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Cationic starch adsorption onto cellulosic pulp in the presence of other cationic synthetic additives

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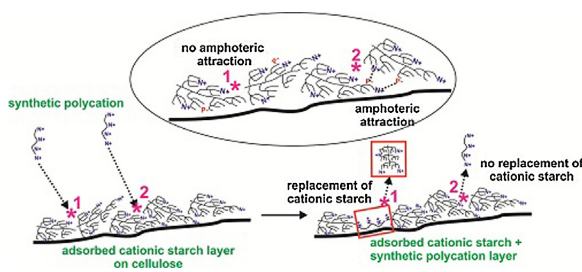
HIGHLIGHTS

- Synthetic polycations interfere with cationic starches at adsorption onto fiber.
- The addition of synthetic polycations after cationic starch results in higher adsorption amounts.
- The replacement of cationic starch depends on molecular properties of the starch itself and of the synthetic polycation.

GRAPHICAL ABSTRACT



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ABSTRACT

The production of paper requires a lot of different raw materials and additives in order to achieve the desired paper properties in a cost-efficient way. Cationic starches are widely used in the wet end process to develop high paper strength and several other additives are also applied to optimize the paper properties or the production process. The aim of this work was to investigate the adsorption behavior of cationic starches on the fiber in the presence of other polycations. Cationic potato starches with three different degree of substitution (DS) of 0.03, 0.065 and 0.09 were compared in the investigations as well as a cationic maize, potato and waxy potato with the same DS (DS = 0.065).

The used synthetic polycations (synth. PC) were polyvinylamine, polyethylenimine, polyacrylamide and poly(diallyldimethylammonium chloride) with three different molar mass. It was found that cationic starches and synthetic polycations compete against each other during fiber adsorption. The higher the cationic charge of the synthetic polycation was, the less cationic starch adsorption occurred. Adding the cationic starch to the suspension before the synthetic polycation minimized this effect. It has been figured out, that a cationic potato starch with a middle DS (0.065) built up the toughest adsorption layer and was less affected by replacement due to synthetic polycations than the other cationic starches. The smaller the pDADMAC, the more cationic starch was adsorbed to the fiber due to the increased pore diffusion of the synthetic polycation.

1. Introduction

The usage of different types of fibers, fillers and specific additives is necessary to achieve the desired properties of the paper. The addition of functional polymers like cationic starches brings better dry strength and for example cationic polyamidoamin resins are used for better wet strength [1,2]. To improve the drainage or the retention of the fibers and fillers, cationic polymers are also widely used. Another important application is the prevention of negative influences from dissolved and dispersed trash compounds and of dissolved electrolytes, too [2–4]. These trash compounds are usually anionic or neutral organic substances and appear in a wide variety due to the differences in pulp qualities, which are used. The dispersed compounds are for instance the leftovers of the printings which could not be sufficiently removed in the deinking process. It is important to optimize the application of the additives

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regarding to the process parameters and the used raw materials. Ecological and economic aspects generated these problems during the last years and the repeated recycling of recovered paper caused a decreasing pulp quality [7–10].

Cationic polymers interact with the anionic fiber because of electrostatic interaction. They adsorb onto the fiber and therefore can interact between the fibers with the result of flocculating the suspension. A network of fibers connected and entangled with each other, because of the cationic polymers, will be created. Hence, the dried paper is more stable because of this network. The adsorption behavior of cationic starches is directly influenced by the starch origin, the process of derivatization and the amount and distribution of the substituents [5,6]. If the additives are used simultaneously, it follows that opposite interaction occurs and the adsorption and flocculation behavior changes. Because of this, cationic multicomponent systems have synergistic and antagonistic influences on the paper properties.

Occasionally, investigations about the changing adsorption behavior of cationic starches have not been done if other cationic polymers are present. The necessity of specific investigations about these interactions was assured. Van de Ven [11] explained the polyelectrolyte adsorption onto porous cellulosic fibers with the "sticky sieve" model which means that the polyelectrolytes can diffuse into the pores if the hydrodynamic volume is small enough. Blocking the entrance of the pores occurs with bigger macromolecules. Polyacrylamide with high molar mass, but linear structure, as well as linear cationic amylose, are able to penetrate the pores as well [12]. Swerin et al. [13] discovered that high molar mass polydiallyldimethylammonium chloride (pDADMAC) achieved lower adsorbed amounts than low molar mass pDADMAC, because of the absence of the pore diffusion. Nevertheless, the adsorption into the pores of cellulosic fibers is certainly very slow and therefore it plays a minor role for the efficiency of the additives at paper production [12]. Shirazi et al. [17] found out that cationic starches adsorbed as big amylose-amylopection-clusters onto the fiber and after a few minutes small clusters were desorbed. The adsorbed starch polysaccharides were found on the fiber surface and in the pores. Ulbrich et al. [5,6] discovered that higher salt amount provides the adsorption of the amylopection fraction. Cationic starches with an amylose content of about 20 percent adsorbed in a higher amount than cationic high amylose starch or waxy starch. In process water with high salt amount, there was no increased starch adsorption with increasing initial starch concentration above 200 μg/ml. The smaller the DS of the cationic starches was, the lesser starch adsorption was figured out in water with high salt amount and the lower was the paper quality.

So far no investigations about the adsorption behavior of cationic additives in multicomponent systems have been done. A few articles have been published about synergistic and antagonistic effects due to the retention of fillers or the paper strength with regard to the use of more than one cationic additive. The adsorption behavior and the building of multilayers of anionic and cationic polymers in combination were documented so far. Possible ways to determine adsorbed amounts of polymers onto cellulosic fibers are by ellipsometry [14], by quartz crystal microbalance with dissipation monitoring (QCM-D) [15,16] and by gel permeation chromatography with multi angle light scattering detection (GPC-MALLS) [5]. The intention of this work was to investigate the interaction between cationic starches and synthetic polycations with regard to their adsorption onto cellulosic fibers and paper strength. The influence of the degree of substitution (DS), starch origin and amylopectin content was also of note. The constitution of the synthetic polycation was different relating to their surface charge and chemical composition. A recovered pulp was compared to a kraft pulp and the water with high salt amount was compared to the water with a low salt amount, in order to assure the relevancy of practice. The influence of dosage order and time of residence was investigated in some experiments.

Table 1
Molar mass [M_w], surface charge [δ], zeta potential [ζ] and particle size [R_h] of the used polyelectrolytes in water 18°dH.

	M_w [10^6 g/mol]	δ [μmol/g]	ζ 18°dH [mV]	R_h 18°dH [nm]
PS 0.03	27.5	+0.30	+12.5	82
PS 0.065	28.8	+0.60	+18.0	85
PS 0.09	25.2	+0.90	+22.4	68
WPS 0.065	28.2	+0.60	+18.5	85
MS 0.07	20.4	+0.65	+18.2	76
pDADMAC-1	0.28	+8.00	+52.0	7
pDADMAC-2	0.11	+8.00	+51.0	3
pDADMAC-3	0.03	+8.00	+50.5	2
PVAm	0.80	+6.00	+45.0	9
PEI	1.50	+3.00	+40.0	17
PAM	3.00	+1.40	+21.0	68

2. Materials and methods

2.1. Materials

Cationic potato starches (PS) with a DS of 0.03, 0.065 and 0.09 (PS 0.03, PS 0.065 and PS 0.09, Grade: 98.2–99.4%) and a cationic waxy potato starch (WPS, Grade: 99.2%) with a DS of 0.065 (WPS 0.065) were used for the investigation. These starch derivatives were produced by BASF Plantscience, Germany. A cationic maize starch (MS) with a DS of 0.07 (MS 0.07, Grade: 99.3%) was obtained from Tereos, France.

The cationic pDADMAC (Grade: 98.3%) was supplied by Katpol Chemicals, Germany and the cationic polyvinylamine (PVAm, Grade: 98.4%), the cationic polyacrylamide (PAM, Grade: 97.8%) and the polyethylenimine (PEI, Grade: 98.0%) were obtained at BASF, Germany. The characteristics of all polyelectrolytes relating to the molar mass [M_w], surface charge [δ], zeta potential [ζ] and particle size [R_h] are listed in Table 1. The above mentioned starches and polymers have not been disclosed by the supplier due to privacy terms.

Two different water qualities were used to implicate the influence of conductivity: first water with 18°dH (W18) and second water with 55°dH (W55). The salt amount, the conductivity and the German hardness [°dH] of both kinds of water are shown in Table 2. The chemicals for the water adjustment were purchased from Carl Roth, Germany: Sodium chloride (Ph. Eur., Grade: 99%), calcium chloride dihydrate (Ph. Eur., Grade: 99%), magnesia chloride hexahydrate (Ph. Eur., Grade: 98%) and sodium sulphate decahydrate (Ph. Eur., Grade: 98.5%).

Two different pulps were used to identify the differences between a kraftpulp and recycled fibers by a specially designed recovered pulp [18]. The characteristics of these two pulps are listed in Table 3. The kraft pulp (KP) was purchased from ZPR Blankenstein in Germany and included 80% spruce and 20% pine (information

Table 2
Salt amount [mg/ml], the conductivity [μS/cm] and the German hardness [°dH] of both kinds of water.

	Conductivity [μS/cm]	German hardness [°dH]	Na^+ [mg/l]	Cl^- [mg/l]	Ca^{2+} [mg/l]	Mg^{2+} [mg/l]	SO_4^{2-} [mg/l]
Water 18°dH	880	18	0.68	254.5	87.4	37.0	–
Water 55°dH	2900	55	347.5	505.7	297.5	–	346.8