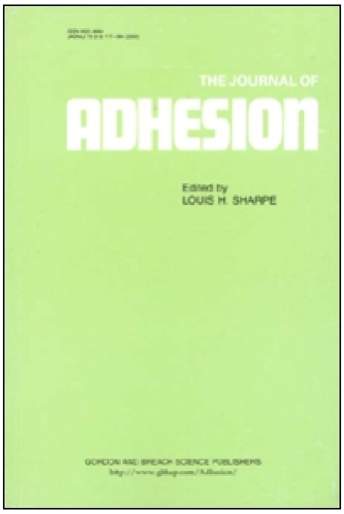

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Hydrophobic Recovery of Plasma-Treated Polydimethylsiloxane*

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Plasma treatment of silicone surfaces is a useful, environmentally-sound method of increasing wettability to improve adhesion. A thin, wettable silica-like layer is produced with various plasma gases such as argon, helium, oxygen and nitrogen. However, in each case the surfaces gradually recover their hydrophobicity. The silica-like layer is brittle and microcracking is evident at more severe levels of plasma treatment. The onset of cracking is a function of plasma gas, RF power, pressure and treatment time. Scanning electron microscopy has been used to characterize the cracks.

The hydrophobic recovery has been monitored by water contact angle changes. It occurs with both cracked and uncracked treated surfaces. There is an initial jump in hydrophobicity at the onset of cracking. Thereafter, the recovery of both cracked and uncracked surfaces broadly parallels each other with virtually complete recovery of original hydrophobicity within one week. These effects can be accounted for by rapid surface diffusion of low molecular weight material out of fresh cracks followed by slower bulk diffusion through the polymer matrix. Significant differences in recovery rates are also evident between different plasma gases.

KEY WORDS PDMS; plasma; surface modification; contact angle; adhesion; SEM; wettability; microcracking; hydrophobic recovery.

1. INTRODUCTION

Plasma modification of polymers is a process of growing importance in material science today. First introduced commercially about twenty-five years ago, it provides a means of controlling the surface properties without affecting the bulk properties. As only a few molecular layers in the surface region are changed by the plasma it offers an environmentally acceptable process without the use of volatile solvents or highly reactive chemical treatments and produces no problematical wastestreams. For these reasons it, and related processes such as corona treatment, are receiving considerable attention at academic and industrial institutions. Many papers at a recent international symposium[1] addressed this topic and two recent issues of a journal[2] were devoted to this subject.

One of the most important uses of plasma modification is to enhance the adhesion or bondability of polymers to adhesives and other substrates. This is particularly so for

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hydrophobic, low-surface-energy polymers such as polydimethylsiloxane (PDMS). Part of the effect may be simple cleaning of the surface of impurities, contaminants and other weak boundary layers that impair adhesion; a part may also be physical and chemical alterations of the surface region such as increasing roughness and introduction of polar functional groups. Liston and co-workers[3] provide a critical review of plasma surface modification for improved adhesion. The first report of plasma modification of PDMS was also directly aimed at improving adhesion.[4] In the earliest studies, Hall and co-workers treated PDMS elastomers in an ammonia plasma. Bonding results with a urethane adhesive were erratic and attributed to a weak boundary layer of low molecular weight PDMS fractions. ATR-IR (attenuated total reflection infrared spectroscopy) on a treated PDMS elastomer gum revealed no NH_2 bonds. Another early bondability study of PDMS was reported by DeLollis and Montoya,[5] who used an oxygen glow discharge plasma treatment. They obtained more consistent adhesion improvement despite the presence of low molecular weight extractable material that might form a weak boundary layer as presumed by Hall and co-workers. Another mechanistically important early contribution was from Hollahan and Carlson.[6] Their IR studies of the effect of oxygen plasma suggested that the polar groups produced in the surface region were predominantly $SiCH_2OH$ groups. They were also the first to describe the close relationship between the effects of corona and plasma treatment of PDMS.

None of these early studies mentioned the hydrophobic recovery or progressive loss of wettability after plasma treatment ceased. This was first reported for corona treated PDMS by Lee and Homan[7] and for plasma treated PDMS by Ikada *et al.*[8] but it remains a controversial topic. Most recent studies acknowledge the problem, for example, the work of Morra and co-workers[9] and Owen *et al.*,[10] but others such as Triolo and Andrade[11] report that the hydrophobic surfaces produced are stable for up to three months storage time in air. At the international symposium mentioned earlier,[1] one contribution[12] claimed that the plasma modified surface of PDMS was stable for a period of at least a week, whereas Owen and Smith[13] presented considerable evidence of hydrophilic recovery of plasma- and corona-modified PDMS surfaces.

Many of the differences in the type of surface modification produced and the nature of the recovery process involved can be attributed to differences in the type of plasma employed. Table I summarizes these differences. The entry "unspecified" means the authors did not provide this information. In the case of Hozbor and McPherson's conference report[12] this omission may well be rectified in the subsequent journal publication. There is no consensus yet on the mechanisms involved even when the same type of gas plasma is used under comparable conditions. The factors involved in the hydrophobic recovery mechanism appear to be:

A. Production of surface hydrophilic groups such as SiOH or $SiCH_2OH$ which can reorientate away from the surface (also called "overturn" of polar groups in the polymer surface).[8]

B. Surface silanol condensation preventing chain reorientation.[7]

C. Development of a silica or silicate-like network in the surface region.[11,14]

D. Cracking of the silica-like region, producing a path for the surface-driven migration of free PDMS chains from the bulk to the surface.[13]

TABLE I

Summary of plasma-treated PDMS surface studies

Year	Authors	Plasma Type	Gases Used	Surface Analysis Techniques
1969	Hall, Westerdahl, Devine, Bodnar	RF	NH_3	IR
1970	Hollahan, Carlson	RF	O_2	IR
1971	DeLollis, Montoya	RF	O_2	IR, contact angle
1976	Feneberg, Krekeler	RF	O_2	contact angle
1983	Triolo, Andrade	RF	He	XPS, contact angle, SEM
1985	Ikada, Matsunaga, Suzuki	RF	Ar	contact angle
1988	Owen, Gentle, Orbeck, Williams	RF	H_2O	XPS, contact angle
1988	Stewart, Urban	Microwave	Ar, CO_2, NH_3	ATR-FTIR, DMA
1990	Gaboury, Urban	Microwave	N_2, Ar	ATR-FTIR
1990	Morra, Occhiello, Marola, Garbassi, Humphrey, Johnson	RF	O_2	ATR-FTIR, SSIMS
1991	Hettlich, Otterbach, Mittermayer, Kaufmann, Klee	Unspecified	O_2, CO_2	XPS, SEM, FTIR
1993	Hozbor, McPherson	Unspecified	Various, unspecified	contact angle
1994	Owen, Smith	RF	Ar, He, O_2, N_2	XPS, contact angle, SEM

E. Migration of untreated polymer chains (particularly low molecular weight species) through the bulk matrix to the surface.
F. Migration of treated polymer chains from the surface to the bulk.
G. Loss of volatile, oxygen-rich or other polar entities to the atmosphere.
H. Changes in surface roughness.
I. External contamination of the polymer surface.

The processes used to make PDMS are generally redistribution processes resulting in an equilibrium between polymer rings and chains and a distribution of molecular weights of both species. Thus, unless special efforts such as rigorous solvent extraction are made, low molecular weight material with the potential to migrate will always be present in PDMS. Central to this potential for migration is the development of the silica or silicate-like surface region. Evidence is mounting that this does occur in many plasma treatments of PDMS. Should it remain intact, its high degree of three-dimensional structure might retard migration but should it be brittle and prone to crack, such cracks could facilitate the migration of low molecular weight material from the bulk to the surface.

Cracking of PDMS surfaces by exposure to plasma was first reported by Hettlich and co-workers.[15] Operating at 600 W, they observed by SEM that fine cracks were induced on the surface by treatment periods of longer than 60 seconds with oxygen plasma, but CO_2 plasma treatment in contrast does not lead to visible surface damage before 600 seconds. Owen and Smith[13] used four different plasma gases: argon, helium, oxygen, and nitrogen. In each case, treatment eventually resulted in cracking although conditions could be found for each gas where the surface becomes completely wettable by water but is free from cracks, *e.g.* helium plasma at 10 W and 70 Pa pressure for 3 minutes.

Given this possibility of treating PDMS to complete water wettability (quasi-static advancing contact angle of zero) both with and without inducing surface cracking, a key mechanistic question concerns the hydrophobic recovery of these two situations. Possibly the uncracked surface might recover its hydrophobicity much more slowly, if at all, than the cracked surface. This could account for the reported differences in hydrophobic recovery. The testing of this hypothesis is the purpose of the research presented here.

2. EXPERIMENTS

2.1 Experimental Materials

The material used in this study was 0.5 mm thick Dow Corning polydimethylsiloxane sheeting, X7-5203. Samples were cleaned by Soxhlet extraction in methanol for a minimum of four hours before treatment. Following treatment, the samples were stored at room temperature in a desiccator at laboratory atmosphere.

2.2 Plasma Treatment

Plasma treatments were performed in a Branson/IPC S4000 Series plasma system which generates a low pressure, radio frequency (13.56 MHz), cold plasma. Controllable parameters include treatment time, gas, RF power and pressure. Typical treatment times ranged from a few seconds to many minutes; typical powers are 5 to 400 W and chamber pressure is variable from 40 to 90 Pa. We studied four plasma gases, oxygen, nitrogen, argon and helium. Gas continually flows into the reactor throughout the plasma treatment process.

2.3 Scanning Electron Microscope Examination

Scanning electron microscopy (SEM) was done with a JEOL JSM-6100 SEM. Samples were coated with 15 nm of Au/Pd prior to examination to prevent charging effects.

2.4 Contact Angle Measurements

Contact angle measurements were taken with a Ramé-Hart, Inc. NRL Model A-100 contact angle goniometer. Measurements were taken with doubly distilled and deionized water having a surface tension (measured by Wilhelmy Plate Method) of 72.6 mN/m. The angles reported are an average of measurements on either side of several drops. The standard deviation was typically ± 5 deg due to the surface roughening induced by plasma treatment.

3. RESULTS AND DISCUSSION

Figure 1 is a scanning electron micrograph of an example of a cracked surface produced by an oxygen plasma after 10 minutes of treatment with 70 W at 70 Pa. It was

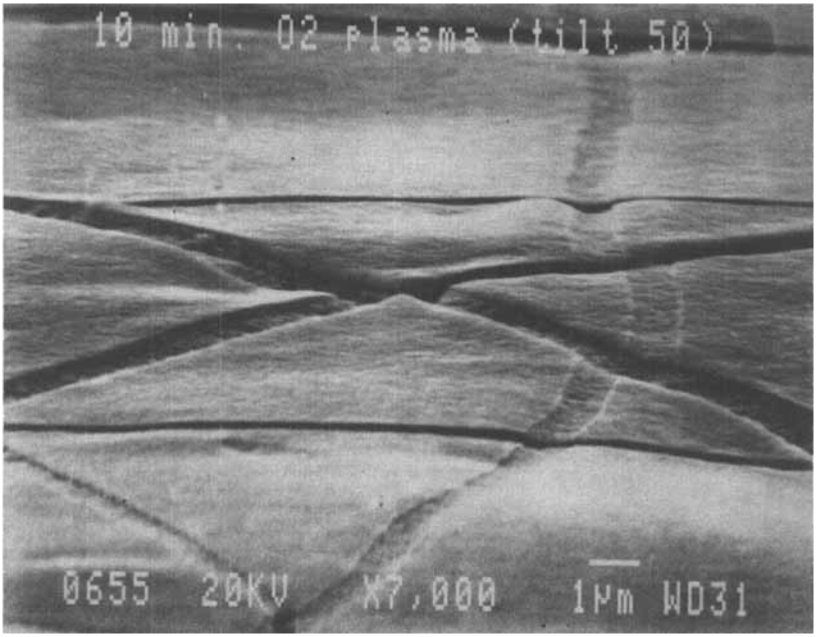


FIGURE 1 SEM micrograph of cracked surface resulting from 10 min. oxygen plasma treatment at 70 W and 70 Pa. Sample has been tilted at 50 deg.

taken at a tilt angle of 50 degrees and the cracks are seen to be of the order of 1 micron wide and 1/3 to 1/2 micron deep, indicating that they should properly be described as microcracks. We attempted a variety of replication and cross-sectional procedures but were unable to get any more precise information on microcrack dimensions. Figure 2 a, b, and c show a series of micrographs which illustrate the effect of treatment time on surface appearance.

The onset of microcracking is a function of the plasma gas used, the RF power level, the pressure in the treatment chamber and the time of treatment. In order to illustrate the difference between the four plasma gases used, pressure and time were held constant at chosen values and the RF power increased until cracking occurred. These data are shown in Table II where it is evident that argon provides the most intense plasma treatment whereas helium provides the least.

The general pattern of hydrophobic recovery is shown in Table III and in Figures 3 to 7. It takes 20–30 seconds to remove the sample from the plasma chamber and take the first contact angle measurement on the freshly treated surface. These are the data termed "initial" in Table III. "Onset of cracking" in this table means that isolated cracks can be seen at this time in the SEM images. "Light cracking" is a later development when sufficient cracks are visible to form a network over the whole surface. In each case, whatever the plasma gas used, there is an initial jump in water contact angle from zero to 10 to 25 deg once cracking begins to occur. A similar rise in

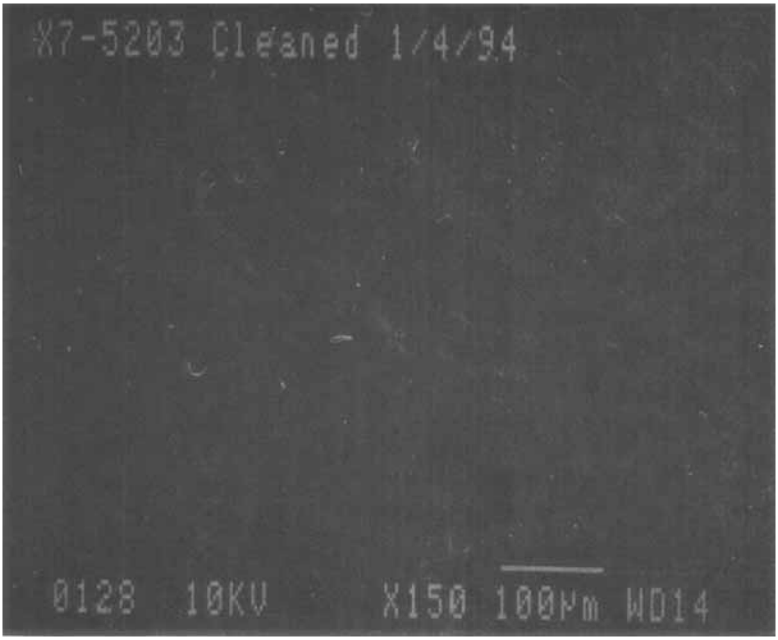
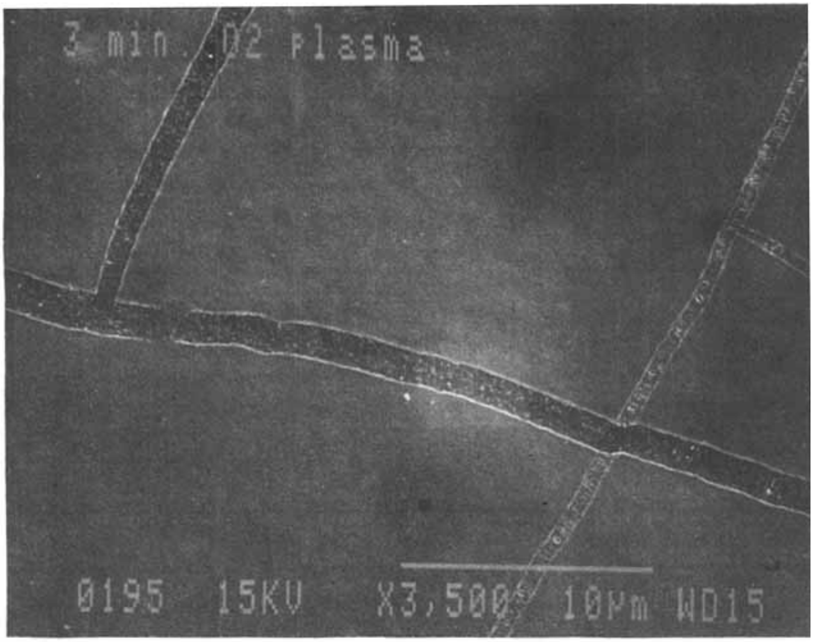
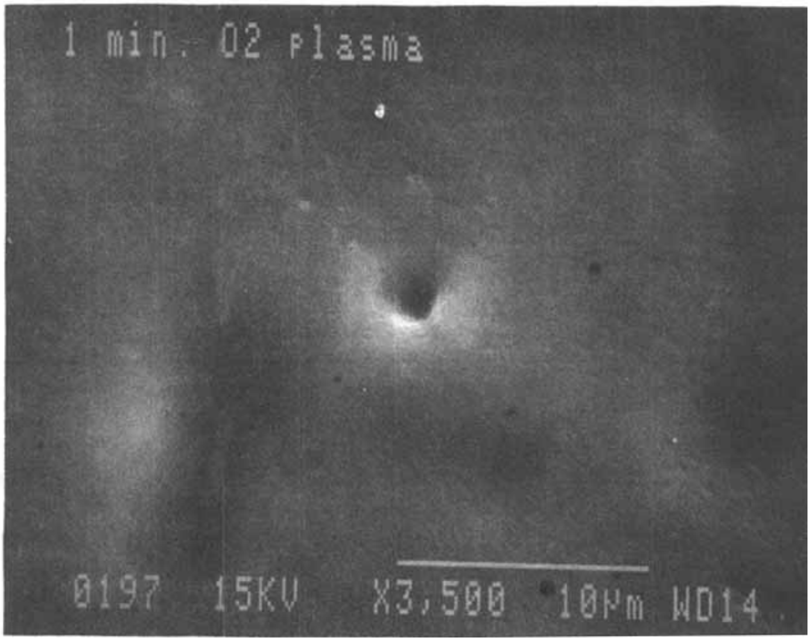


FIGURE 2 a) Untreated control b) 1 min. oxygen plasma at 70 W and 70 Pa c) 3 min. oxygen plasma at 70 W and 70 Pa.



(b)



(c)

FIGURE 2 (*Continued*)

TABLE II

RF power required to produce cracking of PDMS surface (at 70 Pa for 10 minutes)

Gas	Watts
Argon	5
Oxygen	25
Nitrogen	100
Helium	375

TABLE III

Effect of plasma treatment time on PDMS wettability

		Water Contact Angle (deg)	
Plasma Type	Time (min)	Initial	After 24 hrs
Oxygen (70 W, 70 Pa)	1	0	63
	2	< 10	87
	3 (onset of cracking)	21	93
	5	27	94
	8	20	93
	10	30	90
Argon (10 W, 70 Pa)	3	0	33
	5	0	46
	8 (onset of cracking)	0	53
	10	13	72
	12	13	75
Nitrogen (100 W, 50 Pa)	3	0	60
	5	0	57
	8	0	49
	10	0	52
	20 (light cracking)	< 10	64
	30	11	54
Helium (10 W, 70 Pa)	3	0	29
	5	0	37
	10	0	40
	20	0	44
	30 (light cracking)	14	55
	40	14	55

the initial value can be achieved by flexing a treated, uncracked sample to induce surface cracking deliberately. It is as if there is a sub-surface reservoir of material that causes an initial rise in contact angle, but thereafter the changes seem to occur similarly for the first twenty-four hours, with all samples having a contact angle near to 100 deg after one week. The initial contact angle of *circa* 107 deg never seems to be recovered within the timescale of any experiment we have yet conducted (up to several weeks). Various PDMS surfaces show a range of contact angles and *circa* 100 deg may be characteristic of a free film of PDMS whereas 110 deg may be the value for a crosslinked elastomer.

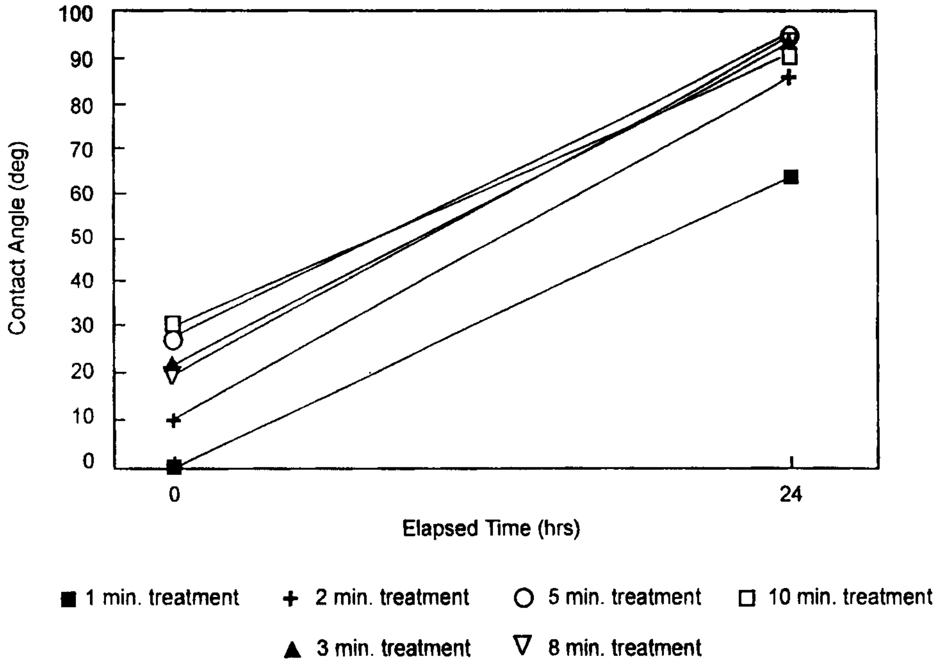


FIGURE 3 Twenty-four hour recovery of oxygen-treated (70 W, 70 Pa) samples at varied treatment times.

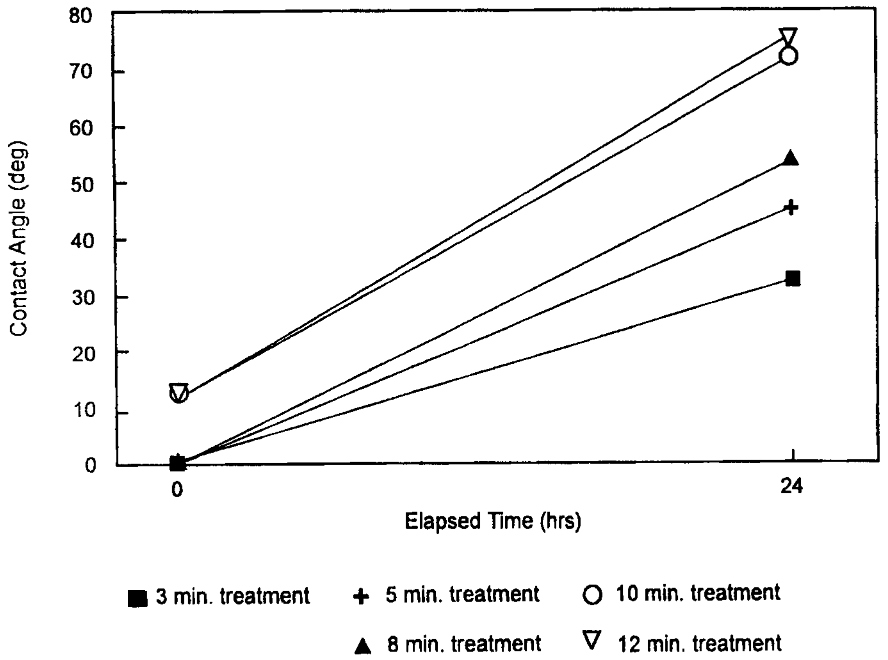


FIGURE 4 Twenty-four hour recovery of argon-treated (10 W, 70 Pa) samples at varied treatment times.

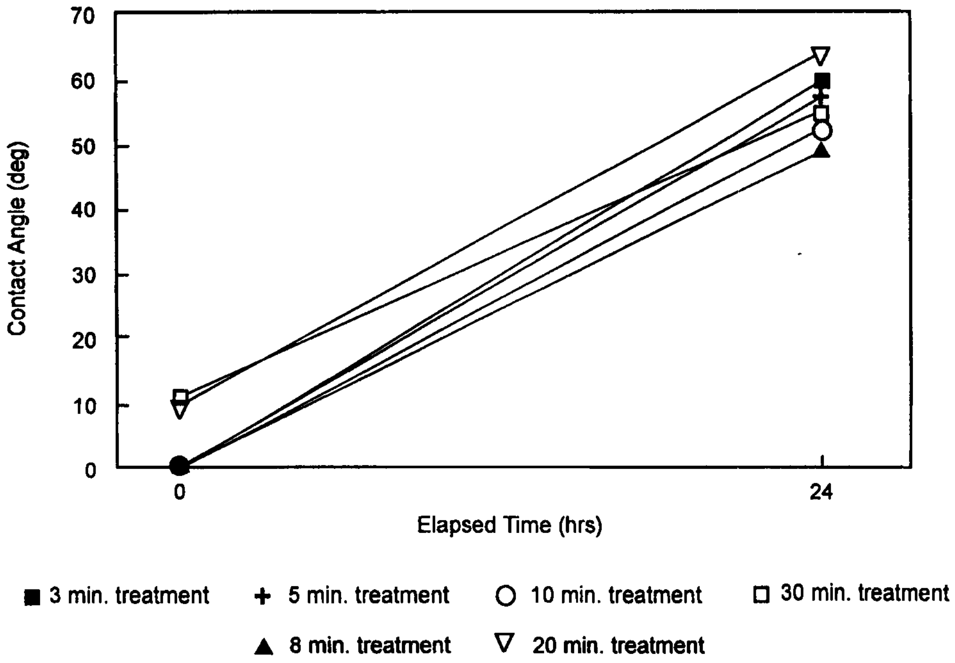


FIGURE 5 Twenty-four hour recovery of nitrogen-treated (100 W, 50 Pa) samples at varied treatment times.

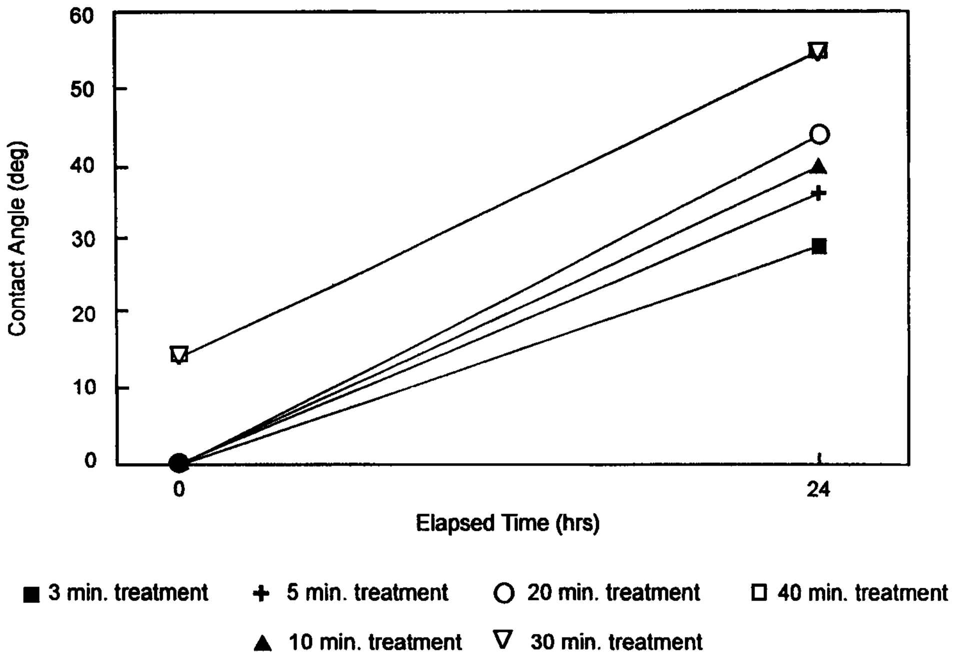


FIGURE 6 Twenty-four hour recovery of helium-treated (10 W, 70 Pa) samples at varied treatment times.

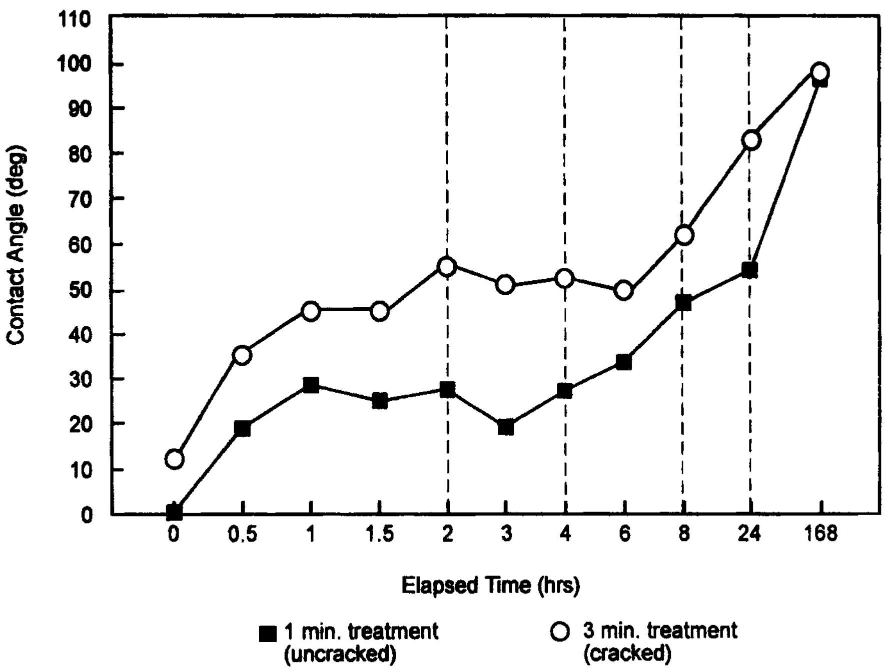


FIGURE 7 Recovery of cracked *vs.* uncracked oxygen plasma-treated (70 W and 70 Pa) samples.

The contact angle increase in the first twenty-four hours differs between the various plasma gases used. This implies different extents of the oxidized region and the pattern of cracking in each case. This oxidation process will depend on the availability of oxygen and the nature of the plasma. Differences in electron and ion energies, types of activated species and UV intensities must account for the detailed differences between the effects of two inert gases such as helium and argon. The oxygen available in such plasmas can come from residual air in the treatment chamber or more likely from dissolved oxygen in the polymer itself. Figures 3–6 illustrate these differences in twenty-four hour hydrophobic recovery of the various plasma gas treatments used. The helium plasma-treated PDMS surfaces recover hydrophobicity the least completely and the oxygen plasma-treated surfaces recover it the most. Argon and nitrogen treatments show intermediate recovery characteristics. Uncracked argon-treated surfaces recover significantly less than similar nitrogen-treated surfaces, but cracked surfaces behave quite similarly. Figure 7 is a more detailed comparison of the hydrophobic recovery of cracked and uncracked surfaces in the case of oxygen plasma treatment. The contact angle values tend to fluctuate up and down during extended recovery studies because several samples were treated at once and plasma treatment varies somewhat over short distances within the reactor. In addition, each sample cracks differently, which results in slightly different contact angle values.

As the cracks are of the order of one micron deep they must penetrate into the unoxidized region. Our previous XPS studies[13] showed a depth of treatment less than the typical 50–80 Angstrom sampling depth of the technique for uncracked but wettable surfaces. It is not likely that even the harshest treatment conditions would affect a region two orders of magnitude greater in depth than this. The shallow treatment depth is also consistent with general plasma-treated polymer surface experience. The cracks must originate as a result of the difference in modulus between the oxidized silica-like layer and the bulk polymer but, evidently, they propagate well beyond this interfacial region. We assume that cracks begin during the plasma treatment process when enough time has elapsed for a sufficient modulus difference to have developed. Presumably, much of this newly-cracked surface is then oxidized by the plasma for the remaining exposure time, *i.e.* to a lesser extent than the original surface. The deepest portion of the cracks will likely be shadowed to the point where little, if any, oxidation can occur.

Such cracks into the untreated region would expose the low molecular weight unbound polymer chains present there. Typically, PDMS elastomers can contain up to 15% of such material. We suggest that the jump in initial hydrophobicity at the onset of cracking is caused by surface-tension-driven surface diffusion from the freshly-cracked surface over the higher-surface-tension, plasma-treated surface. The extent of this diffusion is limited by the amount of free low molecular weight PDMS available on the crack surface and the modest 10–25 deg increase in water contact angle that results indicates a less than complete monolayer coverage. Thereafter, diffusion would be out of the bulk material, evidently a slower process than the initial surface diffusion out of the cracks. It is also conceivable that the sub-surface reservoir of material might also be, at least partially, low-molecular-weight decomposition products of the effect of far-UV and vacuum UV radiation that is part of the plasma process, although UV attack on PDMS results more in methyl group cleavage than in backbone depolymerization.[16]

This bulk diffusion could take place through untreated bulk matrix into the deeper portions of the cracks or through the oxidized region. The former process is likely to be easier than the latter but since the regions between the cracks are more extensive than the cracks themselves, both mechanisms are probably involved. Certainly, the hydrophobic recovery of treated, uncracked samples implies that diffusion is possible through the oxidized region. This region may extend in depth or degree of silica-like 3D structure with increasing treatment and would cause slower hydrophobic recovery of extensively-cracked surfaces compared with lightly-cracked surfaces. There are indications in Table III that this could be so although the variation in contact angle inherent in such cracked surfaces makes it impossible to be certain. The fact that diffusion of polymer chains is possible in this oxidized region is the reason for calling it a silica-like region. The degree of oxidation of much of the region is of a silica-like nature but the structure must be more open than a silica glass to permit the polymer chains to diffuse through it.

The response of plasma-treated PDMS surfaces that have recovered their hydrophobicity to further changes in their environment, such as immersion in water, is an interesting subject that we have yet to study rigorously. The wettability of water-plasma-treated surfaces, such as those reported earlier by Owen *et al.*,[10] can be substantially recovered by boiling in water but we have not established the mechanisms involved. It may be a washing from the surface of diffused material rather than a reversal of the diffusion mechanism from the surface to the bulk of the polymer. This is a promising area for future study.

CONCLUSION

The effect of RF plasma treatment of PDMS elastomer is broadly similar whether the gas is argon, helium, nitrogen or oxygen. Although different plasma conditions are needed, in each case the surface can be treated to zero water contact angle without inducing cracking. Further treatment causes microcracking accompanied by a small rise in water contact angle from zero to 10–25 deg. Both cracked and uncracked treated surfaces recover their hydrophobicity progressively once plasma treatment ceases, eliminating lack of cracking as an explanation of why some reported plasma-treated PDMS surfaces retain their hydrophilicity. The various plasma gases produce significant differences in hydrophobic recovery rates; for example, surfaces treated in argon recover more slowly in the first 24 hours than surfaces treated in oxygen, but all surfaces show virtually complete recovery (water contact angle close to 100 deg) after one week. We believe the small initial jump in hydrophobicity at the onset of cracking is the result of surface diffusion of low molecular weight polymer on the crack surface. The subsequent slower hydrophobic recovery is due to the diffusion of similar material through the bulk polymer matrix and oxidized silica-like surface region.

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