INTRODUCTION

Self-cleaning textiles have many applications for protective uniforms, upholstery and carpets, window blinds, tents and awnings, filter fabrics, agricultural textiles, etc. [1]. Different compounds were tested to improve the photocatalytic self-cleaning efficiency such as TiO$_2$ doped with metals, non-metals, metals-no-metals co-doping, dyes, heterojunctions (ZnO/TiO$_2$; TiO$_2$/SiO$_2$; TiO$_2$/WO$_3$). Recently, doped TiO$_2$-graphene nanocomposites are intensive investigated due their efficiency to decompose pollutants and pathogenic microorganisms under visible light [2–6]. It is largely accepted that the high interfacial contact between graphene sheet and TiO$_2$ nanoparticles facilitates the charge separation and electron transfer from TiO$_2$ to graphene upon irradiation and overcome the fast recombination of the electrons and holes pairs, improving the photocatalytic activity [7].

Different physical and chemical methods were proposed for the immobilization of graphene-TiO$_2$ on textiles such as atmospheric pressure metal organic chemical vapor deposition, electron beam evaporation, reactive magnetron sputtering, spray pyrolysis, sol-gel, and layer by layer assembly technique [8]. The most used method to prepare self-cleaning textiles remains the dip-pad-dry-cure method [9–11] due its large applicability on conventional production lines. The major drawback of immobilized TiO$_2$ composites is the low coating adherence.

The objectives of this study are to investigate the methods to create durable self-cleaning textiles by coating fabrics with TiO$_2$-(1%)Fe-N-graphene (2%). To improve the adherence of the nanoparticles, the polyester/cotton woven fabrics were pre-treated with polyacrylic acid (PA), carboxymethylcellulose (CMC) and polyethylene polyamine resin (EZF). The pre-treated materials were immersed in a doped TiO$_2$ for 30 minutes at 40°C and dried at 125°C. The finished fabrics were stained with methylene blue dye and exposed to visible light.

The SEM images show the presence of particles on polymers layers firmly attached on the material surface. The treatments determine the decrease of the exothermic peak (452.48°C), characteristic of the cellulose decomposition, demonstrating an increase of the thermal conductivity of the materials. The doped TiO$_2$-graphene induces a double degradation of methylene blue in comparison with untreated material and the materials treated with CMC, polyacrylic acid and cationic polymer. The effect is maintained after washing.

Keywords: doped TiO$_2$-graphene, photocatalytic textiles, self-cleaning

Attempts to improve the self-cleaning effect of the textile materials

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EXPERIMENTAL

Materials
Scoured and bleached 33% cotton/67% polyester woven fabric, TiO$_2$-(1%)Fe-N-graphene (2%), polyacrylic acid (MWT = 138.1 g/mol), carboxymethylcellulose (CMC) and polyethylene polyamine resin (ITOFLIX EZF, Fast Colours, UK), sodium dodecylhydrogenesulfate (DHS, Merck), Tween 80 (Sigma Aldrich), ethanol, α-terpineol (Merck), Imerol JSF (Archroma).

Methods
Preparation of 0.7 g/l TiO$_2$-(1%) Fe-N-graphene (2%) dispersion
To prepare the dispersion, in a 2l reactor were successively added under intensive stirring on ultrasonic bath the following compounds: 527 ml of water, 351 ml of ethanol, 88 ml of terpineol, 4.5 ml of EHS, 17.5 ml of Tween 80, 10.5 ml of Imerol JSF, 0.8 g DHS and 0.7g doped TiO$_2$-graphene. The mixture was stirred at 40°C for 60 min. A white-gray dispersion is formed.

Fabric treatment
Cotton/polyester fabrics were separately immersed in 1 g/l carboxymethylcellulose (CMC), 1 g/l polyacrylic acid (PA) and 10 g/l Itofix EZF solutions, kept at 80°C for 20 minutes and then, dried at 120°C. The pre-treated, dried materials are immersed in 0.7 g/l TiO$_2$-(1%) Fe-N-graphene (2%) dispersion, maintained under stirring at 40°C for 30 minutes and dried in the preheated oven at 125°C.

Material abbreviation is the following:
A: cotton/polyester fabric immersed in TiO$_2$-graphene dispersion;
CMC: cotton/polyester fabric immersed in 1 g/l CMC;
B: cotton/polyester fabric immersed in 1 g/l CMC and subsequently in TiO$_2$-graphene dispersion;
PA: cotton/polyester fabric immersed in 1 g/l polyacrylic acid;
C: cotton/polyester fabric immersed in 1 g/l polyacrylic acid and subsequently in TiO$_2$-graphene dispersion;
EZF: cotton/polyester fabric immersed in 10 g/l Itofix EZF;
D: cotton/polyester fabric immersed in Itofix EZF and later in TiO$_2$-graphene dispersion.

Characterization
The morphology of the fabric was investigated by scanning electron microscope (SEM, Quanta 200, FEI, Holland). The wetting ability was determined by measuring the contact angles of 5μl 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/minute and using 10 ml/minute 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 20.7°C and 28.8% relative humidity. The photocatalytic efficiency of the untreated and treated materials was evaluated initially and after 5 washing cycles, by measuring the trichromatic coordinates of materials stained with methylene blue and exposed at UV and visible light on Hunterlab spectrophotometer, with CIELAB 1976 color space and D65-light source.

RESULTS AND DISSCUSSION
Characterization of the fabric by Scanning Electron Microscopy (SEM)
The spreading of the particles and their size on the surfaces of the treated fabrics are shown on the SEM images (figure 1).
SEM images show the TiO$_2$ particles on cotton/polyester woven fabric samples, before and after treatments. The samples CMC, PA, EZF are covered with thick layers of polymers. After the immersion in the doped-TiO$_2$-graphene dispersion, a large number of particles cover the fibers surface. The particles are in a larger number and more uniformly spread on the surface of the fabric coated only with doped TiO$_2$-graphene (A) than on the surface of the samples covered with polymers and TiO$_2$-graphene (B, C, D). As it can be seen from images, the particles are more agglomerated on the fabric B, covered initially with CMC, probably due to porous surface of CMC and carboxyl groups which attract TiO$_2$ particles.

Surface wettability of the treated fabrics

Due to the high content of thin polyester yarns and tight structure of the fabric, the untreated woven material is highly hydrophobic (contact angle of 133°). The hydrophoby of the materials is not significantly changed (table 1) if the materials are covered with polymers. After the TiO$_2$-graphene treatment, the water static contact angle becomes zero, the water droplet being absorbed in less than 60 seconds, indicating a completely water wettability of the fabrics. The increased hydrophilic behavior of the materials could be correlated with the deposition of a large number of TiO$_2$ particles on the materials surface knowing that graphene has water and oil repellency properties [12].

Evaluation of the electrical resistivity

The results of the materials’ electrical resistivity are shown in the table 2. Cotton/polyester fabric has anionic properties due to the hydroxyl and carboxyl groups respectively. By depositing layers of carboxymethylcellulose (sample CMC) and polyacrylic acid (sample PA), the anionic character is accentuated leading to the decrease of the surface electrical resistivity. A smaller decrease of the electrostatic was observed for the fabric EZF covered with polyethylene polyamine layers. The materials coated with polymers and TiO$_2$-graphene show higher electrical resistivities due to the thick layers and large agglomerates formed on the cotton/polyester surface [13].

Thermal conductivity

The thermal behavior of the coated samples is shown in the figure 2 and tables 3 and 4.

![Fig. 2. DSC thermogram: D – yellow; C – purple; B – black; A – green; PA – blue; EZF – blue marine; CMC – red](image-url)
with possible fiber impurities and the third endotherm (452.48°C) associated with the burning of cotton [14]. Covering the materials with polymers and with TiO$_2$-graphene, causes the enthalpy decrease of both fibers. It is possible that this decrease is due to the uneven deposition of the compounds, which leads to localized growth of thermal conductivity.

**Photocatalytic efficiency**

The aspect and the color modifications of the materials stained with methylene blue exposed 4 hours to visible light, are shown in the tables 5 and 6.

As the notes on grey scale demonstrate, the doped TiO$_2$-graphene induces a double degradation (table 6) of the methylene blue in comparison with untreated material and the materials treated with CMC, polyacrylic acid and cationic polymer. The highest lightness difference (dL*) is recorded for sample a, coated with TiO$_2$/graphene. Instead, the highest color difference is recorded on the sample D, initially treated with the cationic polymer, followed in descending order by samples A, C and B. Probably, this effect is determined both by the uneven deposition of polymer layers and the blocking of a portion of TiO$_2$ by the functional groups of the polymers (- carboxyl groups). The hypothesis is confirmed by the dL* and dE* values of samples treated only with polymers that decrease in the order: PA > CMC > EZF.
Carboxymethyl cellulose (CMC) contains several carboxymethyl (-CH₂-COOH) groups linked to the hydroxyl groups of the glucopyranosyl rings and interacts with a larger number of TiO₂ molecules than polyacrylic acid, inhibiting the photocatalytic activity. Consequently, as the results show, the discoloration of methylene blue is more intense on the sample treated with polyacrylic acid and TiO₂/graphene (sample C, dE*=16.26) than that on the sample treated with CMC and TiO₂/graphene (sample B, dE*=15.53). This demonstrates that the discoloration is induced by the photocatalytic effect of TiO₂/graphene and not by any possible absorption of the dye by the polymers although the CMC is amorphous and according to SEM images is deposited in thicker layers than the polyacrylic acid.

The photocatalytic properties of the samples on the degradation of methylene blue (MB), in visible (λ>400 nm) spectral regions (~1 mW; at the irradiance of 2.5 W/m²) were also measured by a PCC-2 (ULVAC RIKO, Chigasaki, Kanagawa, Japan) photocatalytic checker. The absorbance (ABS) is a measure of the photocatalytic efficiency of sample, higher negative values indicating better activity. The ABS values of the samples are depicted in the figure 3. As the graph shows, the most intensive efficiency is demonstrated by the samples c and d (after 2 hours of exposure at visible light, almost 20% of dye is decomposed). No saturation tendency can be observed after 2 hours on irradiation in visible light. The slight differences between the two tests (UV-VIS spectrophotometry and photocatalytic checker) could be attributed to the intrinsic non-uniformity of the textile materials and, accordingly to the deposited composites layers.

**Evaluation of the photocatalytic effect after washing**

The treated materials were subjected to 5 washings at 40°C with distilled water. After drying, they were stained with 0.064 g/l MB for 20 minutes at 30°C. The stained materials were exposed to visible light, the appearance and results of color change measurements being shown in tables 7 and 8.

All the materials treated with TiO₂-graphene preserve their photocatalytic efficiency after 5 washing cycles. According to the values of lightness and color differences, the highest photodegradation is shown by samples C and D, pre-treated with polyacrylic acid and, respectively Itofix EZF and then with doped TiO₂-graphene.

**CONCLUSIONS**

The SEM/EDAX analyses confirm the deposition of TiO₂-graphene on fabrics. The fabrics coated with doped TiO₂-graphene particles are highly hydrophilic due to the deposition of a high number of hydrophilic TiO₂ particles on the materials surface. All the treated fabrics have electrical resistivity in the same range as untreated cotton/polyester.

The coated cotton/polyester fabrics with graphene oxide/TiO₂ nanocomposite show good photocatalytic self-cleaning activity evaluated by degradation of methylene blue under visible light irradiation. The used polymers promote greater adherence of the TiO₂-graphene particles to the substrate demonstrated by the maintenance of the photocatalytic efficiency after 5 washing cycles.

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**TRICHROMATIC COORDINATES OF THE MATERIALS STAINED WITH MB AND EXPOSED 4 HOURS TO VISBILE LIGHT**

| Sample | L*   | a*      | b*      | dL*  | da*  | db*  | dE*  | Strength SUM (%) | Note |
|--------|------|---------|---------|------|------|------|------|-----------------|------|
| Blank  | 67.61| -3.10   | -28.66  | 1.85 | 5.31 | 9.94 | 11.42| 67.49           | 2.00 |
| A      | 77.74| -3.10   | -11.37  | 8.86 | 10.32| 12.62| 18.55| 47.67           | 1.00 |
| CMC    | 63.66| -3.43   | -31.42  | 2.20 | 1.19 | 10.23| 10.53| 72.66           | 2.00 |
| B      | 80.85| -2.19   | -11.47  | 6.62 | 10.48| 9.35 | 15.53| 54.90           | 1.00 |
| PA     | 77.42| -2.22   | -23.73  | 4.93 | 6.15 | 10.67| 13.27| 67.49           | 1.50 |
| C      | 79.52| -1.59   | -10.14  | 6.62 | 10.44| 10.56| 16.26| 55.72           | 1.00 |
| EZF    | 83.41| -0.74   | -16.86  | 0.15 | 8.11 | 3.93 | 9.01 | 78.84           | 1.50 |
| D      | 75.37| -4.88   | -12.03  | 8.68 | 10.19| 14.96| 20.07| 44.98           | 1.00 |

**Table 6**
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Table 7

| Time (hours) | A | B | C | D |
|--------------|---|---|---|---|
| 0            | ![Image of sample A] | ![Image of sample B] | ![Image of sample C] | ![Image of sample D] |
| 4            | ![Image of sample A] | ![Image of sample B] | ![Image of sample C] | ![Image of sample D] |
| 8            | ![Image of sample A] | ![Image of sample B] | ![Image of sample C] | ![Image of sample D] |

Table 8

| Sample | L* | a* | b* | dL* | da* | db* | dE* | Strength SUM (%) | Note |
|--------|----|----|----|-----|-----|-----|-----|-----------------|------|
| A      | 74.92 | -1.07 | -10.60 | 9.36 | 12.01 | 20.98 | 25.92 | 44.35 | 1 |
| CMC    | 66.62 | -2.18 | -21.49 | 5.36 | 3.39 | 19.69 | 20.69 | 58.08 | 1 |
| PA     | 69.43 | -1.29 | -19.75 | 5.79 | 6.83 | 19.84 | 21.76 | 51.78 | 1 |
| B      | 75.89 | -0.73 | -9.75 | 10.44 | 11.84 | 20.92 | 26.20 | 46.13 | 1 |
| C      | 77.30 | -0.42 | -9.87 | 11.53 | 11.80 | 22.77 | 28.12 | 38.13 | 1 |
| D      | 77.96 | -0.50 | -9.13 | 11.50 | 12.21 | 21.37 | 27.17 | 38.19 | 1 |
| EZF    | 84.37 | 2.07 | -12.75 | 3.62 | 12.21 | 9.87 | 16.11 | 73.12 | 1 |
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Authors:

IULIANA DUMITRESCU – In memoriam

OVIDIU-GEORGE IORDACHE1, CORNELIA-ELENA MITRAN1,
ELENA PERDUM1, IRINA-MARIANA SĂNDULACHE1,
LUCIA OANA SECĂREANU1, LAURENŢIU CHRISTIAN DINCĂ1,
ARCADII SOBETKI2, LUCIAN DIAMANDESCU3

1National Research and Development Institute for Textile and Leather – INCDTP,
16 Lucretiu Patrascu Street, 030508, Bucharest, Romania
e-mail: office@incdtp.ro

2National Research-Development Institute for Non-Ferrous and Rare Metals – IMNR,
102 Biruintei Blvd., 077145, Pantelimon, Ilfov, Romania

3National Institute of Materials Physics – NIMP,
405 A, Atomistilor Street, Bucharest-Măgurele, Romania

Corresponding author:

OVIDIU-GEORGE IORDACHE
e-mail: ovidiu.iordache@incdtp.ro