Modification of Poly(ethylene terephthalate) Surfaces by Linear Poly(vinyl amine)

Ralph Wittke[a], Dierk Knittel[a], Robert Kaufmann[b], and Eckhard Schollmeyer[a]

[a] Deutsches Textilforschungszentrum Nord-West e. V. (DTNW), Adlerstraße 1, D-47998 Krefeld, Germany
[b] Deutsches Wollforschungsinstitut an der RWTH Aachen e. V. (DWI), Pauwelsstraße 8, D-52056 Aachen, Germany

Reprint requests to Dr. D. K.; Fax: (02151) 843-143; E-mail: info@dtnw.de, knittel@dtnw.de

Z. Naturforsch. **64a,** 653 – 657 (2009); received July 10, 2008

The feasibility of fixing linear poly(vinyl amine) (PVAm) onto the surface of a poly(ethylene terephthalate) (PET) foil is shown. Pretreatment of the PET foil for PVAm anchoring is UV irradiation generated by an excimer lamp ($\lambda = 222$ nm). Thereby newly formed COOH-groups are able to build up in situ an ionic double layer with PVAm by proton transfer. The properties of the modified PET foil like wetting performance and electric conductivity are significantly improved by this treatment.

Key words: Surface Modification; Poly(ethylene terephthalate); Poly(vinyl amine); Polyelectrolyte; XPS.

1. Introduction

Poly(ethylene terephthalate) (PET) foils are used in many areas like packaging or electronic industry. Many methods are known to modify the surface of a PET foil, which is relatively inert in general, to induce new properties. High-energy irradiation with UV and laser excimers or plasma treatment have been investigated for the activation of the PET surface to change the physical or chemical performance [1 – 3]. Such treatments are able to create new COOH-groups or other oxygenated functions on the surface layer or to change the topography of the surface.

This work presents the functionalization of the PET surface irradiated in a first step by UV light (excimer source) followed of a second step by treatment with strongly polar amino compounds like linear poly(vinyl amine). The changed surface properties are analyzed and possible applications are discussed.

Poly(vinyl amine) and its chemistry is known from paper technology. It is used as a cationic polyelectrolyte to increase the tensile strength of paper products [4, 5].

2. Results and Discussion

After irradiation and finishing with poly(vinyl amine) the PET foil showed an average increase of 0.09 wt% equivalent to 20 μmol amine monomer unit per g foil.

The amino functions anchored onto the PET surface were identified by wet chemical analysis using a specific colour staining test [6].

The surface of the UV-irradiated and additionally PVAm-functionalized PET foil was assessed by XPS measurements for functional recognition (compare [7a]). Figure 1 gives an overview spectrum of a PVAm-functionalized PET foil. In addition to the expected main signals for carbon (285 eV) and oxygen (530 eV) the nitrogen incorporated can be detected by a significant signal at ~ 400 eV. Also impurities of zinc, fluorine and chlorine due to foil preparation are seen as small signals. For assignment of the values literature data were used [7b].

Table 1 shows the chemical composition of different pretreated PET foils and the binding state of carbon, oxygen and nitrogen as given by XPS. The bond energies are put in parentheses.

Figure 2 shows the high resolution $N_{(1s)}$ spectrum of the PET foil modified with PVAm. Due to their chemical shift several nitrogen functions have been assigned to the $N_{(1s)}$ photo lines. The $N_{(1s)}$ photo line with a bond energy of 398.8 eV can be assigned to amine groups, the photo line with a bond energy of 399.9 eV represents nitrogen in an organic matrix (possibly an

Atomic percentage of carbon	C-H, C-C, C-C$_{arom}$	C – O	C-OOR
PET (untreated)	76.0 (285.0)	14.1 (286.0)	9.1 (288.9)
PET (irradiated)	62.3 (285.0)	21.5 (285.5)	16.2 (288.9)
PET (with PVAm)	72.4 (285.0)	19.1 (286.6)	8.6 (289.1)
Atomic percentage of oxygen		O=C	C-O-C
PET (untreated)		– (532.1)	– (533.4)
PET (irradiated)		47.8 (530.7)	52.2 (532.2)
PET (with PVAm)		51.2 (530.6)	40.3 (532.2)
Atomic percentage of carbon	N-C,	N-C	N-C
PET (untreated)	–	–	–
PET (irradiated)	–	–	–
PET (with PVAm)	70.7 (398.8)	22.2 (399.9)	7.1 (400.9)

Table 1. Elementary composition and binding states of untreated, UV-irradiated and with PVAm modified PET foils. Bond energies are put in parentheses.

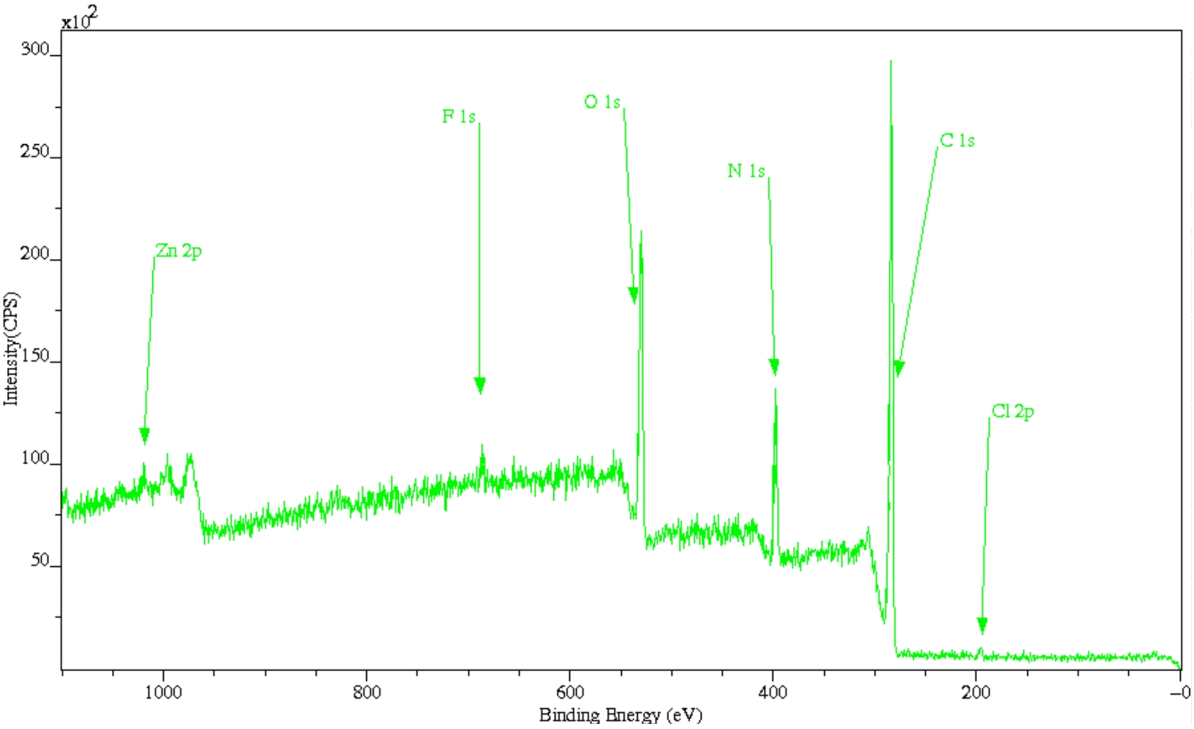

Fig. 1. Overview XPS spectrum of the PET foil functionalized by PVAm.

amide function), and the photo line with a bond energy of 400.9 eV can be assigned to ammonium groups [7b].

To check the quality of the PVAm finishing and also as an example for possible application, the modified PET foil was dyed. Intracronred, a reactive dyestuff for cotton or wool, was used as an indicator which forms covalent bonds with the amine groups fixed onto the PET surface. Figure 3 gives the impression of the PET foil, reactively dyed with intracronred. The colorimetric data of the reactive dyeing are presented in Fig. 4 as remission spectra and as Kubelka-Munk functions.

To characterize the wetting behaviour the contact angle between foil surface and water was determined.

Table 2. Contact angles at the PET foils.

Sample	Contact angle [°]
Extracted PET foil as control value (original)	71
UV-excimer-irradiated PET foil	53
PET foil modified with PVAm	60

Table 2 shows the values for the different PET foils, proving better wettabiliy.

From each extracted and climatized foil [original, irradiated and functionalized with poly(vinyl amine)] the electrical surface resistances according to German standard DIN 54345 were determined (Table 3).

The values of the surface resistances of the original as well as the irradiated PET foils exceed the teraohm

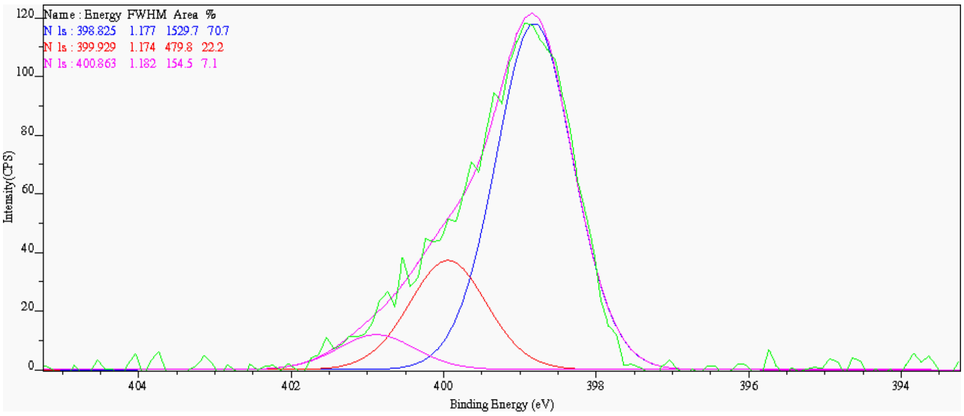

Fig. 2. $N_{(1s)}$ spectrum of a PET foil modified by anchored PVAm.

Table 3. Resistances of the different modified PET foils.

Sample	Resistance [TΩ]
PET foil (original)	> 1000
PET (excimer irradiated)	> 1000
PET (with PVAm)	0.01

Fig. 3. Functionalized PET foil dyed with a reactive dyestuff.

range of the measuring instrument (up to 100 TΩ). Compared to the samples without PVAm linking, the surface resistance of PVAm-modified surfaces is decreased by several orders of magnitude.

The PET surface can be treated by UV excimer irradiation to create a pre-ionic matrix for linking the polyelectrolyte PVAm, thus introducing new physical and chemical functions. The in situ formed complex between carboxylate groups, generated by UV irradiation on the PET surface, and ammonium ions, emerged from PVAm, can be defined as a polyelectrolyte complex or solid state simplex.

XPS measurement shows the chemical composition and the binding state of the functionalized PET surface (foil). Supported by literature values the nitrogen functions generated by PVAm anchoring as amine, ammonium and N in organic matrix can be assigned. The new functionalized surface possesses sufficient free amine groups to operate as an electrophilic centre. So the surface of PET modified with PVAm is available for "amine chemistry". In this context, quaternisation of the amine groups is possible to create a bacteriostatic effect. Also a reaction with nucleophilic centres like chlorotriazinyl- or vinyl sulfonic linkers of reactive dyes offer new perspectives. Other typical reactions with the fixed amine groups are possible.

Figure 5 suggests a chemical model of the anchoring of PVAm onto the PET surface. The model considers the statistical ratio between free amine to (binding) ammonium groups. The shaping of polymer loops is according to a model in paper chemistry, where similar structures of branched polyelectrolytes are formed.

3. Conclusion

The possibility to functionalize the PET surface (foil) with linear PVAm has been proved. The available amine groups were indicated qualitatively by specific staining tests. Characterization of at least three nitrogen species bound to the PET surface has been performed by XPS measurements. In spite of the low amount of add-on a hydrophilic effect was created and the surface resistance was highly decreased. Thus the modified PET foil imparted a distinctive improvement of the antistatic behaviour compared to the original foil. The decreased surface resistance can be explained by the ability of PVAm to retain moisture and improve the dissipation of electric charges.

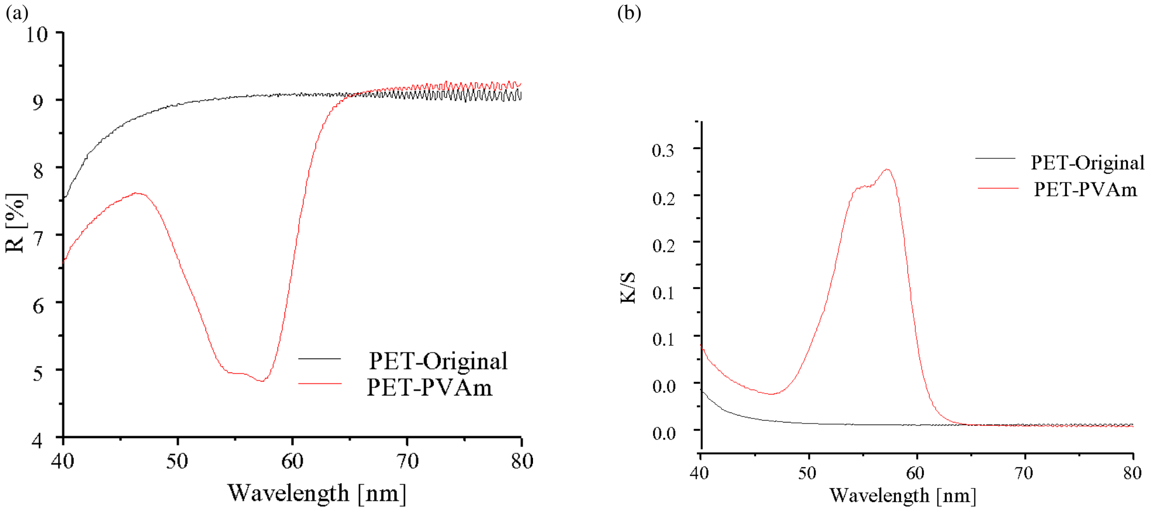

Fig. 4. Reflection data (R) and corresponding K/S values of the (a) treated and (b) reactively dyed PET foil.

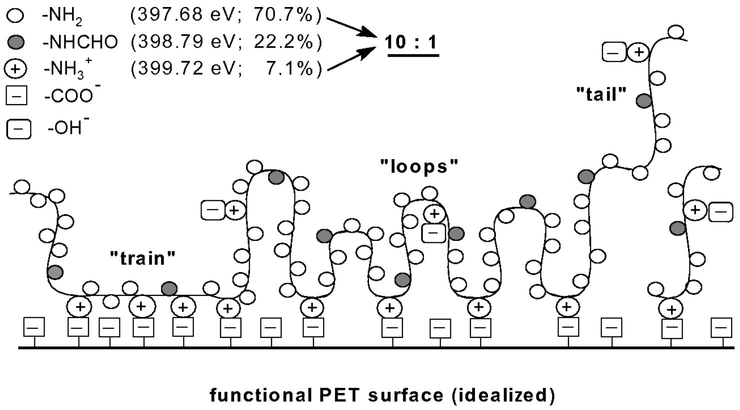

Fig. 5. Statistical model of the ionic linkage of a poly(vinyl amine) chain on an irradiated PET surface.

4. Experimental

4.1. Equipment and Chemicals

PET foil: thickness 36 μm, 50 g/m^2 (Hostaphan® RN36, Mitsubishi-Polyesterfilm).

Poly(vinyl amine): 95% hydrolyzed, desalted by ultrafiltration, 22 wt% solution, average molecular weight 380000 g/mol (Lupamin® 5095, BASF).

Intracronred®: reactive dyestuff (Yorkshire).

Colorimetric measurements: Datamaster DC 3880 (Datacolor), KrCl excimer lamp (Blue Light BLC 222/300, Heraeus Noblelight), $\lambda = 222$ nm, 6000 J/cm^2.

Resistivity measurements: Resistomat Type 2408 (Burster).

XPS measurement: Ultra Axis$^{\text{TM}}$ Spectrometer (Kratos Analytical).

Samples were irradiated by an Al K$_\alpha$ 1,2 beam (1486.6 eV). Spectra were collected with 144 W (12 kV × 12 mA); reference line: aliphatic/aromatic carbon (C-C, C-H or C$_{\text{arom}}$) of C 1s photo line by 285 eV. The spectral resolution of the ester carbon atom of PET is ≤ 0.68 eV for the highest resolved spectrum. The elementary contents are given in atomic-%. The information depth for polymeric materials using this analytical method is approx. 10 nm.

4.2. Treatment of the PET Foils

Each PET foil (10 cm^2) was purified by Soxhlet extraction with a mixture of MeOH/H$_2$O (1 : 1) for 24 h. Prior to irradiation the foils were climatized (22 °C, 65% rel. humidity) and weighed. Irradiation was performed for 10 min in ambient atmosphere with UV light at 222 nm on both sides of the samples, respectively. Due to the energy impact carboxylic groups were created which were converted into carboxylate groups by caustic soda solution (0.1 mol/l). The cationic dyestuff Basic Blue 3 was used for staining and for qualitative characterization of the carboxylate groups formed [8].

Following irradiation the PET foils were immersed in 200 ml of a solution of PVAm (1 wt%) at pH 10.8 for 24 h. 20 μl of a nonionic surfactant were added to this treating solution to improve wetting of the PET surface. As final treatment the foils were extracted for 24 h under the same conditions as described before, climatized and weighed.

4.3. Analysis

In addition to weight determinations of the treated foils other methods were used for characterizsation:

- Wet chemical verification for the presence of amine groups by the reaction with hypochlorous acid forming N-haloamine on the modified surface. After rinsing of the treated foils they were immersed in an iodide/starch solution to release iodine (identified by the blue starch complex) [6].
- Dyeing of the surface with the reactive dye Intracronred®.
- Colorimetric analyses to determine the reflection and K/S-values of stained samples.
- Measuring of contact angles with Microscope G 40 (Krüss).
- Electrical surface resistance measurements.

Acknowledgement

We wish to thank the Ministry for Science and Research of the the country of Northrhine-Westphalia, FRG, for financial support. This support was granted within the project ‘DTNW/Support for attainment of further funds’. The authors express their gratitude for the supply of research chemicals to BASF.

[1] T. Bahners, D. Praschak, and E. Schollmeyer, Appl. Phys. A **71**, 577 (2000).
[2] D. Knittel and E. Schollmeyer, Polym. Int. **45**, 103 (1998).
[3] T. Bahners, E. Schollmeyer, and K. Opwis, Chem. Fibers Int. **54**, 116 (2004).
[4] M. Rübenacker, R. Lorz, R. W. Auhorn, and E. Esser, Das Papier – Science and Technol. **1**, 39 (2001).
[5] BASF AG, Polyvinylamine, Company-Information, Ludwigshafen 2004.
[6] R. Wittke, Darstellung und Untersuchung funktionalisierter Polymeroberflächen, PhD thesis, University of Duisburg-Essen 2005.
[7] a) C. Wagner, W. Riggs, L. Davis, and J. Moulder, Handbook of X-Ray Photoelectron Spectroscopy (Ed. G. E. Muilenberg), Perkin Elmer Corp., Eden Prairie, Minnesota 1995; b) R. Kaufmann and H. Höcker, GIT Fachz. Lab. **4**, 348 (1984).
[8] D. Praschak, T. Bahners, and E. Schollmeyer, Appl. Phys. A **66**, 69 (1998).