

We are IntechOpen, the world's leading publisher of Open Access books Built by scientists, for scientists

6,900

Open access books available

186,000

International authors and editors

200M

Downloads

Our authors are among the

154

Countries delivered to

TOP 1%

most cited scientists

12.2%

Contributors from top 500 universities



WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com



Biopolymer-Based Stimuli-Responsive Polymeric Systems for Functional Finishing of Textiles

Dragan Jocić, Audrey Tourrette and Pavla Križman Lavrič
University of Twente
The Netherlands

1. Introduction

The technological developments of the first decade of 21st century are slowly changing the way we live by controlling our surroundings and regulating our every day life with intelligent objects. *Smart Materials* and *Intelligent Structures* are novel disciplines which are currently rapidly growing into an interdisciplinary technology. This new technology is being incorporated in contemporary engineering and design with the aim to create the path for materials to gain “intelligent” features. Textile materials also benefit from the rapid advances in a new interdisciplinary technology. Development of textile materials with new advanced functionalities is the perfect example where these base technologies can be brought together by using the knowledge involving *surface science* and *surface engineering* at molecular and atomic level. This knowledge is being responsible for developing and creating a new generation of so-called “smart” textile materials. By redesigning textile material surface, operating at microscopic level, many new possibilities emerge for adapting the macroscopic properties of the material to the present needs of the textile industry and thus fulfil current and future end-user expectations. In this context, this book chapter will focus on an innovative strategy for functional finishing of textile materials by application of *surface modifying systems* (SMS) based on *stimuli-responsive polymers*.

2. Stimuli-responsive surface modifying systems for textiles

Among wide variety of materials that nowadays surround us, textile material is considered unique because we have a natural relationship with it. Textile material for clothing is an example of a material which is personal, comfortable, and used almost anywhere and anytime. Clothing is considered as an extension to our physiological characteristics and is very close to the body, so the eternally existing goal was to make clothing material that possesses the extension of qualities of human skin (protection, breathability, sensing). Therefore, gaining “smart” capability for such a material would be the best example of almost always being surrounded by the object that could sense and response to the changes in the surrounding (human and/or ambient) conditions. The main feature of “smart” textile materials is that they could adapt effectively (significantly and automatically) to their local environment by changing the properties due to defined influences (stimuli) from the immediate surrounding. The functional activity of these materials is an important aspect.

“Smart” textiles are expected to act both as sensors and actuators, so they should not be confused with other existing high-performance or multifunctional textiles that are in fact "passive" materials with advanced properties.

With enormous growth in supporting technologies, primarily in the areas of responsive polymers and surface modification techniques, during the last decade the functionalization of textile material has gone quite a few paces forward. However, by being one of the oldest known technologies, traditional textile technology is rather reluctant to essential technology changes, but it is prepared to accept the modifications being based on a number of production steps. In creating paths for such “readily acceptable” solutions, *functional finishing* is one of the most viable alternatives. Functional finishing approach enables producers to continue to use conventional textile fibres and at the same time, by modifying a very thin surface layer of the material, achieve added-value by implementing “smart” features.

In recent times, an increasing amount of research is being done on functional finishing of textile materials by incorporating stimuli-responsive polymeric systems (Liu & Hu, 2005; Crespy & Rossi, 2007; Jovic, 2008). Through this approach, the new added-value textile material can be created containing fibres that maintains 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.

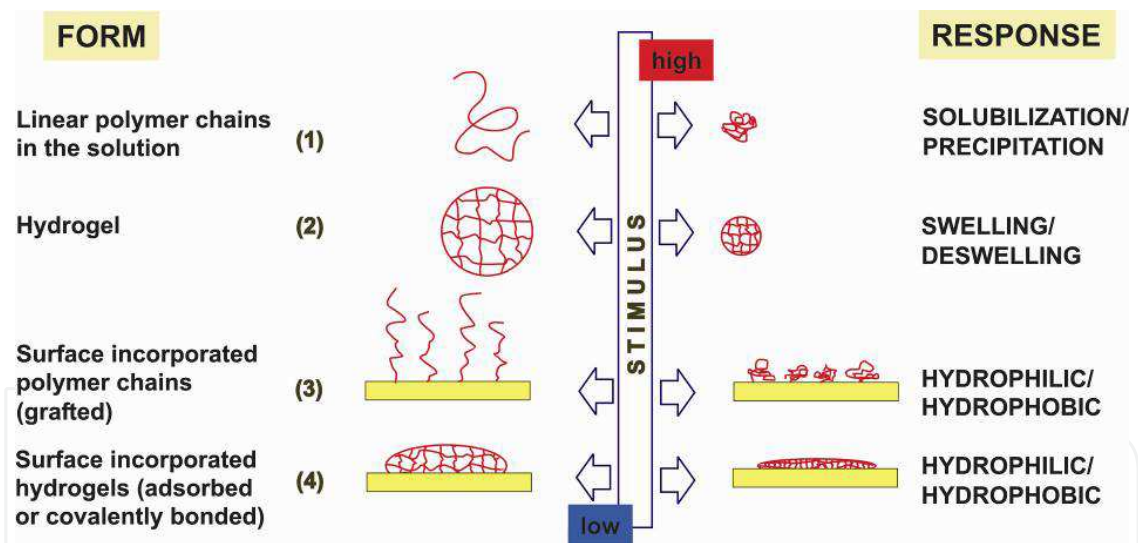


Fig. 1. Different forms of stimuli-responsive polymers and their macroscopic response.

Currently, the most encouraging option for producing efficient surface modifying systems comprises the use of *hydrogels*. This polymeric form exhibits specific volume phase-transition (swelling and shrinking) properties which can be triggered by various stimuli (temperature, pH, humidity, etc.). By incorporation of responsive hydrogels to the surfaces (i.e. textile material), the surface energy or some other property of a material can be switched (on/off). Most often, the switching is between hydrophilic/hydrophobic (Fig. 1). 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 (Kumar et al., 2007; Mano, 2008; Kopecek & Yang, 2007). However, due 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 pH-responsive polymeric component, resulting in dual responsive hydrogel systems (Prabaharan & Mano, 2006).

Among the wide choice of natural polymers, biopolymer *chitosan* is a good option for combining with synthetic stimuli-responsive polymers. Chitosan is a typical pH-sensitive polymer ($pK_a=6.3$) which responds to the changes in the pH of the surrounding medium by protonation/deprotonation that imparts charges on its amino groups (Ravi Kumar, 2000; Rinaudo, 2006). 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.

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 change due to side-chain re-configuration) 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) (Schild, 1992). 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).

3. Biopolymer-based microgel as surface modifying system

The main challenge in achieving the goal of effective functional finishing of textiles with hydrogels lay in the fact that surface modifying system, after its incorporation to the textile material, must exhibit responsive properties without screening the textile's regular performance. Taking in account above consideration, it can be easily concluded that bulk (continuous; macroscopic) hydrogels are not suitable form for functional finishing of textiles, because of slow response time and adverse influence on "textile" properties (flexibility, drapeability, touch, etc.) of the material. Hence, the most modern approach for functional finishing with hydrogels is based on micro- and nano-sized hydrogels, because this polymeric form possesses increased surface area per unit mass and significantly improved response times (Pelton, 2000). Moreover, the submicron particle size of microgels enables their incorporation to textile material surface in a very thin layer, without degrading "textile" properties of the material.

3.1 Synthesis of poly-NiPAAm/chitosan microgel (PNCS)

Microgel is a dispersion of crosslinked hydrogel particles which are swollen by a good solvent. It may also be defined as a disperse phase of discrete polymeric gel particles with sizes ranging between 1 nm and 1 μm . A number of other terms, in addition to the term "microgel", are used in the literature to describe small crosslinked particulate systems, such as "hydrogel microparticles", "hydrogel microspheres", "submicron gel beads", "micro-particulate hydrogels" or "ultrafine microspheres". Microgel has similar properties to both polymers and water-swollen gels (bulk or continuous hydrogels). However, microgel

consists of discrete particles whose characteristics are dependent on the method of synthesis, crosslinking density, monomer concentration, monomer composition and solvency conditions. Microgel particles are insoluble and do not form solutions like linear or branched polymers, but they may be considered to form colloidal dispersions.

The preparation of microgel can be achieved by different methods such as: emulsion polymerization; anionic copolymerization; crosslinking of neighbouring polymeric chains; inverse micro-emulsion polymerization or surfactant-free dispersion polymerization (SFDP). Emulsion polymerization is a versatile technique which yields narrow particle size distributions. Conventional emulsion polymerization enables preparation of very small microgel particles (i.e. particle diameters less than 150 nm) and suffers from the difficulty of completely removing the residual surfactant used for emulsion stabilization. Surfactant-free dispersion polymerization (SFDP) yields microgel particles with diameter range between 100 and 1000 nm, and this method does not suffer from residual surfactant contamination. Some authors call this procedure “precipitation polymerization” or “surfactant-free precipitation polymerization (SFPP)”. The continuous phase must have a high dielectric constant (e.g. water) and ionic initiators are employed. Generally, the polymerization is conducted at 50-60°C in order to generate free radicals by the decomposition of the initiator (e.g. ammonium persulfate – APS). Also, in case where thermoresponsive polymer chains such as poly-NiPAAm chains are present, elevated temperature is required to ensure that growing chains phase separate to form colloidal particles. The key feature of SFDP is that the particle nucleation period is very short (of the order of minutes), which ensures a narrow particle size distribution.

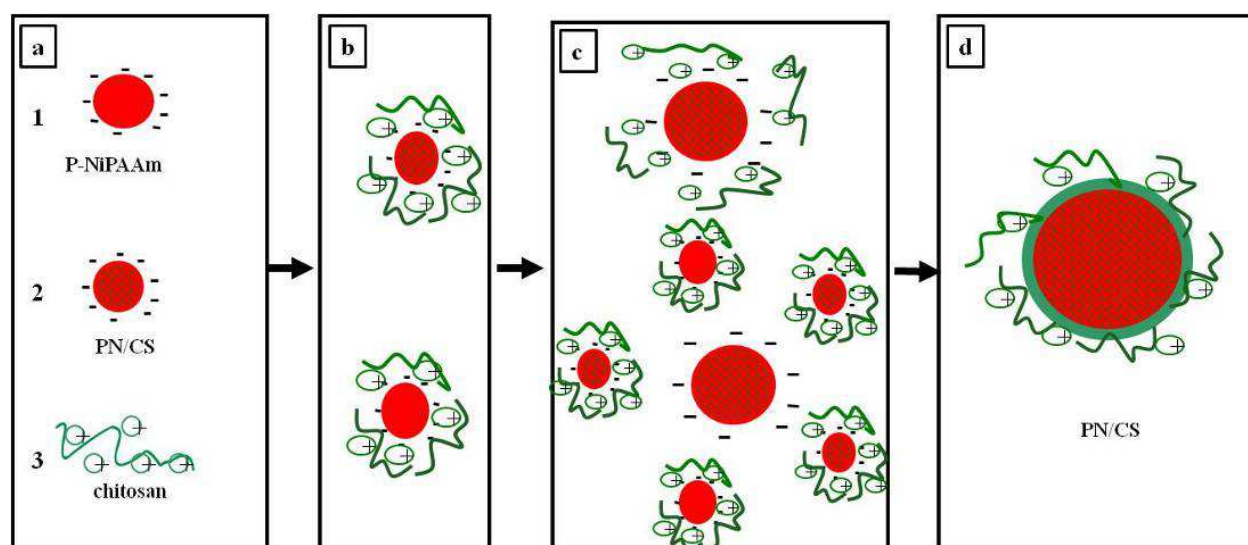


Fig. 2. Synthesis of poly-NiPAAm/chitosan microgel (SFDP mechanism).

The microgel of poly-NiPAAm and chitosan (PNCS), used in our research, was prepared by the surfactant-free dispersion copolymerization method according to the previously reported procedure (Lee et al., 2003; 2004). Three kinds of reactions occur in the reaction system of dispersion copolymerization (Fig. 2). The first reaction is the polymerization of NiPAAm, initiated by APS, which forms negatively charged particles (Pelton & Chibante, 1986) (Fig. 2, a-1). The second reaction is the graft copolymerization of NiPAAm and chitosan, initiated by APS which forms poly-NiPAAm/chitosan complex particles with a

negative surrounding charge (Fig. 2, a-2). The last reaction is the ionization of chitosan which results in positively charged chitosan molecules (Fig. 2, a-3). They might surround the negatively charged poly-NiPAAm or PNCS particles and behave like a surfactant to protect the polymer particles and thus avoid the coagulation (Fig. 2, b). If chitosan molecules are not in vicinity of the particles formed, the other possibility is that the particles coagulate to form larger positively charged particles, until the chitosan molecules are close enough to act like surfactant and prevent coagulation (Fig. 2, c-d).

There are several kinds of possible interactions between chitosan and poly-NiPAAm, such as electrostatic and hydrogen interactions (between chitosan amino and poly-NiPAAm amide groups), as well as covalent bonding due to the formation of radicals. The radical degradation of chitosan is the decisive step in the mechanism of copolymerization reaction. Hsu et al. (2002) showed that the thermal decomposition of an initiator similar to APS (potassium persulfate - KPS) produced free radicals which not only initiate the polymerization, but also break the backbone of chitosan molecules. On the other hand, it has been shown (Harish Prashanth & Tharanathan, 2003) that in free radical initiated copolymerization, NH_2 groups of chitosan were involved in microradical formation, which can interact with electrophilic functional group to create covalent bonding. In addition, Liu et al. (2007) stated that in the chemical structure of the grafting copolymers poly-NiPAAm was attached to the $\text{C}_6\text{-OH}$ reactive group of chitosan and to amino group. In summary, the covalent bonding between chitosan and poly-NiPAAm can be created from different chitosan functional groups: the terminal carbonyl groups of its backbone, its amino groups or its $\text{C}_6\text{-OH}$ reactive groups. The possibility of anionic persulfate (from the initiator) immobilization inside degraded chitosan chains through electrostatic attraction has been also mentioned (Hsu et al., 2002). Hence, chitosan plays multiple roles in the reaction system: in one way it can increase the polymerization rate by serving as a surfactant; on the other hand, the degraded chitosan chain can inhibit free radicals and slow down the polymerization.

3.2 Physicochemical properties of PNCS microgel

3.2.1 Characterization

A SEM image of dry poly-NiPAAm/chitosan microgel, deposited from a solution onto native oxide layer of a silicon wafer, is shown in Fig. 3. The photomicrograph 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.

Since microgel particles are incorporated on textile material not in dry state but in their hydrated state, DLS measurements of diluted PNCS dispersion were performed to determine the particle size (Tourrette et al., 2009). The result was a first proof of the temperature response of the microgel, as the mean microparticle diameter below LCST (426 nm at 25°C) was 2.5 times bigger than above the LCST (166 nm at 38°C). However, the particle size in totally collapsed state was found to be smaller than the one observed in the dry state on SEM picture (Fig. 3). This can be explained by the fact that for SEM analysis the microgel dispersion was deposited onto a native oxide layer of silicon wafer which is hydrophobic. Consequently, the microgel particles interacted strongly with the substrate and did not shrink as much during drying as after collapsing in liquid medium. This finding also shows that the micro-particulate network is not expected to be totally collapsed in dry state, which means that some water remains in the microgel internal structure after drying.

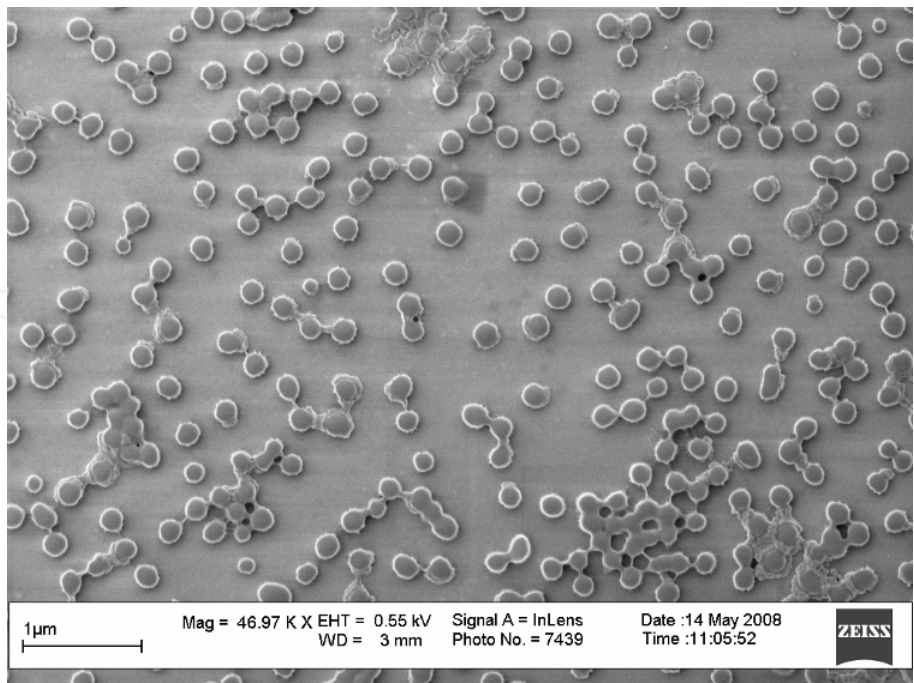


Fig. 3. SEM image of poly-NiPAAm/chitosan microgel particles (PNCS) deposited from a diluted ($3.56 \cdot 10^{-2}$ g/L) microgel dispersion onto a silicon wafer.

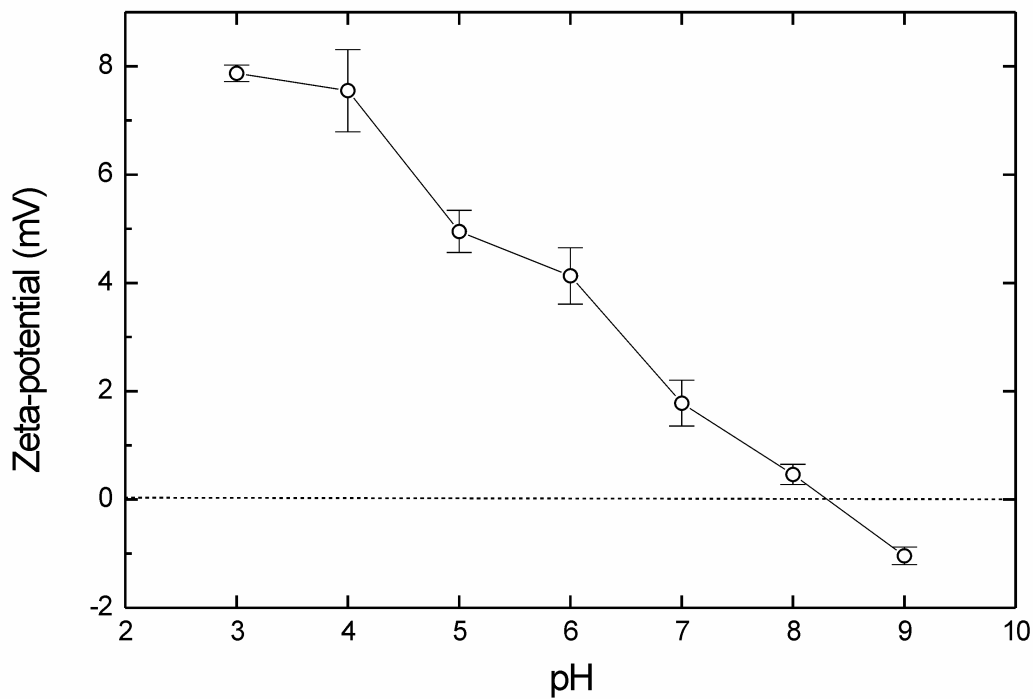


Fig. 4. Variation of zeta-potential with pH for aqueous dispersion of poly-NiPAAm/chitosan microgel dispersion (PNCS) ($1.1 \cdot 10^{-1}$ g/L) at 25°C.

The variation of the zeta-potential with the pH change of aqueous dispersion of PNCS microgel is shown in Fig. 4. Zeta-potential measured at low pH values (pH 3) has clearly positive value. With pH increase, zeta-potential decreases and reaches negative values above pH 8. The observed behaviour can be explained through chitosan pH-responsiveness.

In acidic solutions chitosan behaves as a cationic polyelectrolyte due to protonation of the amino groups. The pKa value of chitosan is 6.3 (as already stated before), but it is known that at pH 6.9 the amino groups ($-\text{NH}_2$) are still partly ($\sim 20\%$) protonated ($-\text{NH}_3^+$) (Muzzarelli, 1977). Therefore, at weak alkaline values (pH 7-8) chitosan is expected to have a very low positive charge. Since chitosan is pH-responsive and the change in its positive charge is detected by zeta-potential analysis, this confirms that chitosan is adsorbed at the surface of microparticles.

3.2.2 Stability

The stability and physical state (hydrophilic or hydrophobic character) of PNCS microgel depends on both temperature and pH. Among all possible interactions between the particles, three of them play a decisive role in microgel stability: electrostatic interaction; van der Waals forces; and steric forces. Hence, the stability of PNCS microgel will depend on the balance of the repulsive and attractive forces that exist between particles as they approach one another. If the particles have a mutual repulsion then they will remain dispersed. However, if the particles have little or no repulsive force, then flocculation, aggregation or coalescence will eventually take place. PNCS microgel stability is controlled by the balance between van der Waals attraction force, which causes aggregation, and steric or electrostatic forces that oppose aggregation. However, below the LCST, thermoresponsive particles are swollen and thus consist mainly of water. Under these conditions, the van der Waals attractive forces are relatively weak. Moreover, polymer tails extend from the gel structure to act as steric stabilizers, further enhancing microgel stability. Charged groups (from chitosan protonated amino groups) incorporated into the particles during polymerization, create electrostatic interactions which contribute to microgel stability. At elevated temperatures the water content of the gels is reduced giving a higher density, thereby increasing the van der Waals forces, which in turn tends to aggregate the microgel.

3.2.3 Stimuli-response

In order to study the stimuli responsive properties (swelling/shrinking behaviour) of PNCS, dynamic light scattering (DLS) analysis was used to study the microgel particle size at different temperatures and pH.

Fig. 5a presents the hydrodynamic diameter of PNCS microgel particles at different pH values. It shows that particle size is very sensitive to pH change as a result of protonation/deprotonation of chitosan. At pH 3 the hydrodynamic diameter is noticeably smaller compared to the values obtained at other pH values, which can be explained by previously reported (Pei et al., 2004) significant pH-dependence of poly-NiPAAm LCST value (it decreases!) in strong acidic medium. Another unexpected result is that the average hydrodynamic diameter of PNCS particles is considerably higher at pH 9, even though this pH value is far above pKa of chitosan (6.3). This result may be attributed to the instrument (DLS) limitation as the consequence of the averaging of a combination of several size distributions which could exist at this particular pH value due to the aggregation of the particles. Indeed, in this case chitosan is not protonated and the particles are slightly negatively charged (Fig. 4). Fig. 5b shows the hydrodynamic diameter of PNCS microgel particles as a function of temperature. The decrease of hydrodynamic diameter of microparticles with an increase of temperature proves their thermoresponsiveness. Polymer network of microgel shrinks gradually with an increase of temperature. Nevertheless, the change of the slope could be noticed around 33°C , which is close to the LCST of poly-NiPAAm.

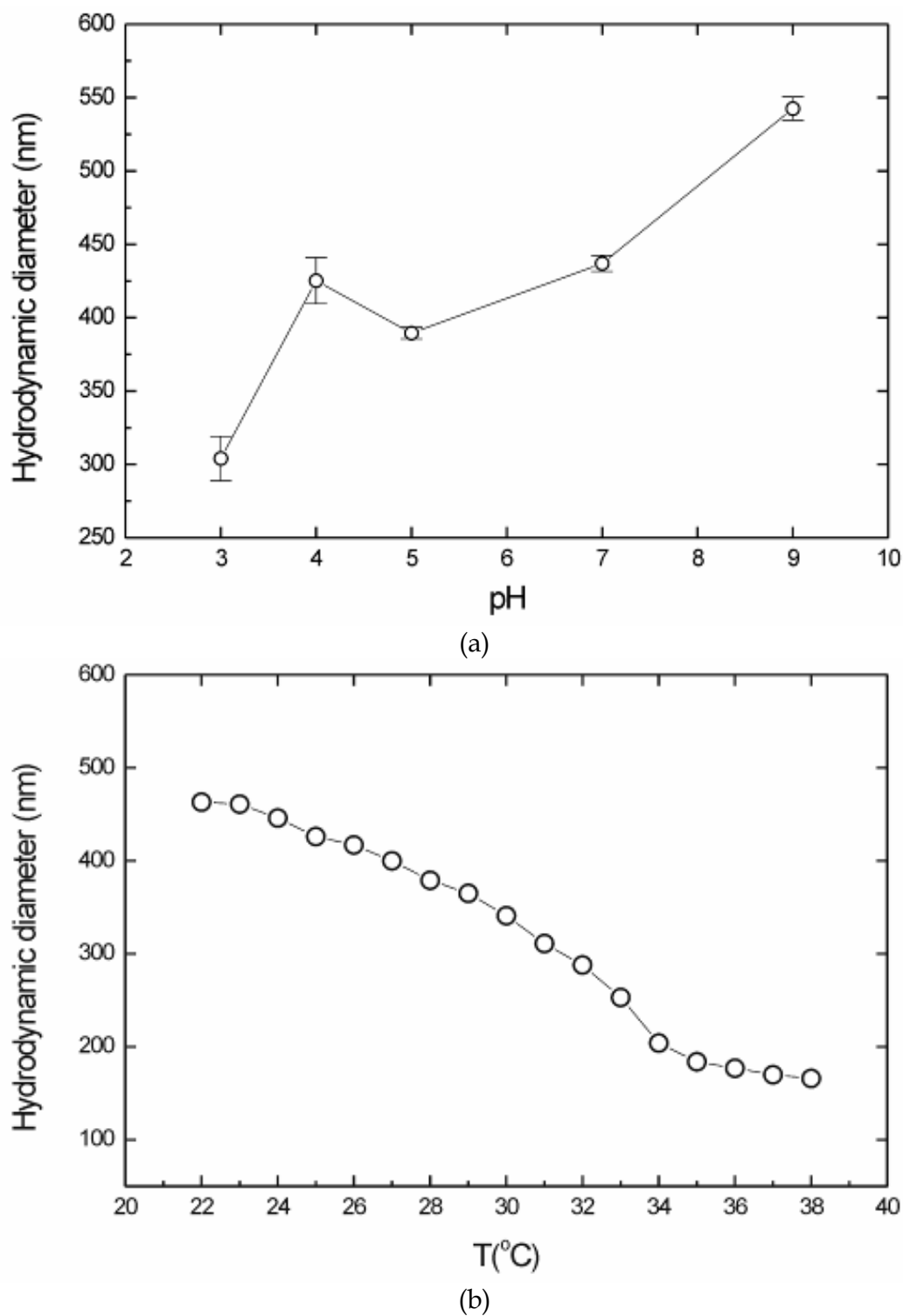


Fig. 5. Hydrodynamic diameter of PNCS microgel dispersion as a function of pH (a) (25°C; $1.1 \cdot 10^{-1}$ g/L) and temperature (b) (pH 7.3; $2.3 \cdot 10^{-1}$ g/L; NaCl 1 mM).

4. Incorporation of surface modifying system to cotton

The incorporation of the surface modifying system based on poly-NiPAAM/chitosan microgel to cotton can be done from aqueous microgel 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 microgel. Two different approaches are available to achieve this goal. One approach is based on cotton activation before the application of the surface modifying system, and both chemical (Jocic et al., 2009) and physical (Tourrette et al., 2009) methods have been previously reported. Another approach, which does not include previous activation of cotton, is based on the use of the additional film-forming agent to produce three-dimensionally linked network between the microgel particles and the substrate (Kulkarni et al., 2010; Krizman Lavric et al., 2010a; 2010b). Hence, the microgel can be bound to the surface of textile fabric directly (without the need for a separate and/or additional crosslinker) or with a crosslinking agent.

4.1 Microgel incorporation to previously activated cotton

4.1.1 Chemical cotton activation

The aim of textile material (cotton fabric) activation is to impart ionic character to cotton cellulose in order to facilitate the incorporation of micro-particulate system.

Among several possibilities for producing ionic active sites on cotton surface, two methods have been chosen as most convenient (Jocic et al., 2009): *anionic cotton* has been produced by reaction with monochloroacetic acid (CAA) to give partially carboxymethylated cellulose (*carboxymethylation*) (Hashem et al., 2003; Racz et al., 1996); *cationic cotton* has been produced by dyeing with reactive dye and subsequent reductive cleavage of the dye attached (*aminization*) (Kim et al., 2007). Thus, aromatic amines are formed on cotton by chemical reduction of covalently attached reactive dye molecules.

The chemical modification of cotton surface has been confirmed by XPS analysis (Jocic et al., 2009). The values for elemental composition and atomic ratio remain similar after carboxymethylation, while after aminization the O/C ratio is significantly increased by a factor 1.6. Both nitrogen and sulphur are detected at aminized cotton, which is the consequence of the presence of the reactive dye's vinyl sulphonic center and the free amino groups on the cotton surface (Fig. 6).

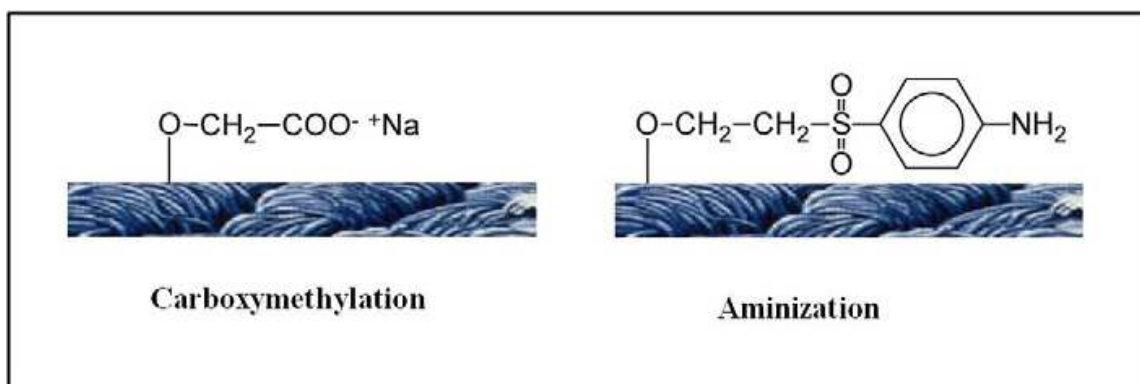


Fig. 6. Chemical activation of cotton.

4.1.2 Physical cotton activation: low-temperature plasma (LTP) treatment

The aim of cotton fabric treatment with LTP is to produce active species on the cotton fabric surface in order to facilitate the incorporation of PNCS microgel. It is well known that

plasma treatment produces chemically active species such as radicals, free electrons and ions, which generate cellulosic radicals on the cotton fabric surface (Li et al., 1997). Depending on the nature of the plasma gas used, different modification is expected. Ward et al. (1978) reported that air, nitrogen and argon as plasma gases produce cotton surface with physical and chemical characteristics that differ significantly from untreated cotton. These three most commonly used plasma gases (air, nitrogen and argon) have been used for the activation of cotton surface (Tourrette et al., 2009).

Examination of surface morphology (SEM) of plasma treated and untreated cotton reveals that the untreated cotton fibres have a smoother surface than plasma treated fibres (Tourrette et al., 2009). Micro-cracks are visible on plasma treated cotton fibres surface no matter which gas is used. These micro-cracks and grooves on the plasma treated fibre surface can be attributed to the ablation effect caused by interaction of plasma species with the fabric surface. As a result, the specimen surface becomes rougher; ablation increases fabric surface roughness, producing clearly visible voids and spaces. However, no significant differences are visible by SEM between the three different plasma gases, which means that there is not a big difference in the physical modification of cotton fibres surface. Anyhow, the nature of the plasma gas can lead to different chemical surface modifications, which cannot be analysed by the SEM technique, but with XPS analysis.

It has been shown by XPS analysis that the O/C atomic ratio obtained for all plasma treated samples is significantly higher than the value obtained for the untreated cotton, confirming that some oxidation of the cotton surface occurred after all plasma treatments. The oxidation processes of nitrogen and argon plasma treated cotton fabric can be related to plasma-created free radicals, which initiate oxidation reactions either during plasma treatment (due to: (1) the nature of the gas used (oxygen contained in air); (2) the presence of small amount of oxygen in the inter-electrode of the instrument or due to the vapour desorption from the cotton sample (Osenberg et al., 1999); or (3) after plasma treatment (as the consequence of the exposure of plasma treated fabric to air after treatment). The influence of the nature of the gas used for the treatment has also been shown with: (1) the value of O/C atomic ratio of air plasma treated cotton which was higher compared to cotton treated with other plasma gases; (2) the elemental composition, where nitrogen plasma treated cotton was the only sample that contained nitrogen at the surface (0.9 at.%).

4.1.3 Microgel incorporation method and surface characterization

PNCS microgel was incorporated by a batch method onto untreated and previously activated cotton fabrics. On untreated and chemically activated (carboxymethylated or aminized) cotton, this process is based on adsorption (van der Waals interaction, acid-base interaction, electrostatic interaction and hydrogen bonding) of the microgel particles onto cotton fibre surface without covalent bonding. However, as the consequence of the presence of radicals at the substrate surface, covalent bonding can be additionally expected between the plasma treated substrate and the microgel particles.

Surface features of untreated and both chemically and physically activated cotton samples with subsequently incorporated PNCS microgel were studied by SEM (Fig. 7). The incorporation of PNCS microgel significantly changed the visual aspect of the fibre surface. This was clearly exhibited in case of previously activated fabrics (chemically or physically) where it was easy to locate surface deposition of PNCS microparticles and to distinguish their form, size and amount present at the fibre surface. It is obvious that hydrated microgel

particles collapsed after incorporation onto the cotton fibre and deformed their shape to “pancake” structure. This is the consequence of volume shrinking because of water evaporation during drying and, possibly, water absorption from micro-particulate hydrogel into the cotton fibre. Previously untreated cotton (Fig. 7a) does not show clear evidence of microgel particle surface deposition, i.e. there is no significant visual change in comparison with the control sample.

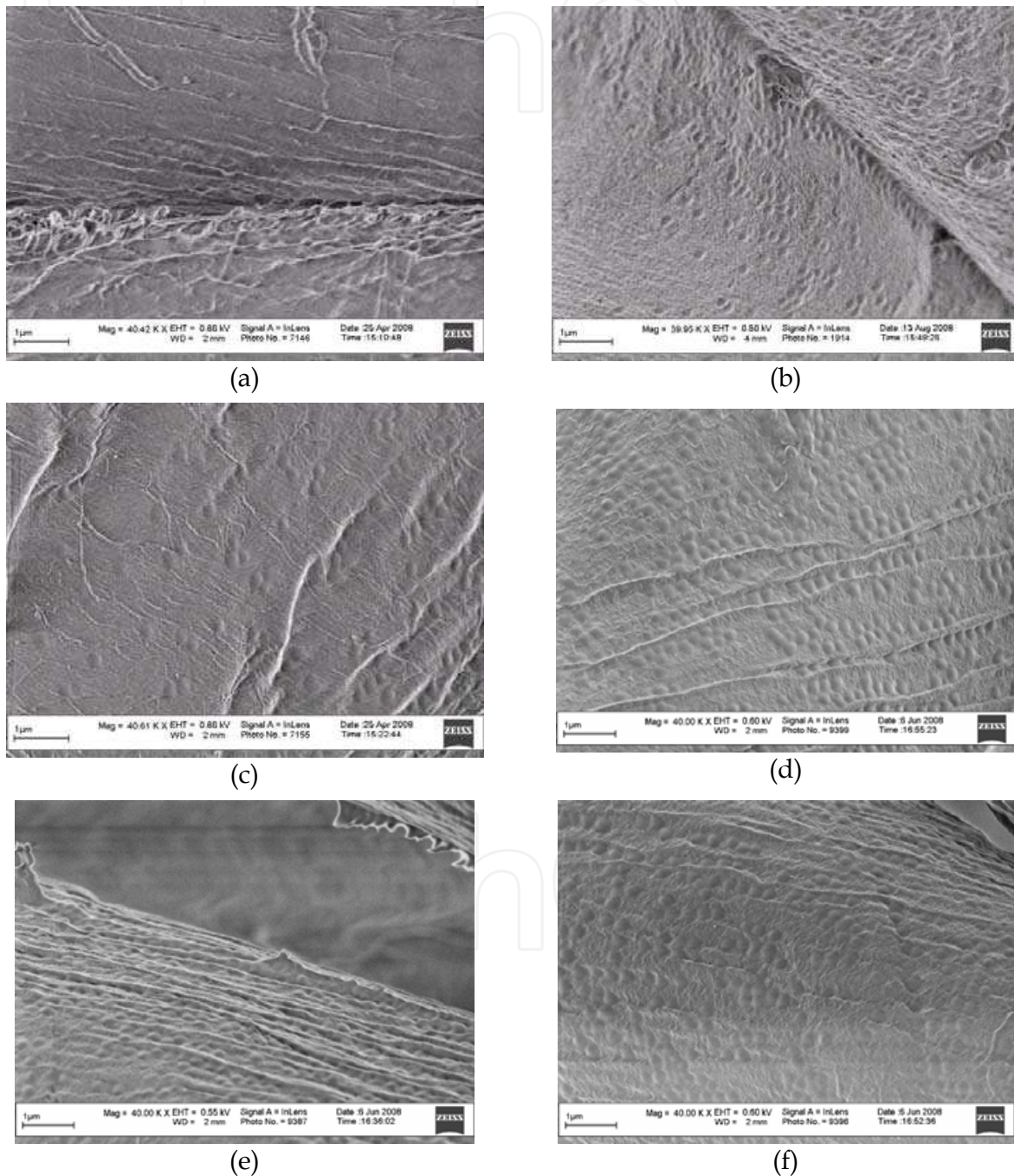


Fig. 7. SEM images after PNCS microgel incorporation: untreated cotton (a); carboxymethylated cotton (b), aminized cotton (c); air plasma treated cotton (d); nitrogen plasma treated cotton (e); and argon plasma treated cotton (e).

XPS analysis was used to determine the surface chemical composition changes of cotton after microgel incorporation (Jocic et al., 2009; Tourrette et al., 2009). After incorporation of PNCS microgel, all samples show the presence of nitrogen in significantly higher amount than in nitrogen plasma treated cotton. This is the consequence of the fact that both poly-NiPAAm and chitosan contain enough nitrogen which can be detected by XPS analysis, thus confirming the incorporation of PNCS microgel to the fibre surface. Therefore, the amount of nitrogen detected can be used as a tool for the estimation of PNCS microgel contents on the fibre surface. However, since previously untreated cotton sample with incorporated microgel shows significant nitrogen content (4.6 at.%), this implies that even without cotton activation some kind of poly-NiPAAm and/or chitosan adsorption occurs. Nevertheless, since SEM analysis did not visually confirm the presence of microgel particles at this sample (Fig. 7a), it can be speculated that a kind of precipitation occurred and polymer(s) have been adsorbed to the nonactivated cotton fibre surface in a thin layer, not in a micro-particulate form. The measured amount of nitrogen is bigger with carboxymethylated sample (5.2 at.%) compared to aminized sample (3.9 at.%), a result which confirms better adsorption of positively charged microparticles (see Fig. 4) on anionic cotton. For plasma treated cotton samples, the highest amount of nitrogen is measured for nitrogen and argon activated samples (6.0 and 6.1 at.%, respectively). Air plasma treated cotton showed nitrogen content similar to previously untreated and chemically activated samples (5.2 at.%). This result implies better microgel incorporation after nitrogen and argon plasma treatment. However, it is difficult to assess at this stage the level of enhancement after nitrogen plasma treatment, concerning the fact that nitrogen plasma treated cotton surface already contains 0.9 at.% of nitrogen as the consequence of the activation step.

These results lead to the conclusion that plasma treatments lead to better incorporation efficiency of PNCS microgel. The enhancement of the adhesion between hydrogel microparticles and plasma treated fibres can be attributed both to physical and chemical modification. The physical modification is the surface roughening of the fibre by the sputtering effect, producing an enlargement of contact area that increases the friction between the fibre and the microgel. The chemical modification increases the functional groups presence at the fibre surface, hence enabling a number of chemical bonds to be formed between the fibre and the microgel. After plasma treatments, there are still a lot of free radicals that remain on the treated fibre surface which can play a role in forming new functional groups and bonds between the fibre and the microgel. In addition, compared to chemical methods, plasma treatment is considered an environmentally friendly process which guarantees the high quality of the material with minimum costs and technological waste (Careiro et al., 2001).

4.2 Microgel incorporation to previously non-activated cotton

In order to obtain satisfying durability of the surface modifying system without previous cotton activation, microgel particles can be covalently bonded to cotton using appropriate crosslinking agent. In textile industry, polycarboxylic acids are well-known crosslinking agents that can serve as formaldehyde-free durable press finishing agents (Welch, 1992; Welch & Andrews, 1990). Among various available polycarboxylic acids, the most effective crosslinking agent for cotton was found to be 1,2,3,4-butanetetracarboxylic acid (BTCA), when combined with catalysts that are inorganic salts of phosphorus-containing acids (Hebeish et al., 2006), among which sodium hypophosphite (SHP) is being the most effective (Gu & Yang, 2000). Polycarboxylic acids have been also used for crosslinking chitosan to cotton, thus adding antimicrobial properties to a durable press finish. It has been reported

(El-tahlawy et al., 2005) that under the action of heat during the curing step, part of BTCA can be consumed for linking chitosan to the cellulosic substrate through esterification. A formation of a covalent bond between the crosslinking agent, chitosan, and cellulosic chains was confirmed (Hsieh et al., 2006; Shin & Ueda, 1999).

Several studies have shown that cellulosic esterification by polycarboxylic acids takes place in two phases. According to Yang & Xu (1998), in the first phase a cyclic anhydride is formed, which forms an ester with the hydroxyl group (-OH) in the cellulose macromolecule (Orhan et al., 2009; Sauperl & Stana-Kleinschek, 2010). This is followed by formation of a second anhydride that subsequently reacts with another cellulose hydroxyl. However, in the presence of SHP, a second mechanism can occur, resulting in formation of a mixed linear anhydride (Gillingham et al., 1999). The number of covalent bonds or linkages which can be formed with cellulose is limited to one less than the number of carboxyl groups in the polycarboxylic acid (Bishof Vukusic & Katovic, 2000). Since BTCA can form at least two ester bonds, two macromolecules can be crosslinked effectively (Xu & Shyr, 2000). Moreover, esterification or amidation with -OH or -NH₂ groups of chitosan can occur, if two -COOH groups remain available (El-tahlawy et al., 2005; Hsieh et al., 2006).

4.2.1 Microgel incorporation method

In practice, the incorporation of PNCS microgel onto the cotton surface is possible by a pad (100% WPU) - dry (70°C, 1h) - cure (160°C, 3 min) process. The reaction mixture is prepared by adding BTCA (crosslinker) and SHP (catalyst) into PNCS dispersion. Ratios used are optimised to the following: PNCS:BTCA = 3.75:1 and BTCA:SHP = 2:1. The effectiveness of the crosslinking procedure of cellulose fibre hydroxyl groups with BTCA and/or chitosan, depends on the amount of crosslinking agent and catalyst, temperature, crosslinking reaction time and pH of the finishing bath (Sauperl & Stana-Kleinschek, 2010). The simplest and quickest way to evaluate the crosslinking efficiency is by using a gravimetric method to determine the add-on finish. A sample's weight is taken before and after the treatment and the percentage of add-on is calculated. However, when the mechanism of crosslinking is taken into consideration, then the quantity of accessible BTCA carboxylic groups indicates the efficiency of the cotton cellulose crosslinking (Sauperl et al., 2009; Sauperl & Stana-Kleinschek, 2010). To determine the content of acid carboxylic groups, a staining test with Methylene Blue (MB) dye can be used. Since each molecule of MB is thought to form a single electrostatic bond with each unit of carboxylic acid on the fabric or, in our case, with BTCA, it is possible to calculate the concentration of carboxylic acid groups present on the fabric after being treated either with BTCA and PNCS microgel (Co-PNCS/BTCA) or with BTCA only (Co-BTCA). The degree of crosslinking was studied by increasing the amount of BTCA from 0 to 3% owf. Fig. 8 shows that the content of carboxyl groups increases with increased percentage of BTCA. Up to 1% a slight increase in carboxyl content is noticed, while the biggest increase is noticed from 1 to 3%. The same tendency could be noticed in the case of Co-PNCS/BTCA, the only difference being that less amount of carboxyl groups has been measured, since part of BTCA is consumed in linking chitosan to cellulose substrate. The degree of crosslinking cotton cellulose to BTCA and PNCS microgel particles increased proportionally to the increase in percentage of BTCA applied. By knowing the number of carboxylic groups available, it is possible to determine the proper concentration of BTCA for efficient crosslinking of PNCS to cotton surface. The methylene blue method proved to be suitable for a quick, simple and accurate determination of the degree of crosslinking of cellulose hydroxyl groups with BTCA and/or chitosan.

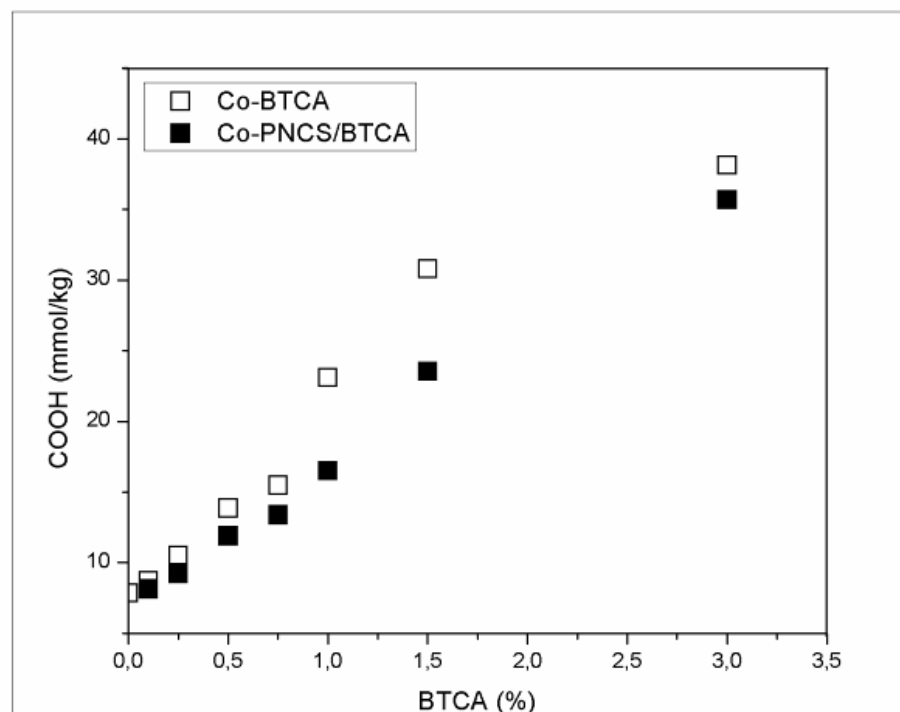
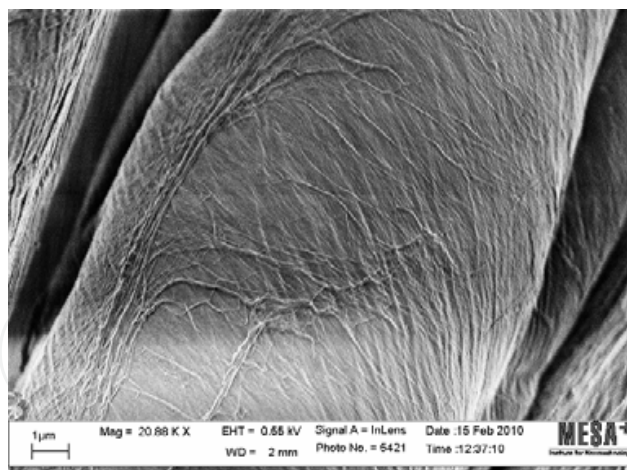


Fig. 8. Carboxyl content (mmol/kg) vs. BTCA concentration (% owf).

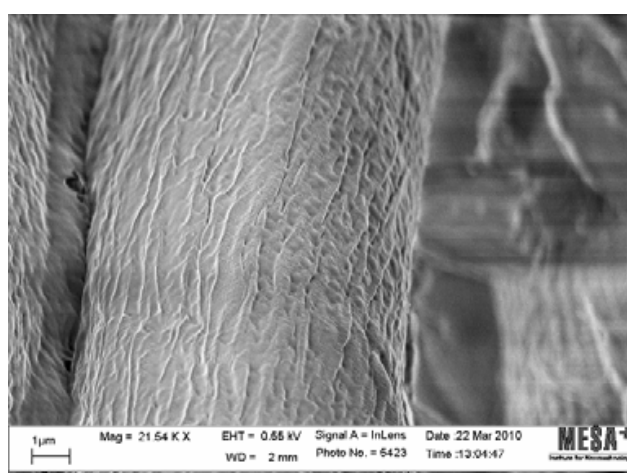
4.2.2 Surface characterization

The surface morphology of cotton treated with BTCA only (Co-BTCA) and of cotton with 3% owf of incorporated PNCS microgel (Co-PNCS/BTCA) was assessed by scanning electron microscopy (Fig. 9). Cotton treated with BTCA only (Fig. 9a) shows the presence of continuous film at the fibre surface, without significant visual difference to the well-known surface morphology of untreated cotton. The incorporation of PNCS microgel particles to cotton (Fig. 9b) significantly changes the visual aspect of the fibre surface. The form, size and amount of microgel particles present are clearly noticeable and they seem to be embedded in the crosslinker film.

The surface chemical composition, determined by XPS analysis, confirms that PNCS microgel was successfully incorporated to cotton (Krizman Lavric et al., 2010a). It can be shown that treatment with BTCA only significantly decreases carbon content (from 66.8 at.% to 59.6 at.%) as the consequence of a BTCA film forming at the fibre surface. After PNCS incorporation, even though a BTCA film was formed at the fibre surface, carbon content again reaches the level of untreated cotton (66.1 at.% vs. 66.8 at.%). This was due to the presence of carbon-rich poly-NiPAAm. Nevertheless, with PNCS incorporation, oxygen content decreased to a level that was below even the initial one (29.7 at.% vs. 33.2 at.%). This was again mainly due to the presence of poly-NiPAAm, as well as on behalf of the newly introduced nitrogen, originating from both poly-NiPAAm and chitosan. As expected, nitrogen was 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.%) (compared to theoretical values for chitosan and poly-NiPAAm) could be explained by specific discrete arrangement of microgel particles at the fibre surface which is estimated to be covered not more than 50% by microgel. The SEM analysis gave visual confirmation for this assumption.



(a)



(b)

Fig. 9. Scanning electron microscope images of cotton treated with BTCA only (Co-BTCA) (a) and of cotton with incorporated PNCS microgel (Co-PNCS/BTCA, 3%) (b).

5. The assessment of pH-, temperature- and humidity-responsiveness of functionalized cotton

5.1 Appropriate methods

Even though many test methods are available to characterize fabric functionality, only a few are in use for assessing the responsiveness of new advanced textile materials which are based on pH and temperature responsive polymers. Recently published book chapter (Hu & Babu, 2008) gives an overview of intelligent textile testing with emphasis on shape memory fabrics and phase change materials. The capability of functionalized material to respond to different stimuli (pH, temperature, humidity) is often studied through swelling/shrinking or hydration/dehydration kinetics and equilibrium using a gravimetric method. The most common gravimetric method used for assessing the responsiveness of thermo- and pH-responsive hydrogels, or materials derived thereof, is the determination of *water uptake*. Interactions between water and textiles affect the comfort of apparel directly, therefore measurements of the amount of water absorbed by fabrics such as moisture regain, moisture sorption isotherms, water retention and absorptive capacities are needed (Zeronian, 1984).

Moisture regain can be used as a measure of the hydrophilicity of fibres, which in turn affects their comfort properties. Moisture sorption isotherm gives us basic information on the relation between moisture and fibre. *Water retention values* (WRV) give an estimate of the swelling capacity of fibres, as determined by the amount of water retained (imbibed water) by water-swollen samples after centrifugation. Data obtained on water retention can be used not only to indicate differences between untreated and treated samples in different environmental conditions in terms of water retention, but also for the degree of crosslinking in cellulosic fibres (Zeronian, 1984). In addition to a good moisture absorption performance, the capacity to discharge the absorbed water during drying is important as well, especially in the case of sportswear (Männer et al., 2004). Drying capability is evaluated by the drying rate of the fabric, the drying time being a function of how much water a fabric absorbs, and depends mainly on the thickness of the fabric (Fangueiro et al., 2010; Li, 2001).

A review of standard test methods for moisture in lint cotton, with emphasis on oven-dry techniques, was given by Montalvo & Von Holven (2008), including a list of moisture related terminology, procedural examples and moisture related formulae. All methods that have been mentioned above can be applied for intelligent textile testing.

5.2 Liquid management properties

Water vapour transport properties of textiles fabrics are of considerable importance in determining thermal comfort properties of clothing systems. Textile fabrics with a higher WVT permeability allow the human body to provide cooling due to evaporation of sweat. If the resistance to water vapour diffusion is high, the moisture movement is impeded and discomfort sensation of dampness and clamminess may arise (Keighley, 1985; Huang & Qian, 2007). The main mechanisms of water vapour transport through textile layers are (Indushekar et al., 2005; Das et al., 2007): diffusion of water vapour through the air spaces between the fibres; absorption, transmission and desorption of water vapour by the fibres; adsorption and migration of water vapour along the fibre surface (wicking); and transmission of water vapour by forced convection. The transport through hygroscopic porous materials is complex, due to the tendency of fibres to take up water vapour and experience swelling that can close off the pores in the fabric. This affects the ability of the fabric layer in passing heat and water vapour, as fibre swelling reduces free air volume within the fabric, affecting both the convective and diffusive transport of energy and mass. The size of pores in the fabric is far more important to moisture transfer than the hydrophilicity of the fabric (Gibson & Charmchi, 1997).

Cotton functionalized with the temperature responsive hydrogel which shows specific volume phase-transition (swelling and shrinking), represents a system that is able to control the evaporative rate at which a material can transport moisture vapour. There are several standard test methods available for measuring the water vapour permeability of fabrics, which can also be applied to microgel functionalized materials (Indushekar et al., 2005; Das et al., 2007; Huang & Qian, 2008; McCullough et al., 2003; Ding, 2008). Even though a number of methods are available for the determination of WVT rate of textile materials, the “pot” test method is still widely used. It involves a lot of work in respect to weighing and timing, but it is recognized as a reliable method.

The methods which have been used in our experiments are thoroughly explained in Krizman Lavric et al. (2010a; 2010b). The *moisture content* of the modified fabrics was measured thermo-gravimetrically, using a moisture analyzer. During the drying process the instrument continually measures the weight of the sample and displays the reduction in

moisture. The final moisture content (MC) is expressed in percentage (mass of the material after drying under specified conditions vs. mass of the material before drying). *Water vapour permeability* was measured according to the standard UNI 4818-26. Weight of the pots was recorded before introducing them into the climatic chamber and after 24 h. The difference in weight gives the quantity of water that was transmitted through the fabric as vapour. The water vapour transmission (WVT) rate is expressed in grams per square meter in 24 h. *Water uptake* was measured gravimetrically by soaking the samples either in acidic (pH 3), neutral (pH 6.5) or alkaline (pH 10) solutions at temperature below (25°C) and above (40°C) LCST of poly-NiPAAm until the swelling equilibrium was attained. The weight of the wet sample was determined after removing the surface water by blotting with filter paper. Water uptake (WU) is expressed in percentage (mass of the material after taking up water vs. mass of dry material).

It has been previously published that the liquid management properties of microgel functionalized textile depend on the temperature and humidity (Jocic et al., 2009; Krizman Lavric et al., 2010a). Because of its poly-NiPAAm core, each microgel particle acts as a temperature sensor and actuator. Therefore, at temperatures below LCST, it is in a swollen state, while above LCST it shrinks, resulting in an increase or decrease of total moisture content of modified cotton, respectively. It is however generally known that ambient moisture concentration is the driving force for moisture absorption, with moisture regain increasing when relative humidity increases (Warner, 1995).

The results obtained on the influence of temperature and ambient humidity on moisture content (MC) and water vapour transport rate (WVT) of untreated cotton (Co-UT) and cotton with incorporated microgel (Co-PNCS/BTCA) are presented in Fig. 10. The humidity values were chosen as low (50% R.H.) and high (80% R.H.), and temperature was chosen to be below (25°C) and above (40°C) 32°C (LCST of poly-NiPAAm). The results show that, when exposed to changes in ambient humidity and temperature, cotton material with incorporated PNCS microgel responds by changes in moisture uptake. The moisture content results (Fig. 10a) 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 microgels, 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 microgel particles are in a "dry" state and the modified cotton does not show a macroscopically observable temperature response. 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°C, where microgel particles are hydrophilic, the moisture content is increased for modified cotton. It is actually the same trend as at low R.H., just with a bigger magnitude of change. At 40°C the microgel particles 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. A similar discussion could be applied to water vapour transport (WVT) rate results (Fig. 10b). At low humidity (50% R.H.) the temperature responsiveness could not be observed. A drop of WVT values is noticed in the Co-PNCS/BTCA sample as a consequence of the microgels presence. It is expected that the microgel at the fibre surface could block water

vapour transport through the material, due to increased roughness. At high humidity (80% R.H.) the responsiveness is clearly evident. At low temperature (25°C), microgel particles swell significantly enough to hinder water vapour passage through the fabric. However, at 40°C (above LCST), hydrophobic microgel particles obstruct moisture absorption (Fig. 10a), which enhances the water vapour transport through the material (Krizman Lavric et al., 2010a). As it was expected, the combined effects of temperature and relative humidity had the biggest impact on water vapour permeability, while relative humidity showed the most significant influence on moisture content (Krizman Lavric et al., 2010b). Water uptake (WU) results confirm increased water uptake capacity at low pH values at room temperature (Fig. 11a), which is the consequence of chitosan pH-responsiveness. A decreased water uptake capacity was noticed at higher temperature (Fig. 11b), due to the influence of poly-NiPAAm, which adds a hydrophobic character to the hydrogel.

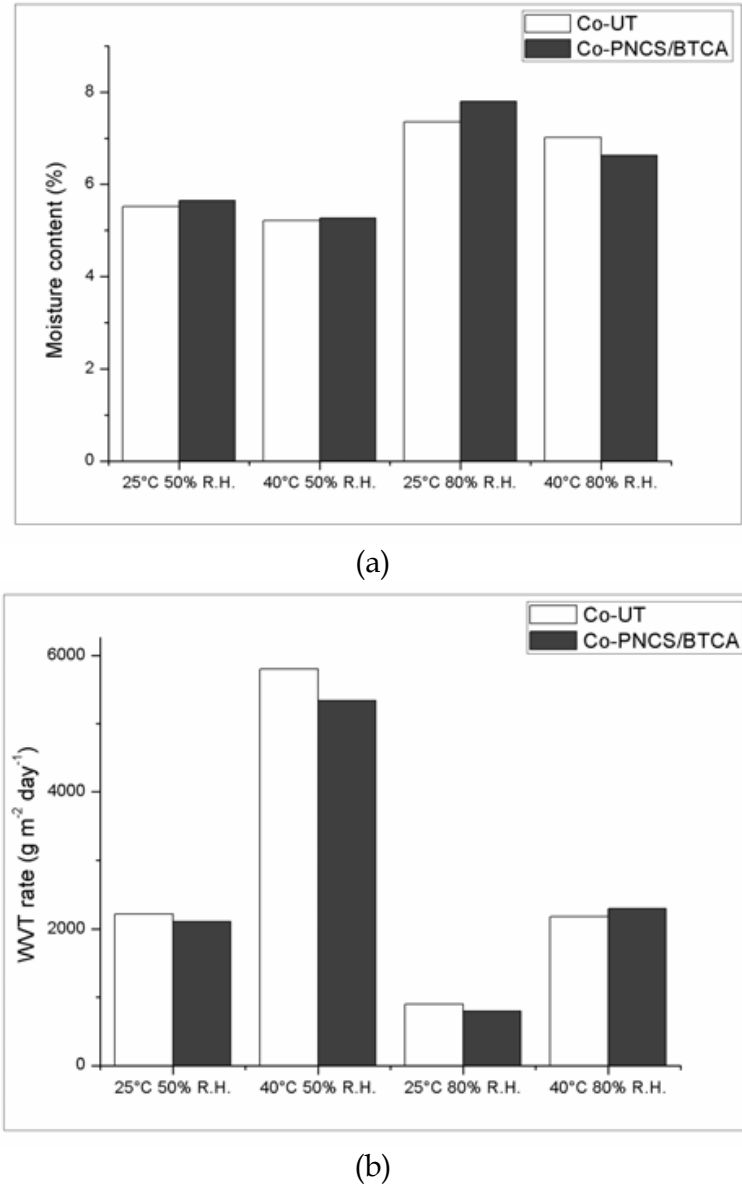
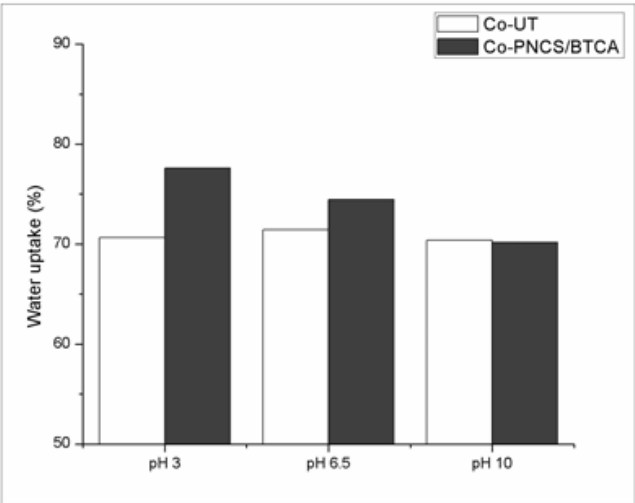


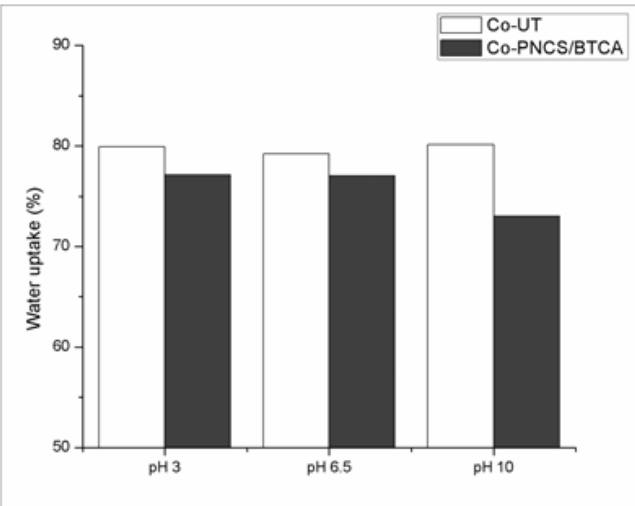
Fig. 10. Moisture content (a) and water vapour transport rate (b) of Co-UT and Co-PNCS/BTCA at different conditioning parameters (Krizman Lavric et al., 2010a).

6. Expected comfort enhancement

Good thermal sensation and comfort are basic demands for the production of performance apparel. Both are closely linked to fibre hygroscopicity, surface energy of fibres (hydrophilic or hydrophobic), and fabric structure and moisture management abilities, such as wicking, wetting and water vapour transport (Zhou et al., 2007). To satisfy the aforementioned demands, clothing materials require a high moisture retention capacity and a high moisture transportation propensity (Li, 2001; Okubayashi et al., 2005). The comfort perception of the wearer depends on the ability of clothing systems to evaporate the accumulated moisture from the skin to the environment. An important mechanism which the body uses to regulate its temperature is by perspiration, its level depending on the level of activity. Since moisture can derive either from sweat or from the environment (e.g. rain, humidity, etc.) it can have an impact on the comfort perception of both cold and hot conditions. During sweating the vapour is transmitted through the micro-porous structure of functional fabric to the outer layer where it evaporates, which makes the wearer feel dry and comfortable (Männer et al., 2004; Li, 2001; Okubayashi et al., 2005).



(a)



(b)

Fig. 11. Water uptake of Co-UT and Co-PNCS/BTCA at 25°C (a) and at 40°C (b).

In our study comfort does not refer to the psychological comfort but to the physiological comfort such as the moisture vapour transport rate. By exposure of the stimuli-responsive microgel to external stimuli (temperature, pH and humidity), it shows swelling/shrinking or hydration/dehydration properties by causing changes in water vapour transmission rate of modified textile material. As the body temperature exceeds the transition temperature (LCST) of the surface modifying system, PNCS microgel particles collapse enabling the transfer of moisture (water vapour) through the material into the environment. In contrast, when the ambient temperature decreases below the body temperature, the microgel tends to swell, preventing perspiration and thereby helping in maintaining the thermal balance of the body. Thus, the controlled expansion or contraction of the surface incorporated microgel particles leads to adjusting the liquid management of textile material and enhances comfort consequently.

7. Conclusions

An encouraging option to meet the goal of achieving “smart” liquid management properties of textiles 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.). The following aspects are reported: the synthesis and characterization of a microgel using the temperature responsive polymer (poly-NiPAAm) and pH-responsive biopolymer (chitosan); the methods for incorporating microgel to cotton, both previously activated and non-activated (with crosslinker); the assessment of pH-, temperature- and humidity-responsiveness of new advanced textile material. The results presented could serve as a proof of the concept and provide a guideline for application of microgel as a surface modifying system in general, with the aim to upgrade the regular textile material quality by providing highly attractive feature of stimuli-responsiveness.

8. Acknowledgement



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. (<http://www.ctw.utwente.nl/efsm/advanbiotex/>)

9. References

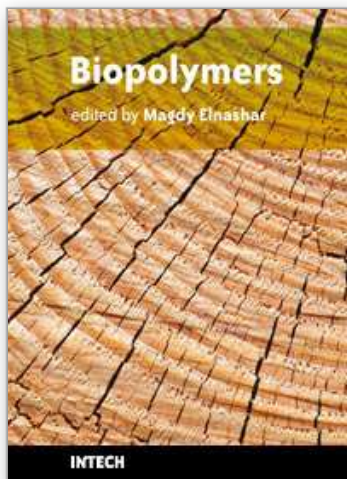
- Bischof Vukusic, S. & Katovic, D. (2000). Creaseproof finishing using phosphono-based catalyst with polycarboxylic acids. *Colourage Annual*, Vol. 47, 87-94, ISSN 0588-5108
- Careiro, N., Souto, A.P., Silva, E., Marimba, A., Tena, B., Ferreira, H. & Magalhães, V. (2001). Dyeability of corona-treated fabrics, *Coloration Technology*, Vol. 117, No. 5, 298-302, ISSN 1472-3581

- Crespy, D. & Rossi, M. R. (2007). Temperature-responsive polymers with LCST in the physiological range and their applications in textiles. *Polymer International*, Vol. 56, Issue 12, 1461-1468, ISSN 0959-8103
- Das, B.; Das, A.; Kothari, V.K.; Fanguiero, R. & de Araujo, M. (2007). Moisture transmission through textiles, Part I: Processes involved in moisture transmission and the factors at play. *Autex Research Journal*, Vol. 7, No. 2, (June, 2007) 100-110, ISSN 1470-9589
- Ding, X. (2008). Fabric permeability testing. In: *Fabric Testing*, Jinlian Hu (Ed.), 189-227, Woodhead Publishing, ISBN 978-1-84569-297-1, Cambridge, UK.
- El-tahlawy, K. F., El-bendary, M. A., Elhendawy, A. G., & Hudson, S. M. (2005). The antimicrobial activity of cotton fabrics treated with different crosslinking agents and chitosan. *Carbohydrate Polymers*, Vol. 60, Issue 4, 421-430, ISSN 0144-8617
- Fangueiro, R.; Filgueiras, A. & Soutinho, F. (2010). Wicking behaviour and drying capability of functional knitted fabrics. *Textile Research Journal*, (March 18, 2010), Available online: <http://trj.sagepub.com>, ISSN 0040-5175
- Gibson, P.W. & Charmchi, M. (1997). Modeling convection/diffusion processes in porous textiles with inclusion of humidity-dependent air permeability. *International Communications in Heat and Mass Transfer*, Vol. 24, No. 5, 709-724, ISSN 0735-1933
- Gillingham, E.L.; Lewis, D.M. & Vončina, B. (1999). An FTIR study of anhydride formation on heating butane tetracarboxylic acid in the presence of various catalysts. *Textile Research Journal*, Vol. 69, No. 12, 949-955, ISSN 0040-5175
- Gu, X. & Yang, C.Q. (2000). FTIR spectroscopy study of the formation of cyclic anhydride intermediates polycarboxylic acids catalyzed by sodium hypophosphite. *Textile Research Journal*, Vol. 70, No. 1, 64-70, ISSN 0040-5175
- Hashem, M., Hauser, P. & Smith, B. (2003). Wrinkle Recovery for Cellulosic Fabric by Means of Ionic Crosslinking, *Textile Research Journal*, Vol. 73, No. 9, 762-766, ISSN 0040-5175
- Harish Prashanth, K. V. & Tharanathan, R. N. (2003). Studies on graft copolymerization of chitosan with synthetic monomers. *Carbohydrate Polymers*, Vol. 54, Issue 3, 343-351, ISSN 0144-8617
- Hebeish, A.; Hashem, M.; Abdel-Rahman, A. & El-Hilw, Z.H. (2006). Improving easy care nonformaldehyde finishing performance using polycarboxylic acids via precationization of cotton fabric. *Journal of Applied Polymer Science*, Vol. 100, Issue 4, 2697-2704, ISSN 0021-8995
- Hsieh, S. H., Lin, E. S. & Wei, H. C. (2006). Effect of Chitosan Addition to BTCA/CA Processed Cotton Fabrics for Adsorbing Metallic Ions from Waste Water. *Journal of Applied Polymer Science*, Vol. 101, No. 5, 3264-3269, ISSN 0021-8995
- Hsu, S.C., Don, T.M. & Chiu, W.Y. (2002). Synthesis of Chitosan-Modified Poly(methyl methacrylate) by Emulsion Polymerization. *Journal of Applied Polymer Science*, Vol. 86, Issue 12, 3047-3056, ISSN 0021-8995
- Hu, J & Babu, K.M. (2008). Testing intelligent textiles, In: *Fabric Testing*, Jinlian Hu (Ed.), 275-308, Woodhead Publishing, ISBN 978-1-84569-297-1, Cambridge, UK.
- Huang, J. & Qian, X. (2007). A new test method for measuring the water vapour permeability of fabrics. *Measurement Science and Technology*, Vol. 18, No. 9, 3043-3047, ISSN 0957-0233
- Huang, J. & Qian, X. (2008). Comparison of test methods for measuring water vapor permeability of fabrics. *Textile Research Journal*, Vol. 78, No. 4, 342-352, ISSN 0040-5175

- Indushekar, R.; Awasthi, P. & Gupta, R.K. (2005). Studies on test methods used to measure water vapor transmission of fabrics by DSC and conventional dish techniques. *Journal of Industrial Textiles*, Vol. 34, No. 4, 223-242, ISSN 1528-0837
- Jocic, D. (2008). Smart Textile Materials by Surface Modification with Biopolymeric Systems. *Research Journal of Textile and Apparel*, Vol. 12, No. 2, 58-65, ISSN 1560-6074
- Jocic, D., Tourrette, A., Glampedaki, P. & Warmoeskerken, M.M.C.G. (2009). Application of temperature and pH responsive microhydrogels for functional finishing of cotton fabric. *Materials Technology: Advanced Performance Materials*, Vol. 24, No. 1, 14-23, ISSN 1066-7857
- Keighley, J.H. (1985). Breathable fabrics and comfort in clothing. *Journal of Industrial Textiles*, Vol. 15, No. 2, 89-104, ISSN 1528-0837
- Kim, S.Y., Zille, A., Murkovic, M., Guebitz, G. & Cavaco-Paulo, A. (2007). Enzymatic polymerization on the surface of functionalized cellulose fibers, *Enzyme and Microbial Technology*, Vol. 40, Issue 7, 782-787, ISSN 0141-0229
- Kopecek, J. & Yang, J. (2007). Hydrogels as smart biomaterials, *Polymer International*, Vol. 56, Issue 9, 1078-1098, ISSN 0959-8103
- Krizman Lavric, P., Warmoeskerken, M.M.C.G. & Jocic, D. (2010a). Microgel Functionalized Textiles Responsive To Ambient Conditions, *Proceedings of AUTEX2010 10th WorldTextile Conference*, pp. 1-4, ISBN 978-609-95098-2-2 (CD-ROM), Vilnius, Lithuania, 21-23 June 2010, Kaunas University of Technology, Kaunas.
- Krizman Lavric, P., Warmoeskerken, M.M.C.G. & Jocic, D. (2010b). Vapour transmission properties of a surface modified textile material with poly-NiPAAm/chitosan microgel, *Proceedings of 41st International Symposium on Novelties in Textiles (ISNT)*, pp. 104-110, ISBN 978-961-6045-80-3 (CD-ROM), Ljubljana, Slovenia, 27-29 May 2010, University of Ljubljana, Ljubljana.
- Kumar, A., Srivastava, A., Galaev, I.Y. & Mattiasson, B. (2007). Smart polymers: Physical forms and bioengineering applications. *Progress in Polymer Science*, Vol. 32, 1205-1237, ISSN 0079-6700
- Kulkarni, A., Tourrette, A., Warmoeskerken, M.M.C.G. & Jocic, D. (2010). Microgel-based surface modifying system for stimuli-responsive functional finishing of cotton. *Carbohydrate Polymers*, in print, ISSN 0144-8617
- Lee C., Wen C. & Chiu, W. (2003). Synthesis of Poly(chitosan-N-isopropylacrylamide) Complex particles with the Method of Soapless Dispersion Polymerization. *Journal of Polymer Science Part A: Polymer Chemistry*, Vol. 40, Issue 13, 2053-2063, ISSN 0887-624X
- Lee C., Wen C., Lin C. & Chiu W. (2004). Morphology and Temperature Responsiveness-Swelling relationship of Poly(N-isopropylamide-chitosan) Copolymers and Their Application to Drug Release. *Journal of Polymer Science Part A: Polymer Chemistry*, Vol. 42, Issue 12, 3029-3037, ISSN 0887-624X
- Li, R., Ye, L. & Mai, Y.W. (1997). Application of plasma technologies in fibre-reinforced polymer composites: a review of recent developments. *Composites Part A: Applied Science and Manufacturing*, Vol. 28, Issue 1, 73-86, ISSN 1359-835X
- Li, Y. (2001). The science of clothing comfort. *Textile Progress*, Vol. 31, No. 1, 1-135, ISSN 0040-5167

- Liu, B. & Hu, Y. (2005). The Application of Temperature-Sensitive Hydrogels to Textiles: A Review of Chinese and Japanese Investigations. *Fibres & Textiles in Eastern Europe*, Vol. 13, No. 6, 45-49, ISSN 1230-3666
- Liu, W., Huang, Y., Liu, H. & Hu, Y. (2007) Composite structure of temperature sensitive chitosan microgel and anomalous behavior in alcohol solutions. *Journal of Colloid and Interface Science*, Vol. 313, No. 1, 117-121, ISSN 00219797.
- Männer, J.; Schuster, K.C.; Suchomel, F.; Gürtler, A. & Firgo, H. (2004). Higher performance with natural intelligence. *Lenzinger Berichte*, Vol. 83, 99-110, ISSN 0024-0907
- Mano, J.F. (2008). Stimuli-Responsive Polymeric Systems for Biomedical Applications. *Advanced Engineering Materials*, Vol. 10, Issue 6, 515-527, ISSN 1527-2648
- McCullough, E.A.; Kwon, M. & Shim, H. (2003). A comparison of standard test methods for measuring water vapour permeability of fabrics. *Measurement Science and Technology*, Vol. 14, 1402-1408, ISSN 0957-0233
- Montalvo, J.G. & Von Hoven, T.M. (2008). Review of standard test methods for moisture in lint cotton. *The Journal of Cotton Science*, Vol. 12, Issue 1, 33-47, ISSN 1523-6919
- Muzzarelli, R.A.A. (1977). *Chitin*, Pergamon Press, ISBN 0080203671, Oxford.
- Okubayashi, S.; Griesser, U.J. & Bechtold, T. (2005). Moisture sorption/desorption behaviour of various manmade cellulosic fibers. *Journal of Applied Polymer Science*, Vol. 97, Issue 4, 1621-1625, ISSN 0021-8995
- Osenberg, F., Theirich, D., Decker, A. & Engemann, J. (1999). Process control of a plasma treatment of wool by plasma diagnostics, *Surface and Coatings Technology*, Vol. 116-119, 808-811, ISSN 0257-8972
- Orhan, M.; Kut, D. & Gunesoglu, C. (2009). Improving the antibacterial activity of cotton fabrics finished with triclosan by the use of 1,2,3,4-butanetetracarboxylic acid and citric acid. *Journal of Applied Polymer Science*, Vol. 111, Issue 3, 1344-1352, ISSN 0021-8995
- Pei, Y., Chen, J., Yang, L., Shi, L., Tao, Q., Hui, B., & Li, J. (2004). The effect of pH on the LCST of poly(N-isopropylacrylamide) and poly(N-isopropylacrylamide-co-acrylic acid). *Journal of Biomaterials Science, Polymer Edition*, Vol. 15, No. 5, 585-594, ISSN 0920-5063.
- Pelton, R. (2000). Temperature-sensitive aqueous microgels. *Advances in Colloid and Interface Science*, Vol. 85, No. 1, 1-33, ISSN 0001-8686
- Pelton, R.H. & Chibante P. (1986). Preparation of aqueous lattices with N-isopropylacrylamide. *Colloids and Surfaces*, Vol. 20, Issue 3, 247-256, ISSN 0166-6622
- Prabaharan, M. & Mano, J.F. (2006). Stimuli-Responsive Hydrogels Based on Polysaccharides Incorporated with Thermo-Responsive Polymers as Novel Biomaterials. *Macromolecular Bioscience*, Vol. 6, Issue 12, 991-1008, ISSN 1616-5187
- Racz, I., Borsa, J. & Bodor, G. (1996). Crystallinity and Accessibility of Fibrous Carboxymethylcellulose by Pad-Roll Technology, *Journal of Applied Polymer Science*, Vol. 62, Issue 12, 2015-2024, ISSN 0021-8995
- Ravi Kumar, M.N.V. (2000). A review of chitin and chitosan applications. *Reactive & Functional Polymers*, Vol. 46, Issue 1, 1-27, ISSN 1381-5148
- Rinaudo, M. (2006). Chitin and chitosan: Properties and applications. *Progress in Polymer Science*, Vol. 31, Issue 7, 603-632, ISSN 0079-6700

- Šauperl, O.; Stana-Kleinschek, K. & Ribitsch, V. (2009). Cotton cellulose 1,2,3,4 butanetetracarboxylic acid (BTCA) crosslinking monitored by some physical-chemical methods. *Textile Research Journal*, Vol. 79, No. 9, 780-791, ISSN 0040-5175
- Šauperl, O. & Stana-Kleinschek, K. (2010). Differences between cotton and viscose fibers crosslinked with BTCA. *Textile Research Journal*, Vol. 80, No. 4, 383-392, ISSN 0040-5175
- Schild, H.G. (1992). Poly(N-isopropylacrylamide): experiment, theory and application. *Progress in Polymer Science*, Vol. 17, 163-249, ISSN 0079-6700
- Shin, H. & Ueda, M. (1999). Fixation of chitosan on cross-linked cellulose fabrics with polycarboxylic acids. *Fiber*, Vol. 55, No. 1, 42-47, ISSN 0037-9875
- Tourrette, A., De Geyter, N., Jovic, D., Morent, R., Warmoeskerken, M. M. C. G. & Leys, C. (2009). Incorporation of poly(N-isopropylacrylamide)/chitosan microgel onto plasma functionalized cotton fibre surface. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, Vol. 352, Issue 1-3, 126-135, ISSN 0927-7757
- Ward, T.L., Jung, H.Z., Hinojosa, O. & Benerito, R.R. (1978). Effect of cold plasmas on polysaccharides, *Surface Science*, Vol. 76, Issue 1, 257-273, ISSN 0039-6028
- Warner, S.B. (1995). Environmental Effects: Solvents, Moisture, and Radiation. In: *Fiber Science*, 99-120, Prentice Hall, ISBN 0-02-424541-0, Upper Saddle River, NJ (USA).
- Welch, C. M. & Andrews, B. A. K. (1990). Catalysts and Processes for Formaldehyde Free Durable Press Finishing of Cotton Textiles with Polycarboxylic Acids. *U.S. Patent Office*, Pat. No. 4 926 865.
- Welch, C. M. (1992). Formaldehyde-Free Durable Press Finishes. *Review of Progress in Coloration and related Topics*, Vol. 22, 32-41, ISSN 0557-9325
- Yang, C. Q.; Xu, L.; Li, S. & Jiang, Y. (1998). Nonformaldehyde durable press finishing of cotton fabrics by combining citric acid with polymers of maleic acid. *Textile Research Journal*, Vol. 68, No. 5, 457-464, ISSN 0040-5175
- Xu, W. & Shyr, T-W. (2000). Durable press finishing of cotton fabrics by polycarboxylic acids after graft copolymerization with hydroxyethyl methacrylate. *Textile Research Journal*, Vol. 70, No. 1, 8-10, ISSN 0040-5175
- Zeronian, S. H. (1984). Analysis of the Interaction between Water and Textiles, In: *Analytical Methods for a Textile Laboratory*, William Weaver (Ed.), 117-127, American Association of Textile Chemists and Colorists, ISBN 978-0-96133-500-7, NC (USA).
- Zhou, L.Y.; Li, Y.; Chung, J.; Tokura, H.; Gohel, M.D.I.; Kwok, Y.L. & Feng, X.W. (2007). Effects of fabric surface energy on human thermophysiological responses during exercise and recovery. *Fibers and Polymers*, Vol. 8, No. 3, 319-325, ISSN 1229-9197



Biopolymers

Edited by Magdy Elnashar

ISBN 978-953-307-109-1

Hard cover, 612 pages

Publisher Sciyo

Published online 28, September, 2010

Published in print edition September, 2010

Biopolymers are polymers produced by living organisms. Cellulose, starch, chitin, proteins, peptides, DNA and RNA are all examples of biopolymers. This book comprehensively reviews and compiles information on biopolymers in 30 chapters. The book covers occurrence, synthesis, isolation and production, properties and applications, modification, and the relevant analysis methods to reveal the structures and properties of some biopolymers. This book will hopefully be of help to many scientists, physicians, pharmacists, engineers and other experts in a variety of disciplines, both academic and industrial. It may not only support research and development, but be suitable for teaching as well.

How to reference

In order to correctly reference this scholarly work, feel free to copy and paste the following:

Dragan Jovic, Audrey Tourrette and Pavla Krizman Lavric (2010). Biopolymer-based Stimuli-Responsive Polymeric Systems for Functional Finishing of Textiles, Biopolymers, Magdy Elnashar (Ed.), ISBN: 978-953-307-109-1, InTech, Available from: <http://www.intechopen.com/books/biopolymers/biopolymer-based-stimuli-responsive-polymeric-systems-for-functional-finishing-of-textiles>

INTECH
open science | open minds

InTech Europe

University Campus STeP Ri
Slavka Krautzeka 83/A
51000 Rijeka, Croatia
Phone: +385 (51) 770 447
Fax: +385 (51) 686 166
www.intechopen.com

InTech China

Unit 405, Office Block, Hotel Equatorial Shanghai
No.65, Yan An Road (West), Shanghai, 200040, China
中国上海市延安西路65号上海国际贵都大饭店办公楼405单元
Phone: +86-21-62489820
Fax: +86-21-62489821

© 2010 The Author(s). Licensee IntechOpen. This chapter is distributed under the terms of the [Creative Commons Attribution-NonCommercial-ShareAlike-3.0 License](https://creativecommons.org/licenses/by-nc-sa/3.0/), which permits use, distribution and reproduction for non-commercial purposes, provided the original is properly cited and derivative works building on this content are distributed under the same license.

IntechOpen

IntechOpen