

Characterization of cellulosic fibers and fabrics by sorption/desorption

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Abstract—Three cellulosic substrates: lyocell (CLY), viscose (CV), and modal (CMD) in the form of fibers and fabrics were subjected to wet/dry or wash/dry treatments. The accessibility of untreated and treated substrates to water and iodine was investigated using dynamic water-vapor sorption, moisture retention, and iodine sorption methods, to study the influence of treatments on sorption–desorption hysteresis, fraction of moisture sorbed as a monomolecular layer, water retention, and iodine sorption. It was found that the sorption properties of untreated and treated substrates differed with sorbate type as well as substrate type and form. © 2008 Elsevier Ltd. All rights reserved.

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1. Introduction

Cellulose from wood pulp is the main component in regenerated fibers. The history of the first commercially available regenerated fiber known as viscose rayon started in 1893 as processing of Chardonnet silk followed by the production of viscose filament yarn in 1905. Further modification of the viscose process led to the production of fibers with a high wet modulus, the modal fibers. In 1984, the first commercial samples of a new generation of cellulosic fibers were produced—lyocell fibers—with a process involving direct dissolution of cellulose in a solution of hot *N*-methylmorpholine-*N*-oxide (NMMO).¹ The different processing routes in the production of lyocell, viscose, and modal result in differences in structure and properties

between the three cellulosic materials. For example, the degree of polymerization, molecular mass, density, crystallinity index, and orientation among the three substrate types are the highest in lyocell, followed by modal and viscose.²

The crystalline arrangement in the regenerated cellulose is labeled ‘cellulose II’ and is characterized by a less compact crystal structure as compared to ‘cellulose I’ that occurs in native cellulose.³ Cellulosic fibers are porous materials, consisting of highly ordered-less accessible crystalline regions and less ordered-more accessible amorphous regions with different abilities to act as sorption centers. The ability of crystalline and amorphous regions to transport reagents to reactive sites and move reaction products out is different, that is their accessibility is different.

The cellulose polymer consists of three hydroxyl groups per anhydrous glucose unit which attract water, and thus celluloses are characterized by high moisture absorption. Moisture content is an important factor,

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as water-retaining cellulose shows different physico-mechanical properties unlike dry cellulose. It was found that void fraction is the greatest in viscose fibers, followed by lyocell and modal.² The study of pore organization and distribution of pore sizes in fibers by TEM showed more porous center of viscose and modal unlike more porous middle zone and compact center of lyocell, and a wider pore size distribution of viscose and modal comparing with lyocell.⁴ Treatments such as drying and wetting affect pores of cellulose. The changes in the pore characteristics of lyocell fibers after repetitive cycles of wetting and drying were studied using inverse size exclusion chromatography (ISEC)⁵ and small angle X-ray scattering (SAXS).⁶ FT-IR⁷ and NMR⁸ methods were also used to investigate the influence of moisture uptake on the internal structure of cellulose. The uptake of moisture causes structural changes in cellulosic substrates resulting in changes to swelling ability, accessibility, and sorption properties of substrate as well as changes of appearance and touch of textiles.

In the present study the influence of wet/dry or wash/dry treatments on the accessibility of different regenerated cellulosic materials—fibers and knit fabrics of viscose type (viscose and modal) and NMMO type (lyocell)—was investigated. The accessibility was determined using dynamic water-vapor sorption and desorption, iodine sorption and swelling in liquid water with a view to assess rearrangements in the substrate structure during wet/dry and wash/dry treatments.

2. Experimental

2.1. Materials

Three types of regenerated cellulosic fibers, kindly supplied by Lenzing AG, were used in this investigation: lyocell (TENCEL[®] Standard)—CLY; viscose (Lenzing Viscose[®])—CV; and modal (Lenzing Modal[®] Standard)—CMD. All fibers were of fineness 1.3 dtex and length 39 mm. Also included in the study were single-jersey knit fabrics made of the same fiber types and specifications.

2.2. Methods

2.2.1. Wet/dry and wash/dry treatment. The fibers were awarded wet/dry treatments and knit fabrics were awarded wash/dry treatments. The wet/dry treatment consisted of immersing fibers in deionized water for 15 h at 40 °C, then drying the wet fibers for 4 h at 105 °C. The wash/dry treatment consisted of subjecting fabrics to a wash with domestic detergent (2 mL/L) for 30 min at 40 °C, in a regular washing machine in easy-care mode without a pre-wash. The washed fabrics were then dried for 30 min at 60 °C, at extra dry mode. One

cycle of wet/dry or wash/dry treatment comprised one combination of wetting or washing and drying. Fibers and fabrics were subjected to 20 wet/dry or wash/dry treatments, respectively.

All treated samples were conditioned for over 48 h in a standard atmosphere at 20 °C ± 2 °C and 65 ± 4% relative humidity (RH) prior to tests.

2.2.2. Dynamic water-vapor sorption/desorption. A detailed description of the instrument and procedure was described previously.⁹ In brief, fiber and fabric specimens were placed in an automatic multisample moisture analyzer SPS11 (Project-Messtechnik, Ulm, Germany) at 25 °C, and the atmosphere in the analyzer at the beginning of measurements was equilibrated at 0% RH. The atmospheric moisture content was then successively increased and equilibrated stepwise at 10% RH intervals up to 90% RH. Thereafter, the atmospheric moisture content was decreased and equilibrated stepwise at 10% RH intervals up to 0% RH. An analytical balance connected to the instrument was used to measure mass change in materials at regular intervals during all moisture sorption and desorption processes.

2.2.3. Water retention values. About 0.5 g of specimens from samples was accurately weighed and immersed in deionized water for 24 h at ambient temperature, then removed and centrifuged at 4000g for 10 min, after which the wet specimens were reweighed (W_w). The wet specimens were dried in an oven for 4 h at 105 °C, allowed to cool in a desiccator over powdery P₂O₅, and the weight of the dried specimen was recorded (W_d). The water retention value (WRV) was calculated according to Eq. 1

$$WRV = \frac{W_w - W_d}{W_d} \quad (1)$$

2.2.4. Iodine sorption method. Iodine sorption capacity of samples was measured according to the method described by Nelson et al.¹⁰

About 0.3 g of specimen was placed into a tared 250 mL stoppered Erlenmeyer flask and the weight of flask plus sample was noted down. A vol of 2 mL concentrated iodine soln (5 g I₂, 40 g KI, 50 mL water) was dropped on the sample and mixed thoroughly by pressing with glass rod. The weight of flask plus sample plus iodine soln was recorded. After mixing iodine soln with sample, the system was allowed to stand for 3 min, consequently 100 mL of saturated sodium sulfate soln was pipetted into the flask. The sample was stirred for 1 h at 22 °C ± 1 °C. The blank soln was prepared by identical procedure omitting sample. After 1 h, the soln was filtered through a tared frit glass crucible. The aliquot amount of sample and blank soln were titrated with 0.01 mol/L Na₂S₂O₃. The sample was washed

on tared crucible thoroughly with deionized water, consequently dried in crucible for 4 h at 105 °C. Finally, the crucible was cooled in desiccator over powdery P₂O₅ for 1 h and weighed. Then iodine sorption value (ISV) in mg I₂/g cellulose was calculated according to Eq. 2

$$\text{ISV} = \frac{(T_s - t_s) \cdot N \cdot F \cdot 126.91}{W} \quad (2)$$

where $T_s = T_b \cdot \frac{I_s}{I_b}$ is the amount of Na₂S₂O₃ soln equivalent to initial iodine in aliquot of sample soln (mL); I_s , the weight of concentrated I₂-KI soln in a sample soln (g); I_b , the weight of concentrated I₂-KI soln in a blank soln (g); T_b , the amount of Na₂S₂O₃ soln for aliquot of blank soln (mL). t_s is the amount of Na₂S₂O₃ soln for aliquot of supernatant filtered from sample (mL); F , the aliquot factor considering that total vol of sample soln was 102 mL; N , the concentration of Na₂S₂O₃ (mol/L); W , the oven-dry weight of sample (g).

3. Results and discussion

The cellulose polymer contains three hydroxyl groups per anhydrous glucose unit, thus cellulosic materials are characterized by high moisture absorption. Absorption of water is accompanied by a change in materials dimensions—swelling. The interactions of substrates with water vapor (moisture), that is, the monitoring of moisture regain (MR) during moisture sorption and desorption was carried out at different relative humidities using an automatic multisample moisture analyzer SPS11. The plot of equilibrium moisture regain versus relative humidity for sorption process for untreated fibers and knit fabrics is shown in Figure 1. The rate of change of moisture regain increases at low relative humidity, consequently there is almost linear part of isotherm followed by a rapid growth at high relative humidity. Untreated knit fabrics show lower moisture regains in comparison with corresponding untreated fiber types. Fibers in yarns of knit fabrics are twisted

and due to tighter construction, the access of water molecules to accessible surfaces is more difficult unlike loose mass of fibers. In both graphs lyocell substrate reaches lower moisture regain than viscose and modal. This fact can occur owing to greater amount of crystalline regions in lyocell. However there is no significant difference in moisture regain between viscose and modal despite their different crystallinity. Therefore it appears that not only crystallinity but also swelling affects moisture regain.

As sorption of water increases with an increase of relative humidity, the cross-links in amorphous cellulose which can be formed where molecules pass near to each other are liable to break and be substituted by the absorption of water molecules on hydroxyl groups. The structure has propensity to remain unchanged, and so there is a hysteresis in the breaking and re-forming of cross-links. Fibers swell during the sorption of water, but because they are not completely elastic there is incomplete recovery after desorption and a hysteresis between sorption and desorption arises. The degree of hysteresis at a particular relative humidity was calculated according to Eq. 3

$$\text{Hysteresis (\%)} = \frac{\text{MR}_{\text{total desor.}} - \text{MR}_{\text{total sor.}}}{\text{MR}_{\text{total sor.}}} \cdot 100 \quad (3)$$

where $\text{MR}_{\text{total desor.}}$ and $\text{MR}_{\text{total sor.}}$ are equilibrium moisture regains in the desorption and sorption phases, respectively, at the same relative humidity.

The effect of relative humidity on the hysteresis of cellulosic fibers as well as knit fabrics untreated and awarded 20 wet/dry and wash/dry cycles, respectively, is shown in Figure 2. All studied materials show a decrease in hysteresis with an increase of relative humidity. While at low relative humidity the diffusion of the vapor is a dominant transport mechanism, capillary flow of water becomes more significant at high relative humidities. The arrangement of less oriented shorter macromolecules with few entanglements contained in viscose substrates allows the material to swell during sorption more than in the case of modal and lyocell substrates that

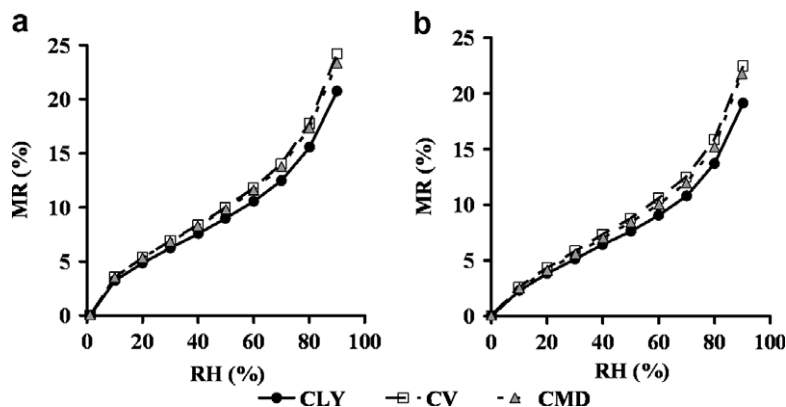


Figure 1. Equilibrium moisture sorption isotherms of untreated (a) fibers, and (b) knit fabrics.

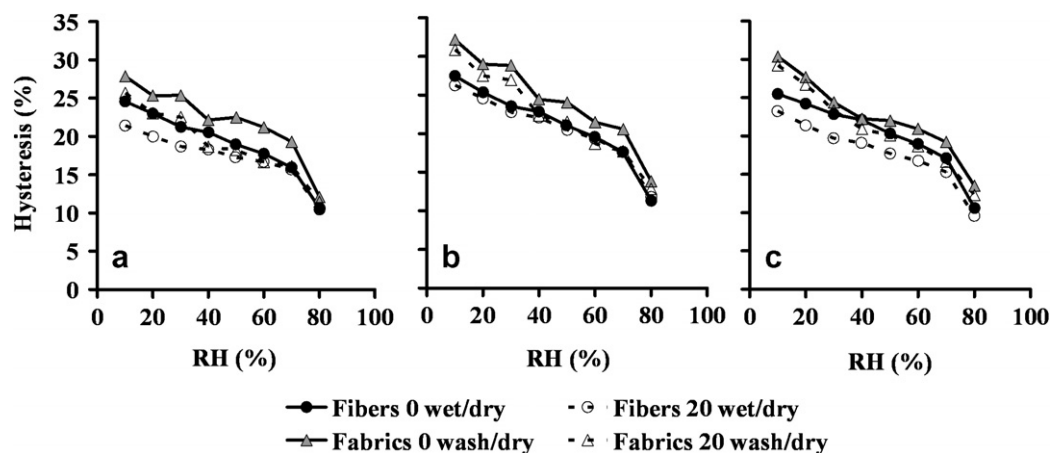


Figure 2. Hysteresis between sorption and desorption isotherms of (a) lyocell, (b) viscose, and (c) modal substrates; fibers awarded 0 and 20 wet/dry cycles, knit fabrics awarded 0 and 20 wash/dry cycles.

are characterized by a higher degree of polymerization and orientation. Desorption process is accompanied with a decrease of swelling to a higher extent for lyocell and modal due to the existence of a greater driving force toward increased orientation. There will be a lack of force which could bring structure closer in viscose substrates, and thus it decreases swelling to a lower extent. These phenomena result in greater hysteresis between sorption and desorption for viscose in comparison with modal and lyocell substrates. The yarns of knit fabrics swell during sorption and the arrangement of fibers in the yarn becomes looser, the construction is more opened. There are more gaps—interstitial spaces—occurring between fibers due to the untwisting of yarns which can retain water. During desorption swelling decreases, but fibers which slipped across each other in the process of opening the yarn structure do not take the original place and interstitial spaces retain water. Thus untreated knit fabrics exhibit higher hysteresis than the corresponding untreated fiber types.

Wet/dry treatment leads to a decline of hysteresis for lyocell and modal fibers, and the difference becomes smaller at higher relative humidity. The applied treatment only slightly affects the hysteresis of viscose fibers. Wash/dry treatment causes the most significant decrease of hysteresis for lyocell fabric among all studied knit fabrics. The other two types of fabrics show lower difference between hysteresis of untreated and wash/dry treated samples in the whole range of relative humidities. The repetition of wetting (washing) and drying leads to a phenomenon known as ‘hornification phenomenon’, at which some voids become ‘zipped’ during drying, by the creation of hydrogen bonds between the elementary fibrils and ‘unzip’ only partially during re-wetting.¹¹ Due to this phenomenon, the accessibility of cellulosic materials to water vapor after 20 wet/dry cycles for fibers and 20 wash/dry cycles for fabrics is diminished.

The water molecules are initially adsorbed directly onto the cellulosic hydroxyl groups forming the first monomolecular layer, followed by an indirect adsorption where water molecules add onto the molecules already adsorbed, creating additional water layers. The Brunauer–Emmett–Teller (BET) equation 4 was used for the determination of the amount of water adsorbed as a monomolecular layer on the surface of material:¹²

$$\frac{x}{V(1-x)} = \frac{1}{V_m C} + \frac{(C-1)x}{V_m C} \quad (4)$$

V_m is the moisture regain in % corresponding to a monomolecular layer, x is the partial vapor pressure of water, V is the moisture regain at x . C is a constant, which is approximately equal to $\exp\{(E_1 - E_L)/RT\}$, where E_1 is the heat of adsorption on the first and E_L that on the succeeding layers.

The BET equation gives a sigmoidal isotherm, which between 0.1 and 0.5 of partial vapor pressure is nearly linear for all studied materials. The values of V_m were calculated from the slope and the intercept of this dependence and they are plotted in Figure 3. According

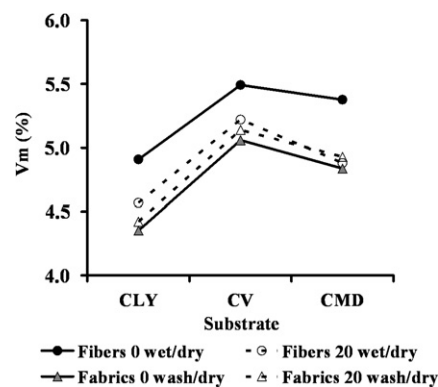


Figure 3. The moisture regain in a monomolecular layer of untreated and wet/dry treated fibers and untreated and wash/dry treated knit fabrics.

to the previous investigation² the characteristics of pores in which the adsorption of water molecules can take place such as pore volume and pore surface area decrease in the order viscose, lyocell, and modal. However in the range of 10% RH to 50% RH generally viscose substrates exhibit the highest moisture regain in a monomolecular layer, followed by modal and lyocell. The apparent divergence could be explained by the limitation in the applicability of BET model for swelling systems. The discrepancies may also arise from the fact that oval lyocell fibers provide smaller available surface for moisture adsorption than modal and viscose fibers with their more irregular surface. The available surface for creating monomolecular coverage of water is found to be greater for fibers than for knit fabrics. This can be explained by the twisted construction of yarns, where the fibers are overlapped and therefore available surface is smaller. After wet/dry (wash/dry) treatment the surface accessible to moisture is expected to be reduced due to the collapse of pores. However no significant decrease of V_m parameter is observed in treated samples. A strict interpretation of the absolute values of V_m is made difficult owing to their sensitivity on curve fitting, that is slightly different values of V_m are obtained if some of the isotherms are fitted with the linear function over the partial vapor pressure interval 0.1–0.5 as compared to an interval of 0.1–0.4.

The interactions of cellulosic substrates with liquid water represent the total swelling of substrates which includes wide expansion of amorphous regions. WRV of fully wetted fibers (fabrics) includes different properties such as effects of capillary water and fiber bulk property as well. It can be seen in Figure 4 that viscose substrates show the highest water retention values among studied substrates. As there is no significant difference in the water retention values of untreated substrates, the modification of substrate by wet/dry treatment results in the decrease of this parameter, more distinct for fiber than for fabric samples. An explanation can be made by re-

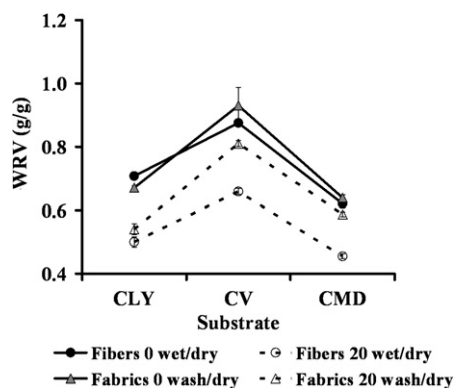


Figure 4. Water retention values of untreated and wet/dry treated fibers and untreated and wash/dry treated knit fabrics.

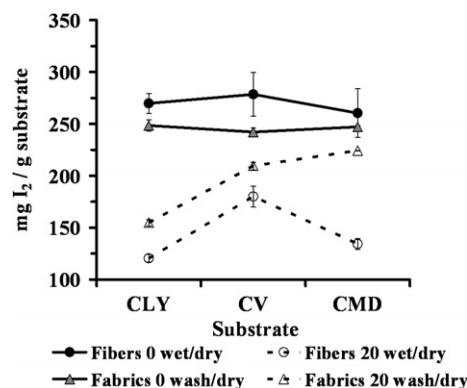


Figure 5. Iodine sorption values of untreated and wet/dry treated fibers and untreated and wash/dry treated knit fabrics.

stricted swelling in fabric, that is the reorganization of structure is limited and thus wash/dry treated fabrics exhibit smaller decrease of WRV in comparison with the corresponding fibers. Generally the expansion and swelling tendency of cellulosic materials decreases during repetitive wet/dry treatment.

Studying the adsorption of iodine which takes place in less ordered amorphous regions of cellulose is a classical method for the determination of surface and sorption properties, and it is used in the present paper. ISV is higher for untreated lyocell and viscose fibers than for untreated fabrics. Modal does not exhibit significant change in ISV between different substrate forms (Fig. 5). After treatment ISV decreases significantly by approx. 55% for CLY fibers, 48% for CMD fibers, and 35% for CV fibers (Table 1). The magnitude of ISV decline for wash/dry treated fabrics is lower because of limited reorganization due to restricted swelling or because of increased accessibility of fabrics after 20 wash/dry cycles (approx. decrease of 38% for CLY, 14% for CV and 9% for CMD). From Table 1 it is evident that the ISV exhibits the highest sensitivity to changes in the treated materials in comparison to all other methods of measuring structure change in materials. In comparison, the water retention value and moisture sorption exhibit relatively lower sensitivity to changes in substrate structure.

4. Conclusion

In this study, a set of molecular probes was applied to investigate sorption properties as a function of accessibility for three regenerated cellulosic substrates in the form of fibers and fabrics. It was found that wet/dry and wash/dry treatments cause the decrease of sorption properties of studied materials. Due to the selectiveness of sorption to defined sites in a cellulose structure the extent of sorption depends on the sorbate as well as on substrate type and form. The effect of molecular

Table 1. Comparison of the changes in investigated parameters for lyocell, viscose, and modal substrates; fibers awarded 0 and 20 wet/dry cycles, knit fabrics awarded 0 and 20 wash/dry cycles

Substrate form		Fibers			Fabrics		
		V_m (mmol/g)	WRV (mmol/g)	ISV (mmol/g)	V_m (mmol/g)	WRV (mmol/g)	ISV (mmol/g)
CLY	0 w/d	2.73	39.27	1.06	2.42	37.22	0.98
	20 w/d	2.54	27.78	0.48	2.46	30.00	0.61
CV	0 w/d	3.05	48.62	1.10	2.81	51.67	0.95
	20 w/d	2.90	36.58	0.71	2.86	45.00	0.83
CMD	0 w/d	2.99	34.47	1.03	2.69	35.48	0.97
	20 w/d	2.71	25.28	0.53	2.74	32.61	0.88

and supramolecular structure of substrates was obvious through all experiments. Changes in sorption sites were most sensitive for iodine sorption, less for water retention value, and the least for moisture sorption.

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