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ORIGINAL CONTRIBUTION

Kinetics of colloidal alkylketene dimer particles deposition on pulp fibers

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Abstract For achieving a certain level of hydrophobicity in paper, sizing agents are added to the paper stock. In alkaline papermaking system, sizing is often performed by the use of alkylketene dimer (AKD)-type sizing agents. Although the key factor for developing sizing properties in paper is the reaction between AKD and cellulose during drying, good retention of size particles in the paper web is required as a prerequisite for later reaction. A mathematical model based on particle collision frequency is used for the description of deposition kinetics of colloidal alkylketene dimer particles on pulp fibers. Modified Langmuir equation was used to describe the retention process in terms of surface coverage, attachment, and detachment rate constants. The values for equilibrium retention predicted by the model are in good agreement with experimental data. The analysis of surface charge in the system also suggests that the extent and efficiency of collisions between colloidal AKD size particles with fibers are one of the key factors for successful retention. Influence of shear on the retention process was also studied.

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Introduction

Paper represents one of the most widely used materials in modern world. Based on the purpose of its use, it has to meet many requirements regarding its quality in terms of mechanical, optical, and printing properties. One of the important properties especially in the field of printing papers is the hydrophobicity of paper obtained by sizing. The sizing of paper is generally performed by sizing agents, which are added directly to the papermaking slurry. With growing production of paper under alkaline conditions with calcium carbonate used as filler in the last 30 years, the use of synthetic sizing agents based on alkylketene dimer (AKD) has dramatically increased. For efficient sizing, two key processes are of specific importance. One is the efficient retention of sizing agent in the paper web, while the other is the reaction of AKD molecules with cellulose. The chemical reaction takes place during the drying process and the amount of AKD that reacts with cellulose is very low (between 10 and 50% of the amount retained in paper) [1, 2]. For this reason, it is very important to obtain good retention of sizing agent in paper and to know what are the key factors that influence the retention process.

For the description of sizing system and sizing mechanism, Gess [3] proposed the “strong bond/weak bond” theory, where the sizing system has four basic components: the size, the precipitator, the catcher, and the substrate. In the AKD sizing system, the first three components are combined in the form of the size dispersion consisting of fine AKD particles with diameter of about 1 μm stabilized by cationic starch. Cellulose represents the substrate where size particles are attached [4]. Because the majority of bonds formed between size particles and fiber surface are labile, AKD is primarily a weak bond size. The retention of AKD on the fiber surface is influenced by many factors such as surface charge on AKD particles and on cellulose, presence of other papermaking components (fillers, retention aids), and particle size distribution in the papermaking suspension.

With cellulose having negative charge on its surface, the retention is improved with AKD dispersions that are stabilized by cationic starch in order to give a cationic character to AKD particles. It was proposed that dissociated carboxylic groups on the cellulose surface are primary anionic sites where AKD particles can attach although their surface density is relatively low [5–7]. The idea is indirectly supported by measurements of AKD retention on pulps with different surface (anionic) charge densities. Higher charge density is supposed to be the result of a larger number of dissociated carboxyl groups, which results in better AKD retention [8, 9].

Presence of other components such as fillers and retention aids can have adverse effect. Low concentrations of retention aids (<0.01% of dry substance in the suspension) in form of cationic polymers generally improve AKD retention, while high concentrations have the opposite effect [9, 10]. This can be explained by possible flocculation of fine particles and their higher overall retention due to polymer addition. Other possible reason is the slightly amphoteric character of AKD particles. Cationic retention aids can namely act as bridge between negatively charged cellulose surface and negative "patches" on the AKD particles and in this way improve their retention [9–11].

The particle size distribution of papermaking suspension also is important. It has been shown that fines (suspended material smaller than 100 μm) present in the system can accumulate a significant amount of AKD. A similar effect was also observed with calcium carbonate. In both cases with increased retention of these components, the retention of AKD has improved [9, 12–14].

The dimensions of dispersed AKD particles and, to some extent, also their electrokinetic properties are similar to those of suspended calcium carbonate particles in the filler dispersion. For the deposition of calcium carbonate on fiber surface, a theoretical model derived from particle collision theory was proposed by Alince et al. [15].

The aim of our work was to test the influence of collisions between AKD size particles and fibers on the retention process. The rate of particle deposition in terms of fiber surface coverage was measured and compared to theoretical values that were calculated following the theory proposed by Alince et al. [15]. The importance of collision frequency in comparison to electrical properties of fibers and AKD size particles was also tested.

Theory

With the majority of bonds formed between AKD and fiber surface being labile bonds (probably van der Waals bonds) that are easily broken, the retention of AKD is strongly influenced by hydrodynamic conditions in the fiber suspension. The retention process can be then modeled as a series of collisions between AKD size particles and fiber surface [15]. Some of the collisions where the size particles remain attached to the fiber surface are successful, while others are not. The particle deposition rate (and consequently retention) is dependent on the particle collision frequency and it can be written as time dependence of the number of particles retained on fiber surface (Nr):

$$\frac{\mathrm{d}N_{\mathrm{r}}}{\mathrm{d}t} = \alpha_0 k_{12} N_{\mathrm{p}} N_{\mathrm{f}} \left(1 - \frac{N_{\mathrm{r}}}{N_{\max}}\right) \tag{1}$$

N_{f} represents the number of fibers, N_{p} is the number of free particles in the suspension, and $N_{\max}$ is the maximum possible number of particles that can deposit on fibers; all values are defined as number concentrations in a unit volume of suspension. Value for k_{12} represents the rate constant of the process, dependent on the shear rate and on the dimensions of colliding particles [16], while α_0 is the collision efficiency depending on the ratio of attractive and shear forces [17].

The ratio of the amount of size particles retained on fibers to maximum possible amount of size particles that could deposit on fiber surface ($N_{\mathrm{r}}/N_{\max}$) can be substituted by surface coverage. The number concentrations of size particles in a unit volume of suspension can be substituted by concentrations of AKD size dispersion expressed in grams of size per gram of fibers and parameter n_0 can be defined as ratio of initial AKD size concentration (c_0) to maximum amount that can deposit ($\Gamma_{\max}$) (both in grams per gram of fibers) [18]. Taking into account possible detachment of particles already attached to the fiber surface, a term describing the rate of particle detachment also has to be included and the final equation for the rate of particle deposition on fibers is:

$$\frac{d\,\theta}{d\,t} = k_{att}(n_0 - \theta)(1 - \theta) - k_{det}\theta \tag{2}$$

In the second term k_{det} represents the detachment rate constant that is generally related to the bond strength E and to the hydrodynamic shear G [18].

For initial condition $\theta=\theta_0$ at time $t=t_0$, Eq. 2 has the following analytical solution [19]:

$$\theta = \frac{2n_0(\lambda - 1) + \theta_0[A(1 - \lambda) + B(\lambda + 1)]}{A(\lambda - 1) + B(\lambda + 1) + \theta_0(1 - \lambda)} \tag{3}$$

Parameters A, B, and λ are defined as:

$$A = K + n_0 + 1 \tag{4}$$

$$B = \sqrt{(n_0 - 1)^2 + 2K(n_0 + 1) + K^2} \tag{5}$$

$$\lambda = e^{Bk_{\mathrm{att}}t} \tag{6}$$

with K is the ratio of detachment to attachment rate constant ($k_{\mathrm{det}}/k_{\mathrm{att}}$). Equation 3 contains three unknowns (K, $\Gamma_{\max}$, and k_{att}), but two of them (K and $\Gamma_{\max}$) can be experimentally determined. A detailed derivation of Eqs. 1–6 is given in the Appendix.

At steady state when $d\theta/dt = 0$, Eq. 2 can be rearranged to [19]:

$$\frac{1}{\Gamma_\infty} = \frac{K}{C_\infty} + \frac{1}{\Gamma_{\max}} \tag{7}$$

$C_\infty (= c_0 - \Gamma_\infty)$ and Γ_∞ are the amount of size left in solution and amount deposited on fibers at steady state (in $\mathrm{g/g_{fibers}}$). By plotting $1/\Gamma_\infty$ as a function of $1/C_\infty$, a linear plot is obtained with slope equal to K and intercept equal to $1/\Gamma_{\max}$. The value for k_{att} can then be obtained by finding a best fit of Eq. 3 to experimental data.

Materials and methods

In our studies, a commercial AKD size dispersion was used with dry matter content of 182 g/l and with average particle size of about 1 μm (as specified by the manufacturer). The dry matter consisted of 64% AKD wax and 36% cationic starch (used as a stabilizer). At pH 6, the dispersion had zeta potential +33 mV and a cationic surface charge density 0.85 meq/g (defined per gram of dry matter).

For the preparation of fiber suspension, bleached sulfate softwood was used. Fibers were first disintegrated for 20 min in distilled water and then washed on a sieve with openings of approximately 100 μm to remove fines. The pulp was analyzed for the fiber length distribution and was found to have an average fiber length of 2.3 mm. From washed pulp, a fiber suspension with fiber concentration of 5 g/l was prepared.

The experiments for AKD size retention were performed in a Britt dynamic drainage jar (DDJ) [20] at room temperature (23 °C) with fiber suspension having pH 8. In each experimental run, 1 l of fiber suspension was first mixed for 2 min in DDJ at 200 rpm. Then the required amount of size dispersion was added, and after a certain time, drainage through the 100-mesh wire was preformed. During drainage, the suspension was still mixed to avoid the formation of fiber mat on the wire. After approximately 30 s, drainage was completed. The fibers retained on the wire were then collected and dried.

For the quantitative determination of size content in filtrate, the latter was extracted with organic solvent by means of liquid–liquid extraction to remove the AKD. For the same purpose, AKD retained on fibers was extracted with organic solvent in Soxhlet apparatus. After extractions, the organic solvent was evaporated and the remaining AKD was converted to corresponding ketones by means of acid hydrolysis. The amount of ketones was then determined by gas chromatography [21], and the quantity of sizing agent in each phase was calculated.

Results and discussion

A series of experimental runs at various initial concentrations of sizing agent in the pulp suspension was performed. From the AKD retention point of view, after 15 min of continuous stirring, the steady state conditions were achieved. The concentrations of free AKD (C_∞) size and of that deposited on fibers (Γ_∞) at steady state are shown in Table 1. A plot of $1/\Gamma_\infty$ as a function of $1/C_\infty$ is shown in Fig. 1. Although at low AKD size concentrations (high $1/C_\infty$ values) a linear dependence is observed, at higher concentrations (low $1/C_\infty$ values) some deviation is present, probably due to flocculation of AKD size particles. Similar deviations from Langmuir plot of adsorption isotherm have been observed by Petlicki and van de Ven [22] with polyethylenimine adsorption on fibers.

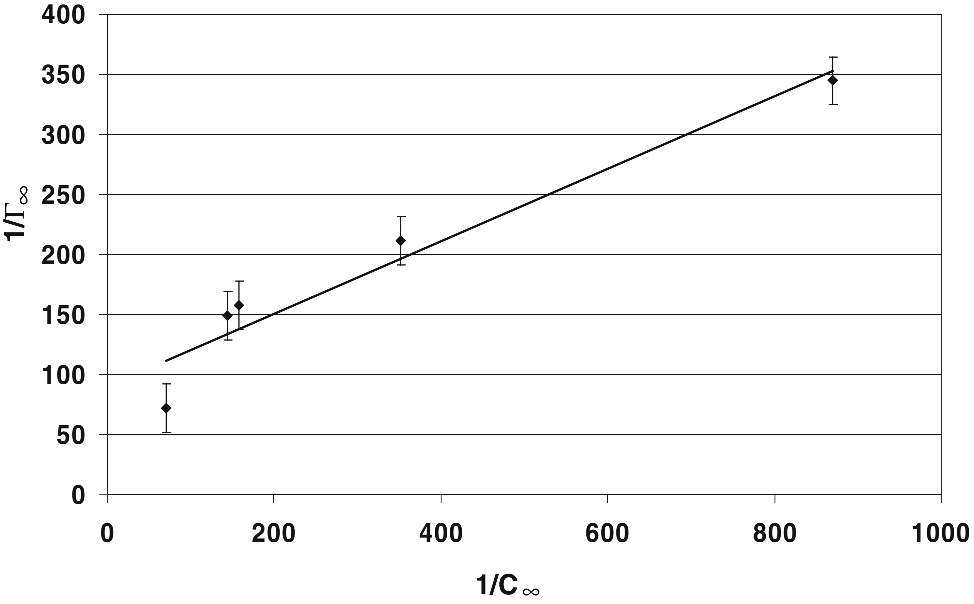
The linear equation that best fitted the experimental data in Fig. 1 was:

$$\frac{1}{\Gamma_\infty} = 0.3021 \cdot \frac{1}{C_\infty} + 90.74 \tag{8}$$

Table 1 Equilibrium amounts of free AKD size (C_∞) and that deposited on fibers (Γ_∞) at pH=8, T=23 °C, and fiber concentration 5 g/l

Size addition ($\mathrm{g/g_{fibers}}$)	C_∞ ($\mathrm{g/g_{fibers}}$)	Γ_∞ ($\mathrm{g/g_{fibers}}$)	$1/C_\infty$	$1/\Gamma_\infty$
0.0041	0.0012	0.0029	869.6	344.8
0.0076	0.0028	0.0047	352.0	211.5
0.0127	0.0063	0.0064	158.0	157.5
0.0137	0.0070	0.0067	143.8	148.9
0.0280	0.0142	0.0139	70.4	72.2

Fig. 1 Plot of $1/\Gamma_\infty$ to $1/C_\infty$

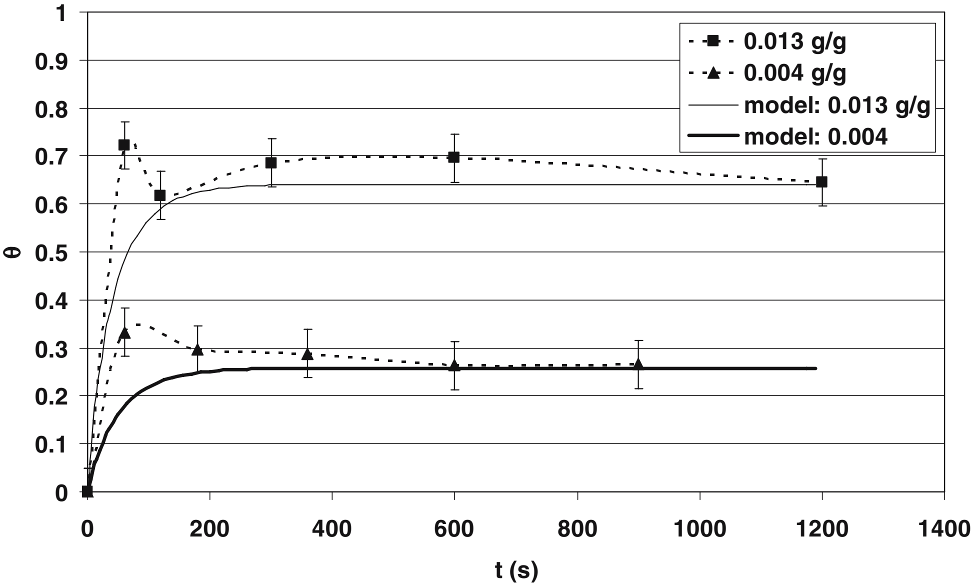


From Eq. 8, the values of 0.3021 and 90.47 can be deduced for K and $1/\Gamma_{\max}$, respectively (within the confidence limit of R^2=0.94). The calculated value for $\Gamma_{\max}$ then equals to 0.01102 g/g$_{\mathrm{fibers}}$ meaning that maximum amount of AKD size particles that can attach to fibers is relatively small.

Using the value for $\Gamma_{\max}$, the time dependency of the amount of AKD size retained on fibers (Γ) can be expressed in terms of fractional coverage θ. The time dependence of fractional coverage for two initial concentrations (0.013 and 0.004 g/g$_{\mathrm{fibers}}$) is shown in Fig. 2.

The steady state with constant surface coverage is achieved rather quickly after 150 to 200 s. Coverage, higher than that at steady state at times before 200 s, can be attributed to nonhomogenous conditions in the fiber suspension. It is reasonable to expect that after addition of the sizing agent, some time is needed before the latter is homogeneously mixed with fibers. During this time frame on microscale, there are parts of suspension with high local concentration of sizing agent due to possible particle entrapment in fiber microflocs. More sizing agent is retained on fibers in these microflocs reaching higher local surface coverage of fibers. With time and due to shearing forces, the flocs are breaking up and a rearrangement process is taking place—AKD size particles are being detached from fibers with high surface coverage and attached to fibers with low surface coverage. If the suspension is dewatered before or during this rearrange-

Fig. 2 Experimental and calculated time dependency of surface coverage for two initial additions of sizing agent. Experiments performed at pH=8, T=23 °C, and fiber concentration 5 g/l



ment process, the average surface coverage on fibers is higher than the surface coverage in equilibrium.

Compared to the sizing agent concentration on fibers at maximum coverage ($\Gamma_{\max}=0.01102$ g/g$_{\text{fibers}}$), the amounts of sizing agent added during first (0.004 g/g$_{\text{fibers}}$) and second (0.0135 g/g$_{\text{fibers}}$) set of experiments represent $0.36\times\Gamma_{\max}$ and $1.22\times\Gamma_{\max}$, respectively. At lower addition level, final surface coverage is 0.26, which means that about 70% of sizing agent remains attached to the fiber surface. While at higher addition level, the surface coverage raises to 0.65–0.69, this represents only 50% retention, although due to surplus of sizing agent 80%, retention would be possible with surface coverage $\theta=1$. Such behavior can be explained by the fact that with higher additions of sizing agent, more and more available sites for attachment of AKD size particles become covered. In general, the number of all suitable sites on the fiber surface is low, and with increasing surface coverage, the remaining free sites are less accessible due to their low number. Furthermore, the retention process by itself is a dynamic process. Because the forces acting between size particles and fiber surface are weak, the particles are being continuously attached and released. For this reason, even with AKD size concentrations higher than $\Gamma_{\max}$, it is hard to obtain full surface coverage once the state of dynamic equilibrium is achieved.

The best fit for time dependence of surface coverage to experimental data was obtained with value of 0.015 ± 0.03 s^{-1} for k_{att}. The value for k_{det}, calculated from experimentally determined ratio between the two constants (K), then equals to 0.0045 ± 0.0009 s^{-1}. The comparison of theoretical fits to experimental data is shown in Fig. 2. Also the calculated time dependencies show that the final (equilibrium) coverage should be achieved rather soon and that higher coverage at times shorter than 100 s does not represent a stable state. It is obvious that the level of equilibrium surface coverage is mainly the consequence of the initial amount of AKD size added to the fiber suspension. Based on Eqs. 3–6 for various initial concentrations, the time dependencies of surface coverage were simulated, and results are presented in Fig. 3.

With increasing initial addition of AKD size at constant fiber concentration, the final surface coverage increases but the time needed to achieve this coverage decreases. Full surface coverage ($\theta=1$) cannot be obtained even with AKD size addition five times higher than the maximum amount of size that can be attached to the fiber surface. These calculations confirm the idea that with increasing surface coverage the remaining free sites are hard to fill. Although at high concentrations of size particles the number of their collisions with fibers is high, only a minor part of collisions are successful due to the low number of free sites suitable for particle attachment. The hypothesis that the number of free sites on the fiber surface is the limiting factor is confirmed by experimental data in Fig. 2, where a 3.375-times higher (0.0135 vs 0.004 g/g$_{\text{fibers}}$) addition of AKD size dispersion results only in 2.5-times increase in final surface coverage. Until the added amounts of size dispersion are lower than $\Gamma_{\max}$ ($n_0<1$), the increase in amount added results in proportional increase in final surface coverage. However, when the added amounts are higher than $\Gamma_{\max}$, the final surface coverage slowly approaches to the full surface coverage.

The importance of fiber surface charge for the deposition of size particles was also tested. It is known that the anionic character of fibers increases with increasing pH (mainly due

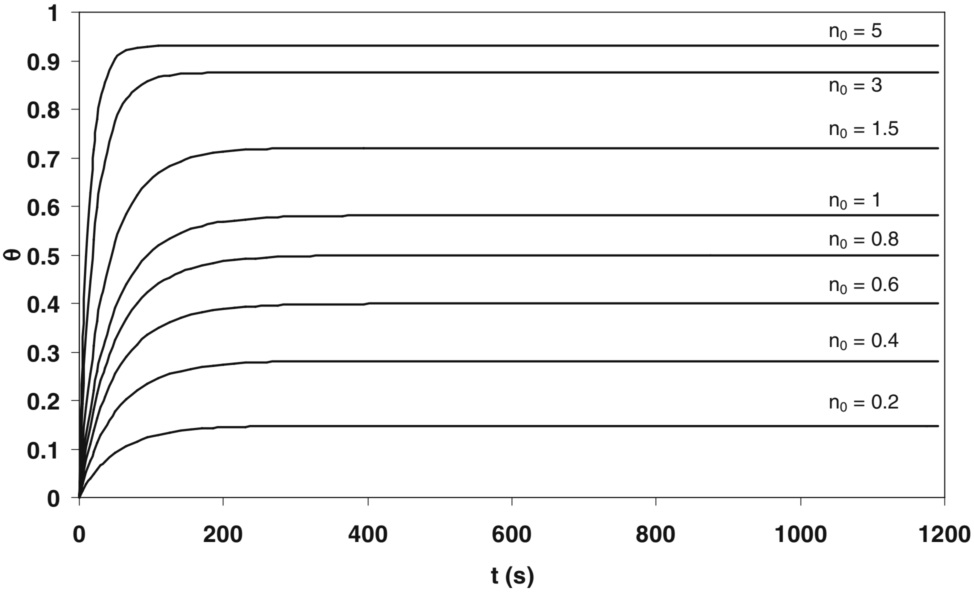


Fig. 3 Simulations of surface coverage for various values of parameter n_0 ($\Gamma_{\max}=0.01102$ g/g$_{\text{fibers}}$, $K=0.3021$)

Table 2 AKD size retention at various pH values (T=23 °C, initial size addition 0.005 g/g_{fibers})

pH	Amount of size retained (g/g_{fiber})	
	Softwood	Hardwood
7	0.0035	0.0043
8	0.0038	0.0049
9	0.0043	0.0043
10	0.0038	0.0037

to dissociated carboxylic groups) therefore the amount of cationic sizing agent retained on fibers could be pH dependent. For this reason, a series of experiments at various (alkaline) pH values was preformed with softwood and hardwood pulp. Although some increase in retained amount of AKD size was observed between pH 7 and 9, but with pH 10, the retained amount again decreased (Table 2). The observations can be explained by lower density of cationic charge on the surface of size particles at alkaline pH, as observed by some authors [23, 24]. The pH-dependent increase in anionic charge on fiber surface and decrease in cationic charge of AKD size particles obviously have opposite effects on the particle retention. Considering that some experimental error is present, the results in Table 2 suggest that increased pH does not improve significantly the deposition of AKD size particles on particular fiber type, although with hardwood, the average amount of size retained on fibers seems to be somewhat higher.

The main sources of anionic charges on fiber surface are supposed to be the dissociated carboxylic groups. They should also be responsible for the successful retention of cationic papermaking additives. While it seems that with more carboxylic groups present in dissociated form at higher pH, this does not contribute to better particle deposition (Table 2); the same can be stated for the increase in carboxylic groups concentration due to fiber structure.

A comparison between softwood and hardwood fibers with carboxylic group concentration of 30±3 and 50±3 $\mu eq/g_{fibers}$, respectively, was made. At pH 8 and initial size addition of 0.0075 g/g_{fibers}, similar retention of AKD size was achieved with both fiber types (0.0046 g/g_{fibers} for softwood and 0.0047 g/g_{fiber} for hardwood, 10% error), although the concentration of carboxylic groups on hardwood fibers is almost twice as high as that on the softwood fibers. Again, as stated above, the increase in concentration of carboxylic groups does not improve the deposition of AKD size particles on the fibers.

To determine the available anionic charge in fiber surface an experiment with poly-diallyldimethyl ammonium chloride (PDADMAC) was made. Based on a Langmuir plot, the value of 0.005 g/g_{fibers} for $\Gamma_{\mathrm{maxPDADMAC}}$ was determined. With PDADMAC having a surface charge of 9 meq/g, this corresponds to surface charge of about 45 $\mu eq/g_{fibers}$. The average molecular mass of PDADMAC was 3×10^5 g/mol (with minimum of 3×10^4 g/mol), indicating that the molecules were too large to penetrate into the micropores of the fibers. If due to the molecule size PDADMAC is retained only on the outer fiber surface, the measured charge density of 45 $\mu eq/g_{fibers}$ could represent the amount of surface charge potentially accessible to the AKD size particles. A comparison to sizing agent surface charge density (0.85 meq/g) suggests that a maximum of 0.05 g sizing agent could be deposited on 1 g of fibers if the main driving force would be the electrostatic attraction. Again the experimentally determined value of 0.01102 g/g_{fibers} indicates that factors other than electrostatic attraction are governing the deposition process.

Within this scope, the influence of shear on the overall deposition rate was tested. A series of experiments at various stirring rates was performed where the amount of AKD size retained on fibers (Γ_{2min}) and surface coverage after 120 s (θ_{2min}) were determined (Table 3). By using Eq. 7, the experimental values for K were calculated. For each stirring speed, the theoretical value for k_{att} was estimated using the following equation [16]:

$$k_{att} = N_f \alpha_0 \frac{4}{3} G\left(a + a_p\right)\left(b + a_p\right)^2 \tag{9}$$

N_f is the number of fibers per unit volume (8.1×10^9 m^{-3} at concentration 5 g/l), G is the shear rate, a is the average fiber length semi-axis (fiber length of 2.3×10^{-3} m=2a), b is fiber radius (fiber diameter of 25×10^{-6} m=2b), a_p is the radius of AKD size particle (0.5×10^{-6} m), and α_0 is the collision efficiency. The values for shear rate were calculated by the following equation [25]:

$$G = \sqrt{\frac{P}{V\eta}} \tag{10}$$

and α_0 was estimated by the relation proposed by van de Ven and Mason [26]:

$$\alpha_0 = 0.8\left(\frac{H}{36\pi\eta G b^3}\right)^{0.18} \tag{11}$$

P represents power input at certain stirring speed, V is the volume of mixing vessel (1 l), η is the viscosity of liquid phase (water), H is the Hamaker constant (10^{-20} J), and b is the fiber radius.

By using theoretical values for k_{att}, the fiber surface coverage θ for various stirring rates was calculated. In the calculations, the experimentally determined values of parameter K for each stirring rate were used. The data used for calculation are shown in Table 3 and the comparison between modeled and experimentally determined depen-

Table 3 Data used for calculation of surface coverage

Stirring (rpm)	G (s^{-1})	Size addition (g/g_{fibers})	Γ_{2min} (g/g_{fibers})	K	θ_{2min}	k_{att} (s^{-1})
200	107	0.0135	0.0072	0.31	0.651	1.34×10^{-2}
500	425	0.0137	0.0045	1.23	0.406	4.15×10^{-2}
750	780	0.0143	0.0043	1.41	0.391	6.83×10^{-2}
1,000	1,201	0.0137	0.0042	1.41	0.380	9.73×10^{-2}

dencies of surface coverage on stirring rate is shown in Fig. 4.

Surface coverage determined at various stirring speeds shows that an increase in the stirring speed strongly affects the attachment of AKD size particles to fiber surface. Increase in the ratio K suggests that with increase in stirring speed and consequent increase in shear, k_{det} increases faster than k_{att} that results in lower surface coverage. The major decrease in θ_{2min} is seen with increase of stirring rate from 200 to 500 rpm, while with further increase in stirring rate, the maximum surface coverage tends to decrease slower (Fig. 4). With k_{det} being exponentially dependent on shear rate in contrast to linear dependency of k_{att}, it seems that the higher the stirring rate, the more the process is influenced by the rate of particle detachment from fiber surface.

Conclusions

With many different factors influencing the process of AKD size retention in paper, their theoretical description is rather complicated. One of the possibilities is to describe the process in terms of the collisions between size particles and fibers. The process is observed to follow Langmuir kinetics, and various influences on the process are combined in the two constants k_{att} and k_{det}, which describe the processes of particle attachment and their possible detachment from the fiber surface. By treating the amount of AKD size particles retained on fibers in terms of surface coverage, we showed that the number of sites on fiber surface suitable for successful attachment of size particles is quite small. An increase in amount of sizing agent does increase the surface coverage, although this effect is less pronounced with amounts higher than the maximum amount of the sizing agent that can be retained on fibers. Among the process parameters that can influence the retention process, the influence of shear in terms of stirring intensity was tested. The results have shown that changes in stirring intensity have a strong impact on the particle attachment and detachment rates, indicating that the bonds formed between fibers and size particles are not very strong. Although starch used to stabilize the AKD dispersion also acts as a retention aid, its efficiency is rather small in terms of strengthening the cellulose–particle bond. To improve retention, a second retention aid, acting as a bridge between fiber surface and size particles, is needed. It would be interesting to expand the study to test how such a potential retention aid influences the maximum coverage of fibers, attachment and detachment rates, and their dependence on shear rate.

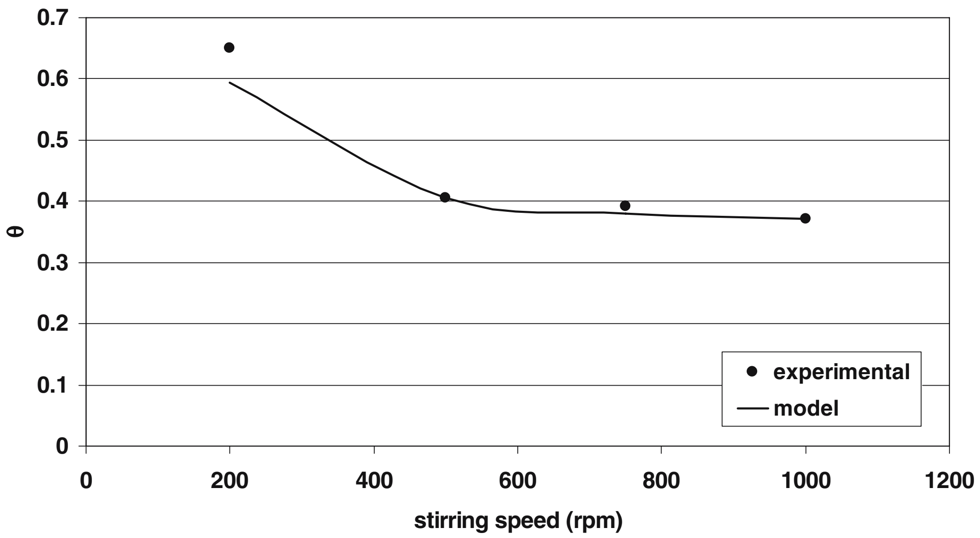


Fig. 4 Dependence of maximum fiber surface coverage (θ) on stirring speed at pH=8 and T=23 °C, fiber concentration 5 g/l; initial size additions are given in Table 3

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Appendix

The particle deposition rate can be written as time dependence of the number of particles retained on fiber surface (N_r) [15–17]:

$$\frac{dN_r}{dt} = \alpha_0 k_{12} N_p N_f \left(1 - \frac{N_r}{N_{max}}\right) \tag{A1}$$

Because the total number of size particles (N_0) remains constant and is equal to the initial number of size particles (at time $t=0$) we can write:

$$N_p = N_0 - N_r \tag{A2}$$

Combining Eqs. (A1) and (A2) and dividing by N_{max} we obtain:

$$\frac{d}{dt}\left(\frac{N_r}{N_{max}}\right) = \alpha_0 k_{12} N_f \left(\frac{N_0}{N_{max}} - \frac{N_r}{N_{max}}\right)\left(1 - \frac{N_r}{N_{max}}\right) \tag{A3}$$

By defining the fractional surface coverage ($\theta = N_r/N_{max}$) and the ratio between total number of size particles in the system and the number of particles deposited on fibers ($\beta = N_0/N_{max}$) Eq. (A3) is rearranged to:

$$\frac{d\theta}{dt} = \alpha_0 k_{12} N_f (\beta - \theta)(1 - \theta) \tag{A4}$$

The term $\alpha_0 k_1 N_f$ in Eq. (A4) can be substituted by attachment rate constant k_{att} and instead of β in Eq. (A4) n_0 is defined as [18]:

$$n_0 = \frac{c_0}{\Gamma_{max}} \tag{A5}$$

Equation (A4) now rearranges to:

$$\frac{d\theta}{dt} = k_{att}(n_0 - \theta)(1 - \theta) \tag{A6}$$

Taking into account possible detachment of particles already attached to the fiber surface also a term describing the rate of particle detachment has to be included:

$$\frac{d\theta}{dt} = k_{att}(n_0 - \theta)(1 - \theta) - k_{det}\theta \tag{A7}$$

The detachment rate constant k_{det} is related to the bond strength E and to the hydrodynamic shear, with $k_0(G)$ representing the rate of shear and kT representing thermal energy [18]:

$$k_{det} = k_0(G) e^{-E/kT} \tag{A8}$$

For initial condition $\theta = \theta_0$ at time $t = t_0$ Eq. (A7) has following analytical solution [19]:

$$\theta = \frac{2n_0(\lambda - 1) + \theta_0[A(1 - \lambda) + B(\lambda + 1)]}{A(\lambda - 1) + B(\lambda + 1) + \theta_0(1 - \lambda)} \tag{A9}$$

Parameters A, B and λ are defined as:

$$A = K + n_0 + 1 \tag{A10}$$

$$B = \sqrt{(n_0 - 1)^2 + 2K(n_0 + 1) + K^2} \tag{A11}$$

$$\lambda = e^{B k_{att} t} \tag{A12}$$

with K being the ratio of detachment to attachment rate constant (k_{det}/k_{att}).

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