Surface Modification of Polytetrafluoroethylene with Tetraethoxysilane by Using Remote Argon/Dinitrogen Oxide Microwave Plasma

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Received 30 October 1998; 9 August 1999

ABSTRACT: The use of remote microwave plasma for the polymerization and deposition of tetraethoxysilane on the surface of polytetrafluoroethylene was investigated using a mixture of Argon and dinitrogen oxide as carrier gas. Layers with thicknesses of 0.5–3 μm were obtained, differing in chemical composition, surface energy, and flexibility/brittleness, depending on the plasma power and both the treatment and aging times. In general, milder treatments and shorter aging times resulted in higher contents of organic structural elements in the layers and greater flexibility and surface energy. Anchoring between the layers and the bulk polytetrafluoroethylene was at least partially caused by fibrils interconnecting the two components. These results were obtained by X-ray photoelectron spectroscopy, Fourier transform infrared spectroscopy in the attenuated total reflection mode, contact angle measurements, and scanning electron microscopy combined with energy dispersive X-ray analysis. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 76: 1207–1216, 2000

Key words: remote microwave plasma; surface modification; surface energy; plasma polymerization; polytetrafluoroethylene; tetraethoxysilane

INTRODUCTION

In recent years, plasma polymerization and deposition of organosilicone compounds has been performed to prepare thin oxide films with good dielectric properties, high thermal stability, and good scratch resistance. Plasma polymerization is generally taken to mean the deposition of organic films at relatively low temperatures. Plasma enhanced chemical vapor deposition is used in the context of the deposition of inorganic chemicals at higher temperatures. Most of the work has been focused on the application of these layers as insulated films for micro-electronic devices. Deposition of the organosilicone monomers, hexameth-

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Journal of Applied Polymer Science, Vol. 76, 1207–1216 (2000)
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yldisiloxane or tetramethylsilane by using glow discharge, radio frequency, and microwave (MW) direct plasma systems has been fully described in the literature.[1–8] In a recent article, plasma enhanced chemical vapor deposition of silicone dioxide (SiO_2) thin films were investigated by using radio frequency (13.56 MHz) plasma, operating at a relatively low plasma power.[9] On the other hand, plasma surface treatment, in the contexts of polymer surface modification, referred to the exposure of polymer to reactive gas or inert gas plasma. Many studies on plasma surface treatment have already been performed.[10–14] The effect of plasma treatment was generally discussed in terms of plasma parameters such as the nature of the gas used, the pressure of the discharge, the power of the plasma, the reactor geometry, and the frequency used for excitation. However, contrary to direct plasma systems, no detailed studies have been reported to date on the effect on the polytetrafluoroethylene (PTFE) surface caused by remote MW plasma, which is known as a developed system capable of plasma deposition. The application of modern MW plasma based surface processing has increased continuously because of the process uniformity and the reliably controlled and highly effective sources of various ions and radicals.[15–17] The slot antenna MW plasma source is beginning to be used for remote plasma deposition of scratch resistance films on polycarbonate substrates with the monomer hexamethyldisiloxane by argon (Ar) and oxygen gases.[18] In this report, the influence of remote plasma activated Ar/dinitrogen oxide (N_2O) gas mixtures on the surface of PTFE foils and the deposition of silicone oxide films on the same substrates using teraethoxysilane (TEOS) has been examined. We have focused the experiments on the surface modification of PTFE by remote MW plasma and its effect on the outstanding thermal and chemical resistance of PTFE. Results, based on our experimental studies, are given for the following points: 1. the effect of MW power on the deposition rate of TEOS using Ar/N_2O gas mixtures; 2. the structure of the interface between the deposited polymer film and the PTFE surface determined by scanning electron microscopy (SEM) equipped with energy dispersive X-ray analysis (EDX); and 3. the chemical composition of the surface of the organosilicone polymer films by Fourier transform infrared spectroscopy in the attenuated total reflection mode (FTIR-ATR) and X-ray photoelectron spectroscopy (XPS).

EXPERIMENTAL

Materials and Analytical Methods

TF 1750, a nonporous film consisting of tetrafluoroethylene homopolymer and produced by Dyneon GmbH, Gendorf, Germany, with the following specifications was used: thickness 100 μm, void content 0.75%, density 2.160 g/cm^3, and crystallinity ≈60%. All foils were cleaned with ethyl acetate, acetone, and methyl alcohol before use. The organosilicone compound used in this study was TEOS (Acros Organics, C_8HO_4Si, molecular mass 208.33 g/mol, MP 37°C, d 0.9350 g/mL, n_d^{20} 1.3825).

Contact angles were measured by a contact angle goniometer. Both advancing and receding angles were measured by using the axisymmetric drop shape analysis of sessile and drops, permitting a simultaneous calculation of contact angles and surface tensions. A Nicolet 5PC FTIR spectrophotometer equipped with Xe/Se detector was used for FTIR spectroscopy. Infrared spectra were recorded at the resolution of 4 cm^{-1} by coding 256 interferograms. XPS measurements were performed in an X-Probe™ spectrometer (model 206, SSI, Mountain View, CA). The samples were excited with monoenergetic Al $_{K\infty 1,2}$ radiation (1486.6 eV) at a power of 175 W. The spectra were recorded with a charger neutralizer set at 20 eV. The aliphatic carbon (C—C, C—H) was used as reference line and set at a binding energy of 285.0 eV. The spectral resolution, i.e., the full width of half maximum of the Au $4f_{7/2}$ line, was 1.55 eV for the survey spectra and 0.9 eV for the elemental spectra. The emission angle of electrons was set at 55° with respect to the sample normal, which results in an information depth of ≈6 nm.[19] For SEM investigations in combination with EDX measurements, the Philips XL 30 type spectrometer was used. A thin Au layer is necessary to prevent surface charging of the PTFE foils.

Remote MW Plasma Processing

Plasma polymerization and deposition on PTFE with TEOS was performed by means of a remote MW plasma system. The dense Ar/N_2O gas plasma was formed using an MW source of the SLAN I type based on the slot antenna principle (JE PLASMA CONSULT GmbH, Germany, 2 KW, 2.46 GHz). Typical experimental conditions are as follows: in the evacuated steel reactor (0.02 mbar) various gas flows of Ar [0.3 up to 1.0 stan-

dard liter per minute (slm)] and N_2O (corresponding to a portion of 8.75 vol % N_2O in the mixture) were introduced to the top inside in a quartz cylinder up to reactor pressures of between 0.2 and 1.0 mbar. The Ar/N_2O gas plasma was ignited by various electrical generator powers (200–1400 W). The TEOS monomer stored in a thermostatic reservoir at 35°C was transferred into the reactor by a gas ring system outside of the Ar/N_2O gas plasma by a constant Ar carrier gas flow (0.05 slm). The deposition time was varied between 15 and 60 min. The PTFE foils and a flat glass substrate (for the purpose of comparison) were positioned downstream of the plasma excitation zone and monomer input system on a steel substrate holder. The deposition temperature was maintained between 26 and 33°C without substrate heating. Before and after plasma polymerization and deposition, some PTFE samples were exposed to the remote MW plasma excited Ar/N_2O gas mixtures without the monomer feed to investigate the effect of the high plasma power on the PTFE surface. The specific conditions, which were used for obtaining the various samples, are given in the Tables.

RESULTS AND DISCUSSION

Deposition Rate, Contact Angle, and Surface Energy

Calculation of the deposition rate was based on the change in weight per unit area and minute

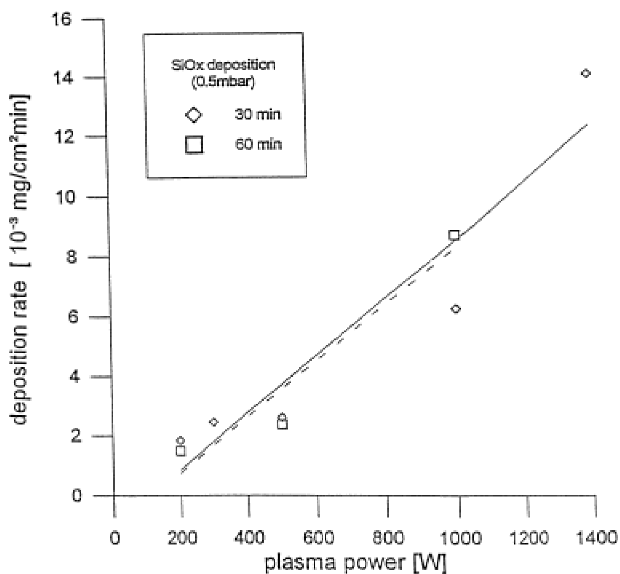


Figure 1 The relationship between the deposition rate of TEOS and plasma power (0.5 mbar, ◇ 30 min, □ 60 min).

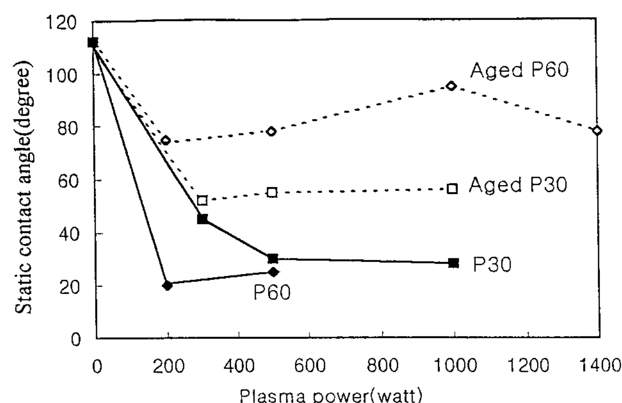


Figure 2 The relationship between plasma power and contact angle for freshly prepared samples and those that were aged for 30 days after preparation. Plasma parameters are as follows: 1. P30 and aged P30, reaction time 30 min, vacuum pressure 0.2 mb, TEOS flow 0.05 slm, plasma gas flow 1.0 slm Ar/8.75% N_2O; 2. P60 and aged P60, reaction time 60 min, vacuum pressure 0.5 mb, plasma gas flow 1.0 slm Ar/8.75% N_2O, TEOS flow 0.05 slm.

($mg/cm^2 \cdot min$) regarding the weight difference on the glass substrate with defined area. The layer thicknesses varied between 0.1 and 3 μm and depend on the deposition parameters, especially on the plasma power. With increasing plasma power, the formation rate of the organosilicone layers also increases (Fig. 1). The contact angle of water on the surface of the treated samples varied between 23 and 94° and decreased with increasing plasma power (Fig. 2). The value of 112° measured for the contact angle of water on an untreated PTFE film was fairly close to the value between 108 and 112° reported in the literature.[20–22] However, as shown in Table I, the advancing angle was found to be greater than the value measured by the contact angle goniometer. The contact angle of the plasma deposited film was recorded at between 20–30° and the measurement was taken up to ≈5 days after the plasma treatment. This value corresponds to that of silica. However, when the measurement was taken immediately after deposition, a much reduced contact angle was observed, which might be attributed to oligomers of silicic acid with a high content of polar end groups.

After plasma deposition of TEOS, samples were aged for 1 month under ambient conditions. Compared with the nonaged samples, the average values of the contact angle increased up to 50–90° because of the aging effect (Fig. 2). Surface energy was calculated by measuring both advancing and

Table I Contact Angle and Surface Energy of Untreated, Plasma-Treated, and Plasma/TEOS-Treated Samples

Item/Sample	Untreated	Plasma Treated (PST 34)[a]	Plasma/TEOS Treated (PPD 23)[b]	Plasma/TEOS Treated (PPD35)[c]
Surface tension (mN/m)	10.2	13.3	60.1	59.4
Advancing angle/water (°)	122.8	116.8	38.6	39.9
Receding angle/water (°)	89.9	61.7	21.3	9.9

Treatment conditions: [a–c] treatment time was 30 min, the vacuum pressure 0.2 mbar, TEOS flow rate (if it applies) 0.05 slm.
[a] 0.3 slm, 8.75 vol % N_2O, 300 W, 30 min.
[b] 0.3 slm Ar, 8.75 vol % N_2O, 1000 W, 30 min.
[c] As PPD 23, but 5 min plasma pretreatment and 10 min aftertreatment.

receding angles. As shown in Table I, the plasma/TEOS-treated samples (PPD35, PPD23) have very reduced contact angles and increased surface energies compared with the sample treated only by Ar/N_2O gas plasma (PST34). To get a better understanding of what happened during the deposition of the TEOS in the layer the plasma/TEOS-treated samples were exposed to the remote plasma once again for 10 min without monomer feeding. As was expected, the contact angles of these surfaces increased compared with those of the surfaces without aftertreatment. It seemed that the oligomers reacted by an additional plasma exposure, which decreased the concentration of polar groups and made the surface more crosslinked. Samples only treated with Ar/N_2O plasma (without TEOS feeding) had a contact angle of 94° compared with a value of 117° before the treatment. This decrease corresponds to that of a typical oxygen plasma process.

SEM with EDX

Scanning electron micrographs of selected samples treated under different plasma conditions and subsequently aged for different periods as well as the starting materials are shown in Figures 3 to 7. Figure 3 shows the surface view of untreated PTFE. It bears the marks of the cutting blade originating from the film processing. Figure 4 shows the surface of a sample after treatment with Ar/N_2O gas plasma for 30 min without monomer feeding. The surface is etched by radicals, which were produced through the plasma gas treatment, resulting in pinholes on the surface. The micrographs shown in Figures 5 to 7 originate from samples that were treated in Ar/N_2O gas plasma with TEOS under different conditions and aged after treatment for different periods. Cracks were generated from a dense layer which forms a relatively regular pattern. On the bottom of the cracks, a gel-like structure can be seen, which in some places appears to be "blown up" (Fig. 5). This is due to the electron beam while SEM was performed. When the films were aged

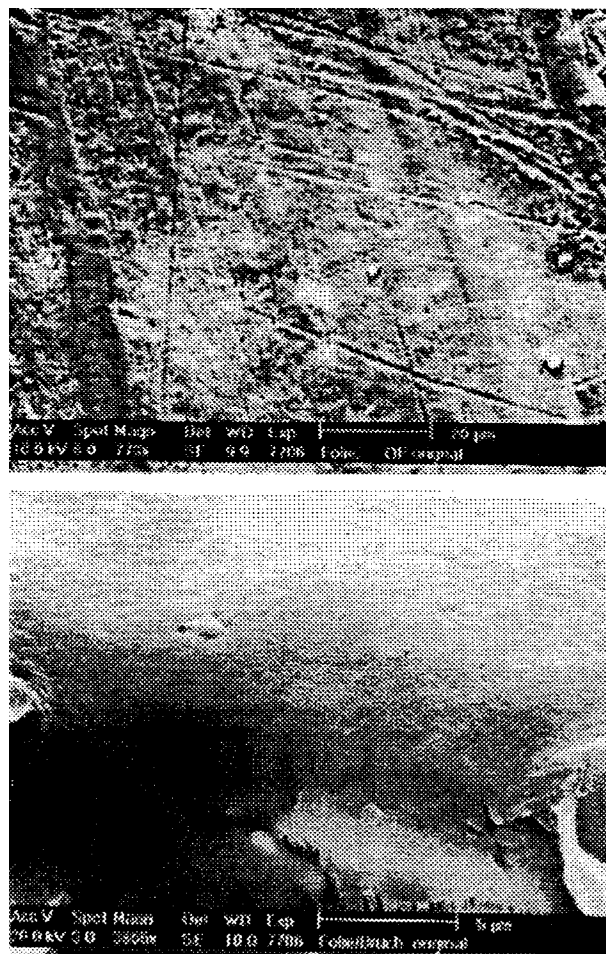


Figure 3 SEM of the surface of untreated PTFE; (top) surface image, (bottom) fracture image (marks of the cutting blade generated through film processing).

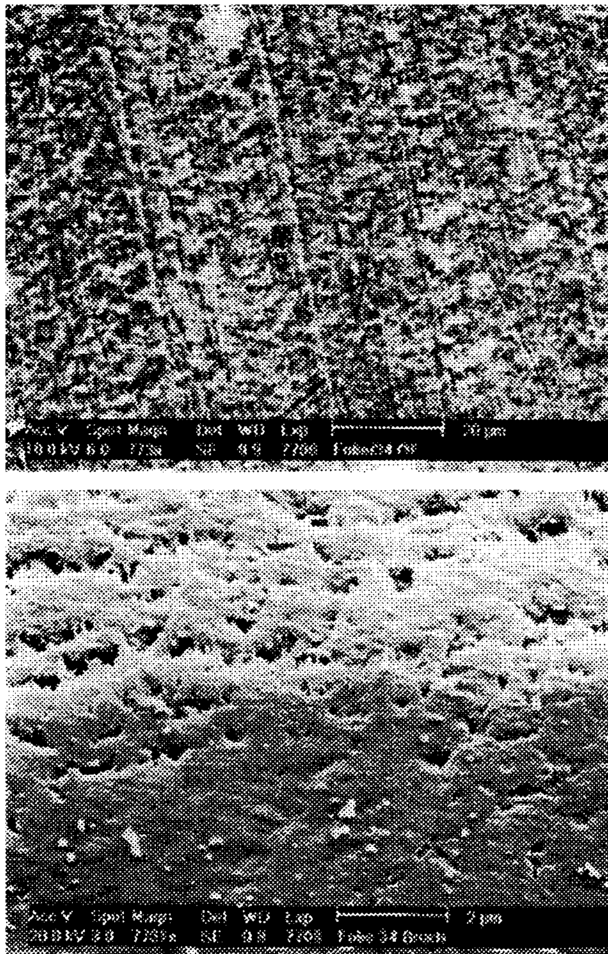


Figure 4 SEM of the surface of PTFE after plasma gas treatment with Ar/N_2O; (top) surface image, (bottom) fracture image (conditions: vacuum pressure 0.2 mb, plasma power 300 W, plasma gas flow 0.3 slm Ar/8.75% N_2O, treatment time 30 min).

for 2 months, many small cracks developed (Fig. 6). Finally, most of the layer peeled off, leaving only parts of the layer behind on the film. Obviously the layer is partly strongly anchored to the bulk because fibrils bind the layer to the PTFE surface (Fig. 7).

EDX spectra show the change in the chemical composition of the layer (Fig. 8). Whereas un-

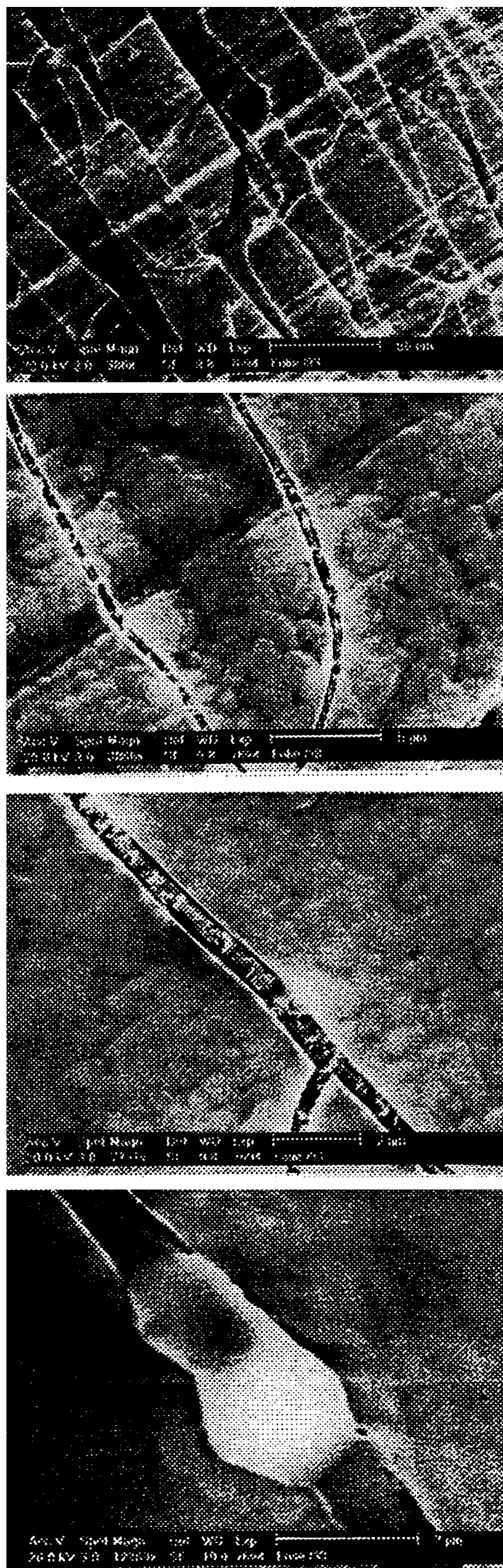
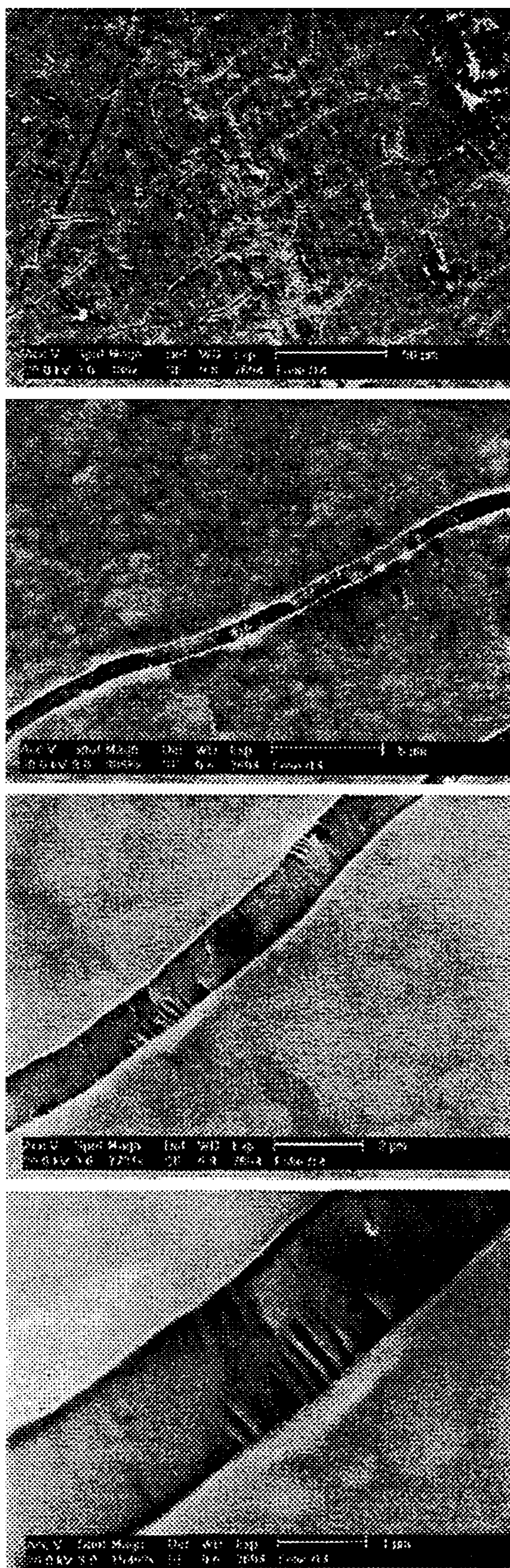


Figure 5 SEM of the modified PTFE surface displaying the cracks after 5 days (conditions: vacuum pressure 0.2 mb, plasma power 300 W, plasma gas flow 0.3 slm Ar/8.75% N_2O, the monomer TEOS flow rate 0.05 slm, reaction time 60 min, 5 days old, at several different magnifications).



treated PTFE shows only peaks for F and C [dotted line (a), left part], peaks typical for Si appeared for the plasma/TEOS-treated PTFE although differing in strength. If the EDX spectrum is taken from the bottom of a crack [Fig. 8, right part, upper line (c)] the intensity of Si and O is lower compared with a spectrum taken from the outer surface (lower line). The filled black area indicates that the layer near to the base of a crack was predominantly composed by organic elements, but there is also some Si. The layer obviously becomes more inorganic toward its outer surface.

XPS

XPS results for the plasma/TEOS modified surfaces and references are shown in Table II (elemental concentrations) and Table III (carbon species). The PTFE reference shows a carbon concentration of 34.6 atomic % and a fluorine concentration of 65.8 atomic %; these values are very close to the theoretical values of PTFE. The small amount of oxygen (0.2 atomic %) results from a negligible contamination. The whole carbon content can be attributed to C—F carbon (cf. Table II).

Plasma treatment without monomer (PST 34) results in an increase of the concentrations of carbon, oxygen, and nitrogen whereas the fluorine content decreases. The attack of the plasma produces reactive sites so that oxygen and nitrogen could form hydrophilic groups on the surface of the sample. The omnipresent atmospheric carbon is both before and after venting adhesively bound at the surface; this is shown by an increase of the aliphatic (C—C, C—H) and C—O carbon content to 12.1 and 2.8 atomic % respectively, whereas the C—F carbon content drops to 25.8 atomic % (cf. Table III).

Plasma treatment in the presence of TEOS leads to the formation of a siloxane layer resulting in a strong increase of the silicon and aliphatic carbon content (C—C, C—H, and C—Si) to 18.5 and 24.0 atomic %, respectively. The ratio of

Figure 6 SEM of the modified PTFE surface displaying the cracks after 2 months (conditions: vacuum pressure 0.5 mb, plasma power 200 W, plasma gas flow 1.0 slm Ar/8.75% N_2O, the monomer TEOS flow 0.05 slm, reaction time 30 min, 2 months old, at several different magnifications).

the silicon to oxygen which is ≈1:2 and the chemical shift of Si 2p photoline of 103.5 eV corresponds to SiO_2 (literature value of SiO_2: 103.4 eV). For the monomeric TEOS, this ratio should be considerably higher. The concentration of the bulk components, fluorine, and C—F carbon, are reduced to 9.6 and 3.2 atomic %, respectively. The residual intensities of fluorine and C—F carbon may result from an incomplete coverage of the surface.

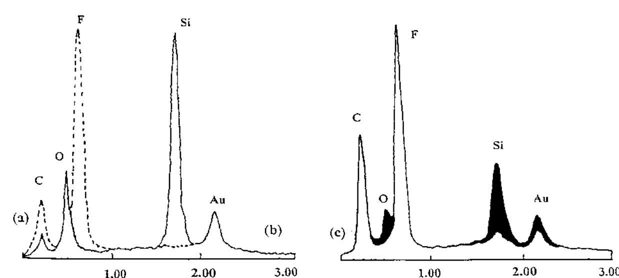


Figure 8 Energy dispersive X-ray spectra. Dotted line (a): untreated PTFE; solid line (b): plasma/TEOS-treated sample, spectrum taken at the bottom of a crack; upper line (c): plasma/TEOS-treated sample, spectrum taken of the surface; lower line (c): plasma/TEOS-treated sample, spectrum taken from the bottom; treatment conditions (b): vacuum pressure 0.5 mb, plasma power 1000 W, plasma gas flow 1.0 slm Ar/8.75% N_2O, the monomer TEOS flow 0.05 slm, reaction time 60 min, (c) vacuum pressure 0.2 mb, plasma power 300 W, plasma gas flow 0.3 slm Ar/3% N_2O, the monomer TEOS flow 0.05 slm, treatment time 30 min.

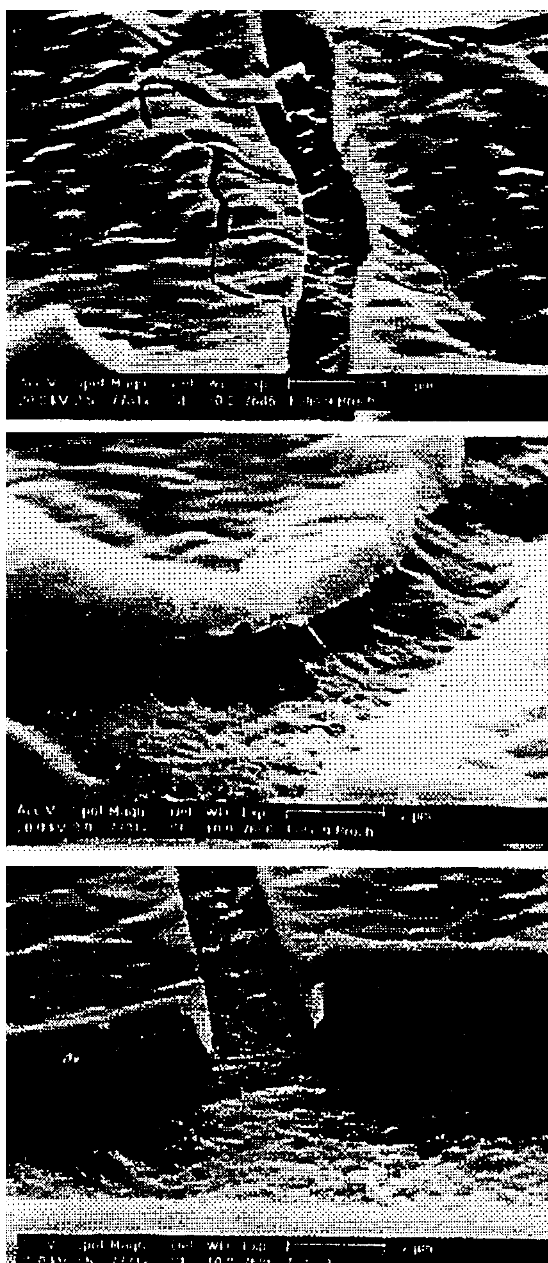


Figure 7 SEM of the layer showing the curling surface (conditions: vacuum pressure 0.5 mb, plasma power 1000 W, plasma gas flow 1.0 slm Ar/8.75% N_2O, the monomer TEOS flow 0.05 slm, reaction time 30 min).

FTIR-ATR

Figure 9 shows two frequency ranges of ATR spectra of plasma/TEOS-treated PTFE and untreated PTFE for comparison. By band assignment, several functional groups (among them also organosilicone structures) could be identified (Table IV).

The two bands in the range 1820–1620 cm^{-1} in the spectra of treated samples correspond to the stretching vibration of the C=O group. Oxygen, with a higher oxidation number than in TEOS, e.g., bound in carbonyl groups, is formed through the plasma treatment. If it is assumed that these

Table II Elemental Composition in Atomic % of PTFE Reference as Well as Plasma-Treated and Plasma/TEOS-Treated Samples

Sample	C 1s	O 1s	N 1s	Si 2p	F 1s
Untreated	34.6	0.2	—	—	65.2
PST 34[a]	40.6	2.4	0.5	—	55.7
PPD 29[b]	30.6	40.1	1.2	18.5	9.6

Treatment conditions: [a] see Table I, sample contains an additional 0.6 atomic % Na; [b] vacuum pressure 0.5 mbar, 300 W, 1.0 slm Ar/8.75 vol % N_2O, TEOS flow rate 0.05 slm, reaction time 60 min.

Table III Carbon Species in Atomic % of PTFE Reference as Well as Plasma-Treated and Plasma/TEOS-Treated PTFE Samples

Binding Energies/ Sample	C-Species			
	C—C, C—H 285.0 eV	C—O 286.5 eV	NH—C=O 288 eV	CF_2/CF_3 292–293 eV
Untreated	—	—	—	34.6
PST 34[a]	12.1	2.8	—	25.8
PPD 29[b]	24.0	2.1	1.4	3.2

[a] Treatment conditions see Table I.
[b] Treatment conditions see Table II.

carbonyl groups form hydrogen bonds with Si—OH, this will result in a shift of the C=O stretching vibration frequency. Accordingly, a band at 1718 cm^{-1} may be attributed to the formation of hydrogen bonds which can, however, also originate from traces of water in the surface. The formation of hydrogen bonds also results in a shift of the Si—OH stretching vibration frequency (3400–3000 cm^{-1}).

The FTIR spectra showed also bands between 1130 and 900 cm^{-1} (Si—O—Si, Si—O—R, Si—C) that belong to organosilicone oligomers and polymers that are present on the PTFE surface.

By taking FTIR spectra on the same surface every other day, the aging under ambient condition was followed. Because of the aging, the strong peak at between 3400–3200 cm^{-1} shifted to lower frequencies with time. The occurrence of intense peaks in the CH_2 stretching region of 2800–3000 cm^{-1} and at 1450 cm^{-1} (shoulder) indicates that aliphatic moieties are present. The intensity of these peaks diminished in aged samples indicating that the products derived from TEOS continue to react during aging. It is well known that the ethoxy groups in the TEOS can react with water, alcohols, and Si—OH groups even in the presence of small amounts of moisture or bases. When organic residues bearing carbon functional groups are attached to the silicone via a heteroatom such as O, this bond is very sensitive to hydrolysis.[23] Thus, when the samples were treated with water and ethyl alcohol for swelling, the hydrolysis and condensation occurred even at room temperature with a

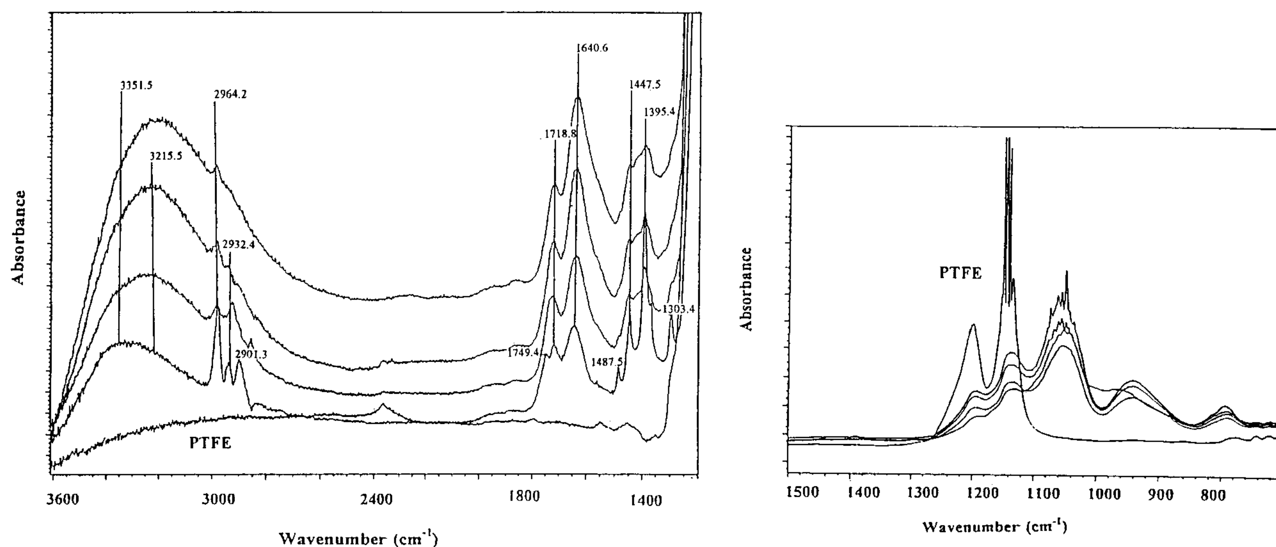


Figure 9 FTIR-ATR spectra of untreated and plasma/TEOS-treated PTFE. The spectra, in order of aging time, from the bottom (untreated PTFE) to the top, 2 h, 24 h, 48 h, and 72 h after plasma polymerization and deposition.

Table IV FTIR Band Assignment

Band (cm^{-1})	Assignment
3400–3200 m (bonded), and 950–830 m	Si—OH, H_2O
3200–3600	OH stretch, bonded
2964	C—H stretch, asym. (CH_3)
2906	Si—O—C_2H_5, C_2H_5—OH, C_2H_5—O^-
2900	O—CH_2
1718 (1749)	C═O stretching mode, hydrogen bonded carbonyl
1450	CH_2 deformation
1421, 1402	Si—CH_3 deformation, asym.
1370	CH_3 deformation
1130–900	Si—O—Si, Si—O—R
1200, 1140	CF_2 stretch

relatively high speed. The ethoxy groups in the TEOS [Si—(O—C_2H_5)$_4$] monomer lose, under mild conditions, ethanol to form Si—O—Si with OH or Si—O^- groups. Furthermore, it can be assumed that the oligomers react also during the plasma treatment by condensation (c.f. Si—O—Si), and oxidation (c.f. C=O) and more complex reactions (c.f. Si—C).

CONCLUSIONS

With Ar/N_2O carrier gas and TEOS as a reactive gas component under appropriate plasma conditions, thin and flexible layers were obtained on PTFE films providing the surface with a controlled hydrophilicity. The flexibility of these layers was attributed to a certain content of aliphatic organic structural elements. By increasing the power and the time of treatment, hard and brittle layers were obtained which contained a far higher concentration of silicone. By aging, formerly flexible layers also became brittle, eventually peeling off. This can be attributed to the hydrolysis of silicone ester groups and their further condensation resulting in crosslinked layers. Oxidation of active sites, resulting from the plasma treatment also played an important role in aging. The anchoring of the layer with the PTFE bulk was nevertheless so strong that even after the layer began to peel off it was still partially attached to the surface with thin strands.

By systematic variation of the plasma conditions and the intervening condensation and oxidation processes, it should be possible to obtain firmly adhering layers, ranging in properties from smooth and flexible to hard and brittle, with a controlled hydrophilicity. Plasma deposition of TEOS with subsequent polycondensation is therefore an alternative to wet chemical PTFE modification with silicon tetrahalogenides delivering PTFE[24] surficially modified by SiO_2.

Financial support from the Deutsche Forschungsgemeinschaft (DFG, German Research Association) through Sonderforschungsbereich (Special Research Unit) 287 “Reactive Polymers in non-homogeneous systems, in melts and at interfaces,” Deutscher Akademischer Austauschdienst (DAAD, German Academic Exchange Service), as well as Fonds der Chemischen Industrie is acknowledged with thanks. The authors are indebted to Dr. Martin Müller, Institut für Polymerforschung Dresden, for looking up the IR spectra.

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