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Water-repellent coating films on glass prepared from hydrolysis and polycondensation reactions of fluoroalkyltrialkoxylsilane

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Abstract

Water-repellent glasses for automotive windows are new glass products in which several kinds of fluoroalkylsilanes are used to modify the surface properties of the glass substrates. We examined the hydrolysis and polycondensation reactions of a fluoroalkyltrimethoxysilane (FAS), $CF_3(CF_2)_7CH_2CH_2Si(OCH_3)_3$, by using gas chromatography, gel permeation chromatography and time-of-flight mass spectroscopy. Dimers, trimers and higher polymerized species of FAS were formed by dehydrating the water-repellent coating solutions after a hydrolysis process. The polymerized species of FAS are preferable for improvement of the durability of the water-repellent glasses. However, the excess polycondensation of FAS deteriorates the abrasion resistance, because of the decrease in the number of silanol groups, which are bound to the glass surface. Therefore, appropriate amounts of the polymerized species of FAS play an important role in improving both the abrasion resistance and the UV-light resistance of the water-repellent glasses. The water-repellent glasses obtained from the dehydrated water-repellent coating solution thus show higher durability than those obtained from the non-dehydrated one.

Keywords: Fluoroalkylsilane; Water-repellent coatings; Hydrolysis; Polycondensation; Dehydration

1. Introduction

Coupling agents such as alkylsilanes and fluoroalkylsilanes are widely used to modify the surface properties of glass. For example, their purposes are for the improvement of the adhesion property between organic compounds and glass substrates and for the addition of new and unique properties onto the glass surface [1–5]. Recently, water-repellent glasses have been produced for automotive windows by using fluoroalkylsilanes and several millions of water-repellent windows have already been installed in actual automobiles [6,7]. The water-repellent glasses are thus the successful new products prepared from fluoroalkylsilanes, because of their high durabilities such as UV resistance, abrasion resistance and chemical resistance.

Fluoroalkylsilanes have coupling groups binding the glass surface and functional groups modifying the surface properties of glass. Therefore, the properties of the glass surface, coupling groups and functional groups are very important for improving the performance of new functional products. Many studies on the preparation conditions for functional products and the structural investigations of fluoroalkylsilanes present on substrates have been reported [8–10]. While there are some reports on hydrolysis and polycondensation reactions of fluoroalkylsilanes [11,12], reports on the influence of polymerization conditions on the durability of water-repellent glasses are hardly found.

In this paper, we examine the hydrolysis and polycondensation reactions of a fluoroalkyltrimethoxysilane (FAS), $CF_3(CF_2)_7CH_2CH_2Si(OCH_3)_3$, by using gas

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chromatography, gel permeation chromatography and time-of-flight mass spectroscopy and discuss the influence of polymerized spices of the hydrolyzed fluoroalkyltrimethoxysilane on the durability of water-repellent glasses.

2. Experimental

2.1. Preparation of water-repellent coating solution

Chemicals grade heptadecafluorodecyltrimethoxysilane, $CF_3(CF_2)_7CH_2CH_2Si(OCH_3)_3$, GE Toshiba Silicone TSL-8233 or Shin-Etsu Chemical KBM-7803, was used as a raw material of water-repellent agents and it is described as FAS in this paper. Nitric acid aqueous solution was used as a source of water and acid catalyst for hydrolysis of FAS. Molecular sieve 4A from Kishida Chemicals was used as a dehydrating agent.

Fig. 1 shows the preparation procedure of water-repellent coating solutions consisting of FAS, water, acid catalyst and 2-propanol. First, FAS (1.0 g, 1.76×10^{-3} mol), water (0.3 g, 1.67×10^{-2} mol) containing 1 mass% nitric acid and 2-propanol (3.7–48.3 g) were mixed and stirred for 2 h at room temperature for hydrolysis of FAS, where the amount of 2-propanol was changed according to the required FAS concentration (2–20 mass%, 2.85×10^{-2}–3.40×10^{-1} mol l^{-1}). Next, the molecular sieve 4A (5.0 g) was added into the mixed solution and allowed to stand for 0–24 h at room temperature. Then the mixed solution was filtered for removal of the molecular sieve, which had previously been added, with a paper No.7 and the water-repellent coating solution was obtained.

2.2. Hydrolysis reaction

The hydrolysis reaction of FAS in the mixed solution consisting of FAS (1.0 g), water (0.3 g) with 0.1, 1.0, 6.0 mass% nitric acid and 2-propanol (23.7 g), where the FAS concentration was 4 mass% (approx. 5.90×10^{-2} mol l^{-1}), was examined by using gas chromatography. At approximately 30-min intervals, approximately 2 μl of the mixed solution was injected. The extent of hydrolysis reaction was indirectly measured by monitoring the volume of methanol generated in the mixed solution. A gas chromatograph, Shimazu GC-14A, was used with a column of Porapak Q (1 m in length) kept at 150°C and with a thermal conductivity detector. The carrier gas was He at a flow rate of 40 ml min^{-1}. The volume of methanol generated was determined by comparing the peak area due to methanol to that due to benzene, which was used as an internal standard material.

2.3. Polycondensation reaction

The water concentration of the mixed solution during the dehydration process was measured with an Aquacounter, Hiranuma AQ-7, which was a coulometric Karl Fischer titrator. The polymerized species of hydrolyzed FAS in the mixed solution after dehydration was measured with a gel permeation chromatograph (GPC), Tosoh HLC-8020. The column of GPC consisted of Tosoh TSK gel types of one G-4000H-HR, one G3000H-HR and two G2000H-HRs (each one, 0.3 m in length), which were connected in series. The detector used was a differential refractometer. The temperatures of the column and the detector were kept at 40 and 38°C, respectively. The mobile phase was tetrahydrofuran, which flowed at a rate of 1 ml min^{-1}. The injected samples were beforehand trimethylsilylated by the Lentz method [13] to avoid further polycondensation of FAS during the GPC measurement and the injected volume was 50 μl. The conditions on the trimethylsilylation were the same for all the experiments, trimethychlorosilane (0.57 g, 5.25×10^{-3} mol) was slowly added into the water-repellent coating solution (5.0 g) with a FAS concentration of 4 mass% (FAS content, approx. 3.55×10^{-4} mol) and stirred at room temperature for 1 h.

The molecular weight of the polymerized FAS species was measured by using a time-of-flight mass spectrometer (TOF-MS), Shimazu KRATOS KOMPACT MALDI series, with a N_2 laser ($\lambda = 337$ nm) as an ionizer.

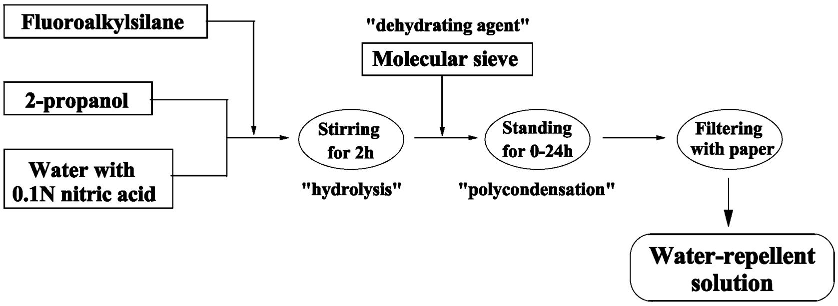

Fig. 1. Preparation procedure of a water-repellent coating solution consisting of FAS, water, acid catalyst and 2-propanol for water-repellent glasses.

2.4. Preparation and characterization of water-repellent glasses

Water-repellent glasses were prepared by coating the water-repellent coating solution on glass substrates, which were polished with cerium oxide and washed thoroughly with water in advance. The coating was carried out by rubbing the glass surface with cotton, moistened with the coating solution obtained (the rubbing method). Next, the coated glasses were heated at 140°C for 10 min and then wiped with a paper towel dampened with 2-propanol.

The characterization of the water-repellent glasses was carried out by measuring the contact angle of a water droplet of approximately 2 μl with a static contact angle meter, Kyowa Interface Science CA-X200, and by measuring fluorine-counts detected with a fluorescence X-ray spectrometer, Rigaku RIX-3000, using the fundamental parameter method [14].

To evaluate the durability of the water-repellent glasses prepared, two kinds of durability tests, a traverse-type abrasion test and a UV-light irradiation test were carried out. The former was performed by rubbing a sample surface with a friction material of canvas cloth referred to JIS L3102-1206 under a load of 0.1 kg cm^{-2}, 3500 times and the latter by irradiating strong UV-light with a power of 76 mW cm^{-2} for 500 h by using an accelerated UV-light irradiation tester, Iwasaki Electric SUV-W11, respectively.

3. Results and discussion

3.1. Hydrolysis reaction of FAS

Fig. 2 shows the molar ratio, MeOH/FAS, of methanol against fluoroalkyltrimethoxysilane as a function of reaction time for hydrolysis of FAS, where the concentration of nitric acid was 0.1 (○) or 6.0 (△) mass%. As described in Eq. (1), the hydrolysis reaction stoichiometrically generated 3 mols of methanol from 1 mol of FAS. Thus, the extent of hydrolysis reaction was indirectly measured by monitoring the molar ratio of methanol generated in the mixed solution by gas chromatograph analysis.

$$Rf\text{-}CH_2CH_2Si(OCH_3)_3 + 3H_2O \rightarrow Rf\text{-}CH_2CH_2Si(OH)_3 + 3\,CH_3OH \quad (1)$$

where *Rf* describes the fluoroalkyl group of $CF_3(CF_2)_7$–.

The volume of methanol generated in the mixed solution increases rapidly with increasing reaction time for both acid concentrations. The hydrolysis reaction under the acid concentration of 6.0 mass% proceeds more rapidly than that of 0.1 mass%. In the former case, more than 2 mols of methanol against 1 mol of FAS have been generated in a few minutes and the molar ratio MeOH/FAS reaches approximately 3.0 in 60–90 min. Even in the latter case, methanol is gradually generated with increasing reaction time and MeOH/FAS reaches 3.0 in 90 min. Therefore, the hydrolysis reaction under the acid catalyst has almost been completed within 90 min, although there is a slight difference depending on acid concentrations at the early stage of hydrolysis reaction. For all the following experiments, the concentration of nitric acid in water used for preparation of the water-repellent coating solution was 1 mass%.

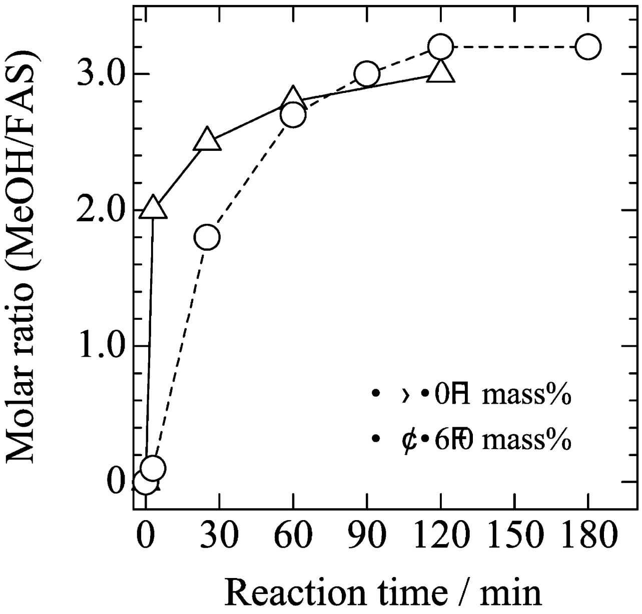

Fig. 2. Molar ratio of methanol to fluoroalkyltrimethoxysilane, MeOH/FAS, as a function of reaction time for hydrolysis of FAS, where the concentration of nitric acid was 0.1 (○) or 6.0 (△) mass% in the water added.

3.2. Water concentration during dehydration process

Fig. 3 shows the water concentration in the mixed solution with a FAS concentration of 4 mass% (approx. 5.90×10^{-2} mol l^{-1}) as a function of time during the dehydration process with molecular sieve 4A as a dehydrating agent. At first, the water concentration is approximately 11 500 ppm, which is almost equal to the value calculated from a batch composition of the mixed solution. By adding molecular sieve 4A, the water concentration rapidly decreases with increasing dehydration time at an early stage and gradually decreases to less than 1000 ppm in 24 h.

As shown in Eq. (2), 2 mols of monomers of hydrolyzed FAS polymerize into 1 mol of dimer and generate 1 mol of water. In the mixed solution, there is a large

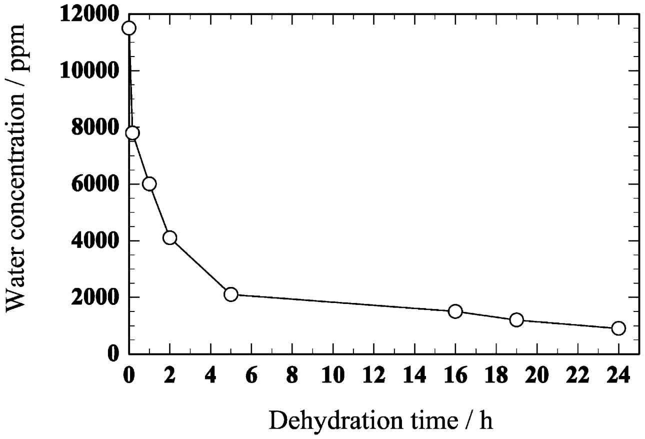

Fig. 3. Water concentration in the water-repellent coating solutions with a FAS concentration of 4 mass% (approx. 5.90×10^{-2} mol l^{-1}) as a function of time during the dehydration process with molecular sieves 4A as a dehydrating agent.

amount of water even after hydrolysis. Under this condition, if water is removed from the mixed solution, the polycondensation reaction between hydrolyzed FAS will proceed more effectively.

$$\text{2 Monomers of FAS-(OH)}_3 \rightarrow \text{Dimer of FAS-(OH)}_2 + H_2O. \qquad (2)$$

To examine whether the polymerized species of FAS are formed or not, measurements by GPC and TOF-MS were carried out in the following section.

3.3. Polycondensation reaction of FAS

Fig. 4 shows the GPC of the trimethylsilylated water-repellent solutions with a FAS concentration of 4 mass% (approx. 5.90×10^{-2} mol l^{-1}) after being dehydrated for 0–18 h. At the dehydration time of zero, two peaks at retention times of 32.5 and 30.7 min are observed. The peak at 30.7 min becomes larger and a new peak at approximately 29.8 min appears with increasing dehydration time. Especially the peak at 29.8 min and the broad band in the earlier retention times, which are due to the higher polymerized FAS, are not observed at the dehydration time of zero and then gradually become stronger with increasing dehydration time. At a dehydration time of 18 h, the broad band at retention times ranging from 27.5 to 30 min is clearly observed, indicating that the polymerized FAS with higher polymerization degrees was formed in the mixed solution during the dehydration process. To estimate the molecular weight for each polymerized FAS, a calibration curve was obtained by measuring chromatograms for standard materials with the known molecular weights under the same measurement conditions as those for the samples. The standard materials used were several kinds of polystyrene with molecular weights ranging from 300 to 400 000. Fig. 5 shows the relationship between the mean molecular weight and the retention time, in which open circles are experimental data and the curve follows a third order equation obtained by a conventional fitting manner as described in Eq. (3);

$$\log M = -1.4147 \times 10^{-3}\, t^3 + 1.2770 \times 10^{-1}\, t^2 - 3.9715\, t + 45.543 \qquad (3)$$

where M is the molecular weight and t the retention time, respectively. Therefore, the molecular weight estimated due to peaks at 32.5, 30.7 and 29.8 min are approximately 600, 1050 and 1400, respectively. Accordingly, those three peaks correspond to the monomer, dimer and trimer of FAS, respectively.

Furthermore, in order to make the above estimation clearer, the TOF-MS measurement was carried out. Fig. 6 shows the mass spectrum of the water-repellent coating solution with a FAS concentration of 4 mass% (approx. 5.90×10^{-2} mol l^{-1}) dried at room temperature for a few minutes after dehydration for 18 h. Four groups, each consisting of several peaks at approximately $m/e = 490$, 1150, 1650 and 2150, are almost periodically observed. For example, the fragments of Rf-$CH_2CH_2Si\equiv$, Rf-$CH_2CH_2SiO=$ and Rf-$CH_2CH_2SiO_2-$ from a monomer of FAS correspond to $m/e = 475$, 491 and 507, respectively. Therefore, the first group with the mass number ranging from $m/e =$ 470 to 510 corresponds to the fragments from FAS monomers. Similarly, the second, the third and the fourth groups on the mass spectrum at approximately $m/e = 1150$, 1650 and 2150 correspond to the fragments from dimers, trimers and tetramers of FAS, respectively. However, in both measurements of GPC

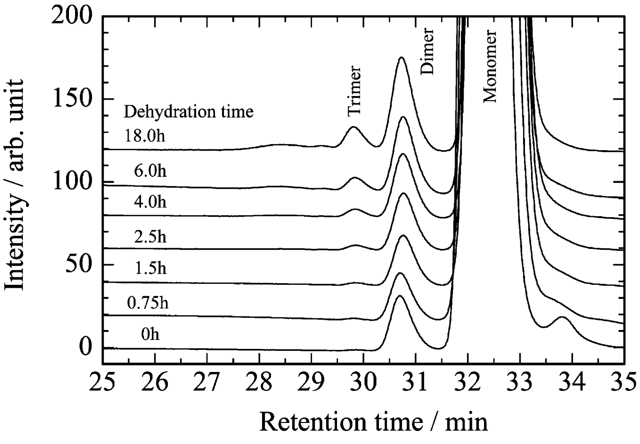

Fig. 4. Gel permeation chromatograms of the trimethylsilylated water-repellent solutions with a FAS concentration of 4 mass% (approx. 5.90×10^{-2} mol l^{-1}) dehydrated for 0–18 h.

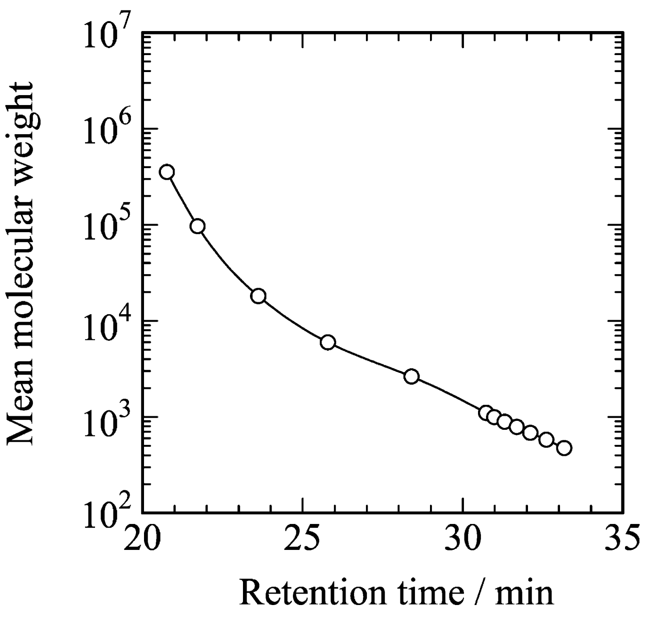

Fig. 5. Relationship between the mean molecular weight and retention time in the GPC measurements.

and TOF-MS, further study is needed to quantitatively discuss about the amounts of each polymerized species in the water-repellent coating solutions. For that quantitative discussion, the progress of the hydrolysis and polycondensation reactions during drying the coating solution should be taken into account.

3.4. Influence of concentration and aging time on polymerization degrees of FAS

Fig. 7 shows the GPC of the trimethylsilylated water-repellent coating solutions prepared with various FAS concentrations ranging from 2 to 20 mass% (2.85 $\times 10^{-2}$–3.40 $\times 10^{-1}$ mol l^{-1}) after dehydration for 18 h. To compare all GPC at the same concentration of FAS, the FAS concentration in the injected solution was adjusted to 2 mass% by adding 2-propanol to the water-repellent coating solutions prepared with various FAS concentrations. With higher FAS concentrations, the peaks due to dimers and trimers become larger. Thus, in the case of FAS concentration of 20 mass%, the peaks at retention time less than 30 min due to the higher polymerized FAS are larger and clearly observed. This indicates that there are tetramers, pentamers and even more polymerized species in the water-repellent coating solutions. On the other hand, with the FAS concentration of 2 mass%, the peaks due to trimers and higher polymerized species are very small, indicating that the polycondensation reaction of FAS does not sufficiently proceed.

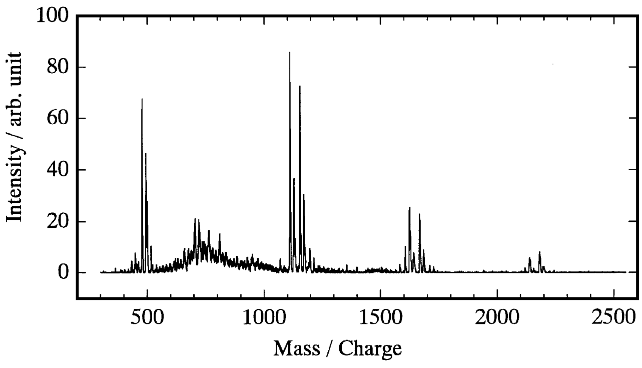

Fig. 6. Time-of-flight mass spectrum of the dried water-repellent coating solution with a FAS concentration of 4 mass% (approx. 5.90 $\times 10^{-2}$ mol l^{-1}) dehydrated for 18 h.

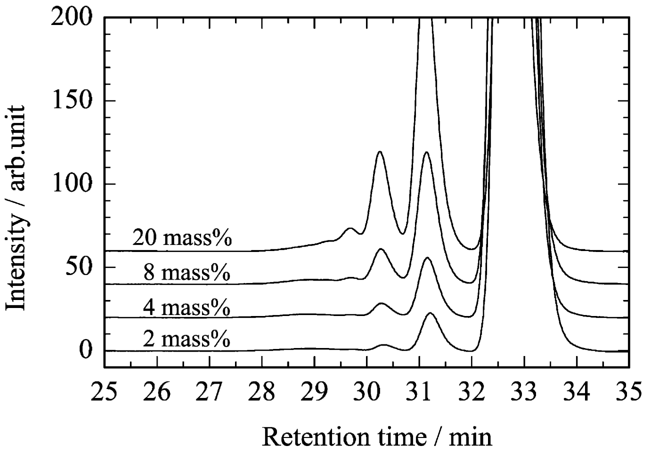

Fig. 7. Gel permeation chromatograms of the trimethylsilylated water-repellent coating solutions with various FAS concentrations ranging from 2 to 20 mass% (2.85 $\times 10^{-2}$–3.40 $\times 10^{-1}$ mol l^{-1}) dehydrated for 18 h.

Fig. 8 shows the GPC of the trimethylsilylated water-repellent coating solutions with a FAS concentration of 4 mass% (approx. 5.90 $\times 10^{-2}$ mol l^{-1}) aged for 0–9 days after dehydration for 18 h and removal of molecular sieve added. The peak due to trimers becomes larger with increasing aging time. Fig. 9 also shows the relationship between the peak area ratio of trimers to dimers and the aging time after preparation of the water-repellent solution, where the peak area ratio is used as a parameter to describe how far the polycondensation reaction of FAS proceeds. The peak area ratio of trimers to dimers increases with increasing aging time, indicating that the polycondensation reaction of FAS still proceeds during storage of the water-repellent coating solutions at room temperature. The water concentrations in the water-repellent coating solutions kept for 0, 3, 6 and 9 days were 660, 1250, 1570 and 2360 ppm, respectively, of which gradual increase was consistent with proceeding of the polycondensation reaction of FAS. The water concentration in the as-prepared water-repellent coating solution was low enough to make the polycondensation reaction of FAS proceed sufficiently.

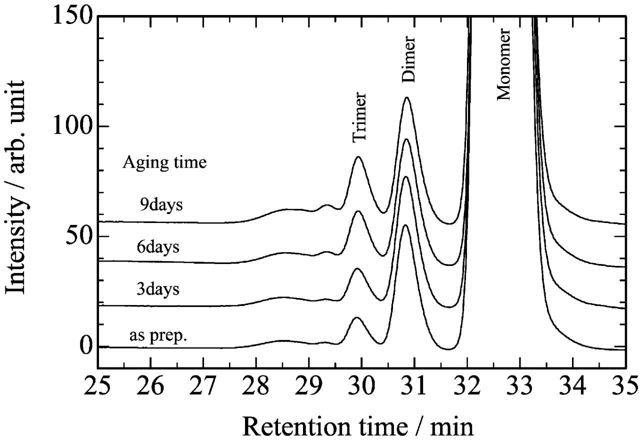

Fig. 8. Gel permeation chromatograms of the trimethylsilylated water-repellent coating solutions with a FAS concentration of 4 mass% (approx. 5.90×10^{-2} mol l^{-1}) aged for 0–9 days after being dehydrated for 18 h followed by the removal of the molecular sieve added.

3.5. Effect of polymerized FAS on durability of water-repellent glass

Fig. 10 shows the effect of the dehydration time on the contact angles after the traverse-type abrasion test of the water-repellent glasses and on the peak area ratio of trimers to dimers of FAS in the water-repellent coating solutions with a FAS concentration of 4 mass% (approx. 5.90×10^{-2} mol l^{-1}). Within approximately 4 h of the dehydration time, the contact angles are still low and widely vary with large fluctuation, indicating that the abrasion resistance is poor for practical uses. On the other hand, at dehydration times of 4 h and more, the contact angles are higher than 100° with much smaller fluctuation and the abrasion resistance of the water-repellent glasses becomes largely improved. At the same time, the peak area ratio of trimers to dimers gradually increases with increasing dehydration time. It can be assumed that the polymerized species of FAS play an important role in improving the abrasion resistance of the water-repellent glasses.

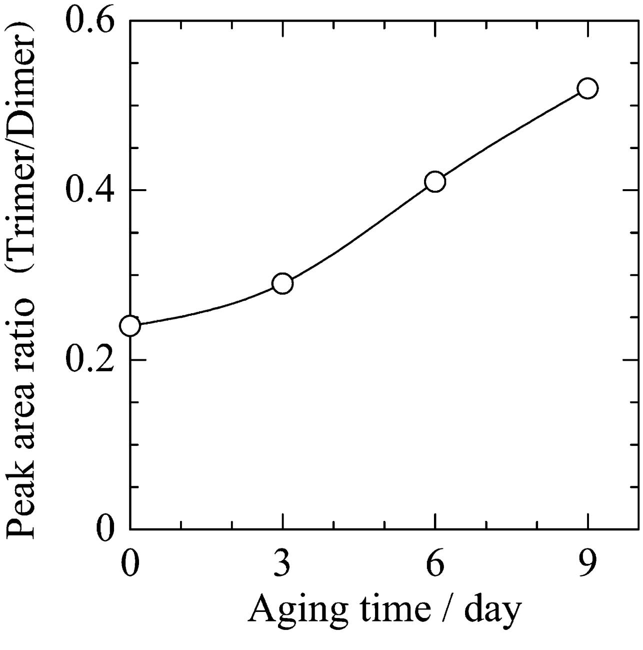

Fig. 9. Relationship between the peak area ratio of trimers to dimers and the aging time after preparation of the water-repellent solution.

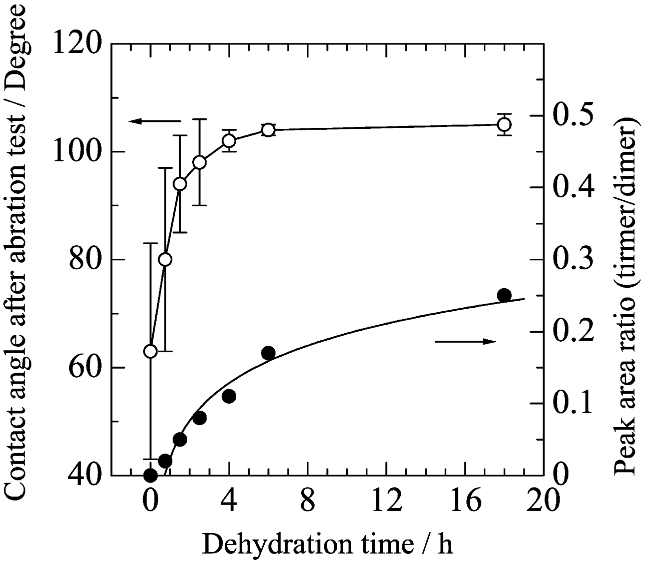

Fig. 10. Effect of the dehydration time on the contact angle after the abrasion test of water-repellent glasses and on the peak area ratio of timers to dimers of FAS in the water-repellent coating solutions with a FAS concentration of 4 mass% (approx. 5.90×10^{-2} mol l^{-1}).

Fig. 11 shows the contact angle after abrasion test of the water-repellent glasses obtained from the water-repellent coating solutions with various FAS concentrations after dehydration for 18 h, of which the peak area ratio of trimers to dimers is also plotted. With lower concentrations of 2 mass% (2.85×10^{-2} mol l^{-1}) and less, the abrasion resistance is very low and gradually improved with increasing FAS concentration. On the other hand, with increasing FAS concentration up to 20 mass% (3.40×10^{-1} mol l^{-1}), the abrasion resistance becomes oppositely lower and the peak area ratio of trimers to dimers increases to approximately 0.52, indicating that the polycondensation reaction of FAS proceeds more effectively. Therefore, an optimum range in the FAS concentration to obtain the appropriate polymerization degrees of FAS for improvement of the abrasion resistance is recognized to be 4–10 mass% (5.90×10^{-2}–1.56×10^{-1} mol l^{-1}).

Fig. 12 shows the contact angle after abrasion test of the water-repellent glasses obtained from the water-repellent coating solutions with a FAS concentration of 4 mass% (approx. 5.90×10^{-2} mol l^{-1}), kept for 0–9 days after dehydration for 18 h and the removal of molecular sieve which had previously been added. As mentioned above, the polymerization degree of FAS became large during aging of the water-repellent coating solution, the peak area ratio of trimers to dimers at 0, 3, 6 and 9 days were 0.24, 0.29, 0.41 and 0.52, respectively. The excess increase of polymerization degrees of FAS results in deterioration of the abrasion resistance of the water-repellent glasses. This effect is also consistent with the result described in Fig. 11.

As another important durability for the water-repellent glasses, the UV-light durability was evaluated. Fig. 13 shows the change in contact angle of the water-repellent glasses obtained from two kinds of the water-repellent coating solutions with a FAS concentration of 4 mass% (approx. 5.90×10^{-2} mol l^{-1}) as a function of irradiation time by UV-light. The symbols of circles and triangles indicate the water-repellent coating solutions with and without dehydration of 18 h, respectively. The UV-light durability of the water-repellent glasses prepared with dehydrated solution is better than the non-dehydrated one, indicating that larger amounts of FAS were fixed on glass substrates in the former case rather than in the latter case. According to quantitative analysis of fluorine present on glass substrates with a fluorescence X-ray spectrum analyzer, the amounts of fluorine fixed on the water-repellent glasses obtained from the dehydrated and non-dehydrated solutions were 0.45 and 0.20 μg cm^{-2}, respectively. The difference between them results from the difference in the polymerization degree of FAS in the water-repellent coating solutions. We can, therefore, expect that the polymerized species of FAS formed by the dehydration process in the water-repellent coating solution were bound to the glass surface and formed the thicker layer by higher polymerized species of FAS, while FAS monomer tends to be thinner one just as a single layer on it. The number of FAS on the glass surface can be calculated from the amounts of fluorine measured by the fluorescence X-ray spectrum analysis. Therefore, the amount of fluorine of 0.45 μg cm^{-2} corresponds to approximately eight or nine hydrolyzed FAS in a unit area of nm^2. Moreover, the maximum number of FAS occupied geometrically with a single layer on the glass surface can be also calculated from the occupied area with one FAS of approximately 0.164 nm^2, which corresponds to the area occupied with three oxygen's of FAS ($= 3 \times 3.14 \times (0.264/2)^2$, a distance of O–O in a unit of SiO_4 tetrahedron, 0.264 nm). The maximum number of FAS in a single layer is approximately six FAS in a unit area of nm^2, which is smaller that that of the result for the water-repellent glass from the dehydrated solution. Therefore, the thickness of the FAS layer on the glass surface is thicker than that of a single layer.

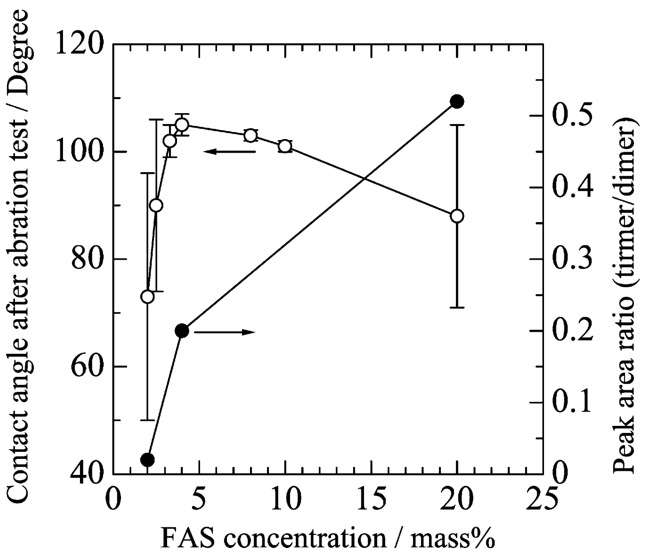

Fig. 11. Contact angle after the abrasion test of the water-repellent glasses obtained from the water-repellent coating solutions with various FAS concentrations after being dehydrated for 18 h, of which the peak area ratio of trimers to dimers is also plotted.

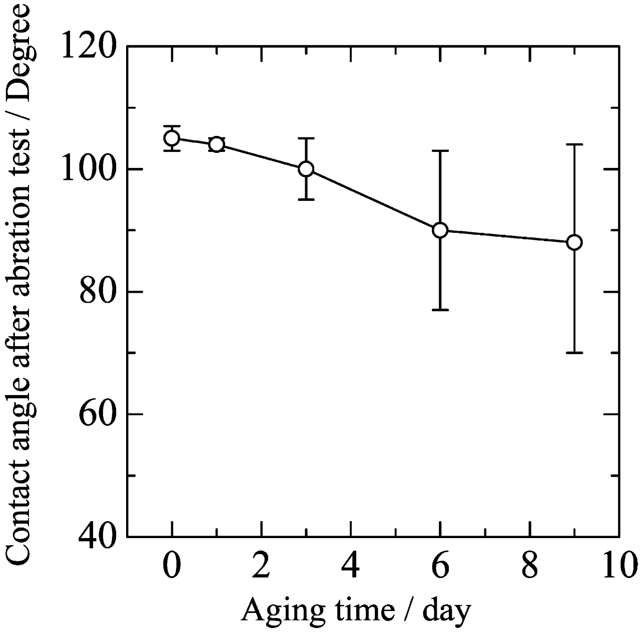

Fig. 12. Contact angle after the abrasion test of the water-repellent glasses obtained from the water-repellent coating solutions with a FAS concentration of 4 mass% (approx. 5.90×10^{-2} mol l^{-1}), kept for 0–9 days after being dehydrated for 18 h followed by the removal of the molecular sieve which had previously been added.

However, as described in Figs. 11 and 12, the excess polymerization degree of FAS leads to deterioration of the abrasion resistance of the water-repellent glasses, because the excess polycondensation of hydrolyzed FAS decreases the number of silanol groups which bind the glass surface. Therefore, an appropriate range of polymerization degrees of FAS is needed to obtain high durability of the water-repellent glasses. For example, the appropriate value of the peak area ratio of trimers to dimers, which is one of the parameters to indicate the polymerization degree of FAS in the water-repel-

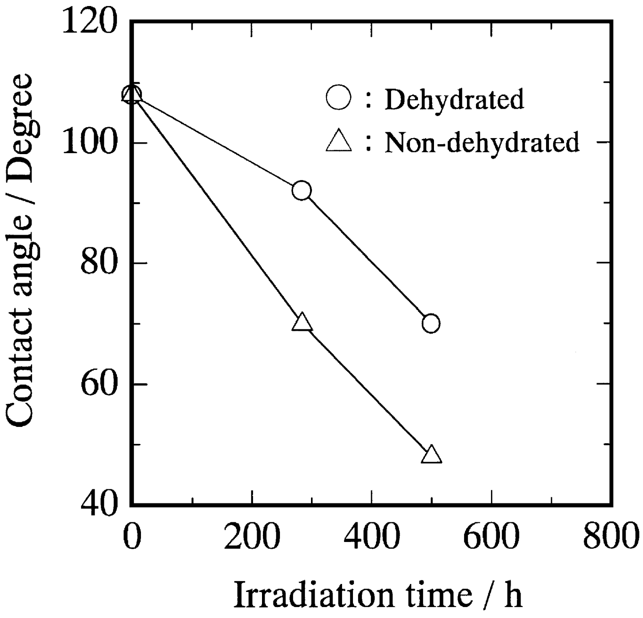

Fig. 13. Change in contact angle for the water-repellent glasses obtained from two kinds of the water-repellent coating solutions with a FAS concentration of 4 mass% (approx. 5.90×10^{-2} mol l^{-1}) as a function of irradiation time by UV-light.

lent coating solutions, ranges from 0.2 to 0.3. In this range, the water-repellent glasses obtained from the dehydrated water-repellent coating solutions show better abrasion resistance and UV-light resistance than those obtained from the non-dehydrated one.

4. Conclusions

We have investigated the hydrolysis and the polycondensation reactions of fluoroalkyltrimethoxysilane, $CF_3(CF_2)_7CH_2CH_2Si(OCH_3)_3$, which is widely used for the water-repellent glasses in an automotive field, by gas chromatography, gel permeation chromatography and time-of-flight mass spectroscopy. Furthermore, the effect of the polymerized FAS on the durability of the water-repellent glasses was examined. The following conclusions were obtained.

1. The hydrolysis reaction of FAS under an acid catalyst was almost completed within 90 min, although there was a slight difference depending on the acid concentration at the early stage of the reaction.
2. The polycondensation reaction of FAS proceeded efficiently during the dehydration of the water-repellent coating solutions with molecular sieve and dimers, trimers and higher polymerized species of FAS were gradually formed during the dehydration process.
3. The polymerized FAS played an important role in improving both the abrasion resistance and the UV-light resistance of the water-repellent glasses and an appropriate range in the polymerization degree of FAS was recognized. For example, the optimum value of the peak area ratio of trimers to dimers in GPC measurements, which was one of the parameters to indicate the polymerization degree of FAS in the water-repellent coating solutions, ranged from 0.2 to 0.3.
4. The polymerized FAS in the water-repellent coating solutions are fixed on the glass surface in the thicker layer, while FAS monomer in a single-layered structure on it. The former (dehydrated) one was preferable for improvement of the durability of the water-repellent glasses than the latter (non-dehydrated) one. However, the excess polycondensation of FAS deteriorated the abrasion resistance because of the decrease in the number of silanol groups by polycondensation, which were bound to the glass surface.

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References

[1] E.P. Plueddemann, J. Adhes. 2 (1970) 184.
[2] B. Arkles, Chem. Tech. 7 (1977) 766.
[3] L. Netzer, R. Iscovici, J. Sagiv, Thin Solid Films 99 (1983) 235.
[4] N. Mino, K. Ogawa, Thin Solid Films 230 (1993) 209.
[5] N. Yoshino, A. Sasaki, T. Seto, J. Fluorine Chem. 71 (1995) 21.
[6] Y. Akamatsu, S. Yamazaki, K. Makita, H. Inaba, Y. Kai, Proceedings of the XVIII International Congress on Glass, E9, 23, San Francisco, USA, 1998.
[7] T. Yoneda, T. Morimoto, Reports Research Laboratory, Asahi Glass Co., Ltd. 48 (1998) 83.
[8] Y. Hayashi, T. Yoneda, K. Matsumoto, J. Ceram. Soc. Jpn. 102 (1994) 206.
[9] N. Yoshino, Y. Yamamoto, K. Hamano, T. Kawase, Bull. Chem. Soc. Jpn. 66 (1993) 1754.
[10] N. Yoshino, Chem. Lett. (1994) 735.
[11] K. Smith, J. Org. Chem. 51 (1986) 3827.
[12] K. McNeil, J. DiCarpio, D. Walsh, R. Pratt, J. Am. Chem. Soc. 102 (1980) 1859.
[13] C.W. Lentz, Inorg. Chem. 3 (1964) 574.
[14] J.W. Criss, L.S. Birks, Anal. Chem. 40 (1968) 1080.