JOURNAL OF APPLIED POLYMER SCIENCE VOL. 19, PP. 451–459 (1975)

A Study of the Contact Angle on RTV-Silicone Treated in a Hydrogen Glow Discharge

MARTIN HUDIS* and L. E. PRESCOTT, *General Electric Company, Schenectady, New York 12301*

Synopsis

A hydrogen glow discharge surface treatment followed by exposure to the atmosphere has been used to decrease the contact angle for distilled water on RTV-silicone. The change in contact angle has been studied in terms of vacuum ultraviolet irradiation, metastable bombardment, free-radical bombardment, and electrostatic charging. The study demonstrates that the decrease in the contact angle is caused by the interaction of the hydrogen atoms produced in the glow discharge with the polymer surface.

INTRODUCTION

Experimental studies of polymer oxidation using an oxygen plasma date back to 1956;[1] but not until 1964 did Mantell and Ormand[2] demonstrate a corresponding change in the contact angle. Since that time, Hansen and Schonhorn[3] have replaced the oxygen plasma with an inert gas plasma and reported improved bondability without a corresponding change in the contact angle. Independent work by Malpass and Bright[4] and Sowell,[5] who also used inert gasses, indicates a change in both bondability and contact angle. Work by at least three independent groups[6,7,8] has demonstrated that plasmas containing no oxygen can produce a larger change in contact angle than plasmas containing oxygen. Sowell et al.[7] claim that a polymer irradiated with vacuum ultraviolet radiation under vacuum can also change the contact angle. In addition, exposure time,[9] polymer temperature,[9] and plasma geometry are parameters that further complicate the problem.

The present work is an attempt to isolate and study the effects of individual plasma energy sources on the change in contact angle. Experiments were conducted with vacuum ultraviolet irradiation, metastable bombardment flux, free radical bombardment flux, and electrostatic charging.

The work has been confined to an RTV-silicone rubber. The silicone rubber samples, RTV-630 (General Electric Polydimethyl RTV-630 Silicone), were molded between aluminum plates lined with polyethylene and cured at room temperature for 24 hr. The resulting samples were 3000 μ thick.

* On leave at NASA–Ames Research Center as a National Research Council Associate.

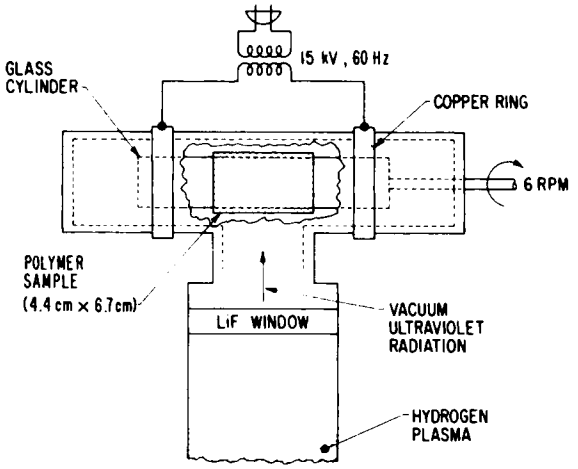

Fig. 1. Plasma discharge apparatus.

EXPERIMENTAL APPARATUS

Plasma System. The plasma system, shown in Fig 1, consists of two discharge chambers separated by a lithium fluoride window. The sample is mounted in the top chamber, which is operated in a diffusive glow mode.[10] The bottom chamber, which is operated in an arc mode, is used as a vacuum ultraviolet lamp. The sample can be exposed to either the glow discharge or the vacuum ultraviolet irradiation. When the ultraviolet irradiation is used, the top chamber is evacuated and flushed with argon.

The hydrogen arc chamber has metal gaskets, stainless steel flanges, and a base pressure of 10^{-6} torr.[11] The hydrogen arc is generated with an induction coil operating at 15 MHz with 350 watts at a gas pressure of 0.6 torr. The glow discharge chamber is sealed with O-rings and has a base pressure of 10^{-3} torr. The diffuse glow discharge is generated with capacitor rings, which operate at 60 Hz with 1–2 watt at a gas pressure of 3 torr.

The polymer samples are mounted on a glass cylinder with double-sided tape and rotated at 6 rpm to ensure uniform treatment.

Contact Angle Measuring System. The contact angle is measured using a low-power Gaertner Toolmakers microscope equipped with a goniometer and crosshairs. The procedure is a standard technique and is described in the literature.[12] Distilled water is dispensed from a medical-type syringe, and the advancing angle is read on the goniometer dial. Four measurements were made on each sample and their values averaged. An accuracy of $\pm 12°$ was achieved, which is adequate to detect substantial changes in the contact angle.

Electrostatic Voltmeter. The electrostatic charge on the sample was measured, before and after the plasma treatment, using an induction plate[13] with a 2-kV electrostatic voltmeter (General Electric Model 518B-841G). The electrostatic charge on the samples could be removed by spraying in the atmosphere a corona discharge generated with a Tesla coil.

EXPERIMENTAL DATA

Glow Discharge Data. The silicone rubber was treated individually in a hydrogen, oxygen, nitrogen, and argon glow discharge. In each case, the glow discharge was run for 1 hr at a pressure of 3 torr. Results by other experimenters demonstrate that 1 hr should be sufficient to guarantee that the surface modification has occurred if it is going to occur at all.[9] The contact angle measurements for the various gases plus the original untreated samples are shown in Table I. For comparison, independent measurements are shown by Sowell et al.[7] Argon was used to estimate the effect of metastable bombardment; oxygen was used to determine the relative effect of direct oxidation; nitrogen was compared to hydrogen and used to determine the importances of hydrogen abstraction. Two additional experiments were conducted to isolate the dominant plasma-coupling mechanism which initiates the change in contact angle. In the first, samples were exposed to ultraviolet irradiation in the absence of a plasma; in the second, samples were exposed to hydrogen atoms, again in the absence of plasma.

Ultraviolet Radiation Data. The silicone samples were exposed to vacuum ultraviolet irradiation for 1 hr in a low-pressure argon background. The pressure in the sample chamber was maintained at 10^{-3} torr while argon was flushed through the chamber. The quantum yield associated with the ultraviolet irradiation can be very small[14] ($<10^{-3}$), thereby producing a slow change in the contact angle. Under these conditions, 1 hr may be too short to produce a measurable change in the contact angle; nevertheless, 1 hr conforms with the other experiments and provides the information to determine the effectiveness of the ultraviolet irradiation.

The vacuum ultraviolet irradiation was provided by a hydrogen arc, which was isolated from the sample by a lithium fluoride window. (The lithium fluoride window, produced by Harshaw Chemical Company, has a cutoff wavelength of 1050 Å.) The samples were immediately exposed to the atmosphere. This procedure is identical with that used for the glow discharge and produces a change in the contact angle wich is less than 10°. Although vacuum ultraviolet irradiation has sufficient energy to produce

TABLE I
Contact Angle Measurements

Gas	Contact angle (distilled water)
Untreated	117°
Hydrogen	44°
Oxygen	46°
Nitrogen	20°
Argon	83°
Untreated[a]	100°
Argon[a]	16°

[a] Data from reference 7.

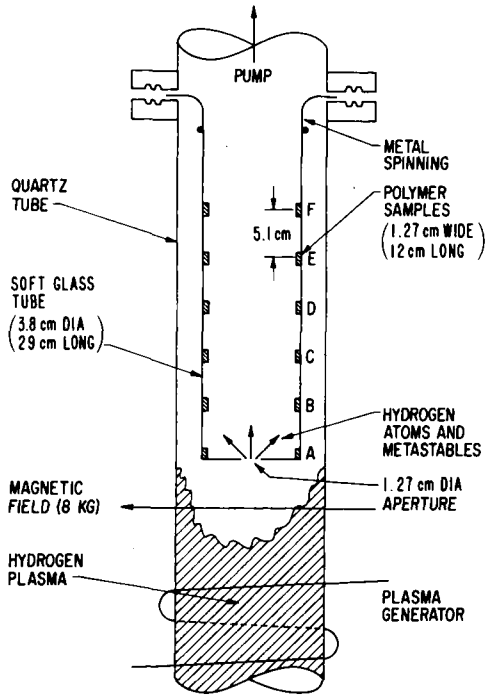

Fig. 2. Hydrogen atom and metastable discharge apparatus.

free radicals within the samples, and produces unsaturation, it does not appear to be the origin for the change in the contact angle.

Sowell et al.[7] have reported that both argon and hydrogen discharges cause rapid changes in the lithium fluoride ultraviolet transmission. They claim this decreases the effect of the irradiation on silicone. A polyethylene sample was exposed to ultraviolet irradiation at the beginning and end of the experiments to estimate the change in radiation flux through the lithium fluoride window. Vacuum ultraviolet irradiation causes polyethylene to crosslink, producing an insoluble component. The mass of this component, which is a function of the radiation flux, can be measured with a Soxhlet extractor. Although detailed ultraviolet spectra of the lithium fluoride window were not measured, the mass of the unsoluble component did not decrease, and therefore no decrease in the radiation flux is expected for wavelengths shorter than 2000 Å.

Hydrogen Atom Data. Hydrogen atoms and metastables were generated and removed from the plasma using the device shown in Fig 2. Again, the hydrogen plasma is generated by the induction coil, but this time in a diffusive glow mode at a pressure of 0.26 torr. The samples are mounted on a soft glass cylinder, which is placed inside the main tube. For identification, the samples are marked alphabetically from A to F, as indicated in the figure. The soft glass cylinder terminates as a soft glass plate with a small aperture. The cutoff wavelength for the glass sample

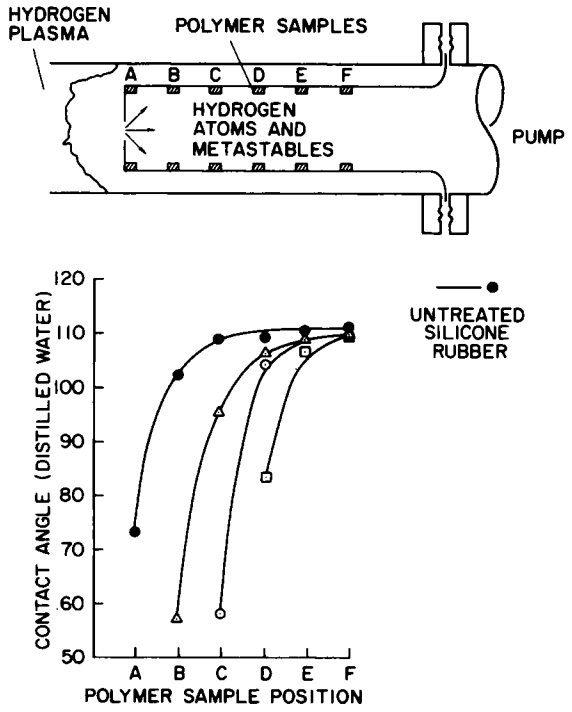

Fig. 3. Curves at bottom of figure are the contact angle measurements for silicone using the hydrogen atom apparatus shown at top of figure. The curve starting with sample A was measured for all six polymers in the sample tube. The curve starting with sample B was measured with samples B through F in the sample tube.

tube is 3150 Å, which eliminates the vacuum ultraviolet irradiation. An 8-kG magnetic field, placed between the aperture of the sample tube and the hydrogen plasma, drives the charged particles into the wall prior to entering the sample tube. The remaining elements, the hydrogen atoms and metastables, pass into the sample tube and bombard the samples. The samples were exposed for 1 hr.

The contact angle measurements are shown in Figure 3. Six separate experiments were conducted. In the first experiment, all six samples (A through F) were mounted and the corresponding contact angles measured. (This corresponds to the left-hand curve in Fig. 3.) In the second experiment, sample A was omitted and only samples B through F were mounted. (This corresponds to the curve that starts at sample B.) This same experiment was repeated four more times until only sample F was mounted on the tube. In each case, the first sample has a small contact angle, while the remaining samples have a large contact angle, corresponding to the untreated material. This behavior is consistent with a hydrogen atom model, which is discussed in the following section.

Electrostatic Charge Data. The electrostatic charge on each rubber sample was measured before and after the glow discharge treatment, using

an electrostatic voltmeter. In many cases, the samples were charged, the amount varying with the gas and the plasma power. The charge on the samples could be neutralized by spraying a charge in the atmosphere from a Tesla coil.

Contact angles were measured on the charged samples and on the neutralized samples. In every case, neutralizing the charge had no effect on the contact angle. The original, untreated samples could be charged by spraying with the Tesla coil, but again the contact angle did not change.

DISCUSSION

Hydrogen Atoms. Direct interaction between hydrogen atoms and a silicone rubber, followed by exposure to the atmosphere, is sufficient to change the contact angle. The data in Figure 3 are consistent with a model in which the reaction is initiated by hydrogen atoms that recombine or that are removed on the silicone surface. Since volume phase recombination can be neglected for the operating pressure of this experiment and the sticking probability for hydrogen on glass is small,[15] the curves in Figure 3 are consistent with a model in which hydrogen atoms are removed on strip A, causing its contact angle to change when exposed to the atmosphere. When strip A is removed, the hydrogen atoms diffuse to strip B, where they are again removed, causing a decrease in the contact angle. The contact angle for sample B (when sample A is removed) is smaller than the contact angle for sample A. This is also consistent with the hydrogen atom model. Because of the aperture, sample A is located in a region where the average hydrogen atom density is smaller than the density around sample B (when sample A is removed).

In a uniform sample tube with steady-state boundary conditions, the hydrogen atom density at the surface of the tube can be estimated following the formulation by Wood and Wise.[15] For a diffusion Reynolds number of 10^{-1} (large recombination), the hydrogen atom density at sample A is about two orders of magnitude smaller than the hydrogen atom density that enters the tube. This suggests that 1% dissociation at glow discharge pressures is sufficient to produce a small contact angle. A dissociation of 1% can be achieved in a large variety of plasma devices, which begins to explain why the plasma reactor has not been a critical parameter. Different results produced by different reactors must be due to differences between other parameters, such as ultraviolet radiation flux, gas contamination, etc.

The same argument can be made for hydrogen metastables, but this seems unlikely. The hydrogen metastable density should be very small compared to the hydrogen atom density, because the metastable energy (10.1 eV) exceeds the dissociation energy (4.5 eV), in which case the metastables would be deactivated by dissociation reactions. The work by Blais et al.[16] serves as additional support. Their work demonstrates that

an argon corona at 1 atm has a large effect on polypropylene, even though the argon metastable density is extremely small.

Although the molecular dissociation model does not explain the contact angle change produced with argon (or any inert gas), it may not be inconsistent with the model. In almost all systems used to date, the molecular gas contamination can be larger than one part in 10^4. The metastable density can be quite large and quite effective in dissociating contaminates, which could then recombine or react on the polymer surface, initiating a change in the contact angle.

Electrostatic Charging. Indirect evidence from this and other experiments supports the observation that electrostatic charging does not change the contact angle. No additional change occurs in the contact angle when the magnetic field is removed, allowing charged particles to flow into the sample region. The silicone samples underwent the same change in contact angle for both the glow discharge system in Figure 1 and the hydrogen atom system in Figure 2.

Sowell et al.[7] have also looked at electrostatic charging. Although they did not detect much charging, they also concluded that electrostatic charging should be unimportant.

The work by Kim and Goring[17] gives additional support for the observation that electrostatic charging is unimportant. Plasmas that produce polymer degradation, such as oxygen, cause surface morphology changes that might be caused by migration of low molecular weight degradation products to electrically charged areas on the surface. Although oxygen may produce more trapped electrostatic charge, it does not lead to a smaller contact angle.

Oxidation. The data in this paper suggest that the reactions that lead to a change in the contact angle for silicone are more complex than direct oxidation. The samples require physical contact with the active neutrals. Vacuum ultraviolet irradiation alone is insufficient to account for the change in the contact angle, at least on a 1-hr time scale. Oxygen does produce a small contact angle, but comparable or smaller contact angles can be produced with gases that contain no oxygen. Although direct oxidation does not explain the process, oxidation cannot be eliminated and, in fact, most likely exists. The change in contact angle appears to occur in two steps. In the first step, the plasma—which need not be an oxygen plasma—activates the sample surface. In the second step, the sample is oxidized either by oxygen in the sample structure or by oxygen from the atmosphere, due to long-lived, polymer-free radicals, which can exist for days after the plasma treatment.[7,18]

Oxygen can contaminate the gases that contain no oxygen and is always a concern, but, for the examples in this paper, does not appear to be an important parameter. The glow discharge chamber has a base pressure of 10^{-3} torr and, correspondingly, could have an oxygen contaminant of about one part in 10^3 (operating pressure of 3 torr and a background pressure of 10^{-3} torr). Under these conditions, oxidation could still be

an important process. The hydrogen atom system has a base pressure of 10^{-6} torr and, correspondingly, an oxygen contaminant of about one part in 10^5 (operating pressure of 0.26 torr and a background pressure of 10^{-6} torr). In spite of the difference in the oxygen contaminant between the flow discharge chamber and the hydrogen atom chamber, both systems produce comparable contact angles for hydrogen on silicone.

CONCLUSIONS

The contact angle for distilled water on silicone rubber (General Electric RTV-630) has been changed by exposing the sample to a hydrogen glow discharge and then to the atmosphere. The change in the contact angle has been studied in terms of vacuum ultraviolet irradiation, metastable bombardment, free-radical bombardment, and electrostatic charging. Results show that ultraviolet irradiation and electrostatic charging do not measurably decrease the contact angle for a 1-hr plasma exposure. The origin of the reaction seems to be the dissociated species within the plasma. The decrease in the contact angle requires physical contact between the plasma (or at least the dissociated species) and the sample, but does not require direct oxidation. Nitrogen and hydrogen plasmas produce small contact angles in silicone. Although an oxygen plasma does not maximize the decrease in the contact angle, oxidation is still a likely process and cannot be eliminated. Oxidation can still occur and most likely does occur through either the oxygen in the samples, as in the silicone, or from exposure to the atmosphere after the plasma treatment.

References

1. K. Rossmann, *J. Polym. Sci.*, **19**, 141 (1956).
2. R. M. Mantell and W. L. Ormand, *Ind. Eng. Chem., Prod. Res. Develop.*, **3**, 300 (1964).
3. R. H. Hansen and H. Schonhorn, *J. Polym. Sci.*, **B**, 203 (1966).
4. B. W. Malpass and K. Bright, in *Aspects of Adhesion*, R. J. Alner, Ed., University of London Press, 1968, p. 224.
5. R. R. Sowell, Effects of rf Activated Inert Gas Plasma on Critical Surface Tension and Bondability of Polydimethyl Silicones and Polyethylene, Sandia Corporation Report No. SC-RR-71-0483, September 1971.
6. J. R. Hall, C. A. L. Westerdahl, A. T. Devine, and M. J. Dodnar, *J. Appl. Polym. Sci.*, **13**, 2085 (1969).
7. R. R. Sowell, N. J. DeLollis, H. J. Gregory, and O. Montoya, *J. Adhesion*, **4**, 15 (1972).
8. A. Bradley and J. D. Fales, *Chem. Tech.*, 232 (1971).
9. C. Y. Kim, J. Evans, and P. A. I. Goring, *J. Appl. Polym. Sci.*, **15**, 1365 (1971).
10. J. A. Thornton, *J. Appl. Phys.*, 3404 (1969).
11. M. Hudis and L. E. Prescott, *J. Polym. Sci.*, **B10**, 179 (1972).
12. A. M. Adamson, *Physical Chemistry of Surfaces*, Interscience, New York, 1960, p. 345.
13. B. Gross, *Charge Storage in Solid Dielectrics*, Elsevier, Amsterdam, 1964.
14. M. Hudis, *J. Appl. Polym. Sci.*, **16**, 2397 (1972).

15. B. J. Wood and H. Wise, *J. Phys. Chem.*, **65,** 1976 (1961).
16. P. Blais, D. J. Carlsson, and D. W. Wiles, *J. Appl. Polym. Sci.*, **15,** 129 (1971).
17. C. Y. Kim and D. A. I. Goring, *J. Appl. Polym. Sci.*, **15,** 1357 (1971).
18. M. M. Millard, J. J. Windle, and A. E. Pavlath, *J. Appl. Polym. Sci.*, **17,** 2501 (1973).

Received June 4, 1974
Revised August 5, 1974