ELSEVIER

Journal of Fluorine Chemistry 79 (1996) 87–91

JOURNAL OF FLUORINE CHEMISTRY

Syntheses and reactions of metal organics. XXI. Syntheses of (1*H*,1*H*,2*H*,2*H*-polyfluoroalkyl)triisocyanate silanes and surface modification of glass

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Received 23 February 1996; accepted 17 March 1996

Abstract

Four silane coupling agents having a fluorocarbon chain and three isocyanate groups as reactive centers, i.e. $CF_3(CF_2)_3CH_2CH_2Si(NCO)_3$ (**1**), $CF_3(CF_2)_5CH_2CH_2Si(NCO)_3$ (**2**), $CF_3(CF_2)_7CH_2CH_2Si(NCO)_3$ (**3**) and $CF_3(CF_2)_9CH_2CH_2Si(NCO)_3$ (**4**), were prepared by the hydrosilylation reaction of trichlorosilane with the corresponding 1*H*,1*H*,2*H*-polyfluoro-1-alkene [$CF_3(CF_2)_nCH{=}CH_2$, $n = 3$, 5, 7 and 9] in the presence of hydrogen hexachloroplatinate(IV), followed by reaction with silver cyanate. Their application to the surface modification of glass was attempted. From measurements of the contact angles θ for water and oleic acid against a modified glass surface, it was found that the isocyanate-type silane coupling agents have a higher surface modification ability toward glass than those of methoxy-type silane coupling agents. The highest contact angle on the glass surface modified by each silane coupling agent was obtained employing both a shorter modification time (1/6) and a lower concentration (1/10) of the silane coupling agent solution in comparison with those of methoxy-type silane coupling agents. The oxidation and acid resistance of the modified glass surface were investigated, and the results of the resistance abilities assessed by measuring the contact angle reduction of water and oleic acid were also higher than those of methoxy-type silane coupling agents.

Keywords: Silane coupling agents; Fluoro compounds; Isocyanatosilanes; Contact angles; Glass surface modification; Oxidation-resistant surfaces

1. Introduction

The use of silane coupling agents to promote surface modification and/or adhesion are most familiar for R_nSiX_{4-n} ($n = 1$, 2 and 3) organosilanes having two types of substituents, R and X. In these compounds, R is a nonhydrolyzable relatively inert organic group such as alkyl or a nonhydrolyzable reactive group such as epoxy-, vinyl- or amino-alkyl group. The X functionality is a hydrolyzable group, often alkoxyl [1].

Recently, we reported the syntheses of silane coupling agents having straight fluorocarbon chains, such as $CF_3(CF_2)_nCH_2CH_2Si(CH_3)(OCH_3)_2$ ($n = 3$, 5, 7 and 9) [2], $CF_3(CF_2)_nCH_2CH_2Si(OCH_3)_3$ ($n = 3, 5, 7$ and 9) [3], $F(CF_2)_n(C_6H_4)C_2H_4Si(CH_3)(OCH_3)_2$ ($C_6H_4 = p$-phenylene, $n = 1$, 3, 5 and 7) [4] and $F(CF_2)_n(C_6H_4)C_2H_4Si(OCH_3)_3$ ($n = 1$, 3, 5 and 7) [4] and other silane coupling agents having branched fluorocarbon chains, $(CF_3)_2CF(CF_2)_nCH_2CH_2Si(CH_3)(OCH_3)_2$ ($n = 4$, 6 and 8) [5] and $(CF_3)_2CF(CF_2)_nCH_2CH_2Si(OCH_3)_3$ ($n = 4$, 6 and 8) [5] were also prepared. From a study of the surface modification of glass using these silane coupling agents, $CF_3(CF_2)_9CH_2CH_2Si(OCH_3)_3$ displayed the highest ability for water and oil repellency. A glass surface modified with this coupling agent also displayed the highest oxidation resistance in hot concentrated nitric acid. These results were assessed by measuring the contact angles of water and oleic acid. As contamination in our daily life has been often thought to be produced from oil and fats, oleic acid was used as an example of oil and fats.

In another recent paper [6], we described attempts to modify some dental-material surfaces using $CF_3(CF_2)_9CH_2CH_2Si(OCH_3)_3$ where an increment in the contact angles of water and oleic acid on the modified material surface was observed. On the basis of these results, we studied the surface modification of a denture to provide stain-protecting ability, and high contamination-protecting ability was observed by wearing the denture in an oral cavity, normally for four months.

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PII S0022-1139(96)03472-0

Composite resins for dental use are prone to coloration by many coloring matters in foods and smoking. The composite resin modified by $CF_3(CF_2)_9CH_2CH_2Si(OCH_3)_3$ also displayed color-preventing ability tested by tea-extract solution, a tobacco-extract solution and an Oil-orange (Sudan I) olive solution [7,8].

Though a composite resin has a natural tendency to show hydrophobic characteristics, bacterial plaques accumulate on its surface. Accumulated plaque may induce recurrent caries and periodontal disease, and contribute to the deterioration of composite materials. The cause of such plaque accumulation is attributed to the adherence of microorganisms on the solid surface brought about by physicochemical interactions. We demonstrated the inhibiting ability of plaque formation and the plaque detachment efficacy of the surface modifier $CF_3(CF_2)_9CH_2CH_2Si(OCH_3)_3$ by using glass and composite resin in vitro [9]. The amount of accumulated bacteria, *Streptococcus mutans* Ingbritt, incubated anaerobically for 24 h at 37 °C on the specimen was determined with an optical densitometer. The efficacy of the detachment ability from the specimen was determined densitometrically through sequential ultrasonic cleansing in test tubes using 10 W for 10 s, 50 W for 20 s, 50 W for 30 s and 200 W for 60 s. After final ultrasonic cleansing, the remaining bacteria on the specimens were determined from SEM photographs. From the results, the remaining bacteria on the modified surface only amounted to 1/1000 of that on the unmodified surfaces.

This paper reports the results of the syntheses and characterization of four silane coupling agents having a fluorocarbon chain and three isocyanate groups as hydrolyzable groups. Applications for the surface modification of glass using these coupling agents have been investigated. The oxidation and acid resistance of the modified glass surface to hot concentrated nitric acid and hydrochloric acid, respectively, were also investigated by measuring the contact angles of water and oleic acid. Shortening the time for a dental operation in an oral cavity is a very important factor for developing a dental surface modifier. The conditions for glass surface modification, such as the modification time and concentration of the modification solution of silane coupling agents, were also investigated.

2. Experimental details

Special precautions were adopted in order to avoid hydrolysis of the starting materials and products; all experiments were carried out under an atmosphere of purified nitrogen to preclude oxygen and moisture.

2.1. Materials

Trichlorosilane was purchased from Tokyo Kasei Kogyo Co., Ltd. and used without further purification. The compounds $CF_3(CF_2)_3CH{=}CH_2$ (b.p. 59 °C), $CF_3(CF_2)_5CH{=}CH_2$ (b.p. 100 °C), $CF_3(CF_2)_7CH{=}CH_2$ (b.p. 148–149 °C) and $CF_3(CF_2)_9CH{=}CH_2$ (b.p. 59–61 °C/345 Pa) were obtained from Daikin Kogyo Co., Ltd. and purified by distillation. The compounds $CF_3(CF_2)_3CH_2CH_2SiCl_3$, $CF_3(CF_2)_5CH_2CH_2SiCl_3$, $CF_3(CF_2)_7CH_2CH_2SiCl_3$ and $CF_3(CF_2)_9CH_2CH_2SiCl_3$ were obtained by the method of the previous paper [3]. Silver cyanate and hydrogen hexachloroplatinate(IV) (Kojima Chemicals Co., Ltd.) were used without further purification. The solvents diethyl ether, benzene and 1,1,2-trichloro-1,2,2-trifluoroethane (F-113) were purified by the usual methods.

2.2. Measurements

FT-IR spectra were measured in a liquid film or by a KBr disk method with a Nicolet 510 spectrophotometer and assigned [10–12]. Each spectrum was recorded at a resolution of 4 cm^{-1} with a total of 10 scans. Pulsed Fourier-transform 300 MHz ^1H NMR spectra were run in $CDCl_3$ with TMS as internal standard using a Bruker AC300D spectrometer at room temperature: pulse repetition time, 3.0 s; number of accumulations, 5. Contact angles θ were measured at 23 °C with a Kyowa CA-X type contact angle meter. The experimental results depicted in the figures are the average of 30 measurements of different points on the modified glass surface. Mass spectra (MS) were measured (70 eV) with a Hitachi M-80A GC–MS spectrometer and the data were analyzed with a Hitachi M-003 data processing system. Elemental analysis (EA) was performed using a Heraeus CHN-O-RAPID.

2.3. Syntheses of silane coupling agents

2.3.1. Synthesis of $CF_3(CF_2)_3CH_2CH_2Si(NCO)_3$ (1)

$CF_3(CF_2)_3CH_2CH_2SiCl_3$ (17.0 g, 44.5 mmol) was added slowly to a dispersion of silver cyanate (25.0 g, 167 mmol) in benzene (100 cm^3) at 80 °C with stirring in a 300 ml flask, and the reaction mixture was then allowed to react for 1 h at the boiling point. After separation of excess silver cyanate and the silver chloride produced by filtration, compound **1** was obtained as a colorless liquid by distillation (13.7 g; yield, 70.6%; b.p. 103–107 °C/390 Pa) IR (cm^{-1}): 2956 (w); 2921 (w) (ν_{C-H}); 2277 (vs) ($\nu_{N=C=O}$); 1468 (m), 1219 (vs), 1135 (s) (ν_{C-F}). ^1H NMR δ: 1.00–1.40 (2H, m, Si–CH_2); 1.55–2.75 (2H, m, Si–CH_2–CH_2) ppm. MS (*m*/*z*) (rel. int.): 401 (0.3) $[M]^+$; 259 (100) $[CF_2CF_2CH_2CH_2Si(NCO)_2+F]^+$; 236 (29) $[CF_2CF_2CH_2CH_2Si(NCO)+2F]^+$; 154 (15) $[Si(NCO)_3]_2^+$; 109 (25) $[CF_2CF_2CH_2CH_2+F]^+$; 69 (8) $[CF_3]^+$. Analysis: Found: C, 26.73; H, 0.79; N, 10.38%. Calc. for $C_9H_4O_3N_3F_9Si$: C, 26.94; H, 1.00; N, 10.47%.

2.3.2. Syntheses of $CF_3(CF_2)_5CH_2CH_2Si(NCO)_3$ (2), $CF_3(CF_2)_7CH_2CH_2Si(NCO)_3$ (3) and $CF_3(CF_2)_9CH_2CH_2Si(NCO)_3$ (4)

The procedures and purification techniques were similar to those for the preparation of compound **1**.

Compound **2**: colorless liquid; b.p. 73–75 °C/41 Pa; yield, 58.0%. IR (cm^{-1}): 2997 (w), 2919 (w) (ν_{C-H}); 2275 (vs)

($\nu_{N=C=O}$); 1466 (m), 1239 (vs), 1206 (vs), 1146 (s) (ν_{C-F}). ^{1}H NMR δ: 1.00–1.40 (2H, m, Si–CH$_2$); 1.55–2.75 (2H, m, Si–CH$_2$–CH_2) ppm. MS (m/z) (rel. int.): 501 (0.4) [M]$^+$; 259 (100) [$CF_2CF_2CH_2CH_2Si(NCO)_2+F$]$^+$; 236 (32) [$CF_2CF_2CH_2CH_2Si(NCO)+2F$]$^+$; 154 (8) [$Si(NCO)_3$]$_2$$^+$; 109 (26) [$CF_2CF_2CH_2CH_2+F$]$^+$; 69 (12) [$CF_3$]$^+$. Analysis: Found: C, 26.13; H, 0.69; N, 8.20%. Calc. for $C_{11}H_4O_3N_3F_{13}Si$: C, 26.36; H, 0.80; N, 8.38%.

Compound **3**: colorless liquid; b.p. 93–95 °C/36 Pa; yield, 74.4%. IR (cm^{-1}): 2958 (w), 2921 (w) (ν_{C-H}); 2279 (vs) ($\nu_{N=C=O}$); 1468 (m), 1445 (m), 1239 (s), 1206 (vs), 1148 (s) (ν_{C-F}). ^{1}H NMR δ: 1.00–1.45 (2H, m, Si–CH$_2$); 1.55–2.80 (2H, m, Si–CH$_2$–CH_2) ppm. MS (m/z) (rel. int.): 601 (0.6) [M]$^+$; 259 (100) [$CF_2CF_2CH_2CH_2Si(NCO)_2+F$]$^+$; 236 (37) [$CF_2CF_2CH_2CH_2Si(NCO)+2F$]$^+$; 154 (7) [$Si(NCO)_3$]$_2$$^+$; 109 (31) [$CF_2CF_2CH_2CH_2+F$]$^+$; 69 (12) [$CF_3$]$^+$. Analysis: Found: C, 26.03; H, 0.59; N, 6.87%. Calc. for $C_{13}H_4O_3N_3F_{17}Si$: C, 25.97; H, 0.67; N, 6.99%.

Compound **4**: colorless solid; b.p. 105–110 °C/37 Pa; m.p. 59.0–59.5 °C; yield, 60.7%. IR (cm^{-1}): 2983 (w), 2954 (w), 2923 (w) (ν_{C-H}); 2285 (vs) ($\nu_{N=C=O}$); 1465 (vs), 1418 (s), 1319 (vs), 1208 (s), 1152 (s) (ν_{C-F}). ^{1}H NMR δ: 1.00–1.45 (2H, m, Si–CH$_2$); 1.55–2.75 (2H, m, Si–CH$_2$–CH_2) ppm. MS (m/z) (rel. int.): 701 (0.5) [M]$^+$; 259 (100) [$CF_2CF_2CH_2CH_2Si(NCO)_2+F$]$^+$; 236 (48) [$CF_2CF_2CH_2CH_2Si(NCO)+2F$]$^+$; 154 (4) [$Si(NCO)_3$]$_2$$^+$; 109 (41) [$CF_2CF_2CH_2CH_2+F$]$^+$; 69 (27) [$CF_3$]$^+$. 154 (7) [$Si(NCO)_3$]$_2$$^+$; 109 (31) [$CF_2CF_2CH_2CH_2+F$]$^+$; 69 (12) [$CF_3$]$^+$. Analysis: Found: C, 25.42; H, 0.62; N, 5.81%. Calc. for $C_{15}H_4O_3N_3F_{21}Si$: C, 25.69; H, 0.57; N, 5.99%.

2.4. *Surface modification of glass*

2.4.1. *Effect of reaction time*

Plates of glass were allowed to react using the silane coupling agents **1–4** in 100 cm^3 of 20 mM F-113 solution for various times at 47 °C (boiling point) under an atmosphere of purified nitrogen. The surface-modified glass was rinsed with fresh F-113 and dried. The glass was treated thermally in an oven at 150 °C for 30 min and then the contact angles of water and oleic acid were measured against these glass samples. The contact angles θ were measured using 0.9×10^{-6} dm^3 of water or oleic acid drops. The contact angles were evaluated by extrapolating to zero time from a plot of the advancing contact angle versus time [13].

2.4.2. *Effect of concentration*

Plates of glass were treated with the silane coupling agents **1–4** in 100 cm^3 of F-113 solution at various concentrations in the same manner as described above. The contact angles of water and oleic acid on the modified glass surface were measured.

2.5. *Measurement of oxidation resistance of modified glass surface*

Plates of glass, which had been treated with the silane coupling agents **1–4** in a 3 mM F-113 solution for 20 min at 47 °C and treated thermally in an oven at 150 °C for 30 min, were dipped into 100 cm^3 of concentrated nitric acid for 30, 60, 90 and 120 min at 100 °C. After oxidation, each sample was rinsed with water and dried at room temperature for 1 d. The contact angles of water and oleic acid on the surface were then measured.

2.6. *Measurement of acid resistance of modified glass surface*

Plates of glass which had been treated as in Section 2.5 were dipped in 100 cm^3 of concentrated hydrochloric acid for 30, 60, 90 and 120 min at 100 °C. After each sample had been rinsed with water and dried at room temperature for 1 d, the contact angles of water and oleic acid were again measured.

3. Results and discussion

3.1. *Synthesis*

The high yield hydrosilylation reactions of trichlorosilane with 1*H*,1*H*,2*H*-polyfluoro-1-alkene were achieved successfully using the reaction in sealed glass ampoules [2,3]. In general, Si–CH$_2$CH$_2$–X-type compounds were mainly formed via the platinum-catalyzed addition reaction of compounds containing Si–H bonds with compounds having the general formula CH$_2$=CH–X, where X is not conjugated with C=C [14–16]. The ^{1}H NMR spectra of the products did not exhibit a proton signal such as Si–C*H* or Si–CH–CH_3. This indicates that the hydrosilylation reaction of trichlorosilane with 1*H*,1*H*,2*H*-polyfluoro-1-alkene is highly regioselective. Syntheses of $CF_3(CF_2)_nCH_2CH_2Si(NCO)_3$ were performed by adding $CF_3(CF_2)_nCH_2CH_2SiCl_3$ to a dispersion of AgCNO. The silane coupling agents obtained were stable in dry air. In the presence of water, however, the silanes were hydrolyzed and polymerized very quickly in F-113 forming a white precipitate at room temperature.

3.2. *Surface modification of glass*

3.2.1. *Effect of reaction time*

For glass-surface modification with methoxy-type silane coupling agents, the reaction time needed was 2 h to obtain the highest constant contact angle [3]. From the results of the relation between contact angle and reaction time for isocyanate-type silanes (Fig. 1), a reaction time of 20 min for glass modification was sufficient. This indicates that the time spent for surface modification using isocyanate-type silane coupling agents is only 1/6 (20 min) by comparison with

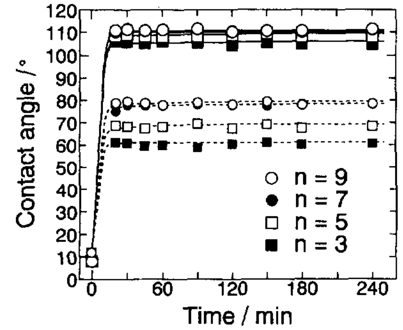

Fig. 1. Relation between the contact angles θ of water (solid line) and oleic acid (dashed line) on the surface-modified glass and the reaction time (min) using 20 mM $CF_3(CF_2)_nCH_2CH_2Si(NCO)_3$. The symbol *n* is the number of CF_2 groups in $CF_3(CF_2)_nCH_2CH_2Si(NCO)_3$ in Figs. 1–4.

that of methoxy-type silanes (120 min). Hence, time shortening for surface modification was accomplished.

3.2.2. *Effect of concentration*

Fig. 2(a) shows the results of contact angle measurements for water and oleic acid on the modified glass surfaces. Fig. 2(b) depicts an enhancement of the low concentration region of Fig. 2(a). To obtain the highest contact angle on glass-surface modification, a 30 mmol dm^{-3} F-113 solution was used for the methoxy-type silane coupling agents [3]. In the case of isocyanate-type silanes, however, only 1/10 concentrations (3 mmol dm^{-3}) were sufficient to permit surface modification of the glass. This indicates that the expensive fluorine-containing compounds could be available economically in the future.

These data also show that contact angles on the modified glass surface were dependent on the fluorocarbon chain length. However, the maximum data for the contact angles of water [$CF_3(CF_2)_9CH_2CH_2Si(NCO)_3$ (4), 113.6°] were slightly less than those for methoxy-type silane coupling agents, i.e. $CF_3(CF_2)_9CH_2CH_2Si(OCH_3)_3$ (118°) [3]. Such contact angle differences were also observed when glass-surface modification was performed using different dilution solution for the silane coupling agent $CF_3(CF_2)_9$-$CH_2CH_2Si(OCH_3)_3$ [17]. For example, values of 118° for F-113, 108° for methanol, 104° for ethanol, 108° for benzene, 108° for hexane, 110° for toluene, 106° for chloroform, etc. were observed. In case of silane coupling agents having different reactive groups such as OCH_3 or NCO, the maximum contact angles of the modified glass surface displayed different values even when the silane coupling agent possessed the same hydrophobic group, e.g. $CF_3(CF_2)_9$-CH_2CH_2–. We are now investigating these phenomena by using atomic force microscopy (AFM), ESCA, and FT-IR spectra measurements.

3.3. *Oxidation resistance of modified glass surface*

Fig. 3 shows the relation between the contact angles θ of water and oleic acid on the oxidized modified glass surface and the time allowed for oxidation in concentrated nitric acid at 100 °C.

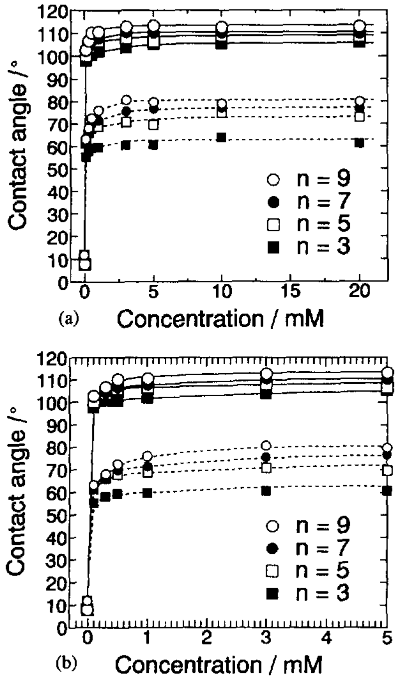

Fig. 2. (a) Relation between the contact angles θ of water (solid line) and oleic acid (dashed line) on the surface-modified glass and the concentration of silane coupling agent. (b) Enhanced low concentration region of Fig. 2(a).

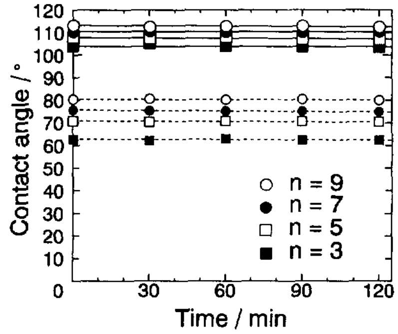

Fig. 3. Relation between the contact angles θ of water (solid line) and oleic acid (dashed line) on the oxidized glass surface and the time allowed for oxidation in hot concentrated nitric acid at 100 °C.

The reduction in the contact angle by oxidation of the glass surface modified with each silane coupling agent was very slight, the difference in the contact angle reduction between 0 min and 120 min being less than 1° in each case (as measured by water and oleic acid). The results show that the oxidation resistance of the glass surface modified with isocyanate-type silane coupling agents having a straight fluorocarbon chain is higher than that with methoxy-type silane coupling agents [ca. 9° for $CF_3(CF_2)_9CH_2CH_2Si(OCH_3)_3$] [2,3].

3.4. *Acid resistance of modified glass surface*

Fig. 4 shows the relation between the contact angles θ of water and oleic acid on the acid-treated modified glass surface

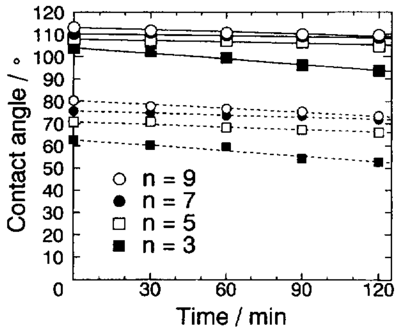

Fig. 4. Relation between the contact angles θ of water (solid line) and oleic acid (dashed line) on the acid-treated glass surface and the time allowed for acid treatment in hot concentrated hydrochloric acid at 100 °C.

and the time allowed for acid treatment in concentrated hydrochloric acid at 100 °C.

The reduction in the contact angle brought about by acid treatment of the glass surface modified with each silane coupling agent was slightly larger than that for oxidation, the difference between the values for 0 min and 120 min being ca. 3° and ca. 7°, respectively, for the glass surface modified with $CF_3(CF_2)_9CH_2CH_2Si(NCO)_3$. In the case of glass modified with $CF_3(CF_2)_3CH_2CH_2Si(NCO)_3$, containing the shortest fluorocarbon chain of all the compounds studied, the difference values for water and oleic acid were ca. 10° and ca. 10°, respectively. These results indicate that the contact angle reduction on the acid-treated glass surface was dependent on the fluorocarbon chain length, the reduction effected by acid resistance on the glass surface modified with isocyanate-type silane coupling agents being slightly inferior to that for oxidation resistance.

4. Conclusions

New four silane coupling agents having a fluorocarbon chain and three isocyanate groups as reactive centers were prepared. The silane coupling agents obtained were stable in dry air. In the presence of water, however, the silanes were very quickly hydrolyzed. In glass-surface modification, time-shortening which is an important factor for dental operation and an economical treatment method for expensive fluorine-containing compounds, was accomplished by the use of the isocyanate-type silane coupling agents. The highest contact angle on the glass surface modified with an isocyanate-type silane coupling agent was obtained employing both a shorter modification time (1/6) and a lower concentration (1/10) of the silane solution in comparison with those of methoxy-type silanes. Glass surfaces modified with the silane coupling agents displayed high water and oil repellency, and the surfaces also had high oxidation and acid resistances.

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