Effects of the Pre-treatment with Atmospheric - Air Plasma Followed by Conventional Finishing

VASILICA POPESCU[1*], ION SANDU[2,3], EMIL IOAN MURESAN[4], BOGDAN ISTRATE[5], GABRIELA LISA[4]

[1]"Gheorghe Asachi" Technical University, Faculty of Textiles, Leather Engineering and Industrial Management, 29 Mangeron Blv., TEX 1 Building, Iasi 700050, Romania

[2]"Alexandru Ioan Cuza" University, ARHEOINVEST Interdisciplinary Platform, 11 Carol I, Corp G demisol, 700506, Iasi, Romania

[3]Romanian Inventors Forum, Str. Sf. P.Movila 3, L11, III/3, 700089, Iasi, Romania

[4]"Gheorghe Asachi" Technical University, Department of Organic and Biochemical Engineering, Faculty of Chemical Engineering and Environment, Management, 73 Blvd. Dimitrie Mangeron, Iasi-700050; Romania

[5]"Gheorghe Asachi" Technical University, Faculty of Mechanical Engineering, 43 Blvd. Mangeron, Iasi, 700050, Romania

The atmospheric-air plasma pre-treatment (the DBD method) determined the creation of a polar group, thus improving the reactivity of some textile supports. The experiments were carried out on fabrics made of 100% polyester (PET) and PET blended with cotton. The subsequent chemical treatment, consisting in grafting three long-chains substances rich in functional groups, occurred much easier. The grafting agents were applied on the textile material pre-treated with plasma, through three successive pad-dry-cure technologies. The FTIR analysis set off the modifications appeared both after the plasma treatment, and at the end of the chemical treatment. The comparative analysis of the contact angles, wrinkle-recovering angles, breaking stresses, treatment durability, dyeability and color measurements was performed on textile supports, both untreated and treated with plasma and then grafted. It was found that the performed physico-chemical treatments are complementary and they have a synergetic effect, resulting in the increase of wettability, dyeability, durability and WRA values.

Keywords: Atmospheric air–plasma, dielectric barrier discharge, pad-dry-cure, grafting, FTIR, water contact angle

Atmospheric-air plasma treatments are used for polymer functionalization, grafting or cross-linking. The cold plasma treatments have the ability to generate new surface characteristics while preserving the polymers bulk properties [1, 2]. Atmospheric-air plasma treatments are responsible for wettability increase due to the generation of functional groups with affinity for water. Such treatments can be performed on both synthetic and genuine polymers.

The polyester is a synthetic polymer with good mechanical properties, but with a marked hydrophobia and poor reactivity. That is why it is often subject to physical (plasma treatments) or chemical (grafting) treatments for functionalization and improved wettability and reactivity. Literature signalizes studies in which PET is functionalized by complementing the physical treatments with grafting chemical treatments. Thus, polyester was grafted with maleic acid [3, 4] or with polyvinyl alcohol [5], with the preservation of the mechanical properties and a good wettability appreciated from the small contact angles [6-10].

The exposure of PET and PET/cotton to dielectric barrier discharge (DBD) plasma in air at atmospheric pressure, under ambient conditions, results in chemical and physical modifications of the surface. The chemical modification of the external layers was proved by the formation of new polar groups (usually COOH and/or OH), due to the process generated by plasma treatment (splitting of ester bound from PET or oxidization at C (6)-OH from cellulose).

The surface physical modifications are more intense and result in a noticeable deterioration by the appearance of a significant amount of surface roughening. Changes of the topography have a great influence on wettability, characterized by the contact angle and surface free energy.

The degree of surface topography change depends both on the discharge power used and the number of treatment repetition cycles. After 20 processing cycles in air at discharge power of 500 W or 1000 W, surface topography changes insignificantly; the modifications become important only after 50 cycles [10, 11]. Usually, the plasma treatment of the synthetic materials is performed in order to diminish their hydrophobia and increase their adhesion to certain products rich in polar groups. In time, to the multiple utilizations of cold plasma were added those of initiating or facilitating the development of cleaning reactions [12], and grafting of genuine polymers of polysaccharide type, in a dry medium [13].

We present in this work the effects of a technology that works in a dry medium (plasma) followed with those of grafting in wet medium (through a pad-dry-cure technology). The utilized grafting agents are: tetrol (T), chitosan (CS) and monochlorotriazine-β- cyclodextrin (MCT-β-CD). The modifications generated at the surface of fabric support were rendered evident by means of the ATR-FTIR analysis. In all the studied cases, the treatment with plasma made functional the support, thus facilitating the grafting. The effects of the performed treatments are confirmed by the values of the taking-in degrees, contact angles, wrinkle- recovering angles and treatment durability/ dyeability and by color measurements.

Experimental part

The textile materials utilized were: polyester fabric (PET) 100% (weight 120g/m^2), PET /Cotton fabric (50/50%; weight 100 g/m^2).

The utilized chemicals were ethylenediamine tetrakis (ethoxylate-block-propoxylate) tetrol, known as Tetronic 701, monochlorotriazine β-cyclodextrin (MCT-β-CD) from

* email: vpopescu65@yahoo.com

Germany, $MgCl_2$ and Na_2CO_3 and C.I. Acid Blue 220. Chitosan (highly viscous) was purchased from Fluke.

The chemical structures of Tetronic 701, chitosan and monochlorotriazine β-cyclodextrin are presented in literature [14-16]. The dye used to highlight the durability of created bonds (C.I Acid Blue 220) during grafting and the increase of dyeability has the chemical structure as in figure 1.

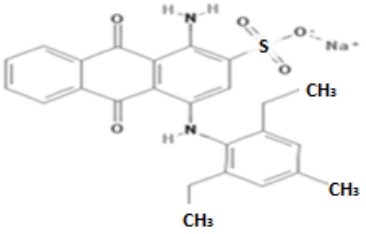


Fig. 1 Chemical structure of C.I Acid Blue 220 dye

Treatment conditions

Plasma treatment was carried out with a DBD (dielectric barrier discharge) - type apparatus COATING STAR produced in Germany. The textile material is passed twice by two electrodes (with the length of 0.5 m and situated at

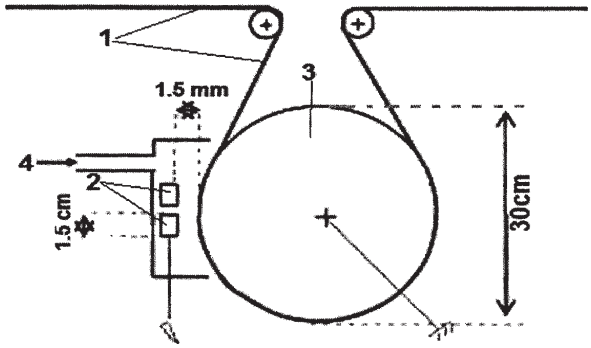


Fig. 2. Scheme of COATING STAR machine:
1. Fabric; 2. Two electrodes (1.5x50cm); 3.Counter- electrode

a distance of 1.5 mm), with each face of the material facing the electrodes), as in figure 2.

The two electrodes and the counter-electrode are responsible for generating plasma- type discharges. The external electrode surfaces are made of ceramic (a dielectric material), such that when the two electrodes are subject to a potential difference, a glow appears, named "discharge with dielectric barrier" (DBD) created when the apparatus is turned on. The atmospheric air was chosen as a gas during plasma treatments. The apparatus parameters were kept constant, namely: 750 W total electric power supplied by electrodes, electric voltage of 15 kV and a frequency of 26 kHz. During plasma pre-treatment, fabric samples are in contact with the counter-electrode and go through the plasma gas present between the electrodes and the counter-electrode gap with passing speed of 2m/min [17].

After plasma treatment, the materials were stored for two days, the time necessary for surface free energy to relax. The main mechanism that explains the phenomenon of surface free energy relaxation in time suggests that the polar groups created on the surface of the modified material migrate (in time) to the greatest extent and thus they will no longer influence the surface free energy, because they are now beneath the external layer of the surface [10]. After the relaxation stage, the textile materials were chemically treated using tetrol, chitosan and MCT-β-CD respectively in a pad-dry-cure technology. Padding - drying (3 min at 120°C) - curing (3 min at 140°C) technologies were performed three times, with each grafting agent. The conditions of application are indicated in table 1.

Method of Analysis

FTIR analysis

FTIR analysis was performed on the Multiple Internal Reflectance Accessory (SPECAC, SUA) using ATR KRS-5 crystal of thallium bromide–iodide, having 25 reflexions and the investigation angle of 45°. For recording the spectra in 4000-600 cm^{-1} area was used the Spectrophotometer FTIR IRAffinity-1 Shimadzu (Japan). After the registration, the absorption spectra have been superposed with KnowItAll software from BIO RAD.

The take-up degree

The taking over of reagents from the solution treatment, at the end of pad-dry-cure technology can be assessed using the take-up degree. The take-up degree, Yp was determined using equation (1):

$$Y_P = 100 \cdot (W_a - W_b)/W_b \quad [\%] \quad (1)$$

Sample's type	Sample's code		Treatment conditions		
			Padding		
	PET 100% (P)	PET /Cotton (PC)	I [1] T (g/L)	II [2] CS (g/L	III [3] CD (g/L)
Control sample 1 [4]	**P0**	**PC0**	-	-	-
Control sample 2 [5]	**PP**	**PCP**	-	-	-
Treated sample [6]	**P1**	**PC1**	150	90	75
	P2	**PC2**	90	150	75
	P3	**PC3**	90	90	90
	P4	**PC4**	90	90	75

Table 1
TREATMENT CONDITIONS AND SAMPLE CODING

[1] I is the pad I; conditions: padding ((T (90-150g/L) and 25g/L catalyst ($MgCl_2$), min.) - drying (3 min. at 120°C) - curing (3 min. at 140°C)
[2] II is the pad II; conditions: padding ((CS 90-150g/L) and 25g/L catalyst ($MgCl_2$), 10 min.) - drying (3 min. at 120°C) - curing (3 min. at 140°C)
[3] III is the pad III; conditions: padding ((MCT-β-CD (75-90g/L), 30g/L catalyst (Na_2CO_3), 10 min.) - drying (3 min. at 120°C) - curing (3 min. at 140°C)
[4] samples without plasma treatment (P0, PC0);
[5] samples with plasma treatment (PP, PCP);
[6] samples P_i, PC_i (when i = 1-4) were pre-treated with plasma followed by conventional treatments using *Ri* receipts

where: Y_p = take-up degree; W_a = mass of fabric before treatment; W_b = final mass of sample, after treatment.

Water contact angles

Contact angles are a measure of the efficiency of plasma treatment [18] and implicitly of wettability of a sample. Contact angles of PET and PET/cotton fabrics were determined on 'Digidrop' and on Balance GBX 3S Tensiometer respectively according to literature [19, 20].

Wrinkle recovering angles (WRA)

Wrinkle-proofing effects produced by the reagents were appreciated by the crease recovery angle values WRA (English Wrinkle Recovery Angle). WRA was determined according to the German standard DIN 53890. The Metrimpex FF-01 apparatus was used to determine the wrinkle recovering angles as the average of 10 measurements along both the warp and the weft directions.

Breaking strength

The breaking strengths were determined on H5K-T dynamometer for fabrics using the software QMAT TEXTILE, according to ISO 9513.

Treatments durability and color measurements

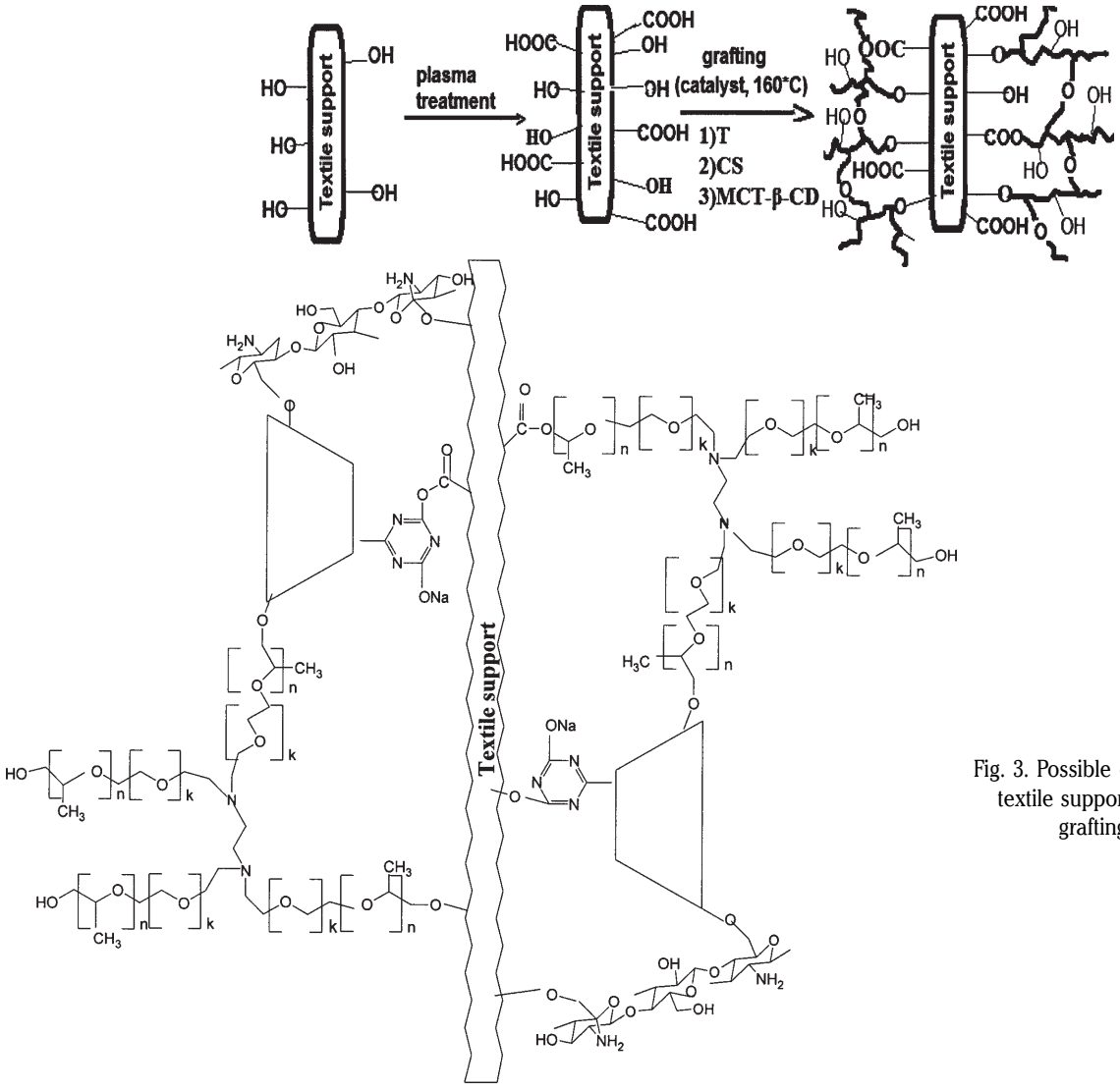
The durability of treatments was tested colorimetric. In order to demonstrate achievement of grafting and the durability of created effects were performed dyeing processes with CI Acid Blue 220, on the Mathis Polycolor 2002 machine. Dyeing with this dye was made possible by prior protonation of the amino groups from chitosan which were then centers of dyeing for this dye. Protonation was carried out for 15 min with acetic acid (*p*H = 4). After dyeing (at 100°C for 90 min) the samples were treated with soap (in a solution de 1g/L DS Lavoton at 100°C for 10 min), rinsed and dried at room temperature. The colour strength (K/S) values were examined using a spectrophotometer Spectroflash type Datacolor SF 300. Colour measurements have been valued by the CIElab graphs, which can be realized by spectrophotometer.

Results and discussions

Mechanism

Plasma pre-treatment generated by DBD in atmospheric air leads to a decrease of contact angle with water and an increase of surface energy due to the creation of more polar groups and more obvious etching occurring on the support surface. In this way, the fabrics made of PET acquire COOH and OH groups, and those of cotton (from PET/cotton fabric) –only COOH groups. These groups come from breaking of some ester bounds of PET, and from oxidization of C (6)-OH from cellulose.

By splitting the ester bound from PET surface, radicals are formed, that react with the radicals present in the plasma gas, and generate hydroxyl, carbonyl and COOH groups [21, 22]. Larger number of polar groups results in smaller contact angles. The smaller the contact angles, the longer the treatment time and discharge power density [23].



(2)

Fig. 3. Possible chemical structure of textile support after plasma and grafting treatments

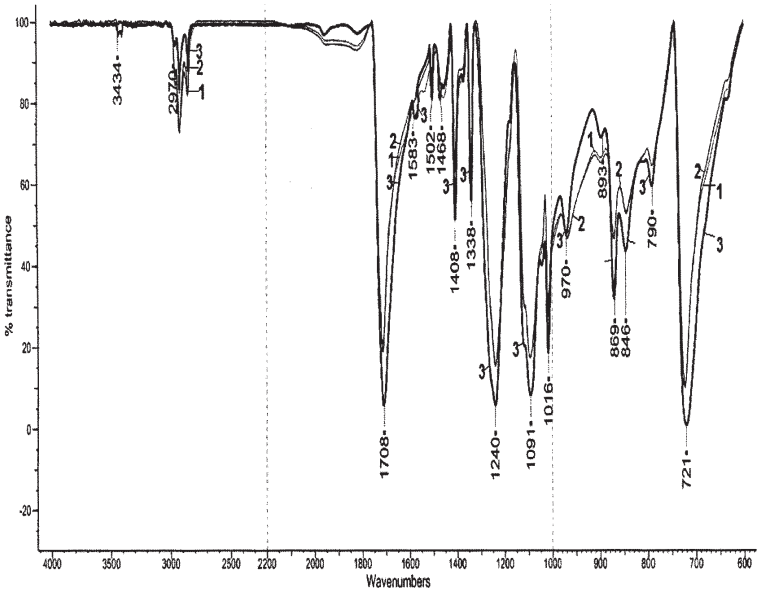


Fig. 4. FTIR spectra for PET fabrics: 1.P0; 2.PP; 3.PP4 (same codes as in Table 1)

The basic mechanism of the treatments applied to the textile supports is schematically represented by the chemical reaction (2).

The COOH and OH groups (from the plasma treated supports) were centers of covalent bonding (through ester/ether bridges) with the OH groups (from T or CS) in the presence of catalysts, the reactions occurring during the curing stages of the pad-dry-cure technologies. In the case of MCT-β-CD, ester/ether bonds were formed between the triazine cycle (the substitution occurred at the level of chlorine atom) and the COOH and OH groups of the support. One can not exclude the interaction between the reagents that can generate partial networks at the material surface, with the generation of ether bridges (see ch.r. 3). Taking into account that the three grafting agents have several OH groups, the structure of this network can be represented as in figure 3.

Spectroscopic analyses: ATR-FTIR

The ATR-FTIR analysis has been used to render evident the chemical modifications appeared on the PET surface after each treatment (fig. 4).

The pre-treatment with plasma did not alter absorption bands of polyester with the exception of peaks in the field 2928-2850cm^{-1} (CH_2 stretchings) as proof of some slight de-structuring at the surface of the fabric, fact highlighted by the appearance of those roughnesses. Acquired functional groups after the pre-treatment are highlighted by slight increases in peak 1712cm^{-1} (for COOH), and in 1408, 1240, 1016, 893 and 846 cm^{-1} (for OH). The tetrol (T) had a dual role: cleaning agent due to the lipofil nature and bridge for CS and MCT-β-CD. After treatment with T, took place a polyester de-structuring highlighted by evident decrease of all the peaks. However, at high concentrations, T was grafted polyester, as evidenced by the appearance of peak at 2970cm^{-1} (metoxy group), 907cm^{-1} (C-skeletal metoxy from the group) and 1240 cm^{-1} (etoxy group).

CS grafting [24] is confirmed by the increase in peaks from the field 2928-2850cm^{-1} (CH_2 stretchings) 1502cm^{-1} (NH bending), 1374cm^{-1} (CH bending (deformation stretch), 1091 cm^{-1} (overlapping C-O stretching of C(3)-OH (s) with CN stretching), 893cm^{-1} (deformation of pyranozic ring from CS and NH2 out-of-plane deformation) and 869cm^{-1} (out-of-phase asym. stretch ring C (1)-O-C (4) glucoside bond from CS). Grafting CS at the level of OH groups of the polyester functionalized with plasma is confirmed by increasing of peaks height from 1016 and 1175cm^{-1} (C-O-C asymmetric and symmetric stretchings).

The presence of MCT-β-CD on the final samples is confirmed by an increase in all peaks but the most obvious increase appears in the fields 2928-2850cm^{-1} (CH_2 stretchings) and 1502cm^{-1} (proving the existence of C=N). The increase of the peak from 1016cm^{-1} confirms the formation of the ether linkage with the polyester. Largest peak height at 1708cm^{-1} leads to the hypothesis of formation of ester bonds between COOH groups (of functionalized polyester with plasma) and the chlorine atom linked to the triazine ring of MCT-β-CD.

Taking-in degrees

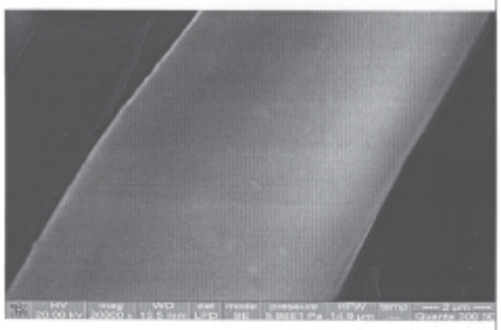
Following the treatments, it has been noticed that the degrees of loading the textile material with the three reagents (T, CS and MCT-β-CD) were higher on the supports that had suffered plasma pre-treatment. For instance, the PET samples (P1- P4) recorded values of 2.87- 3.01%, as compared to 0.07% (for P0); the samples PC1-PC4 had 4.95- 5.30%, as compared to 2.55% in PC0. This proves the favorable effect of the combined treatment (plasma and grafting) on the reactivity of textile support. During the plasma pre-treatment, the material surface will get a certain energy charge originating from some plasma species (ions, electrons, free radicals) with which the textile material is bombarded. Topography (roughness) and chemical modifications (polar groups/free radicals) appear, resulting in the increase of the textile support reactivity, therefore increasing the capacity of grafting with T, CS or MCT-β-CD.

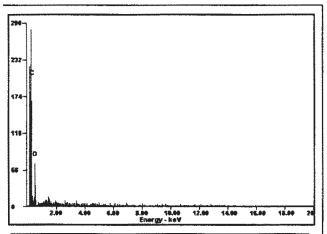
SEM and EDX results

SEM and EDX results (fig. 5) indicate both the existence of many roughnesses on the surface of polyester after plasma treatment and the grafting of T, CS and MCT-β-CD onto surface of polyester. From comparison of PP with P is observed that treatment with plasma determines just increasing the percentage of oxygen and the appearance of some roughnesses. The grafting of T (in PP+T) is confirmed by the appearance of the N atom at a rate of 5.88%.

The presence of CS in sample PP+T+CS is confirmed by the increase of N content at 6.52%. The presence of MCT-β-CD in the sample PP4 is confirmed both the presence of N atoms and Cl atoms (Cl that did not react with COOH groups of polyester functionalized after plasma treatment). Also the presence of the Na atoms (resulted

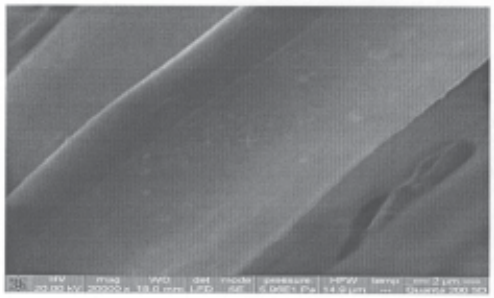
a) P (*Witness without plasma treatment*)

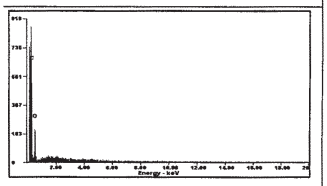




Element	*Wt%*	*At%*

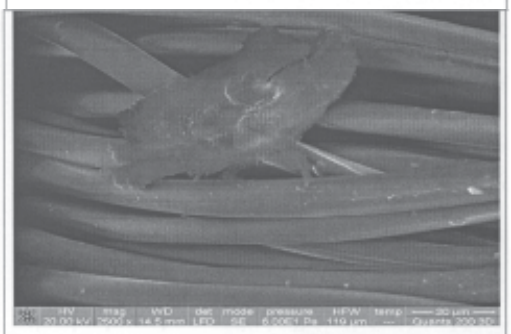
b) PP (*Witness with plasma treatment*)

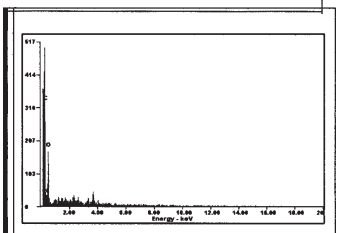




Element	*Wt%*	*At%*
CK	55.05	62.00
OK	44.95	38.00
Matrix	Correction	ZAF

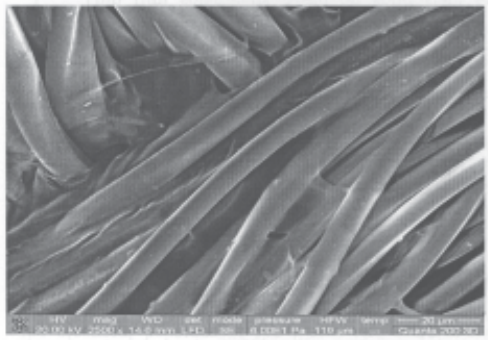
c) PP +T (*PET with plasma treatment +T*)

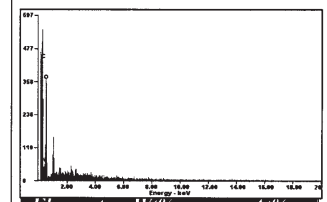




Element	*Wt%*	*At%*
CK	46.79	53.56
NK	05.88	05.77
OK	47.33	40.67
Matrix	Correction	ZAF

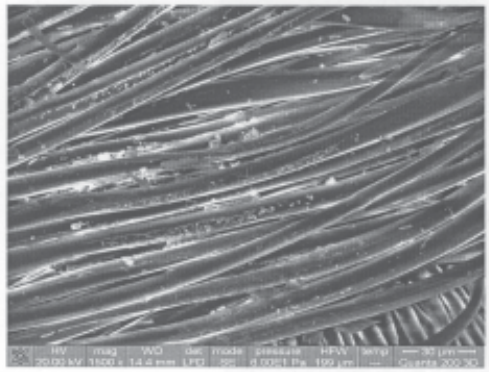
d) PP +T+CS (*PET with plasma treatment +T+CS*)

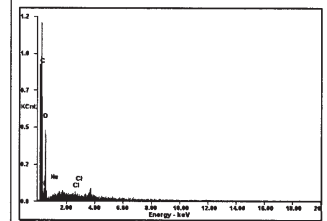




Element	*Wt%*	*At%*
CK	35.60	42.05
NK	06.52	06.61
OK	57.88	51.34
Matrix	Correction	ZAF

e) PP4 (*PET with plasma treatment + T + CS + MCT-β-CD*)





Element	*Wt%*	*At%*
CK	43.58	51.63
NK	05.14	05.22
OK	44.41	39.50
NaK	04.10	02.54
ClK	02.77	01.11
Matrix	Correction	ZAF

Fig. 5. SEM and EDX results

EDX results

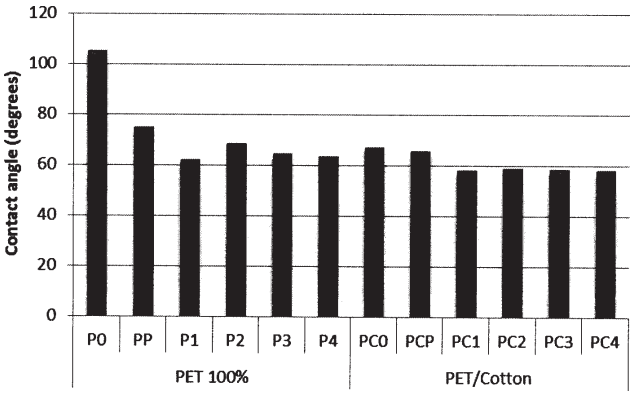


Fig. 6. Values of contact angle

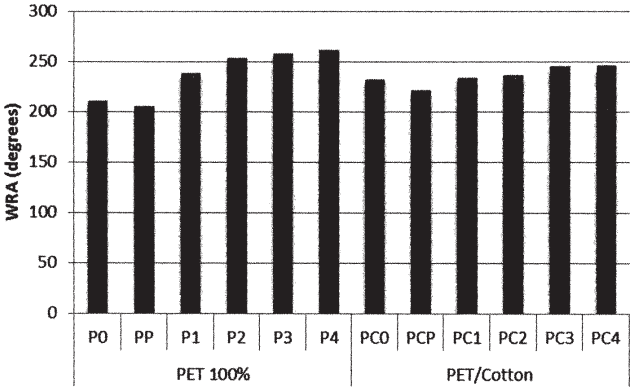


Fig. 7. Values of the wrinkle recovering angles

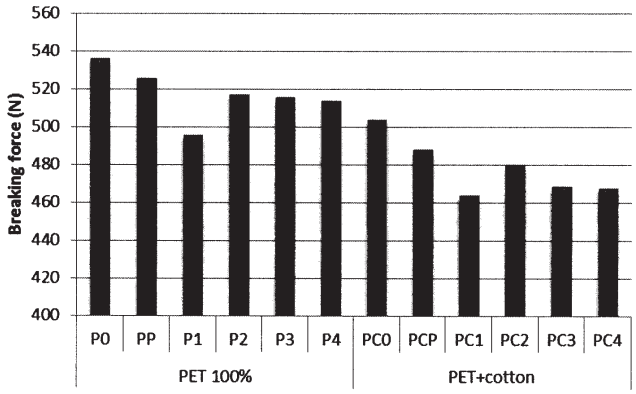


Fig. 8. Values of the breaking forces

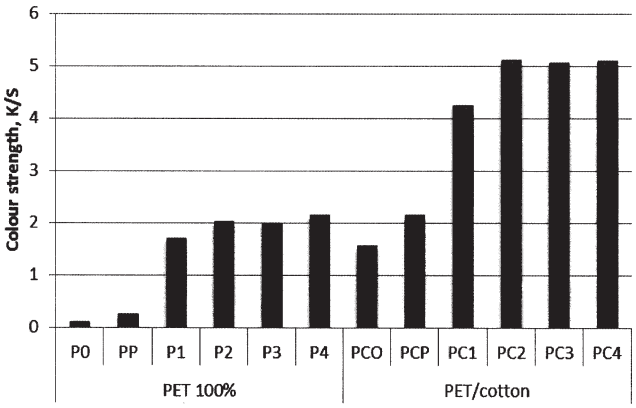


Fig. 9. K/S variation at 630 nm wavelength

from the three cycles MCT attached at cyclodextrine) confirms grafting of MCT-β-CD onto polyester.

The plasma pre-treatment and the performed treatments/graftings have synergetic effects, resulting in the decrease of the contact angle. The contact angle values indicate both the efficacy of both plasma treatment, and the hydrophilizing process produced on chemical way. After plasma pre-treatment, the strongest effect is noticed on untreated PET, where the angle decreases from 105.21 degrees (in P0) to 75.03 degrees (in PP in fig. 6). Grafting also results in the diminution of the contact angles, depending on the concentration of the utilized grafting agents.

In each series, the samples that have a high T concentration determine the lowest contact angles (in the case of P1 and PC1); what concerns CS (P2 and PC2) - on the contrary. The decrease of the MCT-β-CD from 90g/L (in P3 and PC3) to 75g/L (in P4 and PC4) results in the decrease of the contact angles, which shows the important part played by the number of OH groups existing on the textile support; when the number of OH groups is bigger, many OH groups can participate at the formation of a strong network, so only un-participated OH are able to form hydrogen bonds with water and determine the decrease of water absorption capacity. In P4 and PC4 there are many OH groups un-involved in the network and can form hydrogen bonds with water leading at a decrease of the contact angle.

Wrinkle Recovering Angle (WRA)

The samples treated only with plasma (PP and PCP) have smaller WRA than the untreated samples (P0 and PC0). After grafting with T, CS and MCT-β-CD, all the samples easy recover after wrinkling, and the WRA values are higher than for the plasma treated samples (PP and PCP). The highest WRA values are obtained for PET fabrics codified as P2, P3 and P4 (fig. 7).

Breaking resistance

It is known that the species created by the cold plasma treatment DBD have a low energy, therefore a poor material penetration power. The modifications are restricted to the surface, within a thickness of 1-10 nm. Yet, longer treatment duration affects the mechanical properties, because they can determine the breaking of some covalent bonds (through homolytic/heterolytic mechanisms) and the formation of more polar macromolecular structure that still preserves its molar mass (through transposition phenomenon) [1].

In this work, the 2m/min time of passing through the plasma-generating installation has determined a very light destructuring, materialized in a loss of breaking resistance of only a few Newtons, as compared to the witness sample untreated with plasma (fig. 8). Yet, the subsequent treatments resulted in the diminution of the breaking forces, as compared to the witness samples afferent to each series. The justification of these results is based on the occurrence of partial networks on the material surface, produced by graft interaction during the pad-dry-cure processes. At the same time, the destructive action of the acid medium (generated by the decomposition of $MgCl_2$) and of the high temperature during the curing stage results in resistance diminution.

Durability test

The treatments durability was determined by colorimetric tests (fig. 9). The transformations generated by plasma pre-treatments and grafting due to pad-dry-cure technology enable the textile supports dyeing with an acid dyestuff, unspecific for these. The fact that dyeing can be performed and it is uniform and penetrant proves the durability/fastness of the bonds realized between the polar groups resulted after plasma pre-treatment (COOH and OH groups in the case of PET and PET/cotton) and those from the grafting agents (OH or NH_2 groups), even in severe dyeing conditions (110°C for 90 min). It is known that the

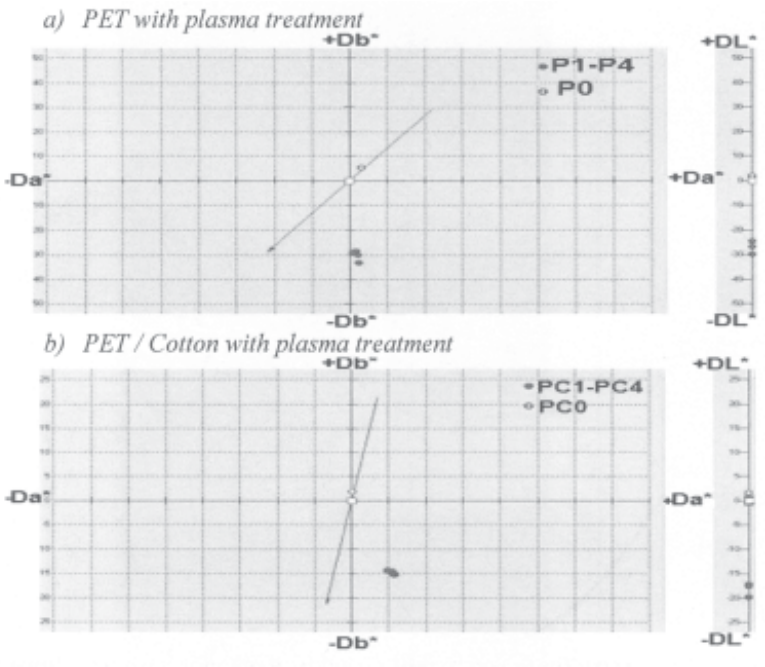


Fig. 10. CIE L*a*b* graphs for the samples treated with plasma, grafted and dyed

high kinetic energy developed during the dyeing process can determine the breaking of some liable superficial bonds.

The dyeing results confirm that all the plasma pre-treated samples have higher K/S values than the witness sample at 630 nm (where the blue color absorption is maxim). Ionic interactions appear between the treated textile supports and the dye (it has NH_3^+ groups acquired during the protonation performed at the beginning of dyeing). At the same time, the bonds between the treated support and the dye can be: hydrogen bonds (between the polar groups) or electrostatic bonds established between the cationic groups of chitosan (the NH_3^+ groups obtained during the protonation stage) and the dye anionic groups (SO_3^{2-}). During the protonation stage can get protonated not only the amine groups from already grafted chitosan, but also part of the NH_2 groups of the dye.

Colour measurements

CIE L*a*b* graphs from figure 10 indicate that all the plasma pre-treated samples and then grafted with T, CS and MCT-β-CD were dyed more intensely than the witness untreated samples (marked with the symbol °), because the brightness differences ΔL^* are negative [25-34].

All the treated samples are much bluer, with slight red hues than the corresponding (untreated) witness samples. Still another favorable aspect of the performed treatments is the existence of very small differences between the component samples of the same series, not only in terms of the color strength K/S, but also in terms of the parameters that characterize the colour (chroma (C), hue (H) and chromatic parameters (**a*** and **b***).

Conclusions

The combination of dry treatments (plasma DBD) with wet treatments (grafting) resulted in the diminution of the contact angles, therefore in a better wettability. The comfort of the materials treated in this way, assessed through the wrinkle-proofing and wrinkle-recovering capacity (WRA) is better than in the case of classical treatments. The mechanical properties are not affected by the plasma pre-treatment, but the subsequent classical treatments determine a diminution of the breaking resistance; this fact can be justified by the creation of partial networks at the material surface and the destructive action of the acid medium generated through the decomposition of the catalyst ($MgCl_2$) due to the high temperature during the curing stage.

In the case of PET, the air-atmospheric plasma pre-treatment superficially modified the morphology, while from a chemical point of view only one modification appears, confirmed by the FTIR analysis: the presence of the COOH groups (at 1708, 1240 - 1016cm^{-1}) and OH groups (at 1236 - 1016cm^{-1}) as the result of breaking some ester groups from polyester under the action of electric discharges during the treatment.

Moreover, this treatments combination (plasma followed by grafting) leads in small wettability variation, even if T, CS and MCT-β-CD have different influences on wettability having a different number of polar groups (the order of favoring the wettability in the classical grafting being T> MCT-β-CD >CS). This fact can be explained by the complementarity and synergy of the two treatments.

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