August, 1982] © 1982 *The Chemical Society of Japan* NOTES *Bull. Chem. Soc. Jpn.*, *55*, *2655—2656 (1982)* 2655

The Effect of Ultraviolet Radiation on Wettability of Silane Coupling Agents Coated on Glass

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

(Received December 16, 1981)

Synopsis. The effect of ultraviolet irradiation on wettability of silane coupling agents coated on glass was studied by using contact angle measurements. The water contact angle for the silane coupling agents decreased due to photooxidation as the irradiation progressed. It was found that silane coupling agents which contain vinyl, allyl, or phenyl groups were easily photooxidated by the irradiation.

Silane coupling agents are well known to alter surfaces from hydrophilic to hydrophobic. There are many papers[1-4] about wettability of silane coupling agents coated on silica particles or glass; these attempt to understand the adhesion mechanism between a matrix and reinforcing medium. Lee[5] determined critical surface tensions for silane coupling agents on glass and found a relationship between the wettability of functional groups of silanes and their solubility parameters.

Silane coupling agents coated on substrates, under normal condition, were put in contact with atmospheric oxygen and exposed to various temperatures, humidities, and lights. It is expected that silane coupling agents on substrates would undergo a photochemical change at their surfaces. Indeed, vinyl and [3-(methacryloyloxy)-propyl] silane agents on glass[6] were found to change very readily in the presence of air at room temperature or at 80 °C and their critical surface tensions increased, presumably due to increase in polarity. Accordingly, it is very interesting to study the stability of silane coupling agents on substrates against different exposure conditions, especially light exposure. To evaluate the change in a surface composition, contact angle measurements have often been used. This work describes the effect of ultraviolet radiation on the wettability of silane coupling agents coated on glass by using contact angle technique.

The silane coupling agents used in this study were chloromethylphenylvinylsilane, chlorodimethylvinylsilane, allyltriethoxysilane, trichloro(1-methyl-2-phenylethyl)silane, chlorotrimethylsilane, and hexamethyldisilazane, which were supplied by Petrarch Systems, Inc. The liquid used for contact angle measurement was deionized water.

A micro slide glass was used as a substrate. The slide glass was cleaned by chromium trioxide solution, washed with distilled water and then dried carefully.

Coating of silanes on slide glass was carried out with about 3 wt% solution of silanes in 2-propanol. The

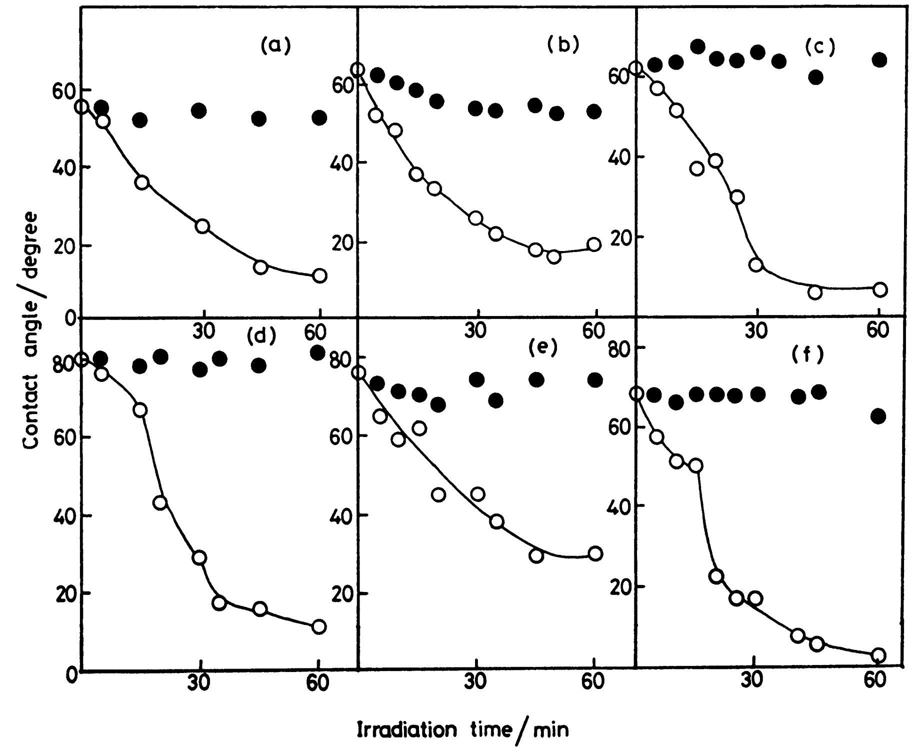

Fig. 1. Water contact angle *vs.* irradiation time.
(○) Water contact angle on irradiated portion, (●) on unirradiated portion. (a) Chloromethylphenylvinylsilane, (b) chlorodimethylvinysilane, (c) allyltriethoxysilane, (d) trichloro(1-methyl-2-phenylethyl)silane, (e) chlorotrimethylsilane, and (f) hexamethyldisilazane.

clean slide glass was dipped into the solution for 30 min, this was followed by washing with 2-propanol and drying *in vacuum*. In the case of hexamethyldisilazane, coating was conducted in vapor state on the slide glass. After exposing the slide glass to the vapor, the treated glass was heated at 100 °C for 20 min to eliminate ammonia generated during the coating.

Contact angles were measured on sessile drops of water by using a goniometer at 20 °C. Three drops for water 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.

Exposures were carried out in air in a hood with a unfiltered radiation from 55.2 W low pressure mercury lamp supplied by Oriel Co. The distance between the sample and the lamp was 5 cm.

The contact angle of water for the silanes on the slide glass was measured as a function of exposure time of ultraviolet irradiation. The results are shown in Fig. 1.

Chloromethylphenylvinylsilane. The initial contact angle of water was 55°. The contact angle decreased with increasing the exposure time and reached to about 10° in 60 min exposure.

Chlorodimethylvinylsilane. The contact angle of water was 60° at initial stage and became 20° during 60 min exposure. During irradiation, however, the unirradiated portion of sample lost hydrophobicity significantly, so that the contact angle on this unirradiated sample went to about 50°.

Allyltriethoxysilane. The contact angle was 60° initially and reached 10° after 30 min exposure.

Trichloro(1-methyl-2-phenylethyl)silane. The initial contact angle was 80°. Irradiation for 30 min dramatically dropped the contact angle to 15°.

Chlorotrimethylsilane. The initial contact angle was 75°. Irradiation for 40 min brought the contact angle down to 30°. This result is somewhat unexpected because methyl groups seem to be stable against ultraviolet irradiation.

Hexamethyldisilazane. The initial contact angle was 65°. The contact angle decreased remarkably to 10° after 40 min exposure.

Generally, the use of a monohalogenosilane[7] prevents the formation of polymeric films on substrates and the coating by the monohalogenosilane is envisioned as a monolayer of silane monomers. On the other hand, trialkoxysilane or trihalogenosilanes undergo the hydrolysis and polymerization to form a polysiloxane network structure, which is much thicker than a monolayer of monomer. Lee[6] studied the conformation of hydrolyzed silanes on glass and concluded that the interaction between the hydrolyzed silanes and the glass surface could take place with the attachment of one hydroxysilyl group to the surface.

In this study, all the silanes except trichloro(1-methyl-2-phenylethyl)silane and allyltriethoxysilane are considered not to form polymeric films on the glass. If chlorotrimethylsilane as a monohalogenosilane is coated on a glass, the water contact angle on the surface would be predicted[8] to be about 73°, while the water contact angle on a fully methylated surface like paraffin wax is taken as 110°. This predictable value of 73° was in good agreement with the experimental value. The above difference of water contact angle between that on monolayer film and that on polymeric film depends on the surface coverage of silane on glass. That is, the polymeric film of silane would give a larger water contact angle than the monolayer of silane.

From Fig. 1, it is seen that by using different silane coupling agents, a variety of functional groups can be exposed on the surface of glass, and each functional group shows a different water contact angle value. When all the samples were irradiated in air by ultraviolet light, the water contact angles decreased as a function of irradiation time. Furthermore, it was found that the water contact angles of silane coupling agents which contain vinyl, phenyl, or allyl groups changed very readily over a short irradiation time.

It is interesting to compare the results obtained with the silane coupling agents on the glass irradiated in air and *in vacuum*. All the silane coupling agents in this study on the glass irradiated *in vacuum* showed no changes in the water contact angles after exposures up to 60 min. This result supports the assertion that during irradiation in air the surface of silane coupling agents on the glass is photooxidated to yield hydrophilic products on the surface.

References

1) P. W. Erickson and E. P. Plueddemann, "Composite Materials," Academic Press, New York (1974), Vol. 6, Chap. 6, 1.

2) W. D. Bascom, *Adv. Chem. Ser.*, **1968**, 87.

3) H. Inoue and S. Kohama, *J. Appl. Polym. Sci.*, **19**, 1939 (1975).

4) E. P. Plueddemann, *Soc. Plastic Ind.*, 19A (1965).

5) L. H. Lee, "Adhesion Science and Technology," Plenum Publ., New York (1975), Vol. 9B.

6) L. H. Lee, *J. Colloid Interface Sci.*, **27**, 751 (1968).

7) M. R. Rosen, *J. Coat. Technol.*, **50**, 70 (1978).

8) J. Laskowski and J. A. Kitchener, *J. Colloid Interface Sci.*, **29**, 670 (1969).