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# The Effect of Ultraviolet Radiation on Wettability of Polymer Surfaces

Kunio Esumi,* Kenjiro Meguro, A. M. Schwartz,† and A. C. Zettlemoyer†
*Department of Applied Chemistry, Science University of Tokyo, Kagurazaka, Shinjuku-ku, Tokyo 162*
† *Center for Surface and Coatings Research, Sinclair Laboratory, Lehigh University, Bethlehem, Pa 18015, U. S. A.*

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**Synopsis.** The wettability of polystyrene and poly(methyl vinyl ketone) surface can be markedly changed by ultraviolet irradiation in air. The contact angle of water on both polymers decreases dramatically as a function of exposure time. This effect is mainly due to increase in the polar component of surface energy. The wettability of irradiated polymers goes back to near original values due to soluble photooxidation products into water after the water extraction.

Polymers, under normal conditions, are in contact with atmospheric oxygen and are subjected to varying temperatures, humidities and exposures to light. A polymer is expected to undergo photochemical induced change at or near its surface.

The wettability of surfaces by liquids of known surface tensions has been determined by many investigators. Contact angle measurements, in particular, have been used to evaluate changes in a surface composition. Fox *et al.*[1)] have reported that with a number of amorphous polymers the changes in contact angles for various liquids with ultraviolet radiation time, not surprisingly, are a function of the nature of the polymers. According to Fox's study, it might be expected that by ultraviolet radiation the wettability of polymer surfaces can be changed from hydrophobic to hydrophilic.

This study describes the effect of ultraviolet radiation on the wettability of two polymers.

The liquids used for contact angle measurements were deionized water and diiodomethane.

Polymers used were polystyrene supplied by Monomer-Polymer and Dajac Laboratories, Inc. and poly(methyl vinyl ketone) by Polyscience, Inc. Films of each polymer were prepared by the evaporation of 2 wt% dichloromethane solution on aluminum plate.

Exposures were carried out in air in a hood with the unfiltered radiation from 55.1 W low pressure mercury lamp supplied by Oriel Co. The distance between the sample and the lamp was 5 cm.

Contact angles were measured with a goniometer at 20 °C. Three drops for a given 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°.

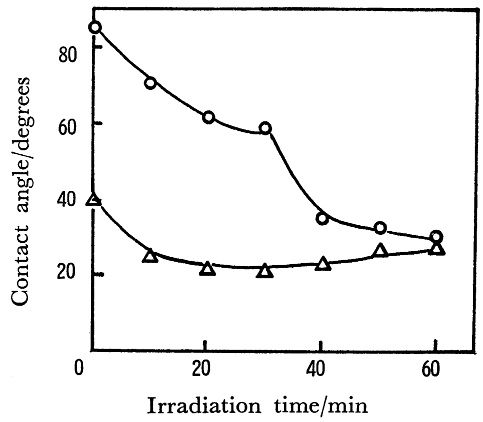

Fig. 1. Irradiation time *vs.* contact angles on polystyrene.
○: Water contact angle, △: diiodomethane contact angle.

To evaluate surface energy, the interfacial term $\gamma_{ab}$ by theory (Owens and Wendt,[2)] Kaelble and Uy,[3)] Wu[4)]), is given as follows:

$$\gamma_{ab} = \gamma_a + \gamma_b - 2(\gamma_a^d\gamma_b^d)^{1/2} - 2(\gamma_a^p\gamma_b^p)^{1/2}, \tag{1}$$

where $\gamma$ is the respective surface energy and the dispersive(d) and polar(p) components of the surface energies for solid a and liquid b are considered to interact only with their own kind. To obtain values for the dispersive and polar components of the solid surface energies, Eq. 1 is combined with the Young equation to give for a solid(a)/liquid(b) pair,

$$\cos\theta + 1 = \frac{2}{\gamma_b}[(\gamma_a^d\gamma_b^d)^{1/2}+(\gamma_a^p\gamma_b^p)^{1/2}], \tag{2}$$

where $\theta$ is the contact angle. If the dispersive and polar components of the surface energies of the various liquids are known,[5,6)] each pair of equations of the form of Eq. 2 yields solutions for $\gamma_a^d$, $\gamma_a^p$. In this study, by using Eq. 2, values of $\gamma_a^d$ and $\gamma_a^p$ for polymers were calculated as a function of ultraviolet irradiation time. Here, literature values of $\gamma_b^d$ and $\gamma_b^p$ for water and diiodomethane are applied in the surface energy analysis:[5,6)] $\gamma_b^d=21.8$ erg/cm$^2$, $\gamma_b^p=50.8$ for $H_2O$, $\gamma_b^d=50.8$, $\gamma_b^p=0$ for $CH_2I_2$.

The wettability of polystyrene and poly(methyl vinyl ketone) was evaluated as a function of exposure time of ultraviolet irradiation. The results for contact angle measurements are shown in Figs. 1 and 2. Compared with the original polymers, oxygenated moieties in the surfaces would be expected to interact more strongly with polar liquid like water, but might be less wet by a nonpolar liquid like diiodomethane. From these figures, it can be seen that the contact angles of water decreased with increase in the exposure time on both polystyrene and poly(methyl vinyl ketone). On the other hand, the contact angles of diiodomethane remained constant as irradiation progressed.

Furthermore, $\gamma_a^d$ and $\gamma_a^p$ are calculated as a function of exposure time, shown in Figs. 3 and 4. For both polymers, the dispersion component of surface energy did not change significantly with exposure time, but the polar component increased remarkably as irra-

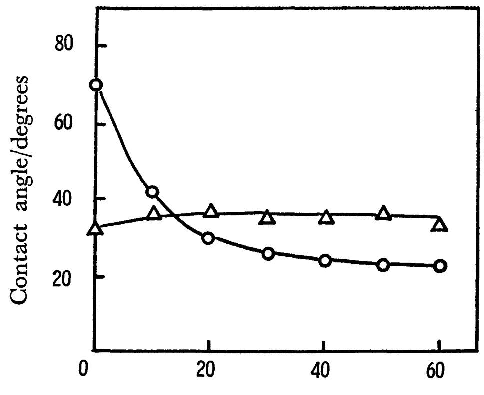

Fig. 2. Irradiation time *vs.* contact angles on poly(methyl vinyl ketone).
○: Water contact angle, △: diiodomethane contact angle.

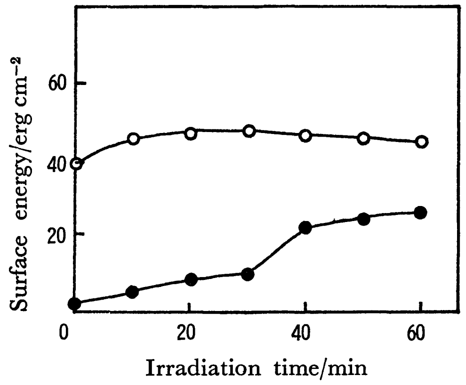

Fig. 3. Irradiation time *vs.* surface energy on polystyrene.
○: $\gamma_a^d$, ●: $\gamma_a^p$.

diation progressed. This increase means that during irradiation the surface of the polymers were photooxidated to yield hydrophilic products on the surface. Also, by means of multiple internal reflectance spectra of irradiated polystyrene film, the carbonyl band due to photooxidation near 1725 cm$^{-1}$ has been observed.[1]

As a next step, to study the stability of irradiated polymer surfaces, two tests were carried out. One was that after irradiation, the samples were kept in a desiccator for 2 d and then contact angles were measured. The other was a water extraction test. The irradiated samples were immersed in distilled water for 15 min and dried *in vacuum*, then the contact angles for the samples were measured. For both polystyrene and poly(methyl vinyl ketone), the contact angles of water after 2 d storage were almost the same as the immediate results. On the other hand, the contact angles of water after the water extraction increased significantly, although they did not come back to the original unexposed values. The increase of the water contact angles might be attributed to water-soluble photooxidation products.

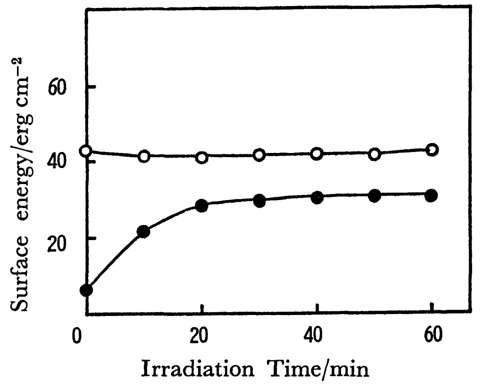

Fig. 4. Irradiation time *vs.* surface energy on poly(methyl vinyl ketone).
○: $\gamma_a^d$, ●: $\gamma_a^p$.

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