

Influence of pulp properties on the adsorption of cationic starch

NEJC ZAKRAJŠEK

ABSTRACT: In most cases, the molecules of a polyelectrolyte such as cationic starch cannot penetrate fiber pores. Therefore, their adsorption depends on the surface properties of fibers and fines. Research has shown that more cationic starch is adsorbed to hardwood than to softwood fibers. A comparison of the properties of both pulp types has determined that the charge on the fiber surface is the key property for the adsorption of cationic starch.

Application: A better understanding of the forces governing starch adsorption to pulp fibers and the relationships between pulp properties and starch deposition could lead to more effective and economical use of cationic starch in pulp and paper operations.

Cationic starch is one of the most frequently used additives in the paper industry. Despite the fact that it represents only a small share of the mass of the end product, it is one of the most important components of paper [1]. It is added to the paper suspension to improve the retention of paper components and the mechanical properties of paper.

Fibers are the basic raw material in paper production. Generally, they can be classified by their process of production: mechanical pulp, chemical pulp, and secondary fibers (waste-paper). Fibers differ both by their content of the chemical components in wood and by their properties. Cellulose is the main component of papermaking fibers. Its chemical structure is that of a polysaccharide on the basis of β D glucopyranoside molecules bound together by hydrogen bonds.

Because adsorption of cationic starch takes place in a suspension, its efficiency is conditioned mainly by the frequency of collisions between starch molecules and particles in the suspension, as well as by the concentration of substances in the suspension. The surface of pulp fibers is composed of fibrils with diameters from 0.1 μ m to 1 μ m, and which are approximately 20 μ m long [2][3]. The fiber surface may be divided into the exterior surface and the interior surface of macropores (75 nm) and of micropores (4 nm), which can be penetrated only by polyelectrolytes with a low molecular mass [4][5]. The average radius of starch molecules is approximately 200 nm [4], which means that cationic starch, when adsorbed, remains on the exterior fiber surface.

One key property of fibers is their surface charge resulting from dissociated acidic groups in cellulose and hemicellulose [6]. With chemically treated fibers, these are mostly carboxylic groups [5], which represent the source of negative charge on a fiber and therefore the site for the adsorption of cationic starch [7].

Adsorption efficiency depends on the specific surface of particles. In the case of pulp fibers, its values range between 0.2 and 5 m²/g, depending on refining [8][9]. Research has shown that a five to thirty times greater amount of cationic

starch can be adsorbed onto fine stock, which has a specific surface that is much larger than the specific surface of fibers, than onto fibers [4][10]. During refining, fibers are fibrillated, and in some cases shortened as well. Although it is not desirable, this shortening cannot be completely avoided because refining is conducted mechanically by mutual friction of individual fibers and refining knives. Consequently, the amount of fines, the total specific surface, and the adsorption of cationic starch are all increased as well [4][11].

The aim of this research was to determine the influence of pulp properties on the adsorption of cationic starch. Adsorption was studied with reference to the type of pulp (softwood, hardwood) and the rate of refining. Results can be used by papermakers to make inferences from fiber properties to process chemical adsorption.

EXPERIMENTAL

For these experiments, we used modified corn starch (i.e., cationic active starch ether with quaternary ammonium groups) with a substitution level between 0.043 and 0.048 mol/mol. In the paper industry, this starch is used as an additive to paper stock. Before use, the cationic starch solution was prepared in accordance with the manufacturer's recommendations. The concentrated base solution, containing approximately 5% starch, was heated to 95°C with continuous stirring. The starch suspension was then mixed at this temperature for another 20 minutes. Distilled water was then used to dilute this solution to 1 g/l. The cationic starch solution was consumed in six hours. Sulfate hardwood (Kotlas) and sulfate softwood (Bohemia) pulps were used to compare pulp properties and their influence on the adsorption of cationic starch. Before use, the pulps were refined at different refining rates. After refining, the pulp suspension to be used in the experiments was further defibered for 15 minutes at 3000 revolutions. We then prepared a suspension with a dry substance concentration of 5 g/l for all experiments except those involving the influence of pulp concentration on the adsorption of cationic starch. The study of the influence of refining on pulp properties and thus

CATIONIC STARCH

on adsorption was conducted on hardwood pulp samples refined to various degrees.

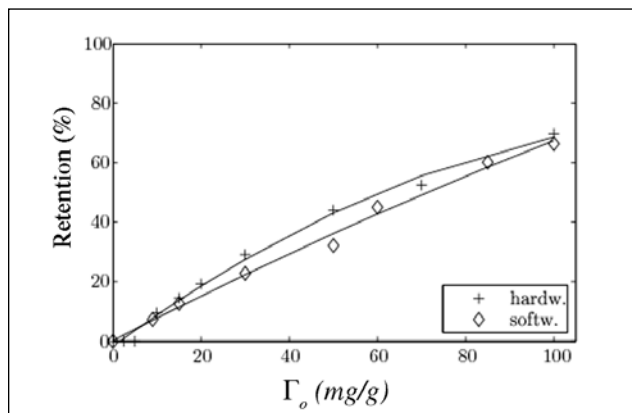
During the experiment, researchers tracked pulp properties including zeta potential, average length, specific surface, and number of carboxylic groups. The extent of pulp refining was determined by the Schopper-Riegler method. The average length of pulp fibers was measured and calculated using the Kajaani FS-200 analyzer, and their specific surface was evaluated using the Tristar 3000 automatic gas analyzer (Micromeritics Instrument Company). Carboxylic groups were determined by conductometric titration (SCAN-CM 65:02). The charge on pulp fibers results from the disassociation of acidic groups. Because the content of sulphonic groups in chemical pulp is negligible, carboxylic groups on fibers can be equated with total acidic groups. The fines content of the samples was measured on the basis of TAPPI 161 pm-80. Quantitative determination of cationic starch in water was conducted in accordance with TAPPI T419 om-02. Starch detection is based on the reaction of starch with J2-KI to form a colored complex that can be detected using a spectrophotometer. Measurements were carried out on a UV/VIS Varian Cary spectrophotometer at 580-nm wavelength. Concentrations of cationic starch in water were calculated by means of calibration curves previously prepared using standard solutions. Zeta potential was measured using a BTG SZP 06, and the adsorption of cationic starch to paper stock was tested using a Britt jar. The basic concept of this device is a mixing jar in which a pulp suspension is prepared and a screen with 100- μ m holes forming the bottom of the jar. A mixer is fixed above the screen and prevents filtering layers of pulp from forming on it. Such conditions provide for dynamic retention and at the same time prevent the influence of filtration effects on the adsorption measurement. Experiments were conducted at room temperature and pH 7.5 with 500 min⁻¹ stirring rate.

RESULTS AND DISCUSSION

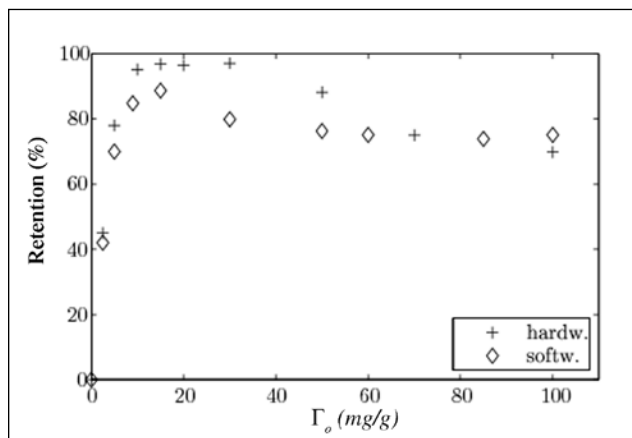
The basic raw material in papermaking is fibers of vegetable origin. The type and quality of wood are important factors that affect both pulp and end-product properties. As expected, comparison of pulp properties showed that at a similar rate of refining, hardwood fibers (2.25 mm) are much longer than softwood fibers (0.89 mm) (**Table I**). In addition, they differ in specific surface and in number of carboxylic groups. Both these fiber properties are especially important in interactions with process chemicals. Softwood fibers have a slight-

Fiber type	Softwood	Hardwood
Refining rate (SR)	28	29
Zeta potential	-42	-40
Specific surface (m ² /g)	2.2	1.8
Average length (mm)	2.25	0.89
Carboxylic groups (μ mol/g)	44.2	76
Fines (%)	8.1	7.9

1. Comparison of softwood and hardwood pulp properties.



1. Mass of cationic starch retained per unit of fiber mass as a function of cationic starch added per unit of mass and of type of fiber.

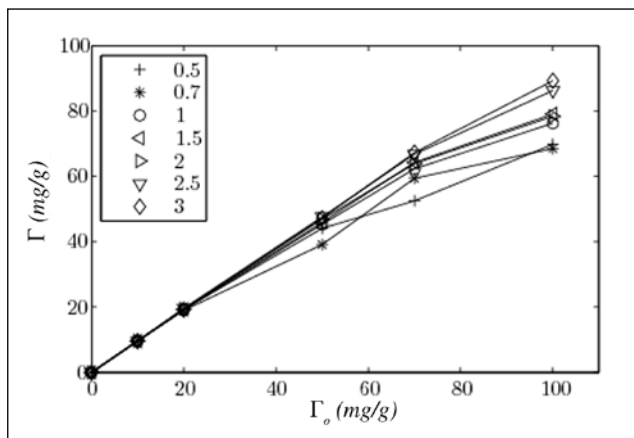


2. Retention of cationic starch in relation to added cationic starch per unit of fiber mass.

ly larger specific surface, whereas hardwood fibers contain more carboxylic groups per g of pulp. Dissociated carboxylic groups on the fiber surface are an important source of negative charge to which cationic starch can be bound [12].

Adsorption is high (more than 20 mg/g) up to an addition rate of 25 mg/g, beyond which it begins to decrease. At an addition rate of approximately 100 mg/g, the adsorption rate is less than 70 mg/g (**Fig. 1**). **Figure 2** shows the retention of cationic starch on fibers. Retention is defined as the ratio of cationic starch absorbed onto fibers to cationic starch added. Up to 10 mg/g, retention increases, after which it maintains a constant value until an addition rate of 25 mg/g, after which it starts to decrease and tends to stabilize below 70% regardless of the addition rate. Figure 2 illustrates that the retention of cationic starch on hardwood is higher than on softwood, in spite of the fact that softwood fibers are longer and have a greater specific surface. The zeta potential of fibers is similar in both cases (approximately -40), which probably results from the higher number of anionic sites on the surface of hardwood pulp fibers (Table I).

A comparison of the properties of both pulp types reveals that fiber surface charge is the key property for the adsorption of cationic starch. The adsorption of a cationic polyelectrolyte is often explained by cationic exchange reactions [13][14] or even by charge neutralization [15]. Theoretically, the adsorp-



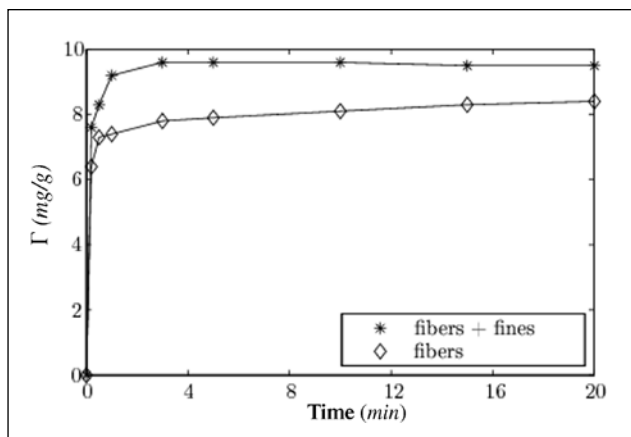
3. Mass of cationic starch retained per unit of fiber mass as a function of starch added per unit of fiber mass (additions of cationic starch in mg/g) and fiber concentration.

tion of polyelectrolytes could continue for long enough for the total charge on the surface to become completely nullified [16]. The adsorption of cationic starch probably takes place in such a way as to enable an individual chain at the beginning of the adsorption process to retain the same configuration as in the solution. Initially, it is bound to the fiber surface only by individual segments, only later changing into a more stable “planar” configuration that occupies most of the fiber surface which was previously filled by a molecule in the initial phase of adsorption. At the same time, the distances between the charges on polymer segments increase [17][18][19]. In addition, this conformation weakens the attractive forces between the charge on starch molecules in water and the charge on the fiber surface [4][20][21].

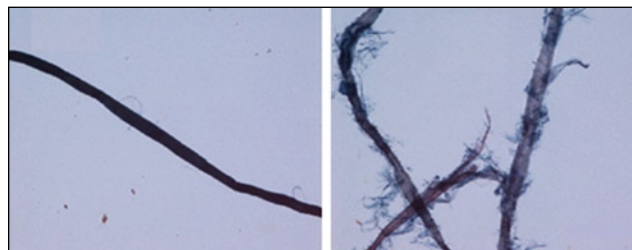
Electrostatic repulsive forces also play an important role among the polyelectrolyte molecules in a solution [22], where, especially at higher concentrations, they prevent individual starch molecules from approaching the fiber surface. With softwood, which has a more negative charge on its surface than hardwood, the influence of repulsive electrostatic forces is reflected in slightly higher addition rates of cationic starch. Consequently, a larger amount of starch is adsorbed.

A higher concentration of fibers in suspension increases the number of potential sites where cationic starch can be adsorbed. The number (frequency) of collisions between starch molecules and fibers increases as well. With lower pulp concentrations, there are consequently fewer anionic sites on fibers and fewer collisions. **Figure 3** shows that with smaller additions of cationic starch, adsorption efficiency is independent of fiber concentration (ranging between 0.5% and 3%). This is especially evident when 100 mg/g are added, because with the same amount of additive and a different fiber concentration in the suspension, adsorption efficiency increases from 60 mg/g to 90 mg/g. Therefore, pulp concentration is an important parameter, both because of the higher number of anionic sites and because of the higher frequency of collisions between fibers and starch molecules.

Fines are fibers shorter than 100 μm that have been formed as a result of mechanical pulping. The influence of fines on the adsorption of modified starch was tested on hardwood



4. Mass of starch retained per unit of fiber mass as a function of time.



5. Comparison of unrefined and refined fibers (magnification 200X).

fibers refined at 29 SR. Pulp was prepared beforehand by the procedure already described. Fines or particles smaller than 100 μm were washed off the pulp with a large amount of distilled water and further removed by vigorous stirring on a 100- μm wire. **Figure 4** shows a comparison of the adsorption of cationic starch to paper suspensions with and without fines. Initially, the proportion of fines in the paper suspension was 79% (Table I), and the maximum amount adsorbed was 9.8 mg/g. In a sample with no fines, the maximum amount adsorbed was reduced to 8 mg/g. Fines within the sample have a positive influence on the adsorption of cationic starch, which probably results from the fact that they have a much larger specific surface than fibers. In addition, this surface is more accessible, enabling more starch per mass of substance to be adsorbed [7][23]. The number of carboxylic groups in a fiber suspension without fines decreased to 59 $\mu\text{mol/g}$. Similar results have been obtained by other researchers [4][7][24] who claim that fines have a higher surface charge than the rest of the substance, which, in addition to the smaller specific surface, could explain a lower adsorption rate to a paper suspension if it does not contain any fines. In both cases, the adsorption of cationic starch is completed very quickly, reaching the maximum level after a few minutes.

In addition to pulp origin, pulp properties are also greatly influenced by the pulping process (chemical, mechanical, and thermomechanical) and by the processes in paper production, especially refining, which is the most important for pulping. During refining, fibers are fibrillated and in some cases

CATIONIC STARCH

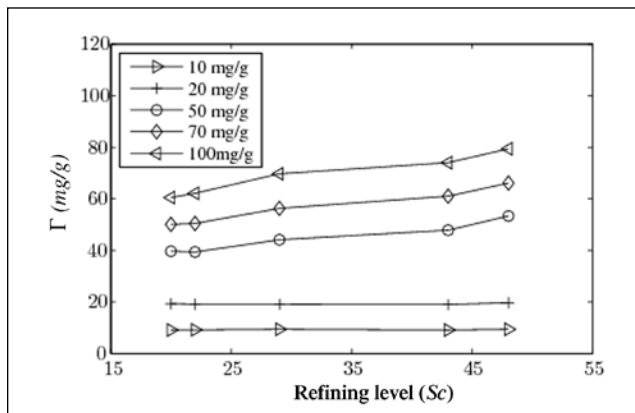
Fiber type	Hardwood				
Refining rate (°SR)	20	22	29	43	48
Zeta potential	-30.3	-36.9	-40	-46.6	-48.1
Specific surface (m ² /g)	1.58	1.6	1.8	2.0	2.14
Average length (mm)	0.92	0.91	0.89	0.86	0.82
Carboxylic groups (μmol/g)	66.8	68.7	76	90	91.3
Fines (%)	5.3	5.9	7.9	11.3	13.2

II. Influence of refining on hardwood pulp properties.

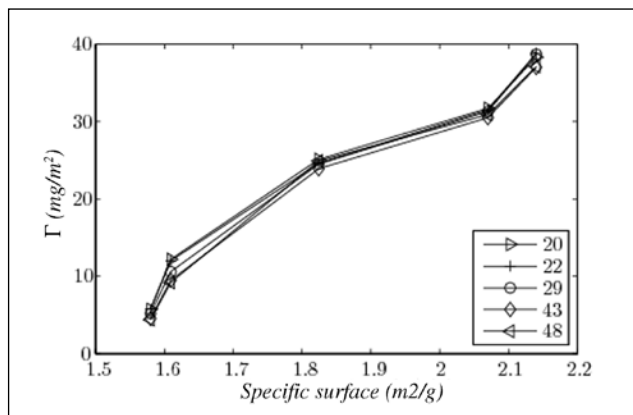
shortened as well. Although it is not desirable, shortening cannot be completely avoided because refining is carried out mechanically by mutual friction of individual fibers and refining knives. During fibrillation, the fibrils composing a fiber may either split off the fiber or remain attached to it (**Fig. 5**).

Fibrillation thus affects the specific surface of fibers and the fines content, which is also evident in **Table II**, which shows that the specific surface increases with the rate of refining. A comparison of the results shown in Tables I and II indicates that the specific surfaces of softwood and hardwood fibers resemble each other only in the case of good hardwood refining (hardwood refining rate 48 SR, softwood 28 SR). The process of fibrillation is evident also in the increasing numbers of carboxylic groups on the fiber surface [4], which results in a greater number of active sites for potential adsorption of cationic starch. According to previous results, there should be only 13% carboxylic groups on the exterior surface of unrefined fibers, with the rest located in pores [7][25]. With refining, however, this percentage may increase. In addition, the zeta potential is positively influenced by refining; that is, refining increases the absolute value of zeta potential. Under the influence of refining, fiber shortening is reflected by a decrease in the average length of fibers.

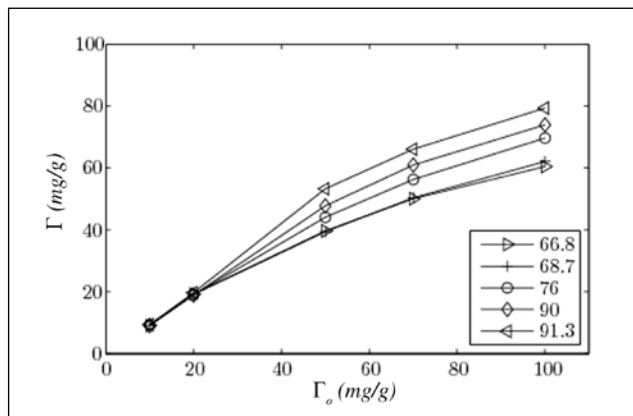
The influence of refining on pulp properties and consequently on the adsorption of cationic polymers was tested with five different additions of cationic starch. **Figure 6** indicates that at low addition rates (10–20 mg/g), refining does not affect adsorption at all. This result was not expected because of the very high retention level in the low addition range for cationic



6. Mass of cationic starch retained per unit of fiber mass as a function of refining rate.



7. Mass of cationic starch retained per unit of fiber surface as a function of specific fiber surface.



8. Mass of cationic starch retained per unit of fiber mass as a function of added starch per unit of fiber mass and the number of carboxylic groups on fibers.

starch. At higher addition rates, however, adsorption efficiency increased with the rate of pulp refining. When 50, 70, and 100 mg/g were added, adsorption efficiency increased by approximately 25 mg/g between the least and most refined pulps.

Average fiber length decreased with refining, whereas fines content increased. Consequently, specific fiber surface increased as well. **Figure 7** shows the adsorbed amounts of cationic starch, expressed per unit of fiber surface. We also noticed a tendency for adsorption to increase with increasing specific surface. A comparison of adsorption at different refining rates shows that at higher refining rates, the same amount of cationic starch per unit of surface is adsorbed. This could be explained by similar levels of charge density on the fiber surface at all refining rates (**Table II**).

The increase in the absolute value of zeta potential with refining rate (**Table II**) is probably a consequence of the increase in the number of carboxylic groups on the surface of the fibers. Because the pulp has a strongly negative zeta potential in all cases, a positive influence on the adsorption of cationic polymers was expected. The lower the absolute value of zeta potential, the lower the adsorption efficiency. At lower addition rates, the adsorbed amount of cationic starch was comparable at all refining rates. With higher addition rates of cationic starch, adsorption efficiency increases with number of carboxylic groups. The amount of adsorbed starch increases with the number of

carboxylic groups on the fiber surface [4]; this relationship is caused by the electrostatic attraction between the cationic starch and anionic groups on the fiber surface.

CONCLUSIONS

The properties of fibers depend on their origin and treatment processes. Despite the fact that softwood fibers are longer and have a slightly larger specific surface than hardwood fibers, a greater amount of cationic starch is adsorbed to hardwood fibers. This is probably caused by the surface charge, which is higher in the case of hardwood fibers. Therefore, the driving force for the adsorption of cationic starch onto fibers is mostly of an electrostatic nature. Fiber refining creates better conditions for the adsorption of cationic polyelectrolyte because the specific surface of fibers is increased, while at the same time more carboxylic groups are present on the surface. Consequently, the amount of cationic starch adsorbed to fibers is increased with refining. The downside of refining, however, is the shortening of fibers, which may result in the deterioration of end-product mechanical properties. **TJ**

Submitted: March 5, 2007

Accepted: June 3, 2008

LITERATURE CITED

1. Banks, W., Greenwood, C.T., *Starch and its components*. Wiley, New York, 1975.
2. Mazeau, K., Heux, L., *J.Phys.Chem.* 107(10):2394(2003).
3. Kroon-Batenburg, L.M.J., Bouna, B., Kroon, J., *Macromolecules* 29(17):5695(1996).
4. Wagberg, L., Bjorklund, M., *Nord. Pulp Pap. Res. J.* 8(4):399(1993).
5. van de Ven, T.G.M., *Nord. Pulp Pap. Res. J.* 15(5):494(2000).
6. Casey, C.P., *Pulp and Paper Chemistry and Chemical Technology*, Third Edition, Volume III, John Wiley and Sons, New York, 1981.

7. Marton, J., Marton, T., *Tappi* 59(12):121(1976).
8. Lindström, T., Soderberg, G., *Nord.Pulp Pap. Res. J.* 1(1):26(1986).
9. Larsson, A., Stenius, P., *Nord. Pulp Pap. Res. J.* 2(3):87(1987).
10. Malton, S., Kuys, K., Parker, I., et al., *Appita J.* 51(4):292(1998).
11. Hernadi, S., Volgyi, P., *Wochenbl. Papierfabr.* 106(10):355(1978).
12. Neimo, L., *Papermaking Science and Technology*, Jyväskylä, Finska Papet Oy, 1999.
13. Winter, L., Wogberg, L., Odberg, L., et al., *J. Colloid Interface Sci.* 111(2):537(1986).
14. Cohen Stuart, M.A., Fleer, G.F., Lyklema, J., et al., *Adv. Coll. Interface Sci.* 34:477(1991).
15. Wagberg, L., Winter, L., Odberg, L., et al., *Colloids Surf.* 27(4):163(1987).
16. Van de Steeg, H.G.M., Cohen Stuart, M.A., de Keizer, A., et al., *Langmuir* 8(10):2538(1992).
17. Wagberg, L., Lindström, T., *Nord. Pulp Pap. Res. J.* 2(4):152(1987).
18. Wagberg, L., Odberg, L., Lindstrom, T., et al., *J. Colloid Interface Sci.* 123(1):287(1988).
19. Lindström, T., *Fundamentals of Papermaking*, Mech. Eng. Publ., London, 1989.
20. Blaakmeer, J., Cohen Stuart, M.A., Fleer, G.J., *J. Colloid Interface Sci.* 140(2):314(1990).
21. Dobrynin, A.V., Rubinstein, M., Joanny, J.F., *Macromolecules* 30:4332(1997).
22. Chen, Y., Liu, S., Wang, G., *J. Colloid Interface Sci.* 303:380(2006).
23. Koethe, L., Scott, W.E., *Tappi J.* 76(12):123(1993).
24. Marton, J., *Tappi J.* 63(4):87(1980).
25. Van de Steeg, H.G.M., de Keizer, A., Cohen Stuart, M.A., et al., *Colloids Surf.* 70(1):77(1993).

INSIGHTS FROM THE AUTHOR

Cationic starch is one of the most frequently used additives in paper chemistry. Not only retention processes, but also the mechanical and surface properties of the final product depend on the efficient adsorption of cationic starch on fibers.

The results of this work support previously conducted research around the world in emphasizing the importance of electrostatic forces and specific surface in polyelectrolyte adsorption. In its use of sulfate pulp, this research differs from most other studies, which have examined mechanical pulps.

Preparation of fibers is important, not only for final paper properties, but because it can influence the efficiency of chemicals. The most surprising results of our work were the high retention of cationic starch with a low initial addition, and the rather low retention with a high initial addition of cationic starch. This appears to prove that the main driving forces for the adsorption of

cationic starch onto fibers are electrostatic in nature.

On the basis of the properties of the raw material (pulp), it is possible to predict to some extent the amount of starch that will be adsorbed on the surface of the fibers and to define additional points where cationic starch could be added in the papermaking process.

The next step in this research will be to determine the adsorption kinetics of cationic starch under different process conditions, as well as the influence of cationic starch on final paper properties.



Zakrajšek

Dr. Nejc Zakrajšek is associated with the Pulp and Paper Institute Ljubljana in Ljubljana, Slovenia, nejc.zakrajsek@icp-lj.si.