Layer-by-Layer Deposition of Poly (Ethylene Imine) Nanolayers on Polypropylene Nonwoven Fabric. Electrostatic and Thermal Properties

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Abstract—The surface properties of many materials can be readily and predictably modified by the controlled deposition of thin layers containing appropriate functional groups and this research area is now a subject of widespread interest. The layer-by-layer (lbl) method involves depositing oppositely charged layers of polyelectrolytes onto the substrate material which are stabilized due to strong electrostatic forces between adjacent layers. This type of modification affords products that combine the properties of the original material with the superficial parameters of the new external layers. Through an appropriate selection of the deposited layers, the surface properties can be precisely controlled and readily adjusted in order to meet the requirements of the intended application. In the presented paper a variety of anionic (poly(acrylic acid)) and cationic (linear poly(ethylene imine), polymers were successfully deposited onto the polypropylene nonwoven using the lbl technique. The chemical structure of the surface before and after modification was confirmed by reflectance FTIR spectroscopy, volumetric analysis and selective dyeing tests. As a direct result of this work, new materials with greatly improved properties have been produced. For example, following a modification process significant changes in the electrostatic activity of a range of novel nanocomposite materials were observed. The deposition of polyelectrolyte nanolayers was found to strongly accelerate the loss of electrostatically generated charges and to increase considerably the thermal resistance properties of the modified fabric (the difference in T50% is over 20oC). From our results, a clear relationship between the type of polyelectrolyte layer deposited onto the flat fabric surface and the properties of the modified fabric was identified.

Keywords—Layer-by-layer technique, polypropylene nonwoven, surface modification, surface properties.

I. INTRODUCTION

THE deposition of thin, mainly organic layers containing functional polyelectrolyte groups, designed for modifying the surface properties of flat objects, is now the subject of a wide interest.

The major idea of the layer-by-layer (lbl) method is in alternately depositing oppositely charged polyelectrolyte layers, which react between themselves due to electrostatic

forces. Using this kind of modification it is possible to obtain products that combine the volumetric properties of the main object with the superficial parameters of a new external layer. Through an appropriate selection of the layer to be deposited one can very precisely control the surface properties of the given product adjusting them to concrete requirements and needs. It has been shown that this method can be also used for textile fabrics.

Our previous papers described the use of the lbl method for the modification of polypropylene and polylactide nonwovens to obtain hydrophilic [1], [2], thermal [3], [5], electrokinetic [4], [5], dyeing [3] and electrostatic properties [5].

Poly (ethylene imine) (LPEI) is one of the most used polymer for gene delivery [6]–[10]. PEI-based polymers have found a number of applications in biotechnology, nano-medicine and pharmacy [11]-[15]. Our previous investigations [4] showed the possibility of deposition of polymeric brushes PEI-PEI and PEI –poly(2-ethyl-2-oxazoline), PEtOx onto PP nonwoven. The present paper describes the effect of surface modification of polypropylene nonwoven fabric by the deposition of linear LPEI, layers using the layer-by-layer method. The effect of the chemical composition upon the thermal resistance properties was explored in detail. The investigation mainly focused on determination of thermal decomposition parameters such as activation energy, reaction order and frequency coefficients which are of vital importance for determining the mechanism of polymer degradation and thermal stability values [16].

The effects of surface modification with LPEI were compared with the effects of the deposition of various polyelectrolytes. Particular efforts were made in order to detect any changes in electrostatic and thermal properties.

II. EXPERIMENTAL

A. Materials

– Polypropylene (PP) nonwoven textile (surface weight = 27.9g/m^2, average filament diameter = 9.65mm) was prepared by the melt blown method (Cenaro – Lodz, Poland) using low viscosity, isotactic PP granules completely free from additives, (Borealis AG, HL604FB, Austria).

– A two-step synthetic procedure was applied for the synthesis of the, LPEI95 [4], [17], [18]. First, PEtOx95 precursors were synthesised, followed by acidic hydrolysis to afford the corresponding LLPEI. The

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PEtOxpolymers were characterized by GPC and 1H NMR. GPC analyses gave monomodal distributions with dispersity indices ranging from 1.1 to 1.3. The degree of polymerizations, DPs of the PEtOx was estimated from the 1H NMR spectra of the polymers in CDCl3. The experimental DPs are in good agreement with the theoretical values and with those calculated from the feed. LPEI was obtained by acidic hydrolysis of PEtOx. Examination of the 1H NMR spectra revealed the degree of hydrolysis to be >95%. The DP of the resulting LPEI was confirmed as equivalent to that of the corresponding PEtOx precursor.

- Poly (acrylic acid) (PAA) was prepared by polymerization of acrylic acid (AA) in toluene initiated with azobisisobutyronitrile (AIBN). The polymer was rinsed several times with toluene and dried under vacuum. Its weight-average molecular weight (Mw= 145 000 g/mol) was determined by gel chromatography.

B. Modification Procedures

1. Activation

The PP nonwoven was activated by immersion in a solution of ammonium persulfate (c = 20g/dm^3, t = 30min, T = 80°C, in nitrogen), followed by thorough rinsing with water. Aiming to produce the first graft poly(acrylic acid) (PAA) layer the activated nonwoven was dipped in concentrated AA aqueous solution, (c = 52g/dm^3, t = 60min, T = 80°C, in nitrogen).

2. Nanolayers Deposition

Samples of the grafted nonwovens were dipped in LPEI solution with a concentration of 10-2 base mol/dm^3 at 80°C for 15min and then rinsed with pure water. Substrates were then dipped in the oppositely charged poly(acrylic acid) (PAA) solution (10-2 base mol/dm^3) for 15min at room temperature.

Prior to every such operation samples were rinsed with distilled water.

C. Characterisation

1. Dyeing Tests

Samples with different numbers of layers were immersed into 0,001 mol/dm^3 methylene blue solution for 10min. After immersion in the dye solution the nonwovens with multilayer films were soaked in water for 1min and then dried with a mild flow of air. All the dyed samples were subjected to measurements of light reemission. Dyed samples were placed in a Spectraflash 300 apparatus (Datacolor International) to measure their light reemission within the range from 400 to 700nm.

2. FTIR Spectroscopy

The FTIR spectra were collected using a Perkin-Elmer 2000 FTIR instrument. A Perkin-Elmer specular reflectance variable angle accessory (VASR) has been used to gather the reflectance FTIR spectra at 60° (16 scans). The unmodified, nonwoven fabric was used as a background for creating spectra of modified nonwoven fabric.

3. Volumetric Titration

The quantitative analysis of acidic groups was determined with the use of a laboratory pH conductometer/salinometer CPC-502 from ELMETRON, operating in pH measurement mode with a combined glass electrode. A weighed portion of nonwoven substrate (about 1 g) was flooded with 5 ml of 0.01 mol/dm^{3}NaOH solution and then 75cm^3 of distilled water was added. The system was titrated by means of 0.01mol/dm^{3}HCl solution (during stirring with a magnetic stirrer). The same procedure was used to titrate samples of modified and unmodified nonwoven fabrics. The latter was used as a reference sample.

4. Thermogravimetric Analysis

The thermal analysis of all samples was carried out with a Perkin Elmer TGA 7 thermal analyser in a platinum measuring cell, with the use of Pyris program for data handling. Measurements were performed in a nitrogen and air atmosphere mainly with the heating rate 15°C min^{-1}. The samples were heated up to 650°C, starting from room temperature. All measurements were repeated at least three times. For each course temperature of 50% degradation (T$_{50\%}$) was determined and after that the average value was calculated.

III. RESULTS AND DISCUSSION

A. Deposition of Polyelectrolyte Layers on the Surface of Polypropylene Nonwoven Fabrics

The surface of polypropylene nonwoven was modified with the use of poly(acrylic acid) (PAA) as a negatively charged layer and poly(ethylene imine) (LPEI) as a positively charged layer. The first layer was deposited on the surface of fabric by grafting acrylic acid. The next layers were deposited by the layer-by-layer technique. The resultant system is shown in Table I.

TABLE I
COMPOSITION OF DEPOSITED LAYERS

Grafting	Type of nanolayer (sample number)	
1	2	3
PAA	PEI	PAA

The structure of modified samples was confirmed using dyeing tests, volumetric analysis and reflectance FTIR spectroscopy.

1. Dyeing Tests

The deposition of polyelectrolyte layers was confirmed by the method of dyeing test with methylene blue dye. This dye belongs to the group of thiazine dyes and is used to dye the surfaces of acidic character. Therefore one should expect considerable differences in the intensity of colour of the test dyed fabrics before modification and those containing the last layer of poly(acrylic acid) or the external layer of polyamine.

The dyed samples show visual differences in the intensity of color: sample 1 and 3 have clearly deeper blue color than samples 0, and 2. Spectrophotometric measurements of

scattered light (S) were also performed. The intensity of reflected color was measured by means of a spectrophotometer within the range of maximum light reemission for methylene blue (550–600nm).

The relationship between K/S (the coefficient of absorption (K) and scattering (S)) and the coefficient of light reflection (R) has been derived by Kubelka and Munk:

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

The dependence of K/S on wavelength is shown on Fig. 1.
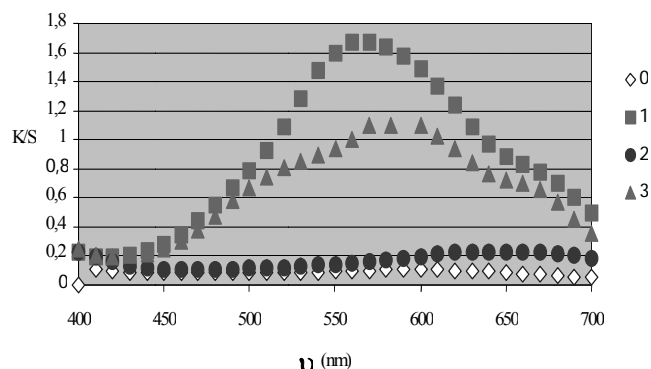

Fig. 1 The results of Kubelka – Munk intensity measurements for PP nonwoven modified according to Table I

As is seen in Fig. 1, the number of acidic groups on the surface with the external PAA layer (samples 1 and 3) is considerably higher than that on the sample with the external LPEI, layer and on the sample with unmodified surface, which is reflected by the measurements of colour intensity obtained with methylene blue.

The use of color tests in the work on the modification of textiles is very useful as it allows a quick and simple control and evaluation of the deposition process, giving results that can be easily and quickly visually interpreted.

2. Volumetric Analysis

The volumetric inverse analysis is a very simple technique, requiring no special apparatus. When a relatively large surface of textile fabric is used (in this case, 1g of sample was used for analysis), it is possible to quantitatively determine the average number of acidic groups that are present in the deposited layers. It is also possible to evaluate the non-uniformity of structure. This technique finds its application in the assessment of changes in surface properties [3], [4].

The determination of the increase in the number of acidic groups was preceded by the analysis of sample 0 (unmodified). The calculated increase in the number of acidic groups is shown in Fig. 2. The concentration of acidic groups in sample 1 (grafted with acrylic acid) considerably depends on the grafting conditions and is contained within the ranges reported in literature [16],[17]. The lower quantity of carboxylic groups in the sample with the second acidic layer

(3) in comparison with the grafted sample suggests some accumulating non-uniformity of the surface cover.

3. FTIR Spectroscopy

In order to quantitatively assess the number of carboxylic groups, the area under the peak corresponding to the carboxylic group in the non-ionized group –COOH in the IR spectra was measured. The relation between this peak area and the number of the deposited layers is shown in Fig. 2.
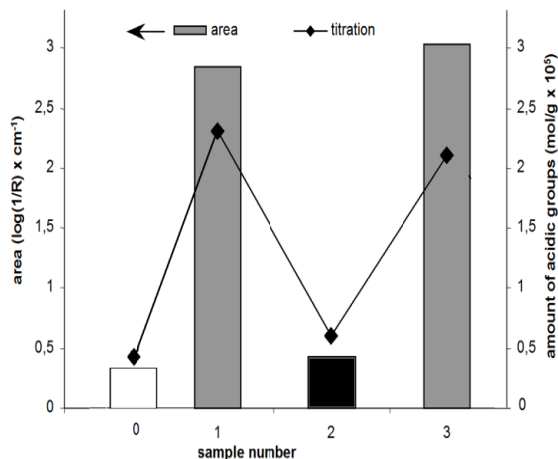

Fig. 2 The results of Kubelka – Munk intensity measurements for PP nonwoven modified according to Table I

The comparison of the amount of accessible acidic groups indicated by the spectrometric technique and pH-metric titration presented in Fig. 2 shows good accordance with the obtained results. External reflectance FTIR is a reliable analytical method for nonwoven PP analysis.

B. Electrostatic Analysis of Samples after Modification

The static electricity is always a negative property of the textile products. Both for personal cloth use and for technical textiles it is important to find the way how to eliminate such disadvantage. PP is a material which has very bad electrostatic parameters. The changes in static electricity can enlarge the possible area of application of this material. The results of time for charge to decrease by 50% are shown in Fig. 3.
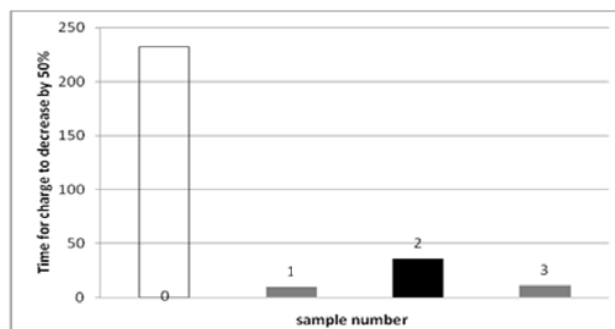

Fig. 3 The electrostatic properties for nonwoven before (0) and after modification (1-3)

The results shown in Fig. 3 show that the application of the LPEI polymers on the nonwoven surface strongly accelerated the loss of electrostatically generated charges.

C. Thermogravimetric Properties

In addition to the well-documented affects upon the surface properties of the material under modification, it has been also observed that this surface modification can also change the thermal resistance of the substrate material [3]. The representative TG curves of samples after each stage of modification are presented in Fig. 4.
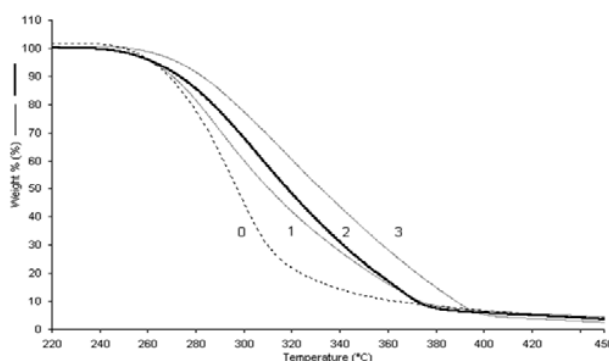

Fig. 4 Representative thermogravimetric curves in air atmosphere

The same phenomenon we have previously found [4] for samples with poly(allylamine hydrochloride) and poly(dimethyl aminoethyl methacrylate) (PDAMA). Deposition of PDAMA has a similar effect on the thermal properties of the above mentioned polyamines. The final difference in temperature of 50% decomposition between unmodified samples 0 and 2 is 22.5°C.

IV. CONCLUSIONS

The investigations performed in this work have shown that the linear poly(ethylene imine) can be use for modification of the polypropylene nonwoven surface in similar way as poly(allylamine hydrochloride) or poly(dimethylaminoethyl methacrylate).

FTIR reflectance analysis can be used for the confirmation of surface structure. The FTIR results are consistent with volumetric tests and methylene blue dyeing tests.

The modified samples have significantly smaller static charge and better thermal stability than unmodified PP nonwoven.

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