

# Modification of Low Energy Polymer Surfaces by Immobilization of Fluorinated Carboxylates with Zirconium-Based Coupling Agents

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**ABSTRACT:** After the photochemical generation of carboxylates onto surfaces of several aromatic polymers, complexes based on zirconyl-(IV)-acetylacetonate are immobilized. These zirconium compounds tend to form strong bonds to carboxylates. Subsequently, zirconium modified surfaces are treated with solutions of a highly fluorinated lithium carboxylate yielding oil- and water-repellent surfaces. It is shown that combined with excimer-UV-laser-

induced micro structuring, the treatments lead to super-repellent surfaces showing contact angles of water up to 160°. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 94: 789–795, 2004

**Key words:** excimer lamp; super-repellent; polyesters; metal-polymer complexes; surface

## INTRODUCTION

Modification of polymer materials by physical and chemical approaches is an active area. The modification of polymer surfaces is of especially high interest. Surfaces with high water and oil repellency are needed for many applications such as textile materials, antifouling coatings, and many more. To achieve this, surface modification techniques aim at the generation of low surface tensions. At the same time, it is desired that the surface modification does not influence bulk properties. Classical surface modification techniques such as chemical or electro chemical refinements or various dipping processes are more and more replaced by modern surface techniques such as, for example, corona or plasma discharge, electron beam, or various photonic techniques. To achieve excellent oil repellency, the employment of highly fluorinated components is mostly irreplaceable. Polytetrafluoroethylene (PTFE), for example, shows surface tensions of 19 mNm<sup>-1</sup>; to achieve lower surface tensions, interfaces must be generated that are enriched with more CF<sub>3</sub> groups than for PTFE. Thünemann reported strategies for preparing polyelectrolyte-surfactant complexes with fluorinated surfactants on the basis of self-organization to create surfaces with surface tensions down to 6 mNm<sup>-1</sup>,<sup>1–4</sup> but this concept is limited to polyelectrolytes.

In this article a concept is shown which allows immobilizing highly fluorinated carboxylated surfactants on the surfaces of various polymers as, for example, poly (ethylene terephthalate) (PET), polyetherimide (PEI), polyetheretherketone (PEEK), aramides, or polyethylene, yielding highly repellent surfaces. By broadening this concept by establishing microstructures on the polymer surfaces, even super repellent properties will be achieved.

## EXPERIMENTAL

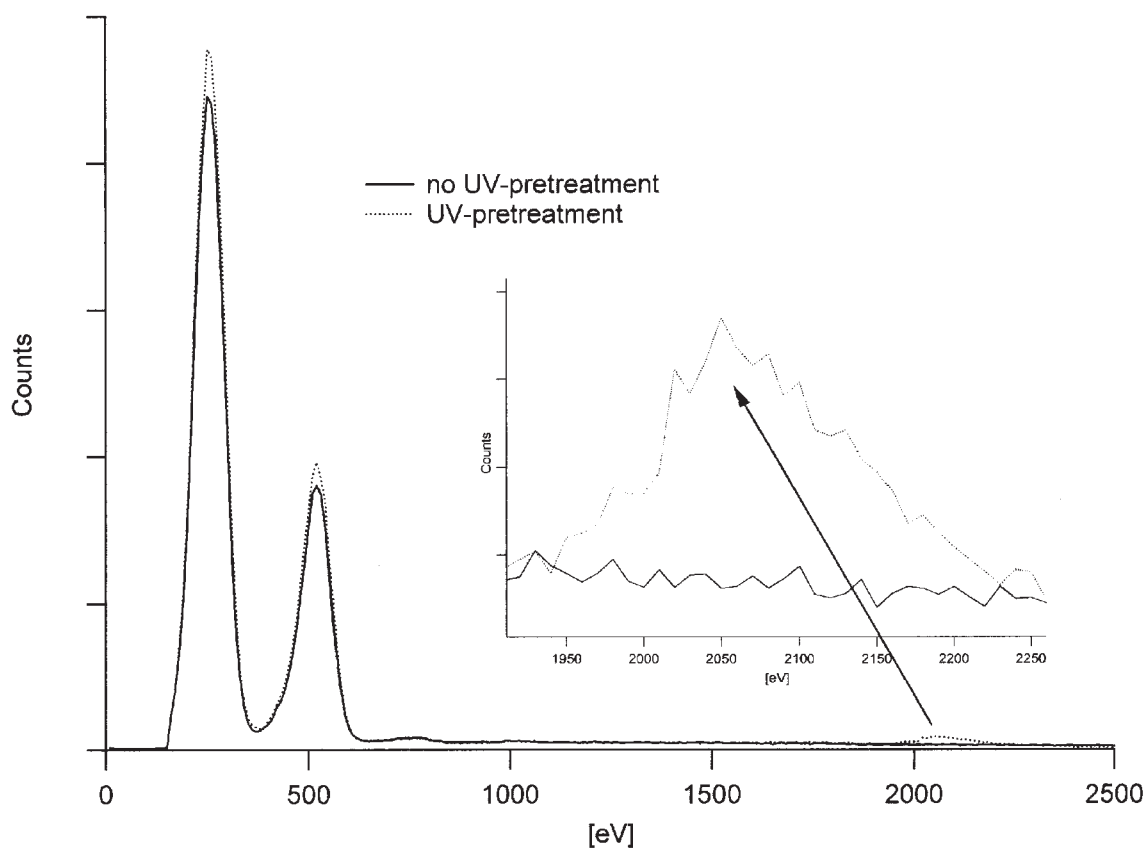
### Materials

Polymer substrates PET, PEI, PEEK, Nomex, and LDPE were received from Goodfellow (Bad Nasheim, Germany). Zirconyl-(IV)-acetylacetonate (Fluka, Germany) and Zonyl FSA (Aldrich; Taufkirchen, Germany) were used as delivered by the supplier.

### Light sources

A quasi monochromatic excimer lamp (BlueLight Härtingsmodul BLC 222/300, Heraeus Noblelight; Hanau, Germany) emitting at 222 nm served as light source. It is equipped with one KrCl\* tube of 30 cm length. Another excimer lamp was used emitting at 172 nm (Xe<sub>2</sub>\*Excimer-UV-Laborsystem Heraeus Noblelight). Microstructures were achieved using a KrF\*-excimer-laser-system LPX 200 (Lambda Physik; Goettingen, Germany).

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**Figure 1** EDX-spectra of poly (ethylene terephthalate) film after treatment with the zirconium complex.

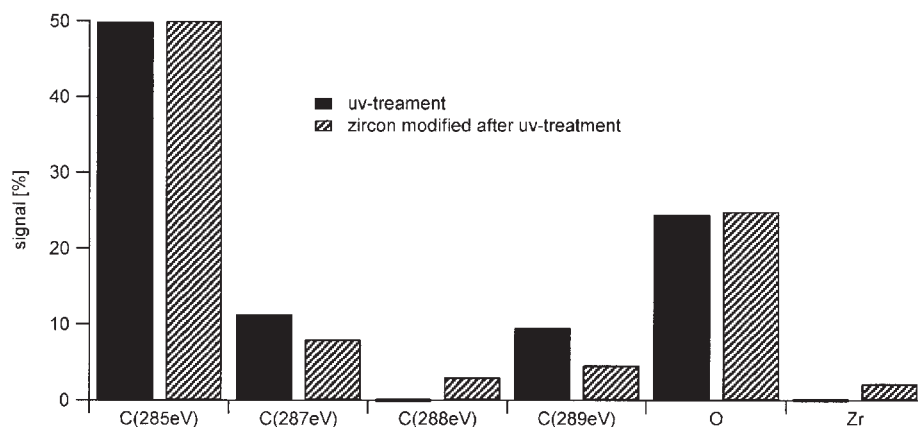
### Analyses

Contact angle measurements were made using a Krüss (Hamburg, Germany) G40 system with distilled water, methylene iodide, and ethylene glycol as testing liquids. Based on these results, surface energies were calculated with the method of Owens, Wendt, Rabel, and Kaelble. XPS analyses were carried out p.p. by the German Wool Research Centre (DWI, Aachen). AFM analyses were made using a Nanoscope III, DI, Santa Barbara. FT-IR studies were carried out using a Biorad FTS 45 spectrom-

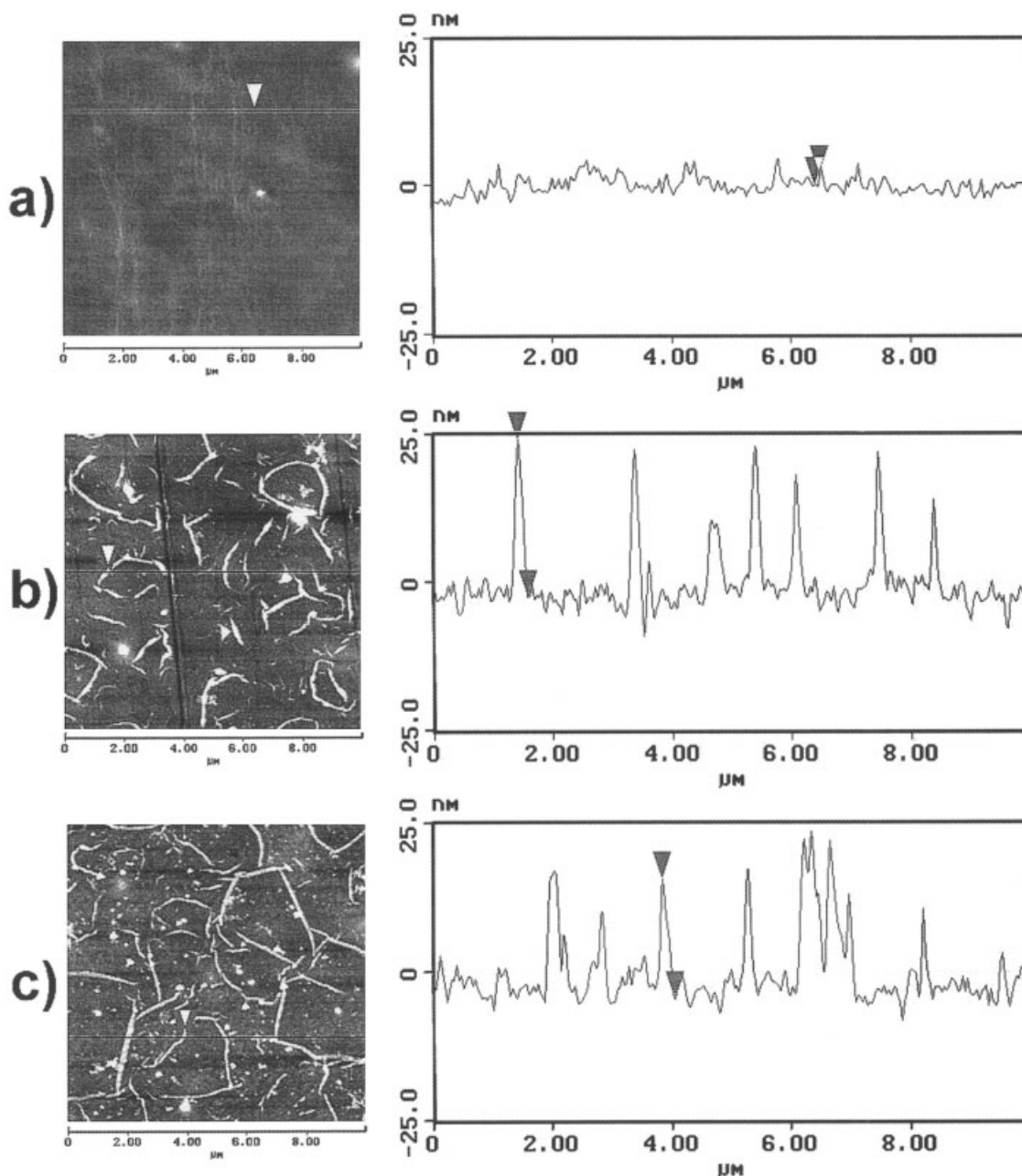
eter equipped with a silver-gate ATR-system (Ge-crystal; Specac, Kent, United Kingdom). The water repellency of textile materials was determined by the TEGEWA drop penetration test, oil repellency by an oil test following AATCC 118 (1972).

### Treatments

In the first step, the polymer films were irradiated with a constant distance of 3 cm between the light



**Figure 2** XPS analysis of UV-treated PET films with and without zirconium complex treatment.



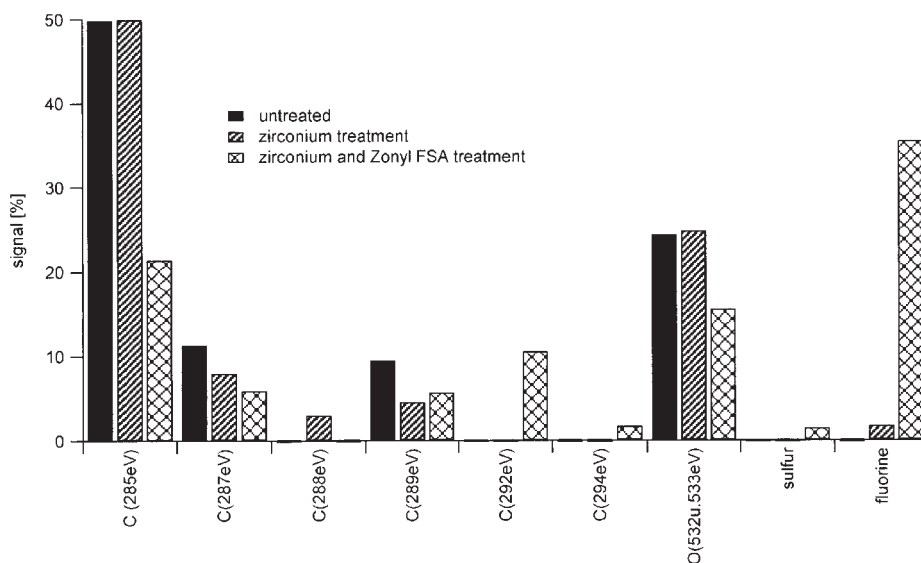
**Figure 3** AFM analyses (dorsal projection and profile) of PET films: a) unmodified film, b) UV-treated and modified with zirconium complex, c) additionally treated with Zonyl FSA.

source and the sample at ambient conditions. After the UV-treatment, the samples were immersed into an ethanolic solution of zirconyl-(IV)-acetylacetonate for at least 10 min and washed with ethanol intensively. After drying in an oven at 80°C, the films were immersed in a water-diluted solution of Zonyl FSA for 10 min, washed with water properly, and dried again.

Microstructures were achieved by exposure of the films to 20 laser pulses with energy of 90 mJ/cm<sup>2</sup>. The films were rinsed with ethanol during the irradiation to prevent the deposition of soot on the surfaces.

## RESULTS AND DISCUSSION

The first step of the treatments, the irradiation with UV-light, causes a hydrophilization of the polymer surface. This effect occurs due to photo-oxidation, which causes the generation of carboxylate functions.<sup>5,6</sup> Focused on poly (ethylene terephthalate) substrates, the generated carboxylates can be observed by increased wettability of the polymer surfaces and by dyeing with Astrazon-Blue-G that selectively dyes carboxylate groups on PET. Following a treatment of only



**Figure 4** XPS analysis of PET films untreated, treated with the zirconium complex only, and additionally treated with a highly fluorinated surfactant.

a few minutes, the contact angle of water decreases from  $75^\circ$  ( $38.4 \text{ mNm}^{-1}$ ) to about  $30^\circ$  ( $48.5 \text{ mNm}^{-1}$ ) for the treated one. As mentioned in the introduction, surface modifications must not change bulk properties. Normally, UV-treatments mean a significant destruction of the poly (ethylene terephthalate) due to bulk penetrating radiation. The KrCl\*-Excimer-UV-lamps emit monochromatic radiation at 222 nm, which is highly absorbed by the polyester, with a penetration depth of about  $1 \mu\text{m}$ . Therefore, no radiation reaches the bulk and only surface modifications are effected. Tests of the tensile strength show no significant decrease even for UV-treatments of more than 20 min.

After the generation of carboxylates at the polymer surfaces, the samples were treated with a zirconyl-(IV)-acetylacetonate solution for a certain time. It is known that most comparable zirconium compounds interact with carbonyl and hydroxy groups. Moles<sup>7</sup> describes the formation of strong covalent bonds, especially for carboxylates. The zirconium treated surfaces were investigated by EDX and XPS studies. The EDX spectra proved a successful immobilization at the polymer surfaces by a weak signal at 2.06 keV ( $L_{\alpha}$ ), which can be identified as zirconium (compare Fig. 1).

XPS-analysis allows study of the effect of the surface modification in greater detail. The data given in Figure 2 refer to the same sample and indicate a zirconium content of 2.2% at the very surface of the sample. Besides this evidence for the existence of a zirconium compound on the surface, an additional signal at 288 eV can be assigned to the acetylacetonate ligand, which indicates the immobilization of a still somehow complexed zirconium at the surface. The modifications of the films lead to topographic changes that can

be proven by AFM analyses. Figure 3a) and b) illustrate the AFM scans of the polymer surface before and after the treatment with the zirconium complex. The untreated films are very flat; the profile shows maximum differences in altitude of less than 5 nm (Fig. 3a). The surface characteristic changes distinctly due to the treatment with the complex. Figure 3b shows steep narrow ridges of 25 nm height and distances in the micrometer range.

As mentioned before, the zirconium compounds are able to form strong covalent bonds to carboxylates. By immersing the zirconium modified films into a solution of Zonyl FSA that consists of different highly fluorinated lithium carboxylates, these fluorinated surfactants can bind to the zirconium at the polymer surface. Figure 4 shows the XPS data of the Zonyl FSA treated PET film compared to the untreated and the zirconium treated ones. An amount of a fluorine component is detected at the Zonyl FSA treated surface. After the Zonyl-FSA treatment, the carbon signal that was identified as a signal of the ligand cannot be detected anymore. Therefore, it can be supposed that the surfactant molecules replaced the ligand. AFM analyses of the surfactant treated samples looked similar to that treated with the complex only (compare Fig. 3c).

The described surface modifications aimed at the generation of low-energy surfaces. The existence of a surface that is rich of  $\text{CF}_3$  functions should guarantee a decreased wettability. The illustration in Figure 5 shows the effects of the UV-treatment and the effect of the UV-treatment combined with the described treatments with the zirconium-complex and surfactant. The photo-oxidation process leads to an increase of

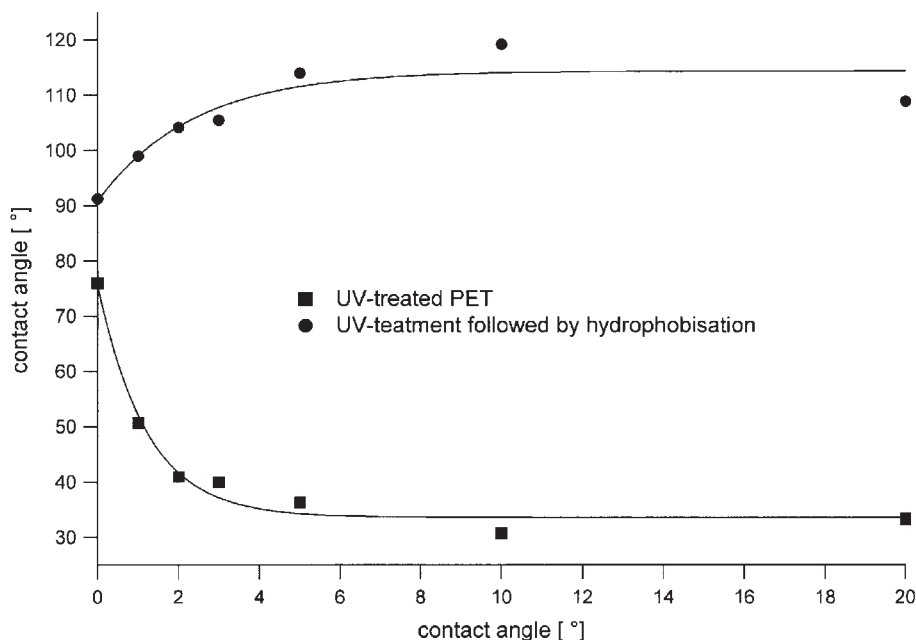


Figure 5 Contact angle of distilled water on a PET surface after UV-treatment and after additional hydrophobization.

the wettability, which means an increase of carboxylate functions at the surface depending on the irradiation time, with saturation after a few minutes. If the samples are treated with the zirconium compound, the increasing number of carboxylates means an increasing number of zirconium compounds, respectively, surfactants immobilized at the polymer surface. This leads to a decreasing wettability of the polymers with contact angles of up to 120°. Comparably low wettability can be achieved even with very strong diluted surfactant solution, concentrations of less than 0.15% with contact angles higher than 100°.

The same effects can be achieved for other polymers than PET. PEI, PEEK, or *m*-aramid are all aromatic polymers with a carbonyl function. For all of these

polymers, irradiation with UV-light of a wavelength of 222 nm at ambient atmosphere leads, among others, to the generation of carboxylate functions; therefore, the above described process will follow the same outline. Table I summarizes the resulting contact angles of water, Table II the surface energies measured for the different treatment stages. Polyethylene does not absorb strongly the radiation of 222 nm; therefore, a weak effect is found for this substrate. Irradiation with a shorter wavelength of 172 nm leads to photo-oxidations of the polymer surface, with ozone yielding to a higher amount of carboxylates. Polyethylene pretreated that way can also be hydrophobized as illustrated in Table I.

These results can be transferred to textile materials. Experiments were carried out with technical PET and *p*-aramid fabrics. The fabrics were all treated as described before. Table III summarizes the consequences

TABLE I  
Contact Angle of Different Polymers, Unmodified, Excimer UV Irradiated for 10 min and Hydrophobized in the Described Manner

Polymer	Contact angle [°]		
	Unmodified	Irradiated	Hydrophobized
PET	75	30	115
PEI	77	27	116
PEEK	72	26	114
<i>m</i> -aramid*	65	34	128
polyethylene	95	90	98
polyethylene (172 nm)	95	41	109

\* The *m*-aramid was used as calendered paper so it was not smooth.

TABLE II  
Surface Energies of Different Polymers, Unmodified, Excimer UV Irradiated for 10 min and Hydrophobized in the Described Manner

Polymer	Surface energy [mNm <sup>-1</sup> ]		
	Unmodified	Irradiated	Hydrophobized
PET	38.4	48.5	12.0
PEI	42.9	59.3	7.08
PEEK	43.8	60.1	13.8
polyethylene	33.2	33.2	21.9
polyethylene (172 nm)	33.2	33.9	18.1

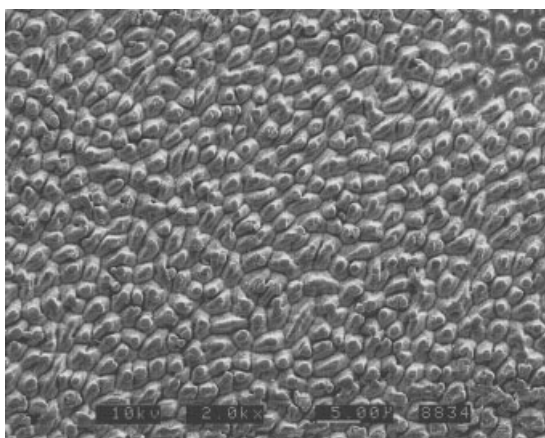
**TABLE III**  
Drop Penetration Time and Oil Test of Hydrophobized Textile Samples

	Fabric	Drop penetration time (TEGEWA)	Oil test (AATCC 118)
PET	unmodified	450s	0
	hydrophobized	>3600s	8
p-aramid	unmodified	25s	0
	hydrophobized	>3600s	7

for the parameters' drop penetration time and oil repellency that are of high interest for textile applications. Drop penetration time describes the time a textile needs to soak up a drop of water totally, and the oil test is a comparable test but with different oils instead of water. According to the testing standard, the best result in the oil test is denoted with an "8," which describes highly oil repellent fabrics. Table III proves that the presented concept yields excellent repellencies for textile materials.

### SUPER-REPELLENCY

Polymer films such as the PET films used are biaxially orientated. The treatment of such films, but also fibers with pulsed excimer-UV-lasers emitting a wavelength that is absorbed by the polymer, leads to the establishment of structured surfaces.<sup>8-16</sup> Other than for the excimer lamps, the pulsed radiation does not effect photo-oxidations and no chemical changes of the treated surfaces can be detected. Figure 6 shows a SEM micrograph of a PET film that was irradiated with a KrF\*-laser emitting with a wavelength of 248 nm. The characteristic surface structures depend on the number of pulses applied and the pulse energy (and the stretch ratio that was kept constant in the investigations). The structures are in a range of micrometers.



**Figure 6** SEM micrograph of a laser treated PET film

**TABLE IV**  
Effect of Different Treatments on the Contact Angle of Water on a PET Film

PET film	Contact angle of water
unmodified	75°
10 min treatment with UV-lamps	30°
Laser treated (20 pulses, 90 mJ/cm <sup>2</sup> )	24°
Laser treatment followed by 10 min treatment with UV-lamp	8-12°
... additionally hydrophobized	130-160°

Applying the above-mentioned hydrophobizing concept to these micro-structured surfaces, one can achieve super-repellent properties with contact angles of up to 160°. The effect of the different treatments on the wettability with water is summarized in Table IV. Corresponding to the Young equation<sup>17,18</sup> or with Cassie and Baxters theory,<sup>19</sup> we find higher wettability for the microstructured but hydrophilic surfaces, and additionally lowered wettability for microstructured and hydrophobic surfaces.

### CONCLUSION

The excimer-UV-lamps are excellent tools to achieve surface photo-oxidations of polymers such as PET, PEEK, PEI, or aramides. The advantage of these monochromatic light sources is in the low penetration depth into the highly absorbing polymers, which prevents destruction of bulk material. The irradiation of the polymers establishes carboxylates at the surfaces that allow immobilizing certain zirconium components from corresponding solutions by forming strong bonds to zirconium. These zirconium-modified surfaces are able to bond carboxylates as presented for the lithium carboxylate Zonyl FSA. This combined surface modification yields interfaces that are enriched with CF<sub>3</sub> functions and, therefore, show low surface tensions. An additional pretreatment with excimer-lasers leads to microstructured surfaces that show super-repellent properties due to the hydrophobic treatment. The described process allows creating highly oil- and/or water-repellent textiles, for instance.

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