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Effect of the Corona Discharge Treatment of Polyester Fabrics on their Adhesive Properties

Abstract
This paper presents the results of studies carried out at the Textile Research Institute, Łódź, Poland with the use of original experimental equipment for the generation and application of corona discharge. The construction of this generator was described in our previous paper. It was found that the treatment of polyester fibres/fabrics with corona discharge brings about some significant changes, both in the physical and chemical structures of the surface layer, which results in considerable changes in the technological and performance properties of textile fabrics. Changes in adhesive properties are of the greatest importance and their range depends on the process conditions of the treatment used, especially on the unit energy of modification, the properties of the fibres modified, the environment in which the discharges occur and the constructional features of the generator. The test results presented concern changes in the physical state of the surface layer, measured by means of scanning electron microscopy (SEM) and atomic force microscopy (AFM). The free surface energy and contact angle were assessed by tensiometric measurements. The wettability of fibres and the chemical structure of the surface layer were also tested. The molar oxygen to carbon ratio (O/C) and the concentration of functional groups containing oxygen were measured by the techniques of photo-electron spectroscopy (XPS) and X-ray micro-analysis. The changes occurring in the technological properties of polyester fabrics, especially the forces of delamination of the coat layers and the quality of polymeric coat bonding, resulting from the corona treatment are also presented. It was found that any change in the charge sign on the activated fabric resulted in an almost double increase in the delamination force.

Key words: *polyester woven fabric, corona discharge, adhesion, surface energy, polarity, wettability, fibre surface properties.*

Introduction

The plasma treatment of textile fabrics results in significant physical and chemical changes [2, 3]. Physical changes concern the state of the fibre surface both at micro- and nano-scales, while the character of these changes is directly dependent on the intensity of the treatment. Depending on this intensity, changes in the micro-scale consist in smoothing the fibre surface by removing various deposits, including oligomers, and its development by the formation of characteristic „creases or wrinkles" located crosswise to the fibre axis. When the treatment intensity is very high, the top layer of fibres is damaged, showing characteristic "scaling". Changes in the nano-scale occur in the form of characteristic nano-roughness [4], and its depth increases with an increase in corona discharge intensity. Chemical changes resulting from plasma treatment consist in creating new functional groups on the fibre surface, which brings about changes in the free surface energy, polarity and wettability of the fibre tested [5]. Both physical and chemical changes in fibres affect their adhesive properties [14]. The low surface energy of many polymeric materials results in their weak adhesion. The problems connected with adhesion issue, especially in the case of fabrics made of synthetic fibres and in particular polyester fibres, which are now important textile raw materials, are revealed when coating, laminating or printing fabrics made of these fibres. As environmental protection and work safety requirements are growing, most of the chemical surface treatments of fabrics, hitherto commonly used to increase their adhesion are becoming increasingly unacceptable due to the toxicity of the agents used as well as the generally high energy and water consumption [14]. In the present state of development, the modification of synthetic fabrics with the use of various types of atmospheric plasma, including corona discharge, offers many advantages and shows great potential as an important method for the preliminary and finishing treatments of textiles.

Experimental

Materials

The fabric used was a woven fabric made of poly(ethylene terephthalate) (PET) filaments, with a mass per unit area of 80 g/m^2 [warp: DTY dtex 84f48 with no twist, spot tacked; weft: DTY dtex 150f215, with no twist], preliminarily washed and stabilised with hot air at 195 °C for 30 s.

Methods

Activation of PET fabric

The activation of PET fabric was carried out by means of a corona discharge generator, designed within the research and development project of the Textile Research Institute and constructed by the Institute of Polymer and Dye Engineering METALCHEM, Torun. The technical parameters of this apparatus are described in [1, 6]. The activation conditions were selected so as to avoid appreciable damage to the PET fabric during modification and the loss of its strength, and to provide the expected physical and chemical changes in the surface properties of the fibres/fabrics at the same time.

In order to find optimal treatment conditions, the PET fabric was treated with corona discharge with the unit activation energy E_j amounting to 18.9 J/cm^2, 37.8 J/cm^2 and 75.6 J/cm^2, respectively.

Unit activation energy E_j – energy of corona discharge per unit area of the fabric activated.

The value of E_j was calculated according to the formula:

$$E_j = P_x B/LA \times 6 \cdot 10^{-3} \text{ in J cm}^{-2}$$

where: P_x – maximal rated power of the generator (2100 W); A – fabric passing

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rate in m/min.; B - discharge power in % ; L – the length of discharge electrode in cm.

Microscopic examination of the fibre surface

This examination was performed at a micro-scale with the use of the SEM method and at a nano-scale by means of the AFM technique.

For the observation of the PET fabric surface, a JSM35C scanning electron microscope from JEOL was used. Fabric samples were dusted with gold by means of a JFC 1100 duster from JEOL.

Morphological and topographic changes in the polyester fibre surface at a nano-scale brought about by corona discharge were examined by means of an atomic force microscope, Nanoscope IIIA from Digital Instruments/Veeco (USA), operated in the tapping mode. Rectangular silicon cantilevers, model RTESP7 (Nanosensors, Wetzlar-Blankenfeld, Germany), were used throughout the study.

Testing the chemical properties of the fibre top layer

Photon-electronic spectroscopy XPS

All spectra were recorded on a Physical Electronics PHI 5000 Versa Probe scanning spectrometer using monochromatic Al Ka X-rays working with a power of 25 W. An X-ray beam was focused to a diameter of 100 μm; the area measured was defined as 250 x 250 μm. The hemispherical electron energy analyser was operated at a pass energy of 117.4 eV for the survey scan and 23.50 eV for all high resolution measurements. All measurements were conducted under a vacuum below 3×10^{-8} mbar, with the use of a neutraliser, working with both low energy electrons and low energy Ar^+ ions. PHI Multipak software was used to evaluate the XPS data (Shirley type background subtraction). For final calibration of the spectra, the peak C1s of an aromatic ring with binding energy values = 284.70 eV was used as an internal standard.

X-ray micro-analysis (EDX)

For the purpose of qualitative and quantitative chemical analysis of the surface composition, the X radiation was recorded by means of an EDX micro-analyser of the ISIS Link System from Oxford Instrument. The topography of the surfaces tested was observed by means of a Vega TS 5135 MM electron scanning microscope from Tesca. The resolution of the X-ray micro-analysis was about 0.5 μm.

Measuring the contact angle and free surface energy

The contact angle of the fabrics tested was measured by the dynamic method using a Sigma 701 tensiometer (KSV Instruments Ltd., Finland). This method consists in recording the force acting on a sample of the fabric tested, which is immersed in and emerged from the measuring liquid at the same rate. Distilled water and ethylene glycol were used as test liquids. The surface free energy and its components were calculated using the Wu equation [6].

$$g_S = g_{SL} + g_L \cdot \cos\Theta_L$$

$$\gamma_S = \gamma_S^d + \gamma_S^p$$

$$\gamma_{SL} = \gamma_S + \gamma_L - 4\cdot\gamma_S^d\cdot\gamma_L^d\cdot(\gamma_S^d + \gamma_L^d)^{-1} + - 4\cdot\gamma_S^p\cdot\gamma_L^p\cdot(\gamma_S^p + \gamma_L^p)^{-1}$$

where:

γ_L – free surface energy of test liquid
γ_L^d – non-polar component of free surface energy of test liquid
γ_L^p – polar component of free surface energy of test liquid
γ_S – free surface energy of fabric
γ_S^d – non-polar component of free surface energy of fabric
γ_S^p – polar component of free surface energy of fabric
γ_{SL} – fabric-liquid interfacial free energy
Θ – contact angle.

Wettability testing

Wettability tests were carried out in accordance with Standard PN-P-04633:1967 [7]. A description of this method and determination procedure are given in [6].

Tensile strength testing

Tensile strength tests were performed according to Standard PN-EN ISO 13934-1:2002 [8] using a Zwick tester, model 1120 (Germany).

Determination of charges on the fabric surface

A sample of the fabric tested was mechanically disintegrated into single filaments with a length not exceeding 1 mm. About 0.25 g of these filaments was immersed in 10 ml of distilled water, intensively stirred and placed in the vessel of a Particle Charge Detector (BTG Műtek GmbH, Germany).

Depending on the charge sign, the filament dispersion was titrated with a solution of poly(acrylic acid) or poly(allylamine hydrochloride). The concentration of the solution to be titrated was 1×10^{-3} mol/dm^3.

Testing the adhesive properties of PET fabrics treated with corona discharge – Determination of the delamination force of laminates

In order to assess changes in the adhesive properties of fabrics treated with corona discharge, the delamination forces of two laminated fabrics were determined. The bonding agent used was a self-crosslinking acrylic-vinyl copolymer in the form of an anion-active 50% aqueous dispersion under the name of Evo-Fin ATR, provided by DyStar (Germany). Tests were carried out in accordance with Standard PN-P-04950:1988 [9]

Results and discussion

The treatment of polyester fabrics with corona discharge with various values of unit energy results in several significant changes in the physical and chemical structures of the surface layer. The range of these changes depends on the process conditions of the treatment used.

Morphological changes in the surface of modified PET fabrics were assessed by means of scanning electron microscopy. The SEM photographs taken allowed us to select preliminary activation conditions, under which one could avoid any noticeable destruction of fibres. ***Figures 1.a, 1.b*** and ***1.c*** (see page 100) show SEM photographs of untreated and modified fabrics with unit activation energies of 37.8 J/cm^2 and 75.6 J/cm^2, respectively

The use of atomic force microscopy (AFM) allowed us to observe, at an nano-scale, changes in the physical state of the surface layer after corona discharge treatment. As is seen in ***Figures 2.b*** & ***2.c*** (see page 100), fibres of the modified fabrics show characteristic changes in the nanotopography of their surface, which are absent in the case of unmodified fibres/fabrics (***Figure 2.a***).

The activation of PET fabrics with corona discharge results in the development of a specific surface structure, as shown by the increase in nanocoarseness RMS.

The RMS value of unactivated fabric amounts to 1.7 nm and increases up to 11 nm after treatment with corona discharge of 37.8 J/cm^2 and can go up to 13 nm when the activation energy is 75.6 J/cm^2. Similar changes in the form of spherical outgrowths with nanodimensions on the surface of polymeric films were observed by Strobel et al. [10] when such films

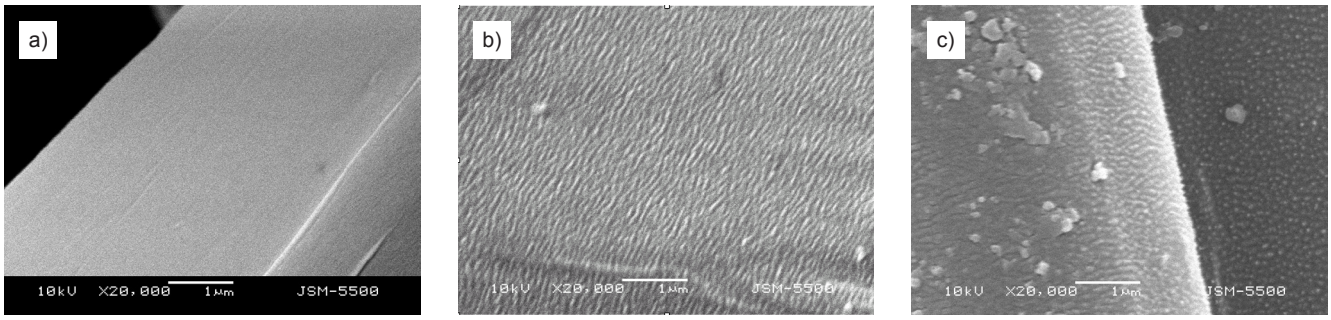

Figure 1. *SEM photographs of PET fibres: a) unmodified fibres, b) fibres activated with corona discharge with a unit activation energy of 37.8 J/cm², c) fibres activated with corona discharge with a unit activation energy of 75.6 J/cm².*

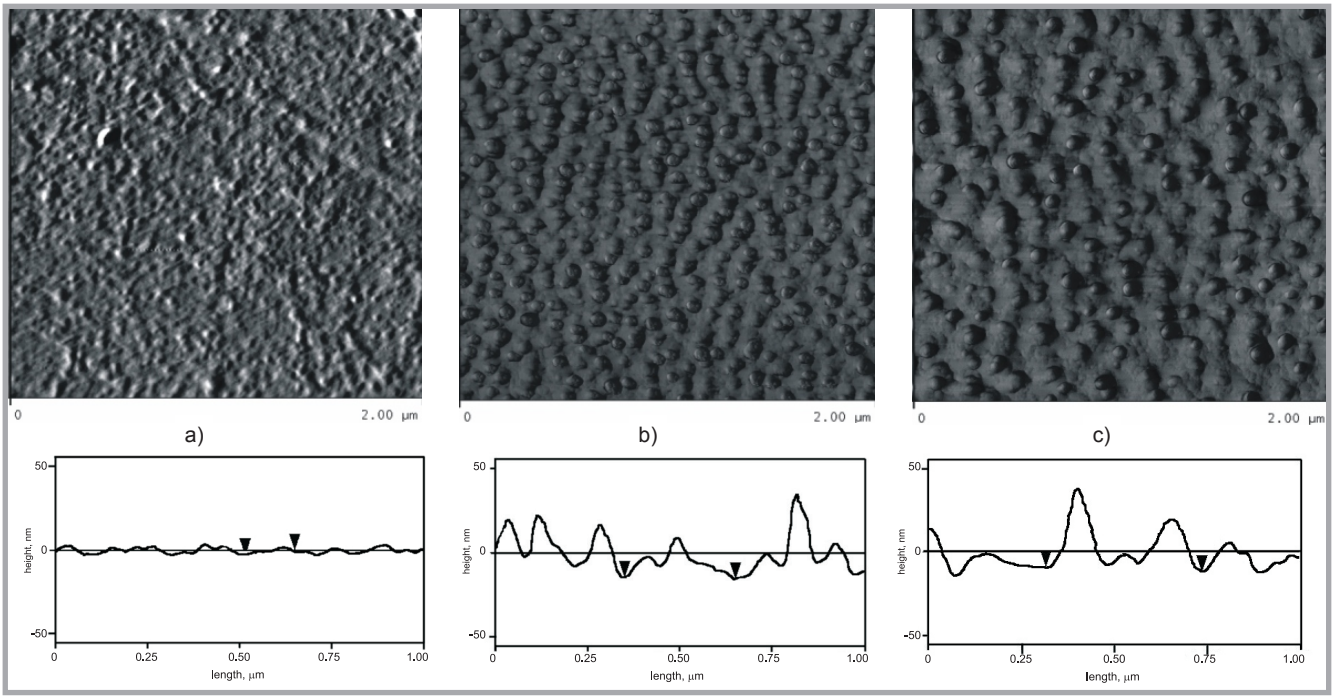

Figure 2. *AFM photographs: a) unmodified PET sample; b) PET sample activated with an energy of E_j = 37,8 J/cm²; c) PET sample activated with an energy of E_j = 75,6 J/cm², showing the profiles of the PET surface coarseness.*

were treated with corona discharge. The authors explained that this phenomenon was due to the formation of water-soluble oligomers. An analogous phenomenon in relation to the effect of the corona discharge treatment of PET film was also reported by Laurens et al. [11].

In order to compare our results with those reported in [10], the sample activated was extracted with hot water. It was found that its surface structure was almost unchanged, and the amount of extract was insignificantly low (lower than 0.5%).

The change in the specific surface of fibres in the PET fabric samples tested also brings about a change in their surface energy. The measurements performed by the tensiometric method show that activation with corona discharge decreases contact angles with both water and ethylene glycol. Based on the contact angle values obtained, the free surface energy, γ_S, was calculated (***Table 1***). An increase in the unit activation energy is accompanied by an increase in both fibre wettability and free surface energy. An increase in the free surface energy is mostly due to an increase in the polar component, which indicates the presence of polar groups in the surface layer of the samples tested.

The changes in wettability were confirmed by wettability tests.

The results of wettability tests are given in ***Table 2***. The analysis of the results obtained shows directly that the samples modified by means of corona discharge are characterised by better wettability than that of unmodified samples. An increase in wettability occurs in both the longitudinal and cross directions, which

Table 1. *Average values of the contact angle and free surface energy, γS, including the dispersive (γSd) and polar (γSp) components of the PET fabric versus the unit activation energy Ej.*

E_j, J/cm²	Contact angle, deg		γ_S, J/cm²	γ_S^d, J/cm²	γ_S^p, J/cm²
	water	ethylene glycol			
0	65.35	59.09	38.45	12.74	25.71
18.90	52.10	53.47	47.60	12.34	35.26
37.80	49.31	55.87	49.03	12.63	36.40
75.60	51.03	58.52	48.16	12.52	35.64

Table 2. *Effect of the unit activation energy, Ej, on the wettability of PET samples in the longitudinal and cross direction.*

Ej, J/cm²	Wettability, cm	
	Longitudinal direction	Cross direction
0	5.45	6.90
18.9	10.3	11.60
37.8	11.9	12.25
75.6	11.7	12.85

Table 3. *Effect of the unit energy of activation (E_j) on the increase in the weight oxygen to carbon ratio (ΔO/C) in the top layer of the samples tested.*

E_j, J/cm²	ΔO/C
0	0
18.9	0.017
37.8	0.021
75.6	0.033

is consistent with the results of the contact angle tests.

Beside changes in the physical state of the fibre surface, there is also a change in the chemical structure of the fibre's top layer. Due to activation with corona discharge, polar groups are formed on the fibre surface, which brings about an increase in the free surface energy. Additionally, the measurements of the molar oxygen to carbon ratio (O/C) show that new functional groups are formed on the surface of the fabric activated . According to previous reports [1, 6], the corona discharge treatment of PET fabrics results in the formation of acid groups on their surface. However, it should be mentioned that an increase in O/C can also be due to the oxygen from other functional polar groups created by the corona discharge treatment. In order to assess what groups are formed on the fibre surface activated, XPS measurements were carried out for an unactivated sample and a sample activated with an energy of 75.6 J/cm². It was found that the O/C of the unactivated sample was 0.269, while that of the activated sample amounted to 0.485. The increase in O/C (ΔO/C) clearly indicates the oxidation of the top layer of the PET fabric. The measurements performed by the EDX method show that corona discharge activation causes the O/C ratio to increase. The results obtained are given in ***Table 3***.

The confirmed changes in the chemical and physical structures of the fibre's top layer, caused by the corona discharge treatment, should considerably affect the technological properties of the fabrics under investigation, including primarily a significant improvement in their adhesive capabilities. According to literature reports [12, 13], this should bring about an increase in the force of delamination of laminated fabrics and, consequently, an improvement in the quality of bonding between the polymeric coats and textile substrate.

Adhesion tests were carried out for three PET fabric samples activated under different conditions. The test results show that the delamination force increases with an increase the unit activation energy. In the case of the most intensive activation, this increase is about 50% compared to the unactivated sample. The results obtained are shown in ***Figure 3***.

In the later part of this work, the adhesion tests were preceded by the determination of the electric charges of both the fabric activated and the emulsion used for bonding laminates. It was found that the bonding agent, in the form of an aqueous emulsion, used for bonding as well as the PET fabric activated showed strong negative charges. This increase in the

Table 4. *Values of the electric charges on the PET fabric surface; * activation with 75.6 J/cm².*

No. of sample	The sequence of operation	Charge quantity coulomb/g ×10⁶
1	Padding with no activation	+ 1,0
2	Padding + activation*	+ 2,8
3	Activation* + padding	+10,5

negative charge of PET fabric obtained by corona activation is brought about by functional polar groups, such as negatively charged O^- and COO^-, formed on the fibre surface under the influence of corona discharge, which is illustrated in ***Figure 4***.

From such a graph, the volume of titrant (V), corresponding to zero potential, is evaluated, and the charge quantity C_q in coulomb/g was calculated according to the formula:

$$C_q = (V \times c)/m$$

where:
c – molarity of the titrant;
m – mass of the sample.

Such monomial charges, irrespective of the development of the fibre's specific surface and the considerably increased surface energy, must negatively affect the quality of laminates obtained and decrease the force of their delamination. This argumentation was confirmed by test results. In this situation, in order to improve the quality of the bonding obtained, it was decided to change the sign of the electric charge of the PET fabric surface from negative to positive. For that end, a series of tests was performed consisting in padding the activated PET fabric with poly(dimethylaminoethylene

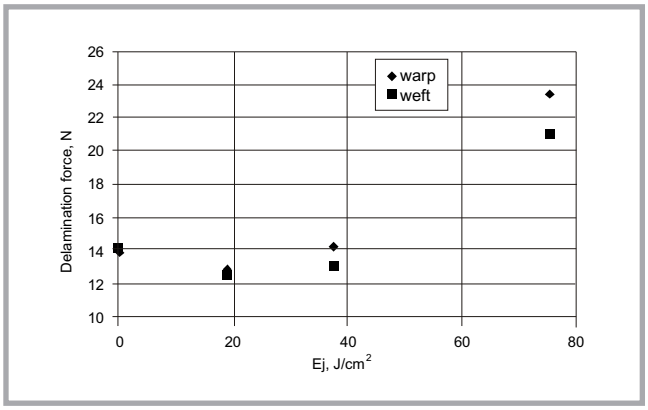

Figure 3. *Effect of the unit activation energy, E_j, on the delamination force of two PET fabrics bonded with a bonding agent.*

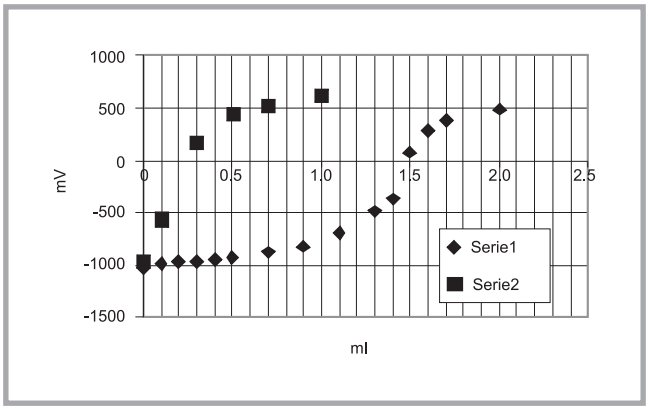

Figure 4. *Titration by 0.001 M poly(allyl-amine hydrochloride): Serie 1 – activated 37.8 J/cm²; Serie 2 – unmodified.*

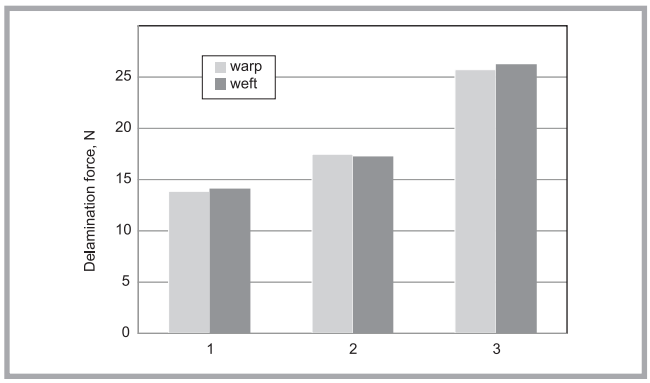

Figure 5. *Delamination forces: 1 – PET fabric; 2 – PET fabric padded with PDAMA; 3 – PET fabric activated with an energy of 75.6 J/cm² and padded with PDAMA.*

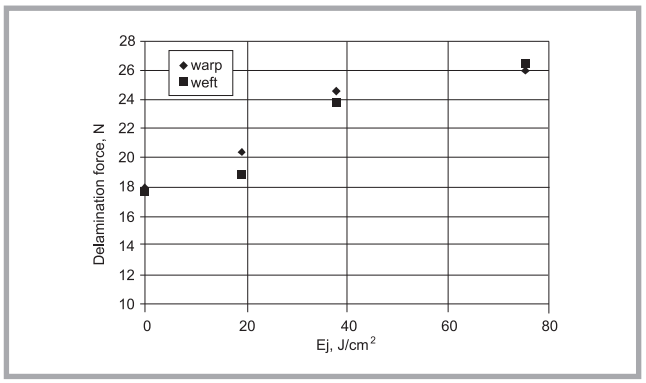

Figure 6. *Effect of the unit activation energy, E_j, on the delamination force of PET fabric, padded with PDAMA.*

methacrylate) (PDAMA), a substance with a strong positive charge, which changes the fabric charge from negative to positive. The charges of the fabric surface after the padding process are given in ***Table 4*** (see page 101).

As is seen, the best variant of treatment consists in activation followed by padding with PDAMA. The charge obtained in this case is positive and amounts to 10.5×10^{-6} coulomb/g.

The use of padding with PDAMA to change the sign of charge on the fabric activated resulted in a considerable, almost double, increase in the delamination force, as shown in ***Figure 5***.

The adhesion test results obtained, i.e. the increased delamination force, can be explained as follows: the padding of fabrics with PDAMA changed the charge accumulated on the activated fabric surface from negative to positive, which brought about a significant improvement in making use of the chemical activation of the fibre's top layer to create a chemical bond with the bonding agent and, consequently, to increase the force of delamination. As is seen, the application of PDAMA quickly increases the delamination force. A further increase is due to the activation process. The larger this increase is, the higher the unit activation energy of the corona discharge is, as illustrated by ***Figure 6***.

Conclusions

Corona discharge causes characteristic changes in the physical and chemical state of the top layer of PET fabrics, resulting in an increase in surface nanocoarsness (RMS) and the formation of polar groups in the fibre's top layer.

The modification of PET fabrics with corona discharge increases the fibre's surface energy, wettability and the wettability of the samples activated.

The increased oxygen to carbon ratio indicates the formation of a great number of functional polar groups in the top fibre layer of PET fabrics activated with corona discharge.

Due to the development of the fibre's specific surface and the elimination of direct contact between the negative charge accumulated on the surface of activated PET fabric and the bonding agent used, the adhesive capabilities of such fabrics are considerably improved, as shown by an appreciable increase in the delamination force.

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