MICROGEL FUNCTIONALIZED TEXTILES RESPONSIVE TO AMBIENT CONDITIONS

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ABSTRACT

Dual-stimuli responsive microgel (PNCS), prepared from poly-NiPAAm - a temperature-responsive synthetic polymer, and chitosan - a pH-responsive biopolymer, were synthesized and incorporated into cotton fabric by a pad-dry-cure method. 1,2,3,4-butanetetracarboxylic acid (BTCA) was used as crosslinker. Surface chemical changes of modified cotton (Co-PNCS/BTCA) were followed by X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM). Material properties were characterized in terms of whiteness and crease recovery. The response to changes of temperature and pH has been analyzed by measuring the water uptake, moisture content and water vapour transmission.

Key words: responsive textile material, poly-NiPAAm/chitosan microgel, moisture management properties

1. INTRODUCTION

The thermal and moisture comfort properties of textile fabrics are closely linked to fibre hygroscopicity, surface energy of fibre (hydrophilic or hydrophobic), fabric structure and moisture management properties. It is well known that these important factors can be controlled by redesigning textile material surface. An encouraging option to meet this goal is the functional finishing by application of microgel based on stimuli-responsive polymers. This surface modifying system shows specific volume phase-transition (swelling and shrinking) which can be triggered by various stimuli (temperature, pH, humidity etc.). Thus, the controlled expansion or contraction of the surface incorporated microparticles is expected to lead to adjusting the liquid management of textiles.
In order to obtain a surface modifying system that is capable of changing its structure as well as its physico-chemical characteristics when responding to small environmental changes, dual-stimuli responsive microgel was prepared from chitosan - a pH-responsive biopolymer and poly-NiPAAm - a temperature-responsive synthetic polymer. Poly-NiPAAm/chitosan (PNCS) microgel was subsequently incorporated onto cotton by a pad-dry-cure process using 1,2,3,4-butanetetracarboxylic acid (BTCA) as crosslinker [1]. Modified cotton fabric has been subsequently tested on surface morphology and surface chemical changes, some material characteristics (crease recovery; whiteness) and responsiveness to temperature-, pH- and ambient humidity.

2. EXPERIMENTAL

2.1 Materials

Cotton fabric (plain weave; 105 g/m^2, double scoured) (Vlisco, The Netherlands); Tanaterge EP5071 (Tanatex, The Netherlands), nonionic detergent; N-isopropylacrylamide (NiPAAm) (Acros, Belgium); chitosan (Chitoclear, DD=95%, η=159 cp) (Primex, Iceland); N,N-methylenebisacrylamide (MBA); ammonium persulfate (APS); 1,2,3,4-butanetetracarboxylic acid (BTCA); sodium hypophosphite (SHP) (all from Sigma-Aldrich, The Netherlands).

2.2 Methods

Poly-NiPAAm/chitosan microgel was prepared by surfactant free co-polymerization of poly-NiPAAm with chitosan as previously described [1, 2]. Modified cotton (Co-PNCS/BTCA) was prepared by incorporating microgel (PNCS) to previously washed cotton fabric,using pad-dry-cure process. The finishing bath consisted of: BTCA; PNCS dispersion; SHP (catalyst) in the ratios: PNCS:BTCA = 3.75:1; BTCA:SHP = 2:1. The pad-dry-cure parameters were: 100% pick-up; drying at 70°C, 1 h; curing at 160°C, 3 min; washing; air drying. The add-on was 2%. A separate sample (Co-BTCA) was prepared without PNCS keeping the same ratios. The surface morphology of air dried PNCS and modified cotton was determined by SEM (1550 HRSEM, Zeiss, Germany). The surface chemical composition was determined by XPS analysis (PHI Quantera Scanning ESCA Micro probe spectrometer, Physical Electronics, USA). Further characterization was done by measuring whiteness (CIE WI) (Spectro-Eye, X-Rite, USA) and crease recovery angle (CRA) (AATCC test method 66-1972). Stimuli responsive properties were determined by measuring water uptake (WU) (gravimetrically; pH 3; pH 6.5; pH 10; room temperature), moisture content (MC) (thermo-gravimetrically; moisture analyzer MS-70, A&D, Japan) and water vapour permeability (WVT) (UNI 4818-26; 24 h; climatic chamber SM-1.0-3800, Thermotron, USA; 25^{o}C; 40^{o}C; 50% R.H.; 80% R.H.). Results are an average of at least three readings.

3. RESULTS AND DISCUSSION

SEM images of modified cotton (not presented here) show that PNCS microparticles are clearly visible on the fibre surface and embedded in the crosslinker film.

Table 1. Elemental composition with atomic ratios of constituent macromolecules (cellulose, chitosan, poly/NiPAAm and BTCA - calculated theoretically) and of untreated (Co-UT) and treated (Co-BTCA and Co-PNCS/BTCA) cotton fabric (experimentally obtained from XPS survey scan spectra)

	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	Co-UT	66.8	33.2		0.50	
	Co-BTCA	59.6	40.4		0.68	
	Co-PNCS/BTCA	66.1	29.7	4.3	0.45	0.07

XPS survey spectra (Table 1) confirm that PNCS microgel was successfully incorporated to cotton (Co-PNCS/BTCA). Treatment with BTCA only (Co-BTCA) significantly decreases carbon content (from 66.8 at.% to 59.6 at.%) as the consequence of BTCA film forming at the fibre surface. After PNCS incorporation, even though BTCA film is formed at the fibre surface, carbon content again reaches the level of untreated cotton (66.1 at.% vs. 66.8 at.%). This is due to the presence of carbon-rich poly-NiPAAm. Nevertheless, with PNCS incorporation oxygen content decreases to the level which is even below the initial one (29.7 at.% vs. 33.2 at.%), again mainly due to poly-NiPAAm presence, but also on behalf of newly introduced nitrogen which originates from both poly-NiPAAm and chitosan. As expected, nitrogen is present only at PNCS treated cotton which could be considered as the indicator of successful microgel incorporation. However, relatively low observed nitrogen content (4.3 at.%) (when compared to theoretical values for chitosan and poly-NiPAAm) could be explained by specific discrete arrangement of microparticles at the fibre surface which is estimated to be covered not more than 50% by microparticles. The SEM analysis gave visual confirmation for this assumption.

Table 2. Whiteness index (WI) and crease recovery angle (CRA) values

Sample	CIE WI	CRA (°)	
		Warp	Weft
Co-UT	77.3	48.1	47.5
Co-BTCA	77.3	50.9	61.6
Co-PNCS/BTCA	76.8	57.0	61.3

Since the PNCS/BTCA incorporation may impart changes not only to the fabric surface but also to the overall fabric appearance and properties, WI and CRA of Co-BTCA and Co-PNCS/BTCA were measured (Table 2). No significant changes were noticed in WI values when comparing either Co-PNCS/BTCA or Co-BTCA to untreated cotton. However, CRA of Co-PNCS/BTCA was slightly bigger than that of Co-BTCA due to the stiffness imparted by the presence of PNCS microgel.

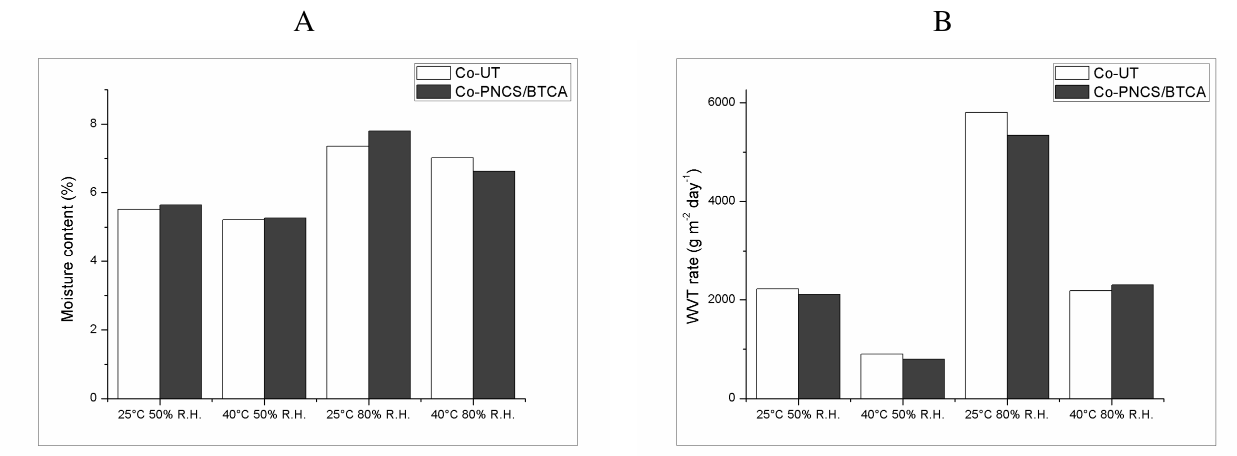

Figure 1. Moisture content (A) and water vapour transport rate (B) of Co-UT and Co-PNCS/BTCA at different conditioning parameters

It has been previously published that the liquid management properties of microgel functionalized textile depend on the temperature and humidity [3, 4]. Water uptake (WU) results (not shown here) confirm increased water uptake capacity at low pH values which is the consequence of chitosan pH-responsiveness. The results obtained for the influence of temperature and ambient humidity on moisture content (MC) and water vapour transport rate (WVT) of Co-UT and Co-PNCS/BTCA are presented in Figure 1. The humidity values were chosen as low (50% R.H.) and high (80% R.H.), and temperature was chosen to be below (25^{o}C) and above (40^{o}C) 32^{o}C (LCST of poly-NiPAAm). The moisture content results (Figure 1A) generally follow the known fact that the MC of the material decreases with temperature increase or ambient humidity decrease, which can be observed with both untreated and modified material. However, since the water presence is the driving force for the temperature responsiveness of microgel, different behaviour can be observed at low and high R.H. At low R.H. (50%), since there is not enough ambient humidity available, the microparticles are in "dry" state and the modified cotton does not show temperature response (or at least it is not macroscopically observable). In fact, it follows the same behaviour as untreated material. However, at high R.H. (80%), when enough humidity is available, there are noticeable differences in the modified cotton behaviour in response to temperature change. Even though the differences are rather small, they clearly imply the responsive property of Co-PNCS/BTCA. At 25^{o}C (where microparticles are hydrophilic) the moisture content is increased for modified cotton (actually the same happens as at low R.H., just at the bigger magnitude). At 40^{o}C the microparticles become hydrophobic, so the moisture content of Co-PNCS/BTCA is consequently significantly decreased (when compared to Co-UT). Therefore, it can be concluded that the responsiveness of the material is more, if not exclusively, pronounced in wet environment. The similar discussion could be applied to water vapour transport (WVT) rate results (Figure 1B). At low humidity (50% R.H.) the temperature responsiveness could not be observed. It is only noticed that the WVT values slightly drop for Co-PNCS/BTCA sample as the consequence of microgel presence. It is expected that the microparticles at the fibre surface could slightly (increased roughness) block water vapour transport through the material. At high humidity (80% R.H.) the responsiveness becomes substantial. At low temperature (25^{o}C), microparticles swell significantly enough to hinder water vapour passage through the fabric. However, at 40^{o}C (above LCST), hydrophobic microparticles obstruct moisture absorption (Figure 1A), which on the other hand enhances the water vapour transport through the material.

4. CONCLUSIONS

Surface morphology characterization and XPS analysis confirmed that poly-NiPAAm/chitosan microgel was successfully incorporated into cotton by a pad-dry-cure method. Crease recovery angle measurements showed that microgel imparted some rigidness to the fabric. No changes in whiteness were noticed. Since the modified cotton is not offering a fixed resistance to the passage of water vapour and shows different liquid uptake properties, its responsiveness to ambient conditions has been confirmed.

5. REFERENCES

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Aknowledgment

The authors are thankful for financial support provided by Marie Curie Excellence Grant (EXT) project ADVANBIOTEX (MEXT-CT-2006-042641), funded by the EU’s Sixth Framework Programme.