

Application of the layer-by-layer Deposition Technique to Improve the Hydrophilic Properties of Polypropylene Nonwoven

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Introduction

Recently, intensive studies have been carried out on the preparation of nanostructured materials using a layer-by-layer deposition technique [1, 2]. The inventor and pioneer of this method, Gero Decher, has published a series of papers describing the technique in detail [3-8]. The formation of the first surface layer is usually performed by grafting, chemical modification or strong adsorption. For example, grafting of acrylic acid (AA) onto fiber activated polyester surfaces is an effective method for the deposition of the first acidic layer [9]. When the grafting of the first layer is complete, a polymer layer containing basic functional groups can be applied leading to the formation of a stable polymer complex onto which oppositely charged layers can be deposited. These results in the formation of new materials with surface characteristics that reflect the properties of the individual layers applied. Through an appropriate selection of the layer(s) to be deposited, the surface properties of the final product could be accurately controlled and thus matched to the requirements of the intended application.

Nowadays, the LBL technique is mainly applied to flat (non-textile) surface modifications in order to obtain materials with antireflective [10], anticorrosive [11], antibacterial [12], hydrophobic or hydrophilic properties [13, 14].

Polyelectrolyte nanolayers can be deposited onto various flat surfaces such as mica [15], glass [16-19], gold [20] or titanium [21], as well as textile fabrics such as: cotton fabric, polypropylene or polyester nonwoven, nylon fibers [22-29].

Improvement of the applicative properties of the fiber surface is of high commercial and industrial importance: polypropylene nonwoven is highly hydrophobic. In order to improve its wettability, a hydrophilic comb-like poly(ethylene imine) polymer (bPEI) has

been deposited onto the nonwoven PP substrates by the LBL method.

The chemical structure of the polymer and its architectural composition are presented in Figure 1. Poly(ethylene imine) has been used in a number of applications in biotechnology, nanomedicine and pharmacy [30-35]. It is, therefore, anticipated that a deeper understanding of the properties of these new composites. It will enable additional practical applications to be identified. Herein we report the results from our studies of three representative samples: sample 1- unmodified PP nonwoven; sample 2- PP nonwoven after grafting with AA; sample 3- PP nonwoven with a deposited bPEI layer. Their properties and behavior will be fully characterized and compared.

1. Experimental

1.1. Materials

Polypropylene nonwoven textile fabric (surface weight=27,9 g/m², average filament diameter=9,65 μm) was prepared by the melt-blown method (Cenaro-Lodz, Poland). The bPEI polymer was synthesized as described elsewhere [36-37]. It is a random sparsely graft polymer of general formula (EI)₆₆-graft-(EI)₄₈, where EI denotes ethylene imine units (see Figure 1).

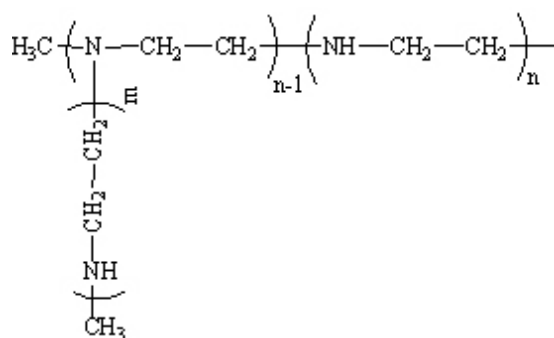


Figure 1: Comb-like poly(ethylene imine), $n = 66$, $m = 48$

The degree of grafting for this polymer was calculated to be approximately 21%. Its solubility in aqueous media are similar to those reported earlier for the linear poly(ethylene imine) (LPEI). Due to its linear, unsubstituted and flexible macromolecules, LPEI is insoluble in water at room temperature and dissolve in solution at 58.5°C to a hydrated state [38]. A water-solubility temperature around 60°C was previously determined for bPEI [37].

1.2. Measurements

- FTIR analysis

The modification of the PP nonwoven was confirmed by FTIR analysis. FTIR spectra were recorded using a Perkin-Elmer 2000 Fourier Transform Infrared (FTIR) instrument with KBr pellets. A Perkin-Elmer reflectance variable angle spectrophotometer was used to gather the specular reflectance FTIR spectra at 60°. The unmodified nonwoven fabric was used as a background.

- Surface wettability

Surface wettability was determined by measuring the contact angle (α) of a liquid droplet applied to the surface. A low contact angle between the fiber and the water indicates the high wettability of the substrate. Wetting is the initial process involved in water spreading. In this process the fiber-air interface is replaced with a fiber-water interface as shown in Figure 2. The forces in equilibrium at a solid-water boundary can be described by the Young-Dupre equation (1) [39]:

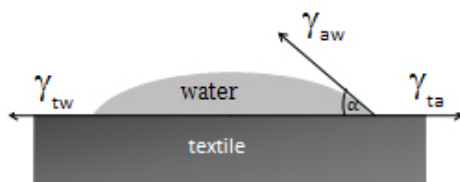


Figure 2: Contact angle of a liquid sample

$$\gamma_{aw} \cos \alpha = \gamma_{ta} - \gamma_{tw} \quad (1)$$

Where:

γ_{ta} - the surface energy between textiles (t) and air (a)

γ_{tw} - the surface energy between textiles (t) and water (w)

γ_{aw} - the surface energy between air (a) and water (w)

For our experiment, a water droplet with a volume of 5 μ l was applied to a sample which had been pre-conditioned ($T = 26^\circ\text{C}$, air humidity 29%, $t = 48$ h). Its enlarged image was observed and photographed using a microscope camera (Micro Ocular) and a program for processing microscope photos (Unlead Photo). The contact angle was calculated graphically using the Image J program.

- Capillarity

The rate of absorption of liquids by fabrics is affected by the nature and size of the small capillaries present in the textiles [40]. Capillarity has very important boosting function in process of sorption water. It happens because capillaries are able to spread H₂O in to areas outside wetting point. Capillarity was examined by applying a colored drop of 0,1% w/v potassium permanganate solution onto a flat surface section of the substrate. The sample was left undisturbed for 24 h, after which the colored fragments of fabric were removed and weighed.

- Moisture absorption

The tested samples were first conditioned for 48 h under the standard conditions ($T = 24,0^\circ\text{C}$, air humidity 36%) and then weighed and placed at maximum humidity ($T = 24,0^\circ\text{C}$, air humidity 99%) for 72 h. After reweighing the samples, the percentage moisture content was obtained from the difference between the two values, according to the following equation (2).

$$W = (Mw - Ms) / Ms * 100\% \quad (2) [41]$$

W- percentage moisture content

Ms- weight of the dry sample

Mw- weight of the wet sample

1.3. Modification of the PP nonwoven

The PP nonwoven was modified as described previously [22, 23, 25].

The nonwoven was activated in a solution of ammonium persulfate ($c = 20$ g/L, $t = 30$ min, $T = 80^\circ\text{C}$), under a nitrogen atmosphere.

In order to produce the first grafted AA layer, the activated PP nonwoven was dipped in the concentrated AA aqueous solution ($c = 52$ g/L, $t = 60$ min, $T = 80^\circ\text{C}$), again under a nitrogen atmosphere. The quantitatively determination of the average number of the acidic groups presented in the grafted AA layer is described elsewhere [36].

Prior to each operation (activated and grafting), the samples were rinsed thoroughly with distilled water [23]. After grafting, the samples were immersed in bPEI aqueous solutions (10-2 mol/dm³), at a temperature between 80-90°C.

2. Results

In order to confirm the modification of the PP nonwoven, FTIR analyses were performed. Figure 3 shows the transmittance solid state spectra of the bPEI polymer before deposition. The characteristic signals due to secondary (-NH-) and tertiary (-N<) amine groups were observed at $\nu = 1134$ and 880 cm^{-1} , respectively.

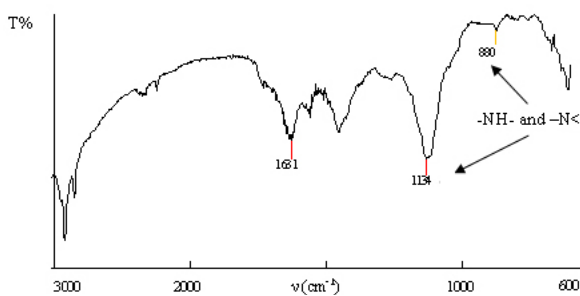


Figure 3: Transmittance FTIR spectrum of bPEI

FTIR reflectance spectroscopy (rFTIR) was performed on the surface after deposition. Comparing the rFTIR spectra of bPEI and the PP nonwoven, the change of the -NH- group signals is clearly apparent, with those of the nonwoven slightly shifted to 1167 cm^{-1} (see Figure 4). Since the reflectance spectroscopy was carried out using unmodified PP nonwoven as a background, the spectrum in Figure 4 indicates successful modification.

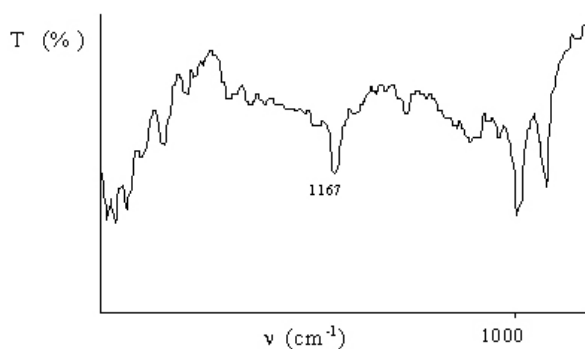


Figure 4: Partial reflectance FTIR spectrum of Sample 3.

- Surface wettability

Figure 5 shows a microscope image of a drop on the surface of unmodified PP nonwoven. The measured contact angle is 134° , which confirms the high hydrophobicity of this material.

For the modified samples (both grafted and post-deposition) the contact angle was impossible to measure due to the increased hydrophilicity of the samples.

- Capillarity

A drop of potassium permanganate (0,1% w/v) placed onto the surface of unmodified nonwoven remained intact. When this test was repeated with the graf-

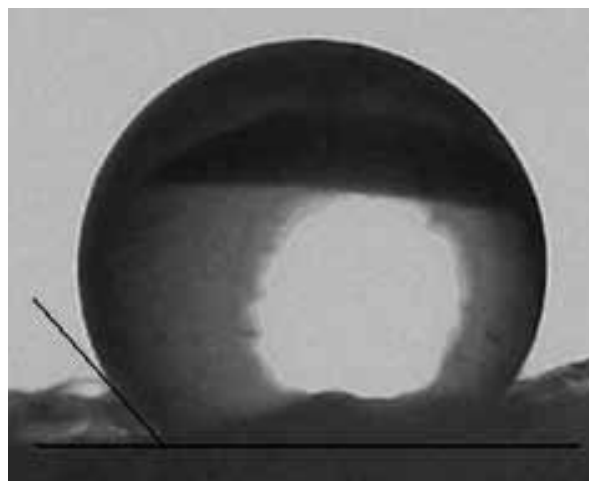
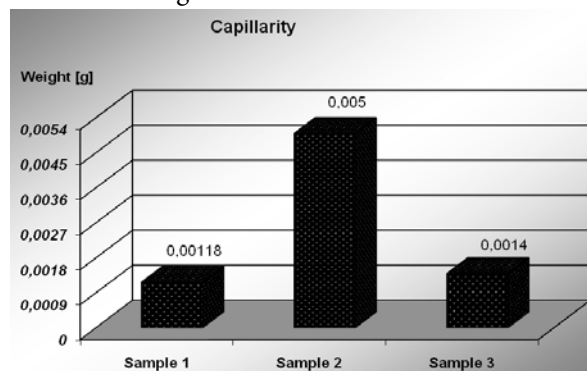


Figure 5: A drop of water ($5\mu\text{l}$) deposited onto Sample 1

ted sample and the sample after deposition of bPEI, the drop was quickly absorbed into the material.

The wet capillary area of each sample was weighed in order to make a direct comparison and the results are shown in Figure 6.



6: Result of capillarity for the Sample No: 1, 2 and 3.

Comparing unmodified and modified PP nonwoven, better capillarity properties were observed for the modified samples (Figure 6). Relative to sample 1, the mass of wetted area for sample 2 increased by several hundred percent, while for sample 3 the increase was approximately twenty percent. It should also be mentioned that samples featuring acidic layers are slightly more hydrophilic than those with amines. The carboxyl group is known to be somewhat more hydrophilic than the amino group, according to previous literature reports [42]. The molar water content, determined by van Krevelen, is also approximately 7% higher for the carboxyl group than for the amino group ($0.375 : 0.35$ mol/repeat unit).

- Moisture absorption

The most frequently determined parameter in moisture absorption tests is the weight of water absorbed by a sample during a given time.

From the data presented in Figure 7, it can be deduced that samples 2 and 3 show an approximately ten-fold increase in hydrophilicity (as measured by sorption). The results are consistent with the recently determined values of water retention for systems where poly(acrylic acid) and poly(4-vinylpyridine) were deposited onto polyester fabric [24]. The highest values were observed for the samples where the layers were deposited using the LBL technique.

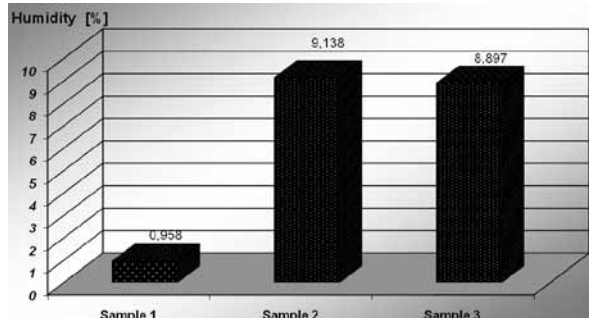


Figure 7: Results of moisture sorption for the Sample No: 1, 2 and 3.

Conclusion

This research confirms that the layer-by-layer (LBL) technique can be successfully utilized for the deposition of bPEI polymers onto PP nonwoven fabric, resulting in a sharp increase in the hydrophilicity of the PP nonwoven. The structures of the modified materials were verified by FTIR spectroscopy. The wetting properties of the textiles are significantly improved after deposition of bPEI. The contact angle, capillarity and moisture absorption measurements clearly indicated a radical increase in hydrophilicity for the samples featuring a deposited layer of bPEI.

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