■ Artykuły naukowo-techniczne

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MODIFIED STARCH DISPERSIONS AS WATER–BASED BINDER SYSTEM FOR PAINTS AND VARNISHES

INTRODUCTION

Since the last decades topics like "sustainable development", "eco-friendliness" and "resource conservation" play an important role in the coating technology development. Water-based paints and varnishes, radiation-curing systems, powder and high solid coatings were the answer to these requests[1]. But still the most commercially available binders are made from oil-based resources. Alkyd systems and modified celluloses, natural resins, like colophony and shellac, and oils are exceptions and represent the minor part of commercial coatings till now[2]. So, there is still a demand of new bio-based binders in the paint and varnish industry.

With its worldwide availability and its low market-price native starch provides the potential for the use as a bio-based material. However, in its native form it is highly hydrophilic, not cold-water dispersible [3], decomposes before it reaches its glass transitions temperature (T_g) (extrapolated: 225–235 °C) [4] and only forms brittle films [5]. So, it is necessary to modify starch by degradation and esterification or etherification reactions to increase its hydrophobicity, improve its water dispersibility and film forming properties. Nowadays the main application fields are the food, paper and adhesive industry [6]. In the coating industry starch is applied on paper or tablets. To our knowledge, starch or its modified form is not in commercial use where starch is the main component in the binder system in the paint and varnish industry.

Thus, our work aimed at the optimization of starch by chemical modification of degraded starch for the application in the coating sector as binder, with the focus on paints and varnishes. For this purpose, cold-water dispersible hydrophobic starch esters with high solid contents ($\geq$ 30 % (w/w)) were synthesized.

MATERIAL AND METHODS

MATERIALS

In the following table only specialty chemicals are listed.

Table 1. Specialty chemicals.

Material	Description	Supplier
Emox TSD/NV	Degraded potato starch[a]	Emsland Group
Bayhydur XP 2655	Isocyanat hardener	Covestro
Tego Foamex 805 N	Defoamer	Evonik Industries
Borchi Gol LA 200	Additive for improved slip, deaeration, flow and leveling	OMG Borchers

[a]: $Mw = 1.80 \cdot 10^5$ g/mol (determined by SEC-MALLS) Carbonyl/Carboxyl-content: 0.13 / 6.26% (investigated by Titration)

METHODS

SYNTHESIS

Two different methods were used to synthesize starch esters. Starch acetates, propionates and butyrates (C_2-C_4) were produced by using carboxylic acid anhydrides in water and a slightly basic pH, as can be seen in 1. The starch hexanoates were synthesized via a transesterification reaction by using carboxylic vinyl esters in DMSO (2) and based on the method of Winkler et al.[7].
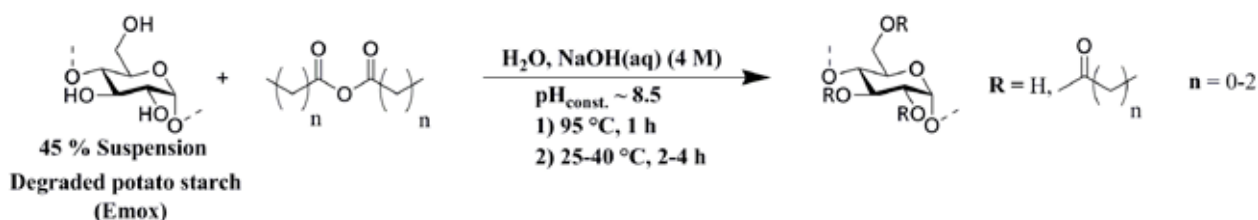

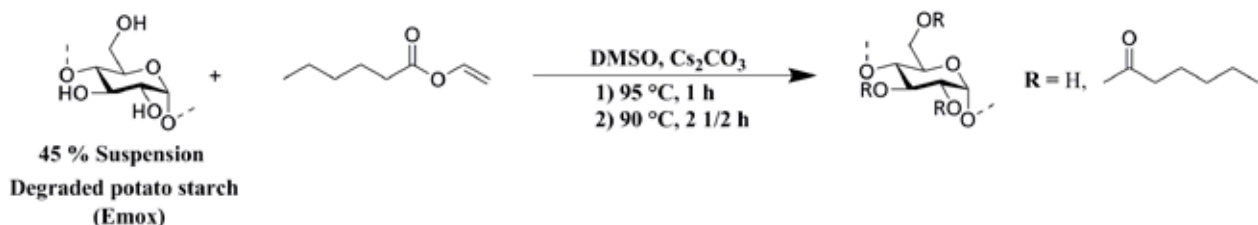Figure 1: Esterification with Carboxylic acid anhydrides.

Figure 2: Transesterification with carboxylic vinyl esters.

CHARACTERIZATION

STRUCTURAL PROPERTIES

DETERMINATION OF DS

The DS values of the short chain esters (starch acetate, propionate, butyrate) was investigated by saponification (1 M KOH, 24 h at room temperature) and back titration (0.5 N HCl) of the excess KOH afterwards. In the same manner the blank test was performed.

PHYSICAL PROPERTIES

WATER DISPERSIBILITY

The maximal possible solid content of the synthesized functionalized starches was investigated in water. The lowest concentration which was tested was 30%. If the water dispersibility was not given with a solid content of 30% the cosolvent diethylene glycol monobutyl ether was used which replaced water as solvent partially. The experiments were performed with a mechanical stirrer at 200 rpm and room temperature.

RHEOLOGICAL MEASUREMENTS

The measurements were performed with a Kinexus pro rotational rheometer (Malvern) and controlled and recorded by the rSpace software. The samples were measured with a cone-plate (cone: angle of slope: 1°, diameter: 6 cm) geometry. The measurement temperature was 25 °C. First an amplitude sweep with a constant frequency of 0.1 Hz was performed to determine the linear area for the following frequency sweep. The shear strain was varied between 0.1 and 100%. In the frequency

sweep the frequency ranged from 0.1 – 10 Hz. The shear viscosity was measured in the shear rate range of 0.1 - 100 s^{-1}.

FILM PROPERTIES

FILM CASTING

Glass plates and a doctor blade with a gap size of 100 µm were used for the film casting. The prepared dispersions were casted in a climate room (23 °C, 50% air humidity (ah)) and dried for 16 h. Afterwards the coated glass plates were brought in laboratory where the climate changed. The temperature (22 °C) as well as the ah (~30–35%) were lower as before. The films which were still continuous after 20 h were treated with 70 °C for 1 h (oven). The brittleness or non-brittleness and the color were evaluated.

The aluminum (Fa. Q-Panel, type: "Al", Q-Lab A-612, 3003 H14) and PBT/PC plates (Fa. Karl Wörwag) were coated using doctor blades with gap sizes of 200 (starch butyrate, DS 0.6) and 250 µm.

LAYER THICKNESSES

The wet layer thickness on glass was determined by a wet film thickness gauge. After the film was casted the wet layer thickness was directly measured at two different positions of the film.

The dry layer thickness on glass plates was evaluated by a Dektak 150 profilometer (Fa. Vecco). The given dry layer thickness was an average value of two measurements which were performed at one sample.

On aluminum plates the dry layer thickness was investigated by an Elcometer 355 (Fa. Elcometer)

WATER PERSISTENCE

The water persistence of the films on glass was tested by using a wet (water) cotton swap and moving this over the film. The number of moves till the coating was dissolved was used as the criterion for the determination of the water persistence. 100 swaps would mean a good water persistence.

On aluminum substrates the water persistence was investigated by exposure of Harrison solution (see corrosion stability) for 20 min and was evaluated by visual inspection after an additional hour. Whitish residuals would mean a bad water persistence and no change in the optical appearance of the coating would imply a good water persistence of the coating.

MECHANICAL PROPERTIES

DECOMPOSITION TEMPERATURE

Pieces of the casted films were dried for 16 h and 75 °C in a vacuum oven, before the thermal gravimetric analysis (TGA) was performed. The decomposition temperatures (T_d) of the modified starches were measured with a Q500 thermogravimetric analyzer (TA instruments). 8–10 mg of the modified starch ester films were heated up to 550 °C in steps of 5 K/min. The degradation was measured by weight loss of the sample. The point of intersection of the elongated lines before and after the first drop of the curve was applied for evaluation.

CORROSION STABILITY

By simulation – based on equivalent circuit models – EIS data can be interpreted regarding loss of the protective properties of coatings like barrier properties, water uptake resistance, undercutting corrosion and delamination. Simulations were performed using the computer program ZView 3.1 (SCRIBNER). EIS is a highly sensitive method, which allows detecting losses of protective properties already in the early stage of coating degradation [8], [9].

Thermocyclic electrolytic loading (TEL) was performed in order to accelerate the corrosive effect of an electrolyte solution and to provoke a built up of internal stress, which occurs under outdoor weathering conditions by the impact of natural temperature cycling. The experimental set-up for this instrumentation, which allows a short-time evaluation of the anticorrosive properties of coating systems [10], is depicted in 3 schematically.
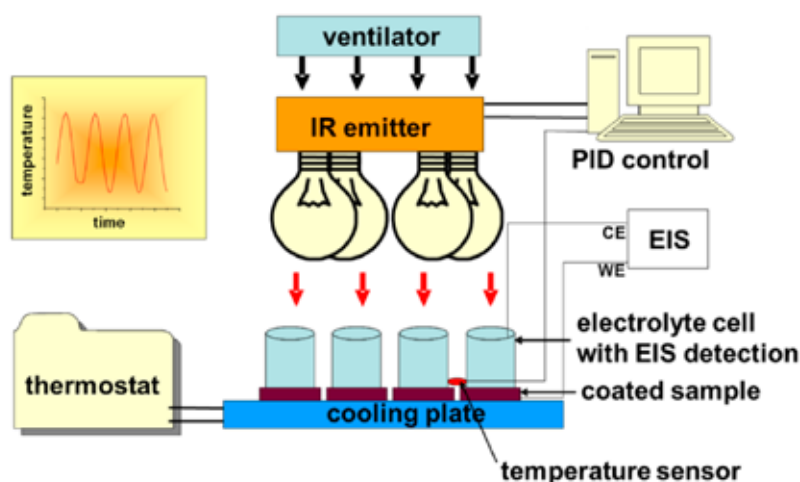
Figure 3: Experimental set-up for the induction of TEL.

Within these studies, thermocycles between 20 °C and 70 °C in sinusoidal periods of 1 h were performed. The temperature of the cooling plate was adjusted to -10 °C; the irradiation was induced by six homogeneously arranged IR emitters (G40, SPRUNGMANN), which were operated by a SIN2-PID tool (ELEKTRONIKA JĄDROWA), whose temperature sensor was tightly applied to the surface of one of the test samples. The electrolyte cells were filled with 7 mL Harrison solution (35 g/L $(NH_4)_2SO_4$, 5 g/L NaCl) and covered with a glass plate (d = 100 µm). Two minutes after the Harrison solution exposure had been started EIS data was recorded from the samples.

Based on a Borchers trial formulation, the starch esters were first dispersed in water (acetate and propionate, c = 45%) or in a mixture of water and DEGBE (1:0.4) (butyrate and hexanoate, c = 30%)

and the additives Borchi Gol LA 200 (1%) and Tego Foamex 805 N (0.3%) were added. Bayhydur XP 2655 was directly added to the starch ester formulation in the case of the butyrate and hexanoate or was dispersed in butylglycol (10%) before and added afterwards to the starch ester formulation.

RESULTS AND DISCUSSION

SYNTHESIS AND DISPERSIBILITY

Starch acetates up to hexanoates could be synthesized in the DS range of 0.05[b] – 1. Solid contents between 30 and 45% could be reached in water with these synthesized starch esters. However, the co-solvent DEGBE was necessary for some samples (2), because the esters had an increased hydrophobicity with increasing DS and chain length and so a decreased water dispersibility.

Table 2. DS and dispersion properties of the synthesized starch esters.

Starch ester	Range of DS	Concentration of dispersion [%]	DEGBE [%]	Optical appearance of dispersion
Acetate	0.1– 0.7	45 - 40	-	clear - milky
Propionate	0.1 – 0.7	45 – 40	20 (for DS 0.7)	clear – turbid - milky
Butyrate	0.2 – 1.1	40 – 30	20	turbid - milky
Hexanoate	0.05 – 0.4[b]	37 - 30	10-20	turbid - milky

[b]: Applied amount of reagent

The different degrees of water dispersibility could be also seen in the optical appearance of the dispersions. While the acetate with the lowest DS showed a milky dispersion, the dispersions with higher DS values of the acetates exhibited a clear appearance till the DS of 0.4. With higher DS values, the water dispersibility became worse again and consequently the dispersion appeared milky. The ester dispersions with longer chains (C_4 and C_6) never possessed clear appearances because of their reduced hydrophilicity.

RHEOLOGICAL PROPERTIES

The tested starch ester dispersions (30–40%) showed viscosities between 20 and 1500 mPa·s (3). The viscosity didn't rise continuously with increasing DS, but decreased first and increased afterwards, for example for the acetate with a DS > 0.4, which can be attributed to the different water dispersibility properties, like described above, and can be seen in 4. Furthermore, the viscosity didn't show an increase with increasing chain length, but the lowest viscosity was given for the propionates (30% dispersions). The flow behavior was influenced by the substituent, its DS and the concentration of the dispersion. While samples with a good dispersibility (clear appearance) showed a newtonian flow behavior, samples with a decreased dispersibility had a shear thinning behavior, which can be seen for the acetate and butyrate in 4.

The frequency sweep measurements showed that all starch ester dispersions had viscoelastic properties and all, with one exception (3), had higher values for the loss than for the storage modulus. Two examples for the frequency sweep (acetate, DS 0.7 and butyrate, DS 0.8) are illustrated in 4.

Table 3. Rheological properties of the starch ester dispersions.

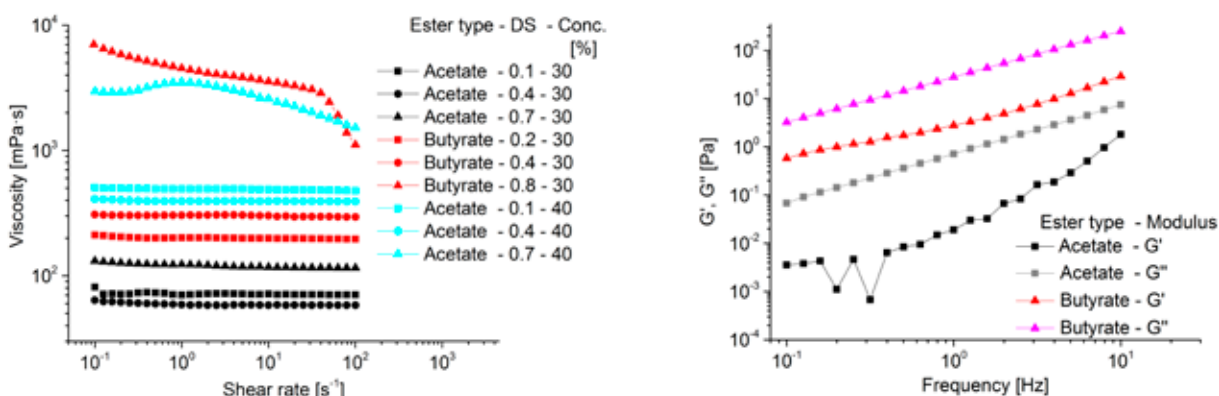| Starch ester	Concentration of dispersion [%]	Shear viscosity (100 s⁻¹) [mPa·s]	Flow behavior	Frequency sweep
Acetate	30 & 40	58 – 1521	newtonian or shear thinning	$G'' > G'$
Propionate	30 & 40^c	17 – 843	newtonian or shear thinning	$G'' > G'$
Butyrate	30^c	196 – 1112	newtonian or shear thinning	$G'' > G'$
Hexanoate	30^c	52 – 527	newtonian or shear thinning (DS 0.2)	$G' > G''$ or $G'' > G'$ (DS 0.1)

c: DEGBE (see 2)

Figure 4: Left: Viscosity of starch acetates and butyrates depending on the shear rate and their DS and concentration. Right: Frequency sweep of starch acetate (DS 0.7) and butyrate (DS 0.8).

FILM PROPERTIES

The following starch ester samples with the given DS ranges formed continuous films based on dispersions with concentrations between 30 und 45% using a doctor blade with a gap size of 100 µm.

Ester-samples
- Acetate   (DS 0.1–0.7)
- Propionate (DS 0.1–0.7)
- Butyrate   (DS 0.4–0.8)
- Hexanoate   (DS 0.4[b])

The optical appearance of the films were clear transparent or turbid, but colorless. In 5 one example of each ester is illustrated.

The wet layer thickness was 25 µm independently on the viscosity of the different dispersions (30%). The measured dry layer thicknesses varied between 8 and 12 µm. Cross cut tests showed a clearly improved adhesion on glass plates with ISO class 0 and 1 for the starch esters in comparison to the starting material (ISO class: 4). Even on PBT/PC substrates the selected starch acetate and propionate possessed a good adhesion. The water persistence of the films on glass was increased about 1 up to 3 moves by the esterification, as can be seen in 4.

The decomposition temperatures (T_d) of the ester films decreased compared to Emox as well as with increasing DS and the temperature values ranged from 178 to 197 °C (4).

Figure 5: From left to right: Acetate, DS 0.7; Propionate, DS 0.7; Butyrate, DS 0.8; Hexanoate, DS 0.4[b].

Table 4. Film properties of starch esters.

Starch ester	DS	Adhesion [ISO class]	Water persistence [number of moves]	T_d [°C]
Emox	-	4	2	200
Acetate	0.1	0	2	-
Acetate	0.2	1 (on PBT/PC)	-	-
Acetate	0.2	0 (on Al)	-	-
Acetate	0.4	0	3	-
Acetate	0.7	1	3	191
Propionate	0.1	0	-	193
Propionate	0.1	1 (on PBT/PC)	-	-
Propionate	0.1	1 (on Al)	-	-
Propionate	0.3	0	3	-
Propionate	0.7	0	3	187
Butyrate	0.4	1	-	190
Butyrate	0.6	0	4	178
Butyrate	0.6	1 (on Al)	-	-
Hexanoate	0.4[b]	0	5	197
Hexanoate	0.4[b]	1 (on Al)	-	-

COATING TESTS ON ALUMINUM PLATES

The cross cut test on aluminum plates resulted in really good (ISO class: 0) and good adhesion (ISO class: 1) for all starch esters (4). Because the ester films were still water sensitive they were crosslinked and their water persistence was tested by treating the coating with Harrison solution. 6 shows that the low substituted and short chain esters were still water sensitive while the higher substituted starch butyrate showed a good and even the hexanoate a really good resistance against water.

In the EIS measurements the tested starch acetate and propionate exhibit medium barrier properties whereas the butyrate showed sound barrier properties, considering its low dry film thickness. The best barrier properties possessed the starch hexanoate, although the high frequency part of the data suggested imperfect film building (7).
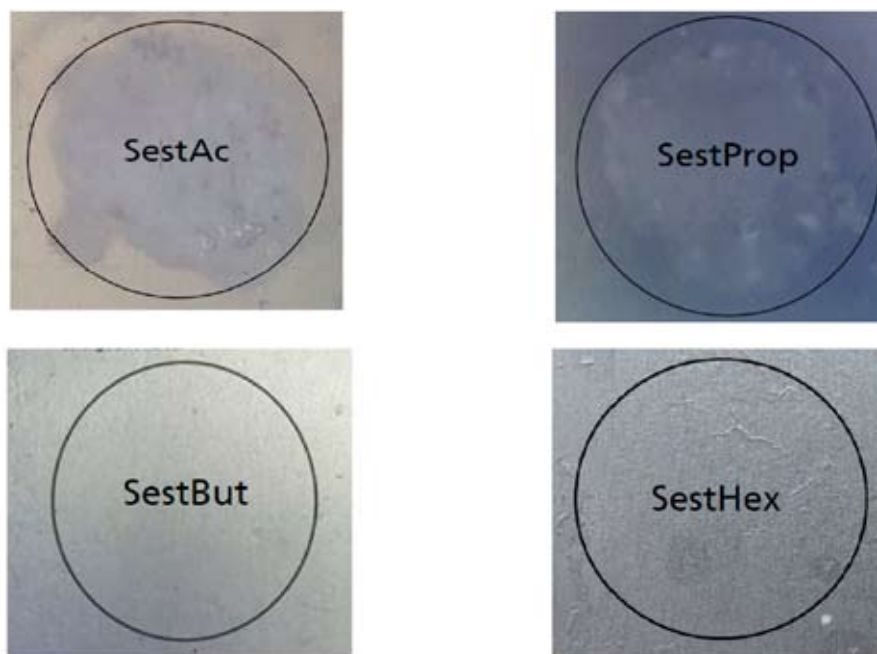

Figure 6: Starch ester coatings (SestAc = Acetate, DS 0.2; SestProp = Propionate, DS 0.1; SestBut = Butyrate, DS 0.6; SestHex = Hexanoate, DS 0.4[b]) after treatment with Harrison solution.
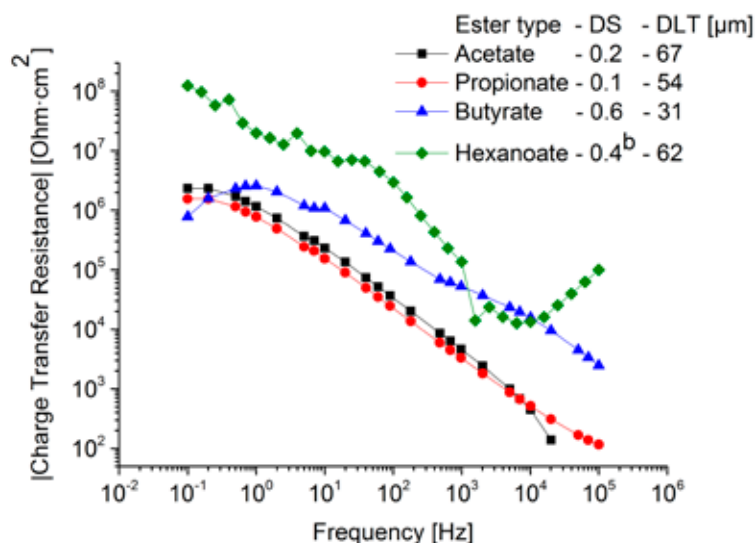

Figure 7: EIS from selected starch acetate, propionate, butyrate and hexanoate.

CONCLUSION

A binder for paint and varnishes should not only bind additives, but also should be able to form a continuous film and possess adhesion on a specific substrate. The two latter properties were studied and could be fulfilled by the synthesized starch esters based on aqueous dispersions with concentrations of up to 45%. Furthermore, the problem of the water-sensitivity of the starch ester films could be solved by crosslinking them with an isocyanate (Bayhydur XP 2655). In the corrosion stability test the starch butyrate with a DS of 0.6 and the starch hexanoate with a DS of 0.4[b] showed sound barrier properties, additionally. In conclusion the synthesized starch esters possess the potential to be an alternative to petroleum-based polymers as binder in paints and varnishes in the future, potentially.

ACKNOWLEDGEMENTS

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