The Effect of the CCl_3F-Treatment on Wettability of Silica Glass Surface by Water and Organic Liquid

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Synopsis. The wettability of silica glass plate by water and some organic liquids was varied by vapor-phase treatment of the surface with CCl_3F at temperatures higher than 450 °C. The critical surface tension γ_c of the treated surface was found to be about 49 dyn cm^{-1} (1 dyn=10^{-5} N).

Previously, two of the authors have found that adsorptive activity of silica powder for both water vapor and gaseous hexane are decreased by vapor-phase treatment with chlorofluorocarbons (CFCs) at higher temperatures.[1] This fact suggests that the silica surface turns to be hydro- and lipophobic with the CFC-treatment. On the other hand, it is well known that the surface properties, such as surface area, surface acidity, and adsorptive activity, of some metal oxides may be modified by surface fluorination with aqueous solution of HF,[2] NH_4F,[3] or NH_4HF_2.[4] However, such a liquid-phase treatment is tedious because of complications arising from the process, including separation and drying. So, it is preferable to apply the CFC-treatment for surface treatment or fluorination instead of the liquid-phase treatment.

Accordingly, this study examines the effect of the CFC-treatment on the wettability of silica glass plate by water and some organic liquids.

Experimental

Materials and Reagents. Quartz glass (QG) and Pylex glass (PG), supplied by Nippon Sekiei Co. and Iwaki Glass Co., respectively, were used as samples after repeated washings by immersion in acetone, nitric acid, distilled water, and $CClF_2CCl_2F$. The fluorination agent, CCl_3F, having a purity of higher than 99.9%, was supplied by Mitsui-Dupont Fluorochemical Co., and used without further purification. All organic compounds used for the wettability test were special grade reagents, supplied by Wako Chemical Co., and they were not further purified.

Measurements. The contact angles (advancing angles), θ_a (°) were measured at 20 °C, by using a Gonio-type apparatus made by Kyowa Kagaku Co. The F content in the surface layer of the treated samples was determined by XPS using Shimadzu ESCA 750. FT-IR spectra of the treated glass plates were measured by attenuated total reflection spectroscopy using a Perkin-Elmer 1760X spectrometer.

Results and Discussion

Contact angles observed for water and organic compounds are listed in Table 1 together with the surface F contents of the glass plates treated with CCl_3F under various conditions. The contact angles of some organic liquids were slightly affected by the CCl_3F-treatment, but that of water was significantly changed from 10° to 73—85° by the surface treatment. The results meant that the hydrophilic surfaces of QG and PG were greatly changed becoming hydrophobic by the CCl_3F-treatment. The degree of hydrophobicity, which is represented by contact angles of water, instead with increasing treatment temperature from 450 to 650 °C. In addition, even after several washes with water and acetone, the contact angle of water for QG treated with CCl_3F at 650 °C was maintained at above 70°.

On the other hand, such a effect on the wettability of the silica glass plate by water was not observed at all when QG was treated using 10 wt% HF solution. As was shown in Table 1, when the treatment temperature

Table 1. Contact Angles θ_a(°) of Water and Some Organic Liquids

Sample[a)]	Treatment temperature	Surface F content	Contact angle θ_a (°)[b)]			
	°C	atm%	Water	Benzene	Decalin	Glycerol
QG-U	—	0	9	9	10	9
QG-CFC	450	0.2	73	—	—	—
QG-CFC	550	0.5	77	10	13	—
QG-CFC	650	0.7	85	10	26	53
QG-CFC[c)]	650	0.6	77	—	—	—
QG-CFC[d)]	650	0.5	76	—	—	—
QG-HF	R.t.	2.4	10	—	—	9
PG-U	—	0	10	11	16	—
PG-CFC	550	0.5	75	19	26	—

a) -U: untreated, -CFC: treated with CCl_3F, -HF: treated with 10 wt% HF solution. b) The parts denoted by (—) were not measured, because the degree of change due to the treatment was predicable from measurements using other organic liquids. c) For the sample treated at 650 °C, and then dipped into water for 2 h, followed by dried at 120 °C. d) For the sample treated at 650 °C, and then dipped into water and acetone for 2 h respectively, followed by dried at 120 °C.

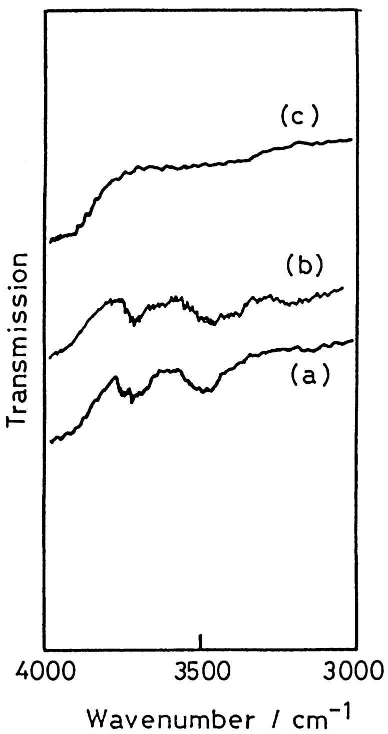

Fig. 1. FT-IR spectra of the various quartz glass plates.
(a): QG-U, (b): QG-HF, (c): QG-CFC.

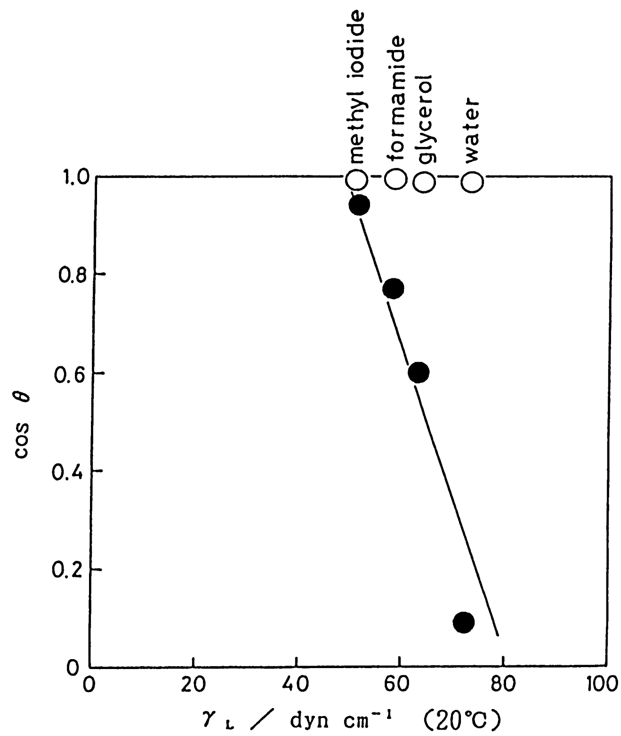

Fig. 2. Zisman plots of the contact angles of various liquids for quartz glass plates before and after CFC-treatment.
○: QG-U, ●: QG-CFC.

was gradually raised, the contact angle of water increased in accordance with an increase in the surface F content. So, the difference in the wettability of the glass plate by water between the HF- and CCl_3F-treated surface seemed to be explained by the surface F content. Namely, the low wettability observed for the CFC-treated QG may be due to a higher F content in the surface layer. However, contrary to the above presumption, the surface F content of the CFC-treated QG was less than that of the HF-treated QG. That is, the difference observed for the wettability was not simply ascribable to F content in the surface layer. As Fig. 1 shows, the IR absorption bands at around 3500—3700 cm^{-1} assignable to the surface OH groups of QG were not varied by the HF-treatment. This result suggested that the difference in the hydrophilic property between CFC- and HF-treated QG may result from the amount of surface OH groups which may attract water molecules through formation of hydrogen bonding. Namely, HF-treated QG having a large amount of surface OH groups can exhibit a high wettability for water, but the CFC-treated QG having few or no OH groups, should not show such a wettability. In addition, the surface of the CFC-treated QG would be expected to be fully covered by F atoms which are able to decrease the surface energy. Hence, the surface of QG treated with CCl_3F could show lipophobicity, besides hydrophobicity, as suggested by the decrease in wettability for some organic liquids (cf. Table 1).

The characteristic surface property of the CFC-treated QG was further revealed by the value of the critical surface tension. As shown in Fig. 2, the contact angles measured for various organic liquids were plotted versus respective surface tensions. Although the liquids used here were not a homolog to each other, a linear relationship was found, and the straight line joining such a Zisman plot,[5] gave the critical surface tension as about 49 dyn cm^{-1}. The value is fairy low compared with a inorganic materials, being comparable to those of organic chloropolymers, such as poly(vinylidene chloride) (γ_c=40 dyn cm^{-1}) and poly (vinyl chloride) (γ_c=39 dyn cm^{-1}). The fact that the γ_c value of the CFC-treated QG was close to those of widely used commercial polymers suggested the suitability of the CFC-treatment for surface treatments of silica, and probably also other inorganic modifiers to be used in blending with polymers.

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