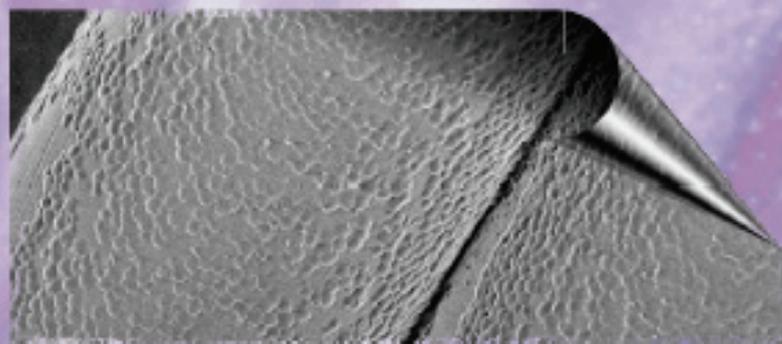
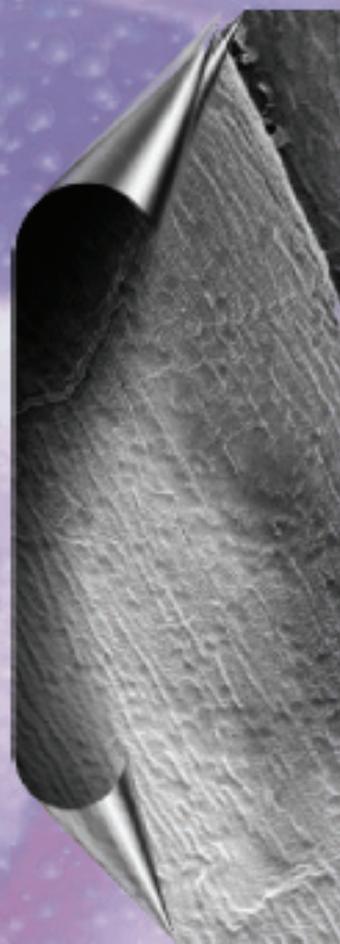


**SURFACE MODIFICATION
SYSTEMS
FOR CREATING
STIMULI RESPONSIVENESS
OF TEXTILES**



Workshop Proceedings

Chapter 4

Functional Finishing of Textiles with Responsive Polymeric Systems

Dragan Jocić
Engineering of Fibrous Smart Materials (EFSM)
Faculty of Engineering Technology (CTW)
University of Twente, Enschede
The Netherlands

1. Introduction

Influenced by constantly evolving consumer lifestyles within the last two decades, textile industry globally adopted a forward-looking approach to create new conceptual textile systems for the 21st century, based on so called *knowledge-based textile materials*. This strategy aims the development of futuristic human-friendly textile products which would redefine the role of textiles and expand the capabilities to affect human life by efficiently fulfilling advanced expectations of modern lifestyle. Nevertheless, in addition to conventional technologies, novel specific technologies are needed to create *knowledge-based textile materials* with new advanced functionalities and environmental responsiveness.

Functional finishing technology is today considered as a specific technology that could provide a technical bridge for achieving 21st century textile technical strategies. It is expected to allow the textiles high-grade functions by adding value to a specific attribute or function or effect. Currently, most functional finishing technologies employed in textile treatments are directly incorporating functional agents to textiles (e.g. fire retardants, antimicrobial agents, UV-blockers, water repellents, etc.). Even though existing functional finishing concepts are capable of creating of textiles with advanced functionalities, they cannot completely meet the specific needs of futuristic textile product's requirements of the advanced functionality coupled with the environmental responsiveness (i.e. sensitivity and the compatibility to surrounding circumstances). Hence, new chemistry and novel functional finishing systems must be explored in order to develop textile materials that sense and react to human and environmental stimuli, and which are able to efficiently protect human body from exterior changes in the environment.

Currently, the main source of inspiration for advances in textile material innovation is rapid development and commercialization of surface modification

and nanotechnology in many other fields. The techniques that are already developed in other fields enhance the creativity in textile research and provide the tools to meet the challenges associated with creating knowledge-based textile materials. Thus, by redesigning textile material surface, operating at microscopic level, new added-value textile material can be created containing fibres that maintain advantageous conventional properties (e.g. mechanical strength, flexibility and wear comfort) but with advanced functionalities and environmental responsiveness implemented by the modification of a very thin surface layer of the material. These concepts are embedded in the Advanbiotex project which aims to develop an innovative strategy for functional finishing of textiles by application of novel surface modifying systems (SMS) based on stimuli-responsive polymers.

2. Knowledge-based textile materials

When talking about *knowledge-based textile materials* it is unavoidable to mention the technology that is creating a sea change in the current practice of materials engineering, which is referred to as "smart" technology. This technology is relatively new, but some areas have reached the stage where industrial application is feasible and viable.

Currently, commonly accepted definition characterizing "smart" materials does not exist, which leads to ambiguities in classifying materials to this group. This term has lately been used in a broad sense especially for marketing purposes. The term "intelligent" is also used frequently, parallel to the ones like: "interactive", "responsive" and "adaptive". No matter how the term is used, it generally refers to a material that reacts (responds, changes) to defined influences (impulses, stimuli) from the local environment (outside, inside) [1-4].

Hence, "smart" textiles are usually defined as textile materials or products that can sense and interpret changes in their local environment, and respond appropriately. According to that definition, knowledge-based textile materials with new advanced functionalities and environmental responsiveness can be regarded as "smart" materials. The functional activity (sense - react - adapt) of these materials is an important aspect. "Smart" textiles act as both sensors and actuators so they should not be confused with other existing high-performance or multifunctional textiles that are actually "passive" materials with advanced properties. The fusion of conventional structural textile materials with advanced properties given by such "smart" technology offers a wide range of high added-value product options to the non-conventional application sectors. These application sectors range from specific technical and biomedical demands to simple transient fashion demands.

The most traditional area of use of textile material is for human clothing. Since many centuries textile material has been acting as the interface between the wearer and the environment, having the role which has always been quite passive. This passive role has been usually overcome by choosing the proper material for certain physical conditions of the body and of the environment.

However, even in such a traditional area as clothing is, the modern lifestyle creates today the situation in which the actual aim of textile materials is changing from traditional simple protection to the necessary functionality and added-value (e.g. appearance; comfort etc.). Textile material is still considered as the interface between the wearer and the environment, but it needs more active role of adapting to the drastic changes of the physiological needs in the accordance with the changes in the environment.

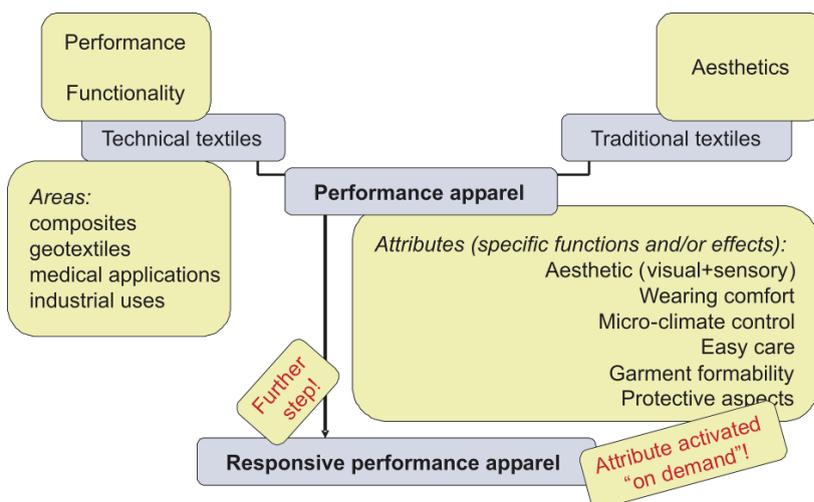


Figure 1. Responsive performance apparel as an example of knowledge-based textile materials.

A good example of modern knowledge-based textile material with new advanced functionalities is material used for the production of performance apparel (Figure 1). As a consequence of a modern lifestyle, performance apparel production represents today one of the fastest growing sectors of the textile industry. It is a typical high added-value textile product that provides consumers with greater levels of comfort, safety, aesthetics and functional performance. Currently it is mostly used for protective clothing, since in many industrial sectors, military and energy services, hospital environments, human beings are subjected to various types of risks (each sector having its own requirements for protective clothing). Another well-known end use of performance apparel is sportswear, through which it is crossing over the boundary to everyday fashion.

The main drivers for the production of the performance apparel emerge from both technical textiles (known for their performance and functionality) and traditional textiles (mainly known for their aesthetics). Not so long ago, the two sectors (technical and traditional textiles) existed totally separated in textile

manufacturing, but today they converged. Hence, the appearance of a new product (performance apparel) made possible to bridge the gap between technical and traditional textiles, making the distinction between them no longer relevant.

However, since the actual trend in producing textile materials is to ensure “smart” capability of interacting with human/environmental conditions, it is necessary to consider further development of materials for performance apparel with environmental responsiveness capability. Hence, the next step in development are materials for so called “responsive performance apparel” where the specific attribute (function or effect) will not be present continuously (i.e. passively), but it could be activated “on demand” by sensing the stimuli in immediate surrounding environment and reacting to the human/environmental conditions.

3. Functional finishing

Technical development strategies for obtaining *knowledge-based textile material* are expected to meet modern societal demands and therefore have to be jointly compiled by government, industry and academia. In this sense, four different categories of development have to be met when putting in practice new development strategies (Figure 2): textiles which are safe and reliable, supporting a higher quality of life; textiles which support recycling; textiles which support energy savings in harmony with the environment; and textiles which support a highly-sophisticated information society.

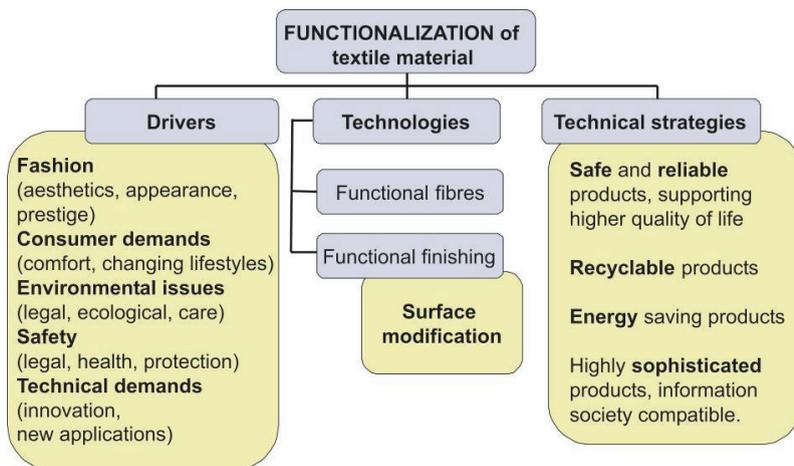


Figure 2. Available technologies for obtaining knowledge-based (functionalized) textile material.

There are two main technologies that are nowadays used to obtain knowledge-based textile material and at the same time to achieve the goals of above mentioned strategies: development and use of functional fibres and functional finishing (Figure 2). Development of functional fibres is based on the process of incorporating active chemicals into the fibre in its manufacturing stage, and this technology is rather increasing today, mainly being supported by fibre manufacturers. However, it is well known that textile finishing, in particular, has a vital role to play in modifying the appearance, texture, handle and performance of all kinds of fabrics to be suitable for the end-use. Therefore, the functional finishing approach is greatly appreciated by textile industry since it involves surface modification technique which can be done at the very last stages of material production. Functional finishing technology enables producers to continue to use traditional textile fibres and at the same time achieve added-value that will be able to stimulate and capture the potential consumer markets for *knowledge-based textile materials*.

Surface structure and the behaviour of textile fibres are of utmost importance to the properties of textile materials in processing and exploitation [5]. By using appropriate surface modification technology on traditional textile materials, new functionalities can be easily implemented and new added-value textile materials can be created to provide consumers with greater levels of comfort, safety, aesthetics and functional performance. The main advantage of modifying a very thin surface layer of the material is that the positive values of the textile material such as mechanical strength, flexibility and wear resistance are maintained.

Generally, surface modification technologies for functional finishing can be divided into two categories: physically based technology and chemically based technology. However, many times the exact classification it is difficult as modifying effects usually come from both physical and chemical reactions. The nature of physical functional finishing is non-contact and non-aqueous treatment. Recently, the numbers of developments in physically based technology, which can harmonize the environment and production, have increased because regulations on chemical substances have become stricter. Some examples of physically based technologies that currently attract high attention are: low-temperature plasma; ozone treatment; UV irradiation; and laser irradiation. The examples of chemically based technologies are: surface activation by incorporation of reactive groups; surface coating by grafting of organic substances; surface coating by incorporation of inorganic substances; sol-gel condensation; etc. At present chemically based technologies are still major, but their combination with physically based technologies is steadily increasing.

4. Functional finishing with responsive surface modifying system

An innovative strategy for functional finishing has been developed within Advanbiotex project. It involves incorporation of thin polymer layers, i.e. application of responsive surface modifying systems (SMS) based on polymers

(Figure 3). This functional finishing technology mainly belongs to chemically based technology, but it also involves the combination with low temperature plasma which is specific physically based technology.

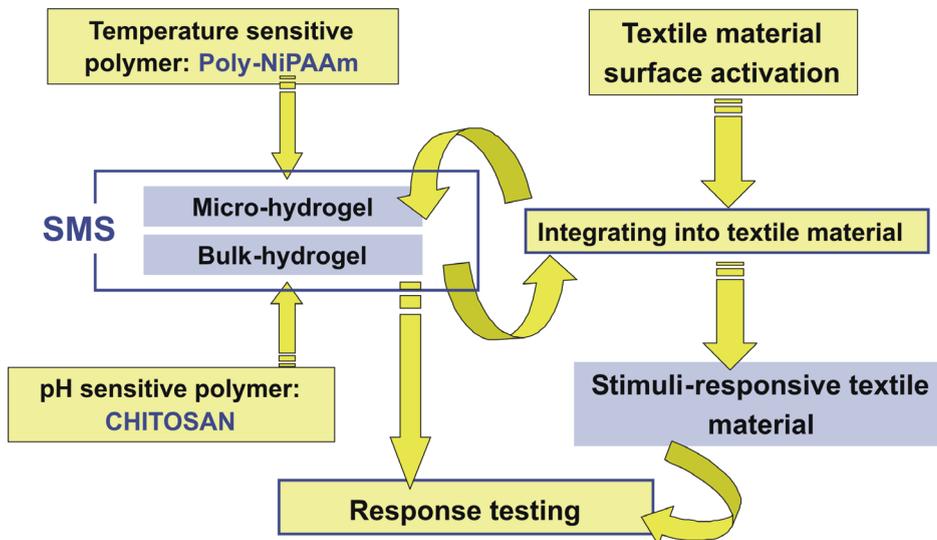


Figure 3. Research scheme of Advanbiotex project.

The efficient and easily applicable surface modifying system can be created by using the specific polymeric form – hydrogel. It is common knowledge that hydrogels exhibit volume phase-transition property (swelling and shrinking) that can be triggered by various external stimuli (temperature, pH, humidity etc.) depending on the responsive properties of the polymers they are made of. According to the research scheme (Figure 3), main challenges in achieving the goal of effective functional finishing of textile material with polymeric system lay in: finding the adequate form of effective surface modifying system (SMS) (bulk- or micro-particulate); achieving efficient surface modification of the textile material (surface activation) for the incorporation of SMS; integrating SMS into textile material surface structure with sufficient durability while still retaining the effectiveness of the SMS (overall responsiveness of the new material). This actually means that surface modifying systems, after their incorporation to the textile material, must exhibit their responsive properties without impairing the intrinsic properties of original textile material. This requirement is successfully fulfilled by the use of micro-sized hydrogels. The submicron particle size enables incorporation to textile material surface in a very thin layer, which possesses increased surface area per unit mass and significantly improved response times in comparison to macroscopic (bulk) hydrogel.

4.1. Microgel as a surface modifying system

Hydrogels are usually defined as three-dimensional cross-linked polymeric networks that can imbibe large amounts of water [6, 7]. Based on their cross-linking chemistry, hydrogels are generally classified into physically cross-linked networks or chemically cross-linked gels. Physical gels are defined as polymeric networks that are bound together via polymer chain entanglement and/or non-covalent interactions that exist between polymer chains. The attractive forces holding these networks together are typically based on hydrogen bonding, electrostatic or hydrophobic interactions and thus, the gels can be reversibly dissolved under certain conditions that would weaken these attractive forces, i.e. a change in pH. Therefore, physical gels are not stable enough to be considered for the surface modifying systems. The other general class of hydrogels, which is appropriate for preparing surface modifying systems, is chemically cross-linked gels. These hydrogels exhibit improved stability due to the formation of covalent bonds between different polymer chains throughout the networks and display endurance with respect to network structure.

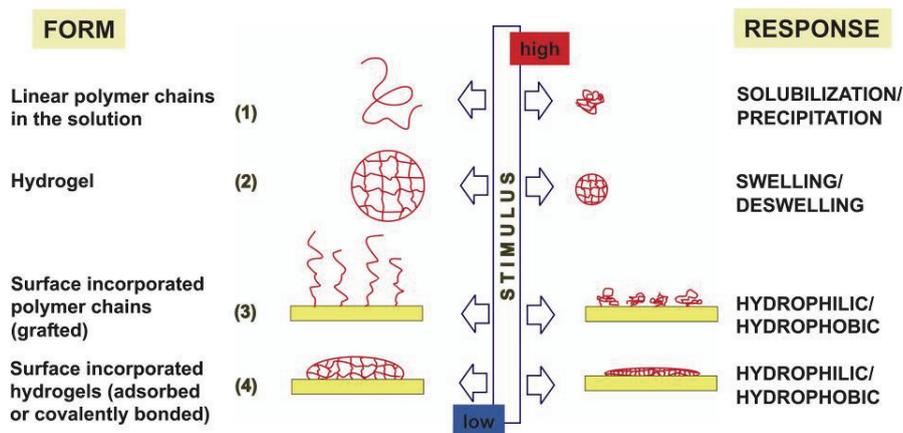


Figure 4. Different physical forms of stimuli-responsive polymers and their macroscopic response.

If hydrogel is prepared from stimuli-responsive polymers it has added functionality and display changes in solvation in response to certain stimuli such as temperature, pH, ionic strength, light, and electric field. Hence, this effect has broad implications in many arenas including biotechnology and biomedicine. 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 the numbers of reviews coming up in this area in recent times address the latest developments [8-10].

Responsive hydrogel 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 (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 (Figure 4).

Another important aspect is categorization based on gel dimensions. Hydrogels can be categorized as either macrogels (bulk) or microgels. Macrogels are bulk, monolithic networks that typically range in size from millimetres or greater. Microgels are defined as colloidally stable, water swellable polymeric networks whose diameter typically ranges from 100 nm to 1 μm [11]. While microgels internally have the same gel structure as their macroscopic version, microgels and macrogels are physically different, which is of ultimate importance for their use as surface modifying systems. Apart from much shorter response times, microgel particles have surface to volume ratios that are several orders of magnitude larger than those existing in bulk gels. They also possess increased surface area per unit and their submicron particle size enables incorporation to textile material surface in a very thin layer. Therefore, taking into consideration also the requirement of maintaining the advantageous conventional properties of initial textile material, it can be suggested that the most efficient polymeric surface modifying systems are expected to be based on micro-sized hydrogels.

4.2. Biopolymer based responsive microgels

We are all aware that nature provides numerous examples of functional materials and there is considerable interest in mimicking nature to generate high-performance, environmentally friendly materials. For this reason, a new generation of environmentally friendly materials in industrial applications has emerged by the use of biopolymers and their mixtures with synthetic polymers. The same occurs in the area of hydrogels where, due to the need for biocompatibility and biodegradability, biopolymer based responsive hydrogels are currently of great interest. Such hydrogels can be prepared by combining a thermoresponsive synthetic polymer with a natural based polymeric component resulting in dual (pH and temperature) responsive hydrogel systems [12].

Among the wide choice of natural polymers, biopolymer chitosan is a good option for combining with synthetic stimuli-responsive polymers. Chitosan is the second largest supply of natural biopolymers after cellulose and for this reason it has found a tremendous variety of real and potential industrial applications. Moreover, it offers unique physicochemical properties: naturally renewable source, non-toxic, non-allergenic, anti-microbial, biocompatible and biodegradable. Owing to these interesting intrinsic properties this biopolymer attracts currently a great deal of interest over a broad range of scientific areas, including use in biomedical, food, textile and various chemical industries. In textile material finishing, chitosan has been applied successfully for modifying the surface topography and thus controlling the surface-related properties of the fibre. It improves the dye coverage of immature fibres in dyeing of cotton [13]; it

can be successfully used as a thickener and binder in the pigment printing of cotton [14]; it can be used as a shrink-resistance agent in wool finishing [15] and as an agent for improving the dyeability of wool [16, 17].

Chitosan is an amine-rich linear β -1,4-linked polysaccharide (similar to cellulose) that is obtained by the partial deacetylation of chitin [18, 19]. Chitin is mostly obtained from the exoskeleton of industrially processed crustaceans, i.e. lobster, crab and shrimp shells, which are waste products from food-processing and contain between 20 to 40% of chitin. Chitin consists of a linear chain of (1–4) linked 2'-acetamido-2-deoxy- β -D-glucopyranose units (N-acetylglucosamine, Figure 5a); however, it is not soluble in common solvents and for its use, generally, chemical modifications are performed. Practically insoluble chitin can be converted into its soluble derivative, chitosan, by partial alkaline N-deacetylation of the parent polymer. Chitosan is in fact a collective name representing a family of chitins deacetylated to different degrees. When the degree of acetylation (DA) is lower than 0.5, chitosan becomes soluble in acidic aqueous solutions and it behaves as a cationic polyelectrolyte. Hence, chitosan can be formally considered as a linear cationic random copolymer containing (1–4) linked 2-acetamido-2-deoxy- β -D-glucopyranose (N-acetylglucosamine, Figure 5a) and 2-amino-2-deoxy- β -D-glucopyranose units (glucosamine, Figure 5b). The content of both structural units is defined by the degree of acetylation (DA) which is different for different chitosans. In fact, chitosan is enough deacetylated chitin to be soluble in diluted acid media.

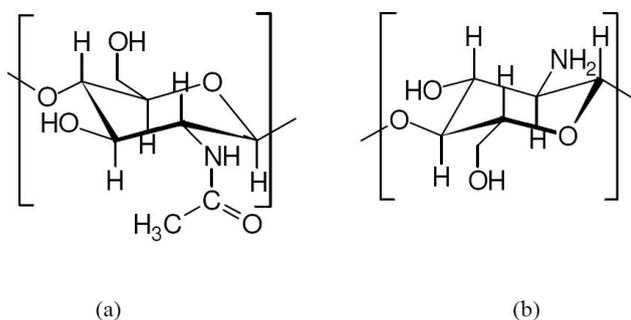


Figure 5. Structural units of chitosan: (a) N-acetylglucosamine unit; (b) Glucosamine unit.

Hence, chemical characteristics of chitosan (molecular weight, its polydispersity, the purity) are greatly dependent on the deacetylation method, the equipment used and also of the source of chitin. Nevertheless, it is important to note that the term “chitosan” does not refer to a single well defined structure, and chitosans can differ in molecular weight, degree of acetylation, and sequence (i.e., whether the acetylated residues are distributed along the backbone in a random or blocky manner).

Chitosan is a typical pH-sensitive polymer because it contains weak basic moieties (primary amino groups that have pKa values of about 6.3) attached to a hydrophobic backbone. It responds to the changes in the pH of the surrounding medium by protonation/deprotonation that imparts charges on its amino groups [20]. Upon ionization of amino groups (at pH values below the pKa, protonation), the charge is imparted over the chitosan molecule, so the coiled chains extend in response to the electrostatic repulsions of the generated charges, making chitosan a water-soluble cationic polyelectrolyte. This phenomenon is known as "pH induced phase transition" which results in increase of the hydrodynamic volume of the polymer as the macromolecules uncoil themselves due to the repulsion forces between multiple positive charges located on the amino groups along the macromolecular chain. At pH values above the pKa, chitosan's amino groups are deprotonated, and it becomes insoluble. When polymer is present in the form of hydrogel, the macroscopic response to the pH-induced phase transition is varying dimensions (swelling/deswelling) of the hydrogel. For this reason, chitosan has been chosen as the main polymer for preparation of surface modifying systems within the Advanbiotex project.

Among synthetic polymers, poly(N-isopropylacrylamide) (poly-NiPAAm) is the most intensively investigated thermo-responsive 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) [21]. 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). It is particularly advantageous that the LCST value of poly-NiPAAm solutions and gels falls between human body temperature and room temperature, this being the main reason why this polymer has been widely investigated in the fields of biotechnology, bioengineering and medicine [22].

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 amide groups) and hydrophobic aggregation of isopropyl groups [21]. The origin of this temperature sensitivity has been fully explained by the cooperative hydration mechanism [23]. Due to cooperative interaction between the nearest - neighbouring - 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.

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. 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.

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 et al. [24, 25] and Fan et al. [26] give the complex microparticles of homogeneous morphology, 50-300 nm in size. Procedures described by Lee et al. [24], Leung et al. [27] and Liu et al. [28] 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.

Theoretically expected dual responsiveness (pH and temperature) of combined chitosan/poly-NiPAAm hydrogel is schematically represented in Figure 6.

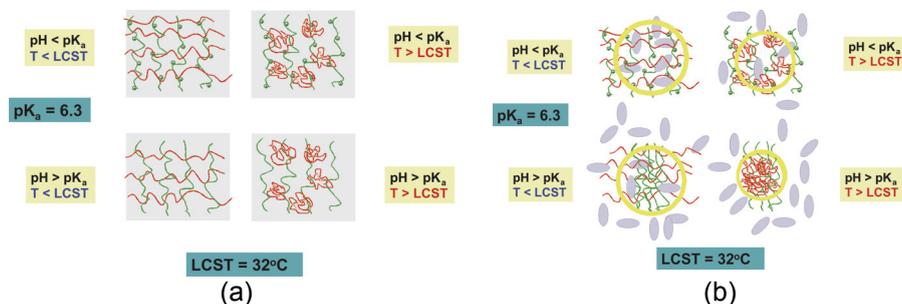


Figure 6. Schematic presentation of phase transition (a) and macroscopic response – swelling/de-swelling (in the presence of water molecules) (b) of dual responsive chitosan/poly-NiPAAm hydrogel in response to pH and temperature change.

However, this simple scheme can be used only for theoretical purposes. The main reason lays in the fact that, when polymer macromolecular domains with functional groups of a different nature are combined (to form hydrogel or microgel), one can expect that the swelling process should be controlled by different mechanisms. While hydrogels based on cationic polyelectrolyte have higher swelling capacity under acidic pH, in the case of polymers with non-ionic functionalities, such as those with amide groups, the swelling capacity depends, fundamentally, on controlled diffusion phenomena driven by concentration

gradients. Then, the final result depends on a balance among the capacity of the response of different functional groups under a determined condition.

Our previous study reported on the influence of the presence and the characteristics of chitosan on the physicochemical properties and the environmental responsiveness of poly-NiPAAm/chitosan (PNCS) microgel [29]. The influence of the degree of deacetylation and the molecular weight of chitosan (three different chitosans) on PNCS microgel properties was studied by dynamic light scattering (DLS) and UV-Vis spectrophotometric method. Dual responsiveness of microgel has been confirmed and correlated to the characteristics of chitosan used.

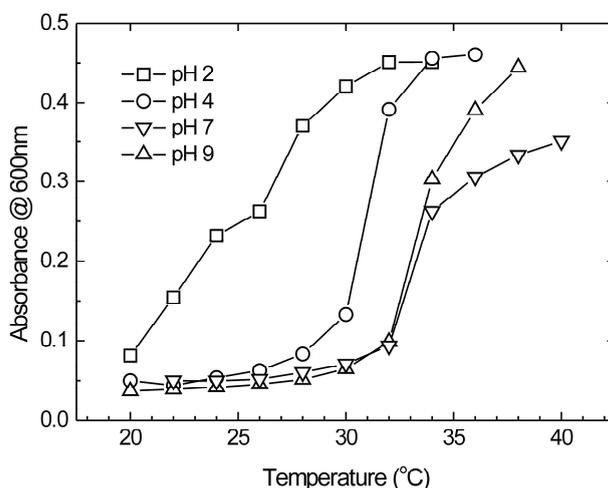


Figure 7. Temperature induced phase transition of PNCS microgel studied by UV-vis spectrophotometry at 600 nm for pH 2, 4, 7 and 9 [30].

The transition temperature (LCST) of PNCS microgel in aqueous system was examined by measuring the absorbance of the microparticle dispersion as a function of pH and temperature [30]. Figure 7 shows the absorbance of PNCS microgel 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 microgel collapses - 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 microgel decreases in acidic medium. Similar effect on LCST of poly-NiPAAm was observed by Pei et al. [31]; however the polymeric system they used was different.

In conclusion, the poly-NiPAAm/chitosan microgel (PNCS) of around 200 nm in size and with homogeneous morphology has been synthesized by surfactant-free dispersion copolymerization method. Its dual (pH and temperature) responsiveness has been confirmed by: reducing of hydrodynamic size with increase in temperature (DLS measurements); swelling in acidic medium and collapsing in alkaline medium. It has been confirmed that transition temperature (LCST) decreases with decrease in pH.

4.3. Incorporation of surface modifying system to textile material

In recent times, an increasing amount of research is being done on functional finishing of textile materials by incorporating stimuli-responsive polymeric systems (i.e. hydrogels), which resulted in publishing two extensive review papers [32, 33]. However, depending on the application field, two different approaches for the incorporation of responsive hydrogels to polymeric or textile materials must be considered.

In the biomedical field, the actual purpose of hydrogel incorporation to other materials is to improve the mechanical properties of the hydrogel [34, 35]. This is necessary because hydrogels with high water content exhibit extremely low mechanical strength, which limits their application. In the development of most biomedical materials biocompatibility and efficiency are the main issues, and polymeric or textile materials are used in this case only for the purpose of reinforcement, as the supporting material. Therefore, there is no issue of limiting thickness of the incorporated layer, which could influence the positive properties of the supporting material.

In the field of material technology, a rather different approach exists. Hydrogel incorporation to other materials is employed with the purpose of obtaining advanced material with responsive properties [36]. Since this material is aimed as consumer product, the characteristics of the material in all stages of production and use, such as performance in textile processing chain, comfort, safety and durability properties of the final product, are of ultimate importance. Moreover, the issue of maintaining the positive properties of the original textile material is present as an additional requirement.

As already mentioned previously, 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. Within the Advanbiotex project it has been confirmed that efficient incorporation of the surface modifying system based on responsive microgel to textile material (cotton, polyamide or polyester) 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. Two different approaches have been applied to achieve this goal. One approach is based on textile material activation before the application of the surface modifying system. Another approach, which does not include previous activation of textile material, is based on the use of the additional film-forming agent to produce three-dimensionally linked network between the surface modifying system and the

substrate. 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 [37]. The aim of textile material activation is to impart ionic character to the substrate (cotton or polyester) in order to facilitate the incorporation of the surface modifying system, and both chemical and physical methods have been used within Advanbiotex project.

4.3.1 Incorporation of surface modifying system to chemically activated cotton

Among several possibilities for producing ionic active sites on cotton surface by chemical methods, two methods have been thoroughly investigated: anionic cotton has been produced by reaction with monochloroacetic acid (CAA) to give partially carboxymethylated cellulose (carboxymethylation); cationic cotton has been produced by dyeing with reactive dye and subsequent reductive cleavage of the dye attached (aminization) [38].

After pad-batch treatment with PNCS microgel dispersion, the presence of microgel on the surface of chemically activated cotton fibres has been visually confirmed by SEM. Surface chemical analysis by XPS indicated that cotton activation and microgel incorporation were successfully achieved. Swelling behaviour and moisture sorption analysis showed that functionalized cotton presents pH, temperature and humidity responsiveness. In terms of difference in swelling between acidic and alkaline pH, the most encouraging result was obtained with previously aminized cotton [39, 40].

4.3.2 Incorporation of surface modifying system to physically activated cotton

Plasma can be defined as a partially ionized quasineutral gas [41]. Non-thermal or low-temperature plasmas (LTP) are particularly suited to apply to textile processing because most textile materials are heat sensitive polymers. It is a versatile technique, where a large variety of chemically active functional groups can be incorporated into the textile surface. By controlling the working parameters of the plasma, such as the nature of the gas, discharge power, pressure and exposure time, a great variety of surface effects can be produced. In the field of textiles, plasma technology has been used for different purposes such as improving hydrophilicity, increasing chemical reactivity of the fibre surface and especially for enhancing the adhesion of coatings [42] and polymer matrices [43].

The enhancement of the adhesion between a polymeric system (in our case surface modifying system) and plasma-treated fibres is due to both physical and chemical modifications. 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 polymer. The chemical modification is the increase of the concentration of functional groups on the fibre surface, hence causing a large number of chemical bonds to be formed between fibre and polymeric system. Special advantages of plasma treatment are reflected in the fact that it allows the selective treatment of the material surface and that the modification remains at a thin surface layer (several tens of

nm) without any influence on the bulk properties of the textile material [44]. With plasma technology it is possible to achieve the surface functionalization of textile material which can result in a variety of active groups on the fibre surface, without the use of any solvents or chemicals. Hence, in contrast to chemical methods, plasma treatment can be considered as an environmentally friendly process, which guarantees the high quality of the material with minimum costs and technological waste [45].

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. Generally, after plasma treatments there are still a lot of free radicals remained on the treated fibre surface which play an important role in forming functional groups and bonds between the fibre and the polymeric system. In case of cotton, the interaction with plasma may induce the formation of radicals or other active groups, such as hydroxyl, carboxyl and carbonyl. The newly formed active sites can initiate chemical reactions with substances brought in contact with the fibre, which are not typically shown by non-modified cotton [46]. Depending on the nature of the plasma gas used (air, nitrogen or argon), different modification is expected that produces cotton surface with physical and chemical characteristics that differ significantly from untreated cotton [47]. These three most commonly used plasma gases (air, nitrogen and argon) have been used for the activation of cotton for subsequent application of PNCS microgel [48]. Examination of surface morphology (SEM) revealed that untreated cotton fibres have significantly smoother surface than plasma treated fibres. The micro-cracks and grooves, observed on the plasma treated fibre surface, can be attributed to the ablation effect caused by interaction of plasma species with the fabric surface. Different plasma gasses led to different chemical surface modification, which has been confirmed by XPS analysis. The O/C atomic ratio obtained for all plasma treated samples was significantly higher than the value obtained for the untreated cotton, confirming that some oxidation of the cotton surface occurred after all plasma treatments. XPS analysis was further used to determine the surface chemical composition changes of cotton after microgel incorporation. These samples showed the presence of nitrogen in significantly high amount as 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. The best results in terms of microgel incorporation were obtained after nitrogen and argon plasma treatment.

4.3.3. Incorporation of surface modifying system to non-activated cotton with the use of additional film-forming agent

Another approach, which does not include previous activation of textile material, is based on the use of the additional film-forming agent to produce three-dimensionally linked network between the microgel particles and the substrate

(cotton) In this way, 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 [49]. 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, among which sodium hypophosphite (SHP) is being the most effective [50]. This system has been used for durable bonding of PNCS microgel to cotton by pad-dry-cure method [30, 51-54].

The crosslinking of PNCS to cotton was confirmed by XPS studies and durability of the surface modifying system was monitored by 5 times washing. It has been observed that after second washing, the add-on of PNCS treated cotton was reduced from initial 3% to 2.7%. After fifth washing it reached the value of 2.4%. This result shows that PNCS microgel particles are attached with satisfying durability to cotton, since ~80% of the surface modifying system still remains incorporated to cotton after 5 washing cycles. 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 poly-NiPAAm, but the contribution of each individual component cannot be established from the survey spectra. However, as obtained nitrogen percentage in PNCS/BTCA treated sample (7.2 at.%) was lower than the theoretically expected values for chitosan (9.0 at.%) and poly-NiPAAm (12.5 at.%), it has been estimated that the PNCS microgel particles cover around 50-60% of the cotton fibre surface, the rest being probably covered with the BTCA three-dimensional network. This assumption was in good agreement with the observation of the surface morphology by SEM.

4.3.4 Incorporation of surface modifying system to polyester

Since the surface of polyester shows strong hydrophobic character, high crystallinity and does not contain any active functional groups, efficient application of the surface modifying system (i.e. microgel) is difficult to achieve without surface initiation and subsequent polymerization (i.e. grafting). Among available grafting techniques, photoinduced grafting has become a very popular because of its significant advantages over other methods, such as: easy operation, mild reaction conditions and permanency of the surface modification. The photoinduced UV grafting onto polyester is a very interesting method because it allows the surface characteristics to be altered without causing serious modifications to the polymer bulk mechanical properties. In addition, UV grafting is an attractive way to impart a variety of functional groups to a polymer [55].

Within Advanbiotex project, photoinduced UV grafting has been used as the method for the incorporation of the surface modifying system to polyester in two different ways: (1) Previous treatment of polyester by photoinduced grafting of

acrylic acid (AA) monomer, which introduces carboxylic groups to polyester surface and thus activates the material, being followed by incorporation of PNCS microgel by the use of sol-gel technology using vinyltrimethoxysilane (VTMS) as a polysiloxane host matrix in a combination with hydrophilic fumed silica. [56]; (2) Direct (without previous activation of polyester) photoinduced UV graft copolymerization of poly(NiPAAm-co-AA) microgel as well as the polyelectrolyte complex of poly(NiPAAm-co-AA) microgel particles with chitosan [57, 58].

The microgel presence on the polyester fibres was confirmed by XPS. It was shown that nitrogen is present on the modified polyester fabric owing to the multiple amide bonds of poly(NiPAAm-co-AA), but also to the chitosan amine groups when the polyelectrolyte complexes were used [57, 58].

5. The effects obtained by functional finishing with responsive surface modifying system

Taking into consideration the basic requirement of preserving the advantageous original properties of the textile material, the incorporation of a surface modifying system has to be done in a manner that the responsive microgel implies stimuli-responsiveness to the textile material without screening its intrinsic properties. Since overall responsiveness observed is the consequence of swelling/collapse of PNCS microgel particles incorporated to the textile material surface, it is expected that there is less space for the microgel particle to expand and that it could not swell as fully as the free microgel particle. Therefore, maintaining the minimum possible coat-thickness has a positive influence on microgel response efficiency (swelling and de-swelling ability).

After careful optimization of the incorporation procedure, the specific discrete arrangement of microgel particles at the fibre surface can be observed, thus being estimated that for best results not more than 50% of the fibre surface should be covered by microgel (Figure 8). This incorporation pattern does impart changes to the fabric (or fibre) surface, but the overall fabric appearance and positive textile properties remain almost unchanged (whiteness; crease recovery angle) [54].

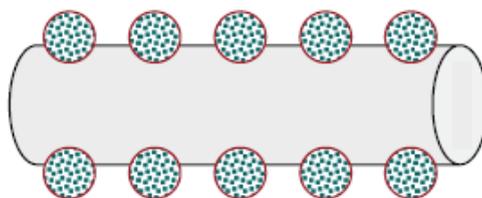


Figure 8. The discrete arrangement of microgel particles at the fibre surface.

The SEM analysis gave visual confirmation for this assumption. When the surface morphology of cotton treated with 3% owf of incorporated PNCS microgel was assessed by scanning electron microscopy, it was obvious that the incorporation of PNCS microgel particles significantly changes the visual aspect of the fibre surface. The form, size and amount of microgel particles present were clearly noticeable. Moreover, XPS analysis showed relatively low observed nitrogen content (4.3 at.%) (compared to theoretical values for chitosan and poly-NiPAAm), which 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 [52].

However, one should bear in mind that the responsive behaviour of microgel can only be observed in the presence of water. This means that water is the driving force which induces the effect of responsiveness. In terms of textiles, the water can appear from rain, water vapour or sweat formed by the wearer.

In general, when a dry cotton material with incorporated PNCS microgel is subjected to an environment containing moisture, both the fibre and the polymeric system absorb the moisture at a rate that depends on a number of physical factors. At the initial stage of moisture uptake, possibly the most important factor is the competition between the fibre and the polymeric system attached. Hence, the polymeric system will certainly be the preferable place where the interaction with moisture will occur. This is because the polymeric system with its very low crystallinity has much higher accessibility to water than the highly crystalline cotton fibre [40].

Moisture permeability is one of the very important criteria to evaluate textile fabric comfort ability. As the main goal of Advanbiotex project was the development of materials with environmental responsiveness capability, it is confirmed that the moisture permeability as specific attribute is not be present continuously (i.e. passively) on the newly developed material, but it could be activated "on demand" by sensing the stimuli in immediate surrounding environment and reacting to the human/environmental conditions. This is a very important step in development of materials for so called "responsive performance apparel".

Figure 9 shows the schematic presentation of water vapour transmission through the textile fabric with incorporated responsive microgel. Under dry conditions this "smart" fabric should always display as normal cloth with open interspaces having good air and moisture permeability, because the incorporated microgel particles are in contracted (de-swollen) state and tightly adhering to the fibre surface. Under severe humid conditions and temperatures below transition temperature of the microgel, interspaces are sealed by swollen microgel particles and fabric becomes resistant to water vapour transmission. By temperature rise over the transition point, the microgel particles contract and expel water, thus opening the interspaces between fibres and yarns. Macroscopically, this responsive behaviour could be certified by the increase in moisture permeability.

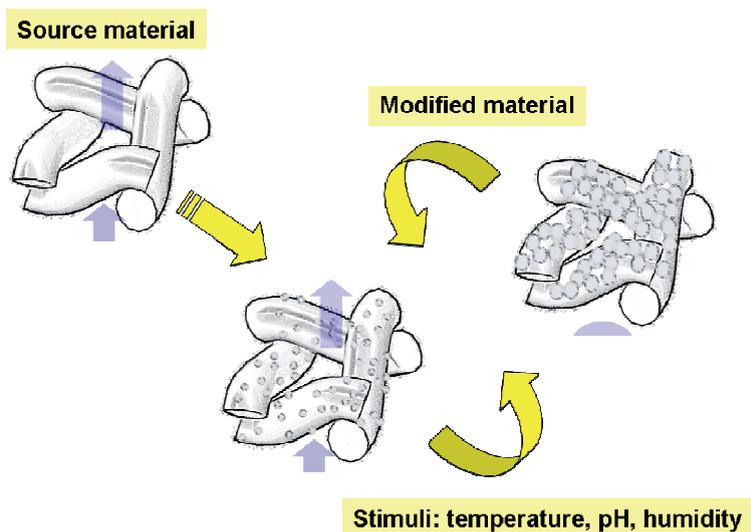


Figure 9. Schematic presentation of water vapour transmission through the textile fabric with incorporated responsive microgel.

Nevertheless, the effects of textile material with incorporated responsive microgel depend on the particular behaviour of each component of the microgel (i.e. chitosan, poly-NiPAAm, etc.) at particular conditions of the stimuli (humidity, temperature, pH). The overall effect is always the combination of swelling and shrinking effects that can occur simultaneously.

Above considerations have been thoroughly presented in various publications, where moisture management and liquid management properties of the newly developed textile material are explained in detail [52-54].

6. Conclusion

There is no doubt that responsive textiles produced by wet chemistry (i.e. functional finishing) will play a significant role in the realization of the “smart” textiles of tomorrow.

Current limitation could be the relatively high cost of the responsive polymers compared to the textile material. However, Advanbiotex project results showed that only a small amount of polymer is required to impart responsive properties efficiently to the textile material as the fabrication of such “smart” textiles is performed by surface modification technique. This fact is of huge interest since the actual production does not require expensive investment for the textile producer.

The results obtained within the frame of Advanbiotex project prove the concept for functional finishing of textiles with responsive microgel. Moreover, they

provide a guideline for the application of hydrogel in the form of micro-particulate systems (i.e. microgels) as a surface modifying system, with the aim to upgrade the regular textile material quality by providing highly attractive feature of environmental responsiveness.

References

- [1] R.R. Mather, Intelligent textiles, *Rev. Prog. Coloration*, **31**, 36-41 (2001).
- [2] T.L. Vigo, Intelligent Fibrous Materials, *J. Text. Inst.*, Part 3, **90**, 1-13 (1999).
- [3] H.R. Matilla (Ed.), *"Intelligent textiles and clothing"*, Woodhead Publishing Ltd., Cambridge, UK (2006).
- [4] X. Tao (Ed.), *"Intelligent fibres, fabrics and clothing"*, Woodhead Publishing Ltd., Cambridge, UK (2001).
- [5] C.M. Pastore, P. Kiekens (Eds.), *"Surface characteristics of fibers and textiles"*, Marcel Dekker Inc., New York (2001).
- [6] N.A. Peppas, A.R. Khare, Preparation, structure and diffusional behaviour of hydrogels in controlled release, *Advanced Drug Delivery Reviews*, **11**, 1-35 (1993).
- [7] A.S. Hoffman, Hydrogels for Biomedical Applications, *Annals New York Acad. Sci.*, **944**, No. 1, 2-73 (2001).
- [8] A. Kumar, A. Srivastava, I.Y. Galaev, B. Mattiasson, Smart polymers: Physical forms and bioengineering applications, *Prog. Polym. Sci.*, **32**, 1205-1237 (2007).
- [9] J.F. Mano, Stimuli-Responsive Polymeric Systems for Biomedical Applications, *Adv. Eng. Mater.*, **10**, 515-527 (2008).
- [10] J. Kopecek, J. Yang, Hydrogels as smart biomaterials, *Polym. Int.*, **56**, 1078-1098 (2007).
- [11] R. Pelton, Temperature-sensitive aqueous microgels, *Advances in Colloid and Interface Science*, **85**, 1-33 (2000).
- [12] M. Prabakaran, J.F. Mano, Stimuli-Responsive Hydrogels Based on Polysaccharides Incorporated with Thermo-Responsive Polymers as Novel Biomaterials, *Macromol. Biosci.*, **6**, 991-1008 (2006).
- [13] J. Rippon, Improving the dye coverage of immature cotton fibres by treatment with chitosan, *J. Soc. Dyers Colour.*, **100**, 298-303 (1984).
- [14] S.A. Bahmani, G.C. East, I. Holme, The application of chitosan in pigment printing, *J. Soc. Dyers Colour.*, **116**, 94-99 (2000).
- [15] M.R. Julia, E. Pascual, P. Erra, Influence of the molecular mass of chitosan on shrink-resistance and dyeing properties of chitosan-treated wool, *J. Soc. Dyers Colour.*, **116**, 62-67 (2000).
- [16] D. Jocić, M.R. Julia, P. Erra, Application of chitosan/nonionic surfactant mixture to wool assessed by dyeing with reactive dye, *J. Soc. Dyers. Col.*, **113**, 25-31 (1997).

- [17] D. Jocić, S. Vilchez, T. Topalović, R. Molina, A. Navarro, P. Jovančić, M.R. Julia, P. Erra, Effect of Low-Temperature Plasma and Chitosan Treatment on Wool Dyeing with Acid Red 27, *J. Appl. Polym. Sci.*, **97**, 2204-2214 (2005).
- [18] M.N.V. Ravi Kumar, A review of chitin and chitosan applications, *Reactive & Functional Polymers*, **46**, 1-27 (2000).
- [19] M. Rinaudo, Chitin and chitosan: Properties and applications, *Prog. Polym. Sci.*, **31**, 603-632 (2006).
- [20] K.M. Vårum, M.H. Ottøy, O. Smidsrød, Water-solubility of partially N-acetylated chitosans as a function of pH: effect of chemical composition and depolymerisation, *Carbohydrate Polymers*, **25**, 65-70 (1994).
- [21] H.G. Schild, Poly(N-isopropylacrylamide): experiment, theory and application, *Prog. Polym. Sci.*, **17**, 163-249 (1992).
- [22] L. Klouda, A.G. Mikos, Thermoresponsive hydrogels in biomedical applications, *Eur. J. Pharmaceut. Biopharmaceut.*, **68**, 34-45 (2008).
- [23] Y. Okada, F. Tanaka, Cooperative Hydration, Chain Collapse, and Flat LCST Behavior in Aqueous Poly(N-isopropylacrylamide) Solutions, *Macromolecules*, **38**, 4465-4471 (2005).
- [24] C.F. Lee, C.J. Wen, W.Y. Chiu, Synthesis of poly(chitosan-N-isopropylacrylamide) complex particles with the method of soapless dispersion polymerization, *Journal of Polymer Science: Part A: Polymer Chemistry*, **41**, 2053-2063 (2003).
- [25] C.F. Lee, C.J. Wen, C.L. Lin, W.Y. Chiu, 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*, **42**, 3029-3037 (2004).
- [26] L. Fan, H. Wu, H. Zhang, F. Li, T. Yang, C. Gu, Q. Yang, Novel super pH-sensitive nanoparticles responsive to tumor extracellular pH, *Carbohydrate Polymers*, **73**, 390-400 (2008).
- [27] M.F. Leung, J. Zhu, F.W. Harris, P. Li, New Route to Smart Core-Shell Polymeric Microgels: Synthesis and Properties, *Macromolecular Rapid Communications*, **25**, 1819-1823 (2004).
- [28] W. Liu, Y. Huang, H. Liu, Y. Hu, Composite structure of temperature sensitive chitosan microgel and anomalous behavior in alcohol solutions, *Journal of Colloid and Interface Science*, **313**, 117-121 (2007).
- [29] A. Tourrette, M.M.C.G. Warmoeskerken, D. Jocić, Influence of chitosan characteristics on the properties of stimuli-responsive poly(N-isopropylacrylamide)/chitosan microgels, *9th International Conference of the European Chitin Society (EUCHIS 2009)*, 23-26 May 2009, San Servolo Island, Venice, Italy, Conference Book, Paper P1-2, 19 (2009).
- [30] A. Kulkarni, A. Tourrette, M.M.C.G. Warmoeskerken, D. Jocić, Microgel-based surface modifying system for stimuli-responsive functional finishing of cotton, *Carbohydrate Polymers*, **82**, 1306-1314 (2010).
- [31] Y. Pei, J. Chen, L. Yang, L. Shi, Q. Tao, B. Hui, J. Li, The effect of pH on the LCST of poly(N-isopropylacrylamide) and poly(N-isopropylacrylamide-co-acrylic acid), *Journal of Biomaterials Science, Polymer Edition.*, **15**, 585-594 (2003).
- [32] B. Liu, Y. Hu, The Application of Temperature-Sensitive Hydrogels to Textiles: A Review of Chinese and Japanese Investigations, *Fibres & Textiles in Eastern Europe*, **13**, No.6, 45-49 (2005).

- [33] D. Crespy, M.R. Rossi, Temperature-responsive polymers with LCST in the physiological range and their applications in textiles, *Polym. Int.*, **56**, 1461-1468 (2007).
- [34] J.O. Karlsson, P. Gatenholm, Cellulose fibre supported pH-sensitive hydrogels, *Polymer*, **40**, 379-387 (1999).
- [35] K-S. Chen, Y-A. Ku, C-H. Lee, H-R. Lin, F-H. Lin, T-M. Chen, Immobilization of chitosan gel with cross-linking reagent on PNIPAAm gel/PP nonwoven composites surface, *Mater. Sci. Eng. C.*, **25**, 472-478 (2005).
- [36] D. Jocić, Smart Textile Materials by Surface Modification with Biopolymeric Systems, *Research Journal of Textile and Apparel*, **12**, No. 2, 58-65 (2008).
- [37] D. Jocić, The perspective of stimuli-responsive surface modifying systems in developing functionalized textile, *The 9th AUTEX Conference*, May 26-28, 2009, Izmir – Cesme, Turkey, Proceedings (CD-ROM), 474-479 (2009).
- [38] D. Jocić, A. Tourrette, P. Glampedaki, M.M.C.G. Warmoeskerken, Application of temperature and pH responsive microhydrogels for functional finishing of cotton fabric, *Materials Technology: Advanced Performance Materials*, **24**, 14-23 (2009).
- [39] A. Tourrette, P. Glampedaki, M.M.C.G. Warmoeskerken, D. Jocić, Surface modification of textile material with biopolymer-based micro- and nano-hydrogels, *AUTEX 2008 World Textile Conference*, June 24-26, 2008, Città Studi, Biella, Italy, CD-ROM of Proceedings, 8 pages (2008).
- [40] D. Jocić, A. Tourrette, P. Glampedaki, M.M.C.G. Warmoeskerken, Functional finishing of cotton with dual-stimuli-responsive chitosan/poly(N-isopropylacrylamide) micro-hydrogels, *The 86th Textile Institute World Conference*, Hong Kong, 18-21 November 2008, Conference Proceedings (CD-ROM), 251-265 (2008).
- [41] S. Luo, W.J. Van Ooij, Surface modification of textile fibers for improvement of adhesion to polymeric matrices: a review, *J. Adhesion Sci. Technol.*, **16**, 1715-1735 (2002).
- [42] R. Shishoo, Plasma treatment – Industrial applications and its impact on the C&L industry, *J. Coated Fabrics*, **26**, 26-35 (1996).
- [43] M. Steffeka, J. Rahel, M. Cernak, Atmospheric-pressure plasma treatment of ultrahigh molecular weight polyethylene fibers, *J. Mater. Sci. Lett.*, **18**, 2007-2008 (1999).
- [44] R. Morent, N. De Geyter, J. Verschuren, K. De Clerk, P. Kiekens, C. Leys, Non-thermal plasma treatment of textiles, *Surf. & Coatings Technol.*, **202**, 3427-3449 (2008).
- [45] N. Carneiro, A.P. Souto, E. Silva, A. Marimba, B. Tena, H. Ferreira, V. Magalhães, Dyeability of corona-treated fabrics, *Color. Technol.*, **117**, 298-302 (2001).
- [46] R. Li, L. Ye, Y.W. Mai, Application of plasma technologies in fibre-reinforced polymer composites: a review of recent developments, *Composites Part A*, **28A**, 73-86 (1997).
- [47] T.L. Ward, H.Z. Jung, O. Hinojosa, R.R. Benerito, Effect of cold plasmas on polysaccharides, *Surface Science*, **76**, 257-273 (1978).
- [48] A. Tourrette, N. De Geyter, D. Jocić, R. Morent, M.M.C.G. Warmoeskerken, C. Leys, Incorporation of poly(N-isopropylacrylamide)/chitosan microgel onto plasma functionalized cotton fibre surface, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, **352**, 126-135 (2009).

- [49] C.M. Welch, Formaldehyde-Free Durable Press Finishes, *Review of Progress in Coloration and Related Topics*, **22**, 32-41 (1992).
- [50] X. Gu, C.Q. Yang, FTIR spectroscopy study of the formation of cyclic anhydride intermediates polycarboxylic acids catalyzed by sodium hypophosphite, *Textile Research Journal*, **70**, 64-70 (2000).
- [51] A. Kulkarni, M.M.C.G. Warmoeskerken, D. Jocić, Adding functionality to cotton by using stimuli-sensitive microparticles, *International conference "Functional materials and nanotechnologies" (FMNT2010)*, March 16-19, 2010, Riga (Latvia), Book of abstracts, OR-53, 85 (2010).
- [52] P. Križman-Lavrič, M.M.C.G. Warmoeskerken, D. Jocić, Microgel functionalized textiles responsive to ambient conditions, *The 10th World Textile Conference (AUTEX2010)*, June 21-23, 2010, Vilnius, Lithuania, Proceedings (CD-ROM), (4 pages) (2010).
- [53] P. Križman Lavrič, M.M.C.G. Warmoeskerken, D. Jocić, Vapour transmission properties of a surface modified textile material with poly-NiPAAm/chitosan microgel, *41st International Symposium on Novelty in Textiles (ISNT2010)*, 27-29 May 2010, Ljubljana (Slovenia), Proceedings (CD-ROM), 104-110 (2010).
- [54] D. Jocić, P. Križman Lavrič, M.M.C.G. Warmoeskerken, Stimuli-responsive cotton by functional finishing with chitosan/poly-NiPAAm microgel, *International Conference on Intelligent Textiles (ICIT2010)*, June 17-18, Seoul, Korea, Proceedings, 15-16 (2010).
- [55] Y-W. Song, H-S. Do, H-S. Joo, D-H. Lim, S. Kim, H-J. Kim, Effect of grafting of acrylic acid onto a PET film surfaces by UV irradiation on the adhesion of PSAs, *J. Adhesion Sci. Technol.*, **20**, 1357-1365 (2006).
- [56] B. Tomšič, this book.
- [57] P. Glampedaki, J. Zhao, C. Campagne, D. Jocić, M.M.C.G. Warmoeskerken, Polyester functionalization using thermoresponsive microparticles, *The 10th World Textile Conference (AUTEX2010)*, June 21-23, 2010, Vilnius, Lithuania, Proceedings (CD-ROM), (4 pages) (2010).
- [58] P. Glampedaki, D. Jocić, V. Dutschk, M.M.C.G. Warmoeskerken, Surface modification of polyester fabrics by grafting pH/thermo-responsive microgels with UV irradiation, *24th International Conference on Surface Modification Technologies (SMT 24)*, September 7-9, 2010, Dresden, Germany, Book of Abstracts, 32 (2010).