

Anja Verbič, Viktor Stojkoski, Brigita Tomšič, Nina Špička, Danaja Štular, Marija Gorjanc, Mateja Kert, Barbara Simončič

University of Ljubljana, Faculty of Natural Sciences and Engineering, Aškerčeva 12, 1000 Ljubljana, Slovenia

Preparation of Functional Stimuli-responsive Polyamide 6 Fabric with ZnO Incorporated Microgel

Priprava funkcionalne odzivne tkanine iz poliamida 6 z mikrogelom z vključenim ZnO

Original Scientific Article/Izvirni znanstveni članek

Received/Prispelo 08-2017 • Accepted/Sprejeto 09-2017

Abstract

A new functional, stimuli-responsive microgel coating on polyamide 6 (PA6) fabric with simultaneous temperature (T)- and pH-responsive moisture management, UV protection and photocatalytic self-cleaning properties was prepared by applying poly-(N-isopropylacrylamide)/chitosan (PNCS) microgel in combination with ZnO nanoparticles to PA6 fabric. Two different application procedures were used: (i) the application of PNCS previously functionalized with a ZnO nanoparticles suspension and (ii) the application of PNCS with the subsequent application of a ZnO nanoparticles suspension. The coatings were fabricated on the untreated PA6 fabric as well as on fabric previously modified by the silica matrix created by the sol-gel precursor iSys MTX in order to increase the adsorption ability and uniformity of the coating. The chemical and morphological properties of the coated PA6 samples were determined by SEM and FTIR analyses. Stimuli responsiveness and functional properties were assessed by the moisture content, water vapour transmission rate, water uptake, UV protection and photocatalytic self-cleaning measurements. The results show that the application procedure as well as the pretreatment of PA6 fabric greatly influenced the properties of the coating. Accordingly, the most appropriate procedure included the creation of a silica matrix on the PA6 fibres followed by the application of PNCS and subsequent application of ZnO. In this case, the modified PA6 fabric exhibited high T and pH responsiveness due to the swelling/de-swelling activity of the PNCS microgel, as well as good UV protection with UPF equal to 18.8 and photocatalytic self-cleaning properties that are even higher than those in the case of the one-component coating with ZnO.

Keywords: polyamide 6, poly-(N-isopropylacrylamide)/chitosan microgel, ZnO nanoparticles, temperature and pH responsiveness, UV protection, photocatalytic self-cleaning properties

Izvleček

Z nanosom mikrogela iz poli-(N-izopropilakrilamid)-a in hitosana (PNCS) na tkanino iz poliamida 6 (PA6) je bila pripravljena nova apretura, odzivna na dražljaje iz okolice, ki se je odlikovala po hkratnem uravnavanju vlage glede na temperaturo (T) in pH, zaščiti pred ultravijoličnim (UV) sevanjem in fotokatalitičnimi samočistilnimi lastnostmi. Uporabljena sta bila dva postopka nanosa: (i) nanos PNCS, ki je bil predhodno funkcionaliziran s suspenzijo nanodelcev ZnO, in (ii) nanos PNCS, ki mu je sledil nanos suspenzije nanodelcev ZnO. Apreturi sta bili naneseni na neobdelano tkanino PA6 in na tkanino PA6, na kateri je bila predhodno oblikovana silicijeva oksidna matrika z uporabo prekurzorja sol-gel iSys MTX, da bi se povečali adsorpcijska sposobnost in enakomernost nanosa. Kemijske in morfološke lastnosti apretiranih vzorcev PA6 so bile določene z analizo SEM in FTIR. Odzivnost na dražljaje in funkcionalne lastnosti apreture so bile proučevane z meritvami vsebnosti vlage, hitrosti prenosa vodne pare, absorpcije vode, UV-zaščite in fotokatalitične samočistilnosti. Iz rezultatov je razvidno, da sta postopek nanosa in tudi predobdelava tkanine PA6 močno vplivala na lastnosti apreture. V skladu s tem je najprimernejši postopek

Corresponding author/Korespondenčna avtorica:

Prof dr. Barbara Simončič

Tel.: +386 1 200 32 31

E-mail: barbara.simoncic@ntf.uni-lj.si

Tekstilec, 2018, 61(0), 00-00

DOI: 10.14502/Tekstilec2018.61.00-00

oblikovanje silicijeve oksidne matrice na vlaknih PA6, ki mu je sledila nanos PNCS in naknadni nanos ZnO. V tem primeru je imela modificirana tkanina PA6 zaradi sposobnosti nabrekanja in krčenja mikrogela PNCS visoko odzivnost na T in pH, kot tudi dobro UV-zaščito z UZF, enakim 18,8, in fotokatalitične samočistilne lastnosti, ki so bile celo boljše od dobljenih pri enokomponentni apreturi z ZnO.

Ključne besede: poliamid 6, mikrogel, poli-(N-izopropilakrilamid)/hitozan, nanodelci ZnO, odzivnost na temperaturo in pH, zaščita pred UV-žarki, fotokatalitične samočistilne lastnosti

1 Introduction

Stimuli-responsive microgels are water-insoluble three-dimensional cross-linked polymers that can absorb and desorb large quantities of water, changing their volume by swelling or de-swelling [1–3]. Microgels can be responsive to different external stimuli, i.e., temperature, pH, ionic strength, light and electric field [1]. For textile functionalization, the most widely studied systems are temperature and pH responsive microgels due to their physiological significance. The most important temperature-responsive polymer used for the formation of microgels is poly(N-isopropylacrylamide) (pNIPAAm), which is known to exhibit a lower critical solution temperature (LCST) that is closest to the surface temperature of human skin (32–36 °C) [3–5]. Among pH-responsive polymers, the polysaccharide biopolymer chitosan is the most popular because of its biocompatibility and biodegradability [1, 6]. A hydrogel with dual functionality, pH and temperature responsiveness can be created by combining pNIPAAm and chitosan polymers.

In textiles, the incorporation of pNIPAAm/chitosan microgel (PNCS) was mostly applied to cellulose, but rarely to polyester or other textile fibres, using the pad-dry-cure method [7–16]. To increase the coating durability, different cross-linkers were used in combination with the PNCS microgel, or they were applied to the fibres in the pretreatment process to increase their adhesion ability. Accordingly, different amounts of 1,2,3,4-butanetetracarboxylic acid (BTCA) and PNCS were applied to cotton fabric to evaluate the liquid management properties and washing fastness of the coating [7, 9–11]. It was found that the PNCS microgel clearly influenced the water retention capacity of the fibres, which was directly dependant on temperature and pH. It did not appear that the presence of BTCA influenced the responsive behaviour of the PNCS [11]. Water retention capacity (WRC) increased by increasing the amount of PNCS, even more in the presence of

BTCA. The PNCS cross-linked with BTCA also showed dual-responsiveness on cotton fabric after five repetitive washings [7]. The modification of fibres with PNCS microgel impaired intrinsic properties but improved textile quality and wicking, especially at temperatures above the LCST [12]. When the PNCS microgel was embedded into the silica matrix previously created on the polyester fabric using a sol-gel technology, it enhanced the stimuli responsiveness of the fabric in comparison to that modified by PNCS without the presence of the silica matrix [14]. Furthermore, air, argon or nitrogen plasma was also used for cotton surface activation before the application of the PNCS, achieving better incorporation of microgel onto the fibres [13].

To enhance the PNCS microgel functionality, controlled-release and bio-barrier formation antimicrobial agents have already been successfully incorporated into its structure by our research group and applied to cotton fibres [8, 17]. The concept of the present research was to create new functional properties that will complement the thermoregulation and moisture management for comfort improvement of textiles by preparing the PNCS microgel with UV protection and self-cleaning properties. To this end, ZnO was chosen as a very promising candidate that could provide these properties and thus contribute to the added value of the PNCS microgel coating. Namely, according to literature, ZnO is well known as an excellent UV protection and antimicrobial agent in different applications on textile substrates [18–25]. The ZnO nanoparticles were also incorporated in different hydrogels, i.e., N,N-methylenebisacrylamide [19], pNIPAAm [20], β -chitin [21] and chitosan [22, 25]. The film produced by incorporating ZnO nanoparticles into a pNIPAAm hydrogel had a homogeneous distribution of nanoparticles and high antimicrobial properties with no cytotoxicity towards a mammalian cell line [20]. The incorporation of ZnO nanoparticles into chitosan film enhanced the antimicrobial activity against *E. coli* and *S. aureus*. Other properties were also improved,

such as UV-blocking and swelling behaviour in different pH solutions [25].

In this research, ZnO nanoparticles (NPs) were incorporated into PNCS microgel and applied to polyamide 6 (PA6) fabric with the aim to create pH- and temperature-responsive fabric with UV-protective and self-cleaning properties. Two different functionalization procedures were used. In the first procedure, the ZnO NPs were incorporated into the PNCS microgel, and both components were applied to the PA fabric together. In the second one, PA6 fabric was first coated by the PNCS microgel, followed by the application of ZnO NPs. Furthermore, to increase the adsorption ability of PA6 fabric, the silica matrix was first created on the fibres in which the PNCS and ZnO NPs were incorporated by both the functionalization procedures. Based on the determination of stimuli responsive, UV protective and self-cleaning properties of the coated fabric, the most effective functionalization procedure was chosen.

2 Experiment

2.1 Materials

Throughout the research, 100% PA6 plain weave fabric with a weight of 75 g/m² per unit area was used. PNCS microgel was prepared with the use of chitosan (Chitoclear, Primex, Iceland), NiPAAm (Acros Organics, Belgium), N,N'-methylenebisacrylamide (Sigma-Aldrich) and ammonium persulfate (Sigma-Aldrich), ZnO suspension by ZnO powder (MK Impex Corp.) and polysiloxane matrix by using iSys MTX (CHT/Bezema Group).

2.2 Synthesis of PNCS microgel

The synthesis of the PNCS microgel via free radical polymerization was performed according to the procedure described by Lee et al. [26]. In 300 mL of distilled water and 3 mL of glacial acetic acid, 1.0 g of chitosan was dissolved and placed in a flask and degassed with nitrogen for 30 minutes. Next, 7.0 g of NiPAAm and 0.21 g of a cross-linking agent N,N'-methylenebisacrylamide were added with intense stirring (320 rpm), and the temperature of the reaction mixture was raised to 50 °C. After 40 min, 0.9 g of ammonium persulfate was added to initiate polymerization, which caused the reaction mixture to turn turbid. The reaction proceeded in a nitrogen

atmosphere at 50 °C for 3 h. Subsequently, the reaction mixture was dialysed against bi-distilled water using a Spectra/Por 4 membrane (Fisher Scientific) for 10 days to remove impurities and unreacted monomers.

2.3 Preparation of the ZnO nanoparticles suspension

The ZnO solution (3% concentration) was prepared by dispersing ZnO powder in bi-distilled water. The solution was stirred for 15 min while 1 mL/L CH₃COOH 30% was added dropwise. Then, the solution was sonicated for 30 min.

2.4 Functionalization of PNCS microgel and its application to the polyamide 6 fabric

Prior to the deposition of the functionalized microgel, a polysiloxane matrix was applied to the PA6 fabric to assure an even distribution of the functionalized PNCS microgel particles. For this purpose, an aqueous solution of a reactive organic-inorganic binder iSys MTX was used in a concentration of 15 g/l. The latter was applied by the pad-dry-cure procedure, which included full immersion of the fabric sample, wringing by 60% wet pick up, drying for 1 minute at 100 °C and curing at 150 °C for 5 minutes.

Functionalization of PNCS microgel was obtained using two approaches. In the first approach, the microgel was functionalized directly in the suspension and applied to the PA6 fabric. In this case, the suspension of the microgel was heated to 50 °C (above the LCST of poly-NiPAAm). The expelled water was removed and replaced with the same amount of ZnO NPs suspension. Afterwards, the obtained suspension was cooled to 20 °C to stimulate the microgel swelling and thus absorb the ZnO NPs into the PNCS microgel. The process of heating and cooling was repeated twice. The functionalized microgel was then applied to the PA6 fabric, using the pad-dry procedure, which included the full immersion of the fabric sample into the corresponding suspension, wringing by 60% wet pick up and drying for 1 minute at 100 °C.

In the second approach, the microgel suspension was firstly applied to the PA6 fabric, using the pad-dry process and the same parameters as described in the first approach. During drying, the fabric samples were exposed to hot air which resulted in the de-swelling of the PNCS microgel particles. Drying was followed by an immediate immersion of the

Table 1: Sample codes according to the chemical modification

Sample code	Chemical modification
PA	No treatment
PA(PNCS-ZnO)	Application of PNCS previously functionalized with ZnO NPs suspension
PA(PNCS+ZnO)	Application of PNCS followed by the application of ZnO NPs suspension
PA-Si	Application of iSys MTX
PA-Si(PNCS-ZnO)	Application of iSys MTX followed by the application of PNCS previously functionalized with ZnO NPs suspension
PA-Si(PNCS+ZnO)	Application of iSys MTX followed by the application of PNCS with subsequent application of ZnO NPs suspension
PA(ZnO)	Application of ZnO NPs suspension

samples into the ZnO NPs suspension at room temperature for approximately 1 minute. Previously dehydrated PNCS microgel particles swelled and absorbed the ZnO NPs suspension. Finally, the fabric samples were dried for 1 minute at 100 °C.

For the purpose of comparison, both approaches were performed on PA6 fabric without the application of the polysiloxane matrix. ZnO NPs were also applied to the fabric individually. Sample codes according to the chemical modification are presented in Table 1.

2.5 Analytical Methods

2.5.1 Scanning Electron Microscopy (SEM)

SEM was conducted on a JSM-6060 LV (JEOL, Japan). Prior to the SEM analysis, samples were coated with a layer of gold to ensure sufficient electrical conductivity. SEM micrographs were taken at 1000x and 3000x magnification.

2.5.2 Fourier Transform Infrared Spectroscopy (FT-IR)

FT-IR spectra were obtained on a FT-IR spectrometer (Perkin Elmer, UK). The spectra were recorded over the range of 4,000–600 cm⁻¹ with a resolution of 4 cm⁻¹. An average of 16 spectra were taken per sample.

2.5.3 Moisture content

Temperature responsiveness was assessed by measuring the moisture content (MC) using a Moisture analyser MLB 50-3C (Kern and Sohn, Germany). Studied samples were pre-conditioned at 65% relative humidity at 20 and 40 °C for 24 hours before they were put in a moisture analyser and dried at 50 °C until constant mass was reached. The value of MC was determined by the following equation:

$$MC = \left(\frac{m_o - m_f}{m_o} \right) \times 100[\%] \quad (1),$$

where m_o is the mass of the preconditioned sample and m_f the final mass of the sample after drying. For each sample, five measurements of MC were obtained and presented as the mean value with standard deviation.

2.5.4 Water vapour permeability

Water vapour permeability was determined according to the standard method UNI 4818-26 and performed at 65% relative humidity at 20 and at 40 °C. The water vapour transmission rate (WVTR) was calculated using the following equation:

$$WVTR = \frac{\Delta m \cdot 24}{S \cdot t} [\text{gm}^{-2} \text{day}^{-1}] \quad (2),$$

where Δm is the change of mass, S is the testing area of the fabric sample (actual value 7 cm²) and t is the time of testing (actual value 24 h). For each sample, three measurements were performed and the mean value was calculated.

2.5.6 Water uptake

To evaluate the dual pH and temperature responsiveness of the PNCS microgel, the samples of known mass were immersed for 30 minutes in the buffer solutions of pH 3 at 20 °C and of pH 10 at 40 °C. Afterwards, the samples were taken from the buffers, and their mass was determined. Water uptake (WU) was determined by the following equation:

$$WU = \left(\frac{m_w - m_o}{m_o} \right) \times 100[\%] \quad (3),$$

where m_w is the weight of the sample taking up water and m_o is the initial weight of the sample.

2.5.6 Ultraviolet protection factor

The ultraviolet protection factor (UPF) of the untreated and functionalized fabric samples was determined according to the AATCC TM 183 standard and measurements were performed using a Varian CARY 1E UV/VIS spectrophotometer (Varian, Australia) containing a DRA-CA-301 integration sphere and Solar Screen software. The transmissions of the ultraviolet radiation through samples were measured in the spectral range between 280 and 400 nm, and the average transmittance (T) with the wavelengths between 315 and 400 nm (UV-A), 280 and 315 nm (UV-B) and 280 and 400 nm (UV-R) were determined from the measurements. UPF was calculated according to the following equation:

$$UPF = \frac{\sum_{\lambda=280}^{400} E_{\lambda} \cdot S_{\lambda} \cdot \Delta\lambda}{\sum_{\lambda=280}^{400} E_{\lambda} \cdot S_{\lambda} \cdot T_{\lambda} \cdot \Delta\lambda} \quad (4),$$

where E_{λ} is the relative erythral spectral effectiveness, S_{λ} is the solar spectral irradiance, T_{λ} is the spectral transmittance of the specimen, and $\Delta\lambda$ is the measured wavelength interval in nm. The UPF rating and UVR protection categories were determined from the calculated UPF values according to the Australian/New Zealand Standard: Sun protective clothing – Evaluation and classification.

2.5.7 Photocatalytic self-cleaning efficiency

The photocatalytic self-cleaning properties of the studied samples due to the presence of ZnO nanoparticles were determined by measuring the fading of coffee stains when exposed to UV light. Samples were immersed in a 2.5% coffee solution and air dried under ambient conditions. The photocatalytic activities of the samples were assessed by monitoring the degradation of the coffee stain after 3, 6 and 9 hours after the exposure of the samples to artificial light at $65 \pm 2\%$ relative humidity and $20 \pm 1^{\circ}\text{C}$ in a Xenotest Alpha (Atlas, USA), equipped with a xenon lamp with an adjustable radiation power region 0.8–2.5 kVA and an expanded range of radiation (300–400 nm). An assessment of the degradation of the stain was performed using the reflectance measurements, R , of the studied samples on a Datacolor Spectraflash SF 600 spectrophotometer (Datacolor, Switzerland) using D 65/10° light. For each sample, ten measurements of the R value were obtained, and the corresponding K/S values were calculated according to the Kubelka–Munk equation [27]:

$$\frac{K}{S} = \frac{(1 - R)^2}{2R} \quad (5),$$

where $\frac{K}{S}$ is the ratio of the coefficient of light absorption (K) to the coefficient of light scattering (S) and R is the reflectance at 400 nm. Based on the $\frac{K}{S}$ values, the stain degradation degree expressed as a $\frac{\Delta K}{S}$ value was determined according to the literature [27, 28]:

$$\frac{\Delta K}{S} = \frac{\left(\frac{K}{S}\right)_1 - \left(\frac{K}{S}\right)_2}{\left(\frac{K}{S}\right)_1} \times 100[\%] \quad (6),$$

where $\left(\frac{K}{S}\right)_1$ belongs to the non-illuminated sample and $\left(\frac{K}{S}\right)_2$ to the illuminated sample.

3 Results and discussion

3.1 Coatings characterization

The SEM images in Fig. 1 reveal the morphology changes of the PA6 fibre surface caused by the applied coatings. Whereas the fibre surface of the PA and PA-Si samples are smooth, indicating that the presence of the silica matrix did not significantly change the topography of fibres, with respect to the magnification scale used, the application of PNCS increased the structured roughness of the fibre surface. Bright spots which are clearly visible on the PA(ZnO) sample are attributed to the ZnO particles, which confirm that smaller to larger agglomerates of ZnO nanoparticles were formed on the fibres. ZnO agglomerates can also be seen in the presence of PNCS, which suggests that the particles were entrapped in the structure of the microgel. Chemical changes of the studied samples were determined using ATR FT-IR spectroscopy (Fig. 2). Sample PA displays absorption bands characteristic for the amide groups, which are present at 1634 cm^{-1} (amide I), 1535 cm^{-1} (amide II) and 1262 cm^{-1} (amide III) [29, 30]. Additionally, absorption bands characteristic for the secondary NH group appear at 3291 cm^{-1} and 3088 cm^{-1} , as well as CH_2 asymmetrical stretching at 2924 cm^{-1} and 2854 cm^{-1} , absorption band characteristic for C=O group at 1744 cm^{-1} , a set of the relatively weak bends associated with the fingerprint of aliphatic polyamides in the region

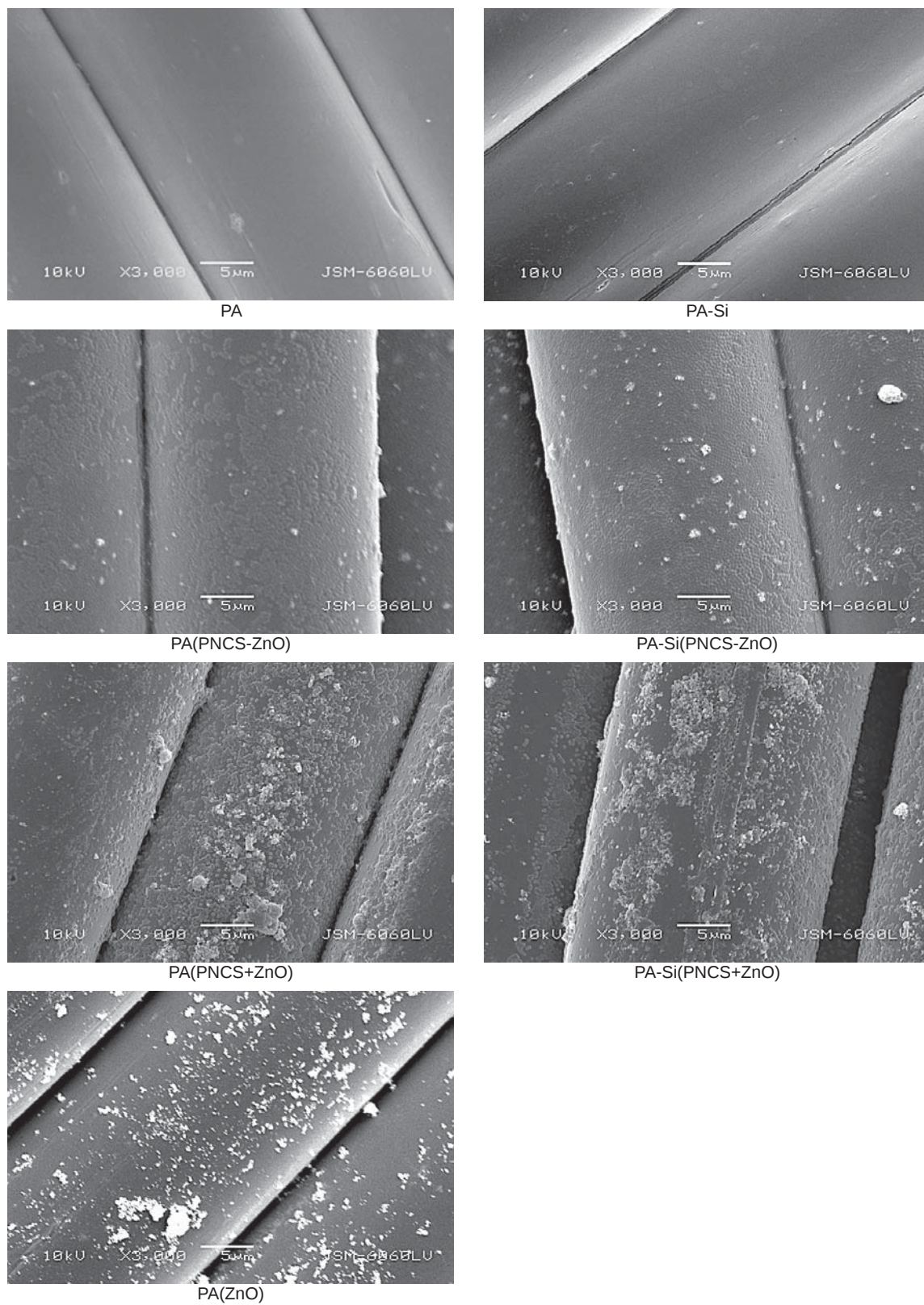


Figure 1: SEM images of untreated and differently coated samples

1500–900 cm^{-1} and an absorption band at 689 cm^{-1} , which can be ascribed to the bending motion of the O=C–N group are clearly evident [29]. Similar spectra were obtained for all of the coated samples, although the intensities of the aforementioned bands decreased. This phenomenon was most prominent at 2924 cm^{-1} , 2854 cm^{-1} and 1744 cm^{-1} . Absorption bands, ascribed to PNCS and Si coatings were overlapped by those of PA6 [29]. Namely, characteristic bands of PNCS microgel, contributed by the presence of N–H stretching vibrations appear at 1456 cm^{-1} and the bands characteristic for amide I and amide II appear at 1645 cm^{-1} and 1535 cm^{-1} , while siloxane chains in the silica matrix could be seen by the formation of an absorption band at 1085 cm^{-1} . Due to the overlapping, no additional bands indicating the presence of PNCS and Si coatings could be observed. Hence, ZnO particles could not be detected from the ATR spectra.

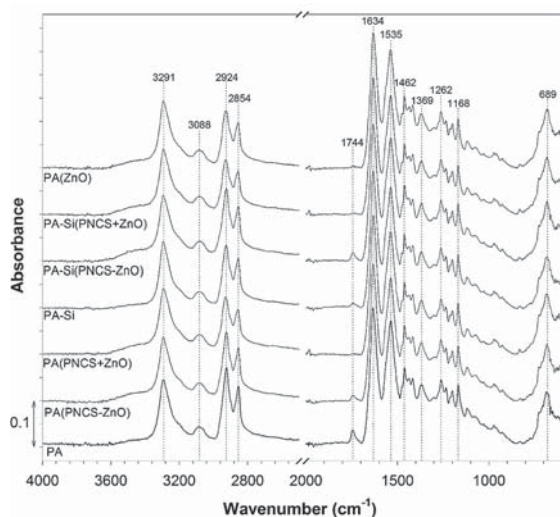


Figure 2: ATR FT-IR spectra of the untreated and coated samples in the 4,000–600 cm^{-1} spectral region

3.2 Functional properties of the coated samples

3.2.1 Temperature responsiveness

To determine the temperature responsiveness of the PNCS microgel on the samples, moisture content (MC) (Fig. 3) and water vapour transmission rate (WVTR) (Fig. 4) at 20 °C and 40 °C (i.e., below and above the LCST of poly-NiPAAm) were investigated. The swelling of the hydrophilic PNCS at 20 °C caused an increase in the MC values for all microgel coated samples, with respect to the PA and PA-Si

samples. Increasing the temperature from 20 °C to 40 °C led to the de-swelling of the PNCS microgel, which resulted in water expulsion from the hydrophobic microgel and, consequently, a decrease in the MC values. However, the results in Fig. 3 show that the MC values of the PA(PNCS-ZnO), PA/(PNCS+ZnO), PA-Si(PNCS-ZnO) samples, gathered at 40 °C were unexpectedly higher, compared to the values of the PA and PA-Si samples. Only the PA-Si(PNCS+ZnO) sample possessed a lower MC value, compared to the untreated PA6 sample. Such behaviour could not be easily explained, although these results suggest that the incorporation of ZnO particles into the microgel slightly hindered the de-swelling ability of the PNCS microgel. The de-swelling ability was most hindered, when PNCS was previously functionalized with ZnO nanoparticles and subsequently applied onto the PA6 fabric.

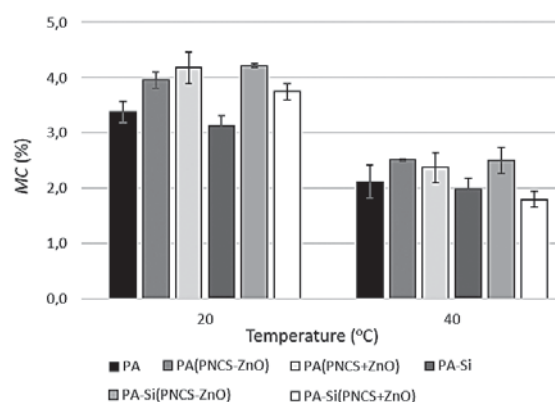


Figure 3: Moisture content, MC, of the untreated and differently coated samples obtained after preconditioning at 65% R.H. and 20 °C and 40 °C

The MC results are in good correlation with the WVTR results, presented in Fig. 4. The swelling of the PNCS on the PA6 fabric at 20 °C increased the closed surface of the fabric and decreased its porosity, which affected the lower water vapour permeability in comparison to the PA and PA-Si samples. The water vapour permeability of all the samples increased at 40 °C compared to 20 °C, although was reduced in the case of the PA(PNCS-ZnO), PA/(PNCS+ZnO), PA-Si(PNCS-ZnO) samples due to the insufficient de-swelling of the microgel. The only exception was the PA-Si(PNCS+ZnO) sample, for which approximately 26% higher WVTR was obtained compared to the PA sample, since the de-swelling of the microgel was unhindered and the

pores between the fibres and yarns in the fabric structure enlarged. Without a doubt, the MC results suggest that the coating created by the application of iSys MTX followed by the application of PNCS with the subsequent application of the ZnO nanoparticles suspension has the highest temperature responsiveness.

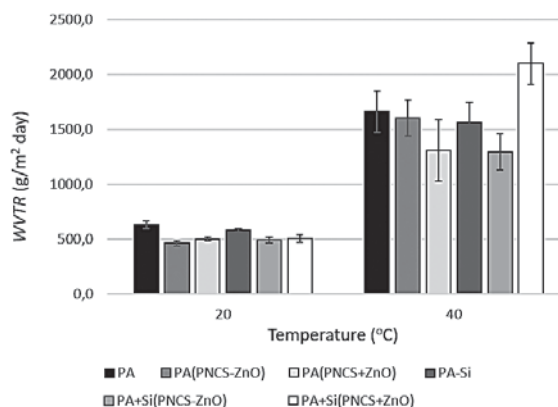


Figure 4: Water vapour transition rate (WVTR) of untreated and differently coated samples determined at 20 °C and 40 °C

3.2.2 Dual temperature- and pH-responsiveness

The WU results presented in Fig. 5 show the dual temperature and pH responsiveness of the PNCS microgel. At pH value 3 and the temperature of 20 °C, both polyNiPAAm and chitosan within the microgel were in hydrophilic form, thus the microgel reached its fully swollen state. On contrary, at pH 10 and 40 °C, both polyNiPAAm and chitosan were in hydrophobic state and the microgel was in the fully de-swollen state. As seen from Fig. 5, the presence of PNCS on the coated samples increased water uptake by 7–12% when samples were immersed in acidic solution at room temperature. The highest increase in WU was obtained for the PA-Si(PNCS+ZnO) sample. In contrast, after the samples were immersed in an alkaline buffer solution at 40 °C, the WU values did not vary significantly, irrespective of the present coating, meaning that the WU of the coated samples were similar to the WU of the untreated PA sample, when PNCS was hydrophobic. These results are reasonable since PA6 fibres are hydrophobic by nature and therefore are poorly swollen and wetted in water. Results are contrary to the one obtained in the case of PNCS microgel applied on the hydrophilic cotton fibres, where the water absorption to the amorphous region of the fibres could have

also occurred, despite the presence of the de-swelled microgel on the fibre surface [10, 17].

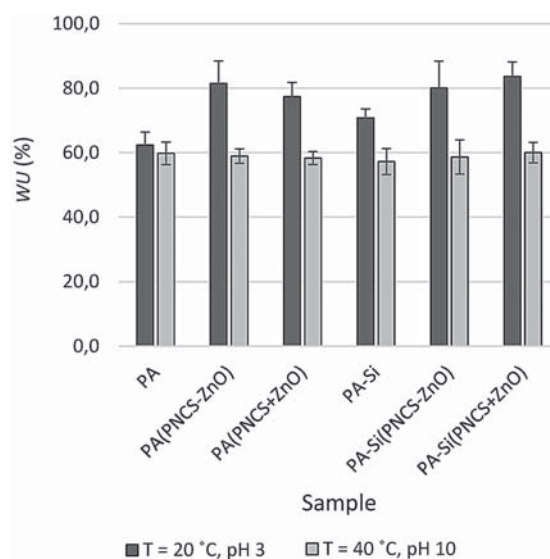


Figure 5: Water uptake (WU) of untreated and differently coated samples obtained after being immersed for 30 min in the buffer solution of pH 3 at 20 °C and in the buffer solution of pH 10 at 40 °C

3.2.3 UV protection

The results of the UV protection properties calculated for the untreated and coated samples (Table 2) show that the lowest UPF values, equal to 4.79 and 4.68, were obtained for PA and PA-Si samples, respectively, indicating that these samples exhibited insufficient UV protection. This suggests that no UV active additives were included in the melt spinning process of the PA6 fibres and that the silica matrix created on the fibres surface did not act as a UV absorber. The UPF of the samples increased in the presence of ZnO, which represented a UV active component in the coating. Accordingly, the UPF value of the PA(ZnO) sample increased to 12.46 which is rated as good UV protection. It is also clearly evident from the results that the finishing procedure significantly influenced the UV protection properties of the fibres. Whereas the UPF values of the PA(PNCS-ZnO) and PA-Si(PNCS-ZnO) samples increased only from 4.79 to 6 ± 0.2 , the UPF values of the PA(PNCS+ZnO) and PA-Si(PNCS+ZnO) samples were much higher and reached values of 15.28 and 18.25, respectively. This indicates that the coatings created by the subsequent application of ZnO suspension to the fabric sample previously modified by

Table 2: Mean UPF, UPF rating and UVR protection categories for untreated and differently coated samples

Sample code	Mean UPF	T(UVA) [%]	T(UVB) [%]	T(UVR) [%]	UVA blocking [%]	UVB blocking [%]	UPF rating	UVR protection category
PA	4.79	31.70	21.45	28.27	68.30	78.55	5	non-rateable
PA(PNCS-ZnO)	6.25	26.18	16.06	22.87	73.82	83.94	6	non-rateable
PA(PNCS+ZnO)	15.28	13.10	6.52	11.02	86.90	93.48	15	good
PA-Si	4.68	31.61	21.93	28.34	68.39	78.07	5	non-rateable
PA-Si(PNCS-ZnO)	5.81	26.93	17.47	23.80	73.07	82.53	6	non-rateable
PA-Si(PNCS+ZnO)	18.80	11.56	5.25	9.58	88.44	94.75	19	good
PA(ZnO)	12.46	15.38	8.03	13.02	84.65	91.97	13	good

PNCS were much more effective against UV radiation in comparison to the coatings including PNCS which was first functionalized by ZnO nanoparticles and afterwards applied to the PA6 fabric, irrespective of the presence of the silica matrix.

3.2.4 Photocatalytic self-cleaning

The results of the coffee stain degradation as a measure of photocatalytic self-cleaning properties of the coatings due to the presence of ZnO nanoparticles are presented in Fig. 6. It was observed that during the illumination of the samples, the colour of the coffee stains became lighter because of their photodegradation, which caused a decrease in the K/S values of the samples. According to equation 5, the greater the decrease in the K/S value is, the higher the $\Delta K/S$ value is, and the greater is the photocatalytic self-cleaning efficiency of the coating.

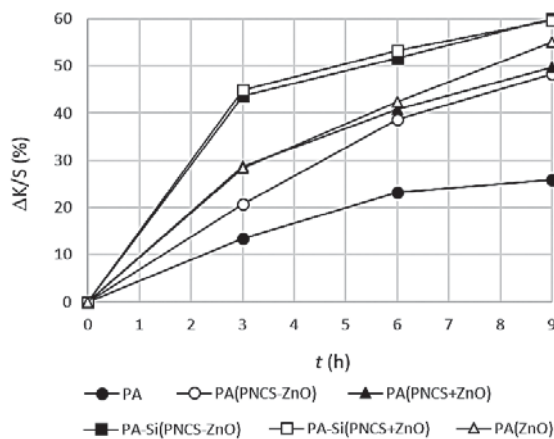


Figure 6: Degree of coffee stain degradation ($\Delta K/S$) on untreated and differently coated samples after their illumination for 3, 6 and 9 hours

The degradation rate of the coffee stain was significantly higher on the coated samples, with respect to the PA sample. Throughout the whole period of the illumination, the maximal degree of stain degradation was observed in the case of the PA-Si(PNCS-ZnO) and PA-Si(PNCS+ZnO) samples with almost the same $\Delta K/S$ values, which were much higher than those obtained for the PA(ZnO), PA(PNCS-ZnO) and PA(PNCS+ZnO) samples. This suggests that the presence of the silica matrix had a greater effect on the ZnO photocatalytic self-cleaning properties, than the method of incorporation of the ZnO particles into the coating. It is well known that SiO_2 does not exhibit a photocatalytic self-cleaning activity [31], therefore the most reasonable explanation for this phenomenon is that the silica matrix increased the uniformity of the PNCS and ZnO coatings on the PA6 fabric and thus contributed to the behaviour of the coatings.

4 Conclusion

In this work, coatings consisting of temperature- and pH-responsive PNCS microgel functionalized with ZnO were successfully fabricated on PA6 fabric, using different application procedures. The results show that the swelling caused the increase in the MC values for all samples with the microgel coating compared to the untreated PA and PA-Si samples. The hydrophilic and hydrophobic character of PNCS was clearly shown when the swelling and de-swelling ability of the microgel was investigated in a buffer solution at pH 3 and 20 °C when pNi-PAAm and chitosan components were in hydrophilic

form and at pH 10 and 40 °C when polyNiPAAm and chitosan components were in hydrophobic form. The presence of ZnO provided the UV protection and photocatalytic self-cleaning properties of the coatings. The results also show that the application procedure of the coating greatly influenced its stimuli responsiveness and functionality. The highest swelling/de-swelling ability with simultaneous good UV protection and the most effective photocatalytic self-cleaning properties was obtained for the coating that was created by the application of PNCS to the PA6 fabric previously modified by the silica matrix followed by the subsequent application of ZnO particles to the PNCS.

Acknowledgement

This work was carried out in the framework of the courses *Advanced Finishing Processes and Chemical Functionalisation of Textiles in the Master Study Programme, Textile and Clothing Planning*. The research was supported by the Slovenian Research Agency (Program P2-0213, Infrastructural Centre RIC UL-NTF).

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