The Role of Vapour Deposition During Internal Sizing: A Comparative Study Between ASA and AKD

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Model surfaces were exposed to vapours of alkyl ketene dimer (AKD), alkenyl succinic anhydride (ASA), stearic acid and methyl stearate. The extent of vapour deposition and the degree of reaction were followed by measuring the contact angle of water on the treated surface. The model surfaces consisted of cellulose acetate, cellulose and glass, while the variables investigated were temperature and the period of exposure. AKD and ASA vapours both deposit on cellulose and glass to render the surfaces hydrophobic, but not on cellulose acetate; hydroxyl groups are required. The critical time of reaction was of the order of hours which, under the conditions investigated, is typical of the formation of a covalent bond by esterification. Compared to AKD and stearic acid, ASA vapour reacts much faster with cellulose. Fatty acid ester vapour rendered glass hydrophobic, but not cellulose. A mechanism of trans-esterification is proposed. A strong bond between the reactive vapour size and cellulose is essential to introduce permanent sizing of cellulose. Vapours play a governing role in internal sizing.

Des surfaces modèles ont été exposées à des vapeurs d'AKD, d'ASA, d'acide stéarique et de stéarate de méthyle. Nous avons suivi l'étendue du dépôt et de la réaction en mesurant l'angle de contact de l'eau avec la surface traitée. Les surfaces modèles ont été l'acétate de cellulose, la cellulose et le verre, et les variables analysées, la température et le temps d'exposition. Les vapeurs d'AKD et d'ASA se déposent toutes deux sur la cellulose et le verre et rendent ces surfaces hydrophobes, mais non l'acétate de cellulose; des groupes hydroxyles sont nécessaires. Le temps de réaction critique se situait autour de l'heure, ce qui est typique de la formation de la liaison covalente par estérification. Comparativement à l'AKD et à l'acide stéarique, les vapeurs d'ASA réagissent beaucoup plus rapidement avec la cellulose. La vapeur d'ester d'acide gras a rendu le verre hydrophobe, mais non la cellulose. Un mécanisme de transestérification est proposé. Un lien solide entre le collage réactif à la vapeur et la cellulose est essentiel à un collage permanent.

INTRODUCTION

Since the pioneering work of Davis et al., from Hercules, Wilmington, DE, USA, who, in 1956 presented alkyl ketene dimer (AKD) as a novel type of size reacting by a covalent bond with the hydroxyl groups of cellulose [1], the mechanism of sizing has drawn tremendous interest. Later, in the 1970s, alkenyl succinic anhydride (ASA) appeared, also promoted as a reactive size [2]. Reactive sizes, mostly ASA and AKD, have since become widely used in industry.

Understanding the precise mechanism of sizing is critical. Such knowledge allows, in the mill, the estimation of the maximum sizing theoretically possible and, therefore, allows improvement of process efficiency. Knowing the mechanism makes it possible to optimize the sizing emulsion by controlling the colloid size distribution, its reactivity and selectivity.

The mechanism of reactive internal sizing is generally believed to involve three steps [3–5]:

— Retention of the polymer-stabilized sizing colloids onto the furnish;
— Wetting of the sizing colloids over the solid surface upon heating; and
— Some reactions and reconfiguration of the sizing molecules to provide water repellence.

The first and second steps are now well understood [6–12]. However, the process by which the size molecules provide hydrophobicity to the paper is not fully understood and still generates much debate [13,14].

Paper hydrophobization is caused by the wetting of the adsorbed size colloids to reach their equilibrium contact angle (θ_E). This phenomenon occurs in the dryer and was analyzed previously [11,12]. The size colloids form hydrophobic patches, preventing water from fully penetrating into the paper. For a typical fine paper sized with AKD, the sizing colloids cover 1–2% of the total surface area of the furnish (0.05–0.1% AKD on paper) [10]. However, sizing with a reactive size such as AKD or ASA might be sufficient at a dosage of only one third of that of rosin sizing. Since a long alkyl chain (C16) is roughly as hydrophobic as a polyaromatic group (rosin), some additional mechanism of sizing distribution on the furnish must be involved. Furthermore, it is known that wetting of a solid by a liquid is dictated by the

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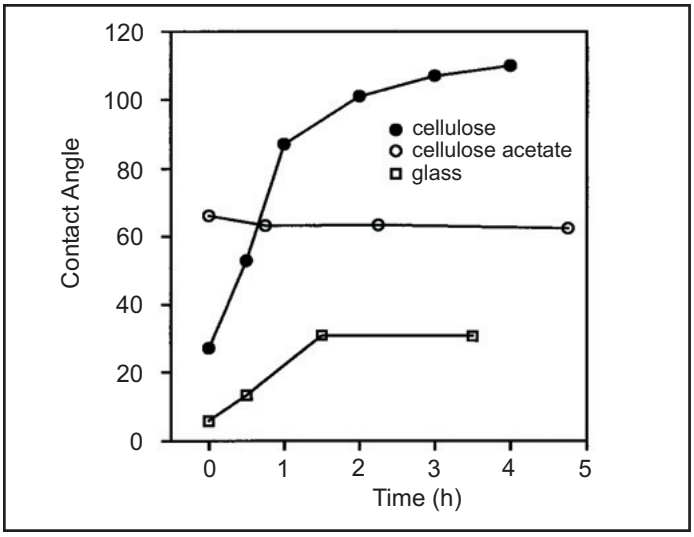

Fig. 1. ASA vapour deposition on model surfaces at 60°C.

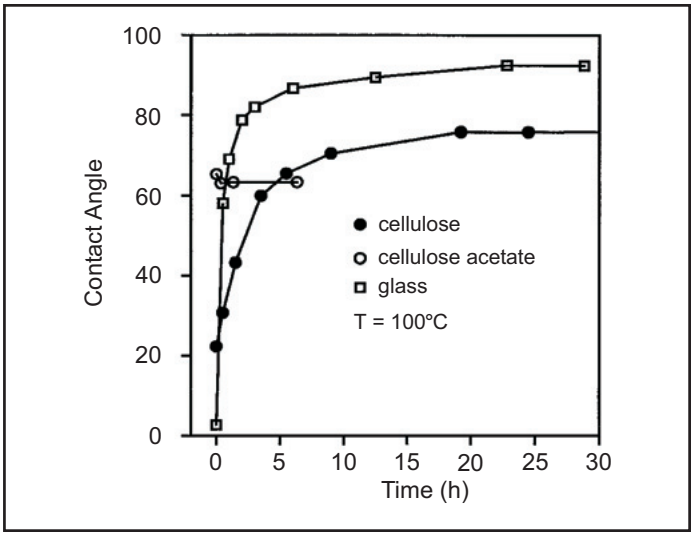

Fig. 2. AKD vapour deposition on model surfaces at 100°C.

chemical composition of the 1 nm outer layer [15]. This dimension corresponds to the characteristic length of an adsorbed AKD or ASA molecule. Assuming that AKD lies flat on the surface of the furnish, it can be easily calculated that there is more than enough AKD to fully coat all of the furnish. If the AKD molecule is chemisorbed standing perpendicular to the surface, 25% of the furnish can be covered. AKD was shown previously not to spread, i.e. θ_E = 0°, on cellulose or on hydrophilic surfaces [10–12]. Thus, a monolayer thickness film of reactive size on the furnish surface can be created only by vapour deposition. Indeed, the physisorption or chemisorption of AKD vapours cannot account for only the high sizing per unit weight, but also for off-machine size development and fugitive nature [9].

Several researchers investigated the sizing performance of hydrophobic vapours on paper [8,16–19]. Swanson [16,17] and Takeyama and Gray [19] concluded that fatty acid vapours can chemisorb onto cellulose, whereas Akpabio and Roberts [8] claimed that AKD vapour could not render paper hydrophobic because a preferential reaction with water vapour takes place. A sizing process relying on the gas phase distribution of ASA on dry paper was studied using a hot-extender nip [20]. More recently, Yu and Garnier [9] investigated the role of AKD vapour deposition in internal sizing and their results showed that the AKD vapour can introduce significant hydrophobicity to paper. Whether this mechanism can be extended to other reactive sizing materials, however, is still unknown. In this investigation, the sizing mechanism and performance of ASA and AKD vapours are compared. We raise the hypothesis that the size vapours play an important role in the mechanism of reactive internal sizing.

EXPERIMENTAL

Materials

Commercial samples of ASA and AKD were provided by Cytec (Brossard, QC, Canada) and Raisio Chemicals North America (Burlington, ON, Canada), respectively. ASA was purified by vacuum distillation, while AKD was recrystallized three times in hexane. Stearic acid (reagent grade, Fisher Scientific) and methyl stearate (MS) (>99.0%, Aldrich) were used as received. Cellulose acetate was from Sigma (now Aldrich, Milwaukee, WI, USA), with 40% acetate group content. All solvents were high-pressure liquid chromatography (HPLC) grade or better. Water was purified from a Millipore Ultrapure System.

Procedures

Complete details of the preparation of the cellulosic films, the model surfaces and the vapour deposition procedure were reported previously [9]. Briefly, cellulose films on glass were prepared by regenerating cellulose acetate coating. For vapour deposition, the substrate of interest was placed in an airtight adsorption cell, which was heated in an oven at a pre-set temperature and time, then quenched. The contact angle of water was measured immediately (within seconds) using a Sigma 70 Surface Tension/Contact Angle Meter (KSV Instrument, Helsinki, Finland) at a temperature controlled at 25 ± 0.5°C. All contact angles reported are advancing contact angles. The data were analyzed as reported previously [9].

RESULTS

Figure 1 presents the evolution of the contact angle formed by water on three model surfaces (cellulose, cellulose acetate and glass) exposed to ASA vapours at 60°C for various periods. The hydrophilic cellulose (θ_o = 25°) becomes highly hydrophobic after 4 h of vapour exposure (θ = 110°); water can still wet glass after a similar treatment to ASA vapours (θ_W = 30°). The increase in contact angle, however, suggests that some ASA vapour may deposit on glass. Exposure to ASA vapour did not affect the hydrophobicity of cellulose acetate as proven by the constant contact angle of water (θ = 65°). Cellulose clearly has the highest reactivity toward ASA vapours. The general trend of ASA vapour reaction with these model surfaces resembles that of AKD (Fig. 2). However, ASA vapour reacts with cellulose much faster than does AKD. Furthermore, ASA shows much less reactivity with glass than does AKD.

Figure 3 compares the hydrophobicity of cellulose as a function of exposure time to ASA vapours (60°C) before and after a severe chloroform solvent extraction. No major differences are observed. The hydrophobicity, and therefore the ASA concentration and orientation at the surface, remains unchanged. The same result was observed previously for AKD [9] and fatty acid vapours [16,17] deposited on glass and cellulose.

MS was chosen as a model representing an unbonded long chain fragment resulting from hydrolyzed AKD. Figure 4 presents the relationship between exposure time to MS vapours at 120°C and the hydrophobicity of the three model surfaces. Water can still wet a cellulose surface exposed to 11 h of MS vapours. A contact angle of 60° is eventually reached when either glass or cellulose acetate are exposed to MS vapours; this value very likely represents the equilibrium contact angle of water on a monolayer of MS. MS vapours adsorb onto glass and cellulose acetate but not onto cellulose. This adsorption behaviour contrasts singularly with that of AKD vapours. By adsorbing onto the hydrophobic cellulose acetate, MS vapours render the surface more hydrophilic; conversely, it increases the hydrophobicity of glass. The time frame of adsorption on glass is similar to that of AKD vapours.

The effect of temperature on the adsorption kinetics of ASA, AKD and stearic acid vapours are shown in Figs. 5, 6 and 7, respectively. For ASA on cellulose, the reactions at 60 and 70°C are significantly faster than at 50°C (Fig. 5). Surprisingly, there is not much difference between 60 and 70°C. The reaction might be mass-transfer limited. The water contact angles of the model surfaces first decrease when exposed to stearic acid vapours, and then increase to level off at 80°, as seen in Fig. 7. The initial behaviour is probably due to volatile impurities or shorter fatty acids. The

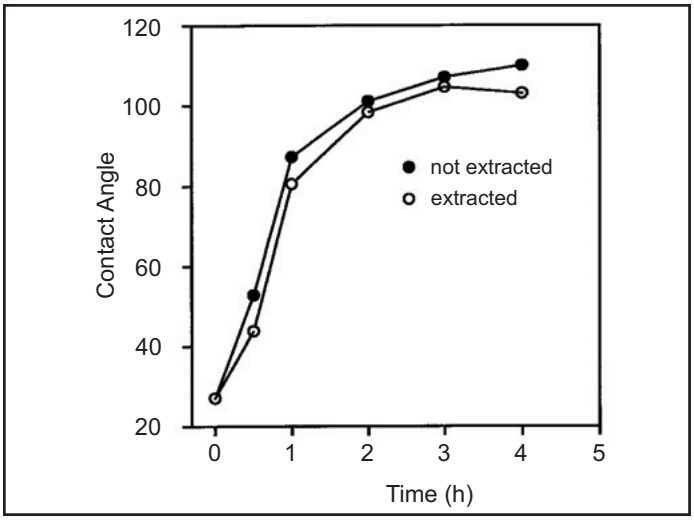

Fig. 3. Effect of chloroform extraction on the ASA vapour deposition on cellulose at 60°C.

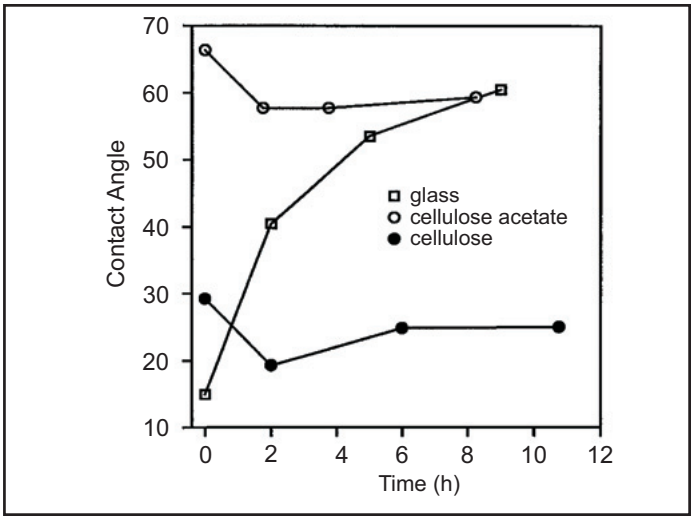

Fig. 4. MS vapour deposition on model surfaces at 120°C.

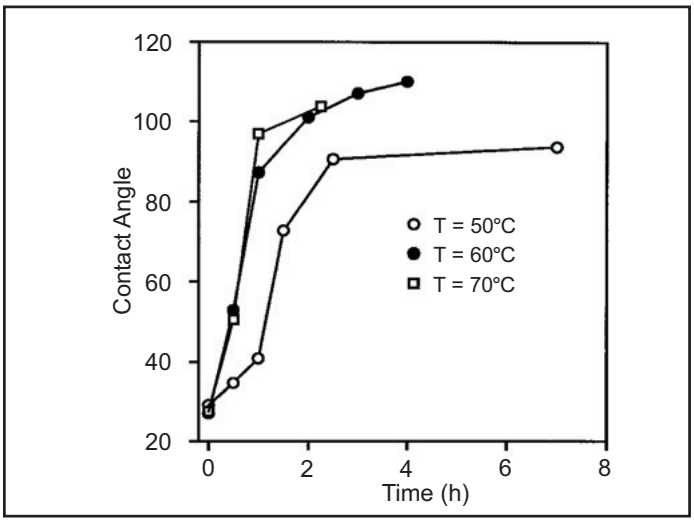

Fig. 5. Effect of temperature on ASA vapour deposition on cellulose.

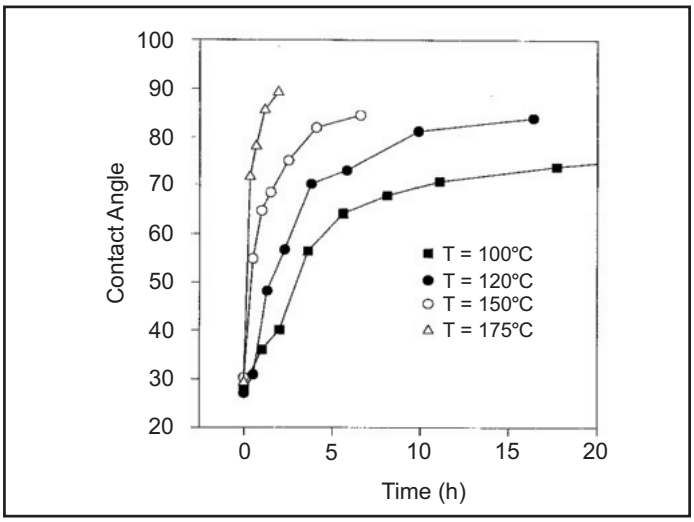

Fig. 6. Effect of temperature on AKD vapour deposition on cellulose.

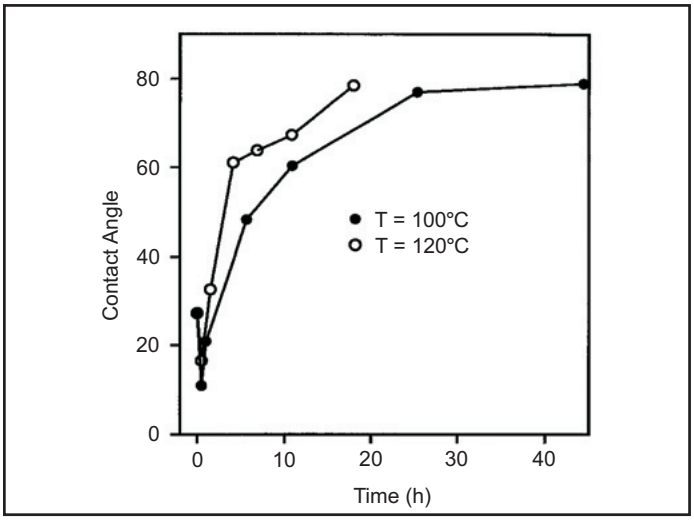

Fig. 7. Effect of temperature on stearic acid vapour deposition on cellulose.

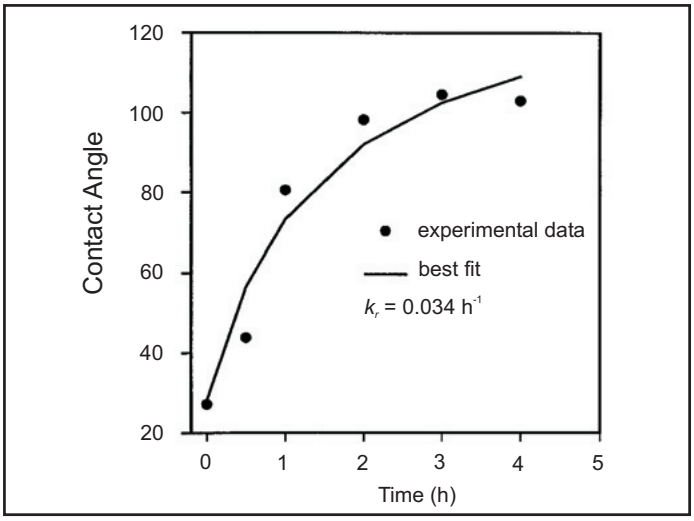

Fig. 8. Comparison of the vapour deposition model [9] with the experimental results.

hydrophobicities of the model surfaces exposed to AKD (Fig. 6) and stearic acid (Fig. 7) vapours exhibit a similar temperature dependence, typical of Arrhenius behaviour.

DISCUSSION

The contact angle formed by water over a hydrophilic surface treated by hydrophobic vapours is a function of four variables: the surface energy of the solid, the surface energy of the vapour, the surface coverage of the solid by the vapour, and the orientation of the alkyl chains at the solid surface. AKD vapours were shown previously to form a covalent bond with the hydroxyl groups of cellulose [9,21], confirming the original claim from Davis et al. [1]. The AKD vapour reaction rate was found to be proportional to the hydroxyl concentration of the solid surface [9]. ASA vapours do not follow this rule (Fig. 1). The usually more reactive silanol groups from glass behave differently from the hydroxyl of cellulose. The reasons are not clear. Two explanations are proposed. In the first, the reaction involving ASA might be chemically specific. In the second, the equilibrium of ASA ring opening and closure might differ between the ASA adsorbed on glass from that on cellulose. In any case, ASA must form a covalent bond with cellulose. Four observations support the esterification mechanism.

— OH groups are required on the solid surface to promote hydrophobicity;
— The reaction rate is temperature dependent;
— Severe chloroform extraction does not decrease the hydrophobicity of treated surfaces;
— The time frame of the reaction (hour) is typical of homogeneous cellulose esterification [22].

Indeed, a chemical reaction between ASA and pulp fibres is widely acknowledged [2, 22–25]. Oddly, this is not true for AKD [13,14]. This work suggests further that ASA vapours might play a governing role in the sizing mechanism.

ASA is well known in industry to be much more reactive toward cellulose fibres than is AKD. This difference in reactivity is best quantified with kinetic reaction constants. We proposed previously a kinetic model to follow AKD concentration on cellulose based on a reversible physisorption followed by a chemisorption (first-order reaction with respect to OH groups) [9]. The extent of the reaction was followed with the development of water contact angle on the vapour-treated surfaces. Swanson further reported that the contact angle formed by water on a monolayer of fatty acid is a function of the length of the alkyl chain and is independent of its cross-section [16]. Therefore, we assumed ASA to have an alkyl chain length similar to that of the AKD studied previously (C 16), and used the model developed [9]. Figure 8 compares the theoretical fit with the experimental points. A reaction constant of 3.4 x 10^{-2} h^{-1} is calculated at 60°C, which is two orders of magnitude higher than the reaction rate of AKD (k_r = 4.8 x 10^{-4} h^{-1}). This confirms that ASA vapours react much faster with cellulose than does AKD.

The reaction behaviours of stearic acid and MS vapours were investigated to better understand the mechanism of AKD internal sizing. Stearic acid vapour deposition on cellulose (Fig. 7) is similar to that reported by Swanson [16]. At 100°C, the hydrophobicity of cellulose exposed to stearic acid vapours is slightly lower than when exposed to AKD vapours. The maximum water contact angles are very similar but the rate at which they are reached is a little faster for AKD. The plateau contact angle of 78° is reached after 20 h of exposure to AKD vapour compared to 25 h for the fatty acid (Figs. 2,7). This suggests that either the vapour pressures or the reactivity of AKD for cellulose is higher than that of stearic acid. The former hypothesis is less likely since, for an homologous series of substances, the vapour pressure is typically a function of molecular weight. Although AKD and ASA are not homologous molecules, the molecular weight of AKD is twice that of stearic acid. The latter premise is more likely: a ketene might be more reactive toward an hydroxyl than a carbonyl. A practical implication is that any fatty acid left unreacted in AKD wax would yield a similar vapour sizing efficiency as AKD. However, fatty acids are known to saponify under alkaline conditions, forming metal soaps which would foam and deposit. Unreacted fatty acids are thus to be avoided in wet-end operations.

At high temperature, MS vapours very likely undergo trans-esterification with the silanol (Si-OH) groups of glass yielding a covalent bond. Equilibration of an ester with an alcohol containing a different alkoxy group is known for converting one ester to another [26]. The process, known as trans-esterification, is normally catalyzed by an acid. Trans-esterification of alcohol on silica has been reported in the literature [27, 28] for temperatures higher than 80°C. This chemisorbed stearate offers alkyl orientation for much improved hydrophobicity. However, MS vapours did not modify the cellulose hydrophobicity: either no vapour deposited or the orientation of the alkyl chain does not provide any hydrophobicity. The hydroxyl of cellulose might not be acidic enough to allow trans-esterification, and thus to create a covalent bond under the conditions investigated. It is unknown if the failure of MS to provide hydrophobicity is due to the lack of molecules chemisorbed or to an improper orientation of the alkyl chains. Physisorbed AKD was shown previously not to provide significant hydrophobicity on cellulose or on glass [29]. A covalent bond is probably required for proper orientation and alignment of the alkyl chains.

CONCLUSIONS

Like stearic acid and AKD, ASA vapour can introduce significant sizing to cellulose. The reaction is temperature dependent and may be interpreted as Arrhenius behaviour. The reactivity toward cellulose increases in the order of stearic acid, AKD and ASA. The concentration of hydroxyl groups and their nature, i.e. silanol versus hydroxyl on carbon, also influence the extent of sizing. Sizing is, however, a subtle function of the surface chemistry combined with the type of vapour. Vapour exposure of a surface without OH groups, such as cellulose acetate, does not produce any sizing. While the sizing reached by AKD is proportional to the OH concentration, that of ASA is not. ASA is more reactive with cellulose than it is with glass. The sizing ability of MS, representing hydrolysis by-products of AKD, is also of interest. Exposure of MS vapours does not render cellulose hydrophobic. MS vapours chemisorb on glass but not on cellulose. A trans-esterification mechanism is proposed. Kinetics data and solvent extraction results suggest that sizing is reached only once a covalent bond has been established between the size vapour and the OH of the surface. Such chemical anchorage must be required to ensure proper alignment of the alkyl chains at the solid–air interface, thus providing hydrophobicity.

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