Thermal Effect of Polymer Layers Deposition on Polypropylene Nonwoven Fabric

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ABSTRACT: To prepare various types of multilayers, polyelectrolytes poly(acrylic acid), poly(allylamine hydrochloride), and poly(dimethyl aminoethyl methacrylate) were prepared and deposited onto polypropylene nonwoven fabrics produced in the melt-blowing process. Each type of external layer deposited was dyed for identification. Utilizing the layer-by-layer method to deposit polyelectrolyte layers considerably strengthens the thermal resistance of the modified fabric (the difference in $T_{50\%}$ is over 40°C). The effect is connected with the type and number of layers. Thermal effects were also observed in both dynamic and isothermal analyses under air atmosphere. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 123: 1340–1347, 2012

Key words: polypropylene; polyelectrolytes; layer-by-layer; multilayers; TGA

INTRODUCTION

Modifying flat surfaces to achieve figures of desired properties is predominant in current materials engineering research. It is now possible to devise products that combine the properties of the primary object with the superficial parameters of a new external layer. To that end, layer-by-layer (LBL) modification method consists of alternately depositing onto a particular material oppositely charged polyelectrolyte layers, which in turn react to each other due to electrostatic forces. Appropriate selection of the deposited layer affords precise control of the product's surface properties, adjusting them to concrete requirements and needs. Gero Decher, inventor and pioneer of this method, published a series of articles describing this technique in the 1990s.[1–6] Since then, many researchers,[7–11] including Decher himself,[12–15] have refined this method.

Electrolyte or polyelectrolyte nanolayers can be deposited on various flat surfaces such as mica,[16,17] glass,[6,13,18–20] quartz,[6] gold,[21] titanium,[22] silicon,[15,18,23–25] pigment particles,[26] polymeric membranes,[25,27,28] microspheres,[29] or finally fibres.[7,24,30–35] It is now possible to modify flat (nontextile) surfaces to obtain the following properties: anticorrosive,[36] antireflective,[37] antistatic-stiffening or nonstiffening,[38] antisoiling,[39,40] hydrophobic or hydrophilic,[41,42] or antibacterial properties.[43,44] The materials produced by the LBL technique are used as selective nanoreactors on membrane surfaces,[45,46] light-emitting diodes,[47,48] or as membranes for selective separation of components.[49,50] However, in published studies concerning the deposition on narrowly selected textile fabrics, the changes in surface properties due to deposited layers were rarely analyzed (e.g., tests of resistivity[30] or electrokinetic parameters[51]).

Polyelectrolytes such as poly(allylamine) hydrochloride and poly(acrylic acid) (PAA) are quite often used to modify the surfaces of different materials due to their model character in such studies and their relatively frequent implementation in the industry. For instance, poly(allylamine) hydrochloride has been used for the modification of mica surface[16,17] and oxidized titanium used in implantation.[17] The deposited layers may also become microreactors or nanoreactors for next chemical reactions.

Our previous articles described the use of the LBL method for the modification of polypropylene and polyester fibres.[7,30,51–53] It has been shown that this method can be also used for textile fabrics. Surface modifications by the LBL technique, as described above, affect mainly the surface properties of the material under modification. However, it has been also observed that this surface modification influences also the thermal resistance of the substrate material. The results of such experiments are shown in this study.

Materials used

A polypropylene nonwoven was prepared by melt-blown method (Cenaro-Lodz, Poland) with a surface weight of 27.9 g m^{-2} and an average filament diameter of 9.65 µm. Nonwovens were produced using low-viscosity polypropylene granulates completely free from additives (HL604FB) produced by Borealis AG, Austria.

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 (M_w = 145,000 g mol^{-1}) was determined by gel chromatography.

Poly(allylamine hydrochloride) (PAH), commercial products from Fluka (M_w= 70,000 and 15,000 g mol^{-1}) was used without purification.

Poly(dimethyl aminoethyl methacrylate) (PDAMA) was prepared by polymerization of dimethyl aminoethyl methacrylate initiated with AIBN. The average molecular weight (M_w = 63,000 g mol^{-1}) was determined by gel chromatography.

Polyelectrolyte layers deposition

Polyelectrolyte layers were deposited as described previously.[30] The nonwoven was activated according to[30] by heating in a solution of ammonium persulfate (20 g dm^{-3}, t = 30 min, T = 80°C, saturated with nitrogen), thoroughly rinsing with water, and grafting with concentrated AA[30] (52 g dm^{-3}, t = 60 min, T = 80°C, saturated with nitrogen).

After grafting, the samples were immersed in an aqueous solution of appropriate polyelectrolyte (10^{-2} mol dm^{-3}). Before every such operation, the samples were rinsed with distilled water.[30]

Characterization

Determination of acidic groups in the surface layer of fibres

The number of acidic groups was determined with the use of a laboratory pH conductometer/salinometer CPC-502 from ELMETRON, operating in the mode of pH measurement with a combined glass electrode. A weighed portion of fibers (from 0.1 to 0.35 g) was flooded with 5 mL of 0.01M NaOH solution and then 75 mL of distilled water was added. The system was titrated by means of 0.01M HCl solution (during stirring with a magnetic stirrer). The same procedure was used for titrating unmodified fibers. Investigators prepared a diagram of the dependence of pH on the volume of the acid added and the equilibrium volume of acid, i.e., its volume at pH 7. The number of acidic groups formed due to the modification was calculated from the difference of titration results between the unmodified (0) and modified samples and recalculated per 1 g of fiber.

Dyeing tests

The samples with different numbers of layers were immersed into 0.001 mol dm^{-3} 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 the dyed samples were subjected to measurements of light re-emission. Dyed samples were placed in a Spectraflash 300 apparatus (Datacolor International) to measure their light re-emission within the range from 400 to 700 nm.

Thermogravimetric analysis

The thermal analysis of all samples was carried out with a PerkinElmer TGA 7 thermal analyzer in a platinum measuring cell, with the use of Pyris program for data handling. The 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, the temperature of 50% degradation ($T_{50\%}$) was determined and then average value calculated.

SEM microscopy

The samples were mounted on the conductive stub with the conductive carbon tape and then sputtered with gold in the ionic sputter JFC 1200 Jeol. The samples were investigated on the scanning electron microscope (SEM; JSM 5500LV firm, Jeol). Observations were conducted in the secondary electron mode. The accelerating voltages were 15 kV and the working distances were 6 mm.

WAXS measurements

Degree of crystallinity was determined using wide angle X-ray diffraction (WAXS) method. Diffraction patterns were recorded in a symmetrical reflection mode using URD 6 Seifert diffractometer and a copper target X-ray tube (λ = 0.154 nm) operated at 40 kV and 30 mA. Cu Kα radiation was monochromized with a crystal monochromator. WAXS curves were recorded in the range 2°–60°, with a step of 0.1° and the registration time of 30 s per step. Investigated fibers were powdered and pressed into a sample holder. Samples with the radius of 2 cm, and the thickness of 1 mm were prepared.

TABLE I
Composition of Deposited Layers

| | Layer number | | | |
| | Grafting | Deposition | | |
Compositions	1	2	3	4
1	PAA	PAH 70 000	PAA	PAH 70 000
2	PAA	PAH 15 000	PAA	PAH 15 000
3	PAA	PDAMA	PAA	PDAMA

The diffraction curves of the fibers were analyzed by means of a computer program WAXSFIT.[54] In the first stage, a linear background was determined based on the intensity level at small and large angles and subtracted from the diffraction curve. Moreover, the curves of the samples were normalized to the same value of integral intensity scattered by a sample over the whole range of scattering angle recorded in the experiment. Next, the diffraction curves were resolved into crystalline peaks and amorphous component. To this aim, a theoretical curve was constructed, composed of functions related to individual crystalline peaks and amorphous halos. The theoretical curve was fitted to the experimental one using a multicriterial optimization procedure and a hybrid system that combines a genetic algorithm and a classical optimization method of Powell.[55] Both crystalline peaks and amorphous halos were represented by linear combination of Gauss and Lorentz profiles. The amorphous component was approximated by two broad maxima located at $2\theta \approx 16.3°$, and $2\theta \approx 34°$.

Degree of crystallinity was calculated as the ratio of the total, integral intensity comprised in the crystalline peaks to the total, integral intensity scattered by a sample over the whole range of measurement, after the background subtraction.

RESULTS AND DISCUSSION

Deposition of polyelectrolyte layers on the surface of polypropylene nonwoven fabrics

The surface of polypropylene nonwoven was modified with the use of PAA as a negatively charged layer and PAH as a positively charged layer. The first layer was deposited on the surface of fabric by grafting AA. The next layers were deposited by the LBL technique according to Ref. [30]. The resultant system is shown in Table I.

Dyeing tests

Test dyeings with methylene blue dye confirmed the deposition of polyelectrolyte. Methylene blue is a thiazine dyes used to reveal acidic surfaces. Therefore, one should expect considerable differences in

the intensity of color of the test-dyed fabrics before modification and those containing the last layer of PAA or the external layer of polyamine. Similar analyses of textiles modified by the LBL method are reported in the literature.[30,35,52]

The dyed samples show visual differences in the intensity of color: Samples 1 and 3 have clearly deeper blue color than Samples 0, 2, and 4. To corroborate naked-eye visual evaluation of color, 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 re-emission for methylene blue (550–600 nm).

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:

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

The dependence of K/S on wavelength for Composition 1 is shown in Figure 1.

As is seen in Figure 1, the number of acidic groups on the surface with the external PAA (1 and 3) layer is considerably higher than that on the sample with the external PAH layer (2 and 4) and on the sample with an unmodified surface (0), which is reflected by the measurements of color intensity obtained with methylene blue. Similar results were obtained for Compositions 2 and 3.

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.

Microscopic analysis (SEM)

SEM makes it possible to visually assess the surface of modified samples. One can obtain important information about the topography of surface, its structure,
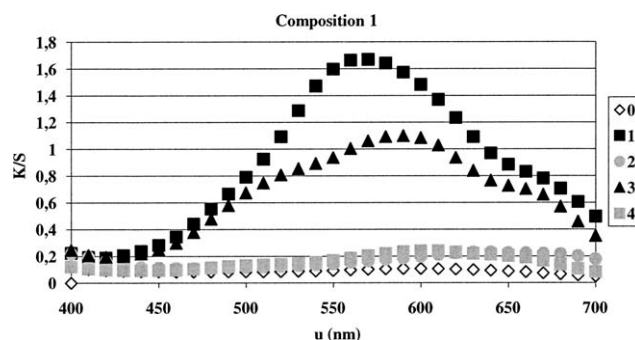

Figure 1 Methylene blue dying tests results for Composition 1 (Table I).
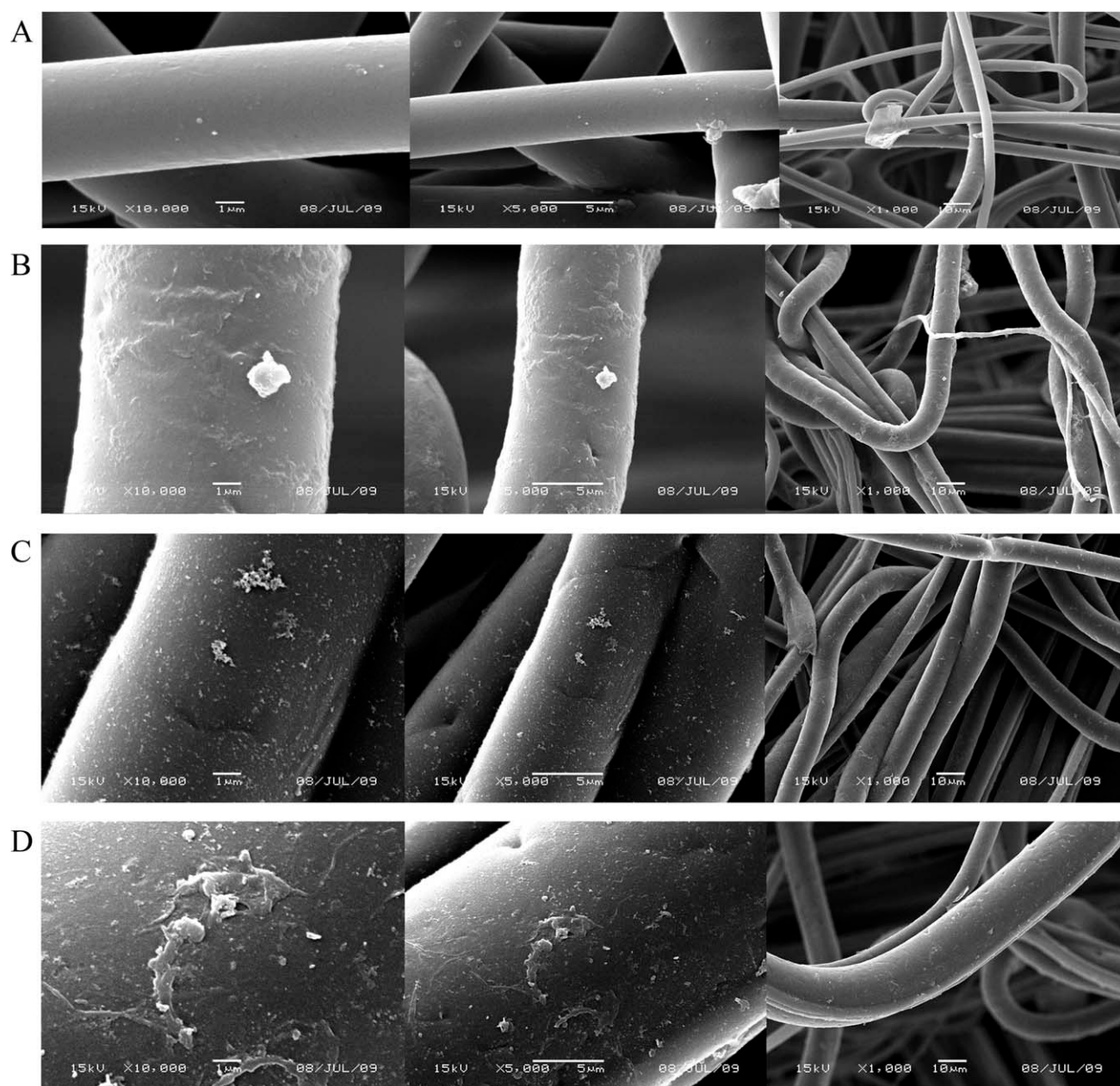
Figure 2 (A) SEM images of Sample 0. (B) SEM images of Sample 1. (C) SEM images of Sample 2. (D) SEM images of Sample 3.

the presence of impurities or uniformity of deposited matter. This technique is also often used to test textile fabrics.[30,54] SEM photographs of samples after various stages of modification, shown in Figure 2, are clearly different from each other.

Figure 2(A) shows the surface of unmodified non-woven (0), which is very smooth with a slight quantity of impurities. In the photograph of grafted nonwoven (1) [Fig. 2(B)], one can observe a clear change in its structure due to the deposition of grafted PAA layer. The surface quality is changed, and the impurities are visible. The photographs of samples after deposition [Figs. 2(C,D)] (2,3) of successive layers show increasing quantities of polycomplexes. The surface structure becomes more and more nonuniform, showing local concentrations of the deposited layers.

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, 1 g 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

TABLE II
Increase in the Number of Acidic Groups on the Surface
of PP Nonwoven after Various Stages of Modification
(Composition 1)

Samples	Amount of acidic groups (mmol g^{-1})
0	–
1 (grafted)	0.023
2 (PAA-PAH)	0.006
3(PAA-PAH-PAA)	0.021
4 (PAA-PAH-PAA-PAH)	0.012

application in the assessment of changes in surface properties.[30,56,57]

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 Table II.

The concentration of acidic groups in Sample 1 (grafted with AA) depends considerably on the grafting conditions and is contained within the ranges reported in literature.[56,57] The lower quantity of carboxylic groups in the sample with the second acidic layer (3) in comparison with the grafted sample, and some quantities in the samples finished with PAH (2 and 4), suggest some accumulating nonuniformity of the surface cover.

The above presented surface characterization data illustrate that the subsequent layers cover the previous ones to radically change the surface properties of the product. There is a strict relationship between the type of polyelectrolyte deposited and dyeing, microscopic, and volumetric properties of this fabric.

Dynamic thermogravimetric analysis

The thermal properties of textiles depend on various factors such as the type of polymeric material, conditions of polymer synthesis, additives used, fabric structure, and many others. Generally, the thermal
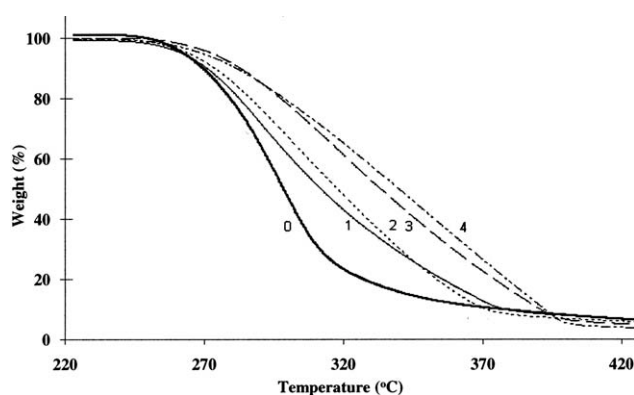
resistance of textiles is connected with the whole volume of product, whereas the structure of its surface influences the thermal characteristics to a relatively small extent. However, even assuming some surface modifications on these parameters, the possible effect would be rather slight. Meanwhile, preliminary thermogravimetric (TG) analyses have shown that significant differences in the run of thermal curves are observed between samples with various degrees of modification. Therefore, the complete TG measurements were carried out to obtain more detailed information about this phenomenon (Fig. 3). To describe TG curves, we selected a temperature of 50% sample decomposition ($T_{50\%}$) as an objective parameter that well describes the quantitative differences between individual curves. The values of average $T_{50\%}$ for samples after various stages of modification are shown in Figure 4.

The differences in $T_{50\%}$ amount to more than 40° for Composition 2. The effect for Composition 2 is slightly better than for Composition 1. It is probably connected with the fact that the smaller PAH macromolecules cover the surface more uniformly.
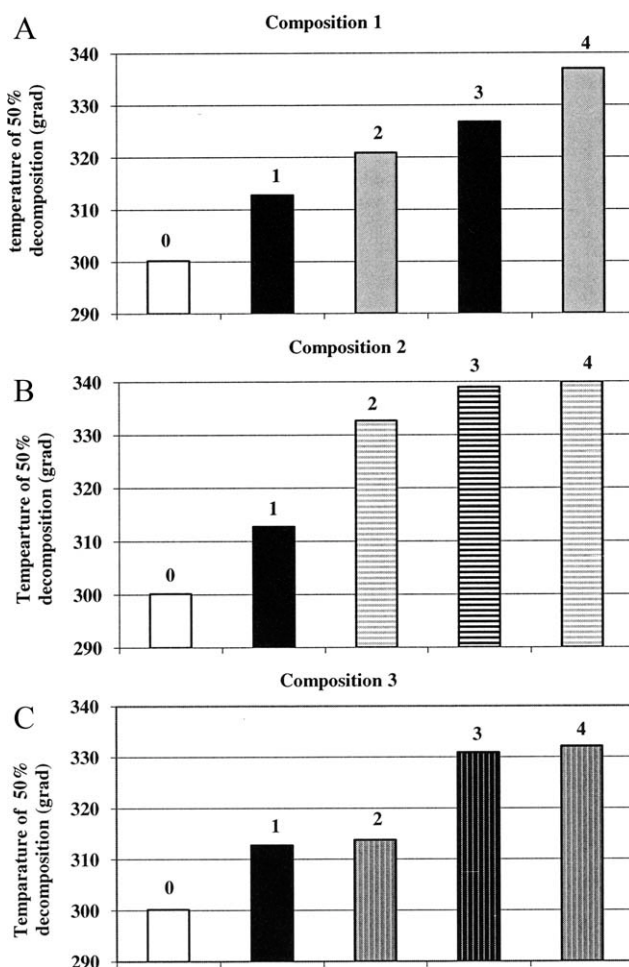

Figure 3 Representative thermogravimetric curves of samples for Composition 1 in air atmosphere.

Figure 4 Calculated temperatures of 50% decomposition (in air) for Compositions 1–3.
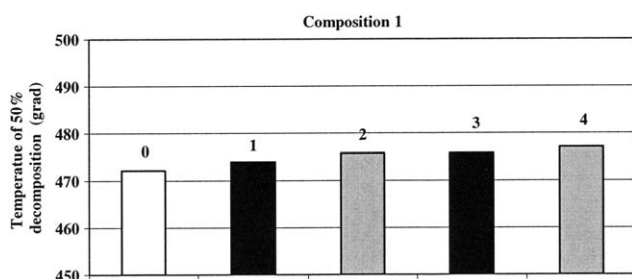
Figure 5 Calculated temperatures of 50% decomposition (in nitrogen) for Composition 1.

Covering with a PDAMA layer which gives similar thermal effects as PAH (at similar molecular weights), the most important being the number of layers.

The effects observed in the TG analysis of nonwovens with polyelectrolyte layers deposited by the LBL method are a surprising fact, practically unreported in the scientific literature. TG analysis was used to assess samples modified by the LBL method in individual cases. The authors of Ref. [25] present the results of TG measurements under the oxygen of unmodified polyelectrolytes (PAA), hydrophobized poly(ethylene oxide), and isolated layer pairs (54 and 82). It has been observed that the thermal characteristics of layers are situated between the results of individual polymers. However, one should remember that these results concern the thermal decomposition of isolated layers and not an object modified by the LBL technique. On the other hand, the article[26] presents contrary results when a differential TG analysis (under oxygen) is used to assess organic pigment particles with silicone layers deposited by the LBL method. In article,[27] minimal changes (below 5°) in TG curves (under nitrogen) were observed after the deposition of PAH and PSS [poly(styrene sulfonate)] layers (up to 40 layers) on the surface of Nafion.

The same TG analyses were carried out under nitrogen. Figure 5 shows the calculated average $T_{50\%}$ values. The differences in the thermal decomposition parameters, measured under the conditions of inert gas, among the samples after various stages of the LBL deposition are minimal at only about 5°. In comparison to the effects obtained in the analyses

TABLE III
Activation Energies Calculated Using Coats-Redfern Method[48] for Composition 1

Samples	Activation energy (kJ mol^{-1})
0	95.6
1 (grafted)	81.4
2 (PAA-PAH)	69.5
3 (PAA-PAH-PAA)	57.5
4 (PAA-PAH-PAA-PAH)	57.4

under oxygen (up to 40° for Composition 2), they are marginal. Moreover, one can notice that the thermal decomposition under nitrogen takes place within a complete different temperature range than that under oxygen. The decomposition under nitrogen begins at temperature about 170° higher.

Based on the above analyses, it seems that the differences in the thermal curves of polypropylene are brought about to a main extent by the fact that the deposited layers form an insulating barrier to protect the main polymeric matter against the access of oxygen and, consequently, they retard the polymer degradation. A minor role is played by the physical insulation against the access of energy. The energetic protection causes differences in the decomposition under inert atmosphere.

The activation energy of samples in Compostion 1 was calculated by Coats-Redfern's method[48] (Table III). In this method, it is assumed that all reactions are zero-order reactions at low rate of conversion. The calculation is only true for zero-order reaction, which results from the former simplifications. The results obtained by this method are true for low conversion degree, but they can be generalized for the whole of the process assuming that the reaction mechanism does not change during reaction duration. The activation energy of PP decomposition decreases for samples with a higher number of layers. Generally, the activation energy for processes that begin at higher temperatures has a higher value, but in the case of samples modified with nanolayers, the contrary happens. It should be also noted that there are significant differences in the values calculated, reaching almost 40 kJ mol^{-1}. This relationship can also be explained by the formation of a protective layer on the modified fabric. This layer retards the PP decomposition and, therefore, the degradation takes place at a higher temperature. As the decomposition of the same material in all the cases begins later, i.e., at a higher temperature, the activation energy needed for its occurrence is lower. At present, the scientific literature contains no reports on the calculation of
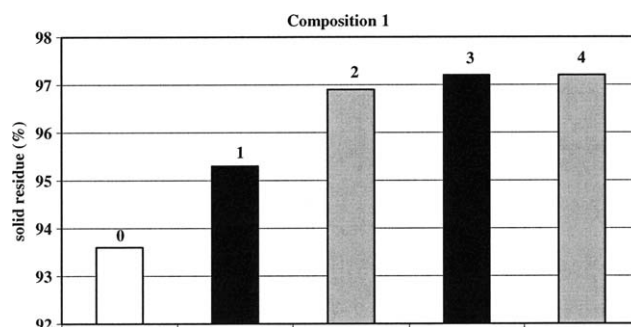

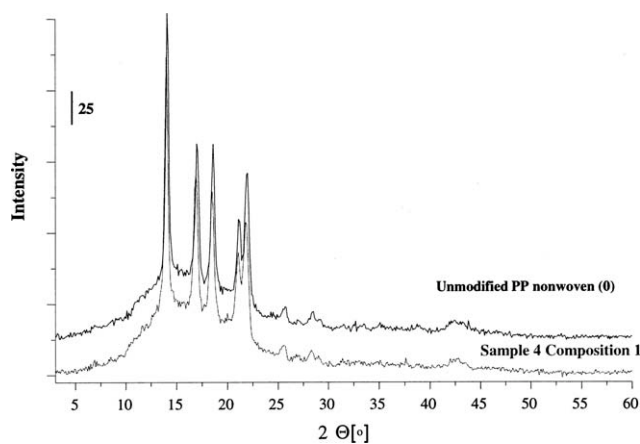**Figure 6** Solid residue for after heating at 158°C (Composition 1).

Figure 7 A comparison of the diffraction curves of modified and unmodified fibers.

activation energy for the decomposition of samples modified by the LBL method.

Isothermal analysis

Practically, it is more important whether the deposited layers protect the modified fabric against thermal degradation within the temperature range closer to realistic applications, i.e., considerably lower than $T_{50\%}$. To that end, fatigue thermal analyses at a temperature of 158°C (300 min) were executed. The results of exemplifying analyses for Composition 1 are shown in Figure 6. Considerable differences in weight loss are observed between individual samples. The highest loss (about 10%) takes place in the case of unmodified sample which is unprotected via a LBL deposition. The calculated average values for all samples are shown in Figure 6. It is seen that the weight losses for the samples modified with polyelectrolyte layers are considerably smaller than that of the initial nonwoven; there is also a correlation between the number of layers deposited and the resistance to prolonged isothermal heating.

Taking into account, the shift of the temperature of 50% decomposition under air in the dynamic analysis, deposited layers constitute an effective protective barrier for the modified nonwoven, retarding its thermal degradation, mainly through obstructing the access of oxygen. Another type of testing thermal properties is analyses in which a sample modified by the LBL method is heated to a specified temperature and then the changes in individual parameters are compared (UV–vis spectroscopy,[49] XPS,[49] fluorescence measurements,[49] and analyses of the second harmonic parameter[28]) between unmodified and modified fabrics.

The solid residues of extreme samples (0 and 4) after isothermal analysis were subjected to the measurements of crystallinity degrees. Thanks to such

measurements, one can find changes in the crystalline structure of polymer resulted from prolonged heating. However, the absolute crystallinity degree of both residues measured on the basis of wide-angle scattering which is identical and amounts to 31.5%. A comparison of the diffraction curves of unmodified and modified (Sample 4) fibers is shown in Figure 7.

CONCLUSIONS

The deposition of polyelectrolyte layers by the LBL method considerably strengthens the thermal resistance of the modified fabric (the difference in $T_{50\%}$ is more than 40°C). The effect is connected with the type and number of layers. Thermal effects were also observed in both dynamic and isothermal analyses under air atmosphere. The values of the activation energy of thermal degradation calculated and the minimal effect obtained in the analysis under inert atmosphere suggest that these effects are due to the formation of a barrier by the deposited layers that insulates the main polymeric matter from oxygen access.

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