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Fabrication of Superhydrophilic Polyester Fabrics Using Various TiO_2 Colloidal Dispersions

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The purpose of this research was to apply four stable colloidal dispersions, combining different TiO_2 core-shell nanoparticles, onto polyester fabric, according to exhaustion procedure, in order to enhance fabrics' water and moisture absorption properties. Firstly, all colloidal dispersions were analysed using transmission electron microscopy (TEM) and dynamic light scattering (DLS) and secondly, the morphologies of TiO_2 modified PES surfaces were evaluated by scanning electron microscopy (SEM). In addition, the superhydrophilic character of fibrous surfaces was investigated by water contact angle measurement. For this purpose, dynamic tensiometry was employed by measuring the changes in the net force on a surface during the repeated immersion and emersion of a solid into a probe liquid. The obtained results show excellent wettability of TiO_2 upgraded PES fabrics depending on the type of applied nano-sized TiO_2-hybride.

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1. Introduction

Polyester (PES) is one of the fastest growing synthetic fibres in the textile industry due to its favourable properties such as superior crease recovery, excellent wash and wear, anti-wrinkle, and quick drying properties [1]. However, it is an exceedingly hydrophobic in character, especially compared to the natural fibres and thus, less desirable material in many textile applications, i.e. sportswear, bedding, under garment. Hydrophobicity is a result of the benzene rings prominence and the presence of -CH_2CH_2- groups [2]. PES is also a highly crystalline fibre consisting of tightly-packed, highly ordered polymer molecules, and with the absence of polar functional groups capable of forming hydrogen bonds with other molecules [3]. With the intention to change the water absorption properties and improve the antistatic behaviour, touch, and moisture transport, the surface modification should be performed. Recently, the application of numerous nanoparticles provided new insights for scientists to develop high-added value products with multifunctional features. TiO_2 has been widely utilised for the surface modification of various textile materials, because of its excellent optical properties, superior thermal stability, long-term lifetime, lack of toxicity, and relatively low-cost, as quoted in [1, 4, 5].

The aim of present paper was, therefore, firstly to characterize four commercially-available colloidal dispersions, which contain rutile crystalline TiO_2 nanoparticles coated by different type and concentration of amorphous shell, and secondly to evaluate the formation of these colloids when applied on PES, by investigating the fabric's morphology as well as its wetting ability.

2. Experimental

2.1 Materials

In the present study, four commercially-available colloidal dispersions were used, combining approximately 20% of rutile crystalline TiO_2 nanoparticles that were superficially coated by different type and concentration of amorphous shell, i) 3 wt.% SiO_2, ii) 5 wt.% SiO_2, iii) 3 wt.% Al_2O_3, and iv) combination of 1 wt.% SiO_2 and 3 wt.% Al_2O_3. All the dispersions were industrially-produced by the Cinkarna Celje, Slovenia. Producer has kindly supplied all colloidal dispersions in the form of pastes as well as disclosed some data about solid TiO_2 nanoparticles concentrations and shell content within individual dispersion. These, so-called TiO_2-hybrides in the above-named stable dispersions were synthesised according to the sol-gel process from metatitanium acid, which is a by-product of the sulphate synthesis process during TiO_2 pigment production. The synthesis procedure is fully described within patents SI 23218A and SI 23547A by Cinkarna Celje.

A series of TiO_2 application trials were accomplished using an industrially-bleached plane-weave 100% polyester fabric (PES) with a mass/unit area of 163 g/m^2, warp density of 20 threads/cm, weft density of 17 threads/cm and fineness of 36.6 tex. Before trials, the fabric samples were washed at 40 °C for 20 min using a neutral non-ionic washing agent, rinsed in warm and then cold water, and dried at an ambient temperature.

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2.2 Exhaustion procedure of TiO_2 nanoparticles application

Individual TiO_2 paste was applied onto polyester fabric in concentration of 9% owf (of weight of fabric) using one-bath exhaustion procedure in a sealed, stainless-steel dye-pot of 250 cm^3 capacity, housed in a Turby (W. Mathis) laboratory-scale device with medium bath circulation. Exhaustion procedure was started at 60 °C, when the combination of individual nano-TiO_2 paste and suitable auxiliaries was put in a dye-pot, followed by a fabric sample at 80 °C using a liquor-to-fabric weight ratio of 20:1 (190 mL of deionized water against 9.5 g of PES). Thereafter, the colloidal bath was heated-up to 130 °C with speed of 2 °C per min, maintained for 60 minutes, and then cooled-down to 70 °C. Finally, the polyester fabric was removed from the bath and rinsed thoroughly in warm and then cold water, neutralized, and dried at an ambient temperature. With the intention to remove unfixed reactants, the treated samples were washed at 50 °C for 5 min (bath-to-fabric weight ratio of 20:1) using 2 g/L of non-ionic wetting agent, rinsed in tap water, and then dried at room temperature.

2.3 Characterization methods

TEM images of selected TiO_2-hybrides were obtained by dropping an individual stable dispersion in concentration of 1% on the Cu-grid, and then after drying out, by observing it by means of a transmission electron microscope (Jeol 2100, 200 kV, LaB_6 as an electron source).

With the aim to determine the particles' size distribution as a function of different shells coated around the TiO_2, the dynamic light scattering (DLS) technique was employed. Measurements were accomplished using a Zetasizer Nano series HT (Malvern, UK), equipped with a light-scattering unit. The working temperature was fixed at 25.0±1 °C. The individual peak was derived from the multi-modal correlation functions.

The surface morphologies of PES fabrics, modified using different nanoTiO_2-hybrides, were analysed by scanning electron microscopy (SEM). Therefore, approximately 1 cm^2 of the selected fabric samples were applied onto an adhesive carbon band fixed to a brass holder for the observation on a Zeiss Gemini Supra 35 VP Scanning Electron Microscope (Carl Zeiss NTS GmbH, Germany) with a maximum scan resolution of up to 1.5 nm at 20 kV.

With the intention to evaluate the influence of different TiO_2 core-shell nanoparticles on the wettability of PES, TiO_2 treated samples were cut into 2×2 cm square pieces and hung on the sample holder in the Tensiometer Krüss K12 apparatus. A total of 10 measurements were taken for each sample in order to calculate a statistical average. Capillary rise measurement procedure has been fully described in [6]. Shortly, the hydrophilic features were determined by measuring the weight increase (m) during liquid (Mili-Q water) penetration on account of capillary effect as a function of time (t). Furthermore, the water contact angle was calculated from the initial slope of the function $m^2 = f(t)$ in accordance with the modified Washburn equation:

$$\cos\theta = \frac{m^2}{t}\frac{\eta}{\rho^2\gamma c}, \quad (1)$$

where $\theta(°)$ is the contact angle between the solid and liquid phases, m(g) is the mass of the absorbed liquid, t(s) is the time, η(Pa s) is the liquid viscosity, $\rho(\mathrm{g\,cm^{-3}})$ is the liquid density, $\gamma(\mathrm{N\,m^{-1}})$ is the surface tension of the liquid, and $c(\mathrm{cm^5})$ is a material constant.

3. Results and discussion

3.1 Analysis of nanoTiO_2 dispersions

The presented study is focused on searching for an appropriate type of TiO_2 core-shell nanoparticles for attaining excellent wettability of PES fabric. For this reason, TEM images of selected four colloidal dispersions at concentration of 0.01 wt.% were taken in order to characterize the surface morphology of diverse nano-sized TiO_2 hybrids for subsequent functionalization of PES fabric. Additionally, DLS measurements were performed for determination of particles size distribution and the average particles size within individual dispersion. The obtained results are presented in Fig. 1.

From the TEM images in Fig. 1a–1d, there can be clearly perceived the presence of small non-spherical TiO_2 crystals of ca. 5 nm in width and > 10 nm in length, which aggregated within individual polycrystalline TiO_2 non-spherical shaped nanoparticles of different sizes, which can therefore be more precisely evaluated from DLS diagrams.

In addition, an amorphous phase between the crystals can be comprehended, that has presumably belonged to residual organic alkyl components or hydrated titanium oxide, originating during the synthesis of nanoparticles, as also reported by Nimittrakoolchai and Supothina [7]. From DLS curves in Fig. 1a–1d, it can be noticed that dispersion combining TiO_2 nanoparticles coated with 5 wt.% of SiO_2, contain exceedingly heterogeneous scattering populations with the widest peak. Herein, the average particles size of 552 nm also proves the presence of large agglomerates of size ca. 5000 nm and thus, this colloidal dispersion is less suitable for fabrics functionalization. On the other hand, the average sizes of the other three TiO_2 hybrids in Fig. 1a, 1c, 1d was 165, 166 and 170 nm, respectively, which indicates a lower agglomeration tendency in water compared to the aforementioned nanoparticles (Fig. 1b).

3.2 Characterization of TiO_2 modified PES fabrics

The surface morphologies of PES fabrics modified according to the exhaustion procedure, using combination of 9% owf of individual TiO_2 paste and adequate auxiliaries, were studied by SEM, and the obtained micrographs are shown in Fig. 2.

Representative SEM images in Fig. 2 demonstrate the different coating morphologies of treated polyester fabric, regarding the employed TiO_2-hybrid. Thus, the most

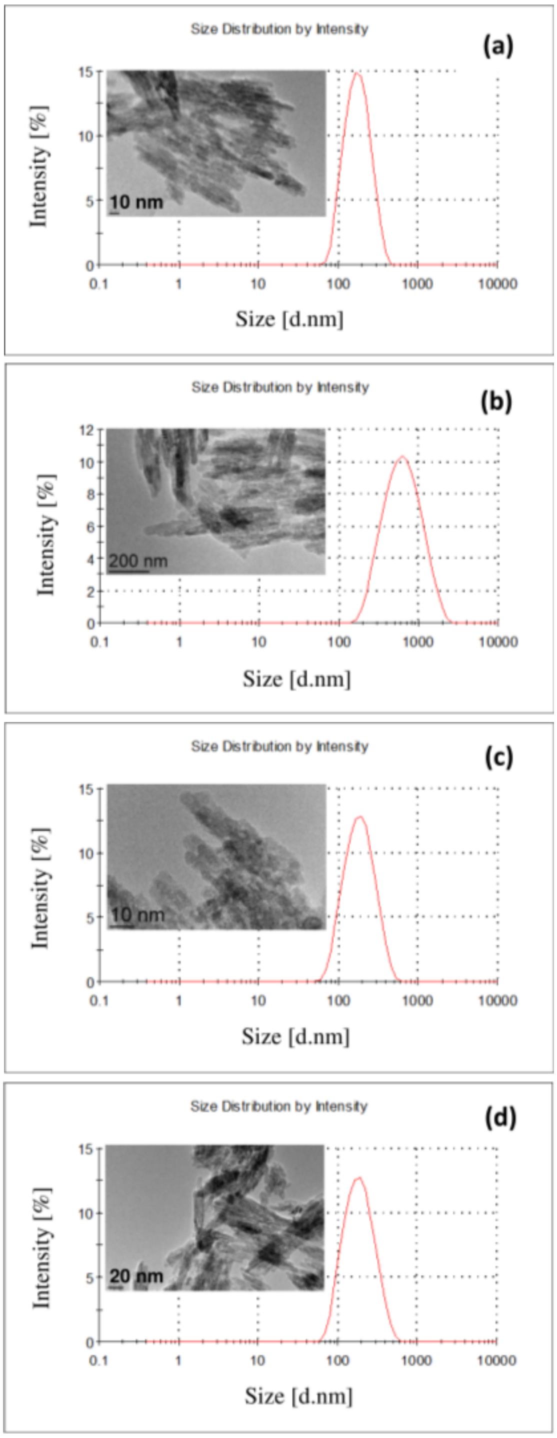


Fig. 1. DLS results and TEM images of rutile TiO_2 nanoparticles coated with (a) 3 wt.% SiO_2; (b) 5 wt.% SiO_2; (c) 3 wt.% Al_2O_3; (d) 1 wt.% SiO_2/3 wt.% Al_2O_3.

homogenous coating can be observed in Fig. 2a when using TiO_2-3 wt.% SiO_2 in comparison to the application of other three colloids. Just the opposite phenomenon can be comprehended from Fig. 2b–2d; namely, PES was obviously covered by larger nanoparticle agglomerates although this could not be expected from the results obtained by TEM and DLS analyses of colloids (Fig. 1b–1d). Moreover, these TiO_2-hybrides did not cover the entire surfaces.

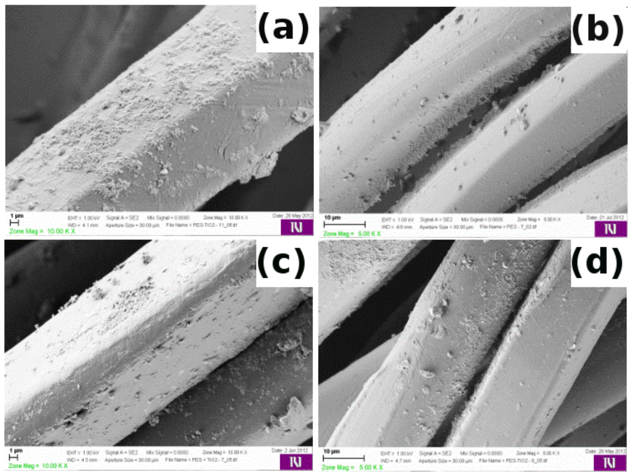
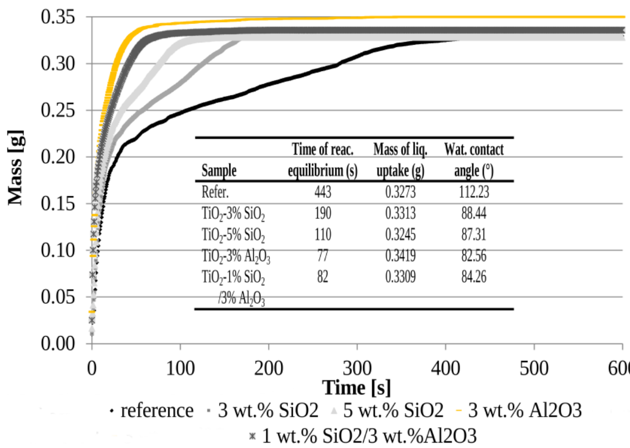


Fig. 2. SEM micrographs of functionalized PES fabrics using 9% owf of: (a) TiO_2 - 3 wt.% SiO_2; (b) TiO_2 - 5 wt.% SiO_2; (c) TiO_2 - 3 wt.% Al_2O_3; (d) TiO_2 - 1 wt.% SiO_2/3 wt.% Al_2O_3.

Additionally, the emphasis was also given to the role of different nano-sized TiO_2-hybrides in the water absorption ability of polyester fabric, which is one of the important functional features of clothes (improvement of anti-static behaviour, moisture transport, and touch). Modified PES samples were thus examined *via* capillary rise method using tensiometer, and the water contact angles were calculated according to Eq. 1. The gained results are graphically represented in Fig. 3.



Sample	Time of reac. equilibrium (s)	Mass of liq. uptake (g)	Wat. contact angle (°)
Refer.	443	0.3273	112.23
TiO_2-3% SiO_2	190	0.3313	88.44
TiO_2-5% SiO_2	110	0.3245	87.31
TiO_2-3% Al_2O_3	77	0.3419	82.56
TiO_2-1% SiO_2 /3% Al_2O_3	82	0.3309	84.26

Fig. 3. Wettability determination of untreated and TiO_2-modified PES.

From Fig. 3 it can be noticed that the mass has increased faster at the beginning of water sorption and has attained a plateau (max. water adsorption) after 443 s (reference-untreated sample), and after 190, 110, 77 or 82 s for TiO_2-treated samples, respectively. Moreover, the calculated average values of fabric-water contact angles were drastically lowered, i.e. from 112.23° (reference sample) to 82.56° (samples modified with TiO_2-hybrides), depending on the type of shell content as also reported by [4]. The lower the water contact angle, the higher the hydrophilicity of the PES fabric is.

4. Conclusions

This research work characterizes four neutral colloidal dispersions, composed of rutile TiO_2 nanoparticles coated with diverse amounts and types of shells, which were industrially-synthesized from metatitanium acid. TEM and DLS results demonstrated polycrystalline non-spherical shape of TiO_2 nanoparticles of different sizes and homogeneities. These so called TiO_2-hybrides were further successfully applied onto polyester fabrics together with suitable auxiliaries during high-temperature exhaustion procedure. SEM images of modified fibrous surfaces have proven that the most uniform nano-scaled coating was achieved when utilising TiO_2-3 wt.% SiO_2 dispersion. Finally, samples functionalized with nano-sized TiO_2-hybrids attained better water sorption at shorter times, as well as superior hidrophilicity (lower contact angles), compared to the untreated sample.

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