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Effect of Plasma Modification on the Chemical Structure of a Polyethylene Terephthalate Fabrics Surface

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Abstract
Investigations focused on physico-chemical modifications of a polyethylene terephthalate (PET) nonwoven fabric fibre surface. To improve the adhesive properties of textile products towards TiO_2, their surface was treated in low-temperature plasma (cold plasma). Plasma treatment of PET fabrics was performed in carbon dioxide and/or argon pressure. Potential changes in the chemical structure of polyester fabric can be caused by the following: a homolytic splitting of the ester bonds, a release of volatile degradation products (mainly CO and CO_2), a cross-linking, reactions of macro radicals [alkyl ($\bullet CH_2$-CH_2~) and phenyl ($\bullet C_6H_4$~)] with oxygen, and a subsequent formation of hydroxy-aromatic rings. Experimental investigations confirmed the fact of modification of the chemical structure of the PET surface caused by plasma treatment of the fibre surface.

Key words: *plasma treatment, poly(ethylene terephthalate) fabrics, nonwovens, surface modification, oxide particles.*

Introduction

The development of new technologies in textile products is closely related to progress in chemistry and polymer processing. The functionalisation of textile polymers and/or textile-products by an insertion of chemical nanomolecules into/or on the surface of their fibres has recently become the main direction of textile product engineering development. Research works on the functionalisation of textile products have focused on the addition of new properties, e.g. antibacterial, absorbing electromagnetic radiation (eg. UV), removal of air pollutants.

Recently many research programs have concentrated on synthetic and physicochemical investigations on modified polyester fibres. An important stage in these research programs is the production of modified textile products and the preparation of a nonwoven fabric support. These include investigations of the fibre surface, especially after prior physico-chemical modifications improving adsorption properties of textile products towards titanium dioxide (TiO_2).

Nanoparticles of metal-oxides (eg. TiO_2) belong to a group of compounds with photo-catalytic properties, which are able to absorb UV radiation and provide an antibacterial barrier. For example, TiO_2 (micronised or in a nanoparticle form) is photostable and non-toxic, and therefore is used in cosmetics as a substance absorbing UV radiation [1 - 3].

Polyesters present a category of polymers based on ester groups forming the main chain of the polymer. Polyesters include naturally occurring chemicals, such as in a cutin of plant cuticles, as well as synthetics through step-growth polymerisation ***(Figure 1)***.

Although there are many polyesters, the term “polyester” as a specific material most commonly refers to polyethylene terephthalate (PET). PET $(C_{10}H_8O_4)_n$ – is manufactured by the polycondensation of purified terephthalic acid (PTA) or its dimethyl ester dimethyl terephthalate (DMT) and monoethylene glycol (GE) (***Figure 1***). With an 18% market share of all plastic materials produced, it ranks third after polyethylene (33.5%) and polypropylene (19.5%) PET is widely used in textiles [78% of the market: applications in staple fibre (PSF) formation, filaments POY, DTY, FDY; technical yarn and tire cord, etc.] and packaging [38% of the market: applications in bottles (for CSD, water, juice, detergents, etc.) formation, A-PET films, strapping, etc.] industry [4-5].

Plasma can be used to modify surfaces of poly(ethylene terephthalate) textiles. Recently many investigations have been directed towards the development of plasma technologies to improve the properties of textile surfaces. Plasma treatment has found numerous applications in the textile industry, namely in dyeing/printing, colour fastness or coating adhesion and many other related applications [6 - 10].

In this paper we present results for the plasma treatment of PET nonwoven as a way to improve their adhesion properties towards TiO_2. The main aim of these research works was the estimation of physico-chemical modifications of a polyethylene terephthalate nonwoven fabric surface after plasma treatment application.

Experimental

Material used

Textile products
Poly (ethylene terephthalate) – PET nonwovens produced according to the spunlace technique (water jet), mass per unit area 100 g/m^2.

Substrates used
Titanium dioxide (TiO_2) of anatase structure: Tytanpol® A-11 (Grupa Azoty

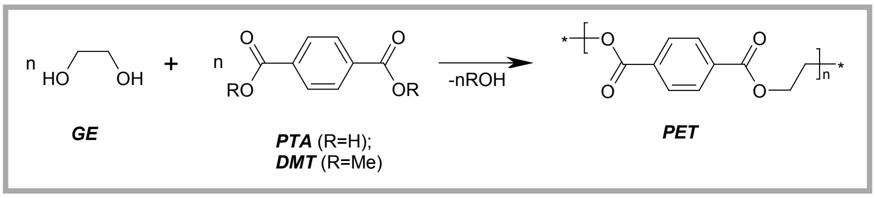

Figure 1. *Formation of PET by polycondensation of DMT and GE.*

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Table 1. *Type of plasma treatment of polyester samples.*

Type of textile used	Type of discharge	Power of discharge, W	Working gas	Gas flow, sccm	Duration of treatment, s
PET nonwoven	AF(40kHz)	2500	Ar	64	15
			CO_2	50	

Table 2. *Type of samples used.*

Textile sample	Type of modification
WPET	Nonwoven polyester fabric
WPET Ar	Nonwoven polyester fabric treated by plasma. Working gas: Argon
WPET CO_2	Nonwoven polyester fabric treated by plasma. Working gas: CO_2
WPET TiO_2	Nonwoven polyester fabric with incorporation of TiO_2
WPET Ar TiO_2	Nonwoven polyester fabric treated by plasma (working gas: Ar) with incorporation of TiO_2.
WPET CO_2 TiO_2	Nonwoven polyester fabric treated by plasma (working gas: CO_2) with incorporation of TiO_2.

Table 3. *UPF values and adsorption of TiO_2, in g/m^2 on the PET nonwoven surface.*

Textile sample type	UPF	Amount of paste deposited onto the nonwoven support, g/m^2	Amount of TiO_2 deposited onto the nonwoven support, g/m^2
WPET	23	-	-
WPET Ar	26	-	-
WPET CO_2	25	-	-
WPET TiO_2	70	18	4
WPET Ar TiO_2	80	30	7
WPET CO_2 TiO_2	126	38	9

Methods used

Plasma treatment

Plasma treatment of PET nonwoven was performed under carbon dioxide and/or argon pressure. This work was done at the Faculty of Process and Environmental Engineering at the Division of Molecular Engineering at Lodz University of Technology.

A detailed list of parameters for the plasma treatment of different options of samples is shown in ***Table 1***.

After applying plasma pre-treatment, TiO_2 particles were easily incorporated into the textile structure.

Coating of polyester nonwoven fabric - incorporation of metal oxide particles: TiO_2

Pastes of homogeneous dispersion and appropriate viscosity based on acryl resins (10% wt.) containing micronised TiO_2 (3% wt.), a densifying agent (3% wt.), and wetting agent 3% (and water to reach 100%) were prepared. The paste was deposited onto the nonwoven support with the use of special kit for the deposition of nanostructural coatings made by Werner Mathis AG (Switzerland), type KTF-350S. The thickness of the coating was controlled by the width of the supply gap; a width of 0.05 mm was used. The samples were dried and heated at 120 °C for 6 minutes. A list of the textile samples tested is presented in ***Table 2***.

Infrared analysis

Changes in the chemical structure of plasma treated polyester products were assessed using FTIR spectroscopy [1]. In the study a spectrometer - Jasco's 6000 series (Japan) was used with a microscopic attachment *Irtron-µ* (Jasco, Japan). The FTIR technique used in the investigation was direct measurement of the absorbance (Abs) of nonwoven polyester fabrics with a microscopic attachment.

UV-VIS analysis and estimation of UV radiation barrier properties

Changes in the physical properties of nonwoven polyester fabric before plasma treatment (a), after plasma treatment (b), and after incorporation of TiO_2 particles into plasma modified polyester (c) were assessed using UV-VIS spectroscopy (***Table 3*** and ***Figure 4***).

UV barrier properties of the modified textile products, expressed in terms of the Ultraviolet protection factor (*UPF*), were evaluated on the basis of UV transmittance (%T) measurements by the spectrophotometric method using the double beam UV-Vis spectrophotometer a V-550 type Jasco (Japan) equipped with an integrating head (Jasco, Japan). The *UPF* value was calculated according to PN-EN 13758-1:2005 from formula (1):

$$UPF = \frac{\int_{\lambda=290}^{\lambda=400} E(\lambda)\varepsilon(\lambda)d(\lambda)}{\int_{\lambda=290}^{\lambda=400} E(\lambda)\varepsilon(\lambda)T(\lambda)d(\lambda)} \quad (1)$$

where:
$E(\lambda)$ – solar irradiance,
$\varepsilon(\lambda)$ – erythema action spectrum (measure of the harmfulness of UV radiation for human skin);
$d\lambda$ – wavelength interval of measurements;
$T(\lambda)$ – spectral transmittance at wavelength λ, in %T.

The *UPF* value of the textile products was determined as the arithmetic mean of the *UPF* values, measured for all samples and reduced by a statistical value dependent on the number of measurements made at a confidence level of 95%.

Results and discussion

The transmittance spectra, in %T of polyester nonwoven samples used in the investigations are presented in ***Figure 2***.

The transmission spectra, in %T of polyester nonwoven samples show no significant change in light transmission in the range of 290 - 400 nm - nonwoven samples before and after plasma pretreatment: WPET, WPET Ar and CO_2 WPET (***Figure 2***) which can be related to no changes in the macro structure of the nonwoven samples. The decrease in light transmission occurs after the modification/introduction of TiO_2 in the samples: WPET TiO_2, WPET Ar TiO_2, WPET CO_2 TiO_2.

The UPF value for the unmodified polyester nonwoven was above 25, but after modification with TiO_2 its value increased above 50.

After plasma treatment and subsequent TiO_2 modification, a significant increase in the *UPF* value was revealed (*UPF* > 100) (***Figure 3, Table 3***).

Table 3 presents the characterisation of representative polyester nonwoven fabric samples coated with paste containing TiO_2, expressed as the adsorption prop-

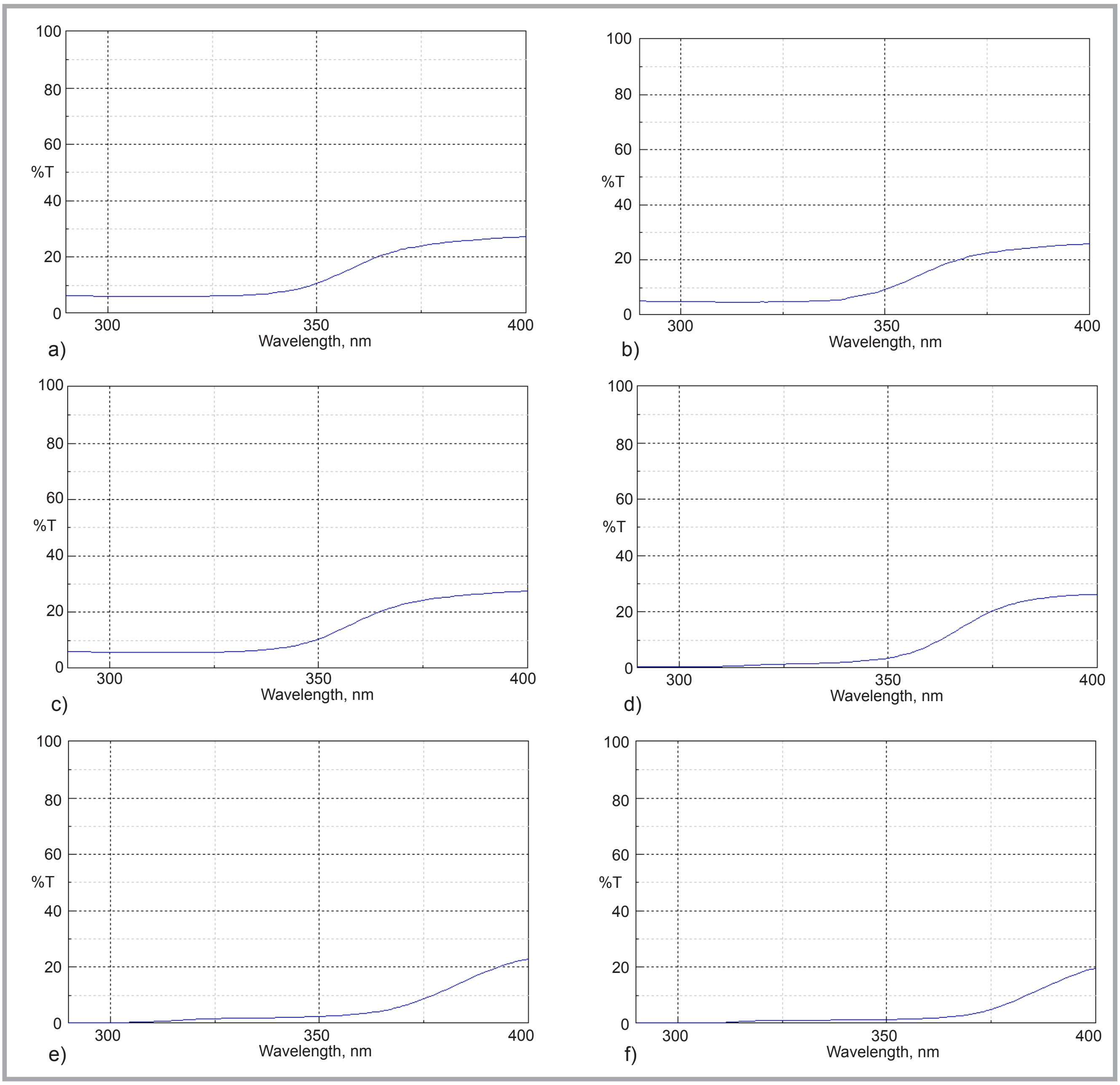


Figure 2. *Transmittance spectra in %T of polyester nonwoven samples a) WPET, b) WPET Ar, c) WPET CO_2, d) WPET TiO_2, e) WPET Ar TiO_2, f) WPET CO_2 TiO_2 in the range λ = 290 - 400 nm.*

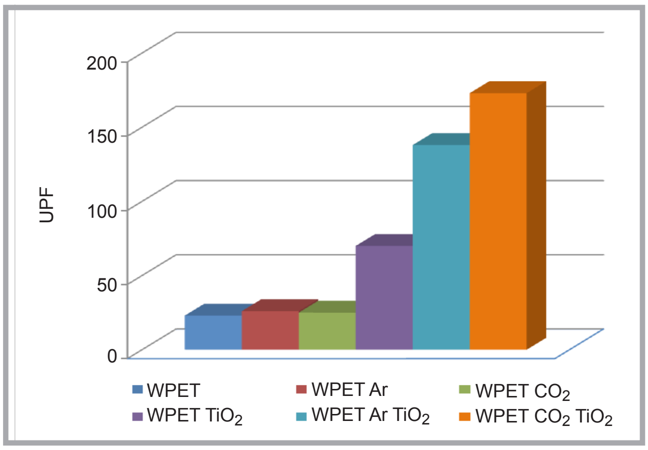


Figure 3. *UPF values of unmodified and modified (TiO_2 incorporated) samples of nonwoven fabrics.*

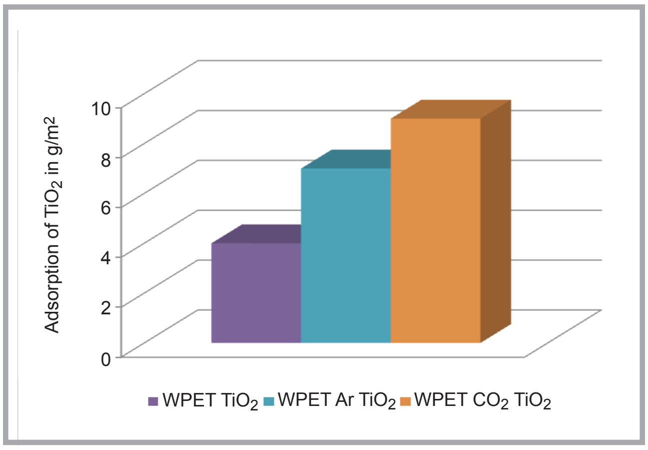
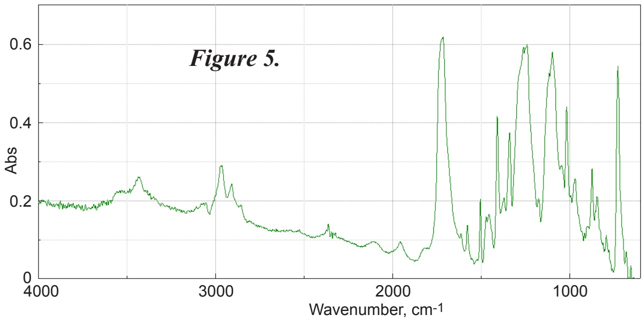
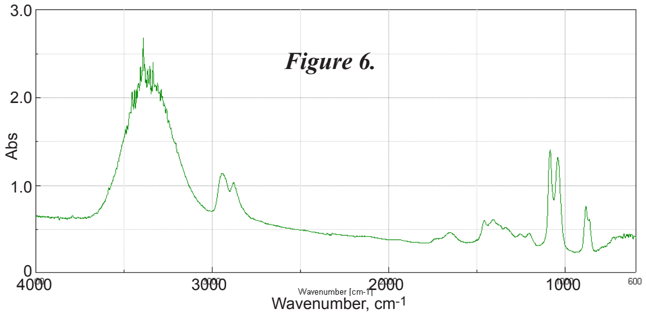


Figure 4. *Adsorption of TiO_2 in g/m^2 onto PET nonwoven surface.*





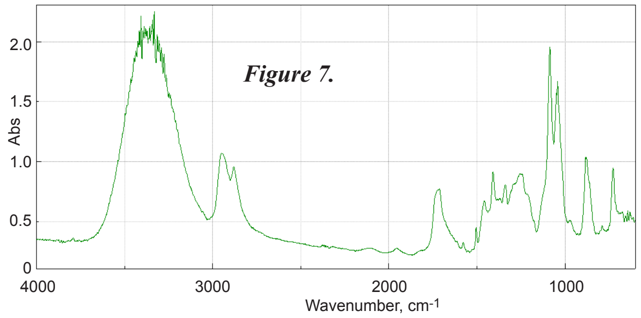


Figure 5. *IR spectrum of nonwoven PET sample (WPET)*

Figure 6. *IR spectrum of nonwoven PET sample treated with plasma (WPET Ar)*

Figure 7. *IR spectrum of nonwoven PET sample treated with plasma (WPET CO_2)*

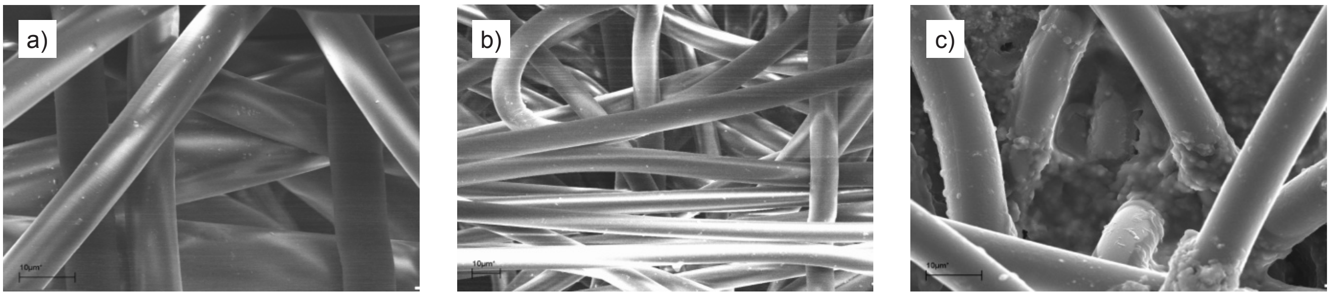


Figure 8. *SEM microphotographs of polyester nonwoven: a.) unmodified (WPET), b.) modified with plasma pre-treatment (WPET Ar), c.) modified with plasma pre-treatment and TiO_2 (WPET Ar TiO_2)*

erties of TiO_2: amount of the paste and TiO_2 deposited onto the nonwoven support and corresponding *UPF* values. The amount of paste and TiO_2 was estimated by the weighing method (the difference in weight of nonwoven before and after deposition of the paste with TiO_2 onto the nonwoven support).

The adsorption properties of polyester nonwoven samples show a significant change in them before (WPET TiO_2) and after plasma pre-treatment: WPET Ar TiO_2, WPET CO_2 TiO_2 (**Figure 4**). The amount of paste with TiO_2 deposited on polyester nonwoven fabric after preliminary treatment with low-temperature plasma (WPET Ar TiO_2, WPET CO_2 TiO_2) is considerably greater than in the case of unmodified samples (WPET TiO_2). Similarly the amount of particles of TiO_2 deposited on polyester nonwoven fabric after preliminary treatment with low-temperature plasma (WPET Ar TiO_2, WPET CO_2 TiO_2) is greater than in the case of unmodified samples (WPET TiO_2).

The resulting high adsorption properties of polyester nonwoven fabric after preliminary treatment with low-temperature plasma prepared by TiO_2 can be related to a better attraction between the nonwoven and TiO_2 particles.

An interesting phenomenon was observed in the FTIR spectra of plasma treated polyester nonwoven samples. IR spectra (Abs) of a nonwoven polyester sample not treated by plasma *(WPET -* ***Figure 5***) and a non-woven polyester sample after plasma modification (WPET Ar, WPET CO_2) showed changes in the IR absorption curves in the range of characteristic OH groups (***Figures 6*** & ***7***).

The broad peak observed at a length of 3000 - 3300 cm^{-1} and the other observed at a length of 1000 - 1150 cm^{-1} corresponding to hydroxyl groups: –OH and >C-O or >C-O· can indicate the more hydrophilic nature of the surfaces of the fibres when in contact with atmospheric water vapor absorbed from the air.

Since the SEM microphotographs (***Figure 8.)*** and UV spectra recorded revealed no significant changes in the macrostructure of nonwoven samples before and after plasma pre-treatment, therefore the changes in adsorption properties may presumably result from surface chemical changes of the polyester nonwoven.

Potential changes in the chemical structure of polyester fabric can be caused by the following: a homolytic splitting of the ester bonds, a release of volatile degradation products (mainly CO and CO_2), a cross-linking, reactions of macro alkyl (•CH_2-CH_2~) and phenyl (•C_6H_4~) radicals with oxygen, and a subsequent formation of hydroxy-aromatic rings (***Figure 9***).

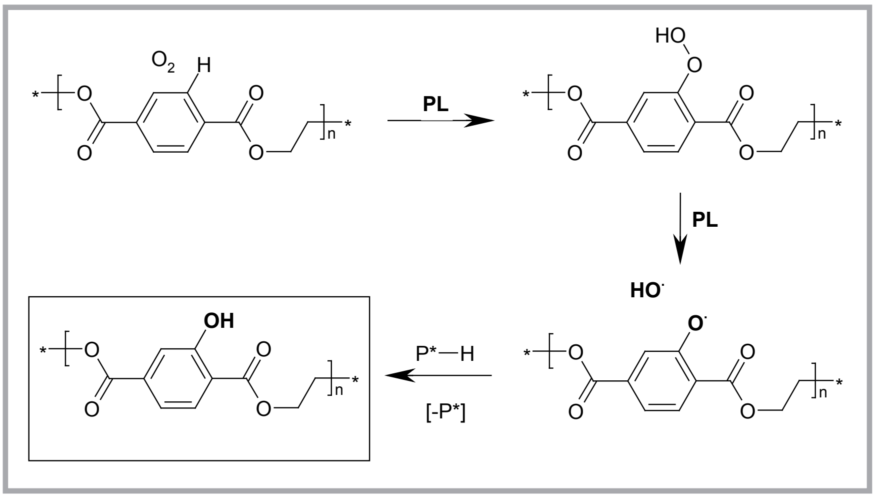


Figure 9. *Proposed mechanism of free radical reactions during plasma modification of PET.*

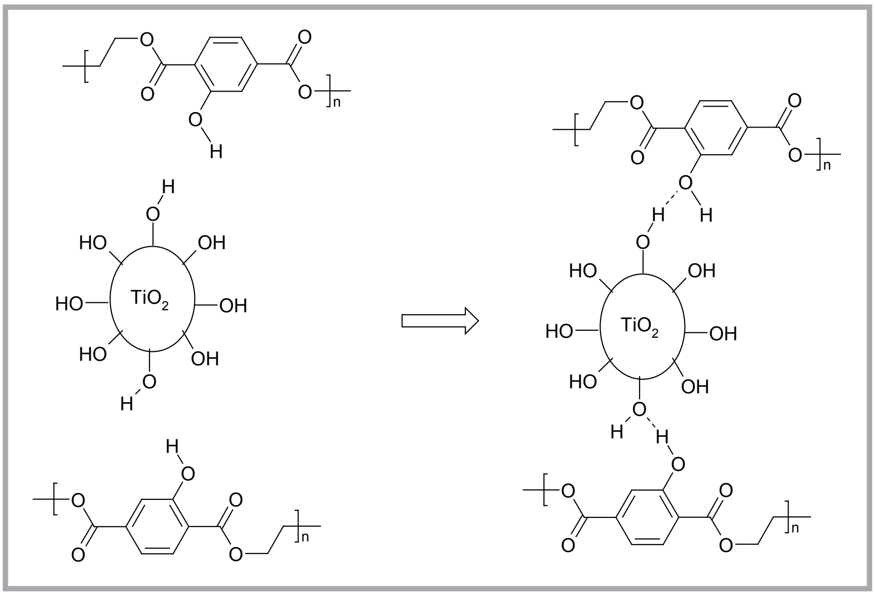


Figure 10. *Complexing ability of PET surface towards TiO_2 proposed.*

Activation with low-temperature plasma treatment increases the amount of hydroxyl and/or carboxyl groups on the surface of polyester fibres, resulting in the improvement of adhesive properties and, hence, in the adsorption of a greater amount of TiO_2 particles to the fabric surface.

An interesting aspect of changes in the chemical structure of PET nonwovens after preliminary treatment with low-temperature plasma is the increase in the complexing ability towards TiO_2. This complexing ability, and therefore affinity towards metal oxides of the nonwoven surface, which is a hypothetical assumption of the authors, can be explained by an enlarging of the level of surface hydroxyl groups (***Figure 10***).

Conclusions

The studies revealed some changes in the structure of polyester (poly (ethylene terephthalate)) nonwoven fabrics after plasma treatment which allow their further modification. The research performed proved that plasma pre-treatment of polyester fabrics and incorporation of TiO_2 particles (anatase structure) in their structure result in very good absorbing properties of UV radiation (whole spectrum) shown by these modified textiles.
Plasma pre-treatment efficiently modifies (textile surface) by way of radical reactions, including oxidation, and prepares the surface to incorporate particles of oxide hybrids into the textile structure (e.g. TiO_2). The better bond between polyester nonwoven and TiO_2 particles results from enhanced adhesive properties of the polyester nonwoven surface after preliminary plasma treatment. The authors suggest potential changes in the chemical structure of polyester fabric caused by the following: a homolytic splitting of ester bonds, a release of volatile degradation products (mainly CO and $C0_2$), a cross-linking, reactions of macro radicals [alkyl (•CH_2-CH_2~) and phenyl (•C_6H_4~)] with oxygen, and a subsequent formation of hydroxy-aromatic rings, with reactions increasing the level of hydroxyl and carboxyl groups on the surface. Changes in the chemical structure of polyester fabric after plasma pre-treatment can efficiently increase the complexing ability towards oxide hybrids of polyester fibres.

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