

## LAYER-BY-LAYER DEPOSITION OF POLY(N-ISOPROPYL-ACRYLAMIDE)/ CHITOSAN MICROGELS OVER COTTON FABRIC

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### ABSTRACT

In this work, we present the innovative strategy of a simple layer-by-layer (LbL) deposition of biopolymer chitosan (CS) and poly-NiPAAm/chitosan microgels (PN/CS) to the previously activated cotton fibre. The PN/CS microgels were prepared by surfactant emulsion polymerization method. The assessment of microgel temperature responsiveness in an aqueous medium was done by spectrophotometric method. Cotton has been activated by a carboxymethylation procedure. Chitosan and PN/CS microgels were incorporated onto cotton surface by a sequential deposition using LbL method. The successful hydrogel incorporation was confirmed by SEM and XPS. The capability of the functionalized material to respond to a change of temperature was studied through moisture uptake kinetics and equilibrium using a gravimetric method.

**Key Words:** Responsive textile material, chitosan, poly-NiPAAm, layer-by-layer deposition

### 1. INTRODUCTION

An innovative strategy to upgrade cotton fabric quality and provide new interesting features comprises surface modification by incorporation of thin layers of stimuli-responsive polymers. Hence, dual stimuli-responsive (pH and temperature) cotton may be prepared by depositing multilayer surface modifying system (SMS) consisting of thermo-responsive synthetic polymer poly(N-isopropylacrylamide) (poly-NiPAAm) and pH-sensitive biopolymer chitosan. Poly-NiPAAm is currently the most investigated thermo-responsive polymer which shows a coil-globule transition at a lower critical solution temperature (LCST) around 32°C [1]. This characteristic is particularly advantageous because LCST value falls between human body temperature and room temperature. Chitosan is a typical pH-sensitive polymer which responds to the changes in the pH of the surrounding medium by protonation/deprotonation events that impart charges on its amino groups [2]. Upon ionization, the coiled chains extend in response to the electrostatic repulsions of the generated charges (pH-induced phase transition) and the hydrodynamic volume of the polymer increases.

A very thin layer deposition of these two polymers is expected to convey the responsive properties of the polymers to the textile material, without screening the textile's regular performance. Currently the most promising technique for achieving this goal is so-called layer-by-layer (LbL) method. In 1992, the area of thin film assembly was revolutionised by the introduction of the versatile LbL technique [3], which uses the sequential adsorption of oppositely charged materials (e.g. polymers or microgels) from solution onto various charged supports (e.g. activated cotton) to construct films in a stepwise fashion. The LbL method readily allows control over the thickness, composition and structure of multilayered films. One of the key advantages of LbL film preparation is that it is simple experimentally and, because water is the main solvent used, the technique is considerably more environmentally friendly than techniques that rely on the use of organic solvents. The LbL method is extremely versatile: most charged materials can be used to construct a multilayered film. Numerous factors determine the composition of the multilayer films and the characteristics of the individual layers. For example, the thickness of a layer appears to be dependent on both the

charge density of the underlying surface and the deposition conditions [4].

Successful deposition of nanolayers onto natural fibres and textiles via LbL can open an avenue to increase their surface functionality without making major changes to the weight, bulkiness, or comfort of the material. Recent research has investigated coating of cellulose-based paper samples [5]. LbL method is especially suitable for potential use on natural fibres due to its self-healing capability providing an increased tolerance to defects [6-8].

In this work, we present the innovative strategy of a simple layer-by-layer deposition of biopolymer chitosan (CS) and poly-NiPAAm/chitosan microgels (PN/CS) to the previously activated cotton fibre. Cotton has been activated by a carboxymethylation procedure, which consists of impregnating cotton fabric with a strong solution of caustic soda, followed by a treatment with an aqueous solution of sodium salt of monochloroacetic acid (CAA). The activated cotton surface (carboxymethylated cotton) was analysed by SEM and XPS in order to study the effects obtained. Chitosan and PN/CS microgels were incorporated onto cotton surface and the new functionalized cotton material was analysed in terms of surface structure and environmental responsive properties.

## 2. EXPERIMENTAL

### 2.1 Materials

The N-isopropylacrylamide (NiPAAm) monomer (Acros Organics, Belgium) was recrystallized from hexane before use. Chitosan (Chitoclear, DD=95%,  $\eta=159$  mPa·s) was purchased from Primex (Iceland). Cotton fabric (100% cotton plain fabric of 105 g/m<sup>2</sup> weight per unit area) was supplied by Vlisco (The Netherlands). The non-ionic detergent Tanaterge EP5071 was supplied by Tanatex (The Netherlands). Crosslinker [N,N-methylenebisacrylamide (BIS)], initiator [ammonium persulphate (APS)], sodium hydrosulphite (Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub>, 85%), monochloroacetic acid (CAA), sodium carbonate, caustic soda (NaOH) and other chemicals were of analytical grade and they were used without further purification.

### 2.2 Preparation of poly-NiPAAm/chitosan microgel

The poly-NiPAAm/chitosan microgel (PN/CS) was prepared by a surfactant-free dispersion copolymerization method according to the procedure reported by Lee et al. [9, 10]. Chitosan solution was prepared by dissolving 1.4 g of chitosan in 280 mL of distilled water containing 3 mL of glacial acetic acid (stirred for 24 hours at room temperature). The NiPAAm/chitosan copolymerization 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 polymerization. The reaction medium turned turbid after 5 minutes and the reaction was allowed to proceed for 3 hours 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.

### 2.3 Cotton fabric surface activation

By knowing that the layer by layer deposition will be done with a successive adsorption of positively charged chitosan solution and negatively charged PN/CS microgel onto cotton surface, the functionalization of cotton material has been done with the aim to obtain anionic or charges at the cotton surface. 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 monochloroacetic acid (CAA) [11, 12]. As first step, cotton fabric was soaked in 20% NaOH aqueous solution for 10 minutes at room temperature, then squeezed (in laboratory padder) to a wet pick-up of 140% and dried for 40 minutes at 60°C. As second step, cotton fabric was immersed for 5 minutes in a solution of reactive anion (1.5M aqueous solution of CAA neutralized by equimolar quantity of Na<sub>2</sub>CO<sub>3</sub>), then padded to a wet pick-up of 140%, sealed in polyethylene bag and held for 60 minutes at 80°C. Finally, the carboxymethylated cotton fabric sample (CmC) was washed several times in deionised water before being dried at room temperature.

### 2.4. Incorporation of microparticulate system to functionalized cotton fabric

Petri dishes were used for the deposition of positive chitosan solution and negatively charged PN/CS microgel. The dishes were filled up to 90% in order to completely immerse the samples. All samples (carboxymethylated cotton, 7×7 cm) were first immersed in acidic chitosan solution (0.16% (w/v) in 1% acetic acid solution) dish for five minutes. The specimen was then transferred to a dish containing deionised water. The sample was allowed to rinse for five minutes and then moved to a dish containing PN/CS microgel suspension (1.7 g/l). After five minutes, the sample was transferred to a dish containing deionised water to be rinsed again for five minutes. The process was continued until a total of eighteen layers had been deposited on the cotton substrates. Samples were dried at room temperature for a period of 24 h.

### 2.5. Characterization methods

The size of air-dried microgel particles and surface characterization 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 prior to the measurements. Cotton fabric samples were analysed without any previous coating.

The particle size and zeta-potential of the PN/CS microgel were determined using Zetasizer Nano ZS system (Malvern Instrument, Inc., Worcestershire, UK). A dialysed PN/CS micro-particle suspension was diluted approximately 100 times with hydrochloric acid or sodium hydroxide aqueous 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 micro-hydrogel suspension (1 g/L) was assessed by spectrophotometric method using Cary 100 Bis (Varian, USA) spectrophotometer equipped with a temperature controller. The absorbance of the polymer suspension was monitored at 600 nm and recorded for the temperature between 20°C and 40°C ( $\pm 0.2^\circ\text{C}$ ).

In order to investigate the surface chemical changes of functionalized cotton and cotton with incorporated micro-hydrogels, 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 energies values calculated were relative to the main O 1s peak at 532.9 eV.

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. Fabrics samples of dimensions 4×4 cm were put in the climatic chamber under conditions of constant temperature (25 and 40°C) and humidity (70 and 80% R.H.) for one hour. Then the samples were weighed with an analytical balance. For calculating moisture regain  $R$  (moisture added to a dry fibre) of the samples, Eq. 1 was used.

$$R = \frac{m_H - m_D}{m_D} \quad (1)$$

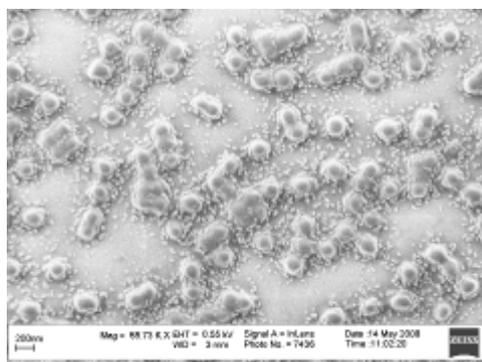
where:  $m_H$  is the mass of sample after humidity exposure;  $m_D$  is the initial mass of dry sample.

### 3. RESULTS AND DISCUSSION

#### 3.1 PN/CS microgel characterization

##### 3.1.1 Morphology (shape and size) analysis

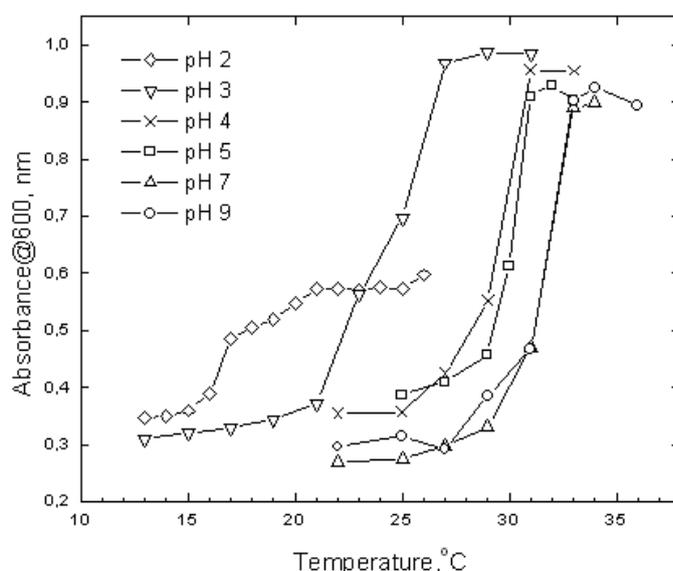
A SEM image of dry poly-NiPAAm/chitosan microgels, deposited from a solution onto the native oxide layer of a silicon wafer is shown in Figure 1. The figure shows that the microgel particles have a homogeneous spherical shape and that the particle size distribution is quite narrow. The diameter in dry state is estimated at 180 nm.



**Figure 1.** SEM image of poly-NiPAAm/chitosan particles (PN/CS) deposited from a diluted ( $3.56 \cdot 10^{-2}$  g/L) solution onto a silicon wafer.

### 3.1.2 Study of pH and temperature responsiveness

The assessment of micro-hydrogel (PN/CS) temperature responsiveness in an aqueous medium has been done by spectrophotometric method. It was observed (Figure 2) that, by increasing temperature of diluted PN/CS suspension from 20 to 40°C, absorbance of the suspension remains almost constant until the critical temperature is reached (LCST), when it rapidly increases, reaching again the constant value. Such an increase in absorbance implies that thermoresponsive PN/CS particles collapse over rather narrow temperature range. This behaviour is well described for poly-NiPAAm, a characteristic polymer that shows a lower critical solution temperature (LCST) as the consequence of change in polymer conformation at  $T > \text{LCST}$ . Measuring of PN/CS suspension temperature responsiveness at different pH values, revealed the LCST dependence on pH (Figure 2). The measurements have been performed at 6 different pH values (pH 2, 3, 4, 5, 7, 9). It can be observed that the LCST value, that we considered to be the temperature for which the absorbance value is doubled, is shifted to lower temperature as a decrease of pH.



**Figure 2.** Absorbance measurements (at 600 nm) of PN/CS suspension (1.1g/L) as a function of temperature.

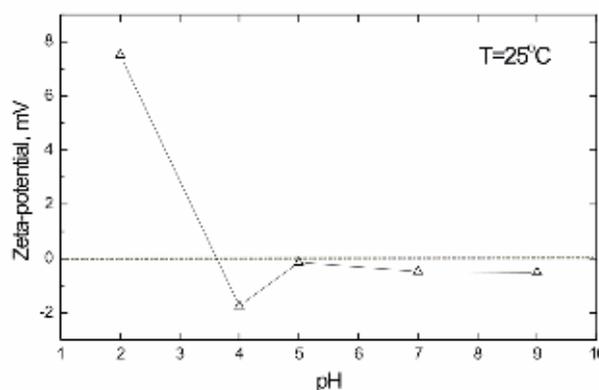
Figure 3 presents the digital photography of the microgel suspension at 25°C and different pH. At pH 2 the particles are precipitated. This finding can be explained by the shrinkage of the whole complex as the consequence of increased amount of  $-\text{NH}_3^+$  groups and decreased LCST of poly-NiPAAm at strong acidic pH [13]. As a result, the whole particle shrinks (i.e. becomes hydrophobic) and precipitates. At pH 3 the hydrophobic state of the microgel is revealed itself by the milky appearance of the suspension. The appearance of the microgel for the rest of the values (pH 4, 5, 7, 9) shows a clear suspension, which is characteristic of hydrophilic and stable particles suspension. This implies that the hydrophilicity of the whole complex increases at higher pH and that the phase transition takes place at higher temperatures. These results show the temperature and pH responsiveness of the PN/CS microgel.



**Figure 3.** Digital photography of a diluted suspension of PN/CS particles (1.1 g/L) (b) (pH 2, 3, 4, 5, 7, 9, from the left to the right).

### 3.1.3 Charge determination

Since layer by layer deposition implies electrostatic interactions the characterization of the charge of PN/CS microgel has been done by zeta-potential measurement. The variation of zeta-potential with the change in pH of aqueous suspension of PN/CS microgel is shown at Figure 4. Zeta-potential measured at low pH values (pH 2) has clearly positive value ( $\zeta=7.4$  mV), which is the consequence of chitosan amino groups protonation in acidic environment. With increase in pH, zeta-potential decreases to negative values and over pH 5 it stabilizes at small negative values ( $<-1$  mV). Hence, since the PN/CS particles have maximum negative charge at pH 4, this condition has been chosen for layer by layer incorporation.

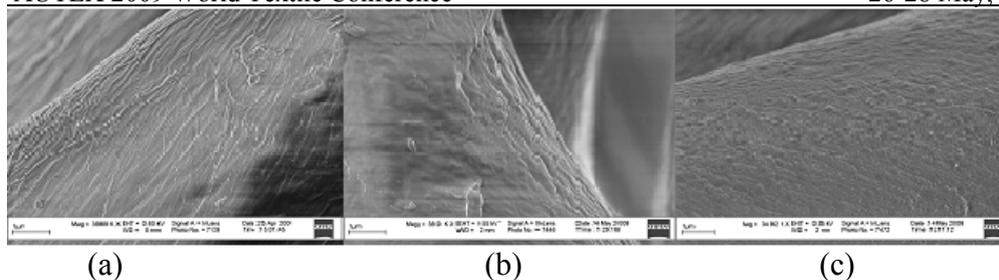


**Figure 4.** Variation of zeta-potential with pH for aqueous suspension of poly-NiPAAm/chitosan particles (PN/CS) ( $3.56 \cdot 10^{-1}$  g/L) at 25°C.

## 3.2 Characterization of new functional textile material

### 3.2.1 Surface analysis

Surface features of untreated (UnC) and carboxymethylated (CmC) cotton, as well as carboxymethylated cotton with incorporated chitosan and PN/CS microgel (CmC-LBL) were studied by SEM. Figure 5, obtained by high magnification of portions of cotton fibre, shows the characteristic wrinkled surface of the cotton primary wall for UnC (a), CmC (b) and CmC-LBL (c). It is obvious that cotton functionalization by carboxymethylation produces a smoother cotton fibre surface. The incorporation of PN/CS microgel significantly visually changed the nature of fibre surface where it was easy to locate microgel surface deposition and to distinguish the form, size and amount of microparticles present at the fibre surface.



**Figure 5.** SEM images of UnC (a), CmC (b) and CmC-LBL (c).

Since chemical composition of the fibre surface cannot be detected 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) cotton fabric before and after incorporation of chitosan and PN/CS microgels are presented in Table 1.

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

Sample	Elemental composition (at. %)			Atomic ratio	
	C 1s	O 1s	N 1s	O/C	N/C
UnC	66.8	33.2		0.5	
CmC	68.1	31.9		0.47	
CmC-LBL	65.9	31.8	2.2	0.5	0.03

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 cellulose chemical composition). This is regular finding because cotton fibre, even though mainly composed of cellulose, contains some non-cellulosic components such as waxes, pectins and proteins which influence the O/C atomic ratio. The values for elemental composition and atomic ratio remain similar after carboxymethylation (CmC). After incorporation of chitosan and PN/CS microgel, CmC-LBL showed presence of a significant amount of nitrogen (2.2%). 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 chitosan and/or PN/CS microgel onto the fibre surface.

### 3.2.2 Moisture uptake study

A kinetic study of moisture uptake has been done in order to determine the time needed to reach the equilibrium. Figure 6 presents the moisture regain of untreated (UnC) and carboxymethylated (CmC) cotton, as well as carboxymethylated cotton with incorporated microgel (CmC-LBL) at 25°C and 80% R.H. It can be observed that functionalization (carboxymethylation) leads to a textile material with better humidity adsorbing property. Carboxymethylated cotton with incorporated microgel (CmC-LBL) regains higher percentage of moisture than its control (CmC). In all cases the moisture uptake is relatively fast during the first few minutes, reaching a plateau after 15 minutes. In the case of CmC-LBL, a second slight increase of moisture uptake can be observed after 35 minutes. Based on these results, it has been decided to leave the samples for 60 minutes in the climatic chamber during further study of temperature influence on moisture adsorbing capacity.

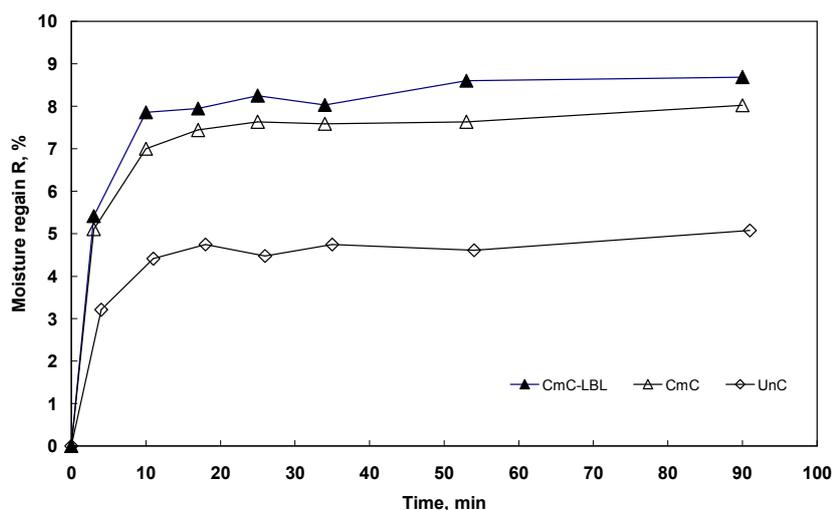


Figure 6. Kinetics of moisture uptake at 25°C and 80% R.H.

When exposed to changes in ambient humidity and temperature, cotton material with incorporated PN/CS microgel responds by changes in moisture regain. The results of the determination of the influence of temperature on the moisture adsorption properties of cotton material with incorporated PN/CS microgel are presented in Figure 7. In general, the quantity of moisture absorbed by all samples (UnC, CmC and CmC-LBL) is higher at 25°C than at 40°C. Once more it can be seen that the functionalization of cotton (CmC) produces a more hydrophilic textile material which adsorbs twice more moisture than untreated cotton (UnC) at 40°C. The sample with incorporated PN/CS microgels (CmC-LBL) presents a thermoresponsive characteristic: the swelling is higher compared to its control (CmC) at 25°C and it is significantly lower at 40°C.

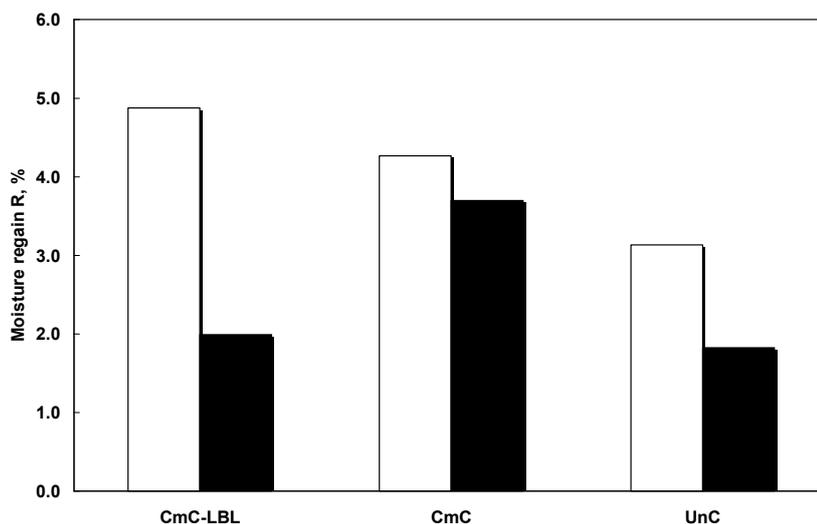


Figure 7. Moisture regain of untreated (UnC), carboxymethylated (CmC) cotton and carboxymethylated cotton with PN/CS microgel (CmC-LBL) at 25°C (white) and 40°C (black) at 70% R.H.

In general, when a dry cotton material with incorporated PN/CS microgel is subjected to an environment containing moisture, both the fibre and the polymeric system 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.

#### 4. 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 functionalized through carboxymethylation, was achieved by layer by layer (LbL) deposition. The presence of the microparticles on the surface of functionalized was confirmed by SEM and XPS analysis. These surface modified textile materials present interesting temperature responsiveness. The presented surface modification method can be considered efficient to obtain new advanced functionalized textiles by biopolymer surface modification.

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### **Acknowledgement**

Financial support for this work was provided by Marie Curie Excellence Grant (EXT) project ADVANBIOTEX (MEXT-CT-2006-042641), funded by the EU's FP6 Programme.