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Hydrophilic/Hydrophobic Characteristics of Different Cellulose Fibres Monitored by Tensiometry

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Wettability and sorptivity improvements for different textile materials are the major tasks during textile finishing. In order to improve the sorption characteristics of a cellulose fabric, different pre-treatment processes are applied, usually washing, bleaching and mercerisation. Differences in the sorption properties of untreated and pre-treated (washed and bleached) regenerated cellulose fibres were obtained using tensiometry and compared with the classical method for determining moisture adsorption. Results show that compared to raw fibres, viscose fibres have the highest moisture and the smallest contact angle whilst modal fibres have the biggest contact angle. Pre-treatment increases the sorption abilities and makes the material more accessible to chemicals used in the finishing processes. Using the conventional method, it can be confirmed that fibres with the highest moisture have the smallest contact angle (tensiometry).

Key words: sorption, tensiometry, pre-treatment, regenerated cellulose fibres.

INTRODUCTION

Moisture, water and dye sorption capabilities are very important for the behaviour of fibres in further finishing processes. The molecular structure (chemical structure, degree of polymerisation, molecular mass) and supramolecular structure (degree of crystallinity, molecular orientation, amor-

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phous regions and void fractions) have a strong influence on sorption properties.[1,2] The amount of adsorbed water is a very important indicator for the determination of sorption characteristics. The water adsorption process shows the equilibrium between moisture adsorption and water adsorption due to wetting.[3,4,5] Water adsorption of fibres, orientated in one particular direction, invariably causes swelling. The bigger the amount of water adsorption, the bigger is the swelling. Swelling also depends on the fibre's structure, on the degree of crystallinity and on the amorphous and void regions. The degree of orientation has a significant influence on the speed of water adsorption. As a result of water adsorption, the fibres start to swell and their volume increases. Most importantly, the diameter of the fibres increases when using orientated fibres and the length increases when using non-orientated fibres.[6,7,8]

Different pre-treatment processes were applied in order to create the proper sorption characteristics of regenerated cellulose fibres. During this work the sorption characteristics of differently pre-treated regenerated cellulose fibres were studied using the powder contact angle method. The results were correlated according to the standard method for determining the moisture adsorption capability.

Pre-treatment of cellulose fibres normally includes alkaline purification, chemical bleaching, alkaline boiling and mercerisation. Pre-treatment is a process that improves some chemical properties, such as uniformity, hydrophilicity, degree of whiteness, ability of dye adsorption as well as some mechanical properties, such as longitudinal and transversal uniformity, dimension stability and smoothness.[9]

Impurities represent a hydrophobic blockage and because of their big influence on fibre wetting, they must be sufficiently removed. The effect of washing, which is one of the pre-treatment processes, depends on many factors, such as the type of textile material, type of impurities, quality and quantity of used water, type of washing agent, mechanical and heat treatment and pre-treatment time.[9] Removal of impurities depends on the morphological structure of the fibres and the location of impurities. In the case of regenerated cellulose fibres, the impurities can be efficiently removed by washing in an alkaline environment.

Regenerated cellulose fibres do not normally reach a sufficient degree of whiteness. The bleaching process eliminates the soft yellow tint of the fibres and the result is a high degree of whiteness without damage to the fibres. During bleaching, a uniform adsorptivity of water, dyes and many other chemicals used in the finishing processes is achieved.[10] Cellulose fibres are usually bleached oxidatively. H_2O_2 is the most important bleaching agent because of its ecological integrity, and its constant whiteness.[10] A problem of

bleaching processes is the catalytic decomposition of H_2O_2, which is caused by transitional metal ions such as copper, iron and manganese. They are usually present in the bleaching bath and in textile fibres. A necessary addition to such a bleaching solution is a stabilizer – organic or inorganic. Organic stabilisers are generally used today. A mineral stabilizer in the bleaching solution avoids decomposition of HO_2^- into OH^- and into active bleaching oxide, which may damage the fibres. A mineral stabilizer works as an active buffer agent, which means that it controls the pH and also deactivates the catalysts of H_2O_2.[11]

The reactivity (adsorption character) of the fibre forming polymers in a polar environment can be measured using tensiometry. The powder contact angle method is used for the measurements of fibre systems (fibre bundles). This method is based on measuring the changed sample mass during adsorption of liquids. The sample mass is squared (m^2) and graphically plotted *versus* time (t). The slope of this curve (m^2/t) is called capillary velocity. In the linear range it is constant and has the value m^2/t (Figure 1).

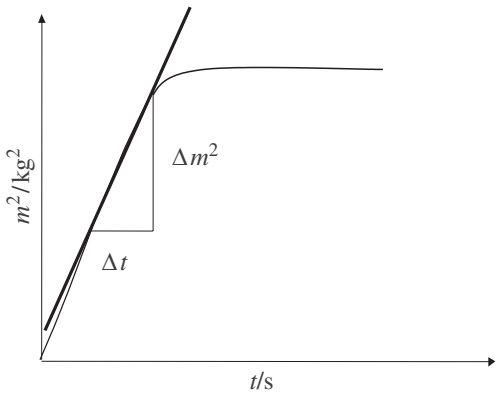

Figure 1. A schematic representation of mass increase as a function of time.[12]

The contact angle φ between the solid (fibres) and the liquid (water/heptane) can be calculated from the slope of the straight line, which depends on the wetting behaviour of the material, using the modified Washburn equation (1):[22]

$$\cos \varphi = \frac{m^2}{t} \frac{\eta}{\rho^2 \gamma c} \tag{1}$$

where t = time / s, η = liquid viscosity / mPa s, ρ = liquid density / g cm^{-3}, γ = surface tension of the liquid / mN m^{-1}, φ = contact angle between solid and liquid phases / °, c = material constant or c factor, m = sample mass / kg.

Constant c can be determined according to equation (2):

$$c = \frac{1}{2} \pi^2 r^2 n_k^2 \quad (2)$$

where r = capillary radius; n_k = number of capillaries.

Constant c (geometric factor in equation 1) depends on the type of the sample measured and the measuring cylinder. It is determined by measuring the wetting behaviour of the solid sample – fibres – with liquid having excellent wetting abilities, such as hexane and heptane, because the liquid completely wets the solid sample. In this case, the contact angle equals zero and cos φ is one, and constant c can be calculated directly using Eq. (1).[13,14] When the material has the ability to be wetted with liquid, then the values of the contact angle are between 0° and 90°. The surface free energy of solids can be calculated from the tensiometric data, using different approximations (Owens, Wendt, Rabel, Kaelble; Zisman; Wu; Oss-Good-Chaundhury).[13,14,15]

Capability of moisture absorption by DIN 54 351 is a long-standing method for the determination of hydrophilic/hydrophobic characteristics of fibres. This method is based on measuring the fibre mass, exposed to standard atmosphere (20±2 °C, relative humidity 65±2%), m_s, and the fibre masses when they are absolutely dry, m_a. The capability of moisture absorption can be calculated using the following equation:[16,17]

$$V_p = \frac{m_s - m_a}{m_a} 100 \quad (3)$$

where V_p = moisture / %, m_s = sample mass in standard atmosphere / g, m_a = mass of absolutely dry sample / g.

EXPERIMENTAL

The sorption abilities of regenerated cellulose fibres, such as standard viscose, modal and a new type of regenerated cellulose fibres called lyocell, were observed. The length of fibres was 40 mm and the linear density 1.7 dtex.

In order to improve the wettability and sorptivity, different pre-treatment processes were applied. First the fibres were washed using a mixed solution of a non-ionic washing agent (Sandoclean PC) and Na_2CO_3, for 30 minutes at 60 °C. Then, chemical bleaching followed using the H_2O_2 bleaching agent and a mineral stabiliser (Tanatex Geo) for 30 minutes at 98 °C. After both pre-treatment processes, rinsing with water took place until constant conductivity of fibres was obtained.

The sorption abilities of untreated and treated regenerated cellulose fibres were monitored using the powder contact angle method, where a certain mass of fibres was put into the measuring glass cylinder (Figure 2) and then into a measuring unit of Tensiometer KRÜSS K12, GmbH, Hamburg (Figure 3). The vessel filled with li-

quid (water or heptane) was placed into the platform drive system. After the Tensiometer KRÜSS K12, GmbH, Hamburg, was turned on, the platform automatically raised the vessel containing liquid up to the cylinder. The sample – fibres – were weighed as the liquid surface was rising, until it just contacted the solid – cylinder. At the moment of contact, the liquid started to penetrate into the cylinder. The liquid wetted the sample – fibres – and caused a steady increase in mass. The K121 software conected and displayed graphically the capillary velocity (m^2/t), which represents the changes in the mass as a function of time.

The capillary velocity for all three types of regenerated cellulose fibres (raw and pre-treated) were measured using water and heptane (to determine the constant c in equation 1). The contact angle φ was calculated from the capillary velocity.[12,18,19]

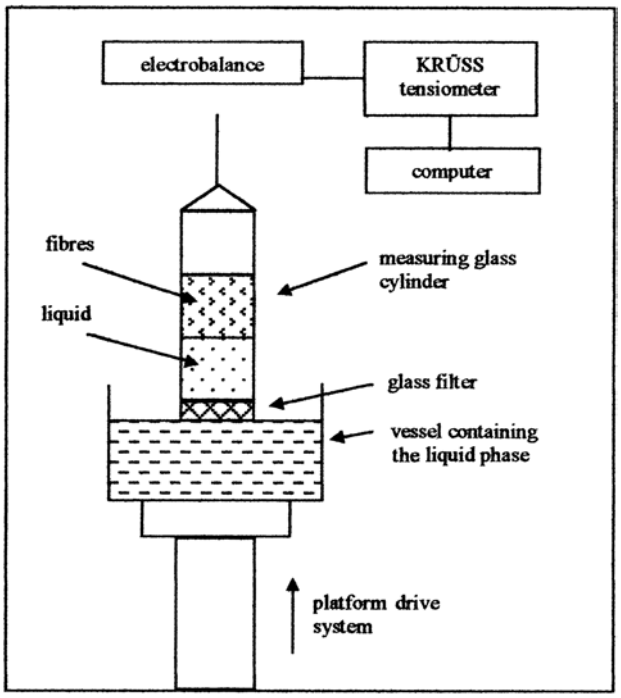

Figure 2. Schematic review of measuring the adsorption behaviour of samples.[12]

The K12 Processor Tensiometer consists of a measuring unit (Figure 3) and a control unit which together measure surface tension or adsorption. The measuring unit consists of a force measuring system, temperature sensor, thermostatic jacket with built-in magnetic stirrer, platform drive system (to raise and lower the sample automatically and determine its position), and a holder for the automatic dosing system. The processor unit contains interface boards to communicate with the measuring unit and to perform calculations, a printer, and a liquid crystal display to present results.

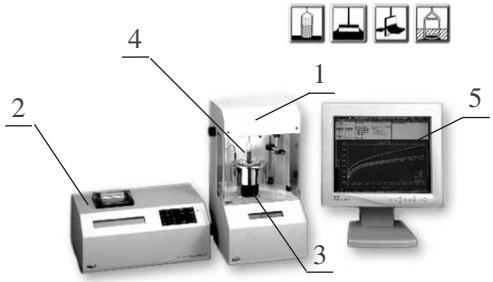

Figure 3. Tensiometer KRÜSS K12, GmbH, Hamburg.[18]

Capability of moisture adsorption was determined according to the standard DIN 54351.[16,17] 1 g of fibres was exposed for 24 hours to standard atmosphere and was weighed (m_s) and transferred into a drying apparatus. Then, the samples were dried for 4 hours at 105 °C, cooled and weighed (m_a). This procedure was repeated four times for each sample (raw and pre-treated viscose, modal and lyocell fibres). The moisture absorption capability was formally calculated according to Eq. (3).[16,17]

RESULTS AND DISCUSSION

In order to determine the sorption abilities, the capillary velocities of non-treated (raw) and pre-treated viscose, modal and lyocell fibres were measured and used for calculations of contact angles according to Eq. (1). As observed in Figure 4, raw modal fibres have the largest contact angle (φ = 77.1°). This relatively high value implies worse sorption characteristics. Lyocell fibres follow with a contact angle of 76.10°, and finally raw viscose fibres have the smallest contact angle (φ = 68.34°). The explanation for this is the fact that the sorption characteristics of both the conventional and the new type of regenerated fibres depend on less ordered regions, where the sorption processes take place. These regions are amorphous and void regions.[6,7,8] It is known[3,20] that viscose fibres are less orientated and less crystalline than modal and lyocell fibres. The amorphous regions of viscose fibres are the biggest (shorter and less orientated macromolecules), and therefore a number of accessible –OH groups are present in these regions. These groups are responsible for the negative charge and better sorption characteristics. A larger number of available –OH groups means a better possibility of interactions between cellulose and chemicals and therefore better sorption properties.[2,21] Modal fibres have smaller amorphous regions than viscose, and the macromolecules are better orientated. They also have fewer available functional groups for interactions, and because of this, they have the poorest sorption characteristics.[2] The lyocell fibres have the smallest

amorphous regions, with longer, highly orientated macromolecules which pass from one crystallite to another through these regions. The sorption phenomena in the aqueous medium of fibres depend predominantly on the void system, *i.e.*, diameter, volume and inner surface of voids. Lyocell and viscose fibres have similar void fractions. The diameter, volume and inner surface of voids are the biggest in viscose fibres, followed by lyocell fibres, which means better sorption properties. Modal fibres have the lowest moisture absorption because of their smaller diameters and volumes of void regions.[2]

Pre-treatment causes an increase of the sorption ability and reduces the contact angle. The second line in Figure 4 shows the contact angles of alkali-washed regenerated cellulose fibres. Alkaline purification has the biggest influence on viscose fibres. The contact angle of raw viscose fibres is 59.17°, which means it decreased by 13% when using alkaline purification. In the case of the lyocell and modal fibres, the influence of alkaline purification is smaller in comparison with viscose fibres and no essential reduction in contact angles can be seen. The contact angle of alkali-washed modal fibres is 75°, which means it decreased by 3%. Using alkaline washing, the contact angle of lyocell fibres is 74.80°, it decreased by 2%. After the washing was done, the alkaline solution of the washing agent easily penetrated into less orientated amorphous regions, and broke down the interactions between the cellulose macromolecules. The diameter of the fibres increased, the structure became looser and the interfaces of fibres became more accessible. The result is a smaller contact angle and wettability and sorptivity improvement of the viscose fibres. In comparison with viscose fibres, modal and lyocell fibres have a higher degree of crystallinity and higher molecular orientation,[3,20] which means that only a small quantity of washing agent can penetrate into less ordered amorphous regions of the fibres. This result

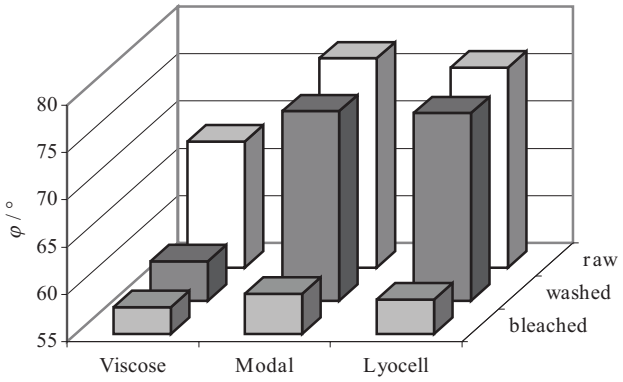

Figure 4. Contact angle, φ, of raw and pre-treated regenerated cellulose fibres.

also implies a smaller pre-treatment effect on the hydrophilic character of the fibres. The improvement of sorption characteristics due to washing in an alkaline medium can be explained by the increase of voids. According to Sugiyama,[10] the gaps between the cellulose crystalline and amorphous parts of the fibres are enlarged into voids by alkaline boiling, so that the adsorption ability is correlated with the increase of the void diameter. Raw viscose fibres have the biggest amorphous regions, so when using alkaline purification they increase much more than the other two types of fibres.[10]

By applying chemical bleaching the wettability properties of regenerated cellulose fibres, especially in the cases of modal and lyocell fibres, can be significantly improved. The contact angles decreased for all three types of regenerated cellulose fibres. The smallest contact angle was obtained by bleached viscose fibres (φ = 57.82°), which decreased by 15% compared to the contact angle of raw viscose fibres. Bleached modal fibres had a slightly bigger contact angle than bleached viscose fibres and were reduced to 59.20°. Using bleached modal fibres, the contact angle decreased by 23% in comparison with raw modal fibres. The contact angle of lyocell fibres was decreased by 23% by chemical bleaching and decreased to 58.60°. A suitable concentration of oxidant and an appropriate pH value applied during chemical bleaching can produce a shortening of the cellulose macromolecule, lowering of the degree of polymerisation and forming of a new hydrophilic group. The main functional groups formed on the cellulose by the H_2O_2 oxidation, appear to be ketones, while very few aldehyde and carboxyl groups are found.[10]

When comparing washed and bleached viscose fibres, there is only a slight decrease in contact angle (2%) in the case of bleached viscose fibres. This results from the fact that, in general, viscose fibres are more hydrophilic than the other two types of fibres. When applying washing to viscose fibres, this process causes a bigger decrease of contact angle than bleaching, but it is just the opposite in the case of modal and lyocell fibres.

Comparison between the sorption ability, represented as a contact angle, and capability of moisture adsorption as the standard method, showed (Figure 5) the same tendency of sorption characteristics and lead to the same conclusions. Raw viscose fibres adsorbed the highest amount of moisture (15.1%) and had the smallest contact angle (68.34°). Raw modal fibres had the biggest contact angle (77.10°) and showed the lowest capability of moisture adsorption (14.4%). The sorption characteristics of all three types of regenerated cellulose fibres were improved by pre-treatment. The results show that the sorption characteristics of viscose fibres were improved by alkaline purification, whilst the sorption properties of modal and lyocell fibres were improved by chemical bleaching.

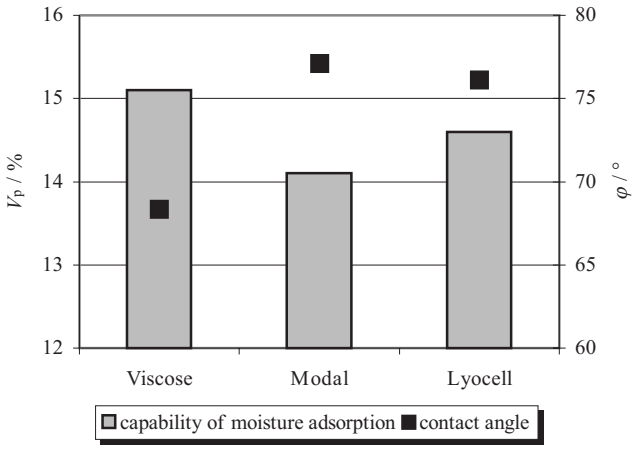

Figure 5. Capability of moisture adsorption, V_p, and the contact angle, φ, of raw viscose, modal and lyocell fibres.

The wettability or sorption characteristics of the fibres are one of the most important practical and technological properties during textile finishing, because most of the treatment processes take place in an aqueous medium.

Tensiometry as an analytical method could replace the conventional methods for determining the sorption abilities of textile materials. Using tensiometry the time needed for the determination of sorption abilities is reduced, but the most important advantage is the possibility of determining the surface reactivity according to different mathematical approximations. Tensiometric data can be also successfully used in many fields of industry, such as pharmacy, printing industry, cosmetics, paper industry, *etc*.

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SAŽETAK

Tenziometrijsko praćenje hidrofilnih i hidrofobnih značajki različitih celuloznih vlakana

Zdenka Peršin, Karin Stana-Kleinschek i Tatjana Kreže

Poboljšanje vlažljivosti i sorptivnosti tekstilnih vlakna najvažnije su zadaće pri završetku izrade tekstila. Kako bi se poboljšale sorpcijske značajke celuloznih vlakana u njihovoj predobradbi rabe se razni postupci, najčešće ispiranje, izbjeljivanje i maceriranje. Razlike u sorpcijskim svojstvima neobrađenih i predobrađenih (ispranih i izbijeljenih) regeneriranih celuloznih vlakana istražene su tenziometrijom i uspoređene s klasičnim postupkom određivanja adsorpcije vlage. U usporedbi sa sirovim vlaknima, viskozna vlakna imaju najmanju vlažnost i najmanji kut kontakta, dok modalna vlakna imaju najveći kut kontakta. Predobradbom se povećavaju sorpcijska svojstva i pristupačnost raznim kemikalijama u završnim postupcima obradbe. Rabljenjem standardnih postupaka potvrdili smo da vlakna najveće vlažnosti posjeduju najmanji kontaktni kut, što je dokazano tenziometrijom.