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Short Communication

Formation of Interpolymer Complexes on Polypropylene Textiles *via* Layer-by-Layer Modification as Revealed by FTIR Method

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Abstract

Oppositely-charged polyelectrolytes such poly(acrylic acid) and poly(allylamine hydrochloride) have been deposited on a polypropylene nonwoven by the layer-by-layer technique. The complex formation of this modified material has been studied by FTIR spectroscopy. It has been found that external reflectance FTIR is an efficient technique for the identification of non-complexed or complexed carboxylic groups in the modified polypropylene material.

Keywords: Layer-by-layer technique, FTIR external spectroscopy, textile material, polypropylene, nonwoven

Introduction

The most important principle of the layer-by-layer (LbL) method consists in alternately depositing oppositely-charged layers of polyelectrolytes, which react between themselves owing to electrostatic forces. Nanolayer films are usually deposited using solution concentrations of several milligrams per milliliter. The adsorption step is followed by a rinsing or an excess removal procedure. The rinsing stage is used to avoid contamination with the next adsorption solution and to remove weakly adsorbed molecules. The coated material, which now possesses an outer layer of a polyelectrolyte, can now adsorb an oppositely-charged layer. The strong electrostatic attraction is the dominant factor in the adsorption of polyions. Multilayer structures may be composed of polyions, charged molecular substances or colloidal materials. Adsorption times per layer vary from minutes for polyelectrolytes to hours for some colloids.

Interpolymer complexes can be obtained as an effect of association of cationic and anionic polymers. The ion proportion can be stoichiometric or non-stoichiometric. The most important factors for the polymeric complexes' durability are their electrostatic attractions, but in addition, there can be hydrogen bonds, and van der Waals interactions.

Recently, the preparation of nanostructured materials using a layer-by-layer deposition technique has been the subject of much research effort [1-4]. Such materials are attracting a great deal of attention and have been widely investigated because of their potential applications, for example, as drug delivery systems or nanoreactors [1-2,5-6].

Direct demonstration of the polycomplex formation as being a result of a polyelectrolyte layer application on the fiber surface is not easy. In the literature, there are only a few attempts to describe the applicability of spectroscopic methods such as IR or UV-Vis for this purpose. Because of the character of the investigated material, only reflective techniques can be used. However, the results of these tests might be negative.

Wang *et al.* [7] did not manage to observe any changes in the IR spectra of the cotton fibers covered alternately with poly(styrene sodium sulfonate) (PSS) and poly(diallyldimethyl ammonium chloride) using the ATR method. It was, however, possible to assign the 226 nm band in the UV spectra and observe the absorbance increase at this wavelength when applying consecutive PSS layers. Dubas *et al.* [8,9] has identified in the ATR-FT spectra of the LbL modified silk, characteristic bands for PSS after depositioning 30 layers. In the investigation of the LbL layer deposition onto lignin-cellulose fibres, photoacoustic FTIR was also used [10]. The presence of the polyacrylic acid on polypropylene fibres, after grafting with acrylic acid, was proven using ATR-FTIR by Zhu and Hirt [11] but it has to be underlined that the degree of grafting was very high and reached 48 %. The creation of the polyion complex was observed using FTIR for the model system on a gold-coated silicon wafer [12]. According to our knowledge, there is no literature data on the creation of thin film polyion complexes in applied systems like textiles, analysed by FTIR.

In this work, we monitor the generation of poly(acrylic acid) and poly(allylamine hydrochloride) (PAA - PAH) polyion complex on polypropylene fibres using an external reflection FTIR method.

Materials and methods

Materials used

A non-woven, polypropylene substrate was prepared by the 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. Non-woven substrates were produced using low viscosity polypropylene (lvPP) granulates, completely free from additives (HL604FB) produced by Borealis AG, Austria.

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-averaged molecular weight (M_w = 145,000 g/mol) was determined by gel chromatography.

Poly(allylamine hydrochloride) (PAH) from Fluka (M_w = 70,000 g/mol and 15,000 g/mol) was used without purification.

Polyelectrolyte layer deposition

Polyelectrolyte layers were deposited as described previously [13]. Briefly: the non-woven material was activated 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, before grafting with concentrated acrylic acid (AA) (52 g/dm^3, t = 60 min, T = 80 °C, saturated with nitrogen). After grafting, the samples were immersed in an aqueous solution of the appropriate polyelectrolyte (10^{-2} mol/dm^3). Prior to each operation, samples were rinsed with distilled water.

Characterization

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 ÷ 700 scans). The unmodified, nonwoven fabric was used as a background for creating spectra of the modified nonwoven fabric. Spectra of the model PAA and PAA-sodium salt layers were performed for adequate layers deposited on aluminium slides.

pH-metric 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 M NaOH solution and then 75 ml of distilled water was added. The system was titrated by means of 0.01 M 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.

Results and discussion

Deposition of polyelectrolyte layers on the surface of polypropylene nonwoven fabrics

The surface of nonwoven polypropylene was modified with poly(acrylic acid) (PAA) as a negatively-charged layer and poly(allylamine hydrochloride) (PAH) as a positively-charged layer. The first layer was deposited on the surface of the fabric by grafting acrylic acid. Subsequent layers were deposited by polycomplex formation using the LbL technique according to reference [13]. The resultant system is shown in **Table 1**.

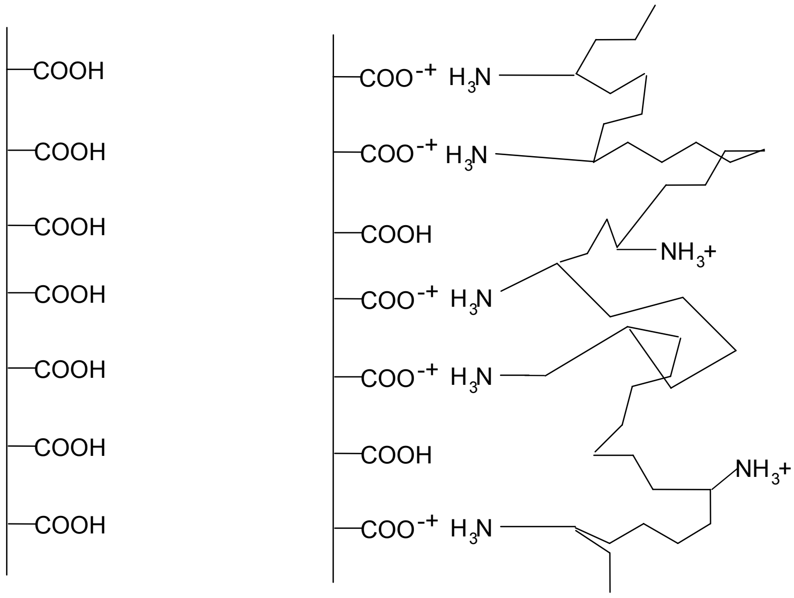
The chemical structure of the material after the first and second steps of modification is schematically shown in **Figure 1**. As shown in the scheme in **Figure 1**, carboxylic groups from the grafted polyacid become ionic as a result of complex formation.

Applications of external reflectance FTIR spectroscopy

The first step of the FTIR spectroscopic analysis, involved taking a spectrum of the unmodified PP unwoven fabric (Spectrum 1, **Figure 2**). Afterwards, spectra of PAA and PAA-sodium salt layers on aluminum slides were obtained (Spectrum 2 and 3, **Figure 2**). The latter two were formed as model layers including carboxylic groups in the non-ionised form (non-complexed) and ionised (complexed) form, which were expected in the investigated nonwoven substrate, after the grafting process, and after the LbL modification respectively.

Table 1 Composition of deposited layers.

Layer number			
Grafting	**Deposition**		
1	2	3	4
PAA	PAA-PAH	PP-PAH-PAA	PAA-PAH-PAA-PAH



PAA Polycomplex PAA - PAH

Figure 1 Poly(acrylic acid) in non-ionised and complexed form.

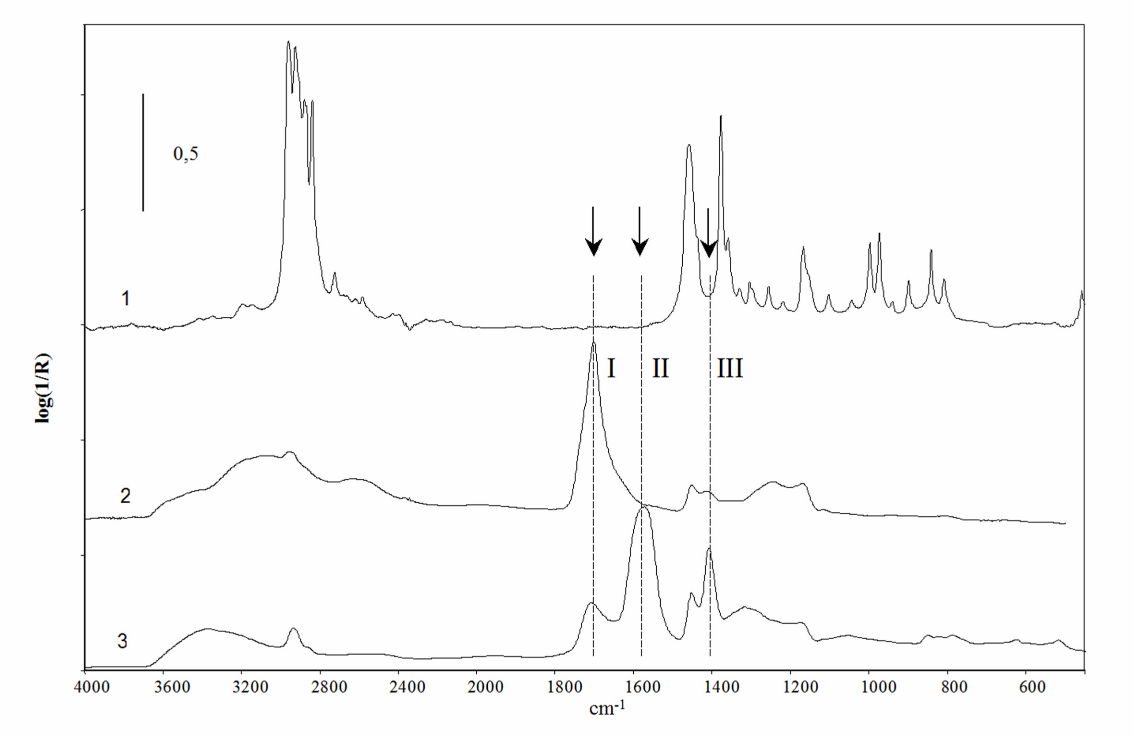


Figure 2 External reflectance FTIR spectra of: 1. unmodified PP nonwoven, 2. poly(acrylic acid) 3. sodium poly(acrylate).

It was concluded, that no signals originating from the polypropylene material were present in the range 2,000 - 1,500 cm^{-1}, in which one could expect bands coming from the ionised and non-ionised carboxylic groups, –COO^{-}. In the spectrum of the PAA layer, a strong signal originating from the –C=O group in the nonionic -COOH coming from polyacrylic acid with the maximum at 1,710 cm^{-1} (I) appears. In spectrum 3 of polyacrylate, there are bands at 1,590 (II) and 1,408 cm^{-1} (III), which correspond to symmetric and asymmetric vibrations of the –C=O group in the ionized –COO$^{−}$ group. Peaks corresponding to the residues of non-ionised carboxylic groups are also visible. It is visible that peaks I and II are localized in slightly different wavenumber ranges (**Figure 2**) and in both cases, they appear in a range in which they do not overlap with the signals coming from the polypropylene material. Signal III is located between the strong polypropylene signals and can be masked by these signals in the investigated complex objects.

Following these measurements, spectra of nonwoven PP after each modification step, were obtained according to the scheme presented in **Table 1**. Spectra of the samples obtained after different modification steps are shown in **Figure 3**. In the spectrum of the sample grafted with polyacid (1), there is a wide signal with the maximum at 1,710 cm^{-1} coming from the –C=O group in the uncomplexed –COOH group (1). In the spectrum of the sample with two layers (2) a signal corresponding to the –C=O of the complexed group (carboxylate) appears (II). Although peak I is also visible, it is significantly smaller than the corresponding peak in spectra 1. It can be concluded that peak II is related to the sequences of complexed PAA units and peak I comes from the separated PAA units as shown in **Figure 1**.

In the spectrum after modification stages 3 and 4, there are both types of signals visible, however, one can observe alternate changes in the proportions of signal I and II. Comparing spectra 1

- 4 the increase of signal II, testifies to the increasing amount of polycomplex. In the case where the final layer comes from the PAA, signal I dominates. However, when the final layer comes from PAH, signal I is much smaller but still visible.

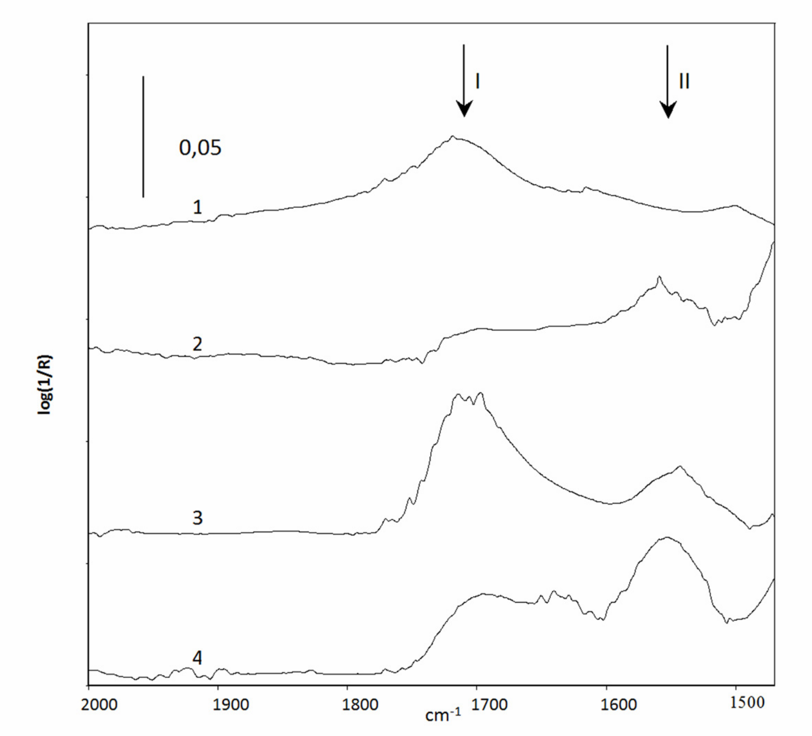


Figure 3 FTIR spectra of PP nonwovens with polyelectrolyte layers (1 – PAA; 2 - PAA-PAH; 3 – PAA-PAH-PAA; 4 – PAA-PAH-PAA-PAH).

The observed changes were compared with the pH-metric titration results obtained after each modification stage. The increment of acidic groups formed due to the modification was calculated from the difference in titration results between the unmodified (0) and modified samples and recalculated per gram of fiber. The calculated increase in the number of acidic groups is shown in **Figure 4**. The concentration of non-ionised acidic groups in sample 1 (grafted with acrylic acid) is contained within the ranges reported in literature [14].

In order to quantitatively assess the number of non-complexed 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 **Figure 4**. The comparison of the amount of accessible acidic groups indicated by the spectrometric technique and pH-metric titration is presented in **Figure 4** are in good accordance with the obtained results. This suggests that external reflectance FTIR is a reliable analytical method for nonwoven PP in determining the carboxylic acid group content in the modified material.

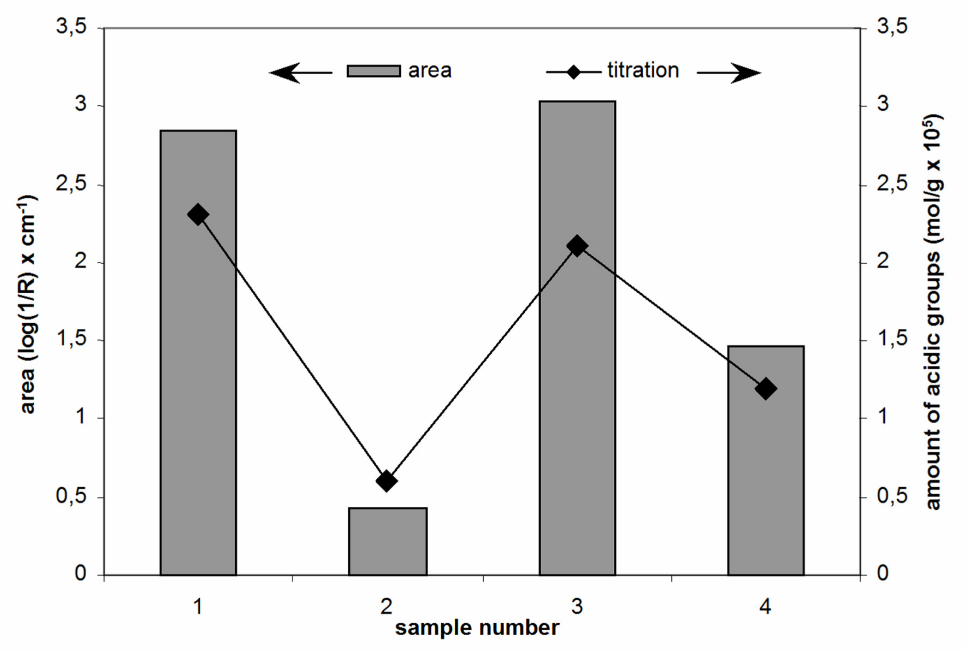


Figure 4 Comparison between average FTIR areas (signal I) and volumetric amounts of non-ionised COOH groups for samples with different number of layers.

Conclusion

A method of analysing PAA-PAH polycomplexes as a result of modification of PP fibers by the LbL method has been demonstrated. External reflectance FTIR is an efficient technique for the determination of non-complexed or complexed carboxylic acid groups in the modified polypropylene material. The results of external reflectance FTIR measurements are consistent with pH-metric analysis.

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