

The Surface Relaxation of Glow Discharge-Treated Silicone Polymer

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SYNOPSIS

The samples of radiationally linked vinyl (1%) methylsilicone elastomer (silicone) were modified in glow-discharge air plasma. Surface relaxation was studied by the data on equilibrium contact angles. The degree of relaxation is shown to increase with increasing plasma treatment duration, probably due to the increase in the destruction degree of the spatial network of chemical bonds in the silicone surface layer. The changes in the chemical composition of the surface were controlled using attenuated total reflectance-infrared spectroscopy. Plasma treatment leads to increase of the polar component of the polymer surface energy and increase of the absorption bands of carboxyl and hydroxyl groups in its spectra. These characteristics disappear when the samples are kept in the open air and can be recovered by putting them into water. Such behavior can be explained by the fact that the polar oxygen-containing groups, forming on the surface due to plasma treatment, pass inside the polymer. Considering the adhesion properties of modified silicone, its biocompatibility was predicted. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

The adhesion interaction of a polymer with the environment is determined by the properties of its surface. As early as 1938, Langmuir¹ stated that the wettability of the surface occurs due to short-ranging forces and depends on surface chemical composition rather than on the characteristics of underlying molecular layers. The conventional method of polymer treatment in plasma²⁻⁹ can be used to modify the characteristics of the surface layer, having no effect on the volume properties of samples, which is especially important for the problem of increasing the biocompatibility of polymers. The term "biocompatibility" is a versatile concept. Thus, different researchers¹⁰ considered the surface roughness, its electric charge, the value of the specific free-surface energy, etc., as factors that affect biocompatibility. At present, the most popular hypothesis is that the polymer adhesion properties, directly related just to those of the surface, have the determining effect on this characteristic.¹⁰⁻¹²

Macromolecules in the polymer surface layer are mobile and can reorientate according to the changes in the surrounding phase. The rearrangement occurs in the direction of the interface free-energy minimization.¹³ Yasuda et al.² considered the relaxation of polymer properties after their modification in oxygen plasma. They demonstrated that the decrease in hydrophilicity is a result of either rotation or diffusion of hydrophilic fragments from the surface inside the sample. Going on with these studies, Yasuda and co-workers³ pointed to the reversibility of the changes in the hydrophilic-hydrophobic properties of nylon 6 and poly(ethylene terephthalate). They also mentioned the importance of the aspect of the mobility of macromolecules at the interface in some applications (e.g., biomedical) of polymers where the materials in use experience an effect of the surrounding medium other than the conventional ones used for testing or characterization.

The mobility of macromolecules in the treated polymeric surface layer can depend on the conditions of its treatment. Of major importance, in this case, are the processes of macromolecule destruction and the formation of links. As follows from the radiation chemistry¹⁴ and photochemistry¹⁵ of polymers, for different polymers under various conditions of their

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irradiation, these processes can compete. When treated in plasma, the surface of the polymer is subjected to UV irradiation and ionic bombarding. However, the authors of the articles, devoted to plasma modification of polymers, usually claim that the modification gives rise to a highly crosslinked surface layer with the thickness of 1–10 μm , and a possible destruction of macromolecules is often neglected. Thus, Hudis⁴ obtained the data confirming the increase of link concentration in the surface layer of polyethylene with increasing time of its treatment in hydrogen plasma. Shimomura et al.⁵ established that the thickness of the linked layer of porous acrylonitrile copolymer films increases with the time of treatment. Vasilets and co-workers⁶ also observed increase in the thickness of the linked layer of polyethylene with increasing time of its treatment in air plasma.

In this article, an attempt has been undertaken to correlate the mobility of silicone surface with the glow-discharge-treatment duration. The changes in the mobility of the silicone surface with its modification are assigned to the break of macromolecules and the formation of their relatively short fragments that exhibit high mobility. Using the method of the analysis of the energy characteristics of interacting substance surfaces, proposed by Kaelble and Moacanin¹¹ and considered in detail in our previous article,¹⁶ we estimated the changes in the adhesion properties of silicone due to modification. This allows us to predict the biocompatibility of modified silicone.

EXPERIMENTAL

The radiationally linked vinyl (1%) methylsilicone elastomer (silicone) with a mean-viscous molecular weight of 35,000 synthesized with a catalyst based on the organosilanolate of tetramethylammonium¹⁷ at the Institute of Organic Chemistry, Novosibirsk, RAN, was studied. Upon linking, the irradiation dose was 12 Mrad. The samples were plates 1 mm thick.

The experimental setup for glow-discharge treatment is schematically depicted in Figure 1. The sample plates of 30 \times 7 mm were placed in a cylindrical glass reactor 45 mm i.d. and 1.1 L in volume with sealed-in nickel electrodes, spaced 600 mm apart. The reactor was supplied with a manometer and two leak-in valves to pump out the reactor and to establish a fixed air-flow velocity. The electrodes were connected to a stabilized constant current source that provides a discharge glow. Discharge parameters are the following: pressure 0.6 Torr, air-

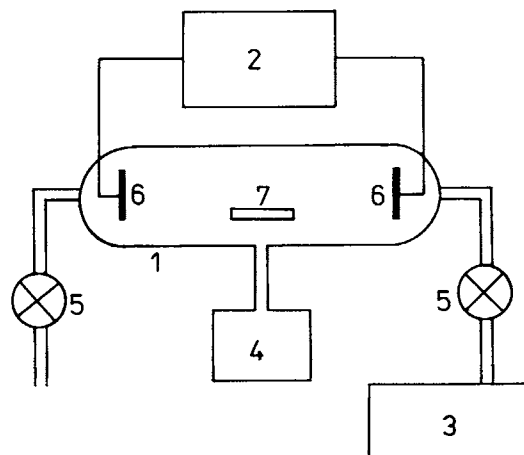


Figure 1 The scheme of the experimental setup: (1) reactor; (2) supply unit; (3) vacuum pump; (4) pressure measurer; (5) leak-in valves; (6) electrodes; (7) sample.

flow velocity through the reactor 1.9×10^{-4} mol/min, and discharge current 8 mA. The time of treatment was varied.

The wettability of silicone was studied using the data on contact angles θ measured through the water phase by either an air bubble or octane droplet (diameter about 1 mm) situated on the silicone surface in water. In all experiments, the contact angle θ was determined using a horizontal microscope with a goniometric ocular during the first minute after the spreading of the droplet (bubble). Each measurement was taken using a separate sample (from one series for one experimental cycle). Experimental points were obtained from the results of no less than 10 measurements. The characteristics of samples belonging to the same series were actually the same, which is confirmed by a minor experimental error.

The data on the chemical composition of the silicone surface in all experiments were obtained by analyzing the attenuated total reflectance-infrared (ATR-IR) spectra. The spectra were recorded with a UR-20 spectrophotometer (Carl Zeiss, Jena) between 800 and 4000 cm^{-1} , scanning being performed at a speed of 160 $\text{cm}^{-1} \text{min}^{-1}$. The KRS-5 prism with angle 45° and the number of reflections 25 was used. The time between the end of treatment and the beginning of the record was no more than 10 min. Each spectrum was recorded using a separate sample from the corresponding series.

RESULTS AND DISCUSSION

When silicone is modified in the glow-discharge plasma, its wettability substantially increases.

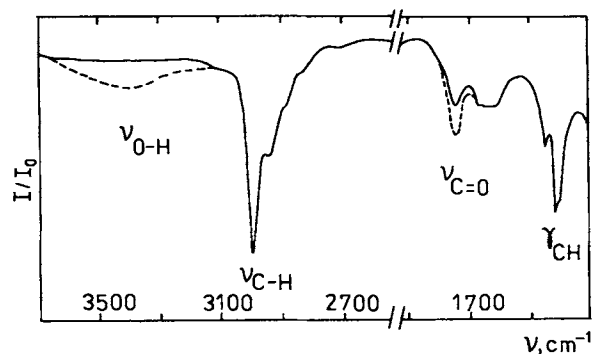


Figure 2 Typical ATR-IR spectra of control (solid line) and glow-discharge-treated (for 90 min) silicone (dotted line).

Thus, the water-air contact angle of the control (untreated) silicone sample is $75 \pm 2^\circ$, and after treatment, this value decreases to about 25° .

Polar groups are known⁷⁻⁹ to appear on a polymeric surface as a result of treatment in the oxygen-containing plasma. As can be seen in Figure 2, the appearance of absorption bands in the range 1740 and 3400 cm^{-1} in the ATR-IR spectra testifies to the presence of carbonyl (C=O) and hydroxyl (O—H) groups. Representing the value of the specific free-surface energy of silicone γ_s as a sum of polar γ_s^p and dispersion γ_s^d components:¹²

$$\gamma_s = \gamma_s^p + \gamma_s^d \quad (1)$$

it is assumed that the appearance of these groups can cause the increase in the γ_s^p value.

We calculated the changes of silicone γ_s and γ_s^p due to its modification. To this end, the data have been used on the wettability of silicone for an air bubble and an octane droplet surrounded by water. The values have been determined by the method of Kaelble and Moacanin,¹¹ considered in detail in our previous article.¹⁶ In this contribution, we are going to give just a brief description.

The adhesion energy $W_{ls(w)}$ of substance L on the surface of polymer S surrounded by water W is described by the expression¹⁸

$$W_{ls(w)} = \gamma_{sw} + \gamma_{lw} - \gamma_{ls} \quad (2)$$

where γ_{sw} , γ_{lw} , and γ_{ls} are the specific surface energies of the polymer/water, substance- L /water, and substance- L /polymer interfaces, respectively. According to the extended Fowkes equation proposed by Owens and Wendt,¹⁹ each of these values can be represented as the γ_{sw} one:

$$\gamma_{sw} = \gamma_s + \gamma_w - 2((\gamma_s^d \gamma_w^d)^{0.5} + (\gamma_s^p \gamma_w^p)^{0.5}) \quad (3)$$

where γ_s and γ_w are the surface tensions of polymer and water, γ_s^d , γ_w^d , and γ_s^p , γ_w^p the contributions of dispersion and polar forces to γ_s and γ_w , respectively.

In the diagram $(\gamma_s^p)^{0.5}$ vs. $(\gamma_s^d)^{0.5}$ (Fig. 3) each point corresponds to a definite substance. As follows from Eq. (3), for such a graphic representation, the value of the interface energy at the boundary of two contacting phases can be expressed as the distance squared between the corresponding points.¹⁶ For instance, for silicone and water (points S and W in Fig. 3), we have

$$\gamma_{sw} = WS^2 \quad (4)$$

The adhesion energy $W_{ls(w)}$ is expressed as the doubled scalar product of vectors WS and WL :¹⁶

$$W_{ls(w)} = 2WS \cdot WL \quad (5)$$

Using the relation between the adhesion energy and contact angle θ , measured through the water phase,

$$W_{ls(w)} = \gamma_{lw}(1 - \cos \theta) \quad (6)$$

as well as Eq. (5) and the relation for γ_{lw} , which is similar to Eq. (4), one obtains

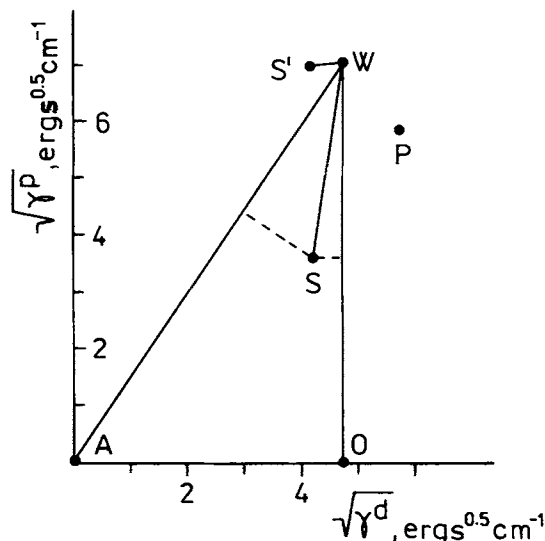


Figure 3 The plot of energy characteristics of the surfaces of interacting substances: (W) water; (A) air; (O) octane; (P) protein albumin; (S) untreated silicone; (S') silicone modified in glow discharge air plasma for 1 min. γ^p , polar component of the surface energy; γ^d , dispersion component.

Table I The Changes of Silicone Properties as a Result of Air-Plasma Treatment

Sample of Silicone	θ_{air}^a (deg)	θ_{oct}^a (deg)	γ_s (ergs/cm ²)	γ_s^p (ergs/cm ²)
Control	75 ± 2	88 ± 6	31.0 ± 4.2	13.7 ± 2.7
1 min treated	22 ± 4	15 ± 5	67.7 ± 1.8	49.3 ± 1.3
90 min treated	26 ± 5	27 ± 9	65.6 ± 2.9	45.6 ± 3.9

^a Contact angles θ are measured either by an air bubble or by an octane droplet in water through the water phase.

$$0.5(\gamma_{tw})^{0.5}(1 - \cos \theta) = \mathbf{WS} \cdot \mathbf{WL} / \mathbf{WL} \quad (7)$$

The right-hand part of expression (7) is the projection of vector \mathbf{WS} onto the vector \mathbf{WL} and the left-hand one can be calculated from the experimental data (γ_{tw} is known and angle θ is measured). If there are wetting data of at least two different substances L and L' , the position of the required point S can be determined unambiguously.

The water-insoluble octane and air bubble (points O and A in Fig. 3) were used as substance L to experimentally determine γ_s^d and γ_s^p of silicone. For water,²⁰ $\gamma_w = 72.8$ ergs/cm² and $\gamma_w^d = 21.8$ ergs/cm². For octane,²¹ due to its nonpolarity, $\gamma_{\text{oct}} = \gamma_{\text{oct}}^d = 21.3$ ergs/cm². Air has no surface tension: $\gamma_{\text{air}} = 0$. Table I gives the values for the contact angles of the air bubble and octane droplet on the surface of the control and modified silicone in the water medium.

For control silicone (point S in Fig. 3), we obtained $\gamma_s = 31.0 \pm 4.2$ ergs/cm² and $\gamma_s^p = 13.7 \pm 2.7$ ergs/cm². For silicone, modified for 1 min (point S' in Fig. 3), the corresponding values were 67.7 ± 1.8 and 49.3 ± 1.3 ergs/cm².

The treatment was observed to substantially increase the polar component of polymeric surface energy, having practically no effect on the dispersion component. This verifies the hypothesis of the increase of the contribution of polar forces to the silicone surface energy after its modification.

The second peculiarity of the influence of treatment on silicone characteristics is a substantial decrease of the polymer/water interface energy γ_{sw} . The value is an important parameter of biocompatibility. Andrade and co-workers²² assumed that the materials with a zero interface energy of the interaction with water must manifest the best biocompatibility because, in this case, the adhesion energy of any substance on the polymer surface in aqueous medium is zero, which prevents the adhesion of the different components of biological liquids causing the rejection of an implant by the organism. For silicone, the γ_{sw} value varies from 12.3 ± 2.0 ergs/cm² in the control sample to 0.25 ± 0.05 ergs/cm²

in the modified (independently of the modification time) one. Hence, the adhesion energy of the substance L droplets decreases on a polymeric surface in aqueous medium. If the data on albumine²³ (point P in Fig. 3) are taken as L , a 1 min treatment, e.g., leads to the decrease in the adhesion energy on the silicone surface in aqueous medium from 8.4 ergs/cm² to (-1) ergs/cm². Thus, it is concluded that silicone, treated by glow-discharge plasma, must display much greater biocompatibility than does the untreated one.

Storage of Silicone in Air After Treatment

The decay of the wettability of the glow-discharge-treated-silicone surface is shown in Figure 4 (solid lines) as a plot of water-air $\cos \theta$ vs. storage time. The degree of surface relaxation increases with the time of treatment. This is confirmed by the fact that the wettability of silicone (Fig. 4) decreases more the longer is the time of treatment. In this case, the most noticeable changes of $\cos \theta$ occur on the first day after modification. Our hypothesis is that the

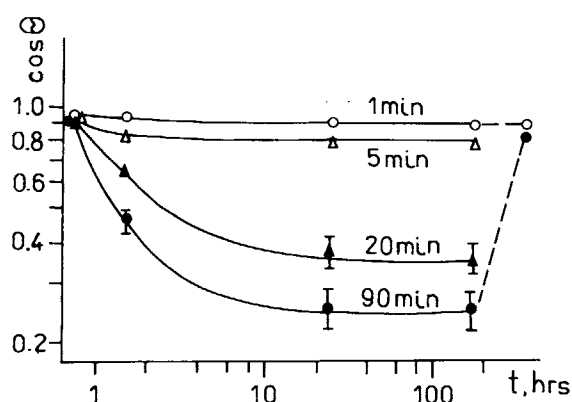


Figure 4 The change of $\cos \theta$ (θ is the water-air contact angle, measured through the water phase) upon keeping of modified silicone in air (solid lines) and further location in water (dotted lines). t , storage time. The lines are drawn for clearness. The time of treatment in the glow discharge is denoted above the curves.

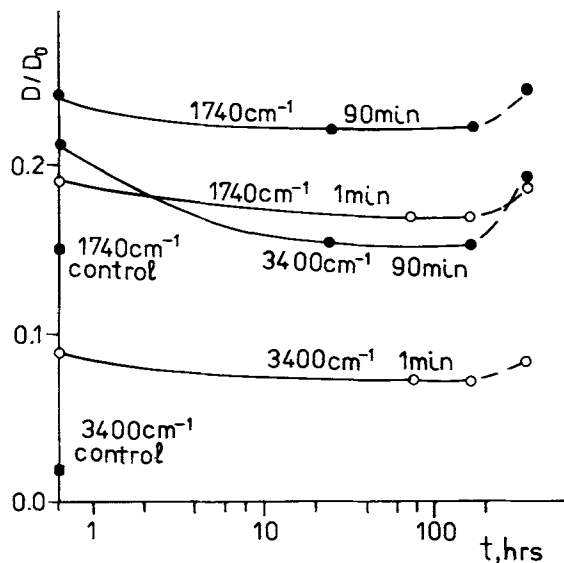


Figure 5 The change of the relative optical density of absorption bands 1740 and 3400 cm^{-1} in the ATR-IR spectra upon keeping of modified samples in air (solid lines) and after further location in water (dotted lines). t , storage time. The lines are drawn for clearness. The time of treatment in the glow discharge is denoted above the curves. Squares correspond to the control sample.

increase of silicone exposition in the glow-discharge air plasma leads to the increase in the destruction degree of the spatial network of chemical bonds in the surface layer and, thus, the formation of the relatively short fragments of macromolecules. The mobility of these fragments with fastened hydrophilic groups increases.

Surface relaxation was also observed using the ATR-IR spectra. The change in the relative optical density of the absorption bands, 1740 and 3400 cm^{-1} , for the samples studied is depicted in Figure 5. As an inner standard (value D_0), we used the absorption peaks in the range of 2990 cm^{-1} , corresponding to the stretching vibrations C—H for the band 3400 cm^{-1} , and at the frequency of 1410 cm^{-1} , corresponding to the deformation vibrations CH for the band 1740 cm^{-1} . A relative optical density of D/D_0 was calculated to exclude the influence of the differences in the condition of sample pressing to the prism on the data obtained. The data testify to the rearrangement of the surface layer of silicone, displaying, however, some differences with the corresponding change of the contact angles which is observed in the different degrees of surface relaxation for these two methods. These differences can be attributed to the difference in the thickness of surface layers that affect the data obtained for both of the methods. When silicone is wetted with water, its

molecules interact with a very thin layer (of the order of one molecular layer) and the existence of hydrophilic groups in it acquires great importance. The depth of the informative layer during the record of the ATR-IR spectra under the given conditions, according to estimates,²⁴ is, depending on the wavelength, $3\text{--}6\text{ }\mu\text{m}$. In this case, some average concentration of such groupings is being determined in the layer. Thus, the hydrophilic groups can leave the surface to provide a fast relaxation by the data of contact angles. However, they can stay informative for the ATR-IR layer, thus determining a smaller decay of the absorption band intensity for the given time of sample keeping after treatment.

In this case, a higher absorption intensity of bands is observed for the sample treated for 90 min compared to that modified for 1 min. Since the band intensity in the IR spectrum is proportional to the concentration of an absorbing group, a higher concentration is attained during the 90 min treatment than during the 1 min one.

Storage of Silicone in Water After Treatment

It is assumed that when the treated samples are placed in water, the hydrophilic groups must be fixed to the surface. The time dependencies of the water-air $\cos\theta$ for silicone located in water just after modification are depicted in Figure 6. In silicone, treated for 1 min, the contact angle decreases to zero for about 4 days. Upon 90 min treatment, the full wett-

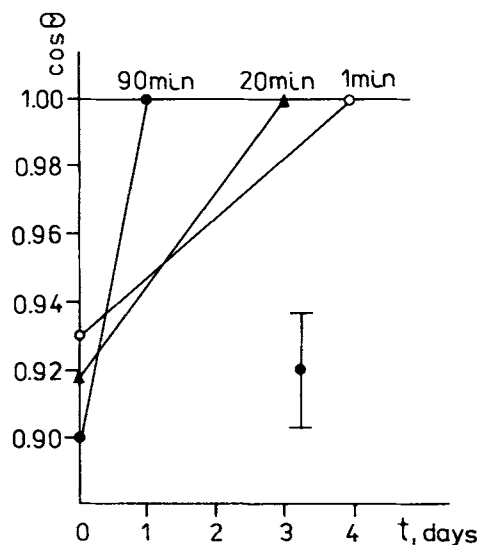


Figure 6 The dependence of water-air $\cos\theta$ on the time t of silicone storage in water after treatment. The time of treatment in the glow discharge is denoted above the curves. The error indicated is typical of all measurements.

ability is reached for 24 h. This is also in accord with the assumption of a higher degree of the destruction of the chemical bond spatial network in the surface layer with increasing treatment duration.

Note that when the control (untreated) silicone sample is kept in water the wettability of its surface increases more slowly than in the cases under study. Thus, during 20 days, the value of $\cos \theta$ varied from 0.26 ± 0.04 to 0.40 ± 0.03 . This can be explained by partial hydrophilization of silicone, which is likely to be due to the passage of macromolecular fragments, containing oxygen atoms, to the surface. A low rate of this process is attributed to a high degree of the link of macromolecules in the surface layer and, hence, to a very difficult reorientation of these fragments for surface rearrangement.

Reversibility of Surface Relaxation

To verify the reversibility of relaxation changes, the samples of silicone, kept in air for 1 week after modification, were put into water. The corresponding changes in the values of the water-air $\cos \theta$ for the samples treated for 1 and 90 min are shown in Figure 4 (dotted lines). The wettability that decreases during the first week then recovers. The $\cos \theta$ value, in this case, varies more strongly for the sample treated for 90 min that for the 1 min one. The data obtained using the ATR-IR spectroscopy (Fig. 5) give more evidence for relaxation reversibility.

The decrease in the intensity of absorption bands under study for silicone kept in air and the following increase with keeping it in water make us assume that the fragments of macromolecules have higher mobility in the layer whose thickness exceeds that of the informative for the ATR-IR one, i.e., in the layer that is more than 3–6 μm .

The relaxation processes that occur on the polymer surface are convenient for control by a graphical method. Two extreme cases were considered: silicone, modified for 1 and 90 min. The change of the contribution of polar and dispersion components to the value of the surface energy of modified silicone was studied. The $(\gamma_s^p)^{0.5}$ vs. $(\gamma_s^d)^{0.5}$ plots of the changes on keeping the treated silicone in water are given in Figure 7(a). It is seen that the energy characteristics of the sample become, in time, identical to those of water (the points, corresponding to silicone *S* and water *W*, coincide). In this case, the polar component γ_s^p increases quite a bit. When the modified silicone is kept in air, γ_s^p decreases substantially [Fig. 7(b), relaxation by solid lines]. In the sample, modified for 90 min, such a decrease is much more dynamic than that on the

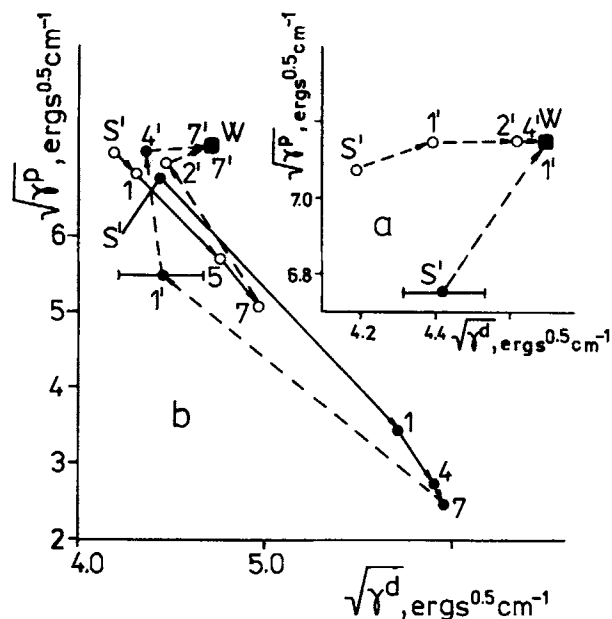


Figure 7 The change of polar γ^p and dispersion γ^d components of the surface energy of modified silicone upon relaxation of its surface: (a) storage in water after modification; (b) storage in air with further location in water. The figures denote the days of silicone storage in air (relaxation by solid lines); the figures with primes denote the days of sample residence in water (relaxation by dotted lines). Arrows show the relaxation changing direction. The letters denote (*W*) water and (*S'*) initial points (just after modification). Empty circles are the points, corresponding to the 1 min-treated sample; full circles are the points, corresponding to 90 min-treated sample. The error indicated is typical of all measurements.

sample treated for 1 min. Thus, the polar component γ_s^p for the sample, modified for 90 min, decreases from 45.6 to 11.9 ergs/cm² for the first 24 h after treatment, whereas for that treated for 1 min, it decreases from 50.0 to 46.9 ergs/cm². The dotted lines in Figure 7(b) show the reverse relaxation on the samples placed in water after being kept 1 week in air. In this case, the dynamics of changes and the treatment duration are in fair agreement. As follows from the plot, the points, corresponding to the samples studied, come back to a water point.

This verifies our hypothesis of the increase in the destruction degree of the spatial network of chemical bonds in the polymeric surface layer with increasing time of its treatment in the glow-discharge plasma and the related changes in the mobility of the fragments of macromolecules in the surface layer.

CONCLUSIONS

The surface of silicone has become hydrophilic after glow-discharge treatment. Its surface energy γ_s increases and that of the polymer/water interface γ_{sw} decreases due to the appearance of oxygen-containing groups in the surface layer. They are attached to the fragments of macromolecules that can penetrate into the polymer. From analyzing the data on wettability, it is concluded that the destruction degree of the spatial network of chemical bonds in the silicone surface layer increases with increasing duration of silicone exposition to air plasma. The relatively short fragments of macromolecules, resulting from long treatment, easily diffuse inside silicone when it is kept in air, thus providing a fast relaxation of surface properties. The relaxation is reversible. When the samples are further put into water, the macromolecular fragments with polar groups again pass to the surface.

The biocompatibility of silicone must increase due to its discharge treatment. This is confirmed by the decrease in the value of polymer/water interface energy and the decrease in the calculated adhesion energy of albumin on the surface of modified silicone in water. As regards biocompatibility, the observed relaxation of surface properties is favorable because the implant in the organism is in aqueous medium, which can favor its characteristics.

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