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Nonwoven fabrics modified with deposited nanolayers

Summary — A layer-by-layer technique was used for deposition of nanolayers of polyelectrolytes onto nonwoven textiles. Polypropylene (PP) and poly(ethylene terephthalate) (PET) nonwoven fabrics grafted by acrylic acid were used as starting materials for deposition of polymer complex layers. It was found that a layer-by-layer technique makes possible to produce the materials with diversified properties. Depending on the layer structure, the hydrophilic properties, electrokinetic potential and absorption of dyes were changed. Remission of methylene blue were measured for samples with different types of deposited layers. It was found that deposited layers are separated. It was found that electrokinetic potential is dependent on the chemical structure of the external layer. Moreover, nanoparticles of gold were deposited onto such layers. It was found that particles of gold are distributed without aggregation. Properties of the obtained materials were tested.

Key words: nonwoven fabric, polyelectrolytes, nanolayers' deposition, optical properties, electrical properties, colloidal gold particles.

MODYFIKACJA WŁÓKNIN PRZEZ NAKŁADANIE NANOWARSTW

Streszczenie — Metodę warstwa-po-warstwie zastosowano do nanoszenia nanowarstwek polielektrolitów na włókniny. Jako materiał wyjściowy zastosowano włókniny polipropylenowe (PP) lub poliestrowe (PET) szczepione kwasem akrylowym. Stosowane włókniny charakteryzowały się gładką powierzchnią monowłókien widoczną na zdjęciach wykonanych za pomocą mikroskopu elektronowego (rys. 1—3). Warstewki wytwarzano z: poli(kwasu akrylowego) (PAA), poli(kwasu itakonowego) (PIA), poli(alliloaminy) (PAH), poli(metakrylanu dimetyloaminoetylenowego) (PDAMA). Wykazano, że w zależności od budowy chemicznej warstw zmieniają się właściwości hydrofilowe i wybarwialność, co ilustrują wyniki pomiaru remisji próbek wybarwianych błękitem metylenowym (rys. 4 i 5). Na tej podstawie stwierdzono, że warstewki otrzymanych kompleksów polimerowych są rozdzielone. Zmierzone potencjał elektrokinetyczny specjalnie spreparowanych próbek (tabela 2). Zaobserwowano, że w zależności od charakteru warstwy zewnętrznej potencjał ten może być dodatni lub ujemny. Ponadto przeprowadzono próby osadzania koloidalnych cząstek złota. Stwierdzono, że osadzone cząstki nie są zagregowane (rys. 7). Badano właściwości tak wytworzonych materiałów.

Słowa kluczowe: włóknina, polielektrolity, osadzanie nanowarstw, właściwości optyczne, właściwości elektryczne, koloidowe cząstki złota.

Preparation of nanocomposites by the layer-by-layer process has already been widely documented in the scientific literature including books [1] and review articles [2].

The process consists of preparation of polymeric complexes mostly on flat surfaces, *e.g.* on specially prepared glass plates. Once the first layer is deposited and combined with the substrate, a polymer is deposited to form a complex with the former layer. For instance, when poly(acrylic acid) (PAA) is deposited as the first layer, the next one can be poly(allylamine), thus a polymer with a basic character. Then, a successive layer with an acidic character can be deposited. Nanometric dimensions result from the fact that coils of macromolecules deposited in the form of layer have just such dimensions and they are combined using only a portion of

their groups that can create bonds such as hydrogen bonds or dipole interactions.

The layer-by-layer technique can be used to make the polymeric composites with various properties. Moreover, the layers can be used as nanoreactors, in which various chemical reactions can be carried out, for example polymerization of aniline, treatment of the layers to make them electro-conductive, reduction of metal salts to deposit the metals or their oxides in these layers in order to form the composites with magnetic or bioactive properties. An additional effect connected with complex-forming polymers is charge transfer when two polymers are mixed, *e.g.* poly(cation exchanger) and poly(anion exchanger). If both polymers are dissociated, a salt-like polymer is formed. As it is known, however, the charge transfer can take place when a group in poly-

mer is not dissociated or the dissociation is negligible, as in the case of the known complex of poly(acrylic acid) and poly(vinyl pyrrolidone).

Recently, the reports on nanocomposites with colloidal particles have appeared in the scientific literature [1, 2].

The electric behavior of particles deposited on surface layers of polymers is connected with two phenomena. The first one concerns the appearance of charge on the surface of polyelectrolyte macromolecules associated with their dissociation. For instance, salts of polyacids are dissociated and the negative ion linked to the $-\text{COO}^-$ group is covalently combined with the macromolecule, while the positive ion, known also as "counter-ion", forms a charge "cloud" more loosely combined. So during the motion of such solutions it results in electrokinetic phenomena such as electrophoresis, electroosmosis etc. Another phenomenon connected with the deposition of particles of colloidal dimensions is the presence of charge on these particles. As follows from the physical chemistry of colloids, colloidal particles have monomial charges on their surfaces and therefore they do not aggregate and the colloidal system is stable. The coagulation of colloids is only possible when ions with opposite charges, *e.g.* derived from salts, especially multivalent salts, are introduced into the system.

The structure and mechanism of deposition of multilayers of polyelectrolytes or nanoparticles have been discussed by Abu-Sharkh [3]. It has been found that nanoparticles can be incorporated into the layers of polyelectrolytes. The formation of such composites takes place as a result of electrostatic interactions. Such particles are attracted and deposited from the colloidal solution.

Another example can be the fabrication of composite of polyaniline and particles of colloidal gold [4]. The authors have found that such composite has a fibrous structure and its electric conduction is higher than that of pure polyaniline. The deposited layer can be used as nanoreactors for the incorporation of colloidal particles of silver [5].

Hybrid micro-gels modified with nanoparticles of silver have been also produced and their physical and chemical properties have been assessed [6]. Composite particles were prepared by the formation of silver nanoparticles in the presence of micro-gels. It has been found that various compositions of hybrid particles could be obtained. These particles are sensitive to temperature and the collapse process is reversible. The presence of silver nanoparticles clearly increases the thermal stability.

Considering the fact that the studies carried out so far concerned mainly the deposition of nanolayers on the flat surfaces or micro-spheres, we have attempted to produce the nanolayers of polymeric complexes on fibers and to perform chemical reactions in such layers as well as to deposit colloidal particles on such layers. Moreover, we decided to use poly(itaconic acid) (not used so far in the layer-by-layer process) that shows interesting

conformation properties as found in our previous studies [7, 8].

EXPERIMENTAL

Materials

Poly(allylamine hydrochloride) (PAH) characterized by $M_w = 70\,000$ supplied by Aldrich.

Poly(acrylic acid) (PAA) was obtained by polymerization of acrylic acid (Merck) initiated by γ rays (3 h; 0.2 MR) in isopropanol. Polymer was precipitated from ether solution and dried under reduced pressure. M_w determined by gel permeation chromatography (GPC) was 169 000.

Poly(dimethylaminoethyl methacrylate) (PDAMA) was obtained by polymerization of fresh distilled monomer — dimethylaminoethyl methacrylate (Aldrich) in toluene, initiated by AIBN. Product was washed many times by toluene and dried under reduced pressure. M_w determined by GPC was 63 290.

Poly(itaconic acid) (PIA) characterized by $M_w = 16\,290$ was obtained by polymerization in 0.5 M HCl aqueous solution, initiated by persulphate ammonium as described in [7].

Three types of nonwoven fabrics were used:

— polypropylene (PP) nonwoven with a specific surface of 35 g/m^2 , made at the Textile Institute, Łódź, designated as IW,

— polyethylene terephthalate (PET) nonwoven made at CENARO company, Łódź, with a specific surface 42 g/m^2 ,

— PP nonwoven made at the "ZGODA" plant, Aleksandrów n/Łódź, with specific surface 60 g/m^2 , designated as Z4.

Preparation of samples

As a smooth surface without pores and irregularities is a requisite for the use of the layer-by-layer process, electron microscope images of nonwoven fabrics were made and shown in Figs. 1, 2 and 3.

As is seen, the nonwoven fabrics are more or less uniform in respect of filament diameter, while the filament shows a smooth surface.

Prior to layer deposition, the nonwoven fabrics were grafted with acrylic acid. The grafting method, described in details in our previous paper [9], consisted of producing of peroxides either by irradiation in air or by heating of the nonwoven fabric in a solution of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ followed by heating of the nonwoven fabric for 1 h in 0.7 mol/dm^3 acrylic acid solution.

Typical procedure of layer deposition consisted of immersing of a wet nonwoven fabric in 10^{-2} mol/dm^3 PAH or PDAMA for 15 min rinsing with water for 1 min and after gentle draining off water, immersing in 10^{-2} mol/dm^3 solution of PAA for 15 min, rinsing for 1

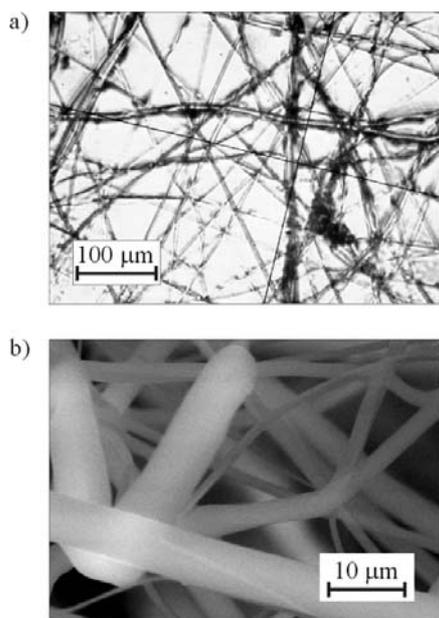


Fig. 1. Electron microscope images of IW nonwoven fabric; magnification: a) 100 times, b) 1000 times

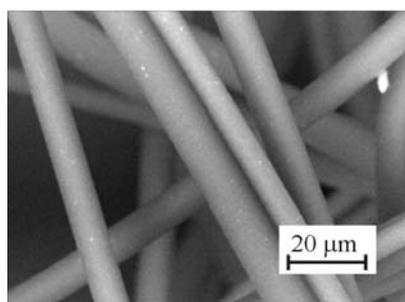


Fig. 2. Electron microscope images of PET nonwoven fabric; magnification 500 times

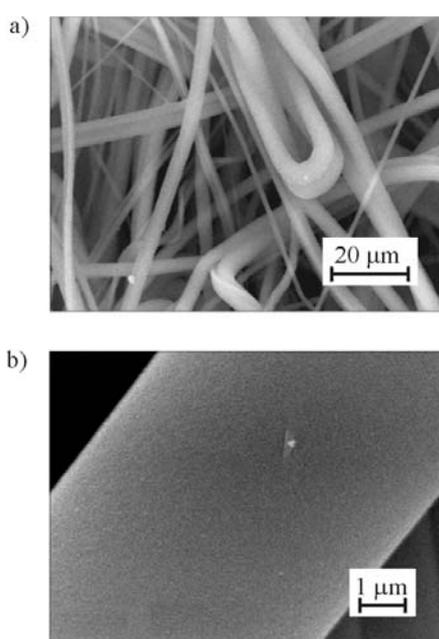


Fig. 3. Electron microscope images of nonwoven fabric Z4 magnification: a) 500 times, b) 6000 times

min and repeating of the whole procedure. In this way from 2 to 6 layers were deposited. The structure of modified fibers are given in Table 1.

Methods of testing

Electron microscope JEOL type JSM 5000 LV was used for microscope examination.

The measurements of light remission were carried out by means of Spectraflash 300 apparatus (Datacolor Int. USA). In order to identify the deposition of layers and the character of surface, the nonwoven fabrics were immersed in a solution of methylene blue for 10 min followed by rinsing with excess of water for 1–2 min and drying in air. The coefficient of reflection (R) of the dyed samples were measured.

In order to measure the electric charge of nonwoven fabric it was necessary to prepare an aqueous dispersion of disintegrated nonwoven fabric. For that purpose PP nonwoven with a surface weight of 30.3 g/m^2 was selected. It was irradiated with a dose of 3.0 MR of γ radiation in an air followed by grafting with acrylic acid. After storage for several weeks, the nonwoven fabric was disintegrated to give the filaments with a length of several millimeters, as shown in Fig. 4.

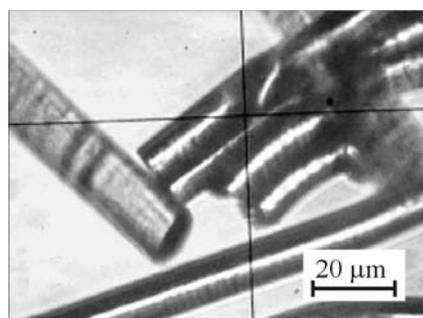


Fig. 4. Nonwoven PP fabric after irradiation with a dose of 3.0 MR of γ radiation, stored in an air for 60 days and then disintegrated

Polymeric layers were deposited on the samples, prepared as above, according to the procedure described previously. Electrical charge was detected by dispersing of 0.05 g of examined sample in 10 mL of water and measuring the electric potential (mV) using Particle Charge Detector (BTG Mütek GmbH, Germany).

Charge quantity (c/g) was estimated by titration of positively charged particles by 10^{-3} mol/dm^3 PAA solution and negatively particles by 10^{-3} mol/dm^3 PAH solution. The same apparatus was used.

RESULTS AND DISCUSSION

Optical measurements

The layers of acidic character become coloured, under the influence of methylene blue while PAH layer

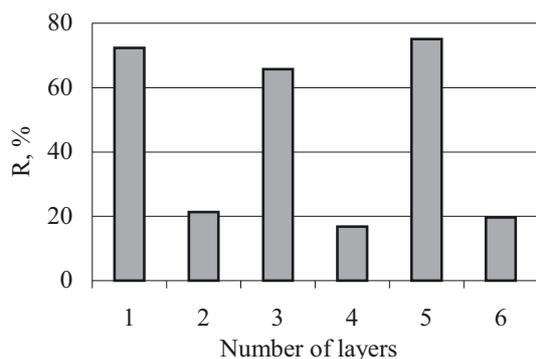


Fig. 5. Coefficient of reflection (R) of IW nonwoven fabric with deposited successive layers: 1 — untreated sample, 2 — sample grafted with PAA, 3 — deposited PAH layer, 4 — deposited PAA layer, 5 — deposited PAH layer, 6 — deposited PAA layer

remained colourless, as confirmed both visually and by measuring the coefficient of reflection of the dyed samples. As an example the coefficients of reflection (R) expressed in %, at 600 nm, of the nonwoven fabric with a surface weight of 30.3 g/m^2 grafted for 1 h at 100°C and dyed with methylene blue (sample IW-5, Table 1) are shown in Fig. 5.

Table 1. The structure of layers deposited on different types of nonwoven fabrics

Symbol of sample	Type of nonwoven fabric	Number of layer					
		1	2	3	4	5	6
PET-6	PET	PAA	PAH	PAA	PAH	PAA	PAH
IW-5	IW	PAA	PAH	PAA	PAH	PAA	PAH
IW-6	IW	PAA	PDAMA	PIA	PDAMA	PKI	PIA
Z4-4	Z4	PAA	PAH	PIA	PDAMA ^{a)}		

^{a)} PDAMA quaternized by allyl bromide.

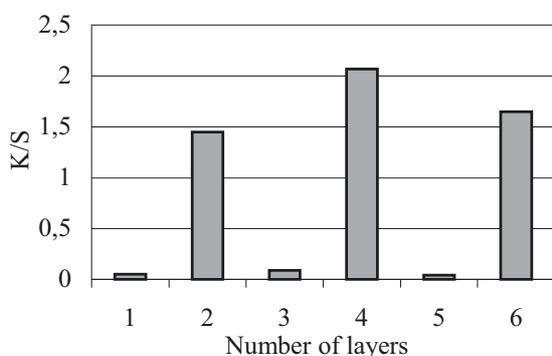


Fig. 6. K/S ratio of the nonwoven fabric with deposited successive layers: 1 — untreated sample, 2 — sample grafted with PAA, 3 — deposited PAH layer, 4 — deposited PAA layer, 5 — deposited PAH layer, 6 — deposited PAA layer

In the case of textiles with the same surface, the dye concentration in a fiber is proportional to the value of K/S ratio defined by Kubelka-Munk's equation [10]:

$$K/S = (100 - R)^2 / 200R \quad (1)$$

where: K — absorption coefficient, S — diffusion coefficient.

Monochromatic light of a wavelength with absorption maximum, *i.e.* reflection minimum was used in the measurements. Results recalculated for the same sample as in Fig. 5 are presented in Fig. 6. From these results we can see that absorption of dyes changes depending on the layers structures.

Electrical charge measurements

The results of electric potential and specific charge quantity measurements for disintegrated PP nonwoven fabric with deposited different layers are listed in Table 2.

Table 2. Results of electric measurements for disintegrated PP nonwoven fabric with different deposited layers

Symbol of sample	Composition of layers	Electric potential mV	Specific charge quantity $\cdot 10^6$, cq/g
PP-1	PAA	-1390	-5.6
PP-2	PPA, PDAMA	+690	+2.9
PP-3	PPA, PDAMA, PIA	-1697	-7.9
PP-4	PPA, PDAMA, PIA, PAH	+625	+2.1
PP-5	PAA, PAH	+270	—
PP-6	PAA, PAH, PIA, PAH, PIA	-480	—
PP-7	PAA, PAH, PIA, PDAMA ^{a)}	+135	—

^{a)} PDAMA quaternized by allyl bromide.

However, experimental error is rather high, so the values presented in the table must be treated as estimation only. We can see from the results presented that electrical potential changes from negative to positive depend on the chemical structure of external layer. These data allowed to anticipate that deposition of colloidal particles with a charge opposite to that of filaments would be possible.

Deposition of colloidal particles

Chloroauric acid with a concentration of 0.16 g/cm^3 was neutralized to $\text{pH} = 7$ with potassium carbonate and heated to its boiling point. Then, a sample of disintegrated nonwoven fabric containing deposited layers (sample PP-7, Table 2) was impregnated with this solution and immersed into 1% solution of tannin to reduce the auric compound (sample A).

A sol of gold was prepared separately by the reduction of a neutralized solution of chloroauric acid with

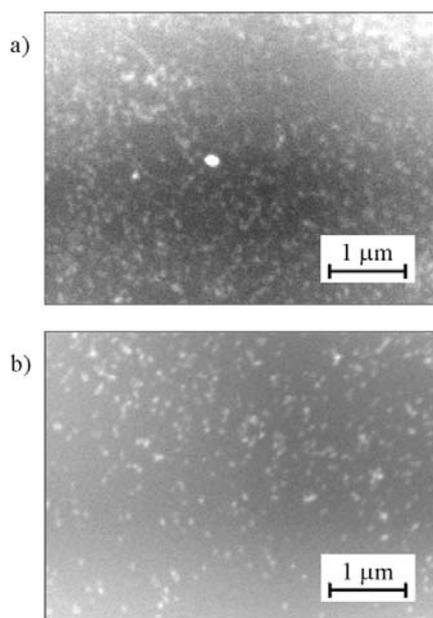


Fig. 7. Samples of nonwoven fabrics with deposited layers of PAA, PAH, PIA, PDAMA and additionally with colloidal particles of gold: a) sample A, b) sample B; designation of samples in the text

tannin. This sol was used then to impregnate a sample of the same nonwoven fabric (sample B).

The photographs in an electron microscope were taken by the technique of secondarily dispersed electrons. As we can see in Figure 7 in both cases the gold particles are separated, without aggregation.

CONCLUSIONS

It has been found that using the layer-by-layer process, polymeric nanolayers can be deposited onto non-

woven fabrics made of PP or PET by the melt-blown method to change the nonwoven fabrics' properties. The deposited layers are isolated, which was confirmed by their dyeing and measuring of the reflected light intensity. It has also been found that the deposition of layers with a suitable chemical structure allowed one to change the character of electric potential of filaments and that this potential could be used to deposit colloidal particles with a charge opposite to that of fibres.

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REFERENCES

1. Multi-author work: "Multilayers Thin Films" (Eds. Decher G., Schlenoff J. B.), Wiley-VCH, 2004.
2. Shi X., Shen M., Möhwald H.: *Prog. Polym. Sci.* 2004, **29**, 987.
3. Abu-Sharkh B.: *Langmuir* 2006, **22**, 3028.
4. Feng X., Yang G., Hou W., Zhu J.-J.: *Macromol. Rapid Commun.* 2006, **27**, 31.
5. Dorn A., Katz E., Willner I.: *Langmuir* 1995, **11**, 1313.
6. Pich A., Karak A., Lu Y., Ghosh A. K., Adler H.-J. P.: *Macromol. Rapid Commun.* 2006, **27**, 344.
7. Stawski D., Połowiński S.: *Polimery* 2005, **50**, 118.
8. Połowiński S.: *Polimery* 2006, **51**, 270.
9. Połowiński S.: *Fibres & Textiles in Eastern Europe* 2005, **13**, 62.
10. Mielicki J.: "Zarys wiadomości o barwie", Fundacja Rozwoju Polskiej Kolorystyki, Łódź 1997, p. 281.