Preparation of Dental Composite Using Hydroxyapatite from Natural Sources and Silica

R A C Razali¹, N A Rahim¹,*, I Zainol¹ and A M Sharif¹
¹Department of Chemistry, Faculty of Science and Mathematics, Universiti Pendidikan Sultan Idris, 35900 Tanjong Malim, Perak, Malaysia
*Corresponding author: saidah@fsmt.upsi.edu.my

Abstract. Dental resin-based composites (RBCs) have been widely used in dental treatment because of their excellent characteristics such as aesthetic, mechanical and biocompatibility properties. The aim of this study was to evaluate the effect of different composition of natural hydroxyapatite (NHAp) and silica as a filler in dental resin. Different ratio of silica (0, 5, 15, 20 wt%) was added to NHAp and mixed with organic resin. The resin used were bisphenol A glycidyl methacrylate (BisGMA)/triethylene glycol dimethacrylate (TEGDMA)/hydroxyethyl methacrylate (HEMA) with their ratio of 50/25/25 wt% respectively. The ratio of fillers and organic resins were 70:30 wt%. The composites were inserted into the mould and cured for 60 s on both sides. The surface roughness, Vickers hardness, flexural and compressive strength were evaluated and compared. The results indicated that the mechanical properties depending on the composition ratio of HAp and silica. The optimum composition with the highest flexural and compressive strength was 85 wt% of HAp and 15 wt% of silica. This result was met the standard requirement of dental composite.

1. Introduction

In modern dentistry, resin-based composites are the material of choice for most restorative procedures since it can be widely used to repair decayed or damaged teeth due to their acceptable mechanical properties, possess better esthetic restoration that matches the color of natural teeth, the ability to bond to tooth tissues and ease of use compared to dental amalgams and dental ceramics (Lezaja et al., 2013; Liu et al., 2015). Despite the significant improvement of resin-based composites, the restorative composite still exhibits deficiencies that impair their longevity because of two key shortcomings which are insufficient mechanical strength properties and high polymerization shrinkage (Chen et al., 2011). The three main parts of resin composite are polymer organic matrix, inorganic fillers, and initiator system.

The polymer matrix is the main organic component consists of monomers that generally are polymerised upon activation by visible light cure, while inorganic filler particles potentially to increase the mechanical and physical properties of resin-based composites. As the main mineral component of hard dental tissues, hydroxyapatite (HAp) is responsible for their hardness and other mechanical properties (Lezaja et al., 2013). Currently, most of the HAp materials used in biomedical applications were synthesized through chemical routes which reported to be expensive due to the high cost of raw materials. Furthermore, synthetic HAp has low bioresorbability in human body which lower the growth of new bones. HAp from natural sources are better and more crystallised than synthetic HAp (Boutinguiza et al., 2012; Mezahi et al., 2011). In addition, extraction process of natural HAp from bio-waste is biologically safe, no chemicals needed and more economical due to
cheaper raw materials. The most important issue is HAp produced from bio-waste is halal for all Muslims around the world (Zainol et al., 2012). However, the characteristics of low fracture toughness, poor tensile strength and brittleness of HAp exclude itself to employ as a load-bearing implants (Bakar et al., 2003; Ozmen & Akin, 2012; White & Best, 2007). To address this problem, the mechanical properties of HAp can be improved by adding a second phase of silica particles. The aim of this study was to evaluate the influence of natural hydroxyapatite and silica as filler incorporation in dental composite resin.

2. Materials and methods
Natural hydroxyapatite powder from fish scale were given by Prof. Dr. Ismail Zainol and silica powder was purchased from Scharlau. Bisphenol A glycidyl methacrylate (BisGMA, Sigma Aldrich), triethylene glycol dimethacrylate (TEGDMA, 95%, Sigma Aldrich), 2-hydroxyethyl methacrylate (HEMA, Aldrich), camphorquinone (CQ, 97%, Sigma Aldrich), ethyl (4-dimethyl amino) benzoate (EDMAB, 99%, Sigma Aldrich) and acetone (C₃H₆O, Systerm) were used without purification.

2.1. Preparation of dental composite
Samples were prepared by mixing the monomer matrix and fillers in a mass ratio of 30:70. The bisphenol A glycidyl methacrylate (BisGMA), triethylene glycol dimethacrylate (TEGDMA) and 2-hydroxyethyl methacrylate (HEMA) were mixed in different ratio 50:25:25 respectively. After one hour, the mixture was taken and kept in a dark room. Then, 0.5 wt% camphorquinone (CQ) as an initiator and 0.5 wt% ethyl-4-(dimethylamino) benzoate (EDMAB) as an accelerator were added and stirred for another 12 hours in a dark ambience (Rahim et al., 2011). Hydroxyapatite as the main filler and silica (Si) were added as inorganic fillers with various mass fractions to the mixture and stirred for six hours to obtain composite resins (Calabrese et al., 2016; Oduncu et al., 2010). After mixing thoroughly with the initiator and the solution, the higher viscosity solution was put in the mould and pressed between a pair of glass slides. The sample was photo-cured using UV-light on both sides for 60 s. The specimens were removed from the mould and polished using silicon carbide paper. Five specimens of each particular composite were prepared. The sample code for the composite was listed in Table 1 that further used in this report.

| Composites group | Organic phase (30 wt%) | Inorganic phase (70 wt%) |
|------------------|------------------------|-------------------------|
|                  | Bis-GMA (wt%) | TEGDMA (wt%) | HEMA (wt%) | HAp (wt%) | SiO₂ (wt%) |
| HASi0            | 50          | 25          | 25        | 100      | 0         |
| HASi1            | 50          | 25          | 25        | 95       | 5         |
| HASi2            | 50          | 25          | 25        | 85       | 15        |
| HASi3            | 50          | 25          | 25        | 80       | 20        |

2.2. Characterisation study
The physical and mechanical properties of dental composite were characterised using Universal Testing Machine (UTM), surface profilometer and Vickers Hardness tester. The surface morphology and distribution of the dental composites were observed using Hitachi SU 8020 UHR SEM. The samples were first coated using platinum to avoid charging and the photographs of representative areas were taken at different magnifications.

The flexural strength test and compressive strength test were evaluated according to the ISO 4049 specifications. Five specimens were prepared in a bar-shaped split steel mould (25 x 2 x 2 mm, n=5) and cylindrical split Teflon mould (6 mm height and 4 mm diameter) for flexural and compressive strength test respectively. All samples were stored in distilled water at 37°C for 24 h before the test.
The dimensions of each specimen were determined with a digital caliper to 0.01 mm. The sample was tested using a Shimadzu Testing Machine at a cross-head speed of 1.0 mm/min with a 10 kN load cell. The values were measured using Trapezium X software.

The surface roughness and Vickers hardness specimens were prepared in cylindrical acrylic mould (2 mm thickness, 5 mm diameter, n=5). The average surface roughness of each composite were determined with a surface profilometer (Surfcom Flex, Accretech, Japan). The specimen was placed below a needle tip and cut-off value was set at 0.08 mm. The speed and length of needle tip to measure the surface of composite across diameter was 0.15 mm/s and 2.00 mm respectively. The surface of the specimen was measured at three different directions for the top and bottom sides. The mean for surface roughness values (R_a) were recorded. While, the Vickers hardness was determined using Vickers Hardness Tester (Model VM 50). The specimens were placed underneath the indenter and 1 kg load was applied for 10s to form square-based diamond point. Every specimen was indented five times at five different surface areas. For each indentation, the lengths of two diagonals were measured and an average was calculated and Vickers Hardness Number (HN) values were recorded.

3. Results and discussion
Fracture of dental resin composites is the main reasons for restoration failure. It is impossible to meet a high mechanical properties value of inorganic filler with HAp alone. Adding other inorganic fillers such as silica possibly to make the materials easy to handle and become viable solution. In this study, natural HAp and commercially silica were used as filler to further improve the mechanical properties of resin composites. Mechanical properties of dental composites containing various mass fractions of natural hydroxyapatite-silica was tested and the results are summarised in Table 2.

Table 2. Mean and standard deviation (SD) values of flexural strength, compressive strength, Vickers hardness and surface roughness of different HASi composites.

| Composites group | Flexural strength (MPa) ± SD* | Compressive strength (MPa) ± SD* | Vickers hardness (HV) ± SD* | Surface roughness (Ra, nm) ± SD* |
|------------------|-------------------------------|---------------------------------|-----------------------------|---------------------------------|
| HASi0            | 30.10±3.86                    | 151.10±13.30                    | 34.8±25.49                  | 47.2±7.73                      |
| HASi1            | 38.97±1.92                    | 165.20±5.01                    | 41.3±1.57                   | 33.4±1.14                      |
| HASi2            | 42.74±1.54                    | 174.28±8.32                    | 43.7±6.23                   | 43.0±3.40                      |
| HASi3            | 29.49±1.37                    | 158.17±26.98                   | 51.9±2.03                   | 65.4±13.85                     |

* Mean and standard deviation for 5 samples.

Flexural strength is a criterion of durability and longevity of composites while the compressive strength is measures the capacity of the sample to withstand loads of chewing forces. As shown in Figure 1 and Table 2, flexural strength and compressive strength of the natural HAp resin composites improved with the addition of silica as a filler compared to natural HAp alone (HASi0). For flexural strength, the value of HASi1 and HASi2 were increased to (38.10±3.86 MPa) and (42.74±1.54 MPa) which were 29% and 42% higher than the resin with only natural HAp (30.10±3.86 MPa), respectively. However, the value decreased to (29.49±1.37 MPa) for HASi3. A similar trend is observed for compressive strength. The HASi2 composites exhibit the highest value (174.28±8.32 MPa) which is 15% higher than HASi0 (151.10±13.30 MPa). These results indicated that a combination of natural HAp and silica as a filler could improve mechanical properties of the resin composites due to their better dispersion in the polymer matrix, especially HASi3. This finding is in agreement with the results of Liu et al. (2015) which the flexural strength and compressive strength increased with the addition of silica into resin composite.
The Vickers hardness is important in the characterisation of dental composites to determine the physical properties and it is widely used to measure the hardness of teeth (Chuenarrom, Benjakul, & Daosodsai, 2009). As shown in Figure 2 and Table 2, the Vickers hardness of composites gradually increased with the increasing of silica filler content. HASi3 exhibited the highest value at (51.9±2.03 HV) compared to HASi2 (43.7±6.23 HV), HASi1 (41.3±1.57 HV) and HASi0 (34.8±25.49 HV), respectively. Calabrese et al. (2016) also reported that similar trends of Vickers hardness value for hydroxyapatite whiskers/silica resin composite. At the ratio HA:Silica 20%, they obtained 77 HV compared to HA:Silica 100% (53 HV). In this condition, HAp act as inhibitors of the photoactivation of resin inducing non-optimal crosslinking.

In aesthetical perspective, roughness of composites have a major impact because it could lead to the bacterial plaque, debris and stain accumulation (Janus et al., 2010; Botta et al., 2008). By comparing all the composites in this study (Figure 2), HASi1 shows the lowest surface roughness value, Rₐ (33.4±1.14 nm) indicates it is the smoothest surface composite. In contrast, HASi3 shows the highest Rₐ value (65.4±13.85 nm) followed by HASi2 and HASi1 with Rₐ value (47.2±7.73 nm) and (43.0±3.40 nm), respectively. According to Bollen, Lambrechts and Quirynen (1997), bacterial plaque accumulation occurred at Rₐ 200 nm inducing caries and periodontal inflammation. Although the Rₐ value differed, the value still below 200 nm and it can be taken for granted that all the composites in this study have a smooth surface which faces no risk of plaque accumulation.

**Figure 1.** Flexural strength and compressive strength of natural hydroxyapatite-silica composite (HASi) as filler.

**Figure 2.** Vickers hardness and surface roughness of natural hydroxyapatite-silica composite (HASi) as filler.
In order to provide a better insight into the morphology of the specimen, scanning electron microscopy (SEM) analysis was performed to investigate the filler distribution in the polymer matrix and the failure pattern of the composites. The morphology seen in Figure 3a represents natural hydroxyapatite is well distributed in the matrix composites (HASi0). Differences in surface features can be seen with the addition of silica in the composites, HASi2 (Figure 3b). HASi2 shows homogenous filler distribution and higher compaction of filler packing in the polymer matrix. Therefore, it related to the good mechanical properties results mention above with high value of flexural strength and compressive strength as well as a smooth surface composite compare to others.

**Figure 3.** SEM images of natural hydroxyapatite-silica dental composites at magnification 50000 (a) HASi0; (b) HASi2

4. **Conclusion**

The study on natural hydroxyapatite-silica as inorganic filler in dental composites were conducted to show their mechanical properties. The properties of composites were evaluated comparing to each other as well other published studies. HASi2 in a composition of 85% natural HAp and 15% silica as a filler enhances the mechanical properties compared to control specimen, HASi0. This composite may be promising material to use as a dental composite. The effect on biocompatibility and water sorption will be further investigated.

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