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Surface Modification of Denture to Provide Contamination-Free Ability by Using Silane Coupling Agent Containing Fluorocarbon Chain

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Silane coupling agent containing fluorocarbon chain, (1H,1H,2H,2H-henicosafluorododecyl)trimethoxysilane, was applied for the surface modification of some dental materials. The contact angles of water and oleic acid on the modified material surfaces were increased. The modified denture teeth worn in an oral cavity displayed a long-range stain-protecting ability.

In general, silane coupling agents to promote surface modification and/or adhesion are the most familiar example of the R_nSiX_{4-n} (n=1, 2, and 3) class of organosilane materials having two types of substituents where R is a nonhydrolyzable organic group that may be relatively inert in one case such as a hydrocarbon radical, or may be reactive to particular organic systems in the other case. The X functionality is a hydrolyzable group, often an alkoxyl group.[1)]

Previously, we reported the syntheses of four silane coupling agents, (1H,1H,2H,2H-polyfluoroalkyl)-dimethoxy(methyl)silanes, and another four silane coupling agents, (1H,1H,2H,2H-polyfluoroalkyl)-trimethoxysilanes, as well as the surface modification of glass plate using these coupling agents.[2,3)] High modification ability of the silane coupling agents and high oxidation resistance ability of the modified glass surface against nitric acid were observed. These results were confirmed by measuring the contact angles on the modified glass surface and the oxidized glass surface with water and oleic acid. In regard to water and oil repellency on the modified glass surface, (1H,1H,2H,2H-henicosafluorododecyl)trimethoxysilane displayed the highest ability, and the largest contact angles of water on the modified glass surface exhibited 118°. This contact

angle was larger than that of poly(tetrafluoroethylene) (110°).[4] The glass surface modified with this coupling agent also displayed the highest oxidation resistance.[3]

In this paper, we tried to modify the surface of some dental materials using (1H,1H,2H,2H-henicosafluorododecyl)trimethoxysilane; the contact angles of the modified surfaces were measured with water and oleic acid. On the basis of these results, we applied the silane coupling agent for the surface modification of a denture to provide stain-protecting ability. The ability was observed by wearing the denture in an oral cavity and normally using it for four months.

First, (1H,1H,2H,2H-henicosafluorododecyl)trimethoxysilane, $C_{10}F_{21}C_2H_4Si(OCH_3)_3$, was prepared as described previously.[3] The dental materials used were a composite material of UDMA polymer containing SiO_2 filler (ca. 32 wt%) for artificial teeth use (the surface was ground #1200) (**1**), PMMA resin for denture base use (ground #1200) (**2**), a composite material of UDMA polymer containing SiO_2 filler (ca. 84 wt%) for restorative use (ground #1200) (**3**), a porcelain tooth (fused finish) (**4**), human enamel (ground #1500) (**5**), and human root dentin (ground #1500) (**6**). These dental materials except for **5** and **6** were obtained from Shofu Co. Ltd. (Kyoto). Human teeth were obtained from patients with periodontal disease and ground. Surface modification of the dental materials was allowed to react with the silane coupling agent at a concentration of 30 mM (1 M = 1 mol dm^{-3}) 1,1,2-trichloro-1,2,2-trifluoroethane (F-113) solution by dipping for 1 h at room temperature. The surface-modified dental materials were rinsed with fresh F-113 and water, and allowed to stand overnight in atmosphere at room temperature. The contact angles of water and oleic acid were measured against these dental materials. The contact angles θ(°) were measured using 1.0×10^{-6} dm^3 of water and oleic acid drops at 23 °C. These angles were evaluated by extrapolating to time zero from a plot of the advancing contact angle vs. time.[5] These data are shown in Table 1.

Table 1. Contact angles θ(°) of water and oleic acid on dental materials

Materials	Water		Oleic acid	
	Untreated	Treated	Untreated	Treated
1	74.7	114.0	2.5	48.3
2	72.0	103.3	6.5	36.7
3	62.3	110.6	4.5	65.3
4	48.0	114.3	12.5	69.7
5	36.3	98.7	11.0	74.7
6	33.3	107.7	12.0	82.3

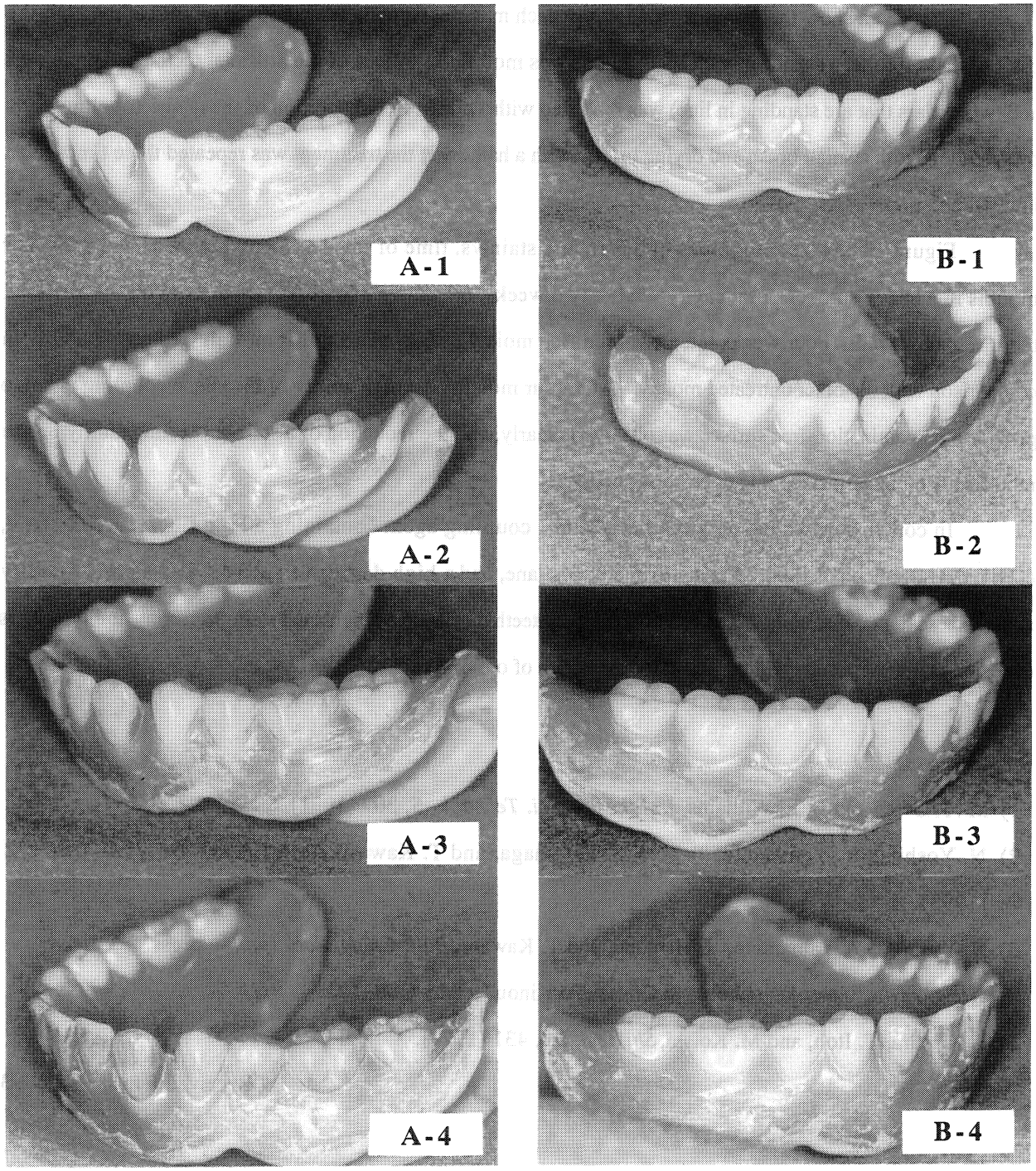

Fig. 1. Photographs of advancing stain vs. time of denture worn in heavy smoker's oral cavity: A-1; untreated (0 h), A-2; untreated (two weeks), A-3; untreated (four weeks), A-4; untreated (four months), B-1; treated (0 h), B-2; treated (two weeks), B-3; treated (four weeks), and B-4; treated (four months).

These data show that the contact angles in each material were increased by the modification. On the basis of these results, a sufficiently cleaned denture was modified. A part of the artificial teeth (two premolars and two molars that are standing in line) was modified with 1.5 mM F-113 solution of the silane coupling agent by spreading with a small brush and drying briefly with a hair drier; the treatment was repeated three times in an interval of 5 min.

Figure 1 shows photographs of advancing stain vs. time of the denture, which was worn for four months in a heavy smoker's oral cavity. After two weeks, no remarkable difference in stain on the artificial teeth was observed. Four weeks later, the modified moiety displayed a significant stain-protecting ability in comparison with the other untreated moiety. After four months, the high ability of the silane coupling agent to provide a contamination-free surface was observed clearly, and the reduction of a stain-protecting ability on the modified denture surface could not be confirmed yet.

In conclusion, we have found that a silane coupling agent containing a long fluorocarbon chain, (1H,1H,2H,2H-henicosafluorododecyl)trimethoxysilane, had a high degree of surface modification ability against these dental materials. The modified denture teeth displayed a heightened stain-protecting ability. It is expected that these results will be useful for the health of our oral cavity.

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