Functionalization of cotton with poly-NiPAAm/chitosan microgel: Part II. Stimuli-responsive liquid management properties

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Abstract An innovative strategy for functional finishing of cotton involves application of stimuli-responsive surface modifying system based on temperature- and pH-responsive poly-NiPAAm/chitosan microgel. The stimuli-responsiveness implied to cotton is the consequence of swelling/collapse of the microgel particles incorporated to the fibre surface, which produces an active liquid management system. The performance of functionalized cotton fabric in terms of liquid management properties was assessed by choosing appropriate techniques (water uptake; thin-layer wicking; water retention capacity; and drying capability) and discussion of the results was based on the types of water that are expected to be present in hydrated cotton and stimuli-responsive microgel.

Keywords Cotton · Stimuli-responsive · Microgel · Chitosan · Poly-NiPAAm · Liquid management

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Introduction

Thermophysiological comfort relates to the ability of the fabric to maintain thermal equilibrium between the human body and the environment through its moisture and liquid management abilities (i.e. wicking, wetting and water vapour transport properties) (Zhou et al. 2007), which can be efficiently controlled by redesigning textile material surface (Pastore and Kiekens 2001).

Currently available approaches to implement moisture and liquid management properties to cotton fabrics are based on composite textile structures (multilayered fabrics; combining fabric and polymer films; combining fabric and membrane; etc.); microencapsulation technology (e.g. encapsulated phase-change materials—PCMs); and moisture management finishes (e.g. silicone microemulsions and thermoreactive polyurethane) (Holme 2007). Nevertheless, the latest concepts from the emerging areas of responsive polymers and surface modification techniques enable taking cotton moisture management one step further—to develop stimuli-responsive material which can actively control material performance by polymer grafting (Hu et al. 2006; Liu et al. 2009; Save et al. 2005) or functional finishing by application of microgel based on stimuli-responsive polymers (Jocic 2008). Microgel based surface modifying system shows specific volume phase-transition (swelling and shrinking) which can be triggered by various stimuli (e.g. temperature, pH, humidity) and it is expected to

lead to adjusting the liquid management of textiles (Jocic 2009; Jocic et al. 2009).

Currently, wide variety of available stimuli-responsive polymeric systems is reported addressing diverse range of applications (Cohen Stuart et al. 2010; Meng and Hu 2010). Since temperature and pH have a physiological significance, versatile dual responsive hydrogels have been reported mainly for biomedical applications (Kopecek and Yang 2007; Kumar et al. 2007; Mano 2008). Simultaneously, an increasing amount of research is being done on functional finishing of textile materials by incorporating stimuli-responsive polymeric systems, which resulted in publishing two extensive review papers (Crespy and Rossi 2007; Liu and Hu 2005). Due to the need for biocompatibility and biodegradability, *biopolymer* based dual responsive hydrogels, prepared by combining with a thermo-responsive synthetic polymer, are currently of great interest (Prabaharan and Mano 2006). Biopolymer *chitosan*, as an amine-rich linear β-1,4-linked polysaccharide (similar to cellulose) that is obtained by the partial deacetylation of chitin, offers unique physicochemical properties: naturally renewable source, non-toxic, non-allergenic, anti-microbial, biocompatible and biodegradable (Ravi Kumar 2000; Rinaudo 2006). Chitosan is a typical pH-sensitive polymer (its primary amino groups have pK_a values of about 6.3) which responds to the changes in the pH of the surrounding medium by protonation/deprotonation of its amino groups (Vårum et al. 1994). This process induces phase transition which results in increase/decrease of the hydrodynamic volume of the polymer which, when polymer is present in the form of hydrogel (or microgel particles), shows the macroscopic response in varying dimensions (swelling/deswelling).

Among synthetic polymers, poly(*N*-isopropylacrylamide) (poly-NiPAAm) is the most intensively investigated thermo-responsive polymer, especially in the fields of biotechnology, bioengineering and medicine (Klouda and Mikos 2008). As a consequence of the rather complex polarity of the molecule (a balance between hydration at amido groups and hydrophobic aggregation of isopropyl groups), it exhibits a volume phase transition at ~ 32 °C (LCST—lower critical solution temperature), which is exactly between human body temperature and room temperature (Schild 1992). The origin of poly-NiPAAm temperature sensitivity has been fully explained by the cooperative hydration mechanism (Okada and Tanaka

2005). Below the LCST, the amide group binds water molecules via hydrogen bonding (i.e. it hydrates to form an expanded structure); above the LCST hydrogen bonds break and the polymer expels water and precipitates (i.e. its chains dehydrate to form a shrunken structure). The result of copolymerization of poly-NiPAAm with an ionizable polymer, such as chitosan, is a microgel that is responsive to both temperature and pH. However, because of its hydrophilic nature (affected by pH), the incorporation of chitosan bearing a large amount of hydrophilic groups into the poly-NiPAAm hydrogel network is expected to greatly influence the above explained interactions.

In this study, dual-stimuli responsive microgel was prepared from chitosan and poly-NiPAAm, with the aim to obtain a surface modifying system that is capable of changing its structure as well as its physicochemical characteristics when responding to changes in pH and temperature. Poly-NiPAAm/chitosan (PNCS) microgel was subsequently incorporated onto cotton by a pad-dry-cure process using 1,2,3,4-butanetetracarboxylic acid (BTCA) as crosslinker (Kulkarni et al. 2010). Both PNCS microgel synthesis and incorporation to cotton are thoroughly explained in Part I of this paper (Krizman Lavric et al. 2011). While the Part I established that moisture management properties of microgel functionalized cotton depend on the temperature and humidity, this study assesses the liquid management properties of the same material, including a pH of the liquid as another stimulus apart from the temperature and humidity.

Since cotton is highly absorptive fibre, both the amount of liquid that can be absorbed (wetting) and the rate of the liquid spreading (wicking) can affect the comfort of apparel directly. The abundant hydroxyl groups of cotton cellulose are responsible for bonding water, but extremely complex morphology of a fibre makes predicting the moisture and liquid transport phenomena a difficult task and the measurements of moisture regain (MR), moisture sorption isotherms, water retention and absorptive capacities are regularly done (Zeronian 1984). However, having in mind that water is the driving force for the microgel responsiveness, in this study some additional techniques are required to investigate liquid management ability of textile material treated with PNCS microgel. The capability of functionalized material to respond to different stimuli (pH, temperature, humidity) is studied through swelling/shrinking or hydration/dehydration

kinetics and equilibrium using a gravimetric method (i.e. the determination of water uptake—WU). The spreading of liquid driven into a functionalized cotton fabric by capillary forces is determined by using a thin-layer wicking (TLW) method. Water retention capacity (WRC) is used to estimate the swelling capacity of fibres, as determined by the amount of water retained (imbibed water) by water-swollen samples after centrifugation. The capacity to discharge the absorbed water during drying is evaluated by assessment of the drying curves of the fabric (Fangueiro et al. 2010; Li 2001; Männer et al. 2004). Above methods can give insight to the question of how much liquid water is held by capillary forces and how much is absorbed within the PNCS functionalized cotton. The understanding of interactions between water (moisture vapour and liquid water) and microgel functionalized cotton on a fundamental level is necessary for further optimization and development of such a material.

Experimental

Materials and procedures

Cotton fabric (100% cotton plain-weave fabric of 105 g/m^2 weight per unit area, desized, double scoured) was supplied by Vlisco (The Netherlands). Poly-NiP-AAm/chitosan microgel (PNCS) has been prepared according to the procedure of Lee et al. (2003) and incorporated to cotton fabric using pad-dry-cure process (Kulkarni et al. 2010). For the purpose of this study, the functionalized cotton sample (Co-PNCS/BTCA) with 2% add-on of the surface modifying system has been prepared (100% pick-up during padding). Untreated sample (Co-UT) was used as the reference in all characterization methods. Moreover, for the purpose of BTCA influence assessment, a sample treated with BTCA only has been prepared (Co-BTCA). Both microgel synthesis and cotton fabric incorporation procedures have been thoroughly described in Part I of this paper (Krizman Lavric et al. 2011).

Characterization methods

Water uptake (WU) measurements

Prior to testing for water uptake, all samples (Co-UT, Co-BTCA and Co-PNCS/BTCA) were conditioned at 20 °C and 65% of relative humidity for at least 24 h, after which the dry weight D was measured. Water uptake was then measured gravimetrically by immersing the samples either in acidic (pH 3), neutral (pH 6.5) or alkaline (pH 10) buffer solutions at temperature below and above transition temperature of PNCS (25 and 40 °C, respectively), until the swelling equilibrium was attained. Equilibrium was reached on average after 1 h and was determined by following the change in weight, the last three consecutive readings being equal. The samples were withdrawn from the solutions, and their weight W was determined after removing the surface water by blotting with filter paper. Water uptake (WU) is expressed in percentage and represents an average of at least three readings (Eq. 1):

$$WU = \frac{W - D}{D} \times 100 \tag{1}$$

where W is the weight of the material after taking up water (g); D is the weight of conditioned (dry) material (g).

Thin layer wicking (TLW)

The spreading of liquid driven into a sample by capillary forces was determined by using a thin-layer wicking (TLW) method (van Oss et al. 1992; Chibowski and Gonzales-Caballero 1993; Simoncic and Rozman 2007). According to the theoretical approach the rate of the liquid penetration (wicking) into a porous solid material can be described by the Washburn equation for the horizontal capillary (Eq. 2):

$$\frac{x^2}{t} = \frac{R}{2\eta} \Delta G \tag{2}$$

where x is the penetration distance (cm); R is the apparent (effective) capillary radius of porous solid (m); t is the penetration time to reach the distance x (s); η is the liquid viscosity (mPa·s); ΔG is the Gibbs free energy change accompanying the liquid penetration process (mJ/m^2). As it can be seen from Eq. 2, the liquid penetration rate (x^2/t), which is proportional to ΔG, represents a quantitative measure of the porous solid material liquid transport ability.

In the main experiment, cotton fabric sample (Co-UT or Co-PNCS/BTCA) was used as a porous solid and water (demineralised water; pH 6.8) as a

wicking liquid. The fabric sample (1 cm × 25 cm) was placed between two glass plates which are equipped with a ruler to enable the determination of the water penetration distance at different penetration time. The whole assembly (the glass plates with the sample between them) is positioned almost horizontally (with $\sim 2°$ inclination), having the lower edge in contact with the liquid. The measurements of the rate of water penetration through the fabric sample were carried out at 20 ± 1 °C. In order to assess the influence of pH of the wicking liquid, the measurements have been done with buffer solutions of different pH values (i.e. 3, 6.5 and 10) as well. Prior to testing, the samples were either dried at 105 °C for 4 h (0% R.H.; absolutely dry samples) or exposed to standard atmospheric conditions (65% R.H.; 20 °C; 24 h). For every fabric sample at least ten measurements were made. The average value of x^2/t was obtained graphically from the slope (k) of the plot of t versus x^2.

The additional experiment has been done in order to assess the apparent capillary radius R values. By measuring the penetration rate of liquids which were expected to spread spontaneously over the solid material (i.e. totally wetting liquids), the value of apparent capillary radius R of the porous solid material could be easily determined from the Eq. 2 as in this case $\cos\theta = 1$ and $\Delta G = \gamma_L$ (van Oss et al. 1992). For this reason n-heptane, as a non-polar totally wetting liquid of a low surface tension ($\gamma_L = 20.1$ mJ/m^2) of known viscosity $\eta = 0.41$ mPa s, was used as a wicking liquid instead of water. To avoid any possible presence of water (i.e. to obtain absolutely dry samples), one series of cotton samples was previously dried for 30 min at 105 °C and pre-contacted with the saturated vapour of n-heptane for 24 h at 20 ± 1 °C before the measurements. In order to assess the possible influence of the moisture present in the samples, another series of samples has been preconditioned at standard atmosphere (65% R.H.; 20 °C; 24 h) before the measurements.

Water retention capacity (WRC)

The water retention capability of the samples (Co-UT and Co-PNCS/BTCA), i.e. the amount of liquid retained by swelling, was determined after removing excess liquid in a centrifuge according to DIN 53814, being expressed through water retention capacity (WRC) parameter (Okubayashi et al. 2005; Siroka

et al. 2008). Prior to testing all samples were conditioned in a standard atmosphere (65% R.H.; 20 °C; 24 h). Each sample of ~ 0.5 g was immersed in buffer solutions of different pH values (i.e. 3, 6.5. and 10) at 25 and 40 °C for 24 h. The wet samples were centrifuged at 4,000 rpm during 10 min and weighed (W_C). The centrifuged samples were then dried in an oven for 4 h at 105 °C and reweighed (D_C). Water retention capacity (WRC, %) was calculated using the Eq. 3 and represents an average of at least three readings:

$$WRC = \frac{W_C - D_C}{D_C} \times 100 \qquad (3)$$

where W_C is the weight of the material after being centrifuged (g); D_C is the weight of the material after drying (g).

By comparing the data obtained for functionalized sample (Co-PNCS/BTCA) with the data obtained for untreated sample (Co-UT) under the same conditions (pH and T), it is possible to calculate the contribution (C_{WRC}) of the functional finishing system to the water retention capability (Eq. 4):

$$C_{WRC} = \frac{WRC_F - WRC_{UT}}{WRC_{UT}} \times 100 \qquad (4)$$

where C_{WRC} is the contribution of the functional finishing system to the water retention capability (%); WRC_F is the water retention capacity obtained for the functionalized sample and WRC_{UT} is the water retention capacity obtained for the untreated sample.

Drying curves and moisture regain

The drying curves and moisture regain were determined by thermogravimetric method, using moisture analyzer (MS-70, equipped with WinCT–Moisture software, A&D, Japan). For both measurements, the samples (Co-UT, Co-BTCA and Co-PNCS/BTCA) were previously conditioned by exposure to different humidity (50% R.H. and 80% R.H.) and temperature (25 and 40 °C, which are below and above the transition point of PNCS, respectively). Based on our previous experience with the measurements done on functionalized cotton (Co-PNCS/BTCA), the actual humidity values are chosen to mimic dry and humid atmospheric conditions in the sense of water availability as the driving force for PNCS microgel responsiveness. The drying curve can be obtained by

measuring the change in weight of the sample over time during drying and it expresses a very important parameter of the moisture present within the material in the course of drying (Su et al. 2007; Fangueiro et al. 2010). For drying curve assessment the conditioned sample was placed in a weighing pan of the moisture analyzer and its weight has been recorded (W_0). Then, the drying process was initiated and the sample weight W_i was measured at 5 s time interval. The drying parameters selected were: drying temperature 105 °C, which was reached in 5 min (ramp drying); weight resolution 0.0001 g; measurement accuracy 0.05%/min; standard mode. Dimensionless (%) water (moisture) remaining in the sample during drying (WRD) is calculated using the Eq. 5:

$$\mathrm{WRD} = \frac{W_i - W_f}{W_0 - W_f} \times 100 \qquad (5)$$

where W_0 is the initial weight of the conditioned sample (g); W_f is the final weight of the sample after being dried (g) and W_i is the weight of the sample recorded at regular intervals (every 5 s) during drying (g). From the obtained results a drying curve (WRD vs. t) can be drawn and drying rates can be obtained as the slopes (k) of the drying curve for each drying stage observed (initial; medium; final).

Since moisture regain (MR) can be used as a measure of the water resorbed by a dried material at specified equilibrium conditions of temperature and humidity, which in turn affects the comfort properties, using the same data it has been calculated according to the Eq. 6:

$$\mathrm{MR} = \frac{W_0 - W_f}{W_f} \times 100 \qquad (6)$$

Results and discussion

Results of water uptake (WU) determination at 25 °C (i.e. below the transition temperature of PNCS) (Fig. 1a) confirm significantly increased water uptake capacity of functionalized cotton fabric (Co-PNCS/BTCA) in acidic environment (pH 3 and 6.5). In alkaline environment (pH 10) water uptake showed nearly the same level as with untreated cotton (Co-UT). This behaviour could be mostly attributed to well-known chitosan pH-responsiveness, but the influence of BTCA has to be considered as well.

The influence of BTCA presence, which was chosen in order to assure anchoring sites for the PNCS microgel particles, can be seen from the results of water uptake determined for the Co-BTCA sample. BTCA film present at the cotton fibre surface generally improves slightly water uptake (when compared to Co-UT), indicating increased hydrophilicity as the consequence of the incorporation of carboxylic groups to the fibres, but the opposite effect has been obtained at 40 °C for pH 6.5 and 10. When measuring WU at ambient temperature (25 °C; Fig. 1a), no greater difference was obtained by raising pH from 3 to 10, while at 40 °C (Fig. 1b) significant decrease of WU was obtained for Co-BTCA sample in comparison to the untreated one. This was unexpected, since at pH 3 carboxylic acid groups act as hydrophobic sites, while showing their hydrophilic character at pH 10 due to the formation of carboxylate anions (Wilson and Whitesides 1988). Contrary, in our study hydrophilic character of Co-BTCA was obtained at pH 3 and hydrophobic character at pH 10. Therefore, the most reasonable explanation for this phenomenon could be
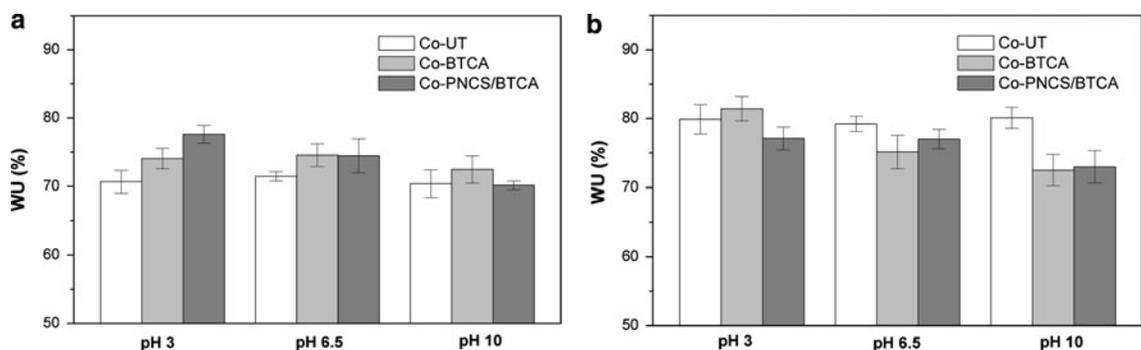
Fig. 1 Water uptake (WU) of Co-UT, Co-BTCA and Co-PNCS/BTCA at 25 °C (**a**) and 40 °C (**b**)

the presence of sodium salt in the buffer solution, since sodium borate was used to prepare the pH 10 buffer solution. Namely, at higher temperature (40 °C) reaction between carboxylic acid group and sodium salt could occur, preventing absorption of water which consequently reflected in lower WU of Co-BTCA at pH 10 and 40 °C (Fig. 1b). However, this phenomenon was not further studied, as it seemed that the observed behaviour of BTCA coated cotton did not influence the responsive behaviour of PNCS, which acted independently, thus influencing the overall pH responsiveness of functionalized cotton (Co-PNCS/BTCA) which was the main focus of the study.

From Fig. 1b overall decrease of water uptake capacity of Co-PNCS/BTCA was noticed at 40 °C (i.e. above the transition temperature of PNCS) in comparison to the untreated sample. This was attributed to the temperature responsiveness of poly-NiPAAm which is being in its hydrophobic state at this temperature. However, since at pH 10 the drop of WU was comparable to the WU obtained for the Co-BTCA treated sample, the presence of BTCA could influence on higher drop of water uptake of Co-PNCS/BTCA sample as well.

By comparing the results obtained at lower and higher temperature, a competitive effect was expected at pH 10 and 25 °C and at pH 3 and 40 °C, due to the competition between the responses of chitosan and poly-NiPAAm. Namely, at pH 10 and room temperature chitosan is hydrophobic (collapsed state) while poly-NiPAAm is hydrophilic. At pH 3 and higher temperature the situation is reversed, chitosan being hydrophilic and poly-NiPAAm being hydrophobic. Taking in account the obtained results, the conclusion could be made that more prominent influence on the responsiveness of the PNCS microgel originates from poly-NiPAAm presence than from the presence of chitosan in the system.

The spreading of liquid driven into a sample by capillary forces was determined by using a thin-layer wicking (TLW) method. The apparent capillary radius R was determined using Eq. 2 from the results of the wicking rate of n-heptane for two series of samples: (A) the samples which were previously saturated with n-heptane (absolutely dry samples) and (B) the samples preconditioned in standard atmosphere (65% R.H.; 20 °C; 24 h). The values obtained for the slope k (estimated from the x^2 vs. t plots) and the apparent capillary radius

Table 1 The slope k and the apparent capillary radius R, obtained from the thin-layer wicking measurements with n-heptane on samples previously saturated with n-heptane (absolutely dry samples) (A) and samples preconditioned in standard atmosphere (65% R.H.; 20 °C; 24 h) (B)

Sample	A		B	
	k	$R \times 10^6$ (m)	k	$R \times 10^6$ (m)
Co-UT	0.24	1.70	0.17	2.40
Co-BTCA	0.21	1.94	0.17	2.40
Co-PNCS/BTCA	0.20	2.04	0.19	2.15

R (calculated from the Washburn equation) are presented in Table 1.

It is evident that the apparent capillary radius R of absolutely dry functionalized cotton fabric (Co-PNCS/BTCA; series A) increases, which could be attributed to the increased capillarity of the surface modifying layer made of PNCS microgel. Another possible explanation is that the contribution of intra-yarn pores (between fibres) to the apparent capillary radius R, is considerably lower than the contribution of inter-yarn pores (between the yarns of warp and weft), since the access of liquids to the intra-yarn pores is expected to be hindered as the consequence of PNCS microgel presence. This bimodal pore size distribution (smaller intra-yarn pores and larger inter-yarn spacings) is the characteristic of woven fabrics manufactured from spun yarns (Rebenfeld et al. 1995). A system of large pores, usually uniform in size and shape, is formed by the interlacing yarns as determined by the weave pattern. Another system of pores, much smaller and in most cases somewhat polydisperse, is formed within the yarn structure between the component fibres.
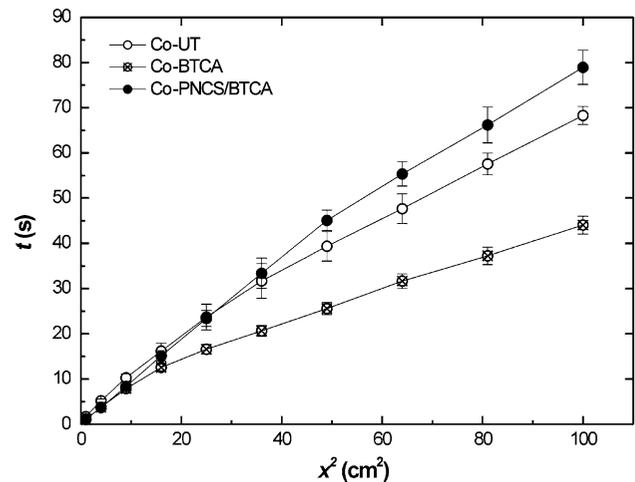
The thin-layer wicking measurements with n-heptane on samples preconditioned in standard atmosphere (65% R.H.; 20 °C; 24 h) (series B) show that the apparent capillary radius R of functionalized cotton (Co-PNCS/BTCA) decreases when compared to untreated cotton (Co-UT). During preconditioning in standard atmosphere both cotton and surface modifying system (consisting of BTCA and PNCS) pick-up moisture, causing certain level of PNCS microgel particles swelling, which consequently hinders the access of the wicking liquid (n-heptane) to both kind of cotton fabric pores (intra-yarn and inter-yarn). As result, a slower penetration rate of n-heptane occurs and lower value of apparent capillary radius R is obtained. The behaviour of the sample treated

with BTCA only (Co-BTCA) is similar to the functionalized sample in both series of experiments (A and B), so the same conclusions apply to this sample.

The penetration rate curves obtained by thin layer wicking experiment with water as a wicking liquid are shown on Fig. 2 (series A; absolutely dry cotton fabric samples) and Fig. 3 (series B; cotton samples previously conditioned in standard atmosphere). Since the TLW technique is based on the theoretical assumption that the porous solid is considered as a cluster of capillary tubes and the liquid spreads over the capillary walls during the wicking (van Oss et al. 1992; Chibowski and Gonzales-Caballero 1993), this in practice means that the penetration rates obtained depend on the rate of diffusion and the mechanism of liquid adsorption onto the material surface. As it can be seen from measurements of water penetration

rates into both absolutely dry samples (Fig. 2) and previously conditioned samples (Fig. 3), the squared penetration distance x^2 is not a linear function of time t over the whole penetration distance measured (10 cm). All curves (Co-UT, Co-BTCA and Co-PNCS/BTCA) consist of two distinct regions in which linear relationship (x^2 vs. t) can be obtained, which in practice means that penetration of water follows two distinct regimes. As the Washburn equation (2) is only valid in the case of linear x^2 versus t relationship, each linear part of the curve was considered as a separate penetration regime, so the corresponding slopes k were separately calculated (k_1 and k_2, Table 2). Generally, with all samples water penetrates the samples initially more slowly, which is then followed by an increase in the penetration rate ($k_2 < k_1$). Apart from k_1 and k_2, Table 2 presents k_{total} which has been determined for

Fig. 2 Water penetration rate curves obtained by the thin-layer wicking measurements on absolutely dry cotton fabric samples (series A)

Fig. 3 Water penetration rate curves obtained by the thin-layer wicking measurements on cotton fabric samples preconditioned in standard atmosphere (65% R.H.; 20 °C; 24 h) (series B)
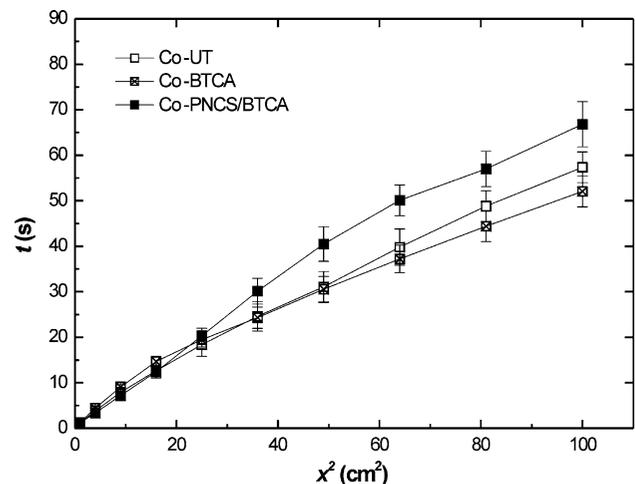
Table 2 Water (demineralised water; pH 6.8) penetration rates, expressed through the slope k estimated from the x^2 versus t plots: (A) absolutely dry cotton fabric samples; (B) cotton fabric samples preconditioned in standard atmosphere (65% R.H.; 20 °C; 24 h)

Sample	A[a]			B[b]		
	k_1	k_2	k_{total}	k_1	k_2	k_{total}
Co-UT	0.85	0.57	0.66	0.71	0.52	0.57
Co-BTCA	0.77	0.37	0.42	0.90	0.44	0.50
Co-PNCS/BTCA	0.92	0.66	0.80	0.83	0.47	0.69

[a] k_1 was determined in the range 0–36 cm^2 for Co-UT, 0–16 cm^2 for Co-BTCA and 0–49 cm^2 for Co-PNCS/BTCA; k_2 was determined in the range 36–100 cm^2 for Co-UT, 16–100 cm^2 for Co-BTCA and 49–100 cm^2 for Co-PNCS/BTCA

[b] k_1 was determined in the range 0–25 cm^2 for Co-UT, 0–16 cm^2 for Co-BTCA and 0–49 cm^2 for Co-PNCS/BTCA; k_2 was determined in the range 25–100 cm^2 for Co-UT, 16–100 cm^2 for Co-BTCA and 49–100 cm^2 for Co-PNCS/BTCA

the whole penetration distance (10 cm), without taking in account the distinction between initial and subsequent penetration regime. Even though the values of k_{total} do not give correct estimation of the slope k as they are determined over a non-linear range, they can be used for simple assessment and comparison between the samples.

Both penetration rate curves (Figs. 2, 3) and corresponding slopes k (Table 2) show that the spreading of water by capillary forces is slower through functionalized cotton (Co-PNCS/BTCA) than through untreated cotton (Co-UT). This behaviour is very obvious with absolutely dry cotton samples (series A, Fig. 2), but similar somewhat less intense trend can be observed on the preconditioned samples (series B, Fig. 3). This result is expected as preconditioned samples already contained certain amount of moisture. It is worthwhile mentioning that BTCA presence obviously improves water spreading (Co-BTCA penetration rate is always increased compared to Co-UT), but this effect is annulled by the PNCS presence in the surface modifying system.

As already mentioned in experimental part, the TLW measurements have been done also with buffer solutions of different pH values (i.e. 3, 6.5 and 10) in order to assess the influence of pH of the wicking liquid. However, when the buffer solution penetration rates in both dry and preconditioned samples were studied, we have seen that pH does not show clear effect on the liquid spreading, since the scattering between the repeated measurements was bigger than the differences obtained between different samples.

The main conclusion that can be drawn from TLW results is that, no matter if the material is dry or preconditioned, the presence of PNCS at the fibre

surface slows down the water penetration rates considerably. This is mainly the consequence of microgel natural ability to absorb water and, as the microgel particles are deposited on the fibre surface, the first contact of the functionalized material with water (at least in the initial stages of material wetting) occurs at the interface created by the microgel particles. This conclusion is in line with the generally known fact that, when water comes in contact with hygroscopic fibres, first adsorption of water present on the fibre surface occurs, followed by the capillary transport to the inner layers.

It is generally known that water soaked by cellulosic material may appear as free molecules and as molecules which are strongly bound energetically with cellulose molecules (i.e. free and bound water). In water-swollen systems, using a simplistic approach, water generally can be divided into *bound water*, subcategorized as being capable of freezing or not, and *unbound water*, subcategorized as being trapped or not (Chaplin 2010). *Bound water* consists of water molecules that are adhering in some way to the surface of polar molecules of the water-swollen system. There are two types of *bound water*: when water molecules are tightly bound (i.e. immobilized) to the polymer molecules, mostly by hydrogen bonding, this is *non-freezing water*; when water molecules are loosely bound to the polymer molecules, by some kind of interaction, this is *freezing water*. On the other hand, *unbound water* (or *free water*), consists of water molecules that do not form hydrogen bonds with the polymer molecules and show great degree of mobility. When present at the material surface, it is called *bulk water* and when present in large pores, cavities or capillaries, it is called *trapped water* (or *capillary*

water). All above mentioned types of water are usually present in hydrated cotton and PNCS microgel, and can be distinguished by the analysis of the results obtained by properly combining several measurement techniques.

The quantity of water, which can be retained by functionalized textile material (Co-PNCS/BTCA) under strictly controlled conditions (pH and T), has been determined by water retention capacity (WRC) measurements (Fig. 4). While the WU and TLW measurements cannot distinguish between *free* and *bound water*, the water retention capacity (WRC) can be used to determine the amount of water present within the cell wall. It gives an estimation of the swelling capabilities of fibres, which is determined by the amount of water retained by water-swollen samples after centrifugation (Zeronian 1984). Hence, the water content measured by water retention capacity— WRC is water that penetrates into the amorphous regions of the fibre causing the fibrous structure to swell. After the excess water is eliminated by the centrifugal action, it can be generally considered that the water retained in the sample consists of following components: *bound water* (both *non-freezing water* and *freezing water* cannot be removed by centrifugation); and certain amount of *free water–capillary water* (held by surface tension in capillary spaces within a fibre and can be partially removed by centrifugation) (Li et al. 2008; Morton and Hearle 1997). The actual amount of *capillary water* removed from cotton fibre depends upon the severity of the centrifugation used in testing and possible obstruction of water diffusion out of the capillaries (e.g. as the consequence of closing the capillaries). In the case of application of crosslinking or film-forming agents to

cotton, the fibre swelling is inhibited and therefore less water is being retained by fibres (Li et al. 2008). The same occurs when BTCA is applied to cotton. It has been shown that the WRC of cotton decreases significantly with an increase in BTCA concentration. The decrease of WRC from 31% (determined on untreated cotton) to 20% for cotton treated with 1% BTCA has been reported (Sauperl et al. 2003).

The results (Fig. 4) show that functionalized cotton (Co-PNCS/BTCA) always possesses increased WRC compared to untreated cotton (Co-UT) no matter at which pH and temperature it is measured. After absorbing the buffer solutions at 25 °C (i.e. below the transition temperature of PNCS), the most pronounced WRC increase can be seen in strong acidic environment (pH 3) (Fig. 4a). This is the result of the synergistic effect of poly-NiPAAm and chitosan, since both polymers are hydrophilic at these conditions. Thus, PNCS microgel particles are in their highly hydrated (i.e. swollen) state, being able to retain a significant amount of water at the cotton fabric surface. At 40 °C (i.e. above the transition temperature of PNCS) in strong acidic environment (pH 3) (Fig. 4b), the difference between Co-UT and Co-PNCS/BTCA becomes smaller due to the antagonistic effect of poly-NiPAAm (hydrophobic) and chitosan (highly hydrophilic). Unexpectedly, a significant increase in WRC was measured for functionalized fabric (Co-PNCS/BTCA), even at the pH values at which chitosan shows limited hydrophilicity (pH 6.5 and pH 10). Based on the synergistic effect of poly-NiPAAm and chitosan, since both polymers are hydrophobic at these conditions (especially at 40 °C and pH 10), it was expected that the sample coated with PNCS microgel will exhibit lower (or at least the
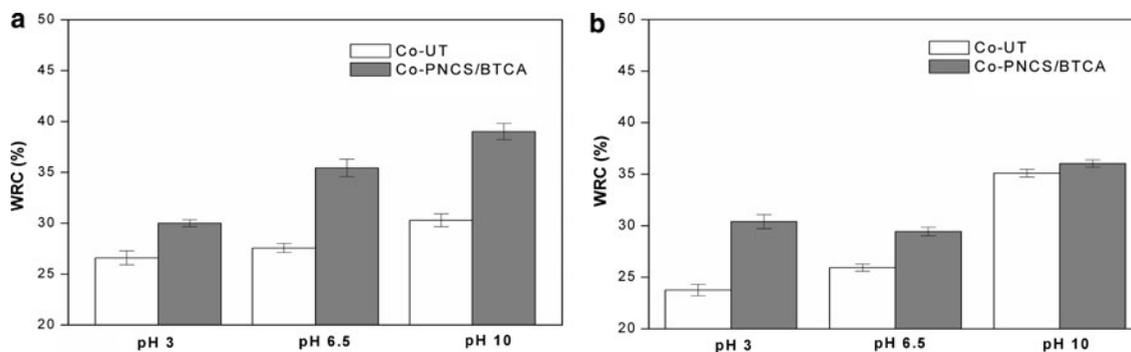
Fig. 4 The influence of pH on water retention capacity (WRC) of Co-UT and Co-PNCS/BTCA at 25 °C (**a**) and 40 °C (**b**)

same) WRC compared to the untreated sample. The explanation for above finding is based on the fact that during preconditioning of functionalized cotton (Co-PNCS/BTCA) in buffer solution (pH 10; 40 °C; 24 h), water is adsorbed by cotton and transported to the inner layers of the fibre by the network of capillaries in a similar way as it occurs with untreated cotton. Since the PNCS microgel covers around 50% of the fibre surface, the presence of collapsed (i.e. hydrophobic) microgel particles does not constrain significantly the penetration of water into amorphous regions of the fibre. When determining WRC, during the centrifugal action, some water held by surface tension in capillary spaces within a fibre (i.e. *capillary water*) is expected to be extracted out of the capillaries by diffusional processes. However, since the surface of the material is covered with hydrophobic microgel particles the mass transfer (i.e. capillary flow) between the fibre bulk and the surrounding is significantly constrained and water molecules remain within the fibre porous structure. Consequently, WRC measured for functionalized cotton (Co-PNCS/BTCA) is increased.

Figure 4 shows that there is a substantial increment of WRC of Co-UT with inreasing pH. The explanation of this behaviour is based on the fact that the cotton cellulose contains abundant hydroxyl groups, one C-6 primary and two C-2 and C-3 secondary on each anhydroglucose unit. These strong polar groups bond water, induce swelling and are generally responsible for the hydrophilic behaviour of the fibre surface. As it has been previously reported (Bellmann et al. 2005), increasing pH produces more negative value of cotton zeta potential, the fact which confirms increased cotton fibre polarity and explains the behaviour of untreated cotton (increased WRC) in alkaline environment.

The hydration of functionalized cotton fabric (Co-PNCS/BTCA), as well as the amount of liquid retained by swelling—WRC, depends both on the intrinsic swelling properties of cotton fibre and on the responsive behaviour of PNCS microgel. Since PNCS microgel is in fact three-dimensional polymer network, its responsive behaviour (i.e. water-absorbing capacity at particular pH and temperature) depends on the balance between the specific behaviour of each component (i.e. chitosan and/or poly-NiPAAm) and specific interactions that exist within the network (crosslinking density, etc.). Hence, the overall effect is

always the combination of swelling and shrinking responses that can occur simultaneously or separately.

Microgels are defined as colloidally stable three-dimensional and hydrophilic polymer networks, whose diameter typically ranges from 100 nm to 1 μm, capable of swelling in water and retaining a large amount of water (approximately 95% by volume) in the swollen state (Pelton 2000). Even in de-swollen state microgels contain approximately 20% of water. Hence, they have special properties and are often referred to be in the intermediate state between a liquid and a solid. As the ability to absorb and to store much water and water solutions makes hydrogels (both as macrogels and as microgels) unique materials for a variety of applications, the state of water in hydrogels has been studied extensively (Muller-Plathe 1998; Capitani et al. 2001; Ostrowska-Czubenko and Gierszewska-Druzynska 2009). PNCS microgel in its hydrated state can contain both *free water* and *bound water*. However, being three-dimensional water swellable cross-linked polymeric network, most of the water molecules present within the microgel particle are regarded as bound (i.e. immobilized) to the polymeric network, either tightly (*non-freezing water*) or loosely (*freezing water*). The amount of *free water* present within the PNCS microgel particle is largely controlled by protonation/deprotonation of the amino groups of chitosan. At low pH values, amino groups of chitosan are protonated, which leads to dissociation of secondary interactions within the polymeric network (such as intramolecular hydrogen bonding), thus allowing more water within the microgel network. On the other hand, when poly-NiPAAm is hydrated, there is ordering of the water molecules that results from hydrogen bonding (at amide groups) which produces reorientation of water molecules around nonpolar areas (at isopropyl groups), resulting in so called hydrophobic effect (Schild 1992). The balance between these two effects is responsible for volume phase transition effect at a lower critical solution temperature (LCST), where the poly-NiPAAm backbone collapses upon itself, thereby expelling water from microgel network. Nevertheless, *free water* within the microgel cannot be easily removed by centrifugal action because it is mostly trapped within the three-dimensional polymeric network.

All above mentioned considerations were confirmed quantitatively by calculating contributions

Table 3 Contribution (C_{WRC}) of the surface incorporated PNCS microgel to water retention capacity of Co-PNCS/BTCA (compared to Co-UT) determined at different pH and temperature

Temperature (°C)	C_{WRC} (%)		
	pH 3	pH 6.5	pH 10
25	27.9	13.5	2.6
40	12.8	28.6	28.8

C_{WRC} due to presence of the microgel on cotton surface (Table 3). Depending on the pH and temperature, the PNCS microgel presence on cotton surface can increase water retention capacity of the functionalized cotton up to ~30%. At 25 °C, water retention is completely regulated by pH responsive behaviour of chitosan, diminishing 10 times from pH 3 to pH 10. At 40 °C, in acidic conditions chitosan still plays the dominant role, enabling increase of 12.8% of water retention capacity. Nevertheless, in weak acidic to alkaline range, the amount of water retained by the functionalized cotton increased for almost 30% as the consequence of constraining the diffusional processes. The obtained C_{WRC} values clearly confirm the stimuli-responsiveness of functionalized cotton.

Apart from centrifugal action, another method for removal of liquid from the material, which is expected to remove both *free water* and *bound water* from the material, is drying. In cotton, drying involves removal of liquid from both fibre lumen and inter-molecular water from cellulose, so the drying capability of cotton is closely related to the macromolecular structure of the fibre. Generally speaking, the structure of wet cotton fabrics consists of a fibre matrix, liquid water, and gaseous phase of water vapour and air. Predicting the drying behaviour

in such a complex system is a difficult task, because the fibre swelling may affect the porosity and the available void space for the liquid and gaseous mixture transport inside the solid matrix (Sousa et al. 2006). After functionalization with PNCS microgel, the system becomes even more complex as it contains at least 50% of the surface covered with microgel particles. Consequently, the evaporation front through which the water vapour is convectively transferred into the airflow is expected to be positioned both at the fibre surface and at the microgel particle surface.

Apart from the wicking ability, moisture regain (MR) plays an important role in the drying capability of the material. It is expected that in the case of similar moisture regain, the material with better wicking ability possesses higher drying rate. The comparison of moisture regain (MR) values, obtained by using thermogravimetric method for different samples (Co-UT, Co-BTCA and Co-PNCS/BTCA), are presented at Fig. 5. Since water is considered as the driving force for the surface incorporated microgel response, the functionalized cotton fabric conditioned at low humidity (50% R.H.; Fig. 5a) does not show the temperature-responsiveness, having at both temperatures the same values of MR as the untreated cotton. When the samples are preconditioned at high humidity (80% R.H.; Fig. 5b), the responsiveness is clearly visible as the difference in MR. In this case the preconditioning parameters (R.H. and T) triggered the PNCS temperature responsiveness which reflects in increase or decrease of MR of the functionalized cotton. Hence, functionalized cotton takes up more or less moisture (when compared to untreated sample) at the temperature below and above the transition point of the PNCS microgel (25 and 40 °C, respectively).
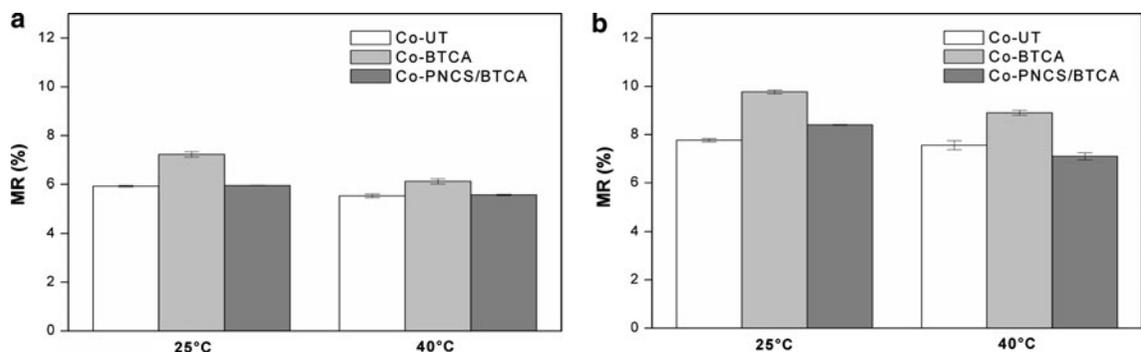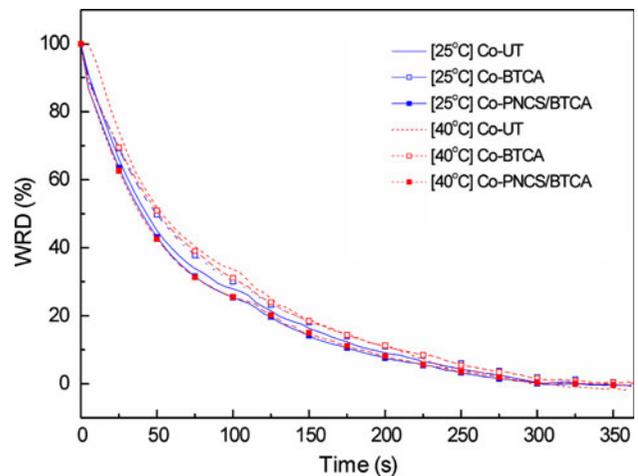

Fig. 5 Moisture regain (%) of Co-UT, Co-BTCA and Co-PNCS/BTCA at 50% R.H. (**a**) and 80% R.H. (**b**)

Fig. 6 Drying curves (*WRD* vs. *t*) of Co-UT, Co-BTCA and Co-PNCS/BTCA preconditioned at 50% R.H. (25 and 40 °C)
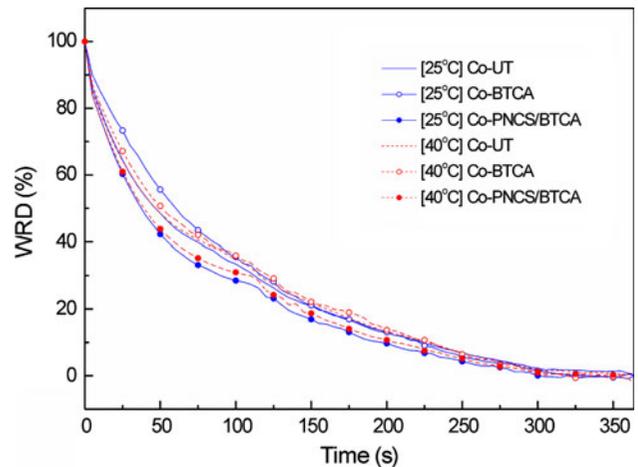
Fig. 7 Drying curves (*WRD* vs. *t*) of Co-UT, Co-BTCA and Co-PNCS/BTCA preconditioned at 80% R.H. (25 and 40 °C)

The moisture liberation of cotton (Co-UT, Co-BTCA and Co-PNCS/BTCA) has been assessed by the drying curves obtained using thermogravimetric method. The comparison of drying curves (*WRD* vs. *t*) for the samples preconditioned at low humidity (50% R.H.) and high humidity (80% R.H.) is presented at Figs. 6 and 7, respectively. It is generally expected that the samples that took up less moisture dry faster. However, in the case of functionalized cotton (Co-PNCS/BTCA), which at low humidity preconditioning (Fig. 5a) shows the same MR as untreated cotton, the *WRD* value during the initial drying stage (up to 1 min of drying time) decreased much more rapidly (Fig. 6). The same trend (but somewhat less pronounced) is observed for the samples preconditioned at high humidity (Fig. 7). These results show that functionalized cotton always dries more rapidly

than regular cotton even if material contains more moisture, like it has been shown for Co-PNCS/BTCA preconditioned at 25 °C and 80% R.H. (Figs. 5b, 7).

The drying curves obviously show the variation of the rates of moisture liberation during drying and, consequently, three stages with different drying rate could be distinguished at the drying curves. During the first minute of drying (initial stage), the large amount of moisture which was present on the surface of the material evaporated quickly. Second stage (medium) is from 1 min of drying to the obvious transition part of the drying curves that could be noticed after ~2 min of drying (i.e. around 70 °C). This medium stage could be attributed to the *free water* present in the material. Since this type of water has a higher level of enthalpy, it gets easily evaporated at lower temperatures.

Table 4 The drying rates determined as the slopes of the drying curves (*WRD* vs. *t*) for the stage 1 (k_1; 0–1 min of drying), stage 2 (k_2; 1–2 min of drying) and stage 3 (k_3; 2–5 min of drying)

Sample	Conditioning parameters		Drying rate		
	RH (%)	T (°C)	k_1	k_2	k_3
Co-UN	50	25	−0.845	−0.264	−0.103
		40	−0.828	−0.253	−0.112
	80	25	−0.988	−0.252	−0.088
		40	−0.980	−0.310	−0.110
Co-BTCA	50	25	−0.778	−0.196	−0.096
		40	−0.820	−0.250	−0.125
	80	25	−0.886	−0.302	−0.087
		40	−0.860	−0.313	−0.093
Co-PNCS/ BTCA	50	25	−0.939	−0.323	−0.112
		40	−0.908	−0.189	−0.100
	80	25	−0.978	−0.246	−0.078
		40	−0.984	−0.225	−0.078

The behaviour of the drying curves with the appearance of 3 stages (initial; medium; final) in which the drying rate may be considered constant, allowed the calculation of separate drying rate constants for each drying stage (i.e. k_1, k_2 and k_3). The results of this calculation are presented in Table 4, where k_1 represents the drying rate in the first minute, k_2 the drying rate from 1 to 2 min (before the transition part), while k_3 represents the drying rate from 2 to 5 min.

The results obtained for k_1 and k_2 show quantitatively that the quantity of water that remains in the material during the initial stage of drying decreases much more rapidly for the functionalized cotton (Co-PNCS/BTCA), at least for the sample preconditioned at 50% R.H. However, in the later stage of drying, when the *free water* is removed from the material, the drying process slows down noticeably without showing significant differences between untreated and functionalized cotton.

By choosing appropriate methods for the assessment of liquid management properties and discussing the results on fundamental level by considering possible interactions between water and the functionalized cotton, it has been confirmed that the redesigning of cotton fabric surface by microgel implements stimuli-responsiveness to cotton. In comparison to existing cotton performance fabrics, the potential

impact of this research lays in making significant progress towards stimuli-responsive cotton, where the important attribute of liquid management will not be present continuously (i.e. passively), but it could be activated "on demand" by sensing the stimuli (temperature, pH and humidity) in the immediate vicinity of the material. Further advantage includes modifying a very thin surface later of the material which, combined with the usage of a regularly industrially available finishing method, should enable textile producers to continue to use traditional cotton processing steps and at the same time achieve added-value that will be able to capture the novel consumer markets.

Conclusion

Several techniques are used to investigate liquid management properties of textile material treated with poly-NiPAAM/chitosan responsive microgel. The results enabled understanding of the interactions between water (moisture vapour and liquid water) and functionalized cotton on a fundamental level, which could help in further optimization and development of such a material. It has been shown that both water uptake capacity and moisture regain of functionalized cotton can be controlled by pH, temperature and humidity of the environment. The spreading of water by capillary forces is slowed down by functionalized cotton fabric, but at the same time the drying capability, at least in the initial stage of drying, is significantly improved. The surface incorporated microgel clearly influences water retention capacity of the material, and its dependence on temperature and pH of the liquid can be easily established. The results obtained show that the functional finishing of cotton with a stimuli-responsive surface modifying system could upgrade the regular textile material quality by providing highly attractive feature of stimuli-responsive liquid management properties.

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