Modification of cotton fabric with temperature/pH responsive hydrogel: influence of particles size

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Abstract. In this study, smart stimuli responsive cotton fabric was tailored by incorporation of temperature and pH responsive hydrogel with two different hydrogel particle size ranges, namely microgel and nanogel. Both hydrogels were based on temperature responsive poly(N-isopropylacrylamide) (poly-NiPAAm) and pH responsive chitosan (PNCS hydrogel). Hydrogels were incorporated onto cotton fabric, in order to study the influence of hydrogel particle size on the stimuli responsive properties, as well as morphological and chemical changes. Regardless of hydrogel particle size, improved air and moisture management activity of the functionalised fabric was achieved. Reduced size of nanogel somewhat influenced swelling ability of the functionalised fabric, although regardless of 4-times smaller concentration of applied hydrogel, comparable responsiveness and great decrease of stiffness was achieved.

1. Introduction

Smart textile materials, which offer improved comfort by interacting with the wearer, can be created by application of stimuli responsive hydrogels. Among them, temperature and/or pH responsive ones are of great importance, since both stimuli, e.g. temperature and pH are of physiological meaning. Thus to assure dual temperature and pH responsiveness, hydrogels based on poly-(N-isopropylacrylamide) (poly-NiPAAm) and chitosan (PNCS hydrogels) can be synthesised. Poly-(N-isopropylacrylamide) (poly-NiPAAm) is the most extensively investigated synthetic temperature responsive polymer, which displays reversible phase transition (hydration-dehydration) at lower critical solution temperature (LCST) in aqueous solution at ~32 °C. Below LCST, the polymer is in coil conformation and is soluble in water. With raising temperature, sharp coil-to-globule transition occurs at the LCST, due to the rather complex polarity of the molecule, hence hydrophobic association is made. Chitosan is polysaccharide, known for its biocompatibility, non-toxicity and pH responsiveness. The latter is based on weak basic moieties (amino groups), attached to a hydrophobic backbone. Upon ionization at pH below ~6.5, amino group protonate and the charge is imparted over the molecule [1, 2]. PNCS hydrogel can absorb and retain moisture when temperatures are below LCST of poly-NiPAAm and below pKa value of chitosan, hence, the hydrogel shrinks and therefore expels water, when temperatures rise above LCST and pH values increases. Thus, when applied on textile, PNCS hydrogel influences moisture content of the fibres as well as air permeability, consequently granting controlled thermo-regulation properties to the fabric [3].
For the chemical modification of textiles, size of the hydrogel particles is of a great importance, since it influences the rate of the volume phase transition \([4, 5]\) as well as handling properties of functionalised fabric, whereas hydrogels of micro- and nanosized particles are used. It is believed that dimensions of the responsive hydrogel particles and the rate of the volume phase transition are inversely proportional \([4]\). Accordingly, smaller particles size reflects in greater control over swelling and shrinking, and thus of releasing of previously incorporated substances, which is ascribed to the greater specific surface area of the hydrogel nanoparticles \([6]\).

To our knowledge, there is no available study on direct comparison of temperature and pH responsiveness of textiles functionalised by the hydrogels of the same composition, but of different particle size. Therefore, in the present research, the influence of the micro- and nano-hydrogel on stimuli responsive properties of surface modifying system, as well as its influence on morphological and handling properties of textile material, was studied. For this purpose, PNCS microgel and PNCS nanogel with proportionate chitosan to poly-NiPAAm ratio were synthesized and applied to cotton fabric.

2. Experimental

2.1 Materials

In this study, 100 % cotton fabric with 165 g/m² mass area was used. For the preparation of the PNCS microgel, chitosan (Chitoclear, Primex, Iceland; DD = 95%; \(\eta = 159\) mPa), glacial acetic acid (Sigma Aldrich), N-isopropylacrylamide (NiPAAm) (Sigma Aldrich), N,N-methylenbisacrylamide (MBA) (Sigma Aldrich) and ammonium persulfate (APS) (Sigma Aldrich), were used. For the preparation of PNCS nanogel, N′-tetramethylethylenediamine (TEMED) (Sigma Aldrich) was added to synthesis.

2.2 Hydrogel synthesis, characterisation and application

PNCS microgel (PNCS_M) was synthesised as reported by Tourrette \([2]\) and synthesis of the PNCS nanogel (PNCS_N) was conducted according to slightly modified method reported by Bashari \([5]\), with preserving chitosan to poly-NiPAAm ratio the same as for the PNCS microgel.

The particle size of dispersed microgel (PNCS_M sample) and nanogel (PNCS_N sample), in correspondence with changes in temperature and pH were determined with dynamic light scattering (DLS) analysis, on Zetasizer Nano S (Malvern, UK), equipped with 4mW He-Ne laser operating at wavelength 633 nm and an avalanche photodiode detector. Scattering light was detected at an angle of 173°. Microgel was diluted 500 times and nanogel 50 times. Particle size was determined at pH 7 and temperatures ranging from 20- to 40°C in 5°C intervals and at pH 3 and 10 at 20- and 40°C. To achieve pH 3 and 10, salts based buffer solutions were used for diluting the samples. 60 µL of sample was used for each measurement, results are an average of 3 measurements.

PNCS microgel (sample CO_PNCS_M) and PNCS nanogel (sample CO_PNCS_N) were applied to cotton fabric using pad-dry procedure with 80% wet pick-up. Coated samples were dried for 5 minutes at 80°C. Sample code for untreated cotton sample is UN_CO.

2.3 Analysis and measurements

Morphological changes of studied samples were determined using scanning electron microscope FE-SEM Zeiss SUPRA 35VP, at an accelerating voltage of 1 kV. Before observation, the samples were coated with Pd.

Temperature responsiveness of the samples was assessed by measuring moisture content using a Moisture analyser MLB-C (Kern & SOHN GmbH, Germany). Studied samples were pre-conditioned at 65±2% relative humidity at 20 and 40°C for 24 h, before they were put in a moisture analyser and dried at 60°C until the constant mass. Moisture content \((MC)\) was determined by following equation:

\[
MC = \left(\frac{m_0 - m_f}{m_o}\right) \times 100\%.
\]

where \(m_o\) denote the initial mass of the pre-conditioned sample and \(m_f\) the final mass of the sample after drying. \(MC\) was reported as mean values of ten measurements. From the results of \(MC\), contribution
of functional coating to the moisture content of cotton fibres ($C_{MC}$), was determined by following equation:

$$C_{MC} = \frac{M_{CF} - M_{CU}}{M_{CU}} \times 100 \% ,$$

(2)

where $M_{CF}$ is $MC$ of functionalized finished sample and $M_{CU}$, $MC$ of unfinished cotton sample.

Water vapour permeability was determined according to the standard method UNI 4818-26, and performed at 65% relative humidity either at 20 or at 40°C. Water vapour transmission rate ($WVTR$) was calculated by next equation:

$$WVTR = \left( \frac{\Delta m \times 24}{S \times t} \right) [g/m^2 \cdot day],$$

(3)

where $\Delta m$ corresponds to the change of mass [g], $S$ is the testing area of the fabric sample [m$^2$] (actual value 70.68 mm$^2$) and $t$ is the time of testing [h] (actual value 24 h). Results represent an average of seven measurements.

In order to evaluate dual, pH and temperature responsiveness of the PNCS microgel and nanogel, the samples of known mass were immersed in buffer solutions of different pH, i.e. 3, 6.5 and 10 for 30 minutes, at two different temperatures, i.e. 20 and 40°C. Afterwards, the samples were taken from the buffers and weighed. Water uptake (WU) was determined by following equation:

$$WU = \left( \frac{m_w - m_o}{m_o} \right) \times 100 \%$$

(4)

where $m_w$ is the weight of the sample taking up water [g] and $m_o$ is the initial weight of sample [g]. WU are reported as mean values of ten measurements.

Stiffness of finished and unfinished samples was determined according to standard ASTM D1388-64. Stiffness in warp direction was determined, using following equation:

$$U_{warp} = T \times \left( \frac{l_{warp}}{2} \right) \times 0.1 [mg \ cm],$$

(5)

where $U_{warp}$ represents stiffness in warp direction [mg cm], $T$ is mass area [g/m$^2$], $l_{warp}$ is bending length in warp direction [cm].

3. Results and discussion

3.1 Hydrogels characterisation

DLS analysis was employed in order to investigate particle size of the studied hydrogels in dependence of changes in temperature and pH of the intermediate environment. Swelling and deswelling ability of PNCS_M and PNCS_N hydrogel particles triggered by the change of temperature and pH is shown in Fig. 1a. Faster and more dramatic response of PNCS_N hydrogel in comparison to the PNCS_M was observed. Namely, when in fully swelled phase (20°C and pH 3) the estimated particle size in the nanogel was of 501 nm, which reduced for 84% by the increase of temperature and pH, when particles where in their full dehydrated phase. In this case, the size of the nanoparticles ranged 87 nm. In the case of PNCS_M particle size of 699 nm was determined at conditions dictating their fully swollen phase. When triggering their deswelling, rapid agglomeration of the microgel particles took place. Dehydrated particles tend to form large clusters, enabling determination of their size at 40°C and pH 10. Nevertheless, when in their partially dehydrated phase, i.e. 40°C and pH 6.5, reduction of particles size up to 405 nm was obtained. In addition, estimation of particle size triggered by only gradual change of the temperature was made (Fig. 1b). In this case a broad LCST of both hydrogels was obtained, ranging from 25 to 35°C for PNCS_M and 25 to 40°C for PNCS_N.
Figure 1. Hydrodynamic diameters of PNCS_M (full line) and PNCS_N (dashed line) as a function of temperature at pH 7 (20, 25, 30, 35 and 40 °C) and pH value (pH 3, 6.5 and 10).

3.2 Morphological and chemical properties

Morphological changes of the functionalised samples were examined by SEM (Fig. 2). PNCS microgel particles appeared in the form of unevenly scattered bulges, of 300–500 nm in diameter on the surface of the CO_PNCS_M sample, which is in agreement with DLS data. Despite high magnifications, the presence of the PNCS nanogel particles could not be observed on the surface of the CO_PNCS_N sample, hence it can be inferred that nanogel must have formed a film, which appeared to smoothened the fibre surface.

Figure 2. SEM images of a, UN_CO, b, CO_PNCS_M and c, CO_PNCS_N at 20 000 times magnification.

3.3 Temperature responsiveness

To study temperature responsiveness of the samples, moisture content (MC) and water vapour transition rate (WVTR) analysis were made at 20°C and 40°C (Fig. 3). While both samples exhibited greater MC at 20°C, reflecting in almost 40% increase in comparison to the untreated cotton fabric, the latter strongly decreased at 40°C (Fig 3a). Decreased MC was less pronounced in the case of the CO_PNCS_N sample, which can be ascribed to the smaller deposition of the nanogel as in the case of microgel application. This assumption was further supported by the add-on determination, which amounted 10.4% in the case of CO_PNCS_M sample and 2.5% in the case of CO_PNCS_N sample. Thus, at 40°C the hydrophilic character of cotton fibres must have hindered the hydrophobic nature of the PNCS nanogel particles, reflecting in only 20% decrease of the MC. WVTR analysis (Fig. 3b) showed greater air retention at lower temperatures and increased air release at higher temperatures of CO_PNCS_M sample in comparison to the CO_PNCS_N sample. Namely, application of nanogel contributed only to the release of water vapour at 40°C, while at swollen state at room temperature WVTR was practically the same as
for the untreated sample. Most likely nano-sized particles of the PNCS_N hydrogel could not close the pores between the fibres, due to film-like distribution of applied nanogel on the fibre surface, thus impairing water vapour retention.

![Graph](image)

**Figure 3.** a. Contribution (C_MC) of the PNCS microgel and nanogel application to the moisture content and b. water vapour transition rate (WVTR) of studied samples, at temperatures of 20- and 40°C.

### 3.4 Temperature and pH responsiveness

*WU* measurements were used to determine dual temperature and pH responsiveness derived from both poly-NiPAAm and chitosan in the PNCS micro- and nanogel. It can be seen from Fig. 4 that both functionalised cotton samples exhibited simultaneous temperature and pH responsiveness, since rising the temperature and pH caused overall decrease of water sorption. Thus, at pH 3 and 20°C, when both poly-NiPAAm and chitosan were hydrophilic and hydrogel particles exist in their swollen state, the highest *WU* was observed in the case of CO_PNCS_M sample. On the other hand, the lowest *WU* was found at 40°C and pH 10, when both components of the PNCS hydrogels were in their hydrophobic state. At this conditions CO_PNCS_N displayed the smallest *WU*, despite 4-times smaller ad-on in comparison to that obtained in the case of the microgel application.

![Graph](image)

**Figure 4.** Water uptake (*WU*) of the studied samples obtained at pH 3, 6.5 and 10, at a, 20°C and b, 40°C.

### 3.5 Handling properties

In Fig. 5 the results of the stiffness of the studied samples are shown. Using the same application procedure, deposition of the microgel influenced 8.8-times higher stiffness of the CO_PNCS_M sample in comparison to the untreated cotton. On the other hand, the nano-sized PNCS particles exhibited lesser
impact on handling properties of the CO_PNCS_N sample, since the stiffness increased by only 2.6-times higher. However, smaller impact on the handling properties of the nanogel in comparison to the microgel, can not only be ascribed to the smaller particles of the PNCS_N, but also to the smaller add-on obtained in the application process, despite the same conditions used.

Figure 5. Stiffness of the studied cotton samples determined in direction of warp yarns ($U_{\text{warp}}$).

4. Conclusion

Regardless of the particle size PNCS hydrogel granted smart temperature and pH responsiveness to the cotton fabric. Irrespective of the impaired water expulsion of the nanogel particles (sample CO_PNCS_N) at conditions where poly-NiPAAm was in hydrophobic phase and smaller water absorption at 20°C and pH 3, reducing the hydrogel particle size from micro to nano level enabled several advantages: (i) 4-times smaller deposition of the hydrogel on the surface of cotton fibres along with (ii) preserved moisture absorption capacity at temperature below the LCST of poly-NiPAAm and (iii) greater water repulsion at 40 °C and pH 10, and lastly (iv) strong increase of handling properties of the functionalised cotton sample.

5. References

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