

Deposition of Polymer Complex Layers onto Nonwoven Textiles

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ABSTRACT: Polymeric complex layers are deposited onto polypropylene and polyester nonwoven fabrics via the layer by layer method. It is found that grafting after previous surface activation with an aqueous ammonium persulfate solution is a beneficial method to form the first acidic layer. In order to form polymer complexes, poly(acrylic acid), poly(itaconic acid), poly(allylamine hydrochloride), and poly(*N*-dimethylaminoethyl methacrylate) are used. The deposition of subsequent layers to form

polymer complexes modifies the properties of nonwovens. Moreover, it is found that the deposited layers can be microreactors for chemical processes such as polymerization of aniline and formation of polymers and copolymers. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 1700–1705, 2007

Key words: nanolayers; polyelectrolytes; polypropylene; polyesters

INTRODUCTION

The grafting process is a method for modifying the surface of textile fabrics. Methods of producing grafted copolymers with the use of acrylic or methacrylic acid have been reported.^{1–6} More recent reports have been concerned with the possibility of depositing several layers onto flat or spherical surfaces using the layer by layer technique.⁷ This method consists of the formation of the first layer on a surface by grafting, chemical modification, or a strong adsorption. Next, a layer of polymer with basic groups is applied onto such a layer, which may have an acidic character, to form a layer of polymer complex, onto which another acidic layer can be deposited.

When using this technique with films or microspheres, we can expect that appropriate layers deposited onto textile fabrics by this method may have changes in their properties such as hydrophilicity, electrokinetic potential, and dyeability. The deposited layers may also become micro- or nanoreactors for chemical reactions such as the polymerization of aniline and the formation of electroconductive layers or the formation of metal or metal oxide particles in these layers.

Our previous articles discussed the possibility of depositing polymer complexes onto polypropylene nonwovens with the use of poly(acrylic acid) (PAA) and poly(allylamine).⁸ The first acidic layer was

formed by grafting AA induced by irradiation. However, the irradiation of a nonwoven with a dose of 2–3 Mrad in air resulted in a considerable decrease in the mechanical strength of the grafted nonwoven. During prolonged storage such a nonwoven crumbles, probably because of oxidation and degradation.

This prompted us to search for new surface grafting methods to form the primary layer, to apply polycomplexes with various structures, and to form nanolayers on other textile fabrics, including polyester fabrics. In addition to a polypropylene nonwoven, a nonwoven made from poly(ethylene terephthalate) by the melt-blown method was also selected. The grafting process was induced by irradiation as well as by the formation of peroxide groups by a chemical, photochemical, or thermal method.

The formation of radicals and active peroxides is possible by heating the fibers in a solution of benzoyl peroxide or other peroxides. This method has been successfully used to graft AA on polyesters.^{3,4}

According to literature data,^{1–3} thin polymeric layers can be formed on polyamide or polyester fiber surfaces with the use of peroxide groups formed previously by heating in air at 80–100°C, followed by grafting with a monomer within a short time to avoid diffusion inside the fibers. Photochemical grafting with UV light and photoinitiators such as benzophenone and related compounds is also reported.⁶

EXPERIMENTAL

Materials

A polypropylene nonwoven prepared by the melt-blown method (Zgoda Works) with a surface weight

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TABLE I
Conditions of Activation and Grafting

Series no.	Type of nonwoven	Activation conditions			Grafting conditions			No. acid groups (mol/g × 10 ³)
		Medium	Temp. (°C)	Time (min)	Conc. of AA	Temp. (°C)	Time (h)	
1	C	γ Rays	1 MR ^a	—	0.3M	100	1	1.53
2	Z	γ Rays	2 MR ^a	—	0.3M	100	1	1.50
3	Z	(NH ₄) ₂ S ₂ O ₈ 20 g/L	80	30	0.3M	80	1	1.50
4	PET	UV + benzofenon	25	2	0.66M in toluene	25	24	1.30
5	PET	(NH ₄) ₂ S ₂ O ₈ 20 g/L	40	10	Concd. AA	40	1	2.80
6	PET	(NH ₄) ₂ S ₂ O ₈ 20 g/L	60	30	0.7M	60	1	1.68
7	PET	(NH ₄) ₂ S ₂ O ₈ 20 g/L	80	30	0.7M	80	1	1.47
8	PET	Air	80	10	Concd. AA	25	4	1.0

^a Dose.

of 77.7 g/m² and an average filament diameter of 2.5 μm was irradiated in air with a dose of 2 Mrad (20 kGy). This sample was designated as sample Z.

A polypropylene nonwoven was prepared by the melt-blown method (Cenaro–Łódź, Poland) with a surface weight of 27.9 g/m² and an average filament diameter of 9.65 μm. This material was named sample C.

A polyester nonwoven was prepared by the melt-blown method (Cenaro–Łódź). Its surface weight and average filament diameter were 60 g/m² and 10 μm, respectively. This nonwoven was designated as PET.

PAA was prepared by polymerization in toluene initiated with AIBN. The polymer was rinsed several times with toluene and dried under a vacuum. Its weight-average molecular weight ($M_w = 145,000$) was determined by the gel chromatography method.

Poly(*N*-dimethylaminoethyl methacrylate) hydrochloride was prepared by polymerization in tetrahydrofuran at 65°C for 5 h and initiated with AIBN (4×10^{-4} M). The polymer was precipitated with *n*-heptane, dissolved in ethanol, reprecipitated with heptane, and dried under a vacuum. Then, the polymer was dissolved in a stoichiometric quantity of HCl.

Poly(allylamine hydrochloride) (PAH) from Fluka ($M_w = 15,000$) was used without purification. Poly

(itaconic acid) (PIA) was prepared as described previously⁹ by polymerization of itaconic acid in water initiated by (NH₄)₂ S₂O₈ ($M_w = 25,210$).

Activation and grafting

In series 1 and 2 (see Table I) the nonwovens were irradiated in air with a γ-ray dose of 1 or 2 Mrad and then grafted by heating them in a solution of AA in water saturated with nitrogen. However, in series 1 the relative strength decreased by 50% of the strength before irradiation, whereas for the sample irradiated by a 2-Mrad dose during prolonged storage the strength decreased even more (sample crumbles).

In series 3 (see Table I) the nonwovens were activated in a solution of ammonium persulfate and then rinsed and heated in the AA solution. In this case the relative strength was 0.85. In series 4 (Table I) the nonwovens were saturated with a solution containing 0.76 g/L of benzophenone and 0.66M AA in toluene followed by irradiation for 2 min with a 37.5-W L6/58 quartz tube from a distance of 25 cm.

In series 5, 6, and 7 the nonwovens were activated by heating in a solution of ammonium persulfate, thoroughly rinsing with water, and grafting with concentrated AA in series 5 and in a 0.7M AA solution in series 6 and 7.

TABLE II
Samples with Deposited Polymer Layers

Sample no.	Activation and grafting series no. ^a	Subsequent layers						
		0	1	2	3	4	5	
1	2	PP ^b	PAA ^c	PAH	PAA	PAH	PAA	
2	3	PP ^b	PAA ^c	PAH	PAA	PAH	PAA	
3	3	PP ^b	PAA ^c	PAH	PKI			
4	2	PP ^b	PAA ^c	PDAMA	PKA			

^a From Table I.

^b Initial sample, polypropylene.

^c A layer derived from grafted PAA.

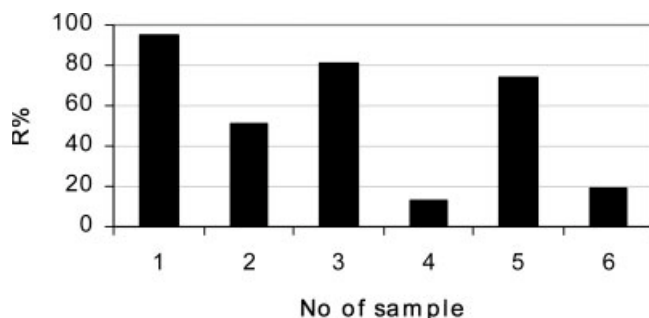


Figure 1 The remission (R%) at 600 nm of series 2 nonwoven samples (activated by irradiation): (1) initial sample, (2) after grafting, (3) with PAH external layer, (4) with PAA external layer, (5) with PAH external layer, and (6) with PAA external layer.

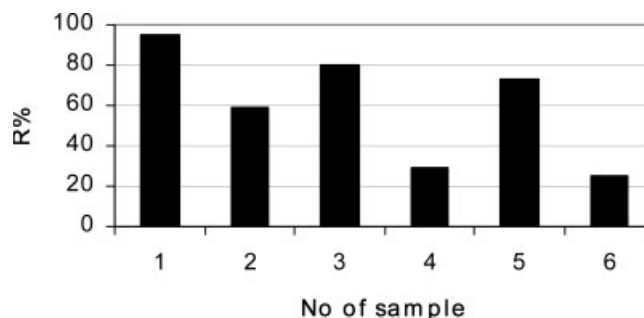


Figure 2 The remission (R%) at 600 nm of series 3 nonwoven samples (activated with persulfate): (1) initial sample, (2) after grafting, (3) with PAH external layer, (4) with PAA external layer, (5) with PAH external layer, and (6) with PAA external layer.

In series 8 the samples were heated in air, immediately saturated with concentrated AA, placed into a polyethylene bag, and saturated with nitrogen. After grafting, all the samples were rinsed with water until the acid reaction disappeared and then dried in air.

The number of acid groups in the samples was determined as follows: 1 g of grafted nonwoven was placed in 100 mL of water and an excess of 0.01M NaOH solution (defined after a preliminary titration) was added. Then, during intensive stirring, the unneutralized base was backtitrated with 0.01M HCl. Such a procedure should be treated as a comparative that characterizes the number of accessible acid groups on the fiber surface. The conditions of activation and grafting are given in Table I.

Deposition of layers

Samples of the grafted nonwovens were dipped in PAH solution with a concentration of 10^{-2} base mol/L for 15 min and then rinsed with pure water. Substrates

were then dipped in the oppositely charged PAA or PIA solution (10^{-2} base mol/L) for 15 min and again rinsed with water. The dipping procedure was repeated (Table II). In order to check the correctness of layer deposition, the samples with subsequent deposited layers were dyed with methylene blue.

Samples with different numbers of layers were immersed in a 10^{-3} M methylene blue solution for 10 min. After immersion in the dye solution, the nonwovens with multilayer films were soaked in water for 1 min and then dried with a mild flow of air. All dyed samples were subjected to the measurements of light remission. The measurements were carried out by means of a Spectraflash 300 apparatus (Datacolor International) within a range from 400 to 700 nm. The results are shown in Figures 1 and 2.

Considering the fact that for methylene blue the minimum remission occurs at about 600–620 nm, one can assume that the lower the remission value within this range is, the higher the amount of adsorbed dye and consequently the higher the number of acid groups on the fiber surface.

TABLE III
Samples with Deposited Layers

Sample no.	Activation and grafting series no. ^a	Subsequent layers					
		0	1	2	3	4	5
4	4	PET ^b	PAA ^c	PDAMA	PANI ^d	PAA ^c	PANI ^d
5	3	PP ^b	PAA ^c	PAH	PKI	PANI ^d	
6	3	PP ^b	PAA ^c	PAH	PKI	SB ^e	
7	3	PP ^b	PAA ^c	PAH	PKI	Copolymer ^f	
8	2	PP ^b	PAA	PDAMA	PAA	PANI ^d	

^a From Table I.

^b Initial sample.

^c The layer derived from the grafted PAA.

^d Polyaniline prepared by the polymerization of aniline.

^e Schiff base.

^f AA-2Vpy copolymer.

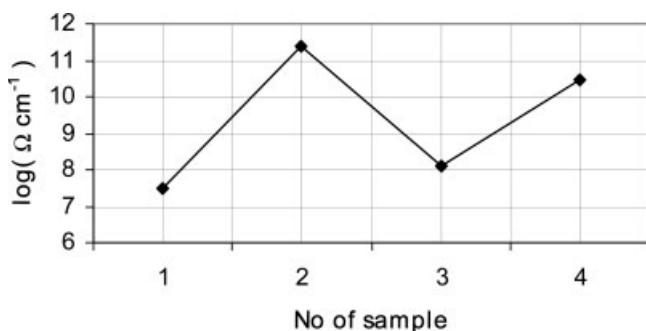


Figure 3 The surface resistance ($\Omega \text{ cm}^{-1}$) of sample 4 (see Table III): (1) initial sample, (2) treated with NaOH, (3) treated with HCl, and (4) treated with NaOH.

Polymerization in layers

In order to examine the possibility of performing the polymerization in the deposited layers, trials were carried out for aniline polymerization, preparation of Schiff bases, and alternating copolymers from AA and 4-vinylpyridine. The structures of subsequent layers on the obtained samples is shown in Table III. Aniline was polymerized on the deposited PIA layer with ammonium persulfate as the oxidizer, as described previously.⁹⁻¹¹

The nonwoven with deposited poly(allylamine) and PIA was immersed for 10 min in a solution of aniline hydrochloride with a concentration of $2.15 \times 10^{-3} \text{ M}$. Then, it was rinsed with water three times, dipped in 0.3M ammonium persulfate solution at 0°C, and left at room temperature for 24 h. Next, the sample was rinsed with water, filtered off on filter paper, and dried.

In order to examine the reversibility of doping (similar to Oh et al.¹²), samples 4 and 8 (see Table III) were alternately placed in 0.1M NaOH and 0.1M HCl solutions. After each operation the sample was rinsed with distilled water to eliminate H^+ and OH^- ions, respectively. The surface resistance ($\Omega \text{ cm}^{-1}$) was measured. Prior to measurements, the samples were dried and conditioned at a relative humidity of 65%. The results are provided in Figures 3 and 4.

According to the reaction shown in Scheme 1, a Schiff base was prepared by immersing the nonwoven sample with deposited layers of poly(allylamine) and PIA into an alcohol solution containing 10 g/L

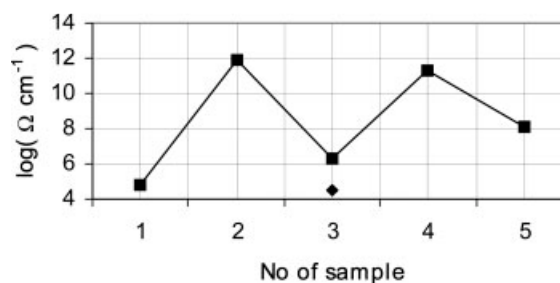


Figure 4 The surface resistance ($\Omega \text{ cm}^{-1}$) of sample 8 (see Table III): (1) initial sample and after treating with (2) NaOH, (3) HCl, (4) NaOH, and (5) HCl. The sample was doped by immersing it in a 0.1M trifluoroacetic acid solution.

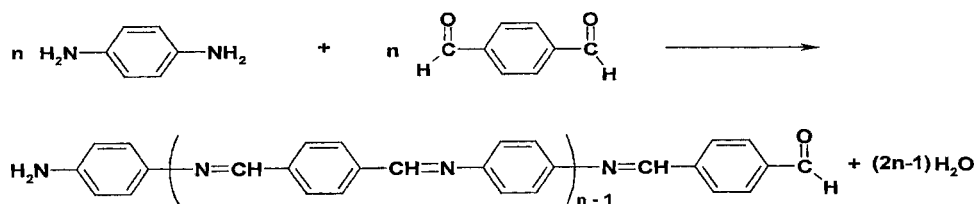
of *p*-phenylenediamine hydrochloride for 10 min, rinsing with alcohol, and immersion in an alcohol solution containing 10 g/L of phenylene dialdehyde. The sample was filtered off and left at room temperature for 24 h, followed by thorough rinsing with alcohol and water and drying.

A spontaneous copolymerization of 4-vinylpyridine with AA (similar to Masuda et al.¹³) was carried out by immersing the nonwoven sample with deposited layers of poly(allylamine) and PIA (sample 3, Table II) into a 0.5M AA solution. The sample was then rinsed with water and immersed in an alcohol solution of 4-vinylpyridine (52.5 g/L) for 48 h at room temperature. Finally, it was rinsed three times with distilled water and dried.

RESULTS AND DISCUSSION

Electron microscope photographs of two types of polypropylene nonwovens are presented in Figure 5. Both polypropylene and PET nonwovens possess filaments with a smooth surface, which is obtained by using the melt-blown method, which is necessary in depositing layers onto these materials by the layer by layer technique. However, nonwoven C shows thicker filaments with more uniform diameters whereas nonwoven Z possesses thinner filaments with more differentiated diameters.

As shown in previous work,⁸ the preirradiation technique allows the preparation of polypropylene nonwovens grafted with AA. The number of acid



Scheme 1 The reaction scheme for the preparation of a Schiff base.

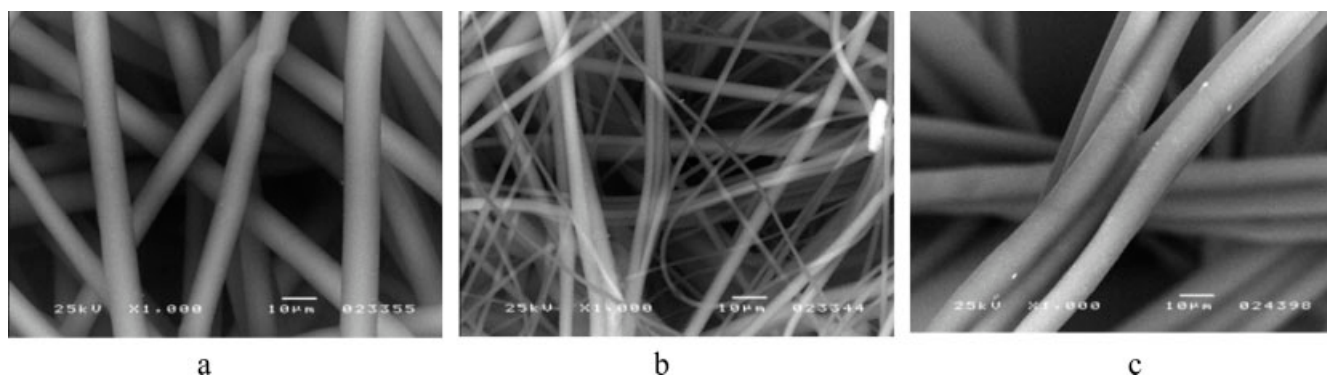


Figure 5 Electron microscope images of nonwovens (a) C, (b) Z, and (c) PET.

groups that makes it possible to form polymer complex layers via the layer by layer method is about 1.5×10^{-5} mol/g. However, the preirradiation technique shows the drawback of a considerable decrease in the mechanical strength of the fiber.

As is seen from Table I, the use of other methods of activation, such as the formation of peroxide in an aqueous medium or thermal or photochemical activation, allowed us to choose such grafting conditions that made it possible to obtain a similar number of acid groups without significant changes in the fiber's mechanical strength.

The grafting methods used here were suitable for the successful deposition of polymer complex layers via the layer by layer method, as confirmed by the remission results of dyed samples shown in Figures 1 and 2. These results illustrate that the subsequent layers effectively cover the previous ones to radically change the properties of the product.

Thus, it is easily possible to form layers consisting of different polymers, resulting in a different product "architecture." According to the literature reports on layers on flat or spherical surfaces,⁷ the deposited layers can become reactors for carrying chemical reactions. The present study demonstrated that in

these layers one can effectively polymerize aniline, prepare polymers of the Schiff base type, or carry out the copolymerization process. In all cases, such layers modified the product properties and were quite stable. The obtained materials with polyaniline layers showed periodical changes under the influence of a changing medium, as demonstrated in the case of the varying surface resistance. Note from the SEM photographs presented in Figure 6 that the deposited layers are distributed rather uniformly on the surface of the nonwoven samples.

CONCLUSIONS

The layer by layer method was used to deposit thin polymeric layers on textile fabrics. A necessary condition for using this method was a smooth surface on the fibers of the fabric. This condition was fulfilled by polypropylene and polyester fibers made by the melt-blown process.

This study showed that the most effective method of depositing the first layer on such nonwoven fabrics was the grafting of AA preceded by fiber activation with an aqueous solution of ammonium persulfate. In this case, the grafting took place on the

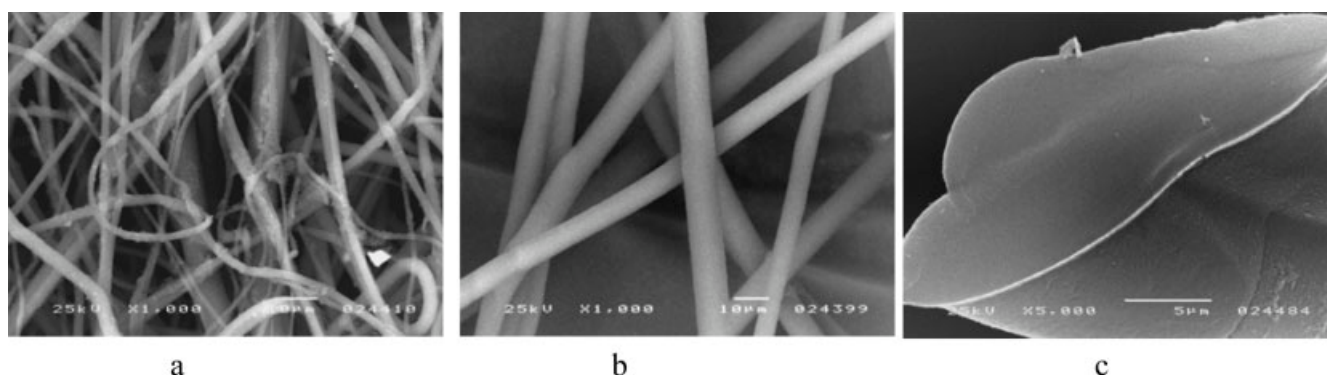


Figure 6 (a) Nonwoven Z with polyaniline (sample 5, Table III), (b) nonwoven PET with PANI (sample 4, Table III), and (c) a cross section of sample 4.

fiber surface and the mechanical properties of fibers were not changed significantly.

The deposited layers of polycomplexes efficiently changed the surface properties from acidic to basic, as shown by the measurement of the remission of samples dyed with methylene blue.

It was demonstrated that chemical reactions such as the polymerization of aniline, synthesis of Schiff bases, or copolymerization of AA with 4-vinylpyridine could be carried out in the deposited layers. This imparted various properties to the textile fabrics, which was shown by the electric conductivity of nonwovens with deposited layers of polyaniline. The dependence of the appropriate properties of treated textiles on the type, sequence, and quantities of deposited layers will be the subject of our further studies.

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