

Studies Regarding the Increase in Hydrophilicity of Some Textile Fabrics through Treatment by Cold Plasma and Grafting with Vinyl Monomers

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Abstract

The polyamide and polyester fabrics have been treated by glow discharge plasma and grafted with 2-hydroxyethylmethacrylate (HEMA) in order to increase the hydrophilicity and to improve the soil release properties. The plasma treatments were carried out at different exposure times. Grafting was obtained with gaseous HEMA and with alcohol or aqueous solution of HEMA at different concentrations. The physical and chemical surface changes were studied using scanning electron microscopy, infrared spectroscopy, colour measurements. The hydrophilicity was assessed through the absorption time of a water drop and the soil removal through washing by remission values.

Introduction

The studies regarding the plasma utilization represent a constantly current domain, taking into account the impact that the plasma has both in research domain and in practical applications.

One of the usual plasma applications developed up to an industrial level is the surface treatment of polymeric materials (particles, granules, films, fibers, fabrics *etc.*) in order to improve the preexisting properties or to create new properties. The consequence of such a treatment is the changing in the surface morphology, as well as the introduction of new functional groups [1-2].

The essential changes caused by the plasma treatment are the basis for a series of chemical reactions initiated by the action of different reactive species existing in plasma (free radicals, ions, electrons, radi-

cal-ions, *etc.*), at the contact with polymeric material. The mechanism of these reactions is mainly a radical one: the primary macro radicals formed through the action of active species in plasma can subsequently serve as centres for graft copolymerization of some monomers introduced in the working environment. The macroradicals can be stabilized through typical reactions or they can react with oxygen, finally forming new oxidized functional groups [3-4].

The judicious selection of the operating conditions (the nature of gaseous atmosphere), the monomers or other reactive compounds introduced in the system, the parameters of plasma treatment process (time, pressure in the reactor, the introduction flow of the reactive compounds, *etc.*) can "a priori" make possible directing the process either in the way of changing the surface morphology of the polymeric fabric (the growth of crystallinity, the rugosity) the consequence being the change of some physical characteristics, or in the way of initiating some chemical reactions with effects regarding not only the change

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of some physical properties, but also the change of surface chemical reactivity.

The modification in surface morphology of some polymeric fabrics resulting from plasma treatments can be explained through the local degradation of the superficial layer of the polymer [5].

A characteristic of plasma utilization in the treatment of the surface of polymers is that the thickness of the affected layer is very low, the changes caused by the active particles from plasma in deeper layers being insignificant [6].

Besides oxygen, the variety of gases used as a plasma medium and as sources of active species is wide, including: air, nitrogen, hydrogen and inert gases [7-9].

The following characteristics can be modified by plasma treatments under different conditions: hydrophilicity, dye ability, stain resistance and conductivity [10-15].

The aim of this work is to study the way in which the treatment in cold air plasma, followed by grafting with 2-hydroxyethylmethacrylate can improve the wettability, dyeability and soil repellency of polyamide and polyester fabrics.

Experimental Part

Materials

Polyamide (nylon 6)-PA, 68 g/m² and polyester (polyethyleneterephthalate)-PET fabric, 132 g/m² were used in these experiments. The sample surface was 20×30 cm².

The fabrics were washed with a 1% nonionic detergent solution (Felosan NOF^(R) - CHT) at 70°C, for 15 minutes and then they were rinsed with distilled water; after that, the samples were dried at room temperature for 24 hours.

The monomer used for grafting was 2-hydroxyethylmethacrylate, which was distilled before use (Merck).

Treatments

The polyamide and polyester samples were treated in plasma with different durations in order to choose the optimum version of activation; then the samples have been grafted with HEMA adopting the following procedures:

- 10 minutes activation in plasma, 10 minutes graft polymerization in plasma with gaseous HEMA;

- 10 minutes activation in plasma, 2 minutes air exposure, treatment with 50 ml solution of HEMA in ethanol, 10 minutes grafting on plasma;

- 10 minutes activation in plasma, 2 minutes air exposure, 5 hours treatment with 100 ml of constantly stirred aqueous HEMA solution at 50°C.

After that, the samples were washed with distilled water in order to remove the homopolymer formed on the surface of the fiber.

Table 1 presents the amounts of HEMA (the gaseous volume, the volume of solution respectively), used according to the approach adopted.

Table 1

Plasma treatment variants and graft polymerization with HEMA for polyamide and polyester samples

Gaseous HEMA		Alcohol solution of HEMA		Aqueous solution of HEMA*	
Version	Volume (cm ³)	Version	Concentration solution (g/l)	Version	Concentration solution (g/l)
V _{1a}	0.5	V _{1b}	50	V _{1c}	10
V _{2a}	1	V _{2b}	100	V _{2c}	20
V _{3a}	1.5	V _{3b}	150	V _{3c}	30
V _{4a}	2	V _{4b}	200	V _{4c}	40

*The treatment in aqueous solution of HEMA was carried out on samples with a surface of 10×10 cm².

The polyamide and polyester fabrics have been treated in plasma set up (Fig. 1), having the following characteristics: air plasma, 2-3 torrs pressure, electrode tension of 2-3 kV, electric field force of 200-300 V/cm, frequency of 1.3 MHz.

Analysis methods

Scanning electron microscopy

The surface morphology of untreated samples and of those treated in plasma and grafted with HEMA has been studied by means of electron microscopy, carried out on a scanning electron microscope (MES-Tesla BS 301). The polyamide and polyester samples were fixed on aluminum supports with an electro-conducting paste and metalized with gold using cathode evaporation.

FTIR analysis

The chemical changes that have appeared on the surface of polyamide and polyester fibers as a result

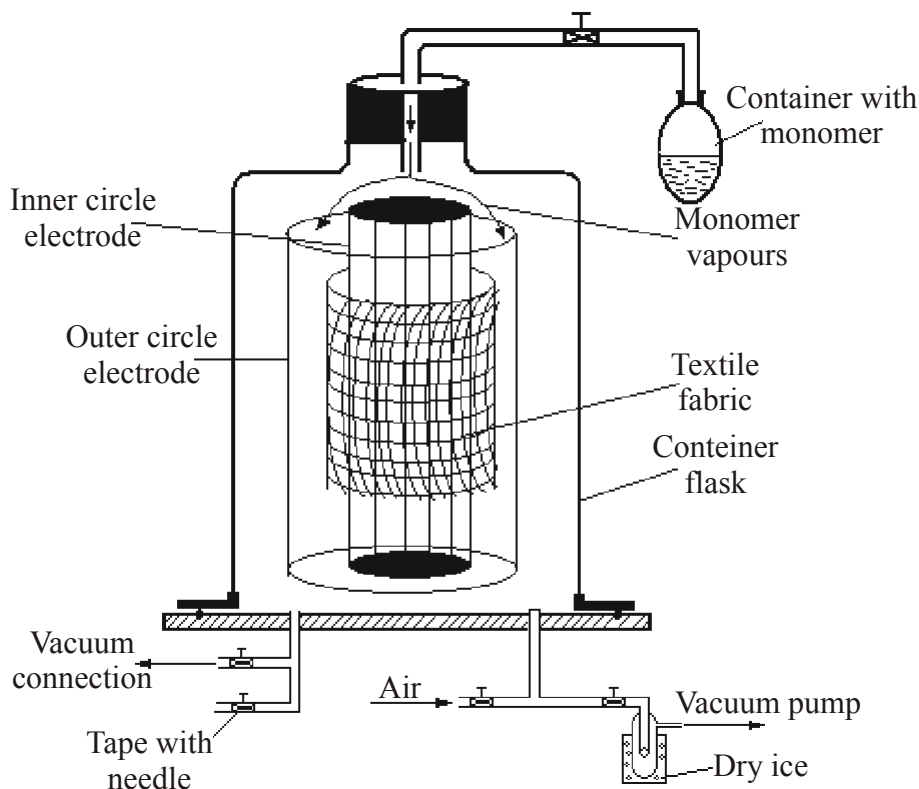


Fig. 1. The scheme of the plasma treatment set up.

of HEMA grafting and activation by plasma treatment were registered using FTIR-ATR spectroscopy. The FTIR spectra were recorded on a spectrophotometer type FTS 2000 Digilab, covering the range 4000-750 cm^{-1} at 4 cm^{-1} resolution, using a special program from MERLIN Digilab family.

The physical-mechanical properties

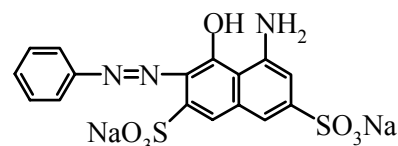
In order to study the influence of the plasma treatment period on the integrity of basic studied fabrics, the breaking strength in warp and weft directions has been determined. The tests were performed on a Met-rimpex-Hungary dynamometer (according SR ISO 5081-1999).

Colour measurements

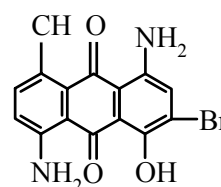
The presence of polar groups introduced on the surface of fibers by plasma activation and graft polymerization with HEMA was emphasized by colour measurements, too.

In this case, the samples have been dyed at a 50:1 liquor ratio, on a Mathis equipment type "Polycolor P 4702[®]". The dyeing of polyamide was performed with a 1% C.I. Acid Red 33 dye (structure 1) at 100°C, pH = 6-7, for 30 minutes; the polyester samples was

dyed with a 1% C.I. Disperse Blue 56 dye (structure 2), at pH = 6 for 30 minutes at 130°C.



Structure 1



Structure 2

After dyeing, the samples were rinsed with warm and cold water and then dried at room temperature.

The reflectance values (R) were obtained using a DATACOLOR Instrument (Model Spectraflash 300[®]), covering the range 400-700 nm. The colour strength (K/S) was established using the Kubelka-Munk equation, where K and S stand for the absorption and scattering coefficients, respectively [16]:

$$\frac{K}{S} = \frac{(1-R)^2}{2R}$$

Hydrophilicity and hygroscopicity

The effect of plasma treatment and graft polymerization with HEMA was estimated by measuring hydrophilicity and hygroscopicity.

Hydrophilicity was evaluated by measuring the absorption time of a drop of distilled water, placed on the fabric surface according to the standard AATC-39-1980. Hygroscopicity (H) is the textile materials capacity of retaining water vapours and it is calculated using the relation [17]:

$$H = \frac{M_u - M_c}{M_c} \cdot 100\%$$

where: M_c is the average mass of five samples with $5 \times 5 \text{ cm}^2$ surface, maintained under 65% humidity and 20°C temperature conditions, for 24 hours and M_u is the average mass of the same five samples maintained under 100% humidity and 20°C temperature conditions for 24 hours.

The hygroscopicity index (i_H) is calculated with the relation:

$$i_H = \frac{M_u - M_c}{S \cdot t} \text{ (g/m}^2\cdot\text{h)}$$

where: S is the sample surface (m^2) and t is the period of 24 hours exposure under 100% humidity conditions.

"Soil release" properties

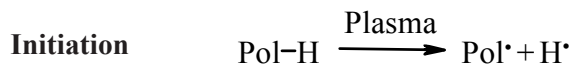
In order to illustrate the influence of HEMA grafting treatment on the capacity of removing soil by washing, the polyamide and polyester fabrics were soiled with used motor oil containing iron oxide and then they were washed out for 30 minutes in a solution

on that contained 2% Felosan NOG[®] and 2% Na_2CO_3 at 60°C .

The capacity of removing soil through washing was evaluated by measuring the reflectance of the washed and unwashed fabrics ($R\%$) on a DATACOLOR Instrument (Spectraflash SF 300[®]).

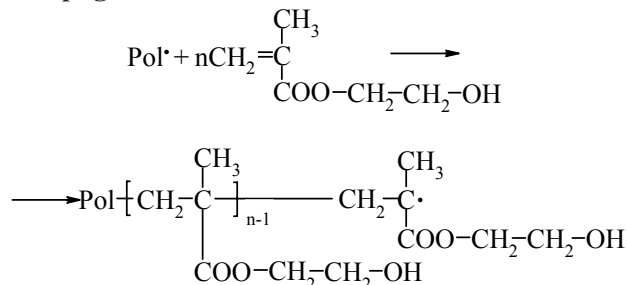
Results and Discussion

The exposure of the textile fabric to plasma has as a consequence the production of some chemical reactions on its surface, via radical mechanism. The active particles in plasma cause the homolytic splitting of C–C bonds and especially of C–H and the appearance of a primary macroradical in polymer.



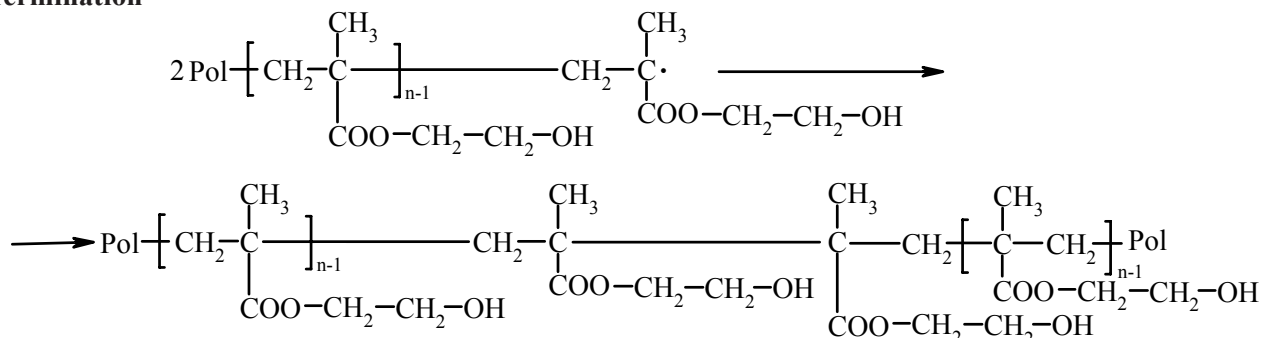
In the presence of the acrylic monomer, a chain of reactions presented in the scheme below is initiated, having as consequence the obtaining of a grafted structure, with new properties unlike the initial polymer.

Propagation



Grafting can be obtained not only when the monomer exists in the gaseous atmosphere in reactor, but also by a previous treatment of the textile fabric in plasma, followed by its rapid immersion in the aque-

Termination

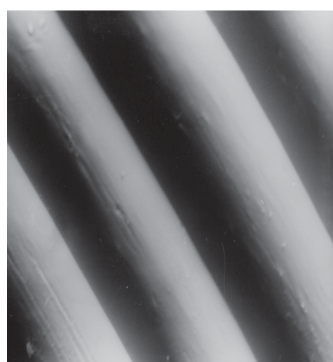


ous or alcohol solution of the monomer. The obtained grafting yield can not be indicated exactly, it is somewhere around 2%.

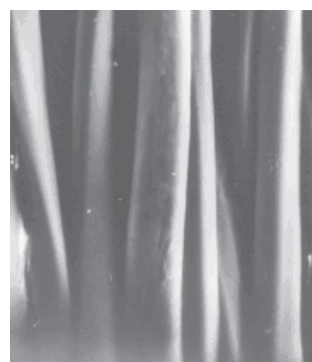
The results of scanning electron microscopy and FTIR-ATR analysis for the polyamide and the polyester samples untreated and treated onto plasma and grafted with HEMA are presented in Figs. 2 and 3.

The SEM photos obtained for the polyamide and the polyester show the surface changes that have appeared.

By analyzing the given results, one can notice that the untreated samples display a smooth uniform surface; for the samples treated on plasma, the surface is slightly etched, with tiny rifts. The surface of the samples treated on plasma and grafted is covered by



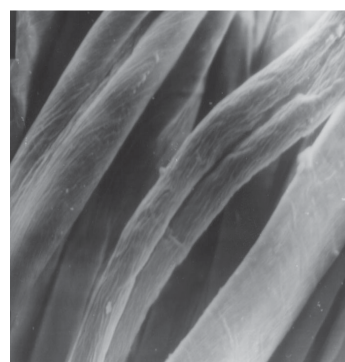
PA untreated (magnification $\times 3000$)



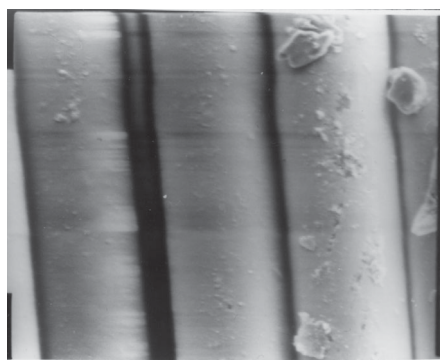
PET untreated (magnification $\times 1500$)



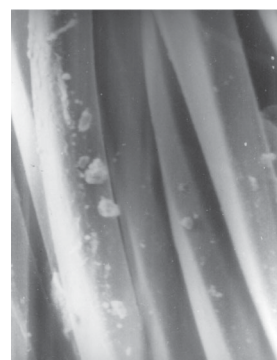
PA treated on air plasma (magnification $\times 2500$)



PET treated on air plasma (magnification $\times 2000$)



PA treated and grafted with gaseous HEMA on plasma (magnification $\times 3000$)



PET treated and grafted with gaseous HEMA on plasma (magnification $\times 2000$)

a

b

Fig. 2. a – SEM photos for the untreated, treated on air plasma and HEMA grafted polyamide fabrics; b – SEM photos for the untreated, treated on air plasma and HEMA grafted polyester fabrics.

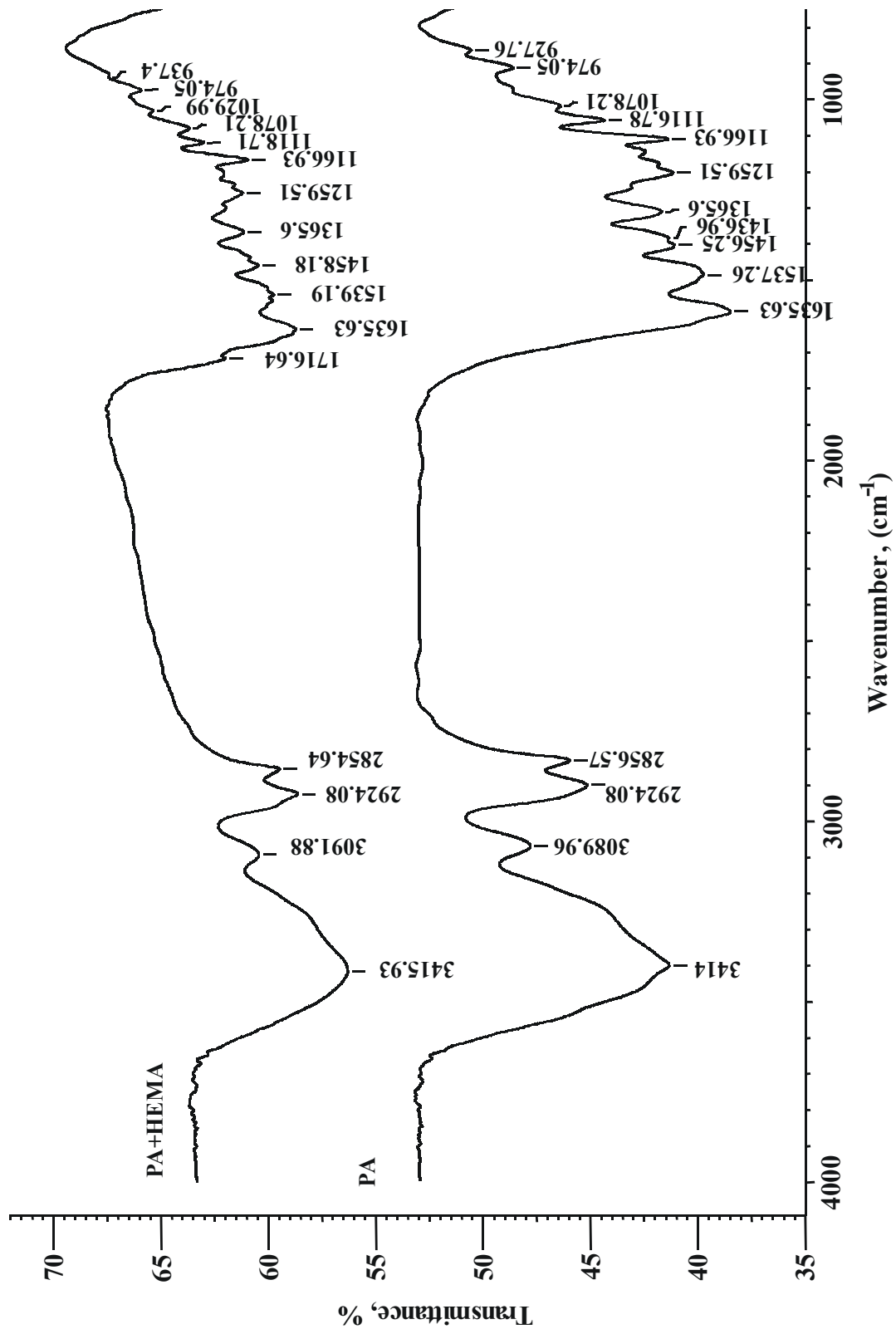


Fig. 3. FTIR spectra of the untreated and grafted in plasma with gaseous HEMA polyamide and polyester fabrics.

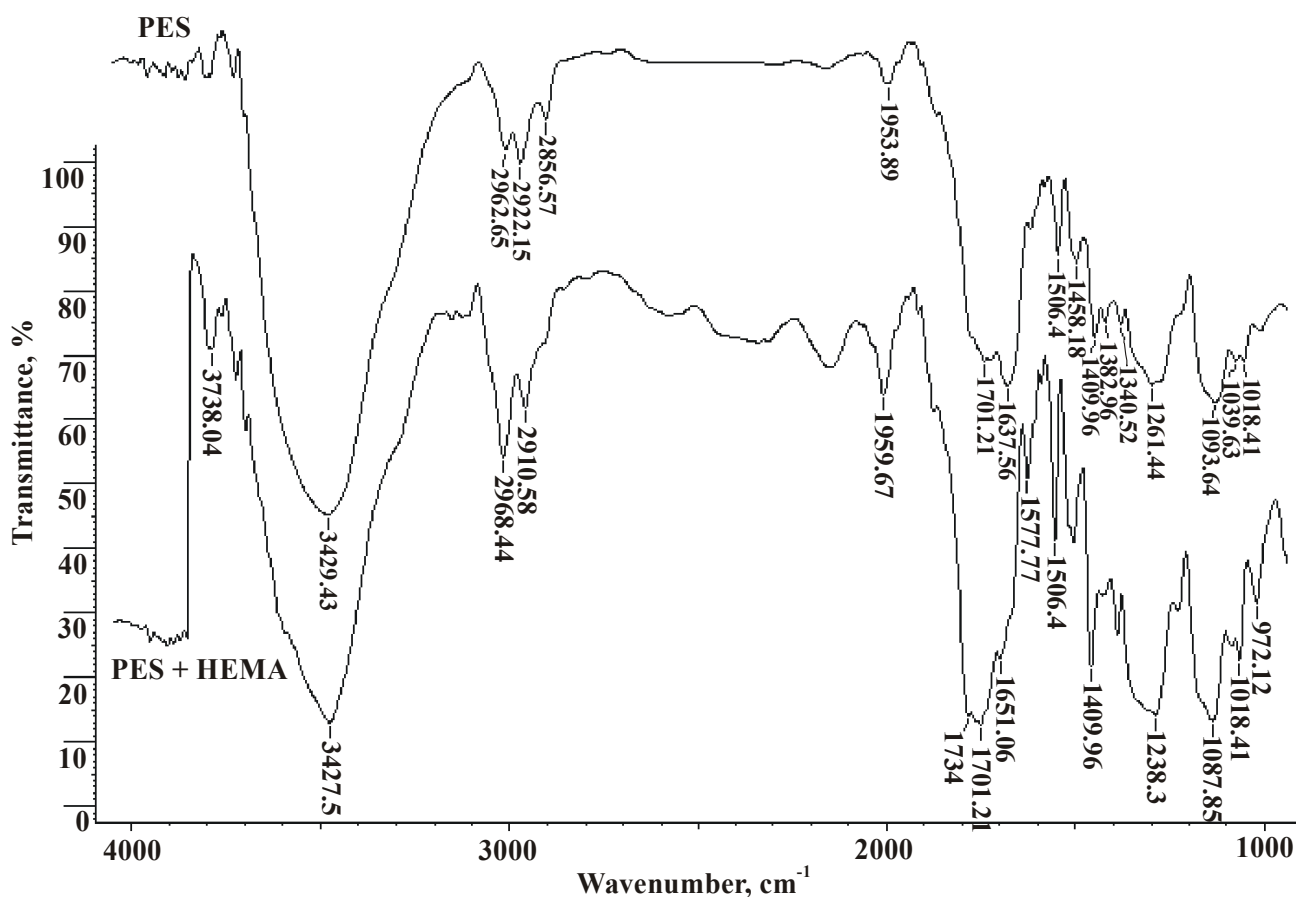


Fig. 3. Continued

some protuberances which are caused only by the grafted polymer.

The FTIR spectra for the grafted samples shows the grafting of the acrylic monomer, confirmed by the appearance of the ester band of HEMA in the case of polyamide and the enlargement of the band in the case of polyester fabrics is $\nu = 1705\text{-}1743\text{ cm}^{-1}$.

The values of the breaking strength for the samples treated in plasma are presented in the Table 2.

Table 2

The influence of plasma treatment duration on the breaking strength of the polyamide and polyester samples

Experimental	Treatment time (min)	Breaking strength (N)			
		Polyester		Polyamide	
		Warp	Weft	Warp	Weft
1	0	1600	1050	1100	930
2	5	1560	1030	1080	900
3	10	1530	1000	1040	880
4	15	1240	850	890	740

By analyzing the given results we have opted for a 10 minutes plasma activation, the degradation of the polyamide and the polyester samples during this time being insignificant. The values of the K/S index for the polyamide and polyester samples treated in plasma and grafted with HEMA and then dyed with the C.I. Acid Red 33 and C.I. Disperse Blue 56 dyes, respectively, are presented in the Table 3.

Table 3

The values of the K/S index for the polyamide samples dyed with the C.I. Acid Red 33 dye and for the polyester samples dyed with the C.I. Disperse Blue 56

No.	The treatment version	K/S (540 nm)	
		PA	PET
1	Untreated sample	0.85	10.26
2	5 minutes plasma treatment	0.99	10.45
3	10 minutes plasma treatment	1.06	10.62
4	15 minutes plasma treatment	1.12	10.74
5	V ₃ a	1.61	11.02
6	V ₃ b	1.33	11.28
7	V ₃ c	1.68	11.27

The higher values for K/S index in the case of polyamide and polyester samples treated in plasma can be explained through the morphological changes or the presence of functional groups that have appeared at the surface of the fiber, groups which favour the dye sorption.

Because of the introduction of the hydroxyl groups

through grafting with HEMA, the hydrogen bonds are probably formed between these and dye, thus obtaining a better dyeing intensity.

The hydrophilic properties of the polyamide and polyester samples obtained as a result of having them treated in plasma and grafted with HEMA are presented in the Tables 4-5.

Table 4

The influence of plasma treatment duration on the hydrophilicity and hygroscopicity of the polyamide and polyester fabrics

No	The treatment of plasma (min)	Time of adsorption of water drop (s)		Hygroscopicity			
				H_s (%)		i_{H_s} (g/m ² ·h)	
		PET	PA	PET	PA	PET	PA
1	0	146	1028	0.36	4.02	0.0081	0.0630
2	5	104	894	0.54	4.40	0.0128	0.0648
3	10	84	816	0.58	4.51	0.0144	0.0739
4	15	82	808	0.59	4.56	0.0146	0.0743

Table 5

The influence of the treatments on air plasma and grafting with HEMA on hydrophilicity and hygroscopicity of PET and PA fabrics

No	Version	Time of adsorption of water drop (s)		Hygroscopicity			
				H_s (%)		i_{H_s} (g/m ² ·h)	
		PET	PA	PET	PA	PET	PA
Treatment of PET and PA fabrics on plasma with gaseous HEMA							
1	V _{1a}	77	782	0.64	4.73	0.0148	0.1103
2	V _{2a}	56	630	0.78	5.76	0.0225	0.1245
3	V _{3a}	40	507	0.89	6.74	0.0402	0.1422
4	V _{4a}	39	504	0.91	6.77	0.0404	0.1427
Treatment of PET and PA fabrics on plasma with solution of HEMA in ethanol							
5	V _{1b}	80	796	0.61	4.52	0.0135	0.0805
6	V _{2b}	58	738	0.73	5.38	0.0160	0.0940
7	V _{3b}	45	580	0.86	6.39	0.0211	0.1151
8	V _{4b}	43	579	0.88	6.43	0.0217	0.1154
Treatment of PET and PA fabrics on plasma with aqueous HEMA solution							
9	V _{1c}	15	215	0.73	5.32	0.0328	0.1380
10	V _{2c}	13	205	0.84	6.33	0.0372	0.1678
11	V _{3c}	12	191	0.98	7.47	0.0430	0.1997
12	V _{4c}	12	190	1.01	7.50	0.0436	0.2000

By analyzing the given results, one can notice that in case of both fibers and all three procedures of treatment, the wetting time decreases whereas the HEMA concentration increases. This can be explained through the growing number of hydroxyl groups from HEMA grafted both on the surface of polyamide and polyester fibers. The water molecules will be fixed by the polar groups from the polymer surface through hydrogen bonds, especially if the number of the latter is larger.

We can explain in the same manner the variation in hygroscopicity expressed by the percentage amount of humidity (H) and by the hygroscopicity index (i_H) respectively; both the characteristics of the fabric increase with the discussed parameter.

The soil release properties conferred to the polyamide and polyester fabrics grafted with HEMA are emphasised by higher remission values for the treated samples unlike the untreated ones (Table 6).

Table 6

The influence of the treatment with HEMA on the soil removal by washing

Version of treatment with HEMA	R, %	
	PET	PA
V ₃ a	72.75	75.93
V ₃ b	64.04	69.98
V ₃ c	73.92	77.62
Untreated	40.44	56.43

This can be explained on the one hand by the presence of hydrophilic groups from HEMA, that restrict the sorption of hydrophobic oil, and on the other hand by the fact that water fastened to the hydrophilic group of the grafted polymer facilitates the removal of hydrophobic soil during the mechanical action that take place during the washing process.

Conclusions

The plasma treatment and grafting with HEMA changes the surfaces characteristics of polyamide and polyester fabrics. The hydrophilicity and the hygroscopicity of the treated fabrics become improved unlike the untreated ones. From the three options

which have been used, the best results were obtained for the treatment with HEMA aqueous solutions and gaseous HEMA, respectively. As for the soil release properties, the best results were obtained for the polyester fabric.

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