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# Surface modification of poly(tetrafluoroethylene) by plasma pretreatment and adsorption of polyelectrolytes

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## Abstract

The adsorption of polyelectrolytes onto plasma-pretreated poly(tetrafluoroethylene) (PTFE) surfaces is reported as a method for fluoropolymer surface modification. PTFE was treated in oxygen or ammonia plasmas in order to introduce oxygen-containing and nitrogen-containing groups, respectively, which increase the surface free energy and make possible the adsorption of polyelectrolytes via electrostatic interactions. We investigated the adsorption of poly(diallyldimethylammonium chloride) and poly(sodium styrenesulfonate) on the plasma-pretreated PTFE. The modification effects were evaluated by means of contact angle and streaming potential measurements. © 1999 Elsevier Science Ltd. All rights reserved.

*Keywords:* Poly(tetrafluoroethylene); Plasma modification; Polyelectrolyte

## 1. Introduction

Poly(tetrafluoroethylene) (PTFE) has a unique position in the plastics industry due to properties such as excellent chemical resistance, high thermal stability and low dielectric constant. These properties are very important for specific applications [1,2]. In addition, PTFE is used for various applications because of anti-adhesive properties resulting from a low surface energy. However, the low surface energy presents considerable disadvantages where adhesion-related and wettability-related problems are concerned. Therefore, surface treatment is needed to improve the wettability of PTFE surfaces by promoting the formation of hydrophilic groups, which increase the surface energy. The most widely used surface modification techniques for fluoropolymers are chemical treatments, e.g. with sodium in liquid ammonia [3] and sodium naphthalene [4]. Low-pressure plasma treatments have become more and more important owing to their high efficiency [5]. The amount of toxic byproducts is low compared to wet chemistry. It has been shown that such plasma treatments can increase the PTFE wettability. The use of various gases such as $O_2$ [6–8], He [9], Ar [8, 10], $NH_3$ [11–15], $H_2$ [13] and $H_2/H_2O$ vapour [16,17] is described in the literature. The wettability produced is influenced by the plasma gas and the processing conditions, such as power, gas flow and treatment time. It was found that in the case of PTFE especially, ammonia plasma treatment renders the surface hydrophilic, leading to an important decrease of the water contact angle. However, it is a potential disadvantage that, in general, plasma-treated polymer surfaces are not stable over extended periods of time. For instance, the wettability with water decreases on storage in air after the plasma treatment [13,14]. The original hydrophobic polymer surface is partially restored in this restructuring process, called ‘hydrophobic recovery’. The driving force of the process is thought to be the minimization of interfacial energy and entropic effects [18]. Thus, plasma-modified surfaces used in applications such as coating and adhesive bonding must be processed further soon after the plasma treatment. It is also impossible to maintain the hydrophilic properties created by plasma treatment over a long period of time without any decrease because of surface restructuring.

The aim of our work is to combine plasma modification with an appropriate post-treatment in order to achieve a permanent hydrophilic surface modification. We think that the adsorption of polyelectrolytes on a plasma-pretreated surface is suitable for this requirement. The adsorption is driven by the electrostatic interaction between the surface charge created by plasma-pretreatment and the oppositely charged polyelectrolyte. If the adsorption is greater than the stoichiometry, the charge on the surface is reversed by ionic groups which do not interact with the oppositely charged plasma-pretreated surface. We assume that this excess of ionic groups in the outermost surface gives rise to an

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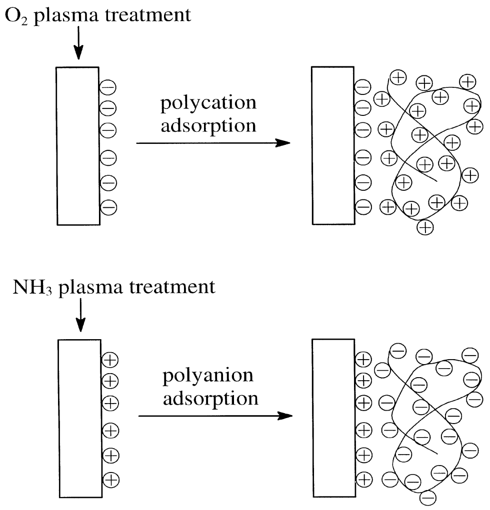

Fig. 1. Modification procedures: oxygen plasma treatment and adsorption of polycations (procedure A); ammonia plasma treatment and adsorption of polyanions (procedure B).

increase of wettability. Furthermore, the decrease in wettability with increasing storage time should be minimized.

The use of polyelectrolytes for fluoropolymer surface modification is described in Refs. [19,20]. Here, polyelectrolyte multilayers were built up on fluoropolymers. $H_2$/$CH_3OH$ plasma functionalization [19] and plasma polymerization of allylamine [20] were used to initiate the polyelectrolyte adsorption.

We investigated both modification procedures illustrated in Fig. 1. In order to create a negatively charged PTFE surface, an oxygen plasma was applied. On the other hand, an ammonia gas plasma was used to obtain a surface with basic properties. For the first investigations reported, we chose poly(diallyldimethylammonium chloride) and poly(sodium styrenesulfonate) as polyelectrolytes for surface modification.

## 2. Experimental

Commercial PTFE skived tape (PTFE Nünchritz GmbH) was used for this study. The PTFE samples were washed in ethanol and deionized water, and then dried at room temperature prior to use. Plasma modifications were carried out in the DARIUS 10 H/M plasma system (Buck plasma electronic GmbH). Treatments were performed under the following conditions: excitation frequency, 13.56 MHz; input power, 130 W; pressure, 15 Pa; gas flow rates, 32 scan ($O_2$) and 20 scan ($NH_3$); treatment time, 3 min. The plasma-treated samples were (a) rinsed three times with water and dried under ambient conditions, and (b) subsequently used for the polyelectrolyte adsorption studies, respectively. The adsorptions were carried out at room temperature in open beakers containing unstirred polyelectrolyte solutions. The pH of the polyelectrolyte solutions was adjusted with either HCl or KOH. Samples pretreated by the oxygen plasma were dipped into a solution of poly (diallyldimethylammonium chloride) (0.001 mol $l^{-1}$ in terms of monomer units; Fraunhofer-Institut für Angewandte Polymerforschung) for 5 min. After the ammonia plasma treatment, the samples were dipped into a solution of poly(sodium styrenesulfonate) (0.002 mol $l^{-1}$ in terms of monomer units; Aldrich, $M_w = 70000$). The modified PTFE samples were subsequently rinsed three times with water and dried at room temperature.

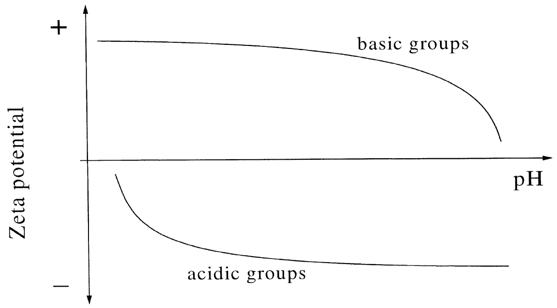

Fig. 2. Typical shapes of zeta potential versus pH curves according to Ref. [21].

Wettability measurements were performed using a Krüss G 40 contact angle measuring system. Advancing and receding contact angles were recorded while the probe fluid (water) was added to and withdrawn from the drop, respectively. The reported contact angle values are an average of at least 10 measurements over the entire sample surface.

Zeta potential measurements were made using an electrokinetic analyzer (A. Paar KG, Graz, Austria). The zeta potential values were determined in 0.001 mol $l^{-1}$ KCl solutions of varying pH values adjusted with HCl or KOH solutions.

## 3. Results and discussion

For the study of the differently modified PTFE surfaces we used an electrokinetic method of surface analysis, measuring the streaming potential. This is measured while the solid surface, e.g. the polymer surface, is in contact with electrolyte solution. Here, an electric double layer is formed at the solid–liquid interface. The origin of this double layer may be attributed to the dissociation of surface groups and the preferential adsorption of cations or anions on the surface. Thus, this method allows the characterization of the polymer surface with respect to polar groups formed by plasma treatment and polyelectrolyte adsorption, respectively. The zeta potential can be determined by streaming potential measurements. Fig. 2 shows typical shapes of the zeta potential–pH curves of acidic and basic polymer surfaces. In the case of acidic groups, the increase in negative zeta potential with increasing pH is due to the increasing number of dissociated groups. Complete dissociation of

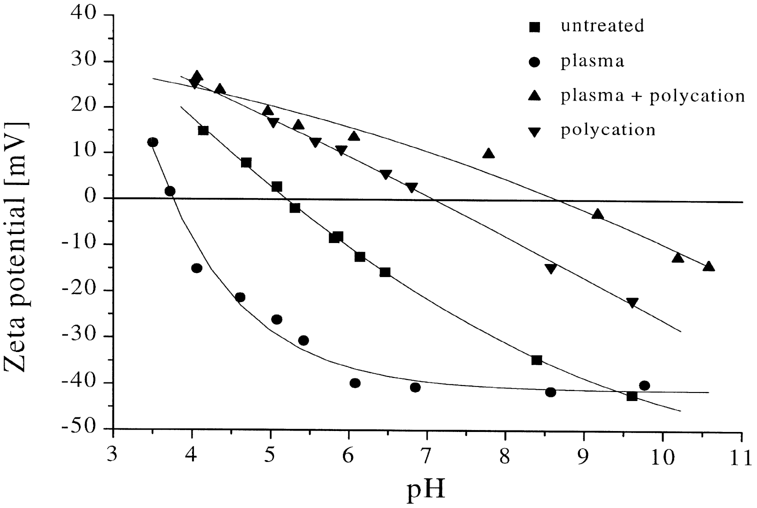

Fig. 3. Zeta potential of PTFE surfaces as a function of pH (procedure A).

the acidic groups at high pH values is connected with a plateau in the curve. If basic groups are only present on the surface, the zeta potential is positive at low pH values. It decreases with increasing pH because the number of positively charged (protonated) groups decreases. Non-polar polymer surfaces show no plateau on the curve. The increase in negative zeta potential with increasing pH is affected by the increasing adsorption of hydroxyl ions.

Fig. 3 shows the experimentally determined zeta potential–pH curves for an untreated and three modified PTFE surfaces. The almost linear dependence of the zeta potential of the untreated sample over a wide pH range proves that an adsorption mechanism dominates on the untreated PTFE surface, which is typical for non-polar solid surfaces. The oxygen plasma treatment effects a remarkable shift of the zero point of charge to a lower pH value and the appearance of a plateau at high pH values. We assume that this change in the curve is caused by the formation of dissociating acid groups on the plasma-treated PTFE surface. After dipping the plasma-pretreated PTFE into the PDADMAC solution, a positively charged surface was observed over a wide pH range due to successful adsorption of the polycation. It is likely that the adsorption of the polycation is enhanced by electrostatic interactions between the negatively charged oxygen plasma-treated PTFE surface and the positively charged groups in the polycation.

Zeta potential–pH curves of PTFE modified using procedure B are shown in Fig. 4. As expected, the PTFE surface treated by the ammonia plasma possesses basic surface properties indicated by the shift of the zero point of charge to a higher pH value compared to the untreated sample. Adsorption of the polyanion in the second modification step is proved by the observed shift of the zeta potential curve in the other direction. It is concluded from the shape and the position of the curve that acidic groups now dominate on the outer surface.

The modified surfaces were also characterized by contact angle measurements. The results of the measurements with

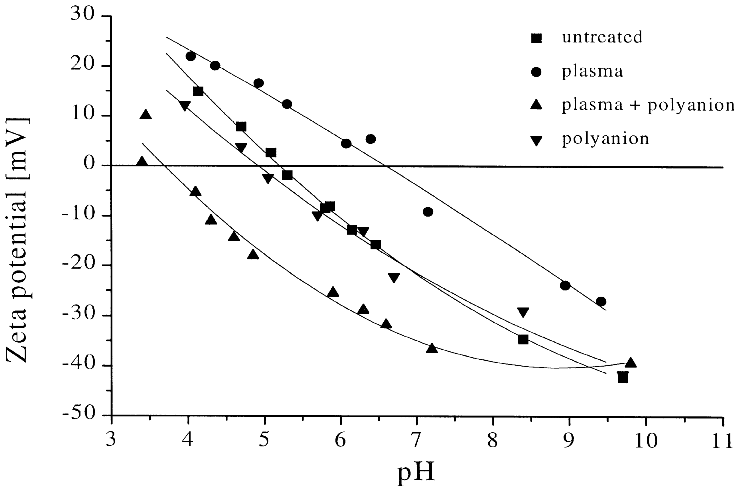

Fig. 4. Zeta potential of PTFE surfaces as a function of pH (procedure B).

Table 1
Advancing ($\theta_a$) and receding ($\theta_r$) contact angles of water on modified PTFE surfaces

| Sample | $\theta_a$ (deg) | $\theta_r$ (deg) |
|---|---|---|
| Untreated | 116 | 91 |
| Polycation-adsorbed | 111 | 74 |
| Polyanion-adsorbed | 113 | 95 |
| $O_2$ plasma-treated | 92 | 50 |
| $O_2$ plasma-treated + polycation adsorbed | 83 | 21 |
| $NH_3$ plasma-treated | 91 | 36 |
| $NH_3$ plasma-treated + polyanion adsorbed | 85 | 14 |

water drops are shown in Table 1. A characteristic of unmodified PTFE is the low surface energy and consequently the high contact angles. The advancing and receding water contact angles of the PTFE sheets used in these experiments were 116° and 91°, respectively. Both the oxygen plasma treatment and the ammonia plasma treatment gave rise to a decrease in the contact angles. The receding angles decreased more than the advancing angles. In other words, contact angle hysteresis increased. The subsequent adsorption of polyelectrolytes caused an additional decrease in both contact angles, which was distinct in the case of receding angles.

Untreated PTFE was also dipped into the polyelectrolyte solution for control purposes. Adsorption of polyanions did not occur, as indicated by contact angle and zeta potential measurements. In the case of the polycation, it is concluded from the corresponding zeta potential curve (see Fig. 3) and the receding contact angle that this polycation is adsorbed on the untreated PTFE. However, we assume that the polycation is adsorbed only to a slight extent because the advancing contact angle remains high and the zero point of charge is shifted to a lower pH value compared to the plasma-pretreated sample. To sum up, it can be said that it is possible to diminish the hydrophobic properties of PTFE using modification procedure A or B.

Table 2
Dependence of the advancing ($\theta_a$) and receding ($\theta_r$) contact angles of water on PTFE modified according to procedures A and B on the pH of polyelectrolyte solutions containing potassium chloride (0.1 mol $l^{-1}$)

| pH | $\theta_a$ (deg) | $\theta_r$ (deg) |
|---|---|---|
| *Procedure A* | | |
| 4.5 | 90 | 15 |
| 6.8 | 87 | 30 |
| 9.8[a] | 90 | 26 |
| *Procedure B* | | |
| 2.2[a] | 54 | 12 |
| 4.7 | 50 | 12 |
| 7.3 | 60 | 10 |
| 9.9 | 73 | 14 |

[a] pH values of the polyelectrolyte solutions used for the experiments summarized in Table 1.

We then investigated whether it is possible to improve the wettability of the PTFE surface additionally by changing the conditions in the second modification step. In detail, we studied the effect of adding potassium chloride to the polyelectrolyte solution used for the modification and the influence of the pH of this solution.

An interesting result was obtained in the case of procedure B by adding KCl to the PSSNa solution. Compared with the corresponding sample described in Table 1 (without KCl), the advancing contact angle was considerably lower (54°). How can this be explained? The ionic strength of the solution is increased by adding KCl. It is known that the conformation of polyelectrolytes in solution is influenced by the ionic strength. At high ionic strength, the polyelectrolytes have a coiled structure because the electrostatic repulsion between the charged chain segments is screened. On the other hand, at low ionic strength the conformations of the polyions are more extended due to electrostatic repulsion. The polyanion is assumed to be adsorbed without changing its structure considerably, e.g. a flatter conformation of the polyanion with a large fraction of segments adsorbed in the form of trains is produced using the polyelectrolyte solution without added KCl. On the other hand, in the case of high ionic strength, many segments of the adsorbed polyion are in loops, and the tails are long. Consequently, in this case there are more sulfonate groups on the outermost ‘surface’ (tails and loops) which do not interact with the oppositely charged ammonia plasma-pretreated surface. This excess of sulfonate groups gives rise to the increase of wettability.

However, we did not observe any considerable effect of KCl on the advancing contact angle in the case of procedure A. This result is not well understood at present. Perhaps the structure of the adsorbed PDADMAC is less influenced by the ionic strength because the PDADMAC used for the modification has a branched structure. We are going to investigate the effect in detail.

Table 2 also shows that the dependence of the advancing contact angle on the pH value of the polyanion solution changes in the case of procedure B. We assume that the contact angle obtained at pH 9.9 was relatively high because the zeta potential of the ammonia-plasma-pretreated surface was negative at this pH value, and the polyanion was not adsorbed preferentially via electrostatic interactions. In the case of procedure A, the pH did not influence the contact angle. We think the reason is that the zeta potential of the oxygen-plasma-modified surface is negative over the whole pH range used for the modification experiments.

## 4. Conclusions

Low-pressure plasma treatments combined with the subsequent adsorption of appropriate polyelectrolytes have been used for the surface modification of PTFE. Modified surfaces with acidic or basic properties were formed by oxygen and ammonia plasma treatments, respectively. It was shown that an oppositely charged polyelectrolyte can be adsorbed on the plasma-pretreated PTFE, diminishing the hydrophobic properties. These experiments indicated that the modification procedure described is a viable tool for fluoropolymer surface modification.

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