

# Surface Lubrication of Polymer Films by Photoinduced Graft Polymerization

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## Synopsis

Films of nylon 6, polypropylene, and ethylene-vinyl acetate copolymers were graft polymerized with acrylamide or dimethylacrylamide to render the hydrated surfaces slippery. Following UV irradiation in air, the films were placed in the aqueous monomer solution and then either heated to 50°C after degassing or UV-irradiated in the presence of a small amount of riboflavin without degassing to effect graft polymerization. The graft polymerization altered the films from the hydrophobic and nonlubricating to the hydrophilic and slippery surfaces. To evaluate the surface lubricity, the coefficient of friction ( $\mu$ ) against a glass plate in water was determined with the help of a tensile testing machine. The  $\mu$  value for the films surface-grafted with acrylamide up to 30  $\mu\text{g cm}^{-2}$  was reduced to less than 0.05, regardless of the substrate polymers.

## INTRODUCTION

Surface modifications of polymer materials have been the objective of a large number of investigations, but little attention has been paid to make a polymer surface frictionless or slippery. Such a frictionless surface is nonetheless important, especially in the field of marine and biomedical technologies. Although there are few widely known man-made materials that have slippery surface, it is not difficult to find slippery surfaces in the biological world. For instance, most of the surfaces of fishes and sea woods are very slippery when contacted with water. There are also many slippery surfaces on tissues and organs in animal bodies. All of these naturally occurring slippery surfaces are extraordinarily hydrophilic, whereas polymers such as cellulose and poly(2-hydroxyethyl methacrylate), although known as hydrophilic, do not become so slippery as the natural organisms when brought into contact with water.

We have been studying surface modifications of polymer through graft polymerization by the use of various initiation methods including glow discharge,<sup>1</sup> corona discharge,<sup>2</sup> high-energy radiation,<sup>3</sup> UV radiation,<sup>4,5</sup> and ozone. It has been found that hydrophobic surfaces of polymer become very hydrophilic and often slippery when grafted with water-soluble monomers.

A coefficient of friction ( $\mu$  value) is commonly used for evaluation of the lubrication of surfaces, but often difficult to determine, especially for elastic and adhesive polymers because of their complicated hysteresis occurring in a cycle of deformation and recovery during the frictional motion, which is probably associated with adhesion force and displacement force.<sup>6</sup> Triolo and Andrade<sup>7</sup> studied frictional properties of various polymers with the aid of a tensile testing machine. They measured the frictional force generated on the

polymer surface during travelling on a glass plate in aqueous environments. They divided the frictional profiles into five types; (1) sharp peaks with steep slopes, (2) sharp peaks with rapid fall but slow rise, (3) low and amplitude high-frequency, (4) relatively smooth curve, and (5) smooth but increasing with time.

The purpose of the present work is to modify polymer surfaces by graft polymerization for reducing their  $\mu$  value in a hydrated state to such an extent as becoming slippery. Polypropylene (PP), nylon 6, and ethylene-vinyl acetate copolymers (EVA) were employed as substrate polymers, and acrylamide (AAM) and *N,N*-dimethyl acrylamide (DMAA) were used as nonionic water-soluble monomers. A UV irradiation technique was chosen for the graft polymerization of the monomers to the surface of the substrate polymers because of its relatively simple procedure.

## EXPERIMENTAL

### Materials

Films of PP and nylon 6 were of commercial grade with thickness of approximately 20  $\mu\text{m}$ . Films of EVA were prepared by casting their toluene solution on a glass plate to have thickness of 0.1 mm. The VA contents of the EVA used were 4, 19, 28, and 33 mol %. Purification of the films was performed by Soxhlet extraction for 24 h with acetone for PP and with methanol for nylon 6 and EVA. The AAM and DMAA monomer were purified before use by recrystallization from the aqueous solution and by distillation, respectively.

### Graft Polymerization

Unless otherwise noted, graft polymerization was carried out as follows. Following UV irradiation in air at room temperature with a high-pressure mercury lamp (75 W, Toshiba SHL-100 UV type,  $\lambda > 254$  nm), they were placed in a deaerated 1.4M aqueous solution of the monomers and kept at 50°C for 1 h for graft polymerization. The grafted films were first washed with running tap water and then immersed in a distilled water at 70°C for 12 h under continuous stirring to remove the homopolymer. The amount of polyacrylamide (PAAm) grafted was determined with the ninhydrin method as described elsewhere.<sup>1</sup> Contact angles ( $\theta$ ) of the films against water were measured at 25°C with a sessile drop method.

To effect graft polymerization without degassing, a preirradiated EVA film was placed in the aerated DMMA solution to which riboflavin was added. Graft polymerization was allowed to proceed under UV irradiation.

### Determination of $\mu$ Value

The  $\mu$  value of the fully hydrated surfaces was measured against a cleaned glass plate using the apparatus illustrated in Figure 1. A slider (A), at the bottom of which a sample film was attached, was allowed to horizontally travel on the glass plate (C) in the distilled water (D). The force needed for the slider to travel at a rate of 10 mm min<sup>-1</sup> was converted by a low-friction

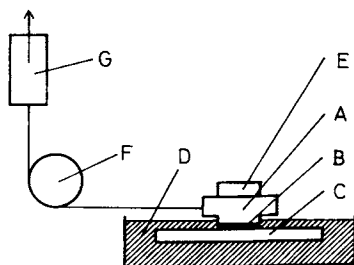


Fig. 1. Schematic of the apparatus used for determining the coefficient of friction,  $\mu$ , of a hydrated surface against a glass plate in water: (A) slider; (B) sample film; (C) glass plate; (D) distilled water; (E) load; (F) pulley; (G) 100 g load cell.

pulley (F) to a vertical force, which was continuously recorded using a 100 g load cell (G). As examples, Figure 2 shows the forces required for a slider attached with films before and after graft polymerization to travel under different loads. As is seen, the force-sliding distance curves for the nongrafted PP film have a high peak at the initial stage of transition from the static state to the dynamic motion and then exhibit many spikes during traveling on the glass plate, whereas the curves for the grafted PP film are very smooth and lack the initial high peak. Appearance of many peaks for the nongrafted film may be due to adhesion or mechanical interlocking between the slider and the

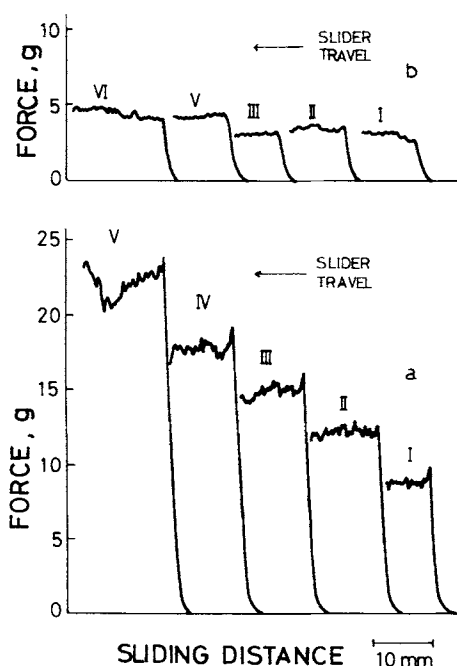


Fig. 2. The force required for a slider attached with the starting PP film (a) and the PAAm-grafted PP film (b) to travel on the glass plate in water. Loads on the slider: (I) 0 g; (II) 10 g; (III) 20 g; (IV) 30 g; (V) 50 g; (VI) 100 g.

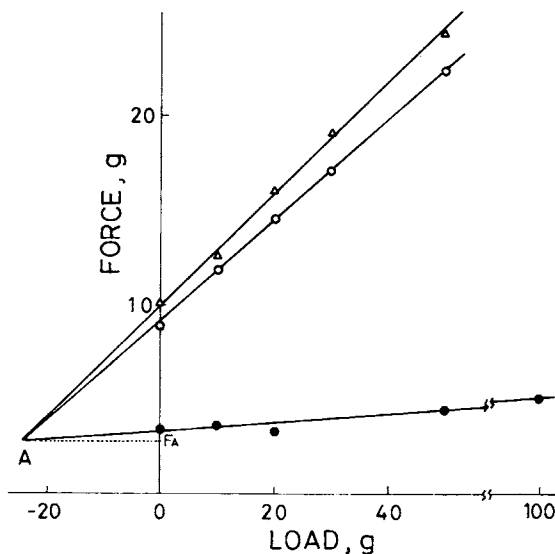


Fig. 3. Plots of the average frictional force against the load put on the slider for the starting PP film ( $\circ$ ) and the PAAM-grafted PP film ( $\bullet$ ). The symbol ( $\Delta$ ) shows the static friction for starting PP film.

film surface. This tendency must become more remarkable as the elasticity of the sample polymer increases.

The average force during sliding and the maximum static force at the initial motion are plotted against the load put on the slider in Figure 3. A small difference between the static and the dynamic friction for the starting PP film suggests that the elastic deformation seems to have little effect on the frictional property of the PP film. The slope of the plots gives the  $\mu$  value. In the following, only the coefficient of dynamic friction will be given, because the difference in  $\mu$  between the static and the dynamic friction is in every case insignificant. When the plots in Figure 3 are extrapolated to the negative loads, all the straight lines cross at a single point ( $A$ ). The frictional force ( $F_A$ ) at  $A$  is probably due to the friction caused by the rotation of the pulley and additional frictions other than that of the tested interface itself.

## RESULTS

### PP and Nylon Films

The observed  $\mu$  and  $\theta$  values for the PAAM-grafted PP films are plotted against the amount of PAAM grafted in Figure 4. It is seen that both the  $\mu$  and  $\theta$  values are remarkably reduced with the increasing graft amount,  $\mu$  reaching virtually zero when the graft amount becomes larger than  $100 \mu\text{g cm}^{-2}$ . The PP films grafted to such a high amount were felt very slippery when touched with wet fingers. Reduction in  $\mu$  was not observed for any grafted films when the friction measurement was performed in the absence of water.

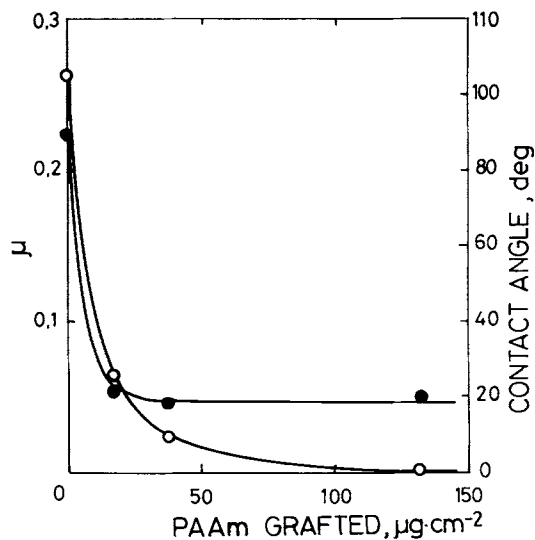


Fig. 4.  $\mu$  and contact angle ( $\theta$ ) values as a function of graft amount for the PAAM-grafted PP films. (○)  $\mu$ ; (●)  $\theta$ .

Figure 5 shows the  $\mu$  and  $\theta$  values observed for the PAAM-grafted nylon films. In this case the plots are given against the UV preirradiation time, because the amount of the PAAM grafted onto nylon could not be determined with the ninhydrin method since amide bonds in nylon interfered with those of PAAM in the quantitative analysis. As can be seen from Figure 5, the  $\mu$  value strongly decreases similar to the PAAM-grafted PP. This is a good evidence for occurrence of graft polymerization of AAM onto the surface of UV-preirradiated nylon films. Straightforward comparison of Figure 5 with

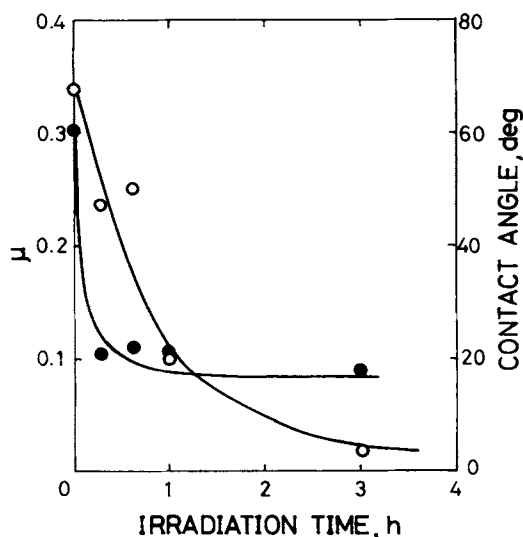


Fig. 5.  $\mu$  and contact angle ( $\theta$ ) values as a function of UV irradiation time for the PAAM-grafted nylon 6 films: (○)  $\mu$ ; (●)  $\theta$ .

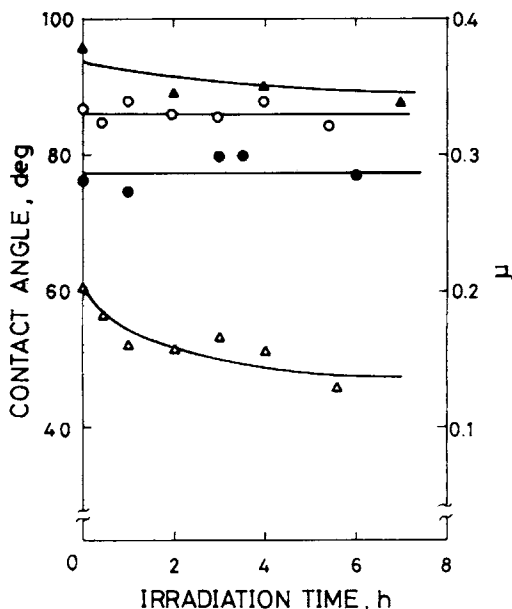


Fig. 6. Influence of UV irradiation alone on the contact angle (open symbols) and the  $\mu$  value (filled symbols) of PP and nylon 6 films: (○, ●) PP; (△, ▲) nylon 6.

Figure 4 reveals that UV preirradiation for 3 h onto the nylon film, followed by graft polymerization of AAm, might yield a graft amount ranging between 50 and 100  $\mu\text{g cm}^{-2}$ .

PP and nylon films treated with UV irradiation alone did not exhibit any significant reduction in  $\mu$  and  $\theta$ . The results are shown in Figure 6, which indicates that the  $\mu$  value practically is not altered upon UV irradiation both for the PP and the nylon film, although  $\theta$  is somewhat reduced for the nylon film. The different change of the contact angle for the PP and the nylon film may be ascribed to different yields of hydrophilic groups on the films upon UV irradiation. As is obvious from Figures 4 and 5, graft polymerization of the water-soluble monomers onto the UV-irradiated films reduced their contact angles in addition to the  $\mu$  values.

### EVA Films

Following UV preirradiation, EVA films with different VA contents were subjected to graft polymerization of the AAm and the DMMA monomer. The condition for graft polymerization was the same as for the PP and the nylon film. The  $\mu$  value of the grafted EVA films is given as a function of the UV preirradiation time in Figure 7. Clearly, the  $\mu$  value decreases with the increasing time of UV irradiation and it takes longer irradiation time for the EVA film of lower VA contents to have a lubricating surface. It is also seen that the PDMAA-grafted films become more slippery than the PAAm-grafted if irradiation is performed for the same period of time.

The higher  $\mu$  values of the grafted EVA films of 14 mol % VA is due undoubtedly to the lower potential of the EVA film for the graft polymerization than that of the film of 28 mol % VA. However, the lower  $\mu$  value of the DMAA-grafted EVA films than those of the PAAm-grafted does not mean

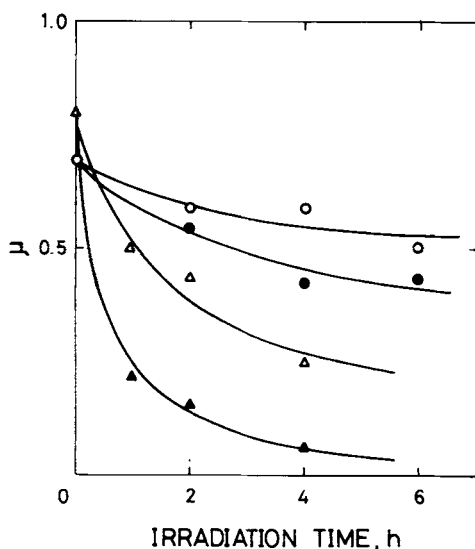


Fig. 7. Influence of UV preirradiation time on the  $\mu$  value of surface-grafted EVA films with different VA contents: (○, ●) VA 14 mol %; (△, ▲) VA 28 mol %; (○, △) PAAm-grafted; (●, ▲) PDMAA-grafted.

that PDMAA should be more capable of producing a slippery surface than PAAm, because the amount of the grafted chains might be different between PAAm and PDMAA, even though the films are irradiated with UV for the same duration. However, as is shown in Figure 8, the  $\mu$  value of the EVA films is practically not dependent on the VA content, if the  $\mu$  value is compared for

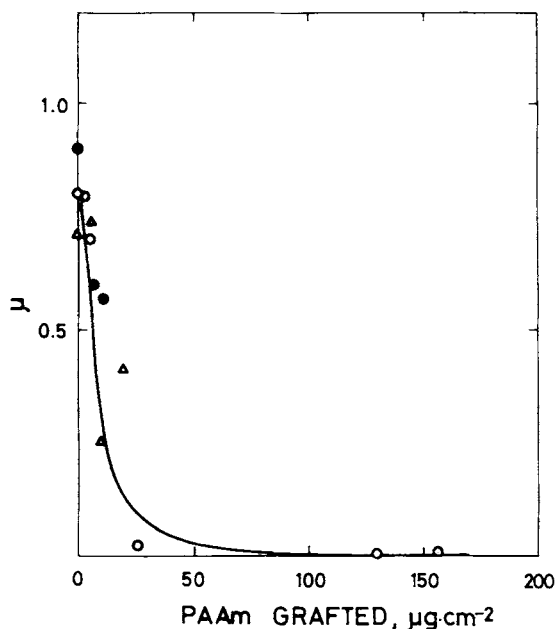


Fig. 8.  $\mu$  values as a function of the graft amount for PAAm-grafted EVA films: (○) VA 28 mol %; (●) VA 19 mol %; (△) VA 14 mol %.

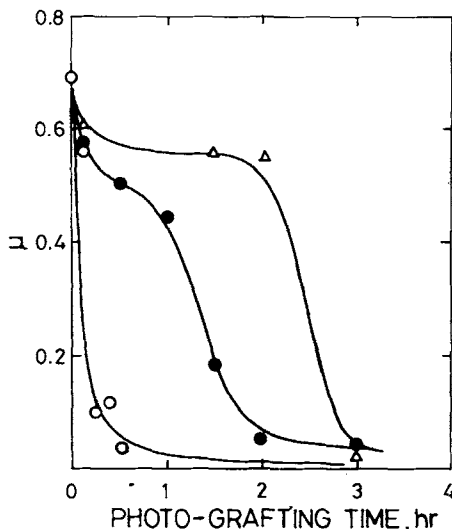


Fig. 9. Effect of photografting time on the  $\mu$  value of the EVA film with VA content of 33 mol % at various temperatures ( $^{\circ}\text{C}$ ): (○) 65; (●) 30; (△) 10.

the PAAm-grafted films at the same graft amount. If it is close to zero, the  $\mu$  value may be still governed by the surface property of the starting EVA substrates which is dependent on the VA content.

Figure 9 shows the effects of duration and temperature of graft polymerization of DMAA on the  $\mu$  value of the grafted EVA film. In this case the EVA film of 33 mol % VA was preirradiated at room temperature for 30 min with a low-pressure mercury lamp (32 W, Riko-32L type), followed by graft polymerization at different temperatures under UV irradiation in the presence of riboflavin without degassing. Riboflavin was employed because it consumed the oxygen present in the monomer aqueous solution upon UV irradiation.<sup>8</sup> Otherwise, the oxygen would inhibit the graft polymerization. As can be seen from Figure 9, raising the polymerization temperature had a large effect on reduction of the  $\mu$  value of the grafted EVA surface. For instance, a highly slippery surface could be achieved without deteriorating the bulk property in a short period of time such as 30 min both for preirradiation and graft polymerization when the preirradiated film was subjected to polymerization at 65 $^{\circ}\text{C}$ .

In an attempt to prepare a catheter which has a slippery surface when hydrated, a tube with a diameter of 5 mm was fabricated by extrusion of the EVA pellet used for the film. The surface of the tube became slippery almost to an extent similar to the film when grafted with DMAA under the same condition as for the film. No significant difference in the observed  $\mu$  value was found between the tube and the film.

## DISCUSSION

Lubrication of a polymeric material in the presence of water appears to be closely related to hydrophilicity (or hydrophobicity) of the surface. Fluorinated polymers are known to have the lowest friction coefficient in air among the conventional polymers, but do not become slippery when hydrated. The



TABLE I  
Contact Angles ( $\theta$ ) and Coefficient of Frictions ( $\mu$ )  
of Various Polymer Films before Graft Polymerization

	PP	Nylon	EVA (VA content)				PTFE <sup>a</sup>
			14%	19%	28%	33%	
$\theta$	89	59	83	80	79	74	119
$\mu$	0.27	0.38	0.68	0.90	0.80	0.68	0.09

<sup>a</sup> Polytetrafluoroethylene.

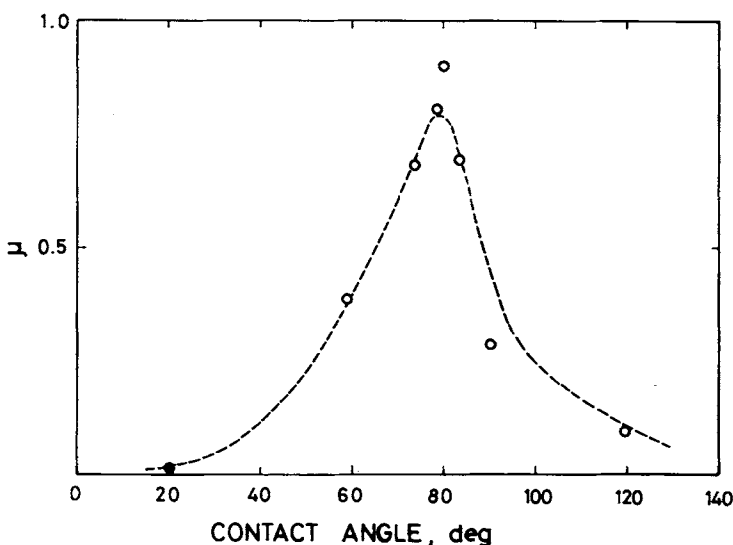


Fig. 10. Relation between the  $\mu$  value and the water contact angle for films: (○) ungrafted; (●) grafted.

substrate polymers employed in the present work are PP, nylon, and EVA with different VA contents. The unmodified surfaces of these films have different contact angles against water and  $\mu$  values, as given in Table I, where those of polytetrafluoroethylene (PTFE) are also given for comparison. Their  $\mu$  value before graft polymerization is plotted against their water contact angle in Figure 10. As is seen, the  $\mu$  value of these ungrafted surfaces determined against a glass plate in an aqueous environment varies in a peculiar manner with the increasing contact angle. A maximum is observed for the  $\mu$  value at a contact angle around  $80^\circ$ . In Figure 10, the average values for the surfaces grafted with AAm or DMAA are also plotted, the contact angle ( $\theta$ ) and the  $\mu$  value being  $20^\circ$  and 0.01, respectively.

Appearance of a maximum in the  $\theta$ - $\mu$  relation reminds us of the dependence of work of adhesion of a reference material to polymer surfaces of various  $\theta$ 's in water.<sup>9</sup> The result is rewritten in Figure 11. In a previous paper<sup>9</sup> the work of adhesion in water,  $W_{12,w}$ , was theoretically derived as a function of the interfacial free energy between a polymer surface and water,  $\gamma_{1w}$ . One of the most proper quantity identifying hydrophilicity (or hydrophobicity) of a surface is the  $\gamma_{1w}$  value. As seen from Figure 11,  $W_{12,w}$  increases with the increasing  $\gamma_{1w}$  or hydrophobicity, but, after passing a maximum,

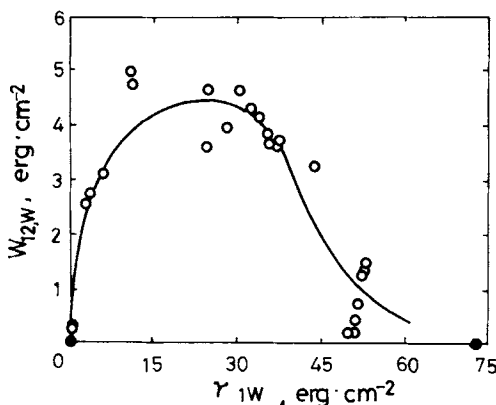


Fig. 11. Work of adhesion of polymer surface 1 with a reference surface 2 in water ( $W_{12,w}$ ) as a function of the interfacial free energy between water and the polymer surface 1 ( $\gamma_{1w}$ ).

decreases as  $\gamma_{1w}$  becomes much higher. This result implies that a quite hydrophobic surface interacts very weakly with the opposing surface, regardless of the presence of water, whereas a quite hydrophilic surface also should be attracted to the opposing surface to an insignificant extent if water is present. This seems reasonable because a water thin layer must be bound to the highly hydrophilic surface, leading to very weak adhesion between the waterlike surface and the reference in the presence of water.

Similar to adhesion, friction must be directly concerned with the attractive force between the two opposing surfaces in contact, if both of them have entirely smooth and undeformable surface. Strong friction may take place if a strong attractive force is operative between the opposing surfaces, whereas friction may be insignificant if the attractive force is weak. In the present work we determined the friction in the presence of water using a glass plate as the reference. It is likely that a more hydrophobic surface has less attraction to the glass plate, resulting in smaller friction. On the other hand, a more hydrated surface with a larger amount of water-soluble graft chains will also interact less strongly with the glass plate, as mentioned above. We may feel a surface slippery upon touching it with fingers, if the  $\mu$  value between the surface and our finger is below a certain value.

### References

1. M. Suzuki, A. Kishida, H. Iwata, and Y. Ikada, *Macromolecules*, **19**, 1804 (1986).
2. H. Iwata, A. Kishida, M. Suzuki, Y. Hata, and Y. Ikada, *J. Polym. Sci., Polym. Chem. Ed.*, **26**, 3309 (1988).
3. M. Suzuki, Y. Tamada, H. Iwata, and Y. Ikada, in *Physicochemical Aspects of Polymer Surfaces*, K. L. Mittal, Ed., Plenum, New York, 1983, Vol. 2, p. 923.
4. Y. Uyama and Y. Ikada, *J. Appl. Polym. Sci.*, **36**, 1087 (1988).
5. E. Uchida, Y. Uyama, and Y. Ikada, *J. Polym. Sci., Polym. Chem. Ed.*, **27**, 527 (1989).
6. B. J. Briscoe and D. Tabor, in *Polymer Surfaces*, D. T. Clark and W. J. Feast, Eds., Wiley, New York, 1978, p. 1.
7. P. M. Triolo and J. D. Andrade, *J. Biomed. Mater. Res.*, **17**, 149 (1983).
8. B. Holmström and G. Oster, *J. Am. Chem. Soc.*, **83**, 1867 (1961).
9. Y. Ikada, *Adv. Polym. Sci.*, **57**, 103 (1984).

Received June 17, 1988

Accepted September 8, 1988