Oxygen Microwave Plasma Treatment of Silicone Elastomer: Kinetic Behavior and Surface Composition

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ABSTRACT: Silicone elastomers were surface modified by oxygen microwave plasma under different conditions and the elemental composition was followed by X-ray photoelectron spectroscopy (XPS). The changes in elemental composition were mapped by a method based on ternary XPS diagrams that we have recently developed. Already at the shortest treatment times, 5 s, the change in surface composition is more than one-half the maximum change obtained on prolonged exposure. After this initial change, the surface gradually oxidizes toward the final composition. Curve resolutions of C1s and Si2p XPS data showed that the initial jump in surface composition is caused by an oxidation of silicon where one of the two methyl groups are replaced by an oxygen. The second methyl group appears to be more difficult to remove, but as the treatment progresses, the number of oxygen bonded to silicon gradually increases. The dominating form of carbon acts as unoxidized methyl groups throughout the process, but the total carbon percentage decreases as the treatment progresses. This indicates either that the methyl groups are removed without prior oxidation or that the methyl groups are removed shortly after oxidation. A silica-like surface layer was formed on prolonged plasma treatment under all the investigated conditions. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 91: 4098–4104, 2004

Key words: silicones; surfaces; ESCA/XPS

INTRODUCTION

Surface modification of silicone elastomers by oxygen plasma and related techniques have been studied from different points of view, including their use as electrical insulation and membranes for selective gas separation and for the improvement of the adhesion of coatings. The long clinical history of silicone elastomers in medical applications has also led to extensive research in the field.

Our main interest is in the surface modification of silicone elastomers intended for use as biomaterials. Plasma treatment has the advantage of modifying only the outermost surface layer without changing the bulk properties of the material. We have previously shown that argon–plasma-treated silicone elastomers can be grafted with well-defined surface structures.[1] The ability to obtain novel plasma modification strategies demands a thorough understanding of the processes involved and of how the resulting structures are formed. Furthermore, the rate of change in surface composition and its dependence on the plasma parameters are also important. To obtain this information, a method of not only analyzing but also evaluating the data is required.

Oxygen plasma treatment of silicone elastomers leads to changes in the elemental surface composition. The relative concentrations of carbon, silicon, and oxygen can be quantified by using X-ray photoelectron spectroscopy (XPS). The results are normally plotted either as three curves of elemental percentages or as two curves of elemental ratios (e.g., C/Si and O/Si), as functions of treatment time. The disadvantage of these methods is that all the curves have to be interpreted together because they are dependent on each another. We have therefore developed a method of evaluating surfaces containing three elements, excluding hydrogen that cannot be detected by XPS, by plotting the data in a ternary diagram.[2] This is a powerful way of presenting each surface composition as a single data point and opens up possibilities for more straightforward interpretations by using simple mathematical expressions.

In the present article, the surface structures formed during oxygen microwave plasma treatment of silicone elastomers are related to the progressing change in total elemental surface composition. This leads to an insight into the behavior of silicone elastomers exposed to plasma that is necessary for the ability to choose suitable conditions for surface modifications. The elemental composition of plasma-treated specimens is characterized by XPS and plotted in ternary XPS diagrams. Furthermore, the oxidative states of carbon and silicon exposed to oxygen plasma are assessed by curve resolution of C1s and Si2p, respec-

tively. The onset of formation of silica-like layers is also of interest because such layers limit the ability to create homogeneous surfaces with suitable mechanical properties.

EXPERIMENTAL

Materials

The raw materials for the polydimethylsiloxane (PDMS) sheet, (30–35%) methylhydro-(65–70%) dimethylsiloxane copolymer (PS123), vinyldimethyl-terminated poly(dimethylsiloxane) (PS442), and platinum-divinyltetramethyldisiloxane catalyst (PC072), were purchased from United Chemical Technologies (USA) and were used as received. The gases were purchased from AGA Gas AB (Stockholm, Sweden) and had a purity of at least 99.996%.

PDMS sheet

Nine grams of PS123, 205 g PS442, and 50 μL PC072 were mixed thoroughly to give a SiH : vinyl ratio of approximately 2. The mixture was immediately cast in glass Petri dishes to a thickness of 3 mm and cured at room temperature for 7 days. The sheet obtained was Soxhlet extracted in analytical reagent hexane from Labscan Ltd. (Ireland), for 7 days, followed by deswelling, and drying in air and vacuum before storage at ambient conditions.

Plasma treatment

The plasma treatment was carried out in a V15-G microwave plasma system from Plasma-Finish GmbH (Germany) operated at 2.45 GHz. The system was connected to a Pfeiffer DUO 035 D C vacuum pump. The plasma treatment chamber was subjected to a cleaning process involving at least 20 min of oxygen plasma treatment before use. Each sample was subjected to at least three degassing cycles where the pressure was decreased below 1 Pa, followed by flushing with oxygen to a pressure exceeding 100 Pa. The plasma treatment was conducted at a preset power, pressure, and treatment time. After the plasma treatment, the chamber was immediately flushed with hydrogen for 300 s at a pressure of about 80 Pa before ventilation to ambient pressure by using argon. The specimens were carefully placed on glass Petri dishes immediately after the plasma treatment.

X-ray photoelectron spectroscopy

An AXIS-HS X-ray Photoelectron Spectrometer (Kratos Analytical, Manchester, UK) was used with a monochromatic AlKα X-ray source operated at 15 kV and 20 mA. The take-off angle was 90° with respect to the sample surface. The pass energies of the spectra used to determine the elemental composition and the curve resolution were 80 and 20 eV, respectively. The pressure was below 10^{-8} Pa during the measurements. Background subtractions were made by drawing a straight line between two suitable points,[3] and the sensitivity factors were supplied by the manufacturer. Curve resolutions were obtained by a least-squares minimization procedure involving simultaneous fitting of all C1s and Si2p peaks of each specimen. The curve shape was assumed to be Gaussian. The Si2p(1/2) was assigned a binding energy 0.61 eV higher than the Si2p(3/2) with an intensity ratio of 1 : 2. All XPS measurements were performed within 24 h after the plasma treatment.

Scanning electron microscopy (SEM)

The specimens were sputter coated with Au/Pd (60/40) by using a Desk II from Denton Vacuum operated at 45 mA for 10 s. A JEOL JSM-5400 scanning electron microscope operated at 10 kV was used to examine the surfaces. Representative pictures were taken and the extent of cracking was determined on an arbitrary scale.

RESULTS AND DISCUSSION

The elemental composition of oxygen–plasma-treated silicone elastomer under various plasma conditions was characterized by XPS. The surface percentages of carbon, silicon, and oxygen for specimens exposed to different plasma conditions were plotted in ternary XPS diagrams. The direction of the trend in the diagrams and the rate of change in elemental composition were followed by defining vectors from the points corresponding to untreated composition to the data points of specimens exposed to oxygen plasma. The presence of a cracked silica-like layer was investigated by SEM. To provide further insight in the molecular structure in the surface region, curve resolution of C1s and Si2p was performed.

Elemental composition

The elemental composition of the oxygen–plasma-treated silicone elastomers is presented in ternary XPS diagrams (Fig. 1).

It is evident in Figure 1 that there is a remarkable change in surface composition already at the shortest treatment times. Although not specifically commented on or discussed, the elemental composition of polydimethylsiloxane exposed to oxygen radiofrequency plasma reported by Owen and Smith[4] also changed rapidly during the first few seconds. Figure 1 also shows that the change on prolonged treatment after this initial process is slower. All plasma treatment
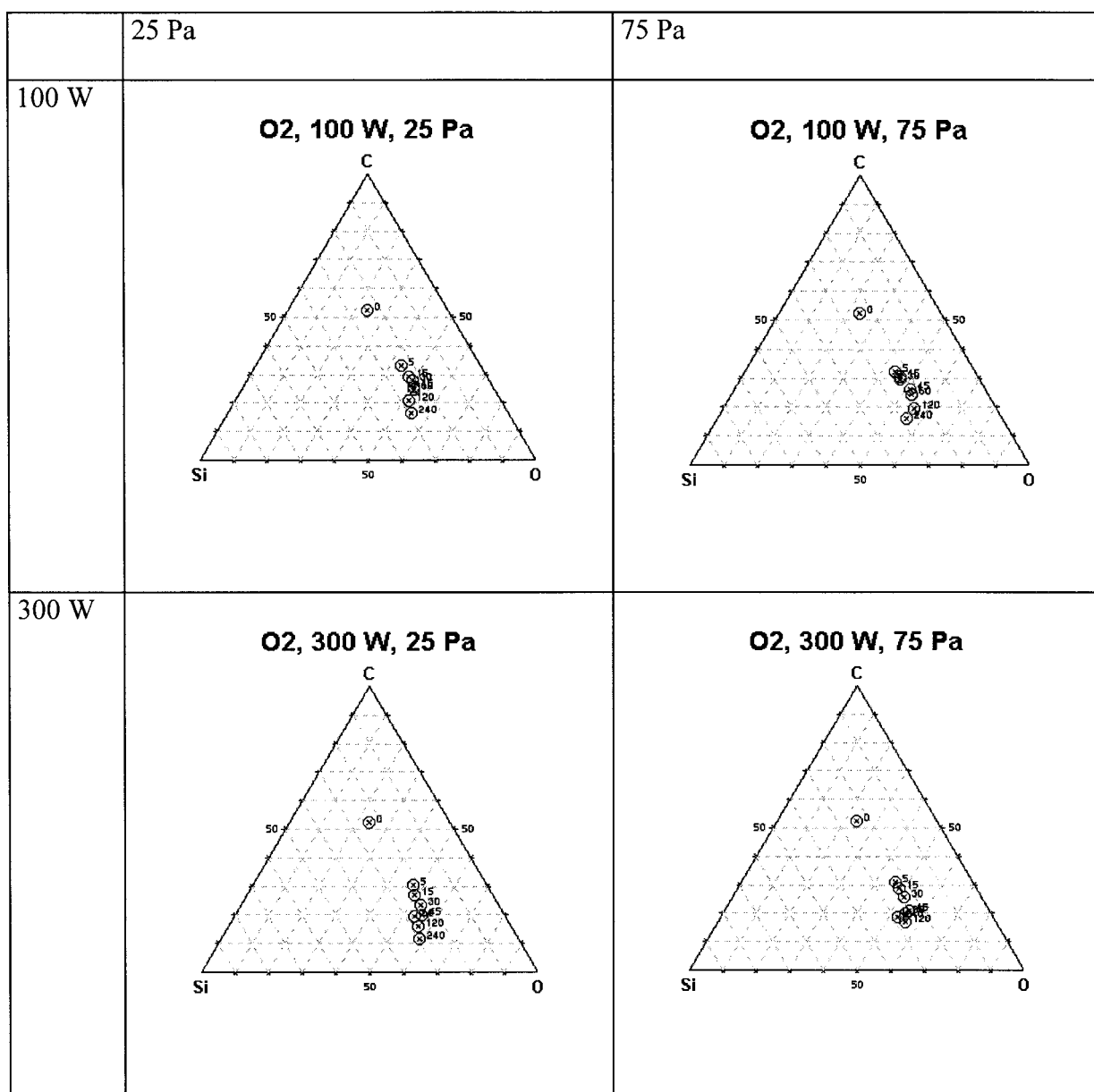
Figure 1 Elemental composition of silicone elastomers treated in oxygen plasma under different conditions plotted in ternary XPS diagrams.

conditions show similar trends. The percentage of carbon decreases and the percentage of oxygen increases, whereas the silicon concentration remains relatively unchanged at shorter treatment times. However, the silicon percentage increases at the longest treatment times.

Rate of change in elemental composition

A vector from the point in a ternary XPS diagram corresponding to untreated composition (subscript 0) to the composition of a treated sample (subscript n) is defined as

$$\mathbf{v}_n = (\Delta C_n, \Delta Si_n, \Delta O_n) \tag{1}$$

where $\Delta C_n = C_n - C_0$, $\Delta Si_n = Si_n - Si_0$, and $\Delta O_n = O_n - O_0$. To follow the change in overall elemental surface composition, we plot the distance between the point of untreated surface composition to the point corresponding to the surface composition at a certain treatment time. The stoichiometric distance is calculated by

$$R_n = |\mathbf{v}_n| = \sqrt{\Delta C_n^2 + \Delta Si_2^n + \Delta O_n^2} \tag{2}$$

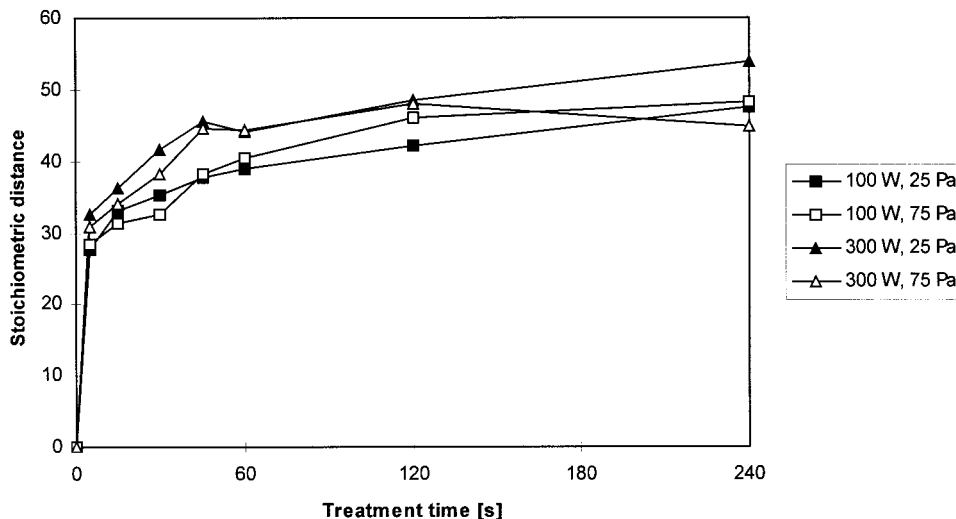and is a measure of the overall change in elemental composition the surface has undergone from the un-

Figure 2 Stoichiometric distance for silicone elastomers treated in oxygen plasma under different conditions.

treated to the composition after a certain plasma treatment time. The stoichiometric distance of silicone elastomers exposed to oxygen plasma under different treatment conditions is plotted as a function of treatment time in Figure 2.

More than one-half the ultimate stoichiometric distance is reached during the first 5 s. This reflects the ease with which silicone elastomers undergo rapid changes in surface composition when exposed to oxygen microwave plasma. As expected, surfaces treated at 300 W undergo a more rapid change in elemental composition than surfaces treated at 100 W. At the lower pressure, the treatment shows a higher rate of change during the first 45 s, which can be due to more reactive species in the plasma because the energy is distributed among fewer species. At longer treatment times, this effect is not pronounced. The stoichiometric distance for the specimens exposed to plasma at 25 Pa, 300 W, and 240 s is shorter than that of the specimens treated for 120 s. This is probably due to the cracked silica-like layer, as will be discussed later. Cracked surface layers may affect the measured compositions both by exposing the less oxidized underlying material and by allowing diffusion of low-molecular-weight silicone species to the surface.

Silica-like surface layers

The crack formation as mentioned in the previous section was confirmed by SEM. The formation of a silica-like surface layer during oxygen plasma treatment of silicone elastomers has been reported by several authors.[4–7] Cracking of these silica-like surface layers eventually occurs on prolonged exposure under all the plasma conditions investigated. The extent of cracking has been expressed by rating each specimen on a scale from no cracks (0) to severe cracking (8). The

scale is arbitrary (i.e., a specimen with a higher crack rating has more cracks than a specimen with a lower number). Surfaces with similar occurrence of cracks are assigned the same number. The results are shown in Figure 3.

The silicone elastomers exposed to oxygen plasma at 100 W were slightly cracked at 120 s, but there was a pronounced formation of cracks at 240 s. The specimens treated at 300 W showed the first cracks already at 60 s, as compared to the ones treated at 100 W, where the onset of cracking is first observed at specimens treated for 120 s. This was not surprising because the higher power leads to a higher rate of change in surface composition than the ones carried out at the lower power.

Hillborg et al. studied the nature of silica-like surface layers formed at the surface polydimethylsiloxane exposed to air plasma at 100 W and found that all specimens were cracked at 180 s, whereas only some of them were cracked at 120 s.[8] This indicates that plasma treatment in oxygen and air is quite similar in this respect.

Our main interest is to create biomaterials and these silica-like surface layers are not desired due to the inhomogeneous surface composition introduced. We therefore desire the shorter treatment times not leading to the formation of these layers.

Curve resolution of Si2p and C1s

The oxygen plasma treatment leads to an increase in the concentration of oxygen in the surface region. Because there are pronounced shifts in the binding energies of silicon and carbon depending on the oxidative state, further insight into the changes in molecular structure of the plasma-treated surfaces can be obtained by curve resolution of the Si2p and C1s XPS regions. The cracking
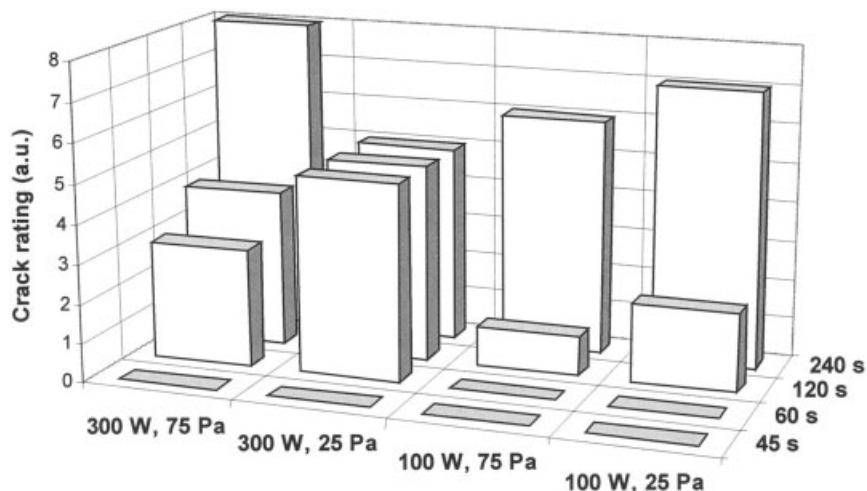
Figure 3 Crack formation at the surface of oxygen–plasma-treated silicone elastomer. The specimens were rated from no cracks (0) to severe cracking (8) on an arbitrary scale based on observations of SEM images.

of the silica-like surface layers discussed in the previous section leads to uncertainty in the interpretation of the curve resolutions, and therefore, we present only the

results from the uncracked surfaces (i.e., 0–120 and 0–60 s for treatments carried out at 100 and 300 W, respectively). The results of the curve resolution for specimens
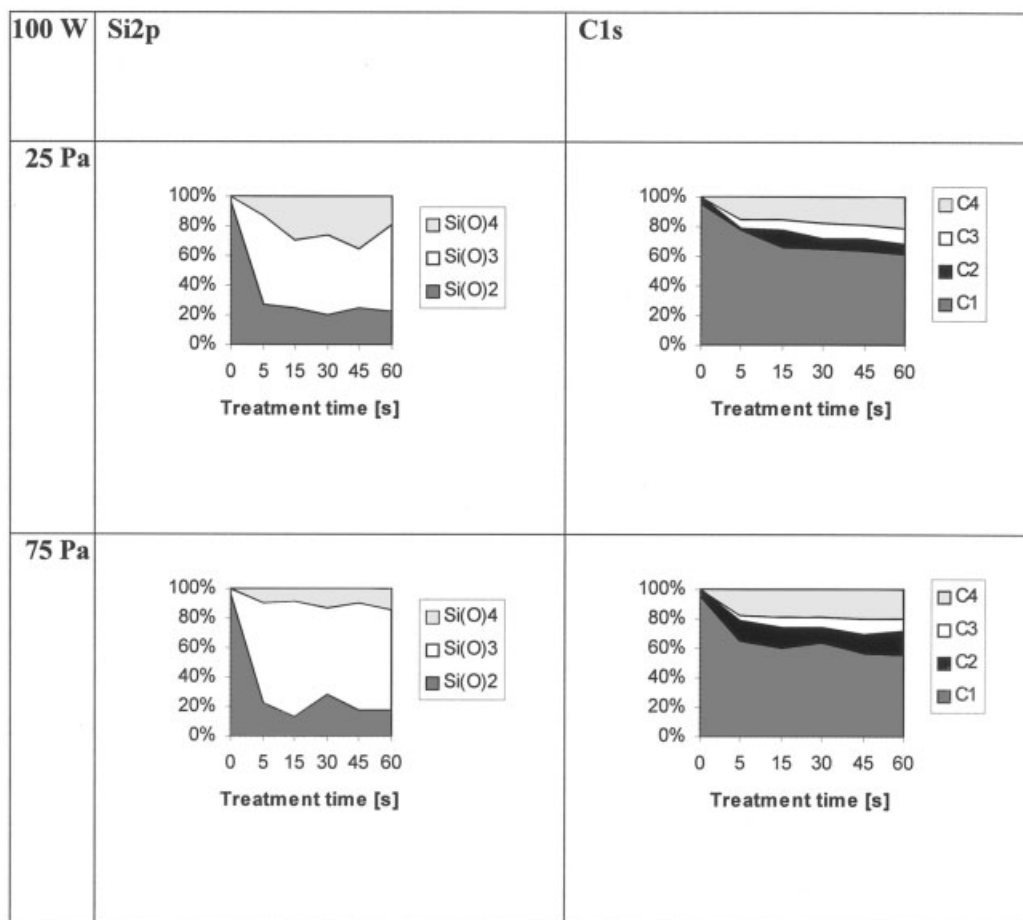

Figure 4 Curve resolution of Si2p and C1s XPS data of silicone elastomer treated at 100 W in oxygen plasma. Si(O)2, Si(O)3, and Si(O)4 denote silicon bonded to two, three, and four oxygen atoms, respectively. C1, C2, C3, and C4 denote zero, one, two, and three bonds to oxygen, respectively.

Figure 5 Curve resolution of Si2p and C1s XPS data of silicone elastomer treated at 300 W in oxygen plasma. Si(O)2, Si(O)3, and Si(O)4 denote silicon bonded to two, three, and four oxygen atoms, respectively. C1, C2, C3, and C4 denote zero, one, two, and three bonds to oxygen, respectively.
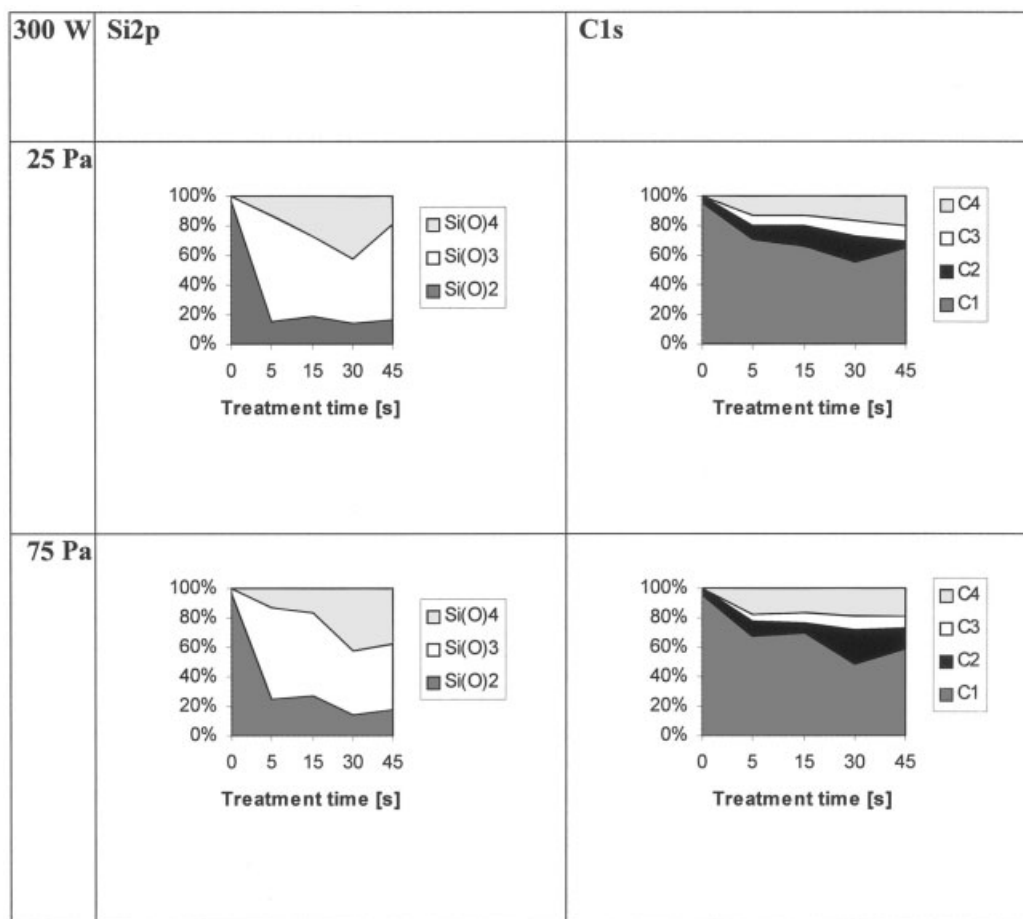
exposed to oxygen plasma at 100 and 300 W are shown in Figures 4 and 5, respectively.

In the original configuration of the silicone elastomer, two methyl groups and two oxygen atoms are bonded to silicon. At both 100 and 300 W, there is a remarkable change from two to three oxygen atoms bonded to silicon already after the first 5 s. This explains the rapid initial change in elemental surface composition already reported. After this initial change in the oxidative state of the silicon, the proportion of silicon bonded to two oxygen atoms remained at a level of about 10–30%. This can be explained either by the presence of low-molecular-weight species at the surface or by the possibility that the analysis depth of XPS is deeper than the modified surface region. All the plasma-treated specimens contained a proportion of silicon bonded to four oxygen atoms (i.e., a silica-like configuration). However, it appears that the preferred configuration of oxygen–plasma-treated silicone is for silicon to be bonded to three oxygen atoms because this is the predominant configuration regardless of plasma parameters or treatment times. This indicates

that the first methyl group is more readily replaced by an oxygen than the second methyl group. The reason for this is not fully understood, although the key to the solution probably lies in changes in the partially positive charges on silicon and partially negative charges on silicon when an electron-donating methyl group bonded to silicon is replaced by an oxygen.

The curve resolution of C1s XPS spectra shows that unoxidized carbon is dominating over the oxidated carbon species during the plasma treatment. This is remarkable considering the fact that the percentage of oxygen increases from 25% to over 50%. This is in agreement with the results Morra et al. obtained with radiofrequency [18]O plasma analyzed with static secondary ion microscopy (SSIMS) and XPS, where they conclude that the oxygen was bonded mainly to silicon and to only a minor extent to carbon.[9]

However, we have to bear in mind that the carbon concentration decreases from 50% to below 20%. The methyl groups cannot therefore be considered to be inert. The explanation for this is either that the methyl groups are removed from the silicon without prior

oxidation or that the oxidized methyl groups are removed shortly after oxidation. The latter alternative is consistent with the explanation we offered in the silicon case. The influence of the electron-donating methyl group leading to strong bonds to silicon bonded to three oxygen atoms will be diminished when oxidized. This oxidized group is expected to have weaker bonds to silicon. However, there is always a distribution of different oxidized carbon species at the surface of an oxygen–plasma-treated silicone elastomer.

CONCLUSION

Silicone elastomers treated in oxygen microwave plasma undergo a rapid initial change in surface composition. More than one-half the total change in overall surface composition as calculated by the stoichiometric distance occurs during the first 5 s. According to curve resolution of XPS, one of the two methyl groups is replaced by oxygen in this initial stage. The subsequent process is slower and leads to a further decrease in carbon and an increase in oxygen concentration. The second methyl group attached to silicon is more strongly bonded when silicon has three bonds to oxygen. This may also explain why the remaining carbon species are found to be remarkably unoxidized. The silicon content remains at about 25% under moderate treatment conditions, but increases to about 30% at the longest treatment times. This increase is caused by the formation of a silica-like surface layer. Cracking of these brittle surface layers was observed at treatment times of at least 120 and 60 s for specimens exposed to 100 and 300 W, respectively. This is due to a more rapid plasma treatment process for specimens exposed to the higher power. These silica-like surface layers are not desired when surfaces are to be tailored for use as biomaterials. The rapid change in surface composition during the initial stage of the oxygen microwave plasma treatment seems to be difficult to avoid even by exposing the silicone elastomers for short treatment times at low power.

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