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Mechanism of Internal Sizing with Alkyl Ketene Dimers: The Role of Vapour Deposition

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ABSTRACT

The role played by AKD vapours during internal sizing was investigated using commercial AKD waxes and model surfaces. The model surfaces consist of cellulose and cellulose acetate films deposited on smooth glass slides. These cellulosic films were exposed to AKD vapours at temperatures ranging from 80°C to 175°C for different periods of time. The extent of sizing was followed by measuring the advancing contact angle of water over the treated surfaces.

A simple model, considering both physisorption and chemical reaction, was developed and validated with experimental data. The energy of activation of 61.4 kJ/mole was derived from the Arrhenius plot. From a series of indirect techniques, it is concluded that the establishment of a covalent bond between cellulose and AKD is essential in order to introduce permanent hydrophobicity to cellulosic surfaces. The effect of “sizing promoters” on the reaction rate was also examined.

Both NaHCO_3 and cationic PEI failed to catalyze sizing between cellulose and AKD vapours. The mechanism proposed and the model will shed new light on the phenomena of AKD sizing treatment and sizing migration.

INTRODUCTION

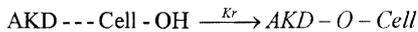
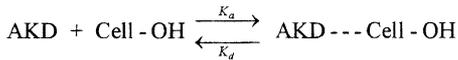
Sizing is the process by which paper hydrophobicity is increased to optimize printability and surface properties. This can be done either as a surface treatment by coating the dry paper with a sizing suspension (surface sizing) or directly during paper making by adsorbing colloids onto the furnish (internal sizing). Alkyl Ketene Dimers (AKD) are among the most widely used internal size. Despite 40 years of intense industrial use, many questions, such as the mechanism of size development with time and whether an AKD-cellulose covalent bond occurs, still remain.

The mechanism of internal sizing with AKD is generally agreed to occur in three distinct steps (1): (i) the retention of the polymer stabilized AKD suspension on the fibres, fines and fillers of the furnish; (ii) the complete wetting of AKD over the solid surface; (iii) some reconfiguration and aging process. While the mechanism in the first step is well known and consists of the hetero coagulation of the positively charged AKD colloids over the negative surfaces, the second and third steps are less understood. This stimulates a strong debate on the occurrence of a AKD-cellulose covalent bond. In this article we investigate the hypothesis by which the deposition of AKD vapours is part of the sizing mechanism. AKD spreading on various surfaces of the furnish could then occur by two mechanisms: wetting and vapor deposition. In an effort to elucidate this spreading mechanism, we have been investigating (1) the wetting of various surfaces by molten AKD and (2) the vapor deposition of AKD on cellulose films. The present study investigates specifically the role played by the AKD vapor deposition during sizing using commercial AKD and model surfaces. Model surfaces were chosen instead of common fibres and fillers to avoid any complication from surface heterogeneity. The model consists of films of cellulose and cellulose acetate deposited on a

smooth glass slide. A purified commercial AKD wax was selected in spite of its important chemical heterogeneity to include all fractions industrially relevant. Variables of interest include temperature, humidity, AKD chemistry (alkyl chain length and contaminant content), hydroxyl concentration of the solid and catalysts (sizing promoters). The objective of this study is to elucidate the mechanism by AKD spreading during internal sizing.

KINETIC MODEL

When AKD vapour is in contact with cellulose, both physical adsorption and chemical reaction can happen. It is assumed that AKD vapour molecules first adsorb on cellulose surface and some of them then react with hydroxyl groups:



where K_a , K_d and K_r are the rate constants of adsorption, desorption and chemical reaction respectively. The physical adsorption rate is given by the AKD concentration and the available adsorption sites:

$$R_{\text{ads}} = K_a [\text{AKD}] N (1 - \theta_a - \theta_r) \quad (1)$$

where N is the total number of sites, θ_a and θ_r are the fractions of adsorbed and reacted sites respectively.

Similarly the desorption rate is:

$$R_{\text{des}} = K_d N \theta_a \quad (2)$$

At equilibrium we have:

$$R_{\text{ads}} = R_{\text{des}} \quad (3)$$

$$K_a[\text{AKD}] N (1 - \theta_a - \theta_r) = K_d N \theta_a \quad (4)$$

which leads to:

$$\theta_a = \frac{(1 - \theta_r) K_a [\text{AKD}]}{K_a [\text{AKD}] + K_d} \quad (5)$$

The AKD concentration can be assumed constant during the reaction by using a large excess and the AKD-cellulose reaction can be modelled as a pseudo-first order:

$$R_r = K_r \theta_a N = \frac{d[\text{AKD} - \text{O} - \text{Cell}]}{dt} = \frac{d(N\theta_r)}{dt} = N \frac{d\theta_r}{dt} \quad (6)$$

Since the AKD vapour concentration is a constant at a given temperature, its temperature dependence can conveniently be included into a modified constant K_a' . Therefore with $K_a' = [\text{AKD}]K_a$ and $K_{\text{eq}} = K_a' / K_d$, equation (5) becomes:

$$\theta_a = \frac{1 - \theta_r}{1 + 1/K_{\text{eq}}} \quad (7)$$

Inserting equation (7) in (6) and integrating gives the expression for the reacted AKD fraction on cellulose surface:

$$\theta_r = 1 - e^{-\frac{K_r t}{1 + 1/K_{\text{eq}}}} \quad (8)$$

Or for convenience:

$$\theta_r = 1 - e^{-\alpha t} \quad \text{where } \alpha = \frac{K_r}{1 + 1/K_{eq}} \quad (9)$$

K_{eq} can be expressed as (13):

$$K_{eq} = A_{eq} e^{\frac{Q}{RT}} \quad (10)$$

where Q is the adsorption energy. Assuming the chemisorption reaction has an activation energy of E_a , and follows Arrhenius behaviour, then:

$$\alpha = \frac{A_r e^{-\frac{E_a}{RT}}}{1 + A_{eq}^{-1} e^{-\frac{Q}{RT}}} \quad (11)$$

Two limiting cases are of specific interest:

Case 1 If $K_{eq} \gg 1$, which means $K_d \ll K_a$, then:

$$\alpha = K_r \text{ and } \theta_r = 1 - \exp[-K_r t] \quad (12)$$

This is the particular case of strong physical adsorption.

Case 2 If $K_{eq} \ll 1$, for weak physical adsorption:

$$\theta_r = 1 - e^{-K_r K_{eq} t} \quad (13)$$

$$\alpha = K_r K_{eq} = A_r e^{-\frac{E_a}{RT}} A_{eq} e^{-\frac{Q}{RT}} \quad \text{or}$$

$$\alpha = A^* e^{-\frac{E_a - Q}{RT}} \quad (14)$$

Where $A^* = A_r A_{eq}$ and a plot of $\ln \alpha$ as function of $1/T$ will still yield a straight line as in case 1.

Unfortunately the amount of reacted AKD is not easy to detect directly using common analytical methods. The approach in this study consists of using some indirect but convenient methods to follow the progress of the reaction. It is well known that water contact angle of a hydrophilic substrate is very sensitive to contamination from low surface energy material. Even with coverage as little as a fraction of a monolayer, low surface energy materials such as fatty acids and AKD on a highly hydrophilic substrate will decrease the surface energy significantly and thus increase the water contact angle. Other advantages of this technique include its simplicity and convenience. Since it is also a non-destructive method, after contact angle measurement the sample can be used for subsequent analysis.

To correlate the measured contact angle (ϕ) to the surface coverage, Swanson's (2) data of fatty acid adsorption on cellulose film was fitted to the following empirical equation:

$$\phi = \frac{a \theta_r}{b + \theta_r} + c \quad (15)$$

where a, b, c are constants to be fitted. It is easy to see that c is the contact angle of pure cellulose, a+c is the contact angle at plateau of the curve (Figure 1).

EXPERIMENTAL

1. Materials and Instrumentation

Cellulose acetate was from Sigma, with ~40% acetate group. All solvents used were HPLC or Spectroscopic grade. Water was purified from a Millipore Ultrapure system. Polyethyleneimine (PEI) was from BASF, Germany with a molecular weight of 500,000 and was used as received. Sodium bicarbonate was reagent grade (Caledon Laboratories Ltd., Ontario, Canada) and was used as received. Commercial AKD, which was made from a fatty acid mixture of C14 to C20 with C18 the main component was donated by Raisio Chemicals, North America. Before use it was recrystallised three times and dried.

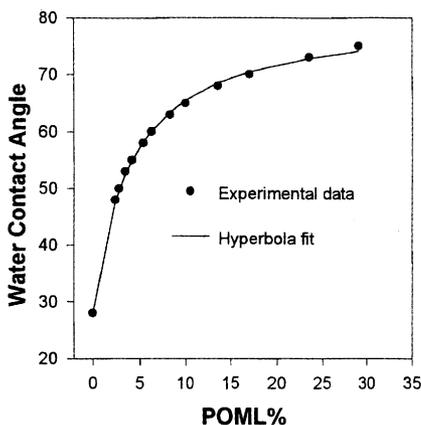


Fig. 1 Swanson's data was fitted into Equation (15), $a = .53.6$, $b = 3.65$, $c = 26.3$.

The Surface tension and contact angle were measured on a Sigma 70 Surface Tension/Contact Angle Meter (KSV Instruments, Finland) at a temperature controlled to 25 ± 0.5 °C. Only advancing contact angles were analysed.

2. Cellulosic Films

Cellulose films on glass were prepared by regenerating cellulose acetate coating. The procedure followed that of Luner et al (3, 4). Briefly, glass slides were cleaned by detergent and nitric acid, rinsed with water, and dried at 120°C. They were always prepared shortly prior to making cellulose acetate films.

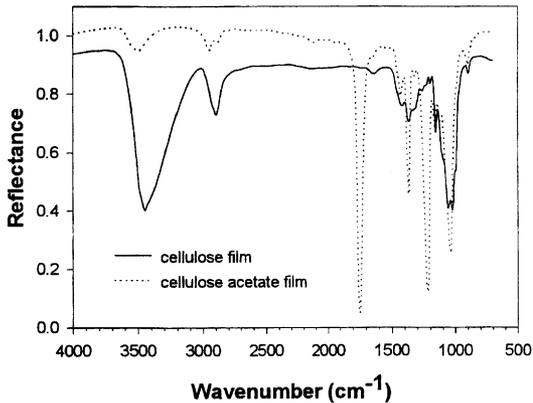


Fig. 2 Internal Reflectance FTIR spectrum of films on gold coated glass.

Cellulose acetate was dissolved in acetone to make a 5% solution. A cleaned glass slide was then dipped slowly into and then withdrew from the cellulose acetate solution. After evaporation of acetone, a smooth cellulose acetate thin film was deposited on the glass slide. The cellulose acetate film was hydrolysed to cellulose by soaking it in 0.5% sodium methoxide for at least 8 hours. The regenerated cellulose film was washed by water and methanol, air dried

and stored in a desiccator at room temperature and ~35% relative humidity. The completion of hydrolysis of acetate into hydroxyl was confirmed by Internal Reflectance FTIR (Figure 2). Tapping Mode Atomic Force Microscopy showed that the films were uniform with a roughness better than 20 nm.

3. Contact Angle Measurements

The substrate of interest was hooked to the micro balance of Sigma 70 Surface Tension/Contact Angle Meter. Then it was brought into contact with water at a velocity of 5 or 10 mm/min. The forces measured by the microbalance F results from the wetting and the buoyancy forces:

$$F = P\gamma \cos\phi - V\rho_1 \quad (16)$$

Where P is the perimeter of the slide (the wetting length), γ is the surface tension of water, ϕ the contact angle and $V(=SH)$ is the wetted volume of cross section S and immersion depth H of the slide respectively. The density of water is represented by ρ_1 . The contact angle can be determined at $H=0$ or more accurately by a series of measurements at a wide range of H and extrapolation to $H \rightarrow 0$, then:

$$\cos\phi = \frac{F}{P\gamma} \quad (H \rightarrow 0) \quad (17)$$

4. AKD Vapour Deposition

For this experiment, a special adsorption cell ($65 \times 38 \times 34$ mm³ outside dimension, without cover) was built. The top view is shown in Figure 3.

The substrate of interest was placed in the centre of the cell. At a distance of 5 mm on both of its sides were mounted two glass slides or filter paper coated with a thin layer of AKD. The cell was air-tight sealed and placed in an oven at pre-set

temperatures for various periods. The contact angle was measured immediately after the cell was cooled down while the sample in the cell.

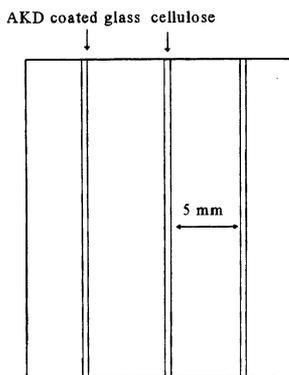


Fig. 3 The sketch of the adsorption cell (top view).

RESULTS

The AKD vapour deposition can be followed as functions of time and temperature by measuring the contact angle formed by water over treated surfaces for different periods of time. The behaviour of AKD vapour deposition on three model surfaces, namely cellulose, cellulose acetate films and glass at 100 °C is shown on Figure 4. While the water contact angle of cellulose acetate remains unchanged after more than 6 hours in contact with AKD vapour, the contact angle of cellulose and glass shows a dramatic increase during the same period. As a matter of fact, the contact angles reach almost the plateau. Glass has a higher contact angle plateau and reaches it faster than cellulose though the two curves have a similar shape.

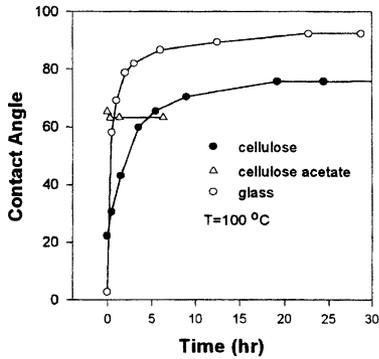


Fig. 4 AKD vapour deposition on model surfaces at 100 °C.

The kinetics of AKD vapour deposition on cellulose is shown at different temperatures on Figure 5.

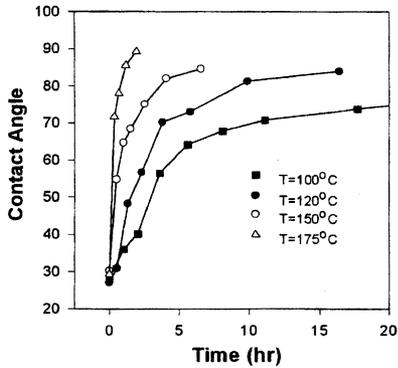


Fig. 5 AKD vapour deposition on cellulose at different temperatures.

All four curves present a similar behaviour: after an initial increase, the contact angle reaches a common plateau. The rate at which the plateau is reached is highly temperature dependent: the higher the temperature, the faster the rate. It should be pointed out that at higher temperatures (150 and 175 °C) AKD decomposed after long heating time. As a result, the water contact angle dropped slightly before it reached the plateau. The data presented here do not show those points.

The experimental results are compared with the developed model on Figure 6 (a, b, c, d for 100 °C, 120 °C, 150 °C and 175 °C respectively). From the best fit, the exponential constants α were obtained. The curve fitting can be regarded as satisfactory considering the experimental error and the assumptions made.

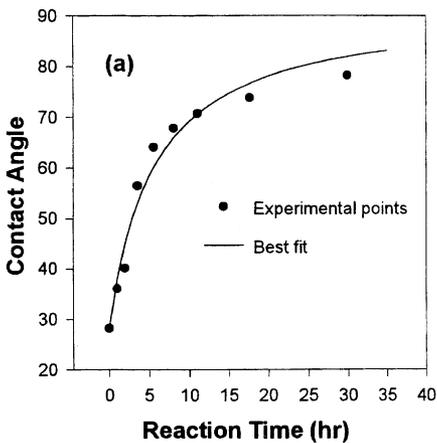


Fig. 5 (continued) AKD deposition on cellulose at various temperatures

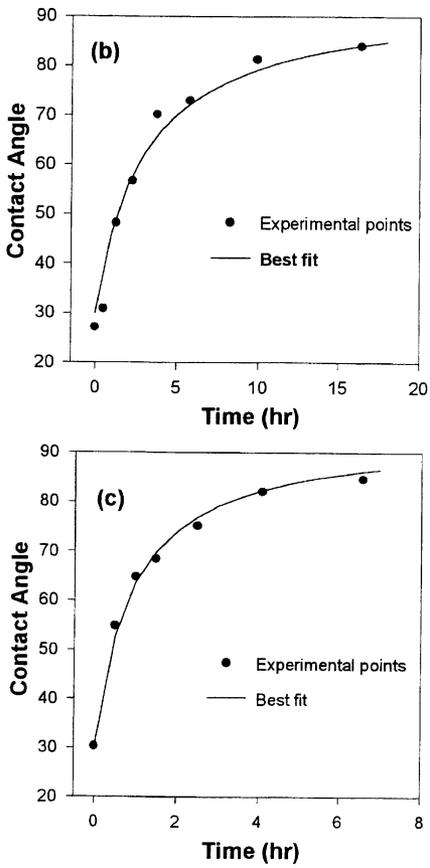


Fig. 5 (continued) AKD deposition on cellulose at various temperatures

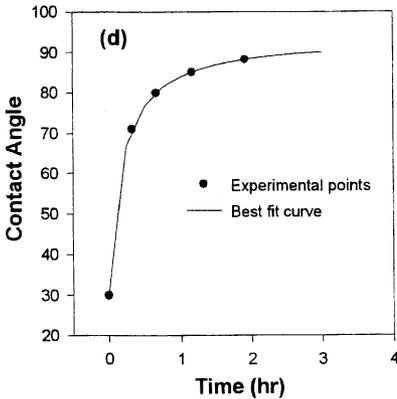


Fig. 6 Best fit of data on Figure 5 at (a) 100 °C, $\alpha = 6.50 \times 10^{-3} \text{ hr}^{-1}$, (b) 120 °C, $\alpha = 0.0121 \text{ hr}^{-1}$, (c) 150 °C, $\alpha = 0.0394 \text{ hr}^{-1}$, and (d) 175 °C, $\alpha = 0.194 \text{ hr}^{-1}$.

In another series of experiments the effect of so called “sizing promoters” was examined. Figure 7 illustrates the results from NaHCO_3 treated cellulose film. The cellulose film was immersed in $3 \times 10^{-3} \text{ M NaHCO}_3$ for 10 minutes and then air dried. The AKD vapour adsorption followed the exact procedure as for pure cellulose. To prevent adsorbed NaHCO_3 from dissolving in water, the contact angle was measured with $3 \times 10^{-3} \text{ M NaHCO}_3$ instead of pure water. The surface tension of $3 \times 10^{-3} \text{ M NaHCO}_3$ is the same as pure water.

Figure 7 shows that NaHCO_3 treated cellulose reacted with AKD vapour almost in the same way as did the pure cellulose: the contact angles are only slightly higher. This small increase is inconsistent with other research results (5)

where NaHCO_3 dramatically increased the cellulose/AKD reaction rate when added to the furnish before making a handsheet.

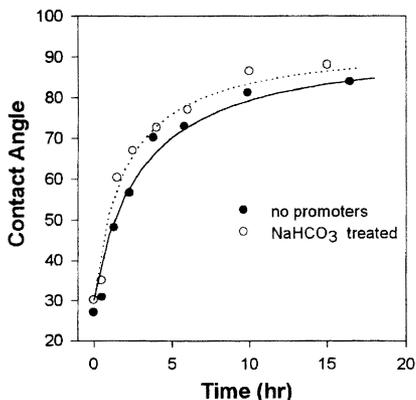


Fig. 7 The effect of NaHCO_3 on AKD vapour deposition on cellulose at 120 °C, $\alpha(\text{NaHCO}_3) = 0.0184 \text{ hr}^{-1}$.

Cationic polyelectrolytes containing amine groups are also reported to catalyse the AKD/cellulose reaction. The polymer chosen for this study was polyethyleneimine (PEI). A cellulose film was immersed in 0.1% PEI aqueous solution for 10 minutes and the excess PEI was washed off with water before the film was air dried. Coating cellulose with PEI increased the initial contact angle from 30° to 50° (Figure 8). Interestingly in both cases (with and without PEI) the contact angle reached the same plateau at about the same time (ca. 15 hours) at 120 °C. These observations again contradict with previous work (5) where PEI was found to increase the reaction rate by a factor of 3 in the absence of NaHCO_3 at pH 8.

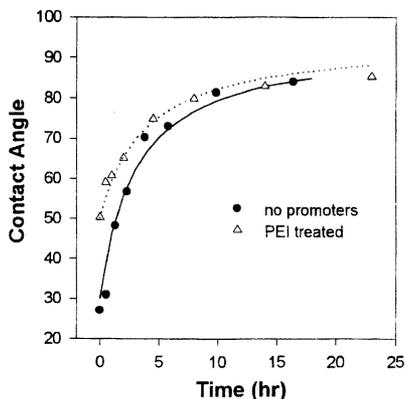


Fig. 8 The effect of PEI on AKD vapour deposition on cellulose at 120 °C, α (PEI) = $9.53 \times 10^{-3} \text{ hr}^{-1}$.

DISCUSSION

1. Measurement of AKD Surface Coverage from Contact Angle Experiments

Because there is no simple way to quantify fractional monolayer concentrations of AKD vapour deposited on cellulose surface, the current study relied on Swanson's results (2) to convert easily measurable contact angle to the AKD surface coverage. It is true that AKD and fatty acids have different chemical structures, but both form the same covalent bond with cellulose. AKD can be seen as a branched fatty acid in this sense. Furthermore, Swanson (2) developed an empirical relationship relating the surface coverage to the fatty acid chain length and the water contact angle:

$$\phi = 17.08(L^2 \text{POML}\%)^{0.15} \quad (18)$$

where L is the molecular chain length. This equation was valid for behenic acid, stearic acid and branched isostearic acid. Equation (16) shows the contact angle to be controlled only by the hydrocarbon chain length and the surface coverage, and to be independent of the detailed chemical structure such as the molecular cross section. Using a relationship developed for fatty acids for AKD is thus justified.

2. Effect of Surface and Covalent Bonds on AKD Sizing

Three different surfaces were examined in this study: cellulose, cellulose acetate and glass. Cellulose and glass displayed a similar behaviour whereas cellulose acetate did not show any increase of hydrophobicity even after long exposure to AKD vapour (Figure 4). This difference is clearly associated with the surface properties of the substrates. Both cellulose and glass have active -OH groups which can form ester covalent bond with AKD whereas cellulose acetate does not have any such functional groups which can associate with AKD. The surface concentration of hydroxyl groups increases from cellulose acetate to cellulose and glass. The contact angle plateau and the rate at which it is reached also increase in the same order after exposure to AKD vapour. Similarly fatty acid vapour can react with cellulose and glass (5-8) and render these surfaces hydrophobic. Fatty acid esters, on the other hand, are hydrophobic materials but their vapours cannot increase the cellulose hydrophobicity (8). AKD hydrolysed products ketones are also highly hydrophobic materials, yet when retained alone on cellulosic fibre in similar amount as AKD or fatty acid, no sizing developed (9, 10). Even very small amount of unextractable AKD (~0.005%) can render cellulose hydrophobic (11). Lindstrom (12) showed that only 4% of a monolayer coverage could provide satisfactory sizing. Under these conditions, some kind of AKD molecular anchoring and orientation must be present. A covalent bond is an efficient means of anchoring though it may not be the only one. No water repellence is expected if a few AKD molecules are randomly physisorbed on the fibre's surface since their polar heads will preferentially orient themselves towards the water because of their higher affinity.

3. Effect of Temperature

The curves of Figure 5 have a common feature: the contact angle of water on cellulose films increases very rapidly initially and then slowly reaches a plateau. The rate of which the plateau is reached is highly temperature dependent. This trend can be seen more clearly from the contact angle-surface coverage plot (Figure 9). In Figure 9 the surface coverage on cellulose film at different temperatures was converted from Equation (15) with constant C adjusted to each case. As expected, all curves fall onto the same line. AKD coverage corresponding to only 5% POML increases the water/cellulose contact angle from 30° to 65°. This curve can be explained in terms of steric hindrance as function of the concentration of bonded AKD and can be separated into three distinct zones. At a low AKD surface concentration, the lateral interaction between AKD molecules is negligible and each of the AKD molecules can freely sweep around its anchoring point thus covering a much larger area than its molecular cross section. This region is represented by the initial linear portion of the curve. As the AKD concentration increases on the surface, the interactions between AKD chains are getting stronger, the mobility and the orthogonal projection of rotation of AKD molecules decrease and thus AKD molecules cover less surface area. Finally the AKD molecules form a full monolayer, and their projections on the surface correspond to their molecular cross section analogue to a L-B film. This region is represented by the plateau of Figure 9. Indeed it was shown that when fatty acid coverage decreased from 100% to 50%, the water contact angle hardly changed (7).

The features shown in Figure 5 and Figure 9 are not consistent with the mechanism of physical adsorption from gas or vapour for three reasons (13). Firstly the physical adsorption generally does not reach the same plateau for different vapour pressures and temperatures. Secondly, the physical adsorption isotherms show the opposite trend: at a given pressure less is adsorbed at higher temperatures. Thirdly physical adsorption is in general very fast except limited by mass transport in the vapour phase (13) which is not the case here. Assuming AKD has the same vapour pressure at 120 °C (0.05 mm Hg), the amount of AKD in the

cell corresponds to a full monolayer coverage of both sides of the glass slide. On the other hand, if a chemical reaction is considered to be the controlling factor these curves are not surprising at all since the water contact angle is mainly determined by the surface coverage of reacted AKD on cellulose. Soxhlet extraction of AKD treated cellulose films with CHCl_3 gave all most the same water contact angle. This suggests that in this experiment the physically absorbed AKD contributes little to the cellulose hydrophobicity.

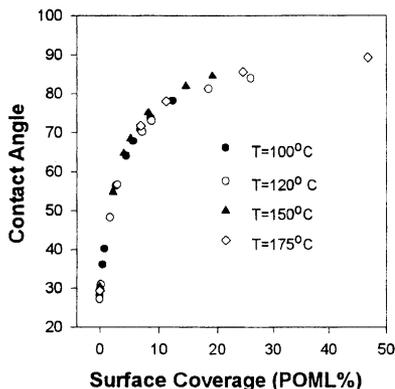


Fig. 9 The relationship between contact angle and AKD surface coverage on cellulose.

It might be of interest to assume the temperature dependence of the chemical reaction and adsorption to exhibit an Arrhenius behaviour. If such is the case a linear relationship is expected by plotting $\text{Ln}\alpha$ as function of $1/T$ in two limiting cases. Such a graph is shown on Figure 10 at 4 different temperatures. A reasonable linearity is observed considering the experimental error. In theory, linearity should be reached for two limiting cases of strong physisorption ($K_{\text{eq}} \gg 1$,

case 1) and low physisorption ($K_{eq} \ll 1$, case 2) but not for median values of K_{eq} . From Figure 10 an energy of activation of 61.4 kJ/mol is calculated. The exact meaning of this energy of activation is debatable. For strong physical adsorption the energy of activation is that of the chemisorption. For weak physical adsorption the calculated energy of activation is $E^* = E_a - Q$.

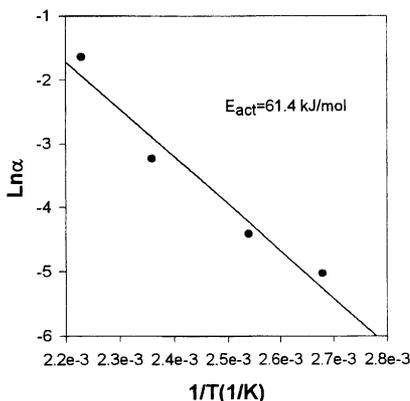


Fig. 10 Arrhenius Equation plot. From the slope, an activation energy of 61.4 kJ/mol was calculated.

The hypothesis of a strong physisorption is favoured. Swanson earlier reported that the amount of fatty acids physisorbed on cellulose was 5 times as much as chemically reacted at 105 °C (2).

As a comparison, Lindstrom (14) measured $E_a=72-54$ kJ/mol for pH=4-10 with $E_a=62$ at pH=6 which is very close to our results. It is interesting to note that though the rate constants of Lindstrom are 2 orders of magnitude higher than in the present study, the activation energies are practically identical. In Lindstrom's

study, AKD suspensions were added to the pulp furnish and handsheets were made and dried at different temperatures. In those conditions, the polymer stabilised AKD particles must first melt and wet the furnish's surface, evaporate and then react by physisorption and chemisorption. Four phenomena are involved. The meaning of an energy of activation in Lindstrom's experiments first appears questionable, and it is striking that linearity is observed by plotting Arrhenius equation. It would suggest that a single phenomena, very likely the reaction of AKD with the hydroxyl groups is much more temperature dependent than the other 3 phenomena.

The energy of activation is defined as the minimum kinetic energy required for colliding molecules to initiate the breaking and the formation of chemical bonds. Assuming the AKD-cellulose reaction to be the controlling step, without any catalysts identical activation energy would then be expected from Lindstrom and the present study.

4. Effect of Sizing Promoters

Industrial practice shows that some chemicals can significantly accelerate the rate or increase the reaction level of AKD during sizing. The sizing promoters generally include CO_3^{2-} , HCO_3^- and polyelectrolytes with imine groups. Lindstrom (5) found that adding 3×10^{-3} M NaHCO_3 and 0.05% PEI to the furnish increased the reaction rate by a factor of 6 and 3 respectively. However, our experiments with both NaHCO_3 and PEI did not result in any sizing enhancement. Deposition of NaHCO_3 did not affect at all the surface hydrophobicity as function of the treatment period with AKD vapour (Figure 7). Similarly adsorbing PEI on cellulose first increased the initial water contact angle of the film, this is due to the less hydrophilic character of PEI than cellulose. Thereafter the PEI treated cellulose exhibits very closely the same reaction behaviour with AKD vapour as

cellulose. The only effect of PEI is to block some cellulose hydroxyl groups otherwise available for reaction with AKD vapour.

These observations suggest that NaHCO_3 and PEI do not catalyse the reaction between AKD vapour and hydroxyl groups of cellulose. The reason for this is not clear yet. These promoters are known to be very efficient in industrial conditions where they are added into the furnish. Water or other polar solvents may play an important role. Formation of two or three molecule complex among AKD, promoter and hydroxyl group have been speculated (5, 15) but without solid physical evidence.

CONCLUSION

Alkyl ketene dimer vapours play a critical role in the mechanism of spreading during internal sizing. The establishment of a covalent bond between AKD and the hydroxyl groups of cellulose was demonstrated with a series of indirect methods. These include: (1) The good experimental fit of the kinetic model; (2) the contact angle of water over AKD sized cellulose films does not vary after severe solvent extraction; (3) the time frame of reaction is characteristic of chemisorption; (4) sizing is proportional to the OH concentration of surface.

A kinetic model was developed and validated with experimental data. It involves the reversible physisorption of AKD vapours on cellulose followed by an irreversible esterification between the adsorbed AKD and the hydroxyl groups of cellulose. The second step is very likely the controlling step. An energy of activation of 61.4 kJ/mol was calculated for the process.

Sizing promoters such as NaHCO_3 and PEI were not found to improve the reaction rate between AKD vapours and cellulose in dry conditions. The presence of water or a polar solvent may be essential for the promoters to function.

Our experimental results with model systems can explain many industrial observations with AKD sizing. For example, Gupta (16) found that as little as 5% of modified fibre can provide full sizing for the whole paper sheet. Rohringer et al (17) concluded from similar experimental observations that AKD could not react with cellulose otherwise it could not transfer. It should be noted that AKD canoes not react completely with cellulose at papermaking or handsheet making conditions. It is the unreacted AKD which migrates through the paper and provides sizing by vapour deposition as shown in our model experiments. In practice, it is also found that AKD sized paper develops most of its sizing off the paper machine. The average bulk paper temperature of a newly formed roll is about 60°C. Furthermore, it was experimentally and theoretically demonstrated that it took several days (up to a week at the centre) for the paper roll to cool down to room temperature (18). From our model, several days at 60°C are favourable conditions to allow physisorbed AKD vapours to diffuse through the roll, physisorb at another site and chemisorb. This fully explains the size development off machine as well as the size migration. By further application of our model, we would expect a sizing variation from the centre to the outer layer considering the non-uniform cooling of the roll. Such measurements were carried out by Jensen and Neogi (19) on a rosin sized paper roll. They measured a substantial increase in sizing in the outer layers compared to the inner layers and identified the temperature gradients during cooling as driving force for the migration. Those evidences further support our mechanism of physisorption and chemisorption.

ACKNOWLEDGEMENTS

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Transcription of Discussion

Mechanism of Internal Sizing with AKD: The Role of Vapour Deposition

Gil Garnier, Research Engineer, Paprican/McGill, Canada

Professor Tom Lindström, Royal Institute of Technology (KTH), Sweden

This is a controversial paper and I would like to take the opportunity to ask the first two questions and you have two claims here. I basically have no difficulty with your experimental data but I have difficulties with the claim that AKD doesn't spread on cellulose. If you take a piece of AKD wax and put it on a piece of paper and leave it there for some time it looks like you have put butter on the paper, I don't know what you're calling it, if it's not spreading.

Gil Garnier

To answer your first question: If you place a droplet of molten AKD on a paper, you have two distribution phenomena. In the first, the droplet can wet ($0^\circ < \theta \leq 90^\circ$) the surface up to a certain equilibrium contact angle governed by thermodynamics. In the second, the droplet can diffuse into the bulk of the sheet by capillary action. This latter effect can easily be calculated with the Lucas Washburn equation. Diffusion by capillarity action into the pores of the paper structure would be the predominant effect in your example. Such mechanism was not possible using the model surfaces of our study.

Tom Lindström

I won't continue that particular part of the discussion. My second question is your claim that it's a vapour deposition process. If you add an AKD emulsion on a piece of paper and then you dry it and leave it in the oven for an hour at 90°C , no AKD will evaporate. I would expect that you could evaporate at least some of the AKD if AKD sizing was a vapour deposition process. You have to take the sheet up to 120°C before any significant amount of AKD evaporates. If you take the sheet of paper down to a low pH value (~ 3) then you can follow evaporation without AKD reacting with cellulose.

G Garnier

OK. If you take a paper sheet sized with AKD and you put a pile of non-sized paper on the top of it and apply some pressure on it for a certain amount of time and then take a

sheet from the pile you will observe that it is somehow sized. Also, if you take a sample roll of paper and take various samples from the core, the middle and the outside you are going to find a gradient of sizing. The explanation for that is diffusion of the vapour and the chemical reaction. We can basically explain the off-machine sizing with our model.

Tom Lindström

That's what I call spreading.

Gil Garnier

No. By definition a liquid spreads a solid surface when a drop of this liquid forms a contact angle of 0° on this solid and spreads until forming a monolayer film thickness.

Kevin Hodgson, Associate Professor, University of Washington, USA

I'm wondering, did you by chance measure the contact angle of water on a pure AKD film, and also, how you think the differences in both morphology and surface chemistry of actual wood pulp fibres would change your conclusions on lack of spreading and importance of vapour deposition?

Gil Garnier

That's a tricky question. First you want to know the equilibrium contact angle of a water droplet placed on a pure AKD film. A year ago the front page of Langmuir was devoted to a picture of a water droplet sitting on such an AKD film. What the Japanese authors proved is that AKD forms a fractal structure, and that the contact angle is a very strong function of this fractal dimension. From what I recall, the contact angles were ranging from 120 - 160° . The maximum contact angle measured in our laboratory was at 95° . To answer your second question, we developed the cellulosic film model to avoid any roughness effect from our study and to only concentrate on the effect of vapour depositional reaction on sizing. I don't intend to try on fibres.

Steve Keller, Associate Professor, Syracuse University, USA

I have a two part question. The first is can you briefly describe your recrystallisation process. What solvent did you use and what temperature did you recrystallise at?

Gil Garnier

I'm afraid I'm not a specialist on this method, since my co-author took care of this experiment. I would prefer not to speculate on this manipulation.

Steve Keller

I would propose to you that if you look at vapour pressure of the recrystallisation solvent and compared that with the vapour pressure of AKD at the temperatures at which you are vapourising, you may find you are looking at the solvent of recrystallisation rather than AKD. Now to prove me wrong you should do chemical analysis on the vapour to prove to us that you are truly depositing AKD.

Gil Garnier

Good point. What I didn't present is that we took some films of AKD reacted over cellulose and we also some films of pure AKD deposited by solvent extraction over glass and analysed the two surfaces by SIMS-TOF. We observed closely the same spectra I can therefore affirm that we deposited the same substance as what constituted the bulk of AKD.

To answer the second point: the role of the recrystallisation was simply to remove most of the unreacted fatty acid present in the wax. We wanted to make sure that we would basically only vapourise AKD and not all the smaller molecular weight contamination present.