viscosity decrease of the starch solution allows for a higher formulation solids content at the same starting viscosity and hence reduced drying cost, which is desirable.

In the current research, SBR latex was replaced by waxy potato starch derivatives as a binding agent in a top coating formulation. Two grades of oxidized waxy potato starch were modified with butyl glycidyl ether (BGE) as the reagent giving BHP starches of different molar substitution (MS-BHP). Formulation viscosity was determined up to 500.000 s^{-1} using four different rheological measurements. Base-paper was coated with a large scale laboratory coating technique and the binding strength and print mottle behavior of the coating layer were assessed, as well as the surface

starch content of the coating. The surface morphology of the coatings was assessed by electron microscopy (SEM).

Materials and methods

Materials

Two commercial grades of oxidized waxy potato starches; Perfectafilm X85 and X55 were kindly supplied by AVEBE Foxhol, The Netherlands. Butyl glycidyl ether (BGE), technical grade (95 %, Sigma) was used as received. HCl (37%, Merck) was diluted to a 6 N solution. Hydrocarb 60, a ground calcium carbonate (GCC, 60 % < 2 μm) coating pigment, was obtained from Omya, (Oftringen, Switzerland) and was homogenized prior to use. Sodium hydroxide (Sigma) was used in a 10% solution. Coating base paper of 82 g/m² was obtained from Burgo Ardennes (Virton, Belgium). Styronal D517, 50 %W solids content (BASF), was used as received. Carboxymethyl cellulose (CMC) type FF10 was obtained from Metsä-Serla, Sweden and used in a 10 %W solution in water.

Preparation of BHP starch

Preparation and characterization of BHP starches was performed as reported earlier in Chapter 4, but at a scale of 10 moles starch (based on anhydroglucose units, AGU). The final products were ground and sieved. The characteristic properties are displayed in Table 1.

Starch	MS-th -	$\mu_{\text{starch}} - 30\%$ mPa.s	γ_{film}^p mN/m	γ_{film}^d mN/m	$\gamma_{\text{total, film}}$ mN/m
X85	0	4850	35.1	21.7	56.8
X85	0.2	1100	17.8	22.3	40.1
X85	0.3	450	16.4	21.9	38.3
X55	0	1170	47.8	16.0	63.9
X55	0.2	450	17.9	24.9	42.8
X55	0.3	550	21.9	20.7	42.6
Styronal D517	-	300 ^a	23.0	20.1	43.1
Hydrcarb 60	-	500 ^b	-	-	-

Table 1: used starches and their viscosity and surface tension.

^{a)} 50 %W in water

^{b)} 78 %W in water

Starch paste preparation

Starch pastes based on oxidized starch products were prepared at 35 W% dispersions in a steel container. Water was added to the modified starch and mixed well to obtain 1200 gram of 35 %W starch suspension. The suspension was heated in a steam-heated water bath of $> 95\text{ }^{\circ}\text{C}$ and mixed for 20 minutes at 600 rpm with a six-hole lab stirrer. In case of foaming, stirrer speed or container-loading were adjusted. After the cooking time, water was added to a weight of 1200 gram to compensate for evaporation. The exact starch concentration was determined by an ATAGO-RX 5000cx refractometer at a sample temperature $< 30\text{ }^{\circ}\text{C}$.

Coating formulation preparation

Coating samples of 2.4 kg at 69 %W solids content were prepared. To 1.5 kg (100 parts) dry solids of Hyrocarb 60 (78 %W suspension), 0.18 kg (12 parts, based on pigment) dry solids of starch as a 35 %W hot paste was added to the pigment suspension while mixing vigorously using a Pendraulic mixer. The pH was adjusted to 8.5 – 9.0 by adding of a 10 %W NaOH solution. The coating formulation was cooled to $30\text{ }^{\circ}\text{C}$ prior to further use. A reference coating with Styronal D517, commercially available SBR latex used for paper coatings, was prepared. The total solids content of the coating formulation was determined gravimetrically with a CEM Labwave 9000 microwave.

Coating viscosity

The viscosity of the coating formulations as a function of the total solids content was determined on a Haake Mars III rheometer with a cone-plate configuration at $20\text{ }^{\circ}\text{C}$. The gap distance (d) was 0.105 mm. The cone diameter was 60.000 mm and the angle was 2° . Two ml of a starch solution was used and measured at 10 s^{-1} shear rate. For this measurement, a small quantity of coating formulation was prepared (100 parts dry solids of pigment = 150 grams) as described above and diluted step- wise from the initial concentration to 50 %W. All other measurements were performed using samples from one formulation, prepared as described above.

For the DIXON application experiments, formulation viscosity was determined at low shear rate by a Brookfield viscometer at 100 rpm. The viscometer was allowed to stabilize for a minimum of 15 seconds before reading the value. High-shear viscosity was measured on a Hercules DV-10 Hi Shear viscometer using a spindle type-A. The shear rate was increased from 0 – 4500 s^{-1} and back to 0 s^{-1} in 20 seconds. 45 grams of the formulation was used per measurement. The viscosity at shear rates, approaching industrial operating conditions around 10^6 s^{-1} , was determined on an A2 ACAV capillary

viscometer. The capillary had a diameter of 0.5 mm and a length of 50.0 mm. The maximum pressure was set to 350 bar. The machine was calibrated with water prior to coating measurements.

Dewatering

The dewatering behavior of the coating formulations was determined on a AA-GWR water retention meter. Eight ml of a coating formulation was air-pressed at 1.5 bar for 15 s through a polyester membrane with a 5 µm pore size (GE water- & process technologies) onto a filter paper. The radius of the sample compartment was 3.192 cm; the mass of water passed through the membrane was multiplied by 1250 to obtain dewatering in g/m².

Coating application

The coatings were applied single-sided to the base-paper by means of a DIXON lab-blade-coating machine. The paper-web speed of the DIXON machine was 50 m/min. Four blade pressures, ranging from 0.5 – 4 bar were applied with each formulation to obtain a series of similar coating-weight on paper (the aim was 10 g/m², a standard amount). The formulation viscosity was set to a Brookfield viscosity of 1200 – 1800 mPa.s (solids content as high as possible) by adding water and subsequent mixing. The dryer was operated at 125°C at a steam pressure of 3 bar. The moisture content of the coated paper after drying was approximately 6%. Prior to further analyses, the coated paper samples were allowed to equilibrate at 23 ± 1 °C and 50 % RH for at least 48h.

The applied coating weight was determined gravimetrically according to ISO-536. The coating weight was calculated by Equation 1:

$$W = \frac{m_{blank} - m_{coated}}{A_{A4} * n} \quad \text{(Equation 1)}$$

Here, W is the amount of coating in g/m², m_i is the mass of n sheets of paper; A is the surface area in m² of 1 A4 sheet and n is the number of sheets; in this case n = 10.

IGT dry pick

Bonding strength of the coatings was determined according to ISO-3738 on a IGT-AIC2-5 machine. IGT pick-test-oil of standard viscosity (520 mPa.s at standard conditions) was used. The ink is rolled

over the paper at increasing speed. The distance at which pick starts to occur was determined visually and relates to the roller speed at that point. The speed at pick, multiplied by the viscosity of the test-oil at this speed yields the 'viscosity-velocity-product (VVP)'. A high VVP value indicates a high bonding strength. Each measurement was repeated 5 times.

Curley porosity

The Curley porosity of coated papers was determined on a Lorenten & Weltre Densometer according to ISO-5636-5. The time required to pass 100 ml of air through the coated paper is a measure for its porosity. This measurement only gives an indication of total free flow area and not about pore size. An increased measuring time means a lower porosity and vice versa. The reported value is the average of 5 measurements.

Print mottle

Print mottle tests were performed on a Prüfbau MZ-II machine. Huber Proofing and Mottling test-ink type 408010 was used. 200 mm³ of ink was homogenized on the machine's roll system for 30 seconds. Then, the ink was transferred to an application-roller during 15 seconds. The ink was transferred to the paper at 0.5 m/s and subsequently rolled over by clean application-rollers; the first immediately after the ink was applied and subsequently 3 times at 10 second intervals. The samples were assessed visually for mottling.

Coating surface starch content

To establish an indication of binder migration, FTIR spectra of the coated papers were recorded on a Bruker Tensor 27 equipped with a platinum ATR. The intensities of the starch peak at 1080 cm⁻¹ (from 1070 to 1090 cm⁻¹) and CaCO₃ (pigment) peak from 855 to 890 cm⁻¹ were determined by direct peak integration using Matlab. The ratio of the integrated starch- and CaCO₃ peaks was used to indicate changes in the coating surface starch content. The measurement only yields qualitative information about the surface starch content of the coating. All coated papers were measured ten times per sample; samples were measured in two-fold (i.e. n = 20). Subsequently, the ratio of the cellulose peak at 1105 cm⁻¹ (1095 – 1120 cm⁻¹) to CaCO₃ was determined to evaluate paper coverage.

SEM

Scanning Electron Microscope (SEM) image for coated paper samples were recorded on a Philips/Fei (XL30) ESEM instrument operating at 3kV acceleration voltage. A small amount of sample was deposited on a double adhesive carbon tab and then coated with 1-2 nm gold to prevent charging. Images were acquired using a secondary electron detector under high vacuum conditions (5×10^{-6} mbar).

Results and discussion

Two commercial grades of oxidized waxy potato starch were reacted with BGE on a 10 mole AGU scale. The MS and pasting behavior were comparable to what was found for small scale samples, see Chapter 4. Coating formulations were prepared and characterized on viscosity (low and high shear) and dewatering behavior. Applied and consolidated coating layers were assessed for bonding strength, porosity, print mottle and surface starch content by FTIR. Samples of two higher coat weights, using X85-0 and X85-0.2 BHP at 15 en 13.5 g/m² respectively, were evaluated as well to assess the impact of coat weight on the layer properties. Standard testing mostly uses 10 g/m². The surface structure of starch- and latex based coatings was investigated by SEM imaging.

Coating viscosity

Two hundred grams of coating formulation was prepared to evaluate the viscosity as a function of total solids content. The result is displayed in Figure 1. The difference in viscosity between the dissolved starch products, for example μ X85-0 > μ X85-0.2 > μ X85-0.3 remain similar for the coating formulations based on these products.

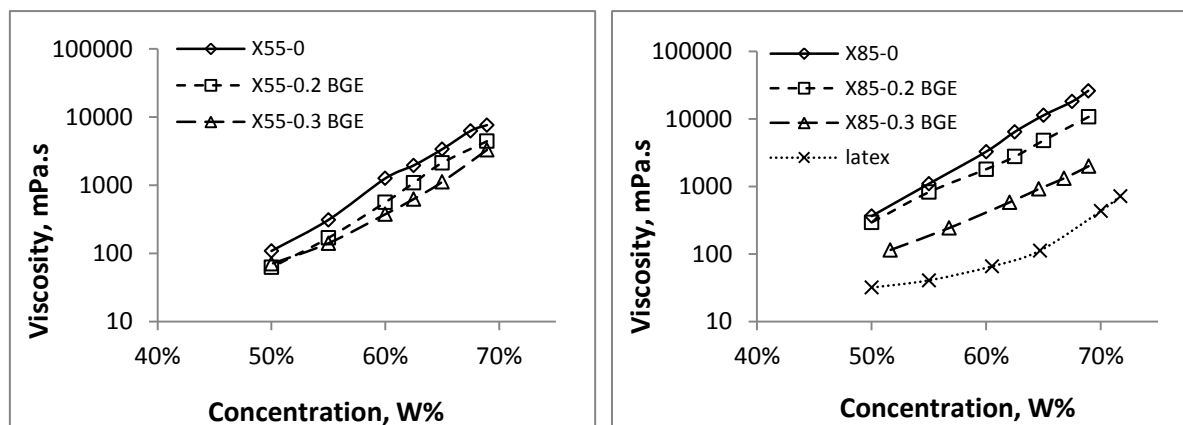


Figure 1: viscosity profiles of starch-based coatings at low shear rate (10 s^{-1})^a.

^a) The profile of a latex-based coating was added for comparison. The profile is measured without addition of CMC to illustrate the difference.

Normally, the viscosity of a suspension at high solids contents can accurately be predicted by the Krieger-Dougherty equation. However, in case of a combination of a polymer (starch), dissolved in the continuous phase (water) with dispersed solids (the pigment), the Krieger-Dougherty equation does not apply [7]. Prior to applying the coatings to the paper by the DIXON lab-coating machine, the coating viscosity as a function of a large range of shear rates was determined as well as the dewatering behavior. The results are presented in Table 2

Starch MS BHP	Solids %W	BrF-100 ^a 30 s ⁻¹	Hercules 400 s ⁻¹	Hercules 4500 s ⁻¹	ACAV 100.000 s ⁻¹	ACAV 500.000 s ⁻¹	Dewatering [g/m ²]
X85-0	63.5	1720	1100	683	283	175	9.8
X85-0.2	66.6	1860	1100	684	339	238	6.5
X8-0.3	67.1	1710	1117	690	300	226	5
X55-0	67.6	1600	950	626	200	143	7.5
X55-0.2	68.9	1400	850	562	189	154	19.6
X55-0.3	68.9	1360	785	513	199	138	20.8
All-latex	71.1	1690	140	75	40	40	77

Table 2: coating properties as applied to paper by DIXON coating machine.

^a) Viscosity by Brookfield at 100 RPM.

All formulations display shear thinning behavior, but there is still a big difference between latex and starch, despite the presence of BHP groups. This is illustrated in Figure 2. Although coatings prepared with X85-0.2 and X85-0.3 were prepared on approximately the same Brookfield viscosity as X85-0, they show a lower viscosity at increasing shear rate while their solids contents are 3-4 % higher than that of the X85-0 coating, as can be seen in Table 2.

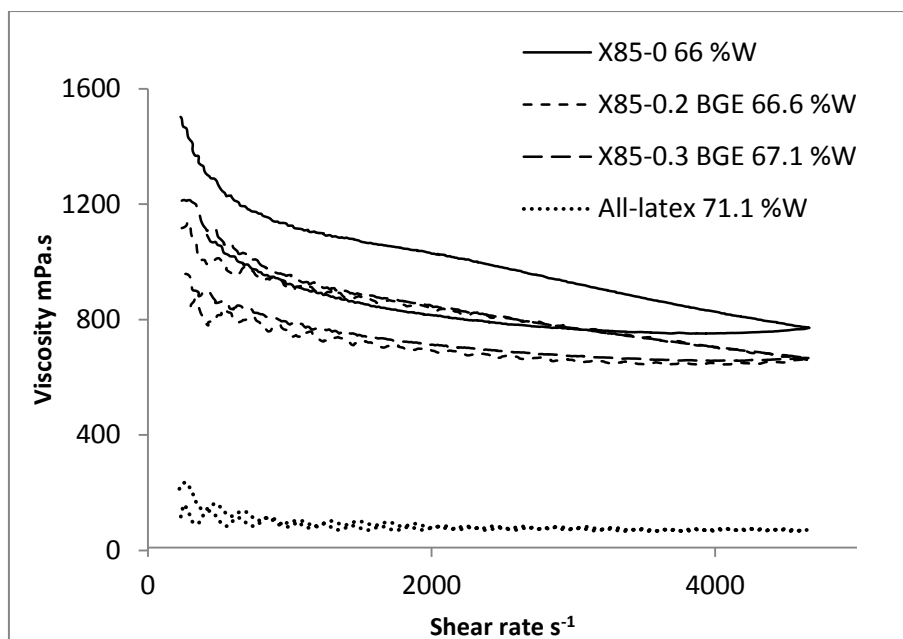


Figure 2: Hercules high shear viscosity profile of X85-based coatings as applied to paper.

An overview of the formulation viscosities at shear rates ranging from $30 - 500.000 \text{ s}^{-1}$ is displayed in Figure 3. The latex based coating was added to illustrate the difference. As can be seen, all starches show shear thinning behavior, but hydrophobic modification does not change this behavior very much. Dilution of the starch-based coatings seems to be the only effective method to obtain the viscosity of the latex based coating at a shear rate of 10^6 s^{-1} .

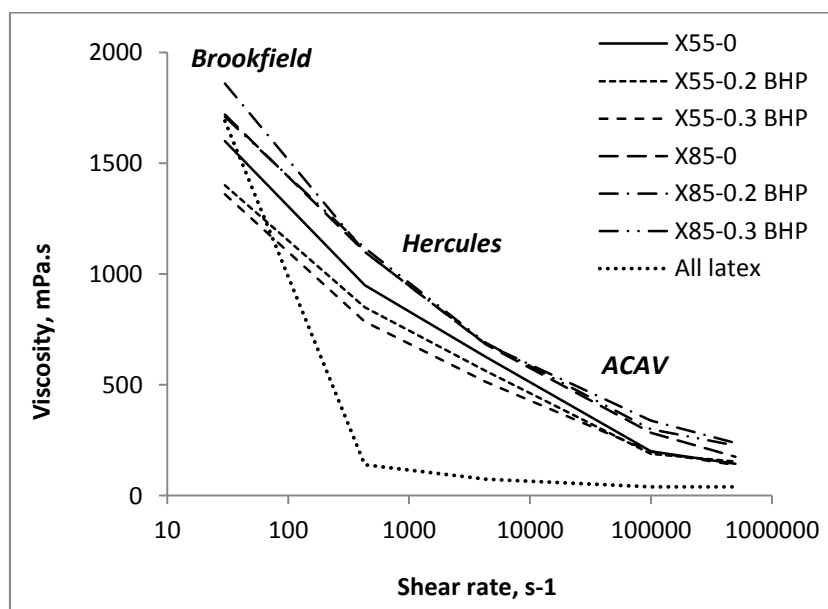


Figure 3: viscosity profile of starch based coatings using three different techniques.

All viscosities were set to a Brookfield viscosity of around $1600 \pm 200 \text{ s}^{-1}$. All formulations showed a similar profile, but at different total solids contents. So while the viscosity of BHP-starch solutions decreases, the shear thinning behavior is not enhanced. This is in agreement with the statement by Buwalda et al. [8] that hydrophobic groups up to a chain length of 10 carbon atoms on the starch back bone are too short to interact. On the other hand, hydrophobic interactions were detected in HBP starches by UV-emission spectroscopy using pyrene as a hydrophobic probe, see Chapter 4. Apparently, this does not result in according rheological behavior.

The dewatering of the starch based formulations was low as can be seen in Table 2. This was expected, since low dewatering is common for coating formulations with dissolved polymers [9]. The dewatering of the formulations of X55 at both MS-BHP of 0.2 and 0.3 is higher than the other formulations, but still well below the latex based coating. Dewatering increases at decreasing molecular weight [2,3]. Usually, dewatering of latex based formulations is even higher but is decreased here by the addition of the rheology modifier, CMC.

Coating properties

After application by the DIXON laboratory coating machine, the paper samples were cut from the roll and allowed to reach equilibrium moisture content for a minimum of 48 hours. By varying the blade pressure, a range of different coating weights was obtained for every used formulation. From this pool a selection was made where the differences in applied coating weight were smallest; preferably around 10 g/m^2 , which is a normal amount for top coatings in the paper industry. Table 3 shows that the average coating weight was $9.2 \pm 0.4 \text{ g/m}^2$ without regarding the two coatings of 13 and 15 g/m^2 .

The IGT dry-pick strength of all samples is higher than that of the base-paper. In addition, the variation between the $9.2 \pm 0.4 \text{ g/m}^2$ is not high: $712 \pm 19 \text{ g/m}^2$. On the other hand, the Curley porosity of all samples in which BHP-starch was used decreased considerably, but no clear trend can be observed. This effect was most pronounced in the X85-series. If, however, the higher coating weights are taken into account, the differences are bigger and much more pronounced; 1135 for X85-0 at 3.5 g/m^2 vs. 968 for X85-0.2 at 15 g/m^2 , which is in agreement with earlier results from Chapter 3 in which the dry pick strength of X85 substituted with benzyl groups at a degree of substitution (DS) of 0.375 also showed a decreased binding strength. However, the porosity of that

starch was much higher. Calculations in Chapter 2 showed that the work of adhesion between the coating compounds decreases as the starch film surface tension decreases.

Starch MS-BHP	Coat weight g/m ²	Dry pick VVP kg/s ²	Curley por. s
Base paper	0	515 ± 13	33 ± 1
X85 0	9.1	695 ± 56	469 ± 17
	13.5	1135 ± 48	n.d.
X85 0.2	9	716 ± 49	923 ± 41
	15.0	968 ± 38	n.d.
X85 0.3	9.4	745 ± 37	805 ± 17
X55 0	9.4	727 ± 43	595 ± 31
X55 0.2	8.6	704 ± 23	719 ± 26
X55 0.3	9.7	697 ± 23	620 ± 31
Latex	9.5	698 ± 32	694 ± 11

Table 3: coating properties of BHP starches.

Surface composition

The causes of print mottle as a consequence of using starch in the coating formulations were comprehensively reviewed in his thesis by Ragnarsson [5] and the literature cited therein. He points out that the surface starch content of a paper coating is influenced by the ease at which starch migrates during the drying process and by the path length, determined by the roughness of the base paper. The latter is kept constant here, since the same base paper was used for all experiments. To study the amount of starch at the coating surface, the starch / CaCO₃ (which is the pigment, Hyrdocarb 60) ratio was determined by FTIR as a measure for migration. The peak ratio was determined by direct integration using MatLab. Note that this method does not yield quantitative data, merely a difference in surface starch content. Dobler et al. [10] did use this method in a qualitative way, but it is unclear how they calibrated their system.

For latex, no starch peak was detected as can be seen from Figure 4. Little variation is observed for the starch based coatings at an applied coating weight of 9.2 ± 0.4 g/m². In some cases, however, starch peaks shifted due to the presence of cellulose peak at 1105 cm⁻¹. Therefore, the cellulose-CaCO₃ peak-ratio was determined as well, which yielded an interesting result. In all samples prepared with 9.2 ± 0.4 g/m² of coating, cellulose was detected. Moreover, the intensity of the cellulose peak showed variations, it becomes less as MS-BHP increases, at least for the X85 series. This suggests that the covering of the paper is enhanced, which may also be concluded by the decreased porosity. Additionally, two samples with a higher coating weight of 13 and 15 g/m² were

evaluated, based on X85-0 and X85-0.2, respectively. The cellulose peak of these samples is almost zero. Moreover, a significant difference appears in the amount of starch detected at the coating surface. At a higher hydrophobic content, the surface starch concentration decreases. The decrease might be considered to be due to the hydrophobic content of the starch; about 10 %W of the modified starch dry matter is accounted for by BHP groups. The starch- CaCO_3 ratio however, decreases by 30%. Therefore, we conclude that less binder (starch) is present at the coating surface if the starch contains BHP groups.

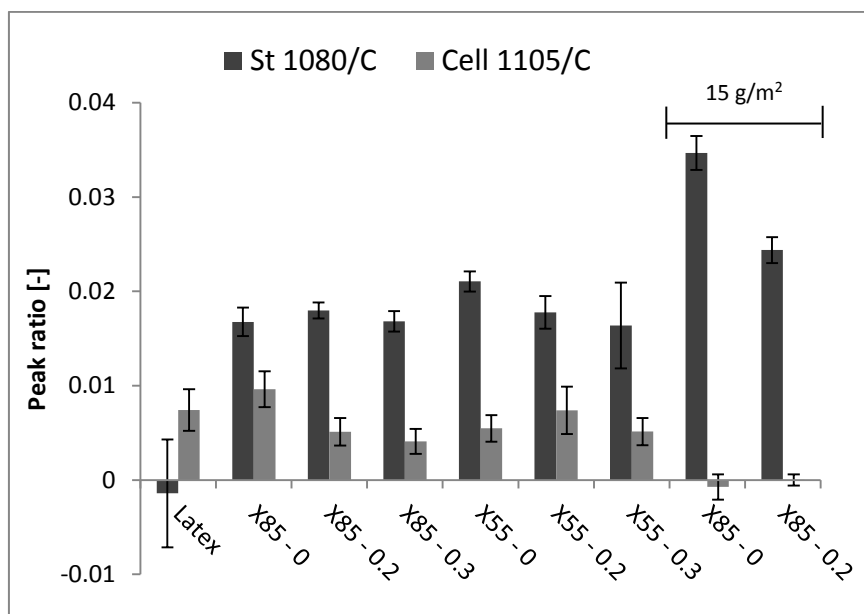


Figure 4: starch – CaCO_3 ratio (left) and cellulose – CaCO_3 ratio (right) by FRIR.

Print mottle

The print mottle test assesses printability as a function of the total set of properties of the tested surface. The printing process is a sequence of related events at the substrate surface; a roller with ink touches the substrate where surface wetting, filtration and film splitting occur within a short time-frame. In an industrial printing process, wet ink is rolled over a few times by clean rolls that transfer other colors to the paper. These separate processes are not easily characterized, let alone the combination. Many variables play a role including the surface energy and porosity of the coated paper and the application roll in combination with the viscosity and surface energy of the ink that transfers shear forces between the coating surface and the printing roll. Changed surface properties of the coated paper because of the introduction of starch may cause problems with the ink transfer and the setting and drying behavior of the ink, resulting in print mottle. Generally, the mottle tests results of the paper samples with 9.2 g/m^2 applied coating were poor; cellulose fibers were clearly

visible as white stripes which hindered the observation of mottle. In Figure 5-a, the mottling test of the latex-based coating is shown. This coating had a coating coverage of 9.2 g/m^2 and the cellulose-peak, determined by FTIR was similar to the starch-based coatings of similar coating weight. Remarkably, white cellulose stripes were not seen in the mottling test for the latex-based coating. In addition, the samples with a coating weight of 13 and 15 g/m^2 were also tested on mottle. Figure 5-b shows the mottle test of X85-0 (13 g/m^2), which clearly shows uneven ink setting. However, a very even and dense coloring was observed for the coating in which X85 – 0.2 BHP (15 g/m^2) was applied, as shown in Figure 5-c. Cellulose fibers were not observed in these samples, which is in agreement with the FTIR observations. The introduction of hydrophobic groups seems to decrease mottling behavior.



Figure 5: images of print mottle tests (enlargement 10X).

SEM imaging

In Figure 6, the SEM images of three coated samples are shown at two magnifications: 1000 and 5000 times. The latex-based coating is somewhat irregular at 1000X magnification and also shows areas of increased and decreased porosity. The areas with decreased porosity are filled with SBR latex, which is the grey substance, as can be seen in the picture of 5000X magnification. Clearly, the surface shows some roughness, especially in comparison to the coating based on X85-0.

As can be seen at 1000X magnification, the X85-0 coating is much smoother than the latex-based coating with little height differences. At 5000 times magnification, it can be seen that the location at which pores should be, in fact there is an accumulation of fine particles, causing a much more regular surface than observed for the latex-based coating with less coarse particles at the surface. Visually, this coating seems less porous, but the Curley porosity is higher compared to the latex-based coating. All three samples have the same coating weight of $9.2 \pm 0.4 \text{ g/m}^2$. The most remarkable difference between the latex and X85-0 is the difference in fine- and coarse particle distribution. The latex-based coating surface seems to have developed according to the prediction of the model by Sand et al. [11]. According to Sand et al. the changed coating structure could be the

consequence of increased viscosity of the continuous phase of the coating formulation, which influences the consolidation behavior.

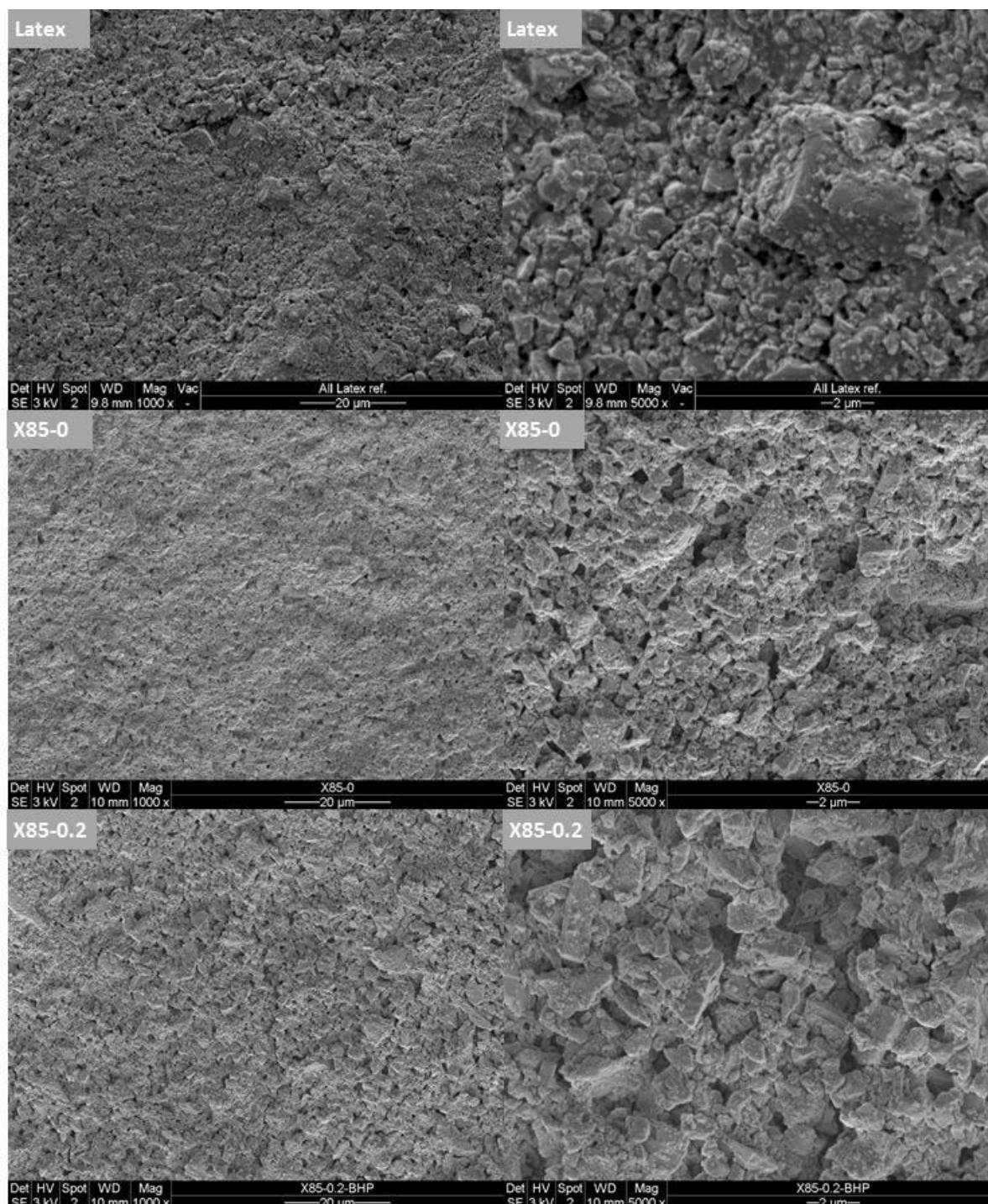


Figure 6: latex based coating, X85-0 based coating and X85-0.2 based coating.

The introduction of BHP groups on the starch backbone causes a change in the surface structure of the coating, as can be seen in Figure 6. It can be observed that the surface of the surface of the

X85-0.2 coating regains some of the roughness that was lost by the replacement of latex by X85-0. In addition, the arrangement of fine-course particle at the surface of the X85-0.2 coating is more like the latex-based coating. Opposite to what the SEM images suggest, the porosity of X85-0 was higher than X85-0.2. In addition, the FTIR measurement revealed that the cellulose peak was less pronounced with the BHP-starches which suggest a better coverage of the paper. This supports the conclusion of Sand et al. [11] that both the internal- and surface coating structure are dictated by rheological behavior and surface energy of the continuous phase. The surface structure of the coating based on X85-0 suggests that material flowed from within the coating layer to the surface while the coating based on X85-0.2 BHP looks like it has settled. This would explain the lower surface starch content, which is supported by the FTIR measurements. Another explanation may be the increased mobility of fine particles when the discontinuous phase, latex, is replaced by a soluble polymer, starch, which is part of the continuous phase. Pan et al. [12] proposed a drying model that describes starch migration as a function of the Peclet number and Capillary number. Their model predicts less capillary transport towards the surface if the surface tension of the continuous phase decreases, which may be the case here but this was not determined.

Aspler and Lepoutre [13] mentioned in their review that uneven binder distribution does not per se lead to print mottle. As can be seen in Figure 6, the surface content of latex varies quite a lot but it should be noted that the DIXON coating machine is a laboratory machine with a relatively low running- and drying speed. Pilot-coater trials show less latex at the surface but it was reported here anyway to illustrate the difference between latex and starch. Despite the surface latex content, no mottling was observed. This raises the question if the mottling test results are caused by the hydrophobic groups on the starch backbone, or by the changed surface structure of hydrophobized starch.

Conclusion

Six starch products, based on waxy potato starch, have been prepared and their properties were evaluated for replacement of SBR latex in paper coatings. The effect of level of oxidation and MS-BHP of the starch on the rheological properties of coating formulations and coated paper samples was evaluated. BHP groups change rheological behavior of the starch solution and of the coating formulation. Exact modeling of the coating formulations at this stage is difficult since most models, like Krieger Dougherty, assume that the viscosity of the continuous phase is constant, which is not the case when starch is used. The consolidation behavior of the coatings seems to change according

to models proposed in the literature by Sand et al. and Pan et al. for latex based coatings, although it may be expected that the consolidation mechanism of starch based coatings is different. SEM images confirmed that the consolidation behavior of starch-based coatings changed after the introduction of BHP groups. The coverage of the base paper increased at increasing BHP content because less cellulose was detected by FTIR. The printability was improved and mottling decreased. Since the porosity of BHP starch was quite low and printing results improved, porosity seems less important than the surface structure regarding mottling behavior. Finally, the amount of applied coating greatly influences the outcome of the performed tests; more than 10 g/m² coating weight is required to minimize the effect of the base-paper on the test outcome.

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Chapter 6

Overview, evaluation, reflection and outlook.

Introduction

In this chapter the findings, described in Chapter 2 to 5 are discussed and compared to evaluate the results regarding starch properties and the replacement of styrene butadiene rubber (SBR) latex in high quality paper coatings by starch. In addition, it is attempted to understand the consolidation process of the starch-based coatings according to the model of Pan et al. [1]. Furthermore, it will be attempted to predict, through calculations, the importance of hydrophobic groups on the starch backbone with respect to printability. The hypothesis on which this research is based “substitution of hydrophobic groups on oxidized waxy potato starch derivatives is required to successfully replace SBR latex in high quality paper coatings”, is re-evaluated with the present knowledge to generate suggestions for further research.

The viscosity of oxidized and hydrophobized waxy potato starches

Rheological behavior of water soluble polymers changes when hydrophobic groups are substituted on its backbone [2]. Below the critical aggregation concentration (*cac*), intramolecular interactions cause the hydrophobic groups to cluster and cause a decrease of the hydrodynamic volume of the polymer molecules, thereby decreasing the viscosity. Above *cac* the viscosity increases faster than the non-hydrophobized material as the concentration increases due to gel-formation by intermolecular interactions of the hydrophobic groups [3]. A schematic representation of this mechanism is displayed in Figure 1. This effect was observed for benzylated (Bn) starch, but not for 1-butoxy-2-hydroxypropyl (BHP) starch, which is remarkable. The viscosity of W-0.2 BHP was equal to that of W-0 and the viscosity of oxidized waxy BHP starches was lower than that of their starting materials X85-0 and X55-0.

Ju et al. [4] reported that acid degraded corn starch, at a slightly higher molar substitution (MS) of BHP groups (MS-BHP), showed thermo responsive behavior. They did however not report on the viscosity of their products. On the other hand, Buwalda et al. [5] suggested that a carbon chain length of at least ten (10) atoms are needed to effectively detect a rheological effect from hydrophobic interactions, both for interactions between hydrophobic groups as well as amylose-

lipid-interaction of hydrophobic groups with potato starch amylopectine. They also state that a minimal degree of substitution (DS) or MS is needed before an effect is measured, but do not give an indication of DS-threshold-values of substituents.

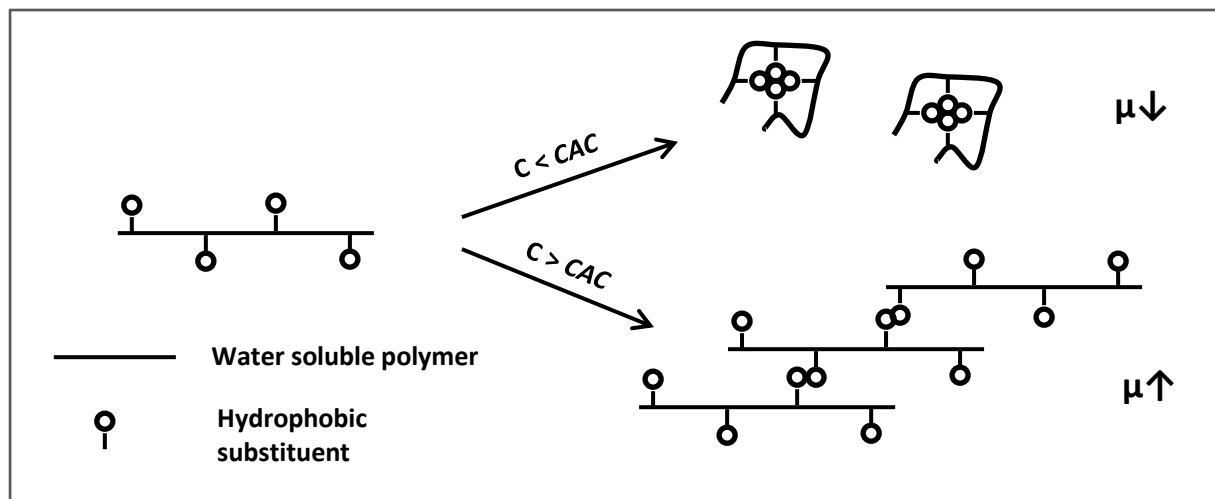


Figure 1: schematic representation of intra- and intermolecular interactions as a function of concentration.

These two statements seem contradictory. The difference between the research described in this thesis and the findings by Ju et al. may be because they used acid degraded corn starch. It is known that acid degraded starch retrogradates very fast [6] while oxidized starches are stabilized by the presence of carbonyl- and carboxyl groups [7]. Still, it is puzzling that the viscosity of oxidized waxy potato, reported in Chapter 4, did not increase after introduction of BHP groups. The molecular weight did not change sufficiently to explain the change of the product viscosity. In addition, hydrophobic interactions were detected for all BHP-substituted starches by means of UV emission spectroscopy using pyrene as a hydrophobic probe. On the other hand, the MS-BHP of products prepared here were lower than that of the products prepared by Ju et al. [4]. If the statement of Buwalda et al. [5] is true, then the chain size of BHP groups is not long enough to generate sufficient interaction to increase solution viscosity. However, this would mean that the findings by Ju et al. are caused by another phenomenon; possibly the preparation method of the starting material. It may also be possible that the viscosity of BHP starches is higher than that of the starting materials at concentrations above 35 %W solution, but this was not investigated in this thesis. For example, the viscosity of X85-0.375 Bn had a higher viscosity than X85-0 above 15 %W concentration, see Chapter 2, Figure 4. For X85-0.3 BHP, this effect could for example take place above 40 %W.

It is not clear why the viscosity of oxidized waxy potato starches decreases after the introduction of BHP groups, while it increases upon benzylation. Aromatic groups interact through π - π -stacking

[8], which is a stronger interaction than the van der Waals forces binding the BHP groups and thus the solution viscosity is increased. Moreover, a benzyl group is shorter than 10 carbon atoms and also shorter than a BHP group (5 vs. 8 carbon atoms). The mobility of the BHP group, which predominantly consists of C-C bonds, is higher than a benzyl group. The latter contains an aromatic ring and is thus much more rigid. The molecular weight of BHP starches was comparable to their starting materials. However, a group with a mass of 130 was substituted on the starch backbone at an MS up to 0.3, so on one in every three starch monomers, there is a BHP group comparable in size to the starch monomer, but with less OH-groups than the starch (1 vs. 3), see Figure 2. The presence of BHP groups could reduce the formation of hydrogen bonding between the starch molecules and thereby reduce the solution viscosity.

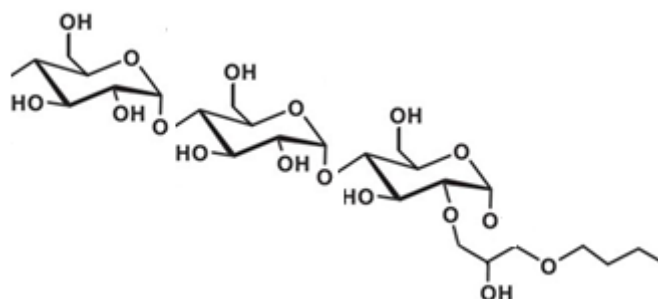


Figure 2: schematic representation of a BHP starch with an MS of 0.3.

In conclusion, the preparation of acid degraded waxy potato starch, followed by substitution with BHP groups at a similar MS as prepared by Ju et al. [4] could prove that oxidation inhibits thermo responsive behavior. In addition, the preparation of oxidized BHP starch according to Ju et al. could provide useful information about the influence of the substitution pattern on the rheological properties and on the validity of the statement by Buwalda et al [5] that at least 10 carbon atoms are needed for clustering of hydrophobic groups.

Development of end-use properties and the role of rheology

The most important end-use properties, of the starch based coating formulations, were the IGT dry pick strength and mottling behavior. It was attempted to understand changes in these properties as a function of the level of oxidation and hydrophobic content of the starches, which in turn changes the rheology of the product solution. The coating porosity (Curley) and coating surface starch content (FTIR) were measured to help understand changes in product quality. The surfaces

structure of the coatings was studied from SEM images of coated paper samples. Correlations between measured properties all proved insignificant (see Chapters 3 & 5).

If the success of a modification is given by the potential to reduce mottling, then PS-0.25 Bn and X55-0.3 Bn (Chapter 2 & 3) and X85-0.2 BHP (Chapter 4 & 5) perform best. The hydrophobic content does not seem to be crucial for decreased mottling, because X55-0.3 Bn has a higher hydrophobic content than PS-0.25 Bn and a different ratio of contributing forces to the total surface tension: 50 % polar vs. 25 % polar, see Table 5. Similarly, the porosity of the X85-0.25 Bn and X85-0.2 BHP coatings were both quite low, around 1150 seconds to pass 100 ml of air, while X85-0.2 BHP showed no mottling whereas X85-0.25 Bn did. The amount of starch at the coating surface, measured by FTIR, was low for the coatings without mottling, as can be seen in Chapter 3, Figure 5 and Chapter 5, Figure 5. It is however not clear *why* a low starch content is detected; because there is less starch present or because less starch is detected due to the surface structure, which was studied by taking SEM images.

The surface structure of a latex-based coating, see Chapter 5, Figure 6, may be considered rough in comparison to the other coatings; there are 'peaks' and 'valleys' and the valleys seem porous, although also accumulation of latex is observed. If the metaphor of a landscape is extended, the coatings based on X85-0 and X55-0 show valleys that are filled with small coating particles. The height-differences between the peaks and the valleys are also lower. Furthermore, it seems that the small particles were transported to the surface, whereas the structure of the latex-based coating suggests the particles settled during drying. One explanation of this was given in Chapter 1: because starch is part of the continuous phase and increases the viscosity of the continuous phase (which is water) whereas latex is dispersed in the water, replacing latex by starch means that small particles have more space to move to the surface and their transport is enhanced by increased viscosity of the water phase. If the SEM images of the coatings based on X85-0.375 Bn and X55-0.3 Bn from Chapter 3, Figure 6 are observed, the X8-0.375 Bn has a very open structure but also some small particles are located at the top of what would be the 'peaks' of the latex-based coating. X55-0.3 Bn shows a similar structure but with increased roughness of the 'landscape'. Similarly, the coating based on X85-0.2 BHP, Chapter 5, Figure 6, shows a similar roughness while there are more fine particles present than when X85-0.375 Bn and X55-0.3 Bn are used; especially the image at 1000X magnification shows the 'roughening' of X85-0.2 BHP vs. X85-0 coating surface. This observation suggests that the surface structure is an important factor for the development of mottling. Regardless of the porosity and the ratio of small and large particles, a certain degree of roughness is required, which is however hard to quantify by the methods applied here.

The coating drying model as presented by Pan et al. [1] takes into account capillary forces, rheology, diffusion and drying speed during the consolidation process. Therefore, an explanation for the formation of a rough structure may be found in the rheological behavior and the surface tension of the corresponding starch solutions. As already mentioned the surface tension of starch solutions at 20 % W was not determined, but it is assumed to be around the value of the starch dry films (around 50 mN/m). This leaves the biggest observed variations to the rheological behavior of the starch solutions. Compared to the solution of X85-0, the viscosity of X85-0.375 Bn increases enormously above 15 %W, see Chapter 2, Figure 4. This high viscosity might have resulted in rapid immobilization of the pigment particles during the consolidation process; particles did not have an opportunity to settle, see Chapter 3, Figure 6. The viscosity of X55-0.3 Bn showed a similar trend, but is generally lower than X85-0.375. In Addition, the viscosity of X55-0.2 Bn is lower than X55-0.3 Bn, but it has nearly the same viscosity at 35 %W. Therefore, these results and observations will be assessed according to the drying model proposed by Pan et al. [1].

They described the drying process by means of a capillary number (Ca) and a Peclet number (Pe). The Ca (Equation 1) balances the flow-forces and the capillary forces while Pe (Equation 2) balances the flow transport and binder diffusion. During the drying process, water is evaporated at the coating-air interface. They also described two drying scenarios. In the first scenario, the evaporation rate of water at the coating surface is higher than the rate of liquid transport in the bulk of the drying coating layer. The coating will then dry 'top-down', as is schematically represented in Figure 3-a. In the second scenario, however, the internal liquid transport capacity is larger than or equal to the evaporation rate. In this case, the coating layer will shrink until the maximum shrinkage is reached as illustrated in Figure 3-b. From that moment on the evaporation rate exceeds the transport capacity and final drying occurs according to case a.

The rate of transport of liquid is influenced by the surface tension and the viscosity of the liquid. In the case of a latex-based coating, the liquid phase is water and its viscosity is, compared to the viscosity of a drying starch solution, constant at around 1 mPa.s if the addition of rheology modifiers such as CMC is ignored. A starch-based coating on the other hand, may very well start its drying process in the regime of high liquid transport rate and ends with a low transport rate. The switch-point from one regime to the other can vary according to the starch solution viscosity and surface tension. One aspect, which is not covered by Pan et al. is the transport of small coating particles to the surface, as observed on SEM images of different starch-based coatings in Chapter 3 and 5. During liquid transport, all coating particles will experience 'drag-forces'. In addition, the viscosity of the aqueous phase is around 1 mPa.s in case of latex, but at least 50 mPa.s at 100 °C for any of the

used starch solutions at 17 %W, which is the minimal initial starch concentration in the water phase of the coating formulation prepared according to the recipes in Chapter 3 and 5 prior to application. This means that the drag-force, experienced by pigment particles is at least 1 order of magnitude higher in case of starch.

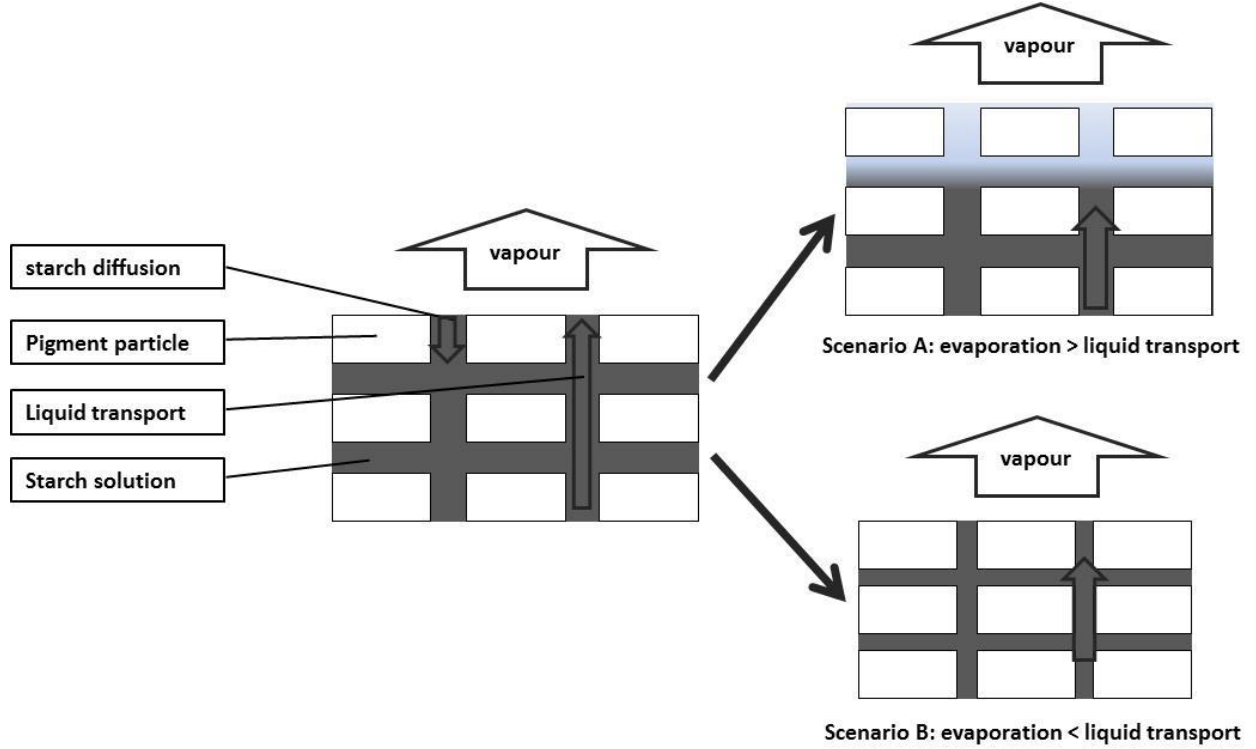


Figure 3: schematic, simplified impression of the drying process according to Pan et al. [1].

Used set of equations:

$$Ca \equiv \frac{\mu WL}{\gamma \rho r_p} \quad (\text{Equation 1})$$

$$Pe \equiv \frac{WL}{\rho D_b} \quad (\text{Equation 2})$$

$$D_b = \frac{1.173 * 10^{-13} * (\phi * M)^{0.5} * T}{\mu * V_m^{0.6}} \quad (\text{Equation 3})$$

$$Re = \frac{\rho * v * D_{pore}}{\mu} \quad (\text{Equation 4})$$

$$F_D = C_D * \frac{1}{2} * \rho * v^2 * D_p^2 \quad (\text{Equation 5})$$

$$C_D = \frac{24}{Re} \quad (\text{Equation 6})$$

$$F_G = D_P^3 * \rho_P * g \quad (\text{Equation 7})$$

Ca is the capillary number, μ is the viscosity (Pa.s), W is the transport speed of water (kg/m²/h), L is the characteristic pathway (coating thickness, m), ρ is the density (kg/m³), r_p is the pore radius, Pe is the Peclet number, D_b is the diffusion coefficient of a solute in a solvent, adopted from [9] (m²/s), φ is an association coefficient for the solvent (2.6 for water), M is the molecular weight of the solvent (g/mol), T is the absolute temperature (K), V_m is the molar volume of the solute calculated from [9] (m³/mol), Re is the Reynolds number, D_{pore} is the average pore size (μm), F_D is the drag force on a pigment particle (N), C_D is the drag-coefficient, v is the free flow velocity of the aqueous phase (m/s), D_p is the particle diameter (assumed cubic), F_G is the gravitational force on a particle.

Basic assumptions, based on initial conditions:

The assumptions on which calculations are based are listed in Table 1.

	Value	Remark
Coating thickness (L)	10 μm	Dry coating layer
Formulation total solids content	67 %W	Based on calculation in Chapter 1
Aqueous phase volume	60 %	Calculated in Chapter 1
Drying time	5 s	After blade coating on DIXON
Water vapor transport		Larger than liquid transport in bulk according to Pan et al. [1]
Water transport speed	$3.3 * 10^{-6} \text{ m/s}$	$2 * 10^{-6}$ corrected for free volume
Average pore size:	1 μm	
Surface tension starch solution	0.05 N/m	Regardless hydrophobicity
Temperature	373 K	100 °C
Molecular weight starch	$1 * 10^6 \text{ kg/kmol}$	
Molecular volume starch	$0.163 \text{ m}^3/\text{kmol}$	Based on [9]
ρ_P	2700 kg/m^3	Density of CaCO_3

Table 1: assumptions for calculations based on the model by Pan et al. [1].

Calculation results:

	Value	Remark
Drying rate, W	0.002 kg/m ² /s 8.4 kg/m ² /h	Based on 20 µm formulation with 0.01 kg water (see Chapter 1).
Re - latex	$3.3 * 10^{-6}$	$C_D = 7.18 * 10^6$
Re - starch low	$1.67 * 10^{-7}$	$C_D = 1.44 * 10^8$
Re - starch high	$3.34 * 10^{-8}$	$C_D = 7.18 * 10^8$
Ca# latex	$3.33 * 10^{-3}$	Viscosity water = 1 mPa.s
Ca# starch low	$6.6 * 10^{-2}$	Using $\mu = 20$ mPa.s
Ca# starch high	0.33	Using $\mu = 100$ mPa.s
D_b starch low	$1.12 * 10^{-11}$	Using $\mu = 20$ mPa.s, 100 °C
D_b starch high	$2.34 * 10^{-12}$	Using $\mu = 100$ mPa.s, 100 °C
Pe - latex	0.103	Viscosity water = 1 mPa.s
Pe - starch low	2.05	Using $\mu = 20$ mPa.s
Pe- starch high	10.3	Using $\mu = 100$ mPa.s

Table 2: calculation results based on the model by Pan et al. [1].

As can be seen from Table 2, the capillary number of a starch-based coatings indicates that for viscosities exceeding 100 mPa.s, capillary forces dominate the process. Moreover, diffusion is leading in case of a latex based coating, as was indicated by Pan et al. However, the diffusivity of starch is so low that in all cases the starch flow in the liquid phase exceeds the rate of diffusion. Note that $Re \ll 1$ so the flow is always laminar, which means that Equation 6 for the calculation of C_D is valid. Moreover, the drag-force that pigment particles experience is always higher than the gravitational force, as can be seen from Figure 4-a and b.

Even in case of a latex-based coating with an aqueous phase viscosity of 1 mPa.s, F_G does not exceed F_D until $D_p > 10$ µm. In addition, for every viscosity, $F_D > F_Z$. These calculations show that for both latex- and starch based coatings, pigment particles can be transported by the liquid flow. While bigger particles experience far more drag force than smaller particles, the small pore diameter prevents them from moving and therefore the smaller particles may move instead. This effect is enhanced by the replacement of dispersed latex by dissolved starch which increases the space between pigment particles and hence the mobility of fine particles as suggested in Chapter 1.

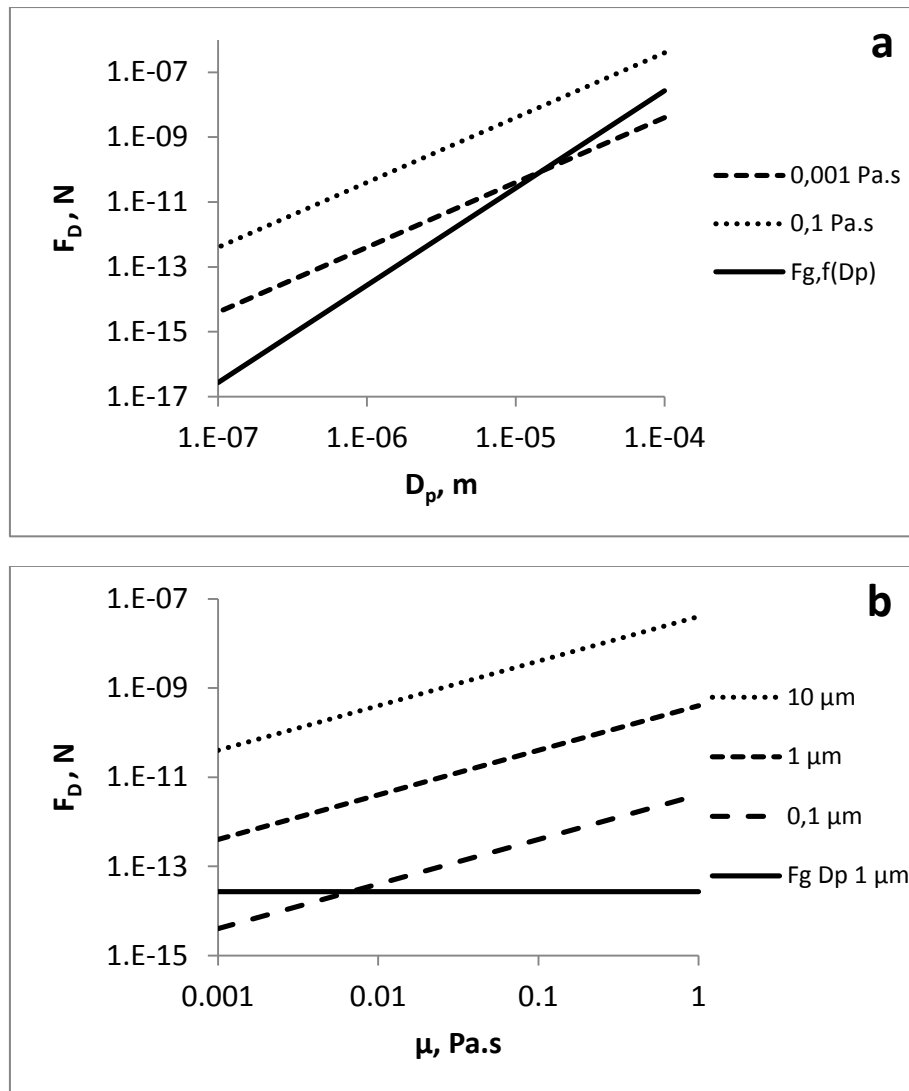


Figure 4: a) drag force as a function of particle size at low and high viscosity, b) drag force as a function of viscosity for small and large particles.

Pan et al. [1] distinguished several migration regimes as a function of low, medium or high Ca and $Pe\#$ as shown in Table 3. If Ca is low (<1) there is opportunity to flow, whereas if Ca is high (>1) there is increasing resistance to flow. High flow means that binder is transported to the coating surface where it deposits. From the calculations, summarized in Table 2 it is evident that the oxidized starch solutions have the tendency to migrate. Only at high viscosity or high drying rate will the coating dry from the surface inwards because the evaporation rate then exceeds the liquid transport. A high Peclet number indicates a high drying rate or low binder diffusivity. From the calculations in Table 2 it can be seen that the binder diffusion of starch is such that the Peclet number is always >1 for starch solutions and that binder migration to the surface is promoted even further. This effect is only counter balanced by a high value of Ca when the coating will dry top-down. Migration to the bottom

occurs if the binder can diffuse well and if the flow to the surface is inhibited by the viscosity and the pores empty top-down. Relatively less binder will then be deposited at the coating surface.

Ca / Pe	Low	Med	High
High	Max to bottom	To bottom	Uniform
Med	To bottom	Uniform	To surface
Low	Uniform	To surface	Max to surface

Table 3: correlation between Pe# and Ca# for binder migration according to Pan et al. [1].

The calculations described above can help explain some of the results from earlier chapters. If the results from Chapter 3 are observed, we see that for low viscosity starches, e.g. X55-0, X85-0 and X85-0.2, many small particles appear at the coating surface as can be seen on the SEM images. This is in agreement with a low Ca (which means relatively low viscosity or low resistance to flow) and thus an opportunity for the aqueous phase to flow and transport starch and fine particles. For example, the viscosity of X55-0 is lowest and its coating has a lot of small particles at the surface, X55-0.2 Bn has a higher viscosity, higher Ca so less opportunity to flow and less small particles appear at the surface. Finally, X55-0.3 Bn is even more viscous and even less fine particles have migrated to the top, which is also reflected in the FTIR measurements, which indicate that the amount of starch at the surface decreases for these three samples: X55-0 > X55-0.2 Bn > X55-0.3 Bn. On the other hand, the viscosity of X85-0.25 Bn is lower than X85-0 and the amount of small particles appearing on the SEM image is also higher. In addition, the starch peak, determined by the FTIR measurements is also higher for X85-0.25 Bn: 0.023 vs. 0.02, and within the experimental error. The coating of X85-0.375 Bn shows even more interesting behavior, since the surface is flat as if it was leveled with the blade. The viscosity probably increased so fast that the coating almost immediately enters the regime of top-down drying, which explains the high porosity and low surface starch content (FTIR); capillary forces could not compact the structure during the drying process.

The model also explains the large amount of fine particles at the coating of X85-0.2 BHP from Chapter 5. The viscosity is fairly low and increases only little at increasing concentration. This indicates that the aqueous phase has the opportunity to migrate to the surface and transport the fine particles there as well, which is also reflected by the low porosity. However, there is a flaw in this argumentation since the X85-0.2 BHP coating also shows a low surface starch content, as determined by FTIR. It is possible that due to the low viscosity, starch is able to diffuse back into the bulk during the drying process and the fine particles cannot because the coating layer has compacted, but this is speculative. Another surprising phenomenon which has to be addressed is the

good printability of X85-0.2 BHP. Since the porosity is low, it was expected that the printability was also poor. However, the mottling test result was remarkably good. One explanation is the uneven coating surface; despite the low porosity, the coating shows a similar 'landscape' as a latex-based coating with some height difference between the peaks and valleys where the ink can settle while it is being rolled over by the clean rollers during the mottling test.

Surface tension of hydrophobized waxy potato starch films

In all cases of hydrophobic substitution, the total surface tension of the starch films decreased and even approximated the surface tension of commercially available SBR latex, as can be seen in Table 1. Remarkably, the contribution of disperse forces to the total surface tension was much higher for the *native* hydrophobized starches; up to 75 % of the total surface tension, while *oxidized* starches would reach a ratio of around 50 % disperse and polar contribution. The difference may be explained by the increased amount of polar carbonyl- and carboxyl groups on the starch backbone in case of oxidized starch. This too could be verified by preparing hydrophobic derivatives based on acid degraded waxy potato starch, just as the effect of acid degradation on the rheological behavior of BHP waxy potato starch, as described in previous paragraphs. Since the same effect is detected for benzyl groups as well as BHP groups based on native starch, it seems that the formation of a dispersion of benzyl starches upon cooking has nothing to do with this phenomenon.

In Chapters 1, 3 and 5 the influence of the liquid surface tension was emphasized for coating drying models through the capillary number, see Equation 1, but this was not investigated during this research. Surface tension measurement by sessile drop tensiometry could not be performed at a concentration relevant in coating formulations; this viscosity of starch solutions >20 %W is simply too high. In addition, the measurement should be performed at increased temperature (around 90 °C) to mimic drying conditions. On the other hand, it may be assumed that the surface tension of the starch solution decreased at increasing hydrophobic content (hydrophobic starches did show foam formation during solution preparation).

On the behavior of benzylated native starches

Aside from the discussion above, there is an interesting feature about the behavior of benzylated native starches, namely: the formation of a dispersion upon cooking while oxidized benzylated starches or other hydrophobic substituents do not. In the literature, the formation of a dispersion

upon cooking of benzylated starch suspensions is repeatedly reported. Berkhout and Guns [10] reported the formation of a dispersion as well as Bohrisch et al. [11] who even reported the formation of a sub-micron dispersion of both degraded corn starch and degraded potato starch prepared both in suspension and in homogeneous reaction mixtures. The viscosity of native benzylated starches was reported to decrease, which was also observed in our research. This is in contradiction to what was observed in the research described in this thesis: that oxidized and benzylated starches dissolve primarily and only leave some granular fragments and at most an opaque solution. Also, W-0.2 BHP yielded a very clear solution upon cooking. Moreover, 1-allyloxy-2-hydroxypropyl (AHP) starch, prepared by Huijbrechts et al [12] was not reported to form a dispersion upon cooking, but the viscosity of native starch with AHP groups increased upon cooling in the RVA profile similar to for example X85-0.375 Bn.

The formation of a dispersion may be caused by the formation of aggregates due to hydrophobic interaction. Also, 'fragmentation' has been used in the literature [10] to describe the formation of a dispersion, which suggests incomplete granular break-up. In both cases, the decreased viscosity is caused by the fact that starch is captured in discrete particles which only contribute little to the total viscosity, which is illustrated by the Einstein-equation or the Krieger-Dougherty equation as described in Chapter 3. If the dispersion is indeed formed by aggregation, then this process takes place in situ, during the cooking process, but this contradicts the observation that other hydrophobic substituents or the use of oxidized potato starch as a base material does not show this behavior. It seems more logic that the viscosity of native benzylated starches also increases upon cooking, similar to that of oxidized and benzylated starches, e.g. X85-0.375 Bn which is supported by the literature, as stated in the previous paragraph. An increased viscosity upon benzylation may also support the formation of a dispersion. If indeed the substitution pattern of benzyl groups is not uniform across the starch backbone in the slurry reaction, which is also supported by the literature [13-15], then the viscosity of the benzylated starch molecules varies greatly within the starch granule. Standard mixing theory states that the difference in viscosity of two compounds cannot be too large, provided that the solubility parameters of the two compounds are alike, since no mixing will then take place. A SEM image was taken from a diluted (10^{-4} %W) solution of PS-0.25 Bn which was freeze-dried on a SEM-sample plate, see Figure 5.

The image in Figure 5 shows spherical to egg-shaped particles with sub-micron dimensions. Most of these particles are incorporated in the 'wires', formed by dissolved starch upon freeze drying. The fact that most of these particles are incorporated supports the hypothesis that a mixing-problem occurred, since the particles are all in connection to starch which was dissolved. Independent

particles would also have deposited separate from any dissolved material, especially at these low concentrations (well below cac).

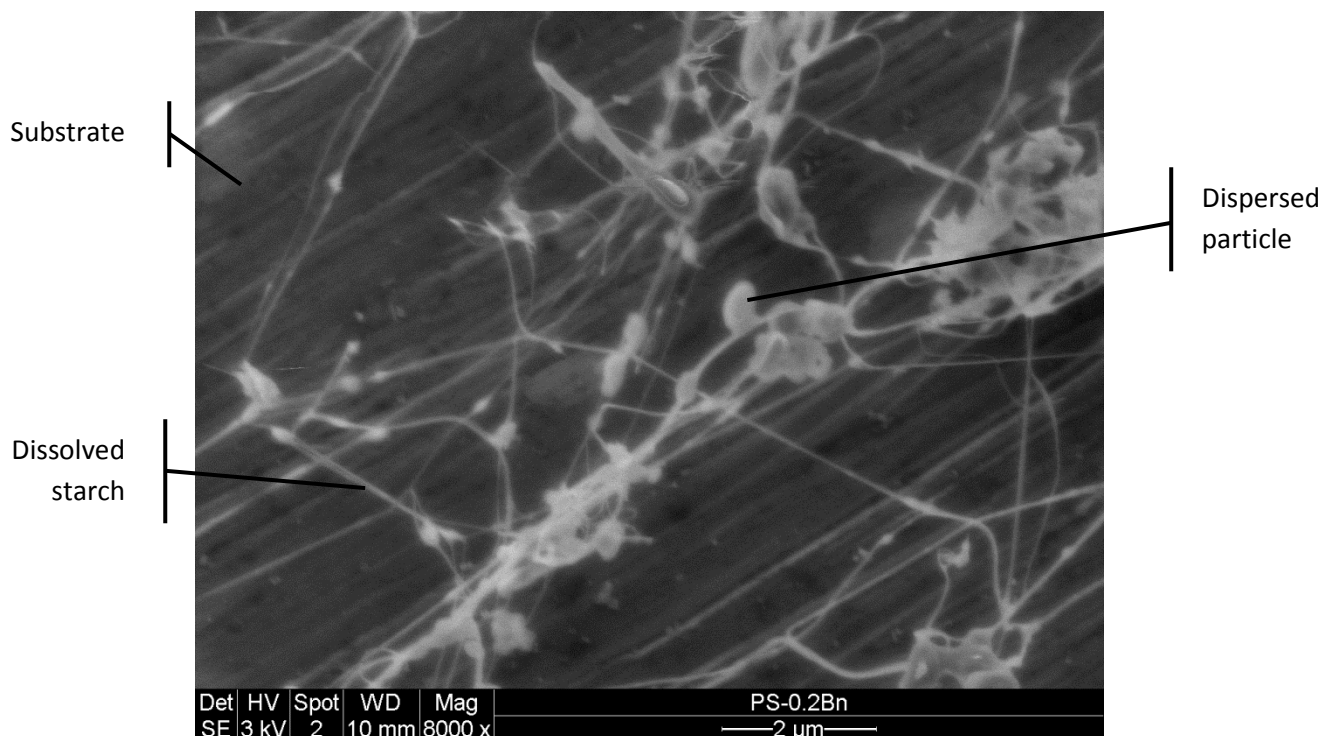


Figure 5: SEM image of freeze dried 10^{-4} %W solution of PS-0.25 Bn.

Is hydrophobicity of starch required?

The central hypothesis, on which the work in this thesis is based, is that hydrophobic groups may provide properties to starch that are beneficial for the replacement of SBR latex by starch. In the end, the question how much hydrophobicity is needed for good printability remained unanswered so far, despite some products that performed reasonably well. Three coatings with very different properties showed good results on the mottling test. PS-0.25 Bn gave a very hydrophobic film ($\gamma^T = 44.9$ mN/m) with an unusual high contribution of disperse forces ($\gamma^D = 37.9$ mN/m). The other coatings were based on X55-0.3 Bn and X85-0.2 BGE, both with similar surface tension ($\gamma^T = 44.9$ mN/m) but different hydrophobic content ($\gamma^D = 29.6$ vs 19.2 mN/m). In this paragraph it is attempted to go a little deeper into the wettability of a surface and the question how hydrophobic the starch should be for good interaction with oil in the ink. If it turns out that low hydrophobicity is sufficient, this is economically favorable since a low DS requires less reagents.

The wetting factor or spreadability (S) between a liquid and a solid surface, is calculated by:

$$S = \gamma_{LV} + \gamma_{SL} - \gamma_{SV} \quad (\text{Equation 8})$$

γ_{LV} is the liquid-vapor surface tension, γ_{SL} is the solid-liquid interfacial tension and γ_{SV} is the solid-vapor surface tension. In this equation, γ_{SL} is unknown but may be calculated through the general equation:

$$\gamma_{12} = \gamma_1 + \gamma_2 - F \quad (\text{Equation 9})$$

A common expression for F is:

$$F = 2 \left[\left(\gamma_1^D \gamma_2^D \right)^{1/2} + \left(\gamma_1^P \gamma_2^P \right)^{1/2} \right] \quad (\text{Equation 10})$$

And assuming:

$$\gamma_i = \gamma^D + \gamma^P \quad (\text{Equation 11})$$

Representing the contribution of disperse (D) and polar (P) forces to the total surface tension of any substance (i). These equations predict the wettability of both oil and water, which is used as a fountain solution in web-offset printing (see Chapter 1). First, the starch-water and starch-oil interactions are calculated and subsequently the water and oil wettability on the starch surfaces as can be seen in Table 5. Equations 8 through 11 were adopted from [16].

Product	μ^a Pa.s	γ^P mN/m	γ^D mN/m	γ^T mN/m	γ_{St-w} mN/m	S-water mN/m	γ_{St-oil} mN/m	S-oil mN/m
X85-0	3.8	35.1	21.7	56.8	170.7	186.7	35.1	-1.7
X55-0	1.2	24.4	26.7	51.1	146.2	167.9	24.9	-6.2
PS-0.25 Bn	1.0	7.0	37.9	44.9	105.3	132.8	11.6	-13.7
W-0.25 Bn	12	9.2	36.1	45.3	98.0	125.9	9.8	-15.1
X85-0.125 Bn	2.0	16.9	31.4	48.3	127.5	152.0	18.2	-10.1
X85-0.25 Bn	13	17.2	29.2	46.4	128.0	154.4	18.1	-8.3
X85-0.375 Bn	720	14.7	30.3	45.0	121.2	149.0	15.8	-9.2
X55-0.2 Bn	10	13.0	30.9	43.9	116.3	145.2	14.2	-9.7
X55-0.3 Bn	83	15.0	29.6	44.6	121.9	150.1	15.9	-8.7
X85-0.2 BHP	1.1	17.8	22.3	40.1	129.1	161.8	17.9	-2.2
X85-0.3 BHP	0.45	16.4	21.9	38.3	125.2	159.7	16.4	-1.9
X55-0.2 BHP	0.45	17.9	24.9	42.8	129.4	159.4	18.2	-4.6
X55-0.3 BHP	0.55	21.9	20.7	42.6	139.8	170.0	21.9	-0.7
D517^{a,b}	0.35	23.0	20.1	43.1	142.5	172.2	23.0	-0.1

Table 5: viscosity, surface tension and calculated spreadability parameters of hydrophobized starches.

^{a)} Viscosity at 30 %W, W and PS at 10 %W, D517 50 %W

^{b)} Styronal D517 is a commercially available latex used by the paper industry and used here as a reference material.

The calculations show that the oil has good wettability on every surface, including the starting materials, X85-0 and X55-0 which is quite a surprise. Actually, the reference material Styronal D517

shows wettability, but is least negative of all surfaces. Probably, this particular property of the latex has been tailored to this value. The water-wettability of all surfaces is low but, also surprisingly, the wettability of PS-0.25 Bn and W-0.25 Bn improved while it was expected that hydrophobic groups would decrease the wettability of water. γ^D and γ^P were varied in Equation 8. From these calculations it was found that for any oil, with a γ^T of 20 mN/m and $\gamma^D = 20$ mN/m and thus no polar contributions, any solid surface tension with a disperse contribution of at least 20 mN/m turned out to show wetting for this particular oil. Generally, for pure disperse liquids, this can be expressed as Equation 12:

$$S < 0 \Leftrightarrow \gamma_s^D \geq \gamma_L^D \quad (\text{Equation 12})$$

Water, however, has a total surface tension $\gamma^T = 72.8$ mN/m with $\gamma^P = 51$ and γ^D mN/m = 21.8 mN/m. Herein lies the reason why the decreased surface tension of films from PS-0.25 Bn and W-0.25 Bn have improved water wettability; their disperse contribution increased considerably. Since the surface tension of water is for almost 30% accounted for by disperse forces, the wettability improves if the disperse contribution of the solid surface increases.

Quo vadis?

In summary, the main conclusion that can be drawn from the previous sections is that the rheological behavior of the starch solution determines the viscosity and consolidation behavior of the coating formulation and thus the end-use properties of the coating. However, the values for the viscosity used in the models (Equations 1, 3, 4 and 6) are estimated values at 100 °C, while these were not measured. In addition, the surface tension of starch solutions was estimated to be 50 mN/m for all starch solutions. This value is close to the average of all measured film surface tensions, however, it is not known either what their exact values are at elevated temperatures. Moreover, calculations showed that the surface tension of the starch film provides sufficient hydrophobicity for good oil wettability. It is true that a starch-based coating which is applied and dried in a similar way as a latex-based coating causes mottling due to changes in the final coating structure, but both the experimental results and the calculations in this chapter show that there is much opportunity for improvement by changing processing conditions as well as starch properties to replace SBR latex by starch. Several suggestions for further research are listed and discussed below.

1. Influence of drying speed.

The calculations show that if the drying speed is increased, the aqueous coating phase containing the starch will be too viscous to flow so the coating will dry top-down, fine particles will remain in the coating layer and the overall result is expected to be a more porous structure.

2. Increase the solids content of the starch in solution.

If the solids content of starch in solution is increased to, for example, 50 %W, the mobility of fine coating particles will decrease because the relative aqueous phase volume is decreased, see Chapter 1, Figure 12. This may not be an economically favorable method, since it would involve an extra production step to produce cold-water soluble starch (the maximum concentration of a granular waxy potato starch slurry is around 37 %W), but an experiment at this concentration would prove the validity of this hypothesis. The viscosity of the starch solution should be low enough to obtain a coating formulation with a solids content >68 %W and a Brookfield viscosity of 1000-1200 mPa.s.

3. Use bimodal molecular weight distribution of starch.

The solution viscosity of benzylated starches X55-0.3 Bn and X85-0.375 Bn showed a rapid increase at increasing solution concentration, which, according to the calculations in this chapter, may be the reason for the development of their coating structure. The viscosity of X85-0, for example, probably remains low quite far into the drying process in comparison to X85-0.375 Bn. Probably, immobilization of fine coating particles takes place at a later moment for X85-0 than for X85-0.375 Bn. One strategy to obtain a starch solution based on oxidized waxy potato starch, with a similar viscosity profile as X85-0.375 Bn, is to use starch with a bimodal molecular weight distribution. This can be achieved by mixing a highly oxidized starch, which provides a low viscosity at a high solids content, with a relatively small amount of less oxidized (native starch will probably degrade due to the high shear forces during the blade coating process) starch. After preparation of a coating formulation, the total starch concentration in the water phase is relatively low, say 17 %W. The contribution of high molecular weight starch to the total viscosity at this stage is low and the highly oxidized starch provides low viscosity, needed for the application process. Upon drying, however, the viscosity of high molecular weight (oxidized) starch will increase much faster than that of the low molecular weight starch. The net-effect should be the mimicking of the drying behavior of, for example, X55-0.3 Bn or X85-0.375 Bn and yield a similar coating surface structure. In addition,

if this experiment succeeds and the coated paper yields good results from the mottling test, this would validate the hypothesis that starch does not require hydrophobic groups for good printability. The addition of high molecular weight starch and the accordingly high viscosity at high solution concentration may also decrease migration due to repeated wetting by other coating layers or by fountain solution (see Chapter 1) during the printing process.

4. Modeling of the consolidation process of starch based coatings.

In the literature, there is substantial information on the drying behavior of latex based coatings [1,17]. Mostly, starch is approached as an additive or as a problem, due to migration and mottling. A latex-based coating contains water and has a constant viscosity through the whole consolidation process. Starch-based formulations, however, are hard to model even with a very common model like the Krieger-Dougherty equation (see Chapter 3) to relate the formulation viscosity to the solids content, since the starch concentration and its viscosity are also variable. This problem continues into the drying process; while Pan et al. modeled for latex and stated that a process is in a certain regime of Ca and Pe , a starch-based coating may start in a regime where there is migration, while it may enter another at any moment during the drying process. Therefore, effort should be made to model the consolidation process of a starch-based formulations as a function of viscosity and surface tension to learn more about its possible behavior and maybe predict in advance what the rheological behavior of the starch solution should be in order to obtain a desired coating structure without migrated starch. Some attention should be given to the heating-up effect during the drying process. How fast can the viscosity of starch decrease at different heating rates? Starch is a large molecule and it may take some time to adjust to the new temperature, which may be of large influence on the drying process and may thus offer an opportunity to manipulate the consolidation process. The modeling would also be aided by the determination of liquid surface tension of different starches at concentrations of $> 20\%$ and elevated temperatures since these are the conditions of the coating- and drying process.

Conclusion

This chapter summarizes the results from previous chapters and an attempt is made to understand the differences in properties of the different starches and different modifications. The most important parameter is the viscosity of starch. The surface tension may need some attention

since its impact is not exactly clear and more research is advisable on this topic. Calculations showed that there is much opportunity for improving the behavior of starch in the paper coating process. Finally, the most important conclusion of this chapter is that starch should not be treated as a problem (cause of mottling, ink setting). Calculations show that starch has the potential to replace SBR latex successfully, without necessarily adding some oil-based material to the starch on top of the oxidative treatment.

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Appendix A

The DIXON lab-coating machine

The DIXON lab-coating machine is a semi-pilot setup for blade-coating research. Figure 1 displays a schematic representation of the Machine. An overview picture is displayed in Figure 2. Paper is led from the reed-roll over a series of rolls to reduce stress on the paper. Eventually, the paper passes the so-called 'backing-roll' where the blade is positioned and the coating formulation is deposited on the paper web, which is displayed in Figure 3. The blade-pressure can be varied to tune the deposited amount of coating on the paper. Subsequently, the paper containing the wet coating is transported into a drying section where steam-heated dryers are operated at 140 °C to evaporate the water. When the paper exits the drying section, the moisture content is typically around 4 – 6 %W. The paper passes a 'leveling-roll' to smoothen the paper-surface and is finally wound on the product-roll. T After the coating process is complete, the paper samples are cut from the product-roll and cut to size, which is shown in Figure 4. The samples are stored at standard conditions (23 ± 1 °C, 50 %RH) for at least 24h to reach equilibrium moisture content.

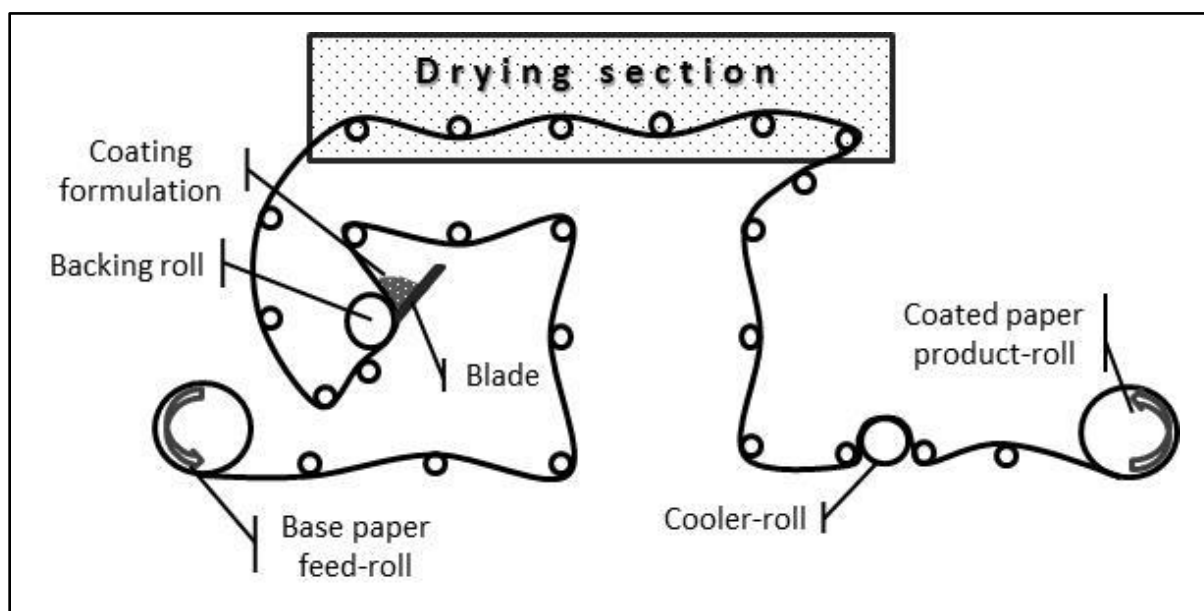


Figure 1: Schematic representation of the DIXON coating machine.

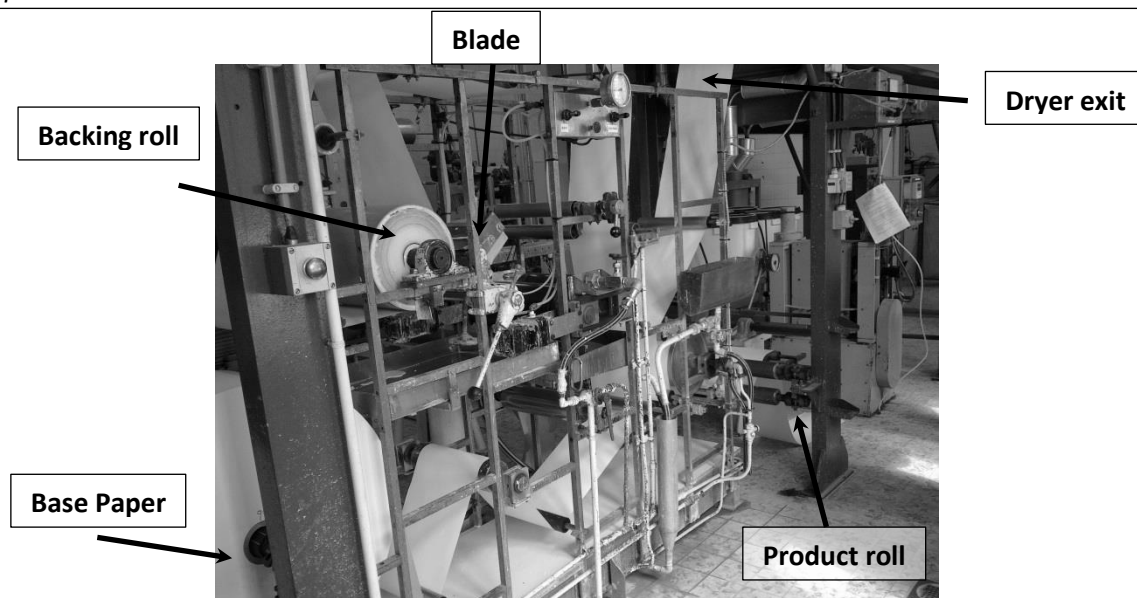


Figure 2: Overview picture of the DIXON coating machine

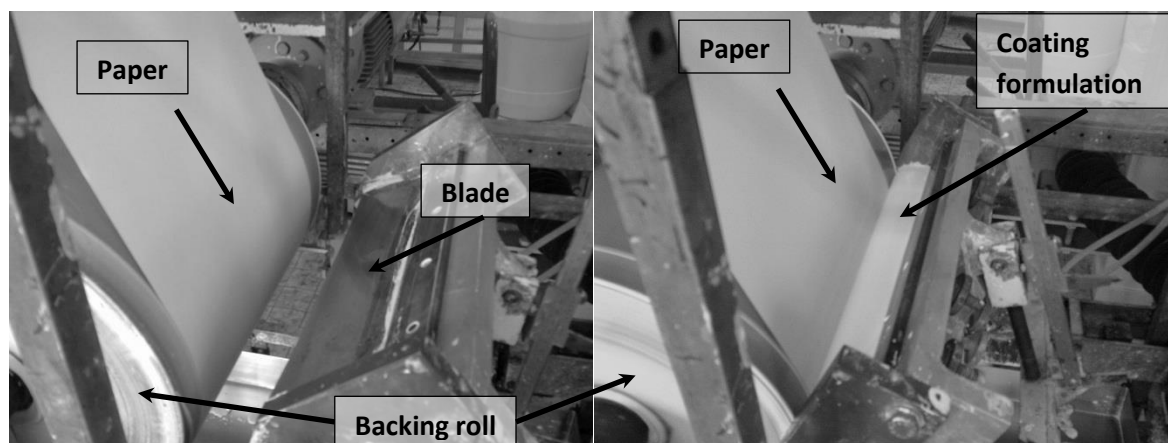


Figure 3: Details of the DIXON coater. Left: without coating, right: with coating.



Figure 4: Cutting samples from the coated paper roll.

Summary

This thesis describes the results of four years of research on the replacement of SBR latex by starch in paper top-coatings. High quality paper coatings are applied to base paper to increase its visual appearance. Up to the Second World War, natural binders like starch and casein were used, but since the petrochemical revolution, tailor made synthetic binders were both lower in cost and superior in performance. However, the starch industry reclaims more and more of the lost terrain. By reducing the viscosity of starch by oxidation, it can already be applied in base- and mid-coats. Increasing oil prices and the trend toward a more bio-based economy enhance this development. Unfortunately, starch has some drawbacks.

The major challenge of the implementation of starch in a high-tech application like paper coating is modifying a -with respect- ill-defined bio-macromolecule to perform similar to a, tailored synthetic product, designed specifically for such a process. The viscosity of starch can be reduced by oxidation, rather than acid degradation. Carbonyl- and carboxyl groups from the oxidation process decrease the tendency of starch to retrograde. A starch film is generally more rigid and brittle than latex-films, but oxidized waxy potato starch were developed which showed improved film forming properties. Still, the molecular structure of (oxidized) starches and SBR latex are very different. It is either this difference or the changing drying behavior of the coating by replacing a dispersed binder (latex) by a dissolved one (starch) that causes, for example, print mottle. Print mottle can be enhanced by the coating structure (roughness, porosity) but also by the presence of starch. It is a fact that starch is able to migrate from the pre- and mid-coating to the top-coat during the application of the latter. Since the ink, used in web-offset printing is oil-based, it is reasonable to assume that if the starch becomes more oil-like, the enhanced interaction with oil will reduce mottling. This is the basis of the central hypothesis of this thesis: the introduction of hydrophobic groups on the starch back-bone will improve its performance in top-coatings.

Chapter 2 deals with the synthesis and characterization of benzylated waxy and oxidized waxy potato starches. It was found in the literature that, for example, corn- and classic potato starch (20 % amylose) form dispersions upon cooking due to the introduction of benzyl groups. For native waxy potato starch, this was also the case, however, oxidized waxy potato starches showed increased solubility and did not form a dispersion. Instead, a viscosity increase was observed, especially at a DS higher than 0.3. At this level of benzylation, native waxy potato starch would no longer dissolve in water. The increased viscosity is expected to be caused by hydrophobic interactions of the benzyl

groups which were detected by UV emission spectrometry. The molecular weight of the products did not increase significantly. The surface tension of the dry product films, casted from solution, decreased upon benzylation as expected. It was calculated that this would decrease the work of adhesion between the starch product and the pigment (CaCO_3), as well as the cellulose in the base paper.

In **Chapter 3**, the products, prepared and characterized in Chapter 2, were used in top-coating formulations. The formulation viscosity and dewatering behavior were measured. The dewatering of coating formulations of all starch products was lower than latex based formulations: <20 vs. ~90 g/m². The viscosity of X85-0.375 Bn showed a strong shear thinning behavior, but also a large recovery at increasing and decreasing shear rates. The coatings were deposited on paper by a laboratory-scale blade-coating machine, called DIXON coater. Bonding strength, porosity and mottling were tested and SEM images were taken. Generally, bonding strength did not decrease; only the highest DS-benzyl of oxidized waxy potato starch showed a decrease. It is not clear if this decrease was caused by the low work of adhesion or by increased porosity of the coating. The SEM images showed that the surface structure of the coatings was different for every product. FTIR measurements showed that the amount of starch at the coating surface decreases at higher DS. Mottling behavior was improved for coatings based on benzylated starches. Especially PS-0.25 Bn and X55-0.3 Bn performed well. X85-0.375 Bn was too porous to obtain good printability. It was concluded that a combination of oxidation and benzylation of waxy potato starch may yield a product that can replace SBR latex.

Chapter 4 is dedicated to the preparation and characterization of a second hydrophobic modification: 1-butoxy-2-hydroxypropylation (BHP) using butyl-glycidyl ether (BGE). Since some environmental- and safety issues disfavor the use of benzyl chloride, it was attempted to use an epoxide instead. The same method of modification as for the benzylation was used: preparation in slurry reaction using Na_2SO_4 as a swelling inhibitor for the starch. Higher chain lengths could not be used due to their insolubility in water which inhibits the reaction. It was found that, in contradiction to benzylated products, the viscosity of BHP starches decreased as the MS increased. Decreased molecular weight was not detected. Hydrophobic interactions on the other hand, were. It is suggested that BHP groups are less bulky than benzyl groups and that shielding of OH groups by BHP may cause the decreased viscosity due to decreased hydrogen bonding. Dry film surface tension of the products was also found to be lower than that of the starting materials.

Chapter 5 deals with the preparation and characterization of BHP-starch-based coating formulations, similar to the work in chapter 3. Subsequently, these formulations were also deposited to base-paper

and characterized according to the methods used in chapter 3. This yielded some interesting results. It was found that the amount of applied coating very much influences the results of the measurements and that, for differences to be detected, a minimum of 12 rather than 10 g/m² is required. In addition, the decreased formulation viscosity resulted in the formation of a dense surface structure, which was shown by the Curley porosity as well as SEM images. Mottling behavior, however, improved despite the low porosity. On the other hand, despite the low porosity of the coatings, the use of BHP starch resulted in a certain roughness of the coating surface, also found in latex-based coatings. It was concluded that BHP-groups on oxidized waxy potato starch may successfully replace SBR-latex.

Finally, in **Chapter 6**, the results of the preceding 4 chapters are compared and evaluated. It was suggested that hydrophobicity may not be necessary to replace SBR latex in top-coatings. This hypothesis is based on the observation that substitution of a less hydrophobic group (BHP) resulted in good coating properties, at a lower content than a highly hydrophobic group (Benzyl) on a different starting material (X55 vs. X85, respectively). The structure of the coatings, based on these products, showed similarities with that of latex-based coatings, based on SEM images. Another argument to support the hypothesis is that it was calculated that the wettability of oil is good on all starch products which have a surface tension of which the disperse contribution is equal to or bigger than the surface tension of the oil, applied in the ink. This only holds for oils with zero polarity.

It was also attempted to explain differences according to a model, proposed in the literature using dimensionless numbers to characterize the coating drying behavior in terms of viscosity, surface tension, diffusion and processing conditions. These calculations supported the findings in earlier chapters that less starch had migrated to the coating surface during the drying process. Optimization of the drying process may further enhance successful replacement of SBR latex by starch. The calculations further supported the hypothesis, stated above, that if the rheological behavior of the starch solution during the drying process indeed determines the final coating structure, than a mixture of high and low viscous starches may be sufficient to yield a starch-based coating that performs as desired. It is advised to model the drying behavior of starch-based coating formulations in more detail to gain insight in the required rheology.

Perhaps it is most important to realize that the subject should be approached from a starch- rather than a latex-point-of-view.

Samenvatting

Dit proefschrift beschrijft de resultaten van vier jaar onderzoek naar het vervangen van SBR latex door zetmeel in top-coatings. Papier coatings van hoge kwaliteit worden op basis-papier aangebracht om zijn visuele eigenschappen te verbeteren. Tot aan de tweede wereldoorlog werden hiervoor natuurlijke bindmiddelen als zetmeel en caseïne gebruikt. Echter, de olie-gebaseerde, speciaal ontworpen, goedkope synthetische bindmiddelen die na de oorlog werden ontwikkeld waren superieur aan de natuurlijke bindmiddelen. Tegenwoordig wordt steeds meer van het verloren terrein teruggewonnen. Toenemende olieprijs en de transitie naar een meer 'bio-based' economie zijn hier oorzaken van. De reductie van de viscositeit van zetmeel door oxidatie heeft ervoor gezorgd dat zetmeel momenteel kan worden ingezet in pre- en midcoats. Helaas heeft zetmeel toch nog enige nadelen die de toepassing in top-coatings in de weg staan.

De belangrijkste uitdaging voor het succesvol vervangen van SBR in een high-tech toepassing als papier coating is het dusdanig modificeren van een, met respect, slecht gedefinieerd bio-macromolecuul zodat het zich net zo gedraagt als een synthetisch product welke speciaal voor deze toepassing is ontworpen. Oxidatie van zetmeel verlaagt de viscositeit van de oplossing. De carbonyl- en carboxyl groepen welke tijdens het oxidatieproces op het zetmeelskelet vormen, zorgen ervoor dat de stabiliteit van de oplossing verbeterd doordat retrogradatie voorkomen wordt. Dit is anders dan bijvoorbeeld zuur-afgebroken zetmeel, welke wel snel retrogradeert door de afwezigheid van deze groepen. Over het algemeen is een zetmeelfilm stijver en breekbaarder dan een film van latex, maar dit gedrag is verbeterd door de ontwikkeling van geoxideerd waxy aardappelzetmeel. Waxy aardappelzetmeel bestaat bijna volledig uit amylopectine. Toch zijn de verschillen op moleculair niveau tussen zetmeel en SBR latex groot. Daarnaast verschillen de verschijningsvormen van beide producten: latex bestaat uit discrete bolletjes met daartussen water en zetmeel is een oplossing. Het verschil tussen de moleculaire structuur en verschijningsvorm ligt ten grondslag aan het ontstaan van een belangrijk probleem wanneer latex door zetmeel wordt vervangen: print mottle (spikkels). Mottle kan worden versterkt door de structuur van de coating (ruwheid, porositeit), maar ook door de aanwezigheid van zetmeel. Het is vastgesteld dat zetmeel uit de pre- en midcoat naar de top-coat kan migreren tijdens het aanbrengen van de laatste. Omdat de inkt, die wordt gebruikt voor het bedrukken van dit soort papieren, is gebaseerd op (hydrofobe) olie, is het logisch om aan te nemen dat de aanwezigheid van (hydrofiel) zetmeel deze problemen veroorzaakt. Vervolgens is het ook een logische gedachte dat het introduceren van hydrofobe groepen op het zetmeelskelet mottling zal verminderen. Vandaar dat de uitgangs-hypothese, waarop het werk in dit proefschrift is gebaseerd,

luit: het introduceren van hydrofobe groepen op het zetmeelskelet zal leiden tot verbeterd gedrag bij toepassing in top-coatings.

Hoofdstuk 2 is geweid aan de bereiding en karakteriseren van gebenzyleerd waxy aardappelzetmeel en een aantal geoxideerde waxy aardappelzetmelen. Uit de literatuur bleek dat bijvoorbeeld mais- en klassiek aardappelzetmeel (met 20% amylose) dispersies vormen na benzylering en koken van het zetmeel. Dit gedrag is ook vastgesteld voor waxy aardappelzetmeel, maar de geoxideerde derivaten waren veel beter oplosbaar en vormden geen dispersie. In plaats daarvan is een sterk toegenomen viscositeit waargenomen, vooral bij een DS hoger dan 0,3. Bij een dergelijk niveau kon natief gebenzyleerd waxy aardappelzetmeel niet meer worden opgelost in water of werd geen dispersie meer gevormd. De toegenomen viscositeit wordt waarschijnlijk veroorzaakt door hydrofobe interactie van de benzylgroepen, wat is vastgesteld door UV-emissiespectrometrie. Het verschil in molecuulgewicht tussen de producten was niet groot genoeg om het verschil in viscositeit te verklaren. De oppervlaktespanning van de gedroogde films van de zetmeel producten daalde voor de gebenzyleerde producten, wat volgens verwachting was. Het was berekend dat hierdoor de adhesie tussen zetmeel en het pigment (CaCO_3) en het papier (cellulose) zou afnemen.

In **Hoofdstuk 3** zijn de producten die gesynthetiseerd en gekarakteriseerd zijn in hoofdstuk 2 gebruikt als bindmiddel in formuleringen van top-coatings ter vervanging van latex. Hierbij zijn de viscositeit en het ontwatergedrag gemeten. Het ontwatergedrag van de coating formuleringen van elk van de zetmeelproducten was laag vergeleken met een latex-gebaseerde coating: <20 tegen $\sim 90 \text{ g/m}^2$. De viscositeit van X85-0,375 Bn nam sterk af bij toenemende shear rate, maar een sterke toename zien wanneer de shear rate weer werd verlaagd. Vervolgens zijn de coatings aangebracht op basispapier met behulp van een laboratoriumschaal blade-coating machine, genaamd DIXON coater. Van deze coatings werden de bindkracht, de porositeit en mottling-gedrag bepaald. Ook zijn SEM foto's gemaakt van de coatingoppervlakken. In het algemeen nam de bindkracht niet echt af naarmate DS-benzyl van de geoxideerde zetmelen toenam, alleen bij de hoogste substitutiegraad was dit het geval. Het kon niet duidelijk vastgesteld worden of deze afname het gevolg was van de veranderde oppervlaktespanning van de zetmeelfilm, zoals berekend, of door de toegenomen porositeit van de coatinglaag waardoor het bindend oppervlak afneemt. De SEM foto's lieten zien dat elk gebenzyleerd zetmeelproduct een andere oppervlaktestructuur veroorzaakte bij de bijbehorende coating. Met behulp van FTIR is vastgesteld dat de hoeveelheid zetmeel aan het coatingoppervlak lager was bij toegenomen DS. Daarnaast vertoonden sommige coatings, gebaseerd op gebenzyleerd zetmeel, verbeterd mottling-gedrag. Voornamelijk PS-0,25 Bn en X55-0,3 Bn gaven goede resultaten. X85-0,375 BN was zo poreus dat de inkt geen goede laag kon vormen. Er is geconcludeerd dat de

combinatie van oxidatie en benzyleren van waxy aardappelzetmeel kan leiden tot een product dat SBR latex kan vervangen.

Vervolgens is in **Hoofdstuk 4** een tweede hydrofobe modificatie uitgevoerd: 1-butoxy-2-hydroxypropylering (BHP) met behulp van butyl-glycidyl ether (BGE). Vanwege het feit dat benzyl chloride omgevings- en gezondheidsrisico's met zich meebrengt is gebruik gemaakt van een epoxide. Dezelfde modificatie-techniek als voor benzylering is gebruikt: de reactie is uitgevoerd in een slurry van zetmeel met gebruik van Na_2SO_4 om zwelling van de zetmeelkorrels te verhinderen. Grotere ketens dan BGE konden niet worden gebruikt vanwege de onoplosbaarheid van deze componenten in water. Dit heeft tot gevolg dat er geen reactie meer optreedt. De introductie van BHP groepen op het zetmeel had tot gevolg dat de viscositeit van de zetmelen afnam bij toenemende moalire substitutie, terwijl een toename was verwacht. Het molecuulgewicht van de producten nam niet af, maar hydrofobe interacties zijn wel waargenomen, net als bij benzylering. Het lijkt erop dat BHP groepen, ondanks dat ze een OH groep dragen, voor minder waterstof-brug vorming zorgen dan hij niet gemodificeerd zetmeel en dat dit de oorzaak is van de afgenomen viscositeit. Dit is echter gespeculeerd. De oppervlaktespanning van de BHP zetmelen was wel lager dan van het basis-zetmeel wat voor de reactie gebruikt was.

Hoofdstuk 5 behandelt de bereiding en karakterisering van top-coating formuleringen, gebaseerd op BHP zetmelen uit Hoofdstuk 4. Karakterisering vond plaats op een soortgelijke wijze als beschreven in Hoofdstuk 3. Dit leverde interessante resultaten op. Ten eerste werd duidelijk dat de standaard-hoeveelheid van 10 g/m^2 coating op het basispapier niet voldoende is om onderscheid tussen de zetmelen aan te tonen met de gebruikte onderzoeksmethoden. Een hoeveelheid van minimaal 12 g/m^2 bleek wel voldoende te zijn. Daarnaast zorgde de afgenomen viscositeit van de formulering voor de vorming van een dichte coating-structuur met een lage curly porositeit. Dit is ook vastgesteld door middel van SEM foto's. Vreemd genoeg nam de mottling sterk af, ondanks de dichte oppervlaktestructuur van de coatings. Ondanks de lage porositeit hadden de coatings, gebaseerd op BHP zetmelen, een oppervlakteruwheid die vergelijkbaar is met een latex-gebaseerde coating. Er werd ook hier geconcludeerd dat het aanbrengen van BHP groepen op geoxideerde waxy aardappelzetmelen succesvol SBR latex zou kunnen vervangen.

Tot slot worden in **Hoofdstuk 6** de resultaten van de vier voorgaande hoofdstukken met elkaar vergeleken en ge-evalueerd. Dit resulteerde in de hypothese dat zetmeel wellicht geen hydrofobe eigenschappen nodig zou hoeven hebben om SBR latex in top-coatings te kunnen vervangen. De basis van deze hypothese is de waarneming dat producten met verschillende substituenten (BHP of Benzyl groepen), een verschillende substitutiegraad, verschillende startmaterialen (natief

aarappelzetmeel of geoxideerde waxy aardappelzetmelen X85 en X55) en met verschillende expressie van de oppervlaktespanning toch goede coating-eigenschappen vertoonden. De structuur van de goed presterende coatings vertoonden overeenkomsten met de structuur van een coating gebaseerd op latex, zoals blijkt uit SEM foto's. Een ander argument dat de hypothese ondersteund is dat door berekening is vastgesteld dat de 'wettability' van olie op alle zetmeelproducten goed is, mits de disperse component van de oppervlaktespanning van zetmeel gelijk aan of groter is dan de oppervlaktespanning van de olie. Dit gaat alleen op wanneer de olie volledig dispers is.

Ook is een poging ondernomen om verschillen tussen de coatings te verklaren op basis van een model uit de literatuur waarin dimensieloze kentallen worden gebruikt om het drooggedrag van de coating te beschrijven. Hierbij wordt gebruik gemaakt van de viscositeit, oppervlaktespanning, diffusie en proces-condities. Deze berekeningen ondersteunen de bevindingen in vorige hoofdstukken waarbij minder zetmeel naar het coatingoppervlak was gemigreerd gedurende het droog-proces. Optimalisatie van het droog-proces kan een positieve bijdrage leveren aan het succesvol vervangen van SBR latex door zetmeel. Verder ondersteunden deze berekeningen ook de bovengenoemde hypothese, omdat het rheologisch gedrag een dominante parameter is en ook van invloed is op de uiteindelijke oppervlaktestructuur van de coating. Het mengen van laag- en hoog visceuze zetmelen zou het rheologisch gedrag van de gehydrofobeerde zetmelen kunnen nabootsen. Als de hypothese klopt, kan op die manier een coating worden verkregen met een vergelijkbare oppervlaktestructuur als bij latex het geval is en waarbij geen mottling optreedt. Het advies luidt om het drooggedrag van coating formuleringen op zetmeelbasis te modelleren om inzicht te krijgen in het gewenste rheologisch gedrag.

De belangrijkste les is wellicht dat gerealiseerd wordt dat het onderwerp wordt benaderd vanuit het 'gezichtspunt' van zetmeel in plaats vanuit dat van de latex.

Dankwoord

English version: Google translate...

“Zo... klaar.” Dat waren de gevleugelde woorden van Shakespeare toen hij klaar was met het stuk ‘Macbeth’ (Finkers, 1993) en dat zijn de woorden die ik na iets meer dan vijf jaar promotie-onderzoek graag zal uitspreken. Voordat ik begin met bedanken van iedereen die direct en indirect hebben bijgedragen aan het gereedkomen van dit boekje, wil ik toch even stilstaan bij wat deze periode voor mij betekent. Toen ik aan het overwegen was of ik een promotie-onderzoek zou willen doen... nee, dat zeg ik verkeerd. Ik wist al jaren dat ik dat wilde, maar toen puntje bij paaltje kwam had ik toch een beetje koud-water vrees. Falen was natuurlijk geen optie dus op zo’n manier leg je de lat voor jezelf eng hoog. Toch maar gedaan, want ja als je potverdorie na een schoolcarrière van MAVO-MTS-HTS-WO eindelijk de kans krijgt om na een paar jaar ploeteren (walk in the swamp...) een uurtje op die stoel te mogen zitten... ja, waar hebben we het dan eigenlijk over?? DOEN! Maar voor mij gaat het verder dan ‘nog een titeltje erbij’. Voor ik begon zat ik in een periode van ‘wat wil ik nou eigenlijk?’ Wetenschap was daarin een belangrijk aspect en daarom heb ik besloten eraan te beginnen. Ik kan me niet anders herinneren dan dat ik aan het prutsen was met van alles en nog wat om iets ‘uit te vinden’, van het maken van een deuralarm met een bel, een lamp, draadjes en een travo tot het mengen van papjes met van alles en nogwat uit het kruidenkastje om van een vervelend mierennest bij de voordeur af te komen (tot op de dag van vandaag daar geen mieren meer gehad...) en dat was vóóordat bovengenoemde schoolcarrière begon. Wetenschap heeft mij altijd gefacineerd. Ten eerste het weten/uitzoeken hoe en waarom iets werkt, maar vooral ook het aspect ‘rede/ratio’, een van de belangrijkste aspecten voor het bedrijven van zuivere wetenschap. Het begrip ‘wetenschapper’ riep bij mij altijd het beeld op van mensen die het altijd bij het rechte eind hebben. Rechte paden, duidelijkheid, precies weten waar ze mee bezig zijn... Ervaring leert dat dat niet per definitie waar is. Ruim vier jaar onderzoeken leert mij ook dat niet zozeer een ‘juiste’ maar een ‘onjuiste’ uitkomst tot inzicht leidt. Als een experiment ‘goed’ gaat (ofwel doet wat je verwacht) heb je eerder de neiging om niet verder te zoeken. Daarnaast is het volgens mij zo dat wanneer je alles weet óf als je je neerlegt bij- dan wel tevreden bent met ‘de huidige situatie’, je geen onderzoek hóeft te doen. In het laatste geval is intrinsieke, academische interesse voldoende om onderzoek te doen. De grootste drijfveer voor ‘ontwikkeling’ is in mijn ogen echter zonder meer non-acceptatie.

Tegelijkertijd wordt ik aangetrokken tot de schijnbare tegenpool van rede en ratio, namelijk ‘gevoel/intuïtie’. Dubbel dankbaar ben ik dus voor het feit dat ik in mijn promotie-periode ook een enorme ontwikkeling door heb mogen maken aan de gevoelskant van het leven, zowel in de vorm van ‘reizen’ als ‘Hoffen’. Fantastisch is het dat wanneer je ratio (in de vorm van het Ego) ‘uitzet’, zich

een nieuwe oceaan aan mogelijkheden voordoet die je stoutse dromen overtreffen. Het mooiste van het kunnen ontwikkelen in deze twee schijnbaar tegengestelde mogelijkheden van het zijn is het besef dat het gevoel en de ratio niet zonder elkaar kunnen. Wanneer je 100% 'in het nu' leeft benut je niet de volle mep van de mentale capaciteiten die je evolutionair gezien gegeven zijn. Hetzelfde geldt voor de ratio, maar dan omgekeerd: sommige dingen zijn (nog) niet of moeilijk rationeel te verklaren. Waarom zou je de ratio uitsluiten als de evolutie heeft besloten dat een mens dat nodig heeft? De kunst is dus om een gezonde balans van beide te vinden. En dat is wel het allermooiste: een rationeel argument om op je intuïtie te vertrouwen 🦋.

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No ego, WEgo!

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– Jan Willem Miel –

Publications:

- J.W.J. Miel and A.A. Broekhuis: "Properties of benzylated native and oxidized waxy potato starch." Submitted to Starch-Starke.
- J.W.J. Miel and A.A. Broekhuis. "Replacement of SBR latex by hydrophobic starch in paper coatings." To be submitted.
- J.W.J. Miel and A.A. Broekhuis. "The effect of oxidation and 1-butoxy-2-hydroxypropylation on the properties of waxy potato starch." In preparation.
- J.W.J. Miel and A.A. Broekhuis. "Oxidized and 1-butoxy-2-hydroxypropylated waxy potato starch in paper coating." In preparation
- J.W.J. Miel. Hydrophobic starch, replacement of SBR in paper coating (63rd starch convention Detmold, Germany, April 2012).