Proceedings of the 4th International Congress APMAS2014, April 24-27, 2014, Fethiye, Turkey

The Role of TiO_2 Nanoparticles on the UV Protection Ability and Hydrophilicity of Polyamide Fabrics

D. Fakin*, K. Stana Kleinschek, A. Ojstršek

University of Maribor, Faculty of Mechanical Engineering, Institute for Engineering Materials and Design, Smetanova 17, 2000 Maribor, Slovenia

The focus of this study was to characterize three industrially-prepared (*via* the sulphate synthesis process) nano-TiO_2 colloidal dispersions with the intention to elucidate their role on the hydrophilicity as well as UV shielding ability when applied onto polyamide fabric. Transmission electron microscopy (TEM) and UV spectrophotometry of the selected dispersions proved the presence of TiO_2 nanoparticles of different shapes and sizes, as well as its imposing absorption capability within the UV region. In addition, TiO_2 dispersions in three concentrations accompanied by selected chemicals and auxiliaries were applied on polyamide fabrics according to standard exhaustion procedure. Scanning electron microscopy (SEM) was adopted in order to analyse the morphological structure of nano-TiO_2-upgraded PA fabrics. Furthermore, the UV-protective ability and hydrophilic properties were evaluated. The gained results show excellent blocking properties against UV-rays (UPF 50+), as well as the (super)hydrophilicity of TiO_2-modified PA fabrics, regarding the type of employed TiO_2 colloidal dispersion.

DOI: 10.12693/APhysPolA.127.943

PACS: 81.05.Lg, 81.70.Fy, 82.70.Dd

1. Introduction

Global trends in textile industry are oriented towards development and manufacturing of novel final high-added value products with multifunctional properties like UV-blocking, anti-microbial, anti-oxidative, self-cleaning, flame-retardation, hydrophilic/hydrophobic, etc., which were also related to the human health and comfort [1]. Polyamide (PA) fibres are linear polymers containing amide bonds [2]. They are rather hydrophobic in character with moisture regain only about four percent; and thus, less comfortable to the wear. Through the surface modification by integrating nanotechnology, the water absorption capacity as well as some other functional properties of textiles could be incorporated or enhanced [3]. Inorganic nano-sized titanium dioxide (TiO_2) has recently attracted significant attention for surface functionalization of different type of textile materials because of its non-toxicity, long-term lifetime, superior chemical and thermal stability, and excellent photoactivity under UV irradiation [1, 4, 5].

Therefore, the purpose of this research was to investigate influence of different type of nano-size TiO_2 colloidal dispersions on the functionality of polyamide fabric: (i) UV protective properties, and (ii) hydrophilic features as one of the important functional properties of clothes.

2. Experimental

2.1. Materials

In the present study, an industrially-bleached plane-weave 100% polyamide fabric (PA) was used with a mass/unit area of 111 g/m^2, warp density of 45 threads/cm and weft density of 36 threads/cm. The source fabric was washed at 40 °C for 20 min., using a neutral non-ionic washing agent, and after that rinsed in warm and then cold water, and dried at room temperature.

Three commercially-available colloidal dispersions of nano-sized TiO_2 were used for this research, produced according to the sulphate synthesis process by the Cinkarna, Metallurgical and Chemical Industry Celje, Inc., Slovenia [6]; (i) CCA100AS (A1A) which includes acidic dispersion (pH 1) of polycrystalline anatase TiO_2 in concentration of 21.8%, (ii) CCA200BS (A2N) which includes neutral dispersion (pH 7) of monocrystalline anatase TiO_2 in concentration of 17%, and (iii) CCR110 (RN) which includes neutral dispersion (pH 7) of rutile TiO_2 in concentration of 24.2% coated by 3 wt.% of hydrated amorphous SiO_2 shell. The information about solid TiO_2 nanoparticles concentration within individual dispersion and shell content were acquired by the producer-supplier.

2.2. PA modification procedure

The application of aforementioned individual nano-sized TiO_2 colloidal dispersion was carried-out according to the exhaustion procedure using liquor ratio of 20:1 (190 ml of deionized water against 9.5 g of PA fabric) in a sealed, stainless-steel treatment-pot of 200 cm^3 capacity, housed in a laboratory-scale apparatus Labomat (W. Mathis). The initial bath composed of 0.5% of amphoteric levelling agent (Keriolan A2N-Bezema), 1 ml/l of pH-regulator (Meropan EF-Bezema) and acetic acid (80%) for pH 5.5–6 adjustment. After 20 minutes of bath circulation at 40 °C, 3, 6 or 9% owf (of weight-of-fabric) of individual TiO_2 paste was added, raising the bath's temperature up to 98 °C with a heating rate of 2 °C/min,

*corresponding author; e-mail: darinka.fakin@um.si

thereon, maintained for 60 minutes and then reduced to 60 °C. Treated samples were rinsed in a warm and then cold water, and dried at room temperature.

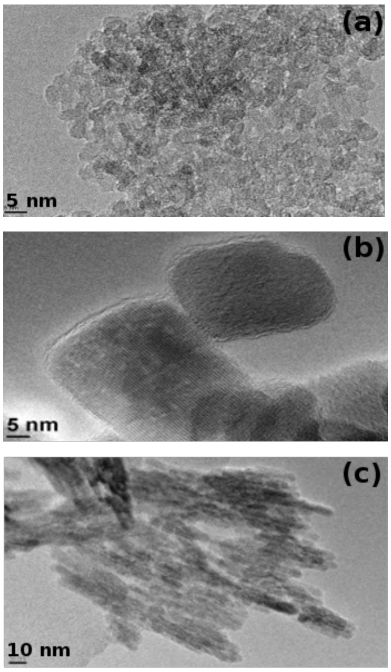

Fig. 1. TEM images of used TiO_2 colloidal dispersions: (a) A1A; (b) A2N; (c) RN.

2.3. Analytical methods

2.3.1. Analysis of TiO_2 dispersions

TEM images were obtained by dropping an individual stable dispersion (of 1% concentration) on the Cu-grid, and thereafter by observing the dried sample using a transmission electron microscope (TEM, Jeol 2100, 200 kV, LaB_6 as an electron source). Absorbance of individual colloidal dispersion, diluted in deionised water in a concentration of 16 mg/l, was recorded by means of a Cary 50 spectrophotometer (Varian) with a quartz cuvette (10 mm optical length) from a wavelength of 200 nm up to 700 nm.

2.3.2. Morphology of TiO_2 modified surfaces

Scanning electron microscopy (SEM) was utilized for the surface morphology of TiO_2 upgraded PA fabric. Approximately 1 cm^2 of the (un)treated fabric was attached on the adhesive carbon band on a brass holder on a Zeiss Gemini Supra 35 VP Scanning Electron Microscope (Carl Zeiss NTS GmbH, Germany) with a maximum scan resolution up to 1.5 nm at 20 kV, and then the SEM images were taken.

2.3.3. Determination of functional properties

The transmission of UVA and UVB rays through differentially treated fabric samples was measured according to the European standard EN 13758-1:2002, over the ultraviolet spectral region (290–400 nm) using a solar-screen Cary 50 spectrophotometer (Varian), equipped with an integrated sphere accessory and a fabric holder accessory. The level of the fabric's shielding capability against harmful UV rays is usually expressed by the ultraviolet protection factor (UPF), which was calculated according to the following equation:

$$UPF = \frac{\sum_{\lambda=290}^{\lambda=400} E(\lambda)\varepsilon(\lambda)\Delta\lambda}{\sum_{\lambda=290}^{\lambda=400} E(\lambda)T(\lambda)\varepsilon(\lambda)\Delta\lambda}, \quad (1)$$

where $E(\lambda)$ is the solar spectral irradiance at Albuquerque [$\mathrm{W\,m^{-2}\,nm^{-1}}$]; $\varepsilon(\lambda)$ is the relative erythema action spectrum; $\Delta\lambda$ is the wavelength interval of the measurements [nm]; and $T(\lambda)$ is the spectral transmittance at wavelength λ.

The hydrophilic feature of untreated and nano-TiO_2-modified fibrous surfaces was investigated by contact angle measurement using a sessile drop technique. Individual sample was placed on a horizontal table attached to a mechanical device on Goniometer (DataphysicApparatus). A micro-drop with the volume of 0.3 μl MilliQ water was poured on the fabric surface. The drop was illuminated by white diffuse light and observed with telemicroscope. A clear image of the drop was directly transferred through a CCD-camera, showing the drop profile. The contact angle was determined from the tangent to the drop at the three phase contact line.

3. Results and discussion

3.1. Characterization of nano-sized TiO_2 colloidal dispersions

Firstly, TEM images of selected three colloidal dispersions were taken and shown in Fig. 1, with the aim of investigating the surface morphology of different types of TiO_2 nanoparticles for subsequent functionalization of PA fabrics. Moreover, to determine the relationship between UV absorbance ability of different type of TiO_2 nanoparticles in dispersions and their UV-blocking properties when applied on the PA fabrics, all three pastes were diluted in water in a concentration of 16 mg/l and measured through UV spectrum from wavelength of 200 up to 400 nm. The obtained curves are graphically presented in Fig. 2.

From the TEM images in Fig. 1, it can be unequivocally perceived the different morphologies, shapes, and sizes of the employed TiO_2 nanoparticles. Figure 1c clearly demonstrates non-spherical shape of nanoparticles of ca. 167 nm in length and ca. 40 nm in width (also confirmed by dynamic light scattering technique - DLS; data not shown). In Fig. 1b, monocrystalline spherical-shaped TiO_2 nanoparticles of 50 nm in diameter were observed as compared to the isotropic morphology of very small spherical crystals of 4–5 nm in Fig. 1a, which aggregated into an individual polycrystalline nanoparticle. Herein, an amorphous phase between the crystals can be noticed that presumably belongs to hydrated titanium oxide or residual organic alkyl components originating from the preparation process of nanoparticles [3].

It is evident from the Fig. 2 that the applied nanoparticles have prominent UV-shielding characteristics, since

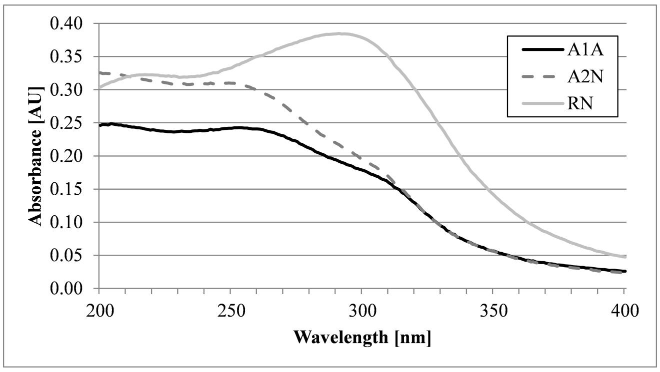

Fig. 2. UV spectrophotometry results of used TiO_2 colloidal dispersions.

they absorb the damaging UV light within a spectral range of between 250 and 400 nm at an exceedingly low concentration of TiO_2 dispersions, with the absorbance maximums at wavelengths of 253 nm (A1A), 246 nm (A2N), and 291 nm (RN). Moreover, it could be noticed that a higher TiO_2 nanoparticles content in dispersion indicates a higher absorbance maximum within the UV region, i.e. 0.2427 AU for A1A (21.8% TiO_2), 0.1264 AU for A2N (17% TiO_2), 0.3849 for RN (24.2% TiO_2), which consecutively influences the higher UV-protection abilities of TiO_2-treated PA, for the same operational parameters during the TiO_2 application procedure.

3.2 Surface functionalization of PA fabrics

Representative SEM micrographs of PA samples before and after modification using 9% owf of individual TiO_2 colloidal dispersion are shown in Fig. 3. In order to assess the role of different type of TiO_2 on the UV-rays blocking ability and wettability of polyamide fabric, UPF values were calculated according to Eq. 1, and the contact angles were determined by means of goniometry. The obtained results are disclosed in Table I.

The surface of the untreated (reference) PA sample, as presented in Fig. 3a, is smooth without any attachments. After application of all three TiO_2 dispersions together with pre-defined auxiliaries, according to exhaustion procedure, the surfaces of the as-modified fibres are covered with small particles (Fig. 3b–3d)). The more homogenous coating is observed in Fig. 3b, 3c using the dispersions of anatase TiO_2 (A1A and A2N), followed by the application of neutral dispersion of rutile TiO_2, coated with 3 wt.% of SiO_2 shell (RN), that obviously did not cover the entire surface of PA (Fig. 3d).

It could be observed from Table I that the hydrophilicity has significantly increased after TiO_2 application, depending on the form of used TiO_2 nanoparticles, their crystallinity, as well as the concentration of applied dispersion, which is in good agreement with the results obtained by [4]. The non-treated (reference) sample shows a contact angle of about 143°. While the rutile TiO_2-SiO_2 (RN) core-shell nanoparticles' application significantly

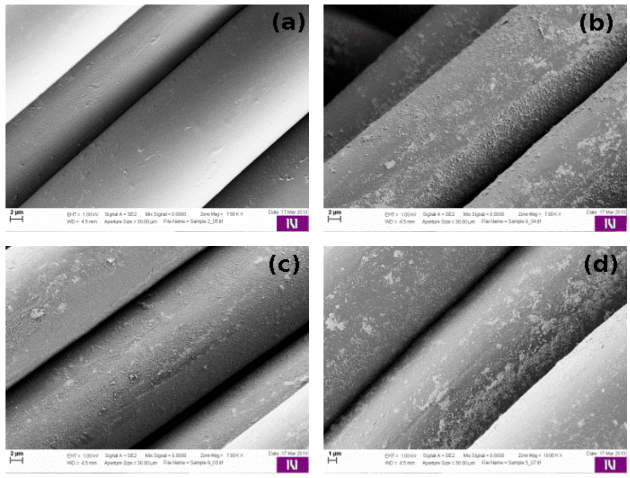

Fig. 3. SEM images of: (a) untreated; and selected TiO_2 modified PA fabrics (9% owf): (b) A1A; (c) A2N; (d) RN.

reduced the water droplet angle to about 98° and polycrystalline anatase TiO_2 to about 63°, monocrystalline anatase TiO_2 rendered the PA fabric super-hydrophilic. Herein, as soon as the water droplet was placed on the surface of PA, the droplet absorbed completely by the modified fabric and the water contact angle could not be determined. Furthermore, some correlations could be done between contact angle measurements and UPF values (Table I). Thus, the lower the water contact angle, the higher the UPF of the TiO_2-modified PA fabric. Also, the UPF increases with the increasing concentration of colloidal dispersion, irrespective of TiO_2 form, although only fabric treated with monocrystalline anatase reaches UPF 50 or more, defining very good or excellent protective properties. When other two types of TiO_2 were applied, the UPF has attained values between 30 and 40, which means that the protective properties are at a low to medium level.

4. Conclusions

The presented study has analysed three colloidal dispersions composed of diverse amounts and forms of TiO_2 nanoparticles, for subsequent functionalization of polyamide fabrics. SEM images revealed successful application of nano-sized TiO_2 onto PA fabric during exhaustion procedure. It should also be concluded, that modified PA fabrics attained super-hydrophilic properties and excellent UV-rays blocking features when using neutral dispersion of monocrystalline anatase TiO_2 in concentration of at least 6% owf.

Acknowledgments

The research leading to these results has received funding from the Slovenian Research Agency (ARRS) under a bigger applied project no. L2-4101, and a programme group for Textile Chemistry P2-0118.

References

[1] D. Mihailović, Z. Šaponjić, M. Radoičić, T. Radetić, P. Jovančić, J. Nedeljković, M. Radetić, *Carbohydr. Polym.* **79**, 526 (2010).

[2] H.R. Kim, H.Y. Seo, *Textil Res. J.* **83**, 1181 (2013).

[3] A. Ojstršek, K. Stana Kleinschek, D. Fakin, *Surf. Coat. Tech.* **226**, 68 (2013).

[4] D. Fakin, N. Veronovski, A. Ojstršek, M. Božič, *Carbohyd. Polym.* **88**, 992 (2012).

[5] H. Zhang, H. Zhu, *Appl. Surf. Sci.* **258**, 10034 (2012).

[6] N. Veronovski, M. Lešnik, D. Verhovšek, *J. Coat. Technol. Res.* **11**, 255 (2014).