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Effect of stimuli-responsive nano hydrogel finishing on cotton fabric properties

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Cotton fabrics have been prepared with smart properties by functional finishing with stimuli-responsive nano gel. A biopolymer (chitosan) and a synthetic polymer (poly-NiPAAm) have been used for the synthesis of nano gel through semi-batch surfactant-free dispersion polymerization (SB-SFDP) method. The incorporation of nano gel to textile fabrics is achieved by pad-dry-cure procedure, using an aqueous nano gel dispersion and 1,2,3,4-butantetracarboxylic acid as a crosslinking agent. With this cross linking method, it is possible to integrate the nano gel into the cotton fabric's structure with good resistance to washing. The changes in physiological comfort parameters of cotton fabric such as the water vapor transmission rate, air permeability and vertical wicking as well properties such as the thickness, crease recovery angle, yellowness index and washing fastness of cotton fabric after smart finishing have also been assessed. The results show that the application of nano gel as a smart finishing system not only impairs the intrinsic properties of cotton but also improves the common textile quality by providing new features of stimuli-responsiveness.

Keywords: Bioplymer, Cotton fabric, Chitosan , Physiological comfort, Stimuli-responsive nano gel, Smart finishing

1 Introduction

Hydrophilic gels called hydrogels are cross-linked polymeric materials absorbing large amounts of water without dissolving. Softness, smartness, and the capacity to store water make them suitable for many applications [1]. Some of hydrogels may exhibit drastic volume changes in response to external stimuli, such as the temperature, *p*H, electric and magnetic field, solvent quality and light [2].

In recent years, more research developments in the functional finishing of textiles by stimuli-responsive polymeric systems are being made. Researchers have proven that they could apply sub-micron hydrogels on textiles in very thin layers. More surface-to-weight ratios of nano- hydrogels than micro-hydrogels or bulk hydrogels make them more sensitive [3]. Through this new finishing method, the new smart textile can be created, containing fibres that maintains conventional properties (flexibility, mechanical strength and wearing comfort) but shows advanced functionalities and/or environmental responsiveness because of the surface modification of textile with a very thin layer of responsive hydrogel.

The general concept of smart textile refers to textile structure that can sense and construe the stimuli in their environment, and respond appropriately. However, they should not be confused with multi-functional or high-performance textiles that are non-active materials with special properties [4]. Stimuli-responsive hydrogels can be grafted onto the surfaces of cotton (CO), polypropylene (PP) and polyester (PET) fabrics by using different techniques[5]. The most often studied methods are pre-activation of textile by chemical (cationization and anionization) or physical (air, N_2, Ar-plasma or γ-irradiation) techniques or by using cross-linking agents (glutaraldehyde and BTCA) for applying hydrogel particle on non-activated textile substrate[6].

The aim of this study is to investigate the conventional properties (especially physiological comfort properties) of cotton fabric after applying the thin layer of *p*H- temperature dual responsive PNIPAAm/Chitosan nano hydrogels.

2 Materials and Methods

2.1 Materials

NIPAAm monomer (99% pure stabilized, Acros, Belgium), chitosan (medium molecular weight, viscosity 1% solution in 1% acetic acid, 200–800 cps), N,N-methylene bisacrylamide (MBA) &

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ammonium persulphate (APS, Sigma-Aldrich, Germany), BTCA, sodium hypophosphite (SHP, Merck, Germany), nonionic surfactant Adrasil HP (P-836, ADRASA, Spain), and N,N,N',N'-tetra methyl ethylene diamine (TEMED) were purchased from LOBA Chemie, India, Methylene blue (MB, Sigma-Aldrich, Germany) and other chemicals were analytically graded and used without further purification. Cotton fabric (100% plain desized cotton fabric of 98 g/m^2) was supplied by Yazbaf Textile Co, Iran.

2.2 Methods

As mentioned earlier[7], the copolymer of PNIPAAm-co-chitosan was synthesized via SB-SFDP method in a three-neck flask equipped with a reflux condenser and a nitrogen inlet/outlet. A mixture of APS (0.08 g) and TEMED (0.025 g) was dissolved in 15 mL of ionized water, and the mixture was stirred for 30 min under nitrogen at 70°C. NIPAAm (1 g) and MBA (0.02 g) as a crosslinking agent were dissolved in 25mL of ionized water. Chitosan (0.25 g) was dissolved in 100mL of acetic acid solution (0.6 V/V%) and then added dropwise to the initiator solution with a rate of 1.042 mL/min at 70°C for 4 h to complete the polymerization reaction. After cooling, the polymer was purified via dialysis (Cellu-Sep dialysis membrane T3, MWCO 12,000–14,000) against frequent changes of stirring ionized water for 3 days at room temperature to remove any unreacted monomer and other impurities. PNIPAAM/Chitosan (PNCS) dispersion concentration was obtained by freeze-drying of proper volume of dispersion and then weighing the final solid particles[7].

The proper amount of PNCS dispersion (4, 6, 8 % owf) with BTCA (1, 1.5, 2% owf) were used for finishing of cotton fabric. It is worth noting that the ratio of BTCA: SHP was maintained at 2:1. The samples were then dried at 70 ºC for 1 h and subsequently cured at 160 ºC during 4 min. All cotton samples were washed in an aqueous solution containing 2 g/L of nonionic surfactant with a liquor ratio of 1:25 at 60°C for 45 min before and after finishing process.

2.3 Characterization

The responsiveness of modified cotton fabric with PNCS nanogels against *p*H and temperature was proved in our previous research. The water uptake (WU) and water retention capacity (WRC) of modified cotton fabric were investigated for evaluation of smart property of textile against two above-mentioned stimuli[7]. The effect of surface modification on thickness of cotton fabric was assessed according to the ASTM D1777 standard with fabric thickness tester SDL O 34 Shirley (England).

The crease recovery angle of smart fabrics was measured according to the ISO 2313:1972. The yellowness index (YI) of modified fabric was measured according to the ASTM E313 – 10 standard method with GretagMacbeth color-eye 7000a spectrophotometer (Canada).

In order to study the stimuli-responsive finishing effect on physiological comfort parameters of cotton fabric, the water vapor transmission rate (WVT), air permeability and vertical wicking of fabric were assessed according to the standard UNI 4818-26, the standard ASTM D737 respectively.

The water vapor transmission (WVT) of cotton fabrics was measured under two different conditions (25°C & 40°C and relative humidity 65%). It is worth noting that the lower critical solution temperature (LCST) of the temperature responsive component of PNCS nanogels is found at around 32°C (ref. 8), and hence we chose two temperature conditions below and above the LCST. The water vapor transmission rate was expressed in g/m^2 in 24 h using the following equation for three readings samples[8]:

$$\text{WVT rate} = \frac{\Delta m \times 24}{S \times t} \quad \dots (1)$$

where WVT is the water vapor transition rate through the fabric (*g/m^2* day); Δm, the difference between the weights (g); *S*, the fabric area (m^2); and *t*, the time of testing (h). An average of three readings was taken.

To check the durability of the functional finishing, the above-described washing procedure was repeated five times and the add-on of samples was calculated after each washing cycle, using the following equation:

$$\text{Add} - \text{on} = \frac{W_a \times W_t}{W_t} \times 100 \quad \dots (2)$$

where W_t is the weight of dry cotton sample before padding; and W_a , the weight of dry cotton sample after padding. For each characterization, samples were assessed three times and the average value of results was taken.

3 Results and Discussion

3.1 SEM Characterization

As it has been previously published, the incorporation of PNCS microgel onto the cotton surface was confirmed by SEM (Fig. 1). The WU and WRC results confirm that due to the thermo-responsiveness of PNIPAAm and *p*H-responsiveness of chitosan, the smart fabric absorbs more water at temperature below LCST (~32°C) and with acidic *p*H (less than pK_b chitosan ~ 6.5), while it absorbs less water when temperature is above LCST and *p*H is basic. Below LCST, the polymer chains, because of predomination of hydrogen bonding, are hydrophilic, whereas a phase separation occurs above the LCST due to predomination of hydrophobic interactions[9].

At acidic *p*H, amino groups of chitosan are protonated, and therefore PNIPAAm's negative charges (due to the polymerization procedure with APS, the PNIPAAm nano particles have negative charges) are neutralized by chitosan. The counterbalance of nano particles leads to higher hydrophobicity in comparison with their charged state, where electrostatic interactions keep them hydrated and stable[7].

3.2 Influence of Nanohydrogel Finishing on fabric Thickness

The results related to the effect of smart finishing on thickness of modified cotton fabrics are listed in Table 1. As already mentioned, samples 1-3 represent the cotton fabrics modified with 4, 6 and 8 (% owf) PNCS and proper amounts of the BTCA and SHP and control sample is the cotton fabric without any hydrogel finishing on the surface.

The increase in thickness of the modified fabrics in comparison with control fabric indicates the presence of the smart nanogel system on fabric. For the thickness measured at 30ºC (below LCST of PNCS nanogel) and at around standard relative humidity of the environment, the effect of hydrogel presence on fabric thickness at temperature below LCST is more than that measured at the temperature above LSCT. However, the increase in the thickness of fabric samples is not more than 5%.

3.3 Influence of Nanohydrogel Finishing on Fabric CRA

Table 1 shows the CRA results of modified and reference fabrics in warp and weft directions. The results show that all modified samples in comparison with control sample have a little larger CRA. This is due to the involvement of the hydroxyl groups of the cellulose chains in cross- linking reaction with PNCS nanogel and BTCA, and consequently decrease of cellusose chain mobility to create wrinkles. As crease recovery angle of modified fabrics in comparison with control does not show significant changes, it cannot be said that the modified fabrics with nanogel have

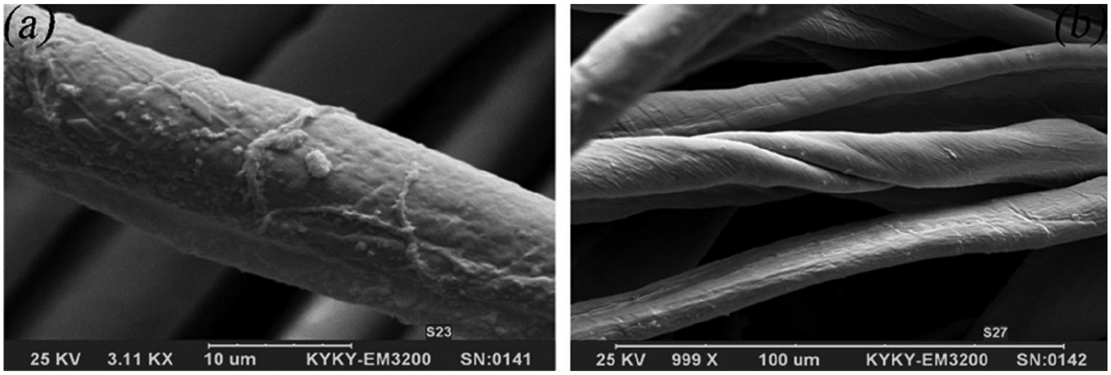

Fig. 1—SEM micrographs of (a) cotton fabric treated with PNCS nano particles, and (b) control fabric.

Table 1—Fabric thickness CRA and the yellowness indices of modified and control cotton fabrics

[30°C and 60% RH]

Sample No.	Increase in thickness, %	Average thickness mm	CRA in direction , deg		Yellowness index
			Weft	Warp	
Control	-	0.248	49.8	50.2	0.94
1	5.242	0.261	57.7	60.6	1.17
2	3.629	0.257	58.3	59.2	1.52
3	4.839	0.260	57.4	61.3	1.41

anti-creasing property.

3.4 Influence of Nanohydrogel Finishing on Fabric Yellowness Index

The yellowness indices of the modified and control cotton fabrics were also measured. The values obtained are the average of three measurements of double-folded (four layers) samples. The results are presented in Table 1.

It is evident that yellowness of cotton fabrics has increased by almost 0.5. Even though visual inspection of the cotton samples does not show sever differences spectrophotometrically it is proven otherwise. Excessive time and temperature of cotton fabric curing may scorch cellulosic fabrics and cause them to become yellow. A temperature of 160-180°C is normally used as the curing temperature for formaldehyde-free durable press agents, such as BTCA, three-propane tricarboxylic acid (TCA) and citric acid (CA). The observed yellowing of the fabric finished with CA combinations is found more severe than that of fabric finished with BTCA combinations[10].

The short curing time and the use of BTCA as a cross-linking agent lead to modification of smart cotton fabrics with minimum yellowness index.

3.5 Influence of Nanohydrogel Finishing on Fabric WVT

Figure 2 shows the results of water vapor transmission rates (WVT) of modified and control cotton fabrics. Water vapor transmission (WVT) through the fabric is possible through following three mechanisms[11]:

(i) Simple diffusion through distances between yarns in fabric structure.
(ii) Capillary transferring from the fibres.
(iii) Diffusion by each fibre.

The WVT results of modified and control cotton fabrics show that the transfer rates of water vapor at 40ºC are more than 25ºC. At temperatures below the LCST of PNCS nanogels, the hydrogel nanoparticles are in swollen state and at temperatures above the LCST, the nanoparticles are shrunk, this leads to increase and decrease in moisture content of the nanoparticles on the surface of the fabric respectively. At 40ºC, the shrinking of nanoparticles allows the water vapor to pass through the fabric easier than under the condition when nanogels are in swelling state.

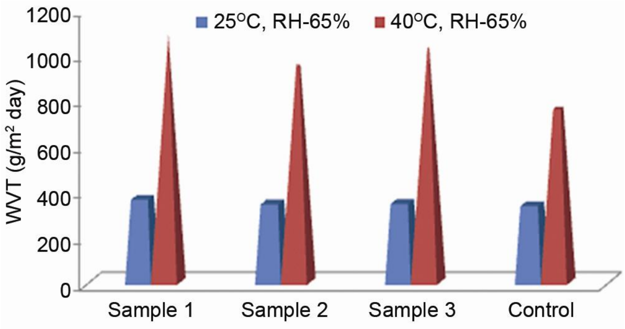

Fig. 2—WVT rates of modified and control cotton fabric [RH 65% , 25°C (<LCST) and 40ºC (>LCST)]

There is no significant difference found between the WVT of modified and control samples at 25ºC. Although the swelling of nanogels at this temperature causes the transmission of less water vapor through the spaces between the fibres (Mechanism 1), but with increasing the moisture content of particles, the probability of water vapor transmission through the surface diffusion and capillary methods (Mechanisms 2 & 3) increases. It seems that these two effects compensate each other and therefore the water vapor transmission rate of the modified textile fabrics at 25ºC is retained near the WVT of control fabric.

3.6 Influence of Nanohydrogel Finishing on Air Permeability of Fabric

Figure 3 shows that the air permeability results of modified and control cotton fabrics. The air permeability of modified fabrics at laboratory conditions (30 ºC, RH 60 %) has fallen slightly compared to the control sample. It may be related to the inherent swelling property of hydrogel nano particle under this condition. On the other hand, as the ambient temperature is below the LCST of PNCS nanoparticles, hydrogel nanoparticles are in swelling form and therefore some parts of spaces between fibres are blocking and the passage of air through the fabric is reduced. However, as the hydrogel is in

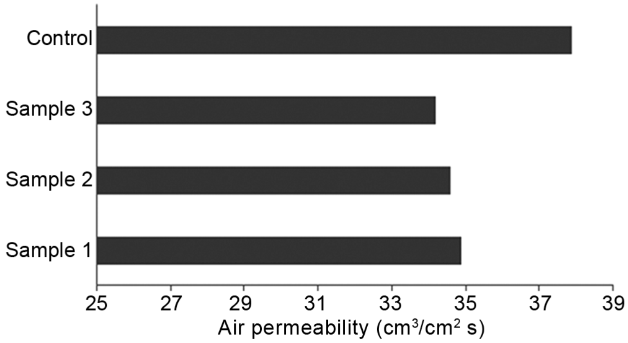

Fig. 3—Air permeability of modified and control cotton fabric [RH 65% , 30°C]

nanoparticle form and amount of this surface modifying system on fabric is not more than 8% (owf), reduction in amount of air permeability through the modified fabrics in comparison with control fabric is not very noticeable.

3.7 Influence of Nanohydrogel Finishing on Fabric Vertical Wicking

The results of vertical wicking behavior of modified and control cotton fabrics are reported in Fig. 4. Factors affecting capillary and the liquid rises in the length of capillary tubes are:

- Contact angle (θ)
- Surface tension (ρ)
- Diameter of the capillary tube (R)[12].

Hydrophilic textiles in comparison with hydrophobic textiles are more able to absorb water. As the contact angle increases when the hydrophilicity of fabric is increased, it causes wetting of more surface area in specific time. Therefore, due to the hydrophilic nature of hydrogel on the surface of the fabric, the wetting time in modified cotton fabric with hydrogel systems are less than in control fabric.

In terms of surface tension's role on fabric wicking, considering that potassium permanganate solution was used in all tests, the surface tension is found similar for both modified and control fabrics. The diameter of capillary tubes is another factor that affects the vertical wicking of fabric. The swelling of the hydrogel system present on the fabric surface can lead to changes in the diameter of the capillary-like tubes (open pores between the fibres) in the fabric.

The fluid speed increases with decreasing the diameter of the capillary tube. As the fabric with a plain weave is used in this study, the structure of fabric is relatively open; closing of pores between the fibres can lead to a significant reduction in the wicking of the fabric. Figure 4 shows that the wicking of modified smart fabric is increased. Therefore, it can be concluded that the increase in hydrophilicity of fabric surface and decrease in diameter of open pores of fabric structure due to nano gel swelling lead to increase in wicking parameter.

3.8 Assesment of Washing Fastness of Modified Fabrics

In order to check the amount of the nanogel finishing system that remains on fabric, washing was done five times on three modified samples according to the mentioned conditions and results are reported in Fig. 5. After five washing process, about 75-80% of the initial hydrogel system has been remained on the fabric surface. This represents the acceptable washing fastness of smart cotton fabric.

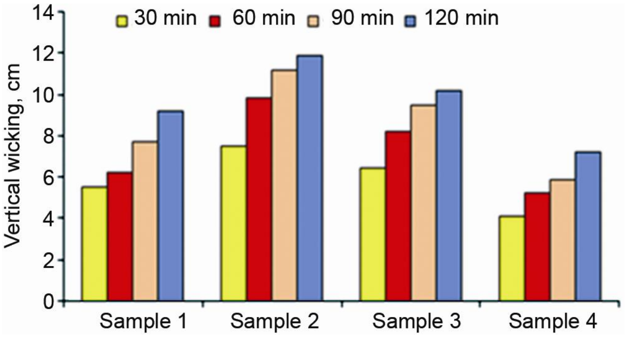

Fig. 4—Vertical wicking of modified and control cotton fabric [RH 65%, 30°C]

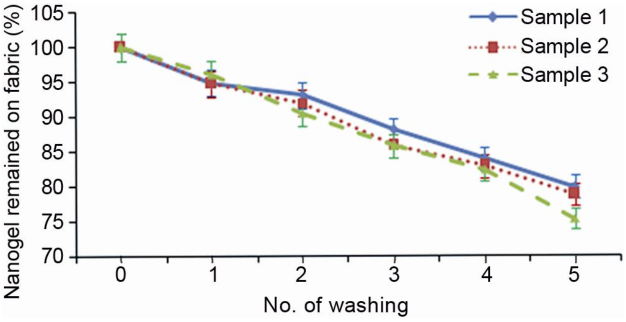

Fig. 5—Wash fastness of modified cotton fabric with smart nanogels after 5 times washing

4 Conclusion

Properties of cotton fabric modified with nanoparticles of PNCS hydrogel show that these fabrics have acquired new smart responsiveness against *p*H and temperature. Due to the small size of nano particles, the thickness of modified fabrics does not show significant difference with control samples. BTCA, used to link the hydrogel nanoparticle to the fabric, does not show crease resistant effect on smart textile. However, because of the involvement of the hydroxyl group in cross-linking process, the CRA of modified fabric has increased in comparison with control sample. Water vapor transition, air permeability and wicking of smart modified cotton fabric are the main properties studied for determining fabric comfort. Surface modification systems containing *p*H and temperature dual-responsive nano hydrogels due to the small size of particles show no negative effects on mentioned comfort parameters and the wicking of modified fabric is increased especially at the temperature above LCST(>32ºC). To conclude, the results confirm that the controlled contraction or expansion of the dual responsive nano particles provides the textile material with smart properties especially in the case of liquid management, and the functional material obtained reacts satisfactorily to the changes in ambient conditions as well as maintains the indivisual comfort. This opens up the possibility of using such smart cotton as an advanced material for sportswear, medical textiles and technical wear.

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