

# Application of temperature and pH responsive microhydrogels for functional finishing of cotton fabric

D. Jocić\*, A. Tourrette, P. Glampedaki and M. M. C. G. Warmoeskerken

This paper discusses the developing of an innovative strategy for functional finishing of cotton by application of surface modifying systems based on stimuli responsive microparticulate hydrogels. Dual responsive hydrogels in the microscale were prepared using a temperature responsive synthetic polymer (poly-NiPAAm) and a pH responsive biopolymer (chitosan). The physico-chemical characterisation and the stimuli responsiveness of the microparticulate systems have been investigated by microscopy and spectrophotometric techniques, and dynamic light scattering. In an attempt to enhance the incorporation of microparticulate hydrogel to cotton surface, carboxymethylation and aminisation methods for cotton activation have been assessed. Surface modified textile material with incorporated microparticles has been characterised by SEM and XPS techniques in order to determine surface morphology and chemical structure. The capability of the material to respond to different stimuli (pH, temperature, humidity) was studied through swelling/shrinking or hydration/dehydration kinetics and equilibrium using a gravimetric method.

**Keywords:** Cotton, Stimuli responsive microgel, Poly-NiPAAm, Chitosan, Hydrogel

## Introduction

The future development of textile materials is based on the need for research driven engineered products with new advanced functionalities. This need has generated many opportunities for the application of innovative chemical finishes to produce high added value textiles that provide consumers with greater levels of comfort, safety, aesthetics and functional performance.<sup>1</sup>

One of the promising strategies to reach the goal of producing high added value textiles involves functional finishing by incorporation of surface modifying systems based on stimuli responsive polymers. Through this approach, the new added value textile material can be created containing fibres that maintain advantageous conventional properties (e.g. mechanical strength, flexibility and wear comfort) but with advanced functionalities and/or environmental responsiveness implemented by the modification of a very thin surface layer of the material.

Currently, the most encouraging option for obtaining efficient surface modifying systems comprises the use of hydrogels based on stimuli responsive polymers. Hydrogels are defined as water swollen three-dimensional networks based on the interactions of hydrophilic

polymer chains in which retained water constitutes at least 20% of the weight. They exhibit specific volume phase transition (swelling and shrinking) properties which can be triggered by various stimuli. Hydrogels responsive to temperature and pH have been the most widely studied systems since these two factors have a physiological significance. Versatile dual responsive hydrogels have been reported mainly for biomedical applications and a number of reviews coming up in this area in recent times address the latest developments.<sup>2-4</sup>

Owing to the need for biocompatibility and biodegradability, biopolymer based hydrogels are currently of great interest. Such hydrogels can be prepared by combining a thermoresponsive synthetic polymer with a natural based polymeric component resulting in dual (pH and temperature) responsive hydrogel systems.<sup>5</sup> Among synthetic polymers, poly(N-isopropylacrylamide) (poly-NiPAAm) is the most intensively investigated thermoresponsive polymer which exhibits a volume phase transition (i.e. hydration–dehydration due to side chain reconfiguration) in response to even slight temperature changes. The coil to globule transition, which is a consequence of the rather complex polarity of the molecule, occurs at a temperature around 32°C, named lower critical solution temperature (LCST).<sup>6</sup> 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). If the physical

Engineering of Fibrous Smart Materials (EFSM), Faculty of Engineering Technology (CTW), University of Twente, Drienerlolaan 5, PO Box 217, 7500AE Enschede, The Netherlands

\*Corresponding author, email d.jocic@utwente.nl

form of the polymer is hydrogel, water is expelled from its interior, thus causing a drastic decrease in volume. It is particularly advantageous that the LCST value of poly-NiPAAm solutions and gels falls between human body temperature and room temperature, this being the main reason why this polymer has been widely investigated in the fields of biotechnology, bioengineering and medicine.<sup>7</sup>

Among the wide choice of natural polymers, polysaccharides are a good option for combining them with synthetic thermoresponsive polymers. Currently, the most interesting polysaccharide is chitosan, i.e. poly-( $\beta$ (1-4)-2-amino-2-deoxy-D-glucopyranose, which is produced through the N-deacetylation of chitin.<sup>8,9</sup> Chitosan is a typical pH sensitive polymer which responds to the changes in the pH of the surrounding medium by protonation/deprotonation that imparts charges on its amino groups. The pH induced phase transition results in varying dimensions of the hydrogel (swelling and deswelling). Furthermore, the interesting intrinsic properties of chitosan are its biodegradability, antibacterial activity and biocompatibility, thanks to which this biopolymer attracts currently a great deal of interest for biomedical applications,<sup>10,11</sup> especially for wound dressings<sup>12</sup> and drug delivery.<sup>13</sup> In textile material finishing, chitosan has been applied successfully for modifying the surface topography and thus controlling the surface related properties of the fibre. It improves the dye coverage of immature fibres in dyeing of cotton;<sup>14</sup> it can be successfully used as a thickener and binder in the pigment printing of cotton;<sup>15</sup> it can be used as a shrink resistance agent in wool finishing<sup>16</sup> and as an agent for improving the dyeability of wool.<sup>17,18</sup>

In recent times, an increasing amount of research is being carried out on functional finishing of textile materials by incorporating stimuli responsive polymeric systems.<sup>19,20</sup> However, depending on the application field, there are two different approaches for the incorporation of responsive hydrogels to polymeric or textile materials. In the biomedical field, the actual purpose of hydrogel incorporation to other materials is to improve the mechanical properties of the hydrogel.<sup>21,22</sup> This is necessary because hydrogels with high water content exhibit extremely low mechanical strength, which limits their application. In the development of most biomedical materials, biocompatibility and efficiency are the main issues, and polymeric or textile materials serve in this case only for reinforcement. Therefore, there is no issue of limiting thickness of the incorporated layer, which could influence the positive properties of the supporting material.

In the field of material technology, a rather different approach exists. Hydrogel incorporation to other materials is employed with the purpose of obtaining advanced materials with responsive properties. Since these materials are aimed as consumer products, the characteristics of the material in all stages of production and use, such as performance in the textile processing chain, as well as comfort, safety and durability of the final product, are of ultimate importance. Moreover, the issue of maintaining the positive properties of the original textile material is also considered as an additional requirement. The main challenges in achieving this goal lay in: finding the adequate form of effective hydrogel (bulk, nano- or microparticles, etc.);

efficient surface modification of the textile material (surface activation) for hydrogel incorporation; integrating hydrogel into fabric structure with sufficient durability while still retaining the effectiveness of the hydrogel (overall responsiveness of the new material). This actually means that surface modifying systems, after their incorporation to the textile material, must exhibit their responsive properties without screening the textile's regular performance.

Taking into consideration this requirement, it can be suggested that modern surface modifying systems for textile materials are expected to be based on micro- or nanosized hydrogels. The submicron particle size of hydrogels enables their incorporation to textile material surface in a very thin layer. Moreover, this polymeric form possesses increased surface area per unit mass and thus significantly improved response times in comparison to macroscopic (bulk) hydrogels.<sup>23,24</sup> Microgels usually achieve equilibrium swelling in less than a second when the temperature is changed, whereas macrogels can take a very long time because shrinking of the exterior layer prevents water transport to the interior.

Very few attempts to improve properties of cellulosic fibres by incorporation of responsive polymers and/or their hydrogels have been reported in literature. Karlsson *et al.*<sup>25</sup> reported on ozone induced graft polymerisation of hydrophilic polymers that impart better absorption properties to cotton. Xie and Hiesh<sup>26</sup> used the cellulose activation by ceric ion treatment which was followed by graft polymerisation procedure to bond thermosensitive poly-NiPAAm hydrogels to cotton non-woven. Hu *et al.*<sup>27</sup> reported the graft polymerisation of NiPAAm and PU anionomer onto the surface of cotton non-woven fabrics initiated by ammonium persulphate. The grafted fabric was capable of responding to pH and temperature.

All the above mentioned examples were realised by the grafting of synthetic responsive polymers on cellulosic fibre substrate. However, Ye *et al.*<sup>28</sup> recently reported on a conventional application method (pad-dry-cure) of novel antibacterial coating for cotton fabrics based on the incorporation of core-shell particles made of poly(*n*-butyl acrylate) and chitosan.

In this work, the authors present the innovative strategy of a simple batch treatment procedure (without grafting) for incorporating dual responsive microparticulate hydrogel (which is based partially on a biopolymer) to the previously activated cotton fibre. The following aspects are reported: the synthesis and characterisation of a microhydrogel using a temperature responsive polymer (poly-NiPAAm) and a pH responsive natural polymer (chitosan); the possibility of incorporating microparticulate hydrogel to cotton previously modified by introducing anionic (carboxymethyl) and cationic (amine) groups; the assessment of pH, temperature and humidity responsiveness of the surface modified cotton material. The aim of this research is to upgrade the cotton fabric quality and provide new and interesting features by functional finishing with responsive microgels.

## Experimental

### Materials

The N-isopropylacrylamide (NiPAAm) monomer (Acros Organics, Belgium) was recrystallised from

hexane before use. Chitosan (Chitoclear, DD=95%,  $\eta=714$  mPa s) was purchased from Primex (Iceland). Cotton fabric (100% cotton plain fabric of  $105 \text{ g m}^{-2}$  weight per unit area) was supplied by Vlisco (The Netherlands). The non-ionic detergent Tanaterge EP5071 was supplied by Tanatex (The Netherlands). Cross-linker [N,N-methylenebisacrylamide (BIS)], initiator [ammonium persulphate (APS)], sodium hydrosulfite ( $\text{Na}_2\text{S}_2\text{O}_4$ , 85%), monochloroacetic acid (CAA), sodium carbonate, caustic soda (NaOH) and other chemicals were of analytical grade and they were used without further purification. The reactive dye Remazol Black B (CI Reactive Black 5) was supplied by Sigma.

### Preparation of poly-NiPAAm/chitosan microparticulate system

The micro-particles of poly-NiPAAm/chitosan hydrogel (PN/CS) were prepared by a surfactant free dispersion copolymerisation method according to the procedure reported by Lee *et al.*<sup>29,30</sup> Chitosan solution was prepared by dissolving 1.4 g chitosan in 280 mL distilled water containing 3 mL glacial acetic acid (stirred for 24 h at room temperature). The NiPAAm/chitosan copolymerisation was carried out in a reactor: three neck round bottom flask placed in a heated bath, equipped with a condenser, stirrer and nitrogen inlet (for maintaining nitrogen atmosphere during the reaction). Reactor was filled with chitosan solution and degassed with nitrogen during 30 min at room temperature. Subsequently, NiPAAm (7 g) and BIS (0.21 g) were added with vigorous stirring, the temperature was raised to 50°C and then APS (0.7 g) was added to initiate the polymerisation. The reaction medium turned turbid after 5 min and the reaction was allowed to proceed for 3 h at 50°C. In order to remove the unreacted monomer and oligomeric impurities, the reaction solution was dialysed (4 spectra/Por, Fisher Scientific) during one week against deionised water.

### Cotton fabric surface functionalisation

The aim of cotton fabric functionalisation was to impart ionic character to cotton cellulose in order to facilitate the incorporation of microparticulate system. Among several possibilities for producing ionic active sites on cotton surface, two methods have been chosen for this investigation: anionic cotton has been produced by reaction with CAA to give partially carboxymethylated cellulose (carboxymethylation); cationic cotton has been produced by dyeing with reactive dye and subsequent reductive cleavage of the dye attached (aminisation).

#### Carboxymethylation

Generally, the carboxymethylation procedure consists of impregnating cotton fabric with a strong solution of caustic soda, which is followed by a treatment with an aqueous solution of sodium salt of CAA.<sup>31,32</sup> As the first step, cotton fabric was soaked in 20%NaOH aqueous solution for 10 min at room temperature, then squeezed (in laboratory padder) to a wet pick-up of 110% and dried for 40 min at 60°C. As the second step, cotton fabric was immersed for 5 min in a solution of reactive anion (1.5M aqueous solution of CAA neutralised by equimolar quantity of  $\text{Na}_2\text{CO}_3$ ), then padded to a wet pick-up of 140%, sealed in polyethylene bag and held for 60 min at 80°C. Finally, the carboxymethylated cotton

fabric sample (CmC) was washed several times in deionised water before being dried at room temperature.

#### Aminisation

The aminisation procedure involves covalent attachment of reactive dye (step 1) to cotton fabric and subsequent reductive cleavage of the dye to free amine (step 2).<sup>33</sup> Thus, aromatic amines are formed on cotton by chemical reduction of covalently attached reactive dye molecules. Dyeing (step 1) was carried out at liquor to goods ratio of 20:1. After the dyebath was set out to the calculated volume, the dye (Reactive Black 5, 2.0%owf), electrolyte ( $\text{NaCl}$ ,  $50 \text{ g L}^{-1}$ ) and cotton fabric were added to the dyebath. The dyebath was held at 40°C for 15 min for the exhaustion. Then, sodium carbonate ( $5 \text{ g L}^{-1}$ ) was added and the temperature increased to 50°C over a 10 min period, when sodium hydroxide (1M,  $10 \text{ mL L}^{-1}$ ) was added and a fixation cycle was run for 45 min. At the end of the fixation cycle, the fabric was removed and rinsed in warm water to remove any salt remained. Then, the sample was treated in a soaping bath (50 L) containing non-ionic detergent Tanaterge EP5071 ( $1.5 \text{ g L}^{-1}$ ) for 20 min at boiling temperature to remove any unfixated dye. After soaping the sample was rinsed with water and dried in air. Reductive cleavage of covalently fixed dye (step 2) was performed in a solution of  $8 \text{ g L}^{-1}$  sodium hydrosulphite ( $\text{Na}_2\text{S}_2\text{O}_4$ ) at 70°C for 2 h. Aminised cotton fabric (AmC) was then again washed in the soaping solution ( $1.5 \text{ g L}^{-1}$  Tanaterge EP5071; boiling temperature; 20 min), rinsed and dried in air.

### Incorporation of microparticulate system to functionalised cotton fabric

Batch method was used for the incorporation of hydrogel microparticles (PN/CS) to untreated (UnC) and functionalised (CmC and AmC) cotton fabrics. A cotton fabric sample of dimensions  $24 \times 24 \text{ cm}$  ( $\sim 6 \text{ g}$ ) was treated in a diluted aqueous suspension ( $1.62 \text{ g L}^{-1}$ ) of microhydrogel (PN/CS) at liquor to goods ratio of 20:1 for 2 h at room temperature with continuous stirring. Samples were then padded with a wet pick-up 80%, dried in air at room temperature and stored under vacuum before characterisation.

### Characterisation methods

The particle size and zeta-potential of the PN/CS microparticles were determined using Zetasizer Nano ZS system (Malvern, UK). A dialysed PN/CS microparticle suspension was diluted approximately 100 times with corresponding buffer solutions (pH 2, 4, 5, 7, 9) for dynamic light scattering (DLS) measurement. Measurements were performed at 25°C. The sample temperature was maintained by a built-in thermostat sample holder with an accuracy of 0.01°C. Particle size results were collected with DTS (nano) software (version 5.0) provided with the instrument. Each sample was measured three times and the average was used as the sample mean diameter.

Temperature responsiveness of the microgel suspension ( $1.42 \text{ g L}^{-1}$ ) was assessed by spectrophotometric method using Cary 100 Bis (Varian, USA) spectrophotometer equipped with a temperature controller. The cuvette was equipped with continuous stirring. The absorbance (at 600 nm) was recorded for temperatures

between 20°C and 40°C ( $\pm 0.2^\circ\text{C}$ ) and in various buffer solutions (pH 2, 4, 5, 7, 9).

The morphology of air dried microgel particles and surface characterisation of cotton samples were determined by scanning electron microscopy. The field emission gun SEM 1550 HRSEM (Zeiss, Germany), operating at 5 kV, has been used. The microgels were deposited onto cleaned silicon oxide substrates before the measurements. Cotton fabric samples were analysed without any prior preparation.

In order to investigate the surface chemical changes of functionalised cotton and cotton with incorporated microhydrogels, X-ray photoelectronic spectroscopy (XPS) analysis was performed using a PHI Quantera Scanning ESCA Microprobe spectrometer (Physical Electronics, USA). The samples were irradiated with a monochromatic Al  $K_{\alpha}$  X-rays (1486.6 eV) using an X-ray spot size with a diameter of 100  $\mu\text{m}$  and a power of 25 W. The standard take-off angle used for analysis was 45°, producing a maximum analysis depth in the range of 3–5 nm. Survey spectra were recorded with pass energy of 224 eV (step size: 0.8 eV), from which the chemical composition the surface was determined. All binding energy values calculated were relative to the main O 1s peak at 532.9 eV.

Liquid porosimetry was used as a procedure for determining the pore volume distribution (PVD) within a cotton fabric sample before and after incorporation of PN/CS microparticles. An autoporosimeter (TRI, USA) was used to measure the intra- and inter yarn pore size distribution in the fabric based on the principles described by Miller and Tyomkin<sup>34</sup> and Rebenfeld *et al.*<sup>35</sup> The PVD typical data output for a single incremental liquid extrusion run was a cumulative curve that represented the amount of liquid remaining in the pores (as the pressure increased). The first derivative of this curve as a function of pore size becomes the PVD plot, showing the fraction of the free volume of cotton fabric sample made up of pores of each indicated size  $R_{\text{eff}}$ . The total wetting liquid ( $\cos\theta=1$ ) used in this study was 0.1% solution of Triton X-100 in double distilled water. Measurements were performed in receding mode in the range of 1–800  $\mu\text{m}$  on three swatches 2.5 cm (weft)  $\times$  3.5 cm (warp) cut randomly from a fabric sample. The PVD taken into consideration was obtained on the basis of averaging of PVDs obtained in this way.

In order to determine pH responsiveness of the cotton material with incorporated microhydrogels, swelling properties were assessed by a gravimetric method. Fabric samples of dimension 4  $\times$  4 cm were immersed in water (pH 7), hydrochloric acid solution (pH 5) and sodium hydroxide solution (pH 9) until the swelling equilibrium was attained (1 h, at room temperature). The weight of the wet sample was determined after removing the surface water by blotting with filter paper. The swelling percentage  $S$  was calculated using the equation (1)

$$S = \frac{m_S - m_D}{m_D} \quad (1)$$

where  $m_S$  is the mass of the sample in equilibrium swelling and  $m_D$  is the initial mass of dry sample.

In order to determine the response of the surface modified cotton samples to temperature and humidity, a climatic chamber SM-1-0-3800 (Thermotron, USA) was

used. Fabric samples of dimensions 4  $\times$  4 cm were put in the climatic chamber under conditions of constant temperature (25 and 40°C) and humidity (60, 70, 80 and 90% RH) for 1 h. Then the samples were weighed with an analytical balance. For calculating moisture regain  $R$  (moisture added to a dry fibre) of the samples, equation (2) was used

$$R = \frac{m_H - m_D}{m_D} \quad (2)$$

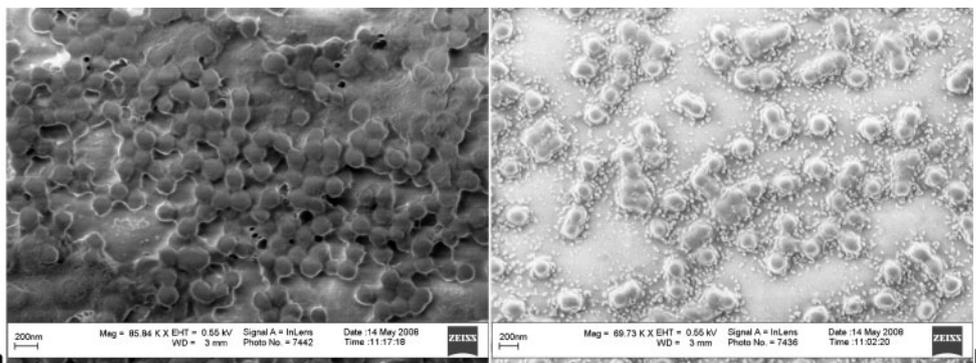
where  $m_H$  is the mass of sample after humidity exposure and  $m_D$  is the initial mass of dry sample.

## Results and discussion

The relatively simple procedure used for the PN/CS microparticles preparation,<sup>29,30</sup> known as ‘precipitation polymerisation’ (first published for microgels based on poly-NiPAAm only),<sup>36</sup> can produce remarkably uniform particles. The reaction is conducted at 50°C in order to generate free radicals by the decomposition of persulfate initiator (APS). Elevated temperature was also required so that growing poly-NiPAAm chains could phase separate to form colloidal particles. At the initial stage of the reaction, before increasing temperature, all reaction components were water soluble and the reaction mixture was homogeneous. Nevertheless, only 5 min after initiating temperature increase, the reaction mixture became heterogeneous and the transparent solution turned into a ‘milky’ dispersion, as the consequence of light scattering caused by formation of complex particles. It is supposed that during the copolymerisation reaction, three different kinds of particles are present in the reaction system (poly-NiPAAm particles, poly-NiPAAm/chitosan complex particles and chitosan molecules) as a consequence of various simultaneous reactions. Since the polymerisation temperature is well above the LCST, the growing poly-NiPAAm and poly-NiPAAm/chitosan complex particles would normally precipitate. However, the precipitation was avoided because the particles were electrostatically stabilised by the negatively charged sulphate groups introduced by the persulphate initiator. It is expected that with prolonged reaction time chitosan molecules with positive charge have been attached gradually onto the larger particles, thus surrounding their negative charged surface, protecting the particles formed and preventing them from coagulating. The authors suggest the above mentioned reaction mechanism based on the findings reported by Lee *et al.*,<sup>29,30</sup> Liu *et al.*<sup>37</sup> and Leung *et al.*<sup>38</sup>

SEM images of dry poly-NiPAAm/chitosan microgels, deposited from a solution onto the native oxide layer of a silicon wafer, are shown in Fig. 1. It is obvious that microgel particles have homogeneous spherical shape and the particle size distribution is quite narrow. The diameter in dry state is estimated at 180 nm. When microparticles are deposited from a concentrated solution (Fig. 1a), they form a closely packed structure which is supposedly stabilised by the charges present at the particle surface.

However, since the microgel particles are usually applied not in dry state but in their hydrated state, DLS measurements of diluted PN/CS suspension were performed to determine the particle size and zeta-potential. The mean value of particle diameter obtained at 25°C in

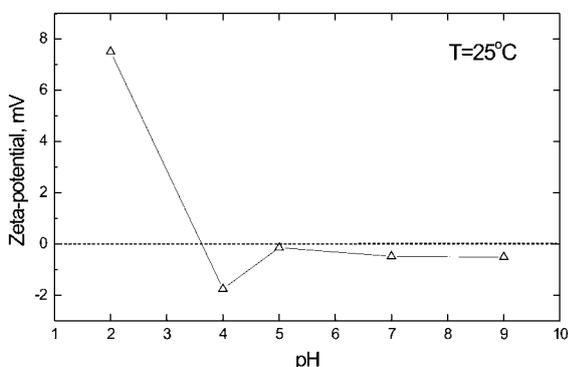


1 SEM images of poly-NiPAAm/chitosan particles (PN/CS) deposited from a concentrated ( $3.56 \text{ g L}^{-1}$ ) and b diluted ( $3.56 \times 10^{-2} \text{ g L}^{-1}$ ) solution onto silicon wafer

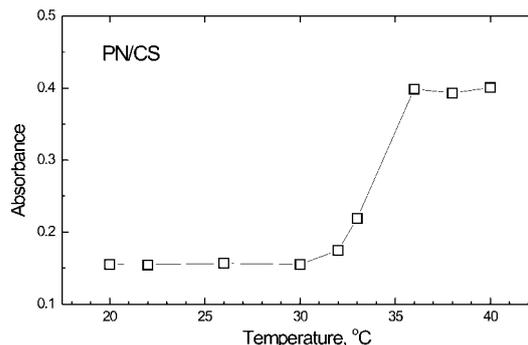
water (pH 7) is 603 nm, which is approximately three times more than in dry state. These data are important from the application point of view since it gives more insight on the actual particle size in aqueous suspension, this being the medium used for the incorporation of the microparticles to textile material.

The variation of zeta-potential with the change in pH of aqueous suspension of PN/CS microparticles is shown in Fig. 2. Zeta-potential measured at low pH values (pH 2) has clearly positive value ( $\zeta=7.4 \text{ mV}$ ), which is the consequence of the chitosan amino groups protonation in acidic environment. With increasing pH, zeta-potential decreases to negative values and above pH 5, it stabilises at small negative values ( $< -1 \text{ mV}$ ). The observed behaviour can be explained through chitosan pH dependence. In acidic solutions, chitosan behaves as a cationic polyelectrolyte due to protonation of the amino groups. Since the pK value of the amino groups of chitosan is 6.3, above pH 5 the amino-groups ( $-\text{NH}_2$ ) should be only partly ( $\sim 20\%$  at pH 6.9) protonated as  $-\text{NH}_3^+$ . Therefore, the amino groups of chitosan are at low pH protonated to form cationic amino groups, but at alkaline pH values, chitosan should have very low positive charge.<sup>39</sup>

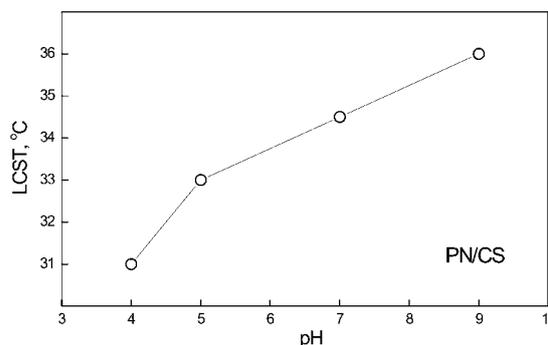
The assessment of the microhydrogel (PN/CS) temperature responsiveness in an aqueous medium has been realised by spectrophotometry. It was observed (Fig. 3) that, by increasing the temperature of the diluted PN/CS suspension from 20 to 40°C, absorbance of the suspension remains almost constant until the temperature reaches 32°C, when it rapidly increases, reaching again a constant value at  $T > 36^\circ\text{C}$ . Such an increase in



2 Variation of zeta-potential with pH for aqueous suspension of poly-NiPAAm/chitosan particles (PN/CS) ( $3.56 \times 10^{-1} \text{ g L}^{-1}$ ) at  $25^\circ\text{C}$



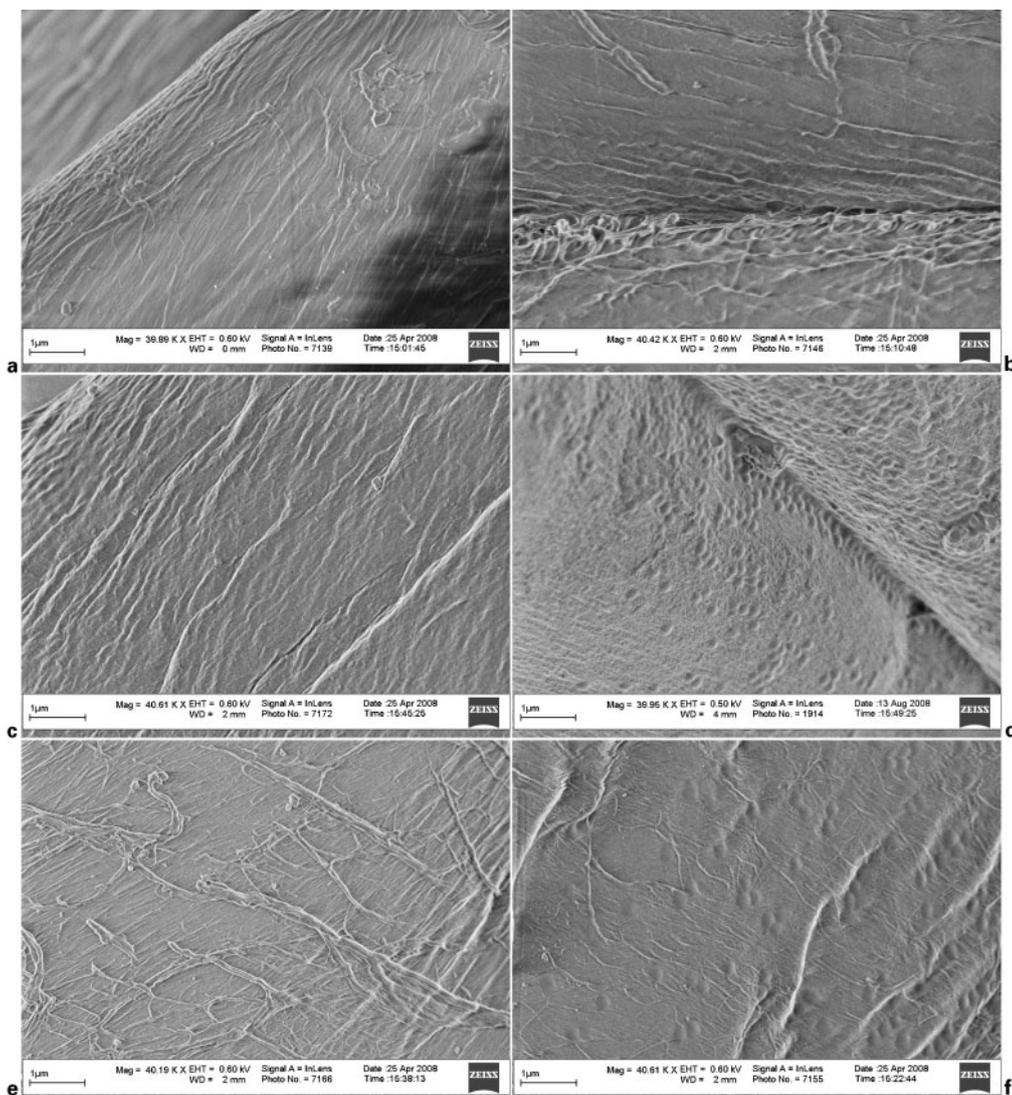
3 Absorbance measurements at 600 nm of PN/CS aqueous suspension (pH 7) ( $1.42 \text{ g L}^{-1}$ ) as function of temperature



4 Dependence of LCST value of PN/CS microparticles ( $1.42 \text{ g L}^{-1}$ ) on pH of suspension

absorbance implies that the thermoresponsive PN/CS particles collapse over a narrow and well defined temperature range. Hence, the presence of a more hydrophilic polymer (chitosan) within the microparticle shifts the LCST from 32°C (observed for pure poly-NiPAAm) to a higher value ( $\sim 34.5^\circ\text{C}$ ).

Measuring of PN/CS suspension temperature responsiveness at different pH values, revealed the LCST dependence on pH (Fig. 4). Although the measurements have been performed at five different pH values (pH 2, 4, 5, 7, 9), the graph presented does not include the data obtained at pH 2 since this sample precipitated immediately at 25°C. This finding can be explained by the shrinkage of the whole complex as the consequence of increased amount of  $-\text{NH}_3^+$  groups and decreased LCST of poly-NiPAAm at strong acidic pH.<sup>40</sup> As a result, the whole particle shrinks (i.e. becomes hydrophobic) and



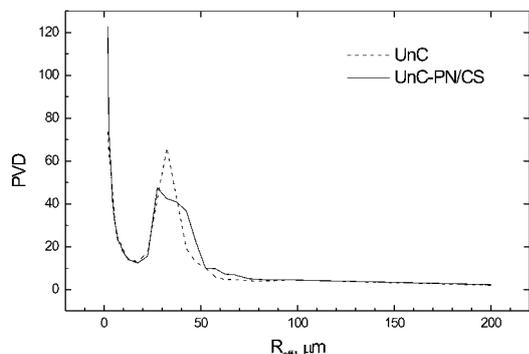
**5 Surface features of untreated cotton: a UnC, c functionalised cotton CmC and e AmC, and cotton with incorporated microparticles: b UnC-PN/CS, d CmC-PN/CS and f AmC-PN/CS**

precipitates. The results obtained for the rest of the values (pH 4, 5, 7, 9) show that there is constant shifting of the LCST to higher values with increasing pH of the suspension. This implies that the hydrophilicity of the whole complex increases at higher pH, so phase transition takes place at higher temperatures.

Since it has been confirmed that PN/CS particles are slightly negatively charged in aqueous solution, and by knowing that untreated cotton fabric (UnC) in aqueous system has also slightly negative charge, the surface functionalisation of cotton has been carried out with the aim to obtain anionic or cationic charges at the material surface and to check whether the ionic charge improves (or diminishes) the microparticle incorporation to the cotton fibre surface.

Surface features of untreated and functionalised cotton, as well as cotton with incorporated PN/CS microparticles, were studied by SEM. Figure 5, obtained by higher magnification ( $\times 40$ ) of portions of cotton fibre, shows the characteristic wrinkled surface of the cotton primary wall for UnC (Fig. 5a) and CmC (Fig. 5c), which in the case of AmC (Fig. 5e) has been covered by some surface deposited material, probably as the consequence of slight fibrillation that occurred

during the amination procedure. It is evident that cotton functionalisation by carboxymethylation and amination do not result in noticeable visual changes of the appearance of the fibre surface. Nevertheless, incorporation of PN/CS microparticles significantly changed the visual aspect of the fibre surface. This is exhibited clearly in the case of previously functionalised fabrics (CmC-PN/CS and AmC-PN/CS, Figs. 5d and f), where it was easy to locate surface deposition of PN/CS microparticles and to distinguish their form, size and amount present at the fibre surface. Moreover, the image of CmC-PN/CS (Fig. 5d) shows that microparticles are deposited not only on the fibre surface, but also in spaces between the fibres. Previously untreated fabric (UnC-PN/CS, Fig. 5b) does not show clear evidence of microparticle surface deposition, i.e. there is no significant visual change in comparison with the control sample (UnC, Fig. 5a). It is obvious that hydrated microgel particles collapsed after incorporation onto the cotton fibre and deformed their shape to 'pancake' structure as the consequence of volume shrinking because of water evaporation during drying and possibly, water absorption from microparticles into the cotton fibre.

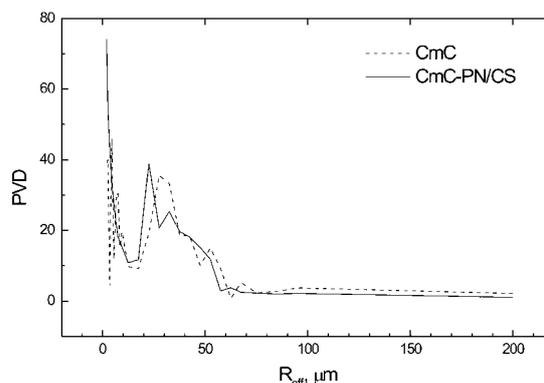


6 Pore volume distribution (PVD) results for untreated cotton fabric with incorporated PN/CS microparticles (UnC-PN/CS) compared with untreated (UnC) cotton as control

Since chemical composition of the fibre surface cannot be analysed by SEM, a low resolution XPS scan was run to determine the chemical modification of cotton surface. The results of elemental composition and atomic ratio for untreated (UnC), carboxymethylated (CmC) and aminised (AmC) cotton fabric before and after incorporation of PN/CS microgels are presented in Table 1.

The O/C atomic ratio found for the untreated cotton fabric (UnC) is 0.5 while the value expected for pure cellulose is 0.83 (theoretical value calculated according to the cellulose chemical composition). This is a normal finding because cotton fibre, even though mainly composed of cellulose, contains some non-cellulosic components such as waxes, pectin and proteins which influence the O/C atomic ratio. The values for elemental composition and atomic ratio remain similar after carboxymethylation (CmC). However, after aminisation (AmC), the O/C ratio is significantly changed (O/C=0.8) and both nitrogen and sulphur are detected, which is the consequence of the presence of the reactive dye's vinyl sulphonic center (S=O) and the free amino groups on the cotton surface.

After incorporation of PN/CS microparticles, all samples (UnC-PN/CS, CmC-PN/CS, AmC-PN/CS) showed the presence of nitrogen in significantly higher amount than in aminised cotton (AmC). This is the consequence of the fact that both poly-NiPAAm and chitosan contain nitrogen, which can be detected by XPS analysis, thus confirming the incorporation of PN/CS microparticles to the fibre surface. Therefore, the amount of nitrogen detected can be used as a tool for the estimation of PN/CS microparticle content on the fibre surface. The measured amount of nitrogen is bigger with



7 Pore volume distribution (PVD) results for carboxymethylated cotton fabric with incorporated PN/CS microparticles (CmC-PN/CS) compared with carboxymethylated cotton (CmC) as control

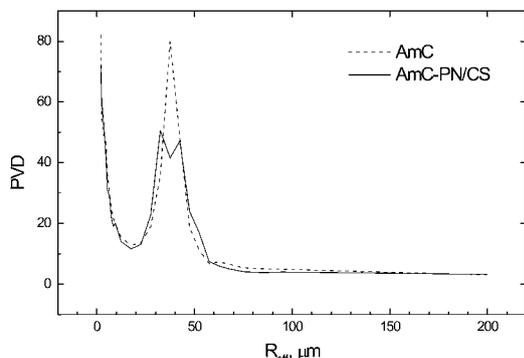
carboxymethylated sample CmC (5.2 at.-%) compared with aminised sample AmC (3.9 at.-%), a result which confirms better microparticle adsorption on cotton with anionic charge. Since previously untreated cotton sample (UnC) shows significant nitrogen content (4.6 at.-%), this implies that even without cotton functionalisation, some kind of poly-NiPAAm and/or chitosan adsorption occurs. Nevertheless, since SEM analysis did not visually confirm the presence of microparticles at UnC sample (Fig. 5b), it can be speculated that a kind of precipitation occurred and polymer(s) have been adsorbed to the non-functionalised cotton fibre surface in a thin layer, not in a microparticulate form.

Knowing the fact that the pore structure in fibrous material contributes directly to some of the key properties of textile material (e.g. liquid absorption, thermal insulation, softness, etc.), the liquid porosimetry method (PVD) has been used to examine the possible effects of PN/CS microparticle incorporation to cotton fabric. The PVD plots for cotton fabrics with incorporated PN/CS microparticles (UnC-PN/CS, CmC-PN/CS and AmC-PN/CS) are presented in Figs. 6–8 together with the plots for corresponding control samples (UnC, CmC and AmC). In general, these plots show the fraction of the free volume of the fabric samples made up of pores of each indicated size (effective radius  $R_{eff}$ ). As it can be seen, the intrayarn pores are always in the range between 1  $\mu\text{m}$  (lower limit of the instrument) and  $\sim 20 \mu\text{m}$ , while interyarn pores range between  $\sim 20$  and 55  $\mu\text{m}$  for all samples studied. Therefore, it can be concluded that both smaller (inrayarn) and larger (interyarn) pores remain distributed in the same range after cotton

Table 1 Elemental composition and atomic ratio for untreated (UnC), carboxymethylated (CmC) and aminised (AmC) cotton fabric before and after incorporation of PN/CS microgels\*

Sample	Elemental composition, at.-%				Atomic ratio		
	C 1s	O 1s	N 1s	S 2p	O/C	N/C	S/C
UnC	66.8	33.2			0.5		
CmC	68.1	31.9			0.47		
AmC	55.1	44.1	0.7	0.1	0.8	0.01	0.002
UnC-PN/CS	68.3	26.7	4.6		0.41	0.06	
CmC-PN/CS	65.5	29.0	5.2		0.44	0.08	
AmC-PN/CS	64.0	31.8	3.9	0.1	0.49	0.06	0.001

\*The error associated with each measurement is <5% of the reported value.



**8 Pore volume distribution (PVD) results for aminised cotton fabric with incorporated PN/CS microparticles (AmC-PN/CS) compared with aminised cotton (AmC) as control**

functionalisation and subsequent PN/CS particle incorporation. Nevertheless, after incorporation of PN/CS microparticles, the average  $R_{\text{eff}}$  represented by the peaks of the interyarn PVD (larger pores) shifts slightly to the left (towards lower values). Moreover, a broader pore size distribution can be observed, covering several orders of magnitude for  $R_{\text{eff}}$ , and in the case of functionalised cotton (Figs. 7 and 8) a slightly pronounced bimodal distribution can be observed. These facts suggest that PN/CS microparticle incorporation reduces slightly the dimensions of large pores (formed by interlacing yarns as determined by the weave pattern), influencing their uniformity in size and probably in shape, too.

In order to determine pH responsiveness of the cotton material with incorporated microparticles, swelling properties were assessed by a gravimetric method (Table 2). The same trials were run on untreated cotton (UnC), carboxymethylated cotton (CmC) and aminised cotton (AmC) for the purpose of control.

Since cotton is a natural hydrophilic material, no significant difference in the swelling behaviour was observed between UnC and AmC samples (both samples gave similar  $S$  values at corresponding pH). Nevertheless, values of swelling percentage for the AmC sample are slightly increased as a consequence of the aminisation procedure (dyeing; reduction) which results in more hydrophilic cotton fabric.

Carboxymethylated (CmC) sample showed behaviour that was rather different from untreated (UnC) and aminised (AmC) cotton fabric, giving much lower  $S$  values at particular pH values. This fact can be attributed to the action of the concentrated solution of caustic soda during the cotton surface functionalisation

**Table 2 pH dependence of swelling percentage  $S$  for untreated (UnC), carboxymethylated (CmC) and aminised (AmC) cotton fabric with incorporated PN/CS microgels (at 25°C)**

Sample	$S$ , %		
	pH 5	pH 7	pH 9
UnC	180	100	152
UnC-PN/CS	178	106	135
CmC	102	84	80.5
CmC-PN/CS	117	78	90.5
AmC	188	111	155
AmC-PN/CS	216	105	172

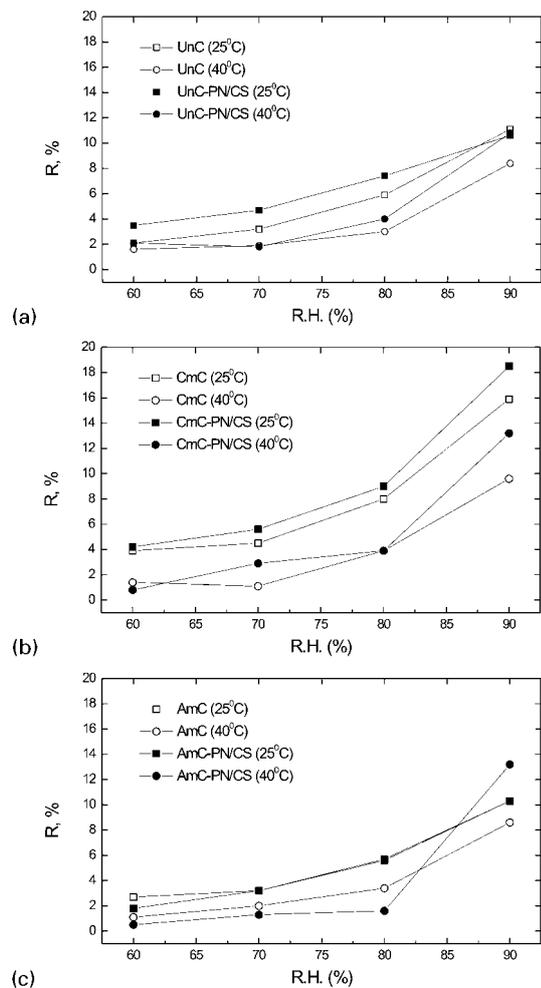
procedure. It is common knowledge that the causticising process causes considerable swelling of the cotton fibre, producing irreversible changes in cellulose physical properties (the size of pores within the fibre is considerably increased). Hence, the fibre stays almost permanently swollen and afterwards it swells considerably less than non-causticised cotton.

Incorporation of PN/CS microparticles to cotton fabric surface caused significant changes in swelling behaviour. Surprisingly, untreated cotton with incorporated microparticles (UnC-PN/CS) showed less swelling ( $S=135\%$ ) in alkaline medium (pH 9) than the control ( $S=152\%$ ). However, both carboxymethylated cotton with incorporated PN/CS microparticles (CmC-PN/CS) and aminised cotton with incorporated PN/CS microparticles (AmC-PN/CS) showed an important swelling increase (compared with the control) in both acidic (pH 5) and alkaline (pH 9) environment. Swelling increase in acidic medium was expected behaviour that could be attributed to the pH responsiveness of chitosan as the consequence of the protonation of amino groups in acidic medium. In alkaline environment, chitosan does not contribute to swelling, but increased swelling can be attributed to poly-NiPAAm swelling (at 25°C). In any case, in terms of difference of swelling between acidic and alkaline pH, the most attractive result is obtained with AmC-PN/CS sample.

Hence, the swelling effect of cotton material with incorporated PN/CS microparticles depends on the particular behaviour of each component (chitosan and poly-NiPAAm) at particular pH values. The overall effect is always the combination of swelling and shrinking effects that can occur simultaneously.

When exposed to changes in ambient humidity and temperature, cotton material with incorporated PN/CS microparticles responds by changes in moisture regain. The results of the determination of the influence of temperature and humidity on the moisture adsorption properties of cotton material with incorporated PN/CS microparticles are presented in Fig. 9. In general, the quantity of moisture absorbed by all samples (untreated, functionalised and with PN/CS incorporated) is higher at 25°C than at 40°C for any relative humidity (RH). As expected, since the moisture concentration in air is the driving force for moisture absorption, moisture regain  $R$  always increased with RH increase.

When PN/CS microparticles were incorporated to untreated cotton (UnC-PN/CS, Fig. 9a) or functionalised cotton (CmC-PN/CS, Fig. 9b; AmC-PN/CS, Fig. 9c), the moisture regain was slightly increased or stayed at similar value compared with the corresponding control samples, except for highest values of RH, where a noticeable increase was observed. This is evident for the following samples: UnC-PN/CS sample at 40°C and 90%RH (Fig. 9a), CmC-PN/CS sample at both temperatures (25 and 40°C) and 90% RH (Fig. 9b) and especially for AmC-PN/CS sample at 40°C and RH > 85%. This phenomenon can be described as unexpected, since the poly-NiPAAm component of the PN/CS microparticle system is expected to be collapsed and more hydrophobic at higher temperature (40°C). The only viable explanation could be that this phenomenon can be attributed to the competition between moisture desorption (drying) and absorption processes which occur simultaneously at higher temperature.



**9 Moisture regain  $R$  of a untreated (UnC), b carboxymethylated (CmC) and c aminised (AmC) cotton fabrics without and with incorporated PN/CS microgels, measured at different humidities and temperatures**

In general, when a dry cotton material with incorporated PN/CS microparticles is subjected to an environment containing moisture, both the fibre and the polymeric systems absorb the moisture at a rate that depends on a number of physical factors. At the initial stage of moisture uptake, possibly the most important factor is the competition between the fibre and the polymeric system attached. Hence, the polymeric system will certainly be the preferable place where the interaction with moisture will occur. This is because the polymeric system with its very low crystallinity has much higher accessibility to water than the highly crystalline cotton fibre.

## Conclusion

In this study, spherical poly-NiPAAm/chitosan hydrogel particles of the submicron scale were prepared with dual sensitivity and responsiveness to temperature and pH changes. Their incorporation to the cotton fabric surface, previously functionalised through chemical methods (carboxymethylation and aminisation), was achieved by the batch method. The presence of microparticles on the surface of functionalised cotton fibres has been visually confirmed by SEM. Surface chemical analysis by XPS indicated that both cotton

functionalisation and microparticle incorporation by a simple batch treatment were successfully achieved. It has been confirmed that microparticle incorporation slightly reduces interyarn pores of cotton fabric. Swelling behaviour and moisture sorption analysis showed that cotton with incorporated PN/CS microparticles presents interesting pH, temperature and humidity responsiveness.

Among a variety of possible applications for such a material, it is worthwhile mentioning the temperature/pH induced adaptive surface materials (hydrophilic/hydrophobic) for performance apparel. Another possibility, of special interest for medical, safety and care applications, is introduction of the controlled release capacity to the material, since the variety of molecules could be easily entrapped in the temperature and pH responsive PN/CS microparticles. However, the results presented prove that the concept of functional finishing of cotton via dual responsive microparticulate hydrogels could lead to the development of a novel material with the highly attractive feature of responsiveness to the environmental stimuli.

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