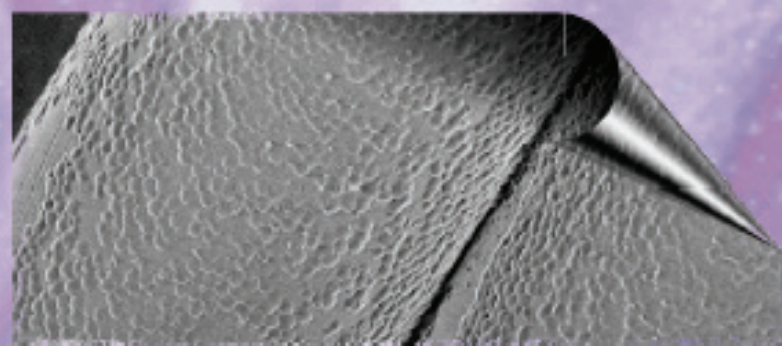


**SURFACE MODIFICATION
SYSTEMS
FOR CREATING
STIMULI RESPONSIVENESS
OF TEXTILES**



Workshop Proceedings

Surface Modification Systems for Creating Stimuli-Responsiveness of Textiles

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



Jocić, D (Ed.)
Surface Modification Systems for Creating Stimuli Responsiveness of Textiles
- Workshop Proceedings -
University of Twente, The Netherlands
ISBN 978-90-365-3122-1

Technical editing: Pavla Križman-Lavrič

Print: Ipskamp Drukkers B.V., Enschede, The Netherlands

© 2010 by Engineering of Fibrous Smart Materials (EFSM)
Faculty of Engineering Technology (CTW)
University of Twente
Drienerlolaan 5
7522NB Enschede, The Netherlands

Surface Modification Systems for Creating Stimuli-Responsiveness of Textiles

Workshop Proceedings

Edited by

Dragan Jocić
Advanbiotex Team Leader

UNIVERSITY OF TWENTE.



Preface

“Even matter called inorganic, believed to be dead, responds to irritants and gives unmistakable evidence of a living principle within. Everything that exists, organic or inorganic, animated or inert, is susceptible to stimulus from the outside.”

Nikola Tesla (1856-1943)

Even though such a great mind - one of the most celebrated scientists of the modern era – already several decades ago affirmed “intelligent” properties of the matter everywhere around us, it is still an enormous challenge to convert such an ordinary material - textiles - in “smart”, “intelligent” or simply - responsive to the stimuli. Over the last decade, researchers from varying backgrounds have come across versatile new methods for obtaining “smart” textile materials and products. Most of suggested approaches have been based on the idea that textile material could be used as a platform for supporting or embedding electronics into textile substrate, which is the consequence of constantly being surrounded with highly sophisticated products of the 21st century information society. However, this approach implies a major technology change in textile production and for that reason it has not been appreciated greatly by traditional textile technology which has always been rather reluctant to essential technology changes.

In creating paths for “readily acceptable” solutions for transforming traditional textile technology to modern textile technology of the 21st century, *functional finishing* is one of the most viable alternatives. This 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, to create modern *knowledge-based textile materials* that are not only keeping us warm, dry and comfortable, but are expected to react and interact with a wide range of stimuli and situations.

The functional finishing approach is nowadays being possible as the consequence of enormous growth in supporting technologies, primarily in the areas of responsive polymers and surface modification techniques. The latest and most influential concepts from these emerging areas are embedded in the Advanbiotex project with aim to develop an innovative strategy for functional finishing of textiles by application of novel *surface modifying systems* based on stimuli-responsive polymers.

The Advanbiotex project has been funded by the Marie Curie Excellence Grant which provided an excellent opportunity to develop a European research team and to stimulate the ideas of what can be done in development of such a novel technology. Moreover, the project itself has been an opportunity for all team members to reach a high level of scientific excellence. The workshop upon which this book is based, is organized on occasion of ending the project with the aim to stress the importance of knowledge-based textile materials for European textile industry by highlighting the exciting area of surface modification systems for creating stimuli-responsiveness of textiles. Part I of this book covers the developments within this dynamic field, drawing together the world-renowned experts in their particular fields of textile research. Part II, comprising five chapters written by Advanbiotex project team members, deals with Advanbiotex project research results and produces an important source of knowledge on textile surface modification systems based on micro-particulate responsive hydrogels.

Both Advanbiotex Workshop and this book have been made possible because a team of authors have contributed. The Team Leader wishes to extend his most sincere gratitude to all the authors for their cooperation and contribution in a joint endeavour to offer the solutions for creating new conceptual textile systems for the 21st century, based on *knowledge-based textile materials*.

November 2010

Dragan Jocić
Advanbiotex Team Leader

Contents

Part I - General aspects

3	An Introduction to the Research Group Engineering of Fibrous Smart Materials <i>Marijn M.C.G. Warmoeskerken</i>
9	Multifunctional Fibers via Manipulation of Nanoscale Phenomena <i>Juan Hinestroza</i>
17	Sol-gel Technology for Chemical Modification of Textile <i>Barbara Simončič, Brigita Tomšič, Boris Orel & Ivan Jerman</i>

Part II - Advanbiotex highlights

37	Functional Finishing of Textiles with Responsive Polymeric Systems <i>Dragan Jocić</i>
61	Tunable Wettability of Polyester Fabrics Functionalized by Chitosan/poly(N-isopropylacrylamide-co-acrylic acid) Microgels <i>Pelagia Glampedaki</i>
77	Thermal and pH-responsive Microgel Incorporation to Previously Activated Cotton <i>Audrey Tourrette</i>
93	Functionalization of Textile Materials with Stimuli-responsive Microgel: A Study of Liquid Management Properties <i>Pavla Križman-Lavrič</i>
107	Modification of PES Fabric by Stimuli-responsive Microgel Using Sol-gel Technology <i>Brigita Tomšič</i>

Contributors

Dr. Marijn M.C.G. Warmoeskerken

Professor - Head of EFSM group
Engineering of Fibrous Smart Materials (EFSM)
Faculty of Engineering Technology (CTW)
University of Twente
Enschede, The Netherlands
m.m.c.g.warmoeskerken@utwente.nl
<http://www.utwente.nl/ctw/efsm>

Dr. Juan P. Hinestroza

Assistant Professor of Fiber Science
Department of Fiber Science and Apparel Design
Cornell University
Ithaca, NY 14850, USA
jh433@cornell.edu
<http://nanotextiles.human.cornell.edu/>

Dr. Barbara Simončič

Professor
Department of Textiles
Faculty of Natural Sciences and Engineering
University of Ljubljana
Ljubljana, Slovenia
barbara.simoncic@ntf.uni-lj.si
<http://www.ntf.uni-lj.si/>

Dr. Dragan Jocić

Senior Researcher
Engineering of Fibrous Smart Materials (EFSM)
Faculty of Engineering Technology (CTW)
University of Twente
Enschede, The Netherlands
d.jocic@utwente.nl
<http://www.utwente.nl/ctw/efsm/advanbiotex>

Professor
Textile Engineering Department
Faculty of Technology and Metallurgy
University of Belgrade
Belgrade, Serbia
drjoc@tmf.bg.ac.rs
<http://www.tmf.bg.ac.rs>

Pelagia Glampedaki, M.Sc.

Research Assistant
Engineering of Fibrous Smart Materials (EFSM)
Faculty of Engineering Technology (CTW)
University of Twente
Enschede, The Netherlands
p.glampedaki@utwente.nl
<http://www.utwente.nl/ctw/efsm/advanbiotex>

Dr. Audrey Tourrette

Assistant Professor
Laboratoire de Pharmacie Galénique
CIRIMAT - UPS-INPT-CNRS
Institut Carnot
Equipe "Phosphates, Pharmacotechnie, Biomatériaux"
Toulouse, France
audrey.tourrette@cict.fr

Dr. Pavla Križman-Lavrič

Postdoctoral Researcher
Engineering of Fibrous Smart Materials (EFSM)
Faculty of Engineering Technology (CTW)
University of Twente
Enschede, The Netherlands
p.krizmanlavric@utwente.nl
<http://www.utwente.nl/ctw/efsm/advanbiotex>

Dr. Brigita Tomšič

Postdoctoral Researcher
Engineering of Fibrous Smart Materials (EFSM)
Faculty of Engineering Technology (CTW)
University of Twente
Enschede, The Netherlands
b.tomsic@utwente.nl
<http://www.utwente.nl/ctw/efsm/advanbiotex>

Assistant Professor
Department of Textiles
Faculty of Natural Sciences and Engineering
University of Ljubljana
Ljubljana, Slovenia
brigita.tomsic@ntf.uni-lj.si
<http://www.ntf.uni-lj.si/>

Part I - General aspects

Chapter 1

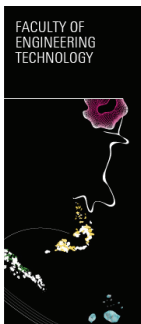
An Introduction to the Research Group Engineering of Fibrous Smart Materials

Marijn M.C.G. Warmoeskerken
Engineering of Fibrous Smart Materials (EFSM)
Faculty of Engineering Technology (CTW)
University of Twente, Enschede
The Netherlands

1. Introduction

The Marie Curie Excellence programme Advanbiotex was hosted by the research group EFSM (Engineering of Fibrous Smart Materials). This group belongs since September 2007 to the Faculty of Engineering Technology of the University of Twente. Before that the name of the group was Textile Technology, TXT, and was hosted by the Faculty for Science and Technology until the reorganization of that Faculty in 2006.

The group as such has been established on the 1st of March 1991 by the Foundation STGM (Foundation for Technology of Structured Materials). After the move from the Faculty for Science and Technology to the Faculty of Engineering Technology the name of the group and of the foundation as well has been changed to EFSM and to the Foundation for EFSM respectively.



2. Foundation EFSM

The Foundation EFSM supports the research chair EFSM. By this chair the Foundation wants to support the industry in their need to develop a strong international position by funding the chair and by directing the long term research objectives of the chair. Building and extending necessary knowledge and expertise and strengthening the European position of the Chair are important strategic objectives. The current members of the foundation are:

- Christeys B.V. (detergents supplier for laundries)
- Colbond B.V. (non-wovens manufacturer)
- Federatie Textielbeheer Nederland (FTN) (branch organisation for Dutch laundries)
- Modint (branch organisation for Dutch textile and clothing companies)
- Saxion (University for Applied Sciences)
- Stork Prints B.V. (ink-jet technology)
- Tanatex Chemicals B.V. (textile chemicals supplier)
- Royal Ten Cate (textile company)
- TNO (materials science)
- Vlisco Helmond B.V. (wax printed fabrics)
- Gamma Holding (technical fabrics).

The driver for these companies to organize themselves in a foundation EFSM to support the academic chair was the loss of the textile industry in the Netherlands and consequently the loss of Dutch textile education and research facilities. As such the Netherlands was an important textile country with many textile mills in, for example, Enschede and Tilburg. However due to the move of these activities to the so called low-wage countries many mills were closed in the sixties and seventies. As a result of that also the polytechnic textile schools in Enschede and Tilburg were closed. At the University of Twente, the Faculty for Chemical Engineering, there was a research group of Prof. Groot Wassink active in the area of textile technology. The focus in that group was on wet textile processes. With the retirement of Prof. Groot Wassink the university decided also to stop this textile research. That meant for still existing textile companies that they finally also lost the possibilities for academic research and education in their area of interest. Therefore, they decided to establish and to maintain an industrial chair at the University of Twente. The first professor of the chair was Prof. Ir. Groot Wassink. His successor in 1995 was Prof. Dr. Ir. Warmoeskerken who is still leading the group.

3. Programme development

The initial programme of EFSM was focused on traditional textiles particularly on textile finishing processes like scouring, bleaching and dyeing. The topics studied were:

- Hydrodynamics in textile materials
- Ultrasonically boosted mass transfer
- Enzymatic treatment processes
- Catalytic bleaching
- Wetting dynamics



In these areas EFSM has built an international recognition. However, in 2006 the board of the EFSM-foundation decided to shift the focus of the programme from traditional textiles towards textiles with added functionality also called smart fabrics. The reason was the international developments on the global textile market with China as a new player. That forced the companies to review their business strategies. One leading theme here was to change their business from a labour intensive one to a knowledge intensive one.

In Europe this has led to the establishment of a Technology Platform for the Future of Textiles and Clothing. This platform aims at reinforcing the research power on textiles in Europe by creating opportunities for different European research groups to work closely together. Since EFSM did not really have expertise in the area of smart fabrics the strategy was to become involved in European projects in this area. The participation in two European projects, Digitex and Advanbiotex enabled EFSM to create a new science base on smart fabrics.

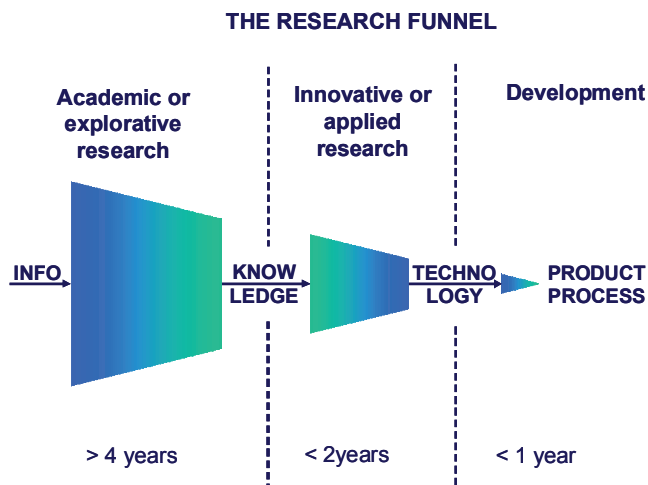
4. Internationalisation

The group EFSM operates in a strong international network. This network has been created by a membership of the European Technology Platform and of the Autex - Association of Universities on Textiles. EFSM has now contacts and collaborations with many universities in Europe. With the board of the EFSM-foundation a strategy is now under development to invite also international companies and research-institutes to become a member of EFSM. Recently a covenant has been arranged with the Leibniz Institute of Polymer Research (IPF) in Dresden (Germany) for scientific collaboration in the field of polymer and related research.



5. Innovative power

For EFSM as an industrial research group it is important that the new knowledge generated by the group is implemented in the industry. However due to the innovation paradox this is not an easy task. The innovation paradox means that there is a gap between the long term academic research at the universities and the short term process and product development in the industry. This gap concerns the development of new technology on basis of academic knowledge.



Big companies, owning their own R&D departments, do this technology development themselves. Therefore many multinationals have science brokers that monitor the latest developments in the academic world to see if a particular university has specific knowledge that could form an input for the company's future key technology. However in the world of fibres and textiles most companies belong to the so called small and medium enterprises, SME-s, that do not have research facilities to develop new technologies. Therefore EFSM has a close collaboration with Saxion University for Applied Science for technology development and to increase the innovation power for the industrial partners.

A good example is the work of G. Bouwhuis. He is employed by Saxion and is allowed to spend two days per week in our group to prepare his PhD-thesis. He works on the industrial implementation of the enzyme-technology that has been developed within EFSM. Recently he has performed successfully full scale experiments in two textile companies. These companies have decided now to implement the EFSM technology in their processes.

Further EFSM do short term bilateral projects for the industrial partners to apply the specific knowledge and expertise to solve particular problems in their company or to develop a proof of concept.

6. Current research programme

The research mission of EFSM is Product Driven Fibre Surface Engineering. This means that the research projects are always directed on a future product or process application.

The current research programme is based on the two European projects mentioned. The first is project Digitex. This project aims at the development of special textile materials applying the principles of inkjets. Our contribution is to study the possibility of slow release systems using cyclodextrin and to study the treatment of single fibres in a fabric by inkjets.

The second project is the Advanbiotex project. In this work the aim is to study biopolymer hydrogels attached to fibres to act as response system to external stimuli.

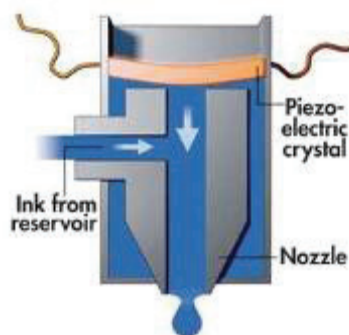
As a result of these efforts in creating a new science base EFSM started recently a new AIO project on anti bacterial finishing systems for the textile service industries.

EFSM participates also in a STW project in collaboration with the TU-Delft and the LU-Wageningen. The aim is to study the fabric cleaning process with dense CO₂ and ultrasound. Since EFSM was in the transition period from TNW to CTW during the time that the STW-proposal for this project was prepared we could unfortunately not apply for an AIO in this work.

As a result of the “old” programme there is also a project on enzymatic treatment of fabrics. In July this year a PhD started her work on the development of antibacterial fabrics for the textile service industries. In September this year a new PhD started his work in EFSM on a generic project initiated by the EFSM-foundation. This work will be focussed totally on the re-engineering of fibre surfaces.

7. Outlook

Nowadays, high performance textile products are demanding, even in the ‘traditional’ clothing and home textiles areas. Functional properties can be defined as all the effects beyond the pure aesthetic, protection and decorative functions. They include a large range of properties that can be also classified as ‘smart properties’ granting to textile materials a capacity to act upon external



stimulations. Multiple functions are often required, leading to multifunctional textile materials, one of the five key technologies at present.

EFSM wants to become an expertise centre in this science area with international recognition. In the next five years a strong science base for fibre surface modification technologies will be developed that can act as a source for new challenging projects. Together

with the board of the EFSM-foundation a strategy will be developed for internationalisation of EFSM.



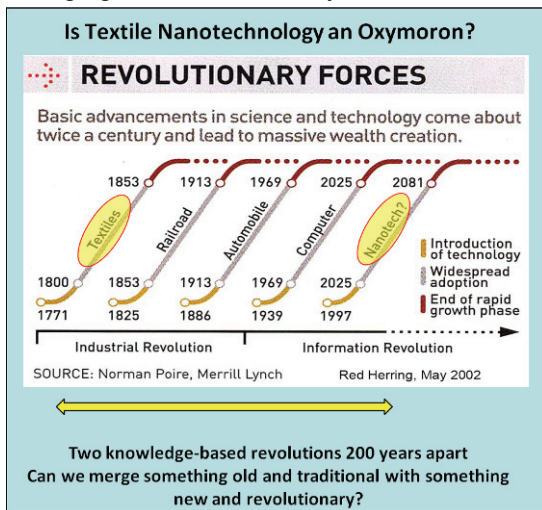
Chapter 2

Multifunctional Fibers via Manipulation of Nanoscale Phenomena

Juan P. Hinestroza, Ph.D.
*Department of Fiber Science & Apparel Design
Cornell University, Ithaca, NY
USA*

1. Introduction

The main focus of the Hinestroza Research Group at Cornell University (<http://nanotextiles.human.cornell.edu>) is to explore the interface between the technologically established and mature field of textile science with the emerging and revolutionary field of nanoscale science. Textile technologies



were the first beneficiaries of the scientific developments from the 18th century industrial revolution while the nanotechnology revolution emerged at the end of the 20th century. Our research group aims at merging two hundred years of innovation history.

We believe that this unusual combination, between an established and an emerging scientific field, can provide unique scientific platforms that can take advantage of the ability of nanoscale science at

controlling the synthesis of materials and probing of unusual phenomena with the time-tested capabilities of textile and fiber processing methods.

In these proceedings we will discuss three different approaches aimed at creating multifunctional cotton surfaces using nanolayers of polyelectrolytes via layer-by-layer deposition, conformal nanolayers of metal oxides using Atomic Layer Deposition and self-assembly of nanoparticles via manipulation of electrostatic and hydrogen bonding interactions. All three approaches allow for

the creation of novel functionalities to the traditional cotton substrate while preserving the comfort and mechanical properties of this natural and abundant fiber.

2. Layer-by-layer assembly of polyelectrolyte nanolayers on cotton substrates

Deposition of polyelectrolyte nanolayers onto natural fibers and textiles via layer-by-layer (LbL) assemblies may open a new avenue to increase the surface functionality of these materials without making major changes to the weight, bulkiness, or comfort. LbL is especially suitable for potential use on natural fibers due to its self-healing capability providing an increased tolerance to defects. The first step in the assembly process includes the creation of a charged surface onto polyelectrolytes of opposite charges can be anchored. Our group works with cationic and anionic cellulose as shown in Figure 1.

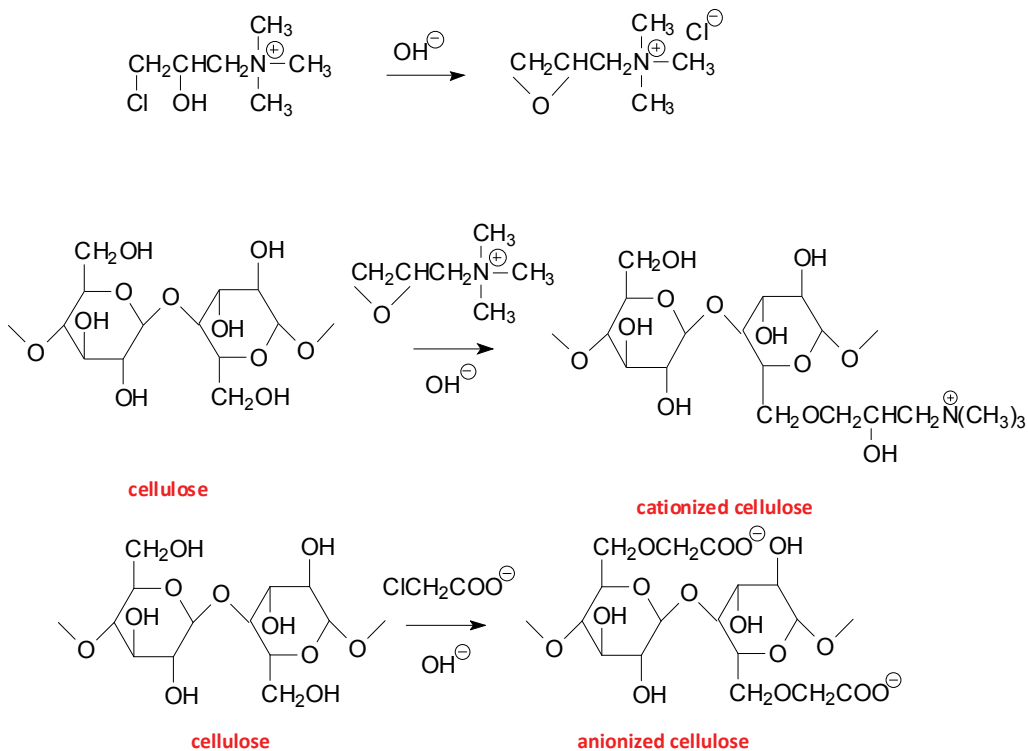


Figure 1. Strategies to create cationic and anionic cellulosic substrates [1, 2].

Once the surfaces are imparted with charged groups, nanolayers of polyelectrolytes can be easily assembled by judiciously manipulating the electrostatic interactions. The assembly process is self-limiting allowing the creation of very thin layers that conform to the irregular and curved surface of the cotton substrates as shown in Figure 2.

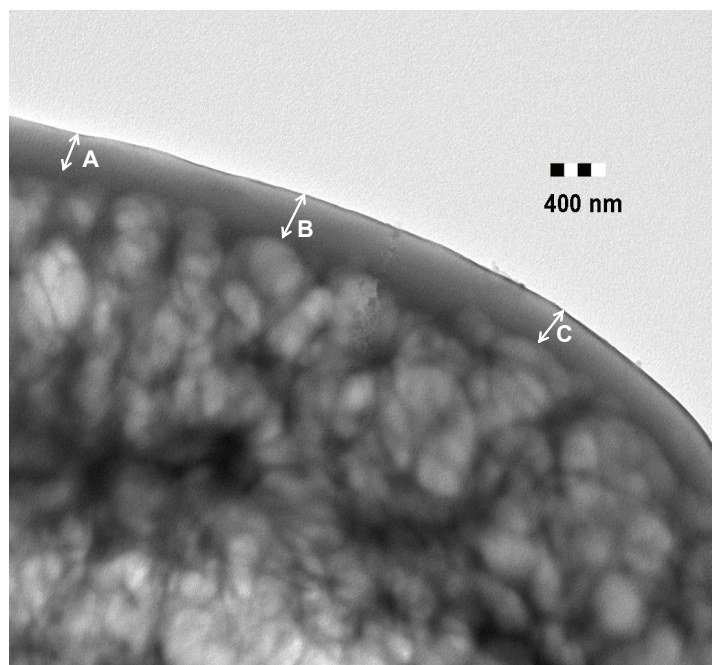


Figure 2. TEM image of a cotton fiber coated with 20 alternating layers of PSS and PAH. Details of the lumen in the cotton fiber can be identified as well as a conformal coating with varied thickness (A=365 nm, B=395 nm and C=313 nm) [2].

Since the layers are usually between 20-80 nm in thickness, special low penetration spectroscopy techniques need to be used to monitor the composition of each layer. Usually X-Ray photoelectron spectroscopy analysis is the preferred method as it provides information of the elemental analysis of the outermost 5 nm of the sample.

3. Atomic layer deposition (ALD) of metal oxide nanolayers on cotton substrates

Due to the high curvature and non-uniform nature of textile fibers, it is difficult to provide a complete coverage to the surface of fibers. The ability to control the

composition of the surface at the molecular level opens the possibility of developing smart textiles for applications such as active filtration, bio-separation of proteins, catalytic mantles, and electronic fabrics as well as novel barrier and anti-counterfeiting materials.

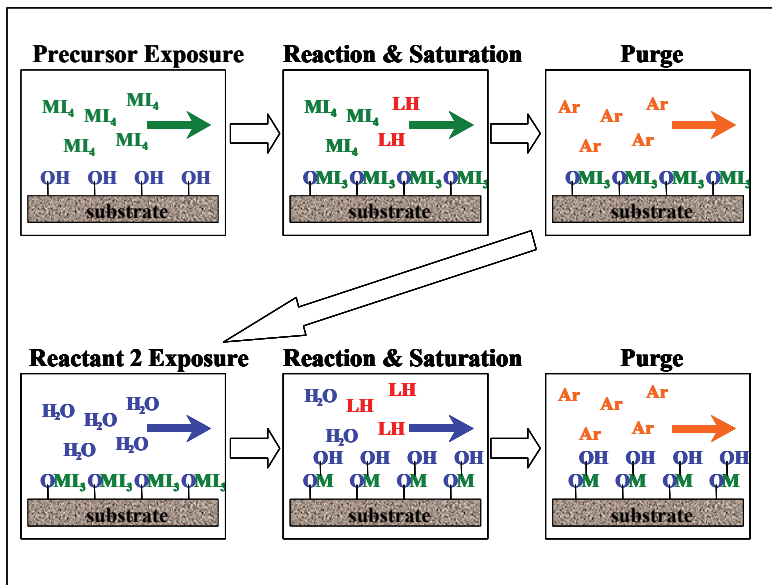


Figure 3. Schematic image of the binary reaction sequence in atomic layer deposition. Repeating this cycle many times results in macroscopic build up of highly conformal and controlled layers with atomic-scale control [3].

There are two key aspects to ALD film growth related to the controlled precursor adsorption: the self-limiting growth enables films with extremely high conformality to be achieved, which is well suited to growth on fiber surfaces; and growth initiation depends strongly on the chemical functionalization of the starting surface [3].

ALD deposition processes involve the repeated sequential exposure of the textile substrates to vapor-phase precursors and secondary reactants. The common method for ALD is to place the substrate of interest into a controlled ambient reactor and to flow the gas in controlled cycles. An alternate method that can also be implemented is to transport the fiber through successive reaction zones. Metal organic precursors are widely available for metals and the thickness of the coatings can be controlled by the number of binary reaction steps. For some fiber structures, the coating procedure may be expected to modify the bulk properties of the fibers. For example, for Al_2O_3 coating of fibers, tri-methyl aluminum precursor may diffuse into the fiber and subsequently react

with the oxidant (typically water) to form isolated islands of hydrated alumina within the fiber network. This may be sometimes desired as a structural modifier or to enhance the barrier properties of the materials.

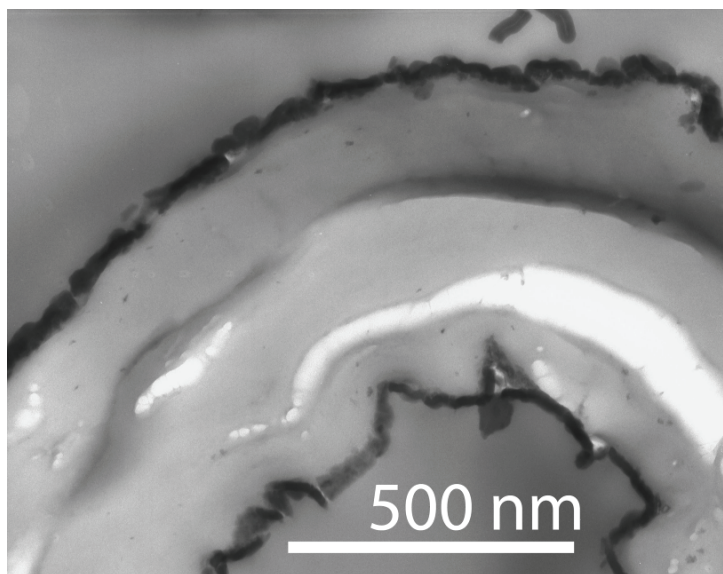


Figure 4. Cross-sectional TEM image of cotton fiber detailing the conformal nature of Al_2O_3 coating deposited via ALD. This specimen was coated with 500 cycles of Al_2O_3 . The coating is observed to be uniform both on concave and convex confined spaces indicating the feasibility of ALD as a coating tool for heterogeneous natural fibers [3].

4. Electrostatic assembly and in-situ synthesis of nanoparticles on cotton substrates.

Assembly of discrete nanomaterials can also be achieved by using electrostatic self-assembly procedures. Our group has used two different approaches to deposit noble nanoparticles as follows: The first method involves electrostatic assembly of citrate-stabilized metal nanoparticles directly onto the cationic surfaces of cellulose. The second method involves the adsorption of negative metal complex ions onto the cationic cellulose followed by reduction reaction [4].

In the first approach, the synthesis involves the use of a soluble metal salt as a precursor, a reducing reagent and a stabilizer. When synthesis of metal nanoparticles involves citrate reduction, citrate groups can serve dual roles as a reducing agent and a stabilizer. The use of citrate groups imparts negative

surface charges to the nanoparticles from weakly bound citrate ions, which prevent agglomeration of nanoparticles in solution. The negative charges on the surfaces of metal nanoparticles are used to immobilize nanoparticles on various substrates or to construct multiple layers of polyelectrolytes/nanoparticles via electrostatic self-assembly [1, 2]. We found that packing density of metal nanoparticles on the surface of fibers appears to increase as the concentration of citrate in the precursor solutions increased from 1% to 2%. This behavior is likely caused by enhanced negative surface potential of nanoparticles capped with more citrate groups [4].

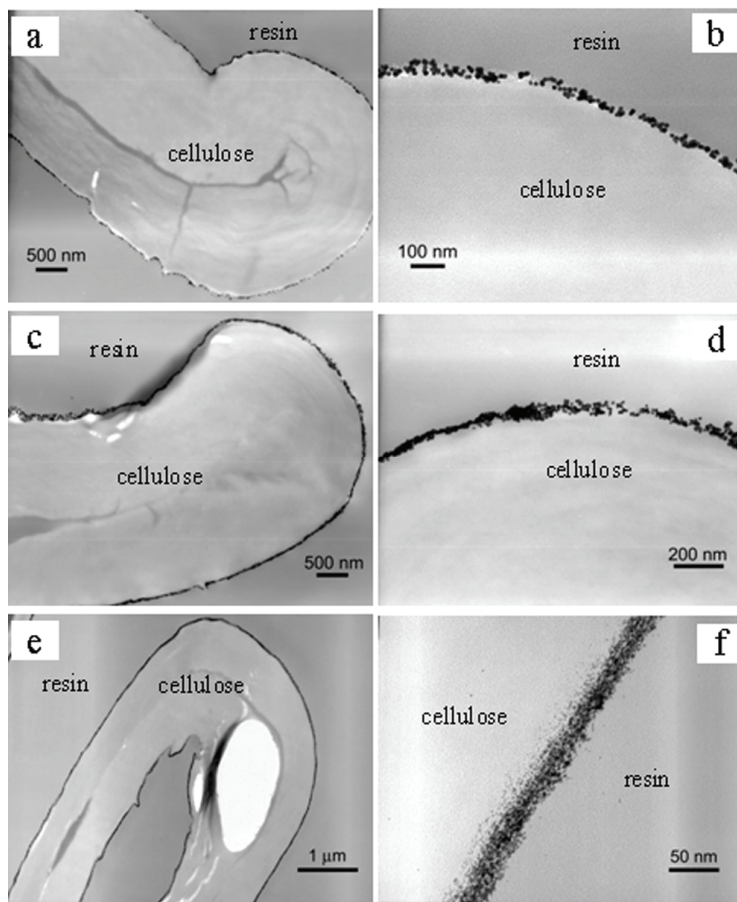


Figure 5. TEM images of the cross sections of cotton fibers coated with (a, b) Au nanoparticles synthesized using 1% citrate, (c, d) Au nanoparticles synthesized using 2% citrate, and (e, f) Pt nanoparticles [4].

Although the electrostatic repulsion between assembled nanoparticles is increased by the presence of more citrate groups, this effect appears to be counterbalanced by a greater attraction of the nanoparticles to the positively charged cellulose surfaces.

The second method, the in-situ synthesis approach, was initiated by adsorption of negative metal complex ions onto the cationically modified cellulose surfaces. Chemical reduction of the metal ions led to the formation of metal nanoparticles on the substrates. Compared with the direct assembly of preformed metal colloids presented in the previous section, the in situ synthesis is absent of protective citrate ions on the surfaces of nanoparticles. This may be of technical importance as it was suggested that the surface coverage of organic species may decrease the reactivity of the nanoparticles in some applications such as catalysis [4].

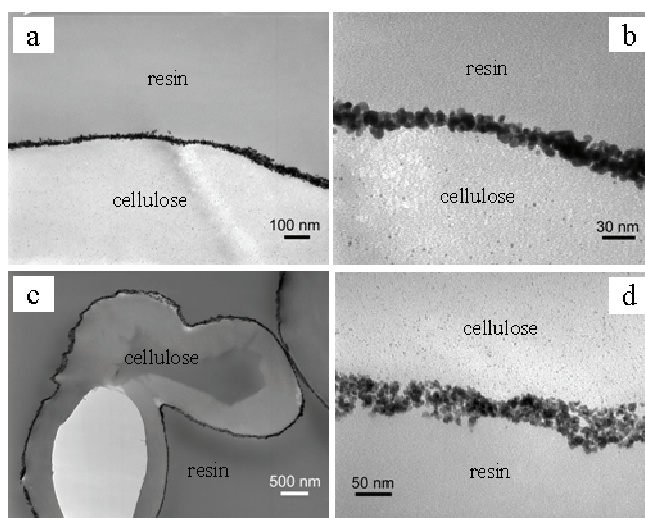


Figure 6. TEM images of a cross-sectional cellulose fiber with (a, b) Au nanoparticles and (c, d) Pd nanoparticles obtained by in situ synthesis [4].

5. Conclusions

While there is evidence that cotton has been a domesticated plant for over 5000 years and thoroughly used across cultures and civilizations, recent advances in manipulating nanoscale phenomena offer new avenues for the creation of novel functionalities in this traditional material. Nanoscale control of the surface chemistry of cellulose molecules present in cotton found a unique platform for the deposition of self-assembled polyelectrolyte nanolayers that can tune the mass transport of gases and liquids; conformal coating of metal oxide nanolayers that

can block dangerous radiations; and high packing surface coating of nanoparticles with antibacterial and catalytic properties. More importantly, all these functionalities can be achieved without compromising the natural comfort, feeling and handle of this unique natural fiber. Future work in our laboratory is aimed at using these techniques to transform cotton fibers into sensors, electrical conductors and structural coloring platforms.

References

- [1] K. Hyde, M. Rusa, J.P. Hinestroza, Electrostatic Self-assembly of polyelectrolytes on natural fibers: Cotton, *Nanotechnology*, **16**, S422-S428 (2005).
- [2] K. Hyde, H. Dong, J.P. Hinestroza, Effect of surface cationization on the conformal deposition of polyelectrolytes over cotton fibers, *Cellulose*, **14**, 615-623 (2007).
- [3] G.K. Hyde, K.J. Park, S.M. Stewart, J.P. Hinestroza, G.N. Parsons, Atomic Layer Deposition of Conformal Inorganic Nanoscale Coatings on Three-Dimensional Natural Fiber Systems: Effect of Surface Topology on Film Growth Characteristics, *Langmuir*, **23**, 9844-9849 (2007).
- [4] H. Dong, J.P. Hinestroza, Metal Nanoparticles on Natural Cellulose Fibers: Electrostatic Assembly and In Situ Synthesis, *ACS Applied Materials and Interfaces*, **1**, No. 4, 797-803 (2009).

Chapter 3

Sol-gel Technology for Chemical Modification of Textiles

Barbara Simončič¹, Brigita Tomšič¹, Boris Orel² & Ivan Jerman²
¹*Department of Textiles,
Faculty of Natural Sciences and Engineering, University of Ljubljana*
²*National Institute of Chemistry, Ljubljana
Slovenia*

1. Introduction

In contemporary life, hi-tech textiles include innovative polymers, whose use is not limited solely to the textile and clothing industry, but has also spread quickly in recent years to other sectors such as pharmacy, medicine, construction, agriculture, transport, tourism and the food industry. Their production is directly related to the introduction of nanotechnology in the textile industry. Nanotechnological processes have been established in the production of fibrogenic polymers and in the chemical finishing of planar textiles, which leads to the creation of products with new or improved properties with high added value.

A special place among nanotechnological processes of fibre functionalization is held by sol-gel technology [1-3], which represents a new approach to the preparation of the composite materials. It enables a creation of nanocomposite polymer films on the surface of the fibres giving the textiles new mechanical, optical, electrical and biological properties that cannot be achieved using conventional finishing agents. It is of great commercial importance in the production of woven fabric, knitwear and unwoven textiles for protective work clothing, textiles for sport and recreation, textiles for the home and the public sector, medical textiles, sanitary materials and technical textiles.

2. Sol-gel chemistry

A sol-gel process, as the name implies, involves the evolution of inorganic networks through the formation of a colloidal suspension (sol) and gelation of a sol to form a network in a continuous liquid phase (gel). The starting compounds for preparation of a sol are precursors, which consist of a metal or metalloid element surrounded by various ligands. For this reason, precursors of various chemical structures can be used, whereas silicon alkoxides ($\text{Si}(\text{OR})_4$)

are the most common [1]. They include reactive alkoxide groups ($-OR$), which react readily with water in the reaction of hydrolysis in the presence of a mineral acid or a base as a catalyst. The hydrolysis reaction replaces alkoxide groups with hydroxyl groups ($-OH$) which in the subsequent condensation reaction produce siloxane bonds ($Si-O-Si$) (Figure 1). This type of reaction can continue to build large silicon containing polymer network with a three-dimensional structure by the process of polymerisation (Figure 2). When the polymers extend throughout the solution, they irreversibly form gel which upon drying affords amorphous xerogel with porous structure. The xerogel reforms into the crystallized polycondensate during heating at temperature of $150^{\circ}C$. The characteristics and properties of a particular sol-gel network are related to a number of factors that affect the rate of hydrolysis and condensation reactions, such as pH, temperature and time of reaction, reagent concentrations, catalyst nature and concentration, H_2O/Si molar ratio, aging temperature and time and drying.

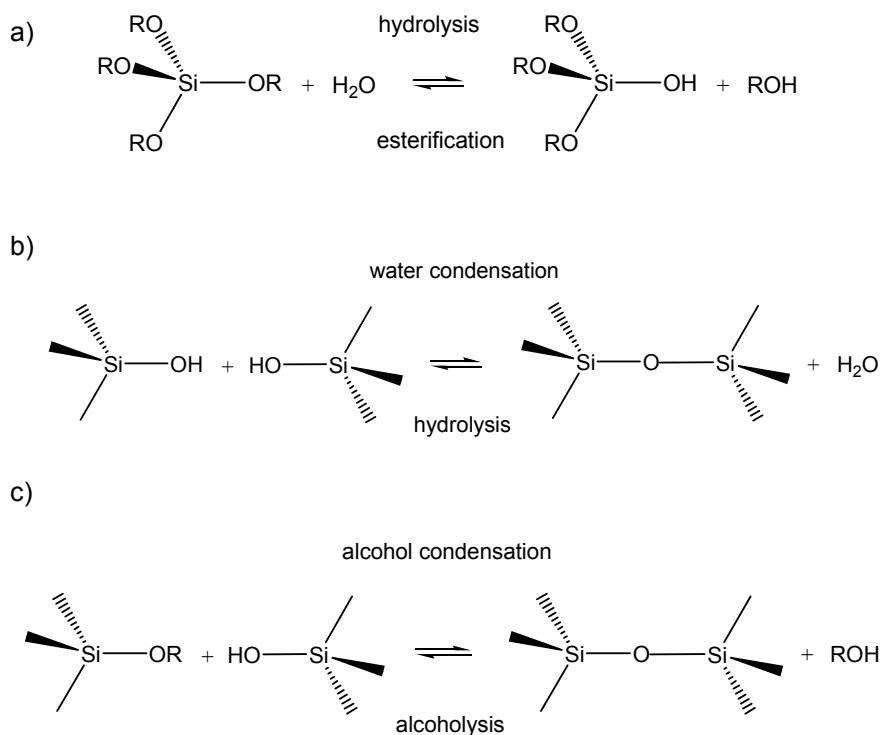


Figure 1. Hydrolysis (a) and condensation (b and c) of tetraalkoxysilanes [1].

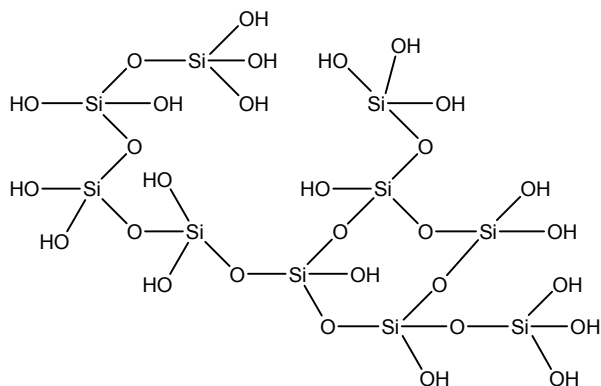


Figure 2. Formation of polymer network by tetraalkoxysilane with a three-dimensional structure [3].

3. Sol-gel technology for chemical finishing of textile fibres

Application of a sol-gel process in the chemical finishing of textiles includes a pad-dry-cure method which consists of the impregnation of textile fibres by the sol following by the fibre drying and curing under the appropriate conditions. During drying and curing, the nanocomposite dense polymer film of thickness of some 10 nm is formed on the fibres surface. The $-\text{Si}-\text{OH}$ groups of precursors can also react with the fibre surface forming hydrogen (Figure 3) as well as covalent bonds (Figure 4). The latter which is formed between the precursor's silanol group and the hydroxyl group of the fibre in the reaction of condensation, strongly increase the adhesion of the polymer film to the textiles as well as the degree of polymer film orientation.

For chemical modification of textile fibres, organofunctional trialkoxysilanes ($\text{R}'-\text{Si}(\text{OR})_3$), polyhedral oligomeric silsesquioxanes (POSS) $((\text{R}'-\text{SiO}_{1.5})_n)$ ($n = 6, 8, 10, 12, \dots$), where R' represents a nonhydrolysable organic functional group, and organically modifies silicates take an important place among silicon alkoxide precursors. They are a class of hybrid organic-inorganic materials which enable facile formation of network polymer films with high level of chemical functionality. The organic group is an integral part of the network architecture (Figure 5) [2]. The organic-inorganic structure gives the polymer film dual properties, i.e. elasticity of polymer and hardness of ceramic. Due to the extremely thin polymer film, it does not cause any significant influence to the physical properties of the textiles such as tensile strength, softness and elasticity. Neither does it penetrate into the pores between the fibres, thus retaining the textiles' breathability. The treatment of textile fibres with hybrid organic-inorganic precursors opens numerous new possibilities for the improvement of their functional and protective properties [4-9], depending on the chemical structure of the organic group. This type of nanocomposite

finishing is noted for its excellent hydrophobicity, oleophobicity, decreased inflammation, improved abrasion stability, electrical conductivity, UV protection, biocatalytic activity, anti-microbial activity and controlled release of oils and flavours. Using a combination of different precursors with synergistic action in the mixture, multifunctional textile properties can be achieved.

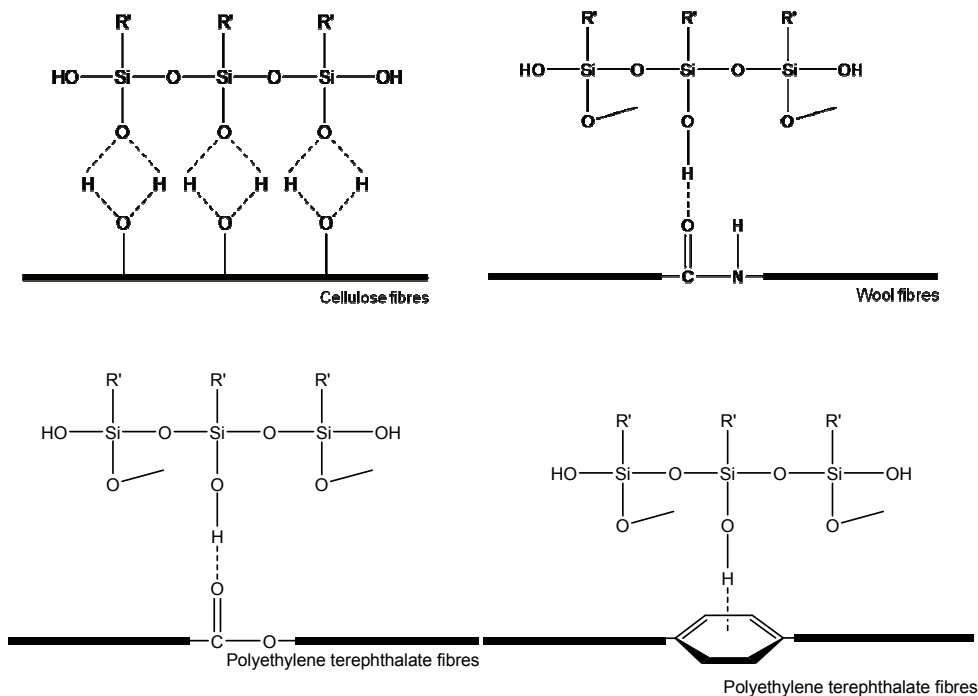


Figure 3. Hydrogen bonding of the precursor silanol group to the fibre surface.

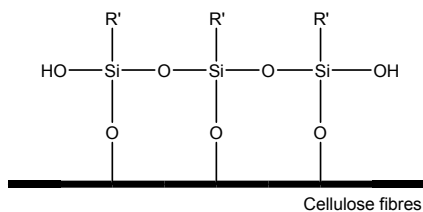


Figure 4. Covalent binding of the precursor silanol group to the hydroxyl group of the textile fibre in the reaction of condensation.

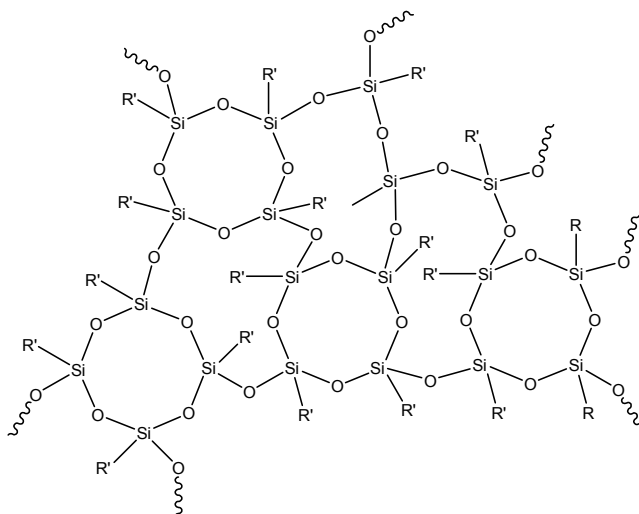


Figure 5. A polymer network formed by the organofunctional trialkoxysilanes [3].

3.1 Sol-gel technology for incorporation of repellent properties

3.1.1 Chemical structures of hydrophobic and oleophobic precursors

Water and oil repellent properties on the textile fibres could be achieved by applying hybrid organic-inorganic precursors with alkyl and perfluoroalkyl groups. While the alkyl groups provide hydrophobicity of the polymer network, the perfluoroalkyl groups assure its hydrophobicity and oleophobicity. The chemical structures of repellent organofunctional triethoxysilanes are presented in Figure 6, and those of bi- and tri-functional POSS based silane precursors synthesized at the National Institute of Chemistry, Ljubljana, Slovenia in Figure 7. In this point it should be stressed that for the industrial use a commercially available fluoroalkylfunctional water-born siloxane (FAS) (Dynasytan F 8815, Evonic Industries, Germany) is of great importance, in spite of the fact that its exact chemical composition is not known.

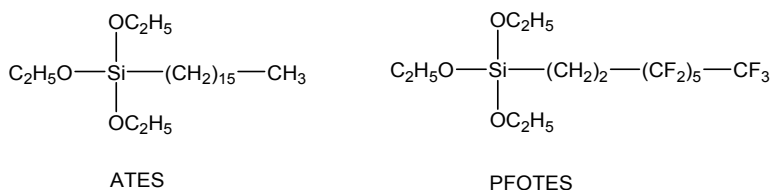


Figure 6. Chemical structures of organofunctional triethoxysilanes: hexadecyltriethoxysilane (ATES), 1H, 1H, 2H, 2H-perfluorooctyltriethoxysilane (PFOTES).

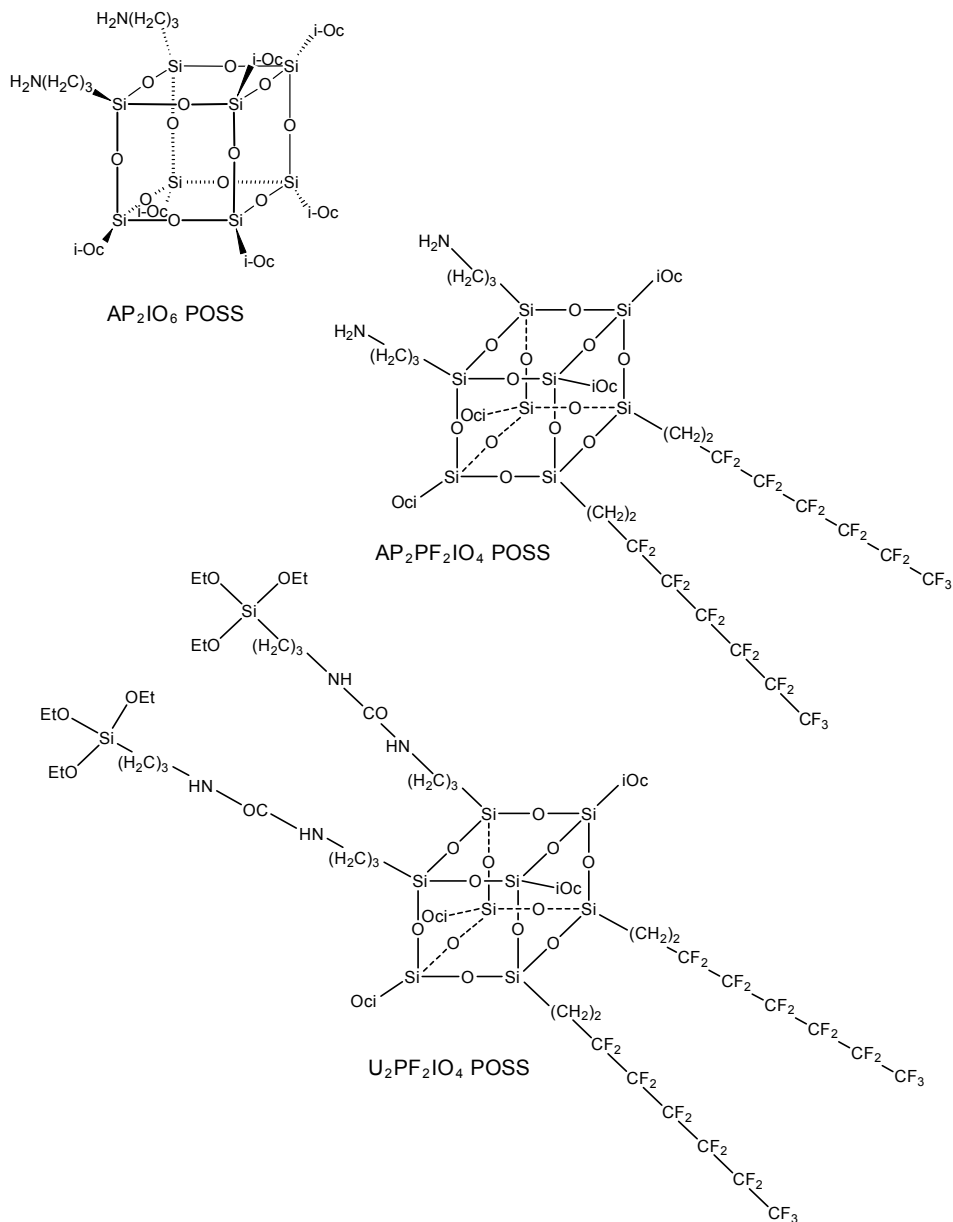


Figure 7. Chemical structures of POSS based silane precursor: aminopropyl-isoocetyl polyhedral oligomeric silsesquioxane (AP₂IO₆ POSS), aminopropyl-perfluoroisooctyl polyhedral oligomeric silsesquioxane (AP₂PF₂IO₄ POSS) and di-(3-(3-(3-triethoxysilyl-propyl)ureido)propyl-perfluoroisooctyl polyhedral oligomeric silsesquioxane (U₂PF₂IO₄ POSS).

3.1.2 Chemical characterisation of the sol-gel polymer films

The molecular groups and species which are present in the sol-gel polymer films obtained by different precursors can be investigated by the Fourier transform infrared (FT-IR) spectroscopy [10]. To avoid the overshadowing of the precursor bands by the bands attributed to the textile fibres, the chemical structure of sol-gel films was studied when deposited on the polished Al/Cu (AA 2024) alloy surface (Al wafer). Because the chemical composition of FAS was not known, the spectra of chemically similar PFOTES were analysed in detail in order to confirm their structural similarity. A closer look at the ATR spectra of PFOTES and FAS presented in Figure 8 revealed that the bands of the perfluoro groups of FAS were slightly shifted with respect to those of PFOTES and appeared at 1238, 1207 cm^{-1} and at 1143 cm^{-1} . However, some bands appeared with different intensities, suggesting that the length of the perfluoro chains slightly differed for FAS and PFOTES. The ATR spectra of FAS and PFOTES also differed regarding the bands at 1672 and 1603 cm^{-1} , and some other bands in the spectral region from 1000–1100 cm^{-1} . Overall, the frequency agreement was surprisingly good, indicating the similar chemical structures of both precursors. After the addition of acidified water, the spectra of PFOTES (Figure 8a, disconnected curve) changed, showing a partial loss of Si-OEt bands at 820 and 778 cm^{-1} and a complete disappearance of the bands at 1105, 1083 and 962 cm^{-1} , suggesting fast (15 minutes) and complete hydrolysis. The latter band became substituted by a band at 910 cm^{-1} ascribed to the silanol groups. The expected silanol band in the spectra of FAS was not observed because of its weak intensity.

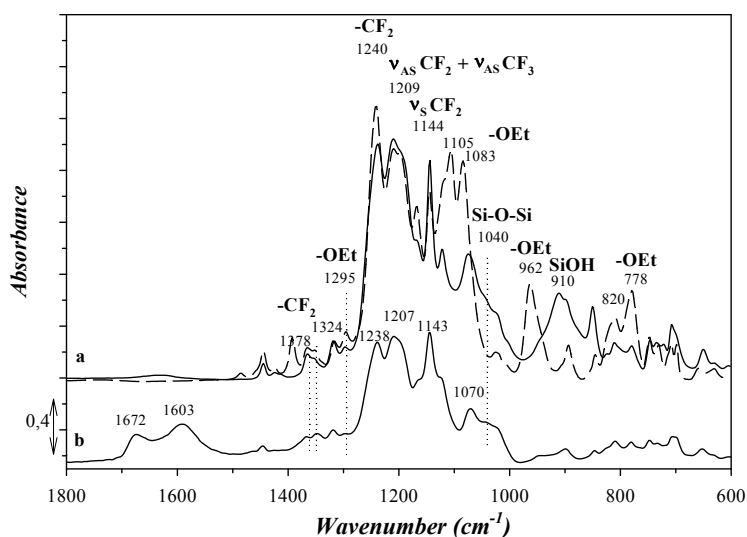


Figure 8. ATR spectra of non-hydrolysed (– –) and hydrolysed (—) PFOTES (a) and FAS (b) deposited on Al wafer.

In the case of the AP_2IO_6 POSS and $AP_2PF_2IO_4$ POSS precursors which do not include reactive silanol groups in the structure, diisocyanatoethyl (DICH) cross-linker was added into the sol to bind the precursors to the solid surface. The ATR spectra in Figure 9 confirmed the interactions between amino functional groups of POSS precursor and DICH. DICH monomer shows an intense band at 2269 cm^{-1} ($-NCO$) and bands at 2940 , belonging to an asymmetric stretching of CH_2 groups, 2861 cm^{-1} noted as a symmetric CH_2 band and weak scissoring and twisting bands of CH_2 at 1462 and 1171 cm^{-1} . As the reaction of POSS and DICH proceeded, the band at 2269 cm^{-1} diminished, accompanied by the appearance of bands of urea groups (Amide I and Amide II bands) in the IR spectrum. The remains of NCO groups are responsible for linkage of the modifier to the textile fibres and ensuring high washing fastness.

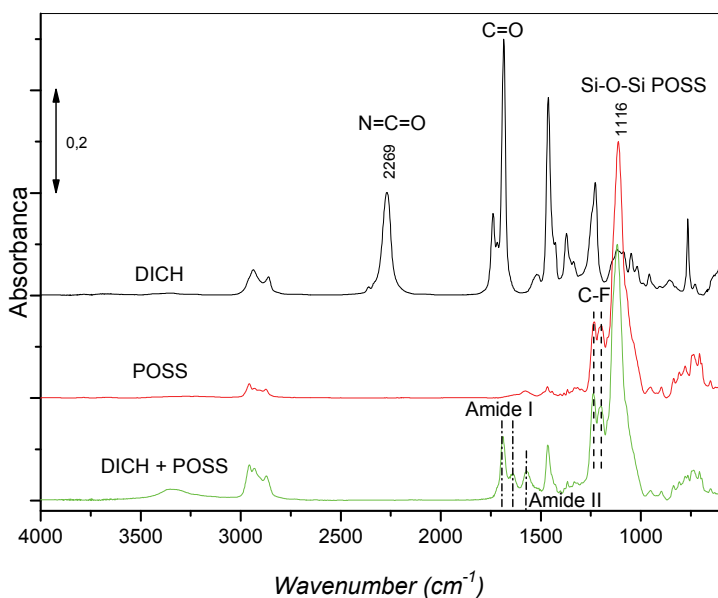


Figure 9. ATR spectrum of DICH, $AP_2PF_2IO_4$ POSS and the mixture of DICH and $AP_2PF_2IO_4$ POSS deposited on Al wafer.

3.1.3 Surface free energy of the of the sol-gel polymer films

The surface free energy of the studied sol-gel polymer films on Al wafer was determined from the results of the goniometric measurements of contact angles of water (W), formamide (FA) and diiodomethane (DIM). The contact angle values were determined using the Young-Laplace fitting. From the contact angle measurements, the total surface free energy of the coatings was determined using the approach of Van Oss and co-workers [11], resolved to the corresponding apolar Lifshitz-van der Waals component, γ_S^{LW} , and the polar

component, γ_S^{AB} , due to the electron-donor, γ_S^- , and electron-acceptor, γ_S^+ , interactions.

In Table 1, the values of surface free energy components of the PFOTES, FAS, AP₂PF₂IO₄ POSS and AP₂IO₆ POSS coatings are presented. As expected, all four precursors form apolar coatings with extremely low values of polar electron-donor, γ_S^- , and electron-acceptor, γ_S^+ , components which are in the range of 0.1 to 0.7 mJ/m². The total values of the surface free energy, γ_S^{tot} , of the PFOTES, FAS and AP₂PF₂IO₄ POSS coatings are lower than 15 mJ/m², indicating that perfluoroalkyl groups in the polymer film assure both the hydrophobicity as well as oleophobicity of the coatings. On the other hand, the value of the AP₂IO₆ POSS coating is much higher than those of the perfluorinated coatings, and is equal to 24.5 mJ/m², proving that the alkyl groups of the precursor could only create the hydrophobic surface.

Precursor	γ_S^{LW} [mJ/m ²]	γ_S^+ [mJ/m ²]	γ_S^- [mJ/m ²]	γ_S^{tot} [mJ/m ²]
PFOTES	14.0	0.7	0.1	14.5
FAS	11.3	0.6	0.5	12.4
AP ₂ PF ₂ IO ₄ POSS	12.0	0.6	0.4	12.9
AP ₂ IO ₆ POSS	23.4	0.5	0.6	24.5

Table 1. The surface free energy components of the sol-gel polymer films formed by the studied precursors on Al wafer.

3.1.4 Finishing of the cellulose fibres by the repellent sol-gel precursors

The reaction of hydrolysis and polycondensation of the precursor PFOTES on the cellulose fibres is presented in Figure 10, and the binding of the POSS precursors to the cellulose fibres over the DICH is shown in Figure 11. The composition of the coatings on the cellulose fibres was investigated by the X-ray photoelectron spectroscopy (XPS) where five characteristic bands which we ascribed to carbon (C 1s) (285 eV), oxygen (O 1s) (533 eV), silicon (Si 2p) (102 eV), fluorine (F 1s) (689 eV) were observed. It should be noted that the XPS spectra of untreated cotton fabric revealed only two characteristic bands belonging to C 1s and O 1s. The results in Figure 12 revealed that, besides the carbon and oxygen, the concentrations of fluorine and silicon significantly increased on cotton fabrics treated with PFOTES, FAS and AP₂PF₂IO₄ POSS, whereas only the increase of the silicon concentration was determined in the case of nonfluorinated AP₂IO₆ POSS.

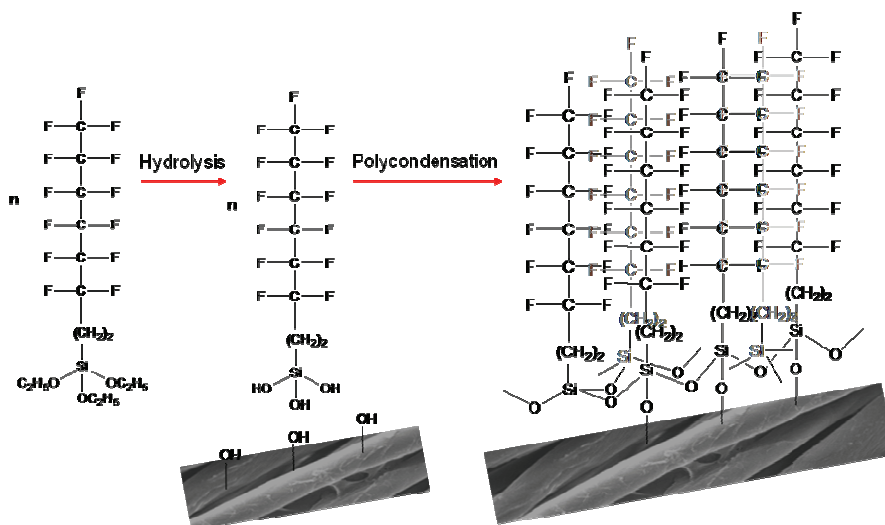


Figure 10. Reactions of hydrolysis and polycondensation of the precursor PFOTES on the cellulose fibres.

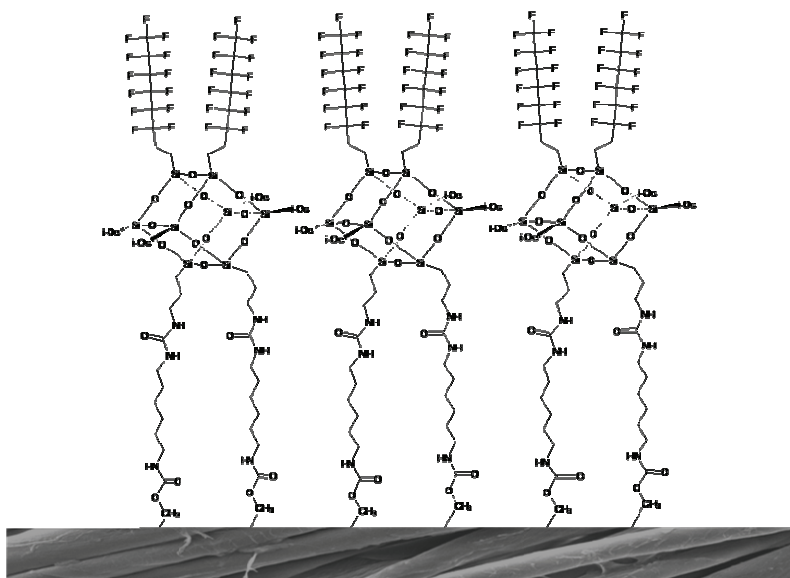


Figure 11. Chemical binding of $AP_2PF_2IO_4$ POSS precursor to the cellulose fibres in the presence of the reactive binder DICH.

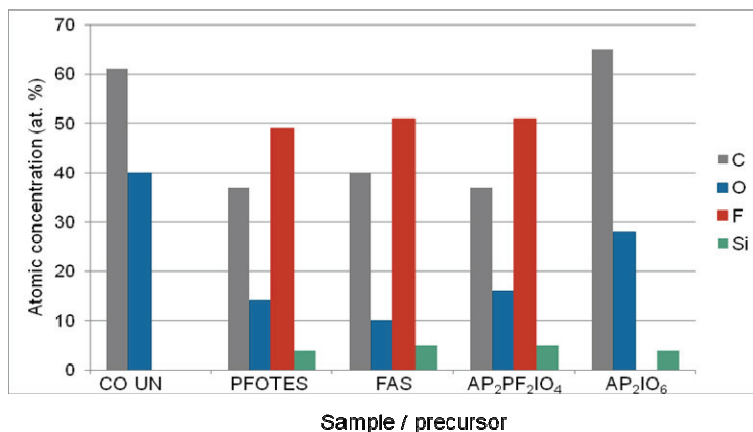


Figure 12. Surface composition of untreated cotton fabric (CO UN) and samples treated with PFOTES, FAS, AP₂PF₂IO₄ POSS and AP₂IO₆ POSS sols, obtained by XPS measurements.

As expected, all four studied coatings provide excellent water repellency of the cotton fabric with the water contact angles from 147° to 153° (Figure 13). The reason for this is attributed to the unique structure of the sol-gel coatings which can provide a micro- and nanoscopic roughness of the cotton fibre surface. SEM micrographs (Figure 14 A and B) showed that the surface roughness of the cotton fibres treated with the FAS sol was increased in comparison to that of the untreated ones. They also substantiated the existence of air pockets, showing that the applied FAS sol did not fill the pores between the individual fibres. Moreover, the AFM measurements (Figure 14 C) revealed that the FAS polymer film creates the fibre surface with the micro- and nanostructured roughness. This phenomenon was clearly noticed for all studied precursors. According to Cassie and Wenzel [12], the roughness of the fibre surface significantly increases its hydrophobicity, due to the air trapped in the fibre texture. This is confirmed by the high water contact angles obtained for cotton treated with AP₂IO₆ POSS ($\theta_w = 153^\circ$) with the lack of perfluoro groups. Such superhydrophobicity is rarely achieved by alkyl functionalized trialkoxysilanes without perfluoroalkyl compounds. Namely, in the case of the cotton/polyester woven fabric treated by ATEs, with twice as long alkyl chain (16 C atoms) as in the case of AP₂IO₆ POSS (8 C atoms), water contact angle of only 131° was obtained when synthesized from tetraethoxysilane (TEOS) or 142° when synthesized from combination of TEOS and 3-(glycidyloxy)propyl triethoxysilane (GLYEO) [13]. The results in Figure 13 also showed that PFOTES, FAS and AP₂PF₂IO₄ POSS coatings repel n-hexadecane confirming their oleophobicity. As expected, n-hexadecane did not form static contact angle on the cotton fabric coated by the AP₂IO₆ POSS, but it penetrated into the porous structure of the fibres, assuring the nonoleophobic properties of this coating.

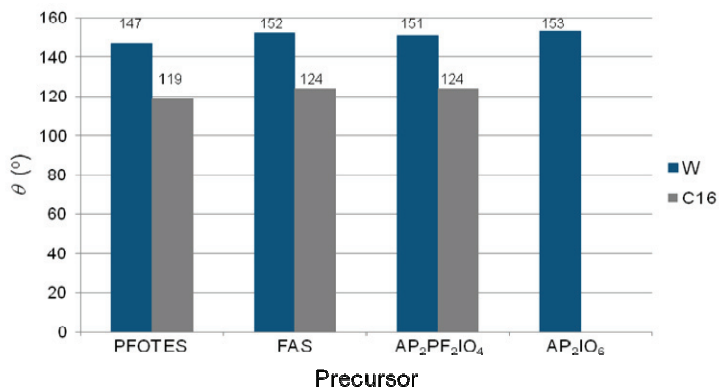


Figure 13. Contact angle, θ , of water (W) and n-hexadecane (C16) on cotton fabric finished by PFOTES, FAS, AP₂PF₂IO₄ POSS and AP₂IO₆ POSS sols.

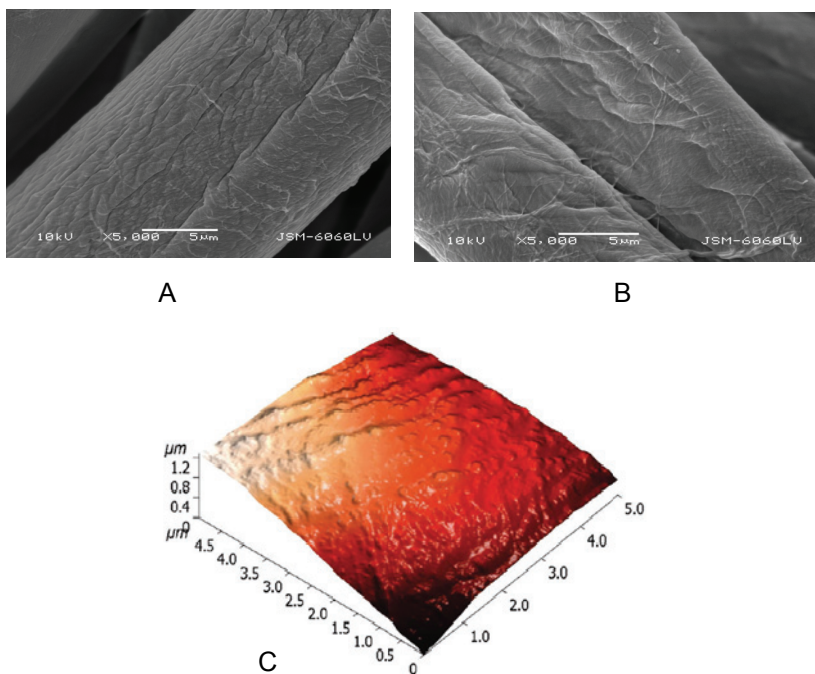


Figure 14. SEM images of cotton fibre surface before (A) and after treatment with FAS sol (B). AFM topographic measurements of cotton fibre treated with FAS sol (C).

3.2 Sol-gel technology for incorporation of antimicrobial properties

3.2.1 Chemical structures of sol-gel networks with antimicrobial properties

Antimicrobial properties on the textile fibres could be achieved by applying hybrid organic-inorganic precursors, such as alkyltrialkoxysilanes with incorporated quaternary ammonium groups (Si-QAC) or quaternary ammonium functionalized polyhedral oligomeric silsesquioxanes (Q-POSS) (Figure 15). Both precursors represent a class of the bound antimicrobial agents, because they are chemically bound to the surface of the textile fibres, where they act as a barrier and control microorganisms which come in contact with the fibre surface. The antimicrobial activity of Si-QAC and Q-POSS is attributed to the presence of the functional cationic alkyl-dimethyl ammonium group in the structure which can create attractive interactions with the negatively charged cell membrane of the microbe resulting in the formation of a precursor-microbe complex, which in turn causes the interruption of all essential functions of the cell membrane, as well as hydrophobic interactions enabling the alkyl ammonium group to physically interrupt all key cell functions [14].

Furthermore, nonfunctionalized TEOS as well as organofunctional Si-QAC and FAS precursors have already been successfully used as a silica matrix for embedment of metallic nanoparticles which act as antibacterial agents (Figure 16). Among nanoparticles, mostly Ag is embedded and held by physical forces, which stabilize nanoparticle structure, control the concentration of released nanoparticles or metal ions, prolong the release time and therefore improve the durability and wash resistance of the antimicrobial coating.

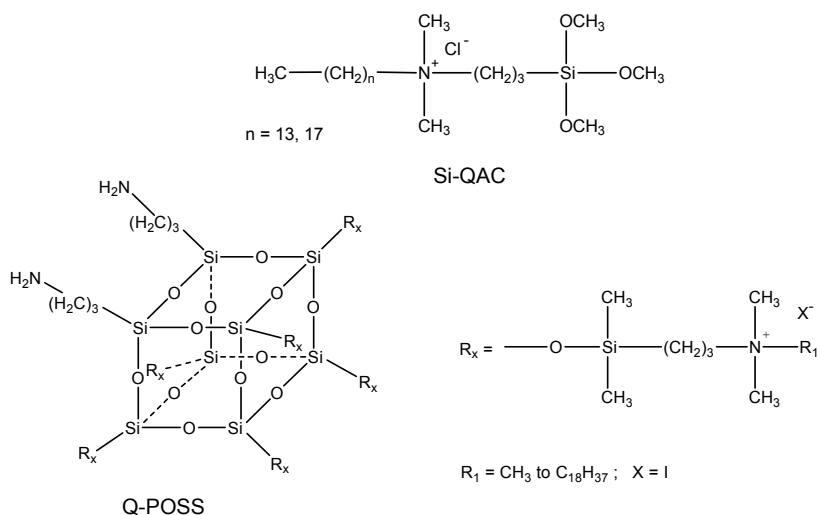


Figure 15. Chemical structures of the antimicrobial precursors: alkyl-dimethyl-3(trimethoxysilyl)propyl ammonium chloride (Si-QAC) and idealized structure of quaternized polyhedral oligomeric silsesquioxanes (Q-POSS).

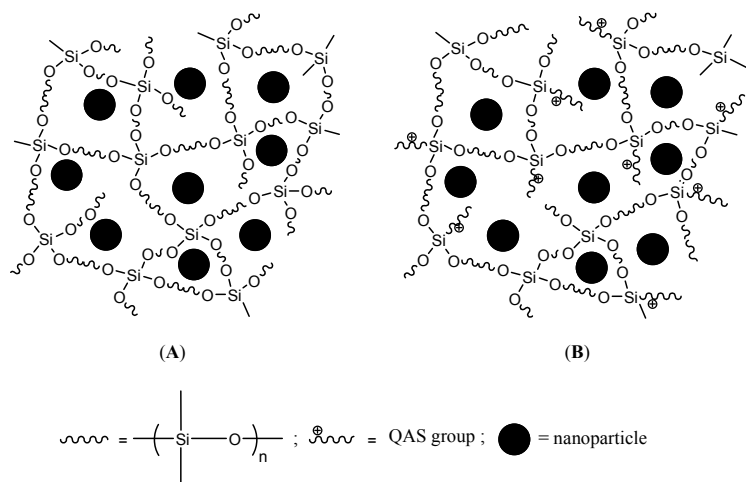


Figure 16. Schematic presentation of metal nanoparticles embedded into nonfunctionalized (A) and quaternary ammonium group functionalized (B) silica matrix.

3.2.2 Finishing of the cellulose fibres by antimicrobial sol-gel precursors

Application of the Si-QAC precursor to the cellulose fibres is presented in Figure 17. To create the multifunctional properties of the cellulose fibres including superhydrophobicity, oleophobicity and active antimicrobial activity simultaneously, a sol consists of the mixture of FAS and Si-QAC precursors was applied. In this case, the polymer film on the cellulose fibre surface (Figure 18) includes two functional organic groups, i.e. oleophobic and hydrophobic perfluoroalkyl groups of the FAS precursor and antimicrobial alkyl-dimethyl ammonium groups of the Si-QAC precursor. In addition, the FAS precursor was also used in combination with commercially available dispersion containing nanosized silver (AG, iSys AG, CHT, Germany) for cellulose finishing.

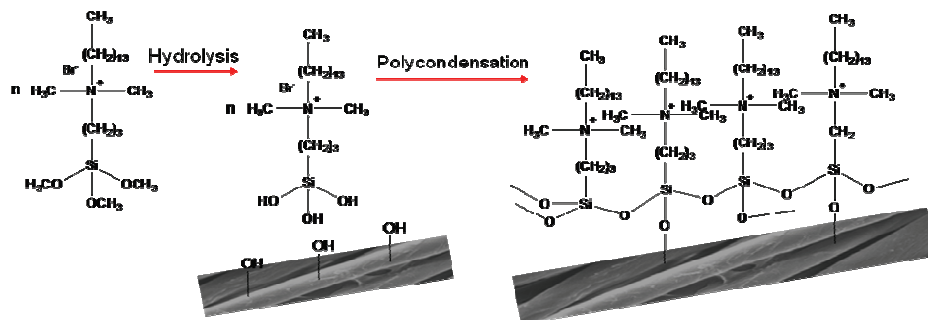


Figure 17. Application of the Si-QAC precursor to the cellulose fibres.

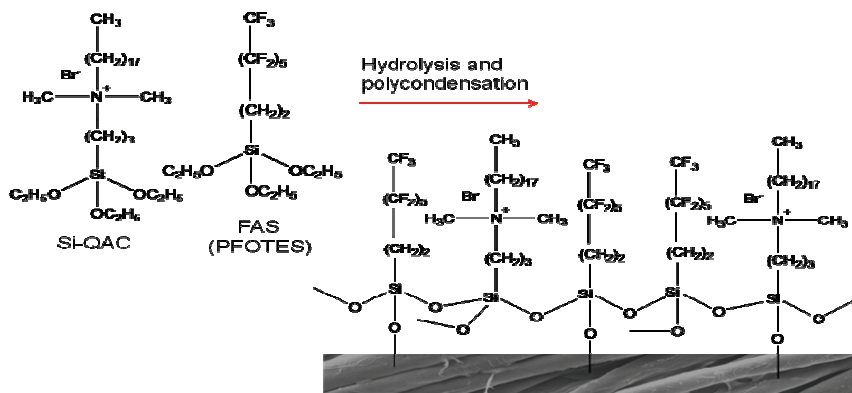


Figure 18. Creation of the sol-gel polymer film on the cellulose fibres by the sol consists of the FAS and Si-QAC precursors.

3.2.3 Antimicrobial activity of the finished cellulose fibres

The antimicrobial activity was studied on the cotton fabric samples treated with the Si-QAC sol, the mixture of FAS and Si-QAC (FAS/Si-QAC) and the mixture of FAS and AG (FAS/AG). Antibacterial activity was estimated for the Gram-negative bacteria *Escherichia coli* (ATCC 25922) according to the EN ISO 20743:2007 Transfer Method. This method enables assessment of the bacterial reduction, R , which is caused not only by the presence of antibacterial active agents in the finishes, but could stem from the low surface energy of the finished textile fibres, which prevents or at least hinders the adhesion of bacteria and their consequent growth and formation of a biofilm on the finished fabrics.

Results for the antibacterial activity of the Si-QAC, FAS/Si-QAC and FAS/AG coatings are presented in Figure 19. In the case of Si-QAC, a bacterial reduction of 46% was obtained on the finished cotton sample, indicating that the antimicrobial activity of the Si-QAC polymer film is biostatic, since it inhibits the microorganisms' growth. The reason for this is ascribed to the chemically bonded alkyl-dimethyl ammonium groups in the coating, where they act as a barrier and control only those microorganisms which come in contact with the fibre surface. The addition of FAS into the FAS/Si-QAC sol significantly enhances a bacterial reduction which reaches a value of 80%. It seems that the presence of the low surface energy FAS precursor strongly hinders the adhesion of bacteria and their consequent growth and the formation of a biofilm on the finished fabrics. The latter effect is called "passive antimicrobial activity". The highest bacterial reduction equal to 100% was obtained on the cotton fabric treated with FAS/AG sol as a result of the dual antimicrobial activity: the biocidal activity of AG during its gradual and persistent release from the silica matrix into the surroundings, and the "passive antimicrobial activity" of FAS.

The results in Figure 20 revealed that contact angle of water obtained on the FAS/AG finished cotton samples decreased in comparison to that obtained with the use of one component FAS sol, causing the impairment of the coating superhydrophobicity. On the other hand, fortunately, the contact angle of water obtained on the FAS/Si-QAC finished cotton samples remained higher than 150° , which clearly indicates that the superhydrophobicity is not impaired in the precursors' mixture and that the synergy between the antibacterial effect of Si-QAC and the superhydrophobicity of FAS is attained in the coating. This enables the FAS/Si-QAC sol to create the biomimetic cotton fabric with the "Lotus-Effect" (Figure 21 B) [15, 16] where the self-cleaning ability of the leaves of the lotus flower *Nelumbo nucifera* is mimicked.

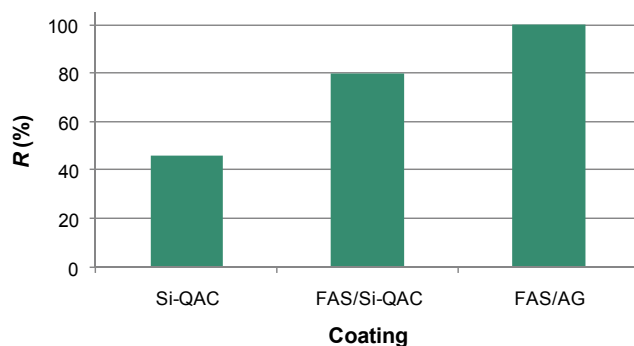


Figure 19. Bacterial reduction, R , determined on cotton fabric samples treated with Si-QAC, FAS/Si-QAC and FAS/AG sols.

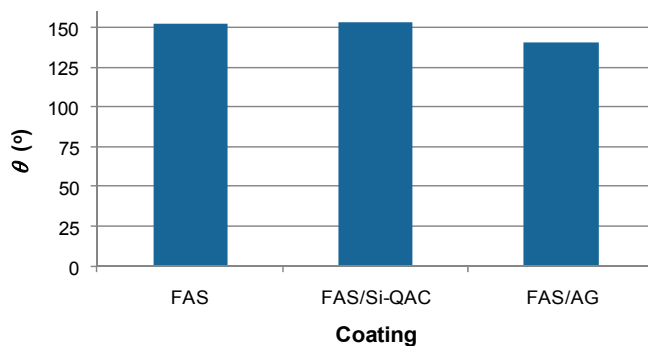


Figure 20. Contact angle, θ , of water on cotton fabric treated with FAS, FAS/Si-QAC and FAS/AG sols (B).



Figure 21. A leaf of the lotus flower *Nelumbo nucifera* (A) and the cotton woven fabric with the “Lotus-Effect” (B).

4. Conclusions

This research work demonstrates the importance of the sol-gel technology in the chemical finishing of textiles, enabling the preparation of nanocomposite polymer film with superhydrophobic, oleophobic and antimicrobial properties. It was investigated that the application of sols consist of PFOTES, FAS, $AP_2PF_2IO_4$ POSS or AP_2IO_6 POSS create apolar coatings with extremely low surface free energy as well as a micro- and nanostructured roughness of the fibre surface resulting in the increased water contact angles. This provides the superhydrophobicity of the coatings as well as its simultaneous oleophobicity in the case of the perfluorinated precursors. A use of the combinations of FAS and Si-QAC or FAS and AG precursors in the coating enabled the upgrading the hydrophobicity and oleophobicity of the fibres with their active antimicrobial properties, where superhydrophobicity was attained only in the coating composed by FAS/Si-QAC mixture, exhibiting their synergistic action.

Acknowledgement

This work was supported by the Slovenian Research Agency (Programme P2-0213 and Project M2-0104) and the Slovenian Ministry of Defence (Project M2-0104). We acknowledge J. Kovač for performing XPS analysis and T. Filipič for AFM measurements.

References

- [1] J.C. Brinker, G.W. Scherer, *Sol-gel Science : the physics and chemistry of sol-gel processing*, Academic Press, San Diego, 908 p. (1990).

- [2] *Handbook of organic-inorganic hybrid materials and nanocomposites*, H.S. Nalwa Ed., American Scientific Publisher, Stevenson Ranch, 386 p. (2003).
- [3] B.M. Novak, Hybrid nanocomposite materials – between inorganic glasses and organic polymers, *Advanced Materials*, **5/6**, 422–433 (1993).
- [4] J. Vince, B. Orel, A. Vilčnik, M. Fir, A. Šurca Vuk, V. Jovanovski, B. Simončič, Structural and water-repellent properties of a urea/poly(dimethylsiloxane) sol-gel hybrid and its bonding to cotton fabric, *Langmuir*, **22/15**, 6489-6497 (2006).
- [5] B. Tomšič, B. Simončič, B. Orel, L. Černe, P. Forte Tavčer, M. Zorko, I. Jerman, A. Vilčnik, J. Kovač, Sol-gel coating of cellulose fibres with antimicrobial and repellent properties, *J. Sol-Gel Sci. Technol.*, **47/1**, 44-57 (2008).
- [6] I. Jerman, B. Tomšič, S. Kovač, B. Simončič, B. Orel, Novel polyhedral oligomeric silsesquioxanes (POSS) as surface modifiers for cotton fabrics, in "4th International Textile, Clothing & Design Conference [also] ITC&DC, Magic world of textiles : book of proceedings". Z. Dragčević Ed., Faculty of Textile Technology, University of Zagreb, Zagreb, 370-375 (2008).
- [7] B. Tomšič, B. Simončič, B. Orel, M. Žerjav, H.J. Schroers, A. Simončič, Z. Samardžija, Antimicrobial activity of AgCl embedded in a silica matrix on cotton fabric, *Carbohydr. polym.*, **75/4**, 618-626 (2009).
- [8] A.Vilčnik, I. Jerman, A. Šurca Vuk, M. Koželj, B. Orel, B. Tomšič, B. Simončič, J. Kovač, Structural properties and antimicrobial Effects of Hydrophobic and Oleophobic sol-gel coatings for cotton fabrics, *Langmuir*, **25/10**, 5869-5880 (2009).
- [9] B. Simončič, B. Tomšič, B. Orel, I. Jerman. Biodegradation of cellulose fibers and its inhibition by chemical modification. In: "*Handbook of carbohydrate polymers : development, properties and applications, (Polymer science and technology series)*", R. Ryouichi (Ed.), Y. Matsuro (Ed.), Nova Science Publishers, Inc., New York (USA), ch. 7, 237-277 (2010).
- [10] G. Socrates G. *Infrared and Raman Characteristic Group Frequencies*. John Wiley & Sons, LTD, New York, 347 p. (2001).
- [11] C.J. Van Oss, R.J. Good, M.K. Chaudhury, Additive and nonadditive surface tension components and the interpretation of contact angles, *Langmuir*, **4**, 884–891 (1988).
- [12] A.B.D. Cassie, S. Baxter, Wettability of porous surface, *Trans. Farad. Soc.*, **40**, 546-551 (1944).
- [13] B. Mahltig, H. Böttcher, Modified silica sol coatings for water-repellent textiles, *J. Sol-Gel Sci. Technol.*, **27/1**, 43-52 (2003).
- [14] J.C. Tiller, C.J. Liao, J. Lewis, A.M. Klibanov, Designing surfaces that kill bacteria on contact, *Proc. Nat. Acad. Sci. U.S.A.*, **98**, 5981–5985 (2001).
- [15] W. Barthlott, C. Neinhuis, Purity of the sacred lotus, or escape from contamination in biological surfaces, *Planta*, **202**, 1-8 (1997).
- [16] T. Stegmaier, V. Von Arnim, A. Scherrieble, H. Planck, Self-cleaning textiles using the Lotus Effect, in "*Biologically inspired textiles*", A. Abbott (Ed.), M. Elison (Ed.), Woodhead Publishing Limited and CRC Press LLC, Cambridge (UK), 137-148 (2008).

Part II - Advanbiotex highlights

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.

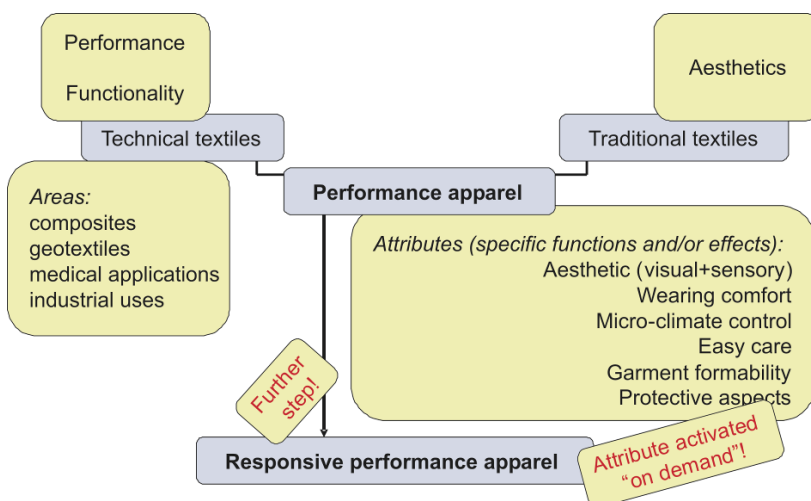


Figure 1. Responsive performance apparel as an example of knowledge-based textile materials.

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.

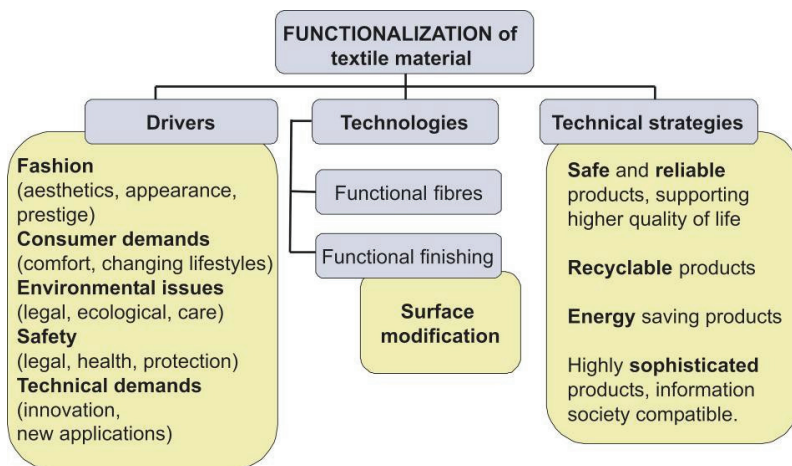


Figure 2. Available technologies for obtaining knowledge-based (functionalized) textile material.

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.

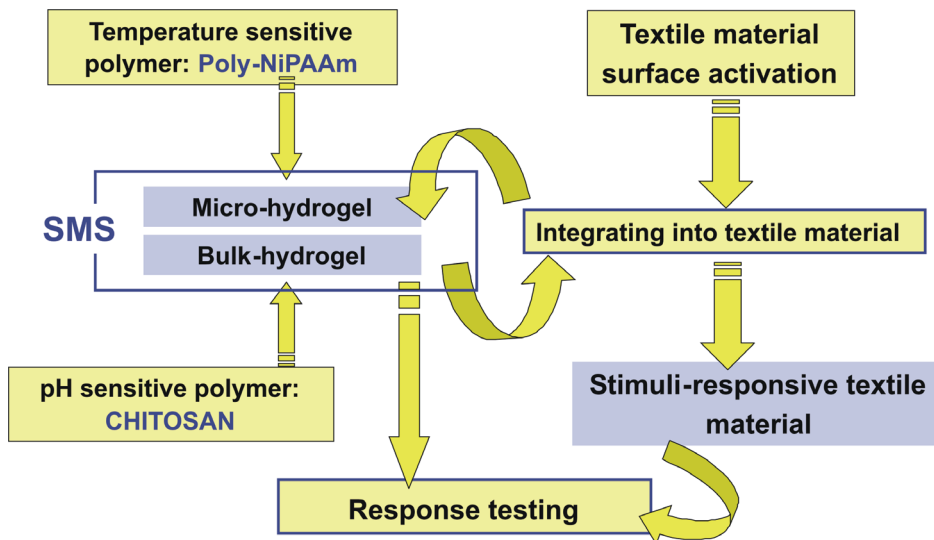


Figure 3. Research scheme of Advanbiotex project.

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.

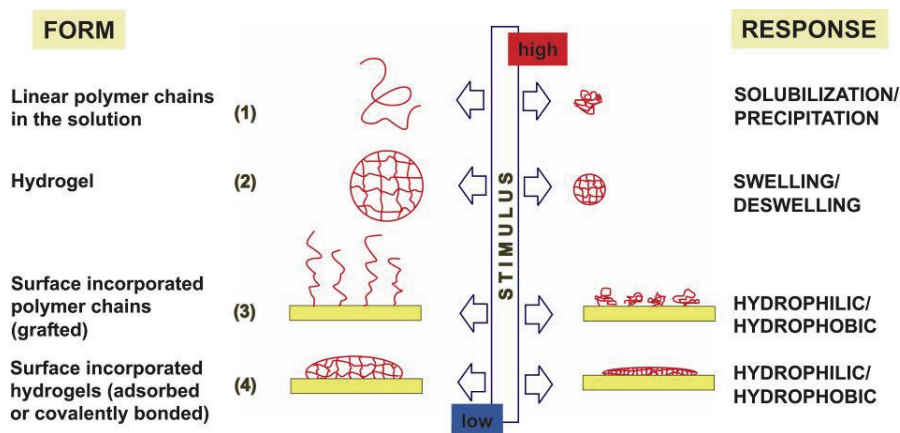


Figure 4. Different physical forms of stimuli-responsive polymers and their macroscopic response.

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.

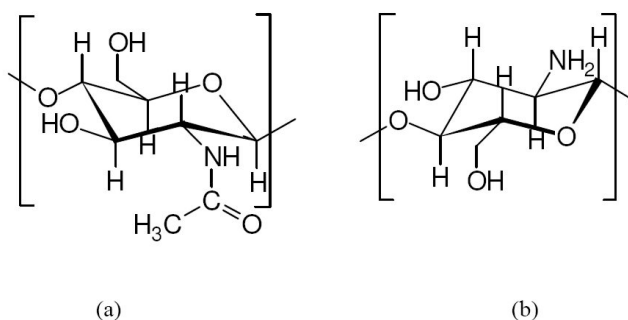


Figure 5. Structural units of chitosan: (a) N-acetylglucosamine unit; (b) Glucosamine unit.

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.

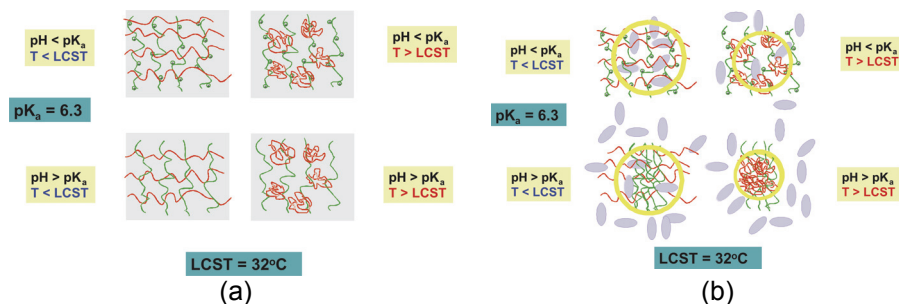


Figure 6. Schematic presentation of phase transition (a) and macroscopic response – swelling/de-swelling (in the presence of water molecules) (b) of dual responsive chitosan/poly-NiPAAm hydrogel in response to pH and temperature change.

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.

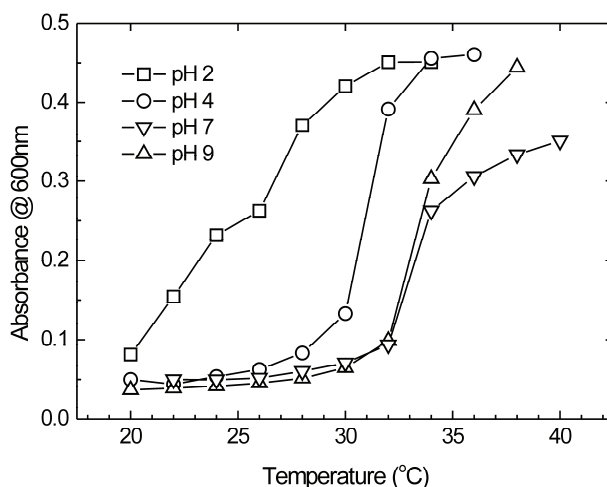


Figure 7. Temperature induced phase transition of PNCS microgel studied by UV-vis spectrophotometry at 600 nm for pH 2, 4, 7 and 9 [30].

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].

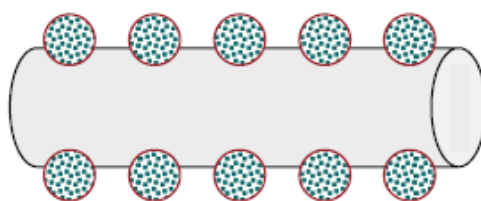


Figure 8. The discrete arrangement of microgel particles at the fibre surface.

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.

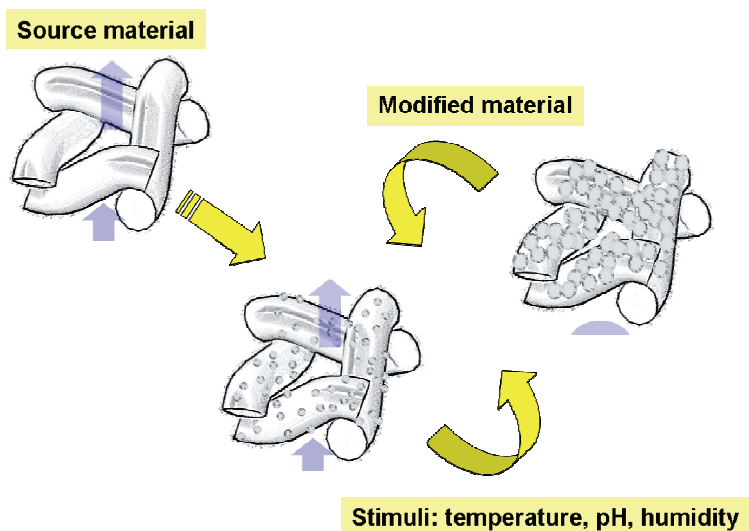


Figure 9. Schematic presentation of water vapour transmission through the textile fabric with incorporated responsive microgel.

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).

Chapter 5

Tunable Wettability of Polyester Fabrics Functionalized by Chitosan/poly(*N*-isopropylacrylamide-co- acrylic acid) Microgels

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

1. Introduction

1.1 Aim and tasks

Functionalization of textiles has been the aim of many studies in the field of intelligent materials. Biomimesis (lotus, pinecone effect etc.), adapting informatics to textile production (integration of computer-controlled electronic sensors), creating new fibres either natural or synthetic (algae biocomposite, ferroelectric polymeric etc.) and convergence of opposites (e.g. hydrophilic with hydrophobic materials) are some of the approaches used for textile functionalization [1-5]. This research focuses on a novel approach for developing advanced textile materials with biopolymer-based functionalities: the use of a hydrophilic stimuli-responsive system based on polyelectrolyte hydrogels for the surface modification of hydrophobic polyester fabrics. The aim was to render textiles responsive to external stimuli such as pH and temperature changes, without affecting dramatically their good intrinsic properties (e.g. mechanical strength). This research involved the following tasks: preparation of surface modifying systems (hydrogels) based on specifically selected polymers; characterization of the surface functionalization; and study of the new functionalities imparted to the textile, expressed as pH/thermo-responsiveness of the material.

1.2 Preliminary work

Prior to the study presented here, extensive tests were performed with different hydrogel types and on different textile substrates, the results of which led to the final selection of an appropriate polymer and textile substrate combination. In all cases, the pH-responsive biopolymer chitosan and the thermo-responsive

polymer poly(*N*-isopropylacrylamide) (PNIPAAm) were used for the hydrogel preparation. The tests included: a) chitosan macro-hydrogels (bulk) with PNIPAAm, in the form of Interpenetrating Polymer Networks (IPNs) for the surface modification of cotton [6]; and b) chitosan macro-hydrogels (bulk) with embedded microparticles of the pH/thermo-responsive co-polymer poly(*N*-isopropylacrylamide-co-acrylic acid) (P(NIPAAm-co-AA)) for the surface modification of polyamide 6,6 fabric [7]. In the first case, crosslinking throughout the hydrogel polymer network was based on physical entanglements of the macromolecular chains and hydrogel attachment on cotton was of physical nature, achieved using a pad-dry method [6]. In the second case, crosslinking within the hydrogel network was achieved through electrostatic interactions between positively charged chitosan and negatively charged P(NIPAAm-co-AA); attachment of the hydrogel on polyamide fabric was of chemical nature, achieved through the natural compound genipin which was used as a crosslinker between the primary amine groups of chitosan and polyamide [7]. In both cases, it was concluded that the stimuli-responsiveness of the functionalized textiles, expressed as water or moisture uptake/loss at different pH and temperature values, was not as pronounced as expected. In fact, substrate interference was so high that hydrogel contribution to the water uptake was not possible to determine with accuracy. In other cases (mostly with cotton trials), the modification gave even opposite effect than expected, i.e. it turned the fabric more hydrophobic than hydrophilic. Moreover, it was observed that the original macroscopic properties of the tested textiles, i.e. of cotton and polyamide, deteriorated. For example, the bulk chitosan hydrogels formed a continuous relatively thick coating layer on the textile surface, as a result of which the functionalized textiles became stiffer, almost paper-like in texture, and their handle much harsher.

1.3 New approach

Based on the above data, it was decided to re-orient research from bulk hydrogels to microgels (i.e. hydrogels in the form of microparticulate suspension) consisting of polyelectrolyte complexes between chitosan and P(NIPAAm-co-AA). Microgels are known to have a faster response to external stimuli [8] and their specific surface area is much bigger compared to a bulk system [9], i.e. more surface modifying material and therefore more functional groups become available per unit area of textile. Polyester was chosen as the most appropriate substrate because its high hydrophobicity, compared to cotton and polyamide, was expected to allow the microgel effect to show. In other words, higher values of water/moisture uptake were expected compared to the previous tests, and a more apparent responsiveness to pH and temperature changes. Moreover, poly(ethylene terephthalate) (PET) was the chosen polyester type and since it is a synthetic polymer, higher homogeneity and less impurities of the substrate surface (e.g. compared to cotton) were advantages for controlling the surface modification. Finally, to test and confirm the polyester functionalization and pH/thermo-responsiveness, the path of wettability

measurements was chosen, instead of water uptake (weight) measurements that were previously the main tool.

2. Polyelectrolyte microgels as surface modifying systems

Taking into account that in this framework textile modification and functionalization were not targeted via novel processing techniques, e.g. weaving or new fibre production, choosing a chemically appropriate finishing was the key parameter to achieve the goal of stimuli-responsive polyester. For this reason, a novel approach for using chitosan was engineered in order to avoid the bulk hydrogel formation and at the same time avoid the chemical modification (e.g. copolymerization) of its macromolecules. As mentioned in the introduction, this approach involved the formation of polyelectrolyte complexes (PECs) between positively charged chitosan macromolecules and the negatively charged P(NIPAAm-co-AA) microparticles (referred to for the rest of the text as "M").

Keeping in mind that textiles for biomedicine or clothing were mainly the target of functionalization, the particular combination of the three components suggested here (chitosan, poly-NIPAAm, acrylic acid) had triple purpose; to prepare a surface modifying system pH-responsive in the entire physiological pH range (4.5-7.5); to prepare a thermo-responsive system with a volume/phase transition temperature as much as possible close to the human body temperature; and to maintain after preparation the desirable intrinsic properties of each component. PEC hydrogels seemed to fit perfectly the above profile. They resemble physiological substrates and therefore are extensively used in biomedicine as e.g. drug carriers, they form very strong networks with reversible electrostatic links (which could also be used for the polyester surface charge management), they are versatile in terms of composition, shape and stimuli-sensitivity, they are easy to prepare, and each of their components keeps its individual characteristics [10, 11].

Indeed the three components used for the PEC formation were chosen for their particular properties; chitosan, because it is an amine-rich pH-responsive biopolymer, abundant in nature and therefore inexpensive, biocompatible and with good bacteriostatic properties [12]; NIPAAm, because in its polymer form it is the most widely investigated thermo-responsive material with a Lower Critical Solution Temperature (LCST) at 32°C [13]; and acrylic acid, because owing to its carboxylic groups it renders its co-polymer with NIPAAm pH-responsive, too. Also, because it is a reagent with which textile industry is familiar and because in its polymer form it is widely used in superabsorbent materials [14]; therefore it was expected to contribute to better moisture management properties of polyester.

2.1 Microgel preparation

M microgel was prepared according to a surfactant-free co-polymerization method yielding negatively charged P(NIPAAm-co-AA) microparticles [15]. The

amount of crosslinker and of the two monomers was thoughtfully chosen in order to achieve low to medium crosslinking extent and at the same time affect the co-polymer hydrophilic/hydrophobic balance in such a way that its LCST is raised from 32 (pure PNIPAAm) to around 36°C. For the first reason, it is known that high crosslinking density results into more rigid hydrogel structures and also hinders hydrogel swelling [16]; therefore it was avoided. For raising the LCST, the reason was to make it approximate more the *average* human body temperature (37.0°C), taking into consideration that each body part differs in temperature but also that skin layer temperature can vary depending on body action and environmental conditions.

After extensive dialysis of the M microgel for removing any unreacted monomers, complexation of P(NIPAAm-co-AA) microparticles with chitosan of 95% deacetylation degree (Chitoclear, Primex) was achieved by adding M microgel to a 0.2% w/v chitosan solution at a ratio 1:2.5 under intense stirring (new microgel formed referred to as “CM”) [17, 18]. Chitosan was chosen to be in abundance in order to possibly bridge microparticles by electrostatically attracting them to the multiple cations of its macromolecular chains but at the same time prevent their aggregation (after charge compensation) by providing an excess of positive charges. However, chitosan excess was kept to a limit in order to avoid bulk gel formation or an increase in the suspension viscosity.

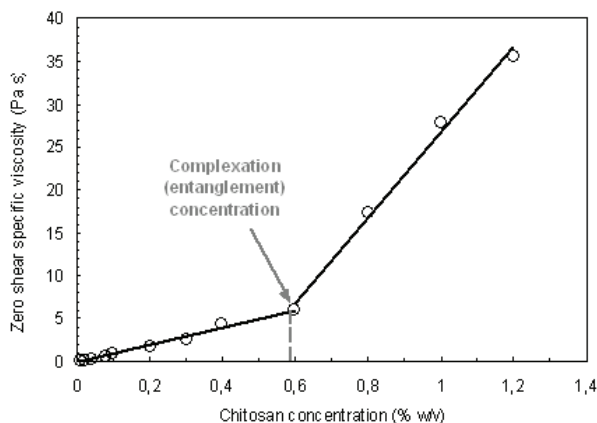


Figure 1. Rheological determination of the complexation (entanglement) concentration of chitosan.

Indeed, rheological measurements showed that the chosen 0.2% w/v chitosan concentration was the only one in a range from 0.01-1.2% w/v that did not alter the microgel viscosity (data not shown), as that would effect the water diffusion and therefore the swelling/shrinking of the microparticles [19]. Also, from shear

rheology measurements performed with an Anton Paar bulk rheometer and according to the protocol described in Hwang et al. (2000) [20], the complexation concentration of the particular type of chitosan used in this study was determined, as shown in Figure 1. That concentration was found to be 0.6% w/v which means that above that value, the polysaccharide chains begin to entangle forming a continuous physical network. It also means that the 0.2% w/v chitosan chosen for this study is far below that value and therefore the bulk gel formation is avoided, as explained above.

2.2 Microgel properties and characterization

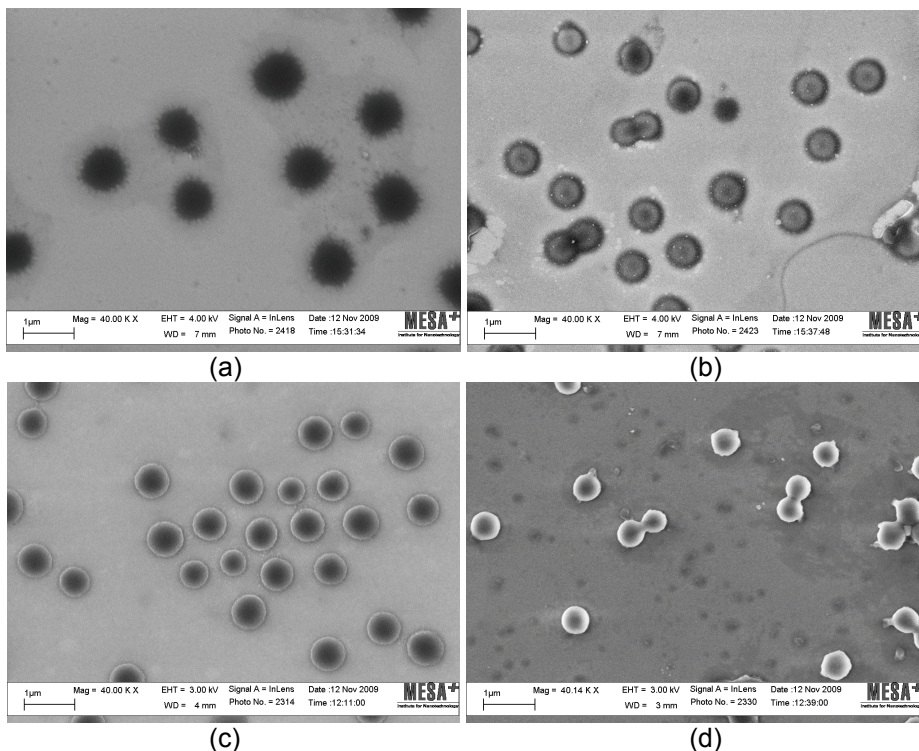


Figure 2. SEM images of: a) microparticles M dried at 20°C and 65% RH; b) microparticles M dried at 50°C and 65% RH; c) suspension of CM complexes dried at 20°C and 65% RH; d) suspension of CM complexes dried at 50°C and 65% RH.

Microgels M and CM were characterized by Differential Scanning Calorimetry (DSC) for determination of the LCST, with high resolution Scanning Electron Microscopy (SEM) for their surface morphology and also for evaluation of the

particle/complex size in dry state, with Dynamic Light Scattering for the particle/complex size in wet state (pH 5), with ζ -potential measurements for determination of the electrophoretic mobility at different pH and temperatures, and with potentiometric titrations for determination of the polyelectrolyte zero-point. It is important to note that based on previous experience, it was decided to study each stimuli effect (pH, temperature changes) on the microgel (and later on polyester) responsiveness separately for a better understanding of each mechanism.

DSC analysis performed as described in Glampedaki et al. (2009) [7] determined the M microgel LCST to be 35.6°C, which upon chitosan addition (CM microgel) shifted to 35.8°C. This slight increase is attributed to the dilution factor when 1 volume of M microgel is mixed with 2.5 volumes of chitosan solution. To characterize the surface morphology of the particles/complexes, SEM images were obtained as shown in Figure 2. To test at the same time the thermo-responsiveness of these particles and to estimate what their size would be in dry state, M and CM aliquots were placed on silicon wafers and were air-dried at 20°C-65% RH and 50°C-65% RH. This would give a better insight of what size to expect on dry textile fibre. As shown in the SEM images (Figure 2) but also in Table 1, the M microparticles are of approximately 700 nm and they undergo about 20% shrinkage above their LCST in dry state. CM complexes have a slightly smaller size at 20°C-65%, which is expected due to the electrostatic attraction forces which contract their structure. However, their shrinkage is 10% higher than that of M particles. To compare with their wet state diameter size, DLS measurements performed with Malvern Nanosizer gave sizes of about 1 μ m for both M and CM in swollen state (pH 5) and 50% shrinkage above their LCST in wet state (Table 1). From the same set of measurements it was confirmed that the CM complexes remained quite uniform in size both at 20 and at 40°C with polydispersity indices of 0.208 and 0.297, respectively.

Sample	Diameter (nm)		
	20°C	40°C	Shrinkage (%)
Wet state (DLS)			
M	944 \pm 89	437 \pm 25	53
CM	968 \pm 39	498 \pm 42	49
Dry state (SEM)	20°C	50°C	Shrinkage (%)
M	656 \pm 24	541 \pm 49	18
CM	629 \pm 34	462 \pm 34	27

Table 1. Temperature-dependence of the M and CM size in wet and dry state.

Potentiometric titrations performed with a Mutek Particle Charge Detector (PCD-03, BTG) over the pH range 3-10 and with NaOH 0.1N as titrant showed that the equivalence point for chitosan used in this study is 6.33, for the M polyelectrolyte particles 3.40 and for the CM complexes 5.97. From these data it is expected that the CM total charge will shift from positive to negative values

within the physiological pH range 4-7, which was a desirable property and further supports the choice of the particular components and ratios. The expected pH-dependence of both M and CM surface charge was also tested with ζ -potential measurements at temperatures below (20°) and above (40°) the LCST as shown in Table 2. For polyelectrolyte complexes the electrophoretic mobility is a more appropriate parameter than ζ -potential values and as shown temperature does not seem to affect it neither in the case of M nor in the case of CM.

Buffer	Electrophoretic mobility ($\text{m}^2 \text{s}^{-1} \text{V}^{-1}$)			
	M		CM	
	20°C	40°C	20°C	40°C
pH 4	-0.21 ± 0.07	-0.37 ± 0.11	2.19 ± 0.34	2.77 ± 0.23
pH 5	-0.92 ± 0.15	-1.21 ± 0.13	1.55 ± 0.09	1.81 ± 0.08
pH 6	-1.09 ± 0.13	-1.46 ± 0.06	0.00 ± 0.08	0.10 ± 0.04
pH 7	-1.21 ± 0.08	-1.44 ± 0.09	-1.05 ± 0.22	-1.41 ± 0.12

Table 2. Temperature and pH dependence of the M and CM electrophoretic mobility.

3. Microgel incorporation into the polyester-fibre surface-layer

Having characterized the pH- and thermo-responsiveness of the CM microgel and having confirmed that both these effects are taking place within physiological temperature and pH range (as it was wished for their application on fabrics) a protocol was established for their incorporation into polyester fibre surface layer. After several trials on different reagent amounts and experimental conditions, a method for using UV irradiation was employed [17, 18].

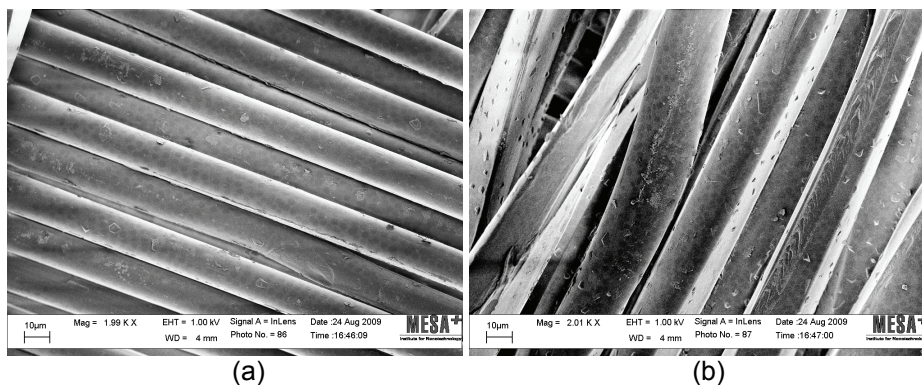


Figure 3. High resolution SEM images of: a) warp yarns, and b) weft yarns of functionalized polyester fabric (PET RCM).

The presence of CM complexes on the polyester fibre surface was visually confirmed by SEM, as shown in Figure 4. Circular formations of less than 1 μm were observed on both warp and weft filaments, rather uniformly spread on the fibres.

Sample	C1s (%)	N1s (%)	O1s (%)	N/C	O/C
R	73.20	-	26.80	-	0.36
RCM	73.98	4.14	21.88	0.06	0.30

Table 3. Polyester surface elemental analysis (atomic concentration (%) and atomic ratio) determined by X-ray Photoelectron Spectroscopy.

The chemical surface composition of functionalized polyester was analysed by XPS [17, 18] and the obtained data are shown in Table 3. Nitrogen presence on the polyester fibres at approximately 4% was confirmed and attributed to the multiple amide bonds of P(NIPAAM-co-AA) but also to the chitosan amine groups. However, no distinction between the two sources could be made solely by these results.

4. Functionalized polyester-textile characterization

4.1 Surface, physical and physico-chemical properties of polyester

After confirmation of the CM complexes on the fibre surface of the functionalized polyester, some of its properties were tested in order to control to what extent the modification altered them. For that reason, electrokinetic analysis for streaming potential measurements were performed using an Electro Kinetic Analyzer (EKA, Anton Paar) and according to the procedure described in Stawski et al. (2009) [21].

The results are shown in Figure 4. The sigmoidal curve of the ζ -potential vs. pH values of the functionalized polyester (RCM), compared to the reference (R), is another clear indication that CM complexes on the polyester fibre surface. As in the case of the complexes themselves, polyester RCM appears to have isoelectric point at around pH 6, so again within the physiological pH range which was the target. This also means that pH-responsiveness is indeed expected from the functionalized polyester.

Sample	Whiteness index (CIE)	Yellowness index (ASTM 313)
R	81 \pm 1	0.4 \pm 0.1
RCM	70 \pm 2	3.2 \pm 0.3

Table 4. Whiteness and yellowness index of reference (R) and functionalized (RCM) polyester fabric.

The whiteness and yellowness indices of the polyester fabrics were also measured using a portable reflectance spectrophotometer (SpectroEye, X-Rite)

and the values obtained were the average of five measurements of double-folded (four layers) samples. The results are presented in Table 4.

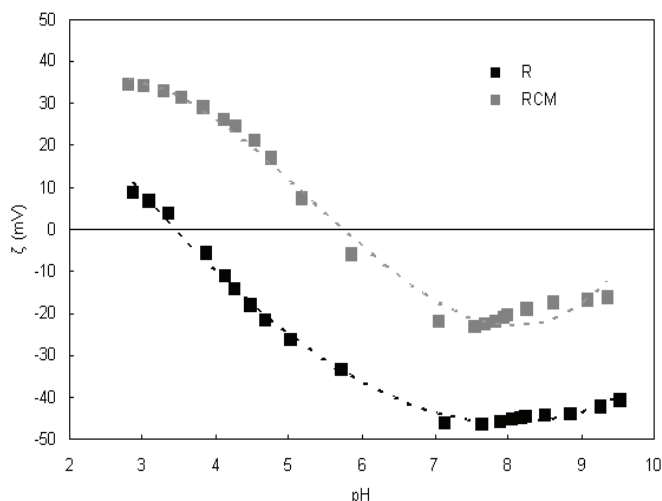


Figure 4. ζ -potential changes of reference (R) and functionalized (RCM) polyester fabric with pH.

It is evident that whiteness of polyester decreases by 10 units and yellowness increases by almost 3. Two parameters can account for these effects; the UV irradiation, even though of low wavelength (254 nm), which may cause degradation of polyester, and the mere presence of chitosan, the solutions and gels of which are by nature coloured yellowish. Even though chitosan is used in a solution of as low a concentration as 0.2% (for reasons explained above), and even though visual inspection of the polyester samples does not show severe differences, spectrophotometrically it was proven otherwise.

Sample	CRA (°) Warp	CRA (°) Weft
R	133 ± 7	142 ± 2
RCM	128 ± 8	135 ± 3

Table 5. Crease recovery angle values of reference (R) and functionalized (RCM) polyester fabric.

Finally, crease recovery angle was measured in both warp and weft directions according to ISO 2313/AATCC Test Method 66-2003. Samples were pre-conditioned at 20°C-65% RH in a climatic test chamber (Thermotron 3800, Climatronic). The results obtained are shown in Table 5. One of polyester main good properties is resistance to wrinkling. Unfortunately, the functionalization

procedure proposed in this study has not left this characteristic unaffected, as a 4-5% decrease was observed in the crease recovery angle in both warp and weft directions. Better insight to an optimized protocol could be given with multiple trials with different CM microgel add-ons and repetition of the physical/chemical characterization.

4.2 Wettability evaluation

Wettability of surfaces is generally influenced and controlled by two key parameters; the surface chemistry and the surface roughness. So far, the former was characterized for the functionalized polyester under study, and it was shown that indeed there are hydrophilic moieties introduced to the polyester surface. In this paragraph the effect of these moieties on the wettability of the fabric is explored in terms of water/buffer drop total absorption time, fabric topography, water vapour transfer and moisture sorption-desorption measurements. In fact, as mentioned in the introduction, wettability is used in this study as an expression of the pH- and thermo-responsiveness of the functionalized polyester.

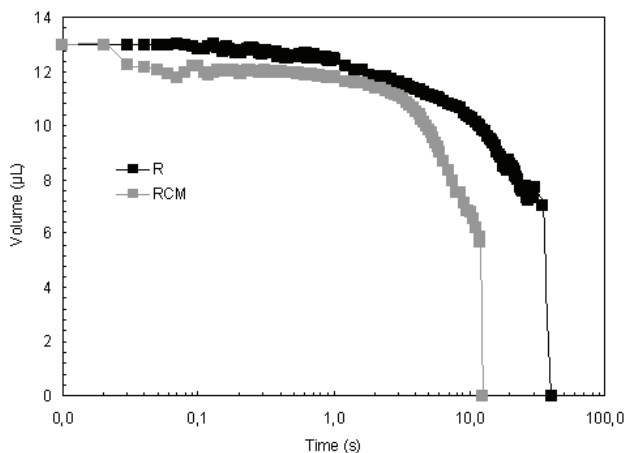


Figure 5. Dynamic wetting curves (drop volume vs. time) of reference (R) and functionalized (RCM) polyester fabric.

In Figure 5, the dynamic wetting curves of polyester R and RCM are presented. They were obtained by dynamic contact angle measurements using the sessile drop technique on a FibroDAT 1100 device (Fibro Systems AB) and according to the protocol described in Dutschk et al. (2003) [22]. It is shown that functionalized polyester (RCM) exhibits almost five times faster absorption of a water drop (13 µL) than reference polyester. It is also indicated that both samples (R and RCM) follow similar wetting regime (first part of the curve) but

water spreading and finally penetration into the functionalized polyester is faster. Using buffer solutions of pH 4-8, the same type of curves were drawn and from them the total absorption time for each sample and at each pH was determined. The results are presented in Table 6.

Solution	Total absorption time (s)	
	R	RCM
Water	65.0 ± 13.0	12.5 ± 1.6
Buffer pH 4	52.0 ± 9.8	7.9 ± 1.5
Buffer pH 6	44.9 ± 18.0	4.6 ± 1.9
Buffer pH 8	40.0 ± 4.4	4.6 ± 1.7

Table 6. Total absorption time determined by the sessile drop method at different pH values for reference (R) and functionalized (RCM) polyester fabric.

As it can be seen, the higher the pH, the lower the total absorption time for both samples. However, in the case of RCM the time decrease is almost double compared to R, ranging from almost 36-64% compared to 20-38%, respectively. It is perceived that the P(NIPAAm-co-AA) microparticles are the ones undergoing swelling when they come in contact with the water drop and that chitosan facilitates the water attraction towards them. Therefore, at pH 4 where chitosan is highly protonated the total absorption time decreases but not as much as at higher pH where the P(NIPAAm-co-AA) microparticles become fully ionized (see equivalence point determination in paragraph 2.1).

Condition	Arithmetic roughness, R_a (nm)	
	RCM Warp	RCM weft
Dry	14	36
Buffer pH 4	22	29
Buffer pH 6	39	28
Buffer pH 8	55	59

Table 7. Micro-roughness in the warp and weft direction for functionalized polyester RCM in dry state and at different pH values.

To confirm this assumption, confocal microscopy was employed for profiling RCM fibres in dry state and after wetting them with buffer solutions of pH 4-8. It was possible to observe the same spot of the fibre by placing the specimen on a glass plate which was glued on a holder to avoid displacement. Measurements were performed using the Nanofocus confocal microscope (Nanofocus μ surf explorer system, Spectra services). Even though only indicative, the derived data on the fibre arithmetic roughness (R_a , Table 7) at different pH confirms the increased swelling (resulting in increased fibre roughness) of the microparticles as pH increases. This is in correlation with capillarity data reported elsewhere [17] which showed that wicking was faster

for polyester RCM compared to R owing to increased capillarity but at the same time the contact angle also increased, indicating increased fibre roughness. However, in Table 7 a discrepancy is observed for the weft filament but this may be attributed to non-uniform deposition of particles on it compared to warp filament.

Topographic parameters	R	RCM
Fabric dimensional change (calculated from the distance between yarns)	0.00%	9.71% (relaxation)
Waviness, W_{max} (μm)	115	82
Inter-yarn porosity, V_o ($\mu\text{m}^3/\mu\text{m}^2$)	0.709	0.702
Intra-yarn porosity ($\mu\text{m}^3/\mu\text{m}^2$) – Warp	0.515	0.726
Intra-yarn porosity ($\mu\text{m}^3/\mu\text{m}^2$) – Weft	0.344	0.438

Table 8. Topographic characterization of reference (R) and functionalized (RCM) polyester fabric.

Topographic measurements (conducted in dry state) according to the procedure described in Calvimontes et al. [23] gave very useful results (Table 8) which help elucidate the effect of the functionalization procedure on the fabric topography. It was derived that the fabric macro-topography was altered as RCM underwent dimensional changes (relaxation of yarns) which was coupled with the observed decreased waviness (i.e. increase in length/width, decrease in height).

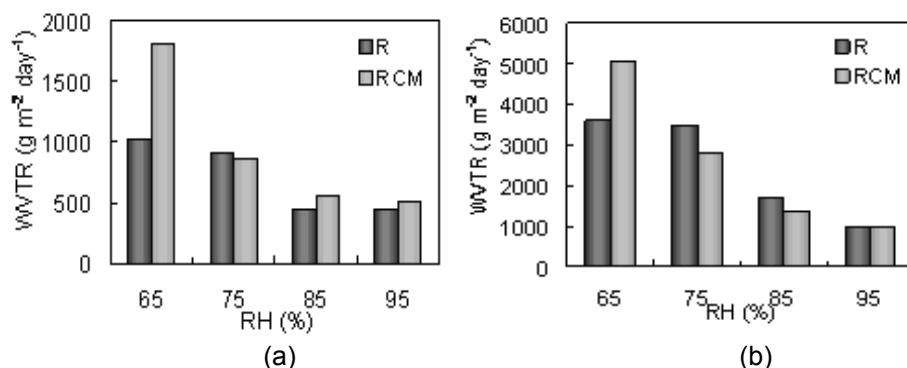


Figure 6. Water vapour transfer rate of reference (R) and functionalized (RCM) polyester fabric at different RH% values and at: a) 20°C, and b) 40°C.

On the other hand, the inter-yarn porosity was not significantly changed, a result which correlates well with data obtained from liquid porosimetry [18]. The intra-yarn porosity, however, in both directions increased.

With the above in mind, explanations can be given about the water vapour transfer results obtained from measurements performed as described in reference [18] at four relative humidity values and at 20 and 40°C. As shown in Figure 6, below the CM LCST, functionalized polyester seems to transfer moisture faster than reference polyester at almost all conditions studied. This fact could be attributed not only to the hydrophilicity of CM but also to the increased intra-yarn porosity that the functionalization treatment caused, as explained above.

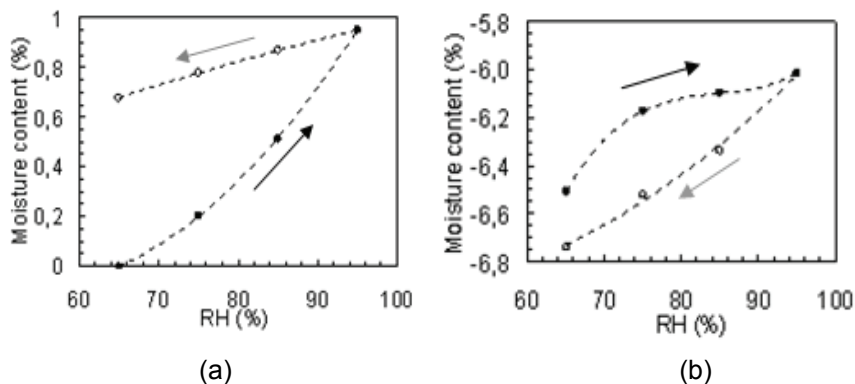


Figure 7. Moisture sorption and desorption of reference (R) polyester fabric at different RH% values and at: a) 20°C, and b) 40°C.

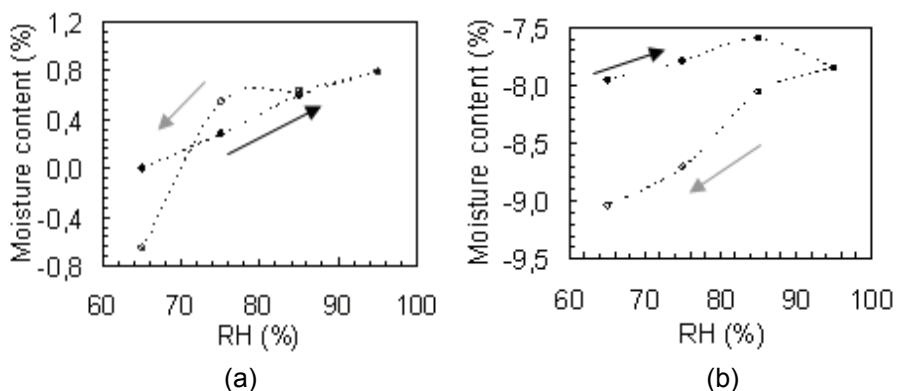


Figure 8. Moisture sorption and desorption of functionalized (RCM) polyester fabric at different RH% values and at: a) 20°C, and b) 40°C.

However, above CM LCST (i.e. at 40°C), polyester RCM transfers moisture faster than R only at low RH. At higher RH where the thermo-responsiveness

may be distinguished better from the mere drying effect due to moisture saturated environment, it is shown that the water vapour transfer rate for RCM is lower than for R. These results agree well with moisture regain data reported elsewhere which showed that hydrophilicity of functionalized polyester was temperature-controlled [17, 18].

Finally, moisture sorption-desorption measurements performed continuously at different temperatures and RH values in a climatic chamber and with direct weight recording of each sample by using a high precision analytical balance (WXS, Mettler-Toledo) gave the results presented in Figures 7 and 8. The thermo-sensitivity of polyester RCM is once more exhibited compared to sample R since it appears to lose more moisture not only during desorption at 40°C (Figure 9b compared to Figure 8b), i.e. at decreasing RH from 95 to 65%, but also during sorption, i.e. at increasing RH from 65 to 95%. At 20°C and lower RH (65-75%), the rate of desorption is higher for RCM than for R as indicated by the abrupt decrease in moisture content. At 40°C and higher RH (85-95%), the rate of desorption is lower for RCM than for R, indicating that even though RCM eventually expels more moisture at the end of the cycle, there is a critical point after which desorption starts.

5. Conclusions

This study conducted in the Advanbiotex framework concluded in the following main achievements: a) knowledge built-up from preliminary work on textile surface functionalization, using from bulk hydrogels to microgels as surface modifying systems, from physical to chemical incorporation techniques, and from cotton to synthetic polyester fabrics as substrates; b) preparation of pH/thermo-responsive microgels as surface modifying systems based on a novel combination of the biopolymer chitosan and the synthetic co-polymer P(NIPAAm-co-AA) in the form of polyelectrolyte complexes; c) functionalization of synthetic polyester fabrics by polyelectrolyte microgel incorporation using a simple technique of UV irradiation; d) confirmation of the pH/thermo-responsiveness of the functionalized polyester through a combination of surface analysis techniques; e) development of synthetic polyester fabrics with tunable wettability as a result of their functionalization and stimuli-responsiveness. These achievements correspond well to the initially appointed tasks; however, the study showed certain limitations regarding alterations in the good properties of polyester (e.g. decreased wrinkle resistance). Even though such alterations were kept to acceptable levels, optimization of the procedures is under way.

Acknowledgements

The scientific contribution, training and advice from Dr. Jürgen Krägel of the Department of Interfaces of the Max Planck Institute of Colloids and Interfaces in Potsdam, Germany, and from Dr. Alfredo Calvimontes and Mrs. Anja Caspari

of the Department of Polymer Interfaces of the Leibniz Institute of Polymer Research in Dresden, Germany, are gratefully acknowledged.

References

- [1] A. Solga, Z. Cerman, B. Striffler, M. Spaeth, W. Barthlott, The dream of staying clean: Lotus and biomimetic surfaces, *Bioinspiration and Biomimetics*, **2**, 126-134 (2007).
- [2] K.J. Sim, S.O. Han, Dynamic mechanical and thermal properties of red algae fiber reinforced poly(lactic acid) biocomposites, *Macromolecular Research*, **18**, 489-495 (2010).
- [3] S. Egusa, Z. Wang, N. Chocat, Z.M. Ruff, A.M. Stolyarov, D. Shemuly, F. Sorin, P.T. Rakich, J.D. Joannopoulos, Y. Fink, Multimaterial piezoelectric fibres, *Nature Materials*, **9**, 643-648 (2010).
- [4] T. Yuranova, D. Laub, J. Kiwi, Synthesis, activity and characterization of textiles showing self-cleaning activity under daylight irradiation, *Catalysis Today*, **122**, 109-117 (2007).
- [5] L. van Langenhove, C. Hertleer, M. Catrysse, R. Puers, H. van Egmond, D. Mattheijs, Smart Textiles, in "*Wearable e-health systems for personalised health management: State of the art and future challenges*", A. Lymberis and D. de Rossi Eds., IOS Press, 344-352 (2004).
- [6] P. Glampedaki, A. Tourrette, M.M.C.G. Warmoeskerken, D. Jocić, Application of bulk and micro-hydrogels for obtaining cotton with responsiveness towards temperature and pH, *2nd International Scientific Conference "Textiles of the Future" – Futurotextiel 2008*, November 13-15, Kortrijk, Belgium, CD-ROM of Proceedings, 10 pages (2008).
- [7] P. Glampedaki, J. de Klein, M.M.C.G. Warmoeskerken, D. Jocić, Surface modification of polyamide via grafted chitosan-based responsive hydrogels, *The 9th World Textile Conference (AUTEX2009)*, May 26-28, Izmir, Turkey, Proceedings, 480-487 (2009).
- [8] B. Saundersa, B. Vincent, Microgel particles as model colloids: theory, properties and applications, *Advances in Colloid and Interface Science*, **80**, 1-25 (1999).
- [9] Basic properties and measuring methods of nanoparticles in "*Nanoparticle technology handbook*", M. Hosokawa, K. Nogi, M. Naito, T. Yokoyama Eds., Elsevier, Amsterdam (NL), 20-23 (2007).
- [10] Y. Shchipunov, I. Postnova, Water-soluble polyelectrolyte complexes of oppositely charged polysaccharides, *Composite Interfaces*, **16**, 251-279 (2009).
- [11] J. Hamman, Chitosan based polyelectrolyte complexes as potential carrier materials in drug delivery systems, *Marine Drugs*, **8**, 1305-1322 (2010).
- [12] M. Rinaudo, Chitin and chitosan: Properties and applications, *Progress in Polymer Science*, **31**, 603-632 (2006).
- [13] Y. Hirokawa, T. Tanaka, Volume phase transition in a nonionic gel, *The Journal of Chemical Physics*, **81**, 6379-6380 (1984).
- [14] F. Buchholz, in *Absorbent Polymer Technology*, Brannon-Peppas and R. S. Harland, Eds., Elsevier, New York (USA), 23 (1990).
- [15] W. Cai, R. Gupta, Fast responding bulk hydrogels with microstructure, *Journal of Applied Polymer Science*, **83**, 169-178 (2002).

- [16] W. Xue, S. Champ, M. Huglin, Network and swelling parameters of chemically crosslinked thermoreversible hydrogels, *Polymer*, **42**, 3665-3669 (2001).
- [17] 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, Vilnius, Lithuania, Proceedings (CD-ROM), (4 pages) (2010).
- [18] 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, Dresden, Germany, Book of Abstracts, 32 (2010).
- [19] D. Saraydin, Y. Çaldıran, In vitro dynamic swelling behaviors of polyhydroxamic acid hydrogels in the simulated physiological body fluids, *Polymer Bulletin*, **46**, 91-98 (2001).
- [20] J. Hwang, H. Shin, Rheological properties of chitosan solutions, *Korea-Australia Rheology Journal*, **12**, 175-179 (2000).
- [21] D. Stawski, C. Bellmann, Electrokinetic properties of polypropylene textile fabrics containing deposited layers of polyelectrolytes, *Colloids and Surfaces A: Physicochem. Eng. Aspects*, **345**, 191-194 (2009).
- [22] V. Dutschk, K. Sabbatovskiy, M. Stolz, K. Grundke, V. Rudoy, Unusual wetting dynamics of aqueous surfactant solutions on polymer surfaces, *Journal of Colloid and Interface Science*, **267**, 456-462 (2003).
- [23] A. Calvimontes, V. Dutschk, M. Stamm, Advances in Topographic Characterization of Textile Materials, *Textile Research Journal*, **80**, 1004-1015 (2010).

Chapter 6

Thermal and pH-responsive Microgel Incorporation to Previously Activated Cotton

Audrey Tourrette
CIRIMAT, UPS-INPT-CNRS
Faculté de Pharmacie, UPS, Toulouse
France

1. Introduction

The objective of the research done was to prepare new-added value cotton textile material, containing fibres that maintain advantageous conventional properties but with advanced functionalities. This advanced textile material should present good mechanical strength and flexibility, as well as wear comfort, but also environmental responsiveness. One of the promising strategies to reach this goal involves the coating of textile material surface with a thin polymeric layer. The incorporation of the polymeric system onto the textile material, must implement fast responsive properties without screening the textile's regular performance. To this end, it has been decided to prepare dual responsive hydrogel in a micro-scale. Such hydrogels were prepared by combining a thermoresponsive synthetic polymer with a natural based pH-responsive polymeric component [1].

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 [2, 3]. 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) [4]. 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).

To reach the goal of the project my main research tasks have been: preparation of the appropriate form of polymeric surface modifying systems (SMS); study of stimuli responsiveness and physicochemical properties of SMS; study of substrate (cotton textile material) surface activation methods (chemical functionalization and low-temperature plasma treatments), and characterization of modified textile material surface.

2. Thermo- and pH-responsive microgel

Poly-NiPAAm (PN) and poly-NiPAAm/chitosan (PNCS) microgels have been simultaneously prepared in order to study the influence of the pH-sensitive polymer on the microgel properties.

2.1 Microgel preparation

The PN microgel was prepared by surfactant emulsion polymerization method [5]. The monomer and the crosslinker were mixed in presence of surfactant in aqueous medium. At this step all the components were miscible. Then the initiator was added at 70°C. In this condition, free radicals were generated by the decomposition of the persulfate initiator. Above the LCST the polymer was hydrophobic and polymerized inside the inverse micelles formed by the surfactant leading to the formation of microparticles with a narrow size distribution.

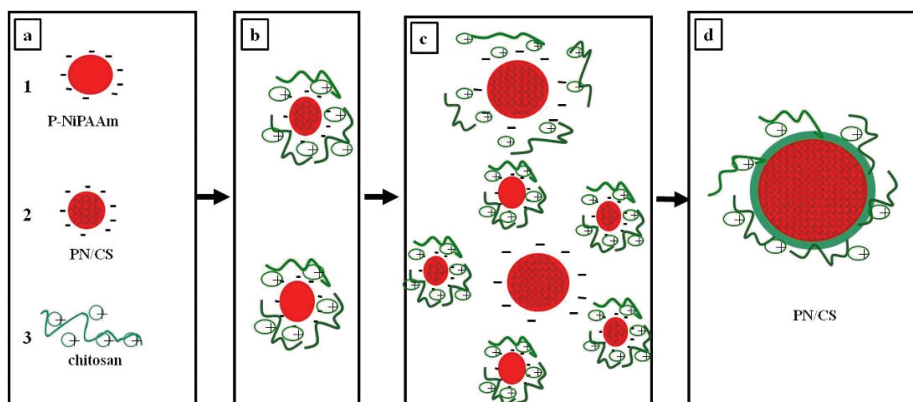


Figure 1. Synthesis of PNCS microgel (SFDP mechanism).

The PNCS microgel was prepared by the surfactant-free dispersion copolymerization method (SFDP) according to the previously reported procedure [6, 7]. Three kinds of reactions occur in the reaction system of dispersion copolymerization (Figure 1). The first reaction is the polymerization

of NiPAAm, initiated by ammonium persulfate (APS), which forms negative particles [5] (Figure 1, 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 (Figure 1, a-2). The last reaction is the ionization of chitosan which results in positively charged chitosan molecules (Figure 1, 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 (Figure 1, 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 (Figure 1, c-d).

2.2 Characterization

2.2.1 Physicochemical characterization

A SEM image of dry PN and PNCS microgels, deposited from a solution onto native oxide layer of a silicon wafer, is shown in Figure 2. The photomicrographs show that in both cases the microgel particles have a homogeneous spherical shape and that the particle size distribution is quite narrow. The diameter of PN and PNCS particles in dry state is estimated at 140 nm and 180 nm, respectively.

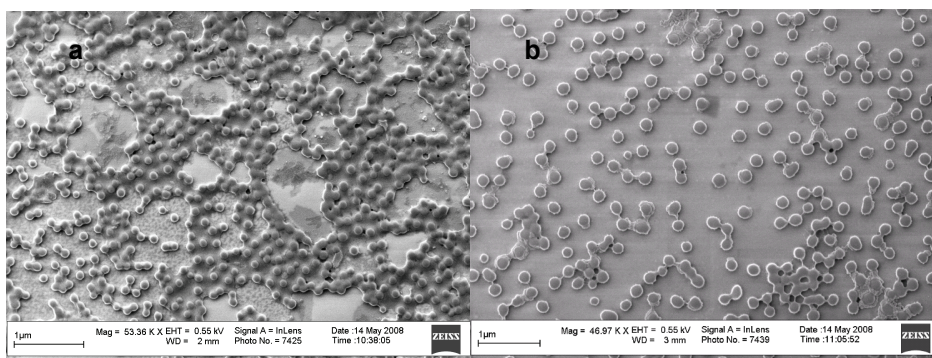


Figure 2. SEM images of poly-NiPAAm particles (PN, 1.11×10^{-2} g/L) (a) and poly-NiPAAm/chitosan microgel particles (PNCS, 3.56×10^{-2} g/L) (b) deposited from a diluted solution onto a silicon wafer.

The variation of the ζ -potential with the pH change of aqueous dispersion of PN and PNCS microgels is shown in Figure 3. PN microgel presents a negative ζ -potential while PNCS microgel is positively charged. The second difference is that ζ -potential values of PN microparticles are quite constant over the whole range of pH measured, while the charge of PNCS particles decreases with an increase of the pH, reaching 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 pK_a value of chitosan is 6.3 (as already stated before), but it is known that at pH 6.9 the amino-groups ($-NH_2$) are still partly ($\sim 20\%$) protonated ($-NH_3^+$) [8]. 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 ζ -potential analysis, this implied that the outer layer of the microgel particles was mainly constituted by chitosan.

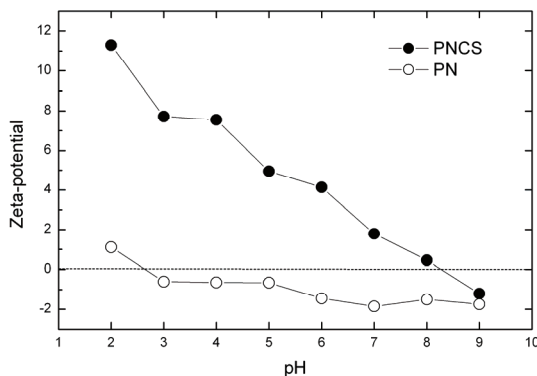
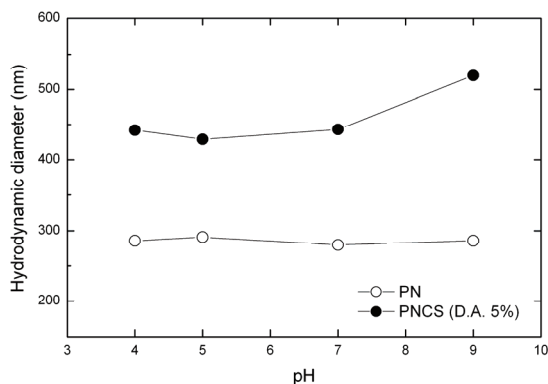


Figure 3. Variation of ζ -potential with pH for aqueous dispersion of poly-NiPAAm (PN) and poly-NiPAAm/chitosan microgel particles (PNCS) (1.1×10^{-1} g/L) at 25°C.

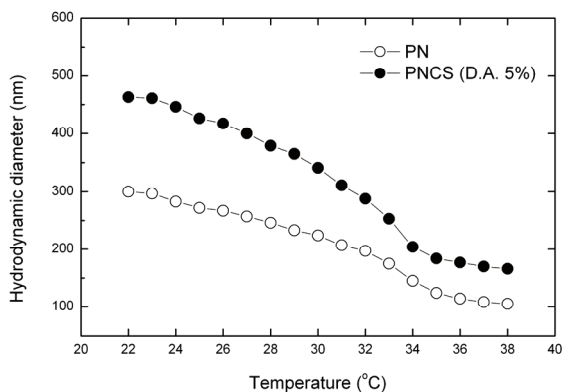
2.2.2 Characterization of thermo- and pH-responsiveness

In order to study the stimuli responsive properties (swelling/shrinking behaviour) of the microgel, dynamic light scattering (DLS) analysis was used to assess the microgel particle size at different temperatures and pH. Figure 4a presents the hydrodynamic diameter of PN and PNCS microgel particles at different pH values. It shows that PN particle size remains constant while PNCS particle size is very sensitive to pH change as a result of protonation/deprotonation of chitosan. An 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 pK_a 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 (Figure 3). Figure 4b shows the hydrodynamic diameter of PN and PNCS microgel particles as a function of temperature. The decrease of hydrodynamic diameter of particles (PN and PNCS) with an increase of temperature proves their thermo-responsiveness.

Microgel polymeric network shrinks slightly with temperature increase. A change of the slope around 33°C for PNCS and around 34°C for PN particles can be noticed, which is close to the LCST of the microgels determined by spectroscopy in the same conditions.



(a)



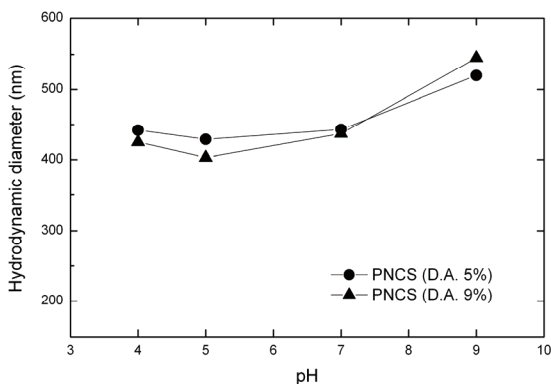
(b)

Figure 4. Hydrodynamic diameter of PN suspension (7×10^{-2} g/L) and PNCS suspension (1.1×10^{-1} g/L) at 25°C as a function of pH (a), and hydrodynamic diameter of PN suspension (9.3×10^{-2} g/L, NaCl 1 mM, pH 7.3) and PNCS suspension (2.3×10^{-1} g/L, NaCl 1 mM, pH 7.3) as a function of temperature (b).

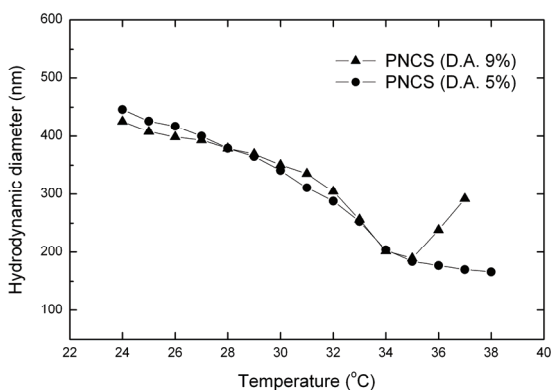
2.3 Improvement of microgel properties

2.3.1 Study of the influence of the degree of acetylation of chitosan on PNCS microgel properties

The intrinsic properties of chitosan polymer depend on its characteristics such as its molecular weight and degree of acetylation (D.A.). Since amine functions play a decisive role in its pH sensitivity property, we studied the influence of the D.A. on the physicochemical properties and the environmental responsiveness of PNCS microgel. To this end, PNCS with two different types of chitosan (D.A. 5% and D.A. 9%) were prepared and characterized.



(a)



(b)

Figure 5. Hydrodynamic diameter of PNCS microgel particle suspension (7×10^{-2} g/L) as a function of pH (a) and temperature (b).

Figure 5 shows the size of PNCS microgel particles prepared with two different types of chitosan as a function of pH (Figure 5a) and temperature (Figure 5b). Significant differences between the two samples concerning their temperature and pH responsiveness cannot be observed. However, it can be observed that PNCS particles made of chitosan with D.A. 9%, present an increase in hydrodynamic diameter above 36°C, which is due to the aggregation of the particles. PN particles are stabilized by the presence of surfactant and do not aggregate above LCST (Figure 4b). PNCS particles made of chitosan with D.A. 5% are more stable because of the presence of protonated chitosan chains at the particles surface which act like surfactants and thereby stabilize them. In the case of PNCS microgel (D.A. 9%), there are less free amino groups on its structure and it is less positively charged. Consequently, the stabilizing property is not enough efficient and the particles aggregate. In conclusion to this study, PNCS microgel (chitosan, D.A. 5%) presents the best properties: interesting pH and thermo-responsiveness and good stability.

2.3.2 PNCS microgel with incorporated carbon nanotubes (CNTs)

Multiwalled carbon nanotubes (MWCNTs) are new materials with unique properties. They have been incorporated into PNCS microgel in order to improve the mechanical properties, thermal and electrical conductivity properties of the system. The composite particles were characterized by SEM. The composite carbon nanotube/poly-NiPAAm/chitosan particles (CNT-PNCS) were prepared by a surfactant-free dispersion copolymerization method according to the procedure reported by Lee and al. [6, 7], in presence of multiwalled carbon nanotubes.

For the synthesis of PNCS microgel particles without MWCNTs, 5 minutes after initiating temperature increase, the reaction mixture became heterogeneous and the transparent solution turned into a “milky” dispersion, as the consequence of light scattering caused by formation of complex particles. In the presence of MWCNTs this phenomena is slower. The reaction mixture turned to a “milky” dispersion only after 30 min. At the end of the reaction (3 h) the dispersion is constituted by a milky dispersion (PNCS particles and MWCNTs coated with both polymers) and by a black dispersion of uncoated MWCNTs.

A drop of composite CNT-PNCS particle dispersion was laid on a silica wafer and dried at room temperature before SEM analysis. It is observed that the hydrogel system consist of PNCS spherical particles of 124 nm diameter and of MWCNTs coated by a polymeric film of chitosan and PNCS particles (Figure 6). The diameter of initial MWCNTs used for the synthesis was between 110-170 nm. After coating this diameter increased until 200 nm. Once dried the composite particles aggregated as clusters.

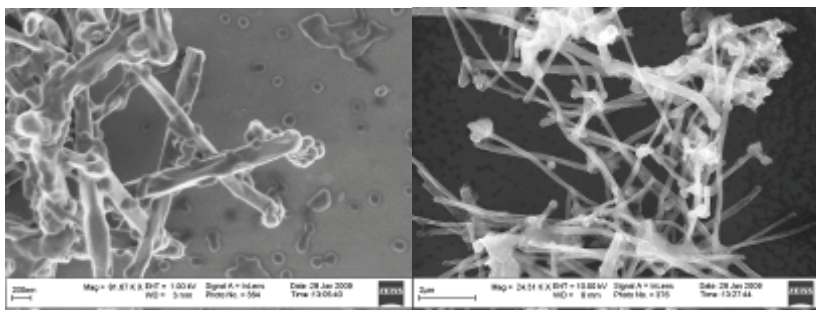


Figure 6. SEM images of CNT-PNCS composite particles (dilution 1/1000).

Unfortunately the synthesis was not complete (presence of coated and uncoated MWCNTs) and a phase separation between PNCS microgel and MWCNTs has been observed after some time. Since the functionalization of MWCNTs is necessary for their use in textile application (biocompatibility issue), we decided to leave this research approach and to work with PNCS microgel (chitosan, D.A. 5%) which presents the best properties.

2.4 Microgel suspension phase behaviour

It has been observed that PNCS microgel in suspension at different pH and temperatures precipitated (destabilized) after some time. A study of the microgel suspension stability was necessary to understand the system. PNCS microgel suspension has been kept one hour (time needed to reach the equilibrium state) at different temperatures and digital photographs have been taken to visualize and study the state of PNCS microgel.

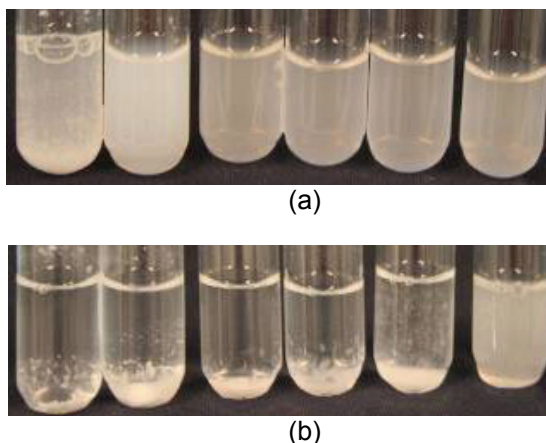


Figure 7. Digital photographs of a diluted suspension of PNCS microgel (1.1 g/L) (pH 2, 3, 4, 5, 7, 9, from the left to the right) at 25°C (a) and 35°C (b).

Figure 7 presents the digital photographs of PNCS microgel suspension at different pH and different temperatures. The stability and physical state (hydrophilic or hydrophobic character) of PNCS microgel depend 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.

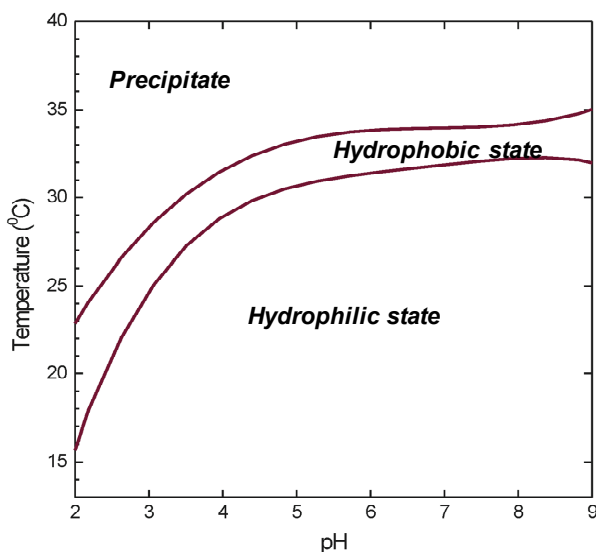


Figure 8. State diagram of a diluted PNCS microgel suspension (1.1 g/L).

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. Below the LCST, thermo-responsive particles are swollen and thus consist mainly of water (Figure 7a). 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 (Figure 7b) the water content of the gel is reduced giving a higher density, thereby increasing the van der Waals forces, which in turn tends to aggregate the microgel. Microgel stability depends

also on pH (Figure 7a). At 25°C and pH 2 (Figure 7a) the particles are precipitated. This finding can be explained by the shrinkage of the whole complex as the consequence of increased amount of $-\text{NH}_3^+$ groups and decreased LCST of poly-NiPAAm at strong acidic pH [9].

Based on above findings and in order to optimize the conditions of incorporation of microgel onto textile fabric of different nature, state diagram of PNCS particles was elaborated (Figure 8) [10]. As already stated before, the boundary line between hydrophilic and hydrophobic state of microgel corresponds the LCST value determined by spectroscopy analysis and the boundary line between hydrophobic state and precipitate was determined by visual observation of PNCS suspension. This diagram will be useful in choosing the temperature and the pH of the microgel suspension for their incorporation onto textile material, depending on the type of substrate used (hydrophobic or hydrophilic).

3. Cotton activation

In order to investigate the activation of cotton for subsequent incorporation of micro-particulate SMS, two kinds of methods (chemical and physical) have been selected.

3.1 Chemical cotton activation

The aim of textile material (cotton fabric) activation was 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 [11]: *anionic cotton* has been produced by reaction with monochloroacetic acid (CAA) to give partially carboxymethylated cellulose (*carboxymethylation*) [12, 13]; *cationic cotton* has been produced by dyeing with reactive dye and subsequent reductive cleavage of the dye attached (*aminization*) [14]. Thus, aromatic amines are formed on cotton by chemical reduction of covalently attached reactive dye molecules.

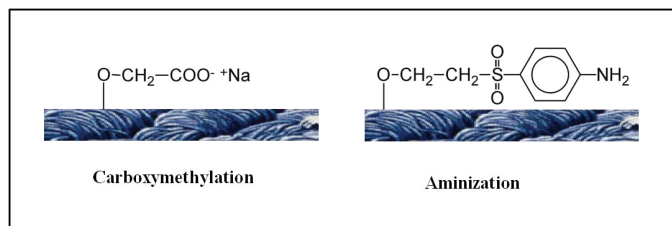


Figure 9. Chemical activation of cotton.

The chemical modification of cotton surface has been confirmed by XPS analysis [11]. 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 centre (S=O) and the free amino groups on the cotton surface (Figure 9).

3.2 Physical cotton activation

The aim of cotton fabric treatment with low-temperature plasma (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 [15]. Depending on the nature of the plasma gas used, different modification is expected. Ward et al. [16] 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 [17].

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 [17]. 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 more rough; 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 fibre 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 (Table 1). 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 containing 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 [18]; 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.%).

Sample	Elemental composition (at.%)			Atomic ratio	
	C 1s	O 1s	N 1s	O/C	N/C
UnC	66.8	33.2		0.5	
Air-PC	57.8	42.2		0.73	
N-PC	59.1	40.0	0.9	0.68	0.015
Ar-PC	58.9	41.1		0.70	

The error associated with each measurement is <5% of the reported value.

Table 1. Elemental composition and atomic ratio for untreated (UnC), air plasma (Air-PC), nitrogen plasma (N-PC) and argon plasma (Ar-PC) treated cotton.

4. Microgel incorporation

PNCS microgel was incorporated by a simple *pad-dry* procedure 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.

The state diagram previously elaborated (Figure 8) has been used to optimize the conditions of incorporation. Since cotton surface is hydrophilic, the first step of the procedure was an immersion of textile samples into a suspension of PNCS microgel at pH 5 and room temperature for two hours.

Surface features of untreated and previously activated cotton samples with incorporated PNCS microgel were studied by SEM (Figure 10). 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 microgel particles 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 (Figure 10a) does not show clear evidence of microgel particle surface deposition, i.e. there is no significant visual change in comparison with the control sample.

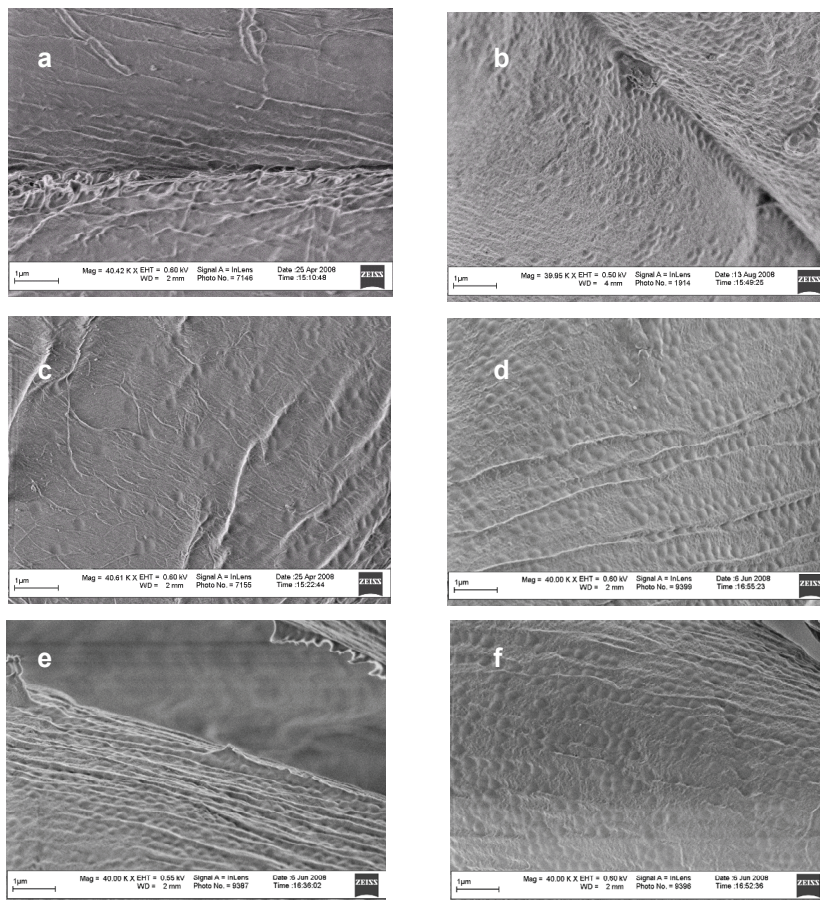


Figure 10. SEM images after PNCS microgel incorporation: untreated cotton (a); carboxymethylated cotton (b), aminated cotton (c); air plasma treated cotton (d); nitrogen plasma treated cotton (e); and argon plasma treated cotton (e).

XPS analysis was used to determine the surface chemical composition changes of cotton after microgel incorporation [11, 17]. After incorporation of PNCS microgel, all samples show the presence of nitrogen in significantly higher amount than in nitrogen plasma treated cotton (Table 2). 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 (Figure 10-a), 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 micro-particles (see Figure 3) 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.

Sample	Elemental composition (at.%)			Atomic ratio	
	C 1s	O 1s	N 1s	O/C	N/C
UnC-PNCS	68.3	26.7	4.6	0.41	0.06
CmC-PNCS	65.5	29.0	5.2	0.44	0.08
AmC-PNCS	64.0	31.8	3.9	0.49	0.06
Air-PC-PNCS	64.9	29.9	5.2	0.46	0.08
N-PC-PNCS	66.3	27.6	6.0	0.42	0.09
Ar-PC-PNCS	65.7	28.2	6.1	0.43	0.09

The error associated with each measurement is <5% of the reported value.

Table 2. Elemental composition and atomic ratio for differently functionalized cotton after incorporation of PNCS microparticles.

These results lead to the conclusion that plasma treatments lead to improved 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 as an

environmentally friendly process, which guarantees the high quality of the material with minimum costs and technological waste [19].

5. Conclusion

This work presents the results obtained for the first two years research period of Advanbiotex project. The first work package (WP1) of the project, which is “the preparation and characterization of the surface modifying system (SMS)” is the main core of the whole project and contains the most important scientific challenges for achieving successful surface modification of textile material. Moreover some of the tasks from the WP2 and WP3 (“modification of the textile material” and “incorporation of the SMS”, respectively) have been also accomplished. The most significant achievements of this research are: (1) the preparation and characterization of the PNCS dual responsive (pH and temperature) hydrogel in a micro-scale; (2) the establishing the innovative strategy of a simple batch treatment procedure (without grafting) for incorporating dual responsive microgel to the previously activated cotton fibre. The capability of functionalized textile material to respond to the different stimuli has been evaluated in the later steps of the project. In addition, in order to obtain satisfying durability of the textile surface functionalization, PNCS microgel can be covalently bonded to textile using appropriate crosslinking agent.

References

- [1] M. Prabakaran, J.F. Mano, Stimuli-Responsive Hydrogels Based on Polysaccharides Incorporated with Thermo-Responsive Polymers as Novel Biomaterials, *Macromolecular Bioscience*, **6**, Issue 12, 991-1008 (2006).
- [2] M.N.V. Ravi Kumar, A review of chitin and chitosan applications, *Reactive & Functional Polymers*, **46**, Issue 1, 1-27 (2000).
- [3] M. Rinaudo, Chitin and chitosan: Properties and applications, *Progress in Polymer Science*, **31**, Issue 7, 603-632 (2006).
- [4] H.G. Schild, Poly(N-isopropylacrylamide): experiment, theory and application, *Progress in Polymer Science*, **17**, 163-249 (1992).
- [5] R.H. Pelton, P. Chibante, Preparation of aqueous lattices with N-isopropylacrylamide, *Colloids and Surfaces*, **20**, Issue 3, 247-256 (1986).
- [6] C. Lee, C. Wen, W. Chiu, Synthesis of Poly(chitosan-N-isopropylacrylamide) Complex particles with the Method of Soapless Dispersion Polymerization, *Journal of Polymer Science Part A: Polymer Chemistry*, **40**, Issue 13, 2053-2063 (2003).
- [7] C. Lee, C. Wen, C. Lin & W. 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**, Issue 12, 3029-3037 (2004).
- [8] R.A.A. Muzzarelli, *Chitin*, Pergamon Press, ISBN 0080203671, Oxford (1977).

- [9] R.H. Pelton, & P. Chibante Preparation of aqueous lattices with N-isopropylacrylamide, *Colloids and Surfaces*, **20**, Issue 3, 247-256 (1986).
- [10] A. Tourrette, M.M.C.G. Warmoeskerken and D. Jocić, Technological importance of poly-NiPAAM/chitosan microgel suspension phase behaviour for functional finishing of textiles (in writing process for *Macromolecular Short Communication*).
- [11] 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**, No. 1, 14-23 (2009).
- [12] M. Hashem, P. Hauser, B. Smith, Wrinkle Recovery for Cellulosic Fabric by Means of Ionic Crosslinking, *Textile Research Journal*, **73**, No. 9, 762-766 (2003).
- [13] I. Racz, J. Borsa, G. Bodor, Crystallinity and Accessibility of Fibrous Carboxymethylcellulose by Pad-Roll Technology, *Journal of Applied Polymer Science*, **62**, Issue 12, 2015-2024 (1996).
- [14] S.Y. Kim, A. Zille, M. Murkovic, G. Guebitz, A. Cavaco-Paulo, Enzymatic polymerization on the surface of functionalized cellulose fibers, *Enzyme and Microbial Technology*, **40**, Issue 7, 782-787 (2007).
- [15] R. Li, L. Ye, Y.W. Mai, Application of plasma technologies in fibre-reinforced polymer composites: a review of recent developments, *Composites Part A: Applied Science and Manufacturing*, **28**, Issue 1, 73-86 (1997).
- [16] T.L. Ward, H.Z. Jung, O. Hinojosa, R.R. Benerito, Effect of cold plasmas on polysaccharides, *Surface Science*, **76**, Issue 1, 257-273 (1978).
- [17] 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).
- [18] F. Osenberg, D. Theirich, A. Decker, J. Engemann, Process control of a plasma treatment of wool by plasma diagnostics, *Surface and Coatings Technology*, **116-119**, 808-811 (1999).
- [19] N. Careiro, A.P. Souto, E. Silva, Dyeability of corona-treated fabrics, *Coloration Technology*, **117**, No. 5, 298-303 (2001).

Chapter 7

Functionalization of Textile Materials with Stimuli-responsive Microgel: Study of Liquid Management Properties

Pavla Križman-Lavrič
Engineering of Fibrous Smart Materials (EFSM)
Faculty of Engineering Technology (CTW)
University of Twente, Enschede
The Netherlands

1. Introduction

The aim of the research presented in this chapter was to prepare cotton fabrics with "intelligent" liquid management properties by functional finishing with stimuli-responsive microgel. The targeted use of these fabrics is in performance apparel, where the added value of controlled ("on-demand") liquid management could enable the transformation of cotton into an advanced material. Functional finishing using the surface modification approach is expected to introduce advanced properties to the material without impairing its intrinsic properties, which currently make cotton the most widely used textile material.

Stimuli-responsive microgel, based on a biopolymer (chitosan) and a synthetic polymer (poly-NiPAAm), has been prepared as described in the chapter 6 of this book. The incorporation of microgel to textile fabrics was achieved by a simple pad-dry-cure procedure, using a surface modifying system that contained aqueous microgel dispersion and 1,2,3,4-butantetracarboxylic acid (BTCA) as a crosslinking agent. With BTCA, a known durable-press finishing agent, we were able to meet our main challenge of integrating the microgel into the fabric's structure and make it sufficiently durable. This application method results in a thin film coating of cotton fibres with good resistance to washing without impairing the beneficial intrinsic properties of cotton.

To accomplish the development and evaluation of this new textile material with advanced functionalities, my research tasks were highly multidisciplinary, combining the fields of material science, polymer chemistry and surface chemistry. My main goals were to study the:

- methods and processes for functional finishing of fibrous materials,
- thermodynamic and kinetic aspects of transport phenomena in responsive functionalized textile material,

- material properties, such as: roughness, handle, wetting and other comfort characteristics.

2. Preparation of poly-NiPAAm/chitosan (PNCS) microgel

A stimuli-responsive microgel based on a thermo-responsive polymer (poly-NiPAAm) and pH-responsive polymer (chitosan) has been prepared by a surfactant-free emulsion polymerization method in the presence of ammonium persulfate and methylenebisacrylamide as reported by Kulkarni et al. [1].

2.1 Surface characterization of PNCS microgel

The surface morphology of air dried PNCS microgel dispersion was determined by scanning electron microscopy (SEM) and the obtained micrographs showed particles of a spherical shape and particle size ~ 200 nm (in dry state) [2]. However, when it comes to determining the size and the structure of microgel particles, transmission electron microscopy (TEM) is often the instrument of choice (Figure 1) and a negative staining method with uranyl acetate (UA) can be used to confirm the morphological features [3]. It is known that uranyl salts bind primarily to the negatively charged groups. However, under usual staining conditions UA does not react exclusively with negatively charged groups. According to the literature [4], positively charged groups also participate in binding with uranyl ions. This is expected because UA is only weakly dissociated and a variety of ionic uranyl complexes (cationic, anionic, and neutral) coexist in aqueous solution.

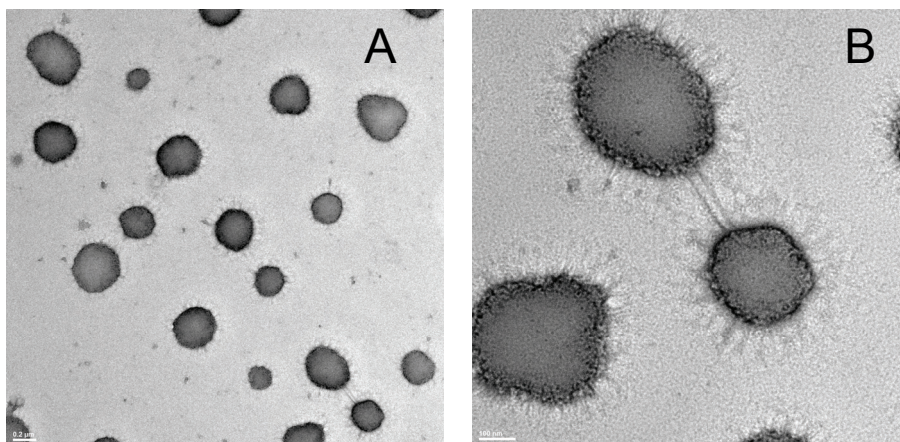
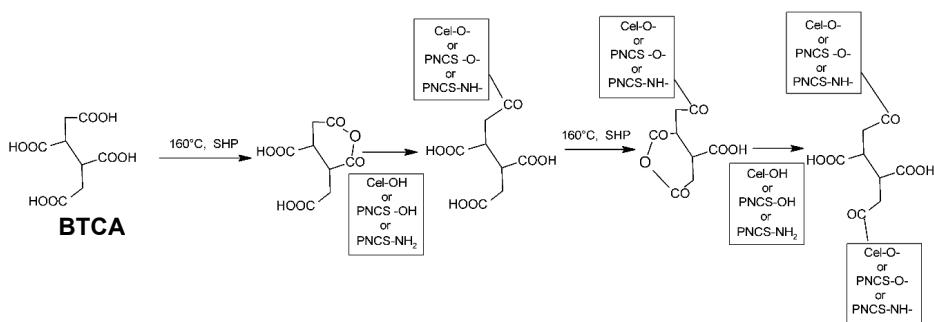


Figure 1. TEM micrograph of poly-NiPAAm/chitosan microgel particles at magnification of 5200x (A) and 16000x (B).

Poly-NiPAAm has no charge by itself. However, when the initiator APS is present, enough negatively charged groups (i.e. sulphonic) are present for UA to bind. Moreover, chitosan's free amino groups are available for binding with UA, which has been characterized as a "pendant complex" [5]. From the results obtained by staining PNCS microgel with UA, it can be seen that the microgel particles have a spherical form (Figure 1A) as it was confirmed by SEM. It is believed, that the particles have a homogenous inner structure containing both poly-NiPAAm and chitosan and that their outer layer consists of chitosan only (Figure 1B). Moreover, it can be noticed that after being stained with UA some leaching trails can be observed in the immediate vicinity of the microgel particle, causing a "sunflower-like" effect. The leaching trails might be the result of the drying process before the TEM image was taken. It seems that the outer layer is bound relatively weakly and that with water even some chitosan leached out.

3. Incorporation of PNCS microgel onto cotton surface

The incorporation of PNCS microgel to cotton fabric was achieved by a simple pad (100% WPU) - dry (90°C, 1h) - cure (160°C, 3 min) procedure, using the surface modifying system that contained aqueous PNCS microgel dispersion and 1,2,3,4-butanetetracarboxylic acid (BTCA) as a crosslinking agent. The main advantage in using BTCA for PNCS microgel incorporation is that previous activation of cotton surface is not needed. The proposed mechanism of PNCS crosslinking on cotton using BTCA was reported by Kulkarni et al. [1]. In short, in the presence of a catalyst, BTCA forms an anhydride during the curing stage which readily reacts either with hydroxyl groups of cellulose or of chitosan present in the shell of PNCS microparticles. It is believed that it can react even with free amino groups of chitosan forming an amide. As a result, PNCS microgel particles become chemically linked to cotton.



Scheme 1. Proposed mechanism of PNCS crosslinking on cotton using BTCA [1].

3.1 Surface characterization of modified cotton (Co-PNCS/BTCA)

The purpose of characterizing the surface of the functionalized material was to determine the efficiency of PNCS microgel incorporation onto cotton surface by using BTCA as a crosslinker. For this purpose two approaches were undertaken. Firstly, the quantity of accessible BTCA carboxylic groups was determined spectrophotometrically by staining the samples with methylene blue dye and secondly, the presence of PNCS microgel was confirmed by SEM, XPS and FT-IR analysis.

In order to establish the most appropriate mass fraction of BTCA and PNCS microgel in the impregnation bath for sufficient crosslinking of PNCS microgel on cotton fibres, various concentrations of BTCA (from 0.1 to 3%) were applied, keeping the amount of PNCS microgel constant (2%). In addition, BTCA was applied on cotton fabric alone, without PNCS microgel. The obtained results are presented elsewhere [6]. As expected, the degree of crosslinking cotton cellulose to BTCA increased proportionally to the increase in percentage of BTCA applied. A similar tendency was noticed in the case of crosslinking cotton cellulose to BTCA and PNCS microparticles (Co-PNCS/BTCA), the only difference being that less carboxyl groups were measured, since part of BTCA is consumed in linking chitosan to cellulose substrate. By knowing the number of carboxylic groups available we were able to determine the proper concentration of BTCA for efficient crosslinking of cellulose hydroxyl groups with BTCA and/or chitosan.

In a second step the efficiency of PNCS microgel incorporation to cotton was studied by varying the amount of PNCS microgel from 1 to 4%, while the ratio BTCA:PNCS was kept constant and equal to 1:3.75.

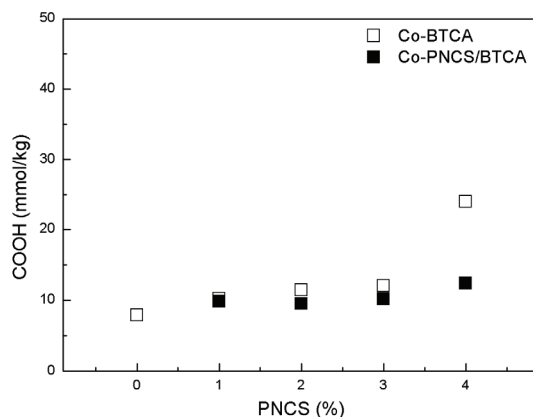


Figure 2. Carboxyl content (mmol/kg) vs. PNCS concentration (% owf).

As it can be seen from Figure 2, sufficient crosslinking of PNCS microgel on cotton fibres occurred at lower concentration of PNCS. If the amount of PNCS

microgel was increased over 3%, it resulted in a higher amount of available carboxyl content, meaning that not all carboxyl groups were included in the crosslinking reaction. These findings, together with our aim to maintain the positive properties of cotton, suggest that 2% of PNCS microgel should be applied, since it covers only up to 50% of the fibre surface. The SEM analysis gave visual confirmation for this assumption.

Furthermore, a structural analysis of the samples treated by BTCA and PNCS microgel of various concentrations (in same manner as for carboxyl content measurement) was done by Fourier transform infrared (FT-IR) spectroscopy. Due to the low concentration of BTCA used, no structural changes were observed from IR ATR spectra of cotton by concentrations of BTCA lower than 1%. However, when more than 1% of BTCA was used, namely 1.5 and 3%, the absorption band at 1720 cm^{-1} characteristic for the ester carbonyl group appeared, whereas its intensity increased by increasing the concentration of BTCA. Since this absorption band overlaps with the absorption band characteristic for the carboxyl carbonyl group of the uncrosslinked BTCA [7-10], dried samples were exposed to the ammonium vapour, causing transformation of the carboxyl groups into the carboxylate, which gave rise to the absorption band at 1565 cm^{-1} . Consequently to the formation of the absorption band at 1565 cm^{-1} , a slight decrease of the intensity of the absorption band at 1720 cm^{-1} occurred, thus showing the presence of ester groups only and undoubtedly confirming the chemical reaction between BTCA and cotton fibres. By increasing the concentration of BTCA the intensity of the carboxylate absorption band increased.

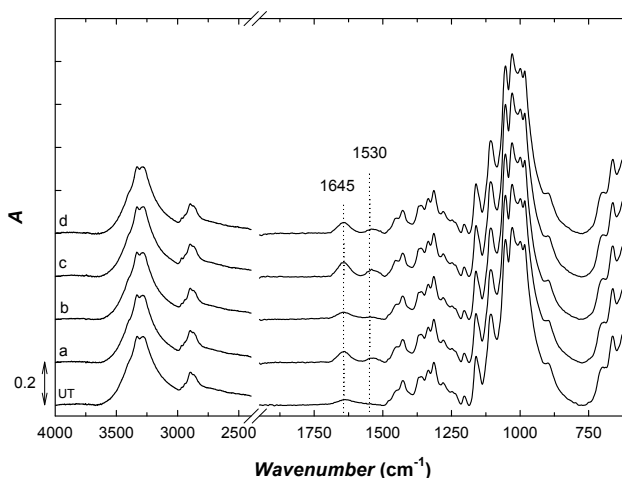


Figure 3. IR ATR spectra of Co-UT and Co-PNCS/BTCA, where the concentration of PNCS was increased and the ratio of BTCA:PNCS was kept at 1:3.75. Samples: UT - untreated, a – 1% PNCS, b – 2% PNCS, c – 3% PNCS, d – 4% PNCS.

Moreover, the structural analysis of the samples treated by BTCA and PNCS microgel revealed the absorption bands belonging to the amide I and II, appearing at 1645 and 1530 cm^{-1} (Figure 3). Since the concentration of applied PNCS increased (from 1 to 4%, while the BTCA:PNCS ratio was kept constant at 1:3.75), it was expected that the intensity of those absorption bands would increase in accordance to the PNCS concentrations. However, a detailed inspection of the IR spectra of the studied samples showed that the intensities of the absorption bands at 1645 and 1530 cm^{-1} did not significantly change by increasing the concentration of PNCS. Thus it can be concluded that, at a certain ratio between BTCA and PNCS, only a certain amount of microgel particles can bind to cotton fibres and that increasing the concentration of PNCS from 1 to 4% had no influence on the increase of the deposition of the microgel particles on the cotton fibres.

The presence of PNCS microgel on cotton was confirmed by XPS analysis as well. The surface chemical composition was determined and presented already elsewhere [11]. In short, XPS survey spectra confirmed that PNCS microgel was successfully incorporated to cotton. 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.%), when compared to theoretical values for chitosan 9.0 and poly-NiPAAm 12.5, 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. Additionally, the surface chemical composition was studied on washed samples. After 5 repetitive washings a satisfying durability was obtained since nitrogen was detected, its content being 1.4 at.%. Since the washings were done at severe washing conditions (60°C, 45 min) with a nonionic detergent, a higher reduction (in this case of 70%) was expected. A visual confirmation of the presence of PNCS microparticles after 5 washings was given by SEM.

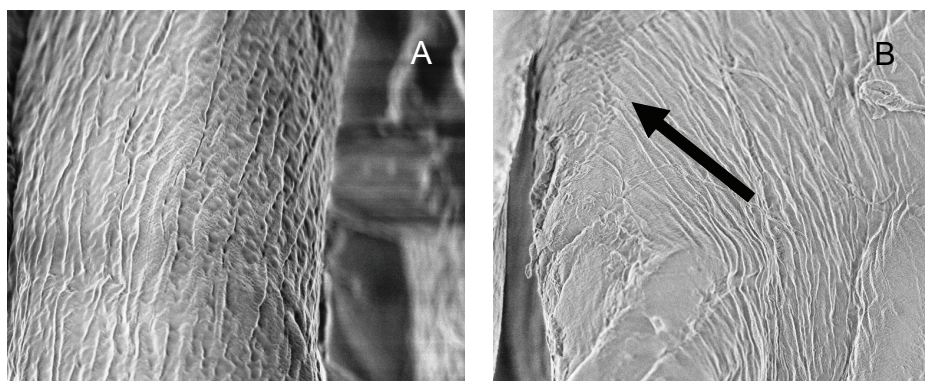


Figure 4. SEM images of Co-PNCS/BTCA after 1 washing (A) and of Co-PNCS/BTCA after 5 washings (B) taken at magnification of 5000x.

On Figure 4 it can be seen that after 1 washing a thin layer of PNCS microgel is still present on the cotton surface. However, after 5 washings, due to severe washing conditions, most of the cuticle is damaged (peeled off) which is the reason of PNCS microgel removal.

4. Assessment of functionalised materials responsiveness

After the incorporation of PNCS microgel onto the cotton surface was confirmed by SEM, XPS and FT-IR, the responsiveness of the functionalized material had to be assessed. 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 is the determination of water uptake. The measurements of the amount of water absorbed by fabrics such as moisture regain, moisture sorption isotherms, water retention and absorptive capacities are of great importance in order to study the interactions between water and textiles [12].

Since liquid management properties often refer to the transmission of both moisture and liquid through the textile material, the methods used and listed in Table 1 will be divided in two subsections according to the form of water used, i.e. moisture and liquid management.

Parameter measured	Abbreviation	Device/Method
Moisture regain	MR	ASTM D 629-77
Moisture content	MC	Moisture analyzer
Water vapour transmission rate	WVT	UNI 4818-26
Water retention value	WRC	DIN 53814
Water uptake	WU	Gravimetric method
Wicking rate	TLW	Thin-layer wicking method [13,14]

Table1. Methods used for studying liquid management properties.

4.1 Moisture management properties

It has been previously published that the liquid/moisture management properties of microgel functionalized textile depend on temperature and humidity [2, 11, 15]. Therefore, 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) of 32°C, which is the lower critical solution temperature (LCST) of poly-NiPAAm.

Our expectations were that due to the thermo-responsiveness of poly-NiPAAm the functionalized material will absorb more water at temperatures below its transition temperature, while absorbing less water when above it. Below LCST

the amide group binds water molecule via hydrogen bonding, above LCST hydrogen bonds break and the polymer expels water.

The results presented in Figure 5 show that, when exposed to changes in ambient humidity and temperature, cotton material with incorporated PNCS microgel responds by changes in moisture regain. Moisture regain results follow the known fact that the moisture content of material decreases with temperature increase or ambient humidity decrease, which can be observed with both untreated and functionalized material. However, since the presence of water (in this case water vapour) is the driving force for the thermo-responsiveness of PNCS microgel, different behaviour can be observed at low and at high ambient humidity. As it can be seen from Figure 4, only at 80%, when enough humidity is available, we can observe noticeable differences in the functionalized cotton behaviour in response to temperature change.

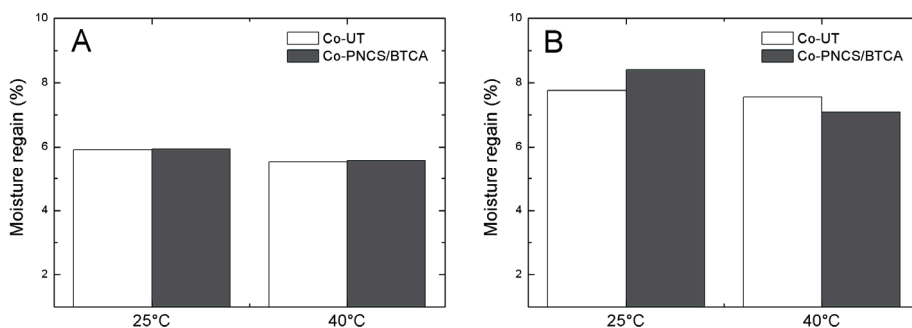


Figure 5. Moisture regain of Co-UT and Co-PNCS/BTCA at 50% R.H. (A) and at 80% R.H. (B).

A similar responsive behaviour was noticed by measuring the moisture content. The combined effect of temperature and ambient humidity on moisture content (MC) and water vapour transport rate (WVT) of Co-UT and Co-PNCS/BTCA, obtained by using statistical software for process optimization (CCD), is presented in Figure 6 [2].

The transfer of moisture (water vapour) through the porous structure of the functionalized material is directly related to the ability of the material to absorb moisture. As expected, the moisture content of the functionalized material increases with decreasing temperature and increasing relative humidity, while the water vapour transmission through the porous structure of the functionalized material increases with increasing temperature and decreasing relative humidity.

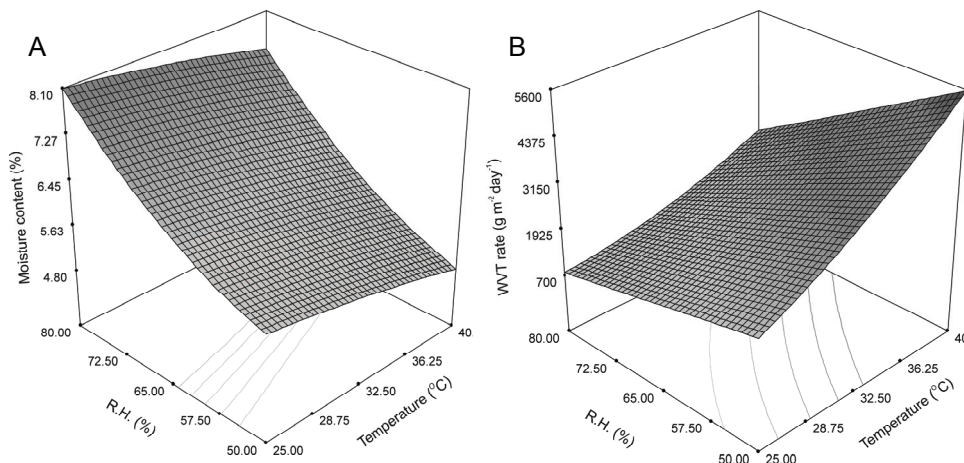


Figure 6. Moisture content (A) and water vapour transport rate (B) of Co-UT and Co-PNCS/BTCA at different conditioning parameters [2].

4.2 Liquid management properties

When referring to liquid management properties, the functionalized material was in contact with water in its liquid form. Parameters measured were water uptake, water retention value and thin layer wicking. The advantage of using water is that both the thermo-responsiveness of poly-NiPAAm and the pH-responsiveness of chitosan can be studied at the same time. Chitosan responds to changes in the pH of the surrounding media by swelling/deswelling. The response is triggered by functional amino groups, which acquire a positive charge in acidic medium. Therefore, three different pH values were chosen, namely pH 3, 6.5 and 10.

It was expected that due to the pH-responsiveness of chitosan more water will be absorbed by the functionalized material in acidic medium, while less water will be absorbed in alkaline medium compared to the untreated sample. Water uptake results, which are presented elsewhere [6], confirmed an increased water uptake capacity of the functionalized material at low pH values at room temperature, which is the consequence of chitosan pH-responsiveness. In an alkaline environment (pH 10) the level is nearly the same as in the case of untreated sample. A decreased water uptake capacity was noticed at higher temperature due to the influence of poly-NiPAAm, which added a hydrophobic character to the microgel. The difference becomes more prominent at higher temperature and at pH 10, since both poly-NiPAAm and chitosan are hydrophobic. Furthermore, a contribution of the surface incorporated PNCS microgel to water uptake was calculated and presented in Figure 7. At 25°C, the pH-responsive behaviour of chitosan prevails and water uptake decreases when pH rises from pH 3 to pH 10. At 40°C, water uptake decreases further, due to the hydrophobic effect of poly-NiPAAm, reaching the lowest value at pH

10 as a result of a synergistic effect of both poly-NiPAAm and chitosan. Same synergistic effect of poly-NiPAAm and chitosan can be clearly seen even in acidic conditions at room temperature, where both of them are hydrophilic. The obtained c_{WU} values confirmed the responsiveness of the functionalized material in response to external stimuli, such as temperature and pH.

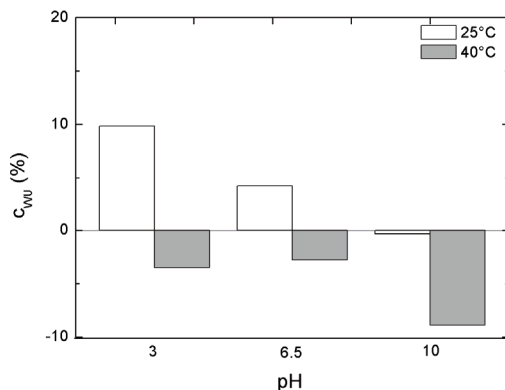


Figure 7. Contribution (c_{WU}) of the surface incorporated PNCS microgel to water uptake (WU) of Co-PNCS/BTCA (compared to Co-UT) determined at different pH and temperature.

However, water uptake gives an estimate how much water is absorbed by the fibres, which means the cumulative amount of both bound and free water. Free water is being held by surface tension in capillary spaces within a fibre and it can be partially removed by centrifugation. Therefore, the quantity of water that can be retained by the fibres can be determined by calculating the water retention capacity of centrifuged samples. In our case, the amount of liquid retained by swelling depends both on intrinsic swelling properties of cotton and on the responsive behaviour of PNCS microgel particles. From the results obtained after immersing both Co-UT and Co-PNCS/BTCA into three different buffer solutions (i.e. pH 3, 6.5 and 10) for 24 hours at temperature below (25°C) and above (40°C) the transition temperature of poly-NiPAAm, with centrifuging the samples after that, we were able to see that the most pronounced WRC was found to be in an acidic environment at 25°C as a result of a synergistic effect of poly-NiPAAm and chitosan. Additionally, these considerations were confirmed quantitatively by calculating contributions due to the presence of PNCS microgel on the surface of cotton (Figure 8). At 25°C, water retention is completely regulated by pH-responsive behaviour of chitosan, since it decreases when pH increases. A similar trend has been confirmed by water uptake measurements. At 40°C, a dominant effect due to chitosan can still be seen at acidic conditions, while at higher pH values, where both chitosan and poly-NiPAAm are hydrophobic, an opposite effect would be expected. The

reason might be in the thin layer of a surface modifying system covering the fibre surface which acts as a barrier obstructing the diffusion processes.

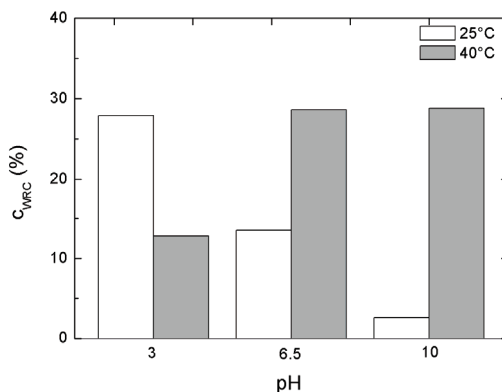


Figure 8. Contribution (c_{WRC}) of the surface incorporated PNCS microgel to water retention capacity (WRC) of Co-PNCS/BTCA (compared to Co-UT) determined at different pH and temperature.

Thin layer wicking (TLW) is often used to determine the theoretical value of the effective capillary radius and to determine how fast a sample gets soaked by a testing liquid. However, in our case it was used to determine the ability of PNCS microgel particles to swell in contact with water. The effective capillary radius (R) was determined from the results of the wicking rate of n-heptane for two series of samples; completely dry and preconditioned samples. The wicking rate was obtained by measuring the liquid penetration distance at different time. R was then calculated according to the Washburn equation, where the liquid penetration rate obtained from the plots of distance vs. time was included.

Sample	Absolutely dry samples		Preconditioned in standard atmosphere (65% R.H., 20°C)	
	k	$R \times 10^6$ (m)	k	$R \times 10^6$ (m)
Co-UT	0.24	1.70	0.17	2.40
Co-PNCS/BTCA	0.20	2.04	0.19	2.15

Table 2. The slope k and the apparent capillary radius R , obtained from the thin-layer wicking measurements with n-heptane on samples previously saturated with n-heptane (absolutely dry samples) and samples preconditioned in standard atmosphere.

The obtained results presented in Table 2 show that when the PNCS microgel particles are in their dry state (absolutely dry samples) R of functionalized material is bigger compared to R of untreated cotton. Two explanations could

be plausible in this case. Firstly, that the increased R is the consequence of an increased capillarity of the surface modifying layer made of PNCS microgel, and secondly, that the contribution of intrayarn pores to the R is considerably lower than the contribution of interyarn pores. When the samples were preconditioned, an opposite effect was noticed. Due to the swelling of PNCS microgel particles, both type of cotton pores (intra-yarn and inter-yarn) were enclosed, which resulted in a slower penetration rate.

5. Material properties

Since the PNCS/BTCA incorporation may impart changes not only to the fabric surface but also to the overall fabric appearance and properties, whiteness index (WI) and crease recovery angle (CRA) of Co-BTCA and Co-PNCS/BTCA were measured. A known drawback in using BTCA is the decrease in cotton whiteness [16]. However, in our case no significant changes were noticed in WI values when comparing either Co-PNCS/BTCA or Co-BTCA to untreated cotton. Even when increasing the PNCS concentration or BTCA concentration, the WI remained almost the same (from 77.3 for untreated to 76.3 for the highest concentration of PNCS or 76.5 for the highest concentration of BTCA).

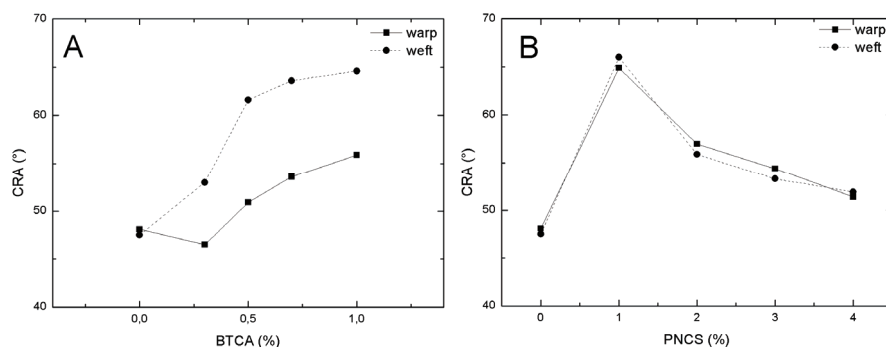


Figure 9. Crease recovery angles (CRA) measured on samples coated with different amounts of BTCA (A) and different amounts of PNCS (B).

However, as it can be seen from Figure 9A, CRA of Co-BTCA increases with increase in the concentration of BTCA. If the concentration of BTCA is kept constant (Figure 9B), CRA of Co-PNCS/BTCA increases with the increase in PNCS up to 1%, decreasing afterwards due to the stiffness imparted by the presence of PNCS microgel. In fact, tactile properties changed with increased PNCS concentration, resulting in increased stiffness of the fabric.

6. Conclusions

In the final year of the Advanbiotex project the focus was mainly on the evaluation of the responsiveness of functionalized materials to ambient conditions (pH, temperature and humidity). As it has been shown in this chapter, by using a simple pad-dry-cure method with BTCA as a crosslinker, the microgel particles bind to cotton via covalent bonds, which offers a satisfactory level of durability. Cotton fibres with a thin film coating that have good resistance to washing are the result of this method. The biggest achievement of this method is that it is simple, efficient and industrially acceptable. It also allows us to control the level of add-on and with that the coverage of fibres with the microgel simply by changing the percentage of wet pick-up. However, in order to maintain the positive properties of cotton, no more than 50% of the surface should be covered by microgel particles.

To conclude, we were able to show that the controlled expansion or contraction of the surface incorporated microgel particles provides the textile material with "intelligent" liquid management properties and that the advanced material obtained reacts satisfactorily to the changes in ambient conditions. This opens up the possibility of using such functionalized cotton as an advanced material for performance apparel, exploiting the controlled ("on-demand") liquid management.

References

- [1] A. Kulkarni, A. Tourrette, M.M.C.G., Warmoeskerken, D. Jocić, Microgel-based surface modifying system for stimuli-responsive functional finishing of cotton, *Carbohydrate Polymer*, **82**, 1306-1314 (2010).
- [2] 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).
- [3] M.F. Leung, J. Zhu, F.W. Harris, P. Li, New route to smart core-shell polymeric microgels: synthesis and properties, *Macromol. Rapid Commun.*, **25**, 1819-1823 (2004).
- [4] M.A. Hayat, *Principles and techniques of electron microscopy: biological applications*, 4th Edition, Cambridge University Press, Cambridge (UK), 345.
- [5] J. Grant, H. Lee, R.C.W. Liu, C. Allen, Intermolecular Interactions and Morphology of Aqueous Polymer/Surfactant Mixtures Containing Cationic Chitosan and Nonionic Sorbitan Esters. *Biomacromol.*, **9**, 2146-2152 (2008).
- [6] D. Jocić, A. Tourrette, P. Križman Lavrič, Biopolymer-based stimuli-responsive polymeric systems for functional finishing of textiles, in *"Biopolymers"*, M. M. Elnashar Ed., Sciyo, Rijeka (Croatia), 37-40 (2010).
- [7] G. Socrates, *Infrared and raman characteristic group frequencies*, New York: John Wiley & Sons, LTD, 347 (2001).

- [8] C.Q. Yang, X. Wang, Formation of Five Membered Cyclic Anhydride Intermediates by Polycarboxylic Acids: Thermal Analysis and Fourier Transform Infrared Spectroscopy, *Journal of Applied Polymer Science*, **70**, 2711-2718 (1998).
- [9] X. Gu and C.Q. Yang, FT-IR and FT-Raman spectroscopy study of the cyclic anhydride intermediates for esterification of cellulose: I. Formation of anhydrides without a catalyst, *Research on Chemical Intermediates*, **24**, 979-996 (1998).
- [10] O. Šauperl and K. Stana-Kleinschek, Differences between cotton and viscose fibres crosslinked with BTCA, *Textile Research Journal*, **80**, 383-392 (2010).
- [11] 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)*.
- [12] S.H. Zeronian, Analysis of the Interaction between Water and Textiles, in *"Analytical Methods for a Textile Laboratory"*, American Association of Textile Chemists and Colorists, NC, 117-127 (1984).
- [13] C.J. Van Oss, R.F. Giese, K. Murphy, J. Norris, M.K. Chaudhury, R.J. Good, Determination of contact angles and pore sizes of porous media by column and thin layer wicking, *J. Adhesion Sci. Technol.*, **6**, 413-428 (1992).
- [14] E. Chibowski, F. Gonzales-Caballero, Theory and practice of thin-layer wicking, *Langmuir*, **9**, 330-340 (1993).
- [15] 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).
- [16] A. Hebeish, M. Hashem, A. Abdel-Rahman, Z.H. El-Hilw, Improving easy care nonformaldehyde finishing performance using polycarboxylic acids via precationization of cotton fabric, *Journal of Applied Polymer Science*, **100**, 2697-2704 (2006).

Chapter 8

Modification of PES Fabric by Stimuli Responsive Microgel Using Sol-gel Technology

Brigita Tomšič^{1,2}

¹*Department of Textiles, Faculty of Natural Sciences and Engineering
University of Ljubljana, Ljubljana
Slovenia*

²*Engineering of Fibrous Smart Materials (EFSM)
Faculty of Engineering Technology (CTW)
University of Twente, Enschede
The Netherlands*

1. Introduction

In this paper, novel method of poly-NiPAAm/chitosan (PNCS) microgel incorporation on textile fabric by the use of sol-gel technology is presented. Namely, among methods for chemical modification of textile fibres, sol-gel technology takes an important place, enabling the preparation of textiles with new or improved functional properties. For this purpose, different sol-gel precursors can be used, with trialkoxysilanes ($R'-Si(OR)_3$), where R' stands for organic functional group, being the most representative ones. In the reaction of hydrolysis and subsequent condensation they form continuous polysiloxane film, which has the ability to physically entrap different additives. For this kind of physically modified polysiloxane matrix, better adsorption and even distribution of additives is characteristic in comparison to conventional finishing. Polysiloxane films are also characterised by thickness of only few 10 nm as well as by their simultaneous elasticity of polymer and hardness of ceramic [1-3].

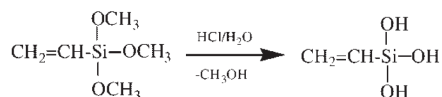
The aim of this work was to introduce new system for durable incorporation of PNCS microgel, which is distinguished by dual pH- and temperature-responsiveness. In this case, textiles with the ability of response to ambient conditions would be created, assuring comfort during wearing. Therefore, in order to achieve desired goal, sol-gel technology was introduced, using vinyltrimethoxysilane (VTMS) as a polysiloxane host matrix in a combination with hydrophilic fumed silica. It was believed, that due to the elastic properties of polysiloxane matrix, PNCS microgel responsiveness would not be affected, while at the same time its good washing durability would be achieved. As a substrate PES woven fabric (kindly supplied by Ten Cate Advanced Textiles,

The Netherlands) was chosen. After deposition of PNCS microgel incorporated into polysiloxane matrix, its morphological and chemical properties were analysed using scanning electron microscopy (SEM) and Fourier transform infrared (FT-IR) spectroscopy. Newly gained responsiveness of PES fabric to ambient conditions was characterised and evaluated applying already established methods, i.e. moisture content, water vapour permeability and water uptake. Washing durability of the functionalized coating was also determined.

2. Hydrolysis of VTMS

In order to obtain polysiloxane matrix, readily for physical incorporation of PNCS microgel, VTMS (Aldrich) precursor was firstly hydrolysed to form reactive silanol groups. As a catalyst 0.1 M HCl was used. The molar ratio between VTMS and acidified water was set to 1:3, so that each methoxy ($-\text{OCH}_3$) group of VTMS would react with one molecule of water. After the addition of acidified water the reaction of hydrolysis proceeded (Figure 1), causing replacement of $-\text{OCH}_3$ groups with hydroxyl ($-\text{OH}$) groups. In the subsequent reaction of condensation $-\text{OH}$ groups reacted between each other, forming siloxane bonds (Si-O-Si) and thus three-dimensional polysiloxane network.

a) Hydrolysis



b) Condensation:

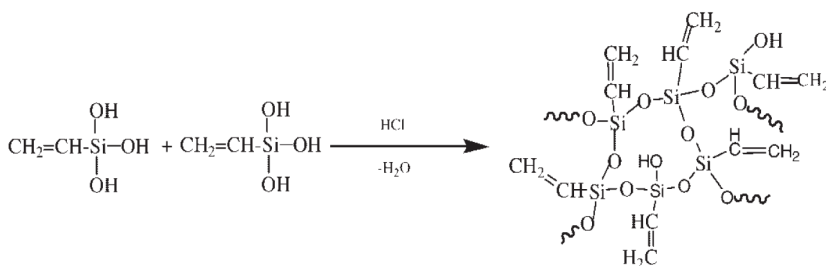


Figure 1. Schematic presentation of hydrolysis and condensation reactions of VTMS [4].

2.1 Assessment of VTMS hydrolysis

In order to confirm the reactions of hydrolysis and condensation, hydrolysed VTMS was applied on a Si-wafer by dip-coating technique and its attenuated total reflectance (ATR) spectrum was recorded using Fourier transform infrared (FT-IR) spectroscopy. From Figure 2 absorption band characteristic for vinyl groups can be seen at 1600 cm^{-1} , while absorption bands belonging to the Si-O and Si-O-Si vibrations appeared at 1010 , 1108 and 1056 cm^{-1} , the latter two undoubtedly confirming the formation of VTMS oxide matrix [4-7]. Beside, the presence of small intensity absorption band at 820 cm^{-1} belonging to the Si-CH₃ vibrations indicated that small amount of VTMS remained unhydrolysed, but its intensity was negligible in comparison to the strong absorption band at 900 cm^{-1} , ascribed to the silanol groups.

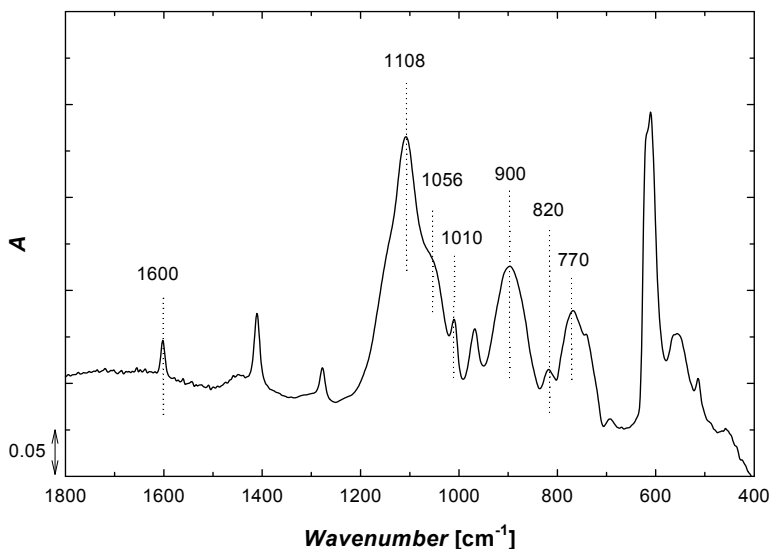


Figure 2. IR ATR spectrum of hydrolysed VTMS deposit on a Si-wafer and subsequently heat treated at 150°C .

3. Application of PNCS microgel to PES fabric

3.1 Chemical activation of PES

It is well known that there is only a small number of functional groups in the structure of PES fibres, which are not sufficient to assure chemical bonding of the polysiloxane matrix to the fibre. In order to overcome this problem, the surface of PES fibres was modified by photo-induced UV grafting. Namely, this is an attractive way to impart a variety of functional groups to a polymer, but without causing serious impairment to the mechanical properties of the bulk polymer [8-10]. Therefore, in order to activate PES fibres procedure according

to Song was used [11]. PES fabric was treated by the solution of acrylic acid (AA) and benzophenone (BP) (90 wt% AA and 10 wt% BP), followed by UV curing. Namely, according to the literature [11] this kind of treatment results in the incorporation of $-\text{OH}$ functional groups onto the PES fibres (Figure 3) as well as their increased surface roughness.

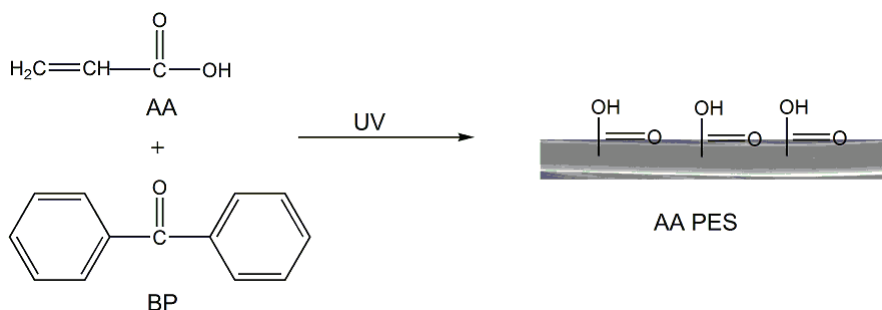


Figure 3. Schematic presentation of the photo-induced acrylic acid (AA) monomer grafting onto PES fibres [11].

3.2 Assessment of PES activation

To confirm chemical and morphological alteration of the PES fibres after UV grafting, ATR FT-IR spectroscopy and scanning electron microscopy (SEM) were performed, and the results were compared to those obtained for the untreated PES fabric.

From the IR ATR spectra of untreated and AA treated PES (Figure 4) the following bands, characteristic for the polyester fibres, could be observed: the absorption bands at 848, 793 and 721 cm^{-1} caused by the C-H and C-C vibrations of the benzene ring; the absorption bands at 1372, 1338, 1240 and 1095 cm^{-1} , belonging to the $\delta(\text{C-O})$ and $\nu_{as}(\text{C-O-C})$ vibrations of the polyester fibres; a band at 1578 cm^{-1} due to asymmetric stretching of the C-O bond of the carboxylate anion; an absorption band at 1720 cm^{-1} due to the strong C=O stretching vibrations of the carbonyl group of the ester bond; absorption bands in the $3000\text{--}2850\text{ cm}^{-1}$ spectral region due to the stretching vibrations of νCH_2 , νCH_3 and C-H; and band at 3430 cm^{-1} belonging to the intermolecular O-H bonds [12-15]. By comparing ATR IR spectra of untreated and AA treated PES fabric no differences could be observed. Namely, it would be expected that absorption band at 3430 cm^{-1} would increase in the spectrum of the activated PES fabric, due to the incorporation of $-\text{OH}$ functional groups. Unfortunately, this did not occur, showing that the degree of grafting and thus the concentration of $-\text{OH}$ groups were too small to be detected by the ATR FT-IR spectroscopy. Nevertheless, influence of AA treatment was undoubtedly confirmed from the SEM images (Figure 5). It can be seen that smooth surface of untreated PES fibres altered and became rougher, allowing better adhesion of the PNCS microgel particles into the rugged surface of fibres.

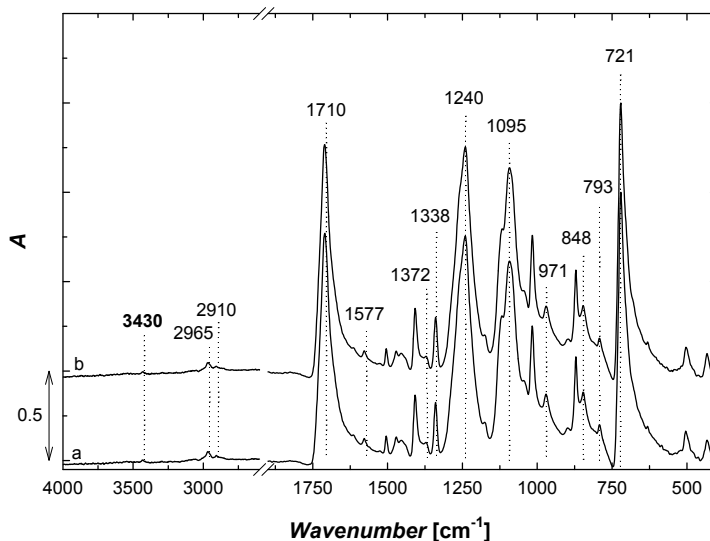


Figure 4. IR ATR spectra of untreated (a) and AA treated (b) PES fabric.

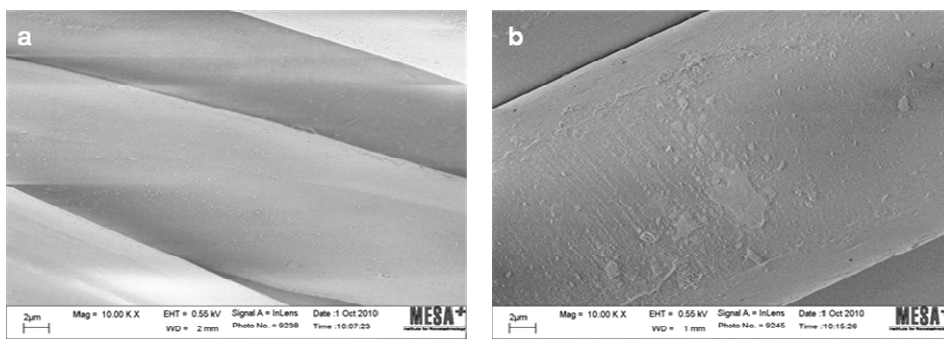


Figure 5. SEM images of untreated (a) and AA treated PES fibres (b).

3.3 Application process

In order to apply PNCS microgel in combination with polysiloxane matrix, two-phase process was used. First of all, hydrolysed VTMS solution was diluted to 4% in ethanol and 0.1% fumed silica nanoparticles (SiO₂) (Aerosil 2000, Evonik, Germany) were added and well mixed. Afterwards, 10% of benzophenone, as a photoinitiator, was added. In this manner prepared finishing bath, was applied to the AA activated PES fabric by the pad-dry-cure method, including full immersion at 20°C, with wet pick-up of 60±1% at 20°C

(laboratory padder) and 5 minute drying at 105°C. Secondly, PNCS microgel (23.7 g/l) was applied, using the same method and conditions as in the first stage. Before drying, finished PES fabric was exposed to the UV-radiation during 40 s, using UV black light (HQV, Osram), placed around 200 mm above the samples. Afterwards, the samples were dried for 5 minutes at 105°C and cured for 3 minutes at 160°C. In addition, PNCS microgel alone was applied as well, using pad-dry-cure method with wet pick-up of 60±1% at 20°C, followed by 5 minute drying at 105°C.

4. Characterisation of finished PES fabrics

4.1 Morphological properties

Morphological properties of the PNCS and VTMS/SiO₂-PNCS finished PES fibres were studied by SEM. In Figure 6 spherically shaped PNCS microgel particles can be observed, with an estimated size ranging up to 200 nm. When comparing SEM images of both studied samples, it can be observed that in the case where VTMS/SiO₂ matrix was present, more even distribution of the PNCS microgel particles was achieved. From Figure 6b (higher magnification), it also appears that PNCS microgel particles were covered by the VTMS polysiloxane matrix, confirming their successful embedding. It can be also seen that SiO₂ nanoparticles agglomerated and were distributed on the top of the VTMS/SiO₂-PNCS coating.

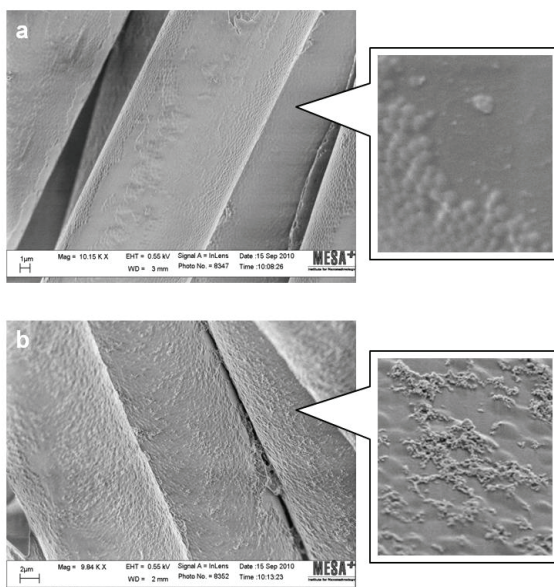


Figure 6. SEM images of the PNCS (a) and VTMS/SiO₂-PNCS (b) finished PES fabrics.

4.2 Chemical properties

The presence of microgel was further confirmed by the ATR FT-IR spectroscopy. From IR ATR spectrum of PNCS and VTMS/SiO₂-PNCS finished PES fabric (Figure 7) the appearance of absorption bands at 1645 cm⁻¹ belonging to the C=O stretching vibration of Amide I and at 1540 cm⁻¹ characteristic for the N-H deformation vibration of Amide II, arriving from poly-NiPAAm (while the latter overlapping with the -NH₂ bending of chitosan) were noticeable [5]. However, since those bands were interfered by the absorption band of PES at 1710 cm⁻¹, differential spectra was obtained by subtracting the IR ATR spectrum of unfinished sample from the IR ATR spectra of the finished samples (insert in Figure 7). It can be seen that both absorption bands were of higher intensity in the case of VTMS/SiO₂-PNCS treated PES sample, indicating that greater amount of microgel was absorbed on the PES fibres previously finished by the VTMS/SiO₂. Most likely, this occurred due to the presence of polysiloxane matrix along with SiO₂ nanoparticles, which made PES fibres more hydrophilic, enabling better absorption of the PNCS finishing bath.

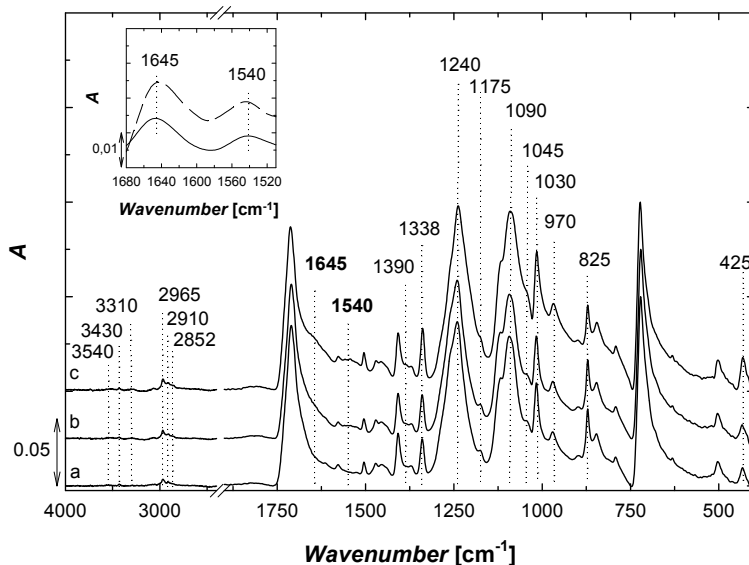


Figure 7. IR ATR spectra of unfinished (a) and PNCS (b) and VTMS/SiO₂-PNCS (c) finished PES samples. Insert: Differential IR ATR spectra obtained by subtracting IR ATR spectra of finished sample from unfinished (— PNCS; --- VTMS/SiO₂-PNCS).

From the spectrum of the VTMS/SiO₂-PNCS treated sample, absorption bands belonging to the VTMS/SiO₂ nanocomposite coating can be also observed, i.e. at 1090, 1030 and 970 cm⁻¹ arising due to the Si-O-Si and Si-O vibrations. Moreover, the absorption bands at 1175 and 1045 cm⁻¹ belonging to the C-O

and ester bond of the PES decreased in the case of VTMS/SiO₂-PNCS treated sample, further confirming the formation of the continuous VTMS film on the surface of the fibres by blurring the bands characteristic for PES. From the IR ATR spectra of both finished samples, the increase of the intensities of the absorption bands in the spectral region from 3000–2800 cm⁻¹, belong to the CH stretching vibration of the N-isopropyl groups, polymer backbone of poly-NiPAAm and chitosan as well as the absorption bands at 1390 and 1338 cm⁻¹, belonging to the CH₃ stretching as well as CH₃ and CH₂ deformation vibrations, were also observed. Besides, the formation of new absorption bands occurred at 3540, 3430 and 3310 cm⁻¹ characteristic for the hydrogen bonding N-H···OH as well as OH vibration [4-7].

4.3 Functional properties

4.3.1 Interaction of water with PNCS microgel incorporated to PES

In order to determine the swelling ability of PNCS microgel due to water absorption, the thin layer wicking (TLW) method was used, which enables the measurement of liquid penetration rate into the porous solid [16, 17]. In this case water was used as a liquid and absolutely dried finished and unfinished PES samples as a porous solid.

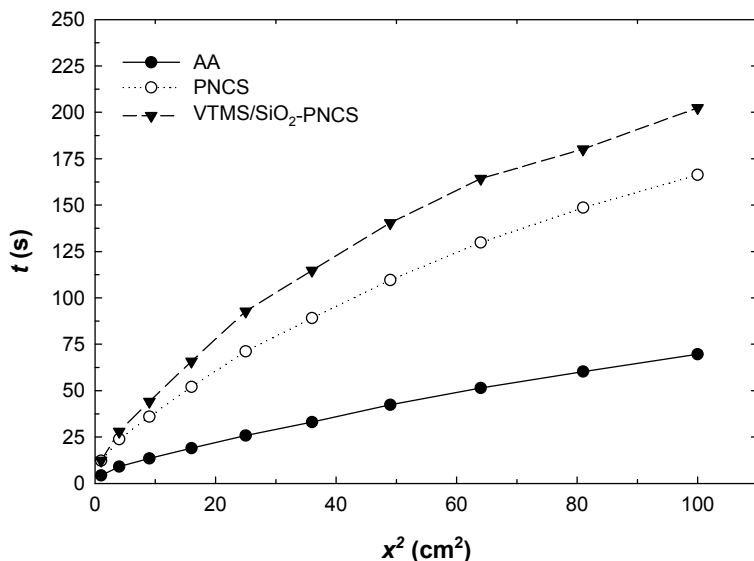


Figure 8. Water penetration rate curves obtained by the thin layer wicking (TLW) measurements on the absolutely dry samples.

As it can be seen from Figure 8, in comparison to the unfinished PES, penetration of water was much slower into the porous structure of PNCS and

VTMS/SiO₂-PNCS finished samples. This was expected, since PNCS microgel particles started to swell, due to the absorption of water, and thus closing the fabric's porous structure occurred, which resulted in a drop of the water penetration rates. This phenomenon was further studied by the determination of the apparent capillary radius, R , which was obtained as proposed by Van Oss and Chibowski [16, 17]. In this case, TLW method was performed by measuring penetration rates of n-heptane into the dry samples which were previously exposed to n-heptane vapour and into the samples preconditioned in the standard atmosphere (65% R.H.; 20°C; 24 h).

Sample	$R \times 10^6$ (m)	
	A	B
AA	3.39	3.37
PNCS	3.43	2.82
VTMS/SiO ₂ -PNCS	3.00	2.66

Table 1. The apparent capillary radius R , obtained from the thin-layer wicking measurements with n-heptane on samples previously saturated with n-heptane (absolutely dry samples) (A) and samples preconditioned in standard atmosphere (65% R.H.; 20°C; 24 h) (B).

From the results obtained for the samples previously exposed to n-heptane vapour, where PNCS microgel particles were in completely dry state (Table 1), it can be seen that after the application of PNCS microgel R did not significantly changed, compared to that obtained for the unfinished PES fabric. On the other hand, when PNCS microgel particles were applied in combination with VTMS/SiO₂, drop of apparent capillary radius R occurred, most likely due to the formation of continuous polysiloxane film layer on the surface of the PES fibres, closing the small pores between the PES filaments. However, when R determination was obtained for the samples previously exposed to the standard atmosphere conditions where PNCS microgel particles were in their swollen state, apparent capillary radius R significantly decreased, undoubtedly proving the expansion of the PNCS microgel particles due to water absorption. Furthermore, results show that slightly lower R value was obtained for the VTMS/SiO₂-PNCS finished samples compared to that obtained for the sample finished with PNCS only, showing that presence of VTMS/SiO₂ had no influence on the expansion capacity of the PNCS microgel particles.

4.3.2 Temperature responsiveness

In order to study temperature responsiveness of the PNCS microgel, due to the presence of poly-NiPAAm, moisture content and water vapour transmission of the PES finished with PNCS and VTMS/SiO₂-PNCS were determined. In the case of both applied finishing methods, the temperature responsiveness of PNCS microgel was obtained below and above transition temperature of poly-NiPAAm, i.e. 25 and 40°C, as well as at different relative humidity (50 and

80%). As expected, hydrophilic character of the PNCS microgel and thus higher moisture content of finished samples was obtained at ambient temperature and 50% R.H., which further increased by the raise of relative humidity (Figure 9). In both cases, i.e. at 50 and 80% R.H., higher moisture content of the VTMS/SiO₂-PNCS samples was obtained, which most likely occurred due to the presence of hydrophilic SiO₂ nanoparticles. Contrary, at higher temperature (40°C), hydrophobic character of poly-NiPAAm in the PNCS microgel predominated, causing water extraction from the PNCS microgel particles, which reflected in a decrease of moisture content of the finished samples. However, this was not the case when VTMS/SiO₂-PNCS treated PES sample was exposed to 80% R.H., where increase of its moisture content occurred. The most reasonable explanation for this was the presence of the hydrophilic SiO₂ nanoparticles on the surface of the coating (see Figure 6b), which blurred the hydrophobic effect of the PNCS microgel in the abundance of moisture, causing the increase of moisture content.

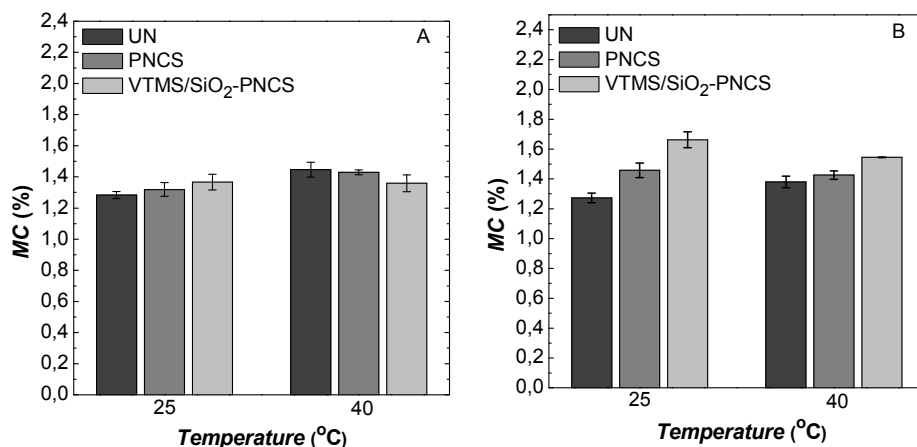


Figure 9. Moisture content (MC) of the studied PES samples obtained at 50% (A) and 80% (B) relative humidity.

Moisture content of the studied samples was inversely proportional to the water vapour transmission. Regarding this, at conditions when high moisture content was obtained (i.e. 25°C), the rate of water vapour transmission decreased (Figure 10). This was expected, as in this case PNCS microgel particles swelled and thus prevented the water vapour passage through the fabric. On contrary, at conditions when decreased moisture content was determined (i.e. 40°C), high water vapour transmission was obtained. Namely, at this temperature, the PNCS microgel particles collapsed and expelled water, allowing the passage of water vapour through the fabric. From Figure 10 it can be also seen that at 40°C and 80% R.H. the highest water vapour transmission was obtained for the

VTMS/SiO₂-PNCS finished PES sample. This undoubtedly confirmed the temperature responsiveness of the PNCS microgel entrapped into the VTMS network at high relative humidity, which could not be obtained from the results of water content, due to the interference of hydrophilic SiO₂ nanoparticles.

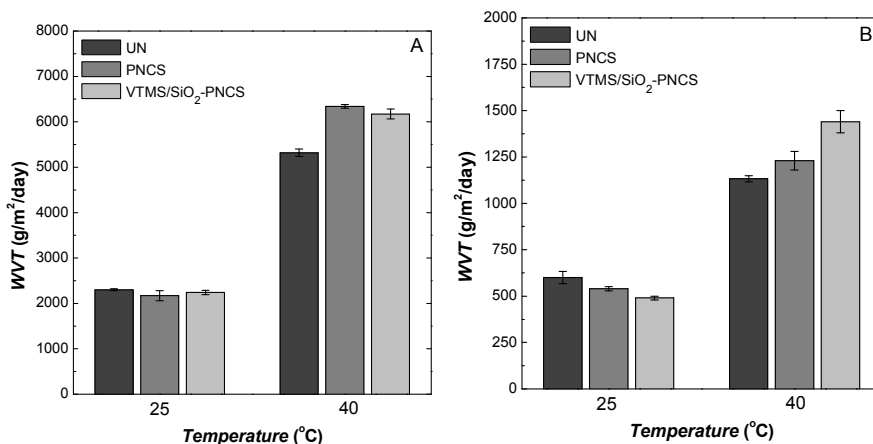


Figure 10. Water vapour transmission (WVT) of the studied samples obtained at 50% (A) and 80% (B) relative humidity.

4.3.3 Dual - temperature and pH - responsiveness

Simultaneous temperature responsiveness, deriving from poly-NiPAAm, and pH-responsiveness, deriving from chitosan, was studied by measuring water uptake. Due to chitosan responsiveness to changes in the pH of the surrounding media, three different pH values were chosen for the measurements, i.e. pH 3, 6.5 and 10. It was expected, that due to the protonation of amino group of chitosan in acidic medium, higher water absorption by studied samples would be achieved at pH 3 and contrary, decreased water absorption would be obtained in the alkaline medium. As it can be seen from Figure 11 the results obtained were in good correlation to the expectation, since a decrease of water uptake was obtained when raising the pH from 3 to 10 at lower temperature (25°C). Accordingly, at higher temperature (40°C) overall decrease of water uptake could also be observed, arising due to the hydrophobic character of poly-NiPAAm, but compared to the unfinished sample this effect was blurred, since in the pH range 6.5–10 hydrophobic character of the unfinished PES sample was obtained.

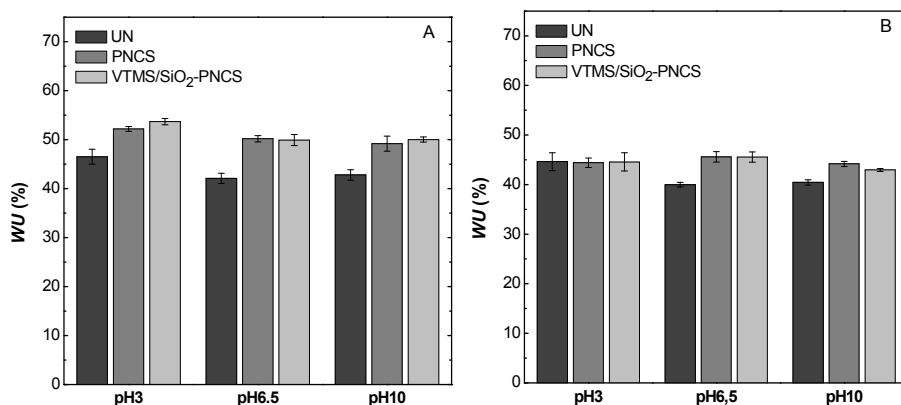


Figure 11. Water uptake (WU) of the studied samples, obtained at 25°C (A) and 40°C (B) for different buffer solutions.

5. Washing durability of the finished PES fabrics

When creating functional textiles, washing durability is of special importance. Therefore, durability of PNCS and VTMS/SiO₂-PNCS finish to repetitive washing was studied according to the ISO 105-C01:1989 (E) standard method using Atlas Linitester, which is widely used for evaluating laundry results on a laboratory scale. One washing in Linitester provides an accelerated washing treatment corresponding to five domestic washings. The finished fabric samples were washed up to 5 times at 40°C. The presence of studied coatings after such treatment was assessed by SEM as well as by determination of temperature- and pH-responsiveness, applying water vapour permeability and water uptake analysis.

5.1 Morphological changes

Morphological changes of the studied finished samples after washing are obtained in Figure 12. It can be seen that certain amount of the PNCS microgel was rinsed away during washing process. Nevertheless, surprisingly high concentration of microgel particles could be still observed after five consecutive washings, indicating their good adherence on the previously activated PES fibres. In the case of VTMS/SiO₂-PNCS finished samples, partial removal of the PNCS microgel particles covered by the VTMS network was observed, while the presence of agglomerated SiO₂ nanoparticles could no longer be detected. However, from the image taken at higher magnification their presence in the silica matrix was clearly seen. Moreover, distribution of SiO₂ nanoparticles was even, which could not be observed from the SEM images taken from the unwashed sample.

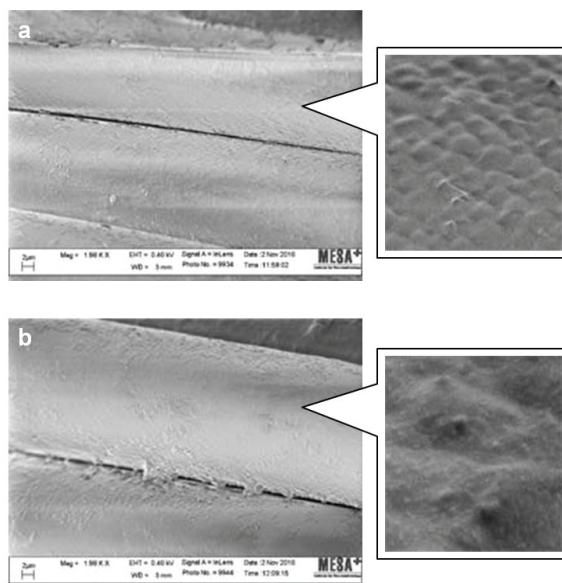


Figure 12. SEM images of the PNCS (a) and VTMS/SiO₂-PNCS finished PES fibres after five consecutive washings.

5.2 Temperature- and pH-responsiveness

In order to study temperature responsiveness of the PNCS microgel particles after their partial removal during washing, water vapour transmission of the studied PES fabrics was measured (Figure 13). As in the case of unwashed finished samples, the same trend of water vapour transport could be observed after five washings. This clearly indicated that the concentration of PNCS microgel was high enough to show thermal responsiveness of poly-NiPAAm. The latter was higher for the PNCS/VTMS-SiO₂ finished PES fabric in comparison to the PES treated by only PNCS. This suggested that higher concentration of PNCS microgel particles remained on the VTMS/SiO₂-PNCS finished PES fibres after washings, confirming the already known fact, that silica matrix hinders the leaching of the physically embedded particles.

Additionally, simultaneous temperature- and pH-responsiveness of the PNCS microgel after washing was also studied, using water uptake determination. Unlike to temperature responsiveness of poly-NiPAAm, where intensive changes between different temperatures were obtained, pH responsiveness of chitosan was hardly detectible after five washing cycles (Figure 14). Nevertheless, despite the fact that small changes were observed between different pH values, certain trend could still be observed. Namely, at lower temperature increase of water uptake of PNCS finished PES sample could be determined at pH 3, which has slightly dropped after raising the pH to 10. In the

case of VTMS/SiO₂-PNCS sample hydrophilic/hydrophobic pH responsiveness could not be obtained, due to the presence of SiO₂ silica nanoparticles, which hindered hydrophobic effect of the chitosan.

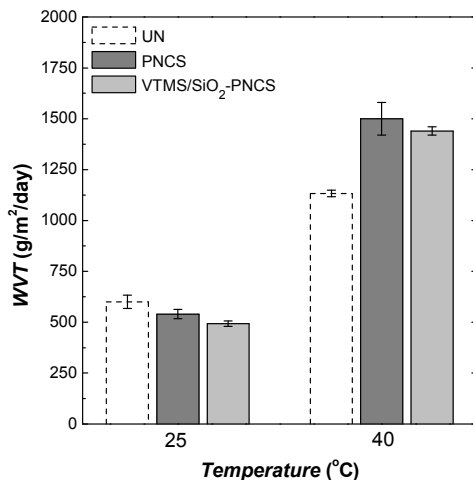


Figure 13. Water vapour transmission (WVT) of the washed studied PES samples obtained at 25°C and 40°C at 80% relative humidity.

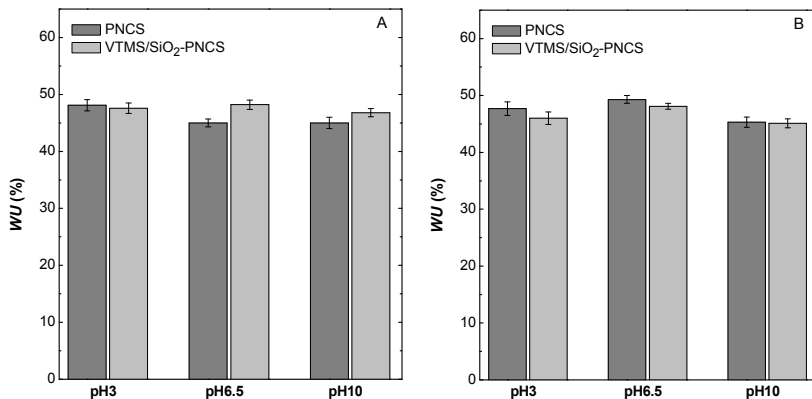


Figure 14. Water uptake (WU) of the washed studied PES samples obtained at 25°C (A) and 40°C (B).

Contrary to the predominant effect of poly-NiPAAm determined at pH 3 and 40°C for the unwashed samples, in the case of washed finished samples chitosan prevalence was observed. Namely, in the case of unwashed PNCS finished sample 15% of water uptake reduction occurred when sample was exposed from lower to higher temperature, while after washing this reduction

significantly decreased to only 1%. In the case of VTMS/SiO₂-PNCS treated PES sample this drop was slightly less intense, namely from 17% to 4%. Regarding this, it can be concluded that during washing, leaching of the chitosan from the PNCS microgel occurred, which was less intense when microgel was applied in combination with VTMS. This is reasonable, since polysiloxane matrix, which covered PNCS microgel particles slightly hindered the leaching of chitosan.

6. Conclusions

By incorporation of PNCS microgel, PES fabric with "intelligent" liquid management properties was obtained, distinguished by good temperature- and pH-responsiveness to ambient conditions. Introduction of sol-gel technology enabled the incorporation of PNCS microgel particles in combination to silica matrix, which due to its elasticity had no influence on swelling/deswelling effect of PNCS microgel, thus retaining its stimuli responsiveness. At the same time, silica matrix prolonged the washing durability of the PNCS microgel incorporated to PES, which is an important feature for maintenance of functional textiles. These results are promising for the future combination of PNCS microgel to a variety of functionalized sol-gel precursors, offering new possibilities for creation of smart textiles with multifunctional properties and high added value.

Acknowledgement

The author thanks to Prof. Dr. Barbara Simončič from Department of Textiles, Faculty of Natural Science and Engineering, University of Ljubljana for constructive discussion as well as to Prof. Dr. Boris Orel from Laboratory for The Spectroscopy of Materials, National Institute for Chemistry, Ljubljana, for introduction into the world of IR spectroscopy.

References

- [1] J.C. Brinker, G.W. Scherer, *Sol-gel Science : the physics and chemistry of sol-gel processing*, Academic Press, San Diego, 908 p. (1990).
- [2] *Handbook of organic-inorganic hybrid materials and nanocomposites*, H.S. Nalwa Ed., American Scientific Publisher, Stevenson Ranch, 386 p. (2003).
- [3] B. Mahltig, T. Textor, *Nanosols and textiles*, World Scientific Publishing Co. Pte. Ltd. Singapore, 224 p. (2008).
- [4] J. He, A. Nebioglu, Z. Zong, M.D. Soucek, K.M. Wollyung, C. Wesdemiotis, Preparation of a siloxane acrylic functional siloxane colloid for UV-curable organic-inorganic hybrid films, *Macromolecular Chemistry and Physics*, **206**, 732-743 (2005).
- [5] G. Socrates, *Infrared and Raman Characteristic Group Frequencies*, John Wiley & Sons, LTD, New York, 347 p. (2001).

- [6] L.F. Chen, Z.H. Cai, L. Zhang, L. Lan, X.J. Chen, J. Zeng, Preparation and properties of silicon oxycarbide fibers, *Journal of Materials Science*, **42**, 1004-1009 (2007).
- [7] J. He, L. Zhou, M.D. Soucek, K.M. Wollyung, C. Wesdemiotis, UV-Curable Hybrid Coatings Based on Vinylfunctionized Siloxane Oligomer and Acrylated Polyester, *Journal of Applied Polymer Science*, **105**, 2376-2386 (2007)
- [8] F. Azizinejad, M. Talu, M. Abdouss, M. Shabani, An investigation of the grafting of acrylic acid/methyl methacrylate mixture onto poly(ethylene terephthalate) fibres, *Iranian Polymer Journal* **14**, 33-38 (2005).
- [9] V. Costamagna, D. Wunderlin, M. Larranaga, I. Mondragon, M. Strumia, Surface functionalization of polyolefin films via the ultraviolet-induced photografting of acrylic acid: topographical characterization and ability for binding antifungal agents, *Journal of Applied Polymer Science*, **102**, 2254-2263 (2006).
- [10] I. Karbownik, J. Bucheńska, B. Lipp-Symonowicz, H. Wrzosek, Studies on the influence of grafting PET fibres with acrylic acid on molecular orientation, *Fibres & Textiles In Eastern Europe* **16**, 108-111 (2008).
- [11] 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, *Journal of Adhesion Science and Technology*, **20**, 1357-1365 (2006).
- [12] B.J. Holland, J.N. Hay, The thermal degradation of PET and analogous polyesters measured by thermal analysis – Fourier transform infrared spectroscopy, *Polymer*, **43**, 1835-1847 (2002).
- [13] M. Parvinezadeh, S. Moradian, A. Rashidi, M.-E. Yazdanshenas, Surface characterization of polyethylene terephthalate/silica nanocomposites, *Applied Surface Science*, **256**, 2792-2802 (2010).
- [14] T. Kijchavengkul, R. Auras, M. Rubino, E. Alvarado, J.R.C. Montero, J.M. Rosales, Atmospheric and soil degradation of aliphatic aromatic polyester films, *Polymer Degradation and Stability*, **95**, 99-107 (2010).
- [15] F.Ł. Kondratowicz, R. Ukielski, Synthesis and hydrolytic degradation of poly(ethylene succinate) and poly(ethylene terephthalate) copolymers, *Polymer Degradation and Stability*, **94**, 375-382 (2009).
- [16] C.J. Van Oss, R.F. Giese, K. Murphy, J. Norris, M.K. Chaudhury, R.J. Good, Determination of contact angles and pore sizes of porous media by column and thin layer wicking, *Journal of Adhesion Science and Technology*, **6**, 413-428 (1992).
- [17] E. Chibowski, F. Gonzales-Caballero, Theory and practice of thin-layer wicking, *Langmuir*, **9**, 330-340 (1993).

advan

BIO

Tex



ISBN 978-90-365-3122-1