Abrasive wear of enamel by bioactive glass-based toothpastes

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Abstract: Purpose: To determine the abrasivity of a 45S5 bioactive glass based toothpaste on enamel as a function of the particle size and shape of the glass. **Methods:** 45S5 glass was synthesized ground and sieved to give various particle sized fractions < 38, 38-63 and 63-110 microns. Two different grinding routes were used: percussion milling and ball milling. The glass powders were formulated into toothpastes and their tooth brush abrasivity measured according to BS EN ISO11609 methodology. **Results:** Enamel loss increased with increasing particle size. The percussion milled powder exhibited particles that had sharp edges and the pastes were significantly more abrasive than the pastes made with round ball milled powders. One interesting observation made during the present study was that there was preferential wear of the enamel at the dentin-enamel junction (DEJ), particularly with the coarse particle sized pastes. (*Am J Dent* 2014;27:263-267).

Clinical significance: The enamel wear for particle size ranges used in existing bioactive glass toothpastes was < 20 microns for 20,000 brushing strokes which we estimate to be equivalent to about 3 years brushing. On this basis there is not a significant abrasivity problem with existing bioactive glass toothpastes. However any abrasivity against enamel is undesirable and reducing the particle size could reduce abrasivity of these particles.

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Introduction

The 45S5 bioactive glass consisting of 46.1 mole% SiO_2, 2.6 mole% P_2O_5, 26.9 mole% CaO and 24.4 mole% Na_2O has been incorporated into toothpastes for treating dentin hypersensitivity (DH) and for the remineralization of enamel.[1-19] The glass used is sold under the trade name NovaMin.[a] Typically a 5-10 weight percent loading of glass is used in the toothpaste. The glass particles used have a broad particle size distribution with a significant fraction (>10%) below about 3 µm, which corresponds to the size of dentin tubules. In addition there are large (< 90 µm) particles present to provide long-term release of Ca^{2+} and PO_4^{3-} ions.

The glass particles dissolve in the saliva releasing Ca^{2+} and PO_4^{3-} ions and are thought to form hydroxycarbonated apatite (HCA) on the surface of the tooth and within the dentin tubules.

These new NovaMin-based toothpastes have been shown to be clinically effective in treating DH[5] and are likely to be more effective than other treatments that use primarily calcium carbonate to occlude the dentin tubules, because of the lower acid solubility of HCA compared to calcium carbonate. The release of Ca^{2+} and PO_4^{3-} ions is also useful for remineralizing incipient caries lesions and other potential benefits include an anti-gingivitis role.[11]

However, one of the potential disadvantages of NovaMin is the 45S5 glass that forms the basis of NovaMin has a hardness of approximately 4.68 GPa,[20] which is considerably harder than enamel at about 3.5 GPa. Consequently during tooth brushing these new NovaMin-based toothpastes are likely to wear enamel. This is of particular concern, since there is circumstantial evidence that at least in part DH may be caused by excessive tooth brushing.[21] Furthermore, DH is most pronounced at the cervical margins where the enamel is thinnest and furthermore the enamel closest to the DEJ is softer[22-24] and is consequently most readily abraded away.

This study examined the abrasivity of the 45S5 glass against enamel and dentin as a function of both the particle size and shape with view to understanding the relative importance of these two parameters in order to be able to design bioactive glass toothpastes with reduced abrasivity.

The focus of this study was therefore on enamel wear since it is the enamel that forms the outer surface of the tooth and is more susceptible to brushing, in particular overzealous brushing habits. As a consequence of this trauma enamel may be removed and the underlying dentin exposed which may result in DH.

Materials and Methods

Glass synthesis - Mixtures of analytical grade SiO_2,[b] P_2O_5,[c] $CaCO_3$,[c] and Na_2CO_3[c] were melted in a platinum-rhodium crucible for 1 hour at 1,380°C in an electric furnace (EHF 17/3.[d] A batch size of approximately 200 g was used. After melting, the glasses were rapidly submerged in water to prevent crystallization. After drying, the glass was ground. The amorphous structure of the glasses was confirmed by powder X-ray diffraction (XRD;[e] 40 kV/40 mA, Cu Ka, data collected at room temperature).

Milling of glass frit - Two different routes were used for comminuting the frit: percussion (Gyro mill[f]) milling also known as puck milling, and ball milling.

The basic working principle of Gyro milling is based on the impact fracture of the glass frit into small particles. The particles produced are angular and irregular in shape with sharp edges. The other method used is ball milling and in this case a rotating cylinder is partially filled with alumina balls, which then grinds the material by friction and low speed impact with the tumbling balls. Here the particles produced are relatively round in shape.

Gyro milling was carried out with a 250 ml pot with 100 g of glass frit for two periods of 7 minutes with the machine set to the highest amplitude setting with a Gyro mill. Ball milling was carried out with 100 g of frit and ball milling with 30 g of

Table 1. Different batches of toothpastes.

Toothpaste name	45S5 particle size	45S5 particle shape
Toothpaste A	63-110 µm	Angular
Toothpaste B	38-63 µm	Angular
Toothpaste C	<38 µm	Angular
Toothpaste D	38-63 µm	Round
Toothpaste E	<38 µm	Round

alumina balls in a 2l ball mill pot[g] with a 30 g charge of alumina balls for a period of 24 hours.

Three different sieve mesh sizes[h] were used to produce three different ranges of particle size; coarse, medium and fine from the ground glass powder. The sieves used were; 38µm, 38 and 63 µm sieve and 63 and 110 µm. Table 1 summarizes the various glass powders that were prepared.

Preparation of the toothpastes - Toothpaste contains active and inactive ingredients in its composition and these inactive ingredients are essential for the formulation of the toothpaste. These inactive ingredients include binders, humectants, detergents, abrasives, flavoring and coloring agents. US patent US 2009/0324516[25] was followed for the formulation of the toothpaste using 10% by weight of the 45S5 glass. Some small changes were made to the toothpaste formulation. The toothpaste formulation includes glycerol, Carbopol, which is polyacrylic acid (molecular weight of approximately 45,000), PEG400 which is polyethylene glycol, which is added to reduce any stickiness and gives smooth texture to the toothpaste, and Syloid 244FP, a silica used as a thickening agent in the toothpaste. K acesulfame as a sweetener and titanium dioxide is also added to improve the luster of toothpaste.

The original patent formulation[26] also included an abrasive in the form of Syloid 63, which is silica abrasive. This was omitted from the toothpaste, since no other abrasive was wanted in the toothpaste other than the 45S5 glass.

The exact amount of the ingredients was weighed and then mixed in a 100 ml plastic container. The 45S5 glass was added last and then mixed thoroughly so that the ingredients dispersed to form the toothpaste. Five batches of toothpaste with the different bioactive glass particle sizes were formulated (Table 2).

Preparation of the tooth samples - Caries free extracted mandibular and maxillary premolars were used for the study. Teeth were obtained from the tooth bank at the Royal London Dental Hospital under agreed Ethics Committee approval (QMREC 2011/99). Teeth were stored in 1% sodium hypochlorite solution. First the teeth were embedded horizontally in an acrylic resin, to make blocks, with dimensions of 3×3×2 cm with the buccal surface of the teeth facing upwards. The facial surface of the tooth was subsequently flattened over the abrasive disc to get the flat and smooth surface of enamel. Afterwards the discs were then polished with 3, 1 and 0.25 µm diamond polishers.[i] The final polished buccal surfaces of premolars were then embedded in acrylic blocks. Two holes of hemi-spherical shape were made on each sample using a dental hand piece with a diamond bur 1.6 mm in diameter. These holes were drilled into the acrylic just below the DEJ region together with un-brushed flat surface to serve as a reference frame for the registration of paired surfaces (before and after brushing). Four premolars were used for each toothpaste.

Particle size analysis – A Malvern particle size analyzer (Malvern Mastersizer[j]) was used for the particle size analysis. This analyzer works on the phenomenon laser diffraction and is based around the principle that particles passing through a laser beam will scatter light.

Table 2. Composition of the toothpaste.

Component	Amount in grams
Glycerine	57.75
PEG400	17.50
K Acesulfame	0.40
Carbopol	0.40
TiO_2	1.00
Syloid 63	6.00
Na lauryl S	0.85
NovaMin	10.00

SEM analysis - The ground glass powders, which had been percussion-milled and ball-milled, were compared with SEM. Samples were observed in a SEM (JCM-500[k]) to qualitatively assess the particle size and shape.

Profilometry - A 3-D surface scanner[l] was used for the surface digitization. This instrument gives high dynamic performance with small scanning deflections and low contact forces. The tip of the contact probe, which explores the surface of the sample, is a 1 mm-diameter sphere made of industrial ruby. The scanning interval used in this experiment is 0.05 mm and speed of the probe was set to 400 mm/second. The teeth samples before and after brushing were digitized with this instrument.

A 3-D image analysis software (Cloud[m]) was used to analyze the samples. Making a fit at the common areas of two hemispheres enabled the registration of the images before and after brushing. The height loss from the area brushed with toothpaste was to be determined. Four measurements were taken from the center of the enamel away from the DEJ and enamel-dentin surfaces.

Brushing of samples - Once the tooth samples were prepared and profiled they were brushed using an automated brushing machine with 10 brushing stations. Each acrylic block having the tooth section embedded in it, was then fixed firmly on each station. The toothbrushes used in this experiment were flat trim brushes with round ended medium textured bristles. Approximately one ml of toothpaste was applied on the brush and the tooth sample was positioned in such a way on the brushing machine so that the direction of brushing strokes was parallel to the root. A mass of 200 grams was used. The brushing machine was programmed to perform 2,000 brushing cycles, but after each 2,000 brushing cycles, a fresh 1 ml of toothpaste was applied. On completion of the 20,000 brushing strokes the samples were removed from each station and washed with water and then profiled again to determine the amount of enamel and dentin wear from each sample. The brushing machine and protocol was based on the BS EN ISO11609 methodology. Note however this standard measures dentin abrasivity, while clinically enamel is more important since it forms the outer layer of the tooth that is exposed to tooth brushing.

Experimental design and statistical methods - The experimental design was chosen to have particle size distributions both larger and smaller than that used in NovaMin in order to obtain significant wear and significant differences. In addition, to

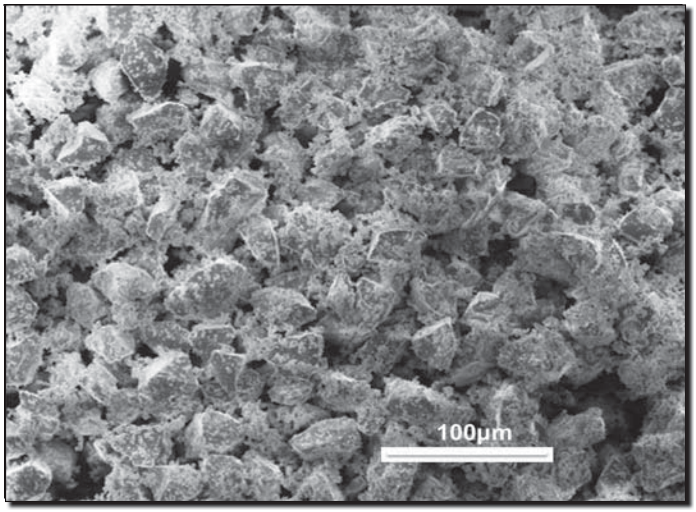

Fig. 1. SEM image of glass B. There are numerous glass particles present < 38 µm in size.

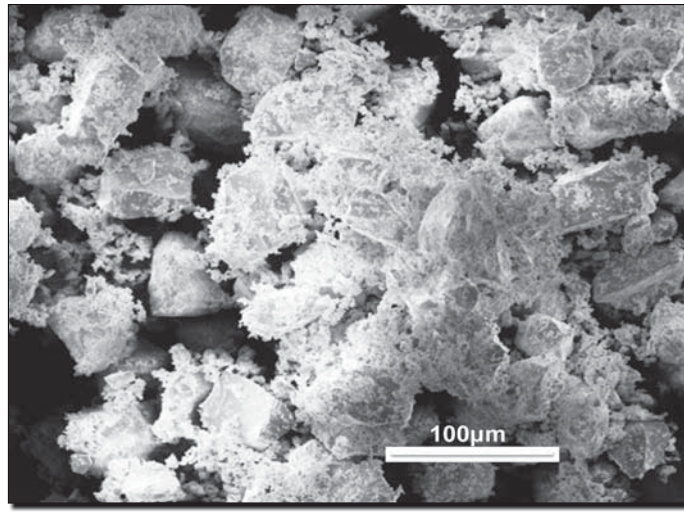

Fig. 2. SEM image of glass A. Small glass particles can be seen adhering to the larger particles and there are also loose agglomerates of small particles.

Table 3. Particle size distribution in batches.

Batch Name	D10	D50	D90
A	1.74 µm	64.68 µm	77.26 µm
B	1.62 µm	41.20 µm	68.47 µm
C	0.91 µm	6.60 µm	28.19 µm
D	1.36 µm	31.28 µm	68.43 µm
E	0.52 µm	5.35 µm	18.63 µm
NovaMin	1.77 µm	14.47 µm	45.55 µm

facilitate obtaining measurable enamel wear, a high glass loading in the toothpaste (10% by weight) was used. Typicallly 2.5 to 10 weight percents of NovaMin are used in commercial pastes. In addition 20,000 brushing strokes were used with a 200 g force on the brush in order to facilitate getting a measure-able enamel loss. The mean and standard deviations were calculated based on the four measurements on four teeth, i.e. based on 16 measurements in total. The error bars on the figures represent twice the standard deviations. Since the error bars are small and the data and associated error bars are well separated, statistical tests were not required to show significance.

Results

Table 3 shows the results of the particle size analysis. All the particle size distributions have a significant fraction of < 1 micron particles present even in samples A, B and D which in theory, the fine particle should have been removed by sieving. The D90 values were all less than the maximum sieve mesh used. For example Toothpaste A was sieved through a 110 µm mesh sieve and has a D90 value of 77.26 µm. The particle size range of the experimental glasses covered the size distributions found in NovaMin. With the NovaMin particle size falling between samples B and C of the Gyro milled samples and samples D and E of the ball milled samples. The glass particle size distributions were deliberately made to give distributions both larger and smaller than that used in NovaMin.

Scanning electron microscopy of the glass powders (Figs. 1, 2) showed that the sieving process was not very efficient and that small glass particles tend to adhere to the surfaces of larger glass particle during sieving. Numerous small glass < 10 µm particles are seen in glass samples A and B despite the fact they

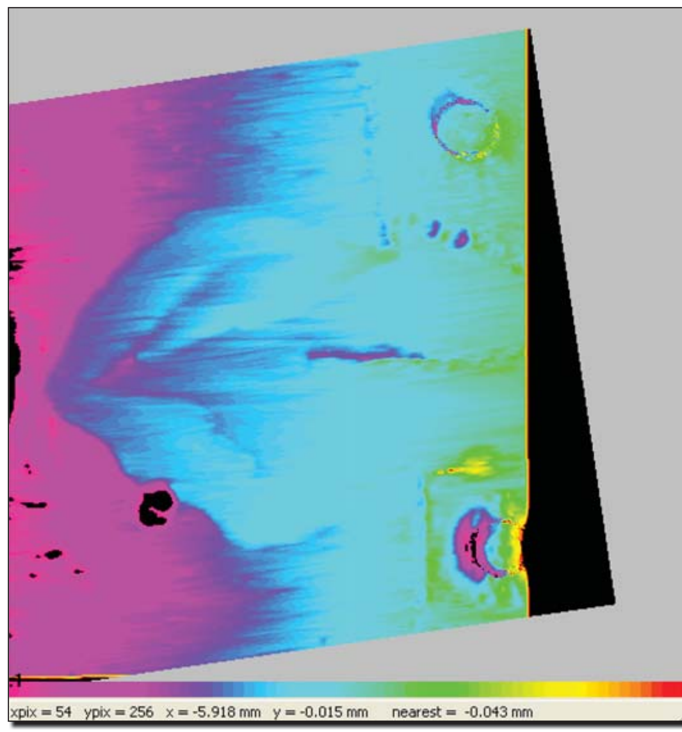

Fig. 3. A color coded image of two registered images of after over before brushing. The color of sea blue, dark blue and purple demonstrates a progression in wear.

should have been removed by the 63 and 38 µm sieves. The presence of these small particles accounts for the low D10 values seen for all the glass powders and was very obvious in Fig. 2. It can be seen that the particle size of the larger particles in Fig. 2 was considerably larger than that of Fig. 1, which is consistent with the D50 and D90 values given in Table 3 obtained from light scattering scanning electron microscopy, and also showed that ball milling made a much rounder particle than Gyro milling.

Figure 3 shows the profilometry data for paste A containing the largest bioactive glass particles. Extensive grooving in the direction of the tooth brushing was evident, and is seen as striations running left to right in Fig. 3. This indicates the coarse sharp glass particles in the particle size distribution were

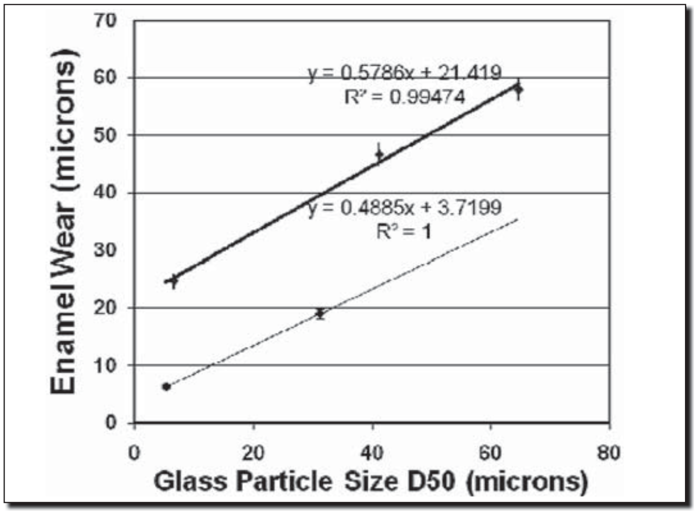

Fig. 4. Enamel wear in microns plotted against the D50 glass particle size.

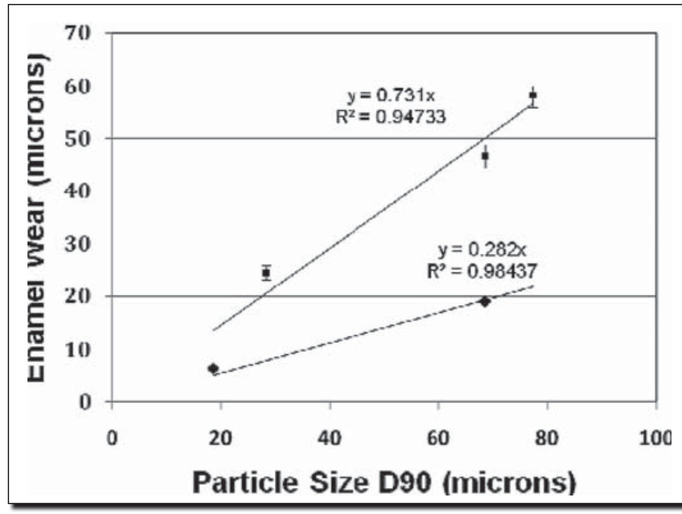

Fig. 5. Enamel wear in microns plotted against the D90 glass particle size.

forming deep scratches on the surface of the acrylic, enamel and dentin. The other three samples for paste A exhibited less marked grooves, but they all exhibited some degree of grooves. Another interesting aspect was that there was preferential wear of the enamel at the dentin-enamel junction (DEJ) which shows up as a deep blue area in the colored image of Fig. 3.

Figure 4 plots the mean wear for each paste against the D50 particle size and Fig. 5 plots the mean wear against the D90 particle size. It can be seen that the errors are small. It can be clearly seen in both plots that the enamel wears less with decreasing particle size of the glass. It also decreases substantially for the ball milled glasses compared to the Gyro milled glasses. The rounder nature of ball milled glasses results in reduced wear compared to the more angular sharper edged particles produced during the impact fractures that occur during Gyro milling. The wear data plotted against the D90 particle size data interestingly extrapolates to almost zero wear for both methods of comminution. In contrast the D50 data extrapolates to approximately 21 µm and 4 µm for the Gyro milled and ball milled data. This extrapolation to zero enamel loss for a zero particle size makes logical sense since a zero particle size indicates no abrasive particles. The plot also suggests that it is probably the larger particle sizes in the particle size distribution that dominate abrasivity and probably largely determines the enamel loss or wear.

Discussion

Ball milling is known to give more rounded ceramic particles than percussion or puck milling.[30] The increased wear at the DEJ occurred particularly with the coarse glass particle sized pastes. There are a number of reports[23,24] that indicate that the enamel at the DEJ is less mineralized and significantly softer than enamel in bulk, and is therefore more likely to be abraded than the bulk enamel.

A typical tooth brushing daily cycle probably involves no more than 20 brush strokes across any one tooth. On this basis, the 20,000 cycles would correspond to 1,000 brushing episodes and assuming two brushing episodes/day this would correspond to about 3 years of brushing. Typically on the crown of the tooth the enamel is 1-2 mm thick, assuming 10 microns abrasion in every 3 years, a 1 mm loss would take more than 300 years. In contrast, the enamel at the cervical margins is much thinner and approximately 50 microns thick, which would only take 15 years to abrade away. However this neglects the fact that enamel close to the DEJ is softer and is likely to be abraded away at a much faster rate which was observed experimentally in the data. In addition, toothpaste abrasivity is likely to be much greater if the tooth is exposed to an erosive challenge such as acidic drinks prior to brushing that removes the hard apatite phase and results in softer enamel.

While the abrasivity of bioactive glass toothpastes is not a major problem on its own, it would still be desirable to reduce the enamel abrasivity, since the outermost enamel layer that becomes fluoridated with use of a fluoride toothpaste is very thin and removal of this protective layer by abrasion is likely to promote caries and acid erosion. Addy[21] suggested that tooth paste abrasivity may be a contributory factor in dentin hypersensitivity particularly when combined with an erosive challenge. The results indicate that reducing the particle size, particularly the D90 value would reduce abrasivity towards enamel. Grinding to a smaller particle size involves an increased cost for the manufacturer. A much better approach would be to reduce the hardness of the glass to a value close to that of enamel. This can be achieved by, for example, incorpora-ting fluoride into the glass that results in softer glasses as well as giving rise to glasses that form fluorapatite,[27,28] which is much more durable than the hydroxycarbonated apatite formed by the 45S5 NovaMin glass that is currently used in toothpastes. The existing data on the efficiency of the NovaMin based toothpastes decreases markedly after an exposure to an acid challenge.[29] Incorporating fluoride into the glass also speeds up the apatite formation process and results in localized fluoride release.[28]

In conclusion, the particle size, grinding process and particle shape strongly influence the abrasivity of bioactive glass based toothpastes. Abrasivity increased with increasing particle size. Abrasivity was also strongly dependent on the particle shape with grinding pathways that produce sharper, more angular particles, making the pastes more abrasive to enamel.

a. GSK, Weybridge UK.
b. Prince Minerals Ltd., Stokeon-Trent, UK.
c. Sigma–Aldrich, Gillingham, UK.
d. Lenton, Hope Valley, UK.
e. X'Pert PRO MPD, PANalytical, Cambridge, UK;
f. Glen Creston London, UK.

g. Pascall Engineering Crawley Sussex, UK.
h. Endecotts Ltd., London, UK.
i. Kemet International Ltd, Maidstone, UK.
j. Malvern Instruments Ltd, Malvern, UK.
k. JEOL, Tokyo, Japan.
l. Incise Dental Scanners, Renishaw Gloucestershire, UK.
m. Medical Physics Dept Unversity College London London, UK.

Disclosure statement: Drs. Gillam, Hill and Mneimne are inventors on patents on bioactive glasses. Drs. Mneimne, Mahmood and Zhou declared no conflict of interest.

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References

1. Du MQ, Tai BJ, Jiang H, Zhong JP, Greenspan DC, et al. Efficacy of dentifrice containing bioactive glass (NovaMin®) on dentin hypersensitivity. *J Dent Res* (Sp Is A) 2003;83:1546.
2. Greenspan DC, Clark A, La Torre GP. In vitro antimicrobial properties of a bioactive glass (NovaMin®) containing dentifrice. *J Dent Res* 2004; 82:1586.
3. Gjorgievska E, Nicholson JW. Prevention of enamel demineralization after tooth bleaching by bioactive glass incorporated into toothpaste. *Aust Dent J* 2011;56:193-200.
4. Layer TM. Development of a fluoridated, daily-use toothpaste containing NovaMin technology for the treatment of dentin hypersensitivity. *J Clin Dent* 2011;22:59-61.
5. Gendreau L, Barlow AP, Mason SC. Overview of the clinical evidence for the use of NovaMin in providing relief from the pain of dentin hypersensitivity. *J Clin Dent* 2011;22:90-95.
6. Earl JS, Leary RK, Muller KH, Langford RM, Greenspan DC. Physical and chemical characterization of dentin surface following treatment with NovaMin technology. *J Clin Dent* 2011;22:62-67.
7. Earl JS, Ward MB, Langford RM. Investigation of dentinal tubule occlusion using FIB-SEM milling and EDX. *J Clin Dent* 2010;21:37-41.
8. Parkinson CR, Willson RJ. A comparative in vitro study investigating the occlusion and mineralization properties of commercial toothpastes in a four-day dentin disc model. *J Clin Dent* 2011; 22:74-82.
9. Wang Z, Jiang T, Sauro S, Pashley DH, Toledano M, et al. The dentine remineralization activity of a desensitizing bioactive glass-containing toothpaste: An in vitro study. *Aust Dent J* 2011;56:372-381.
10. West NX, Macdonald E, Jones SB, Claydon NCA, Hughes N, et al. Randomized in situ clinical study comparing the ability of two new desensitizing toothpaste technologies to occlude patent dentin tubules. *J Clin Dent* 2011; 22 82-89.
11. Tai BJ, Bian Z, Jiang H, Greenspan DC, Zhong J, et al. Anti-gingivitis effect of a dentifrice containing bioactive glass (NovaMin) particulate. *J Clin Periodontol* 2006;33:86-91.
12. Efflandt SE, Magne P, Douglas WH, Francis LF. Interaction between bioactive glasses and human dentin. *J Mater Sci* 2002;13:557-565.
13. Wang Z, Jiang T, Sauro S, Pashley DH, Toledano M, et al. The dentine remineralization activity of a desensitizing bioactive glass-containing toothpaste: An in vitro study. *Aust Dent J* 2011;56:372-381.
14. Gillam DG, Tang JY, Mordan NJ, Newman HN. The effects of a novel Bioglass® 27 dentifrice on dentine sensitivity: A scanning electron microscopy investigation. *J Oral Rehabil* 2002; 29:305-313.
15. Gendreau L, Barlow APS, Mason SC. Overview of the clinical evidence for the use of NovaMin® in providing relief from the pain of dentin hypersensitivity. *J Clin Dent* 2011; 22:90-95.
16. Burwell AK, Litkowski LJ, Greenspan DC. Calcium sodium phosphosilicate (NovaMin): Remineralization potential. *Adv Dent Res* 2009;21:35-39.
17. Litkowski LJ, Quinlan KB, McDonald NJ. Calcium sodium phosphosilicate (NovaMin): Remineralization potential. *J Dent Res* 1998;77(Suppl. 1):199.
18. Wang ZJ, Sa Y, Sauro S, Chen H, Xing WZ, et al. Effect of desensitising toothpastes on dentinal tubule occlusion: A dentine permeability measurement and SEM in vitro study. *J Dent* 2010;38:400-410.
19. Pradeep AR, Sharma A. Comparison of clinical efficacy of a dentifrice containing calcium sodium phosphosilicate to a dentifrice containing potassium nitrate and to a placebo on dentinal hypersensitivity: A randomized clinical trial. *J Periodontol* 2010;81:1167-1173.
20. Cook RJ, Watson TF, Hench LL, Thompson ID. Use of bioactive glass. US2008/0176190.
21. Addy M. Tooth brushing tooth wear and dentine hypersensitivity- are they associated? *Int Nat Dent J* 2005;55:261-267.
22. Gillam DG, Orchardson R. Advances in the treatment of root dentine sensitivity, mechanisms and treatment principles. *Endod Topics* 2006;13:13-33.
23. Cuy JL, Mann AB, Livi KJ, Teaford MF, Weihs TP. Nanoindentation mapping of the mechanical properties of human molar tooth enamel. *Arch Oral Biol* 2002;47:281-291.
24. Jeng YR, Lin TT, Hsu HM, Chang HJ, Shiekh DB. Human enamel rod presents anisotropic nanotribological properties. *J Mech Behav Biomed Mater* 2011;4:515-522.
25. Muscle DP, Burwell KA, La Torre G. Composition and methods for enhancing fluoride uptake using bioactive glass. US 2009/0324516.
26. British Standards Institution. Dentistry-toothpastes - Requirements, test methods and marking, BS EN ISO 11609; 1998.
27. Mneimne M, Hill RG, Bushby AJ, Brauer DS. High phosphate content 1 significantly increases apatite formation of fluoride-containing bioactive glasses. *Acta Biomater* 2011;7:1827-1834.
28. Brauer DS, Karpukhina N, O'Donnell MD, Law RV, Hill RG. Fluoride-containing bioactive glasses: Effect of glass design and structure on degradation, pH and apatite formation in simulated body fluid. *Acta Biomater* 2010;6:3275-3282.
29. Diamanti I, Loeltsi-Kounari H, Mamai_Homata E, Vougiouklakis G. In vitro evaluation of fluoride and calcium phospho-silicate toothpastes on root dentine caries lesions. *J Dent* 2011;39:619-628.
30. Kaya E, Hogg R, Kumar SR. Particle shape modification during comminution. *Kona* 2002; 20:188-194.