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Hydrophobicity recovery of polydimethylsiloxane after exposure to corona discharges

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A high-temperature-vulcanized polydimethylsiloxane (PDMS) elastomer has been subjected to corona discharges for different periods of time in dry air. The loss and recovery of hydrophobicity of the surface have been characterized by contact angle measurements. Immediately after exposure to corona discharges, samples showed a low surface hydrophobicity and, on storage in dry air, a continuous increase in hydrophobicity finally approaching the hydrophobicity of the unexposed material. The activation energy of the hydrophobicity recovery was two to four times greater than the activation energy of the diffusivity of low molar mass PDMS in PDMS elastomers, indicating that the diffusivity properties of the oxidized surface layer were different from that of the bulk. PDMS elastomers quenched in liquid nitrogen or subjected to small mechanical deformation ($<$ 1% strain) after exposure to corona discharges for 1 h or more recovered their hydrophobicity faster than untouched specimens kept under identical conditions. X-ray photoelectron spectroscopy confirmed the early formation of a silica-like surface layer, with a thickness of at least 10–12 nm. The atomic composition of the oxidized surface layer remained essentially unchanged after the first hour of corona discharges. It is suggested that the silica-like surface layer delayed the recovery of hydrophobicity by inhibiting the transport of low molar mass PDMS to the surface. It is also suggested that thermally or purely mechanically induced stresses lead to a cracking of the brittle silica-rich layer and that this in turn facilitates the transport of low molar mass PDMS to the surface and to a more rapid recovery of the hydrophobicity. Data obtained by reflection infrared spectroscopy assessing the outermost micrometer, confirmed the oxidation and the formation of hydroxyl groups at a progressively higher concentration with increasing exposure time of corona discharges. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: polydimethylsiloxane; hydrophobicity; corona discharges)

INTRODUCTION

Elastomers based on polydimethylsiloxane (PDMS) are used as insulating materials in outdoor electrical power applications due to their low weight, good electrical properties and hydrophobic surface properties. Under severe environmental conditions, involving prolonged dry band arcing, the initial hydrophobic surface becomes hydrophilic[1]. Deposition of pollutants on the elastomer surface may also cause a loss of the initial hydrophobicity[2]. After a relatively short period of time with no discharge activity, typically from hours to a few days, the elastomer surface regains its initial hydrophobicity. The loss and recovery of surface hydrophobicity is a key issue also for silicone elastomers used in medical applications. In these applications, a wettable surface is desirable[3].

Plasma treatment is used to increase the wettability of hydrophobic polymer surfaces, but in the case of PDMS the surface hydrophilicity is lost with time after plasma treatment[4,5]. This change from a hydrophilic to a hydrophobic surface is often referred to as 'hydrophobicity recovery'[4]. It is believed that migration of low molar mass PDMS plays an important role in this hydrophobicity recovery[6–9]. Incomplete curing, the addition of silicone liquids as processing aids and ultra-violet (u.v.) and partial-discharge induced reactions are the origins of low molar mass PDMS in the elastomer. Hydrophobicity recovery is also due to a reorientation of hydrophilic groups from the surface into the bulk by torsion about sigma bonds thereby replacing hydroxyl groups by methyl groups in the surface region[9]. PDMS exhibits one of the lowest reported glass transition temperatures ($-$ 123°C)[8], which is indicative of the very flexible nature of the backbone of this polymer.

Several researchers have studied the underlying molecular mechanisms of hydrophobic recovery. Using angle-resolved X-ray Photoelectron Spectroscopy (XPS), Owen and coworkers[5,10] found that a thin wettable, brittle silica-like layer was formed after corona treatment of PDMS in air. The hydrophobicity recovery was explained as being due to a diffusion of unoxidized low molar mass PDMS through cracks in the silica-like surface layer. Toth *et al.*[11] studied silicone rubber surfaces exposed to radio frequency (RF) plasma or corona discharges in air. They found a silica-like surface layer, with a thickness of less than 3 nm, using angle-resolved XPS. They concluded that the diffusion of low molar mass PDMS played a more important role for the hydrophobicity recovery than the reorientation of polar groups into the bulk of the rubber. Using dynamic

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mechanical analysis, Urban and Stewart[12] found that a more mobile surface was formed due to depolymerization as a result of a plasma environment. Morra *et al.*[13] used a combination of static secondary ion mass spectroscopy, XPS and infra-red (i.r.) spectroscopy on O^{18} plasma-modified PDMS, and they proposed that the hydrophobicity recovery was due to burial of polar groups into the bulk and to surface condensation of silanols and consequent cross-linking in the contact-angle-probed layer. No formation of any silica-like phase was detected in this study. Discussions of the chemical reactions occurring during corona discharges have been provided by Hollahan[14] and Scott *et al.*[15]. It has been proposed by Gorur and Yates[16] and Kim and coworkers[17,18] that similar radical reactions occur during dry band arcing.

This paper presents data concerning the influence of mechanical and thermally induced stresses on the hydrophobicity recovery of a high-temperature vulcanized silicone elastomer exposed to corona discharges. Corona discharges made the surface hydrophilic. Mechanical stresses led to a marked increase in the hydrophobicity recovery rate in specimens originally exposed to a sufficiently high dose of corona discharges. The corona discharges led to the formation of an oxidized, silica-like surface layer and it is suggested that mechanical stresses led to a cracking of the brittle silica-rich layer which in turn facilitated transport of low molar mass PDMS to the surface.

EXPERIMENTAL

The corona discharge test cell

An apparatus in which polymer films can be exposed to corona discharges under well-defined conditions has been constructed. It consists of two circular electrodes mounted in a sealed vessel. The geometry of the upper electrode was designed to achieve a homogeneous electric field over the specimen by using the two-dimensional version of the electric field calculation program 'ACE'[19]. Views of the electrode from the side and from below are shown in *Figure 1*.

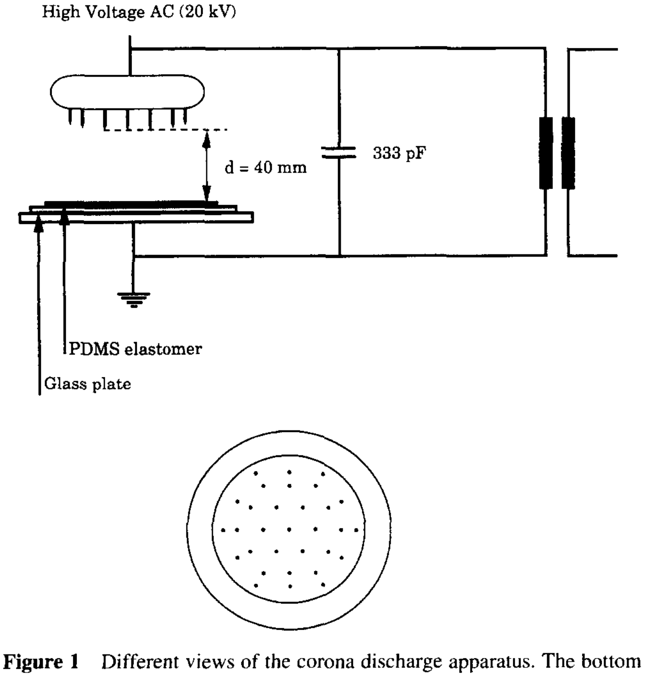

Figure 1 Different views of the corona discharge apparatus. The bottom drawing shows the positions of the needles

The electrode had a diameter of 87 mm. The length of the seven innermost needles was 12 mm, of the 12 outer needles 11 mm and of the 12 outermost needles 9 mm. The tips of the needles had a radius of 56 μm with a standard deviation of 4.2 μm[20]. The distance between the tips of the lowest needles and the surface of the PDMS films was 40 mm. The lower circular electrode had a diameter of 140 mm and was connected to ground. The applied voltage was 20 kV AC at 50 Hz. A visible glow and striations emanated from the tips and impinged on the elastomer surfaces.

The integrated corona charge transfer rate (in Watts), hereafter referred to as the power of the electrode, was obtained according to the method described by Dakin and Malinaric[21]. Two different geometries were used. The films were either positioned directly on the electrode ground plate, resulting in a power of 1.5 W, or on circular glass plates (thickness 3 mm; diameter 120 mm) which were then positioned on the electrode ground plate. The latter geometry resulted in a power of 2.6 W. The electrodes were mounted in a desiccator with a volume of 20.10^{-3} m^3 to provide a control over the surrounding atmosphere. The desiccator was supplied with a continuous flow of dry air, 90×10^{-6} m^3 s^{-1}, and the temperature of all the corona exposures was kept constant at 25 ± 2°C. The times of the exposure to corona discharges were from 20 min to 200 h.

Material

The high-temperature vulcanized silicone elastomer, Elastosil 420/60 from Wacker Chemie, Germany, was based on polydimethylsiloxane. The elastomer contained approximately 20 wt% of silica filler. 1 wt% of PMBP-50-PSI (a mixture of 50 wt% methylated benzoylperoxide and 50 wt% of silicone oil) from Peroxidchemie, Germany, was mixed into the silicone elastomer using a Brabender internal mixer at 20 rpm for 2 min and thereafter at 25 rpm for 5 min at room temperature. The temperature in the mixer never exceeded 50°C. Films with a thickness of 1.6 mm and a diameter of 110 mm were compression moulded and cured between Mylar sheets in a Schwabentan Polystat 400 press for 20 min at 135°C and 6 Mpa. The films were then stored in dry air at 23°C in a desiccator prior to the corona treatment. The films were cleaned with acetone to remove dust particles and fingerprints 40 min before the corona treatment.

Contact angle measurements

Contact angles were measured on specimens taken after the corona treatments. The specimens (1.6 mm thick, 7 mm wide and 30 mm long) were either cut from the films directly after exposure and gently transferred to a substrate to minimize bending during the contact angle measurements or left untouched on the glass plates. The compressive strain on the exposed surface was less than 1% during this procedure. Specimens cut from the films after exposure will hereafter be referred to as 'mechanically deformed' and films that remained on the glass plates during contact angle measurements will be referred to as 'untouched'. The specimens were 'annealed' in dry air at different temperatures (25 ± 2, 50 ± 2 and 90 ± 2°C) and the contact angle measurements were carried out after different periods of time. The contact angle measurements were performed using a Ramé Hart goniometer using the sessile drop technique[22]. Deionized water was used. Each datum point given in the figures is based on at least 12 contact angle measurements at six different positions on the specimen. The error bars in the figures shows a confidence interval of

90%. The advancing contact angles were obtained by keeping the needle in the water droplet after positioning it on the surface and by carefully adding more water until the advancing angle appeared to be maximal. The receding angle was obtained by withdrawing water from the drop until the three-phase line started to recede. The measurements were performed with the needle remaining in the droplet.

X-ray photoelectron spectroscopy

Samples were taken from the unexposed and corona-treated films and were Soxhlet-extracted in hexane (boiling point: 69°C) for 8 h and thereafter dried in an vacuum oven for at least 6 h at room temperature. The XPS spectra were obtained with a Kratos HX instrument using a Mg $K_{\alpha 1,2}$ anode. The X-ray gun was operated at 15 kV and 300 W. The pressure in the sample chamber was between 5×10^{-6} and 1×10^{-5} Pa. Survey spectra were recorded at a 80 eV pass energy and the high resolution spectra at 25 eV pass energy. The spectra were referenced to the C1*s*-line (binding energy = 284.6 eV). Angular resolution was used for some spectra. A low-energy electron flow gun was used to neutralize sample charging.

Infra-red spectroscopy

Silicone elastomers exposed to corona discharges were compared to unexposed material by attenuated total reflection i.r. (ATR i.r.) spectroscopy using a Perking Elmer 1760 spectrometer equipped with a nitrogen-cooled MCT detector. The spectra were based on 100 scans with a resolution of 4 cm^{-1}. A KRS-5 crystal with 45° beam incidence angle from Spectra Tech was used. The spectrum of the KRS-5 crystal was subtracted from all the spectra.

RESULTS AND DISCUSSION

Contact angle measurements

Figure 2 shows that the corona treatment at 1.5 W led to a major reduction in the surface hydrophobicity. The decrease in hydrophobicity occurred even more rapidly during treatment at 2.6 W. One hour of corona treatment at 2.6 W created a surface with advancing and receding angles less than 15°, which are much smaller than the 30–60° obtained after 1 h of 1.5 W corona treatment. The corona discharges caused a uniform surface oxidation over the exposed surface, as is indicated by the small bars associated with the 90% confidence interval.

The surface hydrophobicity was regained on storage of the corona-treated specimen (*Figure 3*). The increase in contact angle was more pronounced in the early stages and it levelled off, finally approaching the contact angle of the virgin, unexposed specimen.

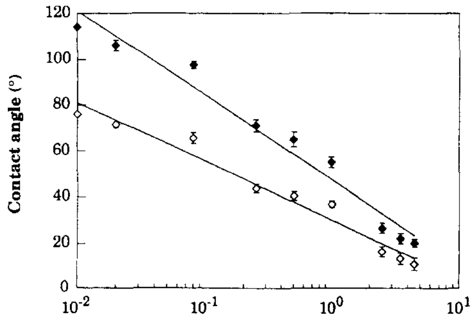

Figure 2 Advancing (◆) and receding (◇) contact angles of water on specimens directly after exposure to corona discharges (1.5 W) as a function of the corona discharge exposure time

Effect of temperature and mechanical/thermal stresses on the recovery rate

The rate of hydrophobicity recovery increased with increasing storage temperature, in accordance with the Arrhenius equation (*Figure 4*). The calculated activation energy for hydrophobicity recovery of a specimen exposed to 2.6 W corona treatment for 0.3 h, cut and removed from the films (i.e. 'mechanically deformed') were 57 kJ mol^{-1} (advancing angle) and 54 kJ mol^{-1} (receding angle). Specimens exposed to 1 h of 2.6 W corona exhibited activation energies of 52 kJ mol^{-1} (advancing angle) and 33 kJ mol^{-1} (receding angle). Specimens subjected to 200 h of plasma exposure showed an even further reduction in the activation energy; to 36 kJ mol^{-1} (advancing angle) and 39 kJ mol^{-1} (receding angle). There is thus a decrease in the activation energy of the recovery process with increasing time for the plasma treatment.

Liang[23] reported that the initial recovery rate increased with increasing corona exposure time. Morra *et al.*[13] obtained a value of 48 kJ mol^{-1} for the activation energy of the hydrophobicity recovery as assessed by the advancing angle after oxygen plasma treatment of PDMS elastomers, which is in agreement with the values reported here. The calculated activation energies for the hydrophobicity recovery were thus at least twice the reported activation

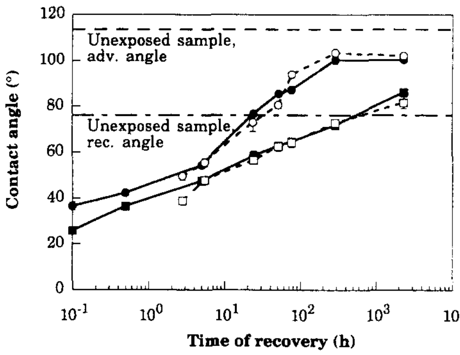

Figure 3 Contact angle of water for specimens exposed to 0.3 h of corona discharges (2.6 W) plotted *versus* storage time at 25°C; 'mechanically deformed': specimen advancing (○) and receding (□); 'untouched' specimen: advancing (●) and receding (■)

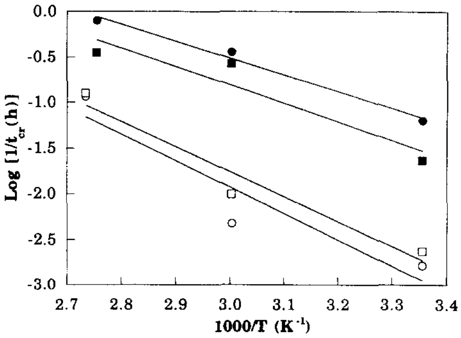

Figure 4 The reciprocal of the logarithm of the time to reach full recovery (t_{cr}) of contact angle of water on 'mechanically deformed' specimens exposed to 2.6 W corona for 0.3 h: advancing (○) and receding (□); and 200 h: advancing (●) and receding (■), as a function of the reciprocal of the recovery temperature

energy of the diffusivity of low molar mass PDMS in PDMS elastomer, 15.5 ± 2 kJ mol^{-1} [24]. The activation energy for the transport of low molar mass PDMS from the bulk to the surface should be very similar to the activation energy for the diffusivity of low molar mass PDMS species from the bulk to the surface, since the heat of mixing of low molar mass PDMS and PDMS elastomer is negligible. This is an indication that the hydrophobicity recovery, if it is controlled by diffusivity, is not a bulk process and that the properties of the oxidized surface of exposed samples is different from those of the bulk.

The hydrophobicity recovery of untouched specimens was markedly slower than the hydrophobicity recovery of 'mechanically deformed' specimens, i.e. the exposed surfaces were subjected to a compressive strain of less than 1%, in the case of samples exposed to corona for one hour or longer (*Figures 5 and 6*). *Figure 3* shows that the rate of hydrophobicity recovery was almost the same for the untouched and for the mechanically deformed specimens that were treated with only a small dose of corona (20 min). Another feature typical of untouched specimens was that the kinetics of the hydrophobicity recovery showed a greater variation under identical conditions, is indicated by the extensive scatter of the data points in the Arrhenius diagram presented in *Figure 7*.

The suggestion by Owen and coworkers[5,10] that a brittle silica-like layer is formed by the corona treatment provides an explanation the data presented in *Figures 5–7*. It may be assumed that the relative free volume and hence the diffusivity of PDMS is considerably smaller in the silica layer than in the bulk of normally crosslinked PDMS. It may also be assumed that the mild bending of the 'mechanically deformed' specimens caused a cracking of the brittle silica layer and hence a more rapid migration of low molar mass PDMS species through the cracks to the surface. The data presented in *Figure 3* seem to indicate that the dense silica layer is not formed during 20 min of corona exposure. The difficulty in obtaining reproducible results for the recovery rates of untouched films under identical conditions may be due to the occasional formation of cracks due to sample handling.

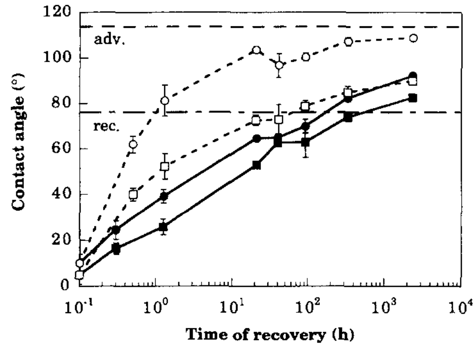

Figure 5 Contact angle of water for specimens exposed to 1 h of corona discharges (2.6 W) plotted *versus* storage time at 25°C: 'mechanically deformed' specimens: advancing (○) and receding (□); 'untouched' specimen: advancing (●) and receding (■). The broken lines indicate the advancing and receding contact angles of the unexposed specimen

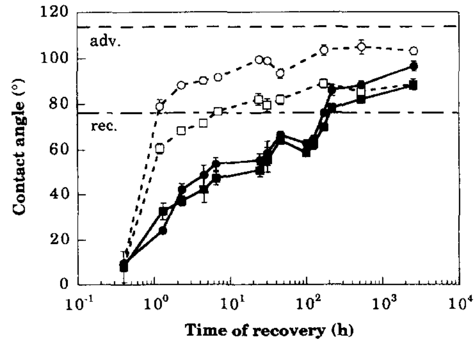

Figure 6 Contact angle of water on specimens exposed to 200 h of corona discharges (2.6 W) plotted *versus* storage time at 25°C: 'mechanically deformed' specimens: advancing (○) and receding (□); 'untouched' specimen: advancing (●) and receding (■). The broken lines indicate the advancing and receding contact angles of the unexposed specimen

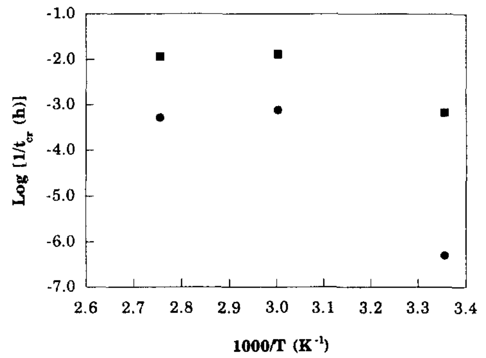

Figure 7 The reciprocal of the logarithm of the time to reach full recovery (t_{cr}) of advancing (●) and receding (■) contact angles of water on 'untouched' specimens exposed to 2.6 W corona for 1 h as a function of the reciprocal of the recovery temperature

The difference in advancing and receding contact angles is a hysteresis effect related to the mobility of the macromolecules at the surface[25]. The initial hysteresis of unexposed samples was 38°. The hysteresis of the samples (both untouched and mechanically deformed samples) immediately after 20 min of exposure to corona discharges was 10°, and this increased to 30° after 20 h of recovery at room temperature (*Figure 3*). After 1 h of exposure to corona discharges, the mechanically deformed specimen exhibited a hysteresis of 20–30°. The untouched film, however, exhibited a lower hysteresis, between 3° and 12°. The same trend was observed after 200 h of corona discharge exposure; the hysteresis directly after the corona treatment was only 1° to 7° for the untouched film whereas the mechanically deformed specimen exhibited a hysteresis between 12° and 20°. A very low hysteresis is indicative either of a very fast reorientation of the polymer chains, as in hydrogels[25], or due to a lack of segmental mobility of the molecules in the surface layer. It is suggested that the 200 h corona treatment yielded a thin surface layer of highly immobilized molecules due to crosslinking by silanol condensation and the formation of Si–O–Si bridges[13]. This effect is further substantiated by the XPS data presented in Section 3.4. *Figures 5 and 6* show that the receding contact angle on long-term storage approaches a value greater than the value obtained for the unexposed specimen, whereas the advancing contact angle approached the value for the unexposed specimen. It was argued by Garbassi *et al.*[26] that the oxidation of the surface layer increased the concentration of hydroxyl groups and that this led to the formation of strong intermolecular bonds (hydrogen bonds). The observed lowering in the hysteresis (i.e. the 'anomolous' high receding angle value) may be due to immobilization of the top-layer molecules attached to the deeper hydrogen-bonded segments. It is remarkable that the extremely small hysteresis for the specimens subjected to 200 h of corona discharges was largely preserved even after recovery of the hydrophobicity as assessed by the advancing contact angle (*Figure 6*). These data imply that the layer of low molar mass PDMS molecules that presumably covers the recovered PDMS specimen is remarkably constrained. It shows a very slow hydrophilication in water which may be due to the aforementioned constraining effect of deeper hydrogen-bonded segments.

Effects of quenching in liquid nitrogen

Storage of corona-treated specimens in liquid nitrogen led to an almost complete suppression of the hydrophobicity recovery, as has been reported by Everaert *et al.*[4] (*Figure 8*). These specimens, originally exposed to 1 h of corona treatment at 1.5 W, showed a faster recovery of the hydrophobicity on storage at room temperature as assessed by the advanced contact angle, than the mechanically deformed specimens at this temperature (*Figure 8*).

The rate of hydrophobicity recovery (advancing contact angle) increased with increasing temperature, in accordance with the Arrhenius equation (*Figure 9*) with activation energies of 51 kJ mol^{-1} (liquid nitrogen-quenched specimens) and 62 kJ mol^{-1} (mechanically deformed specimens). It is suggested that the faster hydrophobicity recovery of liquid nitrogen-quenched samples is due to further cracking of the oxidized surface layer as a result of differences in thermal contraction between the surface layer (high glass transition temperature) and the bulk (low glass transition temperature) during the extensive cooling to the temperature of liquid nitrogen, as that the migration of low molar mass PDMS occurs more readily through the cracks than through the intact silica-rich surface layer.

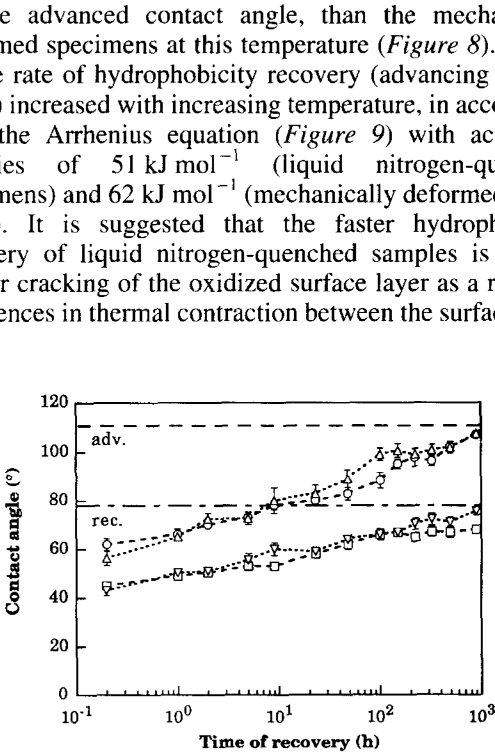

Figure 8 Contact angle of water on 'liquid-nitrogen-quenched' specimens (Δ: advancing, ∇: receding) and for 'mechanically deformed' specimens (O: advancing, □: receding) as a function of the storage time at 25°C after 1 h corona treatment (1.5 W). The broken lines indicate the advancing and receding contact angles of the unexposed specimen

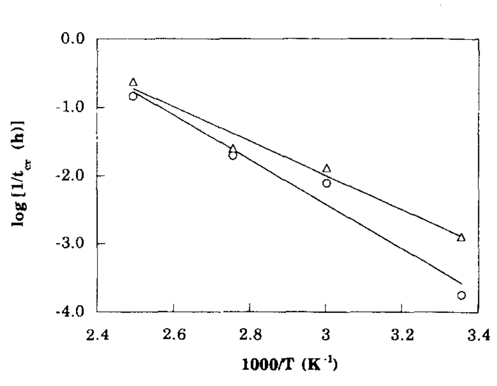

Figure 9 The reciprocal of the logarithm of the time to reach full recovery (t_{cr}) of the advancing contact angle of water on 'liquid-nitrogen-quenched' (Δ) and 'mechanically deformed' (O) specimens as a function of the reciprocal of the recovery temperature. The specimens were originally exposed to 1 h of corona treatment (1.5 W)

X-ray photoelectron spectroscopy

Low molar mass PDMS was largely removed from the silicone rubber samples prior to the XPS analyses, the exposed samples being extracted with boiling hexane after the corona treatment. *Table 1* presents data for the atomic composition of a series of samples exposed to corona discharges for different periods of time.

The estimated depth of penetration was 8–10 nm at normal ($\phi = 0°$; ϕ is the angle between the direction of emitted photoelectrons to the analyser and the surface normal) and 2 nm at grazing angle ($\phi = 60°$)[10]. The theoretical atomic composition of the PDMS is 25% Si, 50% C and 25% O. The atomic composition determined for the unexposed sample differed from the theoretical, presumably due to contamination and surface oxidation (*Table 1*). Short-term (0.3 h) exposure to corona discharges led to a pronounced increase in oxygen content to 41–45% and a decrease in the carbon content to 29–33%. The 2 nm top layer showed a lower oxygen content and higher carbon content than the top 8 to 10 nm. It is clearly possible that a small portion low molar mass PDMS was present in the sample and that low molar mass, unoxidized PDMS migrated through the oxidized layer[10,11]. After 1 h of exposure to corona discharges, the amount of oxygen increased to 53–56% and the carbon content dropped to 15–19% with even greater changes in the top 2 nm layer (*Table 1*). The composition of the surface layer, including data obtained at different angles of resolution, of the sample exposed for 200 hours to corona discharges, was fairly similar to that of the sample exposed for 1 h of corona discharges. This means that the atomic composition of the surface layer remained essentially constant after 1 h of corona treatment.

The pronounced change in composition of samples exposed to corona discharges for 0.3 and 1 h, is demonstrated by the change in shape of the peaks in the Si 2p region. *Figure 10* shows the growth in the exposed samples of the peak at 103.8 eV associated with an inorganic silica-like (SiO_x) phase[11], i.e. a component with Si atoms bonded to more than two oxygen atoms. The Si 2p peak at 102.1 eV is assigned to an organic silicone phase[11]. *Table 2* shows a gradual but strong increase in the relative size of the SiO_x peak with increasing corona treatment time, reaching a relative size of the 103.8 eV peak of 87% of Si 2p peak. The changes in the spectra in the Si 2p region are relatively small between samples exposed for 1 h and for 200 h to corona discharges. The first hour of exposure thus caused

Table 1 Atomic composition of the surface layers according to XPS

Exposure time (h)	Angle ϕ (°)	Atomic Comp. (at.w.%)		
		Si	C	O
0	0	19.5	53.4	27.1
0.3	0	25.7	29.4	44.9
0.3	60	26.5	32.8	40.7
1	0	29.5	14.9	55.6
1	60	28.0	18.7	53.3
200	0	29.7	13.7	56.6
200	60	30.5	13.8	55.7

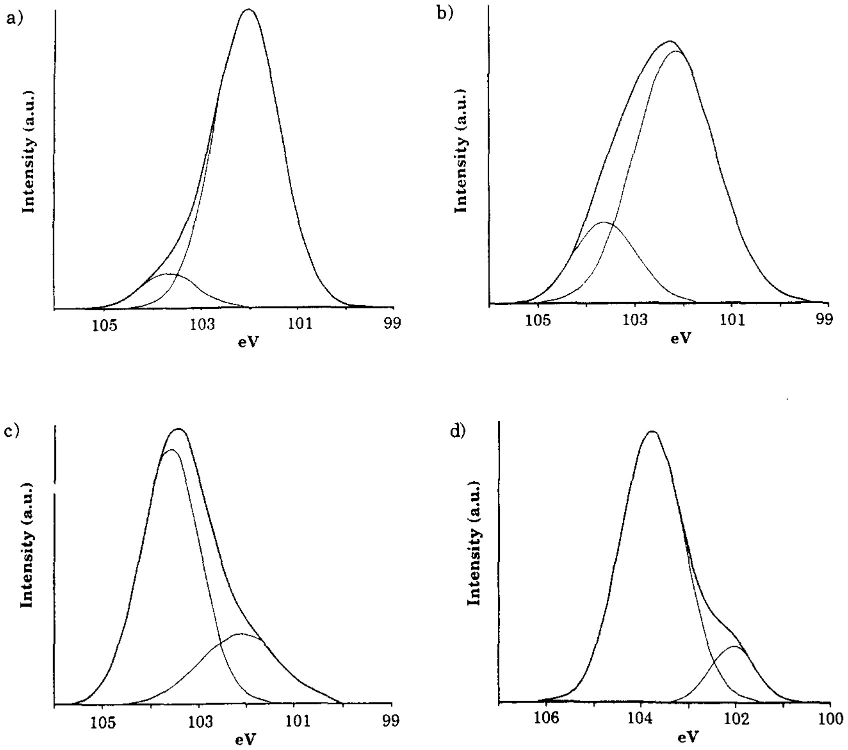

Figure 10 Si 2p spectra (XPS) of samples exposed to corona discharges (2.6 W) for different periods of time: (a) 0 h; (b) 0.3 h; (c) 1 h; (d) 200 h. The Si 2p peak is resolved into the organic silicone 102.1 eV peak and the inorganic silica-like 103.8 eV peak

most of the irreversible changes towards the formation of an inorganic silica-like phase. A small silica peak (constituting 8% of the whole Si 2p peak) was present in the spectrum of the unexposed sample due to the amorphous silica filler added to this polymer. It seems that the more extended corona treatment led to a moderate increase in the thickness of the oxidized surface layer as indicated by the angle-resolved data. The carbon content in the samples exposed to at least 1 h of corona discharges was typically only 26% of the carbon content of the unexposed material (*Table 1*). The content of oxidized carbon atoms (binding energy = 286.1 eV)[11] showed only a minor increase in the exposed samples and it never exceeded 8% of the carbon content (*Table 2*). This suggests that oxidation in the 8–10 nm top layer mainly involved the formation of linkages between Si and O atoms. These findings, combined with the data obtained by contact angle measurements, strongly support the idea of a thin top layer with inorganic, glass-like characteristics in corona-treated silicone rubber. The occurrence of a glassy layer has been suggested by a number of other researchers[4,5,11]. Embrittlement of PDMS elastomers has earlier been reported on aging in well-ventilated situations at temperatures above 250°C[27].

Infra-red spectroscopy

The chemical changes in samples exposed to corona discharges were further studied by ATR i.r. spectroscopy. The depth of the surface layer (d_p) assessed by ATR i.r. is given by[28]:

$$d_p = \frac{\lambda}{2\pi n_1(\sin^2\theta - n_{21}^2)^{1/2}} \qquad (1)$$

where λ is the wavelength in air, θ is the angle of incidence (= 45°), n_1 is the refractive index of the ATR crystal (= 2.38) and n_{21} is the ratio of the refractive index of the sample to that of the ATR crystal (= 0.60). equation (1) yields depths in the range of 0.45 to 4.5 μm depending on the wavelength of the i.r. radiation. The spectra obtained by ATR i.r. are thus not related to the surface in the strictest sense, compared to 'true' surface methods such as XPS. ATR i.r. spectra of unexposed and corona-treated samples are shown in *Figure 11*. The Si–CH$_3$ absorption peak at 1263 cm^{-1} was used as an internal reference. This

Table 2 Analysis of the C 1s and Si 2p peaks

Exposure time (h)	Peak areas (%)			
	C 1s (eV)		Si 2p (eV)	
	284.5	286.5	102.1	103.8
0	100	0	92	8
0.3	98	2	80	20
1	92	8	23	77
200	95	5	13	87

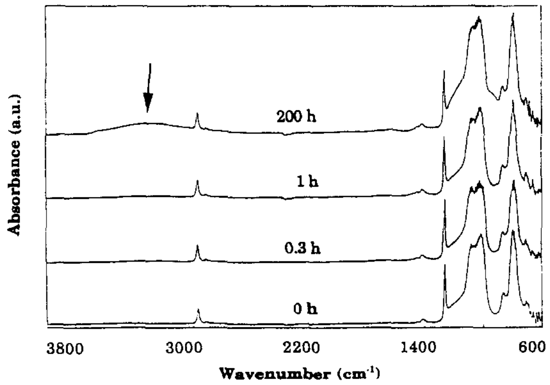

Figure 11 ATR i.r. spectra of samples exposed to corona discharges (2.6 W) for different periods of time. The arrow indicates the hydroxyl absorption peak at 3300 cm^{-1}

absorption was essentially unchanged by the surface treatments, and it was not obscured by other absorption peaks.

Figure 11 shows a corona-discharge-induced increase in the broad absorption peak centered at 3300 cm^{-1} indicating the formation of hydroxyl groups[29]. There is no consensus as to whether the most common type of hydroxyl group formed is Si–OH or $Si-CH_2OH$, as was suggested earlier[14]. According to XPS data, the resolution of the C 1s peak indicated only the presence of minor amounts of oxidized carbon atoms. This suggests that the majority of hydroxyl groups formed were bonded to Si-atoms and not to carbon atoms. The absorption peaks from C–H stretching at 2963 cm^{-1} and bending at 1463 cm^{-1} [30,31] remained almost unchanged, however, even after 200 h, indicating an almost unchanged content of methyl groups in the material within the observed penetration depth. The depletion of carbon atoms detected by XPS is obviously associated with a very thin surface layer (~10 nm) which is hardly noticeable by ATR i.r. spectroscopy. Morra *et al.*[13] showed that the intensity of the C–H stretching, bending, and deformation modes decreased in intensity in PDMS treated with oxygen plasma PDMS. This contradictory result could be explained if the oxidized surface layer formed in our study was very thin, due to the low power used compared with the 100 W RF-plasma used by Morra *et al.*[13]. A broadening of the absorption band at 1100–1200 cm^{-1} was observed in the spectrum of the sample which had been exposed to corona discharges for 200 h. This result indicates a crosslinking of methyl groups into $Si-CH_2-CH_2-Si$ units which would absorb at 1134 and 1058 cm^{-1}, as suggested by Hollohan[14], or recombination of $SiOCH_3$ resulting in a random crosslinking, as suggested by Kim *et al.*[18]. Corona treatment led only to a very minor increase in the carbonyl absorption peak between 1650 and 1700 cm^{-1}. The carbonyl group consists of oxidized carbon atoms in the form of ketones, esters, carboxylic acids and aldehydes[29,30]. This suggests that, during surface oxidation, only minor amounts of carbonyl groups were formed compared to the extensive formation of hydroxyl groups. Absorption peaks at 870–850 cm^{-1} and 840–790 cm^{-1} are characteristic of Si-alkyl groups such as $Si(CH_3)_3$ and $Si(CH_3)_2$, respectively[29]. A decrease in the absorption peak originating from $Si(CH_3)_3$ at 860 cm^{-1} was observed in the spectrum of the sample exposed to 200 h of corona discharges.

CONCLUSIONS

The original hydrophobic surface of a high-temperature-vulcanized polydimethylsiloxane (PDMS) elastomer was changed to a hydrophilic surface when exposed to corona discharges. I.r. spectroscopy showed that the corona discharges led to the formation of hydroxyl groups. Prolonged exposure to corona discharges led to the formation of a ~10 nm thick top layer with silica-rich (Si bonded to more than two oxygen atoms) material. Specimens kept in dry air recovered their original high hydrophobicity. The hydrophobicity recovery rate showed an Arrhenius temperature dependence with an activation energy that was two to four times greater than the activation energy of the diffusivity of low molar mass PDMS in PDMS elastomers. It is suggested that the occurrence of a silica-rich top layer retarded the transport of low molar mass PDMS to the surface and the hydrophobicity recovery. Specimen subjected to a small mechanical deformation ($<$ 1% strain) after corona exposure exhibited a faster hydrophobicity recovery than similar samples subjected to no mechanical stress/strain. It is suggested that mechanical stresses and thermally induced stresses caused a cracking of the brittle silica-layer, which facilitated the transport of low molar mass PDMS to the surface and the hydrophobicity recovery.

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