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The Hydrophobisation of Cellulose Pulp

Abstract
The hydrophobisation of cellulose can be achieved by the treatment of wood fibers with aluminum sulfate and sodium salts of fatty acids. The purpose of the study was to determine the effect of various factors on the resultant hydrophobicity. The investigated variables were fatty acid chemistry and reaction conditions. The hydrophobic property was assessed indirectly by quantifying the wettability of cellulosic material (contact angle) and water retention value (WRV).

Key words: *cellulose pulp, hydrophobicity, contact angle, water retention value.*

Introduction

Wood cellulose pulp is an attractive material due to its abundance in Nature, sustainability and wide range of known and potential applications. Cellulosic fibers are inherently hydrophilic and rendering them hydrophobic may open new avenues for future uses where a high contact angle and low water retention are required. By and large, these very properties have so far been traditionally the main characteristic of most synthetic products.

The main source of cellulose is wood pulp, the starting material for the production of classic paper, textile-like or foam-like nonwovens, as well as a wide variety of chemical derivatives used by many customer industries. The attractiveness of cellulose also has an economic aspect: the price of this material changes at a much lower pace than the rapidly increasing price of crude oil, the source of various synthetic polymers and fibers.

Due to its high porosity and hydrophilic nature, cellulose fluff has excellent hygroscopic properties making it a great absorbent material for personal hygiene uses. Modern hygienic materials are composite products, designed with various functional components. For instance, it is sometimes desirable to have layers exhibiting specific hydrophilic/hydrophobic gradients across the thickness of the absorbent structure. More hydrophobic layers are usually positioned closer to the body of the user for keeping liquid away from the skin. Gaining control over fiber wettability (hydrophobicity) may allow cellulose to be applied in those cases where traditionally only synthetic materials have so far been used. Whole-cellulose composite hygienic materials would be of unquestionable advantage due to the "green" aspects of such products as well as the economy and user friendliness of natural fibers.

A change in the hydrophilic character of cellulose may rely on its surface modification with hydrophobic compounds such as silicones [1, 2], hydrocarbons [3] and fluorocarbons [4]; however, more environmental-friendly and more economical alternatives would be preferred. The growing demand for "greener" products has become an incentive for scientists to further explore natural raw materials including plant triglycerides and oils [5, 6].

Choosing fatty acids and their derivatives from the wide range of hydrophobic compounds seems to be logical due to their safety, availability and relatively low cost.

Materials and methods

Never- dried cellulose pulp from Florida slash pine was supplied by Buckeye Technologies Inc. Aluminum sulfate as well as stearic, palmitic, lauric, oleic, ricinoleic and linoleic acids, all chemical grade, were purchased from Sigma Aldrich. Valpro GM, an industrial grade mixture of saturated fatty acid sodium salts with long alkyl chains (up to C-18) was obtained from Valley Products Company Inc., and the chemical grade citric acid originated from Polskie Odczynniki Chemiczne.

Handsheets of never-dried cellulose pulp with varied aluminum content in th range of 1000 to 10000 ppm were prepared according to the recipe given below. Never- dried pulp was added to distilled water and agitated to obtain slurry at approx. 2.5% consistency. The pH of the slurry was then adjusted to 3.6 - 4.0, the required amount of hydrated aluminum sulfate ($Al_2(SO_4)_3 \times 18\ H_2O$) was added and after 15 min of stirring the pH was brought to 3.5 - 3.7 followed by its adjustment to 5.7.

Handsheets having a basis weight of approx. 300 g/m^2 were prepared using a simple in-house papermaking technique. An aliquot of the pulp slurry was transferred onto a Buchner funnel with polyester scrim circles. The pulp was dewatered on the funnel under reduced pressure, and the wet cellulose sheet obtained was pressed between two layers of tissue to further remove excess water.

Sodium soaps were made as follows. First, a 6 mol NaOH solution was prepared using methanol : distilled water (8 : 2) solvent mixture. Next, 1 gram of a selected fatty acid was dissolved in 50 ml methanol (if needed, at a slightly elevated temperature to obtain a clear solution). Stoichiomertic amounts of the NaOH and fatty acid solutions were admixed and water added to a total volume of 1000 ml. In the case of Valpro GM, 1% solution was obtained by directly diluting the commercial product in hot water.

The sodium soap mixtures were introduced either to the slurry with stirring for 15 minutes, before the handsheet formation, or by spraying on the pre-formed, still wet handsheets. In either case the soaps were used in the form of 1% water dispersion. All the soap mixtures were warmed to 70 °C to obtain homogenous liquids and then were sprayed evenly on the surface of the handsheets. The resulting average soap add-on level was approx. 10 g/kg dry weight of cellulose. The samples were dried at 120 °C for 5 min (to a constant mass).

In the experiments with citric-acid treated cellulose, the citric acid was added to the pulp slurry in distilled water (2.5% consistency) in amounts of 5, 10, 25, 50 and 100 g per 1 kg dry fiber weight. The pulp used for this part of the study contained 7500 ppm Al in the form of aluminum sulfate. Handsheets of the cellulose pulp were formed as described above and then

heated for 5 minutes without pre-drying at various temperatures . The cross-linked sheets were subsequently sprayed with solutions of sodium stearate 1% solution and dried at 120 °C for 5 min. After this procedure the sheets were disintegrated in a Waring blender and new handsheets were formed again from the slurry of the defiberised material as described above and subjected to the contact angle and WRV characterisations.

The hydrophobicity of all the handsheets was assessed indirectly by contact angle measurements, performed with a PG-1 portable goniometer , according to ASTM D724 (Standard Test Method for Surface Wettability of Paper). A drop (0,5 µl) of the test liquid (demineralised water) was placed on the surface of the handsheet being tested. The resultant contact angle was measured visually from the optical micrograph of the drop. Seventy measurements were taken for each sample. The average contact angle and standard deviation were calculated for each set of experiments.

The water retention value (WRV) was measured according to the following procedure: one gram of cellulose of known water content was disintegrated; put into a 200 cm^3 Erlenmayer flask and suspended in 100 cm^3 of distilled water. The suspension was shaken for 1h at 20 °C, then transferred to a G3 sintered-glass funnel to remove excess water under reduced pressure. The sintered-glass funnel was then transferred to a centrifuge tube and centrifuged at 2000G for 15 minutes. Subsequently, the weight of the moist sample was determined. The water retention value was calculated according to the formula:

$$WRV = (m_2 - m_1)/m_1 \times 100\%$$

were:
m_1 - mass of dry sample,
m_2 - mass of moist sample,

Three WRV measurements were conducted in each experimental series to calculate the average value.

Results and discussion

Paper sheets were prepared from cellulose slurries with various Al contents. The deposition of insoluble aluminum hydroxide on the fibers was realised by the alkalisation of the acid cellulose slurry containing aluminum sulfate. The liquid soaps were applied to the wet paper sheets, each with an amount of approx. 10 g/kg of dry cellulose.

Based on known chemical theory, it can be assumed that in these conditions insoluble aluminum salts could be formed on the surface of the cellulose fibers [7].

The contact angles on the experimental sheets were measured using distilled water and the numbers obtained have been presented in Figures 1 and 2. Several characteristic trends can be observed in the data shown here. The highest contact angle values were found for the paper sheets treated with lauryl, palmitic and stearic acid soaps. These acids have long saturated aliphatic chains with various numbers of carbon atoms. The length of the aliphatic chain had a positive effect on the hydrophobicity of the treated samples. On the other hand papers treated with soaps of fatty acids containing the same number of carbon atoms in the alkyl chain (C-18) resulted in different contact angle numbers (Figure 2), depending on the degree of saturation of the aliphatic chain and the presence of hydroxyl groups. In general the double bonds and the hydroxyl group had an adverse effect on the hydrophobicity of the treated cellulose

The use of Valpro GM soap mixture gave relatively high contact angle numbers although not as high as in the case of the treatment with stearic acid soap. This was probably due to the presence of lower aliphatic chains in the commercial product mixture.

As expected, the effect of the aluminum content in the cellulose sheets treated with fatty acid soaps had an important effect on the contact angle. In almost all the cases the contact angle increased with raising the aluminum content up to 7500 ppm. A further increase in aluminum did not enhance the hydrophobicity of cellulose. Interestingly enough, the contact angle became even lower with a further increase in the aluminum content in the samples modified with stearic acid-based soap.

Valpro GM is a representative of industrial soaps commonly used in papermaking. In our study it was used at an amount of 10 g per kg of dry cellulose, either by spraying on the cellulose sheet or by add-

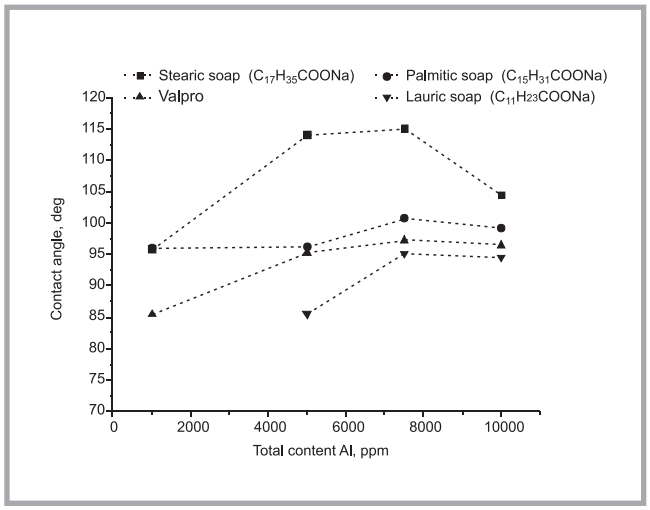

Figure 1. *Contact angle versus aluminium content for aluminium pre-treated sheets coated with various sodium soaps of saturated fatty acids with different lengths of aliphatic chains?. (Valpro GM for comparison).*

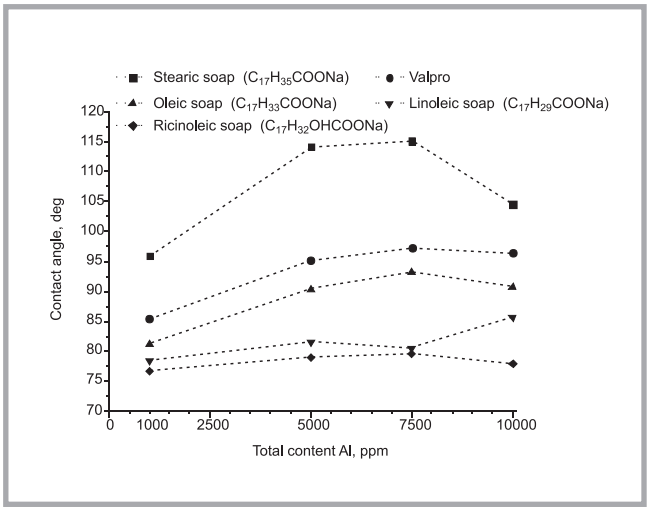

Figure 2. *Contact angle versus aluminum content for aluminum pre-treated handsheets, coated with sodium soaps of unsaturated fatty acids with the same length of aliphatic chain (18 C) and different degree of saturation. (Valpr GM for comparison).*

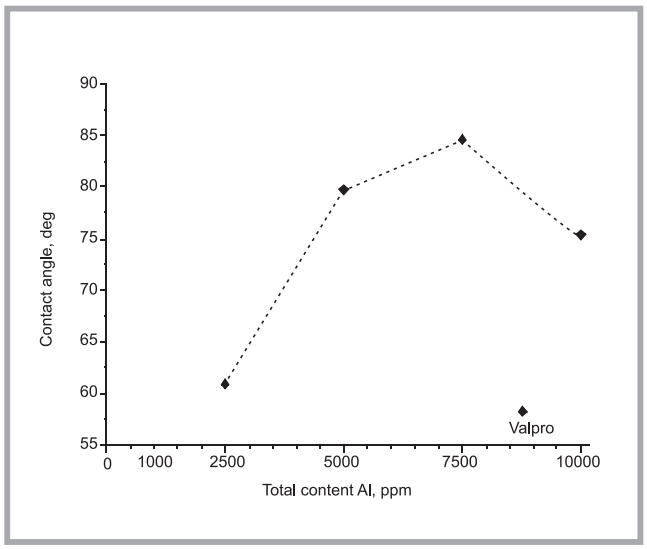

Figure 3. *Contact angle versus aluminum content for samples prepared from never-dried cellulose pulp with various aluminum contents and ValproGM soap added to the slurry.*

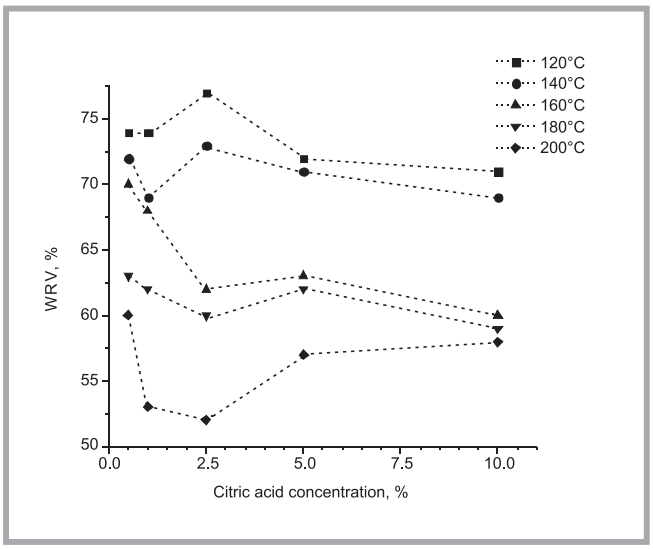

Figure 4. *Water retention value of hydrophobised cellulose cured at various temperatures versus the concentration of citric acid.*

ing it to the slurry. The results obtained are shown in Figures 2 and 3. It can be seen that the treatment was more effective when the Valpro GM was sprayed on the cellulose sheet rather than added to the cellulose slurry.

In some cases, as seen in Figures 1 and 3, when the content of aluminum exceeds 7500 ppm the contact angle of the treated samples decreased. This phenomenon is not well understood and requires more investigation.

In order to get more inside the overall hydrophobic effect of the above treatments, not limited just to the surface properties of the fibers, we also conducted measurements of the water retention value (WRV) of the modified cellulose. The reasoning was that such data would provide information about the penetration of water into the interior parts of the fibers through their capillary system. Low WRV would indicate that the treatment was not only superficial. However, based on our results the water retention of the modified cellulose decreased rather insignificantly, i.e. from 110% down to approx. 90%, regardless of the kind of fatty acid soap used.

The WRV data implied that the hydrophobisation of cellulose with aluminum soaps of fatty acids was restricted to the fiber surface and the internal part was most likely intact retaining the original hydrophilic character. The soap molecules were attached only to the surface and water could still penetrate effectively into the inside capillary structure of the fibers.

A known, effective way of reducing the water retention property of cellulosic fibers is chemical cross-linking of cellulose. Citric acid has been used for a long time as a cross-linking agent in various kinds of cellulosic fibers in paper and textile technologies [8 - 10]. The results of this part of the study showed the effect of cross-linking followed by treatment with aluminum stearate on both the contact angle (Figure 5) and the WRV (Figure 4) of cellulose.

The WRV results obtained indicate that this property depended on the temperature of the curing. The most pronounced effect was obtained at 200 °C. Low temperatures in the range of 120-140 °C did not significantly decrease the WRV of the samples tested. At curing temperatures of 160 - 200 °C and with a citric acid addition of 0.5-2.5% the effect of cross-linking (drop in WRV) was more visible and did not change with higher additions of the cross-linker. The excess amount of citric acid and high temperature led to the degradation of the cellulose (yellowing of the fibres).

Comparing the data shown in Figures 1 and 5, it is interesting to note that the treatment with citric acid did not have a significant bearing on the hydrophobicity of the fibres modified with aluminum stearate. The best results in terms of contact angle and WRV were obtained for samples containing citric acid at an amount of 2.5 and 5% and cured at 160 °C.

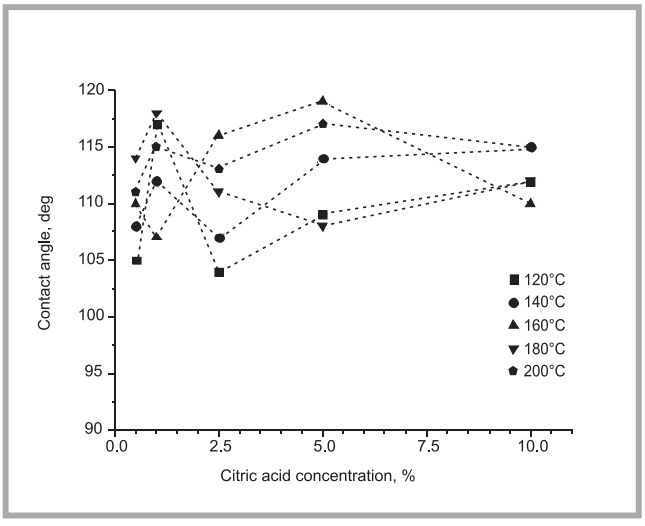

Figure 5. *Contact angle of hydrophobised cellulose cured at various temperatures versus the concentration of citric acid used for cross-linking.*

Conclusions

1. The application of aluminum sulfate and sodium salts of fatty acids is a way to impart hydrophobicity to cellulosic fibers; however, this effect seems to be only superficial.
2. The hydrophobicity obtained depends on the kinds of fatty acids and on the content of aluminum in the fibres. Optimum effect was achieved with sodium stearate when used on the fibers pretreated with aluminum sulfate at 5000 - 7500 ppm Al. Satisfactory hydrophobisation of cellulose can be realised by applying a commercial soap commonly utilised in the paper industry.
3. The cross-linking of cellulose followed by its hydrophobisation with aluminum soap allows both a high contact angle and low water retention value to be achieved.

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