Oxidative Damage and Recovery of Silicone Rubber Surfaces. I. X-ray Photoelectron Spectroscopic Study*

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SYNOPSIS

The oxidative degradation of silicone rubber surfaces in air plasmas obtained by RF or corona discharges and the subsequent recovery process were studied by X-ray photoelectron spectroscopy (XPS or ESCA). Using relatively short treatment times (5 min), the surface oxygen content was found to increase and that of carbon to decrease. Within 1 day some recovery toward the original composition was observed, but it was far from being complete. Angle-dependent measurements have shown an almost total recovery in the topmost layer. The degree of surface degradation of a solvent-extracted sample was much higher while its recovery was much smaller than the corresponding features of the nonextracted sample. According to GC and GC–MS analyses the extract contained a mixture of cyclic, and, in a minor quantity, linear dimethylsiloxane oligomers. Based on the above results the following steps were proposed for the oxidative damage and the subsequent recovery processes on silicone rubber surfaces: first the majority of surface methyl groups is removed and an oxidized layer containing Si atoms bound to 3 or 4 oxygens appears. The surface is later covered by a very thin (2–3 nm thick) "silicone oil" layer due to migration of low-molecular-weight components from the bulk. This diffusion-controlled migration step plays a more important role in the recovery process than the eventual reorientation of the newly formed polar groups from the surface toward the bulk. The proposed model is discussed in the light of published data. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Polyorganosiloxanes have many attractive properties, among others extremely low surface energy.[1] Silicone rubbers,[2–4] due to their unique property combination, became indispensable in various fields of industry and medicine. In certain specific applications, as contact lens materials or implants,[5] low surface energy is not desirable. Therefore, attempts have been made to increase hydrophilicity of silicone rubbers by ion implantation,[6–8] copolymerization.[9,10] Improved wettability achieved by ion implantation, however, decreases with time.[7] The rate of this hy-

drophobic recovery process was different in air and in vacuum. Electron spectroscopy for chemical analysis (ESCA), combined with depth profiling, has shown[6,7] that, in the case of O_2^+ ion-implanted samples, deviation from bulk composition shows a maximum as a function of distance from the surface. At the point of maximum deviation oxygen content was higher; carbon content was lower than either at the surface or in the bulk. The authors explained the changes of wettability by the breaking and recombination of surface bonds.

Fakes and co-workers[9,10] have studied surface chemical changes of contact lenses made of a PMMA/PDMS copolymer in RF oxygen plasma. As siloxane fragments in copolymers tend to concentrate at surfaces, the authors attributed observed changes to this component. They have applied water contact angle, ESCA and static secondary ion mass spectroscopy (SSIMS) measurements. They have

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also detected depleted carbon-content at the surface, with relatively more $C-O$ and $C=O$ oxygens than in the pristine sample. Using different X-ray anodes the authors were able to get some depth profile information. Carbon depletion is the greatest at the surface, where oxygen and silicon enhancement is the largest. A binding energy (BE) shift of Si2p (from 102 to about 104 eV) has been observed, indicative of an *organic–inorganic* transition. (Hereafter "organic" Si means an Si atom bonded to at least to 2 carbon atoms, while "inorganic" means an Si atom bonded to at least 3 oxygen atoms). According to their estimation the inorganic Si content of the surface reached about 90% within 100 s treatment time. ESCA combined with ion sputtering for freshly treated surfaces has shown that oxygen content decreases, while Si content increases monotonously from the surface toward the bulk. SSIMS studies have also revealed carbon depletion and the formation of a silicalike layer at the surface.

Most comprehensive surface analysis of the changes caused by oxygen plasma has been published by Morra et al.[11] They have studied the recovery process of oxygen plasma treated samples not only in air, but also in water, at different temperatures, using contact angle measurements, ESCA, SSIMS, and ATR–FTIR. They have also applied $^{18}O_2$ plasma to elucidate surface oxidation mechanism. Similarly to other cases, improved wettability after treatment has been observed, followed by a hydrophobic recovery. The rate of recovery was temperature dependent, with an Arrhenius-type rate constant. SSIMS and ESCA data have confirmed earlier assumptions that the number of $Si-O$ bonds increases in oxygen plasma, but, from the presence of siloxane-related fragments of varying ^{18}O content, they have concluded that Si atoms bound to 3 oxygen atoms are present in high concentration. They have also reported that during the recovery process newly formed ^{18}O containing groups migrate away from the 1-nm-thick layer probed by SSIMS. According to their observation the composition and wetting behavior of the recovered surface were not identical with those of the original one. Reduced wetting angle hysteresis observed on the recovered surface has been explained by the reduced mobility of the groups involved.

In another large area of application, high-voltage outdoor electrical insulation, loss, and recovery of surface hydrophobicity is again a key problem.[12–17] The main conclusions of the above references can be summarized as follows: (a) The hydrophobic silicone rubber surface, if exposed to electric discharges, looses its water repellency, which leads to the formation of a continuous water film, dry-band arcing, and finally to breakdown. (b) Changes in surface composition after exposure to natural aging, to various accelerated aging tests, or to RF air corona treatment are very similar to those observed in Refs. 6–11. (c) If dry-band activity is intermittent, i.e., if there are 1–2 days (or at least few hours) interval between forced discharging periods, the insulations recover, become hydrophobic again. Recovery has been explained by the diffusion of low molecular silicone oils to the surface. It is understandable that a surface composition similar to polydimethylsiloxane appears not only on aged silicone surfaces,[12,13,15,16] but also on silicone rubbers covered by thin carbon[12] and metal[18] layers. This also explains the hydrophobicity transfer to well-defined pollution layers detected by contact angle and by conductivity measurements.[19,20] In some cases these low molecular oils have been studied by gel permeation chromatography[13,18] (GPC) or gas chromatography[19] (GC). The average molecular weight of the rubber extract in one case[13] was in the order of 10^3. GC analysis of hydrophobic agents transferred from silicone rubber to model pollution layers[19] has detected cyclic and linear siloxanes.

The above summary shows that surface scientists tend to explain the surface recovery of the oxidized silicone rubber surface by a surface mobility mechanism,[21] which has been successfully applied to polymers,[22–24] while electrical engineers by silicone oil migration, which is specific to this group of compounds.

In this article the study of the oxidative damage and recovery process of a typical silicone rubber used in high-voltage insulation is described. The main tool was X-ray photoelectron spectroscopy (XPS or ESCA), which proved to be useful in monitoring ion-induced changes on organosilicon surfaces,[25] in detecting changes of surface composition in organosilicon copolymers,[26] or in detecting lateral diffusion of silicone oils on polymer surfaces.[27] The relative importance of silicone oil diffusion and surface reorientation in the recovery process was assessed by comparing the behavior of solvent-extracted and nonextracted samples. The extract was analyzed by GC–MS. ESCA studies were supported by ATR–FTIR studies, which will be published separately.[28]

EXPERIMENTAL

Materials

The material studied was Powersil 660 (earlier designation VP 7606) of Wacker Chemie AG (Ger-

many), a two-component liquid silicone rubber (LSR), the main constituent of which is polydimethylsiloxane (PDMS). The curing reaction is based on hydrosilylation, catalyzed by Pt compounds.[29] One component contains vinyl functions and the catalyst; the other component contains the crosslinking agent, i.e., oligomeric or polymeric Si–H compounds. The two components have been thoroughly mixed in a static mixer (volume ratio 1 : 1), then plates of 1–2 mm thickness have been cast and cured for 4 h at 100°C. One side of the plate faced air (glossy surface), the other one faced an Al plate (mat surface). Discs with a diameter of 9 mm and a thickness of 1 mm were cut from the samples and the glossy surfaces were studied. Some samples were solvent extracted and dried before plasma treatment and surface analysis.

Solvent Extraction

The extraction was performed in a Soxhlet apparatus, for 8–24 h, using 250 mL benzene or chloroform. Samples showed large swelling during extraction (150–200% size increase). After extraction the solvent from the samples was removed *in vacuo*, until constant sample weight. It usually required 8–10 h. The excess solvent from the solution was removed by distillation (final volume 0.5–1 mL), then 2 μL tetradecane standard has been added for gas chromatographic analysis.

Plasma Treatment

In situ Oxidative RF Plasma Treatment

It was performed in the sample preparation chamber of the ESCA equipment by a home-made inductively coupled RF plasma reactor in the "dark space" region (frequency = 13.56 MHz, power = about 150 W, air pressure = about 0.1 mbar, contact time = 5 or 15 min). After treatments the samples were transferred directly into the analysis chamber, so there was no contact with ambient air before the ESCA measurement.

Ex situ Oxidative RF Plasma Treatment

Samples were treated in a home-made, inductively coupled plasma reactor (frequency = 13.56 MHz, power = about 150 W, air pressure = about 0.1 mbar, contact time = 5 min). The reactor has been designed so that the plasma contacted the sample surface. After the treatment the samples were kept in low-pressure (10^{-3} mbar) air for 1 min, then, after

contacting with ambient air, were introduced into the spectrometer.

Oxidative RF Corona Discharge Treatment

Samples placed on an Al-plate were treated by corona discharge in ambient air using a BD-10AVS type Tesla-coil generator (Electro-Technic Products, Inc., USA) with a conical tip (voltage = 1–5 $\times$ 10^4 V, frequency = 0.5 MHz, treatment time = 5 min). The equipment was fixed on a Bunsen-support in a vertical position so that the tip of the electrode was about 1 cm above the center of the rubber disc. After switching on the generator, sparks from the electrode tip moved around the disc on a conical surface. There seemed to be no direct contact between the corona and the sample surface.

Surface Analysis

ESCA measurements were performed by a KRATOS XSAM800 type spectrometer, using Mg K$\alpha_{1,2}$ (E = 1253.6 eV) radiation. The X-ray gun was operated at 15 kV and 20 mA. Spectra were recorded in the fixed retardation ratio (FRR) mode. The pressure in the sample analysis chamber was 10^{-9} mbar. If not stated otherwise in the text, an electron take-off angle normal to the surface was applied. The spectrometer was calibrated against the Au 4f$_{7/2}$ line fixed at 84.0 eV.[30] The linearity of the energy scale was checked by the dual Al/Mg electrode method using the Ag 3d$_{5/2}$ line (368.2 eV).[30] Data acquisition and processing were performed by a DEC LSI 11/ 23 computer, using the KRATOS DS 300 program package running under the RT-11 FB (V4.00) operation system. The overview spectra were taken between 50 and 1300 eV, with an energy step of 0.5 eV, while the detailed spectra of the lines of interest (O1s, C1s, Si2p, and, in one case N1s) were registered with an energy step of 0.1 eV. The Si KLL Auger peak was recorded using the Bremsstrahlung component of the exciting radiation, with an energy step of 0.2 eV. The spectra were referenced to the hydrocarbon type C1s line (BE = 284.6 eV). The quantitative evaluation of the spectra was performed with the experimentally determined relative differential subshell photoionization cross sections of Evans et al.[31] after correction for the angular distribution effect, using the asymmetry parameters published by Reilman and co-workers.[32]

GC and GC–MS Analyses of the Rubber Extract

The GC analyses have been made on a Hewlett-Packard 5880A type chromatograph equipped with

flame ionization detector (FID). The measuring conditions were as follows: column: 0.33 μm film thickness, methyl-silicone stationary phase, 25 m long, 0.2 mm ID silica capillary; carrier gas: helium; flow rate: 0.8 ml/min; temperature program: 50°C (1 min), from 50 to 300°C at a rate of 10°C/min (25 min), 300°C (40 min); detector temperature: 300°C; injector temperature: 280°C; split ratio: 1 : 25. The identification of the extracted compounds was performed on a Hewlett-Packard 5985B type GC–MS device using the same GC column and conditions as in the GC analyses. The MS conditions were as follows: interface temperature: 300°C; ion source temperature: 200°C; ionization method: electron impact; ionization energy: 70 eV; scanning range: 41–1000 amu.

RESULTS

ESCA Analysis of the Silicone Rubber Surfaces

Table I summarizes the changes in the surface composition of the samples observed before and immediately after plasma treatments under various conditions, and after various periods of recovery. The surface compositions are expressed in terms of stoichiometric ratios: $Si_nC_pO_q$, taking unity for n. In order to evaluate quantitatively the surface compositional changes the concept of stoichiometric distance was introduced:

$$R_{actual} = [(p_{actual} - p_{original})^2 + (q_{actual} - q_{original})^2]^{1/2}$$

where R is the length of the vector defined by the stoichiometric deviation of the actual surface composition (obtained after treatment or after recovery) from that of the virgin sample. Note that R is meaningful for comparison, only if the direction of the deviation vector remains practically constant during the recovery process.

Table I reveals that:

1. The surface composition of the virgin sample is close to the stoichiometric one (Si : C : O = 1 : 2 : 1).
2. In case of short (5 min) exposures to various RF plasmas, the qualitative changes are similar: the oxygen content increases, while that of carbon decreases.

Table I   Surface Composition ($Si_nC_pO_qN_r$, assuming n = 1) of the Silicone Rubber Samples in Virgin State and after Various Surface Treatments, and the Deviation of the Surface Composition from That in the Virgin State (R)

Treatment	Elapsed Time after Treatment (min)	C_p	O_q	N_r	R
Virgin sample	—	2.10	1.03	—	0.000
5-min *in situ* RF plasma	0	1.55	1.49	—	0.717
	45	1.54	1.44	—	0.694
	80	1.54	1.44	—	0.694
	165	1.55	1.42	—	0.674
	300	1.54	1.38	—	0.660
	1350	1.58	1.32	—	0.595
15-min *in situ* RF plasma	0	2.75	1.59	—	0.858
	105	2.22	1.19	—	0.200
	240	2.22	1.17	—	0.184
	5460	2.27	1.16	—	0.214
5-min corona discharge	0	1.85	1.41	0.03	0.439
	75	1.88	1.31	0.03	0.356
	285	1.85	1.33	0.03	0.391
	1320	1.83	1.33	0.03	0.404
5-min *ex situ* RF plasma	0	1.38	1.52	—	0.871
	75	1.41	1.48	—	0.824
	150	1.40	1.46	—	0.813
	270	1.40	1.44	—	0.811
	1440	1.37	1.40	—	0.818

Table II Surface Composition of a Nonextracted and of a Thoroughly Extracted Silicone Rubber Sample before and after the Plasma Treatment

Sample	C_p	O_q	R
Nonextracted			
Virgin sample	2.10	1.03	0.000
After 5-min *ex situ* plasma treatment	1.38	1.52	0.871
After 24-h recovery, take-off angle 90°	1.37	1.40	0.818
After 24-h recovery, take-off angle 30°	1.87	1.10	0.058
Extracted			
Virgin sample	1.88	1.13	0.000
After 5-min *ex situ* plasma treatment	0.34	2.43	2.015
After 24-h recovery, take-off angle 90°	0.42	2.29	1.865
After 24-h recovery, take-off angle 30°	0.79	2.06	1.433

3. The corona discharge treatment results in the appearance of N functionalities on the surface.

4. In case of longer *in situ* air plasma treatments (15 min), the nature of the compositional changes is different: here the silicon content of the surface decreases, the carbon content remains nearly constant, and the oxygen content increases. Due to the $n = 1$ constraint, these changes are reflected in $p > 2$.

5. After about 1 day of staying there is some recovery in all cases, which is, however, far from being total. The least regular trend in the recovery can be observed in the case of the corona discharge treatment.

Table II summarizes the surface compositional data for a nonextracted and for a thoroughly extracted sample obtained before and after standard, 5 min *ex situ* oxidative plasma treatments. Results obtained for the recovered samples at an electron take-off angle of 30° are also reported. Two features seem to be important in this table:

1. The surface damage of the extracted sample is much higher than that of the nonextracted one.
2. The surface composition is much closer to the original one, if a take-off angle of 30° instead of 90° is applied.

Table III summarizes the binding energies of the O1s and the Si2p lines, and the Si Auger parameters for the virgin, the plasma-treated, and the recovered samples. Static chargings of the samples are reported in the last column.

As a rule, after plasma treatments an increase in the Si2p binding energy is observed (from 102.4 eV to values close to 103 eV). This effect is most pronounced in the case of the solvent-extracted sample. Also the shift in the O1s binding energy and the static charging are the largest in the same case. This

Table III Binding Energies of O1s and Si2p Lines and the Si Auger Parameters for the Various Plasma-treated and Recovered Samples

| Sample	O1s eV	Si2p eV	Si Auger eV	St. Charge eV
Nonextracted				
Virgin sample	532.4	102.4	1711.5	8.1
After 5-min *in situ* plasma treatment	532.6	102.8	1711.7	8.3
After 24-h recovery	532.6	102.9	1711.7	8.0
After 15-min *in situ* plasma treatment	532.4	102.5	1711.7	8.0
After 24-h recovery	532.3	102.4	1711.6	7.8
After 5-min corona discharge treatment	532.4	102.4	1711.6	8.2
After 24-h recovery	532.5	102.6	1711.6	8.0
After 5-min *ex situ* plasma treatment	532.7	103.0	1711.3	8.1
After 24-h recovery at 90° take-off angle	532.6	102.9	1711.6	7.9
After 24-h recovery at 30° take-off angle	532.4	102.5	1711.6	7.9
Extracted				
Virgin sample	532.3	102.3	1711.6	8.5
After 5-min *ex situ* plasma treatment	533.0	103.6	1711.5	9.7
After 24-h recovery at 90° take-off angle	532.8	103.5	1711.4	9.9
After 24-h recovery at 30° take-off angle	532.8	103.5	1711.3	9.6
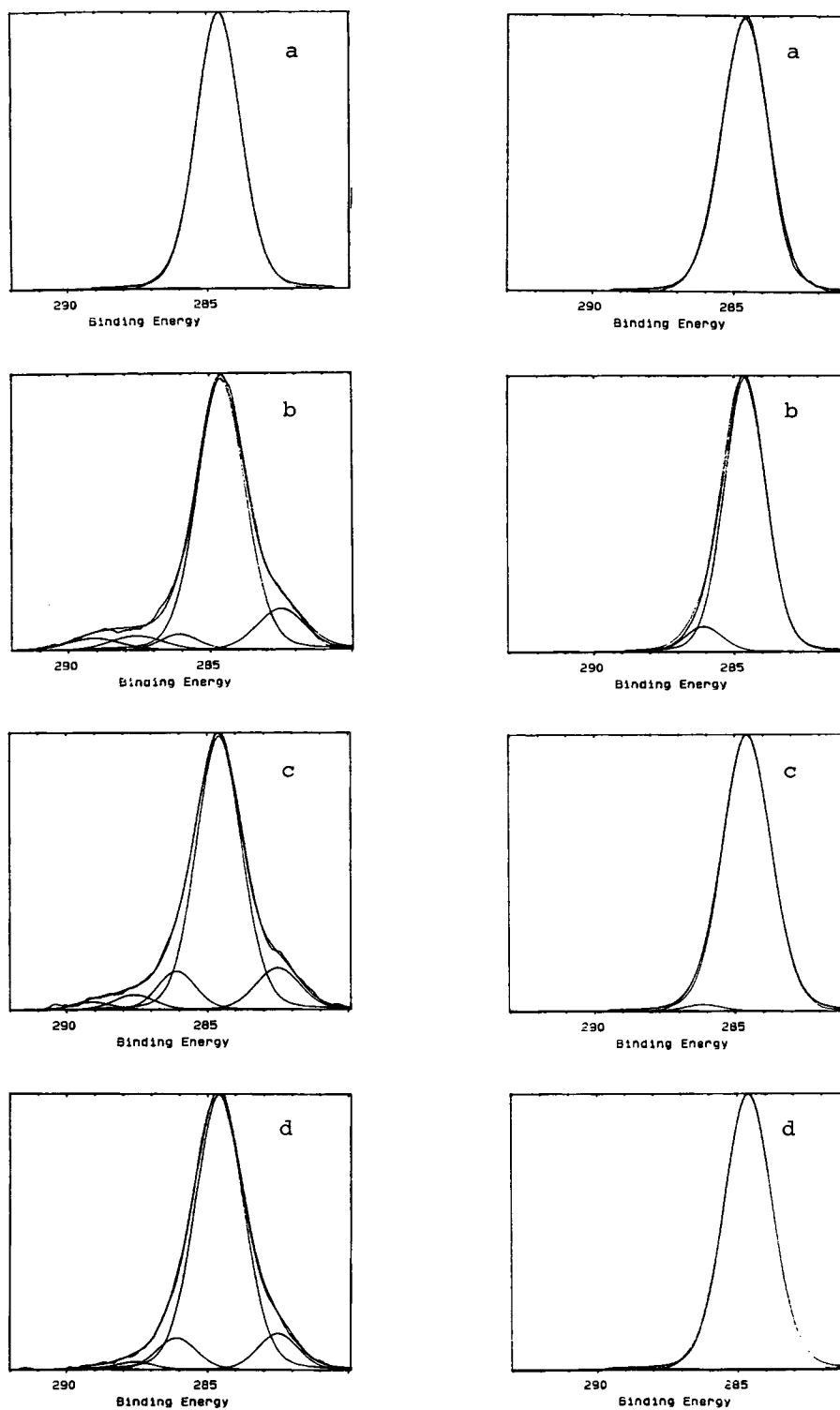
Figure 1   Comparison of the C1s line (a) before treatment, (b) immediately after a 5-min *ex situ* RF plasma treatment, (c) 24 h after treatment, take-off angle = 90°, and (d) 24 h after treatment, take-off angle = 30° for the extracted (left-hand side) and for the nonextracted (right-hand side) specimens.
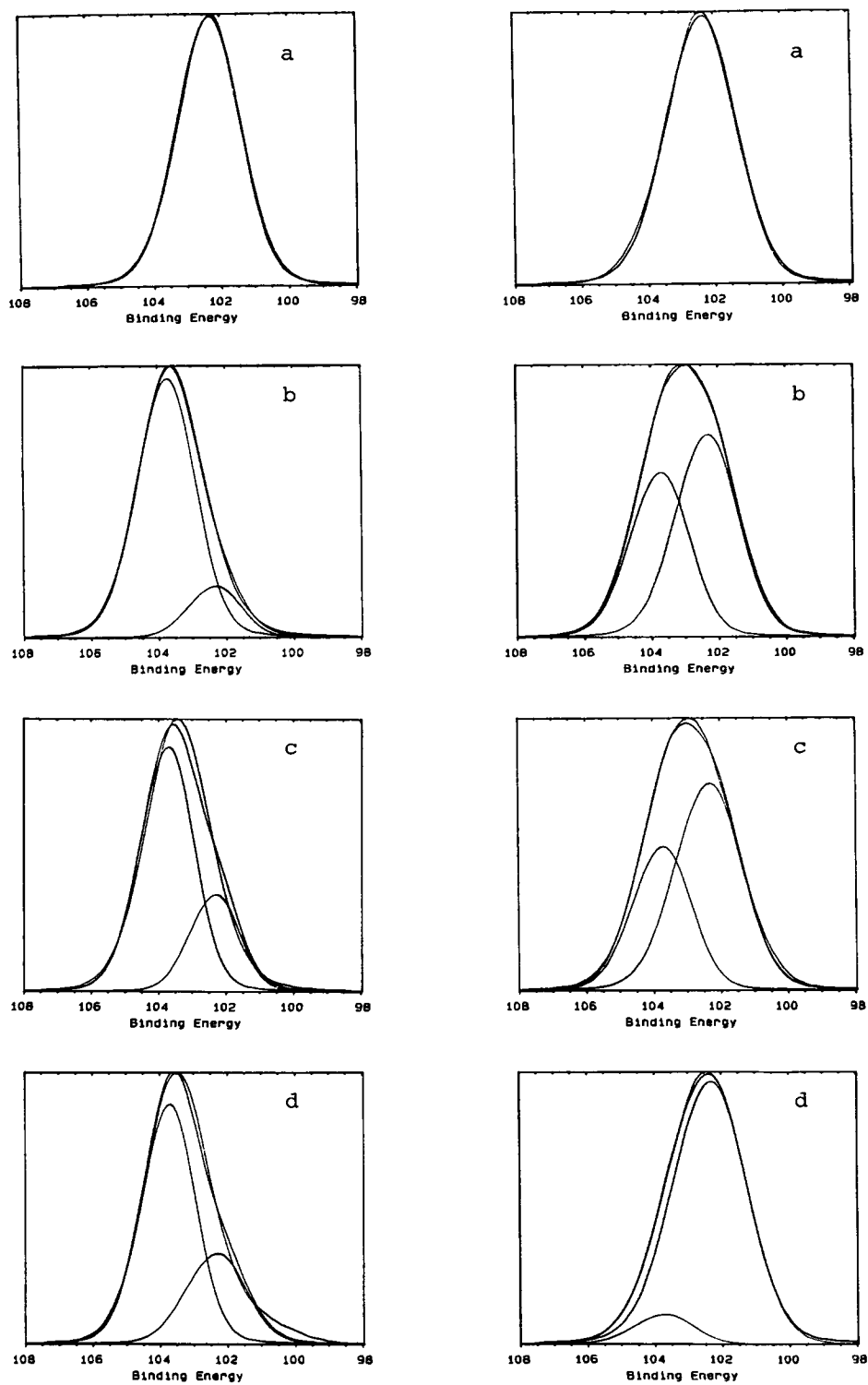
Figure 2 Comparison of the Si2p line (a) before treatment, (b) immediately after a 5-min *ex situ* RF plasma treatment, (c) 24 h after treatment, take-off angle = 90°, and (d) 24 h after treatment, take-off angle = 30° for the extracted (left-hand side) and for the nonextracted (right-hand side) specimens.

Table IV   Peak Synthesis Results of the C1s and Si2p Peaks of the Variously Treated Silicone Rubber Samples

Sample Treatment				Peak Areas (%)						
24 h Extraction by CHCl₃	5 min Air Plasma	24-h Recovery	Take-off Angle	C1s (eV)					Si2p (eV)	
				289.1	287.6	286.1	284.6	282.5	103.7	102.3
−	−	−	90°	—	—	—	100.0	—	—	100.0
−	+	−	90°	—	—	7.8	92.2	—	43.4	56.6
−	+	+	90°	—	—	1.8	98.2	—	37.9	62.1
−	+	+	30°	—	—		100.0	—	8.2	91.8
+	−	−	90°	—	—		100.0	—	—	100.0
+	+	−	90°	3.8	4.5	3.6	76.6	11.5	84.8	15.2
+	+	+	90°	1.8	3.7	8.8	74.7	11.0	73.3	26.7
+	+	+	30°	0.4	1.8	7.7	81.1	8.9	70.3	29.7

is in accordance with the corresponding extensive compositional modification discussed above.

The peak shape analysis gives further information on the chemical changes concerned. Figure 1 shows the C1s peak before, immediately after, and 24 h after a 5-min *ex situ* RF plasma treatment for the nonextracted and for the extracted specimens. Figure 2 depicts the corresponding Si2p peaks. Table IV summarizes the results of peak synthesis for the C1s and the Si2p peaks.

Analysis of the Solvent Extracts

Since the difference in the behavior of the extracted and the nonextracted samples was significant, it seemed worthwhile to check the composition of the solvent extracts. First the effect of solvent and of extraction time was explored. Besides measuring weight changes, the composition of the extract was studied by gas chromatography. Of course, not all siloxane components can be detected by GC, because of volatility limits. Under the conditions described in the experimental section, we were able to detect cyclic siloxane oligomers (D_n) up to $n = 23$. When the injector temperature was raised to 300°C, the relative amount of high-molecular-weight components did increase in the chromatograms, but at this temperature the bleeding of the septa cannot be excluded, therefore we opted for a slightly lower injector temperature. Table V shows the weight changes measured in benzene and chloroform (both good solvents of siloxanes) and the total amount of siloxanes measured by GC after 8 and 16 h of extraction (in the case of chloroform also after 24 h). This latter datum shows that GC detects only a fraction of the total extract, but the molecular weight

range investigated covers that of low molecular antioxidants and other additives. It is also clear that the great majority of extractables can be removed within 8 h. Although a weight change is measurable even after 24 h, the extraction procedure has been stopped, as the extract contained hardly any siloxane component detectable by GC. Figure 3 shows the gas chromatogram of the chloroform extract after 8 h extraction time.

The quantity of the siloxane components has been estimated assuming a relative response factor of 2.6 for n-alkanes versus siloxanes. This is in accordance with published data,[33] and the same value has been measured by us experimentally for pure D5 (decamethyl-cyclopentasiloxane) using n-tetradecane standard. Although the response factor varies somewhat from one siloxane to the other,[33,34] taking into account other sources of error (e.g., truncation of peak height at higher molecular weights), this seemed to be an acceptable compromise. The pres-

Table V   Weight Changes Measured on Silicone Rubber Samples after 8, 16, and 24 h Extraction in Chloroform and Benzene[a]

Extraction Time (h)	Solvent	Total Weight Loss (%)	Total Measured by GC (%)
8	Benzene	3.53	1.30
16	Benzene	3.71	1.42
8	Chloroform	3.90	1.69
16	Chloroform	4.28	1.75
24	Chloroform	4.47	1.76

[a] The quantity of the siloxane components measured by GC is also indicated.
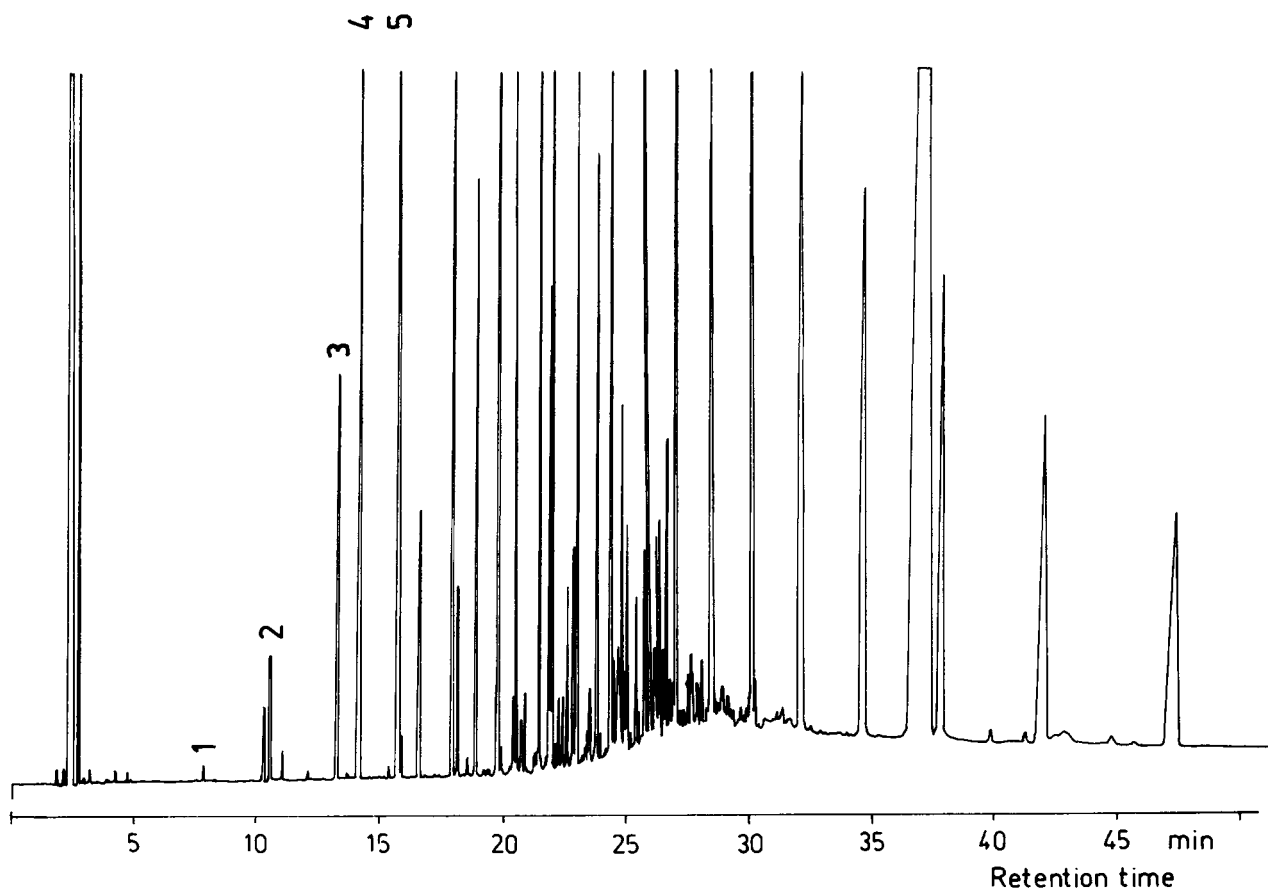
Figure 3   Gas chromatogram of the chloroform extract of the silicone rubber after 8 h of extraction time.

ence of a homologous series is clearly seen in Figure 3. The standard variation of retention times was around 0.4% at the beginning and 1.5% at the end of the chromatogram. The peaks appearing at 10.60, 13.32, 15.78, 17.96, 19.82, 21.50, 23.04, 24.44, 25.73, 27.00, 28.41, 30.05, 32.05, 34.5, 37.7, 41.8, 47.1, 53.9 and 64.0 min, respectively, have been assigned to cyclic dimethyl-siloxane oligomers (from D5 to D23, respectively) by GC–MS. Figure 4 shows the mass spectrum of the first, well measurable peak appearing in the GC–MS total ion chromatogram (due to the high vacuum present in the MS, the retention times are shifted toward somewhat lower values relative to FID detection), as compared to that of a pure D7 standard. The agreement is convincing. Figure 5 shows the gas chromatogram (with FID detection) of a test mixture containing D4, D5, D6, and D7. The retention times of the D5, D6, and D7 components agree very well with those of corresponding components appearing in the extract. Cyclic siloxanes can be well monitored on the mass chromatogram of the m/z 281 fragment ion, while

the linear siloxanes on that of the m/z 73 fragment ion (Fig. 6). The latter fragment peak, corresponding to the trimethylsilyl group, appears in almost all dimethyl-siloxane oligomers[33] (also in cyclic ones, but with lower intensity), so by a comparison of the m/z 281 and 73 mass chromatograms information can be obtained on other, noncyclic siloxane species. The molecular ion did not show up in the mass spectra of the linear oligomers, so their molecular composition cannot be discussed further. Their structure can be identified in a later step by chemical ionization and chemical derivatization. A large peak appeared between the D18 and D19 components, which was identified as a phenylated silicone oligomer. Out of the 16.88 mg/g siloxanes extracted from the sample in chloroform after 8 h the total amount of cyclic oligomers amounted to 11.36 mg/g, linear oligomers to 1.37 mg/g, while the amount of the phenylated silicone oil was 4.15 mg/g, i.e., the most important extractable are the cyclic oligomers. Figure 7 plots the relative weight of the various oligomers against the number of the D units.
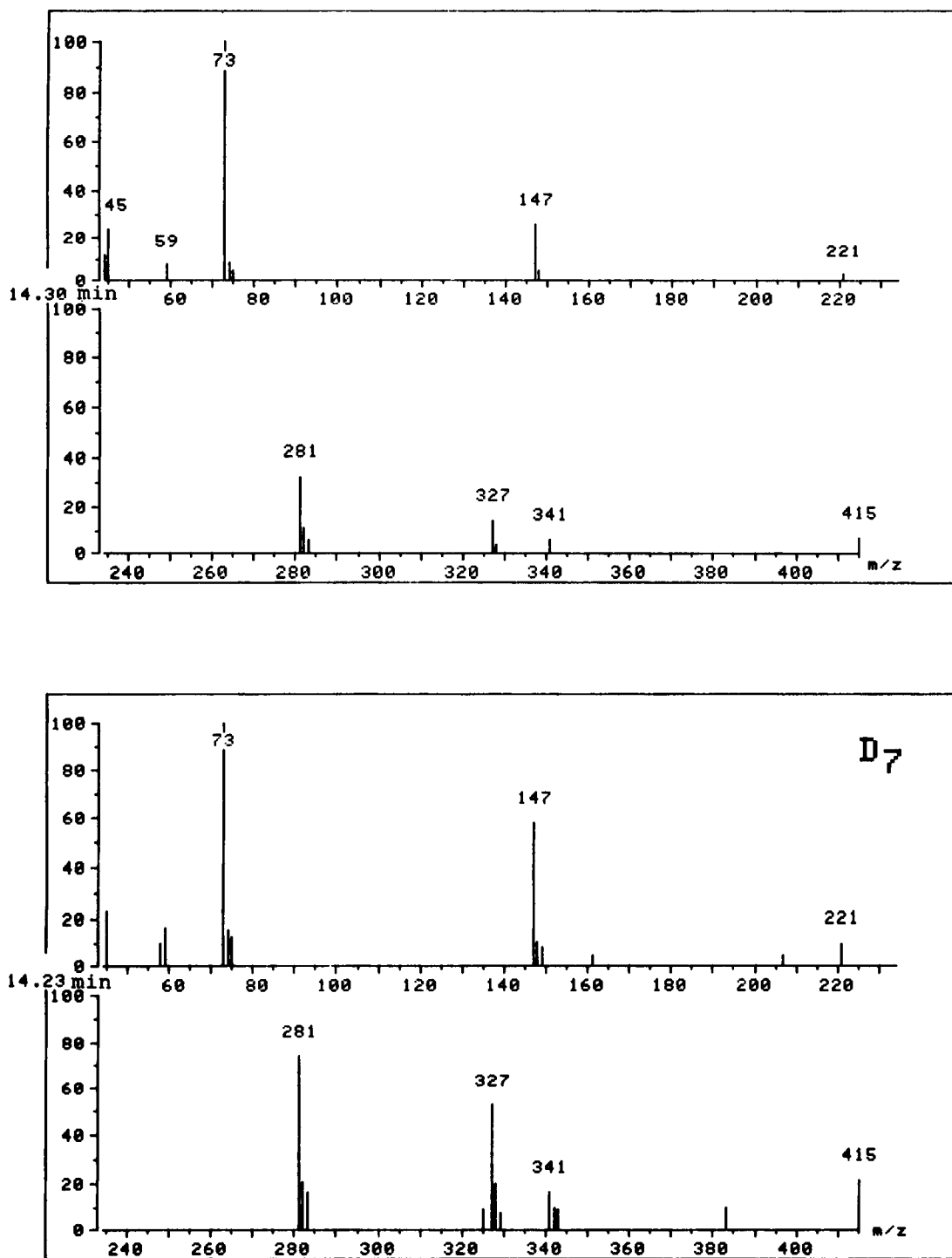
Figure 4   Comparison of the MS of the first, well-detectable peak appearing at 14.30 min in the GC–MS (corresponding to 15.78 min in Fig. 4) with that of a pure D7 (tetradeca-methyl-heptasiloxane) standard.

A bimodal distribution is well discernible. The presence of low molecular antioxidants could not be confirmed.

In order to check whether low molecular siloxanes are present on the surface due to oxidative degradation or they are purely the result of diffusion mi-
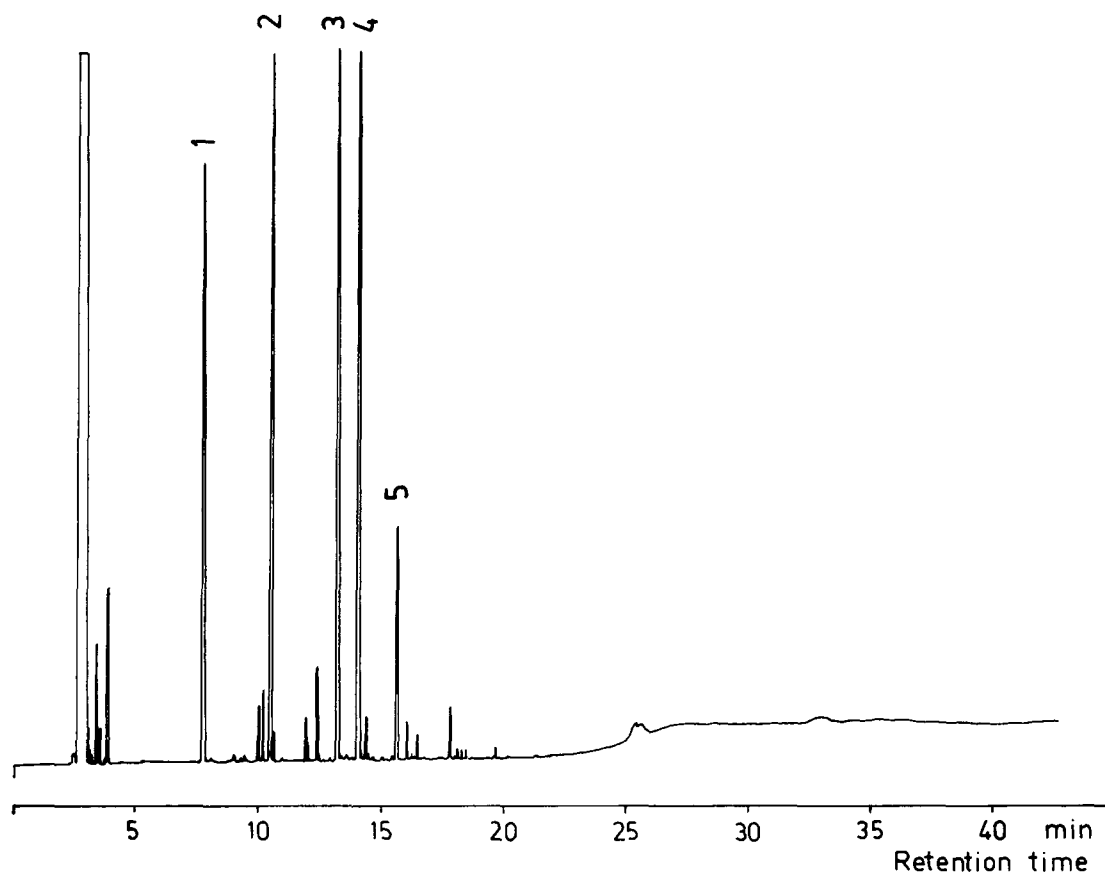
Figure 5 Gas chromatogram of a mixture of D4, D5, D6, and D7, measured under identical conditions as in Fig. 4. The peak appearing at 14.21 min corresponds to the tetradecane internal standard.

gration, we tried to analyze the low molecular species formed on the surface of the extracted silicone rubber sample after oxidative plasma treatment. A piece of the well-extracted sample surface, after being exposed to the *ex situ* oxidative plasma, was washed with 10 mL chloroform, then soaked in an other 10 mL chloroform for 1 h. Volume of both aliquots of solvent has been reduced from 10 mL to 30 μL, then analyzed by GC. The washing solvent contained about 2 μg, the soaking solvent about 8 μg, chromatographically detectable siloxane. (Detectability limit within these conditions was about 0.5 μg.) This experiment has shown that the oxidative damage itself does also produce low molecular siloxanes at the surface, but much less than that quantity, which can migrate from the bulk to the surface.

DISCUSSION

The detected trend of the surface compositional changes of the air plasma treated silicone rubbers

(i.e., increasing O content, decreasing C content) is in accordance with most of the earlier observations.[6-17] The reverse tendency at longer exposure times, observed by us in the case of a 15-min *in situ* treatment, has already also been reported.[25] The degree of deviation (or stoichiometric distance R), however, depends strongly on the details of treatment and recovery.

Suzuki et al.[6-8] did not publish ESCA compositions for the nontreated samples, so we could calculate the deviation from the ideal stoichiometry (SiC_2O) only. It is interesting to note that in the case of the combined ion-sputtering/ESCA data published by Suzuki et al.[6,7] for O_2^+ ion treated surfaces even the composition belonging to the longest sputtering time is far from the ideal stoichiometry (R value is 1.0–1.2). (This may be due to the presence of fillers or other nonsiloxane component.) At the point of the maximum deviation, R increases to 1.4–1.8, i.e., the degree of damage is between the corresponding values of the extracted and nonextracted samples. R value calculated from the data
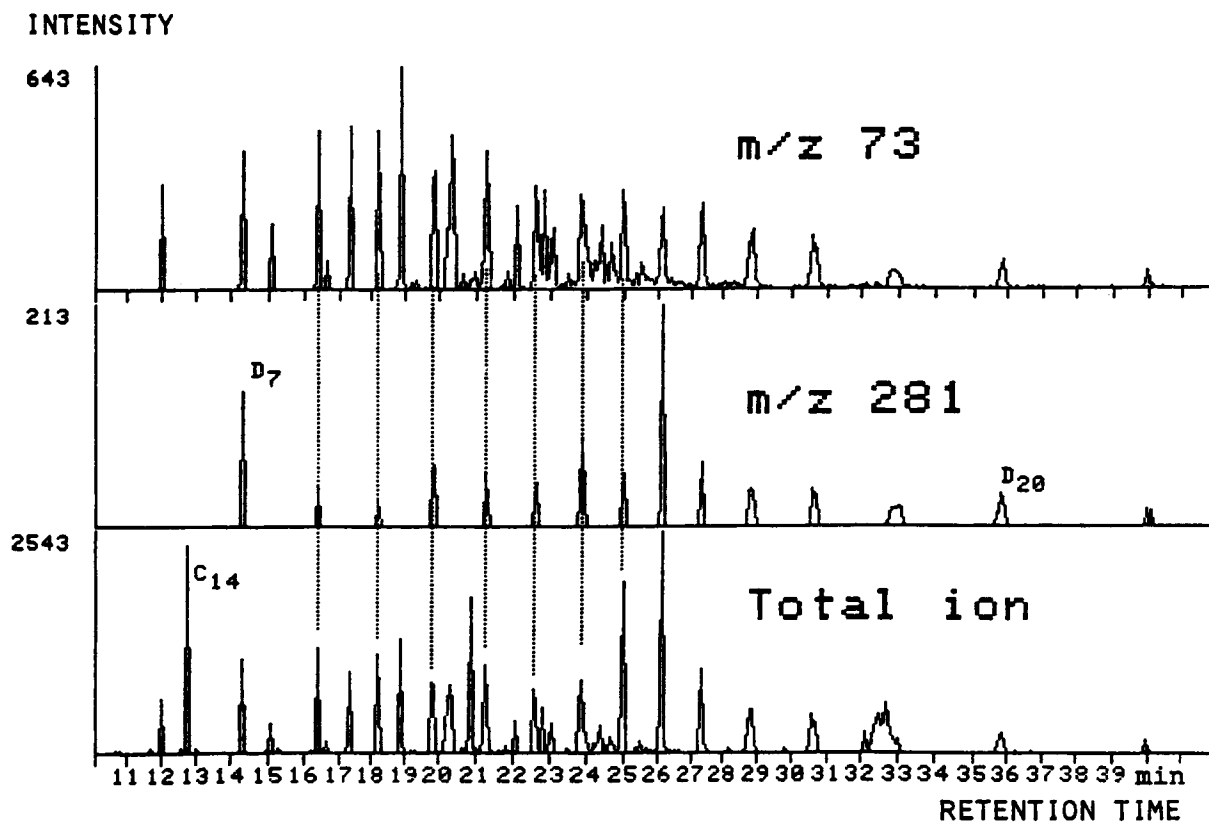
Figure 6 Comparison of the total ion chromatogram with the m/z 73 and m/z 281 fragment chromatograms of the 8 h chloroform extract.
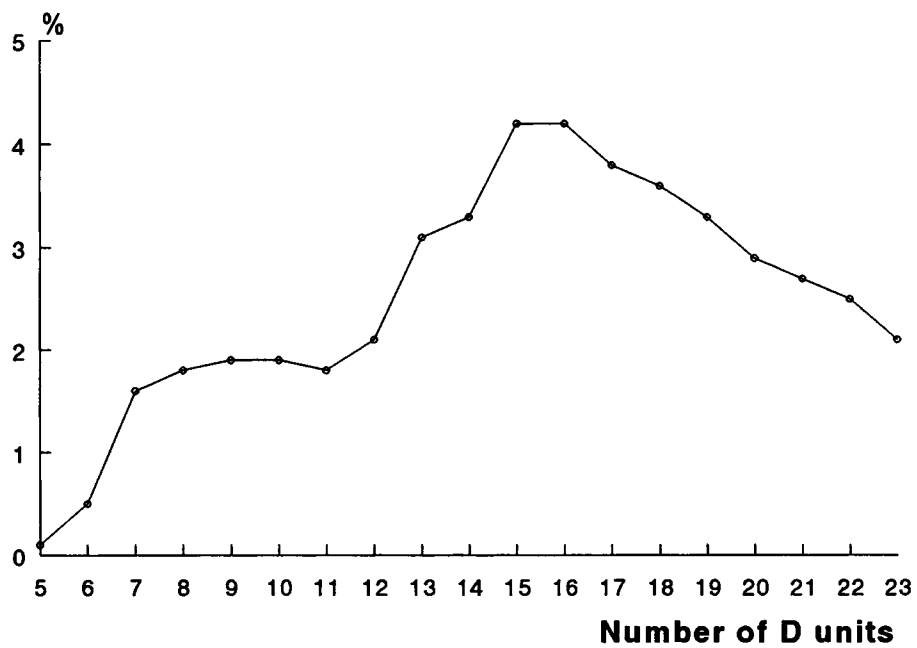

Figure 7 Distribution of the cyclic siloxane oligomers in the chloroform extract, expressed as a percentage of the total extracted quantity.

published by Morra et al.[11] is 1.3 immediately after the treatment, which decreases to 0.6 after 120 h recovery at room temperature. This datum is in agreement with our own observation that the recovery is not total. The degree of oxidative damage after 20 h exposure to high voltage in a fog chamber[16] is quite substantial; calculated R value is 2.1, which decreases to 0.4 in 24 h.

It is clear from the data presented in Table II that the recovery is not uniform: it is much more advanced in the topmost layer than in the subsurface region. Data supporting this conclusion can also be found in Suzuki et al.'s publications,[6,7] but without any further discussion. Since they did not publish etch rates, their etch times cannot be converted into thickness values. From the present angle-dependent ESCA measurements the thickness of the recovered layer can be estimated. The photoelectron sampling depth is about 6 nm in the case of 90° of take-off angle,[9,35] which is reduced to 6 nm $\times$ sin 30° = 3 nm in the case of 30° of take-off angle. This recovered layer closely resembles the bulk: its Si content, and the distribution of the organic and inorganic type silicon atoms are closer to the initial values (measured before plasma treatment), than to those measured after treatment at 90° of take-off angle (Table IV). Morra et al.[11] have also observed that the number of inorganic Si atoms increased from 17 to 79% after the oxidative plasma treatment, which decreased to 57% after 120 h of room temperature recovery. They did not estimate the in-depth distribution of these atoms by XPS, but got a similar information from SSIMS measurements performed after the $^{18}O_2$ plasma treatment and also concluded that the composition of the recovered layer was closer to that of the bulk than to that of the degraded layer.

The fact that the extent of recovery of the topmost layer is much less in the case of the solvent-extracted sample (Table II) suggests that the recovery is mainly caused by the diffusion of organic siloxane oligomers (with an elemental composition practically identical to that of the polymer) onto the surface. Moreover, it seems that the low molecular silicone oils play a role not only in the recovery but also exert a definite protecting effect against the oxidative plasmas. This is shown by the fact that the surface damage detected right after the plasma treatment is much more pronounced in the extracted sample than in the nonextracted one. Obviously, during short-term oxidative plasma treatment, it is just these low-molecular-weight compounds that undergo fragmentation and evaporation from the surface, thus protecting the latter from an extensive damage.

The distribution of the C1s components of the degraded surfaces is remarkably different for the extracted and the nonextracted samples (Fig. 1 and Table IV). In the case of the nonextracted sample it is only the concentration of the singly oxidized carbon atoms (BE = 286.1 eV) that increases slightly after the plasma treatment, while in the case of the solvent-extracted sample the relative amounts of the highly oxidized carbons (BE = 287.6 and 289.1 eV) increase substantially, and another line also appears at BE = 282.5 eV. This latter may be due to amorphous or to graphitic carbon, since such species were already detected by Suzuki et al.[8] by Raman spectroscopy.

In the Si2p region a new component appears after air plasma treatment (Fig. 2 and Table IV). In the literature the Si2p peak around 103 eV is assigned[9,36] to an "inorganic, silica-like phase." The percentage of inorganic silica after plasma treatment reaches 85% in the extracted sample, while it is only 43% in the nonextracted one. Thus, the results of the peak fitting for both the Si2p and the C1s peaks corroborate the conclusion drawn above from the compositional changes: the siloxane network of the extracted sample is much less resistant to oxidative damage than the original rubber containing organosiloxane oligomers.

The recovery process probably cannot be attributed exclusively to silicone oil diffusion, since the extracted sample also exhibits a measurable, albeit slight, recovery. The percentage of organic Si atoms offers a good measure of the recovery, as it is 100% in the initial state. The organic Si content of the top layer of the nonextracted sample after 24 h reaches 92%, while the corresponding value in the extracted sample is only 30%, so one can assume that roughly about one-third of recovery is due to the reorientation of the polymeric chains and about two-thirds of it to the diffusion of low molecular siloxanes. The pronounced decrease of the strongly oxidized carbons in the top layer of the recovered extracted sample (cf. the last three rows of Table IV) lends support to the suggestion that the recovery of the extracted sample is due to group reorientation. The slightly oxidized carbon and the newly formed amorphous (or graphitic) carbon, however, remain in the top layer of the recovered sample. This is reasonable, since they are less polar and do not increase the surface energy substantially. The reorganization of the surface structure, driven by surface energy minimization, has been observed in other

systems, not containing low molecular additives (see, e.g., Refs. 22–24), and differences between the aging behavior of oxygen ion-implanted silicone rubbers in air and *in vacuo*[7] indicate that air and airborne water and other components may also play some role in the recovery process.

As to the chemical composition of the heavily oxidized surface layer obtained immediately after the oxidative plasma treatment, both "silicalike" structures and Si atoms bound to 3 oxygens have been suggested.[11] Both seem acceptable: the binding energies of Si2p and O1s levels shift toward higher energies in the polydimethylsiloxane–methylsiloxane T resin–SiO$_2$ series.[36] In addition, Auger parameters measured in the present work (Table III) are closer to the published value for silica gel[36] than to that for crystalline silica.[36] Silica gel has a less ordered, partially hydrated structure, which is closer to the expected degraded siloxane structure than the crystalline or amorphous silica. Furthermore, silica or silica gel may be present not only as degradation products of polydimethylsiloxane, but also as filler residues, since silica aerogel (e.g., Aerosil) or finely ground silica is frequently added to silicone rubber formulations.[1–3]

CONCLUSION

In the present XPS study of the oxidative damage and recovery of silicone rubber surfaces, certain findings are in agreement with previous results, but new features have also been found.
The points that are in agreement with earlier results are as follows:

1. Under the effect of oxidative plasma the oxygen content of surface increases, the carbon content decreases.
2. This is due the formation of Si atoms bound to 3 or 4 oxygens (inorganic or silica-type Si atoms) instead of 2, as in PDMS (organic type Si atoms).
3. The portion of inorganic Si atoms decreases with increasing recovery time, but the recovery is only partial.

The comparison of the behavior of extracted versus nonextracted samples revealed the basic importance of low molecular silicone oils both in the oxidation and in the recovery processes, which was supposed, but only partially proved, by earlier investigators. Some important new findings are listed below:

1. The compositions of the oxidized and of the recovered surfaces differ significantly in the extracted and in the nonextracted samples.
2. The percentages of inorganic Si and of highly oxidized carbon atoms are much higher, the degree of recovery is much lower in the extracted sample.
3. The in-depth composition profile of the recovered surface is not constant.
4. The estimated thickness of the almost totally recovered top layer on the nonextracted samples is less than 3 nm.
5. The solvent extract of the silicone rubber contains predominantly cyclic dimethylsiloxane oligomers and some linear silicone oil components.

According to the above-mentioned facts the recovery process observed in silicone rubbers is predominantly due the migration of low molecular silicone oil components to the surface rather than to group reorientation assumed in the hydrophobic recovery of other polymers. The percentage of organic Si atoms offers a good measure of the recovery, since it is 100% in the initial state. The organic Si content of the top layer of the recovered nonextracted sample reaches 92%, while the corresponding value in the extracted sample is only 30%, so one can assume that roughly about one-third of recovery is due to the reorientation of the polymeric chains and about two-thirds of it to the diffusion of low molecular siloxanes.

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