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Deposition of poly(ethylene imine)/poly(2-ethyl-2-oxazoline) based comb-branched polymers onto polypropylene textiles using the layer-by-layer technique. Selected properties of the modified materials.

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Abstract

Well defined comb-branched poly(ethylene imine)/poly(2-ethyl-2-oxazoline), (PEI-PEtOx) and homo poly(ethylene imine), (bPEI) polyelectrolytes with varying degrees of polymerization (DP) of the main chain and branches have been successfully deposited on a polypropylene fabric (PP) using a layer-by-layer technique. The surface properties of the nanocomposites have been studied by Fourier transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS) spectroscopy. Changes in the net surface charge and the electrostatic behaviour have been studied by employing electrokinetic and electrostatic measurements. The deposition of the electrolytes increased the thermal stability of the nanocomposites and enabled the deposition of copper ions. Moreover, the materials obtained were found to have properties which could be correlated with the particular polymers deposited.

1. Introduction

Recently, the preparation of nanostructured materials using a layer-by-layer deposition technique has been the subject of much research effort [1,2]. Such materials in particular have attracted a great deal of attention and have been widely investigated because of their potential applications, for example, as drug delivery systems or nanoreactors [1-4].

The process of nanofabrication is based on the preparation of polymer complexes mostly on specially prepared flat surfaces such as glass plates, silicon wafers [5], on microspheres [6] or fibers [7-9]. The first layer is commonly formed either by grafting of a polymer onto the surface or by chemical modification. The successful grafting of acrylic acid onto polyester surfaces is a well-established procedure [10-11]. Once grafting is completed, a layer of a polymer containing basic functional groups can be applied leading to formation of a stable polymer complex onto which another oppositely charged layer can be deposited.

The deposition of polyelectrolyte layers onto various surfaces has been also studied. This method makes it possible to obtain materials with the combined properties of both surface and layer. By the inclusion of appropriate layers, it is possible to fine tune the properties of the surfaces e.g their hydrophilicity [12], dyeability [7], surface resistance [7], thermal stability [8] and electrokinetic properties [13]. Variations in the surface acidic or basic strength depending on the properties of deposited layers were also observed with the aid of an appropriate dye [7].

This paper continues the research described in recent publications on the deposition of polymer-complex layers onto various textile fabrics [7,8,12,13]. In order to understand how the type, composition and architecture of the deposited polymer layer influences the properties of the prepared materials, previously synthesized and well-characterized PEI-PEtOx and bPEI polymers [14-15] have been used for deposition on nonwoven polypropylene substrates. This research has also been inspired by some interesting publications concerning the incorporation of gold, silver, platinum [8] or magnetic particles [9] into similarly prepared systems. Since PEI-based polymers have found a number of applications in biotechnology, nanomedicine and pharmacy [16-21], a deeper understanding of the properties of these new composites is essential in order to efficiently explore potential practical applications.

2. Experimental

Materials

Polypropylene (PP) nonwoven textile (surface weight = 27.9 g/m², average filament diameter = 9.65 μm) was prepared by the melt blown method (Cenaro – Lodz, Poland) using low viscosity, isotactic, PP granules completely free from additives, (Borealis AG, HL604FB, Austria).

Polyacrylic acid, (PAA) was synthesized by free-radical polymerization of acrylic acid (AA) in toluene initiated with azobisisobutyronitrile (AIBN). The PAA was purified and dried under a vacuum. The weight-average

molecular weight ($M_w = 115000$ g/mol) was determined by gel permeation chromatography, (GPC), using Waters 410 light scattering detector (Viscotek T60A) in 0.05 mol/L Na_2SO_4 .

The polyelectrolytes (Fig.1a) were synthesized as described elsewhere [14,15]. There are random branch polymers with the main backbone of linear poly(ethylene imine) and with either poly(2-ethyl-2-oxazoline), or poly(ethylene imine) side chains for PEI-PEtOx and bPEI, respectively. The DPs of the main chain and the branches varies from 20 to 96. The composition, nominal total molecular weight, degree of grafting and the codes of the polymers are given in Table 1.

Figure 1, Table1

The PEI-PEtOx and bPEI polymer layers were deposited onto PP (nonwoven) using previously described method [7]. The nonwoven was activated by immersion in a solution of ammonium persulfate ($c = 20$ g/L, $t = 30$ min, $T = 80$ °C, nitrogen atmosphere), followed by thorough rinsing with water. Aiming to produce the first graft PAA layer the activated nonwoven was dipped in concentrated AA aqueous solution, ($c = 52$ g/L, $t = 60$ min, $T = 80$ °C, nitrogen atmosphere), followed by thorough rinsing with water. After grafting, the samples were immersed in aqueous solutions of PEI-PEtOx or bPEI (1×10^{-5} g/cm³), in the temperature range of 80-90 °C. Special care was taken to ensure that the polymers were fully dissolved [15]. Prior to every such operation samples were rinsed with distilled water [7].

Measurements

FTIR spectra were recorded using a Perkin-Elmer 2000 Fourier transform infrared (FTIR) instrument. Transmission spectra were carried out in KBr pellets. Reflectance FTIR spectra were carried out using Perkin Elmer reflectance variable angle specular at 60° (50 scans). The unmodified nonwoven was used as a background.

XPS experiments were performed with an AXIS ULTRA spectrometer (Kratos Analytical, U.K.) equipped with a monochromatic Al $K\alpha$ X-ray source of 300 W at 20 mA. The wide-scan spectra and high resolution spectra were obtained at analyzer's pass energy set value of 160 eV and 20 eV, respectively. During all measurements electrostatic charging of the sample was compensated by means of a low-energy electron source working in combination with a magnetic immersion lens. Later, all recorded peaks were shifted by the same amount which was necessary to set the C 1s peak to 285.00 eV for saturated hydrocarbons. Quantitative elemental compositions were determined from peak areas using experimentally determined sensitivity factors

and the spectrometer transmission function. The high-resolved spectra were deconvoluted by means of a computer routine. Free parameters of component peaks were their binding energy (BE), height, full width at half maximum and the Gaussian-Lorentzian ratio.

Electro Kinetic Analyzer (EKA) (Anton Paar GmbH, Graz, Austria) was employed for electrokinetic measurements carried out as streaming potential experiments [22-23]. A cylindrical measuring cell was equipped with Ag/AgCl disc electrodes. The measurements were performed by streaming of the measuring fluid (electrolyte solution) through a fiber plug insert between the two electrodes of the measuring cell. The zeta-potential values, ζ was calculated according to Smoluchowski [24]:

$$\zeta = -\frac{dU}{dp} \frac{\eta\kappa}{\varepsilon_r\varepsilon_0} \quad (1)$$

Where the quotient dU/dp is the streaming potential. It was determined from the voltage (U) measured in dependence on the pressure (p) driving the liquid flow through the fiber plug. The symbols ε_r , η and κ are the dielectric constant, viscosity and conductivity of the electrolyte solution and ε_0 is the permittivity of free space. In all experiments the pH-dependence of zeta-potential was determined in the presence of 0.001 mol/L KCl solution.

The electrostatic measurements were made using the Static Meter I (Haug, Germany) apparatus (distance to the sample 2 cm). The samples were preconditioned for a prolonged time (at least one week) at a temperature of 22 °C and 33 % humidity. Each calculation was repeated at least three times and the results averaged.

Thermal analysis was carried out with Perkin–Elmer TGA 7 thermal analyser in a platinum measuring cell, using the Pyris programme for data handling. Measurements were performed in an air atmosphere (gas flow of 20 cm³/min, heating rate of 15 °C/min). The samples (about 5 mg) were heated up to 650 °C, starting from room temperature. All measurements were repeated at least three times. For each of them $T_{50\%}$ was determined and an average value was calculated with an uncertainty of about 1%.

Sorption properties of Cu²⁺ ions were analyzed from water solution of CuSO₄ (1.0 wt. %) during 48 hours in static conditions at room temperature after calibration (807 nm absorbance vs. CuSO₄ percentage). The nonwoven area was 32 cm² (0.07g). The sorption process was monitored using a Lambda 2 (Perkin–Elmer) UV-VIS spectrometer.

3. Results and Discussion

3.1. Structure of the deposit substrate

3.1.1. XPS analysis

Fig. 2a shows the high-resolution C 1s XPS spectrum of the unmodified PP fiber substrate. The shape of the spectrum is characterized by a single component peak *A*, which appears from photoelectrons of saturated hydrocarbons. Self-oxidation reactions introduced small amounts of oxygen (elemental ratio determined from the wide-scan spectrum [O]:[C] = 0.011) in the polypropylene surface.

Figure 2

The grafting of AA strongly changes the shape of the corresponding C 1s spectrum (Fig. 2b). According to the chemical structure of AA and its polymerized form PAA three component peaks are expected. The component peak (*A*) showing the methylene groups of the polymer backbone is on the same position as the main component peak of PP. Component peak *F* appears from carbon atoms of carbonic acid (COOH) and component peak *B* from carbon atoms in α -position to the carbonic acid groups (C-COOH). Surprisingly, the C 1s spectrum in Fig. 2b showed two further component peaks cannot explained by the PAA structure. It can be assumed that the PP surface is slightly oxidized during its activation with ammonium persulfate. Immediately formed alcoholic groups or peroxy groups decomposed during the AA polymerization are able to react with few of the carbonic acid groups of the PAA. The carbon atoms of resulting carbonic ester groups cause the two component peaks *E* (O=C-O-C) and *D* (O=C-O-C). Carbon atoms in α -position to the carbonic ester groups contribute to component peak *B*. According to the stoichiometric ratio of the ester group the intensities of the two component peaks *E* and *D* was found to be [*E*]:[*D*] = 1. The intensity of component peak *B* equals the sum of the intensities of two component peaks *E* and *F* ([*E*] + [*F*] = [*B*]).

Table 2

The C 1s spectrum of the PEI-PEtOx sample No. 1 (Fig. 2c) does not appear very different from the C 1s spectrum of the PAA-modified sample. However, that spectrum does not show the presence of carbonic acid groups (COOH). Obviously the adsorption of the PEI-PEtOx polymer converts these groups. The presence of ester groups, which are analyzed by the two component peaks *E* (O=C-O-C) and *D* (O=C-O-C) shows that the

PAA-modified nonwoven surface is not homogeneously covered by a thick PEI-PEtOx film. The intensity of component peak *E* is slightly higher as the intensity of component peak *D* ($[E]:[D] = 1.15$) because the amide groups of the PEI-PEtOx polymer also contribute to component peak *E*. Compared with the C 1s spectrum of the PAA-modified sample component peak *B* is more intensive due to numerous $\underline{C}-\underline{N}$ bonds of the secondary and tertiary amino groups of the PEI-PEtOx polymer.

The high-resolution N 1s spectrum of the nonwoven modified with PEI-PEtOx shows two component peaks. The component peak *Y* having the fewer intensity appears from electrically neutral $\underline{C}-\underline{N}$ bonds of amines and amides. The component peak *X* results from protonated amino groups ($\underline{C}-\underline{N}^+$). The findings indicate that the adsorption of the PEI-PEtOx polymer endows the fiber surface with a high number of positive charge carriers. The protonation of the amino groups can origin from the hydronium ion (H_3O^+) adsorption from the aqueous PEI-PEtOx solution or/and the formation of salt pairs between accessible carboxylic groups of the PAA layer and amino groups of the PEI-PEtOx polymer ($-\text{COO}^\ominus \cdots \oplus \text{HNC}-$). The formation of salt pairs drives the dissociation reaction of the carbonic acid groups and convert them into a carboxylate structure. The de-localizing negative charge increases the electron density on the carbon atom and shift the binding energy of its electrons slightly to lower values. Hence, in the C 1s spectrum of the PEI-PEtOx-modified nonwoven component peak *F* is disappeared. The strong attractive electrostatic interactions inside of the salt pair fixes the adsorbed PEI-PEtOx molecules on the PAA-modified nonwoven surface.

The very surface sensitive XPS method is an element-oriented method, which allows to discuss the binding states of some of the detected elements. A more molecularly oriented method is the infrared spectroscopy, which is able to give fingerprints of molecular ensembles.

3.1.2. FTIR analysis

In order to compare the polymer samples before and after deposition onto PP nonwovens surfaces, solid state transmittance and reflectance FTIR spectroscopy analysis have been performed. The transmittance FTIR spectra of the solid PEI-PEtOx and bPEI (Samples 1-4) polymer powders before deposition are presented on Figure 3. The characteristic signals of $-\text{CH}_3$, $-\text{CH}_2-$, $-\text{NH}-$ and $-\text{N}<$ groups can be seen, the latter appearing at 815 and 1100-1200 cm^{-1} [25-28].

Figure 3

Fig. 4 shows the FTIR spectra of the deposited layers. For clarity, the structure of one of the deposited layers was compared with that of the sample before deposition- Fig. 5. As seen, although slightly shifted (1196 cm^{-1} , see

Figure 4) the signals due to –NH– groups are clearly visible in the both spectra. Since, the reflectance spectroscopy was carried out using unmodified PP nonwoven as a background, the spectra on Fig. 4 and 5 are related only with the deposited layers (not with the main PP material). The presence of the same peaks assigned to –NH– groups are indicative for the successful coating of the surfaces on each nonwoven with polymer.

Figures 4 and 5

3.2. Properties of modified materials

3.2.1. Electrokinetics

Of considerable importance for a range of applications are the electrokinetic properties of the modified textiles' surfaces [29]. The investigations of the electrokinetic properties give information on the sign of net surface charge and the possibility to change it by changing the environment of the differently modified fibres. The variation of the pH values in an aqueous solution, which is in contact with the fibres provides hydronium ions (H_3O^+) and hydroxyl ions (OH^-) to drive adsorption and/or dissociation reaction on the fiber surface. On this way it is possible to study the surface charging mechanism. The dependence of the zeta-potential values on the pH of an interacting aqueous KCl solution for the untreated and the modified nonwoven samples are shown in Fig. 6.

Figure 6

The strong dependence of the zeta-potential values on the pH values ($\zeta = \zeta[\text{pH}]$, Fig. 6) clearly show that the hydronium ions (H_3O^+) and hydroxyl ions (OH^-) are potential determining ions. The $\zeta = \zeta[\text{pH}]$ function of the unmodified nonwoven sample is typical for solid with a hydrofobic surface, which does not contain a considerable amount of functional groups. At $\text{pH} < 4$ the sign of the zeta-potential values is positive. That means, hydronium ions (H_3O^+) are preferably adsorbed on the fiber surface. With increasing the pH values the number of available hydronium ions decreases and a preferable adsorption of hydroxyl ions are enforced. Hence, with increasing the pH values the zeta-potential and the corresponding surface potential become more and more negative. The constant slope of the $\zeta = \zeta[\text{pH}]$ at $\text{pH} > 4$ is typical for OH^- ion adsorption because water molecules enclosing the charge carriers cannot be stabilized on the hydrofobic surface and will be successively removed. The released space can be occupied by further charge carriers increasing the net surface charge. The pH value

where the zeta-potential equals zero is called the isoelectric point ($\text{pH}|_{\zeta=0} = \text{iep}$). For the unmodified nonwoven sample the iep was $\text{iep} \approx 4$, what is also a typical values for surfaces do not contain functional groups. The grafting of AA strongly changed the $\zeta = \zeta[\text{pH}]$ function (Fig. 6). The negative sign of all zeta-potential values indicates a negative surface charge. Considering the interpretation of the high resolution C 1s XPS spectrum (Fig. 2b) the negative surface charge results from the presence of carboxylic groups, which are able to undergo dissociation reaction in presence of an aqueous solution (the XPS method is working under ultra-high vacuum condition where water is not present on the sample surface). With increasing the pH value the increased OH^- concentration forwards the dissociation reaction and the formation of negatively charged surface sites. Hence, the amounts of zeta-potential values increase with increasing the pH values. However, the number of carboxylic groups on the sample surface is limited. If all groups, which are able to undergo the dissociation reaction are dissociated the net surface charge must remain constant. The $\zeta = \zeta[\text{pH}]$ plot flows into a plateau phase.

The adsorption of the amino groups containing PEI-PEtOx and bPEI polymers turns the net surface charge over a wide pH range from negative to positive. Obviously, at low and moderate pH values the amino groups of the adsorbed polymers are protonated. These findings correspond to the XPS results, where the N 1s spectrum of sample No. 1 shows a considerable amount of protonated species. As mentioned above, these protonated species can be formed by salt formation between carbonic acid groups of the PAA layer and amino groups of the adsorbed polymer. However, these ions pairs exhibit a net charge of zero and do not contribute to the positive net surface charge found in the electrokinetic experiments. The positive charges observed here origin from amino groups protonated by the adsorption of hydronium ions. With increasing the pH value the OH^- ions increases and deprotonation reaction are forwarded. Hence, at higher pH values the amounts of zeta-potential are decreased. Compared to the nonwoven grafted with AA the isoelectric points of the samples modified with PEI-PEtOx and bPEI polymers are shifted to higher values. The highest isoelectric point was found for sample No. 1 ($\text{iep} = 7.7$), whereas the other samples 2,3 and 4 had iep of 5.0, 5.5 and 5.9 respectively. According to the well established Stern theory of the electrochemical double layer [30] the iep corresponds to the number of functional surface groups can be undergo dissociation or protonation reactions. The electrokinetic experiments showed that the adsorption of PEI-PEtOx and bPEI polymers allow to adjust the pH value of the fiber surface.

3.2.2. Electrostatic investigations

The phenomenon of static charging is one of the major disadvantages of man-made fibres and textiles made from. Particularly, PP is a material, which can be easily charged up, e.g. by a simple contact to an other polymer or by slight rubbing. The generated charges remain stable on the PP surface largely independent of the environmental conditions [31]. Even a storage in an atmosphere of high humidity (e.g. 90 %) does not significantly increase the rate of charge dissipation [31]. As mentioned above, the application of the PEI-PEtOx and bPEI polymers on the nonwoven/PAA fibre surface is linked with the formation of ionic surface groups. Salt pairs as well as protonated amino groups are laterally fixed and cannot transport the charge carriers themselves. But the ionic structures enable the stabilisation of water films on the fibre surface, which have the ability to transport charge carriers. Hence, the application of the PEI-PEtOx and bPEI polymers should increase the rate of sample's discharging or prevent an electrostatic charging. In order to evaluate the electrostatic charging the time of the charge half-disappearing was selected as a quantitative factor (Table 2).

Table 2

The results shown in Table 2 show that the application of polyions on the nonwoven surface strongly increase the disappearing of electrostatically generated charges, even at moderate humidity of $\varphi = 30\%$. Hence, the PEI-PEtOx and bPEI polymers seem to be suitable antistatic agents. In contrast to ammonium salts commonly used to prevent electrostatic charging the polymer layer are fixed on fibre surface and cannot be spilled off.

3.2.3. Thermogravimetric analysis

The thermal stability of the materials after deposition has been studied by thermogravimetry. Typical thermogravimetric curves for unmodified, grafted with AA and materials obtained after the deposition of PEI-PEtOx or bPEI polymers are presented in Figure 7.

Figure 7, Table 3

The data derived from the curves in Figure 5 are listed in Table 3. An increase in the thermal stability measured by the temperature for 50% decomposition by up to 30° C after deposition onto the PP nonwovens. Although differences were small, slightly higher values were found for the bPEI structures. It has been assumed that polymer layers serve as a barrier, preventing decomposition of the underlying material. This strongly implies that

the polymer architecture and composition of the new deposited nanolayers are appropriately chosen for the preparation of materials with a significant surface stability.

3.2.4. Sorption properties of copper ions

According to the literature [32, 33] the materials containing tertiary amine groups show good sorption abilities for Cu^{2+} ions and find a great number of applications. In order to investigate these particular properties for the surface-modified nonwovens, the sorption of Cu^{2+} from 1.0 wt. % aqueous solutions of CuSO_4 was studied under static conditions at room temperature for 48 hours. The results are collected in Table 4.

Table 4

As can be seen, higher sorption efficiency was observed for all the modified nonwoven structures. In spite of the higher values, an increase of sorption could potentially be achieved by shaking or by pH manipulation of the solutions. The improved surfaces could be used as sorption filters in the future. The sorption of other metal ions or different biocides, such as proteins [34] or DNA [35] is planned to be considered.

4. Conclusions

Our current research confirms that layer-by-layer technique can be successfully applied for the deposition of PEI-PEtOx and bPEI polymers onto PP nonwoven. As a result new materials with the desired characteristics were subsequently produced. The structure of the modified products was analyzed and verified by XPS and FTIR spectroscopy. The electro kinetic studies reveal that as a result of deposition the nonwovens have significantly higher values of isoelectric point and the pH of the fiber surfaces could be adjusted. It was also observed that the modified materials can be exploit as antistatic agents. The sorption properties were tested for copper ions and it was discovered that the tertiary amine groups can be utilized as an effective sorbent. A clear increase in the thermal stability was confirmed, leading to formation of an insulating barrier preventing further decomposition of the main material.

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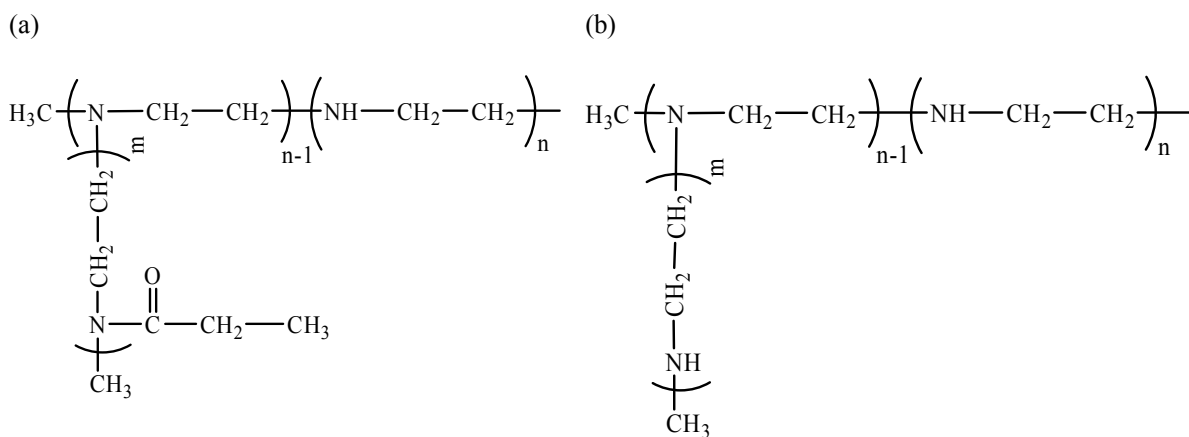


Fig.1. Structural formulas of (a) PEI-PEtOx and (b) bPEI polymers.

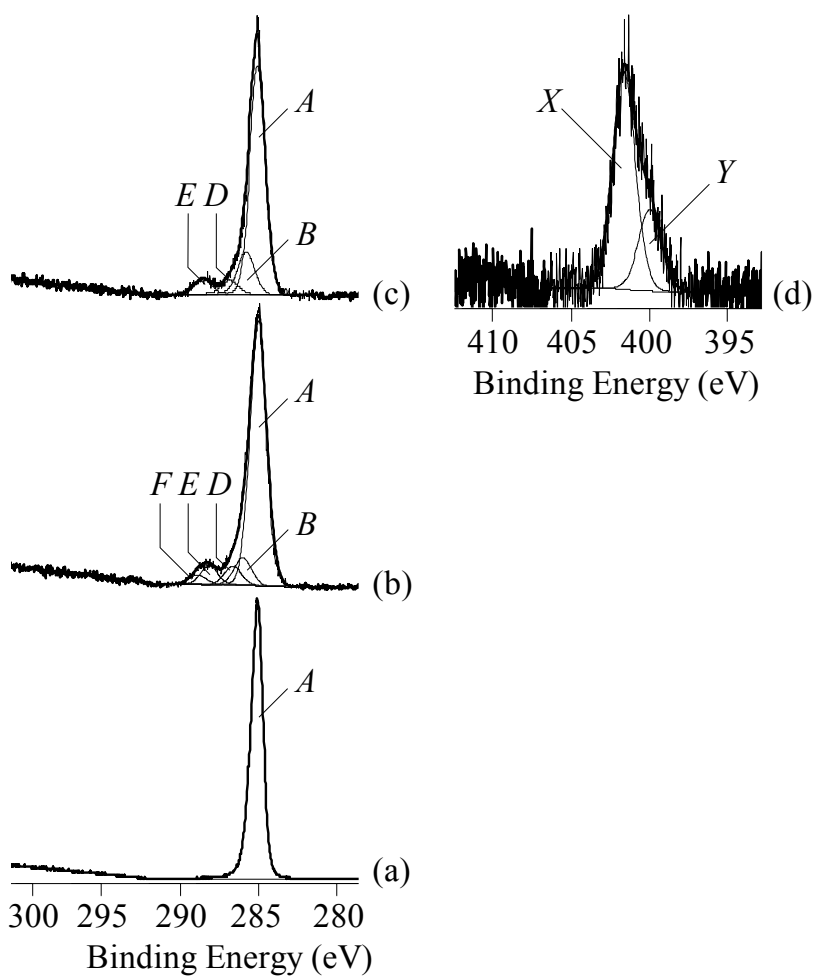


Figure 2 High-resolution C 1s XPS spectra of unmodified nonwoven (a), nonwoven grafted with AA (b) and PEI-EtOx adsorbed on the nonwoven/PAA sample (c). Fig. 2d

shows the high-resolution N 1s XPS spectrum of the nonwoven/PAA/PEI-EtOx – sample 1.

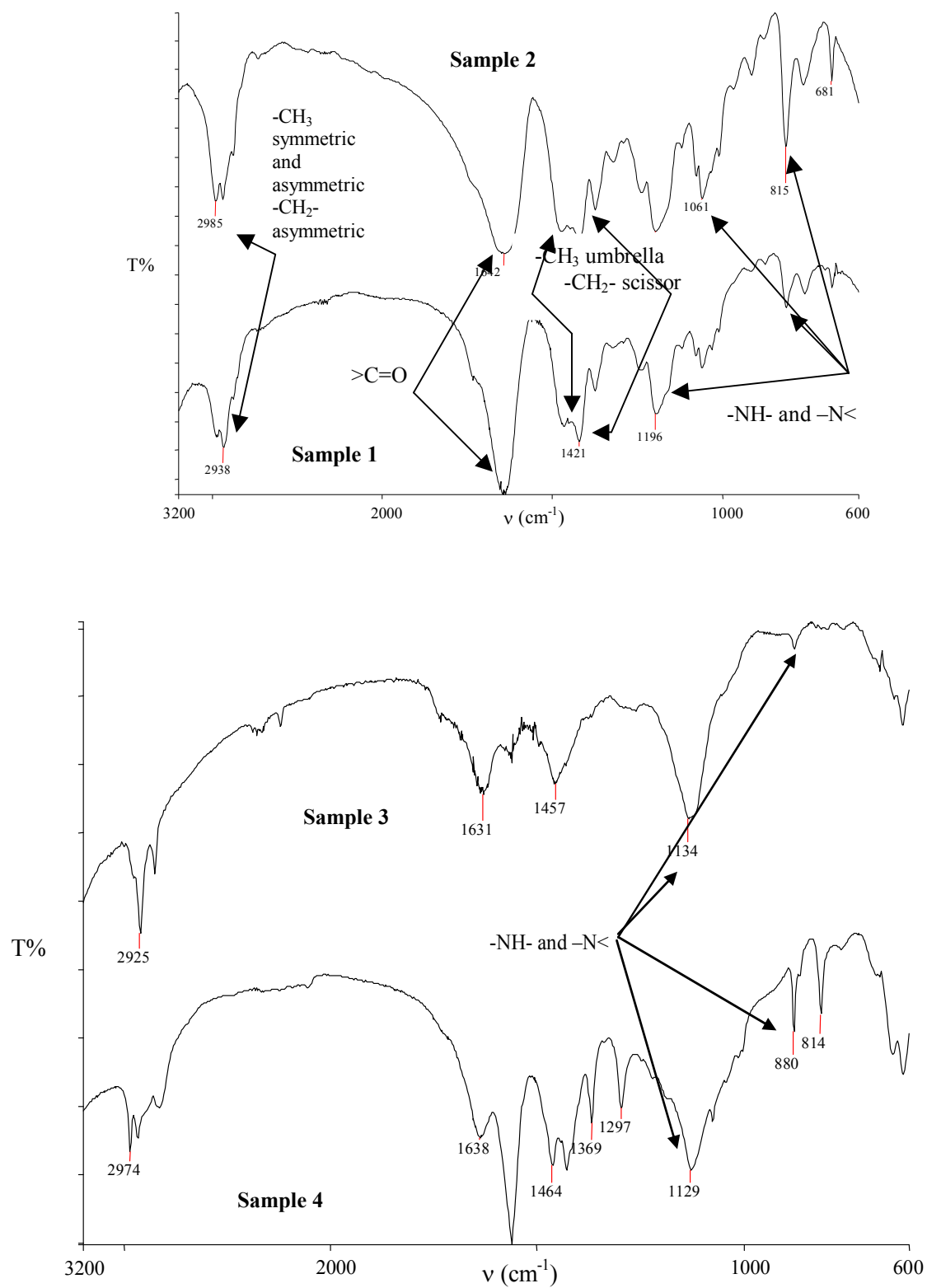


Figure 3. Transmittance FTIR spectra of PEI-EtOx and bPEI polymers in solid state before deposition (KBr pellets).

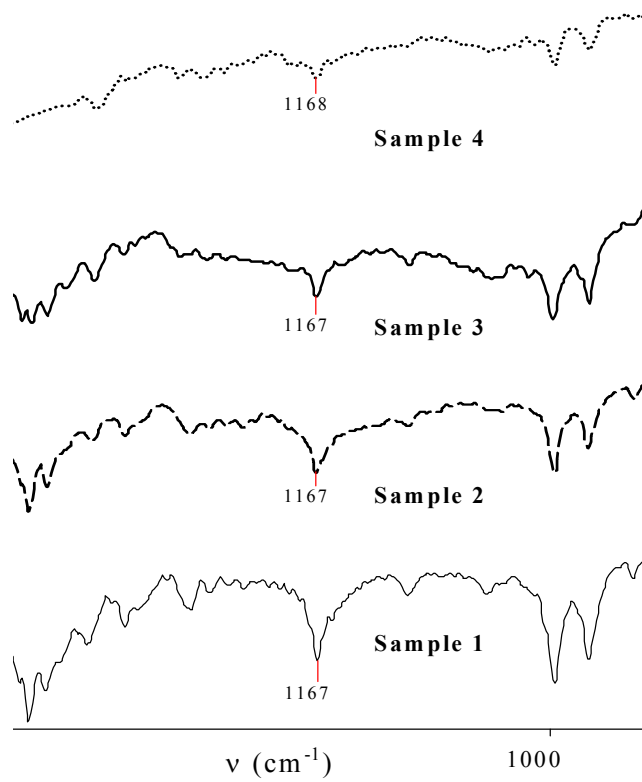


Figure 4. Partial reflectance FTIR spectra of the nonwovens after Samples 1-4 deposition. The characteristic signals at 1167 cm^{-1} are marked.

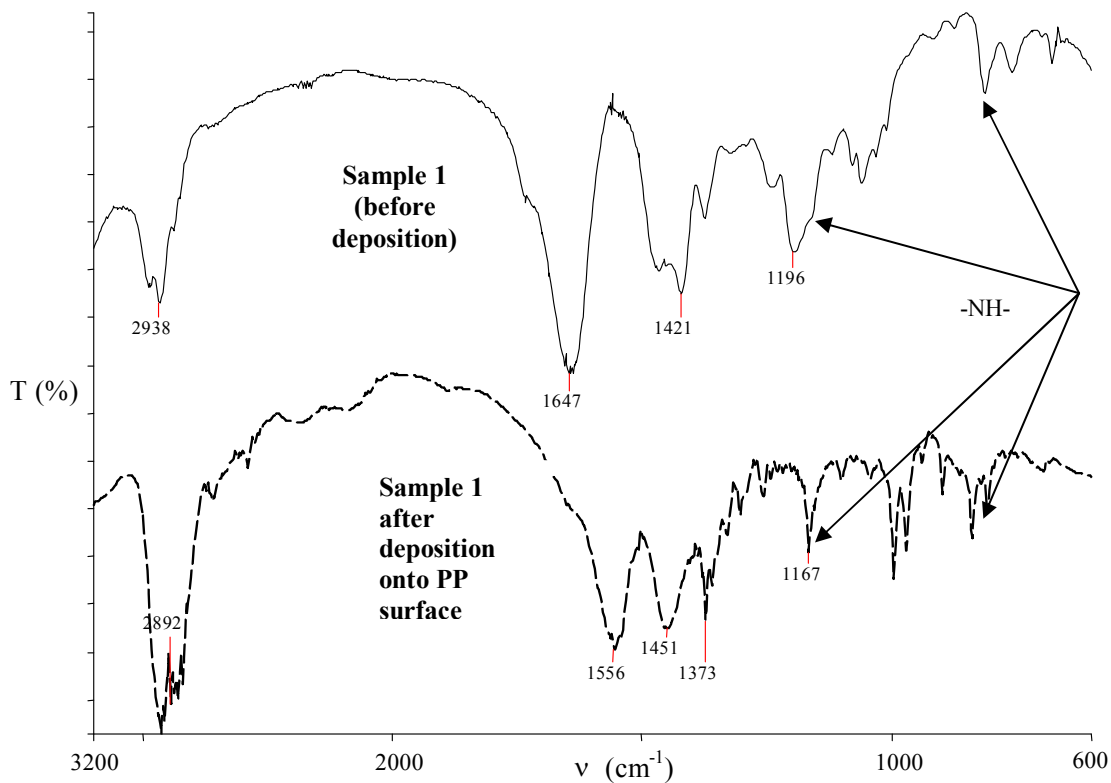


Figure 5. Transmittance FTIR spectrum of Sample 1 (PEI-PEtOx 5-5) before deposition and reflectance FTIR spectra of the surface after Sample 1 deposition.

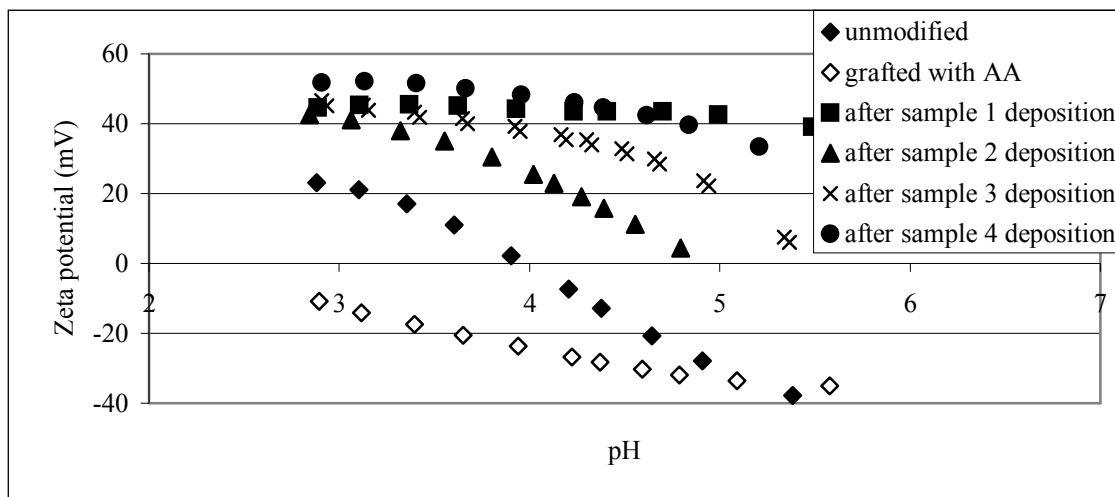


Fig. 6. pH dependence of zeta-potential for untreated and modified samples.

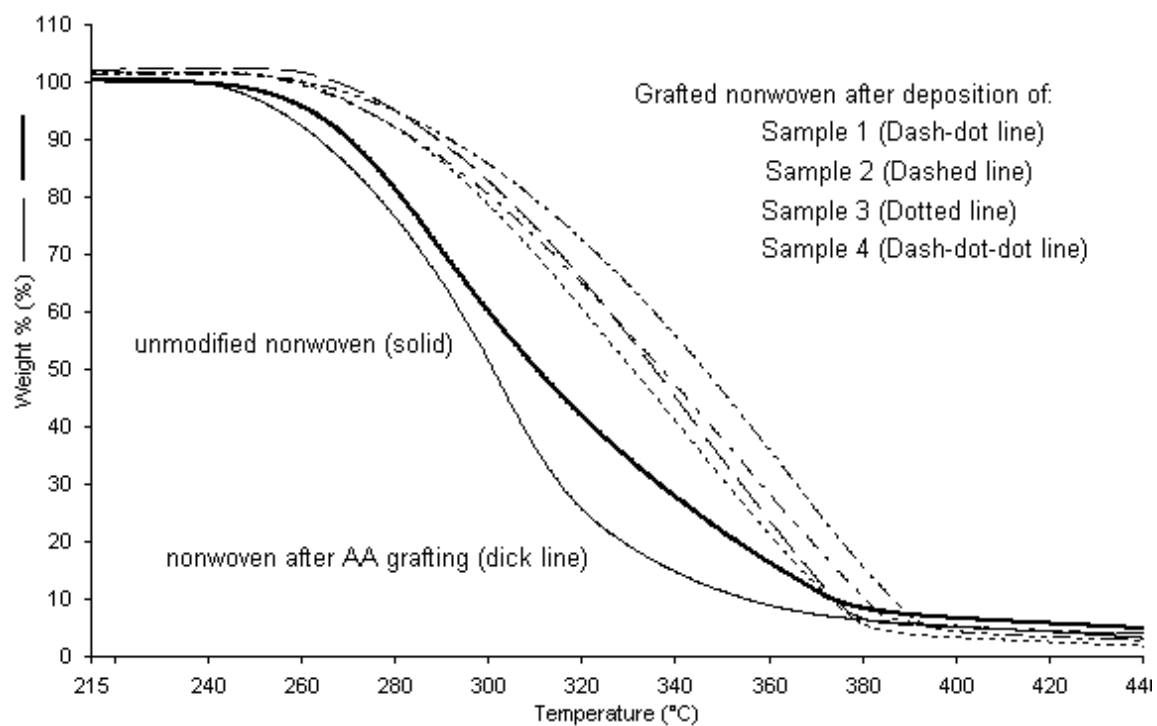


Figure 7. Thermograms for unmodified PP-nonwoven, AA-grafted nonwoven and the structures obtained after layer deposition.

Table1

Characterization data for PEI-PEtOx and bPEI polymer samples

DP of the main chain	DP of the branches	Degree of grafting,	Molecular weights	Code	Sample №
48	48	4%	11628	PEI-PEtOx 5-5	1
66	66	7%	35617	PEI-PEtOx 7-7	2
66	48	3%	7128	bPEI 7-5	3
96	48	7%	14784	bPEI 10-5	4

The first and last digits of the abbreviation codes multiplied by 10 give the approximately degree of polymerization of the polymer backbone and each of the branches, respectively.

Table 3

The electrostatic properties for nonwovens before and after modification

Structure №	The time of the charge half- disappearing (min)
unmodified	229.91
grafted with AA	4.89
1	13.50
2	12.14
3	14.12
4	18.90

Table 4

Temperatures of 50% mass loss for PP nonwovens before and after modification.

Structure №	T of 50% mass loss (°C)
Unmodified	304
grafted with AA	312
1	337
2	331
3	335
4	344

Table 5

Sorption of Cu²⁺ ions for nonwovens before and after modification

Structure №	Sorption of Cu ²⁺ ions (mg/cm ²) x 10 ³
unmodified	0.0
grafted with AA	0.5
1	1.8
2	2.4
3	2.4
4	3.6