

INFLUENCE OF THE MATRIX TYPE ON THE TEMPERATURE RESPONSIVENESS OF A POLY-NIPAAm/CHITOSAN MICROGEL FUNCTIONALIZED PES FABRIC

VPLIV VRSTE MATRICE NA TEMPERATURNO ODZIVNOST POLI-NIPAAm/HITIZAN MIKROGELA NA PES-TKANINI

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In this paper, the temperature responsiveness (swelling/de-swelling) of the poly-NiPAAm/chitosan (PNCS) microgel applied to a PES fabric in combination with two different matrixes, i.e., 1,2,3,4-butanetetracarboxylic acid (BTCA) or vinyltrimethoxysilane (VTMS) with hydrophilic fumed-silica nanoparticles (SiO₂) was studied. While a BTCA-based matrix enables chemical bonding of the PNCS microgel particles, resulting in a formation of a rigid surface-modified system, a VTMS/SiO₂ polysiloxane matrix has the ability to physically entrap the PNCS microgel particles and stimulate, due to its elasticity, a formation of a more flexible coating on the surface of PES fibres. Morphological and chemical properties of differently finished samples were studied with the SEM and XPS analyses. To determine the swelling/de-swelling ability of the PNCS microgel, the moisture contents of the samples, before and after five repetitive washings, were obtained for the samples conditioned at two different temperatures, i.e., at 25 °C and 40 °C, when the PNCS hydrogel was in its swollen or collapsed phase. The results showed that the rigid structure of the BTCA-based matrix restricted the swelling ability of the microgel particles, resulting in a 12 % lower moisture content of the corresponding sample in comparison to the moisture content determined for the sample with the PNCS microgel particles physically entrapped within the polysiloxane matrix. Due to its elasticity, the polysiloxane matrix enables the microgel particles to fully expand, which is the consequence of a partial removal of the PNCS microparticles during the washing procedure.

Keywords: hydrogel, microgel, poly-NiPAAm/chitosan, 1,2,3,4-butanetetracarboxylic acid, vinyltrimethoxysilane, responsiveness

V prispevku je preučevana temperaturna odzivnost (nabrekanje/skrčenje) poli-NiPAAm/hitozan (PNCS) hidrogela, nanesenega na PES-tkanino v kombinaciji z dvema različnima matricama, in sicer z 1,2,3,4-butanetrakarboksilno kislino (BTCA) ter viniltrimetoksi silanom (VTMS) s hidrofilnimi nanodelci silicijevega dioksida (SiO₂). Medtem ko je BTCA-matrica omogočila kemijsko vezanje PNCS-mikrogela ter nastanek bolj togega apreturnega filma na površini vlaken, so se delci PNCS-mikrogela v VTMS/SiO₂-matrico vezali fizikalno, pri čemer se je zaradi prožnosti in raztegljivosti matrice na površini vlaken tvoril elastičen apreturni film. Morfološke in kemijske lastnosti apretiranih vzorcev so bile preučevane s SEM- in XPS-analizama. Sposobnost nabrekanja/krčenja PNCS-mikrogela je bila določena z meritvami vsebnosti vlage nepranih in 5-krat pranih apretiranih vzorcev, klimatiziranih pri 25 °C in 40 °C, ko se je PNCS-hidrogel nahajal v nabrekli oziroma skrčenem stanju. Rezultati so pokazali, da je toga struktura BTCA-matrice vplivala na zmanjšano sposobnost nabrekanja delcev mikrogela, saj je bila vsebnost vlage teh vzorcev za 12 % nižja od vsebnosti vlage, določene pri vzorcih, na katere je bil PNCS-mikrogel fizikalno vezan v polisiloksanjsko matrico. Slednja je zaradi svoje elastičnosti omogočila neovirano nabrekanje delcev mikrogela, kar se je bolj izrazilo pri pranih vzorcih. Med pranjem je namreč prišlo do delne odstranitve PNCS-mikrogela iz vlaken, zaradi česar so imeli delci mikrogela, ki so ostali na vlaknu, več prostora za polno nabrekanje.

Ključne besede: hidrogel, mikrogel, poli-NiPAAm/hitozan, 1,2,3,4-butanetrakarboksilna kislina, viniltrimetoksi silan, odzivnost

1 INTRODUCTION

In the production of textiles special attention is devoted to the creation of the apparel with specific properties that could be activated "on demand" by sensing and reacting to the stimuli in the immediate environment. The creation of such textiles involves, among other methods, an application of hydrogels, where a hydrogel based on chitosan and poly-(N-isopropylacrylamide) (poly-NiPAAm) is of great importance since it ensures a dual pH and temperature responsiveness.¹⁻³ Namely, due to weakly basic moieties (primary amines that have the *pKa* values of about 6.3) chitosan can respond to the changes in the pH of the surrounding medium with a

protonation/de-protonation of the amino groups.⁴ A pH-induced phase transition of chitosan results in the varying dimensions (swelling and de-swelling) of the hydrogel made of it. Poly-NiPAAm exhibits a reversible temperature-sensitive phase transition in aqueous solutions at a lower critical-solution temperature (LCST) of 32 °C. At the temperatures below the LCST, poly-NiPAAm is water-soluble, i.e., hydrophilic, so the hydrogel made of it exists in the swollen phase. At the temperatures above the LCST, poly-NiPAAm becomes hydrophobic and, consequently, the hydrogel collapses.^{5,6} Therefore, after combining the swelling and shrinking effects, applied to textile materials, a poly-NiPAAm/chitosan (PNCS) hydrogel is expected to provide com-

fort to the wearer due to its moisture-management and liquid-management properties, as well as the thermo-regulating ability.

An advanced approach to the textile-material functionalization is based on microsized and nanosized hydrogels because their polymeric form has an increased surface area per unit mass, significantly improving the response times. When creating a stimuli-responsive textile, the main challenge is to apply the microgel onto the textile fibres in such a way as to create a sufficient durability while still retaining the effectiveness of the hydrogel. In our previous research a PNCS hydrogel was successfully applied to cotton in combination with the crosslinking agent 1,2,3,4-butanetetracarboxylic acid (BTCA).⁷⁻⁹ During the curing process, the chemical bonding of the PNCS microgel was obtained. Namely, the carboxylic groups of BTCA reacted with the hydroxyl groups from both cotton and chitosan by forming stable ester bonds, possibly reacting also with the free amino groups of chitosan via a formation of an amide.^{10,11} Even though good moisture-management properties of the functionalized cotton were obtained, the question arose whether these chemical bonds formed between the cotton, BTCA and PNCS hydrogel, resulting in the formation of a rigid, surface-modified system, restricted the expansion ability of a microgel particle in such a way that it could not swell as fully as a free particle. Therefore, in the continuation of the research, a PNCS microgel was applied to a PES fabric with the sol-gel technique, using the vinyltrimethoxysilane (VTMS) and hydrophilic fumed-silica nanoparticles (SiO₂) as the precursors.¹² In the application process, VTMS formed a continuous network on the surface of the fibres, enabling a physical entrapment of the PNCS microgel. Besides, SiO₂ nanoparticles acted as possible anchoring sites for the PNCS microgel particles, thus enabling their enhanced incorporation into the surface of the PES fibres. Since the polysiloxane precursors are known by their ability to form an elastic film on a solid surface of only ≈10 nm thickness,¹³ it was found out that the presence of a VTMS/SiO₂ matrix did not influence the responsiveness of the PNCS microgel particles.¹²

The aim of this work was to study the influence of the chemical structure and composition of the matrix on the performance of the PNCS microgel particles. For this purpose the PNCS microgel was first applied in combination with a matrix based on the crosslinking agent (BTCA), which enabled a covalent bonding of the microgel particles and, later, in combination with a VTMS/SiO₂ polysiloxane matrix, where a physical embedment of the microgel particles was obtained. The thermal responsiveness (i.e., the swelling/de-swelling ability) of the PNCS microgel particles was studied using the moisture-content determination. For this reason, a PES woven fabric was chosen as the substrate due to its non-polarity and a low moisture regain in order to avoid any interference with the results of the moisture-content determination of the studied samples. In the application process, a simple pad-dry-cure procedure was used since

it is especially interesting for an application in industrial conditions.

2 EXPERIMENTAL WORK

A 100 % woven (plain weave) PES fabric with a mass per unit area of 153 g/m², supplied by Ten Cate Advanced Textiles (The Netherlands) was used throughout the experiment. The surface of the PES fibres was chemically activated using the UV grafting of the acrylic acid AA (Sigma-Aldrich) in the presence of benzophenone BP (Sigma-Aldrich) as the initiator, according to the procedure of Song et al.¹⁴ In this way the pre-treated fabric was referred to as the activated PES (PES-AA) and was used as the starting material for all the subsequent experiments.

The PNCS microgel was prepared according to the slightly modified¹⁵ procedure of Lee et al.¹⁶ For its application with the matrix based on the crosslinking agent (BTCA), the finishing bath was prepared by adding 1,2,3,4-butanetetracarboxylic acid BTCA (Sigma-Aldrich) and sodium hypophosphite SHP (Sigma-Aldrich) (as a catalyst) into the PNCS dispersion (23.7 g/l). The ratios used were PNCS : BTCA = 3.75 : 1 and BTCA : SHP = 2 : 1. The finishing bath was applied with the pad (60 % WPU) – dry (105 °C, 5 min) – cure (160 °C, 3 min) method. The PES sample treated in this manner is henceforth referred to as BTCA-PNCS.

To apply the PNCS microgel in combination with a polysiloxane matrix, vinyltrimethoxysilane VTMS (Sigma-Aldrich) was acid-catalysed. The finishing bath was prepared by adding 0.1 % fumed-silica nanoparticles (SiO₂) (Aerosil 2000, Evonik, Germany) and 10 % benzophenone BP – photoinitiator (Sigma-Aldrich) into a 4 % VTMS solution in ethanol. The prepared finishing bath was applied by the pad (60 % WPU) – dry (105 °C, 5 min) method. Subsequently, the PNCS microgel (23.7 g/l) was applied (60 % WPU) and the samples were UV treated for 40 s using a UV lamp (HQV, Osram). Afterwards, the samples were dried (105 °C, 5 min) and cured (160 °C, 3 min). This PES sample is referred to as Si-PNCS.

The washing fastness of the BTCA-PNCS and Si-PNCS finished samples was determined after five repetitive washings in Atlas Linitester according to the ISO 105-C01:1989(E) standard method. The washing was carried out in a solution of the SDC standard detergent with a concentration of 5 g/l, previously heated to 40 °C, at a liquor ratio of 50 : 1. The duration of a washing cycle was 30 min. After each washing cycle the samples were thoroughly rinsed in cold running tap water.

A microscopic evaluation of the morphological changes occurring after the finishing and washing of the PES samples was carried out using a SEM 1550 HRSEM (Zeiss, Germany), operating at 5 kV. Before SEM images were taken, the samples were dried in a vacuum.

An X-ray photoelectron spectroscopy (XPS) analysis was carried out using a PHI Quantera Scanning ESCA Microprobe spectrometer (Physical Electronics, USA) with monochromatic Al $K\alpha$ radiation (1486.6 eV) at 25 W. The quantification of the surface composition was obtained from the XPS peak intensities measured on five different spots of a sample, taking into account the relative sensitivity factors provided by the instrument manufacturer.

In order to study the thermal responsiveness of the PNCS microgel, the moisture content (MC) was determined. The method was performed on the samples pre-conditioned at 80 % relative humidity, at 25 °C and 40 °C (i.e., the temperatures below and above the transition temperature of poly-NiPAAm) during a period of 24 h. MC was measured thermogravimetrically with a moisture analyser (MS-70 Moisture Analyser equipped with the WinCT-Moisture software, A&D, Japan) by drying the samples at 105 °C until a constant mass was obtained. The measurements were done on the finished samples and five-times washed samples. The final moisture content (MC) was calculated as follows:

$$MC = \frac{W_0 - W_f}{W_0} \cdot 100 (\%) \quad (1)$$

where W_0 is the mass of a sample before drying (g) and W_f is the mass of a completely dried sample (g).

In order to determine the share of the measured MC, which can be attributed to the responsiveness of the PNCS surface-modified system only, the swelling ability (SA) parameter was introduced. By using the results of the moisture content determined for the samples pre-conditioned at 25 °C and 40 °C, the swelling ability of the PNCS microgel particles was calculated as follows:

$$SA = \frac{MC_{(BTCA-PNCS;Si-PNCS)} - MC_{(PES-AA)}}{MC_{(PES-AA)}} \cdot 100 (\%) \quad (2)$$

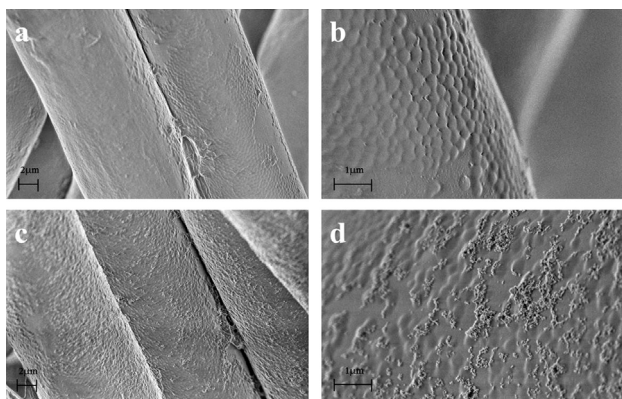


Figure 1: SEM images of: a), b) BTCA-PNCS and c), d) Si-PNCS functionalized PES samples taken at a lower (10000x) and higher (45000x) magnification

Slika 1: SEM-posnetki: a), b) BTCA-PNCS ter c), d) Si-PNCS funkcionaliziranih vzorcev PES-tkanine, posnetih pri manjši (10000-kratni) in večji (45000-kratni) povečavi

where $MC_{(BTCA-PNCS;Si-PNCS)}$ is the moisture content of the functionalized PES samples (BTCA-PNCS or Si-PNCS) and $MC_{(PES-AA)}$ is the moisture content of the activated PES (PES-AA).

With such a calculation, the contribution of the PES substrate to the measured MC can be avoided and the response efficiency of the PNCS surface-modified system can be easily assessed.

3 RESULTS AND DISCUSSION

To be able to prove that the incorporation of the PNCS hydrogel in a combination with BTCA and VTMS/SiO₂ took place, the SEM images of the functionalized PES samples were taken. On **Figure 1** the spherically shaped microgel particles with an estimated size of up to 200 nm could be clearly seen on the surface of the BTCA-PNCS and Si-PNCS finished PES, thus indicating a successful deposition of the PNCS microgel particles, regardless of the matrix used (BTCA or VTMS/SiO₂). A detailed assessment of the SEM images of the Si-PNCS finished sample also revealed that the SiO₂ nanoparticles agglomerated and distributed on the top of the coating (**Figures 1c** and **1d**). However, after five consecutive washings the SiO₂ agglomerates were rinsed away, as evident in **Figure 2b**. Moreover, the clearly present PNCS microgel particles became smoothened, while their shape change could be observed on the surface of the washed BTCA-PNCS sample (**Figure 2a**). This could be a consequence of the volume transition (swelling/de-swelling) of the microgel particles during the washing procedure. While the VTMS/SiO₂ matrix, due to its elastic properties, allowed such transition

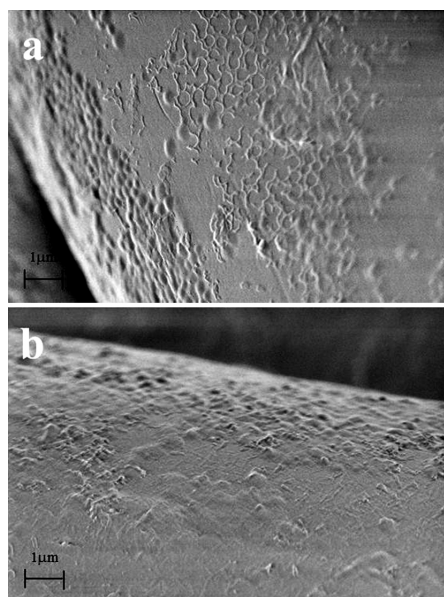


Figure 2: SEM images of: a) five-times washed BTCA-PNCS and b) Si-PNCS functionalized PES samples

Slika 2: SEM-posnetki: a) 5-krat pranih BTCA-PNCS in b) Si-PNCS funkcionaliziranih vzorcev PES-tkanine

behaviour of the PNCS microgel, the rigid structure of the BTCA-based matrix might have been the reason for the PNCS-particle rupture on certain parts of the BTCA-PNCS finished fibres.

Further evidence of a successful deposition of the PNCS hydrogel was obtained with the XPS analysis (Figure 3). While only two bands were obtained in the XPS spectrum of the activated PES (PES-AA), ascribed to carbon (C1s) (285 eV) and oxygen (O1s) (533 eV), the XPS spectra of both finished samples also displayed a band ascribed to nitrogen (N1s) (400 eV), while in the case of the Si-PNCS sample, a band belonging to silicon (Si2p) was observed as well. It can be seen from Figure 3 that the application of the PNCS microgel in combination with BTCA resulted in an increase in the carbon concentration and a decrease in the oxygen concentration, indicating an efficient crosslinking of the BTCA agent. On the other hand, a simultaneous decrease in the carbon and oxygen concentrations occurred in the XPS spectrum of the Si-PNCS sample, indicating a formation of a continuous polysiloxane matrix. Nevertheless, an effective incorporation of the PNCS microgel particles could be confirmed by detecting nitrogen, which was present in both poly-NiPAAm and chitosan. In the XPS spectra a higher concentration of nitrogen was detected for the Si-PNCS sample, which decreased after the washing, indicating a partial removal of the PNCS microgel. This was expected, since the PNCS microgel particles were mostly physically entrapped into the VTMS/SiO₂ matrix. On the other hand, in the XPS spectra of the unwashed and five-times washed BTCA-PNCS samples, the concentrations of nitrogen were almost unchanged, proving that, in the application process, a covalent bonding of PNCS to BTCA took place. In any case, comparable concentrations of nitrogen were determined for both the finished samples and washed samples, showing that each time approximately the same concentration of the PNCS microgel particles remained on the fibres.

The influence of the type of the bonds formed between the microgel particles and the BTCA crosslinking agent or the VTMS/SiO₂ polysiloxane matrix on the swelling/de-swelling ability was studied by determining the moisture content (MC). It can be seen from Figure 4

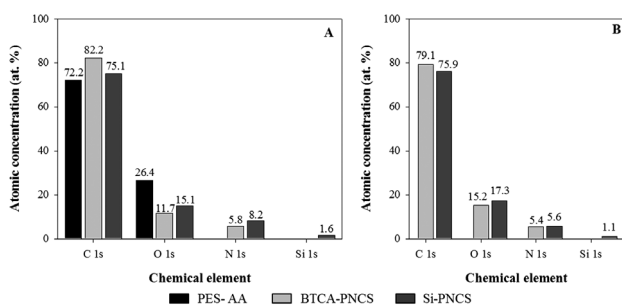


Figure 3: Surface chemical compositions of the studied PES samples: a) before and b) after five consecutive washings

Slika 3: Kemijska sestava površine preučevanih vzorcev PES-tkanine: a) pred 5-kratnim zaporednim pranjem in b) po njem

that the comparable temperature responsiveness of the PNCS microgel for BTCA-PNCS and the VTMS/SiO₂-PNCS finished samples was observed. Namely, irrespective of which type of matrix was used, the hydrophilic character of the PNCS microgel was observed (Figure 4a). With the samples preconditioned at 25 °C, the PNCS microgel particles were in their highly swollen state, resulting in a significantly higher moisture content of both finished samples in comparison to the bare activated PES (PES-AA). As expected, after the conditioning at 40 °C the hydrophobic character of poly-NiPAAm in the PNCS hydrogel predominated. The PNCS microgel particles were in their collapsed phase, causing water expulsion from the PNCS hydrogel, which resulted in a general decrease in the moisture content. After five consecutive washings the same trend could be observed for both sample types (Figure 4b). However, it can be seen that for the samples conditioned at ambient temperature (25 °C) a 12 % higher moisture content of Si-PNCS was obtained in comparison to the BTCA-PNCS sample, even though the results of the XPS analysis showed the same concentration of the PNCS microgel after the washing. This indicated that the PNCS microgel particles applied with BTCA absorbed less water under ambient conditions, which could occur due to a mechanical rupture of the PNCS microgel particles during the washing procedure as seen on the SEM images (Figure 2a).

The hindered responsiveness of the PNCS microgel particles due to the rigidity of the BTCA matrix became more expressed with a calculation of the swelling ability (SA). From the results shown in Figure 5 it can be seen that the difference in SA obtained by subtracting the SA determined at 40 °C from the SA determined at 25 °C, which could be the measure for the amount of expelled water, was approximately the same for both unwashed samples, i.e., 20 % and 22 %. However, after the washing the difference in the amount of the expelled water between differently finished samples became more pronounced being 14 % for the BTCA-PNCS sample and 30 % for the Si-PNCS sample. This undoubtedly proved that, due to its rigidity, the BTCA matrix did not allow a

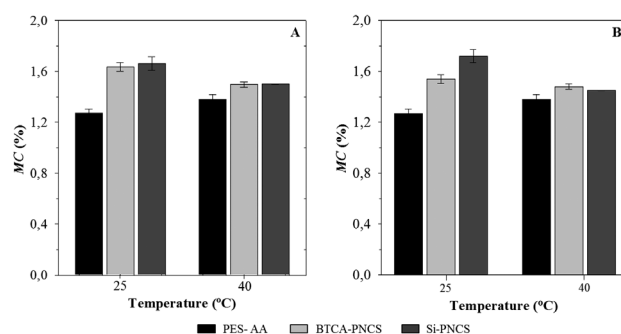


Figure 4: Final moisture content, *MC*, of the studied PES samples determined: a) before and b) after five consecutive washings

Slika 4: Vsebnost vlage *MC* preučevanih vzorcev PES-tkanine, določena: a) pred 5-kratnim zaporednim pranjem in b) po njem

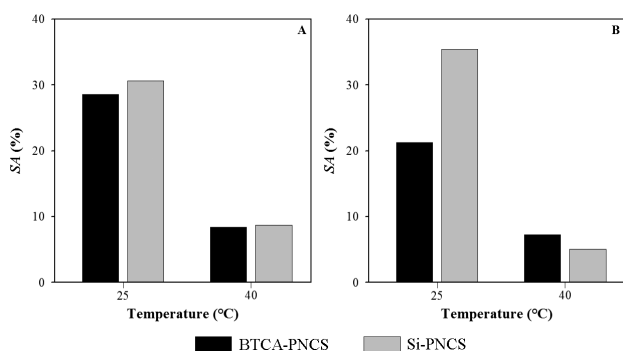


Figure 5: Swelling ability, SA, of the PNCS microgel particles, determined: a) before and b) after five consecutive washings of the samples
Slika 5: Zmožnost nabrekanja SA delcev PNCS-mikrogela, določena: a) pred 5-kratnim zaporednim pranjem vzorcev in b) po njem

flexible volume transition of the PNCS microgel particles during the washing process performed at 40 °C (the microgel particles were in their collapsed phase) and the rinsing of the samples in cold running tap water (the microgel particles were in their swollen phase). On the contrary, in the case of the Si-PNCS sample, the amount of expelled water increased after the washing. The most reasonable explanation would be a partial removal of the PNCS microgel particles, giving the microgel particles remaining on the fibres more space for expansion at the conditions below the transition temperature, which was reflected in a higher amount of expelled water at 40 °C. In this case, the physical entrapment of the PNCS hydrogel acted beneficially on the response efficiency. Namely, as it was pointed out before, for better results not more than 50 % of the fibre surface should be covered with the microgel.¹⁷ This means that with the physical incorporation of the PNCS microgel particles into the VTMS/SiO₂ polysiloxane matrix, a gradual leaching of the microgel with every washing cycle could occur, giving the remaining microgel particles on the fibre surface more space to fully swell at ambient temperature. At this point, it also has to be taken into account that after a certain number of washings the concentration of the PNCS microgel particles falls under the limit necessary to retain the response efficiency.

4 CONCLUSIONS

From the results obtained it can be concluded that the use of the matrix based on an BTCA crosslinking agent, results in a decreased swelling ability of the PNCS microgel particles, which consequently leads to a reduced capacity of water absorption under ambient conditions (25 °C) and thus less water can be expelled at 40 °C. This behaviour is attributed to the formation of chemical

bonds between the PNCS hydrogel and BTCA, creating a rigid surface-modified system on the PES fibres. The rigid nature of this matrix hindered the volume transition (swelling/de-swelling) of the PNCS microgel particles during the washing procedure, resulting in a shape change of the microgel particles. Consequently, after five washings, a 12 % smaller moisture content of the BTCA-PNCS sample, preconditioned at ambient temperature, was obtained in comparison to the corresponding Si-PNCS sample. On the other hand, when being physically entrapped into the VTMS/SiO₂ matrix, the PNCS microgel particles can expand quite freely. After five washings their swelling ability became even more pronounced, due to a partial removal of the microgel particles, giving the remaining ones more space on the fibre surface to fully expand at ambient conditions.

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