Original Article

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Fluoride release, rechargeability, and coating retention of surface pre-reacted glass ionomer coating on thermoplastic orthodontic retainers over a 35-day period

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Purpose: This study aimed to evaluate the fluoride releasing and recharging abilities, along with the coating retention of Surface Pre-Reacted Glass-Ionomer (S-PRG) coating on thermoplastic retainer material.

Materials and Methods: Samples were prepared by applying S-PRG paste (PRG Barrier, Shofu) onto orthodontic thermoplastic sheets (Essix A+, Dentsply). Fluoride release and recharge were alternately assessed in 10 coated and 10 non-coated samples over three cycles (each cycle consisted of a 5-day release followed by a 5-day recharge period). Adhesion testing was performed on Days 0 and 35, and surface characteristics were evaluated on Days 0 and 35. Statistical analyses were conducted at a significance level of $p<.05$.

Results: Fluoride release from S-PRG-coated samples was measured over multiple recharging cycles. On Day 1, fluoride release was highest (6.67 ± 1.73 μg/cm²), rapidly decreasing by Day 5. During the first recharging period (Days 6-10), fluoride release peaked at 4.25 ± 1.46 μg/cm² on Day 6, declining to 1.03 ± 0.39 μg/cm² by Day 10. Similar trends were observed in subsequent cycles, with peaks on Days 16 and 26, followed by steady declines. Fluoride levels dropped to low but detectable concentrations on Days 1 and 2 post-recharging (0.19–0.25 μg/cm² on Day 1; 0.07–0.09 μg/cm² on Day 2). Adhesion testing demonstrated no coating removal, indicating excellent coating retention. No changes were observed on the surface of coated samples before and after fluoride tests.

Conclusion: S-PRG paste demonstrates excellent coating retention on the thermoplastic retainer material, excellent short-term fluoride release and rechargeability, and sustained low-level fluoride release, suitable for extended use with periodic fluoride recharging over the 35-day experimental period.

Keywords: clear retainer, fluoride recharging, fluoride releasing, surface pre-reacted glass-ionomer filler (S-PRG filler), thermoplastic

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Introduction

Orthodontic treatment aims to improve dental occlusion, facial aesthetics, and masticatory function, contributing to patients' overall quality of life [1]. However, orthodontic appliances are associated with adverse effects including periodontal disease, root resorption, and dental caries [2]. In particular, enamel demineralization and white spot lesions (WSLs) represent a significant complication, affecting both aesthetics and long-term dental health of orthodontic patients [3-6]. Dental caries is a biofilm-mediated disease driven by acidogenic bacteria, resulting in enamel demineralization under low pH conditions [4, 5, 7, 8].

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Following active orthodontic treatment, thermoplastic clear retainers are widely prescribed due to their aesthetic advantages and patient acceptance [9-11]. These appliances are typically worn for extended periods, making the retention phase clinically significant with respect to caries risk [9, 10]. Unlike fixed appliances, the enclosed design of thermoplastic retainers limits natural salivary clearance and promotes microbial colonization, including cariogenic bacteria [12]. Studies have demonstrated a significant increase in Streptococcus mutans and Lactobacillus counts on tooth surfaces during the retention period, with counts significantly elevated even at 60 days of retainer wear [13]. Clinical case reports have further documented severe enamel demineralization and dental caries developing in patients wearing thermoplastic Essix-type retainers [14]. Despite this recognized risk, compliance-independent caries prevention strategies specifically targeting the retention period remain limited [15-18].

Fluoride remains the cornerstone of caries prevention by enhancing remineralization, inhibiting bacterial activity, and promoting fluorapatite formation [19-22]. Even very low fluoride concentrations (0.014–0.1 ppm) have been shown to significantly reduce enamel demineralization [19, 23]. Therefore, sustained fluoride delivery systems that do not rely on patient compliance have gained increasing attention [24, 25]. A fluoride-releasing thermoplastic retainer material would offer the dual benefit of mechanical tooth position maintenance and passive caries prevention throughout the retention period.

Another material that has shown potential for caries prevention in orthodontic patients is the Surface Pre-Reacted Glass-Ionomer (S-PRG) filler with fluoride releasing and recharging abilities. This filler is produced as the result of an acid-base reaction between polyacrylic acid and fluoroboroaluminosilicate glass. Besides fluoride, S-PRG filler releases ions such as strontium, boron, sodium, aluminum, and silicon dioxide, which contribute to remineralization, pH buffering, and resistance to decay. S-PRG fillers, when incorporated into a range of dental materials such as toothpaste [26] and dental sealants [27], can inhibit tooth demineralization, and can promote the remineralization of early caries lesions [28]. Although these materials differ in formulation from the surface coating evaluated in the present study, they share the same S-PRG-derived ion-release mechanism underlying their anticariogenic effect. Tokunaga *et al.* [24] demonstrated that orthodontic resin containing S-PRG filler showed fluoride release and recharging ability positively correlated with filler concentration, and recommended 30 wt% S-PRG for clinical use.

As the thermoplastic retainers are meant to be used over a prolonged retention phase of 6 months to 1 year which may lead to a positive association with caries incidence [9-11], integrating a fluoride-releasing and rechargeable S-PRG coating onto thermoplastic retainer sheets may offer a clinically meaningful caries prevention approach. Therefore, this study aimed to compare the fluoride releasing and recharging ability, coating retention, and surface quality of a commonly used thermoplastic retainer material with and without an S-PRG coating

Materials and Methods

Sample Preparation

This study employed 10 S-PRG-coated and 10 non-coated thermoplastic polyethylene terephthalate glycol (PETG) sheets (Essix A+, Dentsply Sirona, NC, USA) (Table 1). Thermoforming of both groups was performed under identical parameters, with the sole difference being the PRG barrier coat application.

Table 1 Specifications and composition of the PRG-barrier coating and Essix A+ (PETG) substrate.

Material	Manufacturer	Specifications	Composition	
			Active	Base
PRG Barrier Coat (S-PRG coating)	Shofu Inc., Kyoto, Japan	PN 1786; LOT 012301; Exp. 2025-08-31	• Phosphonic acid monomer • Methacrylic acid monomer • Bis-MPEPP • Carboxylic acid monomer • TEGDMA • Reaction initiator	• S-PRG filler (30% by weight) • Distilled water • Methacrylic acid monomer
Essix A+ (PETG substrate)	Dentsply Sirona, Charlotte, NC, USA	REF 10046; LOT 062480087; PETG, 125 mm	Polyethylene terephthalate glycol-modified (PETG)	

S-PRG-coated specimens were prepared by applying one layer of PRG Barrier Coat (Shofu Inc., Kyoto, Japan) unilaterally onto the inner surface of 1.0 mm thick copolyester thermoplastic sheets (Essix A+, Dentsply Sirona, Sarasota, FL, USA) using a disposable silicone paddle with horizontal strokes. It should be noted that PRG Barrier Coat is intended by the manufacturer for direct application to the tooth surface; its use as a coating on thermoplastic sheets in the present study therefore represents a modified, off-label application. While the coating itself was light-cured following the manufacturer's recommended parameters—10 seconds with a dental LED light-curing unit (440–490 nm, ≥1,000 mW/cm²) in overlapping sections to ensure complete coverage—the substrate and overall application protocol were adapted for the purposes of this study. The coated sheet was then placed with the coating facing downward toward the smooth stainless-steel platform of the pressure thermoforming machine and thermoformed (Biostar, Scheu Dental, Iserlohn, Germany) at 220°C and 6 bar pressure. Specimens were subsequently cleaned in an ultrasonic bath.

The decision to apply and polymerize the S-PRG coating before thermoforming was guided by our pilot studies, which showed that post-thermoforming application resulted in a moist, sticky, and viscous coating that persisted for a week. Similar to the pre-thermoforming application, the coated layer remained moist and sticky following light curing, prior to thermoforming. However, after thermoforming, the coating became completely dry and non-sticky, displaying a visibly scattered pattern. Therefore, we chose the pre-thermoforming application method to ensure complete polymerization and achieve a stable, dry finish post-processing.

Optical and Physical Characteristics of S-PRG-coated Specimens

A visually observable change in optical appearance was noted following PRG Barrier Coat application and thermoforming. While the non-coated specimens remained clear and transparent (Figure 1A), the S-PRG-coated

specimens exhibited a uniform whitish, opaque appearance with reduced light transmission across the coated surface (Figure 1B).

Post-thermoforming thickness was verified at three measurement points (center and two opposing edges) and remained unchanged from pre-thermoforming measurements, as measured using a digital vernier caliper (resolution: 0.01 mm; Mitutoyo, Kawasaki, Japan). Specimens were sectioned into 1×1 cm² squares using sharp scissors.

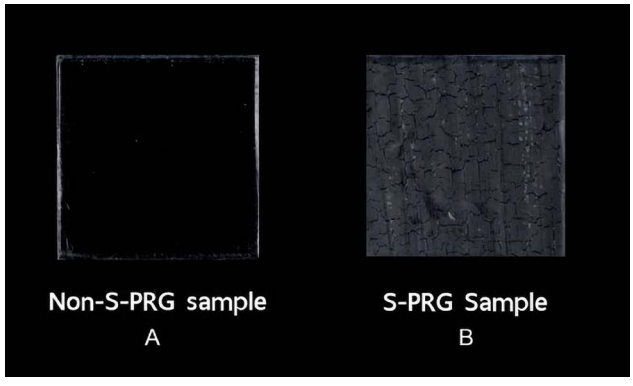


Figure 1 Macroscopic appearance of thermoplastic specimens after thermoforming: (1A) Non-S-PRG-coated specimen showing a transparent surface; (1B) S-PRG-coated specimen showing increased opacity following PRG Barrier Coat application and thermoforming. Both specimens are 1×1 cm² flat PETG sheets (Essix A+, 1.0 mm).

Fluoride Releasing and Recharging Ability Testing

Ten 1x1 cm² square samples were cut from S-PRG-coated and non-coated thermoplastic sheets. The fluoride release and recharging protocol was adapted from Tokunaga *et al.* [24], which was in turn modified from Kamijo *et al.* [25], with the modification of three recharging cycles instead of one. Fluoride release was tested by immersing the samples in 3 mL of non-ionized water at 37°C, with daily water changes for 5 days, alternating with a 5-day fluoride recharge period. During recharging, samples were immersed in 3 mL of a commercially available 1,000 ppm sodium fluoride solution (Thermo Fisher Scientific, Waltham, MA, USA) for 8 hours, followed by immersion in non-ionized water for 16 hours. After the third recharge cycle, samples were immersed in non-ionized water for 5 days. During each water change, samples were cleaned with ultrasonic cleaning for 1 minute, rinsed with deionized water, and stored in deionized water at 37°C to simulate intraoral temperature conditions. The 8-hour recharge followed by 16-hour immersion within each 24-hour interval was adopted from the source protocol [19, 21] and was selected to approximate a clinically realistic daily exposure pattern, in which a fluoride-recharging agent (e.g., a fluoride mouthrinse or gel) contacts the retainer for a limited period each day, while the appliance remains in a predominantly aqueous oral environment for the remaining hours. Fluoride measurements were taken at the end of each 24-hour interval to capture the cumulative amount released over that day.

Fluoride ion measurements were taken from Day 1 - Day 35 using a calibrated fluoride electrode (Orion Versastar Pro, Thermo Fisher Scientific, MA, USA) using 1/10 TISAB III (Orion Ionplus, Thermo Fisher Scientific, MA, USA) as the ion selective electrode, with a detection limit of 0.02 ppm (0.06 μg/cm^2) or less.

Adhesion Testing (Days 0 and 35)

Coating adhesion was evaluated using the cross-cut tape test according to American Society for Testing and Materials (ASTM) D3359-22 Standard Test Methods for Measuring Adhesion by Tape Test (Table 2). This standard assesses the adhesion of coating films to a substrate by applying a cross-hatch lattice pattern, removing

the cut area with a pressure-sensitive tape, and rating the proportion of coating detached on a 0B-to-5B visual scale, where 5B indicates no coating removal and 0B indicates removal of more than 65% of the coating. Test Method B (the cross-cut method) is applicable to coating films up to 125 µm thick and requires two sets of eleven parallel cuts made perpendicular to one another, producing a uniform lattice grid where a cut spacing of 1 mm is used for coatings up to 50 µm thick and 2 mm for coatings between 50 and 125 µm.

In the present study, 10 S-PRG-coated thermoplastic specimens were tested at Day 0 and Day 35 using Test Method B. Eleven parallel cuts were made in each of two perpendicular directions through the coating to the substrate using a cutting guide, producing a uniform 10×10 cross-cut grid of 100 squares. A strip of transparent film tape (3M Scotch Transparent Film Tape 600, 3M Company, St. Paul, MN, USA) was applied firmly over the grid and removed rapidly at a 180° angle after 90 seconds. A new tape strip was used for each test, and the coating adhesion was rated according to the classification scale in Table 2.

Table 2 Adhesion rating scale and assessment criteria based on ASTM D3359-22.

Rating	Percentage (%)	Description	Operational Criteria (Assessment Method)
5B	0%	Edges of cuts are completely smooth	Visual estimation of the cross-cut area under standardized lighting; tape-strip (pressure-sensitive tape) applied and removed per ASTM D3359; grade assigned by consensus of two independent assessors.
4B	Less than 5%	Minor flaking of coating at intersections	Visual estimation of detachment at lattice intersections after tape removal; tape-strip assessment per ASTM D3359; grade confirmed by consensus of two independent assessors.
3B	6-15%	Minor flaking of coating along edges and intersections	Visual estimation of detachment along cut edges and intersections after tape removal; tape-strip assessment per ASTM D3359; grade confirmed by consensus of two independent assessors.
2B	16-35%	Flaking along edges and parts of squares	Visual estimation of the affected lattice area after tape removal; tape-strip assessment per ASTM D3359; grade confirmed by consensus of two independent assessors.
1B	36-65%	Significant flaking along edges, with large ribbons and entire squares detaching	Visual estimation of the proportion of detached lattice squares after tape removal; tape-strip assessment per ASTM D3359; grade confirmed by consensus of two independent assessors.
0B	More than 65%	Flaking and detachment more severe than 1B	Visual estimation confirming detachment exceeding the 1B threshold after tape removal; tape-strip assessment per ASTM D3359; grade confirmed by consensus of two independent assessors.

Qualitative Surface Assessment (S-PRG-coated sample at Day 0, 35 and Non-S-PRG-coated sample)

The surfaces of 1x1 cm^2 thermoplastic sheet samples were analyzed at different stages: immediately after S-PRG coating (Day 0), on the 5^{th} day after the 3^{rd} fluoride recharging cycle (Day 35), and on non-S-PRG-coated sample. Scanning electron microscopy (SEM) in backscattered electron mode was used (JSM-6610LV, JEOL Ltd., Tokyo, Japan) to enhance the differentiation of surface composition.

Statistical Analysis

Sample size was determined based on a pilot study using the same coating material and protocol (29). Using the mean fluoride release on the first day of the initial recharging cycle (Day 6) in the S-PRG-coated group (mean ± SD: 5.51 ± 1.01 μg/cm^2) as the primary outcome, a sample size of 9 specimens per group was calculated to achieve 80% statistical power at a two-sided significance level of $\alpha = 0.05$, assuming a minimum detectable difference of 1.5 μg/cm^2. The sample size was therefore set at 10 specimens per group to account for potential specimen loss during the 35-day experimental period. Statistical analyses were carried out using the Statistical Package for Social Sciences software (SPSS version 23.0, IBM Corp., NY, USA). Normality was assessed using the Shapiro–Wilk test.

T-tests of unequal variance were used to determine if there were any significant differences in the amount of fluoride ions detected between S-PRG-coated and non-coated groups during recharging cycles.

A one-way repeated measures ANOVA was conducted to compare the amount of fluoride released by the S-PRG-coated groups on the 1^{st} (Day 6, 16, 26), 2^{nd} (Day 7, 17, 27), 3^{rd} (Day 8, 18, 28), 4^{th} (Day 9, 19, 29), and 5^{th} (Day 10, 20, 30) days of the 1^{st}, 2^{nd}, and 3^{rd} recharging periods, as well as on the 1^{st} (Day 11, 21, 31) and 2^{nd} (Day 12, 22, 32) days after each recharging period. All pairwise contrasts were tested, and Tukey's Honestly Significant Difference (HSD) test was used for multiplicity.

Results

Optical and Physical Characteristics

Following PRG Barrier Coat application and thermoforming, the S-PRG-coated specimens showed a uniform whitish, opaque appearance with reduced light transmission, in contrast to the clear, transparent non-coated specimens (Figure 1). This change in opacity was consistent across all coated specimens, with no visually detectable color change or yellowing over the 35-day experimental period. Post-thermoforming thickness, measured at three points (centre and two opposing edges), remained unchanged from the pre-thermoforming measurements, with all specimens maintaining a thickness of 1.00 mm.

Fluoride Releasing and Recharging Ability Testing

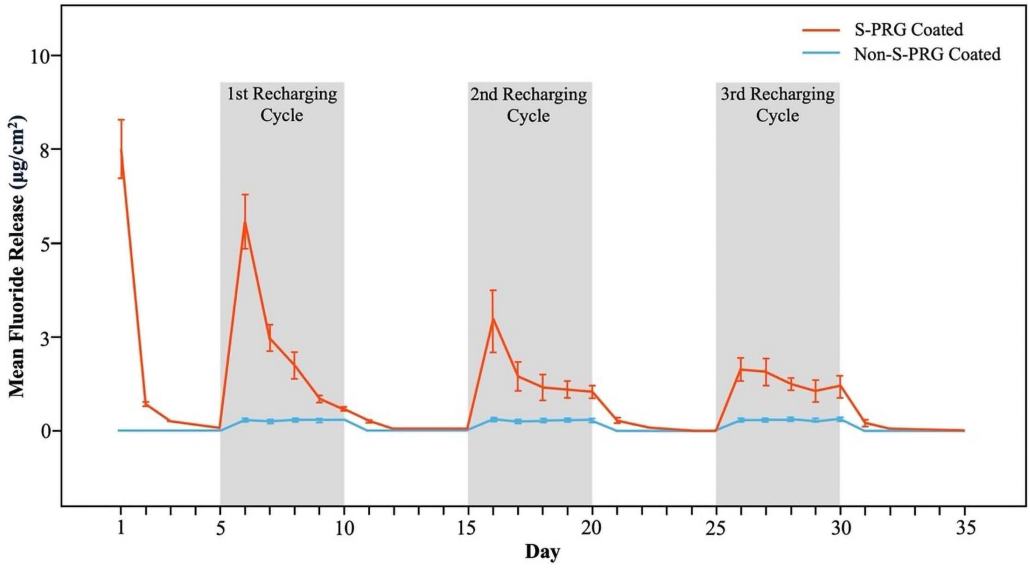


Figure 2 Mean fluoride release (µg/cm²) in S-PRG-coated group (red line) and Non-S-PRG-coated group (blue line) from Day 1 to Day 35, across three recharging cycles (shaded regions: Days 6–10, 16–20, 26–30). Error bars represent standard deviation (n=10).

S-PRG-coated group

From Day 1 to Day 5 (Figure 2), the fluoride release from the S-PRG-coated group peaked on Day 1 (6.67 ± 1.73 µg/cm²) and rapidly declined to 0.07 ± 0.02 µg/cm² by Day 5. During the first recharging period (Days 6–10), fluoride release spiked on Day 6 (4.25 ± 1.46 µg/cm²), then steadily decreased to 1.03 ± 0.39 µg/cm² by Day 10. A similar pattern was observed in the second (Days 16–20) and third (Days 26–30) recharging periods, with initial spikes on the first day of the second and third recharging cycles (Day 16: 2.91 ± 1.14 µg/cm² and Day 26: 1.64 ± 0.4 µg/cm²), followed by gradual declines, stabilizing at 1.03 ± 0.23 µg/cm² and 1.17 ± 0.39 µg/cm² on the last day of the second and third recharging cycles (Day 20 and Day 30, respectively).

In all three recharging cycles, significant differences in fluoride release between each recharging cycle were observed on the 1st days (Days 6, 16, and 26, respectively) (p<.05). For the 2nd days of each recharging cycle (Days 7, 17, and 27), significant differences were found only between Day 7 and Day 17 (p<.05). However, no significant differences between cycles were noted for the 3rd (Days 8, 18, and 28), 4th (Days 9, 19, and 29), and 5th days (Days 10, 20, and 30) in each cycle.

Regarding the days after each recharging cycle of 5 days, the fluoride release on the 1st day after each cycle (Day 11: 0.24 ± 0.05 µg/cm², Day 21: 0.25 ± 0.09 µg/cm², Day 31: 0.19 ± 0.12 µg/cm²) and 2nd day after each cycle (Day 12: 0.07 ± 0.01 µg/cm², Day 22: 0.09 ± 0.04 µg/cm², Day 32: 0.07 ± 0.02 µg/cm²) showed no significant differences (p>0.05). On the 3rd (Days 13, 23, and 33), 4th (Days 14, 24, and 34), and 5th (Days 15, 25, and 35) days after each recharging cycle, the fluoride levels were below the detection limit (< 0.06 µg/cm²).

Non-S-PRG-coated group

In the non-coated group, fluoride levels did not differ significantly across the days of the recharging period showing trace amounts ranging from 0.23 to 0.31 μg/cm². On the first day after each recharging cycle (Days 11, 21, and 31), fluoride levels were below the detection limit and were undetectable by the second day after each cycle.

S-PRG-coated VS Non-S-PRG-coated group

Fluoride levels were significantly different between the coated and non-coated groups throughout all recharging cycles ($p < 0.05$).

Adhesion Testing

Adhesion testing per ASTM D3359-22 showed that all 10 specimens were rated 5B on both Day 0 and Day 35 (Figure 3), indicating that the adhesion of the S-PRG coating remained intact and unchanged throughout the 35-day testing period.

Qualitative Surface Assessment

The SEM analysis of the non-S-PRG sample revealed a smooth, featureless surface across all magnifications (Figures 4A–4C). In the S-PRG group, the ×100 magnification images showed a discontinuous coating layer forming island-like regions separated by gaps that exposed the underlying PETG surface, observed immediately after thermoforming on Day 0 (Figure 4D) and persisting through Day 35 (Figure 4G). At ×1000 magnification, these gaps were more clearly delineated (Figures 4E, 4H), with no apparent increase in gap width or further coating disruption over the 35-day period. At ×5000 magnification, filler particles (manufacturer-stated size, 3 μm) were observed embedded within the coating matrix on both Day 0 (Figure 4F) and Day 35 (Figure 4I), indicating that the filler was retained within the coating throughout the experimental period.

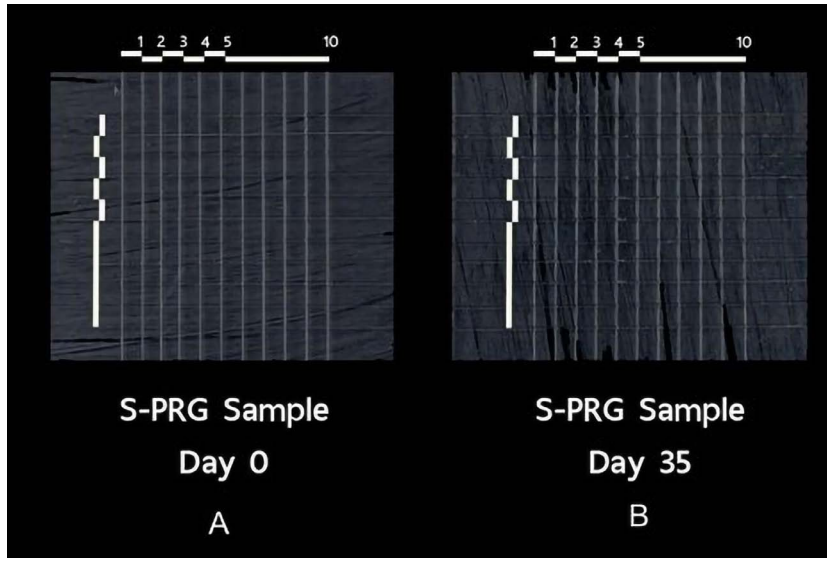


Figure 3 Representative images of S-PRG-coated specimens following cross-cut tape testing per ASTM D3359-22 (Test Method B) at Day 0 (3A) and Day 35 (3B).

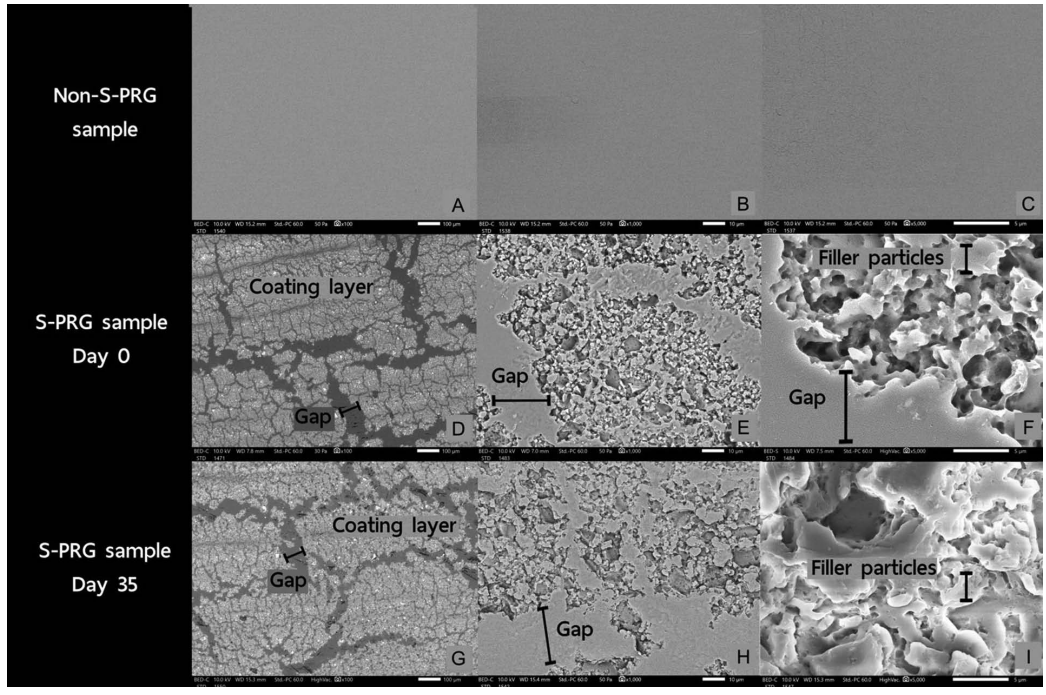


Figure 4 Non-S-PRG sample (4A–4C) and S-PRG-coated samples on Day 0 (4D–4F) and Day 35 (4G–4I) under ×100, ×1000, and ×5000 magnification. (4A) Non-S-PRG ×100; (4B) Non-SPRG ×1000; (4C) Non-S-PRG ×5000; (4D) S-PRG Day 0 ×100; (4E) S-PRG Day 0 ×1000; (4F) S-PRG Day 0 ×5000; (4G) S-PRG Day 35 ×100; (4H) S-PRG Day 35 ×1000; (4I) S-PRG Day 35 ×5000.

Discussion

S-PRG fillers have been widely incorporated across various dental materials; however, their application in thermoformed appliances such as clear orthodontic retainers remains limited.

Kaga *et al.* [30] demonstrated that S-PRG-containing materials effectively prevented enamel demineralization in acidic conditions through pH neutralization. Similarly, Kiatsirirote *et al.* [31] reported that 20% S-PRG dentures temporarily increased salivary fluoride levels, although the effect diminished over time, emphasizing the need for regular fluoride recharging. Amaechi *et al.* [26] found that toothpaste containing 30% S-PRG provided the greatest inhibition of mineral loss, consistent with Tokunaga *et al.* [24], and recommended lower concentrations (1–5%) for long-term caries prevention depending on caries risk. Ma *et al.* [32] showed that PRG Barrier Coat forms a ~200 μm protective layer that inhibits root surface demineralization and reduces acidogenic activity of *S. mutans*, likely due to ion release and buffering effects. Supporting this, Spinola *et al.* [33] reported that varnishes containing 30–40% S-PRG effectively preserved enamel microhardness during pH cycling. The present results extend these observations to a thermoformed retainer substrate, demonstrating that the rechargeable fluoride behaviour of S-PRG is retained when the filler is delivered as a surface coating on PETG.

S-PRG Filler as a Fluoride Reservoir

The recharging behaviour observed in this study indicates that the S-PRG filler functions as a finite but renewable fluoride reservoir rather than a single-use fluoride source. This reservoir capacity arises from the unique surface pre-reacted glass-ionomer (PRG) architecture of the filler, in which an acid–base reaction between polyacrylic acid and fluoroboroaluminosilicate glass produces a stable glass-ionomer phase surrounding a glass core. This pre-reacted surface layer contains ion-exchange sites that can both release fluoride into, and re-uptake fluoride from, the surrounding medium, allowing the filler to be repeatedly replenished upon exposure to an external fluoride source [34, 35]. The mechanism is conceptually similar to that of conventional glass-ionomer cement (GIC) and resin-modified glass-ionomer (RMGI) materials, which are also recognised for their fluoride release and recharge capabilities. However, in GIC and RMGI, fluoride recharge depends largely on the bulk porosity and water-sorption of the set cement, whereas in S-PRG–based materials the rechargeable behaviour is governed specifically by the pre-reacted glass-ionomer surface phase of the filler particles [36]. In the present coating, this surface-PRG architecture is what enabled the repeated fluoride uptake and release observed across the three recharging cycles, supporting the use of S-PRG–coated thermoplastics as a rechargeable, compliance-independent fluoride delivery platform during the retention period.

In addition to the S-PRG filler itself, the thermoplastic substrate may contribute a secondary, lower-capacity reservoir effect. PETG-based thermoplastics are known to absorb water [37-40], and this water-sorption behaviour allows fluoride ions to diffuse into and out of the bulk material during immersion and recharging. This is supported by the present findings in the non-S-PRG group, in which low but measurable fluoride was detected during the recharging cycles despite the complete absence of S-PRG filler, indicating that the PETG substrate alone is capable of taking up and subsequently releasing a small amount of fluoride. Although this substrate-derived contribution was minor and short-lived compared with the release from the S-PRG coating, it suggests that in the coated specimens the overall reservoir behaviour reflects the combined contribution of the S-PRG filler and the inherent water-sorption capacity of the underlying thermoplastic.

Coating Polymerization and Thermoforming

Essix A+ is described by the manufacturer as possessing compatibility with acrylic materials, although its detailed composition is not disclosed by the manufacturer [41]. In our study, we observed that the PRG Barrier Coat (acrylic-based) remained sticky and easily removed even after light-curing according to the manufacturer's instructions. This suggests that proper polymerization was not yet achieved by the light-curing alone. However, after the same coated thermoplastic sheet was subjected to thermoforming, the coating turned dry and its adherence was improved. These suggest that the heat applied during thermoforming may enhance the polymerization or the bonding of the S-PRG coat. Nevertheless, this hypothesis remains speculative and requires confirmation in future studies.

Overall specimen thickness, measured with a digital vernier caliper (0.01 mm resolution), remained unchanged after thermoforming. However, the thickness of the S-PRG coating layer itself was not quantified, as its sub-micrometre-to-micrometre scale is below the resolution of the caliper; therefore, fine dimensional changes within the coating layer cannot be excluded, and this is acknowledged as a study limitation.

Coating Integrity and Surface Morphology

SEM analysis showed that thermoforming did not visibly disrupt the continuity of the coating at the macroscopic level, yet at higher magnification the coating presented as discontinuous island-like regions separated by gaps that exposed the underlying PETG surface (Figure 4), likely resulting from contraction of the coating as it conformed to the deformation of the thermoplastic sheet during thermoforming. These gaps were already present immediately after thermoforming (Day 0) and persisted without apparent widening or further disruption through Day 35, indicating that the coating morphology remained stable across the experimental period. The influence of these gaps on fluoride diffusion and on coating durability under intraoral conditions remains unclear and warrants further investigation. Clinically observable opacity changes on archform specimens are presented for illustrative purposes (Figure 5) but should be interpreted with caution, as formal testing was conducted on flat sheet specimens. Adhesion testing demonstrated a 5B rating per ASTM D3359-22, confirming that the coating was not removed under standardised cross-cut tape test conditions, and SEM analysis confirmed resistance to structural detachment after multiple recharging cycles. Notably, the durability of the coating under repeated mechanical loading during clinical insertion and removal has not been evaluated and represents an important direction for future research.

Initial Fluoride Burst and the Plateau During Days 3–5

During the initial 5-day release period, the S-PRG–coated group exhibited a pronounced fluoride burst on Day 1 (6.67 μg/cm²; 2.22 ppm), followed by a rapid decline to a low, stable plateau by Days 3–5 (reaching 0.07 μg/cm²; 0.023 ppm by Day 5), consistent with previous findings [24]. This early plateau is consistent with the two-phase release behaviour characteristic of S-PRG–based materials, in which an initial rapid burst is followed by a slower, diffusion-limited phase. The Day 1 burst reflects the dissolution of fluoride that is loosely held at, or immediately adjacent to, the coating surface, whereas the plateau phase reflects the progressively slower release of fluoride

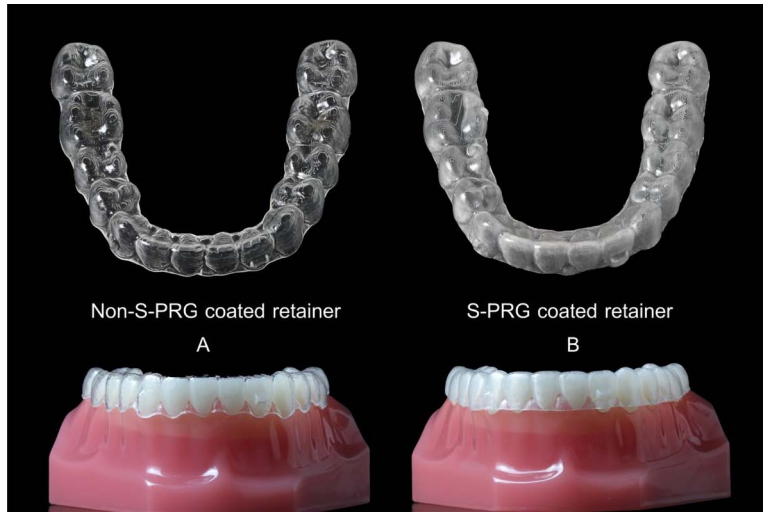


Figure 5 Illustrative photographs of archform thermoplastic retainers: Non-S-PRG-coated retainer (5A) and S-PRG-coated retainer (5B). Note: these specimens are presented for illustrative purposes only; all formal testing was conducted on flat 1×1 cm² sheet specimens.

that must diffuse from deeper within the filler matrix. As the most readily accessible ion-exchange sites in the S-PRG filler become depleted, the remaining sites release fluoride at a much lower and more constant rate, producing the observed plateau [35, 36]. Importantly, even these low fluoride concentrations (<0.03 ppm) have been shown to inhibit demineralization and promote remineralization [19], indicating that the coating may continue to provide a baseline protective effect even between recharging events. In contrast, no fluoride release was observed in the non-S-PRG group during this initial period. Based on our observations and comparison with Tokunaga's findings [24], the pronounced fluoride burst on Day 1 may be attributed to an excessively high initial surface fluoride concentration introduced during manufacturing or early processing of the coating.

Recharging Behaviour and Progressive Decline of Recharge Peaks

During the recharging period, the S-PRG group exhibited a significant peak in fluoride release on the first day of the initial cycle (Day 6), which progressively declined in subsequent cycles, with reduced release observed on the first day of the second (Day 16) and third (Day 26) cycles. On the 3rd (Days 8, 18, 28), 4th (Days 9, 19, 29), and 5th (Days 10, 20, 30) days of each recharging cycle, fluoride release showed no significant differences. Fluoride release continued after each recharging cycle, with low but measurable concentrations only on the 1st (Day 11, 21, 31; mean range 0.19–0.25 μg/cm²) and 2nd (Day 12, 22, 32; mean range 0.07–0.09 μg/cm²) days post-recharging. By the 3rd to 5th days (Day 13, 14, 15; Day 23, 24, 25; Day 33, 34, 35), fluoride levels were below detection limits, indicating that fluoride release lasts up to 2 days after recharging.

The absence of any rise in fluoride release during Days 3–5 of each recharge cycle despite continued daily immersion in fresh 1,000 ppm fluoride solution reflects the finite, saturable nature of the ion-exchange sites in the pre-reacted glass-ionomer surface phase of the S-PRG filler. Fluoride re-uptake proceeds by a ligand-exchange mechanism limited by the number of available binding sites rather than by solution concentration [34, 35], and uptake from solution approaches an equilibrium beyond which further immersion does not increase bound fluoride [35]. Once these surface sites became saturated early in each recharge period, subsequent release was rate-limited by slow diffusion from the filler matrix rather than by external fluoride availability [35, 36], producing the observed concentration-independent plateau on Days 3–5.

The progressive decline in the recharge peaks across the three cycles (Day 6 > Day 16 > Day 26) is consistent with the behaviour of a finite, rechargeable fluoride reservoir. With each cycle, the most readily accessible ion-exchange sites release their fluoride during the 5-day measurement period, and a single 8-hour recharge does not appear to fully replenish the reservoir to its initial state, so the subsequent peak is lower than the preceding one. Importantly, the magnitude of the decline diminished with successive cycles: the drop from Day 6 to Day 16 was substantially larger than that from Day 16 to Day 26, and the release stabilised at a comparable plateau (approximately 1.0–1.2 μg/cm²) by the end of the second and third cycles. This pattern suggests that the readily depletable surface fraction is exhausted within the first one to two cycles, after which the coating settles into a lower but more reproducible steady-state release. Extrapolating from this trend, a further two to three cycles would be expected to yield recharge peaks at or slightly below the Day 26 level, approaching a stable equilibrium rather than continuing to decline sharply, although

longer-term cycling studies are required to confirm this projection. This behaviour initially differs from the relatively stable early-cycle release reported by Tokunaga and Kamijo [24, 25]; however, by the third cycle our results converged toward the more stable release pattern described in those studies.

Mechanisms of Gradual S-PRG Filler Loss

This reduction may also be attributed to the gradual loss of S-PRG filler during the testing period, which we were unable to precisely quantify, potentially diminishing the material's ability to release fluoride during subsequent recharging cycles. Two mechanisms may underlie this gradual loss. First, surface-exposed S-PRG particles may undergo partial dissolution during repeated immersion, as the acid–base reactive glass phase is inherently water-sensitive and progressively releases its constituent ions into the surrounding medium. Second, particles that are incompletely embedded within the coating matrix may become physically dislodged during the repeated immersion, rinsing, and ultrasonic-cleaning steps. Both processes would reduce the population of rechargeable ion-exchange sites available at the coating surface, which is consistent with the progressively lower recharge peaks observed across the three cycles. As the SEM analysis confirmed that the bulk of the filler particles were retained within the coating after 35 days, any such loss is likely to have been confined to the outermost surface layer rather than reflecting wholesale delamination of the coating.

Moreover, the fluoride release observed during our third recharging cycle (1.0–1.6 μg/cm²) was slightly higher but still comparable to the values reported by Tokunaga [24] (0.8–1.0 μg/cm²). This small difference may result from the greater water absorbability of thermoplastic materials (37-40), as evidenced by fluoride detection in the non-S-PRG-coated group during recharging, combined with the fluoride-releasing ability of the S-PRG coating, unlike the 30% S-PRG orthodontic resin used alone in Tokunaga's findings [24].

Clinical Relevance

The S-PRG group showed superior fluoride release and recharging ability compared to the non-S-PRG group, with a strong initial release suitable for short-term use in clear retainers. Despite declining fluoride levels, it maintained low but consistent release when paired with regular fluoride recharge, aligning with Kiatsirirote's findings [31], making it suitable for prolonged use in clear retainers. Orthodontic retainers are often worn for extended periods, typically 6 months to several years [9, 10], suggesting that sustained fluoride rechargeability may provide meaningful caries protection, particularly in high-risk patients. Although our 35-day model simulated repeated exposure cycles, longer-term studies are required to better reflect clinical use. Thermoplastic retainers such as Essix-type appliances have relatively short clinical lifespans due to deformation, discoloration, and hygiene-related issues, and are commonly replaced every 6–12 months [9, 10]; therefore, the short- to mid-term fluoride rechargeability demonstrated in this study may still offer clinically relevant benefits within typical replacement intervals.

Limitations

This study has several limitations. First, the in vitro design does not replicate the complex oral environment, where mechanical loading from insertion and removal, salivary pellicle formation, thermal cycling, and microbial activity may all influence coating retention, fluoride release kinetics, and filler integrity. Second, only three fluoride recharging cycles were evaluated; extended cycling is needed to determine the

coating's long-term fluoride reservoir capacity and effective clinical lifespan. Third, although overall specimen thickness was verified with a digital vernier caliper and remained unchanged, the thickness of the coating layer itself was not quantified at the micrometre scale, so fine dimensional changes within the coating cannot be excluded. Fourth, the study was limited to a single thermoplastic material (Essix A+, PETG), while behavior on other thermoplastic compositions may differ. Fifth, the long-term esthetic stability of the S-PRG coating has not been evaluated. Future studies should specifically assess: (1) color stability by spectrophotometry (CIE L*a*b*) over extended wear periods; (2) opacity changes using translucency parameter measurement; (3) surface discoloration from staining agents commonly consumed during orthodontic retention; (4) coating degradation and delamination assessed by SEM and surface profilometry after simulated clinical wear; and (5) fluoride recharge efficiency across extended cycles to determine the effective clinical lifespan of the coating. Finally, formal assessment of enamel demineralization inhibition using pH cycling models is required to confirm the anticariogenic clinical relevance of the fluoride levels observed in this study.

Conclusion

Within the limitations of this in vitro study, S-PRG coating applied to copolyester thermoplastic sheets used for orthodontic retainers achieved a 5B rating on the ASTM D3359-22 cross-cut tape test at both Day 0 and Day 35, indicating that the coating was retained without removal under standardised test conditions, even after thermoforming and repeated immersion.

Additionally, S-PRG-coated copolyester thermoplastics showed promising short-term fluoride release and recharging capabilities. These materials also maintained a consistent low-level fluoride release, making them suitable for extended use with regular fluoride recharging, as observed over the 35-day experimental period.

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