Effect of fluoride addition on the properties of dental alginate impression materials

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Fluoride-containing dental alginate impression materials can exert a considerable reduction in enamel solubility. The objective was to evaluate the effects of fluoride addition in the alginate impression materials on the properties and subsequent release of fluoride. Four experimental alginate impression materials were studied. Materials were mixed with distilled water (control) or 100-ppm fluoride solution. One or two percent NaF, or 1% SnF_2 was added to the materials, which were mixed with distilled water. Fluoride release, flexibility, recovery from deformation, setting time, compressive strength and elastic modulus were determined in accordance with the ISO 1563 and ANSI/ADA Spec. 18. Fluoride release increased after addition of fluoride, and the released amount was 0.762–14.761 ppm. Addition of NaF or SnF_2 resulted in higher fluoride release than the control group ($p < 0.05$). After fluoride addition, flexibility was 15.45–20.27%, and the recovery from deformation did not change except one material. Compressive strength after fluoride addition was 0.36–1.12 MPa. Addition of NaF or SnF_2 in an alginate impression material may result in effective release of fluoride without deteriorating the properties of material itself.

1. Introduction

The caries preventive effect of fluoride is mainly attributed to the effects on demineralization/remineralization at the tooth and oral fluid interface. Sub ppm levels of fluoride in saliva are effective in shifting the balance from demineralization, leading to caries, to remineralization. This is attributed to the fluoride-enhanced precipitation of calcium phosphates, and the formation of fluorhydroxyapatite in the dental tissues [1]. Research questions for the future perspectives for dental fluoride applications should be found in the retention and slow release of fluoride after various combinations of fluoride treatment and the combination of fluoride and antimicrobial treatment [1].

A predominant part of the cariostatic activity of fluoride is a function of its concentration in the fluid environment around the tooth. The fluoride exposure results in a slightly elevated steady-state level of fluoride in the oral fluids, primarily in saliva and plaque fluid. Following fluoride intake, fluoride remained in the oral cavity is diluted by the saliva pool. It is well-established that plaque, after fluoride exposure, becomes a fluoride reservoir, which stores for some time and releases fluoride [2].

A variety of fluoride releasing products designed for topical use are currently available. Following their use, a varied amount of fluoride is systemically absorbed depending on the fluoride concentration and the manner of its use. Pharmacokinetic data should, therefore, form part of the basis for the optimal and safe use of fluoride products [3].

The addition of fluoride compound in dental alginate impression materials was shown to produce a firmer and more definite set, and the surface condition of the stone cast improved [4, 5]. It is well-known that some commercial alginate impression materials contain high concentration of fluoride, part of which is readily transferred to the surface of tooth, saliva and plaque fluid after impression taking. Fluoride containing alginate impression materials have been shown to exert a considerable reduction in enamel solubility [6, 7]. Therefore, alginate impression material is a generally unrecognized source of fluoride in the oral cavity. An experimental alginate impression material was tested as a vehicle for topical application of 1% fluoride. The material was mixed with water and the resulting mass was topically applied to rat's teeth for 5 min twice a week for 8 weeks. As a result, the treatment induced a significant reduction in caries scores [8]. Commercial alginate impression materials contained 0.44–1.87% fluoride, and the final fluoride concentration in the mixture was about 0.13–0.50%. Therefore, the use of alginate-based materials as a vehicle for topical application of fluoride offers a valuable means of increasing the enamel resistance against acid demineralization [9]. So far, however, little is known on the

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fluoride release from alginate impression material in which fluoride was added to deliver effective level of fluoride, and the effect of fluoride addition on the properties of alginate materials.

The objective of this study was to evaluate the effects of fluoride addition in experimental dental alginate impression materials on the fluoride release, flexibility, recovery from deformation, setting time and compressive properties.

2. Materials and methods

2.1. Preparation of alginate impression materials

Four experimental compositions of alginate impression materials were prepared. The ingredient materials are listed in Table I, and the compositions are given in Table II. Two kinds of sodium alginate were used; the viscosity of 1 wt/vol % aqueous solution at 20 °C of one was 300–400 cp which was used in WM3 and WM4, and that of the other was 500–600 cp which was used in WH3 and WH4. The composition of WM3 and WH3, and that of WM4 and WH4 were the same except for the viscosity of the sodium alginate.

Experimental alginate impression materials were mixed with a ball mill (YJB-10, Young Hana, Korea) for 4 h at 160 rpm to obtain homogeneous mixture. Then the mixed powder was sieved with a No. 140 standard sieve. Mixing of the impression materials with water or fluoride solutions was performed with a vacuum-mixing machine (Combination unit, Whip-mix, USA) for 10 s. Mixing ratio was 5 g of powder with 12 ml of water or fluoride solutions.

Four methods of fluoride addition were employed. The addition methods are listed in Table III.

2.2. Methods

Fluoride release, flexibility, recovery from deformation, setting time and compressive properties were determined in accordance with the ISO Specification 1563 and the ANSI/ADA Specification 18 [10, 11].

Fluoride release was measured *in vitro*. Specimen was made by pouring the mixed material into Teflon mold (6 mm in diameter and 2 mm in height). The set specimens were placed in polyethylene tube (three specimens per tube) containing 3 ml of distilled water. The tube was sealed and placed on a shaker (LSB-0455, Daihan, Korea) for 5 min at 120 rpm. After removing the specimen, the leached solution was mixed with TISAB buffer (Lot. BB51, pHoenix Electrode Company, USA) by the ratio of 1 : 1 for 20 s with a minishaker (MS1, IKA Works, Malaysia). TISAB buffer was composed of 1.4% acetic acid, 8.2% sodium acetate, 5.8% sodium chloride, 0.4% *trans*-1, 2-diamino cyclohexane tetra-acetic acid (CDTA) and water. The fluoride concentration was measured with an ion-specific electrode (Fluoride Ion Electrode, pHoenix Electrode Company, USA) and a pH/ion meter (DP-880 M, Dongwoo Medical, Korea) at 20–23 °C. The fluoride concentration was determined from a standard curve of 0.1, 0.5, 1.0, 5, 10 and 20 ppm fluoride prepared in distilled water.

Flexibility was measured according to the ISO 1563 (6.6 Strain in compression), and recovery from deformation was measured according to the method in 6.5 clause of the same Specification.

Setting time was measured according to the ANSI/ADA Specification No 18 (6.4 Initial Setting Time). After filling the mold with mixed material, an end of the poly (methylmethacrylate) test rod was placed into momentary contact with the unset material. The test rod was withdrawn, and was cleared of any material left from the contact. The contact/withdrawal steps were

TABLE I Ingredient materials

Material	Batch No.	Manufacturer
Borax	S9101281	Shinyo, USA
Calcium sulfate	111090	Sigma, USA
Diatomaceous earth	04531KU	Sigma, USA
Magnesium oxide	20922-3	Yakuri, USA
Potassium chloride	M9301283	Shinyo, USA
Sodium acetate	311147	Yakuri, USA
Sodium alginate (high viscosity; 500–600 cp)	KSF1417	Wako, Japan
Sodium alginate (medium viscosity; 300–400 cp)	ELN4168	Wako, Japan
Sodium fluoride	820842	Shinyo, USA
Sodium fluoride	820842	Shinyo, Japan
Sodium phosphate	03126BS	Sigma, USA
Sodium silicofluoride	1E4073	Junsei, Japan
Stannous fluoride	H2N5C Q23	Sigma, USA
Zinc fluoride	04727MU	Sigma, USA
Zinc oxide	2G1587	Junsei, Japan

TABLE II Composition of experimental alginate impression materials

Code	Sodium alginate	Calcium sulfate	Diato-maceous earth	Borax	MgO	KCI	Sodium acetate	Na_3PO_4	ZnF_2	ZnO
WM/H3*	11.4	11.6	65.7	1.9	1.9	1.9	1.9	2.0	1.9	—
WM/H4	11.4	11.6	65.7	1.9	1.9	—	1.9	2.0	1.9	1.9

*In WM, sodium alginate of which the viscosity of 1 wt/vol % aqueous solution at 20 °C was 300–400 cp was used, and in WH 500–600 cp was used.

TABLE III Methods of fluoride addition

Group	Fluoride addition
Gr. 1	Mix with distilled water (Control)
Gr. 2	Mix with 100-ppm fluoride solution
Gr. 3	Add 1% NaF to the material
Gr. 4	Add 2% NaF to the material
Gr. 5	Add 1% SnF_2 to the material

repeated until the rod separated cleanly from the material.

Compressive properties were measured by the ISO 1568 (6.7 Compressive strength) with a universal testing machine (Instron 4465, England). Elastic modulus was determined from the stress–strain curve.

2.3. Statistical analyses

Differences in the fluoride release, flexibility, recovery from deformation, and compressive properties by the method of fluoride addition were analyzed by ANOVA and Scheffe's multiple range tests (SPSS 7.0, SPSS, USA, $p = 0.05$).

3. Results

3.1. Fluoride release

Fluoride release before and after fluoride addition are in Table IV and Fig. 1. In the control group (Gr. 1), the released fluoride was 0.438–0.702 ppm. In the test groups (Gr. 2–5), the amount was 0.762–14.761 ppm, which was varied by the material and the method of fluoride addition ($p < 0.05$). Mixing the materials with 100-ppm fluoride solution (Gr. 2) resulted in no significant increase in fluoride release compared with Gr. 1 ($p > 0.05$). Adding 1% or 2% NaF resulted in higher fluoride release regardless of the composition of materials ($p < 0.05$).

3.2. Flexibility, recovery from deformation and setting time

These properties are summarized in Table V. After adding fluoride to WM3, flexibility was 15.45%–19.43%, which was within the range of the Specification (5%–20%). Recovery from deformation was reduced, and setting time was shortened after fluoride addition.

After adding fluoride to WM4, flexibility was 16.52%–18.51%. Recovery from deformation and setting time were not changed significantly compared with Gr. 1 ($p > 0.05$).

After adding fluoride to WH3, flexibility remained within the range of the Specification except for Gr. 2. Recovery from deformation was not changed significantly; however, setting time was shortened significantly ($p = 0.05$).

After adding fluoride to WH4, flexibility remained within the range of the Specification except for Gr. 2. Recovery from deformation and setting time were not changed compared with Gr. 1 ($p > 0.05$).

3.3. Compressive properties

Compressive properties are in Table VI. After adding fluoride to WM3, the compressive strength was 0.690–1.137 MPa, which was higher than the lower limit of the Specification (0.35 MPa). In the cases of WM4, WH3 and WH4, similar trends to those of WM3 were found. Elastic modulus of Gr. 4 was reduced significantly in all four materials ($p < 0.05$).

4. Discussion

Fluoride compounds are fundamental ingredients of alginate impression material. Fluoride salts accelerate the setting reaction of gypsum products, and aid in the production of a hard stone cast surface [5]. Fluoride concentration of commercial alginate impression materials ranged from 0.86% to 3.5%, whereas the fluoride content of the most popular topical fluoride gels was 1.23% or less [12]. Therefore, an unexpected source of fluoride to which many dental patients are exposed is alginate impression procedure. The high concentrations of fluoride in alginate impression materials can result in substantial elevation of fluoride in body fluid and surface enamel [3].

To determine the efficacy of fluoride in alginate impression material, volunteers received alginate impressions and APF gel applications during separate visits. As a result, significant increases in salivary, urinary, and enamel fluoride concentrations were observed following APF gel applications, but only in whole saliva following alginate impressions [13]. In the aforementioned report, the efficacy of fluoride in alginate impression material was doubted. However, in other reports, fluoride-containing alginate materials were tried for topical or subcutaneous application of fluoride, and the use of alginate impression material as a fluoride vehicle was advocated [8, 9]. Fluoride contents of ten alginate impression materials in powder form were found

TABLE IV Fluoride release (ppm) from the fluoride-added alginate impression materials

Code	Control (Gr. 1)[a]	100 ppm-F (Gr. 2)	1% NaF (Gr. 3)	2% NaF (Gr. 4)	1% SnF_2 (Gr. 5)	DG[b]
WM3	0.702 (0.023)[c]	1.381 (0.125)	10.120 (1.852)	14.371 (1.033)	3.462 (0.319)	1.2 < 5 < 3.4
WM4	0.652 (0.063)	1.876 (0.284)	10.457 (0.980)	13.168 (1.652)	7.917 (1.196)	1.2 < 5 < 3.4
WH3	0.438 (0.010)	0.762 (0.054)	11.867 (2.600)	14.761 (1.507)	6.808 (0.230)	1.2 < 5 < 3.4
WH4	0.441 (0.039)	0.892 (0.132)	13.932 (1.793)	12.592 (1.980)	6.771 (0.250)	1.2 < 5 < 4.3

[a]Gr. is used in DG section.
[b]DG; Different groups and '' < '' means significantly different group marker from the Scheffe's multiple comparison test ($p < 0.05$).
[c]Standard deviations are in parentheses.

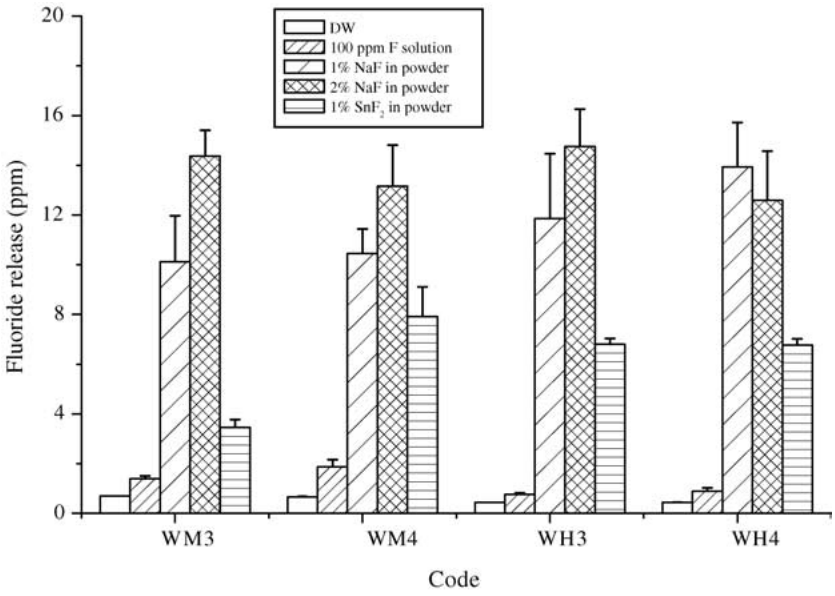

Figure 1 Fluroide release from the experimental alginate impression materials.

TABLE V Flexibility (%), recovery from deformation (%) and setting time (minutes)

Code		Control (Gr. 1)[a]	100 ppm-F (Gr. 2)	1% NaF (Gr. 3)	2% NaF (Gr. 4)	1% SnF_2 (Gr. 5)	DG[b]
WM3	FX[c]	12.75 (1.11)[d]	19.43 (2.45)	15.45 (1.81)	15.64 (1.42)	19.22 (2.27)	1 < 5.2
	RD	94.03 (0.10)	92.76 (0.18)	93.18 (0.36)	93.33 (0.24)	93.29 (0.18)	2.3.5.4 < 1
	ST	2.92 (0.22)	1.92 (0.29)	2.03 (0.31)	2.33 (0.14)	2.19 (0.25)	2.3.5 < 1
WM4	FX	19.20 (1.32)	18.51 (2.09)	17.04 (1.53)	16.52 (1.07)	18.39 (1.98)	N.S.[e]
	RD	93.69 (1.80)	92.98 (0.03)	93.00 (0.16)	92.19 (0.45)	91.80 (2.26)	N.S.
	ST	1.79 (0.08)	1.83 (0.15)	1.92 (0.20)	1.89 (0.38)	1.92 (0.17)	N.S.
WH3	FX	17.73 (2.28)	20.24 (2.02)	17.34 (2.07)	17.91 (1.52)	18.48 (2.69)	N.S.
	RD	93.09 (0.55)	94.28 (2.31)	93.24 (0.29)	92.43 (0.32)	92.76 (0.24)	N.S.
	ST	3.25 (0.69)	1.92 (0.22)	2.25 (0.10)	1.88 (0.25)	2.06 (0.25)	4.2.5.3 < 1
WH4	FX	18.45 (0.93)	20.27 (2.45)	18.87 (1.05)	19.62 (0.90)	17.73 (0.84)	N.S.
	RD	93.45 (0.71)	92.56 (0.36)	92.82 (0.39)	92.57 (0.18)	93.37 (0.69)	N.S.
	ST	1.88 (0.21)	1.92 (0.20)	2.08 (0.32)	1.92 (0.23)	2.00 (0.26)	N.S.

[a]Gr. is used in DG section.
[b]DG; Different groups and '' < '' means significantly different group marker from the Scheffe's multiple comparison test ($p < 0.05$).
[c]FX means flexibility, RD means recovery from deformation and ST means setting time.
[d]Standard deviations are in parentheses.
[e]No significantly different groups.

TABLE VI Compressive strength (MPa) and elastic modulus (MPa) of experimental alginate impression materials

Code		Control (Gr. 1)[a]	100 ppm-F (Gr. 2)	1% NaF (Gr. 3)	2% NaF (Gr. 4)	1% SnF_2 (Gr. 5)	DG[b]
WM3	CS[c]	1.261 (0.197)[d]	1.137 (0.127)	0.839 (0.124)	0.690 (0.083)	0.945 (0.109)	4.3 < 2. 4.3.5 < 1
	EM	4.304 (1.167)	3.569 (0.178)	1.553 (0.198)	2.079 (0.383)	2.486 (0.375)	3.4.5 < 2.1
WM4	CS	1.246 (0.098)	1.066 (0.116)	0.788 (0.053)	0.493 (0.170)	1.155 (0.190)	4 < 3 < 2.5.1
	EM	1.211 (0.130)	1.610 (0.398)	1.298 (0.198)	0.928 (0.251)	1.931 (0.610)	4 < 5
WH3	CS	1.053 (0.145)	0.867 (0.083)	0.703 (0.116)	0.457 (0.049)	1.059 (0.117)	4 < 2.3 < 1.5
	EM	1.861 (0.263)	1.191 (0.027)	1.376 (0.263)	1.082 (0.340)	1.397 (0.461)	4 < 1
WH4	CS	1.013 (0.262)	0.807 (0.100)	0.618 (0.074)	0.488 (0.037)	0.921 (0.175)	4 < 5.1. 3 < 1
	EM	1.272 (0.096)	1.356 (0.333)	1.556 (0.023)	0.732 (0.116)	1.491 (0.451)	4 < 5.3

[a]Gr. is used in DG section.
[b]DG; Different groups and '' < '' means significantly different group marker from the Scheffe's multiple comparison test ($p < 0.05$).
[c]CS means compressive strength and EM means elastic modulus.
[d]Standard deviations are in parentheses.

to range from 0.44% to 2.42%, and the bioavailability of fluoride from the alginate was about 55% of the total fluoride in the administered dose. Accidental ingestion of alginate raised the plasma fluoride concentration, but it was still far below that reported for fluoride gels [14]. In the present study, the control groups released 0.438–0.702 ppm of fluoride (Table IV, Fig. 1). The released amount is influenced by the surface area to immersion solution ratio, and the ratio in the present study was fixed as 31.4 mm^2/ml. After adding 1% and 2% NaF in the materials, the released amount was increased more than 20-fold. Though the effectiveness of released fluoride in caries prevention should be further studied, the released amount increased significantly ($p < 0.05$). In the present study, fluoride was added by the weight percentage to the impression material. The amounts of released fluoride from 1% NaF added group (Gr. 3) of four materials were significantly higher than those from 2% SnF_2 added group (Gr. 5). There are more fluoride ions in NaF than in the equivalent weight of SnF_2, and this might explain the difference in the amount of released fluoride between sodium and stannous fluoride added groups.

As a method for the continuous supply of fluoride, alginate was implanted subcutaneously. *In vivo* studies on rats, fluoride was continuously released from implanted alginate for up to 3 weeks [15]. This is a new method that can deliver fluoride continuously, and can be applied as a method of fluoride application in a combined fluoride treatment scheme.

Fluoride release of alginate impression materials was determined after soaking materials in water for 24 h, and approximately 6% of the total fluoride leached out [6]. To determine the fluoride release within short time, diffusion coefficient of fluoride-containing materials were measured. As a result, the diffusion coefficient of fluoride from alginate was about 10-fold greater than that of fluoride varnish or fluoride gel. Fluoride was diffused rapidly in the first few minutes, decreased afterward [16]. Therefore, shaking time of 5 min employed in the present study can be justified, and routine alginate impression time of 4–5 min [17] can be regarded as a sufficient time for the fluoride transfer from alginate impression material to tooth. The fluoride contents of alginate powders were about 1.9% and 1.5%, and approximately 6.5% and 5.8% leached out [7]. The results indicated a significant increase in the fluoride concentration of the first enamel layer after both 5 min and 18 h exposure. Due to this diffusion characteristic of alginate, contact time during clinical impression procedures, which is about 4–5 min, may be sufficient to transfer fluoride from alginate impression material to tooth surface. In the present study, addition of fluoride into alginate impression materials resulted in minor changes in mechanical and physical properties. However, the final properties were generally within the range of the Specifications [10, 11], except some materials and methods of fluoride addition. Therefore, addition of fluoride may be an effective method of fluoride delivery. Moreover, intimate contact with alginate impression material and tooth may enhance the fluoride transfer compared with fluoride gels, which are too flowable to contact intimately with tooth.

The efficacy of topical fluoride applications was compared in several studies. The effects of commercial alginate impression materials and fluoride gels on enamel solubility were determined by 4 min topical application on partially demineralized enamel surfaces. Every topically applied material except APF-gel exerted a considerable reduction in enamel solubility ranging between 41.4% and 61.5%, and no simple correlation was found to exist between the fluoride content of these products and their antisolubility effect. This was attributed to the mode of fluoride incorporation and distribution in enamel [9]. Thirty minutes after routine alginate impressions, plasma fluoride levels increased by an average of 2.6 times, and average whole saliva fluoride level at 15 min were over 100 times the average control concentration. The relatively high levels of fluoride in whole saliva following alginate impressions suggested the possibility of significant fluoride uptake by surface enamel [15]. Hattab and Frostell [6] reported that 18-h exposures of human premolars to alginate resulted in an average increase of 620 ppm in surface enamel. In addition to the great variation in the rate of salivary flow between individuals, which may lead to varied fluoride levels following the alginate impression, difference exist between various alginates not only in their fluoride content but also in the type of fluoride salt added [18]. The clinical implications of released fluoride from alginate impression materials should be further studied, especially on the difference of effectiveness by the type of fluoride compound added.

Due to the strong activity of fluoride ions and their affinity to Ca ions, fluoride solutions decomposed silicate cement, very likely by reversing the original setting reaction [19]. As this, fluoride may have some destructive effect on the alginate impression material. Hardened pieces of alginate impression materials were exposed to 2% sodium fluoride solution, and it was found that within a few minutes liquefaction of material was observed. By mixing alginate with a 0.05% sodium fluoride solution instead of water, setting was delayed from 3 to 5 min [19]. In the present study, mixing alginate impression material with 100 ppm-F solution (Gr. 2) resulted in slight but not significant increase in fluoride release (0.438–0.702 ppm versus 0.762–1.876 ppm). Flexibility of Gr. 2 of WH3 and WH4 was 20.24% and 20.27%, respectively, which were slightly higher than the upper limit in the Specification (20%, Table V). Although compressive properties were within the range of the Specifications, mixing alginate impression materials with fluoride solution has no benefit.

If the amount of released fluoride increases after intentional addition of fluoride without changing the properties of alginate impression material, routine alginate impression procedure with fluoride-added material could transfer caries preventive dose of fluoride to tooth surface. In this respect, the results of the present study can be adopted as a valuable tool of fluoride delivery in a combined fluoride treatment scheme. Conclusively, the present study substantiated previous studies on the efficiency of using alginate-based materials as a carrier of fluoride in topical application [6, 7].

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