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The Effect of Ultraviolet Radiation on the Wattability of Silicone Polymers

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Synopsis. The effect of UV radiation in air on the wettability of silicone polymers was studied by measuring the contact angles. From the contact-angle data, the surface energies were also calculated. As the irradiation progressed, the surface energy of the polar component increased, while the surface energy of the dispersive component remained constant, for all the samples. This increase in surface energy is attributable to a surface photooxidation of the silicone polymers. Especially, poly(diphenylsiloxane) showed a remarkable increase in the surface energy of the polar component after the irradiation.

The wettability of surfaces by liquids of known surface tensions has been determined by many investigators.[1,2] In particular, contact-angle measurements have been used to evaluate changes in surface composition.[3] We have ourselves previously reported that the water-contact angles on polystyrene and poly(methyl vinyl ketone) surfaces decreased dramatically as a function of the UV exposure time because of the photooxidation of the surfaces.[4] Generally, it is known that silicone polymers have relatively low surface-energy values. If the surface energy of a silicone polymer could be increased by UV radiation, the adhesion between liquids and the surface of the silicone polymer irradiated would be enhanced by an increase in the work of adhesion.

This report will describe the effect of UV radiation in air on the wettability of silicone polymers.

The silicone polymers used in this study were poly(methyl)3—7%(diphenyl)0.5—1.0%(methyl vinyl) siloxane, poly(diphenyl-siloxane), poly(dimethyl)1—2%(methyl vinyl)siloxane, and poly(methyl vinyl)siloxane, all supplied by Petrarch System, Inc. (U.S.A.). A film of each polymer was cast from its benzene solution on an aluminum plate. Then, the plate was cured at 100 °C in an oven for 15 min. The plate was exposed in air with a low pressure mercury lamp (55.2 W, $1\ \mathrm{W}=1\ \mathrm{J\ s^{-1}}$) supplied by the Oriel Co. (U.S.A.). The distance between the plate and the lamp was 5 cm.

The liquids used for contact-angle measurements were octane and diiodomethane. The contact angles were measured on the irradiated plate by using a goniometer at 20 °C. Three drops of the liquid were measured on both sides of the drops, and the six values were averaged. The overall variation in the contact-angle measurement was about ±3 degrees.

The free energy γ, of any interface can be regarded as the sum of two terms; one, designated γ^{d}, attributed to dispersion forces, and the other, γ^{p}, to polar forces. The value of $\gamma_{\mathrm{s}}^{\mathrm{p}}$ can be calculated from the octane-water contact angle θ_{ows}, by means of Hamilton's[5] equations:

$$\cos\theta_{\mathrm{ows}} = \frac{\gamma_{\mathrm{w}} - \gamma_{\mathrm{o}} - \gamma_{\mathrm{sw}}}{\gamma_{\mathrm{ow}}}$$

and:

$$I_{\mathrm{sw}} = 2\sqrt{\gamma_{\mathrm{s}}^{\mathrm{p}}\gamma_{\mathrm{w}}^{\mathrm{p}}},$$

where γ_{w} and γ_{o} are the surface tensions of the mutually saturated water phase and octane phase respectively, where γ_{wo} is the interfacial tension of the two phases, where $\gamma_{\mathrm{w}}^{\mathrm{p}}$ is the polar component of water-surface tension, and where I_{sw} is the term of polar interaction with water.

The value of $\gamma_{\mathrm{s}}^{\mathrm{d}}$ can also be calculated from the diiodomethane-air contact angle, θ_{m}, using an equation developed by Fowkes:[6]

$$\gamma_{\mathrm{s}}^{\mathrm{d}} = \gamma_{\mathrm{m}}\frac{(1+\cos\theta_{\mathrm{m}})^2}{4},$$

where γ_{m} is the surface tension of diiodomethane. Here, literature values[6,7] are applied in the surface-energy analysis:

$$r_{\mathrm{w}} = 72.6\ \mathrm{erg/cm^2}\ {}^{**},\ \gamma_{\mathrm{o}} = 21.8,\ \gamma_{\mathrm{wo}} = 50.8,\ \gamma_{\mathrm{w}}^{\mathrm{p}} = 50.8,$$
$$\text{and}\ \gamma_{\mathrm{m}} = 50.8\ \text{at}\ 20\ ^{\circ}\mathrm{C}.$$

Five different compositions have been made into plates, irradiated, and measured according to the above procedures. These compositions are:

1. Poly(dimethyl)3—7%(diphenyl)0.5—1.0%(methyl vinyl)siloxane. This material is referred to as "PS 264".
2. Poly(diphenylsiloxane).
3. Poly(methyl)1—2%(methyl vinyl)siloxane.
4. PS 264+poly(diphenylsiloxane), 1:1 in weight.
5. PS 264+poly(methyl vinyl)siloxane, 5:1 in weight.

Tables 1—5 present the primary data and the derived results for compositions #1—#5. In each table, the last column, headed γ_{s}, is simply the sum of $\gamma_{\mathrm{s}}^{\mathrm{p}}$ and $\gamma_{\mathrm{s}}^{\mathrm{d}}$. From these tables, it can be seen that the values of $\gamma_{\mathrm{s}}^{\mathrm{p}}$ are increased as a function of the irradiation time for all the samples, while the values of $\gamma_{\mathrm{s}}^{\mathrm{d}}$ remain almost constant. Two reasons for the increase in $\gamma_{\mathrm{s}}^{\mathrm{p}}$ may be considered; a surface cracking due to UV irradiation and a surface photooxidation.

If a surface cracking has occurred during UV irradiation, the contact angle of octane-water might increase, for water can penetrate into such a crack and make the surface more hydrophilic. Also, if the silicone polymer surface is photooxidized during UV irradiation, the contact angle of octane-water is likely to be

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** $1\ \mathrm{erg}=1\times10^{-7}\ \mathrm{J}$.

Table 1. Composition #1. Poly(dimethyl)3—7%(diphenyl)0.5—1.0%(methyl vinyl)siloxane

UV irradiation time/min	Octane/Water contact angle θ/°	CH_2I_2 contact angle θ/°	γ_s^p / erg cm^{-2}	γ_s^d / erg cm^{-2}	γ_s / erg cm^{-2}
0	21	73	0.1	21.2	21.3
10	24	68	0.1	24.0	24.1
20	42	65	0.8	25.7	26.5
30	60	61	3.2	28.0	31.2
40	70	59	5.5	29.1	34.6
50	77	59	7.6	29.1	36.7
60	79	58	8.3	29.7	38.0

Table 2. Composition #2. Poly(diphenylsiloxane)

UV irradiation time/min	Octane/Water contact angle θ/°	CH_2I_2 contact angle θ/°	γ_s^p / erg cm^{-2}	γ_s^d / erg cm^{-2}	γ_s / erg cm^{-2}
0	34	24	0.4	46.5	46.9
10	89	50	12.3	34.3	46.6
20	98	57	16.5	30.3	46.8
30	115	40	25.7	39.6	65.3
40	117	44	26.9	37.5	64.4
50	119	39	28.0	40.1	68.1
60	119	38	28.0	40.6	68.6

Table 3. Composition #3. Poly(dimethyl)1—2%(methyl vinyl)siloxane

UV irradiation time/min	Octane/Water contact angle θ/°	CH_2I_2 contact angle θ/°	γ_s^p / erg cm^{-2}	γ_s^d / erg cm^{-2}	γ_s / erg cm^{-2}
0	8	82	0.0	16.5	16.5
10	37	67	0.5	24.5	25.0
20	57	60	2.6	28.6	31.2
30	68	62	5.0	27.4	32.4
40	75	58	7.0	29.7	36.7
50	77	63	7.6	26.8	34.4
60	88	61	11.8	28.0	39.8

Table 4. Composition #4. PS 264+poly(diphenylsiloxane), 1:1 in weight

UV irradiation time/min	Octane/Water contact angle θ/°	CH_2I_2 contact angle θ/°	γ_s^p / erg cm^{-2}	γ_s^d / erg cm^{-2}	γ_s / erg cm^{-2}
0	8	68	0.0	24.0	24.0
10	39	62	0.6	27.4	28.0
20	61	62	3.4	27.4	30.8
30	80	60	8.7	28.6	37.3
40	82	59	9.4	29.1	38.5
50	87	59	11.4	29.1	40.5
60	87	59	11.4	29.1	40.5

Table 5. Composition #5. PS 264+poly(methyl vinyl)siloxane, 5:1 in weight

UV irradiation time/min	Octane/Water contact angle θ/°	CH_2I_2 contact angle θ/°	γ_s^p / erg cm^{-2}	γ_s^d / erg cm^{-2}	γ_s / erg cm^{-2}
0	45	92	1.1	11.8	12.9
10	56	57	2.5	30.3	32.8
20	71	57	5.8	30.3	36.1
30	76	61	7.3	28.0	35.3
40	81	61	9.0	28.0	37.0
50	91	64	13.2	26.3	39.5
60	93	63	14.1	26.8	40.9

increased as a result of the formation of surface hydrophilic groups. To check whether or not cracks are formed after UV irradiation, SEM micrographs for the samples were obtained. No cracks were observed. Furthermore, all the samples irradiated *in vacuo* showed no changes in the octane–water contact angles after exposures of up to 1 h. Therefore, the increase in γ_s^p values after UV irradiation in air is attributed to the surface photooxidation of the silicone polymers. Especially, it is found that Composition #2 is easily photooxidized by UV irradiation.

Accordingly, it can be anticipated from the above results that the adhesion between liquids and irradiated silicone-polymer surfaces is enhanced by the increase in polar-polar interaction which is attributed to the work of adhesion.

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