

Analysis of Modified Starch Adsorption Kinetics on Cellulose Fibers via the Modified Langmuir Adsorption Theory

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Dedicated to the memory of Professor Dr. Valentin Koloini

The kinetics of starch adsorption on cellulose fibers is one of the most important criteria regarding the efficient application of papermaking additives due to the continuous nature of paper production and the concomitant need to determine optimum residence times. This study presents an analysis of the kinetics of modified starch adsorption onto cellulose fibers via the application of the modified Langmuir adsorption theory (i.e. the collision theory). A model based on this theory was used to describe the kinetics of starch binding, and to obtain the adsorption rate constant under different process conditions, which closely correspond to the conditions commonly encountered in industrial production of paper and board. The model predictions were then correlated with the experimental data. The adsorption of modified starch was found to increase by increasing the fiber consistency, shear forces (via stirring frequency) and the refining degree of fibers. The results also demonstrate that, at least in the studied range of process variables, the modified Langmuir adsorption theory can be applied to describe the adsorption kinetics of modified starch on cellulose fibers.

Key words:

(Cationically) modified starch, fibers, adsorption, collision theory, Langmuir adsorption theory

Introduction

Its beneficial influence on the retention of various components, but most particularly fibers and fines, makes starch one of the most widely used process chemicals in the paper and board production. In the past, the most commonly used starch was non-modified native starch that is weakly negatively charged in an aqueous solution. Due to the ever higher paper machine speeds and, consequentially, also increasing hydraulic forces that occur during the dewatering on the paper machine wire, about 60 % of starch remained in the water, thus increasing the chemical oxygen demand of the process water and exacerbating the problems related to the microbiological contamination, since starch is a perfect food source for the primary metabolism of many microorganisms.^{1,2} Moreover, lower starch retention adversely affects the properties – especially mechanic – of paper. In this case, the binding of starch depended exclusively upon the mechanical entrainment of starch molecules between the cellulose fibers.

Relatively low price, biodegradability, and structural similarity to cellulose, which makes starch a more suitable additive for paper production than various synthetic chemicals, contributed to the appearance of differently modified starches on the market.^{3,4} In the wet end section of the paper machine, the most commonly applied modified starches are characterized by their cationic charge. This significantly increases their adsorption onto negatively charged cellulose fibers by enabling the positively charged starch macromolecules to be bound also via the electrostatic forces.^{5,6}

Modified starch is employed in paper production as:

- Retention aid,
- Additive for improving the mechanical strength of paper,
- Binder or co-binder in coating formulations for surface sizing and coating of paper.

The adsorption of modified starch on cellulose fibers is a complex process. The range of factors that influence this process is very wide, and includes:

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– The characteristics of the polymer chain (charge density, molecular weight, degree of branching, etc.).

– The characteristics of the fibers (surface charge density, fines content, specific surface, etc.).

– Chemical (pH, conductivity, interfering substances – i.e. “anionic trash”), and

– Physical properties of the system (e.g., hydrodynamic forces, temperature).

Since the adsorption of modified starch occurs in a suspension, its success also depends on the frequency of collisions between the starch molecules and cellulose fibers. The fiber surface has many pores that are only accessible to the relatively low molecular weight polyelectrolytes,^{2,7} which, however do not include the modified starch macromolecules. Consequently, the starch adsorption is most affected by the properties of the fiber’s outer surface. The specific surface area of cellulose fibers is commonly in the range of about 0.2–5 m² g⁻¹,^{8,9} and depends on both the type of cellulose, as well as the fiber treatment (refining). During refining, the fibers are fibrillated and shortened.³ This latter process is usually not desirable; however, it can never be completely prevented, since the refining proceeds via the mechanical friction between the individual fibers, and between fibers and the refiner plates. Consequently, the fraction of fines – and concomitantly also the total specific surface area – increase during refining thus promoting the modified starch adsorption.^{2,10} Previous studies have shown^{2,11} that the fines fraction can bind from 5 and up to 30 times more modified starch than cellulose fibers.

Another important parameter influencing the adsorption of polyelectrolytes is the nature and magnitude of the electrostatic forces. The cellulose fibers have negatively charged functional groups on their surface in aqueous suspensions. In the case of chemically treated fibers, these are predominantly the carboxyl groups,⁷ and represent a source of anionic charge, and hence potential sites for the adsorption of modified starch.¹² Besides the charge on the fibers and starch macromolecules, the electrostatic forces are also affected by the presence of many soluble or even sparingly soluble compounds in the paper stock suspension (mineral fillers, inorganic salts, process chemicals, and functional additives).

Fibers and modified starch molecules in the paper stock suspension are in a state of constant movement under the influence of thermal (Brownian motion) and shear forces, which causes incessant collisions among them. The collision frequency per unit volume depends on the number concentration of both starch molecules and substrate particles. In

a system composed of oppositely charged particles, it is assumed that the positively charged modified starch molecules will be successfully retained only on the surface of negatively charged particles (fibers, fines). The time evolution of the modified starch adsorption depends on the balance between the attractive (electrostatic) and shear forces.^{13,14} In unmixed paper suspension it depends primarily on the diffusion, i.e. the size of starch molecules and fibers. More commonly though, the paper stock suspension is mixed vigorously during the paper production, in which case the adsorption rate constant also depends on the shear forces.^{15,16}

If we assume that the adsorbed molecules can also desorb, we obtain the Langmuir adsorption isotherm^{17,18} in the following form:

$$\frac{d\Theta}{dt} = k_{\text{ads}} \cdot (n_0 - \Theta) \cdot (1 - \Theta) - k_{\text{des}} \cdot \Theta \quad (1)$$

The n_0 parameter in the above equations represents the ratio between the initial (Γ_0) and maximum amount of modified starch molecules (Γ_{max}) that can be bound on the fiber surface. Both parameters are defined per unit mass of fibers. The introduction of n_0 is particularly important in cases when the suspensions contains less starch molecules than can be bound on the surface and thus represents a correction to the Langmuir adsorption theory.^{17,18}

The rate constant of desorption (k_{des}) depends on the strength of bonds and the hydrodynamic forces.^{18,19} With the initial boundary conditions $\theta = \theta_0$ at $t = 0$, eq. 2 has the following analytical solution:^{18,20}

$$\Theta = \frac{2n_0(\lambda - 1) + \Theta_0[A(1 - \lambda) + B(\lambda + 1)]}{A(\lambda - 1) + B(\lambda + 1) + \Theta_0(1 - \lambda)} \quad (2)$$

In the above equation the parameters A , B and λ are defined as:

$$A = K + n_0 + 1 \quad (3)$$

$$B = \sqrt{(n_0 - 1)^2 + 2K(n_0 + 1) + K^2} \quad (4)$$

$$\lambda = e^{Bk_{\text{ads}}t} \quad (5)$$

Where K denotes the desorption/adsorption kinetic rate constants ratio, $k_{\text{des}}/k_{\text{ads}}$. In equilibrium the rates of both processes are equal so that the surface coverage remains constant with time (i.e. $d\theta/dt = 0$), and eq. 2 can then be rearranged to:^{16,20}

$$\frac{1}{\Gamma_{\infty}} = \frac{K}{\gamma_{\infty}} + \frac{1}{\Gamma_{\text{max}}} \quad (6)$$

Where Γ_{∞} and Γ_{\max} denote the equilibrium and the maximum relative* concentration of modified starch adsorbed on the fibers, respectively, and γ_{∞} denotes the equilibrium relative concentration of modified starch in the paper stock suspension. The values of K and Γ_{\max} are determined from the $1/\Gamma_{\infty} = F(1/\gamma_{\infty})$ diagram. Eq. 6 does not include the influence of the reformation of adsorbed modified starch molecules. Nevertheless, studies have shown^{14,16} that this equation is applicable for times shorter than the times required for the reformation of polyelectrolyte on the fiber surface. The reformation process is relatively slow when compared to the adsorption;¹⁷ according to some studies, the polyelectrolyte requires as much as 200 min for reformation,⁵ while adsorption takes place in less than one minute.¹⁸ It thus follows that during adsorption each modified starch molecule can be treated as a spherical particle.¹⁶

The goal of this study is to analyze the kinetics of modified starch adsorption onto cellulose fibers. Previous studies into starch adsorption on cellulose fibers focused mainly on the experimental determination of the maximum amount of starch that can be adsorbed, commonly at different salt concentrations of the dispersing medium. Consequently, the present study also focuses on the calculation of the starch binding times, as well as the maximum amount of starch adsorbed under different conditions. Furthermore, the study is focused on elucidating the influence of those process variables, which are most commonly exploited to influence the adsorption of cationically modified starch and other papermaking additives in real papermaking systems – i.e. mixing, substrate (fiber) and adsorbent (starch) concentration, and fiber refining. By applying the collision theory, we obtained the adsorption rate constant under different process conditions, which correspond to the conditions commonly encountered in the production of paper and board. A model was further developed to describe the kinetics of binding, and the model predictions were correlated with the experimental data.

Experimental

Materials

(Cationically) modified starch

In all the experiments, a commercially available cationically active modified cornstarch (Papiran SKW-42) was used, with the degree of substitution 0.043, supplied by the Helios, d.d. The

product is commonly applied as an additive dosed into the paper stock. The modified starch solution was prepared in accordance with the producer's instructions, and used within six hours.

Fibers

Commercially available hardwood sulphate short fibers (mixture of 50 % birch and 50 % poplar), were used in all experiments reported in this study. Before application, the fibers were refined (in PFI refiner) to varying refining degrees. After refining, the fiber suspension was additionally defibrillated for 15 min at 3000 rpm, before the preparation of a suspension with suitable dry matter content.

Measuring methods and equipment

The kinetics of modified starch adsorption was studied using the Britt-jar apparatus. 1 L of fiber suspension was prepared in the Britt-jar container, and stirred for a few minutes before adding the modified starch. Other process parameters, common to all the experiments (unless stated otherwise), were: fiber stock consistency 5 g L⁻¹, the refining degree 29 SR (Schopper-Riegler), suspension temperature 25 °C, and the stirring frequency 500 rpm. The solution pH was not regulated and was 7.5 ± 0.2 in all experiments.

Analyses

The quantitative determination of the modified starch content in water was carried out in accordance with the procedure described in the "Tappi T419 om-02" standard. The starch detection is based on its reaction with iodine into a colored complex that can be detected on the spectrophotometer. The latter analyses were executed on the UV/VIS Varian CARY 50, at 580 nm wavelength. The adsorbed amounts of modified starch were calculated via:

$$\Gamma = \frac{V(\gamma_0 - \gamma)}{m} \quad (7)$$

Where Γ denotes the relative amount of adsorbed starch (in mg of starch per g of fibers), V is the vessel volume, γ_0 and γ are the (relative) concentrations of modified starch in water at the beginning and end of an experiment respectively, and m is the mass of fibers.

The degree of refining was determined according to the well-known Schopper-Riegler method, according to the "SIST EN ISO 5267-1 (2000)" standard.

The specific surface area of fibers was measured on an automatic gas analyzer Tristar 3000 (Micromeritics Instruments Co.).

* All relative concentrations in this study are given as the concentration of the particular component (e.g. the modified starch) per unit mass of cellulose fibers.

The carboxyl group content was determined with a conductometric titration in accordance with the “SCAN-CM 65:02” standard.

The fines are defined as the fraction of fibers passing through the mesh 200 sieve. The fines content in the samples was determined according to the procedure described in “Tappi 161 pm-80”.

Results and discussion

The kinetics of modified starch adsorption on cellulose fibers was studied via a theoretical model based on the collision theory. The model is based on the frequency and efficiency of collisions between the fibers and modified starch. However, the model does not include the possible influences of temperature and electrostatic forces. Consequently, the first part of the experimental work was devoted to establishing the range in which the influence of these two parameters can be regarded as negligible.

Temperature effects

Temperature of the paper stock suspension is one of the most important and influential process parameters. In the papermaking process waters it is commonly about 35 °C, depending on the degree of water-circuit closure, and other more mundane factors, such as the season of the year (water temperatures rise significantly – some 10 °C or more – during the summer months, making it the least favorite season for all papermakers), the production program, and the process equipment. In the present study, the influence of temperature on the adsorption of modified starch on fibers was researched in the range between 20 and 60 °C: the adsorption isotherms for this range are shown in Fig. 1. As can be seen from this diagram, the influence of the temperature is negligible in this range.

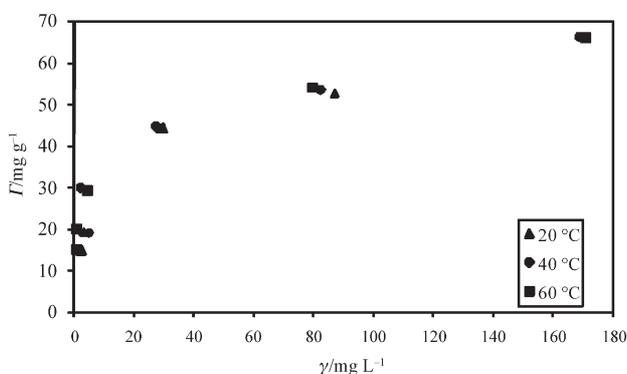


Fig. 1 – The (relative) adsorbed amount of modified starch (per unit fiber mass) in dependence on the initial (relative) concentration of starch in the paper stock suspension at three different temperatures (fiber consistency: 5 g L⁻¹, stirring frequency: 500 rpm)

The influence of inorganic salts (conductivity)

Inorganic salts are present in dissolved form in the papermaking waters, originating mostly from fillers and various process chemicals. The amount of dissolved inorganic salts in the papermaking process waters is usually expressed via the solution conductivity, and is commonly below 1.5 mS cm⁻¹.^{21–23} Fig. 2 demonstrates the influence of different concentrations (expressed as the solution conductivity) of different inorganic salts (i.e., with different valences of the cation) on the adsorption of modified starch on cellulose fibers.

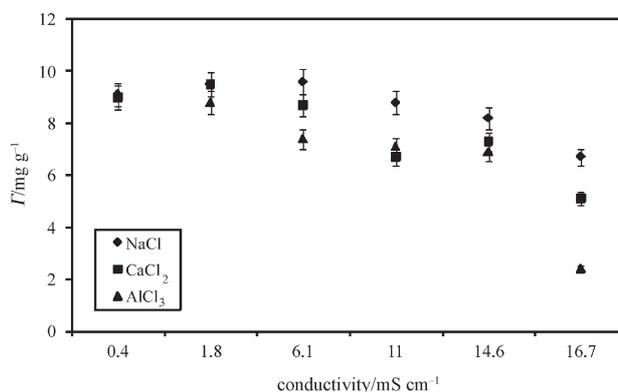


Fig. 2 – The relative amount of starch adsorbed on the fibers in dependence of the inorganic salt concentration (solution conductivity) for different salts commonly encountered in papermaking (initial starch concentration: 10 mg g⁻¹, stirring frequency: 500 rpm)

It is evident from Fig. 2 that the adsorption of modified starch is significantly affected by solution conductivity. It remains fairly constant up to about 1 mS cm⁻¹, then begins to fall with rising conductivity. This effect is more pronounced the higher the valence of the cation; at conductivities above approximately 15 mS cm⁻¹ the adsorbed amount of starch on fibers can be decreased by up to 80%! This indicates that the adsorption of modified starch primarily depends on the magnitude of electrostatic forces between the modified starch molecules and the fiber surface.²⁴ On the other hand, it is also interesting to note that in the case of NaCl and CaCl₂ (but not the chloride salt with a trivalent Aluminum ion), the adsorbed amount of starch initially rises with the rising salt concentration, although in those cases it also begins to fall off quite precipitously once some critical value is exceeded. The reasons for such adsorption behavior could be related to the swelling of fibers and fines,^{11,25–27} and the reduction of the hydrodynamic radius of starch molecules due to the decrease of repulsive forces between the charged segments on the macromolecule (i.e. the electric double-layer compression or the charge screening effect),^{16,27–31} which can then penetrate

into the fiber pores. Considering these findings, we can conclude that in the range of inorganic salts concentrations that are commonly encountered in papermaking (i.e. solution conductivities approximately in the range of 0.5–1 mS cm⁻¹), their influence on the adsorption of modified starch is rather insignificant.

Consequently, in the continuation of this work, the temperature was kept constant at 25 °C, and the solution conductivity was below 1mS cm⁻¹, so as to eliminate or at least minimize any possible influence of these two parameters.

The modified Langmuir adsorption model

In the following series of experiments, the initial dosage of modified starch in the paper stock suspension was varied. The equilibrium state was attained after a few minutes, in good accord with the previously published results.^{22,33–35} The relation between the inverse relative concentration of starch adsorbed on fibers ($1/\Gamma$) and the inverse value of the relative concentration of starch in the solution ($1/\gamma_\infty$) is shown on Fig. 3.

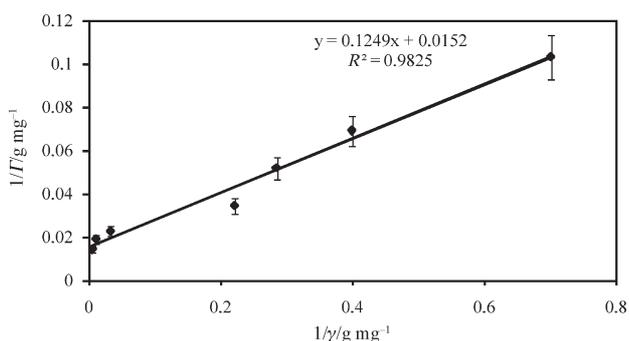


Fig. 3 – The inverse relative concentration of starch adsorbed on fibers in dependence of the inverse value of the relative starch concentration in the solution (fiber consistency: 5 g L⁻¹, stirring frequency: 500 rpm)

The equation, which gives the best fit ($R^2 = 0.98$) to the above-observed adsorption behavior of modified starch on the hardwood fibers was found to be:

$$\frac{1}{\Gamma_\infty} = \frac{0.125}{\gamma_\infty} + 0.0152 \quad (8)$$

From the y-axis intercept, Γ_{\max} can be estimated at 66 mg g⁻¹. This is much higher than the maximum adsorbed amounts of modified starch reported in other studies: 20 mg g⁻¹ on microcrystalline cellulose,¹⁶ and 33 mg g⁻¹ on sulphate hardwood fibers. The reasons for this discrepancy are most likely related to the differences in the characteristics of fibers (specific surface area, fines

content) and modified starch used in the respective studies. In both studies cited here,^{16,24} the modified starch had a degree of substitution approximately 0.030, compared to 0.043 in the present study.

The slope of the line in Fig. 3 equals the equilibrium constant for desorption (i.e. the ratio between desorption and adsorption kinetic rate constants), $K = 0.025$. Considering the low value of K , we can conclude that the adsorption of modified starch on cellulose fibers proceeds at significantly higher rates than its desorption. This is in agreement with previous findings that the adsorption of polyelectrolytes onto the oppositely charged surfaces is virtually irreversible.¹⁶

Theoretically, the fiber surface coverage with the modified starch can be calculated via eq. 2. The only unknown parameter in this equation is the kinetic rate constant of adsorption (k_{ads}), which can be calculated from:³⁵

$$k_{ads} = \alpha \cdot k_{12} \cdot N_f \quad (9)$$

Both the rate constant (k_{12}), as well as the collision efficiency factor (α), depend on the shear velocity. The container volume ($V = 1$ L) and the stirrer diameter (0.062 m) were the same in all experiments. To a first approximation, the solution viscosity (μ) and density (ρ) can be equated to that of water at the defined temperature. The Reynolds number (Re) exceeded 10.000 in all experiments, thus indicating turbulent flow conditions in the mixing vessel. The shear velocity under these conditions can be calculated via eq. 10:³⁵

$$G = \sqrt{\frac{P}{V\mu}} \quad (10)$$

Where P denotes the average power input, V the mixing vessel volume, and μ the viscosity of medium. The average power input depends on the stirring frequency (N) via

$$P = P_0 \cdot N^3 \cdot D^5 \cdot \rho \quad (11)$$

In the above equation P_0 is the geometrical factor of the stirrer, which for the stirrer used in this work equals 0.34. D denotes the stirrer diameter, and N the stirring frequency. The rate constant k_{12} can be estimated theoretically by taking into account the shear velocity (G) and the radii of starch molecules (a_1) and fibers (a_2)¹⁷

$$k_{12} = \frac{4}{3} G(a_1 + a_2)^3 \quad (12)$$

The radius of starch molecules can be estimated at 0.2 μm.² Previous studies have shown that

the deposition of small spherical particles on large particles of various shapes proceeds in very much the same manner as their deposition on large spherical particles.¹⁷ Since eq. 13 assumes that the substrate particles are spherical, while cellulose fibers are in fact oblong in shape, their average radius must be corrected via³⁶

$$a_2 = \left(\frac{3}{4} R^2 L \right)^{\frac{1}{3}} \quad (13)$$

In eq. 13 R denotes the average fiber radius, while L , the average fiber length, depends on the refining degree and fiber characteristics. The number concentration of fibers can be calculated from the ration between the concentration (consistency) of fibers in the paper stock suspension, their average length (L), and linear density (0.1 mg g^{-1}).³⁷

The collision efficiency factor (α) can be evaluated via the following empirical relation:^{20,38}

$$a = 0.8 \left(\frac{H}{36 \cdot \Pi \cdot \mu \cdot G \cdot b^3} \right)^{0.18} \quad (14)$$

Where H denotes the Hamaker constant between the modified starch and cellulose fibers and b the particle radius. The Hamaker constant can be calculated from the Hamaker constants for pure components:^{39,40}

$$H = (\sqrt{H_{11}} - \sqrt{H_{33}})(\sqrt{H_{22}} - \sqrt{H_{33}}) \quad (15)$$

In the above equation, H_{11} is the Hamaker constant for starch ($8 \cdot 10^{-20} \text{ J}$),^{41,42} H_{22} for the cellulose ($9 \cdot 10^{-20} \text{ J}$),³⁹ and H_{33} for the water ($5 \cdot 10^{-20} \text{ J}$).³⁹ Thus calculated value must be multiplied by the factor 4.6 to take into account the dielectric constant of the medium (water).⁴⁰ The Hamaker constant calculated via eq. 15 for the system under investigation is then $0.72 \cdot 10^{-20} \text{ J}$.

The fiber surface coverage by the modified starch in dependence of the contact time is shown in Fig. 4. The experimental results (dots of different styles) are calculated as the ratio between the amount of starch adsorbed under the defined conditions and the experimentally determined maximum amount of modified starch that can be adsorbed under these conditions ($\Gamma/\Gamma_{\text{max}}$). At stirring frequency of the paper stock suspension of 500 rpm and fiber consistency of 5 mg L^{-1} , the collision efficiency factor (calculated via eq. 16) equals 0.38, while the rate constant k_{12} (calculated via eq. 14) is $8.6 \cdot 10^{-11} \text{ m}^3 \text{ s}^{-1}$. The theoretical adsorption rate constant (k_{ads}) of modified starch on the cellulose fibers is thus 0.183 s^{-1} .

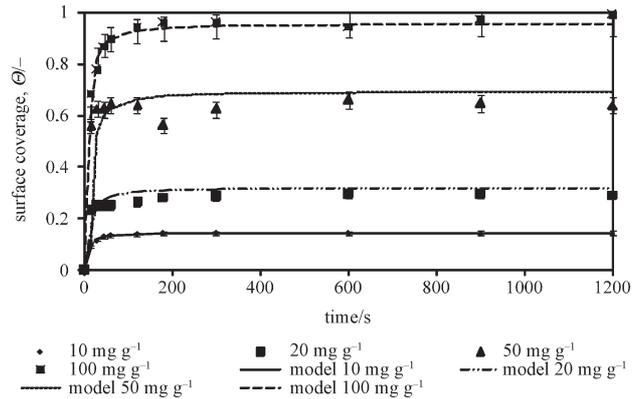


Fig. 4 – The fiber surface coverage by the modified starch molecules in dependence of time at different initial starch concentrations (stirring frequency 500 rpm, fiber consistency 5 g L^{-1}). The experimental results are denoted by dots of various forms, while the theoretical model predictions for different initial starch concentrations are depicted as lines.

As expected, the times required to attain the equilibrium state are relatively short (less than 200 s). The starch dosages of 10, 20, and 50 mg g^{-1} correspond to surface coverage of 0.15, 0.30, and $0.77 \Gamma_{\text{max}}$, respectively. This indicates that there should be plenty of free adsorption sites available to the starch molecules on the surface of the fibers. In spite of this, Fig. 4 shows that the best agreement between the experimental results and the theoretical model predictions can be observed at the low (10 mg g^{-1}) and high (100 mg g^{-1}) end of the starch dosage range. In between, the theoretical predictions are slightly higher than the experimental values. The main reason for this discrepancy could be because the presented model does not take into account the repulsive electrostatic forces between fibers, which occur when the modified starch has already been adsorbed on the fibers. The modified starch adsorption on the cellulose fibers most likely proceeds in such a manner that the individual molecular chains at first keep the same “extended” conformation they had in the solution, and thus initially bond only with the individual fiber segments. Later on, a more stable “planar” conformation is adopted. Concomitant with this relaxation into the planar conformation is the increase in the distance of separation between the charged segments on the polymer,^{30,41,43} which consequently decreases the attractive forces between the starch molecules in the water and the fiber surface.^{2,44,45} At the starch dosage of 100 mg g^{-1} , which corresponds to $1.35 \Gamma_{\text{max}}$, most, if not all of the initially available adsorption sites, have been occupied. Moreover, at such almost complete surface coverage, the repulsive forces between the charged segments of the starch molecules in the solution and adsorbed on the surface begin to exert an influence, thus further hindering the adsorption.

The influence of fiber consistency on the adsorption kinetics

Higher fiber concentration in the paper stock suspension, besides raising the number of surface sites available for the adsorption, also increases the collision frequency between the starch molecules and fibers. The results of modified starch adsorption (i.e. the parameters of the modified Langmuir adsorption isotherm) at different fiber consistencies are gathered in Table 1.

Table 1 – Parameters of the modified Langmuir adsorption isotherm at different fiber consistencies of the paper stock suspension (stirring frequency 500 rpm)

Fiber consistency/ mg L ⁻¹	5	10	20	30
K	0.125	0.181	0.1185	0.182
$\Gamma_{\max}/\text{mg g}^{-1}$	65.8	80.6	81.3	166.7
$N_f/10^{10} \cdot \text{m}^{-3}$	5.5	12	22	34
$k_{\text{ads}}/\text{s}^{-1}$	0.183	0.366	0.718	1.11

As can be seen in Fig. 5, the adsorption rate constant increased proportionally (almost linearly) with the fiber consistency; at fiber consistency of 30 mg L⁻¹ the adsorption rate constant was 6-times higher than at 5 mg L⁻¹. The maximum amount of adsorbed starch (Γ_{\max}) also rises together with the rising fiber consistency; however, its increase is not nearly linear (see Table 1). At fiber consistency of 30 mg L⁻¹ the Γ_{\max} increased only 2.5-times in comparison with the fiber consistency of 5 mg L⁻¹. This is most likely due to the mechanical flocculation of fibers, which can occur at higher consistencies, thereby decreasing the fiber specific surface area, and hence hindering the starch adsorption.

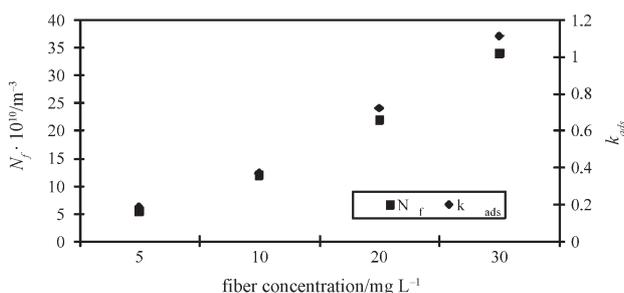


Fig. 5 – The number concentration (N_f , left-hand scale) and the adsorption rate constant (k_{ads} , right-hand scale) depending on fiber consistency

The influence of shear forces on the adsorption kinetics

Beside the fiber consistency, the collision frequency between the modified starch and fibers is also affected by the stirring frequency. The shear forces affect both kinetic rate constants of desorption and adsorption. As can be seen from the results presented in Table 2 and Fig. 6, the equilibrium constant of desorption (ratio between the kinetic rate constants of these two opposite processes) fell – the adsorption increased – as the stirring frequency increased.

Table 2 – The parameters of adsorption at different stirring frequencies (fiber stock consistency 5 mg L⁻¹)

Stirring frequency/min ⁻¹	200	500	1000	1200
Shear velocity/s ⁻¹	107	424	1183	1549
K	0.200	0.125	0.090	0.075
$\Gamma_{\max}/\text{mg g}^{-1}$	60.6	65.8	70.4	72.2
$k_{\text{ads}}/\text{s}^{-1}$	0.047	0.183	0.413	0.521

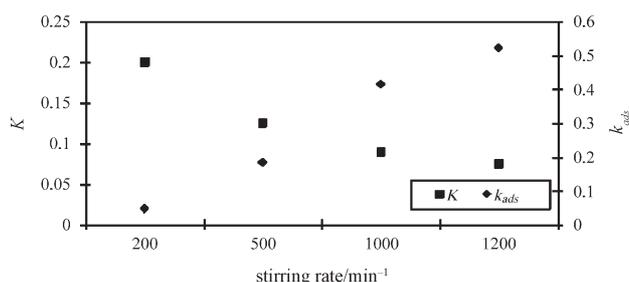


Fig. 6 – The equilibrium constant of desorption (left-hand scale) and the kinetic rate constant of adsorption (right-hand scale) in dependence of the stirring frequency

These results strongly indicate that the rate constant of adsorption increased faster than the rate constant of desorption, despite the theoretical assumption that k_{des} increases exponentially, while k_{ads} increases only linearly with the increasing stirring frequency.¹⁹ It seems that, at least in the studied stirring frequency range, the increase in collision frequency more than offsets the influence of increasing shear forces, thus favoring adsorption over desorption. On the other hand, in spite of the low contact times, this could also partly reflect the influence of polyelectrolyte reformation, which increases the contact surface between the fiber and the polymer molecule.^{46,47} This strengthens the bond between them and all but prevents desorption of starch.¹⁶ Γ_{\max} also increased in conjunction with the increasing stirring frequency; Γ_{\max} increased about 16 % from the lowest to the highest stirring frequency at the same fiber consistency (i.e. the same total number of available discrete adsorption

sites on the fiber surface). This indicates that at lower stirring frequencies there remain some unoccupied adsorption sites, which are inaccessible to the starch molecules, most likely due to the repulsive electrostatic forces between the like-charged segments of starch molecules.

The influence of fiber surface characteristics on the adsorption kinetics

Another important factor influencing the adsorption of modified starch is the characteristics of the fibers themselves. The papermaking operation that exerts the most profound influence on the fiber characteristics is the refining process. During refining, the fibers are fibrillated, and in some cases also shortened. The consequence of both these processes is an increase in specific surface area and the content of fines (the fiber fraction with fiber length under about 0.1 mm), as can be seen from Table 3.

Table 3 – The effect of the refining degree on fiber characteristics

Refining degree/SR	20	22	29	43	48
Specific surface area/ $\text{m}^2 \text{g}^{-1}$	1.58	1.6	1.8	2.0	2.14
Carboxyl group content/ $\mu\text{mol g}^{-1}$	66.8	68.7	76	90	91.3
Carboxyl group surface density/ $\mu\text{mol m}^{-2}$	42.3	42.9	42.2	43	42.6
Fines content/%	5.3	5.9	7.9	11.3	13.2

According to some researchers, the outer surface of the fiber contains no more than some 13 % of all carboxyl groups, while the remainder is situated within the pores,^{12,48} however this share can be significantly raised by refining. It is evident from Table 3 that the carboxyl group content increased in concert with the increasing refining degree, which indicates the fibrillation of fibers.² However, when the carboxyl group content is expressed per unit area of fiber surface (i.e. as the surface density), it is obvious (see Table 3 and Fig. 7) that this remains constant during the refining. Refining only increases the specific surface area of cellulose fibers via defibrillation and/or fiber shortening, but it does not seem to have a noticeable effect on the density of carboxyl groups on the surface. Since these groups are thought to represent the surface sites for the modified starch adsorption, this also promotes its adsorption on the fibers.

The adsorption of cationic polyelectrolytes is often explained on the basis of cation exchange reactions^{49,50} or even charge neutralization.⁴⁶ The adsorption of polyelectrolytes via the electrostatic

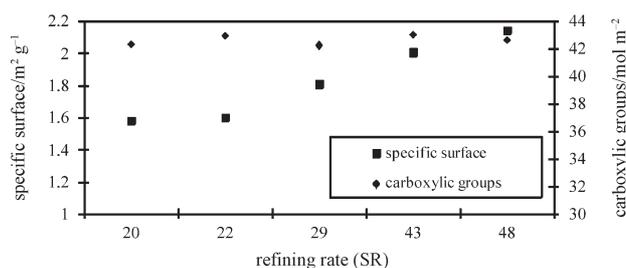


Fig. 7 – The influence of the refining degree on the specific surface area (left-hand scale) and the surface density of carboxyl groups (right-hand scale)

forces could theoretically proceed until the entire surface charge has been neutralized.⁵¹ This is in agreement with the results presented on the Fig. 8, which shows the maximum adsorbed amount of modified starch (Γ_{\max}) in dependence on the fiber specific surface area. The full black bars in this Figure show the maximum adsorbed amount expressed per unit fiber mass ($\Gamma_{\max1}$). It is obvious that this quantity increases significantly with the increasing specific surface area. However, when expressed per unit area of the fiber (i.e. as the maximum surface density of adsorbed starch, $\Gamma_{\max2}$) it remains virtually constant, regardless of the specific surface area, and hence also the refining degree of fibers.

Table 4 shows the adsorption parameters for cellulose refined to different degrees. Both the desorption equilibrium constant K and the adsorption rate constant slightly decreased with increasing refining degree.

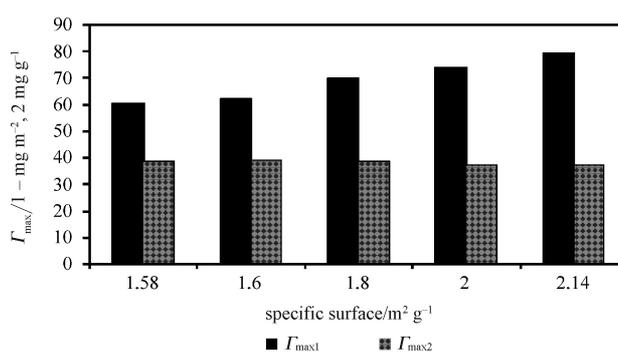


Fig. 8 – The maximum amount of adsorbed modified starch: per unit fiber mass $\Gamma_{\max1}$ (full bars), and per unit surface area (surface density) $\Gamma_{\max2}$ (dotted bars). Stirring frequency: 500 rpm, fiber consistency: 5 g L⁻¹.

Table 4 – The comparison of adsorption parameters at different refining degrees

Refining degree/SR	20	22	29	43	48
K	0.2475	0.226	0.125	0.140	0.080
Γ_{\max} /mg g ⁻¹	65.3	64.1	65.8	84	90.1
k_{ads} /s ⁻¹	0.187	0.186	0.183	0.177	0.168

Conclusions

The results of this study demonstrate that, at least in the studied range of process variables, the modified Langmuir adsorption theory can be applied to describe the adsorption kinetics of modified starch on cellulose fibers. This theory includes the effects of the substrate concentration, hydrodynamic forces, and even some characteristics of the substrate (e.g. specific surface area). However, even the modified theory cannot take into account the influence of temperature and detrimental substances (anionic trash) in the suspension. Fortunately, the results of this study also show that, under the experimental conditions closely corresponding to those commonly encountered in the industrial paper production, these factors exert very little influence on the adsorption of modified starch. The main findings of this study can be summarized as follows:

1. Increasing the fiber consistency in the suspension increases the collision frequency between fibers and modified starch molecules, which results in enhanced adsorption.

2. Increasing the shear forces (by increasing the stirring frequency) also enhances the modified starch adsorption. This result indicates that, at least in the studied range of stirring frequencies, the increase of adsorption due to the increased collision frequency more than balances the increased desorption due to the increasing shear forces.

3. The refining of fibers significantly influences the fiber characteristics and, consequently, the modified starch adsorption. Refining increases the specific surface area via fibrillation and/or fiber shortening, thus increasing the total available content of carboxyl groups (the sites for starch adsorption), and hence also the starch adsorption. On the other hand, the cellulose refining does not seem to have any appreciable influence on the surface density of carboxyl groups.

4. The results of this study have also shown that relatively short contact times (below 60 s) are required to bind the cationically modified starch on the surface of cellulose fibers. As noted in the introductory section, this is a vital parameter in the analyses and construction of adsorption equipment.

We hope that the findings presented in this study will contribute to the understanding of complex interactions occurring during the adsorption of modified starch on cellulose fibers, and also help in the optimization of application of this most important additive in the production of paper.

Symbols and abbreviations

a_p , b_i	– characteristic linear particle dimensions, m
γ	– concentration, stock consistency, mg L ⁻¹
G	– shear velocity, s ⁻¹
H	– Hamaker constant, J
k_{ads}	– kinetic rate constant of adsorption, s ⁻¹
k_{des}	– kinetic rate constant of desorption, s ⁻¹
m_i	– mass of component i, g
N_i	– number concentration of species i, m ⁻³
P	– average power input, N m s ⁻¹
SR	– Schopper Riegler refining degree, /
T	– temperature, K, °C
V	– volume, m ³

Greek symbols

α	– collision efficiency factor, /
Γ	– relative concentration of a component, mg g ⁻¹
Θ	– surface coverage, /
μ	– viscosity, Pa s
ρ	– density, g m ⁻³

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