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Microgel-based surface modifying system for stimuli-responsive functional finishing of cotton

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ABSTRACT

An innovative strategy for functional finishing of textile materials is based on the incorporation of a thin layer of surface modifying systems (SMS) in the form of stimuli-sensitive microgels or hydrogels. Since the copolymerization of poly(N-isopropylacrylamide) with an ionizable polymer, such as chitosan, results in a microgel that is responsive to both temperature and pH, the microparticulate hydrogel of poly-NiPAAm-chitosan copolymer (PNCS) was synthesized using surfactant-free emulsion method. The microparticle size in dry (collapsed) state is estimated at 200 nm by SEM and TEM, and effect of temperature and pH on microparticles was investigated by DLS and UV–vis spectrophotometry. The incorporation of PNCS microparticles to cotton material was done by a simple pad-dry-cure procedure from aqueous microparticle dispersion that contained 1,2,3,4-butanetetracarboxylic acid (BTCA) as a crosslinking agent. This application method provided sufficient integrity to coating by maintaining the responsiveness of surface modifying system. The stimuli-responsiveness of modified cotton fabric has been confirmed in terms of regulating its water uptake in dependence of pH and temperature.

1. Introduction

In a constant search for ways of improving products, nowadays textile producers turn to advanced technologies that can fully exploit the novel uses of textile materials. The fusion of conventional structural textile materials with advanced properties given by “smart” functional finishing technology offers a wide range of high added-value product options. The technologies used to incorporate certain functionalities in the textile and to develop “smart” textile for the non-conventional application sectors such as technical, biomedical, sportswear and protective uses include microencapsulation, hydrogel film coating, sol–gel technology, etc. (Boczkowska & Leonowicz, 2006; Mondal, 2008; Textor, Bahners, & Schollmeyer, 2003; Textor & Mahltig, 2010). The “smart” functional finishing approach is currently greatly appreciated since it enables producers to continue to use conventional textile fibers and at the same time achieve added-value that will be able to stimulate and capture the potential consumer markets for such textile materials.

An innovative strategy for functional finishing of textile materials is based on the incorporation of a thin layer of surface modifying systems (SMS) in the form of stimuli-sensitive microgels or hydrogels (Crespy & Rossi, 2007; Jocic, 2008; Liu & Hu, 2005). In the past decades, stimuli-responsive hydrogels have been extensively investigated because of their responsiveness to environmental stimuli (i.e. temperature, light, pH, electric field and magnetic field) as well as their wide range of applications in biomedical field (Mano, 2008; Kopecek, 2009; Kopecek & Yang, 2007; Kumar, Srivastava, Galaev, & Mattiasson, 2007). The variety of polymers used include synthetic polymers like poly(N-isopropylacrylamide), polyacrylic acid, polyoxazoline and some biopolymers like chitosan and carrageenan (Klouda & Mikos, 2008; Prabaharan & Mano, 2006).

Chitosan is a polyaminosaccharide, obtained by alkaline deacetylation of chitin, which is the principal component of living organisms such as fungi and crustaceans (Rinaudo, 2006; Tolaimate, Desbrieres, Rhazi, & Alagui, 2003). It has key properties such as biocompatibility, non-toxicity, the ability to absorb liquids and to form protective films and coatings (Rinaudo, 2006). Hence, chitosan has been reported to be a promising polymer not only in the chemical field but also in biomedical and industrial areas where it is being evaluated in a number of medical, safety and care applications, including wound dressing, dialysis membranes and fibers for resorbable sutures (Aranaz et al., 2009; Hirano, 1999; Ravi Kumar, 2000). Chitosan shows pH-responsiveness as it is a linear polymer of mainly anhydroglucosamine which behaves as a polyelectrolyte at acidic pH, carrying a high positive charge density at pH below ∼6.5 (one charge per glucosamine unit).

Currently, most of the studies of synthetic temperature-responsive polymers focus on poly(N-isopropylacrylamide),

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poly(N-alkylacrylamide), poly(N-vinylcaprolactam), poly(vinylmethyl ether) and their derivatives (Liu, Fraylich, & Saunders, 2009). Among these polymers, poly(N-isopropylacrylamide) (poly-NiPAAm) is the most widely explored as it has the peculiarity of possessing a LCST (a reversible coil to globule transition in solution when the temperature is set beyond the so-called lower critical solution temperature) in the physiological range (~32 °C), which is notably important for biomedical or clothing applications (Pelton, 2000; Schild, 1992).

Both chitosan and poly-NiPAAm can be used for microgel preparation. The result of copolymerization of poly-NiPAAm with an ionizable polymer, such as chitosan, is a microgel that is responsive to both temperature and pH. Several surfactant-free dispersion copolymerization methods for the poly-NiPAAm/chitosan microgel synthesis have been reported, confirming that the morphology of the complex microparticles depends on the mechanism of polymerization which is being affected by the initiator used. Procedures described by Lee, Wen, and Chiu (2003), Lee, Wen, Lin, and Chiu (2004) and Fan et al. (2008) give the complex microparticles of homogeneous morphology, 50–300 nm in size. Procedures described by Lee et al. (2003), Leung, Zhu, Harris, and Li (2004) and Liu, Huang, Liu, and Hu (2007) give the microparticles of core–shell morphology, having the core zone of poly-NiPAAm and shell zone of either chitosan or grafted copolymer of poly-NiPAAm/chitosan. However, no matter which morphology the microparticles possess, chitosan with its free amino and hydroxyl groups gives the possibility of attaching to the substrate (e.g. textile material) or loading/absorbing some agents (e.g. drugs, antimicrobial agents, etc.).

The incorporation of the surface modifying system based on poly-NiPAAM/chitosan microparticles to cotton material can be done from aqueous microparticle dispersion by simple pad-dry or pad-dry-cure procedure, which is of special interest for the application in industrial conditions. The main challenge during incorporation procedure is: to integrate the surface modifying system into textile substrate with sufficient durability while still retaining the effectiveness (responsiveness) of the microparticles. Two different approaches are available to achieve this goal. One approach is based on cotton functionalization before the application of the surface modifying system, and both chemical (Jocic, Tourrette, Glampedaki, & Warmoeskerken, 2009) and physical (Tourrette et al., 2009) methods have been previously reported. Another approach, which is the aim of this research, is based on the use of the additional film-forming agent to produce three-dimensionally linked network between the microparticles and the substrate.

In textile industry, polycarboxylic acids such as 1,2,3,4-butanetetracarboxylic acid (BTCA) are well-known crosslinking agents that can serve as formaldehyde-free durable press finishing agents (Welch, 1992; Welch & Andrews, 1990). Under the action of heat (curing step) carboxylic groups of BTCA can react with hydroxyl groups from both cotton and chitosan (present in the microparticle) by forming stable ester bonds (Hsieh, Lin, & Wei, 2006; Sauperl, Stana-Kleinschek, Voncina, Sfiligoj-Smole, & Majcen-Le Marechal, 2003; Yang & Wang, 2000) and possibly additionally react with free amino groups of chitosan via formation of amide. Suitable catalysts for this process are mainly alkali metal salts of phosphorus-containing acids (e.g. hypophosphites). It has been reported that this method can be successfully used for grafting ethylcellulose microcapsules (Badulescu, Vivod, Jausovec, & Voncina, 2008), N-halamine diol precursor (Ren, Kocer, Worley, Broughton, & Huang, 2009), β-cyclodextrin (Voncina & Majcen Le Marechal, 2005) and hydroxyl-functional organophosphorus oligomer (Cheng & Yang, 2009) onto cotton.

In this study, an attempt has been made to develop pH- and temperature-responsive cotton fabric by functional finishing with the surface modifying system based on stimuli-responsive poly-NiPAAm/chitosan (PNCS) microparticulate hydrogel. In order to obtain durable coating, microparticulate hydrogel was covalently bonded to cotton fabric using polycarboxylic acid (BTCA) as crosslinking agent. The simple pad-dry-cure application method provided sufficient integrity to coating by maintaining the responsiveness of surface modifying system. The stimuli-responsiveness of functionalized cotton fabric has been confirmed in terms of regulating its water uptake in dependence of pH and temperature.

2. Experimental

2.1. Materials

The N-isopropylacrylamide (NiPAAm) monomer (Acros Organics, Belgium) was recrystallized from hexane before use. Chitosan (Chitoclear, DD = 95%, η = 159 mPa s) was purchased from Primex (Iceland). Cotton fabric (100% cotton plain fabric of 105 g/m^2 weight per unit area) was supplied by Vlisco (The Netherlands). N,N-methylenebisacrylamide (MBA), ammonium persulphate (APS), 1,2,3,4-butanetetracarboxylicacid (BTCA) and sodium hypophosphite (SHP) were purchased from Sigma–Aldrich (The Netherlands). The nonionic surfactant (Tanaterge EP5071) was purchased from Tanatex Chemicals B.V. (The Netherlands). All other chemicals were of analytical grade and they were used without further purification.

2.2. Synthesis of PNCS microparticles

The microparticles of poly-NiPAAm/chitosan hydrogel (PNCS) were prepared by a surfactant-free dispersion copolymerization method according to the procedure reported by Lee et al. (2003, 2004). At first, chitosan solution was prepared by dissolving 1.0 g of chitosan in 300 ml of distilled water containing 3 ml of glacial acetic acid (stirred for 24 h at room temperature). The graft copolymerization of poly-NiPAAm with chitosan was carried out in three-neck round-bottom flask equipped with a condenser, mechanical stirrer and nitrogen inlet (for maintaining nitrogen atmosphere during the reaction). The flask was filled with chitosan solution and degassed with nitrogen for 30 min at room temperature. Subsequently, NiPAAm monomer (7 g) and crosslinking agent MBA (0.21 g) were added with vigorous stirring (320 rpm), the temperature was raised to 50 °C when APS (0.9 g) was added to initiate the polymerization. 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 monomers and oligomeric impurities, the reaction solution was dialyzed (4 spectra/Por, Fisher Scientific) during 10 days against deionized water.

2.3. Incorporation of PNCS microparticles to cotton

The PNCS microgel particles were incorporated and durably crosslinked to cotton using a pad-dry-cure method. The conditions for BTCA crosslinking have been taken from the literature (Sauperl et al., 2003). The ratio of BTCA:PNCS was maintained at 1:3.75 and of BTCA:SHP at 2:1. The required amount of BTCA (0.6 wt.%) and the catalyst SHP (0.3 wt.%) were added into 10 ml PNCS microgel dispersion to prepare the reaction mixture, which was then stirred for 15 min. Previously washed cotton fabric samples (5 cm × 5 cm) were dipped in the reaction mixture for 10 min and subsequently squeezed (with 100% pick-up) using laboratory padder ($v = 3$ m/min; p = 1.5 kP/cm^2). The samples were then dried (70 °C) and subsequently cured at 160 °C during 7 min in the oven. After curing, the samples were washed for 45 min in an aqueous solution containing nonionic surfactant (2 g/L Tanaterge EP5071) with a liquor-to-goods ratio of 25:1 at 60 °C, and then rinsed twice in cold tap water. It is worthwhile noticing that the same washing procedure has been used for cleaning cotton samples before the microparticles incorporation. After washing, samples were dried at room temperature and then put into the desiccator (sample code: c-PNCS/BTCA). The same procedure (excluding PNCS microparticles) has been used to obtain reference cotton treated with BTCA only (sample code: c-BTCA).

The pick-up (P) and add-on (A) of the coated fabrics were calculated using the Eqs. (1) and (2), respectively:

$$P = \frac{W_p - W_t}{W_t} \times 100 \tag{1}$$

$$A = \frac{W_a - W_t}{W_t} \times 100 \tag{2}$$

where, W_p is weight of wet cotton sample immediately after padding; W_a is weight of dry cotton sample after padding and W_t is weight of dry cotton sample before padding.

To check the durability of coating, the above-described washing procedure was repeated five times and samples were analyzed with scanning electron microscopy for the presence of the surface modifying system. Additionally, the add-on (A) has been calculated after each washing cycle.

2.4. Scanning and transmission electron microscopy (SEM and TEM)

The morphology of air-dried microgel and of cotton samples was determined by scanning electron microscope 1550 HRSEM (Zeiss, Germany) operating at 5 kV with the field emission gun. The samples were prepared as following: a drop of 500 times diluted (4.5×10^{-4} mg/ml) PNCS microgel dispersion was placed on silicon wafer and dried at room temperature; in case of c-BTCA and c-PNCS/BTCA samples, the small centre-piece of fabric sample (3 mm × 3 mm) was cut, mounted on sample holder and analyzed without further preparation.

The internal structure of microparticles was studied by TEM. The drop of 500 times diluted PNCS microgel dispersion (4.5×10^{-4} mg/ml) was placed on copper grid with holy carbon film. After drying, the samples were analyzed by CM30 Twin (S) TEM (Philips, The Netherlands) with 300 kV field emission gun and using bright field imaging mode.

2.5. Dynamic light scattering (DLS)

The effect of temperature and pH on hydrodynamic diameter of the microparticles was determined by dynamic light scattering (DLS) method at the wavelength of 532 nm using a Zetasizer Nano ZS system (Malvern, UK). A dialyzed PNCS microgel dispersion was diluted 500 times (4.5×10^{-4} mg/ml) for the study. For studying the effect of temperature, a built-in thermostat sample holder with an accuracy of 0.01 °C was used. The temperature was varied from 20 °C to 40 °C and corresponding hydrodynamic size was measured. For studying the effect of pH, the temperature was maintained constant (20 °C) and the diluted microgel dispersion was titrated from the starting value (pH 6.5) to pH 2 and to pH 10 by regular addition of small aliquots of 0.25 M HCl or 0.25 M NaOH solution, respectively, using a MTP-2 multi-purpose titrator (Malvern, UK). Particle size was analyzed with Dispersion Technology Software (DTS) version 5.00, provided with the instrument. Each sample was measured three times and the average value of hydrodynamic size was taken. The polydispersity index (PDI) was calculated from cumulate analysis of intensity autocorrelation function measured by DLS. The broader the microparticle size distribution, the bigger is the value of PDI.

2.6. UV–vis spectrophotometry

Temperature-responsiveness of the microgel dispersion was assessed by spectrophotometric method using Cary 100 Bis (Varian, USA) UV–vis spectrophotometer equipped with a temperature controller. PNCS microgel dispersion was diluted 100 times (2.25×10^{-3} mg/ml) with different buffer solutions (pH 2, 4, 7, 9) and 2 ml was taken for each measurement. The absorbance (at 600 nm) was recorded for temperatures between 20 °C and 40 °C (±0.2 °C).

2.7. X-ray photoelectronic spectroscopy (XPS)

In order to investigate the surface chemical changes of untreated cotton (c-UT), cotton treated with BTCA only (c-BTCA) and cotton with incorporated PNCS microgel (c-PNCS/BTCA), X-ray photoelectronic spectroscopy (XPS) analysis was performed using a PHI Quantera Scanning ESCA Microprobe spectrometer (Physical Electronics, USA). The samples were irradiated with monochromatic Al K_α X-rays (1486.6 eV) using an X-ray spot size with a diameter of 100 μm 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 of the sample surface was determined.

2.8. Environmental scanning electron microscopy (ESEM)

The samples of cotton with incorporated PNCS microparticles (c-PNCS/BTCA) were investigated with environmental scanning electron microscopy (ESEM) XL30 ESEM Tungsten filament electron microscope (Philips, The Netherlands). The small centre-piece of the sample was put into the sample chamber without any further preparation and the drop of degassed water was placed on it. The chamber was then immediately closed and adjusted to a desired pressure. The ESEM images were collected at an accelerating voltage of 20 kV at different temperatures between 20 °C and 40 °C. The care must be taken that, if vacuum is too high or if the sample stays for a long time in the ESEM chamber the water could be evaporated, so the effect observed could be due to vacuum conditions, not due to increased temperature.

2.9. Water uptake

The gravimetric method for measuring water uptake was employed to study the temperature sensitivity of cotton with incorporated PNCS microparticles (c-PNCS/BTCA) in the temperature range 24–42 °C (with 2 °C steps). At first, the fabric samples were kept in thermostatic bath for 30 min to achieve equilibrium. Further on, at each temperature interval the samples were kept in water bath for 5 min, then taken out and gently blotted with wet filter paper to remove surface water, followed by immediate weighing. The water uptake (U) was determined using the following equation (Eq. (3))

$$U = \frac{W_u - W_t}{W_t} \times 100 \tag{3}$$

where W_u is weight of the sample after taking up water; W_t is weight of dry sample.

The same procedure was repeated with acidic (pH 3), nearly neutral (pH 6.5) and alkaline (pH 10) solution to study the effect of pH (and temperature) on water uptake of cotton with incorporated PNCS microparticles. For the purpose of control, the same measurements have been done on untreated cotton (c-UT) and cotton treated with BTCA only (c-BTCA).

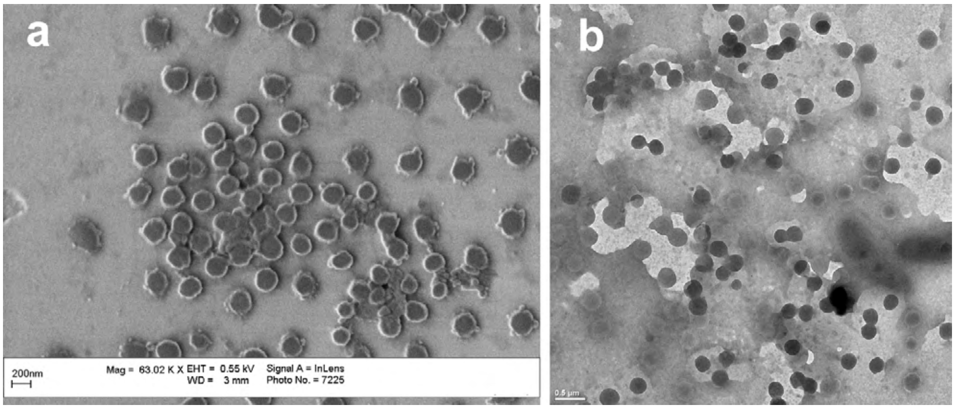

Fig. 1. Scanning electron microscope image (a) of PNCS microparticles deposited on a silicon wafer and transmission electron microscope image (b) of PNCS microparticles deposited on a copper grid.

3. Results and discussion

3.1. Synthesis and characterization of PNCS microparticles

According to the literature (Lee et al., 2003, 2004), when APS is used as initiator, at first two types of reactions occur: reaction one – formation of APS initiated poly-NiPAAm particles with a negative surface charge; and reaction two – graft copolymerization of NiPAAm and chitosan which forms the poly-NiPAAm/chitosan (PNCS) complex particles with a negative surface charge. As reaction medium is acidic, chitosan is in ionized state (–NH_3^+). Hence, remaining chitosan molecules (positively charged) surround the negatively charged surface of the poly-NiPAAm and poly-NiPAAm/chitosan particles, being adsorbed there and thus preventing the particles from coagulating. As the consequence, small particles (micro-scale) are formed. However, if chitosan molecules are not in the vicinity of the poly-NiPAAm and poly-NiPAAm/chitosan particles, then particles coagulate to form larger particles until enough chitosan molecules get absorbed onto particle surface to prevent further coagulation. The advantage of this polymerization reaction over conventional emulsion polymerization is that, as it is surfactant-free polymerization, subsequent purification of the microparticles is simple and relatively pure microparticle dispersion can be prepared.

The PNCS microparticle morphology and size were investigated by scanning electron microscopy (SEM). The SEM image (Fig. 1a) of diluted PNCS microparticle dispersion reveals that microparticles are well separated from each other, spherical in shape, with the average diameter of around 200 nm. As the SEM image is taken in high vacuum and dry conditions, this size of PNCS microparticles corresponds to the size of the totally collapsed microparticles.

Transmission electron microscopy (TEM) was used to investigate internal structure of PNCS microparticles. TEM image of microparticles coated on copper grid (Fig. 1b) reveals monodisperse spheres with regular size, similar as determined by SEM. The appearance of uniformly dark microparticles indicates that there are no differences in electron density within the microparticle structure. This confirms homogeneous morphology of the microparticles, i.e. that poly-NiPAAm is mixed with chitosan homogeneously within the microparticle structure. Nevertheless, by knowing the mechanism of polymerization (Lee et al., 2003, 2004), it is expected that chitosan molecules are absorbed onto the surface of the microparticles.

Fig. 2a presents the effect of temperature on average diameter (hydrodynamic size) of PNCS microparticles studied by dynamic light scattering at pH 6.5. The results show that swollen microparticles at 20 °C have average diameter of 760 nm, while the fully collapsed microparticles at 40 °C have average size of 190 nm, which is similar to the value obtained for dry microparticles (Fig. 1). By stepwise increasing temperature from 25 °C to 34 °C, the PNCS microparticle size reduces gradually until complete collapse, which was observed at 35 °C. Above 35 °C the microparticle size does not vary significantly with increase in temperature. Normally poly-NiPAAm homopolymer microparticles should show sharp collapse (LCST value) at 32 °C. Nevertheless, in case of PNCS microparticles the shift in the transition temperature and appearance of broad transition temperature range (25–34 °C) can be attributed to the presence of chitosan. Even slight ionization of chitosan amine

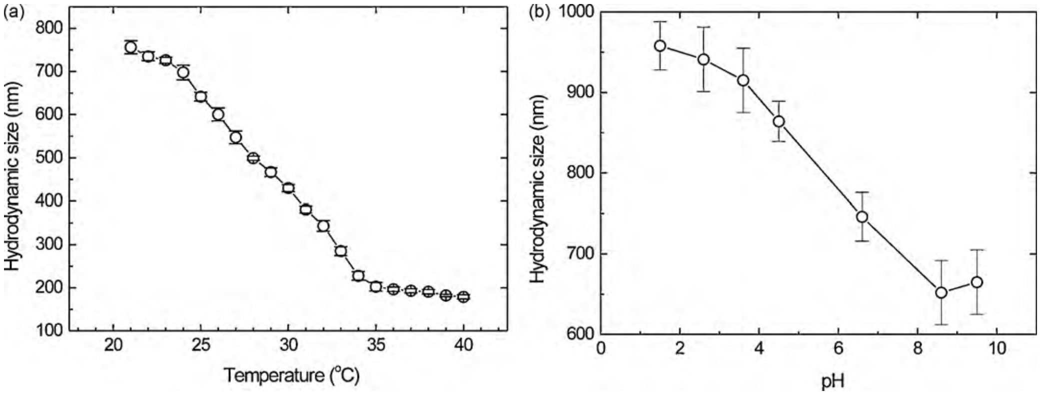

Fig. 2. Average hydrodynamic size (diameter) of PNCS microparticles studied by dynamic light scattering: effect of temperature at pH 6.5 (a) and effect of pH at 20 °C (b).

Table 1
Average hydrodynamic size (nm) and polydispersity index (PDI) of PNCS microparticles at different temperatures determined by dynamic light scattering at pH 6.5.

Temperature (°C)	Hydrodynamic size (nm)	PDI
24	697	0.328
28	499	0.254
32	343	0.241
36	195	0.230
40	175	0.269

groups (at pH 6.5) results in increased hydrophilicity of the whole system and it imparts charge repulsion between the microparticles. Further, we observed that over the temperature range from 20 °C to 40 °C, the size distribution measured as polydispersity index (PDI) does not vary significantly even though the average hydrodynamic size of PNCS microparticles reduces to ¼ of the average size at 24 °C (Table 1). This indicates that the microparticles are well separated from each other over the whole temperature range assessed.

Effect of pH on hydrodynamic size of PNCS microparticles was studied using dynamic light scattering at 20 °C (Fig. 2b). The results show that at low pH PNCS microparticles are in swollen state, having at pH 2 the hydrodynamic size of 960 nm. With pH increase the hydrodynamic size of PNCS microparticles gradually decreases, reaching 650 nm at high pH values. This swelling/de-swelling effect of microparticles is purely due to the presence of chitosan. At low pH the amino groups of chitosan are protonated and it acts as cationic polyelectrolyte (soluble in acidic medium – swelling). By increasing pH, the amino groups become non-protonated and, as the rest of backbone chain of chitosan is relatively hydrophobic, chitosan becomes insoluble (Vårum, Ottøy, & Smidsrød, 1994). As the consequence, PNCS microparticles de-swell in basic medium due to pH sensitivity of chitosan.

The transition temperature (LCST) of PNCS microparticles in aqueous system was examined by measuring the absorbance of the microparticle dispersion as a function of pH and temperature. Fig. 3 shows the absorbance of PNCS microparticle dispersion (pH 2, 4, 7 and 9) studied within the temperature range 20–40 °C. The results show that by lowering pH (in acidic pH range) the temperature at which PNCS microparticles collapse decreases. Hence, at pH 2 the transition temperature is estimated at 26 °C, at pH 4 it is around 30 °C and at pH 7 and pH 9 it is 33 °C. Therefore, it can be concluded that the LCST of PNCS microparticles decreases in acidic medium. Similar effect on LCST of poly-NiPAAm was observed by Pei et al. (2003), however the polymeric system they used was different.

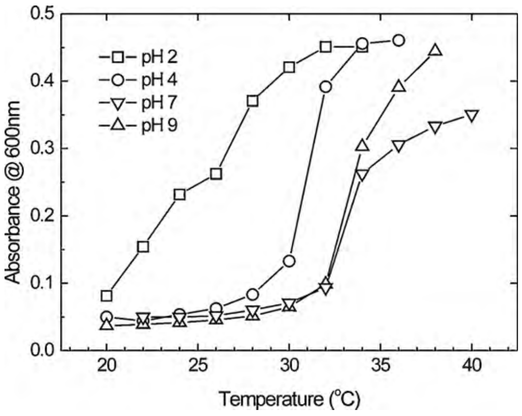

Fig. 3. Temperature induced phase transition of PNCS microparticles studied by UV–vis spectrophotometry at 600 nm for pH 2, 4, 7 and 9.

3.2. Incorporation of PNCS microparticles to cotton

As described previously, PNCS microparticles were coated and crosslinked on cotton using pad-dry-cure method. When cotton fabric is treated with PNCS/BTCA reaction mixture, at first – due to absorptive property cotton – it adsorbs hydrophilic BTCA and PNCS microparticles. During the curing stage at 160 °C BTCA forms anhydride. Anhydrides readily react with hydroxyl group and amine to form the esters and amide, respectively (El-tahlawy, El-bendary, Elhendawy, & Hudson, 2005) as shown in Fig. 4. There are two types of hydroxyl groups available for reaction with BTCA: hydroxyl groups of cellulose (cotton) and hydroxyl groups of chitosan from PNCS microparticles. It is expected that BTCA crosslinking occurs via esterification with these hydroxyl groups as well as via formation of amide with free amino groups of chitosan. During cotton coating with PNCS/BTCA reaction mixture the pick-up was maintained to 100%, so after crosslinking the add-on (A) value for treated cotton samples was calculated. The measured add-on (A) for PNCS coated cotton (c-PNCS/BTCA) was 3%, while for cotton treated with BTCA only (c-BTCA) it was 1.3%.

To confirm that the PNCS microparticles are chemically linked to cotton fabric, c-PNCS/BTCA and c-BTCA samples were analyzed by XPS and the results obtained for surface elemental composition are compared to the untreated cotton sample (c-UT). Table 2 shows both theoretically calculated elemental composition of polymers and crosslinker involved, as well as the experimentally obtained values (by XPS survey scan) for surface elemental composition of cotton samples. The calculation of theoretical corresponding values as a function of known chemical composition of the repeating units of cellulose, chitosan,

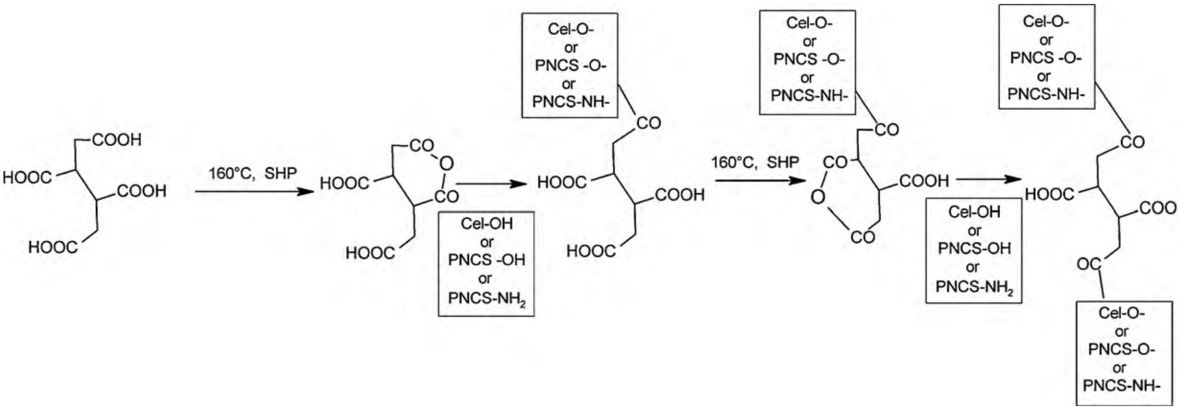

Fig. 4. Proposed mechanism of PNCS crosslinking on cotton using BTCA.

Table 2
Elemental composition and atomic ratios of constituent macromolecules (cellulose, chitosan, poly-NiPAAm) and crosslinker (BTCA) calculated theoretically and experimentally obtained from XPS survey scan of cotton with incorporated PNCS microparticles (c-PNCS/BTCA).

Sample	Elemental composition (at.%)			Atomic ratio	
	C 1s	O 1s	N 1s	O/C	N/C
Theoretical					
Cellulose	54.5	45.5		0.83	
BTCA (crosslinked)	55.0	45.0		0.81	
Chitosan (DD 95%)	54.7	36.3	9.0	0.66	0.16
Poly-NiPAAm	75.0	12.5	12.5	0.17	0.17
Experimental					
c-UT	66.8	33.2		0.50	
c-BTCA	61.5	38.1		0.62	
c-PNCS/BTCA	70.4	22.4	7.2	0.32	0.10

poly-NiPAAm and crosslinked BTCA (by taking in account the deacetylation degree of chitosan) (Table 2) has been necessary for the interpretation of the results of surface elemental analysis. The results obtained by XPS survey spectra of untreated cotton, BTCA treated cotton and PNCS/BTCA treated cotton indicate, as expected, that nitrogen is present only in PNCS/BTCA treated cotton. The appearance of nitrogen can be attributed both to chitosan and to poly-NiPAAm, but the contribution of each individual component cannot be established from the survey spectra. However, as obtained nitrogen percentage in c-PNCS/BTCA sample (7.2 at.%) is lower than the theoretically expected values for chitosan (9.0 at.%) and poly-NiPAAm (12.5 at.%), it can be estimated that the PNCS microparticles cover around 50–60% of the cotton fiber surface, the rest being probably covered with the BTCA three-dimensional network. This assumption is in good agreement with the observation of the surface morphology by SEM (Fig. 5a and b). Another important finding is the significant lowering of the O/C ratio (0.32) of the c-PNCS/BTCA sample, when compared to both c-UT and c-BTCA (0.50 and 0.62, respectively). This is another clear indication of the incorporation of PNCS microparticles, as the result is the consequence of increased concentration of unoxidized carbon that originates from poly-NiPAAm – the compound rich in carbon-containing groups (O/C = 0.17).

The surface morphology of PNCS/BTCA treated cotton was examined by SEM and compared to the surface morphology of cotton treated with BTCA only (Fig. 5). The incorporation of PNCS microparticles to cotton significantly changes the visual aspect of the fiber surface (Fig. 5a and b; taken at various magnifications). The form, size and amount of microparticles present is clearly noticeable and the microparticles seem embedded in the crosslinker film. This suggests that the microparticles are linked both to cotton surface and crosslinked with each other via BTCA. The images also show that the thin film of the surface modifying system covers the whole cotton fiber surface with existence of some irregular fragments visually observed as clusters of microparticles on the fiber surface (Fig. 5b). Furthermore, at such a low add-on level (3%) the twisted ribbon form of cotton fibers was still observable (Fig. 5a). The image of cotton treated with BTCA only (Fig. 5c) shows the presence of continuous film at the fiber surface, without significant visual difference to the well-known surface morphology of untreated cotton. To check the durability of coating on cotton, the PNCS/BTCA treated cotton samples were washed five times (45 min; 60 °C; nonionic surfactant), then dried at room temperature and SEM image was taken (Fig. 5d). The image shows that even after five times washing, significant amount of the surface modifying system is present on cotton and the surface morphology is very similar to the original sample (c-PNCS/BTCA, Fig. 5a).

In order to check the amount of the surface modifying system that remains after washing, the add-on (A) has been measured after each washing cycle. It has been observed that after second washing, the add-on of PNCS treated cotton was reduced to 2.7% and

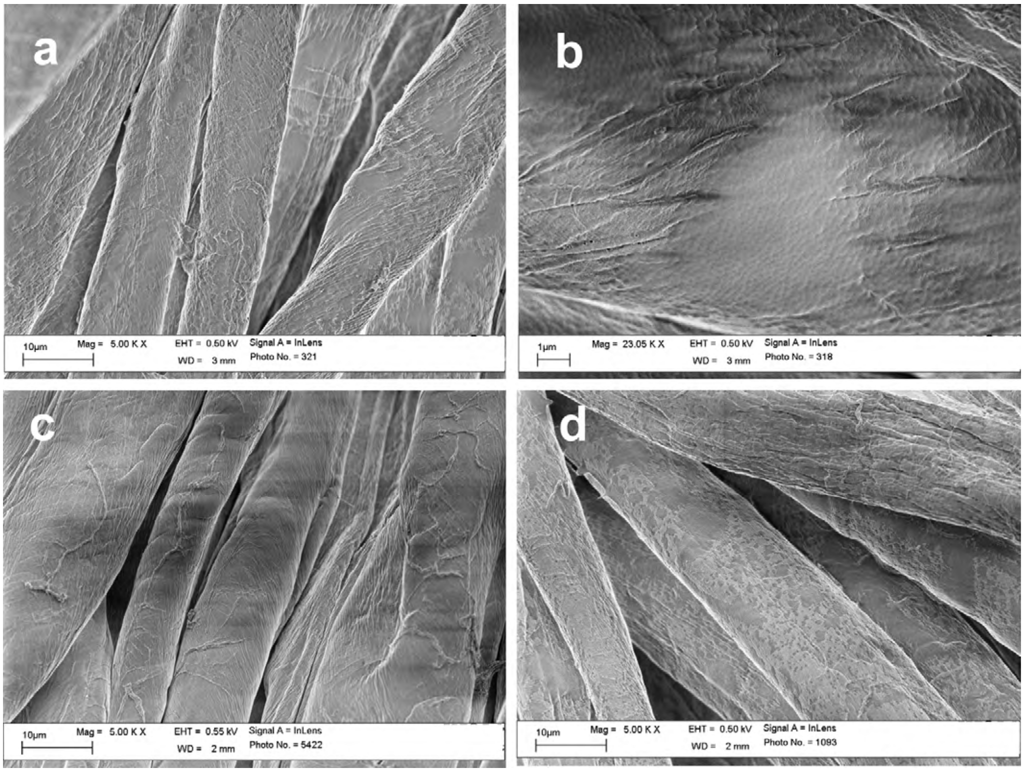

Fig. 5. Scanning electron microscope images of cotton with incorporated PNCS microparticles (c-PNCS/BTCA) (a and b); cotton treated with BTCA only (c-BTCA) (c) and cotton with incorporated PNCS microparticles (c-PNCS/BTCA) after five times washing (d).

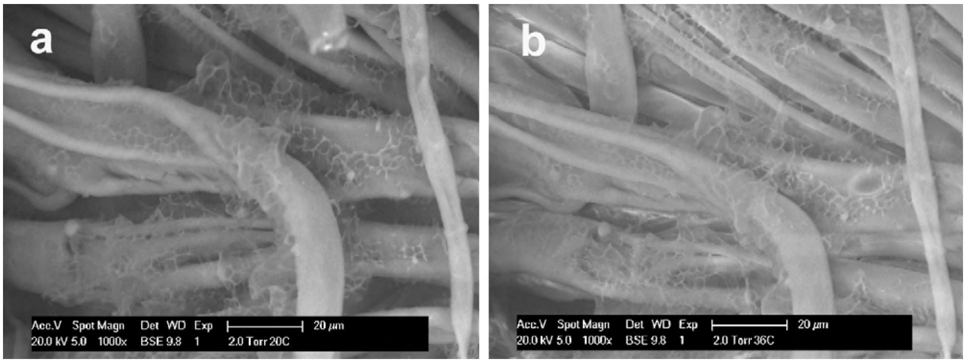

Fig. 6. Environmental scanning electron microscope images of cotton with incorporated PNCS microparticles (c-PNCS/BTCA) at 20 °C (a) and 36 °C (b).

after fifth washing it reached the value of 2.4%. This result shows that PNCS microparticles are attached with satisfying durability to cotton, since ~80% of the surface modifying system still remains incorporated to cotton after 5 washing cycles.

3.3. *Stimuli-responsiveness of PNCS coated cotton*

Stimuli sensitivity of modified cotton was investigated using environmental scanning electron microscopy (ESEM) and by measuring water uptake capacity. ESEM allows taking images of samples at relatively low vacuum, so one can study microscopically the morphology of samples in moist environment. Fig. 6 shows ESEM images of the same spot of c-PNCS/BTCA sample at the temperatures below (20 °C; Fig. 6a) and above (36 °C; Fig. 6b) transition temperature of PNCS microparticles. The images show that the microparticle layer incorporated to cotton surface is in swollen state at low temperature and in collapsed state at higher temperature, clearly indicating the temperature-responsiveness of the coating.

Furthermore, the stimuli-responsiveness of functionalized cotton fabric was investigated macroscopically by measuring water uptake of the c-PNCS/BTCA samples at various temperatures (24–42 °C) and pH (3, 6.5 and 10). The type of experiment done is so-called “shrinking experiment” where the samples were initially swollen and with raising the temperature they start to de-swell. The graphs presented in Fig. 7a–c compare the water uptake values obtained for c-PNCS/BTCA to corresponding values for c-BTCA sample, latter being considered as the reference for the purpose of establishing quantitatively the response, i.e. the contribution of the incorporated PNCS microparticles to the overall effects observed. For the reason of keeping the clarity of the graphs, the values for the original cotton sample (c-UT) are not presented, but it is worthwhile mentioning that its water uptake was nearly constant (between 95% and 105%) over the whole temperature range and for each pH measured. Similarly, the water uptake of c-BTCA sample remains relatively constant over the whole investigated temperature range, but showing slightly different average water absorption capacity at different pH values (~110% at pH 3; ~100% at pH 6.5; ~115% at pH 10).

The most obvious temperature sensitivity of the functionalized cotton fabric was observed at pH 6.5 (Fig. 7b). The transition occurs within the relatively narrow temperature range (29–32 °C), with water uptake decrease from 125% to 95%, and with further temperature increase it remains constant. Moreover, it is worthwhile noticing that at temperatures below 29 °C the significant response of 20–30%, measured by increase of water uptake compared to c-UT or c-BTCA, is achieved with only 3% add-on of the surface modifying system.

Similar overall effect, with existence of relatively sharp transition (30–32 °C), has been observed in acidic environment (pH 3, Fig. 7a), but with significantly weaker response (~10% instead of 20–30%). In alkaline environment (pH 10, Fig. 7c) the significant water uptake increase (~20%) was recorded at 24 °C. With further temperature increase, water uptake decreases gradually until 32 °C (there is no sharp transition) and it remains constant afterwards. It is interesting to note that when the surface modifying system is in collapsed state, water uptake is always lower (~10%) than in original/reference cotton samples (c-UT and c-BTCA). This finding confirms that, once the transition temperature attained, the surface modifying system becomes hydrophobic, thus imparting increased hydrophobicity to modified cotton.

The effects observed are the consequence of swelling/collapse of PNCS microparticles incorporated to the cotton surface. When PNCS microparticles are incorporated to cotton, it is expected that there is less space for the microparticle to expand and that it could not swell as fully as the free microparticle. Nevertheless, clearly observed sharp transition and pH-/temperature-responsiveness in spite of the heterogeneity of the whole system (cotton + PNCS + BTCA) is an encouraging result.

When rising the temperature, poly-NiPAAm undergoes collapse transitions with accompanying sharp change in polymer conformation which results from a balance between hydrogen bonding of water onto the chain (hydration at amido groups) and hydrophobic aggregation of isopropyl groups (Schild, 1992). The origin of this temperature sensitivity has been fully explained by the cooperative hydration mechanism (Okada & Tanaka, 2005). Due to cooperative interaction between the nearest – neighboring – bound water molecules, sequential hydrogen bonds are formed along the polymer chain. As a result, consecutive sequences of bound water appear along the chain, which leads to a pearl-necklace type chain conformation. When the chain is heated up, the hydrogen bonds are broken and each sequence is dehydrated as a whole, resulting in the sharp collapse of the chain as the consequence of the hydrophobic interactions among the isopropyl groups, which become dominant. As a result, entrapped water molecules via hydrogen bonds in hydrogel are released from the network, leading to de-swelling. However, because of its hydrophilic nature (which is affected by pH of the solution), the incorporation of chitosan bearing a large amount of hydrophilic groups including hydroxyl and amino groups into the poly-NiPAAm hydrogel network is expected to greatly influence the above explained interactions. Moreover, when incorporated to cotton, the surface modifying system contains crosslinking agent (BTCA) beside poly-NiPAAm and chitosan (PNCS microparticles). Thus, both crosslinked structure and the presence of carboxyl groups (from BTCA) in the system are also expected to influence the responsive behavior of poly-NiPAAm and chitosan.

In order to explain the effects observed (Fig. 7a–c), the main factors to be considered are: the initial level of water uptake at low temperature; and the transition behavior with rising the temper-

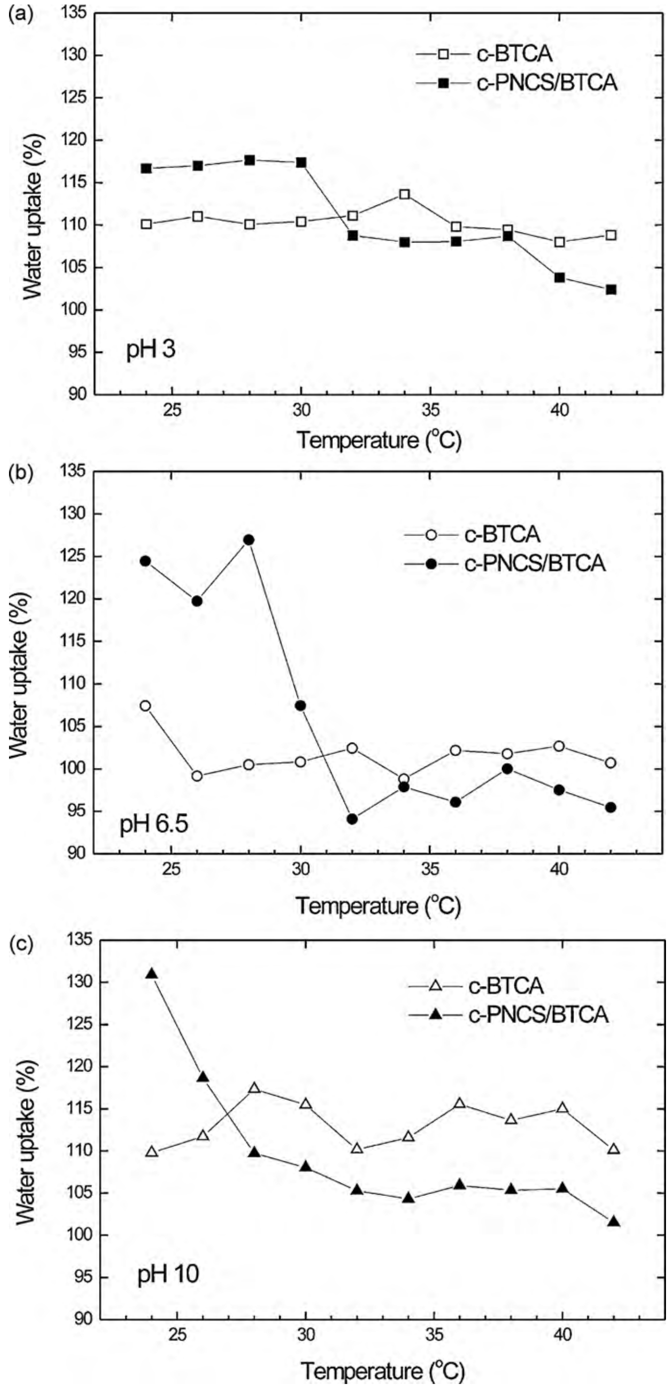

Fig. 7. Temperature dependence of water uptake of cotton with incorporated PNCS microparticles (c-PNCS/BTCA), studied at pH 3 (a), pH 6.5 (b) and pH 10 (c), compared to the corresponding values for cotton treated with BTCA only (c-BTCA).

ature. The initial water uptake (measured at 24 °C) is significantly affected by pH value, showing unexpectedly the lowest value at pH 3 (Fig. 7a). The observed behavior can be explained by understanding the effect of pH on collapse temperature of PNCS microparticles (studied by absorption spectrophotometry, Fig. 3). At lower pH, PNCS microparticles collapse at lower temperature than expected, thus meaning that at pH 3 even at such a low temperature (24 °C) PNCS microparticles are in slightly collapsed state. Hence the initial water uptake observed at 24 °C for pH 3 is lower than that of weak acidic condition (pH 6.5; Fig. 7b). However, at higher temperatures (above 30 °C), PNCS microparticles are predominantly in collapsed state, hence the water uptake measured above 30 °C for all three different pH conditions (pH 3, 6.5 and 10) is almost same.

At pH 6.5 (Fig. 7b) initial water uptake ability (at 24 °C) of the surface modifying system is increased due to the strong hydrogen bond interaction between amide group (from poly-NiPAAm) and water molecules. Thus, poly-NiPAAm contribution to water uptake can be considered as predominant, so the shape of the water uptake temperature dependence curve with the relatively sharp transition phase, can be attributed mainly to known poly-NiPAAm temperature-responsiveness.

At alkaline conditions (pH 10; 24 °C; Fig. 7c), the initial water uptake ability was not influenced by hydrophobic nature of chitosan. Moreover, instead of showing well-defined transition with increasing temperature, the water uptake decreases gradually until 32 °C. The effect observed can be discussed in terms of PNCS microparticle morphology which suggests that the microparticles are of homogeneous structure. By gradually increasing the temperature, the microparticle starts to shrink (consequence of poly-NiPAAm temperature-responsiveness) and expels water. However, this process is being slowed down due to hydrophobic chitosan chains present in the surrounding of poly-NiPAAm chains, which prevents water molecules from migrating easily out of the PNCS microparticle. Hence, the de-swelling occurs – but in a much slower rate than at pH 6.5 – because water cannot be easily overtaken by nearby chitosan and transported outside the microparticle. This means that the de-swelling rate is regulated by the chitosan state in the microparticle.

4. Conclusion

The poly-NiPAAm/chitosan microparticles (PNCS) of around 200 nm in size and with homogeneous morphology have been synthesized by surfactant-free dispersion copolymerization method. Dual (pH and temperature) responsiveness of PNCS microparticles has been confirmed by: reducing of hydrodynamic size with increase in temperature; complete collapsing that occurs at 34 °C; swelling in acidic medium and collapsing in alkaline medium; transition temperature (LCST) decreasing with decrease in pH. The stimuli-responsive PNCS microparticles have been used for functional finishing of cotton in the form of surface modifying system that contained polycarboxylic acid (BTCA) as an additional film-forming agent to produce three-dimensionally linked network between the microparticles and the substrate. The industrially acceptable pad-dry-cure method has been used. The crosslinking of PNCS to cotton was confirmed by XPS studies and durability of the surface modifying system was monitored by five times washing. The pH and temperature sensitivity of functionalized cotton fabrics was qualitatively and quantitatively investigated by ESEM and by water uptake studies, respectively. It has been confirmed that the stimuli-responsive surface modifying system imparted pH- and temperature-responsiveness to cotton fabric in terms of regulating its water uptake in dependence of these two stimuli.

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