Original paper

Effects of Polysiloxane Coating of NaF on the Release Profile of Fluoride Ion from Bis-GMA/TEGDMA Resin Containing NaF

Satoshi NAKABO, Yasuhiro TORII, Toshiyuki ITOTA, Masahiro YOSHIYAMA, Kunio ISHIKAWA1 and Kazuomi SUZUKI1
Department of Operative Dentistry, 1Department of Biomaterials, Okayama University Dental School
2-5-1 Shikata, Okayama 700-8525, Japan

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The aim of this study was to regulate fluoride release from restorative resin containing NaF using N-(β-aminoethyl)-γ-aminopropylmethyldimethoxysilane (AMMS) and evaluate factors that regulate fluoride release from the resin. ESCA analysis, FT-IR measurements along with SEM observations demonstrated that a polysiloxane layer was formed on the surface of NaF treated with AMMS. Bis-GMA/TEGDMA resin containing NaF powder treated with AMMS released lower concentrations of fluoride for longer periods when compared with that containing untreated NaF. However, AMMS treatment of NaF was less effective for the regulation of fluoride released from the resin than γ-methacryloxypropyltrimethoxysilane (γ-MPTS) treatment, despite its higher hydrophobic polysiloxane layer formation. These findings may have been caused by the higher density of polysiloxane prepared with γ-MPTS than that prepared with AMMS. The present findings suggested, therefore, that alkoxysilane should be chosen based not only on hydrophobicity but also the density of polysiloxane to effectively regulate fluoride release from the restorative resin containing NaF.

Key words: Fluoride release, Resin, Regulation

INTRODUCTION

Prevention of caries is an important goal of dentistry. Although mouth rinsing with fluoride solution, tooth brushing with toothpaste containing fluoride and topical fluoridation of teeth at dental clinics are recommended by dentists, one of the drawbacks of these treatments is that the tooth would be exposed to fluoride for only a limited period. Low and constant levels of fluoride are required to effectively suppress the occurrence of caries1. In addition, it was suggested that low and constant levels of fluoride are effective in preventing the occurrence of secondary caries2-5. Furthermore, with respect to remineralization of incipient carious lesions, a slow and sustained release of fluoride is recognized as more beneficial than periodic high-concentration fluoride applications6. Release of fluoride from sealant or restorative materials is one of the ideal ways to allow low and constant levels of fluoride release. Basically fluoride would be released from the resin simply by loading fluoride into the resin. However, regulation of the rate of fluoride release is difficult since the kind of fluoride which can be used in the oral cavity is limited. Sodium fluoride (NaF) is one of the fluoride compounds commonly used and approved for use in the
oral cavity. However, the solubility of NaF is very high. Therefore, the resin rapidly releases fluoride ions and results in significant decreases of its physical properties with time if NaF is simply loaded into the resin\(^7,8\). We previously reported that release of NaF from bis-GMA/TEGDMA resin could be regulated by coating NaF powder with a hydrophobic polysiloxane layer\(^9\). The bis-GMA/TEGDMA resin containing NaF without hydrophobic polysiloxane coating released a high concentration of fluoride ions for a short period. In contrast, the bis-GMA/TEGDMA resin containing NaF that was coated with a hydrophobic polysiloxane layer released fluoride ions at a lower concentration for a longer period.

In our previous study, we coated NaF powder with a polysiloxane layer using \(\gamma\)-methacryloxypropyltrimethoxysilane (\(\gamma\)-MPTS). We chose \(\gamma\)-MPTS among many alkoxysilane compounds since \(\gamma\)-MPTS is commonly used in dental products as a silane coupling agent. There are many alkoxysilane compounds with different properties. Thus, the polysiloxane layer formed on the surface of NaF will be regulated by simply changing the type of alkoxysilane compound. One of the alkoxysilanes commonly used in industry is aminoalkoxysilane prepared from \(N\)-(\(\beta\)-aminoethyl)-\(\gamma\)-aminopropylmethyldimethoxysilane (AMMS) because it forms polysiloxane that has an active amino site in its structure.

In the present study, therefore, we chose AMMS for formation of the polysiloxane layer and evaluated the release of fluoride ions from bis-GMA/TEGDMA resin containing NaF to further clarify the possible usefulness of the hydrophobic polysiloxane layer as a regulating device of fluoride release.

**MATERIALS AND METHODS**

*Treatment of NaF with \(N\)-(\(\beta\)-aminoethyl)-\(\gamma\)-aminopropylmethyldimethoxysilane (AMMS)*

NaF (Wako, Osaka, Japan), acetic acid (Wako), ethanol (Wako) and AMMS (Shin-Etsu Chemical, Tokyo, Japan) were obtained commercially and used without further purification. Various amounts of AMMS and 99.5% ethanol were mixed and 99.7% acetic acid was added into the solution so that the concentration of acetic acid became 1 wt%. The solution was allowed to hydrolyze for 30 minutes followed by addition of an equal amount NaF powder. For the formation of a polysiloxane layer on the surface of the powder, the suspension was exposed to air to allow evaporation of ethanol. Some of the NaF powder further received heat treatment at 130°C for 24 hr.

*Analysis of NaF powder treated with AMMS*

The surface of NaF powder treated with AAMS was analyzed with an S-Probe ESCA (SSX-100S, Fisons Instruments, East Grinstead, UK) equipped with an Al K\(\alpha\) source. The analysis was performed under the following conditions; a vacuum reading of \(10^{-8}\)–\(10^{-9}\) Torr, spot size of 250×100 mm\(^2\), flood gun reading energy of 5 eV and pass energy of 50 eV. Energy calibration was effected with reference to carbon C 1S
A high-resolution spectrum of Si 2P was determined to assess the bonding environments surrounding the Si atoms. For the decomposition of spectra, curve fitting with a Gaussian function supplied with the S-Probe ESCA was performed.

To further identify the coat formed on the surface of the NaF powder, NaF powder treated with AMMS was immersed in distilled water to dissolve NaF. The distilled water was replenished several times to dissolve and remove NaF completely. For the SEM observation, the vacuum-dried powder was gold-coated using an ion coater (JFC-1100E, JEOL, Tokyo, Japan) and subjected to SEM (DS-720, Topcon, Tokyo, Japan) observation. For the FT-IR measurement, the vacuum-dried powder was mixed with KBr (E. Merck, Darmstadt, Germany) so that the concentration of powder became approximately 0.5 wt%, and was pressed to prepare transparent KBr disks. Then the disks were subjected to FT-IR (FTIR-8300, Shimadzu, Kyoto, Japan) measurement.

For the qualification of hydrophobicity of NaF powder treated with AMMS, the contact angle was measured. The contact angle of each compacted NaF powder was measured using a sessile drop technique. Five specimens were tested in each group.

The density of the polysiloxane formed using AMMS or γ-MPTS was measured as follows. In brief, the solution mixed with 65 wt% AMMS or γ-MPTS solution, 99.5% ethanol and 1 wt% acetic acid was allowed to hydrolyze for 30 min at room temperature and heated at 130°C for 24 hr to obtain bulk polysiloxane. The density was measured based on Archimedes method using a specific gravity bottle (Shibata, Tokyo, Japan).

Fluoride-release from the bis-GMA/TEGDMA resin

Bis-GMA (Shin-nakamura, Wakayama, Japan), TEGDMA (Wako), camphor quinone (Wako), 2-(dimethylamino)ethyl methacrylate (Wako) and 2,6-di-t-butyl-4-methylphenol (Wako) were obtained commercially and used without further purification. A experimental resin consisting of 49 wt% bis-GMA, 49 wt% TEGDMA, 0.98 wt% camphor quinone, 0.98 wt% 2-(dimethylamino)ethyl methacrylate and 0.04 wt% 2,6-di-t-butyl-4-methylphenol was prepared. The resin will be called bis-GMA/TEGDMA resin in the following text for simplicity. Then the 50 wt% of NaF powder treated with various concentrations of AMMS were mixed with bis-GMA/TEGDMA resin. A mixture of NaF powder and bis-GMA/TEGDMA resin was poured in a plastic splitting mold with a diameter of 6.0 mm and thickness of 2.5 mm. Both sides of the splitting mold were clamped with slide glass and cured using a light-curing unit (Visilux2, 3M Co., St. Paul, MN, USA) from both sides for 80 s each. The specimens were kept in an incubator at 37°C and 100% relative humidity for 24 hr, and both surfaces of the specimens were ground flat with 1000-grit silicon carbide paper.

The specimens thus prepared were placed in plastic vessels that contained 5 mL distilled water at 37°C. Distilled water in the vessels was exchanged every week and retained for measurement of the fluoride concentration. The fluoride concentration
in the retained solution was measured using an ion meter (290A, Orion Research) equipped with a fluoride specific electrode (Orion 9609BN, Orion Research).

RESULTS

Fig. 1 shows typical SEM images of NaF powders before and after AMMS treatment and the remnant powder obtained when NaF powder treated with AMMS was immersed in water. We observed no significant change in the appearance of NaF powder before and after AMMS treatment. When we added NaF powders before and after AMMS treatment to water, the former dissolved completely but the latter did not, at least within 24 hr. The SEM image of the remnant powder revealed that the particles were shell like.

![Fig. 1 Scanning electron micrographic images.](image)

(a) NaF powder before AMMS treatment; (b) NaF powder after 10 wt% AMMS treatment; (c) remnant powder obtained when NaF powder treated with 10 wt% AMMS was immersed in distilled water. Scale bar=2 μm.

![Fig. 2 Infrared spectra.](image)

(a) AMMS; (b) remnant powder obtained when the NaF powder treated with 10 wt% AMMS receiving heat treatment was immersed in distilled water.
Fig. 2 shows the FT-IR spectra of AMMS (Fig. 2-a) and the remnants obtained when the NaF powder treated with AMMS was immersed in distilled water (Fig. 2-b). Although the remnants showed spectra similar to AMMS, the new absorption band at 1040 cm⁻¹, attributed to Si-O-Si, was determined, in addition to that at 1080 cm⁻¹ attributed to Si-O-C. These findings indicated that polysiloxane compound was formed on the surface of NaF due to AMMS treatment.

Fig. 3 shows high-resolution spectra of Si 2p of NaF powder after treatment with AMMS. The spectra showed an asymmetric peak and could be decomposed into two peaks at 100.12 eV and 101.47 eV when curve fitting was performed. The peak at 100.12 eV, attributed to Si-O-C, and the peak at 101.47 eV was attributed to Si-O-Si, which was consistent with the finding of FT-IR spectra.

Fig. 4 summarizes the contact angles of the disks compacted with NaF powder treated with various concentrations of AMMS with and without heat treatment. The contact angles of NaF powder treated with γ-MPTS in the presence of heat treatment are also shown for comparison. The contact angle of the disks of the NaF treated with 1 wt% AMMS powder significantly increased. The NaF powder treated with AMMS in the presence of heat treatment showed a larger contact angle when
compared with that in the absence of heat treatment regardless of the concentration of AMMS. Also, the NaF powder treated with AMMS showed a higher value than that treated with γ-MPTS, indicating that AMMS treatment formed a polysiloxane layer of higher hydrophobicity.

Table 1 summarizes the density of alkoxysilane, γ-MPTS and AMMS, and polysiloxane prepared from each alkoxysilane. The density of polysiloxane was higher than that of the corresponding alkoxysilane. In addition, the density of γ-MPTS and polysiloxane prepared from γ-MPTS was higher than AMMS or polysiloxane prepared from AMMS.

<table>
<thead>
<tr>
<th>Alkoxysilane</th>
<th>Density (g/cm³)</th>
<th></th>
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</thead>
<tbody>
<tr>
<td></td>
<td>Liquid</td>
<td>Polysiloxane*</td>
</tr>
<tr>
<td>γ-MPTS</td>
<td>1.04</td>
<td>2.07</td>
</tr>
<tr>
<td>AMMS</td>
<td>0.97</td>
<td>1.14</td>
</tr>
</tbody>
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*Polysiloxane was formed with heat treatment at 130°C for 24 hr.

Fig. 5 Cumulative amounts of fluoride release from bis-GMA/TEGDMA resin containing AMMS treated NaF powder with heat treatment. Cumulative amounts of fluoride released from bis-GMA/TEGDMA resin containing γ-MPTS treated NaF powder with heat treatment reported in our previous study (Nakabo et al., in press) are shown for comparison. □: no treatment, ○: 1 wt% AMMS treatment, △: 5 wt% AMMS treatment, ◇: 10 wt% AMMS treatment, •: 1 wt% γ-MPTS treatment, ▲: 5 wt% γ-MPTS treatment, ●: 10 wt% γ-MPTS treatment.
Fig. 5 shows cumulative amounts of fluoride released from bis-GMA/TEGDMA resin containing NaF powder treated with various concentrations of AMMS. During AMMS treatment, NaF powder received heat treatment in this case. Fluoride release from bis-GMA/TEGDMA resin containing NaF powder treated with γ-MPTS is also shown for comparison in Fig. 5. As shown, the resin containing NaF powder without AMMS treatment released the largest amount fluoride. However, the amounts of fluoride released from the resin markedly decreased with time. In contrast, smaller amounts of fluoride were released from the resin containing NaF treated with higher concentrations of AMMS at least until 30 weeks. The bis-GMA/TEGDMA resin containing NaF treated with AMMS released larger amounts of fluoride than that containing NaF treated with γ-MPTS.

Fig. 6 shows cumulative amounts of fluoride released from bis-GMA/TEGDMA resin containing NaF powder treated with various concentrations of AMMS when no heat treatment was performed during AMMS treatment. Fluoride released from bis-

Fig. 6 Cumulative amounts of fluoride release from bis-GMA/TEGDMA resin containing AMMS treated NaF powder without heat treatment. Cumulative amounts of fluoride released from bis-GMA/TEGDMA resin containing γ-MPTS treated NaF powder without heat treatment reported in our previous study (Nakabo et al., in press) are shown for comparison. □: no treatment, ○: 1 wt% AMMS treatment without heat, △: 5 wt% AMMS treatment without heat, ◇: 10 wt% AMMS treatment without heat, ●: 1 wt% γ-MPTS treatment without heat, ◆: 5 wt% γ-MPTS treatment without heat, ⊙: 10 wt% γ-MPTS treatment without heat.
GMA/TEGDMA resin containing NaF powder treated with γ-MPTS is also shown for comparison in Fig. 6. Basically fluoride released from bis-GMA/TEGDMA resin containing AMMS treated NaF without heat treatment was similar to that with heating during AMMS treatment. However, fluoride released from bis-GMA/TEGDMA resin containing AMMS treated NaF powder without heat treatment was faster when compared with the corresponding finding in Fig. 5. In other words, fluoride ions were released for longer periods from bis-GMA/TEGDMA resin containing AMMS treated NaF with heat treatment. However, fluoride release was regulated more effectively when NaF was treated with γ-MPTS than AMMS regardless of the alkoxysilane concentration or the presence or absence of heat treatment.

DISCUSSION

The findings obtained in the present study along with those obtained in our previous study demonstrated clearly that hydrophobic polysiloxane coating of NaF was very effective for the regulation of fluoride release from bis-GMA/TEGDMA resin. Although the bis-GMA/TEGDMA resin containing untreated NaF released high concentrations of fluoride, most fluoride loaded into the resin was released within 10 weeks. In contrast, the resin containing NaF treated with AMMS or γ-MPTS released lower concentrations of fluoride at least until 30 weeks. In other words, the resin containing NaF treated with 10 wt% AMMS or γ-MPTS still contained approximately 6 and 23 wt% fluoride in the resin even after 30 weeks, respectively. Thus, the duration of the fluoride release period from the resin will be significantly extended based on the formation of a hydrophobic polysiloxane layer. However, the rate of fluoride release from the bis-GMA/TEGDMA resin containing treated NaF powder depended on the origin of the hydrophobic polysiloxane layer. In other words, the bis-GMA/TEGDMA resin containing NaF powder treated with AMMS released fluoride ions at relatively higher concentrations for shorter periods when compared with NaF powder treated with γ-MPTS. The mechanism of fluoride release from the resin containing fluoride compound involves the penetration of water into the resin, resulting in the dissolution of the fluoride compound and diffusion of fluoride to outside the resin. In addition, diffusion of water becomes slower in a more hydrophobic matrix. When the NaF compound was treated with alkoxysilane, the NaF would be coated with hydrophobic polysiloxane; this resulted in slow water penetration around the NaF and slow fluoride release from the resin. However, the bis-GMA/TEGDMA resin containing NaF treated with AMMS released fluoride faster than that containing NaF treated with γ-MPTS when compared with the same alkoxysilane concentration even though NaF treated with AMMS showed a larger contact angle, i.e. higher hydrophobicity than NaF treated with γ-MPTS. These contradictory findings may have been because the hydrophobicity of the siloxane layer was not the sole factor but one of the factors that regulated the diffusion of water in the matrix. Another important factor regulating the diffusion of water in the matrix may be the density of the matrix. If the matrix is dense, water is difficult to diffuse whereas water can
diffuse easily if the matrix is not dense$^{13,14}$. When the densities of AMMS and γ-MPTS were compared, γ-MPTS showed a larger density than AMMS as shown in Table 1, which may have been due to the existence of the branch methyl group in the AMMS. In addition, the methacryl group of γ-MPTS could polymerize and form a denser matrix$^{15}$. In fact, the density of the polysiloxane prepared from γ-MPTS was 2.07 g/cm$^3$ whereas that prepared from AMMS was 1.14 g/cm$^3$.

Although it was suggested that both the hydrophobicity and density are important factors for the regulation of water diffusion in the matrix, it appeared that the density of the polysiloxane played a more dominant role when compared with the polysiloxane coating prepared from AMMS and γ-MPTS. Heat treatment during the AMMS treatment contributed to increase both the hydrophobicity and the density of polysiloxane coating. Therefore, heat treatment was recommended during the NaF treatment with alkoxysilane compound.

In conclusion, we found that we should choose alkoxysilane based not only on the hydrophobicity but also the other factors including the density of the polysiloxane to effectively regulate the release of fluoride from the resin. Constant and durable fluoride release without decreasing other physical properties may not be so easy, further studies are awaited based on the findings obtained in the present study since prevention of secondary caries is definitely beneficial to patients.

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