Impact of particle morphology on abrasion, polishing and stain removal efficacy in a tooth cleaning model system

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Impact of Particle Morphology on Abrasion, Polishing and Stain Removal Efficacy in a Tooth Cleaning Model System

Short title: Abrasive Particle Morphology Affects Dental Cleaning

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Highlights

- Spherical silica gel particles achieved greater dental stain removal compared with standard angular silica particles.
- Spherical alumina particles demonstrated greater dental stain removal compared with angular alumina particles.
- The main factor influencing stain removal, abrasivity and surface finishing was abrasive particle morphology compared with particle concentration and size.

Abstract

Toothbrushing with toothpaste is used for daily maintenance of oral hygiene, and aims to remove food debris, the dental plaque biofilm and dental stains from tooth surfaces. However, toothpastes can also cause tooth abrasion as different particle morphologies are known to exert differential cleaning and abrasivity. Consequently, silica and alumina particles with spherical and angular morphologies, at comparable size ranges and concentrations, were used to brush polished, partially roughened or stained bovine enamel specimens and their impact on tooth abrasion, surface polishing and stain removal *in vitro,* was determined. Spherical silica gel particles at concentrations as low as 0.5% (w/w) achieved greater dental stain removal and higher surface polishing compared with 15% (w/w) standard abrasive silica without producing significant increases in enamel wear. Comparable results were also found for alumina abrasive particles, whilst spherical alumina particles at concentrations as low as 0.25% (w/w) showed greater stain removal compared with 1% (w/w) angular alumina particles. Both particles achieved similar surface polishing and produced less enamel wear. These findings are important in underpinning the development of

dentifrices which aim to achieve optimal cleaning whilst minimising dental hard tissue damage.

Keywords

Bovine enamel; Toothbrush abrasion; Surface polishing; Stain removal; Particle morphology

1. Introduction

Dental diseases, such as caries and periodontal disease, remain the most prevalent chronic disease in both children and adults despite being preventable [1]. Clear causal links are well established between the presence of dental plaque and disease progression [2]. In dentistry, toothbrushing with toothpaste is the most common method used for daily maintenance of oral hygiene and aims to remove food particulates, the plaque biofilm and stain from tooth surfaces [3]. Notably, there is also an increasing demand for improved dental aesthetics using dental whitening products [4]. It is now widely recognised that toothpaste abrasivity is necessary for the prevention and removal of extrinsic stain [5]. However, the abrasivity of the toothpaste needs to be moderated as excessive wear can lead to loss of mineralised tissue, resulting in dentine hypersensitivity and poor aesthetics [6], [7]. Consequently, it is not only important to determine the stain removal efficacy of toothpaste but also to determine its potential wear on dentine and enamel [8], [9].

A typical toothpaste formulation consists of multiple components, each with their own purpose and also with the potential to influence the behaviour and performance of other ingredients in the formulation [10]. Of all the ingredients in dentifrices or toothpastes, dental abrasive particles are regarded as being the key particles responsible for the physical cleaning and polishing of the tooth surface [11], [12]. Dental abrasives typically used in toothpastes include hydrated silica, calcium carbonate, dicalcium phosphate, alumina, sodium carbonate, perlite, hydroxyapatite and diamond [5], [8], [13], [14], [15], [16], [17], [18]. Data indicate that the properties of the abrasive particles, including their hardness, concentration, size distribution and morphology, are key to cleaning performance [9], [11], [16], [19], [20], [21].

Notably, particle morphology has also been reported as being an important factor in determining abrasivity [22]. In engineering studies, it has been widely established that angular particles cause higher wear than spherical particles [23]. Previously, large differences in abrasivity were identified when polymethylmethacrylate (PMMA) substrates abraded with calcium carbonate and silica abrasives. This outcome was largely attributed to differences in particle shape with spherical particles causing the lowest abrasion [22]. Similarly, a greater reduction in abrasive damage of stainless steel occurred due to spherical alumina filled polytetrafluoroethylene (PTFE) compared with angular alumina filled PTFE [24].

Currently, there is limited knowledge with regard to the influence of abrasive particle morphology on tooth wear and stain removal. However, some *in vitro* and *in vivo* data has indicated that compared with angular particles, spherical particles demonstrate a decrease in volume loss of enamel and higher stain removal properties [25], [26]. Ideally, a toothbrushing regime should show excellent cleaning efficiency for dental plaque and stain removal, as well as for polishing ability, while exerting minimal tooth wear [19]. Consequently, we hypothesised that small quantities of spherical particles in toothpastes could achieve similar or greater stain removal compared with standard angular abrasive particles. The aim of this work, therefore, was now to investigate the effect of spherical silica gel and spherical alumina abrasive particles on tooth abrasion, polishing and stain removal.

2. Materials and methods

2.1. Characterisation of silica and alumina abrasives

Three silica abrasives and three alumina abrasives were used in the present study (Table 1). Scanning Electron Microscopy (SEM, EVO MA10, Zeiss) was used for particle morphology characterisation. The abrasive particles were adhered to carbon tape on an aluminium stub (Agar Scientific Ltd., UK). Ultra-thin sputtered gold coating (EMITECH K550X, Emitech, United Kingdom) was applied to the particles prior to SEM observations to prevent specimen charging. Representative images were captured at a range of magnifications.

A Malvern Mastersizer 2000 laser diffraction particle size analyser (Malvern Instruments Ltd., United Kingdom) was used to perform the particle size analysis. Silica and alumina abrasives were added in distilled water to an agitated flask attached to the diffraction machine and the particle size distribution of the abrasives were determined. Particle size distribution data (Table 1) are shown as d10, d50 and d90, average values of three measurements. The d10, d50 and d90 values indicate that 10%, 50% and 90% of the particles measured were less than or equal to the size stated.

2.2 *Preparation of bovine enamel samples*

Freshly extracted permanent bovine incisor teeth were stored in 0.1% (w/w) thymol (Sigma-Aldrich, UK) solution at 4 °C prior to use. A custom-built diamond-edged saw with water cooling was used to dissect tooth crowns (approximate 12mm × 18mm) from the bovine teeth. The tooth crowns then were embedded in Ø25 mm blocks of epoxy resins (Buehler, UK). Eight bovine enamel specimens per treatment group were prepared (approximate 10mm × 10mm of the enamel surface was exposed) on a Phoenix Beta Grinder/Polisher (Buehler, UK) using Silicon Carbide grinding paper (SiC) abrasive discs (Buehler, UK). A roughened surface group was prepared with a 280-grit SiC ground finish for *in vitro* stain removal. A partially roughened surface group was prepared with a 400-grit SiC ground finish for surface polishing. A polished surface group was prepared using 600-grit SiC grinding paper followed by 3 µm diamond finishing for enamel abrasion. Any residual grinding/polishing materials on the sample surfaces was removed by 5 minutes ultrasonication in tap water.

2.3. Tooth staining on the roughened surface group

The tooth staining assay previously reported was used [2]. Freshly combined solutions of 0.1% (w/w) tannic acid (ACS reagent, Sigma-Aldrich) and 0.1% (w/w) of diammonium iron (II) sulphate 6-hydrate (Sigma-Aldrich), a dark colloidal iron (III) tannic acid complex ("ferric-tannate") forms on contact with air, were used to mimic a dietary tannin stain. Data showed that no statistically significant differences in stain removal efficacy were detected between 3 to 10 layers of stain [2], and 10 layers of stain were used in the present study which gave reproducible results. The fresh mixture was applied as 10 successive layers on the enamel specimens. For the initial layer, a 40 µl aliquot of the mixture was pipetted onto each specimen and dispersed evenly over the specimen surface. For the subsequent 9 layers, 10 µl aliquots of the solutions were applied as described above. Each layer was dried in an oven (D-63450 Hanau, Kendro Laboratory Products Ltd, Germany) at 40 °C for 10 mins before application of the subsequent layer.

2.4. Toothbrushing procedure

The *in vitro* toothbrushing protocol used here is well established and has previously been reported [2], [27], [28]. A test band of the enamel specimen was exposed and an unbrushed reference area was generated by coverage of the tooth surface with ADA/ISO standard tape. Oral B P35 medium toothbrushes were used for the brushing. Eight bovine enamel specimens per treatment group were mounted in two brushing channels of the brushing simulator.

Slurries were freshly prepared with the addition of 0.1% (w/w) to 15% (w/w) silica or alumina abrasives (Table 1) in 10% (w/w) Glycerol (VWR International BVBA, Belgium) and 0.5% (w/w) Hercules 7 MF Carboxymethyl Cellulose (Hercules Incorporated, USA). Concentration as low as 0.1% (w/w) was selected for the spherical abrasives, 4% (w/w) AC 43 and 15% (w/w) Zeodent 113 as these levels are commonly used in commercially available toothpastes. A 150 g brushing load was applied on each toothbrush head and 150 g slurry was added in each channel. Specimens were "brushed" for up to 5,000 strokes at a brushing speed of 120 rpm. The temperature was maintained at 20 °C throughout the brushing procedure. All specimens were washed under tap water after brushing and any residual tape was removed.

2.5. Surface profiles of enamel specimens

A Talysurf Series 2 inductive gauge profilometer (Taylor-Hobson, UK) was used to obtain surface profiles before and after brushing. The inductive gauge profilometer uses a conical probe with 2 µm diamond tip to accurately measure surfaces at the sub-micron level, it has a resolution of 16 nm and a 1 mm range in the z-axis. Linear profiles (2D) were obtained on the surfaces with a point spacing of 0.25 µm and at a measurement speed of 0.5 mm/s. The arithmetic mean surface roughness (Ra) and wear depth values were calculated (µltra version 5.1.14, Taylor-Hobson, UK).

2.6. Gloss measurements

Gloss measurements before and after brushing were determined using a Novo-Curve small area glossmeter (Rhopoint Instruments Limited, UK) at intervals of 90 degree rotations about the centre point of each specimen.

2.7. Colour evaluation

All surfaces were consistently dried prior to colour measurements and changes in colour were determined as previously described [2]. Colour values (L*, a*, b*) for each tooth specimen before staining (=Initial), after 10 layers of stain application (=Stained) and after the brushing treatments (=Brushed) were measured. A calibrated spectrophotometer (Minolta CM-2600d, Konica Minolta Sensing Americas, Inc, USA) was used for the colour measurements. The L* value represents the value of 'brightness/darkness' of a colour and values indicated by a* and b* represent two colour axes, with a* the red-green axis and b* the yellow-blue axis. A perfect black body has an L* value of zero and the perfect reflecting diffuser has an L* value of 100. Stain removal was assessed using the following formula:

$$\%\,Removal = \frac{L^*\,(\text{Brushed}) - L^*(\text{Stained})}{L^*\,(\text{Initial}) - L^*(\text{Stained})} \times 100$$

Where L* (Initial), L* (Stained) and L* (Brushed) is the brightness before staining, after 10 cycles of stain application and after toothbrushing for the requisite number of strokes with the silica or alumina abrasive slurry, respectively.

A Nikon D7000 camera (Nikon Corporation, Japan) was used to digitally capture images of the enamel surfaces before staining, after 10 layers of stain and post-stain removal with 1,000 brush strokes to visually demonstrate the effects of stain removal.

2.8. Statistical analyses of the data

The data from abrasivity, polishing and stain removal were analysed using a single factor ANOVA with a significance level of $p \leq 0.05$ applied.

3. Results

3.1. Morphology and particle size of silica and alumina abrasive particles

Representative SEM micrographs of the test silica and alumina abrasives are shown in Figure 1 and the particle size distributions of the abrasives are shown in Table 1. The d10, d50 and d90 values indicate that 10%, 50% and 90% of the particles measured were less than or equal to the size stated. Differences in particle size and range of morphologies for the silica and alumina abrasives can be clearly observed. All the angular abrasive particles (AC 43 silica and Zeodent 113 silica; P10 alumina and 3 μm alumina) exhibited irregular morphologies and consisted of a range of particle sizes. SEM micrographs clearly demonstrated that the spherical silica gel and spherical alumina were of the reported morphology, and also contained a range of particle sizes. Particle size distribution data (d50) indicated that Zeodent 113 silica abrasive had the largest particle size (20.5 μm), followed by the spherical silica gel (9.3 μm) and spherical alumina abrasives (6.7 μm), AC 43 silica (6.2 μm), P10 Feinst alumina (5.3 μm) and 3 μm alumina (4.3 μm) had the smallest particle sizes. Notably, Zeodent 113 silica had the largest d10 (6.2 μm), d90 (38.3 μm) particle size, which also showed the largest relative particle size span. The two spherical abrasives had the smallest d10 particle size (<1 μm), and the 3 μm angular alumina had the smallest d90 (7.8 μm) particle size and revealed the smallest relative particle size span.

3.2. Abrasivity of test silica and alumina abrasives on polished enamel

Tables 2 and 3 provide wear depth and surface finishing data for the polished enamel specimens after brushing at 5,000 strokes with the silica and alumina abrasives, respectively. Wear occurred for all the tested enamel specimens. Statistically significant differences ($p<0.05$) were detected in wear depth between the tested silica abrasives. The 0.1% (w/w) spherical silica gel, 4% (w/w) AC 43 silica and 15% (w/w) Zeodent 113 silica resulted in the least wear (least abrasive), followed by the 0.5% (w/w) spherical silica gel abrasive (medium abrasive), while the 3% (w/w) and 5% (w/w) spherical silica gel produced the most wear (most abrasive). Statistically significant differences (p<0.05) were also detected in wear depth between the test alumina abrasives. The 1% (w/w) P10 alumina caused the least wear (least abrasive), then followed by the 0.25% (w/w), 0.5% (w/w) and 1% (w/w) spherical alumina abrasives (medium abrasive), while the 1% (w/w) 3 µm alumina abrasive produced the most wear (most abrasive). Interestingly there were no statistically significant differences in wear depth between the spherical silica gel and spherical alumina with the same concentration of 0.5% (w/w) although 0.5% (w/w) spherical silica gel caused more wear than the 0.5% (w/w) spherical alumina.

There was a decrease in gloss for all of the polished enamel surfaces after toothbrushing with all test silica and alumina abrasives. Statistically significant differences were detected for the decreases in gloss when the polished enamel specimens were brushed with the test silica and alumina abrasives. There was a trend for the decrease in gloss to be greater when the polished enamel specimens were brushed with the spherical silica gel and alumina abrasive particles.

The polished enamel surfaces became roughened following toothbrushing and there was an increase in the surface roughness for all of the polished enamel surfaces. The abrasive particles generated grooves in the polished enamel surfaces which resulted in a roughening of the polished enamel surfaces, hence, resulting in increases in surface roughness. The increase in surface roughness of the polished enamel specimens brushed with silica abrasives was lowest for the 0.1% (w/w) spherical silica gel, 4% AC 43 silica and 15% (w/w) Zeodent 113 silica abrasives, followed by the 0.5% (w/w), 3% (w/w) and 5% (w/w) spherical silica gel particles. When brushed with the test alumina abrasive particles, the 1% (w/w) P10 alumina caused the lowest increase in surface roughness of the polished enamel specimens, and no statistically significant differences in roughness increase was detected between the spherical alumina and 3 μm alumina abrasives.

3.3. Polishing effect of silica and alumina abrasives on partially roughened enamel

The polishing effects for the silica and alumina abrasives on the partially roughened enamel specimens after brushing for 3,000 strokes are shown in Tables 4 and 5, respectively. There were no appreciable differences in wear depth after 3,000 brushstrokes.

There was an increase in gloss for all of the roughened enamel surfaces due to wear and removal of asperities, and these specimens also showed a decrease in surface roughness. The most abrasive particles increased gloss and decreased the surface roughness at a greater rate than the least abrasive particles.

Notably, when brushed with the spherical silica gel, there was a continual increase in gloss and decrease in surface roughness for roughened enamel surfaces with the increasing concentrations from 0.1% (w/w) to 3% (w/w). There was no further increase in gloss and decrease in surface roughness with further concentration increases up to 5% (w/w). A similar trend was also found with the spherical alumina abrasives, and no statistically significant differences in gloss increase and surface roughness decrease were found between 0.25% (w/w) and 0.5% (w/w) spherical alumina.

3.4. Stain removal from partially roughened enamel

The *in vitro* stain removal efficacy results for silica and alumina abrasives are presented in Figures 2a and 3a, respectively. Data indicate that the spherical silica gel demonstrated the greatest cleaning power, and the concentration as low as 0.5% (w/w) removed similar or more stain than the 4% (w/w) AC 43 silica and 15% (w/w) Zeodent 113 silica abrasives. The stain removal data from spherical silica gel abrasives also showed that increases in the concentration of spherical silica gel from 0.1% (w/w) to 5% (w/w) continuously increased the stain removal efficacy. Compared with the angular alumina abrasive particles, the spherical alumina abrasive also exhibited greater cleaning power. However, there was no change in stain removal efficacy when the concentration of spherical alumina increased from 0.25% (w/w) to 0.5% (w/w). The images of enamel surfaces before staining and post-stain removal following application of 1000 brush strokes with silica and alumina abrasives are shown in Figures 2b and 3b, respectively. A trend indicating that spherical abrasive particles removed more stain from the enamel surfaces compared with the angular abrasives was observed. No obvious differences can be seen from the enamel surfaces post-stain removal between the spherical silica gel with concentrations of 0.5% (w/w) or above and the spherical alumina abrasives as no stain was apparent on the enamel surfaces.

3.5. Cleaning efficiency index (CEI)

The cleaning efficiency index (CEI) was used for further analysis of the correlation between the abrasivity and stain removal. The CEI emphasized the importance of good stain removal and low dentine abrasivity, which was calculated according to the following equation [29]:

$$CEI = (RDA + PCR - 50) \div RDA$$

Where RDA is relative dentine abrasion, PCR is pellicle cleaning ratio.

The following modified equation was used in the present study for the CEI calculation by using the enamel wear depth and *in vitro* stain removal data.

$$CEI = (\text{Wear depth} + \text{Stain removal} \times 100 - 50) \div \text{Wear depth} \div 100$$

Different specimens were used for the abrasivity and stain removal measurements. The CEI values that were calculated from the enamel wear depth (Tables 2 and 3) and stain removal data (Figures 2 and 3) are presented in Figure 4. The CEI values range from -2.47 to 4.69. The negative CEI value indicated that the stain removal efficacy was lower than 50%. It is interesting to see that 0.5% (w/w) spherical silica gel showed greater CEI value than the commercially used 15% (w/w) Zeodent 113, although 4% (w/w) AC 43 performed the best. Spherical alumina as low as 0.25% (w/w) performed better than 1% (w/w) compared with the other two angular alumina abrasives.

4. Discussion

Freshly extracted bovine enamel specimens were used in the present study. Bovine enamel has similar physical properties and chemical composition compared with human enamel and is routinely considered as a suitable human model in toothbrush abrasion studies [2], [19], [21], [25], [29], [30]. A dentifrice or toothpaste should have the ability to remove extrinsic stain effectively without causing unnecessary and damaging tooth abrasion. Additionally, it should also have the ability to produce a smooth and highly polished tooth surface which inhibits stain and plaque accumulation [2], [29]. It is now apparent that the morphology of the particles used in toothpastes is an important factor in determining abrasivity and stain removal [25], [26]. In the present study, the silica and alumina particle morphology effects were investigated on tooth abrasion, polishing and *in vitro* stain removal. Results under these experimental conditions demonstrated that relatively small quantities of spherical silica gel or spherical alumina showed similar or greater stain removal compared with standard angular abrasive particles and data support the original hypothesis underpinning this study.

4.1. Influence of particle morphology of the tested silica and alumina abrasives

4.1.1. Particle morphology impact on abrasivity of polished enamel

The practice of designing effective toothpaste abrasive systems is complex and is dependent on a variety of properties of the abrasives, mainly the chemical composition, particle size and size distribution, morphology, particle structure, as well as concentration of the abrasive particles within the toothpaste [31]. Abrasive particle morphology is a key factor which impacts on the behaviour of the particles during toothbrushing and thus the wear depth. In engineering, it is reported that spherical particles are less damaging or less abrasive than angular particles [22], [23], [24]. Consistent with this, recent data has also reported that spherical particles cause a lower volume loss of enamel compared with angular particles [25], [32], [33].

In the present study, abrasivity data did not indicate a clear trend on enamel abrasivity when brushed with spherical and angular particles. The enamel wear depth was mainly dependent on the chemical composition and physical structure of the abrasive concentration and shape. Indeed, it has been widely accepted that the harder the particle the more abrasive it is. However, there were no statistically significant differences in wear depth between spherical silica gel and spherical alumina with the same concentration (0.5% (w/w) and this might relate to their spherical morphology.

A low concentration (0.1% (w/w)) of spherical silica gel produced similar or less wear of enamel with no statistically significant differences compared with 4% (w/w) AC 43 angular silica and angular Zeodent 113 silica. However, the spherical silica gel generated more wear at higher concentration (0.5% (w/w) to 5% (w/w)) compared with that produced by 4% (w/w) AC 43 and 15% (w/w) Zeodent 113. A similar trend was found for alumina abrasives with a low concentration (0.25% (w/w)) of spherical alumina causing more enamel loss compared with 1% (w/w) P10 angular alumina. However, 3 µm angular alumina were more abrasive than spherical alumina abrasives. There was no clear trend of spherical particles causing less wear than angular particles under the current experimental conditions, and this highlights the complexity of toothpaste abrasive systems. Indeed, abrasivity is dependent on multiple factors including abrasive particle structure, size distribution, shape, and concentration.

Toothpaste concentration affects abrasivity of enamel and dentine, although only small changes on enamel abrasion when toothpaste concentration increased have been previously reported [34]. Data in the present study demonstrated that the wear depth for polished enamel increased with the increase in concentration of the spherical silica gel. This wear depth increased up to a content of 3% (w/w) for the spherical silica gel, subsequently the effect was reversed with further increases in the concentration of spherical silica gel up to 5% (w/w). Similar results on enamel loss were previously reported when enamel specimens were brushed with an experimental toothpaste containing silica abrasives [35]. Notably, no statistically significant differences were detected with the wear depth of enamel between spherical alumina abrasives with different concentration.

Particle size effect is a well-known phenomenon in abrasion [36] and there is reportedly a minimum abrasive particle size or critical particle size which allows maximum abrasive action [19]. Unfortunately, it is not straightforward to isolate the separate effects of particle size and shape from wear depth data. However, a concentration as low as 0.5% (w/w) of spherical silica gel produced more enamel wear than the test angular silica abrasives, while 1% (w/w) 3 μm angular alumina caused the most wear among the test alumina abrasives. It is noteworthy that the spherical silica comprised of extremely small particles and the 3 μm angular alumina had the smallest d90 particle size and smallest relative particle size span.

Further work needs to be performed to isolate the separate effects of particle shape, size and size distribution effects within dentifrices.

4.1.2. Particle morphology effects on polishing

More highly polished enamel surfaces appear whiter due to their enhanced ability to reflect light [37]. Notably, and more importantly, these polished and smoothed tooth surfaces are less receptive to the build-up and retention of dental plaque [29]. These properties are important for the aesthetics of the dentition and studies on the effects of enamel surface finish on *in vitro* stain removal have shown that polished surfaces require fewer brush strokes to remove stain compared with roughened enamel surfaces [2].

Dulled enamel specimens have also been used to study polishing effects of toothpastes and previous work has used tooth specimens etched with acid prior to toothbrushing [8], [29]. In our current study, partially roughened enamel specimens were also generated and used to analyse the polishing effects of spherical silica gel and spherical alumina. After brushing with the test abrasives, a proportion of the peaks and troughs on the partially roughened enamel surfaces were removed. The partially roughened enamel surfaces subsequently became smoother, consequently, the gloss increased and the surface roughness decreased. Data in the present study clearly demonstrated the greater polishing power of the test spherical abrasives when compared with the angular silica abrasives. In addition, the spherical alumina exhibited greater polishing ability compared with the spherical silica gel due to their hardness differences with alumina being harder than silica. It was notable that there was a continual increase in gloss when concentration of the spherical silica gel increased from 0.1% (w/w) to 5% (w/w), while no obvious differences were detected when the concentrations of the spherical alumina increased from 0.25% (w/w) to 0.5% (w/w). As alumina is harder than silica, therefore, spherical alumina was more efficient than spherical silica to remove asperities and achieved similar gloss performance at lower concentrations, with the plateau effect occurring at a lower concentration.

4.1.3. Particle morphology effects on stain removal

It has been reported that abrasivity and stain removal are correlated [11]. Usually, more stain is removed when brushing is performed with more abrasive particles and a linear relationship between wear depth and stain removal was previously reported when alumina abrasive particles were used [19]. Under the experimental conditions used in the present study, the abrasivity and stain removal were correlated when brushing with spherical silica gel abrasives. However, no such relationship was found between the 0.1% (w/w) spherical silica gel, 4% (w/w) AC 43 angular silica and 15% (w/w) Zeodent angular silica. There was also no such correlation observed between the spherical alumina and 3 μm angular alumina.

Stain removal data from the present study showed that toothpaste slurry containing relatively minor quantities of spherical abrasives resulted in similar or greater stain removal compared with slurries used at a higher concentration of angular abrasives. One potential explanation for this outcome may be due to the shape and particle structure differences. However, more work needs to be undertaken to investigate the interaction between the toothbrushes and spherical abrasive particles in tooth cleaning. A further potential explanation may be that the spherical silica gel and spherical alumina abrasives also comprise extremely small particles, including a d10 particle size of 0.8 μm for spherical silica gel and d10 0.7 μm for spherical alumina. These slurry properties would consequently provide more particles per tooth area to clean the stained enamel surfaces. Consequently, lower concentrations of abrasive particles may be used to achieve similar or improved stain removal compared with angular abrasives.

4.2. Wear pattern observation of the brushed polished enamel

Particle morphology plays an important role in the behaviour of granular materials and is also important in the mechanics of contact [38]. By definition, angular particles have ‘sharp’ edges resulting in highly concentrated contact stresses which can chip or fracture enamel, whereas spherical particles due to their morphology, penetrate the enamel less [25]. Therefore, the morphology of worn enamel surfaces depends on the shape of the abrasive particles contacted. Reportedly, spherical particles generate round craters (indents) and smooth grooves while angular particles produce sharp indents and narrow cutting grooves [39]. Our data (Figure 5) clearly demonstrated the differences in wear patterns on the polished enamel due to the differences in morphology of the abrasive particles. A considerable number of indents were observed when surfaces were brushed with spherical alumina particles (0.5% (w/w)) which may relate to their rolling wear (three-body wear) on the enamel surfaces, while narrow and sharp grooves (two-body wear) were found on the enamel surfaces after brushing with the angular alumina, especially 3 µm alumina due to the sharp edges. However, notably, the majority of wear occurred as grooving wear (two-body) wear.

5. Conclusions

The properties of the abrasive particles in a toothpaste system, including their hardness, concentration, size distribution and morphology, are key to cleaning performance and abrasion. Data in the present study demonstrated that spherical abrasives at lower concentration achieved similar or better stain removal efficacy compared with angular standard abrasives. Abrasive morphology (spherical vs angular shape) also affected the wear of the polished enamel surfaces and the polish of the partially roughened enamel surfaces.

The novel findings reported here provide new information on abrasive morphology for modification and control of toothpaste abrasivity, polishing and cleaning. This information can now be used in the development of novel and more efficacious toothpaste formulations.

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Table 1 Abrasives used in this study indicating material, individual particle shape, particle size distribution, concentration in the slurry and manufacturer information*

Abrasive	Material	Shape	d10 (µm)	d50 (µm)	d90 (µm)	Concentration, % (w/w)	Manufacturer
Zeodent 113	Silica	Angular	6.2	20.5	38.3	15	Evonik Industries AG
AC 43	Silica	Angular	3.1	6.2	15.0	4	PQ Corporation
Spherical silica gel	Silica	Spherical	0.8	9.3	20.3	0.1, 0.5, 3, 5	Asahi Glass SI-Tech. Co. Ltd
P10 Feinst	Alumina	Angular	1.5	5.3	16.6	1	Almatis GmbH
3 µm alumina	Alumina	Angular	2.3	4.3	7.8	1	Almatis GmbH
Spherical alumina	Alumina	Spherical	0.7	6.7	15.6	0.25, 0.5, 1.0	Denka Company Limited

* Particle size data are average values of three measurements. The d10, d50 and d90 values indicate that 10%, 50% and 90% of the particles measured were less than or equal to the size stated by the manufacturer.

Table 2 Surface finish and wear depth of polished bovine enamel brushing with silica abrasives (n=8, mean ± standard deviation)

Brush strokes	**Parameters**	**0.1% (w/w) spherical silica gel**	**0.5% (w/w) spherical silica gel**	**3% (w/w) spherical silica gel**	**5% (w/w) spherical silica gel**	**4% (w/w) AC 43 silica**	**15% (w/w) Zeodent 113 silica**
Before	Gloss, GU	100.0±2.1	100.5±2.5	100.2±1.1	103.5±0.8	101.5±2.0	102.1±2.4
	Roughness, µm	0.019±0.002	0.020±0.002	0.023±0.004	0.021±0.002	0.020±0.001	0.021±0.002
5000	Gloss, GU	84.1±9.8	67.4±8.1	69.0±3.5	73.9±4.6	76.9±2.7	92.0±5.8
	Gloss change, GU	-15.9±9.0	-33.1±6.9	-31.3±3.0	-29.5±4.8	-24.6±2.9	-10.1±4.4
	Roughness, µm	0.042±0.014	0.090±0.040	0.096±0.020	0.088±0.021	0.039±0.006	0.044±0.012
	Roughness change, µm	0.022±0.014	0.070±0.040	0.074±0.019	0.067±0.020	0.020±0.006	0.023±0.012
	Wear depth, µm	0.089±0.039 Bcd	0.224±0.146 ACE	0.379±0.100 aBef	0.332±0.048 aef	0.083±0.027 Bcd	0.113±0.047 cd
Column names		A	B	C	D	E	F

Statistically significant differences were found in wear depth. Upper-case letters to indicate results significant at the *p* values of 0.05 level and lower-case to indicate results significant at the *p* values of 0.001 level.

Table 3 Surface finish and wear depth of polished bovine enamel brushing with alumina abrasives (n=8, mean ± standard deviation)

Brush strokes	**Parameters**	**0.25% (w/w) spherical alumina**	**0.5% (w/w) spherical alumina**	**1% (w/w) spherical alumina**	**1% (w/w) P10 alumina**	**1% (w/w) 3 µm alumina**
Before	Gloss, GU	106.5±0.9	106.1±0.7	106.5±1.3	106.7±0.3	106.4±0.6
	Roughness, µm	0.014±0.001	0.014±0.001	0.014±0.001	0.014±0.001	0.014±0.001
5000	Gloss, GU	89.8±3.9	90.0±2.3	89.5±5.8	99.7±1.5	89.4±5.5
	Gloss change, GU	-16.7±3.6	-16.1±2.4	-17.1±6.1	-7.0±1.5	-17.0±5.2
	Roughness, µm	0.059±0.007	0.056±0.007	0.057±0.013	0.040±0.005	0.062±0.011
	Roughness change, µm	0.046±0.007	0.042±0.007	0.043±0.014	0.026±0.005	0.047±0.012
	Wear depth, µm	0.176±0.033 de	0.182±0.029 de	0.220±0.072 dE	0.119±0.028 abce	0.320±0.101 abCd
Column names		A	B	C	D	E

Statistically significant differences were found in wear depth. Upper-case letters to indicate results significant at the *p* values of 0.05 level and lower-case to indicate results significant at the *p* values of 0.001 level.

Table 4 Surface finish and wear depth of partially roughened bovine enamel brushing with silica abrasives (n=8, mean ± standard deviation)

Brush strokes	Parameters	0.1% (w/w) spherical silica gel	0.5% (w/w) spherical silica gel	3% (w/w) spherical silica gel	5% (w/w) spherical silica gel	4% (w/w) AC 43 silica	15% (w/w) Zeodent 113 silica
Before	Gloss, GU	17.6±5.3	16.9±4.4	12.6±2.3	16.1±4.2	16.4±4.6	16.0±3.7
	Roughness, µm	0.147±0.029	0.149±0.033	0.176±0.031	0.150±0.025	0.151±0.029	0.172±0.025
3000	Gloss, GU	39.1±6.8	59.2±11.0	69.7±4.2	73.0±6.2	31.1±5.8	27.7±8.0
	Gloss change, GU	21.5±5.5	42.3±8.8	57.1±3.3	56.9±8.2	14.7±7.2	11.7±6.5
	Roughness, µm	0.111±0.016	0.097±0.025	0.100±0.039	0.079±0.014	0.123±0.027	0.142±0.035
	Roughness change, µm	-0.037±0.016	-0.053±0.019	-0.075±0.032	-0.071±0.018	-0.028±0.012	-0.030±0.025
	Wear depth, µm	0.239±0.056	0.249±0.049	0.354±0.095	0.266±0.061	0.258±0.050	0.260±0.038

Table 5 Surface finish and wear depth of partially roughened bovine enamel brushing with alumina abrasives (n=8, mean ± standard deviation)

Brush strokes	Parameters	0.25% (w/w) spherical alumina	0.5% (w/w) spherical alumina	1% (w/w) P10 alumina	1% (w/w) 3 µm alumina
Before	Gloss, GU	15.9±3.2	12.0±3.0	16.4±5.0	11.6±2.1
	Roughness, µm	0.153±0.022	0.184±0.038	0.163±0.030	0.192±0.040
3000	Gloss, GU	70.4±7.7	69.9±8.1	49.1±17.8	67.4±10.8
	Gloss change, GU	54.5±7.8	57.9±6.8	32.7±13.8	55.8±10.2
	Roughness, µm	0.082±0.018	0.095±0.018	0.109±0.032	0.100±0.025
	Roughness change, µm	-0.072±0.018	-0.089±0.026	-0.054±0.014	-0.092±0.027
	Wear depth, µm	0.254±0.063	0.310±0.062	0.255±0.066	0.381±0.073

Figure legends

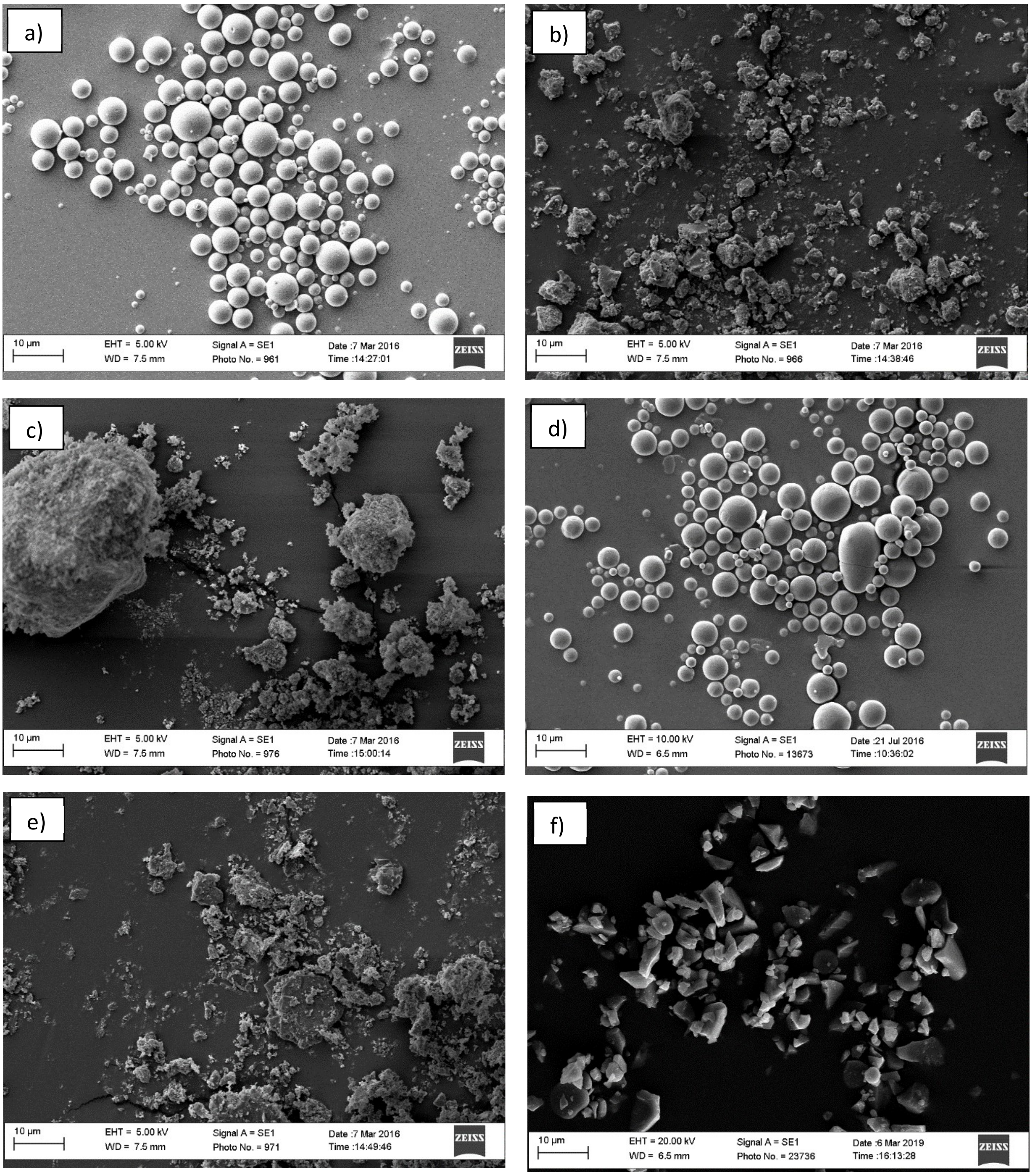
Figure 1 Representative SEM micrographs of the tested abrasives particles. a) spherical silica gel; b) AC 43 silica; c) Zeodent 113 silica; d) spherical alumina; e) P10 Feinst alumina; and f) 3 µm alumina. Differences in particle size and range of morphologies for the abrasives can be clearly observed. The spherical silica gel and spherical alumina were of their reported morphologies and AC 43 silica, Zeodent 113 silica, P10 Feinst alumina and 3 µm alumina displayed an angular shape.

Figure 2 a) Stain removal efficacy for roughened bovine enamel specimens after 1000 strokes when brushed with the test silica abrasives; b) Representative images of enamel surfaces before staining, after staining and post-stain removal with 1000 brush strokes. (left to right, upper row): before stain; after staining; stain brushing with 0.1% (w/w) spherical silica gel; stain brushing with 0.5% (w/w) spherical silica gel; (left to right, lower row): stain brushing with 3% (w/w) spherical silica gel; stain brushing with 5% (w/w) spherical silica gel; stain brushing with 4% (w/w) AC 43 silica; stain brushing with 15% (w/w) Zeodent 113 silica.

Figure 3 a) Stain removal efficacy for roughened bovine enamel specimens after 1000 strokes when brushed with the test alumina abrasives; b) Representative images of enamel surfaces before staining, after staining and post-stain removal with 1000 brush strokes. (left to right, upper row): before stain; after staining; stain brushing with 1% (w/w) P10 alumina; (left to right, lower row): stain brushing with 1% (w/w) 3 µm alumina; stain brushing with 0.25% (w/w) spherical alumina; stain brushing with 0.5% (w/w) spherical alumina.

Figure 4 Cleaning efficiency index (CEI) data of the tested abrasives based on the equation in the text by using the enamel wear depth and stain removal data. Negative CEI value indicated the stain removal efficacy was lower than 50%.

Figure 5 Representative SEM micrographs of wear patterns on the polished enamel surfaces after 5000 strokes when brushed alumina abrasives. Red arrows indicate the brushing direction. The majority of the wear occurred as two-body wear (grooving wear) and also a considerable number of indents were evident due to the three-body wear (rolling wear). a) 0.25% (w/w) spherical alumina; b) 0.5% (w/w) spherical alumina; c) 1% (w/w) spherical alumina; d) 1% (w/w) P10 Feinst alumina; e) 1% (w/w) 3 µm alumina.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10 µm
EHT = 5.00 kV
WD = 7.5 mm
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Time :14:27:01
ZEISS
b)
10 µm
EHT = 5.00 kV
WD = 7.5 mm
Signal A = SE1
Photo No. = 966
Date :7 Mar 2016
Time :14:38:46
ZEISS
c)
10 µm
EHT = 5.00 kV
WD = 7.5 mm
Signal A = SE1
Photo No. = 976
Date :7 Mar 2016
Time :15:00:14
ZEISS
d)
10 µm
EHT = 10.00 kV
WD = 6.5 mm
Signal A = SE1
Photo No. = 13673
Date :21 Jul 2016
Time :10:36:02
ZEISS
e)
10 µm
EHT = 5.00 kV
WD = 7.5 mm
Signal A = SE1
Photo No. = 971
Date :7 Mar 2016
Time :14:49:46
ZEISS
f)
10 µm
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Date :6 Mar 2019
Time :16:13:28
ZEISS

Figure 1

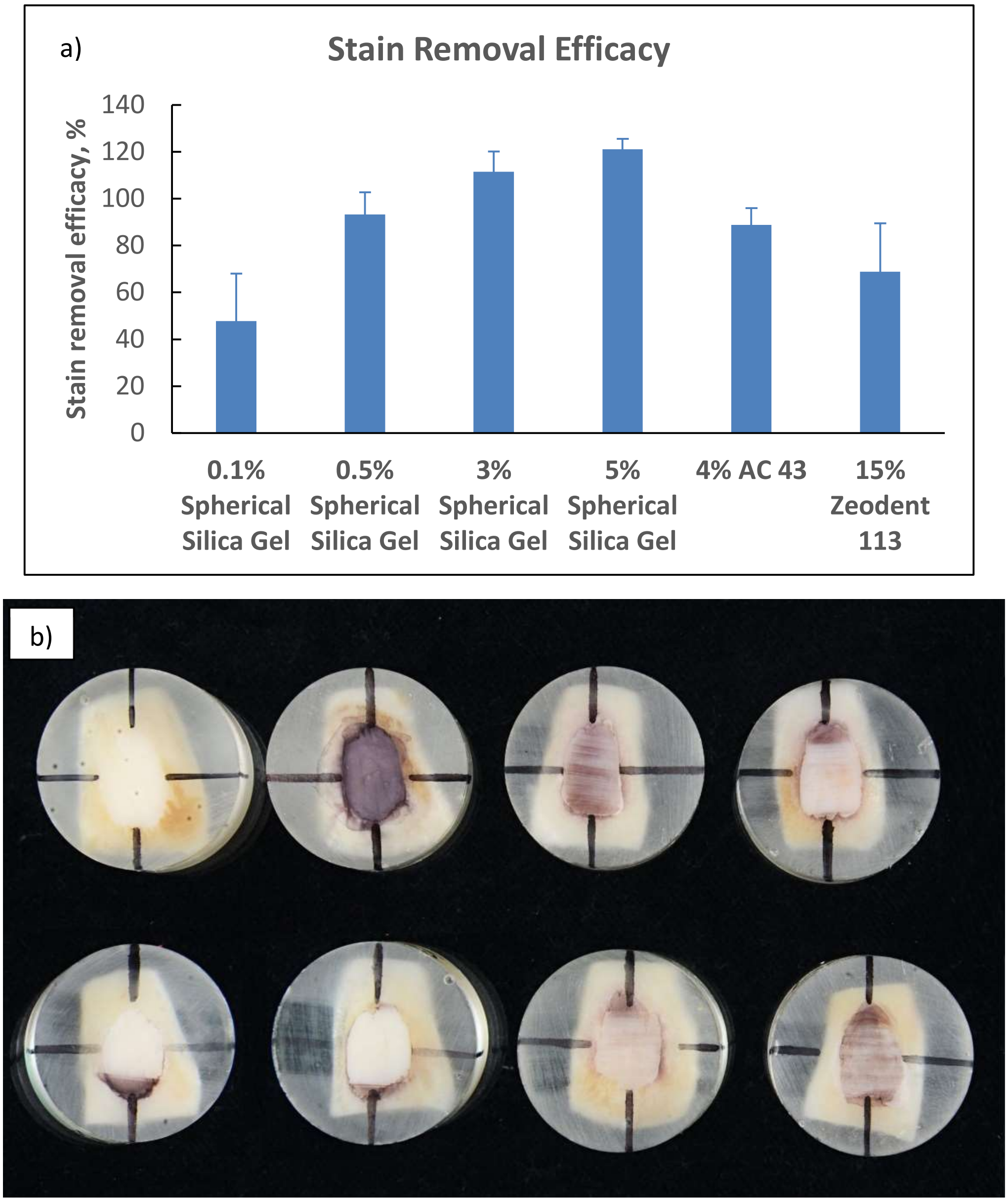

a)
Stain Removal Efficacy
Stain removal efficacy, %
0
20
40
60
80
100
120
140
0.1% Spherical Silica Gel
0.5% Spherical Silica Gel
3% Spherical Silica Gel
5% Spherical Silica Gel
4% AC 43
15% Zeodent 113
b)

Figure 2

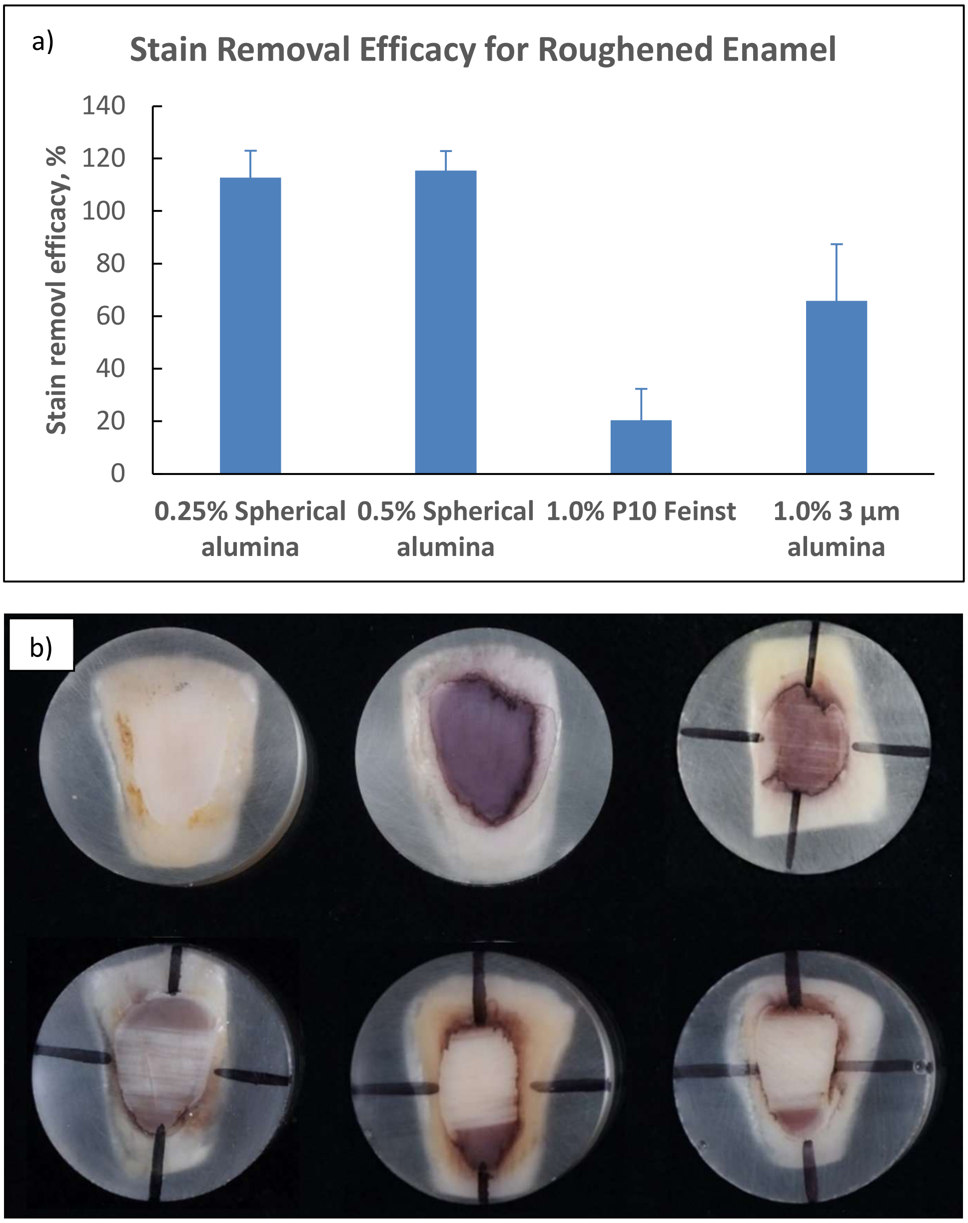

a)
Stain Removal Efficacy for Roughened Enamel
Stain removl efficacy, %
140
120
100
80
60
40
20
0
0.25% Spherical alumina
0.5% Spherical alumina
1.0% P10 Feinst
1.0% 3 µm alumina
b)

Figure 3

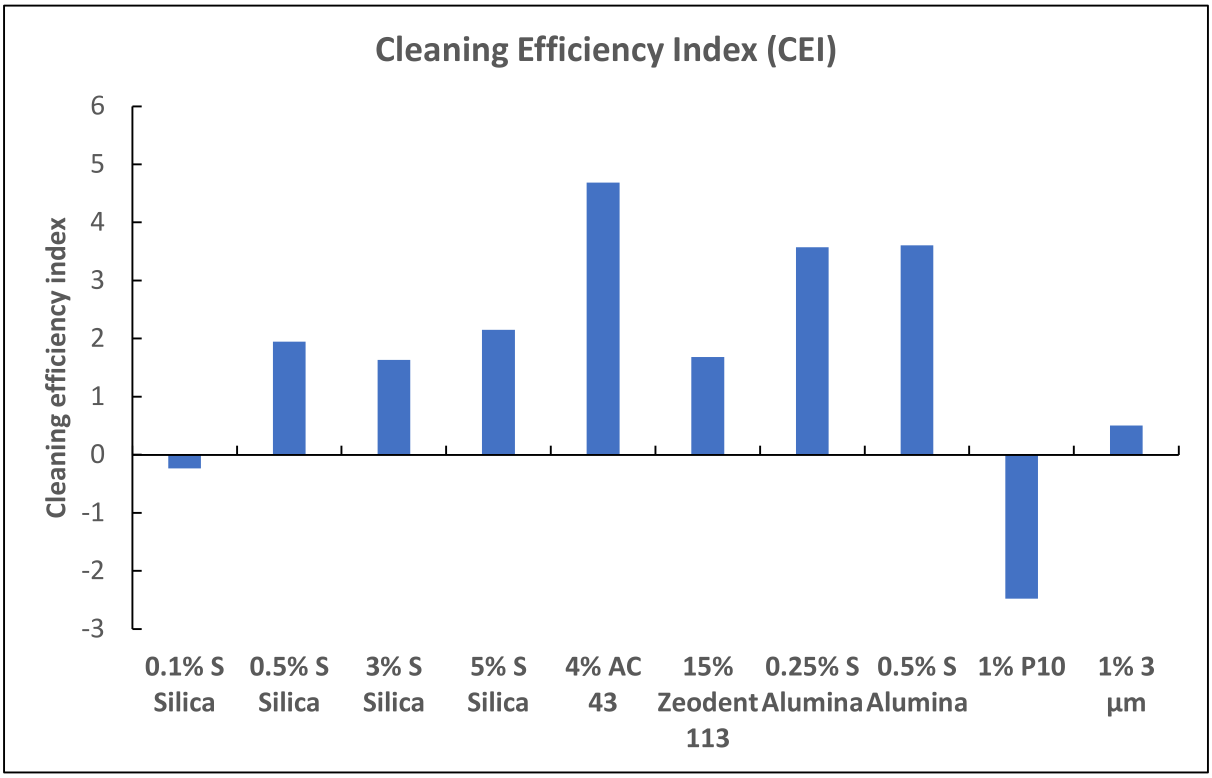
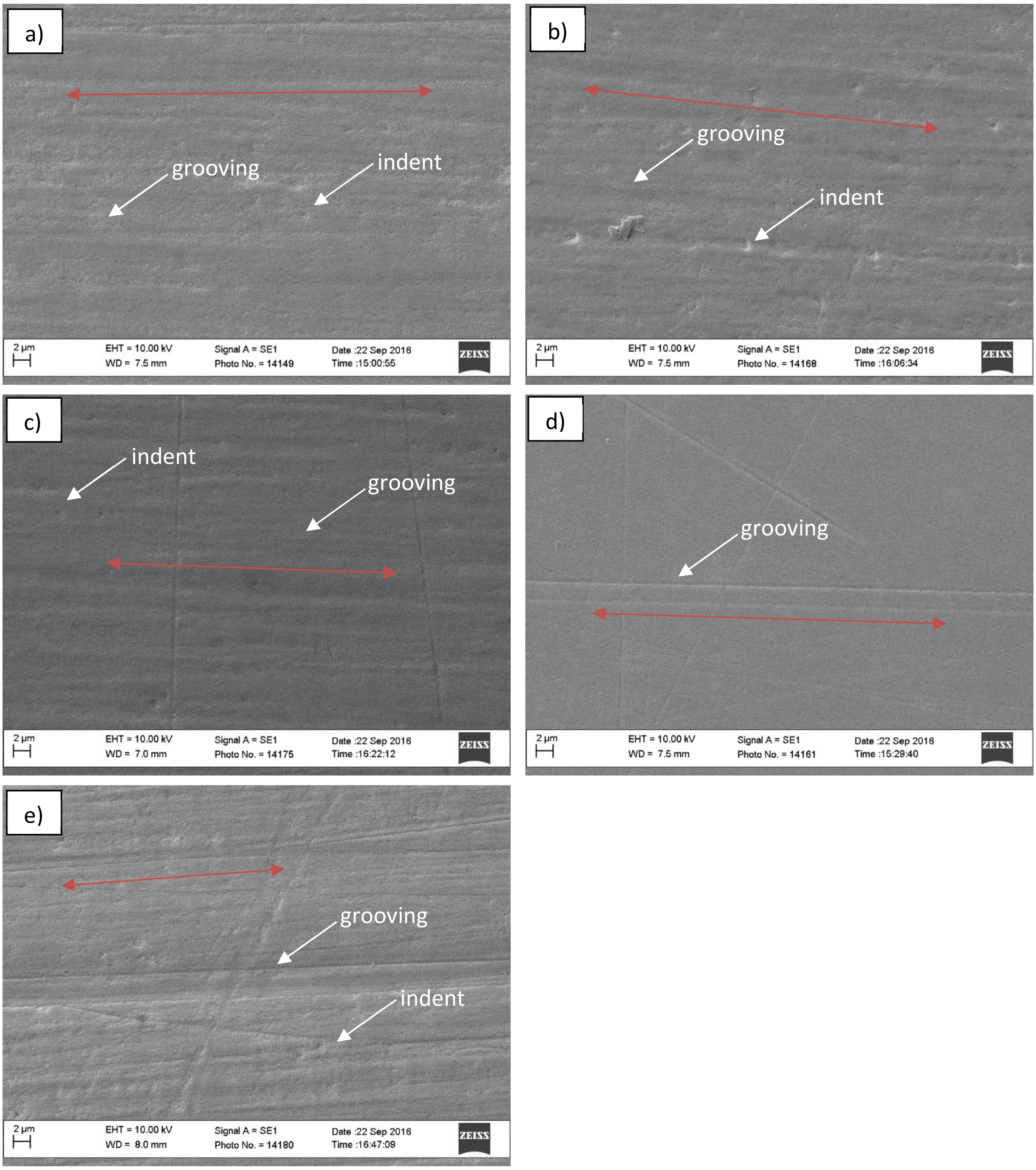

Cleaning Efficiency Index (CEI)
Cleaning efficiency index
6
5
4
3
2
1
0
-1
-2
-3
0.1% S Silica
0.5% S Silica
3% S Silica
5% S Silica
4% AC 43
15% Zeodent 113
0.25% S Alumina
0.5% S Alumina
1% P10
1% 3 µm

Figure 4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grooving
indent
2 µm
EHT = 10.00 kV
WD = 7.5 mm
Signal A = SE1
Photo No. = 14149
Date :22 Sep 2016
Time :15:00:55
b)
grooving
indent
2 µm
EHT = 10.00 kV
WD = 7.5 mm
Signal A = SE1
Photo No. = 14168
Date :22 Sep 2016
Time :16:06:34
c)
indent
grooving
2 µm
EHT = 10.00 kV
WD = 7.0 mm
Signal A = SE1
Photo No. = 14175
Date :22 Sep 2016
Time :16:22:12
d)
grooving
2 µm
EHT = 10.00 kV
WD = 7.5 mm
Signal A = SE1
Photo No. = 14161
Date :22 Sep 2016
Time :15:29:40
e)
grooving
indent
2 µm
EHT = 10.00 kV
WD = 8.0 mm
Signal A = SE1
Photo No. = 14180
Date :22 Sep 2016
Time :16:47:09

Figure 5