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# Modifying of Polyester Fabric Surface with Polyelectrolyte Nanolayers Using the Layer-by-layer Deposition Technique

## Abstract

*Polyelectrolytes such as poly(4-vinylpyridine) and poly(acrylic acid) with opposite charges have been deposited on a polyester fabric by the layer-by-layer technique. The first acidic layer with carboxylic groups were produced by grafting acrylic acid onto the polyester fabric according to the previously established grafting conditions. Selected fibre properties connected with the character of the deposited nanolayer of polyelectrolyte were tested. It has been found that the content of methylene blue dye in fibre and water retention depend on the character of the deposited nanolayer, as they are always considerably higher when the top nanolayer consists of poly(acrylic acid). Electron microscope photographs show that the fibre surface in the fabric becomes smoother after polyanion and polycation nanolayers are deposited.*

**Key words:** polyelectrolyte layers, polyester fabric, grafting, multilayer.

## Introduction

In recent years, intensive studies have been carried out on the preparation of repeated nanolayer systems by the so-called layer-by-layer method, as well as for practical applications [1 - 3]. The technique of depositing successive, very thin layers makes it possible to produce materials with complex properties. In typical processes, two water-soluble polyelectrolytes possessing groups with opposite charges are alternately deposited on flat surfaces such as glass plates, films or spherical surfaces by electrostatic attraction. High-quality multi-layer films with controlled thickness can be obtained by repeating successive cycles of adsorption. This method has been successfully used to produce multilayer films of water-soluble polyelectrolytes with various polymeric architecture and functional groups, using suitable commercial polyelectrolytes [4, 5]. So far, the literature has reported only a few studies on the preparation of multilayers on textile fabrics [6, 7]. In this case, it is important to produce the first layer containing active groups that could react electrostatically with a polyelectrolyte. Such a first layer can be produced, for example, by grafting monomers such as metacrylic acid or vinylpyridine on the surface of a fibre, woven or non-woven fabric. Vinyl monomer grafting is a well-known method of textile surface modification. The literature contains extensive studies concerning the grafting of vinyl monomers onto polyamide or poly(ethylene terephthalate) PET fibres [8 - 14]. However, there are serious difficulties in grafting monomers onto PET. The chemical nature of PET does not allow the formation of its macrochains of an appreciable quantity of radicals

which can initiate grafting, and the high extent of crystallisation and ordering of amorphous regions retard monomer diffusion inside the material. These radical sites that are necessary for the initiation of grafting can be generated by radiation [12] or chemical methods [14]. The main purposes of grafting various vinyl monomers onto PET fibres are to improve their inferior properties and to furnish them with new properties.

The aim of the present study was to deposit repeated nanolayers onto polyester fabric by the successive deposition of poly(acrylic acid) and poly(4-vinylpyridine) through their electrostatic attraction. The first acidic layer with carboxylic groups was produced by grafting acrylic acid onto polyester fabric under the previously established conditions. Some selected fabric properties connected with the character of the deposited polyelectrolyte nanolayer were also tested.

## Experimental

### Materials

Polyester fabric (from Uniontex) with a surface weight of about 75 g/m<sup>2</sup> was dipped into dichloroethane for 2 h at 90 °C. After treatment, solvent on the fabric was removed by blotting between filter papers, and put into the polymerisation medium.

Acrylic acid (AA) was dried over CaCl<sub>2</sub>, and distilled in a vacuum at 45 °C. Benzoyl peroxide (Bz<sub>2</sub>O<sub>2</sub>) was twice precipitated from a chloroform solution in methanol and dried in a vacuum for 48 h.

Poly(acrylic acid) (PAA) was prepared by polymerising acrylic acid in an isopropanol,

as described in paper [15]. Its molecular weight was  $M_w = 258,000$  g/mol. Poly(4-vinylpyridine) (P4-VP) was obtained from Aldrich with  $M_n = 170,000$  g/mol.

### Grafting procedure

The graft polymerisation was carried out in thermostatted tubes equipped with a reflux condenser and a nitrogen gas inlet. The mixture containing the polyester fabric (10×10 cm, about 0.75 g), monomer and Bz<sub>2</sub>O<sub>2</sub> at the required concentration in 2 cm<sup>3</sup> acetone was made up to 50 cm<sup>3</sup> with deionised water. The mixture was immediately placed into the water bath adjusted to the polymerisation temperature. After the grafting procedure, the polyester fabrics obtained were purified by extracting the unreacted monomers and homopolymers with boiling ethanol.

### Nanolayer fabrication

A typical procedure for depositing very tiny layers (nanolayers) consists in immersing polyester fabric, previously grafted with PAA, in an ethanol solution of PVP with a concentration of 10<sup>-2</sup> base mol/dm<sup>3</sup> at a temperature of 20 °C for 2 h, rinsing with ethanol for 10 min. and after filtering off the water, immersing it in an aqueous solution of poly(acrylic acid) with a concentration of 10<sup>-2</sup> base mol/dm<sup>3</sup> for 2 h, rinsing with water for 10 min and then repeating the whole procedure. About 5 layers of polyelectrolytes were deposited in this way.

In order to check that the layer were deposited correctly, the samples with subsequent deposited layers were dyed with methylene blue. Samples of polyester fabric with different numbers of layers were immersed into 10<sup>-3</sup> mol/dm<sup>3</sup> methylene blue solution for 10 min. After

immersion in the dye solution, the polyester fabric with nanolayer films were soaked in water for 5 min and then dried with a mild flow of air.

### Measurements

The number of carboxylic groups in all samples was determined as follows: 0.2 g of the grafted of polyester fabric was weighed accurately into a 100 cm<sup>3</sup> flask, 25 cm<sup>3</sup> of 0.01 M NaOH solution was added, and the flask was stoppered. Contents were allowed to stand for 24 h with occasional shaking. Then, during intensive stirring, the un-neutralised base was back-titrated with 0.01 M HCl. The carboxylic group content was then calculated from the titre values.

For the dyed fabric samples, the light diffuse reflectance measurements within the range from 400 to 700 nm were performed with a Spectra-flash 300 apparatus manufactured by Datacolor International, and the colour yield values were calculated according to the Kubelka-Munka function (K/S) by equation [16]:

$$(K/S) = (1-R)^2 / (2R) \quad (1)$$

where:  $R$  – reemission,  $K$  – absorbance,  $S$  – scattering.

**Table 1.** Effect of time and temperature;  $[AA] = 0.7 \text{ mol/dm}^3$ ;  $[Bz_2O_2] = 3.5 \times 10^{-3} \text{ mol/dm}^3$ .

Time (min)	Carboxylic groups content, mmole/100g			
	45 °C	55 °C	65 °C	70 °C
60	4.01	4.73	4.12	3.87
90	-	5.30	4.94	-
120	5.16	6.03	-	4.56
180	5.19	6.10	5.23	4.53

**Table 2.** Effect of initiator concentration;  $[AA] = 0.6 \text{ mol/dm}^3$ ,  $T = 55 \text{ °C}$ , and  $t = 180 \text{ min}$ .

$[Bz_2O_2] \times 10^{-3} \text{ mol/dm}^3$	Carboxylic groups content, mmole/100g
1.0	2.15
2.0	4.43
3.0	6.10
4.0	5.91
6.0	5.07

**Table 3.** Effect of monomer concentration;  $[Bz_2O_2] = 3.0 \times 10^{-3} \text{ mol/dm}^3$ ,  $T = 55 \text{ °C}$ , and  $t = 180 \text{ min}$ .

$[AA] \text{ mol/dm}^3$	Carboxylic groups content, mmole/100g
0.2	3.44
0.3	5.12
0.6	6.10
0.9	5.99
1.0	5.85

Surface images of the polyester fabric were taken with a Quanta 200 scanning electron microscope made by FEI Corporation (USA).

The water retention value (WRV) was determined by relating the mass of water stored by polyester fabric centrifuging the samples over 10 minutes at an acceleration of about 10,000 ms<sup>-2</sup>, to the dry sample mass. Prior to centrifuging, the fabrics were kept for 48 hours in water.

## Results and discussion

The effect of some grafting parameters such as grafting time, temperature, initiator concentration and monomer concentration on the content of carboxylic groups combined with the fibres of polyester fabric was assessed in order to find the optimal reaction conditions.

### Effect of time and temperature

The results of assessing the effect of grafting time and temperature on the content of carboxylic groups on polyester fabric after grafting with AA are given in Table 1.

The graft copolymerisation was carried out at four different temperatures ranging from 45 to 70 °C for various durations. From the experimental data given in Table 1, it clearly follows that the content of carboxylic groups increases with temperature up to 55 °C, while any further increase in temperature decreases the grafting degree of polyester fabric samples. The higher grafting efficiency at raised temperatures may be connected with the higher decomposition rate of Bz<sub>2</sub>O<sub>2</sub> and a possible reaction between the macro-radical of AA and the radical of PET. On the other hand, the decrease in carboxylic groups content at temperatures above 55 °C may be associated with facilitating the reaction termination resulting in the formation of the PAA homopolymer. Similar results have been obtained for the graft copolymerisation of acrylamide on PET fibres with the use of Bz<sub>2</sub>O<sub>2</sub> as initiator [17]. Moreover, the data given in Table 1 shows that after 120 min of graft copolymerisation, the number of added carboxylic groups remains at almost a constant level.

### Effect of initiator concentration

Table 2 shows the results of assessing the effect of Bz<sub>2</sub>O<sub>2</sub> concentration on the content of carboxylic groups connected with PET fabric. From this data, it follows that this content increases with the initiator concentration up to about 3.0×10<sup>-3</sup> mol/dm<sup>3</sup>,

while it decreases with the further increase in the initiator concentration. The initial increase is probably connected with the formation of a higher number of free radicals on the PET fabric, allowing more monomer molecules to be combined with the fabric. The increase in the carboxylic group content with the increasing Bz<sub>2</sub>O<sub>2</sub> concentration to some extent allows us to conclude that the primary free radicals may first participate in the direct hydrogen atom abstraction from the carbon chain of PET, in order to form radicals which are capable of initiating the grafting process.

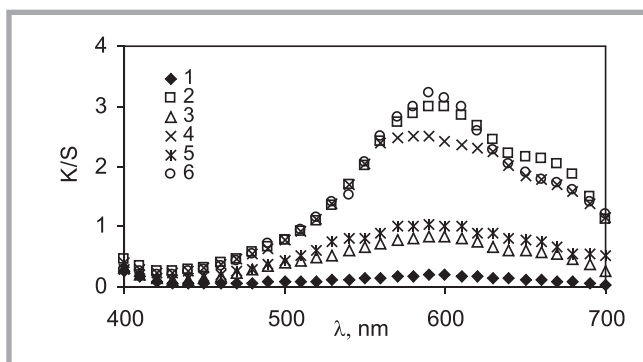
### Effect of monomer concentration

Table 3 contains the results of assessing the effect of AA concentration on the content of carboxylic groups combined with the PET fabric. The quantity of grafted PAA increases gradually with the increasing monomer concentration up to about 0.6 mol/dm<sup>3</sup>, and then it remains at an approximately constant level. With the increase in AA concentration, the diffusion of monomer molecules into PET fibres is also increased, resulting in a higher quantity of grafted polyacid. The degree of PAA grafting on PET remaining at an approximately constant level at higher AA concentrations may be connected with the formation of homopolymers in the reaction medium, which causes the medium viscosity to increase and makes diffusion of the monomer into the PET structure difficult.

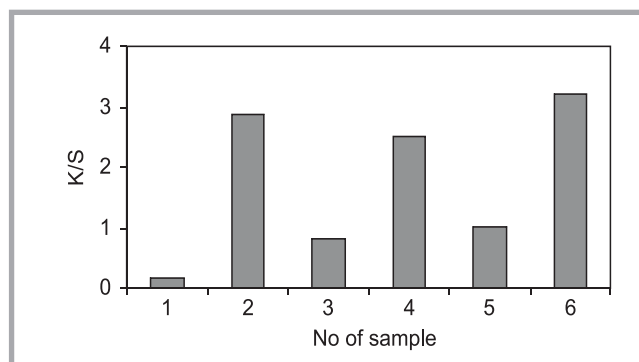
The maximum quantity of PAA covalently combined with PET fabric was obtained by performing the copolymerisation under the following optimal conditions:  $[Bz_2O_2] = 3.0 \times 10^{-3} \text{ mol/dm}^3$ ,  $[AA] = 0.6 \text{ mol/dm}^3$ ,  $T = 55 \text{ °C}$ ; and  $t = 180 \text{ min}$ .

In order to identify the deposited nanolayers and the character of the surface, PET fabric samples with various numbers of nanolayers were immersed in a solution of methylene blue for 10 min, washed with excess distilled water for 5 min and then dried in air. The acidic nanolayers were intensively dyed, while those of P4-VP showed a clearly decreased intensity of colour. This was confirmed by measuring the value of K/S of the dyed samples, which is a quantitative measure of the content of dye combined in the sample.

Figure 1 shows the dependence of K/S versus wavelength. From the course of the curves, it follows that the maximum absorption appears at 590 nm. The change in K/S depending on the type and



**Figure 1.** Dependence of  $K/S$  versus  $\lambda$  for: 1 – initial PET fabric; 2 – PET fabric grafted with PAA; 3 – PET fabric with P4-VP nanolayer; 4 – with PAA nanolayer; 5 – with P4-VP nanolayer; 6 – with PAA nanolayer.



**Figure 2.**  $K/S$  values at  $\lambda_{max}$  for: 1 – initial PET fabric; 2 – PET fabric grafted with PAA; 3 – PET fabric with P4-VP nanolayer; 4 – with PAA nanolayer; 5 – with P4-VP nanolayer; 6 – with PAA nanolayer.

the number of deposited nanolayers is illustrated in Figure 2. When depositing successive layers of an acidic character, the  $K/S$  value clearly increases, illustrating the combination of a higher quantity of methylene blue dye with base properties. In the case of the top nanolayers of base character, a clear decrease in the  $K/S$  value can be observed.

From literature [4], it follows that the thickness of a layer deposited by the technique under discussion is about 5 nm.

Representative scanning electron micrographs of unmodified PET fabric grafted with PAA and of those after deposition successive layers of polyanion and polycation (sample 6) are shown in Figure 3. As can be seen, the surfaces of elementary fibres of unmodified PET fabric (Figure 3.a) and PET fabric grafted with PAA (Figure 3.b) are rough in both cases, while the samples with 5 deposited nanolayers shows a smoother surface (Figure 3.c), which additionally confirms the deposition of successive nanolayers.

The results of testing the water retention of samples with deposited layers are

given in Table 4. These data show that when the top nanolayer deposited on the fibres of PET fabric is of acidic character, its water retention is clearly higher.

The study concerning the deposit of colloidal particles and formation of catalytic systems on the fabric surface will be continued.

### Conclusion

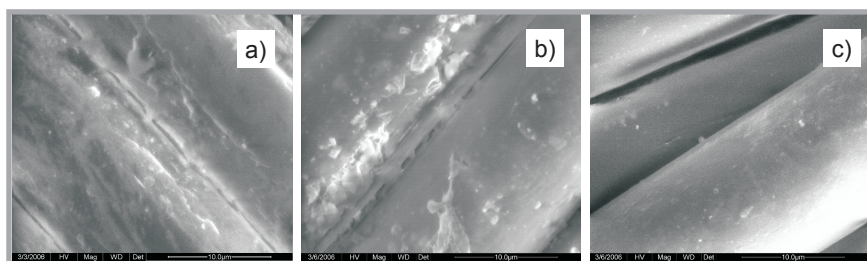
The method we have developed can be successfully used for depositing very thin polyelectrolyte nanolayers on PET fabric to change its properties connected with the fibre surface. The content of methylene blue dye in the fibres of PET fabric and the value of water retention clearly depend on the character of the deposited nanolayer, which is always higher when the top nanolayer consists of PPA. It has also been established that the surface of fibres in the fabric becomes smoother after depositing PAA and P4-VP nanolayers.

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**Figure 3.** SEM photographs of the surfaces of: a – initial PET fabric, b – PET fabric grafted with PAA, c – PET fabric with 5 deposited nanolayers, magnification 10,000 $\times$ .

**Table 4.** WRV values depending on the layer character; No of sample (see Figure 1).

No of sample	1	2	3	4	5	6
WRV, %	20.20	25.00	20.59	24.12	20.26	22.56

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