Moisture Sorption/Desorption Behavior of Various Manmade Cellulosic Fibers

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ABSTRACT: The kinetics of dynamic water vapor sorption and desorption on viscose, modal, cotton, wool, down, and polyester fibers and lyocell knit fabrics were investigated according to the parallel exponential kinetics (PEK) model. The total equilibrium moisture regain ($M_{\text{inf(total)}}$) in all the materials decreased with increasing temperature. However, the partial equilibrium fast sorption, determined by PEK simulation at 60% relative humidity (RH) and 36°C, was larger than that at 20°C, whereas the partial equilibrium slow sorption was smaller. The characteristic times in fast sorption (τ_1) and in slow sorption (τ_2) for lyocell were reduced when the conditions were changed from 60% RH and 20°C to 36°C, whereas those for the other fibers increased. Lyocell exhibited the highest $M_{\text{inf(total)}}$ value and the lowest τ_1 and τ_2 values, and this suggested high equilibrium moisture content and fast moisture uptake/release, that is, high moisture accessibility for lyocell. The relationships between the moisture regain, hysteresis, water retention capacity, and Brunauer–Emmett–Teller surface volume in the materials were also examined. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 97: 1621–1625, 2005

Key words: fibers; kinetics (polym.); modeling; thermodynamics

INTRODUCTION

Clothing materials require a high moisture retention capacity and a high moisture transportation propensity to provide good wearing comfort. Moist fibers can act as heat reservoirs, and thus the moisture transfer rate is an important function for temperature and humidity control in textiles. Furthermore, fiber properties are changed by moisture sorption, which causes fiber swelling in hygroscopic materials such as cellulosics, which also affects the general dyeing and finishing behavior of fibers. The lyocell fiber, a regenerated cellulosic fiber manufactured by pulp dissolution in *N*-methyl morpholine *N*-oxide and coagulation, has a high crystallinity and a fibrillar morphology. Lyocell fibers have a high fibrillation tendency, which leads to rope marking defects in hank finishing, graying of dyed fabrics, and changes in the handle of clothes.[1] The fibrillation occurs when water is adsorbed into the lyocell fibers, causing a change in the fiber structure.[2] Hence, an understanding of the mechanism of water

sorption onto lyocell fibers may provide valuable information to improve not only wearing comfort but also textile processability.

Moisture sorption, especially by hydrophilic fiber materials, is a comparatively complex process because it involves a continuous change in the structure and hence properties of the fiber due to swelling. High internal temperature changes caused by the heat of sorption with large amounts of moisture also complicate the kinetics of the sorption process.[3] Kohler et al.[4] reported that water exchange in natural fibers such as flax and hemp could be modeled by two parallel independent first-order processes defined as the parallel exponential kinetics (PEK) model. We also reported in a recent article[5] that moisture sorption/desorption kinetics on lyocell and cotton (Co) fibers could be described by the PEK model and suggested that at low RHs the mechanism of moisture sorption in the lyocell fibers was distinctly different from that in the Co fibers.

Here we describe moisture accessibility in lyocells, viscose, wool (W), down (D), Co, and polyester (PES) fibers quantitatively with the PEK model and compare it with the apparent equilibrium and kinetics of moisture sorption. The thermodynamics of moisture sorption in fibers is also discussed, with consideration given to the effect of the temperature on the PEK parameters.

TABLE I
Technical Parameters of the Substrates

Material	Yarn count (tex)	Yarn twist (T/m)	Yarn type	Fiber fineness (dtex)	Fiber length (mm)	Loop density (cm^{-2})	Mass/area (g/m^2)	Fiber type	Crosslinking treatment
L1	14.7	930	Ring yarn	1.3	40	330	163	Lyocell	None
L2	14.7	930	Ring yarn	1.3	38	322	149	Lyocell	Crosslinker A
L3	14.7	930	Ring yarn	1.4	38	329	162	Lyocell	Crosslinker B
CV$_f$1	14.7	930	Ring yarn	1.3	40	—	—	Modal	None
CV$_f$2	14.7	930	Ring yarn	1.3	39	—	—	Viscose	None
Co	14.7	930	Ring yarn	Combed	—	—	—	Unbleached	None

EXPERIMENTAL

Materials

Co, W, PES, and D fibers, two viscose fibers (CV$_f$1 and CV$_f$2), and three varieties of lyocell knit fabrics (L1, L2, and L3), supplied by Lenzing AG (Lenzing, Austria), were used in the experiments. The technical parameters of the substrates are given in Table I. The diameters of the W and PES fibers were approximately 30 μm.

Measurements

Dynamic water vapor sorption and desorption were measured gravimetrically with an SPS11 automatic multisample moisture sorption analyzer (Project-Messtechnik, D-Ulm, Ulm, Germany) at 20 and 36°C. The instrument parameters were set as described previously.[5] The water retention value (WRV) was evaluated by a centrifugal method according to a previous work.[5]

RESULTS AND DISCUSSION

The regain and loss of moisture in fibers with stepwise increases and decreases in the relative humidity (RH) were measured gravimetrically with the automatic moisture sorption analyzer. The profile of the time (t) versus the mass change at t (M_t) of a full sorption/desorption cycle for L1 is shown in Figure 1. The fibers reached an equilibrium state at each moisture interval. The values of the individual equilibrium states [i.e., the total moisture regain at the equilibrium state ($M_{inf(total)}$)] were plotted against RH to draw the equilibrium moisture sorption/desorption isotherm shown in Figure 2. The hydrophobic PES fiber showed an extremely low moisture uptake in comparison with that of the hydrophilic fibers. The moisture regain in Co fibers was distinctly lower than that in the regenerated cellulosics and W and D fibers because of the fewer amorphous regions in Co.[6] The total equilibrium moisture regain of D fibers was lower than that in regenerated cellulosics and W fibers at high RHs;

this might be due to the internal structure of the D fibers.[7]

The equilibrium moisture isotherms show a distinct hysteresis between the sorption and desorption cycles, indicating structural changes in the fibers caused by interaction with water. The extent of the hysteresis was calculated as described in a previous study[5] and is plotted against RH in Figure 3. The extent of the hysteresis clearly decreases with increasing RH, and this suggests that the fiber structure strongly changes when moisture is adsorbed by the dry fiber or when all moisture is desorbed from the fiber. Obviously, this structural change becomes less distinct after some moisture has been absorbed by the fiber. This phenomenon has been observed not only in hydrophilic fibers but also in hydrophobic PES fibers. The Co fiber showed less distinct hysteresis than the other fibers especially at low humidity. This result indicates that the fiber structure of Co is more stable than those of the other fibers. Water can invade the structure less easily at low RHs, and this can be explained by the high crystallinity of Co. The hysteresis for PES was the lowest because water is hardly absorbed by this hydrophobic polymer.
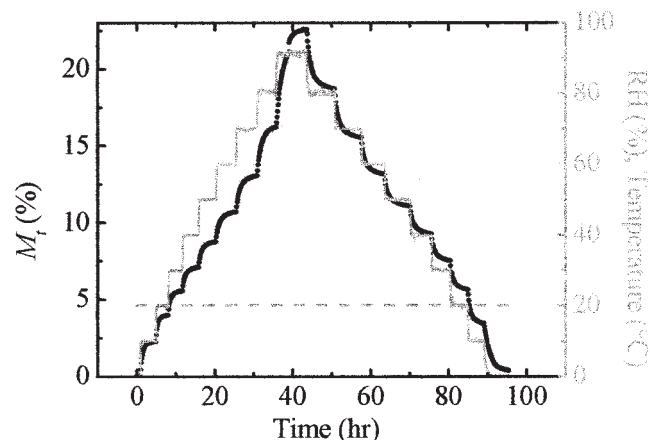

Figure 1 (●) Profile of M_t over the full sorption/desorption cycle (interval method) for L1 at (- - -) 20°C. The steplike curves show the course of RH.
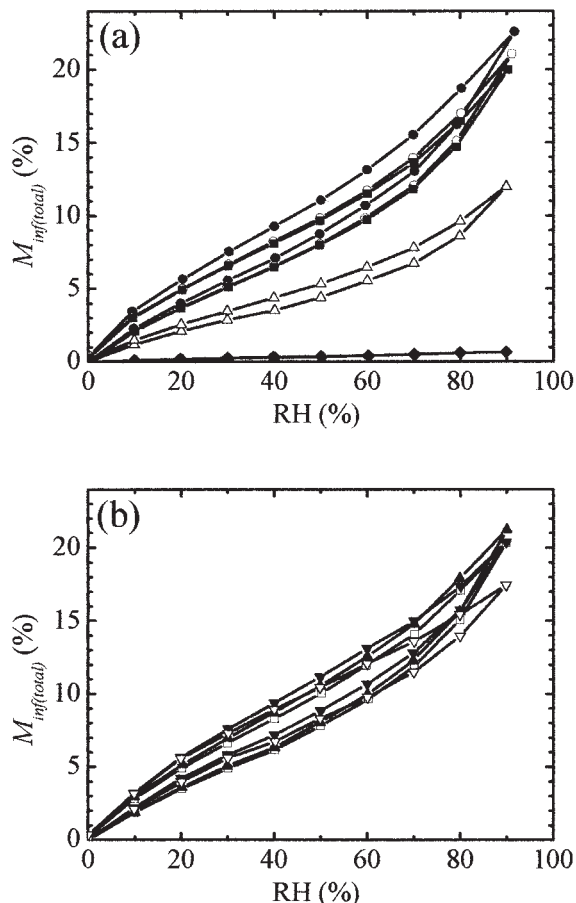
Figure 2 Equilibrium moisture sorption and desorption isotherms at 20°C for (●) L1, (○) L2, (■) L3, (△) Co, (◆) PES, (□) CV$_f$1, (▲) CV$_f$2, (▼) W, and (▽) D.
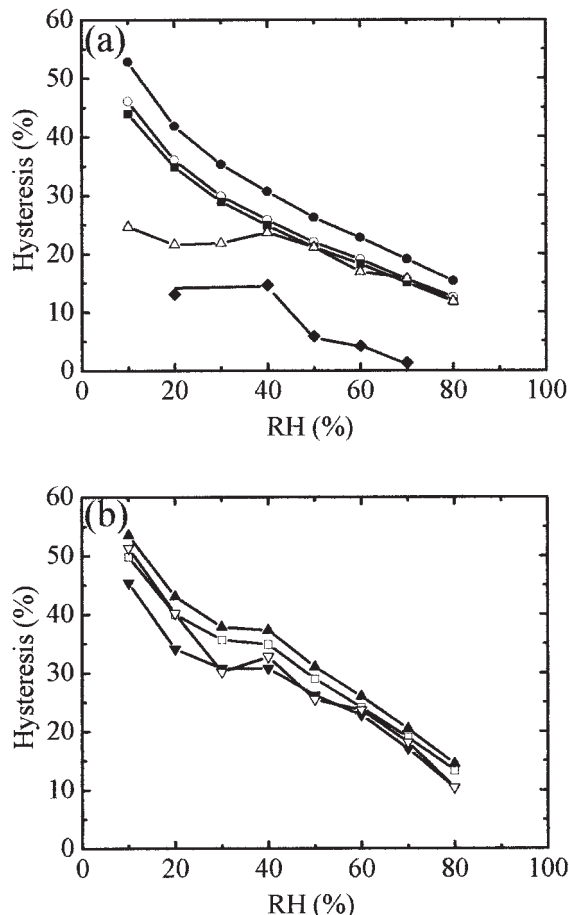
Figure 3 Plots of the relative hysteresis between the moisture sorption and desorption cycles versus RH at 20°C for (●) L1, (○) L2, (■) L3, (△) Co, (◆) PES, (□) CV$_f$1, (▲) CV$_f$2, (▼) W, and (▽) D.

$M_{\text{inf(total)}}$ values for various fibers at 60% RH and at 20 or 36°C are given in Figure 4. The higher moisture regain at 20°C versus that at 36°C indicates that the moisture sorption process in these fibers is an exothermic reaction. This result is consistent with the results reported in the literature.[8] The temperature effect on the total moisture regain for the lyocell fibers is more distinct than that for CV$_f$1, CV$_f$2, W, and D fibers. It is presumed that a larger quantity of heat is generated when water adsorbs onto lyocell fibers, and this retards moisture sorption.

The effect of temperature on the hysteresis at 10% RH is shown in Figure 5. The hysteresis in all the fibers was lower at the higher temperature, except for Co and W fibers. Additional experiments are required to study details of the temperature effects on hysteresis.

We have previously reported that water exchange in lyocell and Co fibers can be modeled well by two parallel independent first-order processes, the parallel exponential kinetic (PEK) model.[5] The PEK parameters obtained from the curve fittings characterize the kinetics of moisture sorption and desorption.[4] The model involves two different mechanisms for the ex-

change of water vapor relating to different sorption sites. The quantity of partial equilibrium moisture sorption and the characteristic time (τ) were estimated from simulations of experimental data.[5] The results

Figure 4 Effect of the temperature on the moisture regain at 60% RH.

Figure 5　Effect of the temperature on hysteresis at 10% RH.

TABLE III
Water Accessibility and PEK Parameters in Various Fibers at 20°C

Material	$M_{inf(total)}$ at 60% RH (%)	Hysteresis at 10% RH (%)	V_m (%)	WRV (g/g)
L1	10.7	52.8	5.64	0.943
L2	9.85	46.1	5.27	0.816
L3	9.72	43.9	5.19	0.799
CV_f1	9.64	49.9	5.36	0.642
CV_f2	9.98	53.5	5.61	0.891
Co	5.54	24.7	2.86	0.555
W	10.7	45.4	6.41	0.464
D	9.76	51.4	6.29	0.399
PES	0.41	—	0.76	0.122

for the partial equilibrium fast sorption (M_{inf1}), the partial equilibrium slow sorption (M_{inf2}), the characteristic time to obtain 63% M_{inf1} (τ_1), and the characteristic time to obtain 63% M_{inf2} (τ_2) obtained at 60% RH are summarized in Table II..
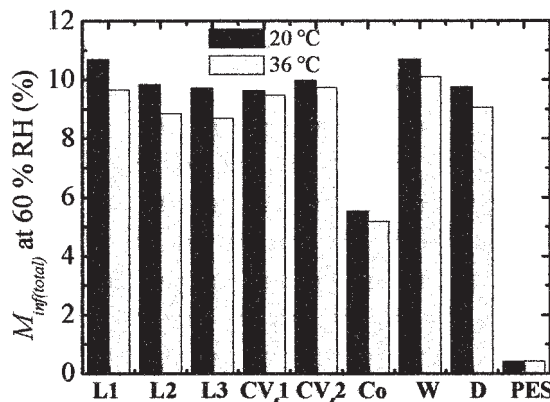
All fibers exhibited a larger M_{inf1} value at 36°C than that at 20°C, whereas M_{inf2} was smaller. This result indicates that extent of fast moisture sorption increased with increasing temperature, whereas that of slow moisture sorption decreased. The specific times τ_1 and τ_2 of CV_f1, CV_f2, Co, W, and D fibers were distinctly smaller at 20°C than at 36°C, and this suggested that the rate of moisture sorption and penetration into the fibers was higher at lower temperatures. On the contrary, the lyocell fibers showed larger τ_1 and τ_2 values at 20°C; that is, the rate of moisture sorption and penetration was lower at 20°C than at 36°C. The results imply that heat promoted the rate of moisture sorption in the lyocell fibers but retarded it in other fibers. A comparison of the values of the different types of fibers is striking in that τ_1 and τ_2 of the lyocell fibers at 36°C were smaller than those of other fibers. The moisture sorption and penetration in the lyocell fibers were thus clearly faster than those in all other fibers. The difference in the τ values of the

materials at 20°C was not significant, but τ of the lyocells was smaller than the τ values of the other materials; this indicated the higher rate of moisture sorption in the lyocell fibers even at 20°C.

The quantities of moisture adsorbed in a monomolecular layer on the surface of the material (V_m) were determined according to the Brunauer–Emmett–Teller (BET) model.[9] The V_m results are given in Table III with the $M_{inf(total)}$ values at 60% RH, the hysteresis at 10% RH and 20°C, and WRVs.

The hysteresis, V_m, and WRV of the cellulosic fibers increased in proportion to $M_{inf(total)}$. WRV for W and D fibers was not high as that for regenerated cellulosics, although the W and D fibers showed high $M_{inf(total)}$ and V_m. The penetration of liquid water into the fibers was obviously hindered by the unique surface structures in W fibers with characteristic scales and in D fibers with typical barbs.[7,10]

CONCLUSIONS

In this study, the effects of the temperature on the degree and kinetics of dynamic water vapor sorption and desorption on W, D, and PES fibers and different cellulosics were investigated with the PEK model. The total amount of moisture sorption on the fibers gener-

TABLE II
Effects of Temperature on PEK Parameters at 60% RH

Material	20°C at 60% RH				36°C at 60% RH			
	M_{inf1} (%)	M_{inf2} (%)	τ_1 (min)	τ_2 (min)	M_{inf1} (%)	M_{inf2} (%)	τ_1 (min)	τ_2 (min)
L1	0.78	1.19	22.9	93.2	1.26	0.39	19.8	80.9
L2	0.96	0.85	22.4	89.7	1.15	0.34	15.4	53.2
L3	0.84	0.91	22.1	87.5	1.10	0.31	16.6	56.0
CV_f1	0.65	1.22	28.3	108.3	1.15	0.59	59.4	810.8
CV_f2	0.95	1.02	43.8	145.2	1.10	0.65	58.7	617.4
Co	0.70	0.41	13.1	100.1	0.76	0.26	18.2	677.2
W	0.80	1.02	11.4	95.5	0.86	0.74	28.1	601.8
D	0.64	0.84	10.4	107.7	0.69	0.55	54.5	886.5
PES	—	—	—	—	—	—	—	—

ally decreased with increasing temperature. However, the partial amount of moisture sorption due to the fast process was enhanced at higher temperatures, whereas that of the slow process was reduced. The rate of moisture sorption and penetration into the lyocell fibers was promoted by heat, whereas it was retarded in both the fast and slow sorption processes in the other fibers. Furthermore, the results of the hysteresis between sorption and desorption isotherms showed that all the investigated fibers exhibited the highest relative hysteresis values at 10% RH, indicating that the fiber structure strongly changed as the moisture adsorbed on the dry fibers, whereas the changes became less distinct at higher RHs. A rise in temperature lowered the hysteresis in all the fibers except the Co and W fibers.

The analysis of water accessibility, V_m, and WRV of the fibers showed that V_m, WRV, and hysteresis increased in proportion to $M_{\text{inf(total)}}$ for the cellulosic fibers. The difference in the water accessibility between the three different lyocell fabrics was not significant. The lyocell knit fabric, for which M_{inf1}, M_{inf2}, τ_1, and τ_2 at 60% RH and 36°C, V_m, and WRV were 1.26%, 0.39%, 19.8 min, 80.9 min, 5.64%, and 0.943 g/g, respectively, showed a higher equilibrium uptake and a higher rate of moisture sorption. In other words, the lyocell fibers clearly exhibited higher moisture accessibility than the viscose, Co, W, and D fibers.

The definition of sorption sites in fast and slow processes is not simple at this stage. However, the temperature dependence of the partial components of the moisture content estimated by PEK simulation was different between fast and slow sorption. Besides, the temperature dependence of the partial components of the sorption rate was distinct among the different sample materials. These results suggest that the PEK model can be applied to investigate fiber structure.

NOMENCLATURE

Co	cotton
CV_f1	viscose modal fiber
CV_f2	viscose fiber
D	down
L1	lyocell 1
L2	lyocell 2
L3	lyocell 3
M_{inf1}	mass change at equilibrium state in fast sorption/desorption (%)
M_{inf2}	mass change at equilibrium state in slow sorption/desorption (%)
$M_{\text{inf(total)}}$	total moisture regain at equilibrium state (%)
M_t	mass change at t (%)
PEK	parallel exponential kinetics
PES	polyester
RH	relative humidity (%)
τ	characteristic time (min)
τ_1	characteristic time to obtain 63% M_{inf1} (min)
τ_2	characteristic time to obtain 63% M_{inf2} (min)
t	time (min)
V_m	Brunauer–Emmett–Teller surface volume (%)
W	wool
WRV	water retention value (g/g)

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