UV light-shielding properties of TiO_2-based materials coated flax samples

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The use of nanomaterials in textile area already showed considerable potential with economic and environmental benefits. In the present study, Ag-TiO_2 and Ag-TiO_2/reduced graphene oxide powders were prepared by a combined chemical/thermal approach followed by deposition onto flax samples by immersion from ethanol solution. TiO_2 P25 (Degussa)-coated flax blank sample was obtained and examined for comparison. The morpho-structural properties of flax samples were investigated by Scanning Electron Microscopy (SEM), X-ray powder diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR). The transmittance measurements of the coated flax samples were performed and the ultraviolet (UV) light-shielding ability was evaluated. TiO_2 P25 coated flax sample showed a good UV light-shielding property (UPF = 15.536).

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1. Introduction

In recent years, the nanotechnology opened new opportunities to create innovative textile products without degradation of comfort properties of the substrate. Nanomaterials as coatings over the fabric surfaces induce multifunctional properties, such as wrinkle resistance, water repellence, antibacterial activity, electrically conductive and antistatic, self-cleaning or UV protective [1-3]. Among these, TiO_2-based nanomaterials have gained a wide research interest as photocatalysts in various applications [4, 5]. However, TiO_2 exhibits high sensitivity under UV light due to its large bandgap (3.0-3.2 eV). In order to improve its photocatalytic ability, various modification strategies of TiO_2 have been proposed, such as doping with non-metal or metals, combining with other semiconductors, surface treatments etc. [6].

Silver (Ag) and TiO_2 nanoparticles showed enhanced antimicrobial and photocatalytic activities and they are used in UV protection, self-cleaning, textile or water treatment applications [7, 8]. Moreover, an interesting perspective was opened using the graphene-like materials to modify textile surfaces due to their unique characteristics (high specific surface area, excellent mechanical properties and electrical conductivity, thermal stability, biocompatibility) [9, 10]. Already, some studies reported the Ag/TiO_2 nanocomposites onto cotton fabric with high antibacterial activity and UV protective ability [11, 12], photocatalytic TiO_2–SiO_2-coated cotton textiles [13], nano-TiO_2 coated textiles to combat nosocomial infections [14], graphene and reduced graphene oxide-modified cotton fabric with electrostatic properties for protective cloths in the environment with explosive atmosphere [15], graphene-based wearable e-textiles *via* associated activity monitoring sensor [16], graphene/titanium dioxide nanocomposite for electroconductive, self-cleaning, antibacterial and antifungal cotton fabric [17], graphene/TiO_2 nanocomposite treated wool fabrics with antibacterial activity and photocatalytic self-cleaning property [18], reduced graphene oxide and TiO_2 coatings on polyester fabrics with photocatalytic activity [19]. Therefore, it has been proposed to investigate the UV light-shielding ability of modified flax samples covered by Ag-TiO_2 and Ag-TiO_2/reduced graphene oxide powder composites in comparison with TiO_2 P25 (as widely used commercial nanoparticles) - coated flax sample.

2. Experimental

2.1. Materials

TiO_2-P25 was supplied from Degussa (Germany). Triton X-100 (Fluka, Switzerland) and acetylacetone (Merck, Germany) were used as organic additives. Silver nitrate ($AgNO_3$), ascorbic acid and ethanol were purchased from Alfa-Aesar (Germany), Merck (Darmstadt, Germany) and respectively, Fluka (Germany).

2.2. Preparation of Ag-TiO_2, Ag-TiO_2/reduced graphene oxide, and coated flax samples

The Ag-TiO_2, Ag-TiO_2/reduced graphene oxide (Ag-TiO_2/RGO) composites were obtained by a protocol already reported [20]. Briefly, an appropriate amount of

TiO_2 nanoparticles (P-25 Degussa) was added into a mixture of double-distilled water, Triton X-100 and acetylacetone (5:1:1.5 vol. ratio). After homogenization by magnetic stirring, the corresponding metal source ($AgNO_3$) and the reducing agent (ascorbic acid) were added in order to obtain Ag:Ti = 1:40 molar ratio of final composite. By increasing of temperature up to 80°C, the suspension changed its color from white to dark gray, as a result of chemical reduction of Ag^+ to Ag^o. After drying of suspension and thermal treatment at 450°C for 2 h (in the air) of powder, the Ag-TiO_2 material was obtained. Further, graphene oxide and Ag-TiO_2 (initial Ag-TiO_2:graphene oxide = 10:1 weight ratio) were dispersed in 20% ethanol solution by sonication, then dried and annealed at 300°C for 15 min, under argon atmosphere, obtaining Ag-TiO_2/RGO material.

The 100% flax fabric was subjected to the preliminary conventional treatment in successive stages consist of two hot alkaline treatments and two successive bleaching. The flax samples (4 x 5 cm) were immersed in dispersions consisting of composite powders (2mg/ml) in 25% ethanol solution for 10 minutes. Small pieces of filter paper were placed around the edge of the flax samples to absorb the excess of ethanol solution, and then the samples were dried on a hotplate at 80°C. Similar flax samples covered with TiO_2 P25 (Degussa, Germany) were used for comparison. The final samples were denoted: flax sample (without powder coating), TiO_2 P25 coated flax, Ag-TiO_2 coated flax and Ag-TiO_2/RGO (RGO means reduced graphene oxide) coated flax, according to with composite used for surface coating of flax samples.

2.3. Morpho-structural characterization of coated flax samples

The morphological characteristics of flax samples were investigated by Scanning Electron Microscopy (SEM) using an H-7650 120 kV Automatic Microscope Hitachi, Japan. The X-ray powder diffraction (XRD) patterns were recorded on a Bruker X-ray diffractometer, Germany, with CuK_α radiation (λ =1.54056 Å), in order to identify the crystalline phases of the flax samples. The Fourier-Transform Infrared (FTIR) absorption spectra of flax samples were recorded using the Jasco FTIR-6100 spectrometer. Small pieces of flax samples were ground and mixed with KBr (Merck) and then pressed into transparent discs.

2.4. UV light-shielding measurements of coated flax samples

The UV transmittance through coated flax samples were recorded using Varian Cary®50 UV-Vis spectrophotometer and the Ultraviolet Protection Factor (UPF) was calculated using mean percentage transmission in the UVA region (315–400 nm) and mean percentage transmission in the UVB region (280–315 nm) according to the equation (1):

$$UPF = \frac{\sum_{\lambda=280}^{400} E\lambda \; x \; S\lambda \; x \; \Delta\lambda}{\sum_{\lambda=280}^{400} E\lambda \; x \; S\lambda \; x \; T\lambda \; x \; \Delta\lambda} \qquad (1)$$

where: $E\lambda$ is the relative erythemal spectral effectiveness, $S\lambda$ is the solar spectral irradiance, $T\lambda$ is the average spectral transmission of the sample and $\Delta\lambda$ is the measured wavelength interval (nm).

3. Results and discussion

3.1. Morpho-structural characterization of coated flax samples

The SEM images of coated flax surfaces (Fig. 1) showed a non-homogenous coverage and agglomeration of particles. However, the distribution of particles influences the UV properties of the obtained flax samples.

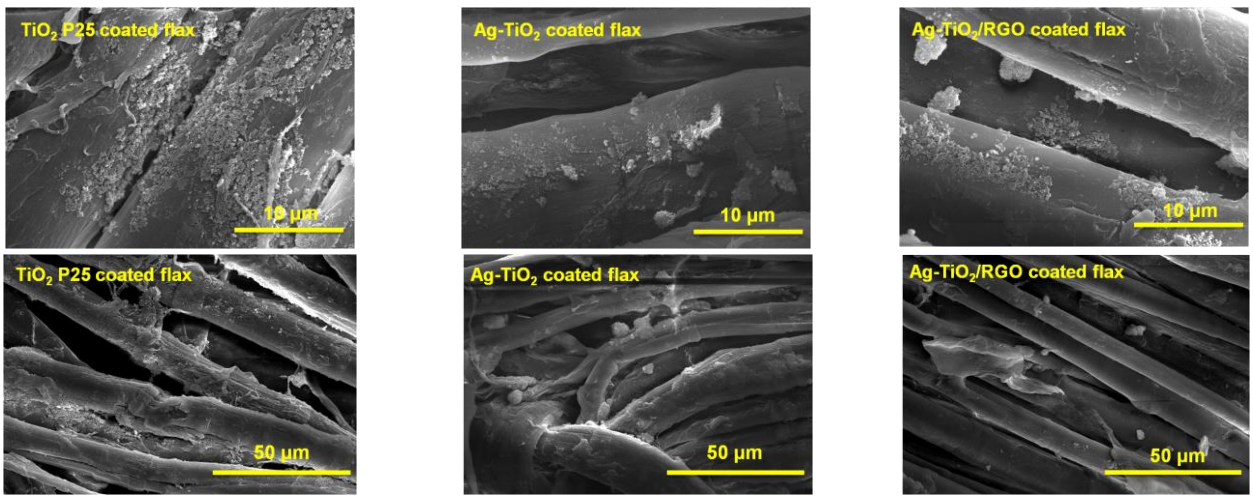

Fig. 1. SEM images of coated flax samples.

The XRD patterns of coated flax samples were shown in Fig. 2. All diffraction peaks perfectly assigned to the native cellulose structure. According to the literature data [21-25], the peaks at 2θ = 14.6°, 16.8° and 22.5° were assigned to the (1-10), (110) and (200) crystallographic plane of cellulose I. The peak at 2θ = 34.3° was attributed to structures with hydrogen bonds due to the free hydroxyl groups from cellulose macromolecules [22]. No characteristic peaks associated to the crystalline forms of TiO_2 (anatase and rutile) were detected in the XRD patterns. Also, no XRD peaks due to crystalline form of silver nanoparticles were observed.

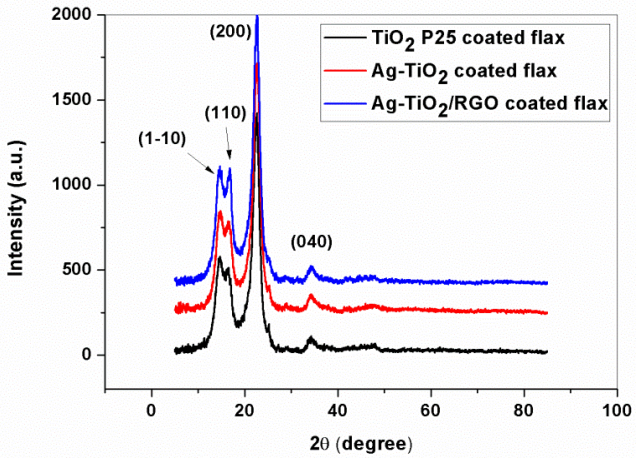

Fig. 2. XRD patterns of coated flax samples.

Since the flax fibers content 64.1-76% cellulose, 11–20.6% hemicelluloses, 2–5% lignin,1.8–2.3% pectin, 1.5-1.7 % wax [26, 27], the FTIR spectra of flax samples (Figure 3) were typical for natural cellulosic materials: O–H stretching modes (3422 cm^{-1}), asymmetric and symmetric –CH_3 and –CH_2 stretching (2921, 2853 cm^{-1}), -CH deformation (1628, 1453 cm^{-1}), C–O stretching (1065 cm^{-1}) [21-24]. The broad vibration band at 585 cm^{-1} was attributed to Ti-O-Ti vibration [24] that demonstrates the presence of TiO_2 particles at the surface of flax samples.

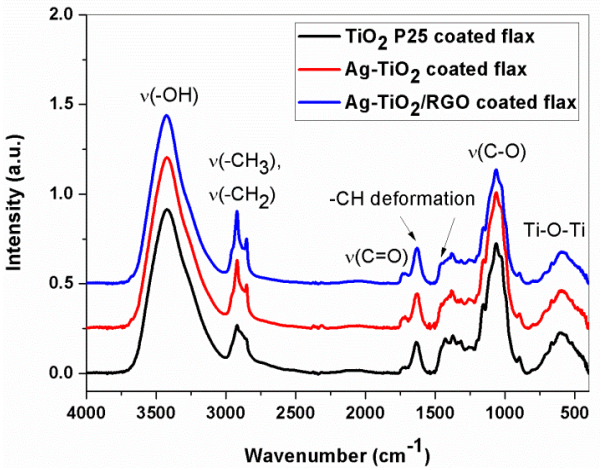

Fig. 3. FTIR spectra of coated flax samples.

3.2. UV light-shielding ability of coated flax samples

The curves in Fig. 4 showed that the UV transmittance in the range of 280–360 nm of uncoated flax has a poor UV-shielding ability mainly due to the lignin content since the cellulose (as a major component of flax fibers) cannot absorb UV radiation [29]. The TiO_2 P25 coated flax exhibited some better UV light-shielding than those of Ag-TiO_2 and Ag-TiO_2/RGO coated flax samples.

Based on the UV transmission data, the UPF was determined. The higher UPF value shows increased UV protective characteristics and a greater protection level of fabrics. According to the Australian/New Zealand Standard (AS/NZS 4399:1996) [30], European Norm (DIN EN 13758-1) [31] and the American Standard (AATCC TM 183) [32], the UPF value describes textiles providing good (UPF = 15-24), very good (UPF = 25-39) or excellent (UPF > 40) UV protection.

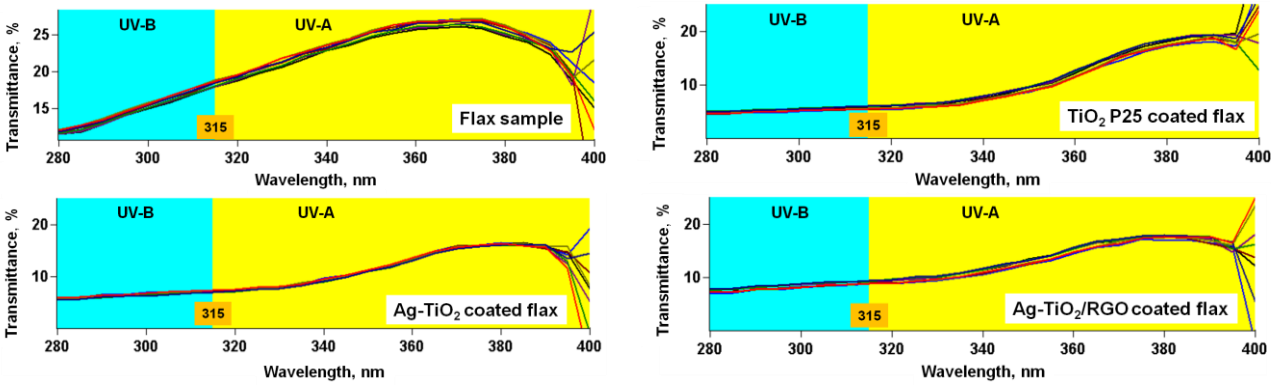

Fig. 4. UV transmission of flax samples.

From Table 1, it can be observed that the uncoated flax showed an extremely low UPF value. Among coated flax samples, only the UPF of TiO_2 P25 coated flax increased to a good protection level, the rest ones were all classified as not UV protective properties.

The different ratio of solar erythemal ultraviolet radiation between Australia, USA and Europe should be

taken into account. For example, the AS/NZS 4399 uses the solar spectrum measured in Melbourne, whereas EN 13758-1 and AATCC 183 uses a solar spectrum of Albuquerque, where the solar radiation is similar to that of southern Europe. More detailed, in European countries, such as the UK, a UPF of 15 is considered that would be sufficient [33].

Table 1. UPF values and UV transmission parameters of uncoated and composite-coated flax samples.

Sample	Mean UPF	Mean UVA Transmission	Mean UVB Transmission	Calculated UPF	UPF Rating
Uncoated flax	5.680	23.164	15.843	5.558	Nonrateable
TiO_2 P25 coated flax	16.285	12.338	5.494	15.536	Good protection
Ag-TiO_2 coated flax	13.447	11.713	6.800	13.123	Nonrateable
Ag-TiO_2/RGO coated flax	10.806	13.656	8.587	10.397	Nonrateable

The UV protectiveness depends on textile composition (natural, artificial or synthetic fibers), textile construction (porosity, mass, and thickness), dyeing (natural/synthetic nature, concentration, UV-absorbing properties) [34], physico-chemical properties of additives or particles that cover the textile surface, uniformity of coatings, etc. As a consequence, further experiments should be designed to obtain flax fabric providing excellent ultraviolet protection.

4. Conclusion

Flax samples were covered with TiO_2 P25 (Degussa) nanoparticles, Ag-TiO_2 and Ag-TiO_2/reduced graphene oxide powder composites using a simple dipping coating method. The data obtained using XRD, FTIR techniques and SEM images proved the presence of nanocomposites on the surface of the coated flax samples even if the coating was not uniform. The UV transmission measurements and corresponding UPF values showed improved UV protection only for TiO_2 P25 flax sample. However, the UPF values of Ag-TiO_2 and Ag-TiO_2/reduced graphene oxide coated flax samples were close enough to be further considered for a good UV light-shielding ability. The experimental research will be continued by taking into account various factors (i.e., textile composition/construction, dyeing, the additives/particle coating).

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References

[1] J. K. Patra, S. Gouda, J. Eng. Technol. Res. **5**(5), 104 (2013).
[2] S. K. Chinnammal, K. V. Arun Kumar, J. Nanosci. Nanotechnol. **2**(4), 404 (2014).
[3] A. K. Yetisen, H. Qu, A. Manbachi, H. Butt, M. R. Dokmeci, J.P. Hinestroza, M. Skorobogatiy, A. Khademhosseini, S. H. Yun, ACS Nano **10**, 3042 (2016).
[4] W. Zhang, J. Yang, X. Pei, Optoelectron. Adv. Mat., **12**(3-4), 227 (2018).
[5] V. Purcar, V. Raditoiu, C. A. Nicolae, A. N. Frone, A. Raditoiu, F. M. Raduly, R. Somoghi, R. A. Gabor, S. Caprarescu, J. Optoelectron. Adv. M. **21**(3-4), 281 (2019).
[6] W. Chang, X.Z. Huang, M.J. Zhang, Y.P. Du, Y.X. Yang, J. Optoelectron. Adv. M., **13**(7-8), 487 (2019).
[7] M. Radetić, J. Photoch. Photobio. C **16**, 62 (2013).
[8] P. J. Rivero, A. Urrutia, J. Goicoechea, F. J. Arregui, Nanoscale Res. Lett. **10**(501), 1 (2015).
[9] J. Molina, RSC Adv. **6**, 1 (2016).
[10] S. Lan, H. Zhang, J. Hu, S. Geng, H. Lan, J. Optoelectron. Adv. M. **20**(5-6) 337 (2018).
[11] M. Gorjanc, M. Šala, Cellulose **23**, 2199 (2016).
[12] S. Li, T. Zhu, J. Huang, Q. Guo, G. Chen, Y. Lai, Int. J. Nanomedicine **12**, 2593 (2017).
[13] T. Yuranova, R. Mosteo, J. Bandara, D. Laubb, J. Kiwi, J. Mol. Catal. A Chem. **244**, 160 (2006).
[14] K. Kowal, P. Cronin, E. Dworniczek, J. Zeglinski, P. Tiernan, M. Wawrzynska, H. Podbielska, S. A. M. Tofail, RSC Adv. **4**, 19945 (2014).
[15] D. Kowalczyk, W. Fortuniak, U. Mizerska, I. Kaminska, T. Makowski, S. Brzezinski, E. Piorkowska, Cellulose **24**, 4057 (2017).
[16] N. Karim, S. Afroj, S. Tan, P. He, A. Fernando, C. Carr, K.S. Novoselov, ACS Nano **11**, 12266 (2017).
[17] L. Karimi, M. E. Yazdanshenas, R. Khajavi, A. Rashidi, M. Mirjalili, Cellulose **21**, 3813 (2014).
[18] M. A. Shirgholami, L. Karimi, M. Mirjalili, Fiber. Polym. **17**(2), 220 (2016).

[19] J. Molina, F. Fernandes, J. Fernández, M. Pastor, A. Correia, A. P. Souto, J. O. Carneiro, V. Teixeira, F. Cases, Mater. Sci. Eng. B **199**, 62 (2015).
[20] M. C. Rosu, C. Socaci, V. Floare-Avram, G. Borodi, F. Pogacean, M. Coros, L. Magerusan, S. Pruneanu, Mater. Chem. Phys. **179**, 232 (2016).
[21] B. Duchemin, A. Thuault, A. Vicente, B. Rigaud, C. Fernandez, S. Eve, Cellulose, **19**(6), 1837 (2012).
[22] L. I. Mikhalovska, V. M. Gun'ko, A. A. Rugal, O. I. Oranska, Y. I. Gornikov, C. Morvan, N. Follain, C. Domas, E. M. Pakhlov, S. V. Mikhalovsky, RSC Advances **2**, 2032 (2012).
[23] M. Poletto, V. Pistor, A.J. Zatter, Chapter 2. Structural characteristics and thermal properties of native cellulose, in: T. van de Ven, L. Godbout (Eds.) Cellulose-Fundamental Aspects. Intech, 45–68, Rijeka, 2013.
[24] M. Poletto, H. L. O. Júnior, A.J. Zattera, Materials, **7**, 6105 (2014).
[25] J. Gong, J. Li, J. Xu, Z. Xiang, L. Mo, RSC Adv. **7**, 33486 (2017).
[26] L. Yan, N. Chouw, K. Jayaraman, Compos. B Eng. **56**, 296 (2014).
[27] B. D. Lazić, B. M. Pejić. A. D. Kramar, M. M. Vukčević, K. R. Mihajlovski, J. D. Rusmirović, M. M. Kostić, Cellulose **25**, 697 (2018).
[28] A. Mirabedini, S. M. Mirabedini, A. A. Babalou, S. Pazokifard, Prog. Org. Coat. **72**, 453 (2011).
[29] T. Afrin, T. Tsuzuki, X. Wang, The Journal of The Textile Institute **103**(4), 394 (2012).
[30] Standards Australia/Standards New Zealand: AS/NZS 4399: Sun protective clothing – Evaluation and classification 1996.
[31] PrEN 13758: Textiles - Solar UV protective properties. Method of test for apparel fabrics. European standard, Brussels, Belgium (1999).
[32] AATCC TM 183: (R2014), Transmittance or blocking of erythemally weighted ultraviolet radiation through fabrics, American Association of Textile Chemists & Colorists (2010).
[33] D. Grifoni, L. Bacci, G. Zipoli, G. Carreras, S. Baronti, F. Sabatini, Photochem. Photobiol. **85**, 313 (2009).
[34] D. Grifoni, L. Bacci, G. Zipoli, L. Albanese, F. Sabatin, Dyes Pigm. **91**, 279 (2011).

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