

Silicone Elastomers with Controlled Surface Composition Using Argon or Hydrogen Plasma Treatment

Björn Olander, Anders Wirsén, Ann-Christine Albertsson

Department of Polymer Technology, Royal Institute of Technology, SE-100 44 Stockholm, Sweden

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ABSTRACT: Plasma treatment of poly(dimethyl siloxane) (PDMS) leads to changes in the surface composition that can be followed by X-ray photoelectron spectroscopy (XPS). Prolonged plasma treatment in argon or hydrogen leads to an increase in oxygen, a decrease in carbon, and only minor changes in the silicon content. The extent of the change in elemental composition is dependent on the plasma conditions (e.g., the power and pressure during the treatment). We have determined how these parameters influence the surface composition of PDMS exposed to argon and hydrogen microwave plasma as a function of treatment time. A model has been developed describing the extent of change in surface composition under different plasma conditions. The

power had a large impact on the rate of change in elemental surface composition, whereas the pressure had only a minor influence. We show that the rate of change in elemental composition can be described by one factor common for all treatments and one factor specific for each plasma condition of power, pressure, and gas. Using this model we can determine the plasma parameters and treatment time to obtain any desired extent of surface modification. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 1378–1383, 2003

Key words: silicones; surfaces; ESCA/XPS; elastomers; plasma treatment

INTRODUCTION

Silicone elastomers are well-established materials used in fields ranging from biomaterials to electrical outdoor insulation. In many of these applications, the surface properties are crucial for the performance of the product. Plasma treatment is one of the methods used to alter the surface without changing the bulk properties of the material. Regardless of the purpose of the modification, its characterization is important for the ability to design a process leading to desired surface properties. The processes taking place must be understood and the parameters affecting the results should be identified. It is also important to quantify to what extent the parameter settings affect the surface composition. Some of the reports of earlier surface modification processes we have developed to obtain surfaces for use as biomaterials also include quantitative information as to how the most important process parameters affect the surface structure.^{1,2} This knowledge has enabled us to obtain the desired surface compositions in a straightforward way.

We are currently interested in plasma surface modification followed by a grafting step.³ This procedure for grafting onto the surface of poly(dimethyl siloxane) (PDMS) using microwave plasma treatment in

argon illustrates the importance of further investigations of how the surface is affected by the different conditions.^{4,5} Hydrogen plasma treatment is also potentially interesting for this type of surface modification.⁶

Our aim is to tailor the surface composition by plasma treatment of silicone elastomers with subsequent grafting of molecules suitable as biomaterials. In this article, we present a method to choose suitable parameters to obtain desired elemental surface compositions of PDMS plasma treated in argon or hydrogen. The influence of the different plasma conditions on the resulting surface was followed by X-ray photoelectron spectroscopy (XPS). Using methods based on the ternary XPS diagrams previously reported, we have been able to quantify to what extent the parameters of power and pressure in argon and hydrogen plasma affect the surface composition as a function of treatment time.⁷ A simple mathematical model of the extent of change in surface composition has been developed. This makes it possible to choose suitable parameters to obtain the surface compositions we desire.

EXPERIMENTAL

Materials

The raw materials for the PDMS sheet, (30–35%)methylhydro–(65–70%)dimethylsiloxane copolymer (PS123), vinyl dimethyl-terminated poly(dimethyl siloxane) (PS442)

Correspondence to: A.-C. Albertsson (aila@polymer.kth.se).

and platinum–divinyltetramethyldisiloxane catalyst (PC072), were purchased from United Chemical Technologies (Bristol, PA) and were used as received. Analytical reagent grades of hexane from Labsan Ltd. (Dublin, Ireland) were used as received. Argon ($\geq 99.996\%$) and hydrogen ($\geq 99.9999\%$) were purchased from AGA (Stockholm, Sweden).

PDMS sheet

PS123 (9 g), PS442 (205 g), and PC072 (50 μL) were mixed thoroughly to give a SiH : vinyl ratio of approximately 2.⁸ The mixture was cast onto petri glass dishes to a thickness of 3 mm and cured at room temperature for 7 days. The sheet was cut into 10-mm strips and Soxhlet-extracted in hexane over 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 plasma system from Plasma-Finish GmbH (Schwedt, Germany) operated at 2.45 GHz microwave frequency. The system was connected to a Pfeiffer DUO 035 DC 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 the treatment gas (argon or hydrogen) to a pressure exceeding 100 Pa. The plasma treatment was conducted at a preset power, pressure, and treatment time. The chamber was immediately flushed with hydrogen for 300 s at a pressure of about 80 Pa before ventilation to ambient pressure.

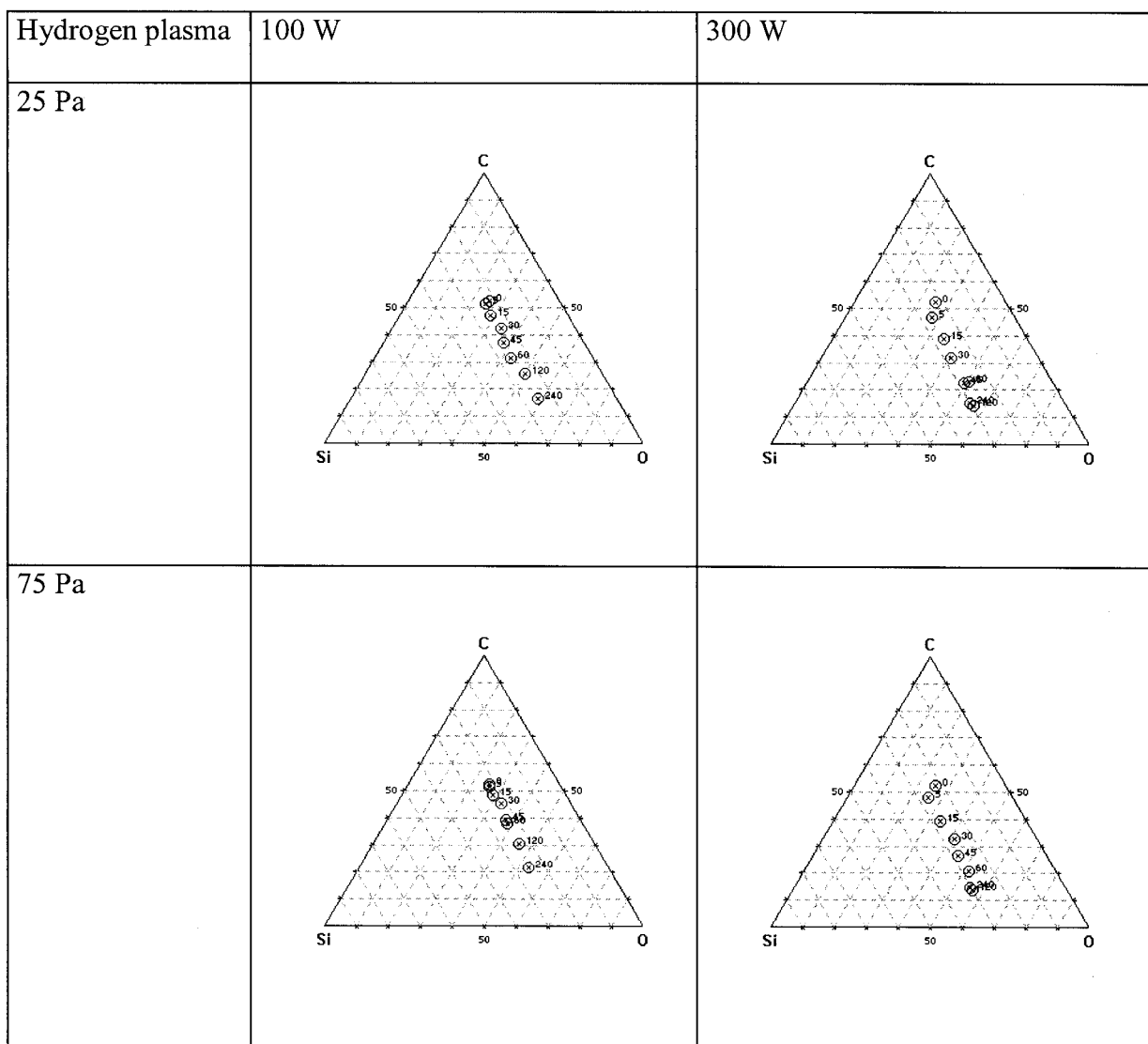


Figure 1 Elemental composition of hydrogen plasma-treated PDMS at different treatment times for four combinations of power and pressure.

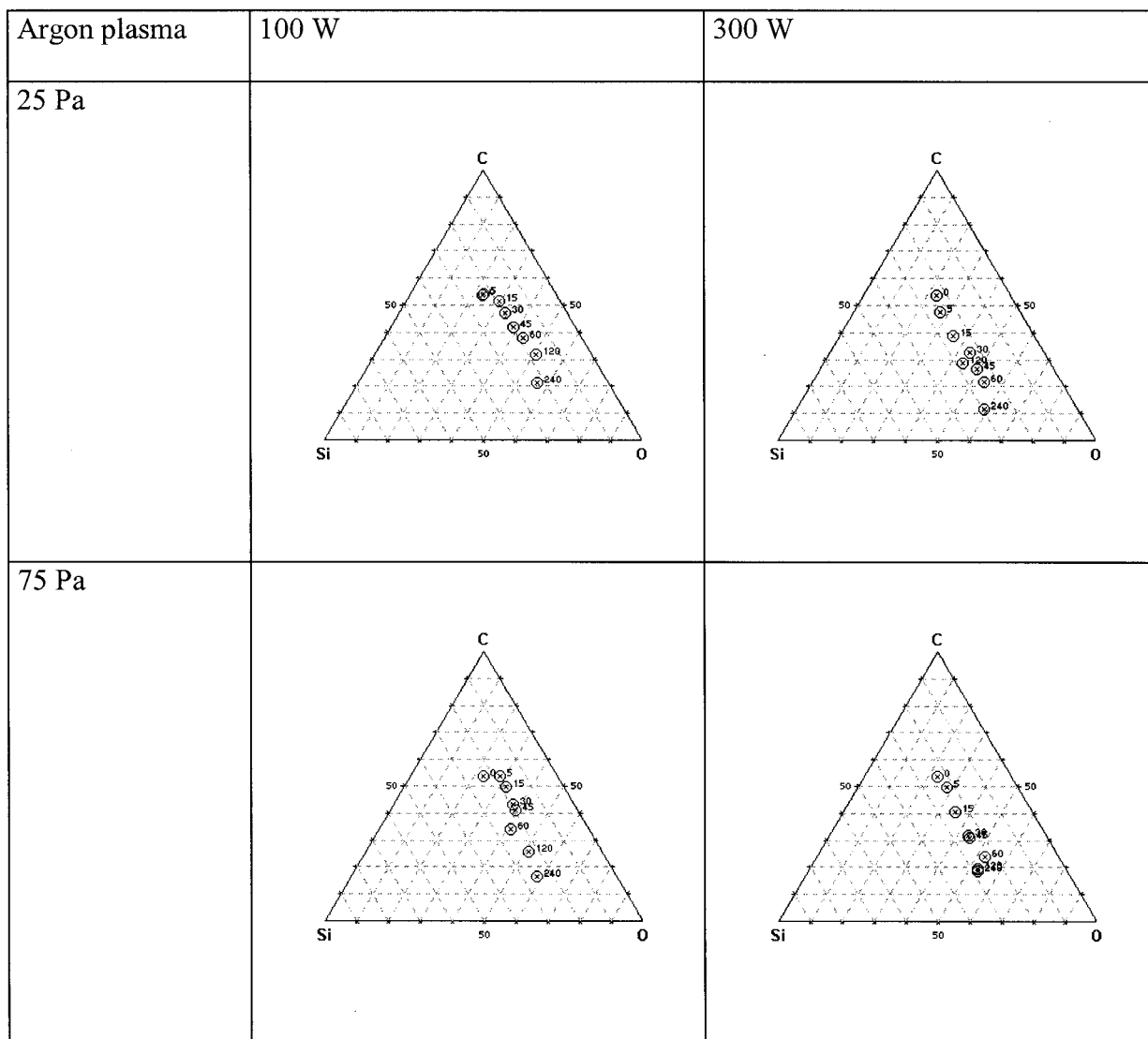


Figure 2 Elemental composition of argon plasma-treated PDMS at different treatment times for four combinations of power and pressure.

X-ray photoelectron spectroscopy (XPS)

An AXIS-HS X-ray photoelectron spectrometer (Kratos Analytical, Manchester, UK) was used with a monochromatic Al- K_{α} X-ray source operated at 15 kV and 20 mA. The take-off angle with respect to the sample surface was 90°. All spectra were acquired at a pass energy of 80 eV. To minimize the possible effects of hydrophobic recovery and oxidation resulting from exposure to air, the specimens were transferred to the XPS vacuum chamber within 4 h after the plasma treatment and analyzed on the following day at a pressure below 10^{-6} Pa. Background subtractions were made by drawing a straight line between two suitable points.⁹

RESULTS AND DISCUSSION

The surface composition of hydrogen- and argon-microwave-plasma-treated polydimethylsiloxane (PDMS)

was determined by XPS. The investigated plasma parameters were power (100 and 300 W), pressure (25 and 75 Pa), and treatment time (0, 5, 15, 30, 45, 60, 120, and 240 s). The elemental percentages after the plasma treatments were plotted in ternary XPS diagrams as previously described,⁷ using the present XPS data for PDMS treated in hydrogen plasma at 100 W and 25 Pa. Each set of elemental percentages of carbon, silicon, and oxygen is plotted in a ternary diagram as a single data point, and this makes it possible to study the changes in surface composition in a straightforward way.

Elemental percentage

Figure 1 shows the elemental percentages of the PDMS surfaces treated in hydrogen plasma for different times for different combinations of power and pressure.

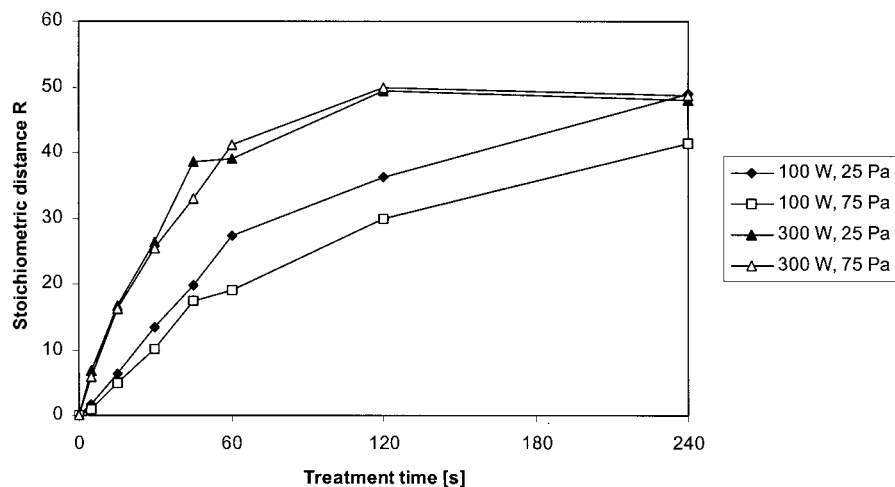


Figure 3 Stoichiometric distance (R) representing the change in surface composition of hydrogen plasma-treated PDMS under different conditions of power and pressure plotted against treatment time.

The original surface composition is close to what is expected from the stoichiometric composition: 50% carbon, 25% silicon, and 25% oxygen. The general trend in all cases is that the carbon decreases, the oxygen increases, and the silicon concentration changes to only a minor extent. Similar changes are observed for PDMS treated in argon plasma, as shown in Figure 2.

Although both the argon and the hydrogen were substantially free from oxygen-containing species, a remarkable increase in the proportion of oxygen in the surface was observed. Removal of methyl groups will result in a higher oxygen concentration, but if this were the only process taking place the silicon concentration would also increase substantially. This has not been observed. The argon data points appear to be more scattered than the data points from the hydrogen

plasma-treated PDMS. One possible explanation for this behavior is that hydrogen to some extent can participate in reactions during the plasma treatment, whereas the reactive sites formed during argon plasma treatment have to be terminated by internal surface reactions.

Stoichiometric distance

The elemental percentages of carbon, silicon, and oxygen are plotted in a ternary diagram and a vector 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 $\Delta O_n = O_n - O_0$. The subscripts 0 and n denote untreated and

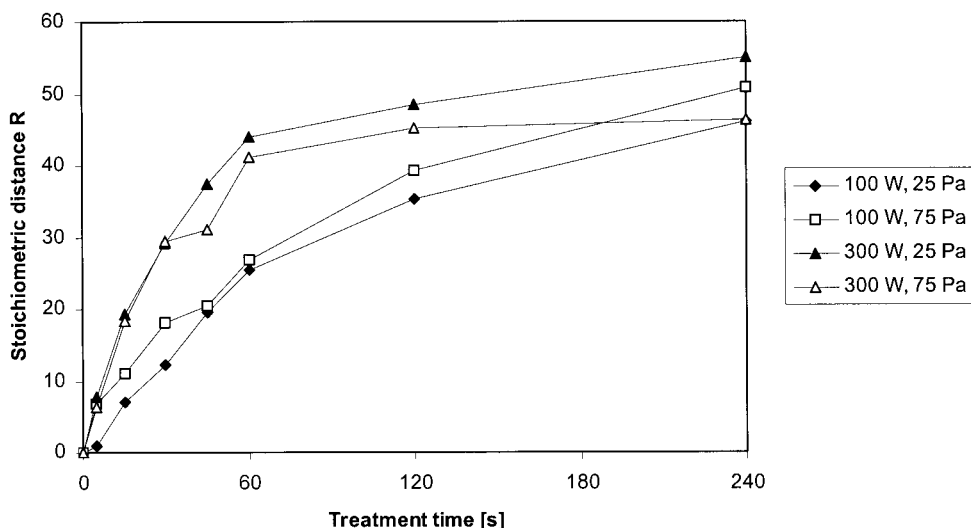


Figure 4 Stoichiometric distance (R) representing the change in surface composition of argon plasma-treated PDMS under different conditions of power and pressure plotted against treatment time.

treated samples, respectively. We define the stoichiometric distance R_n in the ternary diagram as

$$R_n = |\mathbf{v}_n| = \sqrt{\Delta C_n^2 + \Delta S_i^2 + \Delta O_n^2} \quad (2)$$

which is the length of the vector \mathbf{v}_n . This makes it possible to characterize the extent of change in elemental surface composition with a single value. Tóth et al.¹⁰ introduced a similar expression for the stoichiometric distance for modified silicone rubber surfaces where the silicon content was not included.

The stoichiometric distance according to our definition is a measure of the overall change in elemental surface composition. This stoichiometric distance for hydrogen plasma-treated PDMS under different conditions of power and pressure is plotted against treatment time in Figure 3.

The stoichiometric distance increases gradually as the treatment time is extended until a limiting value of about 50% is obtained. With a higher power, the change in composition is more rapid but the effect of pressure is much less by comparison. The stoichiometric distance for argon plasma-treated PDMS presented in Figure 4 shows a similar pattern of behavior.

The relations between the stoichiometric distances for the different plasma conditions are discussed further in a later section.

Kinetic study

The stoichiometric distance R shows the magnitude of the change in the total elemental composition. This can be used to follow the change in surface composition as a function of treatment time. It is also possible to compare the rates at which different plasma conditions change the surface composition. However, in-

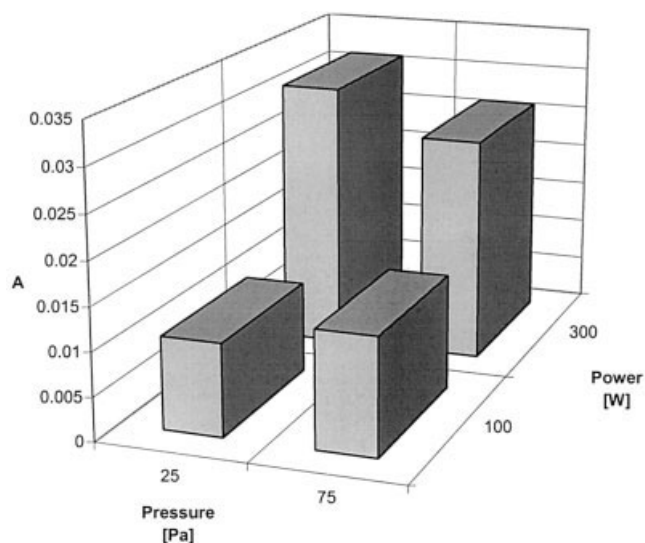


Figure 5 The constant A for different power and pressure conditions for argon plasma treatment.

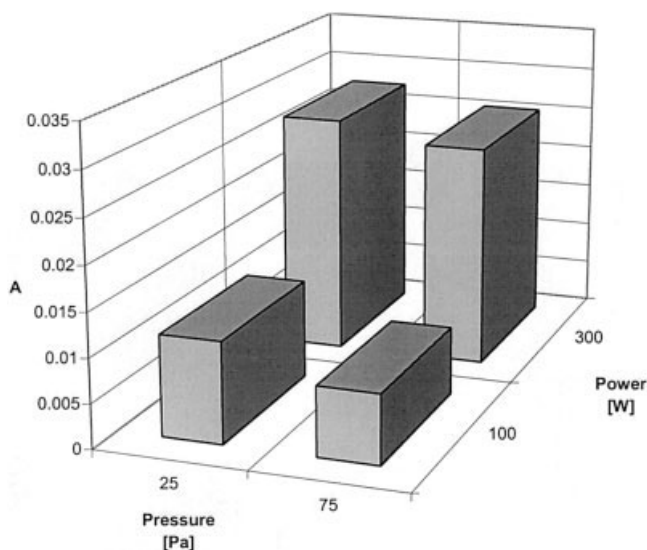


Figure 6 The constant A for different power and pressure conditions for hydrogen plasma treatment.

stead of performing a visual comparison of the curves, it is desirable to be able to obtain values that characterize the shape of the curve. This leads to a “kinetic” understanding of how the plasma treatment affects the composition of the surface. The shapes of the curves in Figures 3 and 4 suggest the expression

$$R = R_{\max}(1 - e^{-At})$$

where R_{\max} is the asymptotic stoichiometric distance approached with long treatment time, t is the treatment time and A is a constant specific for each plasma condition. The experimental data was fitted to eq. (3) using a least-squares minimization procedure to determine the values of R_{\max} and A . Each plasma condition (i.e., gas, pressure, and power) was assigned an individual value A . All conditions were given the same value R_{\max} . This resulted in $R_{\max} = 50.2$. The values of A obtained for the argon plasma treatment are shown in Figure 5 and the corresponding values for the hydrogen plasma treatment are presented in Figure 6.

The constant A can be interpreted as a measure of how fast the elemental composition changes under given plasma conditions. The power is found to have a large impact on the rate of change in surface composition. The value of A is about three times higher at 300 than at 100 W. The pressure is found to have little impact on the rate. In Figure 7 the experimental stoichiometric distances for all the treatments presented in Figures 3 and 4 are plotted against At .

Figure 7 shows that the rate constant A is sufficient to describe the kinetic behavior of all the investigated plasma treatment processes regardless of gas (hydrogen or argon), power (100 or 300 W), or pressure (25 or 75 Pa). In combination with the fact that the stoichio-

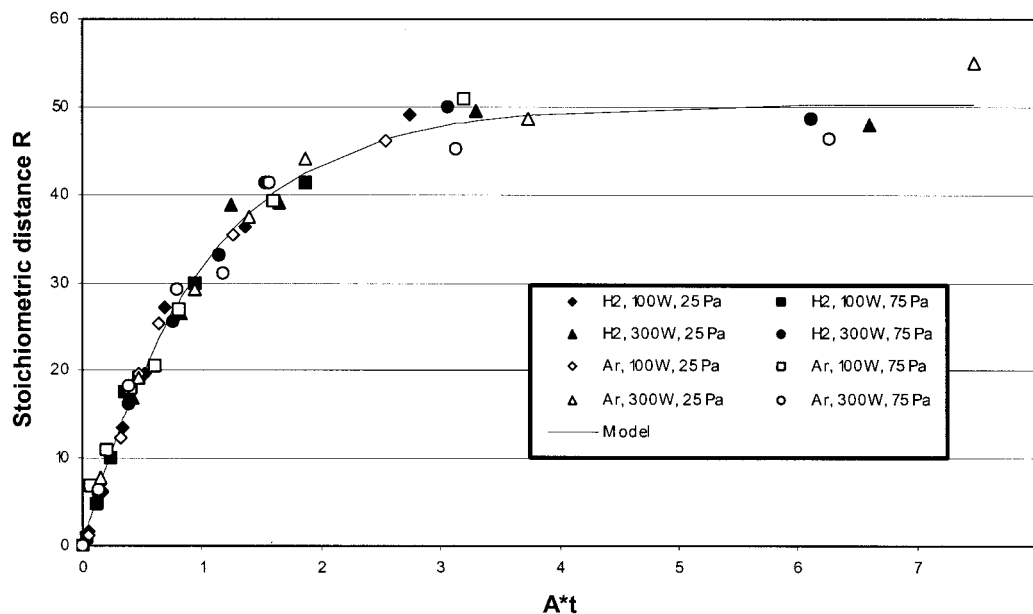


Figure 7 Experimental stoichiometric distance plotted against $A \cdot t$.

metric angles of the different treatments are similar, this clearly indicates that all the investigated treatments follow the same general trends in terms of elemental surface composition as the treatment progresses. The main difference between the treatments is in the kinetic behavior, that is, the rate of change in composition under the given conditions.

CONCLUSIONS

Controlled surface composition of silicone elastomers by plasma treatment in argon and hydrogen is obtained using a method to determine the influence of the plasma parameters power, pressure, and treatment time. The plasma treatment of PDMS argon or hydrogen was followed by XPS and the results were plotted in ternary diagrams. The change in surface composition on prolonged treatment follows the same trend for all plasma conditions: the carbon decreases, the oxygen increases, and the silicon content varies only a little. The rate of change in elemental composition is dependent on the plasma conditions: the type of gas, power, and pressure. The influence of the different parameters is quantified using a simple model describing the rate of change as a function of treatment time for the different plasma conditions. The power had a large influence on the rate of change in surface composition, whereas the effect of the pressure was only minor. The model also makes it possible to

compare the different conditions in terms of stoichiometric distance. The similarities between the two gases in this respect are remarkable. Regardless of the gas, power, or pressure used during the plasma treatment, the changes in elemental composition can be described by a parameter common to all treatments and a parameter specific for each plasma condition. The model describing how the elemental composition changes with different plasma conditions can be used to choose plasma conditions for tailoring surfaces to a desired structure.

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