Characterization of fabrics coated with doped TiO_2-graphene

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ABSTRACT – REZUMAT

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This study presents the results of laboratory experiments to prepare cotton woven fabrics with photoactive properties. The fabric was treated with TiO_2 – Fe(1%) – N + 2% graphene by exhaustion followed by a fluorocarbon polymer treatment. The fabric was analyzed by Scanning Electron Microscope coupled with Energy Dispersive Spectroscopy (SEM/EDAX), Differential scanning calorimetry (DSC), Contact Angle measurement, physical properties (weight, thickness, breaking strength, elongation, air/water permeability, electrical resistance). The photocatalytic activity was determined initially and after 5 washings by measuring the trichromatic coordinates of the treated fabrics stained with methylene blue and exposed to UV and visible light on a Hunterlab UV-Vis spectrophotometer.

The results demonstrate a uniform deposition of doped TiO_2-graphene particles on material surface. The thermal stability of the coated cotton fabric is practically unmodified in comparison with blank cotton fabric.

The decrease of the surface resistivity demonstrates the deposition of graphene layer, known for its good electrical conductivity. The wetting capacity of initial hydrophilic cotton fabric is dramatically modified, the fabric becoming hydrophobic after treatment. The photocatalytic efficiency is higher under visible light than under UV-radiation due to the TiO_2 doping and decoration with graphene, which extend the light absorption from UV to visible range. The good photocatalytic activity under visible light is maintained after 5 washing cycles.

Keywords: *doped TiO_2-graphene, photocatalytic textiles, cotton fabrics, physical properties*

Caracterizarea ţesăturilor acoperite cu TiO_2-grafen dopat

Studiul prezintă rezultatele experimentelor de laborator pentru obținerea ţesăturilor din bumbac cu proprietăţi fotocatalitice. Ţesătura a fost tratată cu TiO_2 – Fe(1%) – N + 2% grafen, prin exhaustare, urmată de un tratament cu polimer de fluorocarbon. Ţesătura a fost analizată prin Microscopie Electronică de Baleiaj cuplată cu Spectroscopie de Raze X cu dispersie de energie (SEM/EDAX), Calorimetrie de Scanare Diferenţială (DSC), măsurarea unghiului de contact şi determinarea valorilor caracteristicilor fizico-mecanice (masă, grosime, rezistenţă la rupere, alungire la rupere, permeabilitate la aer/apă, rezistenţă electrică). Activitatea fotocatalitică a fost determinată iniţial şi după 5 spălări prin măsurarea coordonatelor tricromatice ale ţesăturilor tratate, pătate cu albastru de metilen şi expuse la UV şi lumina vizibilă, pe un spectrofotometru UV-Vis Hunterlab.

Rezultatele demonstrează o depunere uniformă a particulelor de TiO_2-grafen dopat pe suprafaţa ţesăturii. Stabilitatea termică a ţesăturii din bumbac acoperite este practic nemodificată, comparativ cu ţesătura din bumbac netratată.

Scăderea rezistenţei de suprafaţă demonstrează depunerea unui strat de grafen, cunoscut pentru conductibilitatea electrică bună. Capacitatea de umectare iniţială a ţesăturii din bumbac este dramatic modificată, aceasta devenind hidrofobă după tratare. Eficienţa fotocatalitică este mai mare în lumina vizibilă, decât în radiaţie UV, datorită dopării TiO_2 şi acoperirii cu grafen, care extind absorbţia luminii din domeniul UV în domeniul vizibil. Activitatea fotocatalitică sub lumina vizibilă se menţine şi după 5 cicluri de spălare.

Cuvinte-cheie: *TiO_2-grafen dopat, textile fotocatalitice, ţesături din bumbac, proprietăţi fizice*

INTRODUCTION

Titanium dioxide was intensively investigated to prepare textiles with new functionalities such as self-cleaning, hydrophilicity, antibacterial, UV-protection, etc. [1–3]. As it is well known, the major drawback of TiO_2 is the efficiency only under UV light ($\lambda < 387$ nm) due its large band gap of 3.2 eV [4]. To extend the absorption under visible light, TiO_2 was doped with metals, non-metals and recently with carbon nanotubes, graphene oxide, graphene [5].

The composition TiO_2-graphene has an improved photocatalytic efficiency due to the fast transfer electrons from the conduction band of TiO_2 to graphene sheets, suppressing the recombination of the formed electron-hole pair formed and, therefore increasing the lifetime of the pair and generation of a higher number of active species involved in photo-degradation. More than that, graphene having a huge surface area, allow a better contact with the contaminants, which are absorbed and decomposed by the generated radicals [6].

The studies show antimicrobial, photocatalytic self-cleaning and UV blocking activity of the cotton fabrics treated by dip-drying technique with graphene oxide/ TiO_2 nanocomposites [7–8]. Polyester fabric coated with multiple layers of reduced graphene oxide and TiO_2 demonstrates light absorption, conductivity, electro-activity and photocatalytic properties [6].
Wool fabric coated with graphene/TiO_2 nanocomposite, besides the improved antibacterial activity and electrical conductivity, has a good photo-catalytic self-cleaning property under sunlight [9].
While almost all the researches are directed to analyses the functional properties, few of them investigate the physical modifications of the treated fabrics. The present study is focused on the physical properties and photocatalytic activity of the cotton woven material coated with doped TiO_2-graphene composite.

EXPERIMENTAL

Materials

The following materials were used for the experiments: 100% cotton woven fabric which characteristics are shown in the table 1; TiO_2 – Fe(1%) – N + 2% graphene (average diameter: 17.8 nm) hydrothermal synthetized by National Institute of Materials Physics, Romania; sodium dodecylhydogensulphate (DHS); poly(ethylenebenzensufonic) acid (PBS); Nuva® 4200 liq.(perfluorocarbon polymer).

Methods

The fabric was introduced into 0.49g/L doped TiO_2-graphene dispersion prepared by sonication 0.5 g TiO_2 – Fe(1%) – N + 2% GO powder in 1000 mL solution containing 0.19 g DHS, 15mL ethanol and 0.6 mL PBS for 3 hours at 30ºC. The fabric was immersed in the above prepared dispersion, maintained at 40ºC for 30 minutes and then, dried at 100ºC for 2 minutes. The fabric so treated was named S6G. The dried fabric is immersed in 20 g/L Nuva® 4200 liq., at pH 5, dried at 110°C, and thermofixed at 170°C for 40 seconds. The fabric was abbreviated S6.

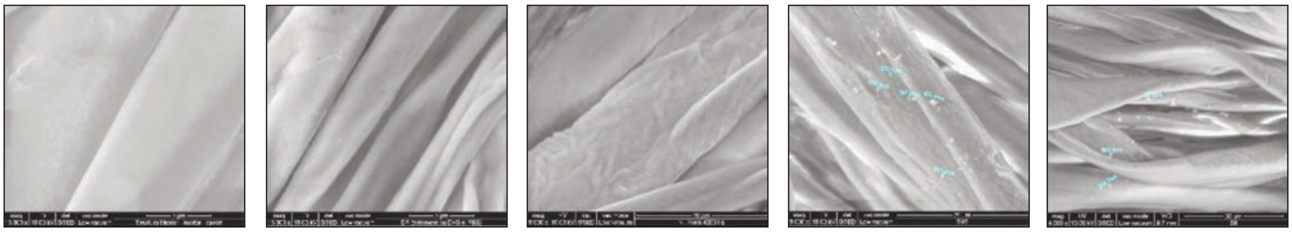
Characterization

The fabric morphology and chemical composition of deposited layers were investigated by scanning electron microscopy coupled with Energy Dispersive Spectroscopy (SEM/EDAX, Quanta 200, FEI, Netherlands). The wetting capacity was determined by measuring the contact angles with a 5 μl distilled water droplet on a VCA Optima (AST Products Inc., USA) instrument. The results are the average of 5–10 measurements in different points on the samples surface. The thermal properties of the coated fabric were measured on DSC (Pyris Diamond, Perkin Elmer, USA) instrument, with a heating rate of 10°C/min. and using 10mL/min. air as a purging gas. The electrical resistivity was measured with PRS 801 digital multi-meter (Prostat Corporation, USA), according standard SR EN 1149-1: 2006, at 19.5°C and 35.1% relative humidity. The physical properties of the fabrics (weight, thickness, breaking strength, elongation, air/water permeability) were analyzed according to specific ISO standards. The photocatalytic efficiency of the untreated and treated materials was evaluated by measuring the trichromatic coordinates of materials stained with methylene blue and the exposed at UV and visible light on Hunterlab spectrophotometer, with CIELAB 1976 color space and D65-light source. The nanoparticles adherence on the fabric surface and efficiency to washing was investigated by subjecting the fabric to 5 washing cycles, staining with methylene blue, exposing to visible light and evaluation of the color changes.

Table 1

PHYSICAL-MECHANICAL PROPERTIES OF THE FABRICS

Analysis		Blank	S6	Standard
Weight (g/m^2)		253	249	SR EN 12127:2003
Thickness (mm)		0.568	0.635	SR EN ISO 5084:2001
Water vapor permeability (%)		31.6	34.3	STAS 9005:1979
Air permeability at 100Pa (Lm^{-2}s^{-1})		75.66	75.92	SR EN ISO 9237:1999
Fabric density (number of yarns/10 cm)	Warp	414	420	SR EN 1049-2:2000-Method A,B
	Weft	214	214	
Breaking force (N)	Warp	710	1051	SR EN ISO 13934-1/2013
	Weft	470	511	
Breaking elongation (%)	Warp	15.10	20.2	
	Weft	15.10	15.26	
Surface resistivity (× 10^{13} Ωsq)		18.9	6.96	SR EN 1149-1: 2006
Volume resistivity (× 10^{14} Ωcm)		11.5	18.8	
Contact angle, left/right (degrees)		0	146.16	Sessile drop method



a *b* *c* *d* *e*

Fig. 1. SEM images of untreated and treated fabrics: *a* – untreated; *b* – treated with DHS & PBS; *c* – treated with NUVA 4200 liq.; *d* – S6G; *e* – S6

RESULTS AND DISSCUSION

Surface morphology investigation of coated fabric by SEM

The SEM images of fabric untreated and treated with TiO_2 – Fe(1%) – N + 2% graphene are shown in figure 1.

The SEM images of the materials untreated (figure 1, *a*) and treated with DHS & PBS (figure 1, *b*) show a clean, smooth surface. The fluorocarbon polymers, NUVA4200 liq., form a thick layer on the fibers surface. On the surface of the S6G fibers (figure 1, *d*) the polymer layer (PBS) is observed on which random particles of 221.6 nm, 265.2 nm, 257.6 nm, 495.4 nm are dispersed. It is possible that the sheets present on certain fibers are graphene because the particles attached to doped TiO_2 are seen on their edges. After treatment with fluorocarbon polymer, on the fibers surface (figure 1, *e*) a small number of particles (72.9 nm, 262.7 nm, 364.3 nm) are observed due to their inclusion in the thick polymer layer.

EDAX quantification of the elements on the treated cotton fabric

The spectra and chemical composition of nanoparticles present on the fabric coated with TiO_2 – Fe (1%) – N + 2% graphene are shown in the figure 2 and table 2.

The results demonstrate the presence of Ti as major element on the coated fabrics, in larger amount on the sample S6G than on sample S6. After the treatment with NUVA 4200, almost 62% Ti is removed due to the low adherence of particles on the fabric surface.

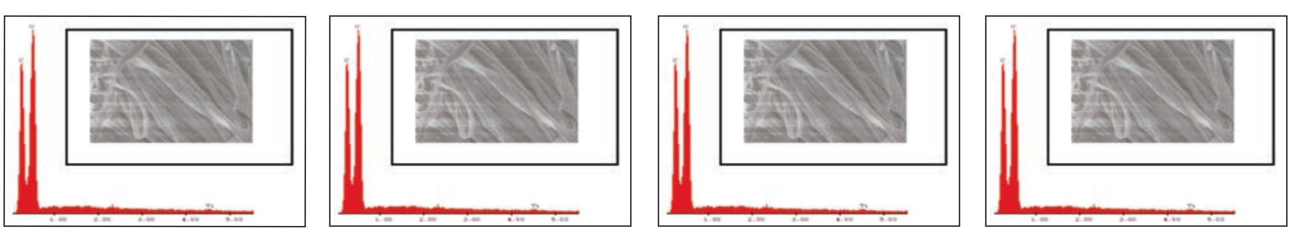
DSC analysis of the coated fabrics

The thermal behavior of the coated samples is shown in the figure 3 and table 3. The TiO_2-graphene composite powder shows an exothermic peak at 256°C, associated with thermal decomposition and oxidation of organic matter resulting from the doped TiO_2 synthesis process. Iron doping causes the exothermic point to drop, which is higher as the amount of iron is higher. Thus, studies [10] have shown that TiO_2 doped with 1% Fe shows an exothermic peak at

Table 2

QUANTIFICATION OF THE ELEMENTS ON THE FABRICS SURFACE BY EDAX

Sample	Untreated fabric		Treated with DHS and PBS		Treated with N Nuva 4200liq.		S6		S6G	
Element	Wt (%)	At (%)	Wt (%)	At (%)	Wt (%)	At (%)	Wt (%)	At (%)	Wt (%)	At (%)
C K	45.83	52.99	46.75	53.91	43.71	51.15	40.02	47.37	42.55	50.53
O K	54.17	47.01	53.25	46.09	51.96	45.65	58.86	52.30	54.50	48.59
F K	-	-	-	-	4.33	3.20	-	-	-	-
TiK	-	-	-	-	-	-	1.12	0.33	2.95	0.88
Total	100	100	100	100	100	100	100	100	100	100



a *b* *c* *d*

Fig. 2. EDAX spectra of the fabrics surface: *a* – untreated; *b* – treated with DHS and PBS; *c* – treated with NUVA 4200 liq.; *d* – S6G

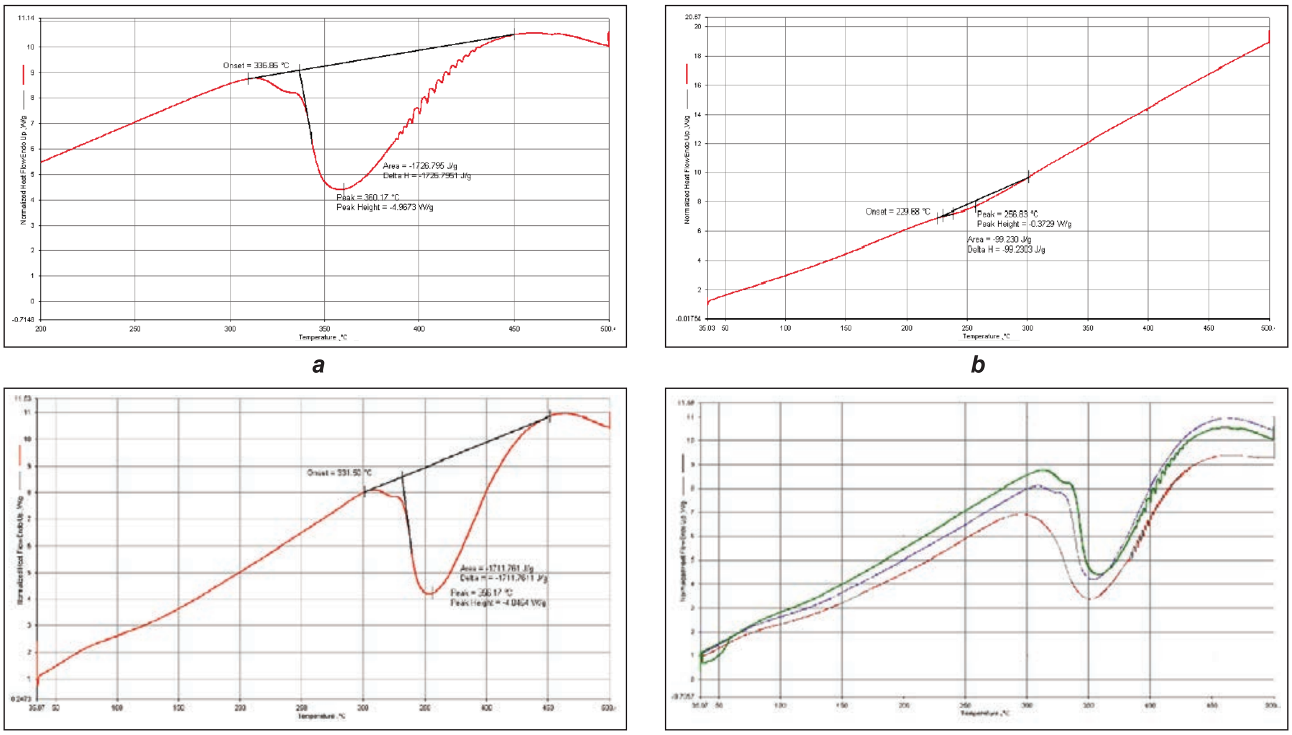


Fig. 3. DSC curves of fabrics: *a* – Blank, untreated cotton fabric; *b* – TiO_2–Fe(1%)–N + 2% GO powder; *c* – S6G; *d* – superimposed DSC Thermograms: blue – S6G, red – S6, green – blank

Table 3

DSC ANALYSIS DATA OF FABRICS AND DOPED TIO_2-GRAPHENE POWDER				
Sample	**Blank**	**TiO_2-Fe (1%)-N +2% G powder**	**S6**	**S6G**
Weight (mg)	7.3	5	7.2	7.1
Temp. max. (°C)	360.17	256.83	354.51	356.17
ΔH (J/g)	–1726.795	–99.2303	–1833.5558	–1711.761
Onset t (°C)	336.86	229.68	315.36	331.50
Final t (°C)	450	300	450	452

223°C. If the dopant is nitrogen, the exothermic point is shifted to higher values, respectively 274°C [11] attributed to the evaporation of solvent, the N precursor and its derivatives. Graphene, which, theoretically has two peaks between 200–300°C (decomposition of oxygen-containing groups) and 550–650°C (oxidation of carbon residues), also contributes to the temperature change. The untreated cotton fabric has an exothermic peak (360.17°C) attributed to cellulose decomposition [12]. After treatment with doped TiO_2-graphene, the temperature drops by 4–6°C demonstrating that treatment does not essentially influence the thermal behavior of cotton.

The physical-mechanical characteristics

The physical-mechanical properties of the initial and treated fabrics are shown in the table 1. Except the weight, all the physical characteristics analyzed show slightly modifications. The results demonstrate an increase of thickness (11.79%), fabric density on warp (1.45%), breaking force (48% on warp and 8.72% on weft) and elongation at breaking (33.77%). The water vapor and air permeability are slightly changed, increasing by 8.5% and respectively 0.35%. Instead, the surface and volume resistivity are decreased, mainly due to graphene.

The initial cotton fabric is highly hydrophilic, the water being absorbed instantaneously. Also, the fabric treated with doped TiO_2-graphene is hydrophilic, probably due to the high content of TiO_2 deposited on the material surface. After coating with fluorocarbon polymer, the material becomes hydrophobic, due to the polymer, specially used to provide oil and water repellency to the textile materials.

The evaluation of photocatalytic effect

The aspect and the color changes of the materials stained with methylene blue under visible and UV light are shown in the tables 4–7.

As it can be seen, methylene blue suffers a very slight photo-degradation on the untreated material after 8 hours of exposure to UV light. Instead, the

Table 4

ASPECT OF THE FABRICS STAINED WITH METHYLENE BLUE AND EXPOSED AT UV LIGHT (365NM)	
Initial	8 hours
	
Blank	
	
S6G	
	
S6	

Table 5

THE ASPECT OF THE FABRICS, STAINED WITH METHYLENE BLUE, EXPOSED AT VISIBLE LIGHT	
Initial	4 hours
	
Blank	
	
S6G	
	
S6	

Table 6

TRICHROMATIC COORDINATES OF THE FABRICS STAINED WITH METHYLENE BLUE, EXPOSED 8 HOURS AT UV LIGHT

Sample	L*	a*	b*	dL*	da*	db*	dE*	Note
Blank unexposed	87.52	–13.39	–7.69					
Blank exposed	87.92	–13.10	–7.46	0.40	0.29	0.23	0.55	4.5
S6 unexposed	83.01	–17.54	–10.46					
S6 exposed	84.69	–15.28	–9.00	1.68	2.25	1.46	3.17	3.50
S6G unexposed	84.70	–10.77	–5.02					
S6G exposed	85.94	–8.73	–3.26	1.24	2.04	1.76	2.96	3.50

Table 7

TRICHROMATIC COORDINATES OF THE FABRICS STAINED WITH METHYLENE BLUE, EXPOSED 8 HOURS AT VISIBLE LIGHT

Sample	L*	a*	b*	dL*	da*	db*	dE*	Note
Blank unexposed	87.01	–13.97	–8.63					
Blank exposed	89.91	–5.96	–4.09	2.90	8.01	4.54	9.66	1.5
S6 unexposed	83.62	–16.08	–9.89					
S6 exposed	86.77	–5.82	–4.72	3.15	10.27	5.18	11.92	1.5
S6G unexposed	84.57	–10.68	–4.88					
S6G exposed	84.85	–3.20	–0.94	0.29	7.48	3.93	8.45	1.50

notes on gray scale demonstrate a more intense photo-degradation of methylene blue existing on the treated fabrics (S6 and S6G).

According to the value of light and color differences (dE*), the fabric coated with TiO_2-graphene and fluorocarbon polymer (S6G) is more strongly photodegraded than the material treated with only TiO_2-graphene.

Under the visible light, the most intensive degradation is shown by the fabric S6 due to the deposited photo-catalyst on the material surface. According to dL* and dE* values, the sample S6G is less degraded than the blank. The results could be influenced by the black color of graphene and the lower amount of TiO_2 present on the material surface.

Evaluation of the photocatalytic effect after washing

The durability of the photocatalytic efficiency was tested by subjecting the materials to 5 washing cycles under the following conditions. Trichromatic coordinates of the washed fabrics exposed to UV and visible are shown in tables 8–10.

After 5 washings and exposure to UV light, the color fading of methylene blue on both fabrics is very low, as it could be seen from the notes on gray scale, which is similar for treated and untreated fabric. The

Table 8

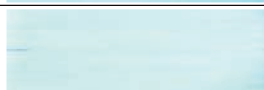
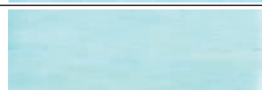
ASPECT OF THE FABRICS AFTER 5 WASHINGS, EXPOSED TO UV AND VISIBLE LIGHT				
Exposure time	Exposed 8 hours to UV light		Exposed 4 hours to visible light	
	Blank	S6	Blank	S6
Initial				
8 hours				

Table 9

TRICHROMATIC COORDINATES OF THE FABRICS AFTER 5 WASHINGS, EXPOSED 8 HOURS TO UV LIGHT								
Sample	**L***	**a***	**b***	**dL***	**da***	**db***	**dE***	**Note**
Blank unexposed	86.57	–14.90	–10.72					
Blank exposed	86.73	–12.85	–9.95	0.15	2.05	0.76	2.19	4.00
S6 unexposed	81.50	–17.78	–14.79					
S6 exposed	82.60	–17.57	–13.03	1.10	0.21	1.76	2.08	4.00

Table 10

TRICHROMATIC COORDINATES OF THE FABRICS AFTER 5 WASHINGS, EXPOSED 4 HOURS TO VISIBLE LIGHT								
Sample	**L***	**a***	**b***	**dL***	**da***	**db***	**dE***	**Note**
Blank unexposed	84.09	–15.13	–12.10					
Blank exposed	88.61	–5.30	–5.45	4.52	9.84	6.65	12.71	1
S6 unexposed	81.22	–17.53	–14.41					
S6 exposed	83.78	–7.92	–9.04	2.55	9.61	5.37	11.30	1.5

higher dL*value of sample S6 indicates a higher degradation of dye on the treated material.

After 5 washings, the photocatalytic efficiency is lost, probably due to the removal of TiO_2-graphene.

CONCLUSIONS

The SEM/EDAX analyses confirm the deposition of TiO_2-graphene on fabrics. The treated fabrics show a more intensive photo-degradation under visible light than under UV light. The photocatalytic effects were preserved after five washing cycles, demonstrating the capacity of polymer to fix the particles on the fabric surface. The genuine characteristics of the textile materials are not significantly modified by the chosen treatment method.

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