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Deposition of Polymer Complex Nano-Layers onto Polyester Fabrics Activated with Corona Discharges

Abstract

A polyester fabric was treated by corona discharges. Surface modification was carried out using a laboratory prototyped device. A quantity of acid groups formed on the surface of fibres was determined and normalised activation energy $[E_a]$ was selected, required to apply the Layer-by-Layer (L-b-L) method. Contact angles were established and components of the surface free energy were calculated for the samples activated. A significant growth in polar components of the surface free energy was found, caused by the corona discharges. The L-b-L method was used for deposition nano-layers of poly(allylamine hydrochloride) [PAH] and polyacrylic acid [PAA]. Using the test dye method, it was found that the method can be applied to polyester fabrics activated by corona discharges and modified by the deposition of polymer complex nano-layers.

Key words: nanolayer deposition, corona discharge, polyester fibres, surface energy.

Introduction

Recently, there have been a number of articles and monographic evaluations published [1, 2] concerning the deposition of multi-polymer layers of nanometer thickness onto flat surfaces, such as glass, mica or polymer surfaces [1, 2]. The method, known as Layer-by-Layer (L-b-L) method, not only leads to the modification of polymer surfaces but also enables to introduce layers of metal, metal oxides, and to carry out chemical reactions in the layers, using these layers as nano-reactors. Layer thickness in L-b-L method is connected with dimensions of polymer coils used for deposition, which, depending on the pH, is about 10-100 nm.

There have also been some reports about applying the L-b-L method in the modification of textile materials [3 - 9]. However, corona discharge was not applied as activation before the L-b-L process.

Although monographs have already been written on this method [3], there are still many problems concerning the application of this method onto foils used in textiles, problems emphasised even by the authors of the publications themselves. The authors [10] write that "Not all approaches can be automatically transformed from plane substrates onto fibres or textiles".

The basic difference in using the L-b-L method for textiles as opposed to deposition on flat surfaces is the uncovered part of the surface on the threads or fabrics that result from the specific structure of the textiles.

As is well-known [11, 12], nano-layers of polyester complexes are not durable and are subject to erosion in an aqueous environment with a high or low pH, and also in salt solutions. As has already been established [6], in layers deposited on fibres, reactions can be carried out, i.e. polymerisation or polycondensation, treating the layers as nano-reactors.

The first stage of polymer deposition with the L-b-L method is activation, thus forming functional groups on the outer surface, whose purpose is to anchor the first layer. Such activation may be carried out by a chemical reaction using acids, bases or surface grafting. These processes are usually carried out in a liquid environment, most often in aqueous solutions. Recently, activation by corona discharges, carried out under atmospheric pressure in air or in an atmosphere of other gases, such as N_2 , NH_3 , fluorinated hydrocarbons, has become more and more significant. This is connected with the fact that corona discharge treatment is a dry process and does not require the use of water or chemicals. In this work, we decided to test the possibilities of applying corona discharge activation on polyester textiles, followed by nanolayer deposition of polymer complexes using the L-b-L method.

Experimental part

Materials

Polyester textile (PET), washed and stabilised, surface mass 80 g/m², warp 84 dtex f 48, weft 150 dtex f 216, plain weave.

Aldrich poly(allylamine hydrochloride) PAH had a molecular weight of

$M_w = 55.0$ kDa. Poly(acrylic acid) PAA was obtained by radiation polymerisation in isopropanole, which had a molecular weight of $M_w = 258.0$ kDa; other reagents (p.a.) were from POCH Ltd. (Poland).

Research methods

The treatment of polyester fibres by corona discharge was carried out with the use of a laboratory device constructed by METALCHEM (Toruń, Poland) and specially adapted for textile material treatment. The new device for corona treatment under atmospheric pressure is described in detail in [13, 14]. In short the construction of the device developed makes it possible to activate a corona discharge under conditions allowing one to obtain the required level of modification of the top layer of the fibre without any damage to the fabric. This was accomplished by using four co-operating 5-segment electrode sets. In this way the total discharge energy necessary to obtain the level of modification required, which according to our experience amounts to 40 J/cm², was divided into 20 portions, which eliminates the possibility of damage.

Calculating the concentration of acid groups

Samples of activated material were immersed in 50 ml of water, and 5 ml of 0.01 mol/L of NaOH was added to each sample. After 30 minutes, the solution was refilled to 100 ml and titrated pH-metrically in a 0.01 mol/L solution of HCl. From the difference between the untreated sample and the result of titration, the concentration of acid groups in 1g of the fabric was calculated.

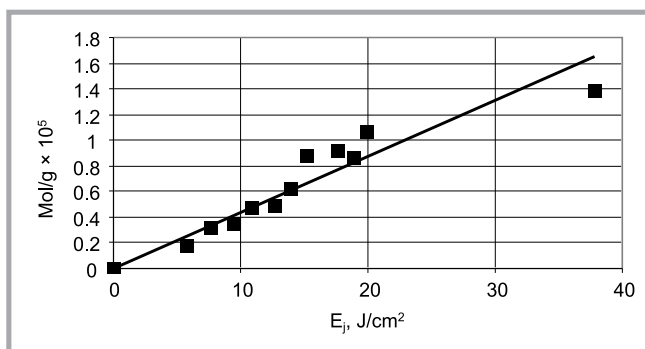


Figure 1. Concentration of acid groups on the surface of PET textile, obtained in various conditions of treatment by corona discharge.

Deposition of layers

Polymer deposition on the activated textile was carried out in a way described in previous publications [5, 6], only the time of dipping was prolonged from 10 to 30 minutes in comparison with the procedure applied on nonwovens. PAH and PAA was selected as the most commonly used polymers in the L-b-L process.

The samples were dipped into a solution of PAH with a concentration of 10⁻² base mol/L for 30 min at about 20 °C and subsequently rinsed with pure water. They were then dipped into the oppositely charged solution (10⁻² base mol/L PAA) for 30 min., followed by rinsing with water. The dipping procedure was then repeated. (Samples 4 and 5 in **Table 3**).

Test dyeing

Samples with different numbers of layers were immersed into 10⁻³ mol/L methylene blue solution for 10 min. After immersion in the dye solution, the samples with multilayer films were soaked in water for 1 min. and then dried in a mild flow of air. All the dyed samples were subjected to light remission measurements. The dyed samples were placed in Spectraflash 300 apparatus of *Datacolor International* to measure their light remission within a range of 400 nm to 700 nm.

Measurements of the contact angle and calculation of the surface free energy

The contact angle of the materials tested were established by the dynamic method,

Table 1. Changes in the concentration of acid groups in the outer layer of the samples tested and in the Kubelka-Munk (K/S) coefficient, depending on the normalised activation energy (E_j).

Sample number	E_j , J/cm ²	Concentration of acid groups, mol/g × 10 ⁵	K/S at $\lambda = 600$ nm
1	-	0	0.035
2	18.9	0.92	0.09
3	37.8	1.39	0.20

using a tensiometer. This method is based on force measurements of the interaction of a probe with the interface of a test liquid. Deionised water and ethylene glycol were used as test liquids. Results of the contact angle measurements were used to calculate the surface free energy of polyester fibres. The calculations were done according to the method presented in [14].

Measurements of infrared spectra

FT-IR spectra were carried out with a Perkin-Elmer spectrometer "System 2000"

Results

As mentioned earlier, surface activation is an introductory stage of polymer deposition using the L-b-L method. This activation is done to form an amount of functional groups on the surface of the modified product which would allow to anchor the first layer of the deposited polymer.

In order to select the most appropriate activation conditions, the concentration of acid groups formed in the outer layer of PET textile, modified in various conditions of treatment by corona discharge, was established. The results obtained are presented in **Figure 1**.

On the basis of the results obtained, it can be stated that together with the increase in normalised activation energy (E_j), there is a gradual increase in acid groups on the surface of the modified polyester fabric.

In the previous work [6] it was stated that in order to deposit the polymer complex layers, a number of acid groups in the order of 1 × 10⁻⁵ mol/g is necessary. The number of acid groups ($\geq 10^{-5}$ mol/g) required in the L-b-L method was obtained during the treatment with corona discharge with energy exceeding 18 J/cm². Due to that fact and for further research, two samples were chosen, activated with

energy of 18,9 and 37,8 J/cm². Conditions of modification and concentration of acid groups in the outer layer of the samples activated are presented in **Table 1**.

These samples were later dyed with methylene blue, according to the method described earlier. Values of the Kubelka-Munk (K/S) coefficient as a result of light remission measurements are presented in **Figure 2**.

As can be seen from **Figure 2**, the K/S values are relatively small, but significantly different from the result obtained for the untreated sample. This confirms the appearance of acid groups on the surface of the activated samples earlier, which can be later used to anchor the nano-layers of polymer deposited using the L-b-L method. The differences in K/S values obtained for the non-modified sample are evidence of hydrophilic changes in the activated samples. During the modification of outer PET textile, an increase in its wetting takes place, which enables it to absorb more dye. The increase in wetting was also confirmed by the tests of the contact angle, carried out using the tensometric method. Results of the contact angle measurement with two measurement liquids are presented in **Table 2**. Values of contact angles with both water and ethylene glycol are lower as a result of activation; however, more significant changes are observed for contact angles which are measured in water. The values of contact angle measurements obtained were used to calculate the surface free energy (**Table 2**). A significant increase in the value of surface free energy was found in all the range of E_j used. It can be concluded from those tests that an increase in the value of surface free energy is mainly caused by the polar component, as the disperse value changes only slightly. An increase in surface free energy proves the presence of

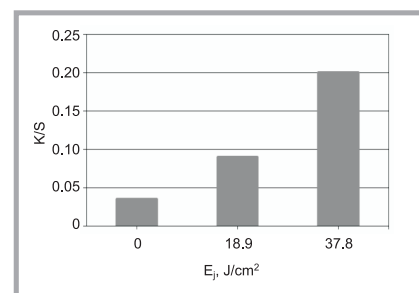


Figure 2. Values of Kubelka-Munk (K/S) coefficient for activated and not activated samples (see **Table 1**) after dyeing with methylene blue.

polar groups in the outer layer of the test samples, caused by the corona discharge.

In the subsequent part of this work, layers of polymer were deposited onto activated samples of polyester textile using the method described previously. The composition of the samples with the deposited layers is presented in **Table 3**.

Samples with deposited layers were then dyed with methylene blue, and the remission was measured, as described above. For instance, for samples 5 and 5a (see **Figure 3**), all reflected light spectrum within the range of 400 to 700 nm was presented. As can be seen, the maximum K/S coefficient is about 600 nm.

Thus, in **Figure 4** there are only K/S values for this wavelength for all samples from **Table 3**.

As can be seen from **Figure 4**, for non-activated sample (1) and for samples with outer PAH layers (2 and 4), the K/S values are very small, which shows a lack of dye bond with the surface. On the other hand, for samples with an outer layer containing PAA, there is a visible dye bond manifested in a high K/S value. It is worth noting that K/S values for the sample activated with higher normalised energy (37.8 J/cm²) are a little higher.

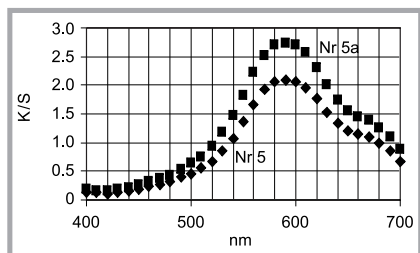


Figure 3. Reflected light spectrum for samples 5 and 5a.

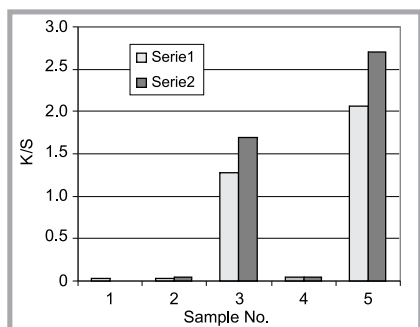


Figure 4. Values of Kubelka-Munk coefficient for samples with deposited layers (see **Table 3**), dyed with methylene blue; Serie 1 and 2 - samples activated with an energy of 18.9 J/cm² and 37.8 J/cm², respectively.

Table 2. Values of surface free energy and its components: dispersive and polar, and average values of contact angles for PET textile, depending on the normalised activation energy E_j .

E_j , J/cm ²	Contact angle, deg		Surface free energy, mN/m	Dispersive component, mN/m	Polar component, mN/m
	water	ethylene glycol			
0	65.35	59.09	38.45	12.74	25.71
18.9	52.10	53.47	47.60	12.34	35.26
37.8	46.21	54.56	52.16	11.61	40.55

Table 3. Activated samples with the deposited polymer layers; PAH- poly(allylamine hydrochloride); PAA- poly(acrylic acid).

Sample number	E_j , J/cm ²	Type of deposited layer	K/S at $\lambda = 600$ nm
1	-	-	0.035
2	18.9	PAH	0.03
2a	37.8	PAH	0.05
3	18.9	PAH + PAA	1.28
3a	37.8	PAH + PAA	1.69
4	18.9	PAH + PAA + PAH	0.05
4a	34.8	PAH + PAA + PAH	0.05
5	18.9	PAH + PAA + PAH + PAA	2.07
5a	37.8	PAH + PAA + PAH + PAA	2.71

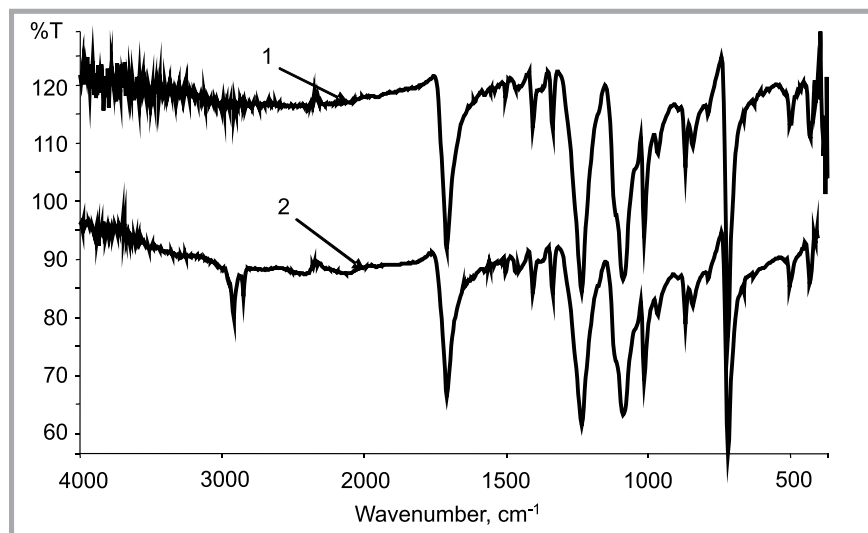


Figure 5. FTIR reflective spectrum of the not activated sample (1) and activated sample (2) with an energy of 37.8 J/cm² with a deposited PAH layer.

The results are evidence that the PAH and PAA layers cover the surface of fibres in PET textile efficiently. Following layers 'cover' the previous ones, giving those layers either an acid or base character.

Additionally, a FTIR reflective spectrum was performed for the non-activated sample (PET) and the sample with a deposited PAH layer. The result, in the form of a spectrum ranging from 4000 to 500 cm⁻¹, is presented in **Figure 5**.

As can be seen, these spectra are not much different, and the amide group band of 1600 cm⁻¹ is absent. In the activated sample and the one with a deposited PAH layer, there are wide bands ranging from

2000 - 2500 cm⁻¹, characteristic for primary amine hydrochlorides, whereas a band of around 3000 cm⁻² is probably characteristic for a hydrate. However, these bands are very weak, which confirms the little thickness of the deposited layer.

Conclusion

Concluding, corona discharges can be used for the activation of polyester fabrics as a first step for depositing very thin polymer complexes. It was shown that normalised energy sufficient for the application of the L-b-L method is about 20 J/cm². Applying this level of energy, a significant decrease in the contact angle and increase in the polar component

of surface free energy was found for activated fabric. The concentration of acid groups on the surface of activated fabric was measured. The additional presence of acid groups was confirmed by test dyeing. The test was also used for the determination of deposited layer composition. The results obtained are evidence that the deposited layers cover the fiber surface in polyester fabric and change its properties.



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References

1. Decher G., Schlenoff J. B., (ed.) "Multilayers Thin Films; Wiley-VCH (2004).
2. Shi X., Shen M., Mohwald H.; *Prog. Polym. Sci.*, Vol. **29**, (2004), p. 987.()
3. Brown P. J., Stevens K. (Eds.), "Nanofibres and nanotechnology in textiles" Woodhead Pub. Lim. Cambridge, England 2007.
4. Połowiński S.; *e-Polymers 2006*: http://www.e-polymers.org/papers/Połowiński_P_004.
5. Połowiński S.; *Fibres & Textiles in Eastern Europe*, Vol. 13 (2005), No 6(54) pp. 50.
6. Połowiński S.; *J. Appl. Polym. Sci.* Vol. 103 (2007) p. 1700.
7. Połowiński S.; *Polimery* Vol. 52 (2007) p. 37.
8. Jantas R., Połowiński S.; *Fibres & Textiles in Eastern Europe*, Vol. 15, (2007), No. 2(61) pp. 97.
9. Połowiński S., Stawski D.; *Fibres & Textiles in Eastern Europe*, Vol. 15(2007), No. 4(63) pp. 82.
10. Minko S., Motornov M.; Chapter 18 p. 489 in P.J. Brown, K. Stevens (Eds.) "Nanofibres and nanotechnology in textiles" Woodhead Pub. Lim. Cambridge, England 2007.
11. Sukhishvili S. A., Kharlampieva E., Izumrodov V.; *Macromolecules* Vol. 39 (2006) p. 8873.
12. Kovacevic D., van der Burgh S., de Keizer A., Cohen Stuart M. A.; *Langmuir* Vol. 18 (2002) p. 5607.
13. Brzeziński S., Żenkiewicz M., Połowiński S., Kowalczyk D., Karbownik I., Lutomirski S., Malinowska G.; *Polimery* (2009) No 6 (in press).
14. Brzeziński S., Żenkiewicz M., Połowiński S., Kowalczyk D., Karbownik I., Lutomirski S., Malinowska G.; *Polimery* (2009) No 8 (in press).

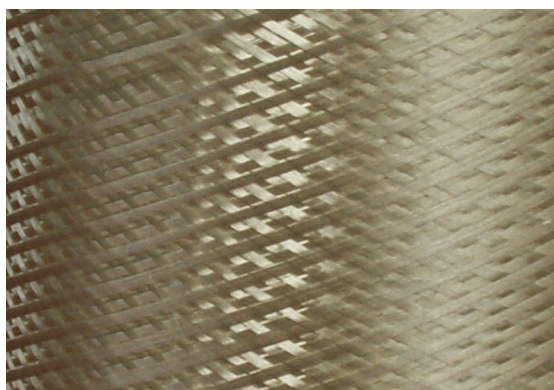
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