

EFFECT OF YTTRIA STABILISED ZIRCONIA ADDITION IN NATURAL HYDROXYAPATITE COMPOSITES FOR DENTAL RESTORATION

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ABSTRACT

Resin based composite (RBC) resembles the color of teeth has been used as a popular dental materials to repair or restore damaged teeth. In this study, the RBC were prepared using a hydroxyapatite from fish scales and yttria stabilised Zirconia as reinforcement fillers, while the organic resin are the blended monomers of Bis-GMA, TEGDMA and UDMA. The aim of this study is to assess the effect of addition of yttria stabilised Zirconia (YSZ) on the mechanical properties of natural hydroxyapatite resin-based composites for dental restoration. The composites were prepared in ratio 30:70 wt% of organic resin and inorganic filler, respectively. For inorganic filler, different ration of YSZ (0, 10, 25, 50 and 75 wt%) was added to the natural hydroxyapatite (HAp) powder and mixed with the blended resin. The RBC was inserted into mould and light cured with LED polymerization unit for 60 s on the both sides. The flexural strength, compression strength, Vickers hardness and surface roughness of composites were measured. The HAp-YSZ composite with 10 wt% YSZ filler content exhibited satisfactory mechanical strength with a flexural strength, compression strength, Vickers hardness and surface roughness of 65.61 MPa, 158.20 MPa, 50.80 HV and 120.00 nm, respectively. These results suggested that the strong mechanical properties of RBCs are important for the long-term clinical application of dental restorative materials.

Keywords: natural hydroxyapatite; hydroxyapatite; Zirconia; dental composite

INTRODUCTION

One of the most important issues in dentistry is repairing the tooth structural using the proper materials especially for dental resin-based composites (RBCs). Since 1960s, a great number of researches have been attempted to improve the physical and mechanical properties of dental composites. Compared to amalgam, the RBCs possess better esthetic, less safety concern and excellent mechanical properties [1]. People nowadays are attracted to esthetic restoration that matches the colour of natural teeth. RBCs encounter this demand and have become the most frequently used in dentistry. Most RBCs generally consist of organic matrix and inorganic filler that improve the strength of composite [2-5]. In this study, hydroxyapatite and yttria stabilised Zirconia are used as the inorganic filler while bisphenol A glycidyl methacrylate (Bis-GMA),

triethylene glycol dimethacrylate (TEGDMA) and diurethane dimethacrylate (UDMA) are used as the organic matrix.

Hydroxyapatite (HAp) with a chemical composition of $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ and the ratio $\text{Ca/P} = 1.67$ is the main mineral component of bone and teeth which can be used as implant in various biomedical applications, especially in orthopedics and dentistry field [6-8]. The development of HAp powder becomes more attractive to researchers since it can simply prepare either from natural sources or synthetic process. The sources of natural hydroxyapatite are varied such as eggshell [9], bovine bone [10], fish bone and scales [8, 11, 12]. Meanwhile, synthetic process of HAp utilized various techniques include precipitation, sol-gel approach, hydrothermal and electrodeposition [6]. HAp from natural sources are better and more crystallized than synthetic HAp [12].

However, the characteristics of low fracture toughness, poor tensile strength and brittleness of HAp exclude itself to employ as a load bearing implants [13]. To address this problem, the mechanical properties of HAp can be improved by adding a second phase of Zirconia into HAp during the synthesis process [14,15]. The presence of yttrium oxide (Y_2O_3) in the Zirconia can stabilise the tetragonal phase at room temperature which plays a major role in the increase of fracture toughness and higher bending strength. This widely used of yttria stabilised Zirconia (YSZ) has been proved by researchers that it is suitable for tissue repair due to its good mechanical strength without degrading the biocompatibility of HAp [15-17].

The aim of this study was to evaluate the mechanical properties such as flexural strength, compression strength, Vickers hardness and surface roughness of natural hydroxyapatite-yttria stabilized Zirconia (HAp-YSZ) as filler in dental resin-based composites. The composites were made from a different organic matrix and filler ratios, but under the same curing time and testing conditions. The null hypothesis was there would be no significant difference in mechanical properties between composites when subjected to the same curing time and testing conditions.

EXPERIMENTAL

Materials

The chemicals of camphorquinone (CQ), ethyl-4-dimethylamino (EDMAB), bisphenol A glycidyl methacrylate (Bis-GMA), triethylene glycol dimethacrylate (TEGDMA) and diurethane dimethacrylate (UDMA) were purchased from Sigma Aldrich. Natural HAp powder from fish scales was obtained from Assoc. Prof. Ismail Zainon, Universiti Pendidikan Sultan Idris and yttria stabilised zirconia (YSZ) was purchased from Maju Saintifik Sdn.Bhd. All the reagents were used without further purification.

Preparation of composites

The composites were prepared by mixing the monomers matrix and fillers of 30:70 wt% respectively. The monomers of Bis-GMA, TEGDMA and UDMA were blended in different ratio 30:50:20 wt%. This mass ratio was selected because it gives the most

suitable mechanical properties for composites [2, 3]. CQ as an initiator and EDMAB as co-initiator was added in the ratio of 0.5 wt%, respectively and stirred in a dark ambience [4,5]. Different ratios of HAp and YSZ as state in Table 1 were added into the mixture and stirred for six hours to obtain composite resins. The homogenised composite was inserted into mould and light cured with LED polymerisation unit (Bluephase N[®] MC) at an intensity of 800mW/cm². The light was illuminated on the top and bottom sides through clear microscope glass for 60 s [4]. The specimens were removed from the mould and polished using silicon carbide paper. Five specimens of each particular composite described in Table 1 were prepared for each different measurement.

Table 1: Phase ratios of HAp-YSZ composites

Specimens group	Organic phase (30 wt%)			Inorganic phase (70 wt%)	
	Bis-GMA (wt%)	TEGDMA (wt%)	UDMA (wt%)	HAp (wt%)	YSZ (wt%)
C1				100	0
C2				90	10
C3	30	50	20	75	25
C4				50	50
C5				25	75

Characterisation of HAp-YSZ composites

Flexural strength

The specimens were prepared in a bar-shaped split Teflon mould (25 x 2 x 2 mm) and stored in distilled water at 37°C for 24 h. Then, the test was performed according to ISO 4049 for polymer-based restorations [18]. The flexural properties were quantified by a three-point bending test (Shimadzu Testing Machine, Japan) at a crosshead speed of 1 mm/min and span length of 20 mm. The flexural strength (σ) was obtained by measuring the load at fracture under 10-kN load cell and calculated in megapascal (MPa) according to the Eq. 1:

$$\sigma = \frac{3LF}{2BH^2} \quad (1)$$

where, L is the distance between the supports (mm), F is the maximum load (N), B is the width of the specimens measured (mm) and H is the height (mm).

Compressive strength

The specimen from cylindrical split Teflon mould were prepared with 6 mm height and 4 mm diameter and stored in distilled water at 37°C for 24 h before perform the test [19]. The dimensions of each specimen were determined with digital caliper to 0.01 mm. The specimens were subjected to a compression test at a crosshead speed of 1

mm/min and 10-kN load cell using Shimadzu Testing Machine. The compression strength was calculated by the following equation Eq. 2:

$$CS = \frac{4P}{\pi d^2} \quad (2)$$

where, P is the load at fracture (N) and d is the diameter of the cylindrical specimen (mm).

Vickers hardness

The specimens were prepared in cylindrical acrylic mould with 2 mm height and 5 mm diameter and subjected to hardness testing using Vickers hardness tester. The specimen was placed underneath the indenter and 1 kg load was applied to form square-based diamond point. Every specimen was indented three times at three different points for each surface of top and bottom sides. For each indentation, the lengths of two diagonals were measured and an average was calculated.

Surface roughness

The average surface roughness of each specimen was determined with profilometer tester (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 for needle tip to measure the surface of specimen across diameter was 0.15 mm/s and 2.00 mm. The surface of each specimen was measured at three different directions for the top and bottom sides. The mean surface roughness parameter of each specimen (R_a) was recorded

Statistical analysis

The acquired data of mechanical properties were analyzed with one-way ANOVA and significant differences were determined with Tukey's post hoc test using SPSS software version 21.

RESULTS AND DISCUSSION

The characteristics of RBCs have a great influence upon their final properties and clinical performance. The filler content, size, type, and distribution of particles and matrix influence their mechanical properties [20]. The strong mechanical properties of RBCs are important for the long-term clinic application of dental restorative materials. In this study, the RBCs were prepared under identical LED polymerization conditions with similar mass ratio of monomer matrix composition but different concentrations of inorganic fillers. To evaluate the reinforcing effect of YSZ addition in HAp composites, flexural strength, compression strength, Vickers hardness and surface roughness of composites were measured and the results are summarized in Table 2.

Table 2: Mean and standard deviation (SD) values of mechanical properties of five different HAp-YSZ composites

Specimens group	Flexural strength (MPa) $\pm$ SD	Compressive strength (MPa) $\pm$ SD	Vickers hardness (HV) $\pm$ SD	Surface roughness (R_a , nm) $\pm$ SD
C1	38.34 $\pm$ 3.98	128.96 $\pm$ 6.04	39.80 $\pm$ 2.86	133.40 $\pm$ 10.01
C2	65.61 $\pm$ 19.14	160.34 $\pm$ 7.71	50.80 $\pm$ 3.28	120.00 $\pm$ 9.46
C3	59.85 $\pm$ 2.89	144.54 $\pm$ 3.33	47.54 $\pm$ 2.93	124.20 $\pm$ 6.76
C4	32.43 $\pm$ 0.91	118.11 $\pm$ 4.94	40.40 $\pm$ 4.33	126.60 $\pm$ 12.07
C5	26.65 $\pm$ 1.70	68.76 $\pm$ 11.96	29.04 $\pm$ 6.37	129.80 $\pm$ 9.81

Flexural strength

During the recent years, flexural strength testing has become increasingly in demand as a suitable technique to assess the strength of materials. The test of flexural strength was performed using three-point bending test because of its lower coefficient of variation, lower standard deviation and less complex crack distribution compared to biaxial flexural test [21]. In order to examine the mechanical properties of dental composites, this test combines the effect of compression deformation (adjacent to the point of applied load) and tensile deformation (on the opposite side of composite) [22]. Bending strength is one of the particular interests since it is more sensitive to defects than compression strength.

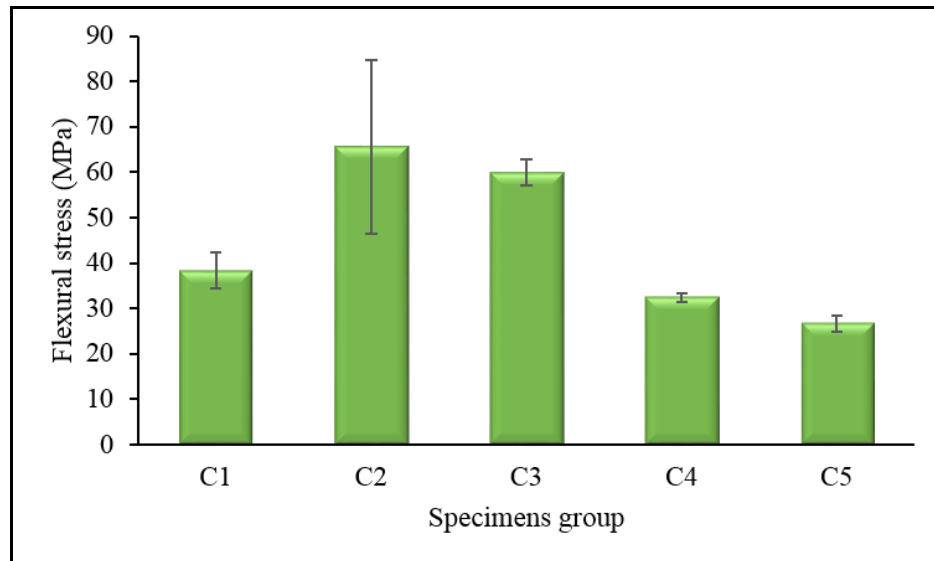


Figure 1: Flexural strength mean values of composites for each specimens group

As shown in Table 2 and Figure 1, RBC with 10 wt% YSZ (C2) revealed the highest mean value of flexural strength. Then, the bending strength slightly drops to about

59.85 MPa for C3. It further decreases gradually to 32.43 MPa (C4) and 26.65 MPa (C5) with further addition of YSZ. The C2 specimen has significant differences in flexural strength mean value with the control group of C1 (unfilled YSZ), C4 and C5 specimen, but has no significant difference with C3 specimen. Therefore, the flexural strength of HAp-YSZ composites was detected to decrease with the increasing of YSZ filler content. This result was agreed with the other research, where the strength undergoes decreasing trend at higher YSZ content [23]. The lower flexural strength causes the mechanical strength decreases with the increased of porosity. In addition, the minimum requirement of ISO 4049 for dental restorations is 50 MPa. The mean flexural strengths of C2 and C3 specimens (65.61 MPa and 59.85 MPa) were above this minimum requirement of ISO 4049, indicating that these materials are appropriate in some stress-bearing areas such as certain occlusal restorations.

Compressive strength

Compressive strength is particularly important as well as flexural strength because of it chewing forces and one of the material strength measurements in different force conditions [24]. In other words, compression strength measures the capacity of the sample to withstand loads.

Similar trends in flexural strength are observed for compression strength (Figure 2). The C2 specimen exhibit highest mean value (160.34 MPa) followed by the gradual decrease of C3 (144.54 MPa) and C4 (118.11 MPa), respectively. The lowest mean value of compression strength belongs to C5 with 68.76 MPa. The one-way ANOVA result revealed that the C2 specimen has a significant difference in mean value of compression strength between C1, C4 and C5 specimens ($p < 0.05$), but has no significant difference between C3 specimen ($p > 0.05$). The compression strength was decreased in addition of YSZ filler due to the increasing of porosity and bonding between HAp and YSZ grains is not strong. The structure of YSZ cracked as well as the HA as a composite matrix cracked [25]. The minimum requirement of standard specification of ISO 9917 for dental restorations is 100 MPa. All the specimens result were above the minimum requirement except C5. This indicated that the materials are appropriate in some other load bearing areas.

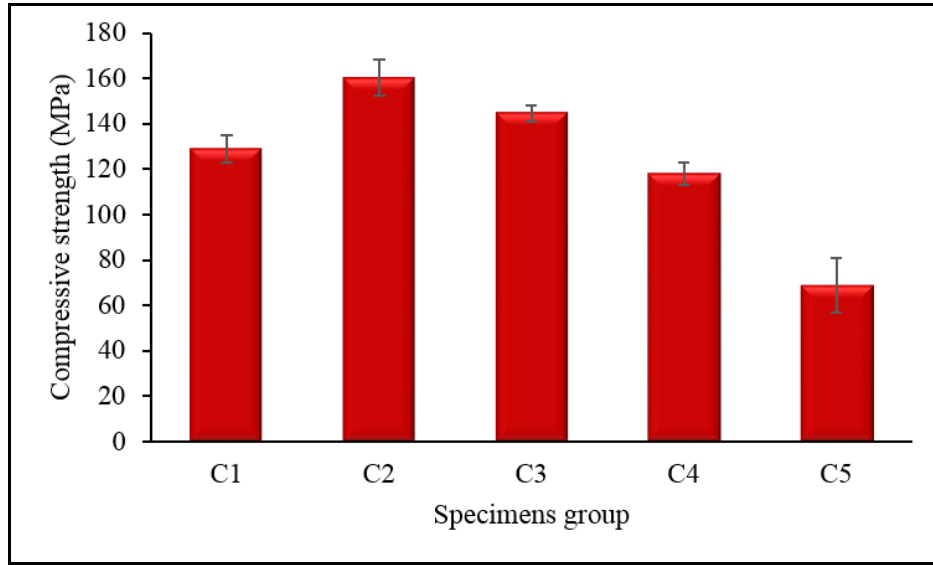


Figure 2: Compressive strength mean values of composites for each specimens group

Vickers hardness

The hardness test was also performed to determine the degree of deformation of composite and it is generally valuable parameter of comparison with the enamel tooth structure [26]. As shown in the Table 2, 10 wt% of YSZ in C2 specimen exhibited the highest Vickers hardness value at 50.80 HV ($p < 0.05$). The one-way ANOVA result revealed that the C2 specimen has a significant difference in mean value of Vickers hardness between C1 (39.80 HV), C4 specimen (40.40 HV) and C5 specimen (29.04 HV), but has no significant difference between the C3 specimen (47.53 HV). As shown in Figure 3, the Vickers hardness increased with increasing YSZ filler content up to a maximum at 10 wt% of YSZ and then decreased with further increase in the YSZ filler content. The slight drop in the hardness observed in the HAp-YSZ composites above 10 wt% YSZ filler was probably due to the YSZ additives disrupted the structure of HAp where HAp decomposition occurred [27].

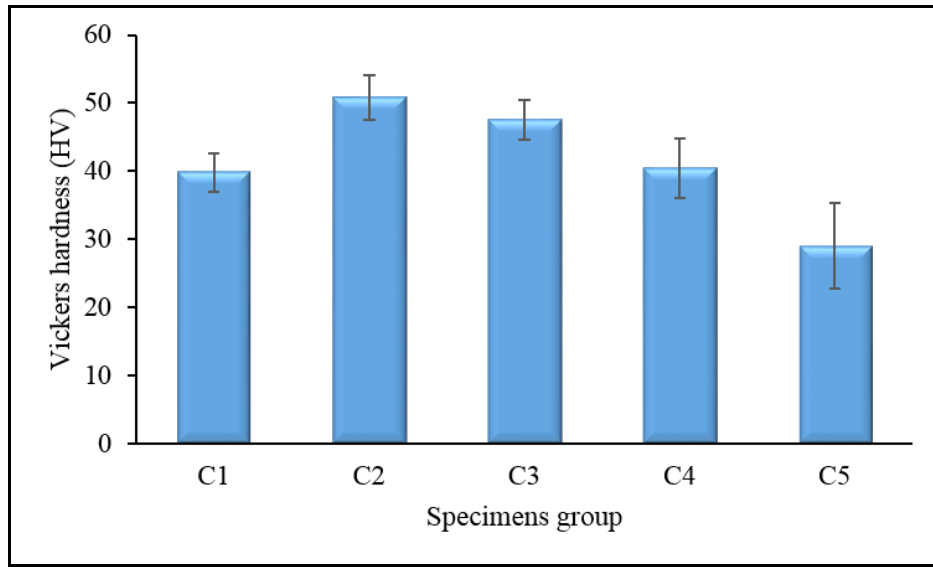


Figure 3: Vickers hardness mean values of composites

Surface roughness

The mechanical property of surface roughness is also important parameters in dental study because the surface smoothness of the restoration is one of the main factors of aesthetic success [28]. In the oral cavity, the surfaces of RBCs are subjected to a variety of factors that may alter the quality of surface. The surface texture of RBCs has an influence on the aesthetic appearance, discoloration of restorations and accumulation of plaque which may lead to secondary caries, superficial staining, gingival and periodontal inflammation.

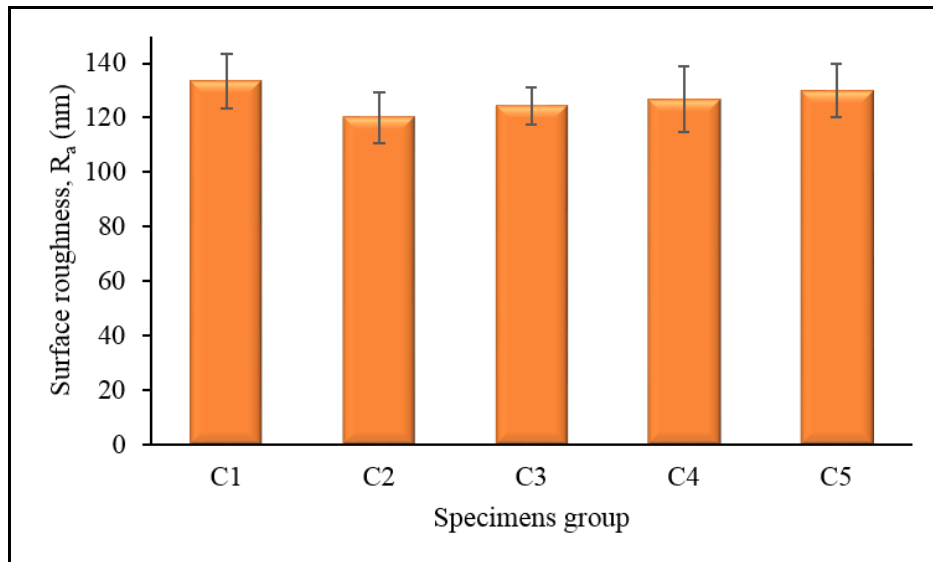


Figure 4: Surface roughness mean values of composites for each specimen group

In this study, the surface roughness (R_a) value was significant higher for C1 (133.40 nm) specimen compared to other specimens group as shown in Table 2 and Figure 4. The R_a mean values started to increase from the addition of 10 wt% to 75 wt% of YSZ filler in HAp composites. By comparing of all composites, the C2 specimen (10 wt% YSZ) showed the lowest significant surface roughness (120.00 nm) which were the smoothest specimen and there was not significant difference of R_a mean values between C2 with the other specimens HAp-YSZ composite ($p < 0.05$). The accumulation of plaque increased simultaneously as well as increased of the risk of caries and periodontal inflammation when the surface roughness is above 200 nm [29]. Due to obtain and maintain a surface as smooth as possible, every dental material actually needs its own treatment modality. Thus, the composite surfaces in this study can be assumed to have a smooth surface which may cause no risk of plaque accumulation.

CONCLUSION

HAp-YSZ composites were prepared by mixing the inorganic fillers with the blended monomer system to form a homogenous paste. Regarding to the trends observed, the performance of mechanical properties decreases with the increment of YSZ filler content in the inorganic phase of the RBC. However, the mechanical properties of HAp-YSZ composite with 10 wt% YSZ filler content (C2) exhibited satisfactory results (Flexural strength 65.61 MPa; Compressive strength 158.20 MPa; Vickers hardness 50.80 HV; Surface roughness 120.00 nm) with the minimum requirement given by ISO standards. The C2 specimen also shows a good property compared to the control specimen, C1 and it is potential to use as dental filler.

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