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Fluoride Release, Recharge and Mechanical Property Stability of Various Fluoride-containing Resin Composites

S Naoum • A Ellakwa • F Martin
M Swain

Clinical Relevance

Fluoride containing resin composites and especially those containing pre reacted glass ionomer fillers could be employed to great benefit in treating high caries risk patients in situations where glass ionomers may be unsuitable; particularly in high load bearing or aesthetically critical locations.

SUMMARY

Aim: To determine the fluoride release and recharge of three fluoride-containing resin composites when aged in deionized water (pH 6.5) and lactic acid (pH 4.0) and to assess mechanical properties of these composites following aging.

Methods: Three fluoride-containing resin composites were analyzed in this study; a new giomer material named Beautifil II, Gradia Direct X, and Tetric EvoCeram. A glass ionomer cement, Fuji IX Extra, was also analyzed for comparison. Specimens were fabricated for two test groups: group 1 included 10 disc specimens initially aged 43 days in deionized water (five specimens) and lactic acid (five specimens). The fluoride release from these specimens was measured using a fluoride-specific electrode on nine specific test days during the aging period. Following 49 days of aging, each specimen was recharged in 5000 ppm neutral sodium fluoride solution for 5 minutes. Specimen recharge was then repeated on a weekly basis for 3 weeks. The subsequent fluoride rerelease was measured at 1, 3,

Steven Naoum, BDSc, Grad Dip, The University of Sydney, Faculty of Dentistry, Westmead Oral Health Centre, Sydney, Australia

*Ayman Ellakwa, BDS, MDS, PhD, FRACDS, The University of Sydney, Faculty of Dentistry, Westmead Oral Health Centre, Sydney, Australia

Fjelda Elizabeth Martin, BDS(Hons), MDS, PhD, FRACDS, The University of Sydney, Faculty of Dentistry, Westmead Oral Health Centre, Sydney, Australia

Michael Swain, BSc, PhD, The University of Sydney, Faculty of Dentistry, Westmead Oral Health Centre, Sydney, Australia

*Corresponding author: The University of Sydney, Faculty of Dentistry, Westmead Oral Health Centre, Level 1, Faculty Office, Darcy Road, Westmead Hospital, Sydney, Westmead 2145, Australia; e-mail: ayman.ellakwa@sydney.edu.au

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and 7 days after each recharge episode. Group 2 included six disc specimens aged for 3 months in deionized water (three specimens) and lactic acid (three specimens). The hardness and elastic modulus of each specimen was measured using nano-indentation at intervals of 24 hours, 1 month, and 3 months after fabrication. Two-way factorial analysis of variance (ANOVA) and post-hoc (Tukey) testing was used to assess the influence of storage media (two levels) and composite type (three levels) on the fluoride release, fluoride rerelease, hardness, and elastic modulus of the assessed materials. The level of significance was set at p=0.05.

Results: All three composites demonstrated fluoride release and recharge when aged in both deionized water and lactic acid. The cumulative fluoride released from Beautifil II into both media was substantially greater than the fluoride released from Gradia Direct X and Tetric EvoCeram after 43 days aging and was significantly ($p<0.05$, ANOVA, Tukey test) greater during several analysis periods. Beautifil II demonstrated the greatest recharge ability of the three composites over the 3-week recharge period in both media. Fuji IX Extra demonstrated a significantly ($p<0.05$) greater fluoride release and recharge compared with the three resin composites. The elastic modulus and hardness of the three composites did not decrease significantly ($p<0.05$) with fluoride release or fluid uptake over the 3-month aging period, in either media.

Conclusion: The three composites in the present study demonstrated fluoride release (Beautiful II > Gradia Direct X > Tetric EvoCeram) and fluoride recharge (Beautiful II > Gradia Direct X > Tetric EvoCeram). This capability raises the possibility of fluoride-containing composites exhibiting a lower incidence of recurrent caries than non fluoride–containing composites. The mechanical properties of each composite did not diminish with aging and fluoride release over the testing period.

INTRODUCTION

Recurrent caries is a common mode of failure of directly placed resin composite restorations.[1,2] Resin composite restorations are particularly susceptible to recurrent caries due to polymerization contraction that occurs during curing[3] and the difficulty of attaining reliable adhesion between resin composites and dentin.[4] These phenomena can result in marginal disruption and subsequent marginal biofilm formation. Recurrent caries result in significant loss of tooth structure, both through the actual carious process and through replacement of affected restorations. The need to replace a restoration is especially destructive for teeth containing a tooth-colored restoration. Such replacement can result in an increase in cavity size by up to 37%.[5]

Several studies have demonstrated a lower incidence of recurrent caries associated with restorative materials capable of fluoride ion release.[6-8] This potential of fluoride-releasing restorative materials to inhibit the initiation and progression of recurrent caries has stimulated development of new materials, including the giomer class of restorative materials. Giomers are dental restorative materials containing prereacted glass ionomer (PRG) filler particles within a resin matrix.[9,10] PRG filler is formed by an acid-base reaction between fluoride-containing glass particles (fluoro-boro-alumino silicate glass filler) and polyalkenoic acid in the presence of water prior to integration into the resin.[11] Two types of PRG filler are available: surface reaction type PRG filler (S-PRG filler), as assessed in this study, and full reaction type PRG filler (F-PRG filler). S-PRG filler particles exhibit a three-layer structure. The glass core is enveloped by a stable glass-ionomer hydrogel. This hydrogel is then surrounded by the "reforming phase," which provides structural protection for the hydrogel.[9] Giomers, therefore, differ from compomers because the glass ionomer hydrogel within compomers forms only after water uptake by the compomer resin matrix after polymerization.[12]

The chemistry of giomer materials facilitates fluoride ion release and recharge with the potential for a lower incidence of recurrent caries. However, few studies have assessed the fluoride release and recharge of giomers, and no studies have assessed the effect that fluoride release and aging has on the mechanical properties of giomer materials.

The aim of this study, therefore, was to determine the fluoride release and recharge of three fluoride-containing resin composites, including a giomer, when aged in deionized water and lactic acid as well to assess mechanical property stability of these composites following aging and fluoride release.

MATERIALS AND METHODS

Three fluoride-containing resin composites were analyzed in this study: Beautifil II (Lot 060854; A2;

Shofu Inc, Kyoto, Japan) containing prereacted glass ionomer filler, Gradia Direct X (Lot 0805142; A3; GC Co, Tokyo, Japan) containing fluoro-alumino-silicate glass, and Tetric EvoCeram (Lot L24180; A2; Ivoclar Vivadent, Schaan, Liechtenstein) containing fillers holding ytterbium trifluoride. A glass ionomer cement, Fuji IX Extra (Lot 0804151; A3; GC), was also analyzed for comparison (Table 1). Specimens were fabricated for two test groups.

Group 1 - Fluoride Release and Recharge

Ten disc-shaped specimens of each material were prepared using a polytetrafluoroethylene mold (inner diameter 10.0 mm, thickness 1.5 mm). A glass plate (thickness 1.0 mm) was placed over the dispensed material, and finger pressure was applied to each specimen to ensure removal of air and material excess. Each composite specimen was cured using a halogen curing light (Optilux 501, Kerr Co, Orange, CA, USA) at a measured intensity of 400 mW/cm^2 (curing radiometer, Demetron Research Corporation, Danbury, CT, USA) for 40 seconds. Each glass ionomer specimen was retained in the mold with a 200-g mass maintaining pressure on the glass slide for 10 minutes after mixing. Following fabrication, each specimen was placed in an incubator at 37°C and 100% relative humidity for 30 minutes. The specimen edges were then lightly polished with dry 600 grit silicon carbide paper, and dimensions were measured with calipers before the specimens were placed into storage medium. The specimens were initially aged in individual plastic jars containing 20 mL of storage media for 43 days at 37°C. Five specimens of each material were aged in lactic acid solution (pH 4.0), and five specimens were aged in deionized water (pH 6.5) (Milli Q plus, 18.2 Mcm, Millipore, New York, NY, USA). Following each measurement of released fluoride ions, the storage medium of each specimen was discarded. Specimens were then placed in a clean jar containing 20 mL of fresh storage medium. Measurement and subsequent medium replacement took place at nine analysis intervals on days 1, 2, 4, 8, 15, 22, 29, 36, and 43 (Figure 1). Following 49 days of aging, each specimen was recharged in 5000 ppm neutral sodium fluoride solution (NeutraFluor 5000 Plus, Colgate, New York, USA) for 5 minutes. Specimen recharge was then repeated weekly for 3 weeks. The fluoride rerelease that occurred subsequently was measured at 1, 3, and 7 days after each recharge episode.

To determine the release (and rerelease post recharge) of fluoride ions after specimen removal, 2 mL of Total Ionic Strength Adjustment Buffer II buffer solution was added to the 20 mL of storage media. A fluoride ion selective electrode (Radiometer Analytical, Copenhagen, Denmark) was used to measure the fluoride concentration. Standards containing 0.025-0.25 mg/L fluoride in 0.025 mg/L fluoride steps were used for calibration at each testing interval. The results attained were expressed as the quantity of fluoride released per unit area of specimen (μg/cm^2).

Group 2 - Mechanical Properties Analysis

Group 2 comprised six specimens of each material. These were prepared identically to specimens of group 1, except that a mold of dimensions 7.0×2.0 mm was used for logistical reasons. Importantly, due to the very smooth surface of the pressing glass, each specimen exhibited a highly smooth, flat "mirror"

Table 1: *Materials Assessed in This Study*

Material	Key Contents	Manufacturer
Tetric EvoCeram Lot L24180	Filler particles consisting of barium glass, ytterbium trifluoride, mixed oxide, and prepolymer, unspecified dimethacrylate monomers (17% weight)	Ivoclar Vivadent, Schaan, Liechtenstein
Gradia Direct X Lot 0805142	Fluoro-alumino-silicate glass, prepolymerized filler, silica, UDMA, unspecified dimethacrylate comonomers (23% weight)	GC Co, Tokyo, Japan
Beautifil II Lot 060854	S-PRG glass filler, fluoride-containing fluoro-boro-alumino silicate glass filler particles, TEGDMA, Bis-GMA (17% weight)	Shofu Inc, Kyoto, Japan
Fuji IX Extra Lot 0804151	Fluoro-alumino-silicate glass, copolymer of acrylic and maleic acid, tartaric acid, water	GC Co, Tokyo, Japan

Abbreviations: Bis-GMA, 2, 2-bis [4-(2′-hydroxy-3′-methacryloxy-propoxy) phenyl] propane; S-PRG filler, surface reaction type prereacted glass ionomer; TEGDMA, triethylene glycol dimethacrylate; UDMA, urethane dimethacrylate.

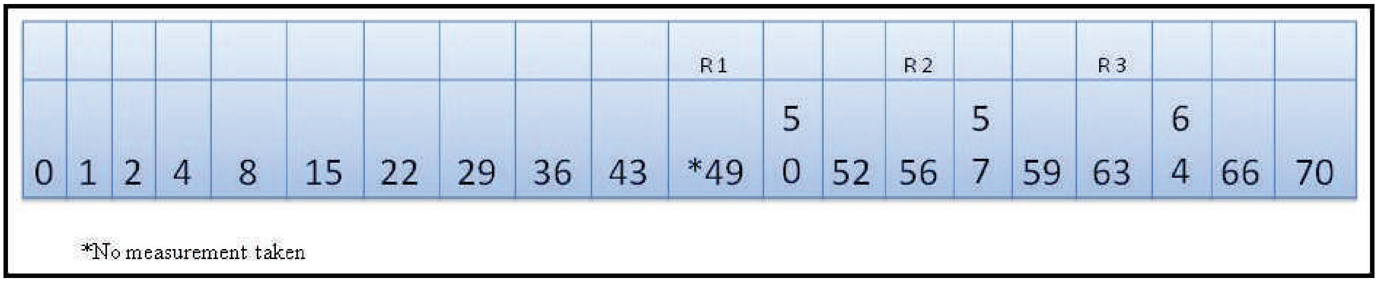

Figure 1. *Days of fluoride ion measurement and fluoride recharge treatment (R).*

surface suitable for nano-indentation without polishing.[13] By avoiding polishing, a more accurate evaluation of the hardness and elastic modulus of each resin composite was able to be attained. The polishing process results in heat production, even when water is used, so potentially adding to surface polymerization. An applied load of 50 mN was used, enabling a substantially larger penetration depth to be achieved compared to any specimen surface roughness.[13] Following fabrication, each specimen was placed into 20 mL of storage media and aged for 3 months: three specimens in deionized water and three in lactic acid. The aging solutions were renewed monthly. The hardness and elastic modulus of each specimen was measured using nano-indentation at intervals of 24 hours, 1 month, and 3 months after fabrication.

Indentations were made using an ultra-micro indentation system (UMIS 2000, CSIRO, Canberra, Australia). A calibrated diamond Berkovich indenter tip was used to apply loads of 50 mN, 25 μm apart. For each indentation, the maximum force was held for 30 seconds before unloading. This hold period at maximum load ensured minimal creep during unloading, therefore, producing more reliable elastic modulus values.[14] Sixteen indentations were made on each specimen in a 4×4 array, providing 48 data points for each material, from each storage medium at each testing interval. This distribution and number of indentations was sufficient to identify any variation in the properties of the material, should a material not be homogenous. The hardness and the elastic modulus for each material were calculated using the UMIS software. The hardness was calculated by dividing the applied load by the surface area. The elastic modulus was calculated using the equation[13] $1/E_r = (1 - v_m{}^2)/E_m + (1 - v_i{}^2)/E_i$ where E_r is the reduced modulus from the nano-indenter determined from the recovery rate on unloading at maximum load, where v_m and E_m are the Poisson's ratio and elastic modulus of the composite material, and V_i and E_i are the elastic modulus and Poisson's ratio of the indenter. A Poisson's ratio of 0.325 was used, adapted from Chung and others.[15]

Two-way factorial analysis of variance (ANOVA) and post-hoc (Tukey) testing was used to assess the influence of storage media (two levels) and composite type (three levels) on the fluoride release, fluoride rerelease, hardness, and elastic modulus of the assessed materials. The level of significance was set at $p=0.05$.

RESULTS

The results relating to the analyzed resin composites will be outlined first, after which a comparison to Fuji IX Extra will be undertaken. Figure 2 shows the cumulative fluoride ion release from each composite in both media. The cumulative fluoride release by giomer Beautifil II into both deionized water and lactic acid exceeded the release by Gradia Direct X (water difference, 89%; lactic acid difference, 23%) and Tetric EvoCeram (water difference, 170%; lactic acid difference, 172%) after 43 days aging. The fluoride release by Beautifil II was significantly ($p<0.05$) greater than the release by Tetric EvoCeram into water during days 1, 2-15, and 22–36, and into lactic acid during days 0–36. The fluoride release by Beautifil II was significantly ($p<0.05$) greater than the release by Gradia Direct X into water during days 1 and 2-15 and into lactic acid during days 0–2, 8-15, and 29–36. All three composites continued to release fluoride for the 43-day aging period, with the exception of Tetric EvoCeram, which stopped releasing fluoride into water after 36 days. Each composite demonstrated greater fluoride release when aged in lactic acid. The rate of fluoride release by each composite in both media decreased with time at a rate approximately proportional to the square root of time ($x = \sqrt{t}$).

Figure 3 presents the weekly cumulative fluoride ion rerelease by each composite aged in the different media, following a weekly 5-minute fluoride re-

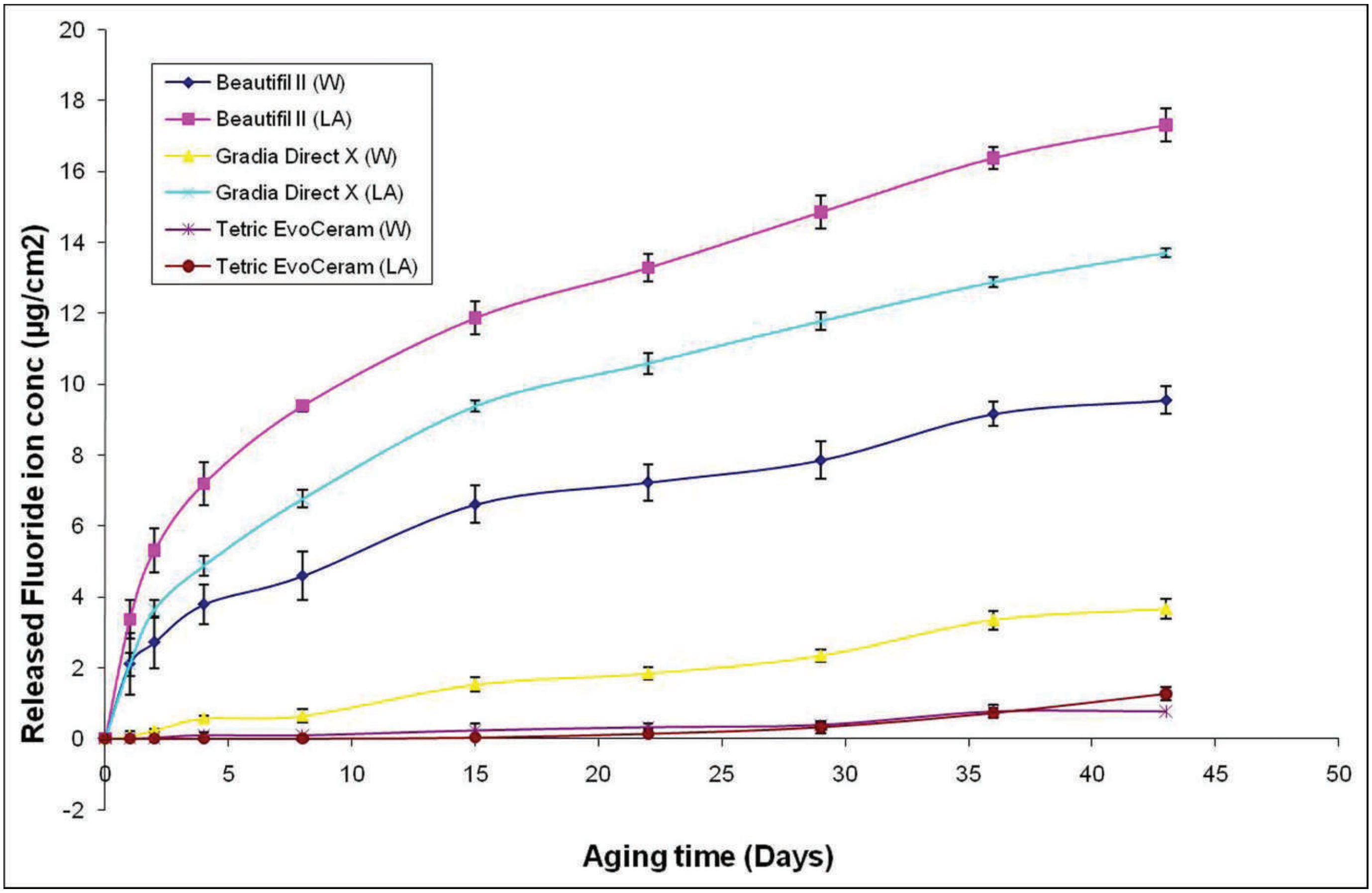

Figure 2. *Cumulative fluoride ion release by each composite aged in deionized water (W) and lactic acid pH 4.0 (LA) over 43 days.*

charge (5000 ppm) in the 3 weeks following 49 days of aging. All three composites demonstrated fluoride recharge, with subsequent rerelease of fluoride following recharge. The fluoride rerelease by Beautifil II was significantly ($p<0.05$) greater than the rerelease by Tetric EvoCeram and Gradia Direct X into water between days 0 and 3 during each of the 3 weeks of recharge analysis. Beautifil II demonstrated the greatest cumulative rerelease of the composites, in both media, at the completion of the 3 weeks: the rerelease percentage difference for Tetric EvoCeram being 57% (water) and 76% (lactic acid) and for Gradia Direct X 39% (water) and 1% (lactic acid). Gradia Direct X and Beautifil II exhibited a greater cumulative rerelease into acid compared to that into water. With each subsequent fluoride recharge, each composite rereleased a greater quantity of fluoride in the week following fluoride treatment despite previous aging. The greatest average daily fluoride rerelease from each material was during the first 24 hours post recharge (Figure 4). Figure 5 shows the hardness and elastic modulus of each composite aged in deionized water and lactic acid over 3 months. The hardness of Tetric EvoCeram in water and of Beautifil II in both acid and water did not change significantly ($p>0.05$) over the 3-month aging period. Likewise, no significant change was observed in the elastic modulus of Beautifil II and Tetric EvoCeram in acid over the 3 months. A significant ($p<0.05$) increase in the elastic modulus of Beautifil II and Tetric EvoCeram in water and an increase in the hardness and elastic modulus of Gradia Direct X in both media was observed after 3 months of aging.

The fluoride release by Fuji IX Extra during the initial 43 days of aging and following fluoride recharge was significantly ($p<0.05$) greater than that of the three analyzed composites (Figure 6). Notably, the average daily post recharge rerelease by Beautifil II in the first 24 hours after recharge was comparable to the daily fluoride release by Fuji IX Extra at 21 days of aging and beyond (Figure 6). The hardness of Fuji IX Extra, which remained stable in both media over 3 months of aging, and the elastic

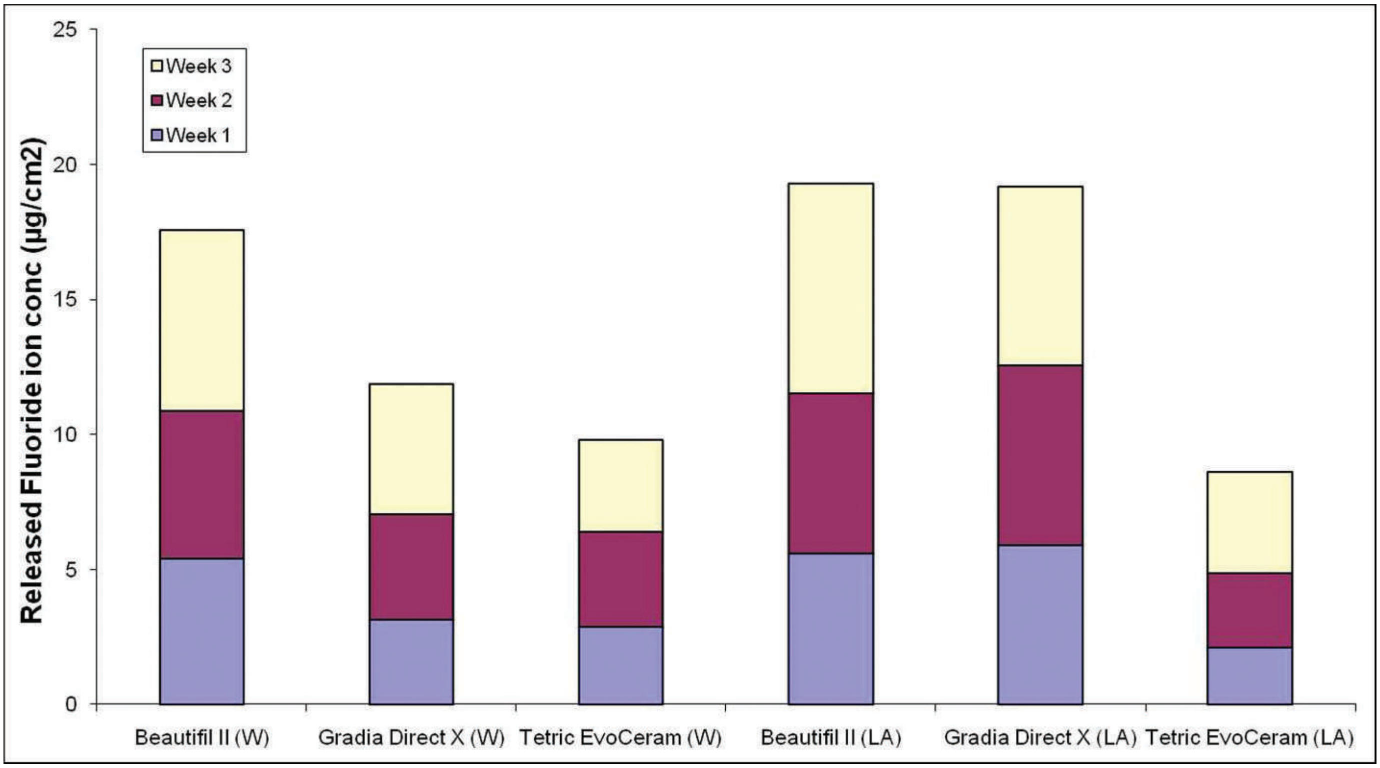

Figure 3. *Weekly cumulative fluoride ion release by each composite aged in lactic acid (LA) and deionized water (W) after weekly 5 minute fluoride recharge (5000 ppm) following 49 days aging.*

modulus were substantially lower than the analyzed resin composites at each testing interval. In contrast to the resin composites, Fuji IX Extra displayed a significant reduction ($p<0.05$) in the recorded elastic modulus with aging in both media.

DISCUSSION

In the present study, all three fluoride-containing resin composites demonstrated fluoride ion release and recharge capability. Additionally, the analyzed composites exhibited no significant ($p<0.05$) reduction in mechanical properties in either lactic acid (pH 4.0) or deionized water (pH 6.5) for the 3 months of the study.

Beautifil II exhibited the greatest fluoride ion release of the resin-based materials in both deionized water and lactic acid. The fluoride-releasing ability of S-PRG filler particles would be the primary reason for this finding; Gradia Direct X, Tetric EvoCeram, and Beautifil II have a comparable filler loading and resin matrix hydrophobicity.

The filler particles of the three composites analyzed have the ability to release fluoride into their resin matrix and surrounding media as a result of storage media dissolution of filler particle surfaces.[16] However, S-PRG particles have an additional source of fluoride for release—the fluoride complexes within their glass ionomer hydrogel.[10] Further, the acidified water within the hydrogel surrounding the inner glass of S-PRG particles facilitates fluoride release through continual dissolution of the fluoride-containing glass core.[17,18]

The greater fluoride release in lactic acid compared to release in water by each composite is significant in terms of potential inhibition of recurrent caries. This ability indicates that the composites in the present study are most capable of providing fluoride to surrounding tooth structure at the moments when adjacent enamel is most susceptible to demineralization. Such "smart behavior"[19] points clinicians to consider the timing in addition to the quantity of fluoride release when assessing the caries inhibition potential of fluoridated restorative materials.

The ability of a material to exhibit fluoride recharge depends on its ability to retain fluoride.[20,21] The hydrophobic nature of the resin matrices of the analyzed composites implicates the glass ionomer hydrogel of S-PRG particles as the key reason for the additional recharge demonstrated by Beautifil II

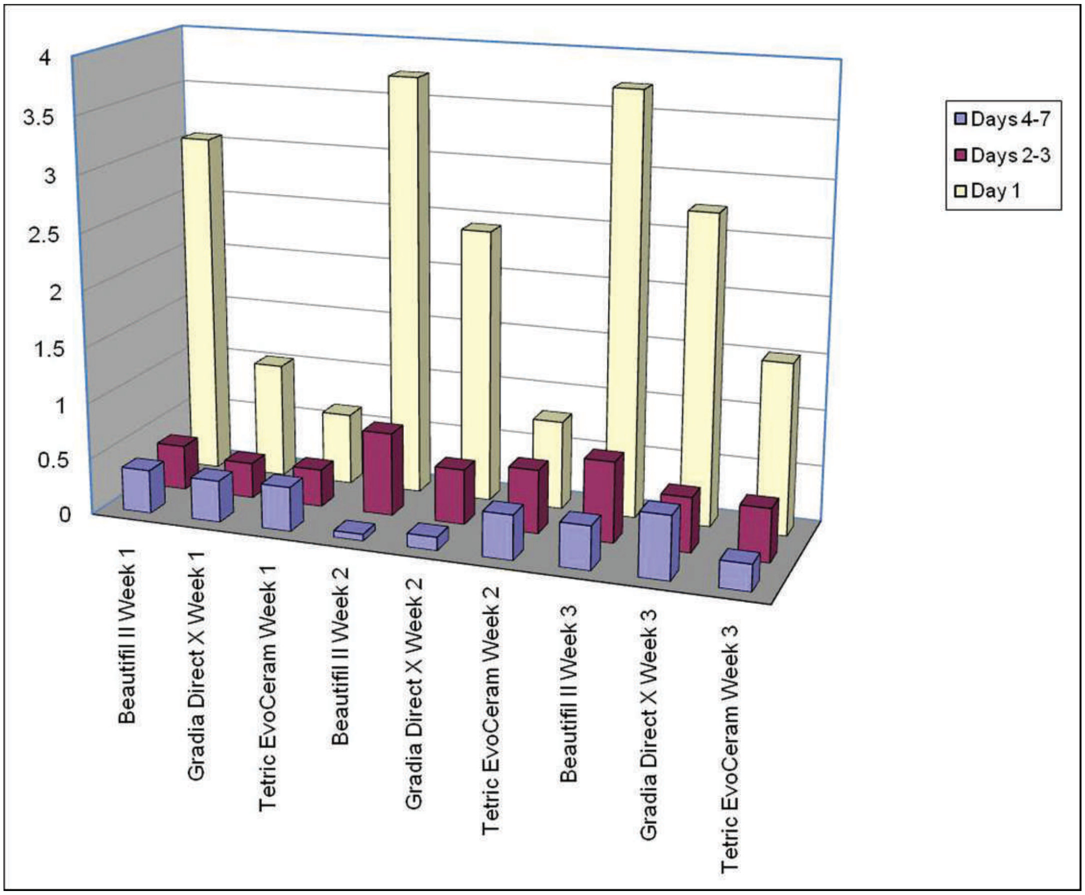

Figure 4. *Average daily fluoride ion release by each composite aged in deionized water following 5 minute fluoride recharge (5000 ppm) after 49 days aging.*

compared with Tetric EvoCeram and Gradia Direct X. The hydrogel of S-PRG particles exhibits a higher permeability and porosity than resin matrices.[22,23] This hydrogel provides Beautifil II with areas within its structure capable of greater fluoride uptake relative to a composite not containing a glass ionomer phase.

The increased level of recharge by each composite with each additional fluoride treatment reported in this study, despite aging, is consistent with previous studies.[16,24] Likewise, the positive relationship between pre recharge release levels and post recharge rerelease levels was in concert with previous data.[24-26] These findings point to rechargeabilty being governed by the number of sites available within a material able to retain absorbed fluoride.[18]

The relationship between the fluoride recharge ability and pre recharge fluoride release of the analyzed composites also explains the increased recharge demonstrated by Beautifil II and Gradia Direct X in lactic acid compared to water. In contrast to expectations from previous studies, Tetric EvoCeram demonstrated a higher recharge in water compared to lactic acid.[22,27] Further, Beautifil II, while exhibiting a 0greater cumulative rerelease in acid by the end of the 3-week recharge analysis, demonstrated a greater rerelease into water during three of the nine testing periods. These findings may be a result of the dissolving action of acid facilitating additional cation release from the filler within Tetric EvoCeram and Beautifil II. These cations have the capability to form fluoride complexes with fluoride ions introduced through recharge into the resin.[28,29] Such complexes are of greater molecular size than free fluoride ions and therefore may experience resistance to movement as well as increased retention time within the resin matrix.

A delayed release of such complexes points to a possible enhanced ability of resin composites sustaining a fluoride release, which might increase with time and so enhance the potential inhibition of recurrent caries.

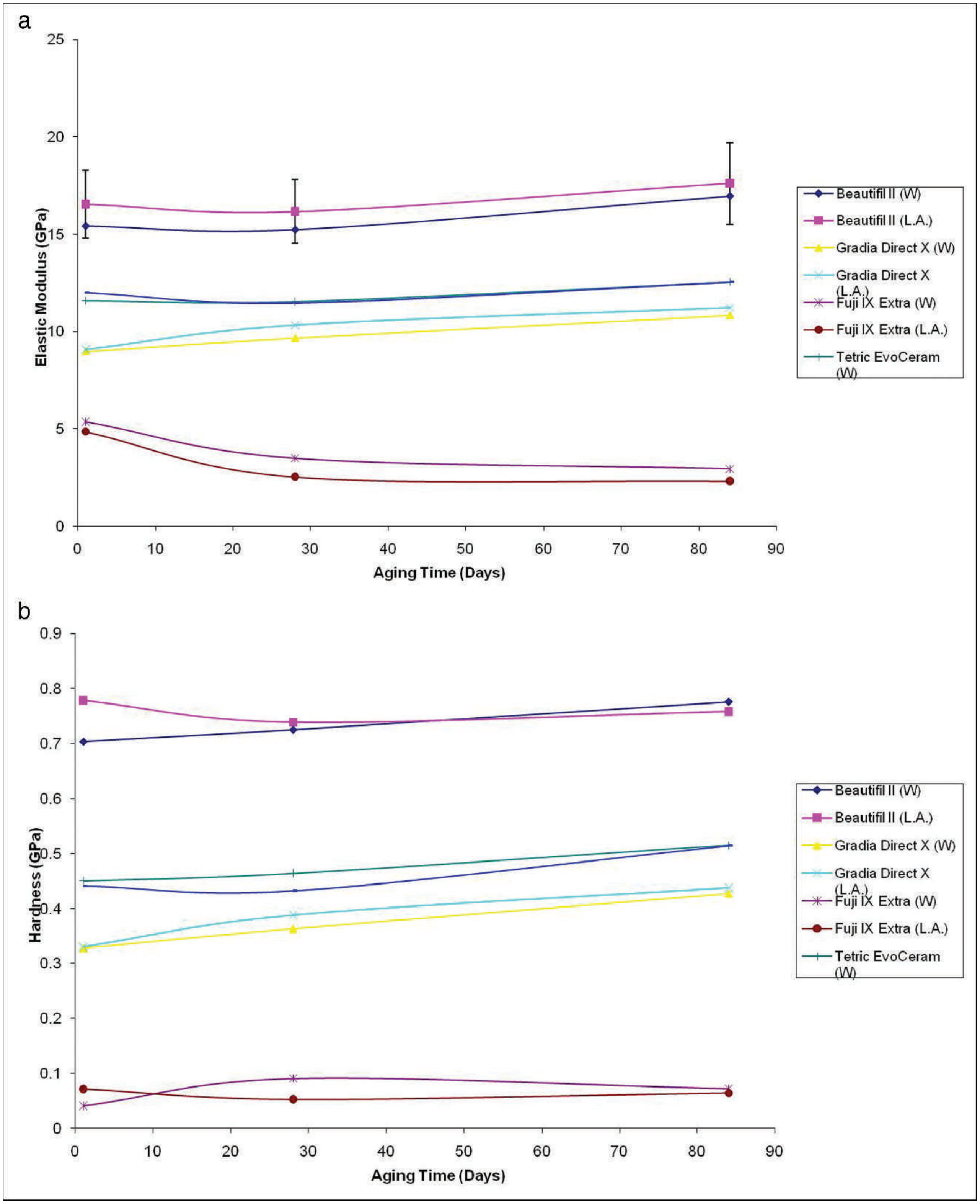

Figure 5a. *Elastic modulus of each composite aged in deionized water (W) and lactic acid pH 4.0 (L.A.) over 3 months.*
Figure 5b. *Hardness of each composite aged in deionized water (W) and lactic acid pH 4.0 (L.A.) over 3 months.*

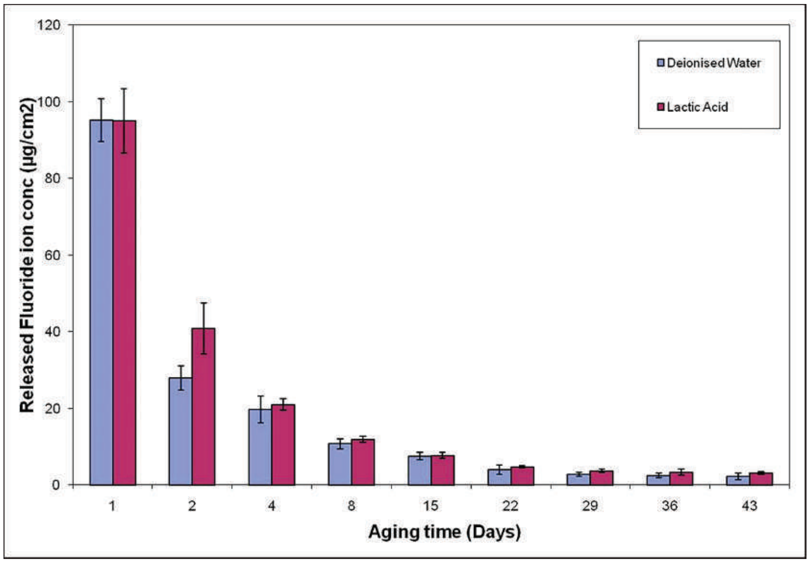

Figure 6. *Average daily fluoride ion release by Fuji IX Extra aged in deionized water and lactic acid (pH 4.0) over 43 days.*

Results of the present study affirm that glass ionomers have a significantly ($p<0.05$) greater fluoride release and recharge capacity relative to the analyzed fluoride-containing resin composites. This result was expected due to the nature of the setting reaction of glass ionomers. During this reaction, polyacrylic acid actively dissolves the fluoride-containing glass particles, enabling fluoride ion release.[17,30] This differs from the setting reaction of composites in which no intentional acidic treatment of the glass filler particles occurs. Additionally, glass ionomer cements are significantly more porous and permeable than resin composites, thus enhancing media interaction with glass particles and therefore substantially enhancing glass ionomer fluoride release and recharge.[23]

The present study indicates that by recharging Beautifil II utilizing a daily recharge regimen of 5000 ppm for 5 minutes, a regimen feasibly employed by patients, the fluoride release by Beautifil II approaches the "plateau release" of Fuji IX Extra (Figures 4 and 6). Importantly, this long-term daily "plateau release" from glass ionomers is regarded as contributing to recurrent caries inhibition.[31,32] The capacity for a fluoride rerelease from Beautifil II comparable to the "plateau release" from Fuji IX Extra gains greater relevance when considering the extremely high quantity of fluoride released by Fuji IX Extra compared to other glass ionomers that have displayed caries inhibition.[33] Further, since the placement of unfilled resin over glass ionomers reduces the level of fluoride release by a factor of 1.5 to 4 times,[34-36] it follows that the post recharge fluoride release from Beautifil II would be comparable and would potentially exceed the "plateau release" of glass ionomers that have demonstrated caries inhibition.[6,7]

While the greater permeability and porosity of glass ionomers contributed to the significantly ($p<0.05$) higher fluoride release of Fuji IX Extra, these characteristics also contributed to the observed reduction in elastic moduli of Fuji IX Extra with aging. This is in contrast to the three resin composites which displayed no significant ($p>0.05$) reduction in their elastic moduli or hardness with time. The greater permeability of the hydrogel enables a greater volume of storage media to contact and break down the glass fillers within glass ionomers, in turn affecting their mechanical properties.

Fluoride-containing resin composites and especially those containing prereacted glass ionomer fillers could be employed to great benefit in treating patients at high risk for caries in situations where glass ionomers may be unsuitable; particularly in high load-bearing or esthetically critical locations. To provide the maximum possibility for recurrent caries inhibition, a sustained level of fluoride release by a restorative material is necessary. This requirement arises from carious tooth destruction resulting from alternating episodes of remineralization and demineralization over time.[37] From the present study, a regular regimen of fluoride recharge would be recommended to achieve this from fluoridated resin composites. Should the weekly recharge regimen described in the present study be adopted, fluoride-releasing resin composites have the potential to exhibit a sustained long-term fluoride release necessary for recurrent caries inhibition.[38] An *in vivo* study investigating recurrent caries incidence when various fluoride recharge regimens are undertaken by patients could confirm this potential.

CONCLUSIONS

Within the limitations of the current study, the three composites tested demonstrated fluoride release (Beautifil II > Gradia Direct X > Tetric EvoCeram) and fluoride recharge (Beautifil II > Gradia Direct X > Tetric EvoCeram). This capability raises the possibility of fluoride-containing composites exhibiting a lower incidence of recurrent caries than non fluoride–containing composites. The mechanical properties of each composite did not diminish with aging and fluoride release over the testing period.

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REFERENCES

1. Wilder AD Jr, May KN Jr, Bayne SC, Taylor DF & Leinfelder KF (1999) Seventeen-year clinical study of ultraviolet-cured posterior composite Class I and II restorations *Journal of Esthetic Dentistry* **11(3)** 135-142.
2. Collins C, Bryant R & Hodge K (1998) A clinical evaluation of posterior composite resin restorations: 8-year findings *Journal of Dentistry* **26(4)** 311-317.
3. Botha C & de Wet F (1994) Polymerisation shrinkage around composite resin restorations—An *in vitro* study *Journal of the Dental Association of South Africa* **49(5)** 201-207.
4. Van Meerbeek B, Perdigao J, Lambrechts P & Vanherle G (1998) The clinical performance of adhesives *Journal of Dentistry* **26(1)** 1-20.
5. Millar B, Robinson P & Davies B (1992) Effects of the removal of composite resin restorations on Class II cavities *British Dental Journal* **173(10)** 210-212.
6. Dijkman G & Arends J (1992) Secondary caries *in situ* around fluoride-releasing light-curing composites: A quantitative model investigation on four materials with fluoride content between 0 and 26 vol% *Caries Research* **26(5)** 351-357.
7. Hsu C, Donly K, Drake D & Wefel J (1998) Effects of aged fluoride-containing restorative materials on recurrent root caries *Journal of Dental Research* **77(2)** 418-425.
8. Rebitski G & Donly KJ (1993) Dentin pretreatment and caries inhibition by a fluoride-releasing resin *American Journal of Dentistry* **6(4)** 204-206.
9. Shinno K, Nagafuji A, Nakatsuka T, Deguchi M & Negoro N (2007) A new fluoride releasing bonding material applying S-PRG filler *Journal of Dental Research* **86(Special Issue A)** Abstract Number 1589.
10. Tay F, Pashley E, Huang C, Hashimoto M, Sano H, Smales R & Pashley DH (2001) The glass-ionomer phase in resin-based restorative materials *Journal of Dental Research* **80(9)** 1808-1812.
11. Gordan V, Mondragon E, Watson R, Garvan C & Mjör I (2007) A clinical evaluation of a self-etching primer and a giomer restorative material: Results at eight years *Journal of the American Dental Association* **138(5)** 621-627.
12. Meyer J, Cattani-Lorente M & Dupuis V (1998) Compomers: Between glass-ionomer cements and composites *Biomaterials* **19(6)** 529-539.
13. Fischer-Cripps AC (2002) *Nanoindentation* 2nd ed Springer-Verlag, New York.
14. Angker L, Nockolds C, Swain MV & Kilpatrick N (2004) Correlating the mechanical properties to the mineral content of carious dentin—A comparative study using an ultra-micro indentation system (UMIS) and SEM-BSE signals *Archives of Oral Biology* **49(5)** 369-378.
15. Chung SM, Yap AU, Koh WK, Tsai KT & Lim CT (2004) Measurement of Poisson's ratio of dental composite restorative materials *Biomaterials* **25(13)** 2455-2460.
16. Itota T, Carrick TE, Yoshiyama M & McCabe JF (2004) Fluoride release and recharge in giomer, compomer and resin composite *Dental Materials* **20(9)** 789-795.
17. De Moor RJ, Verbeeck RM & De Maeyer EA (1996) Fluoride release profiles of restorative glass ionomer formulations *Dental Materials* **12(2)** 88-95.
18. Attar N & Onen A (2002) Fluoride release and uptake characteristics of aesthetic restorative materials *Journal of Oral Rehabilitation* **29(8)** 791-798.
19. Itota T, Al-Naimi O, Carrick T, Yoshiyama M & McCabe J (2005) Fluoride release from aged resin composites containing fluoridated glass filler *Dental Materials* **21(11)** 1033-1038.
20. Preston AJ, Higham SM, Agalamanyi EA & Mair LH (1999) Fluoride recharge of aesthetic dental materials *Journal of Oral Rehabilitation* **26(12)** 936-940.
21. Han L, Cv E, Li M, Niwano K, Ab N, Okamoto A, Honda N & Iwaku M (2002) Effect of fluoride mouth rinse on fluoride releasing and recharging from aesthetic dental materials *Dental Materials Journal* **21(4)** 285-295.
22. Attin T, Buchalla W, Siewert C & Hellwig E (1999) Fluoride release/uptake of polyacid-modified resin composites (compomers) in neutral and acidic buffer solutions *Journal of Oral Rehabilitation* **26(5)** 388-393.
23. Preston AJ, Agalamanyi EA, Higham SM & Mair LH (2003) The recharge of esthetic dental restorative materials with fluoride *in vitro*—Two years' results *Dental Materials* **19(1)** 32-37.

24. Xu X & Burgess JO (2003) Compressive strength, fluoride release and recharge of fluoride-releasing materials *Biomaterials* **24(14)** 2451-2461.

25. Attar N & Turgut MD (2003) Fluoride release and uptake capacities of fluoride-releasing restorative materials *Operative Dentistry* **28(4)** 395-402.

26. Gao W & Smales R (2001) Fluoride release/uptake of conventional and resin-modified glass ionomers and compomers *Journal of Dentistry* **29(4)** 301-306.

27. Vieira AR, de Souza IP & Modesto A (1999) A fluoride uptake and release by composites and glass ionomers in a high caries challenge situation *American Journal of Dentistry* **12(1)** 14-18.

28. Nicholson JW & Czarnecka B (2004) The release of ions by compomers under neutral and acidic conditions *Journal of Oral Rehabilitation* **31(7)** 665-670.

29. Williams JA, Briggs E, Billington RW & Pearson GJ (2003) The effects of adding fluoride compounds to a fluoride-free glass ionomer cement on subsequent fluoride and sodium release *Biomaterials* **24(7)** 1301-1308.

30. Vermeersch G, Leloup G & Vreven J (2001) Fluoride release from glass-ionomer cements, compomers and resin composites *Journal of Oral Rehabilitation* **28(1)** 26-32.

31. Wiegand A, Buchalla W & Attin T (2007) Review on fluoride-releasing restorative materials—Fluoride release and uptake characteristics, antibacterial activity and influence on caries formation *Dental Materials* **23(3)** 343-362.

32. Toumba KJ & Curzon M (1993) Slow-release fluoride *Caries Research* **27(Supplement 1)** 43-46.

33. Pereira PN, Inokoshi S & Tagami J (1998) *In vitro* secondary caries inhibition around fluoride releasing materials *Journal of Dentistry* **26(5–6)** 505-510.

34. Vercruysse CW, De Maeyer EA & Verbeeck RM (2001) Fluoride release of polyacid-modified composite resins with and without bonding agents *Dental Materials* **17(4)** 354-358.

35. Mazzaoui SA, Burrow MF & Tyas MJ (2000) Fluoride release from glass ionomer cements and resin composites coated with a dentin adhesive *Dental Materials* **16(3)** 166-171.

36. Castro GW, Gray SE, Buikema DJ & Reagan SE (1994) The effect of various surface coatings on fluoride release from glass-ionomer cement *Operative Dentistry* **19(5)** 194-198.

37. Kidd E & Joyston-Bechal S (2005) *Aetiology of Dental Caries Essentials of Dental Caries: The Disease and Its Management* 3rd ed Oxford University Press, New York.

38. Duckworth RM & Morgan SN (1991) Oral fluoride retention after use of fluoride dentifrices *Caries Research* **25(2)** 123-129.