Investigation of the nanomechanical and tribological properties of dental materials

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Abstract: This study utilises nanoindentation and nanoscratch for testing the human enamel and dentine and three biocompatible dental filling materials: epoxy nanocomposite, glass ionomer, and silver amalgam. Nanoindentation gave hardness and Young's modulus. Nano-scratch gave critical load in the scratch test, and resistance to sliding wear. The results show that the silver amalgam filling has a higher modulus of elasticity, hardness and wear resistance than the nanocomposite. These relatively nondestructive mechanical characterisation techniques may assist in better understanding the mechanical behaviour of the dental fillers and thus facilitate the design of robust fillers with excellent mechanical properties.

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1 Introduction

The American Dental Association (ADA) Council on Scientific Affairs had prepared charts comparing the important features of many of the popular direct and indirect restorative materials (ADA, 2003). The service life of dental restoratives depends on a number of patient, material and procedure-related factors. Material’s related factors include strength (Lohbauer et al., 2006), hardness (Meerbeek et al., 1993) toughness ((Denny and Holl, 2004), wear resistance (Perry et al., 2000), tolerance to water (Santos et al., 2002), dimensional stability (Okamura et al., 2006), translucency, and colour stability (Kim et al., 2007; Lee, 2007).
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The human tooth is composed of different calcified tissues, namely the enamel, dentine and cementum (Ratner et al., 1996) as shown in Figure 1. The hardest and most brittle part is enamel and covers the outer part of coronal tooth. The inner portion is composed of dentine, which is less calcified than enamel. Its microstructure consists of tubules with a circular like cross-section that has diameters of 1–3 µm. Cementum covers the tooth root by firmly adhering to dentine.

Figure 1  Tooth axial section (see online version for colours)

A large number of different materials are used in dentistry for a wide spectrum of applications.

*Dental amalgams* are filling composites that consist of silver/tin powder mixed with mercury/gallium. The mercury free amalgam is referred to as *Galloy*. The gallium dissolves the outside layers of the metal powder particles forming a matrix of silver-tin-gallium that hardens to form the finished amalgam composite. The advantages of amalgam restorations over other direct-placement materials include resistance to wear, tolerance to wide range of clinical placement conditions such as wet fields, and excellent load-bearing properties. However, amalgams have been reported to be capable of sealing tooth-restoration margins with corrosion products. Also, due to its metallic nature it is unable to mimic the translucency of natural teeth and its silver-grey colour limits its use to anterior teeth (ADA, 2003).

*Dental cements* are made from a nonmetallic powder that dissolves partially in a liquid that serves as glue that is used to cement crowns and posts. *Silicate cement* is made by mixing a powder of Alumino-Flouro-Silicate glass with phosphoric acid (ACI Committee 440, 2006). This acid dissolves the glass and chemically combines with it creating a hard and brittle matrix. Due to itsbrittleness and lack of translucency and weak wear resistance this material is not used as restorative in stress bearing areas. Its usage mainly is limited to front teeth. The advantage of this cement is the prevention of further decay due to its rich content of fluoride.

The *glass ionomer cements* consist of a mixture of polyacrylic acid and Alumino-Flouro-Silicate glass (ADA, 2002). The acid-base reaction between these two ingredients results in the formation of metallic-polykenoate salt which precipitates and begins to gel until the cement sets hard. Unlike the silicate cement, this matrix is reasonably translucent allowing the colour of the glass particles to dominate the aesthetics. Also it is less brittle making it less prone to chipping and crasing. The strong
ionic interaction with the dental hard tissues will yield an ion-enriched layer of cement that is firmly attached to the tooth. The glass powder has a natural rich fluoride content that has been credited with providing a cavity–inhibiting environment to protect the tooth from decay (Fischman and Tinanoff, 1995). On the negative side, the glass ionomer cements are less hard than the silicate cements so the restorations wear faster. They also lack fracture resistance, hence, they are excellent fillings on the surfaces of front teeth, but should not be used to rebuild the top edges of the teeth due to their weakness.

*Resin cements* are composed of powder glass filler in a hard matrix (mostly acrylic) which binds together. The hard matrix is composed of a refined form of acrylic known as BIS-GMA (bisphenol -A -glycidyl dimethacrylate). These fillings are usually cured through hardening the acrylic by adding a hardening catalyst or photoinitiator that will harden the acrylic when illuminated under a strong light (ex. UV) (ADA, 2002). The acrylic cannot be used by itself because it tends to shrink while it is setting. This shrinkage will lead to generation of stresses that might either break the tooth or create spaces between the filling and the walls of the cavity in the tooth. Moreover, acrylic on its own has low wear resistance. Therefore, the addition of rigid glass particles prevents most of the shrinkage associated with the resin, and enhances the wear resistance significantly. The size of the glass particles determines the over all properties of the resin-filled composites. Using macro particles such as crystalline glass (8–12 microns in diameter, 70–80% by weight) will make the macrofill not very polishable. Large particles are also easily dislodged from the surface of the restoration. This tendency to abrade away makes macrofills unsuitable for posterior restorations.

*Microfill composites* use particles very small in size (about 0.04 microns in diameter, 35–50% by weight). This type is usually used in front teeth because it is polishable quite well. However, having that many small particles might make the composite stiffer to work with (Ratner et al., 1996). In order to overcome the limitations of the micro and macrofilled composites, it is better to use a layer of microfilled composite over a bulk of macrofill in order to spatially increase the strength of the structure and provide a more polishable restoration and a translucent enamel-like appearance. Another approach utilises ‘Hybrid’ composites that are cross between microfilled and macrofilled composites. Hybrid composites contain particles between 0.6–1 microns in diameter and 70–75% by weight. Hybrid composites are formulated to be layered. Often, hybrid composites are formulated with more resin than fillers (flowable composites), to form a loose mix that can be delivered to cavities using a syringe. Flowable composites are used to seal the dentine of a tooth prior to placing the filling material. Due to the low level of fillers, they are more prone to shrinkage, so they are not recommended by themselves to fill large cavities.

Nanocomposites can be considered solid structures with nanometer-scale dimensional repeat distances between the different phases that constitute the structure (Ajayan et al., 2003). These materials typically consist of an inorganic (host) solid containing an organic component or vice versa. Or they can consist of two or more inorganic/organic phases in some combinatorial form with the constraint that at least one of the phases or features is of nanosize.

*Hybrids nanocomposites* fillers were synthesised by sol-gel processing of hydrolytically condensable silica (silicon oxides) (Moszner and Klapdohr 2004). However, the particles size was in average of 50–100 nm, and the authors did not characterise the improvement in the mechanical properties or the biocompatibility. Mitra et al. (2003) synthesised two nanofillers particles: nanometric particles and
nanoclusters. These are particles that are monodisperse nonaggregated and nonagglomerated silica nanoparticles, respectively. In that investigation, the authors used aqueous colloidal silica sols to synthesise dry powders of nanosized silica particles 20 and 75 nm in diameter. The study showed that nanofillers outperform the micro and hybrid fillers in compressive strength, wear resistance and polish retention. However, the investigators relied on macroscale techniques to quantify the mechanical behaviour of the nanofillers, and that usually leads to underestimating the actual mechanical behaviour of the nanofiller. Beun et al. (2007) investigated three commercially available nanofilled composites. While the investigation confirmed that the nanofilled resin show higher elastic modulus than those of microfilled composites, the investigation did not indicate improvement on the flexural strength. The use of nanoparticles was not limited to resin based fillings, Prentice et al. (2006) studied the effect of ytterbium fluoride and barium sulphate nanoparticles (10–25 nm in diameter) on the reactivity and strength of glass ionomer cement. These nanoparticles modified the setting characteristics, strength and surface hardness of commercial glass ionomer cement.

All the different dental fillers behave differently under loading conditions. Knowledge of the mechanical properties of the dental materials is crucial for understanding how masticatory strains are distributed throughout a tooth, and for predicting how stresses and strains are altered by dental restorative procedures, age and disease (Kinney et al., 1996). It is expected that under masticatory loadings, a restoration with sufficient and identical mechanical properties to that of the adjacent tooth structure will have a longer lifetime (Angker and Swaina, 2006). The mechanical properties of calcified tissue have been also shown to reflect the level of mineralisation (Bosch and Angmar-Mansson, 1991). Most diseases affecting dental hard tissue, such as caries, impinge on tooth mineral assemblages and compositions, which subsequently alter the physical and mechanical behaviour of the tooth. Changes in the mechanical properties of the dental calcified tissues have been shown to be associated with many of these pathologic conditions (Bosch and Angmar-Mansson, 1991).

In the past, in order to measure the mechanical properties, (hardness and elastic modulus) of a dental material, conventional mechanical tests such as compressive (Caul et al., 1963), tensile (Rider et al., 1977), and three–points bending tests were performed on different sections of the tooth such as enamel, dentine, and cementum. Recently, indentation tests are becoming most commonly applied means of testing the mechanical properties. Nanoindentation usage for dental hard tissue studies began in 1992 (Meerbeek et al., 1993); since then several studies have been published using this technique (Cuy et al., 2002; Lippert et al., 2003; Angker and Swaina, 2006; Guidoni et al., 2006). The instrumented nanoindentation systems enable the measurement of the mechanical properties, hardness and elastic modulus, on the surface of dental materials. The nanoindentation technique is a much simpler procedure compared with other micro and macroscale mechanical tests such as compressive, tensile, bending, and punch shear tests, particularly on small complex-shaped samples such as enamel and dentine.

Nanoindentation tests are relatively nondestructive, and the specimen preparation is less time consuming than regular tests. Of particular importance, it allows probing the mechanical properties of a very small concise selected region of the specimen, the dimension of which may arrange between several nanometers to micrometers which is of crucial importance for measuring the local properties of nonhomogenous structures such as dental calcified tissues. Indentations on enamel rods and interods, and peritubular
and intertubular dentine are achievable, which have greatly contributed to our current understanding of the mechanical behaviour of dental hard tissues in association with their microstructural compositions (Angker and Swaina, 2006). Furthermore, we contend that the difference in elastic behaviour between the enamel and the dentine can only be determined using nanoscratch tests.

The objective of this study is to investigate the mechanical properties and wear resistance of the different natural dental materials and dental filling materials using the nanoindentation and nanoscratch techniques, respectively.

2 Experimental

Only molar teeth were used for this project. All teeth tested were mounted in Acrylic Fast Set mounting kit (PSI-234, Precision Surfaces International). Teeth samples were disinfected with NaClO prior to the drilling procedure. Teeth were drilled about 5 mm in depth and then filled according to the following procedures.

2.1 Nanocomposite

The tooth sample was etched with 35% Phosphoric Acid (Ultra-Etch, Ultradent Products Inc) to expose the tubules and clean out any dust. Following this, the sample was rinsed with water and blow-dried with air. Equal parts of Primers A and B were mixed (All-Bond 2, Bisco Dental Products Inc). Two coats of this primer mixture were applied to facilitate bonding. Solvents were evaporated with an air syringe. A thin layer of bonding resin was applied (D/E Resin, Bisco Dental Products, Inc.) to seal the tubules. The resin was UV-light cured for 20 s (QHL75 Lite, Dentsply International). Lastly, the cavity was filled with the nanocomposite restorative (Filtek Supreme Plus, 3M ESPE) and UV-light cured for 20 s every 2 mm.

2.2 Silver amalgam

The tooth sample was coated with varnish two times (Copalite, Cooley & Cooley, Ltd.) to help desensitise the tooth. Trituration of the silver amalgam was done by mixing the capsule in an amalgamator (Caulk Vari-mix II, Dentsply International). The mixture was then condensed inside the cavity and burnished. Tooth sample was left to dry for 48 hours.

2.3 Glass ionomer

The tooth sample was etched with 35% Phosphoric Acid (Ultra-Etch, Ultradent Products Inc). Capsule containing the glass ionomer mixture (GC Fuji IX–GP FAST, GC Corp.) was mixed in vortex for 10 s. The ionomer was then injected into the cavity and packed in. The sample was cured at room temperature for 5 min.
2.4 Nanoindentation

To prepare the samples for nanoindentation the bottom of the mounted teeth was ground to about one-third of its height using a 120-grit disk. The top of the teeth was ground using a motorised grinding wheel starting with 600-grit disk and finishing with the 2000-grit. Diamond paste (0.1 micron) was used for the final polish. The samples were rinsed with running water during the 600-grit polishing and with distilled water during the 2000-grit grinding.

Nanoindentation tests were carried out using a Nano Test 600 from Micro Materials, Inc., Wrexham, UK. The NanoTest is a pendulum-based depth-sensing system with the sample mounted vertically and the load applied electromagnetically as shown schematically in Figure 2. Current in the coil causes the pendulum to rotate about its frictionless pivot so that the diamond probe penetrates the sample surface. Test probe displacement is measured with a parallel plate capacitor achieving sub nanometer resolution. Indentation data were obtained for the dentine, enamel, and each of the three different fillings using maximum loads of 2, 6, and 10 mN for each different material. The loading rate was set to 0.1 mN/s. Each test was repeated three times. A Berkovich diamond tip (three-sided pyramidal) diamond indenter was used for all indentations.

The trace of a series of indentation on the dentine surface is shown in the AFM scan in Figure 3. The largest traces represent the indentations carried out at 10 mN; the medium traces correspond to 6 mN indentation load while the smallest traces represent the 2 mN maximum indentation load. The optical microscope of the Nano test system was used to accurately locate the regions of interest. Indentations were spaced sufficiently far apart so that the indentation behaviour was not affected by the presence of adjacent indentations. The instrument’s software corrected all data for thermal drift and instrument compliance. Figure 4 shows sample nanoindentation tests of the different materials at maximum load level of 10 mN. The scattering in the curves for samples like ionomer and silver amalgam is indication of the inhomogeneous nature of these materials.

Figure 2 Nano Test 600 setup (see online version for colours)
Figure 3  AFM scans for series of 2, 6 and 10 mN indentations on the surface of the different dental materials (see online version for colours)
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Figure 4  Nanoindentation curves for three different loading-unloading cycles at a maximum load of 10 mN on the surface of different dental filling materials (see online version for colours)

2.5 Nanoscratch test

Nanoscratch tests were performed using the scratch option available in the Nano Test 600™ machine to assess the scratch resistance and deformation behaviour of the enamel, dentine, and the three fillings. For each scratch test, a set of surface profiles along the track was measured, including the track profile before scratch (BSP), during scratch (DSP), and after scratch (ASP). At constant load, the BSP profile was obtained by a pre-scan of the sample across the full length of the scratch route (75 µm) at a small constant load of 0.05 mN, and then the indenter was returned to the starting point. For constant load scratching, a testing load of 20 mN was applied instantly after the pre-scan and kept constant for the rest of the 75 µm scratching. Figure 5 shows constant load scratch profiles on the surfaces of the different dental materials using Atomic Force Microscopy (AFM).

During the constant load scratch tests, the specimen was moved against the static and loaded indenter (Spherical) at a constant speed of 500 nm/s for a total length of 75 µm. Several probes can be used for scratch testing including trihedral diamond indenter, small radius spherical diamonds or various fractured ceramic probes can also be used. The choice of spherical indenter with relatively large diameter was to ensure that the indenter will encounter some of the nanoparticles for the nanocomposite filler.

After the scratch test, the indenter was lifted and moved back to the starting point. Then, the scratch track was scanned again under 0.05 mN so that the ASP profile was obtained.
3 Results and analysis

Modulus and hardness for each material were calculated using the Oliver-Pharr method (Oliver and Pharr, 1992) from the load-displacement curves during unloading. The Oliver-Pharr method was proven to be an efficient tool for mechanical characterisation of soft or hard dental materials (Cuya et al., 2002; Angker and Swaina, 2006; Drummond, 2006).

The Oliver-Pharr method is based on analytical solutions for other indenter geometries. It accounts for the curve in the unloading data and provides a method of finding the contact area at peak load using a determined depth and indenter shape function. They note that like the conical indenter, the Berkovich has a cross-sectional area which varies as the square of the depth of contact. Important parameters for this method are shown in Figure 6.
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Figure 6  Schematic representation of load vs. indenter displacement showing quantities used in the analysis as well as a graphical interpretation of the contact depth

The total depth is \( h \), which is the total indentation depth, made up of \( h_c \) – the contact depth, and \( h_s \) – the displacement of the surface at the perimeter of the indent.

\[
h = h_c + h_s
\]  

(1)

\( P_{\text{max}} \) is the max load; \( h_{\text{max}} \) is the depth at \( P_{\text{max}} \), and \( S_{\text{max}} \) – the initial unloading contact stiffness. The contact area of the indenter is determined using the relation

\[
A = F(h_c)
\]  

(2)

where \( F \) is \( F(h) \), an area function of the tip relating the area of the cross section to the distance from the indenter’s tip. The typical contact area equation for a Berkovich indenter is given by

\[
A = 3\sqrt{3}h_c^2 \tan^2 65.3 = 24.5h_c^2
\]  

(3)

where the contact depth is given by

\[
h_c = h_{\text{max}} - h_s
\]  

(4)

The reduced modulus is given by

\[
\frac{1}{E_r} = \frac{1-\nu^2}{E} + \frac{1-\nu'^2}{E'}
\]  

(5)

where \( \nu \) is the Poisson’s ratio and \( E \) the Young’s modulus of the sample, and \( \nu' \) and \( E' \) are the values for the indenter (for diamond \( E' = 1141 \) GPa and \( \nu' = 0.07 \)). This reduced modulus is related to the stiffness through the equation
where $S$ is determined from the upper portion of the unloading data. The hardness of the sample is determined by using the maximum load applied divided by the projected area found from equation (3).

$$H = \frac{P_{\text{max}}}{24.5h_c^3}$$  \hspace{1cm} (7)

The Elastic modulus of the sample may be calculated through

$$E^* = \frac{dP}{dh} \frac{1}{2h_c} \frac{1}{\beta} \frac{\pi}{24.5}$$  \hspace{1cm} (8)

where $\beta$ is 1.034 for a Berkovich indenter tip (Fischer-Cripps, 2002).

The conclusion is that with a Berkovich indenter, unloading curves can be described by the power law relation of

$$P = A(h - h_f)^m$$  \hspace{1cm} (9)

where $P$ is the indenter load and $(h - h_f)$ is the elastic displacement, and $A$ and $m$ are material constants.

The nanoindentation results—modulus, $E$, and hardness, $H$, were calculated using the Oliver-Pharr method given above. Table 1 reports the average values and standard deviation for each of the materials tested. Compared to enamel and dentine, nanoindentation of the two fillings composites, using a $3 \times 3$ matrix of indentations, resulted in a wide range of measured values for the elastic modulus and hardness (more than 10% error) because of the size of the filler particle, the location of indenter within the filler particle, and the composition of the filler particles.

The results obtained from the nanoindentation experiments confirm enamel as the hardest material from all tested. The measured hardness and modulus ($H = 5.16 \pm 0.64 \text{ GPa}$, $E = 112.85 \pm 8.73 \text{ GPa}$). For enamel are comparable to those obtained by other investigators; $H = 4.9 \pm 0.21 \text{ GPa}$, $E = 108.2 \pm 5.8 \text{ GPa}$ measured by Lippert et al. (2004). Similarly the measured mechanical properties of dentine are consistent with those reported with other studies (Angker and Swaina, 2006).

<table>
<thead>
<tr>
<th>Material</th>
<th>Hardness (GPa)</th>
<th>Modulus (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Enamel</td>
<td>5.16 ± 0.64</td>
<td>112.85 ± 8.73</td>
</tr>
<tr>
<td>Dentine</td>
<td>0.85 ± 0.13</td>
<td>36.39 ± 2.53</td>
</tr>
<tr>
<td>Nanocomposite</td>
<td>0.78 ± 0.17</td>
<td>15.71 ± 1.69</td>
</tr>
<tr>
<td>Silver Amalgam</td>
<td>2.34 ± 0.27</td>
<td>107.00 ± 12.00</td>
</tr>
<tr>
<td>Glass Ionomer</td>
<td>1.93 ± 0.20</td>
<td>37.36 ± 4.00</td>
</tr>
</tbody>
</table>
Among the three fillers, the silver amalgam filling had the highest modulus of elasticity at 107 GPa, which is comparable to the modulus of the enamel. The nanocomposite filling had the lowest modulus at 15.71 GPa. The composite filling also had the lowest hardness at 0.78 GPa. Therefore, the commercial nanocomposite clearly has the lowest mechanical properties of the fillings tested while the silver amalgam filling displayed clear superiority.

The difference between ASP and BSP represents the depth of the scratch groove remaining on the sample surface after the scratch tests. It is termed as scratch depth in this study, which reflects the permanent damage caused by the scratching.

For each scratch test, a set of surface profiles along the track was measured, including the track profile before scratch and after scratch. The difference between the two scans for different dental materials is shown in Figure 7. The glass ionomer composite is the least wear-resistant among the four materials tested, followed by the nanocomposites. The jump in the silver amalgam scratch profile is an indication of severe plastic deformation. The same observation was observed for the nanocomposite due to the viscoelasticity of the polymeric matrix. The rest of the dental materials are behaving ceramics–like (brittle); therefore, their corresponding scratch profiles did not attain higher depths.

Figure 7 Scratch curves under constant loading. DSP profile being the recorded depth profile during scratch track under 20 mN constant load along 75 µm track (see online version for colours)

4 Conclusions

Nanoindentation is an attractive method for measuring the mechanical behaviour of small specimen volumes in dental hard tissue and dental fillings. Using this technique,
the mechanical properties of enamel, dentine, glass ionomer, nanocomposite and silver amalgam fillers were investigated.

This technique evaluates only the mechanical properties of a very shallow surface region of a specimen that may have undergone damage associated with mechanical preparation required to achieve a satisfactory flat sample for testing. The technique is also very surface sensitive with a fine-polished surface as a prerequisite. In addition, the inhomogeneous and anisotropic nature of the dental materials add further complications that, to date, have barely been addressed.

The nano characterisation verified that the human enamel has the highest hardness and modulus of all materials (tooth and fillings) tested. Traditional silver amalgam was proven to have better mechanical properties than the nanocomposite filler. Nanoscratch tests also suggested that the silver amalgam is more wear resistant than nanocomposites. The glass ionomer is the least wear-resistant among the four materials tested. This conclusion is also supported by the fact that among the three filler the glass ionomer has the lowest hardness. The poor properties of the nanocomposites might be due to the low amount of the nanoparticles, agglomeration, and poor dispersion in the polymeric matrix.

References
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