Evaluation of Short-Term Fluoride Releasing and Recharging in S-PRG-Coated Thermoplastic Aligners

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Abstract

Clear aligners provide an aesthetic, comfortable, and removable orthodontic option, yet recent studies highlight issues with plaque buildup impacting oral health. Incorporating fluoride directly into aligners presents a novel method for enhancing oral health during orthodontic treatment. With limited research in this area, this study explores the feasibility of fluoride-releasing aligners as a self-sustaining fluoride delivery system. This study aims to evaluate the short-term fluoride-releasing and recharging properties of thermoplastic aligner materials coated with surface pre-reacted glass-ionomer (S-PRG) filler, along with examining the surface characteristics of the coated samples. Samples were prepared by coating thermoplastic sheets typically used for aligners with S-PRG paste, followed by thermoforming according to manufacturer instructions and cutting them into 1 cm^2 squares. Fluoride release was assessed over five days, followed by a five-day recharge cycle and a subsequent five-day fluoride release evaluation, comparing 10 coated and 10 non-coated samples. Statistical analysis utilized a significance level of $p<0.05$. The S-PRG-coated group showed significantly elevated fluoride release on Day 1, with levels gradually decreasing each subsequent day. Fluoride recharge from Day 6 to Day 10 successfully elevated fluoride levels again, which steadily declined by Day 15. Non-coated samples demonstrated no initial fluoride release; however, minor fluoride detection occurred briefly after immersion during recharge, ending by Day 11. SEM analysis revealed no difference in changes between Days 0 and 15 in S-PRG-coated samples. The coated thermoplastic exhibited effective short-term fluoride release and recharge, making it suitable for aligners typically worn for a few weeks, with SEM confirming strong adhesion.

Keywords: *surface pre-reacted glass-ionomer (S-PRG), fluoride releasing, fluoride recharging, clear aligner, thermoplastic materials*

1. Introduction

Clear aligners have become a popular alternative to traditional fixed braces due to their aesthetic appeal, comfort, and removability. Unlike metal brackets and wires, aligners offer a nearly invisible orthodontic treatment option, making them especially attractive to adult patients seeking discreet correction of malocclusion. Additionally, clear aligners are often marketed as being more hygienic than fixed appliances, as they can be removed for eating and oral hygiene maintenance (Papadopoulou et al., 2019). However, recent research has highlighted concerns regarding plaque accumulation and bacterial biofilm formation on aligner surfaces, which may contribute to oral health issues (Gracco et al., 2009).

Plaque accumulation on aligners is influenced by several factors, including material composition, surface roughness, and patient compliance with cleaning protocols. Studies have shown that the inner surfaces of aligners, which remain in close contact with teeth, tend to retain more plaque and bacteria compared to their outer surfaces (Yan et al., 2021). This buildup can lead to increased risks of dental caries, gingivitis, and periodontal disease, particularly in patients with poor oral hygiene habits. Furthermore, aligners create an enclosed environment around the teeth, limiting saliva circulation, which is essential for natural plaque control and enamel remineralization.

Several studies have investigated the microbial composition of plaque that accumulates on aligners. A previous study found that after prolonged use, aligners harbor a significant increase in cariogenic bacteria such as *Streptococcus mutans* and *Lactobacillus spp.* (Yan et al., 2021). These bacteria thrive in acidic conditions and contribute to enamel demineralization, leading to the formation of white spot lesions and cavities. Additionally, prolonged wear of aligners without adequate cleaning has been associated with the growth of anaerobic bacteria, which are linked to bad breath and gum inflammation (Fournier et al., 1998).

To mitigate plaque accumulation and its consequences, many studies have explored various modifications to aligner materials, including antimicrobial coatings such as gold-nanoparticle coated aligners for reducing bacterial adhesion (Zhang et al., 2020), the incorporation of fluoride-releasing materials remains relatively unexplored.

Fluoride strengthens enamel, making it more resistant to acid attacks and reducing tooth decay risk in both children and adults through multiple mechanisms such as forming fluoroapatite, reducing enamel solubility, slowing enamel dissolution in acidic environments, promoting remineralization, and exerting antibacterial effects by inhibiting bacterial enzymes, lowering plaque acidity, limiting sugar uptake, and disrupting bacterial metabolism which collectively help maintain oral health when regularly using fluoride-containing products like toothpaste or mouth rinses.

Surface Pre-Reacted Glass Ionomer (S-PRG) is an advanced dental material engineered to continuously release and recharge fluoride, providing long-term protection against enamel demineralization and dental caries. It is synthesized through an acid-base reaction between polyacrylic acid and fluoroboronaluminosilicate glass, resulting in a stable matrix capable of sustained fluoride ion release while also absorbing fluoride from external sources such as toothpaste and mouthwash. In addition to fluoride, S-PRG filler releases beneficial ions, including strontium, boron, sodium, aluminum, and silica, which aid in enamel remineralization, neutralize acids, and exhibit antibacterial properties.

When exposed to water, S-PRG filler facilitates fluoride release or recharging, depending on the fluoride concentration gradient between the giomer restoration and the surrounding environment (Okuyama et al., 2006). The effectiveness of S-PRG filler depends on factors like concentration, particle size, and material integration, with studies recommending a minimum of 30 wt% for optimal performance (Amaechi et al., 2017; Spinola et al., 2020; Tokunaga et al., 2013). Its application in orthodontic adhesives, sealants, and restorative materials highlights its potential to enhance oral health.

Incorporating fluoride directly into aligners presents a novel approach to enhancing oral health during orthodontic treatment, particularly benefiting patients with inconsistent oral hygiene by providing continuous fluoride exposure through self-sustaining S-PRG-coated thermoplastic aligners; however, this approach has not yet been investigated, and this study addresses that knowledge gap by investigating the feasibility of combining fluoride-releasing thermoplastic materials with S-PRG filler to enhance the protective function of orthodontic aligners.

2. Objectives

This study aims to evaluate the short-term fluoride-releasing and recharging properties of thermoplastic aligner materials coated with surface pre-reacted glass-ionomer (S-PRG) filler as well as evaluate the surface features of the coated samples.

3. Materials and Methods

3.1 Experimental Design

This study followed a structured approach to evaluate fluoride release and recharging in S-PRG-coated thermoplastic aligners. The methodology was adapted from previous studies (Kamijo et al., 2009; Tokunaga et al., 2013) on fluoride-releasing dental materials. The experimental design included multiple test phases to assess both the initial fluoride release and the capacity for recharging over repeated cycles.

3.2 Sample Size Calculation

Statistical analyses were performed using the Statistical Package for Social Sciences software (SPSS version 23.0, IBM Corp., NY, USA). Sample size calculation was based on pilot data from Day 10 when the difference between groups was smallest, yet fluoride release in the non-S-PRG group remained above zero. The mean fluoride release at that time was 0.59 ± 0.06 µg/ml in the S-PRG group and 0.30 ± 0.05 µg/ml in the non-S-PRG group. A minimum of 3 samples per group was determined to provide 80% power at a significance level (α) of 0.05. However, to enhance reliability and account for potential variability, a sample size of 10 per group was selected in the same amounts as the previous study (Tokunaga et al., 2013).

3.3 Sample Preparation

S-PRG-coated thermoplastic samples were fabricated by applying a PRG barrier coat containing 30 wt% S-PRG filler (Shofu) onto a 0.035" thick acrylic-bondable copolyester thermoplastic sheet (Essix A+, Dentsply). The coating was applied uniformly using a silicone paddle to ensure consistent thickness across the samples, as Figure 1a. The coated sheets underwent light polymerization for 40 seconds to achieve proper adhesion and hardness. After curing, the coated sheets were thermoformed using a Biostar thermoforming machine (Scheu) under controlled temperature and pressure conditions, as shown in Figure 1b. The final samples were thoroughly rinsed with non-ionized water to remove any unpolymerized material.

For the non-coated control group, samples were prepared using uncoated Essix A+ thermoplastic sheets, thermoformed in the same manner. 10 square samples, each measuring 1 × 1 cm², were prepared from both S-PRG-coated and non-coated thermoplastic sheets. To ensure proper solution exposure during testing, all samples were suspended in test tubes using a 0.014-inch NiTi wire, keeping the coated surfaces in constant contact with the solution as in Figure 1c.

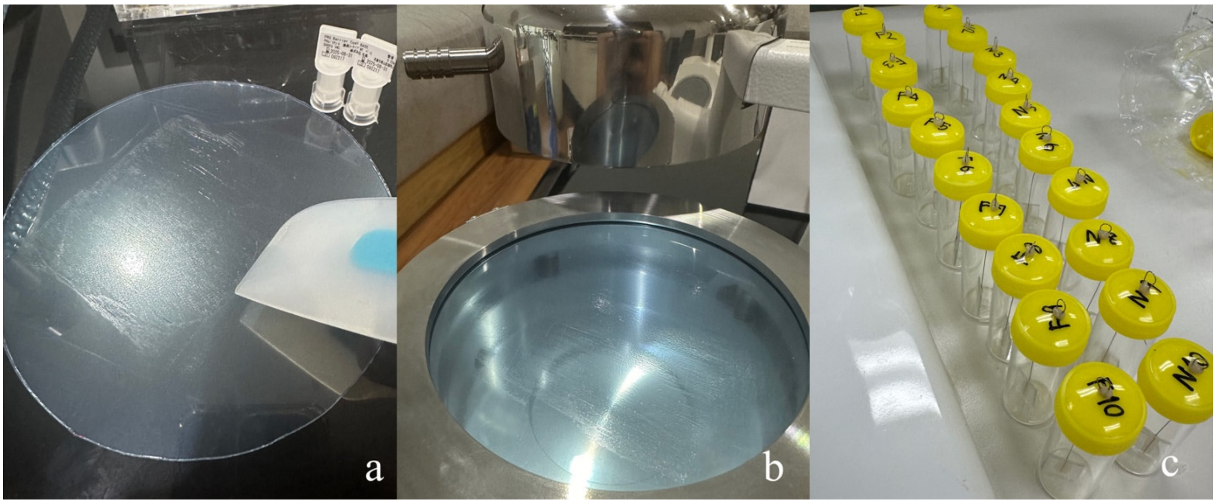

Figure 1 Application of S-PRG paste on a thermoplastic sheet (1a), thermoforming process (1b), and preparation of 10 S-PRG-coated and non-coated samples (1c)

3.4 Fluoride Release and Recharging Testing

The fluoride release and recharging process was evaluated in three distinct phases:

1. **Initial Release Phase (Days 1–5):** Samples were immersed in 3 mL of non-ionized water at 37°C, with daily water replacement. Fluoride release was measured each day.
2. **Recharging Phase (Days 6–10):** Samples were immersed in 3 mL of 1000 ppm fluoride solution for 8 hours, followed by immersion in non-ionized water for 16 hours daily.
3. **Post-Recharge Release Phase (Days 11–15):** Samples were again immersed in 3 mL of non-ionized water, with daily solution changes, to assess fluoride retention after recharging.

Samples were washed before each solution change. All non-ionized water solutions were mixed with 10% TISAB III as the ion-selective as in Figure 2. Fluoride ion concentration was determined using a calibrated fluoride electrode (Orion Versastar Pro, Thermo Scientific) electrode as in Figure 3.

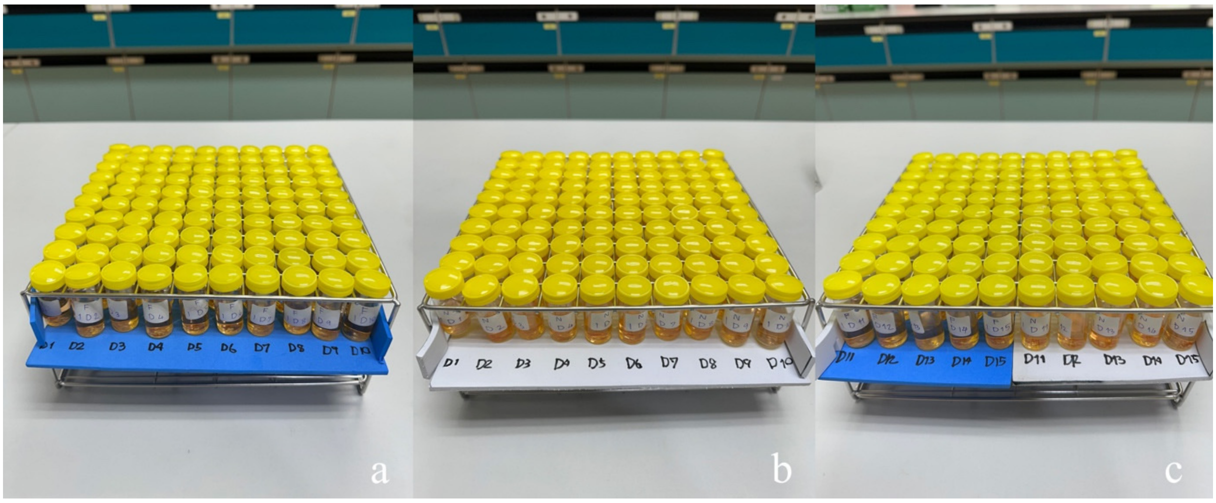

Figure 2 Non-ionized water immersed with S-PRG coated samples from Day 1 to Day 10 (2a), non-ionized water immersed with non-S-PRG coated samples from Day 1 to Day 10 (2b), and non-ionized water immersed with both S-PRG coated and non-coated samples from Day 11 to Day 15 (2c)

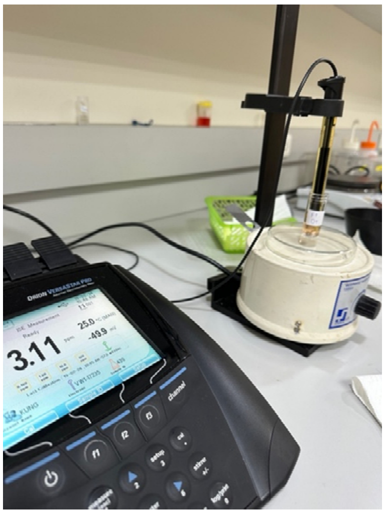

Figure 3 Fluoride ion measurement using Orion Versastar Pro electrode

3.5 PPM to µg/cm² Conversion

Fluoride concentration, measured in parts per million (ppm) within a known water volume, was used to determine the total fluoride ion release from the specimens. In this study, each sample was immersed in **3 mL** of water, and the sample disk had a surface area of **1 cm²**.

After each measurement, the total fluoride released (in micrograms) was calculated by multiplying the ppm value (1 ppm = 1 µg/mL) by the **3 mL** water volume. Since the sample area was **1 cm²**, the total fluoride release per unit area was obtained by dividing by **1 cm²**, simplifying the calculation to **ppm** × **3**, resulting in fluoride release in micrograms per square centimeter (µg/cm²).

3.6 Qualitative Surface Assessment

The surface morphology of thermoplastic sheet samples (1x1 cm²) was examined by Scanning Electron Microscopy (SEM) in backscatter electron mode, chosen for enhanced visualization of compositional contrasts, immediately after S-PRG coating (Day 0) and following the completion of fluoride recharge cycles (Day 15).

3.7 Statistical Analysis

Statistical analyses were carried out using the Statistical Package for Social Sciences software (SPSS version 23.0, IBM Corp., NY, USA). Shapiro–Wilk tests indicated that most data were normally distributed; however, Levene's test showed unequal variances between groups. Therefore, Welch's t-test (t-test for unequal variances) was used to determine significant differences in fluoride ion concentrations between S-PRG coated and non-coated groups on days 6, 10, and 11. Paired t-tests were applied to compare fluoride release within the coated groups between Day 6 and Day 10.

4. Results and Discussion

4.1 Result

4.1.1 Fluoride Test

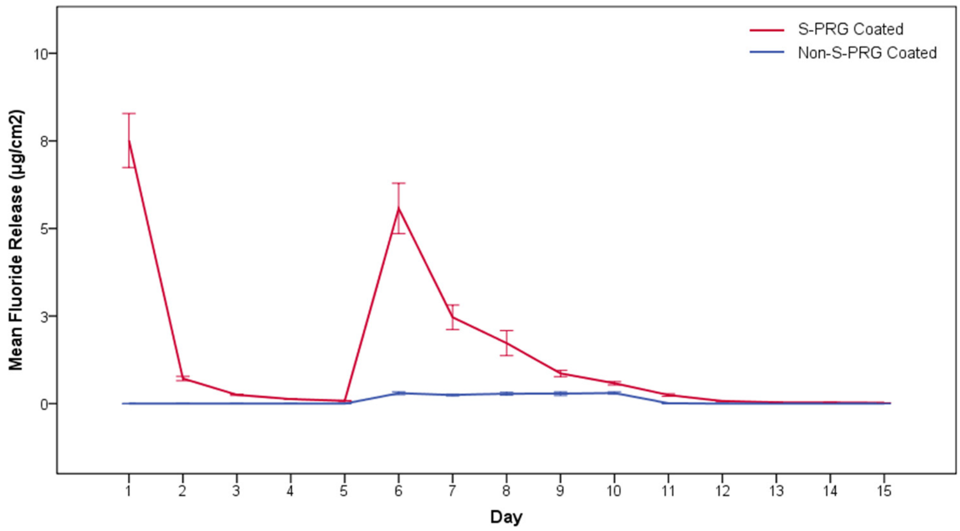

Figure 4 Mean fluoride amount in S-PRG-coated group and the non S-PRG coated group from Day 1 to Day 15

From Figure 4, Day 1 to 5 clearly showed the fluoride release from S-PRG-coated group, while no fluoride was detected in non-coated group. In the coated group, the mean concentration of fluoride release was highest on Day 1 (7.51 ± 1.08 µg/cm^2) and gradually declined until Day 5 (0.08 ± 0.01 µg/cm^2).

The amount of fluoride released from the coated group rose rapidly on the first day of fluoride recharging (Day 6: 5.51 ± 1.01 µg/cm^2) but did not reach the levels on Day 1. The fluoride levels again declined over the next four days until Day 10 (0.58 ± 0.07 µg/cm^2). During this period, a trace amount of fluoride was detected from the non-coated group, ranging from 0.24 to 0.30 µg/cm^2. The fluoride levels were significantly different between the coated and non-coated groups throughout the recharging period from Day 6 to 10 ($p<.05$).

When comparing within the groups between Day 6 and Day 10, a significant difference was observed in the S-PRG coated group, while no significant difference was found in the non-coated group.

From Day 11 onwards when the samples were immersed in the non-ionized water, fluoride levels were still detected from the S-PRG-coated group (Day 11: 0.24 ± 0.05 µg/cm^2), but reduced even further to below the detection limits by (Day 13: 0.03 ± 0.00 μg/cm^2). In the non-coated group, fluoride was completely undetectable in all samples after Day 11 onwards.

4.1.2 Qualitative Surface Assessment

At 100x magnification, The S-PRG-coated samples revealed noticeable gaps in the coating immediately after thermoforming on Day 0 (Figure 5a), which remained visible on Day 15 (Figure 5d). Under 5000x magnification, filler particles measuring approximately 3 μm, as specified by the manufacturer, were consistently observed at both Day 0 (Figure 5c) and Day 15 (Figure 5f).

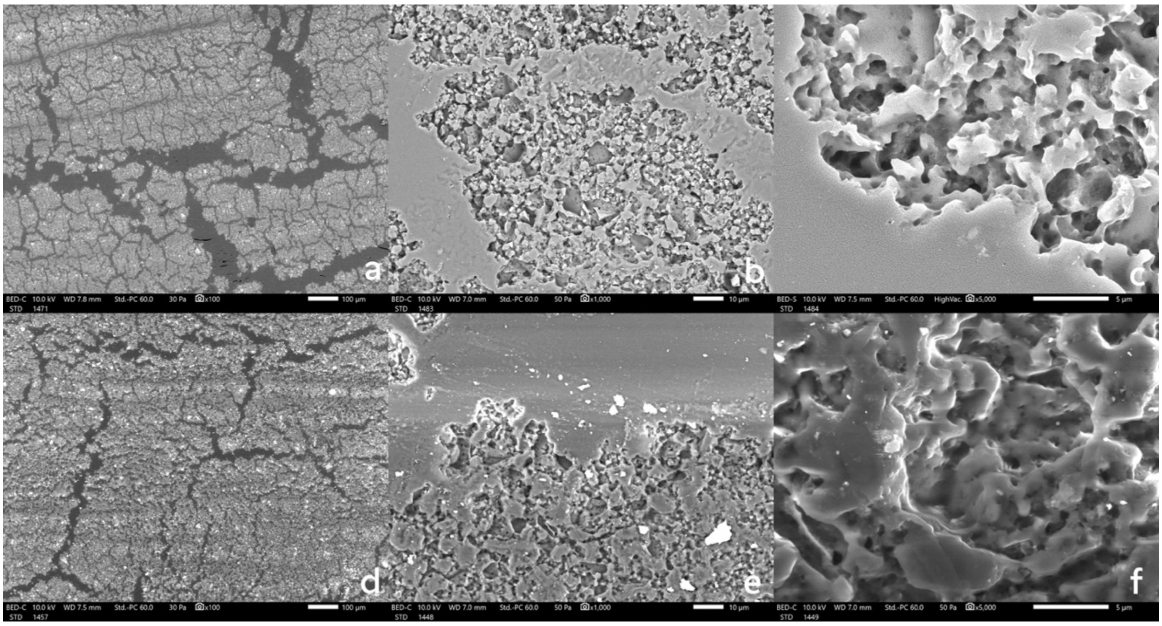

Figure 5 Surface morphology of S-PRG-coated samples observed at magnifications of 100x, 1000x, and 5000x on Day 0 (top row) and Day 15 (bottom row)

4.2 Discussion

In our preliminary study, we investigated the optimal timing for applying S-PRG coating onto thermoplastic sheets. Contrary to the manufacturer's claims regarding acrylic compatibility, directly applying and curing the acrylic-based S-PRG paste onto previously thermoformed plastic led to incomplete curing, leaving the coating moist, sticky, and easily removable even after one week. However, applying and fully polymerizing the coating before thermoforming resulted in a stable, dry, and thoroughly cured coating, although slight unevenness in the coating pattern was visually observed after thermoforming.

SEM analysis confirmed the effectiveness of this method, showing strong adhesion and excellent coating integrity even after fluoride recharge cycles. Although thermoforming heat may have affected bond strength or polymerization, thermal expansion and contraction during heating and cooling created scattered micro-gaps (<100 μm) within the coating, which were not visible before thermoforming.

On Day 1 of fluoride release testing in the S-PRG coated group, the recorded amount of released fluoride was 7.512 μg/cm^2, equivalent to 2.5 ppm, and this amount rapidly decreased daily until Day 5, when the amount of fluoride was less than the detection limit of <0.03 ppm. Even so, it has been suggested that low fluoride concentrations of less than 0.03 ppm can still reduce demineralization and enhance remineralization in the plaque fluid (Ten Cate, 2004).

During the fluoride recharging period from Day 6 to 10 of the S-PRG-coated group, the results of our study were similar to those of Kamijo et al., (2009), who immersed poly(methyl methacrylate) denture material containing 30 wt% of S-PRG filler into a 9000 ppm fluoride solution for 8 hours. The amount of fluoride release from our samples shot up rapidly from the first day of fluoride recharge (Day 6) and significantly declined daily despite repeated recharging from Days 7 to 10. In contrast, Tokunaga et al., (2013) reported only a slight daily reduction during the recharging period of their 30 wt% S-PRG incorporated orthodontic resin and found non-significant differences between Days 6 to 10. We deduce that the lower amounts of fluoride release during our recharging period could be due to a saturation limit of S-PRG filler and that this aspect would need more investigation in future studies.

In our non-coated group, a low but stable amount of fluoride ions of about 0.09 ppm was detected from Days 6 to 10. This demonstrated the thermoplastic's water absorbability, enabling fluoride ions to disperse after being soaked in a fluoride solution, supporting Ryu et al., study (Ryu et al., 2018). When the immersion solution was changed to non-ionized water on Day 11, the fluoride amount in this group dropped below the detectable limit and became completely undetectable from Day 12 onwards.

On the other hand, even though the fluoride release from the S-PRG group at Day 11 was significantly reduced compared to Day 10, a slow release of fluoride ions below 0.02 ppm still continued from Days 13 until 15.

Our findings confirmed that S-PRG-coated thermoplastic aligners effectively release fluoride upon initial use and can be recharged through fluoride exposure. The observed release trends align with previous studies on S-PRG filler materials, which demonstrate a sharp initial fluoride release followed by gradual depletion. Recharging cycles successfully replenished fluoride levels, although subsequent releases declined progressively.

This study introduces a novel approach of embedding fluoride-releasing materials directly within orthodontic aligners, highlighting a promising preventive measure, especially for patients with heightened caries risk. The sustained fluoride delivery demonstrated here uniquely maintains continuous enamel protection, effectively reducing the risk of enamel demineralization during orthodontic treatment. Additionally, due to their prolonged daily use, these aligners uniquely offer continuous, direct fluoride exposure to teeth and reduce bacterial adhesion on their surfaces.

Future research should address key limitations identified in the current study, such as the relatively short duration, lack of durability testing for the coating, and absence of in vivo validation. Extended trials evaluating long-term fluoride recharging cycles and coating durability under simulated oral conditions, including temperature fluctuations, mechanical forces from mastication, and exposure to salivary enzymes, are essential. Additionally, future studies should consider using a more clinically realistic fluoride recharge duration of approximately 2 hours, rather than the 8-hour period used in this study for comparative purposes with previous protocols. Detailed analysis of the chemical interactions between S-PRG filler and thermoplastic materials is needed to ensure stable fluoride incorporation and enhance overall material stability. Mechanical assessments should focus on the coating's adhesion and integrity over prolonged wear periods. Furthermore, biocompatibility studies in vivo, specifically examining cytotoxicity, allergenicity, and interactions with oral microbiota, are crucial to verify the clinical safety and efficacy of S-PRG-coated aligners.

5. Conclusion

The S-PRG-coated thermoplastic materials demonstrated short-term fluoride releasing and recharging abilities which rapidly declined within a few days, suggesting that their use is suitable for short-term appliances as a thermoforming aligner.

6. Acknowledgements

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7. References

Amaechi, B. T., Key, M. C., Balu, S., Okoye, L. O., & Gakunga, P. T. (2017). Evaluation of the caries-preventive effect of toothpaste containing surface prereacted glass-ionomer filler. *Journal of Investigative and Clinical Dentistry*, *8(4), e12249.* https://doi.org/10.1111/jicd.12249

Fournier, A., Payant, L., & Bouclin, R. (1998). Adherence of Streptococcus mutans to orthodontic brackets. *American Journal of Orthodontics and Dentofacial Orthopedics*, *114*(4), 414-417. https://doi.org/10.1016/s0889-5406(98)70186-6

Gracco, A., Mazzoli, A., Favoni, O., Conti, C., Ferraris, P., Tosi, G., & Guarneri, M. P. (2009). Short-term chemical and physical changes in invisalign appliances. *Australian Orthodontic Journal*, *25*(1), 34-40.

Kamijo, K., Mukai, Y., Tominaga, T., Iwaya, I., Fujino, F., Hirata, Y., & Teranaka, T. (2009). Fluoride release and recharge characteristics of denture base resins containing surface pre-reacted glass-ionomer filler. *Dental Materials Journal*, *28*(2), 227-233. https://doi.org/10.4012/dmj.28.227

Okuyama, K., Murata, Y., Pereira, P. N., Miguez, P. A., Komatsu, H., & Sano, H. (2006). Fluoride release and uptake by various dental materials after fluoride application. *American Journal of Dentistry*, *19*(2), 123-127.

Papadopoulou, A. K., Cantele, A., Polychronis, G., Zinelis, S., & Eliades, T. (2019). Changes in Roughness and Mechanical Properties of Invisalign(®) Appliances after One- and Two-Weeks Use. *Materials (Basel)*, *12*(15). https://doi.org/10.3390/ma12152406

Ryu, J. H., Kwon, J. S., Jiang, H. B., Cha, J. Y., & Kim, K. M. (2018). Effects of thermoforming on the physical and mechanical properties of thermoplastic materials for transparent orthodontic aligners. *Korean Journal of Orthodontics*, *48*(5), 316-325. https://doi.org/10.4041/kjod.2018.48.5.316

Spinola, M. D. S., Moecke, S. E., Rossi, N. R., Nakatsuka, T., Borges, A. B., & Torres, C. R. G. (2020). Efficacy of S-PRG filler containing varnishes on enamel demineralization prevention. *Scientific Reports*, *10*(1), 18992. https://doi.org/10.1038/s41598-020-76127-w

Ten Cate, J. M. (2004). Fluorides in caries prevention and control: empiricism or science. *Caries Research*, *38*(3), 254-257. https://doi.org/10.1159/000077763

Tokunaga, Y., Nakano, T., Kato, K., & Fukuta, O. (2013). Fluoride Release and Recharge Capabilities of Orthodontic Resin Containing S-PRG Filler. *The Japanese Journal of Pediatric Dentistry*, *51*, 1-7.

Yan, D., Liu, Y., Che, X., Mi, S., Jiao, Y., Guo, L., & Li, S. (2021). Changes in the Microbiome of the Inner Surface of Clear Aligners After Different Usage Periods. *Current Microbiology*, *78*(2), 566-575. https://doi.org/10.1007/s00284-020-02308-5

Zhang, M., Liu, X., Xie, Y., Zhang, Q., Zhang, W., Jiang, X., & Lin, J. (2020). Biological Safe Gold Nanoparticle-Modified Dental Aligner Prevents the Porphyromonas gingivalis Biofilm Formation. *ACS Omega*, *5*(30), 18685-18692. https://doi.org/10.1021/acsomega.0c01532