Effect of Sulfuric Acid and Chromic Acid Mixture Treatments of Plastics on their Wettability towards Water

By Teruo TSUNODA, Tsutomu SEIMIYA and Tsunetaka SASAKI

(Received April 6, 1962)

The wettability of polymer surfaces has been studied by several workers with reference to the theoretical problems of surface chemistry as well as the practical processes of printing, adhesion, friction, anti-electrification, surface electrical conductivity, etc., and many problems of the surface chemical and physical treatment of a polymer substance and plastics have been studied along these lines¹⁾.

In most of these experiments with surface treatment, however, no full attempt has been made to establish a definite relation between the amount of surface attack and the magnitude of the surface properties affected thereby. In the present experiment, the effect of the sulfuric acid treatment of polystyrene and of the chromic acid mixture treatment of polyethylene on their wettability towards water was studied.

Experimental

Materials.—The plastics used in this experiment were polystyrene (" Styron-666-General Purpose " made by the Asahi-Dow, Ltd.) and polyethylene ("Hi-Zex" made by the Mitsui Chemical Ind. Co.), both 0.2 cm. in thickness and cut into 2×1 cm. plates. Sulfuric acid of a pure grade and a chromic acid mixture prepared from commercial potassium dichromate, sulfuric acid and water in the ratio of 5 : 100 : 8 by weight were used for the surface treatment of polystyrene and polyethylene respectively.

Procedure.—Sample plates cleaned with a soap solution were immersed, under varying conditions of dipping time and temperature, into a sulfuric acid solution in the case of polystyrene and into a chromic acid mixture in the case of polyethylene; they were then withdrawn, rinsed with distilled water, dried in a desiccator, and used for the contact angle measurement by a Wilhelmy-type torsion balance, in a manner similar to that reported previously²⁾. The cobalt adsorption on the treated polystyrene surface was measured by the radiotracer method, using a cobaltous chloride solution tagged with ^{60}Co. The details of this, as well as the results of the measurement, have already been reported in a preceding paper³⁾.

Contact Angles.—Figure 1 shows the change in the contact angles of water on polyethylene with the time of immersion in a chromic acid mixture at 23 and 13°C. In both cases, the polyethylene surfaces are rendered wettable soon after immersion into the chromic acid mixture. This can reasonably be explained by the oxidation of the polyethylene surfaces by the chromic acid mixture, as may be seen from a similar oxidation reaction which constitutes the basic reaction of the quantitative determination of the number of side chains in a polyethylene molecule⁴⁾. A similar oxidation is observed in a surface treatment by an aqueous solution of chromic acid and

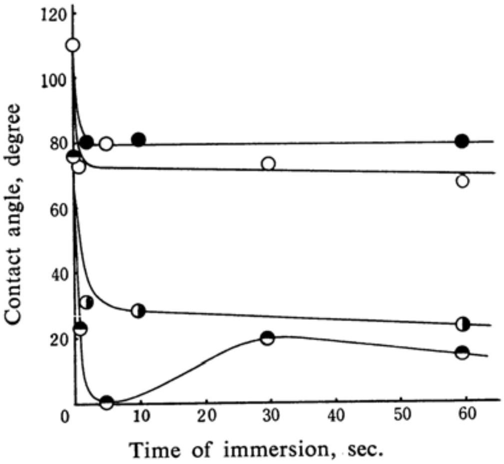

Fig. 1. Change of wettability of polyethylene towards water with time of immersion into chromic acid mixture.
- ● Advancing contact angle; immersion temperature 13°C
- ○ Advancing contact angle; immersion temperature 23°C
- ◑ Receding contact angle; immersion temperature 13°C
- ◓ Receding contact angle; immersion temperature 23°C

---

1) E. G. Shafrin and W. A. Zisman, *J. Phys. Chem.*, **64**, 519 (1960); R. G. Craig, G. C. Berry and F. A. Peyton, ibid., **64**, 514 (1960); F. E. Bartell and B. Roger Ray, *J. Am. Chem. Soc.*, **74**, 778 (1952); K. Kawasaki, *J. Colloid Sci.*, **15**, 402 (1960); B. Roger Ray, J. R. Anderson and J. J. Scholz, *J. Phys. Chem.*, **62**, 1220, 1227 (1958).

2) T. Sasaki, H. Kumanomido and T. Tsunoda, Second. International Congress of Surface Activity, III, Butterworths, London (1957), p. 153.

3) T. Seimiya and T. Sasaki, This Bulletin, **35**, 1567 (1962).

4) K. Tani, *Kobunshikagaku*, (in Japanese) **28**, 104 (1948).

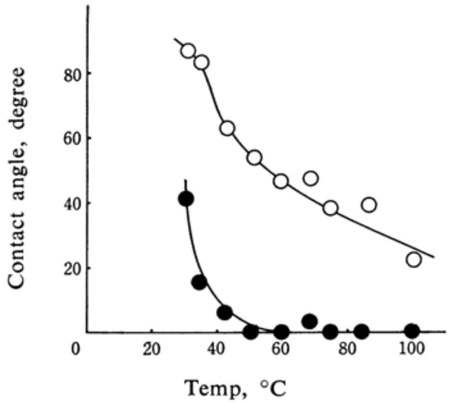

Fig. 2. Change of wettability of polystyrene towards water with temperature of immersion into sulfuric acid.
Time of immersion 10 sec.
○ Advancing contact angle
● Receding contact angle

potassium permangante, while no increase in the wettability can be seen in a treatment by sulfuric acid or phosphoric acid. The relation between the contact angle of the water and the temperature of the sulfuric acid treatment for polystyrene is given in Fig. 2, which shows a zero receding contact angle for temperatures above 50°C. The higher the temperature of treatment is raised, the more wettable becomes the polystyrene surface towards water. The sulfonation of the polystyrene surface by the sulfuric acid may reasonably be considered responsible for this wettability[5]. The change in the contact angle of water on polystyrene with the time of immersion into sulfuric acid was also measured at the immersion temperatures of 30°C, from 85 to 88°C and at 100°C (Figs. 3 and 4). For the cases of both 85 to 88°C and of 100°C, a rapid increase in wettability is observed within 10 sec. of immersion, while a rather gradual increase in wettability is exhibited at 30°C.

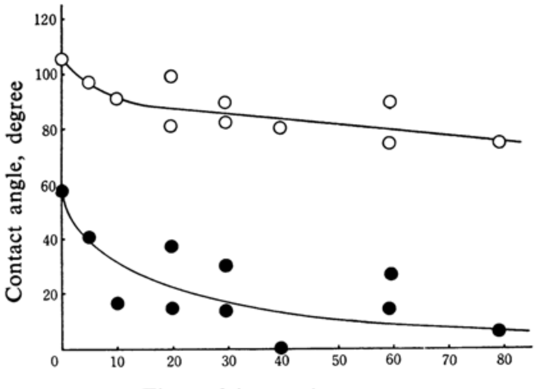

Fig. 3. Change of wettability of polystyrene towards water with time of immersion into sulfuric acid.
○ Advancing contact angle } immersion temp. 30°C
● Receding contact angle } immersion temp. 30°C

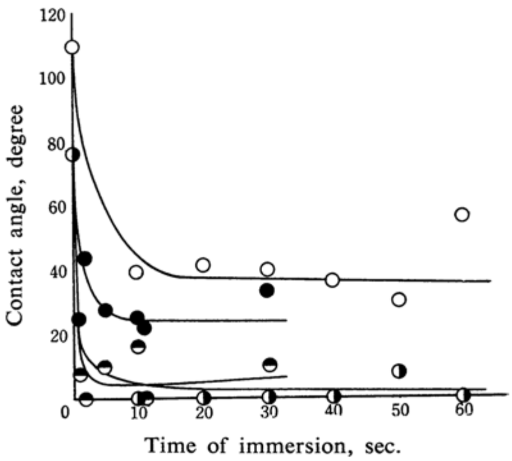

Fig. 4. Change of wettability of polystyrene towards water with time of immersion into sulfuric acid.
○ Advancing contact angle; immersion temperature 85~88°C
● Advancing contact angle; immersion temperature 100°C
◑ Receding contact angle; immersion temperature 85~88°C
◓ Receding contact angle; immersion temperature 100°C

The Relation between Wettability and the Degree of Surface Attack.—Various equations for the relation between the wettability of a solid surface and the adsorption of the liquid or solute upon it have been proposed[6].

We ourselves have presented the following equation[2]:

$$\cos\theta=\frac{\sigma_1+\sigma_{\mathrm{w}}}{\sigma_1}(a\Gamma+b)-1 \qquad (1)$$

where θ is the contact angle of the wetting liquid (aqueous solution) with a surface tension of σ_1 on the surface of a solid where the solute adsorption of the amount Γ takes place, σ_{w}, the surface tension of the solvent (water), an a and p, constants. The value a is positive or negative according to whether the adsorption renders the surface hydrophobic or hydrophilic. This equation can be reduced

---

[5] For example, H. Shimizu, "Ion-Exchange Resin", Kyoritsu Pub. Co., Tokyo (1958) (in Japanese).

[6] P. A. Rhebinder et al., *Kolloid-Z.*, **65**, 268 (1933); M. A. Cook et al., *J. Phys. Colloid Chem.*, **55**, 1219 (1951); K. S. Doss et al., *Proc. Ind. Acad. Sci.*, **7A**, 117 (1938); M. Wada, *Nippon Kogyo Kaishi*, **59**, 681 (1943) (in Japanese); L. S. Bartell et al., *J. Phys. Chem.*, **64**, 514 (1960).

to Doss' Eq. 5 for wetting by a pure liquid (water) where $\sigma_1=\sigma_w$ and $\Gamma=0$.

We have already confirmed that Eq. 1 is valid both in the case of the wetting of a paraffin surface by an aqueous ethyl alcohol solution and in the case of the dewetting of a galena surface by an aqueous xanthate solution$^{2)}$. Now let us apply this equation in the present case to explain the wetting of a polystyrene surface by water. Here σ_1 is equal to σ_w and the equation is simplified to:

$$\cos\theta=2(a\Gamma+b)-1 \qquad (2)$$

In the original Eq. 1, Γ represents the amount of adsorption, which can be interpreted to be the extent of the portion of the surface suffering from the change in wetting properties. It is quite legitimate here to equate Γ with the extent of the surface rendered wettable by the sulfuric acid, or with the degree of surface sulfonation if such an expression may be used for the sake of brevity. Then we can interpret Eq. 2 as the wetting isotherm for the sulfonation of a polystyrene surface. Now if we assume that the amount of cobalt adsorption, x, for the sulfonated surface is proportional to Γ, we have

$$\cos\theta=2(apx+b)-1 \qquad (3)$$

where p is the proportionality constant. We should, however, notice that the untreated surface also gives a cobalt adsorption of the amount x_w. This, together with x, gives the total cobalt adsorption, X, namely

$$X=x+x_w \qquad (4)$$

From Eqs. 3 and 4, we obtain

$$\cos\theta=\cos\theta_w+2ap(X-x_w) \qquad (5)$$

Here $X-x_w$ expresses the net amount of surface sulfonation. From Eq. 5 we should expect a linear relation between $\cos\theta$ and $X-x_w$. Figure 5 shows the experimental results. Here the values of θ were those measured one minute after the samples were dipped in water, and the corresponding X values were measured by the radiotracer method$^{3)}$. Now, we can observe a linear relation as a whole, in the cases of both an advancing and a receding contact angle, thus confirming a linear change of wettability with the degree of sulfonation as far as the present experiment is concerned. We can, of course, expect in this diagram that the region of saturation may appear on further attack, where the incerase of $X-x_w$ will no longer result in an increase in $\cos\theta$. This may be explained chiefly by the fact that, under such a condition, the attack may proceed deep under the surface, thus contributing little to the wetting properties of the surface.

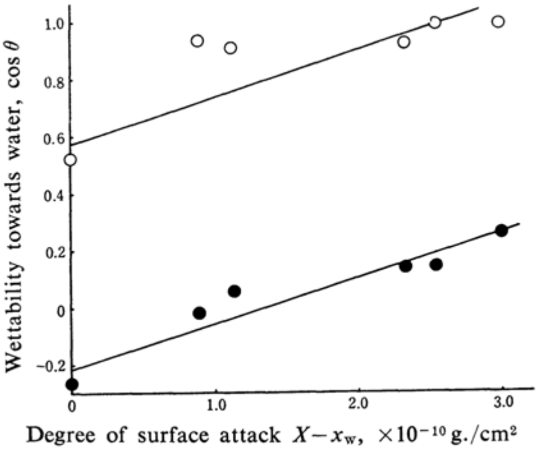

Fig. 5. Change of wettability with degree of surface attack of polystyrene.
○ Receding contact angle
● Advancing contact angle

The authors wish to express their thanks to the Ministry of Education for the Scientific Research Expenditure given to T. Sasaki. They also wish to thank the Asahi-Dow, Ltd., and the Mitsui Chemical Ind. Co. for the samples given to them.

Department of Chemistry
Faculty of Science
Tokyo Metropolitan University
Setagaya-ku, Tokyo