PREPARATION AND CHARACTERISATION OF RESIN-BASED DENTAL COMPOSITES USING NATURAL HYDROXYAPATITE AND SILICA FILLERS

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UNIVERSITI PENDIDIKAN SULTAN IDRIS

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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 aims of this study were to prepare and characterise the resin-based dental composite using natural hydroxyapatite (NHA) and silica fillers. The effect of different compositions of these materials on the properties of dental resin composite was investigated. RBC was prepared by varying the composition of silica (0, 5, 15, 20 wt%) in the filler mixture of NHA and silica. The ratio between fillers and organic resins was fixed at 70:30 wt%. Two different ratios of organic resins of bisphenol A glycidyl methacrylate (BisGMA)/triethylene glycol dimethacrylate (TEGDMA)/hydroxyethyl methacrylate (HEMA) were used i.e. 50:25:25 wt% (CB50) and 25:50:25 wt% (CT50). The composites were inserted into the mould and cross-linked using visible light for 60 seconds on both sides. The degree of conversion, flexural and compressive strength, surface roughness, Vickers hardness, water sorption of composites, and cytotoxicity test were evaluated and compared. The surface morphology and distribution of the dental composites were also observed and examined by field emission scanning electron microscope (FESEM). The data were analysed using one-way ANOVA and the Tukey's post hoc test at the significance level of 0.05. The results indicated that the CB50 with 15 wt% silica in filler mixture exhibited satisfactory mechanical and physical properties compared to CT50 with the value of flexural strength (42.74 MPa), compressive strength (174.28 MPa), surface roughness (43.0 nm), Vickers hardness (43.7 HV) and water sorption (34.84 µg/mm^3). Cytotoxicity test demonstrated no toxic effects released from the composites. In conclusion, this result has complied with the standard requirement of dental composite. The implication, combination of NHA and silica is promising as reinforcing filler for dental resin composite application.

PENYEDIAAN DAN PENCIRIAN KOMPOSIT GIGI BERASASKAN RESIN MENGGUNAKAN PENGISIAN HIDROKSIAPATIT SEMULA JADI DAN SILIKA

ABSTRAK

Komposit berasaskan resin pergigian (RBC) telah digunakan secara meluas dalam rawatan pergigian disebabkan oleh ciri-ciri mereka yang sangat baik seperti sifat estetik, mekanikal dan bioserasi. Tujuan kajian ini adalah untuk menyediakan dan mencirikan komposit gigi berasaskan resin menggunakan pengisian hidroksiapatit semula jadi (NHA) dan silika. Kesan komposisi bahan-bahan ini terhadap sifat komposit resin gigi diselidik. RBC disediakan dengan mengubah komposisi silika (0, 5, 15, 20 wt%) dalam campuran pengisi NHA dan silika. Nisbah antara pengisi dan resin organik ditetapkan pada 70:30 wt%. Dua nisbah berbeza resin organik bisfenol A glisidil metakrilat (BisGMA)/trietilena glikol dimetakrilat (TEGDMA)/hidroksietil metakrilat (HEMA) telah digunakan iaitu 50:25:25 wt% (CB50) dan 25:50:25 wt% (CT50). Komposit dimasukkan ke dalam acuan dan ditaut-silang menggunakan cahaya tampak selama 60 saat pada kedua-dua bahagian. Darjah penukaran, kekuatan lenturan dan mampatan, kekasaran permukaan, kekerasan Vickers, penyerapan air oleh komposit dan ujian kesitotoksikan dinilai dan dibandingkan. Morfologi permukaan dan taburan komposit pergigian juga diperhatikan dan diperiksa menggunakan mikroskop elektron pengimbas pelepasan medan (FESEM). Data dianalisis menggunakan ANOVA satu arah dan ujian post hoc Tukey pada tahap penting 0.05. Keputusan menunjukkan bahawa CB50 dengan 15 wt% silika dalam campuran pengisi mempamerkan sifat mekanikal dan fizikal yang memuaskan berbanding dengan CT50 dengan nilai kekuatan lenturan (42.74 MPa), kekuatan mampatan (174.28 MPa), kekasaran permukaan (43.0 nm), kekerasan Vickers (43.7 HV) dan penyerapan air (34.84 $\mu g/mm^3$). Ujian kesitotoksikan menunjukkan tiada kesan toksik yang dibebaskan daripada komposit. Kesimpulannya, keputusan ini telah memenuhi keperluan piawai komposit pergigian. Implikasinya, gabungan NHA dan silika mempunyai harapan sebagai pengisi penguat untuk aplikasi komposit resin gigi.

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LIST OF ABBREVIATIONS

µg	Microgram
µm	Micrometer
ANOVA	Analysis of Variance
Bis-GMA	Bisphenol A Glycidyl Methacrylate
C	Celsius
cm	Centimetre
CQ	Champhorquinone
DC	Degree of Conversion
EDMAB	Ethyl-4-Dimethylamino Benzoate
FTIR	Fourier Transform Infrared Spectrometer
GIC	Glass Ionomer Cement
HA	Hydroxyapatite
HA/SiO_2	Hydroxyapatite/Silica
HEMA	2-Hydroxyethyl Methacrylate
ISO	International Standard Organisation
kN	Kilonewton
min	Minutes
mm	Millimeter
MPa	Mega Pascal
mW	Milliwatt
NHA	Natural Hydroxyapatite

nm	Nanometer
RBC	Resin-Based Composite
s	Second
SD	Standard Deviation
SEM	Scanning Electron Microscope
SiO_2	Silica
TCP	Tricalcium Phosphate
TEGDMA	Triethylene Glycol Dimethacrylate
UTM	Universal Testing Machine

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CHAPTER 1

INTRODUCTION

1.1 Research Background

One of the most important issues in dentistry is repairing the tooth structural using the proper materials. Since the 1960s, a great number of researches have been attempted to improve the physical and mechanical properties of dental filling materials. Nowadays, dental resin-based composites (RBC) have become very popular since it can be widely used in dentistry as restorative material to repair decayed or damaged teeth due to their acceptable mechanical properties, superior aesthetics and the ability to bond to tooth tissues (Liu et al., 2015; Chen, Yu, Wang, & Li, 2011). Before their introduction as a dental filling material, metallic dental amalgams were the materials of choice for more than 150 years which have a long record of clinical success. According to Chadda et al. (2016), the average life span of amalgam restorations is approximately 13 years compared with approximately 5 to 7 years for composite resin restorations.

However, the metallic amalgam materials have drawbacks such as the possibility of toxic reactions, lack of aesthetics, and lack of adhesion to the tooth which can cause the formation of cracks (Wille, Hölken, Haidarschin, Adelung, & Kern, 2016). People nowadays are attracted to an aesthetic restoration that matches the color of natural teeth. The RBCs possess a better aesthetic, less safety concerns, and acceptable mechanical properties (Chen et al., 2011). Besides that, resin-based composite can be directly bonded to the tooth structure without removing healthy tissue (Schneider, Cavalcante, & Silikas, 2010).

RBCs, which are the main focus of this research, composed of an organic matrix, inorganic filler particles, coupling agents and initiator-accelerator system (Chen et al., 2011; Zandinejad, Atai, & Pahlevan, 2006). The organic 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. However, the polymerisation shrinkage is one of the major problems for clinicians during the restoration, which is responsible for the shorter median survival lifetime of resin-based composites (Chen et al., 2011).

The problems creates at the margins (Figure 1.1), because the restoration will tend to shrink away from the margin (Oduncu, Yucel, Aydin, Sener, & Yamaner, 2010; Roulet, 1997). This shrinkage problem are influenced by the composition of the resin composite, properties of resin composite and the application techniques (Roulet, 1997). Fillers and chemical composition of resin composite plays an important role over the polymerisation shrinkage, elastic modulus and degree of conversion. For example, if the filler ratio is increased, then the value of the composite elastic modulus is higher; a resin with higher molecular weight will result in lower shrinkage value (Schneider et al., 2010; Chen et al., 2008; Sideridou, Tserki, & Papanastasiou, 2002). Many studies have focused on these components to reduce shrinkage and improve mechanical properties.

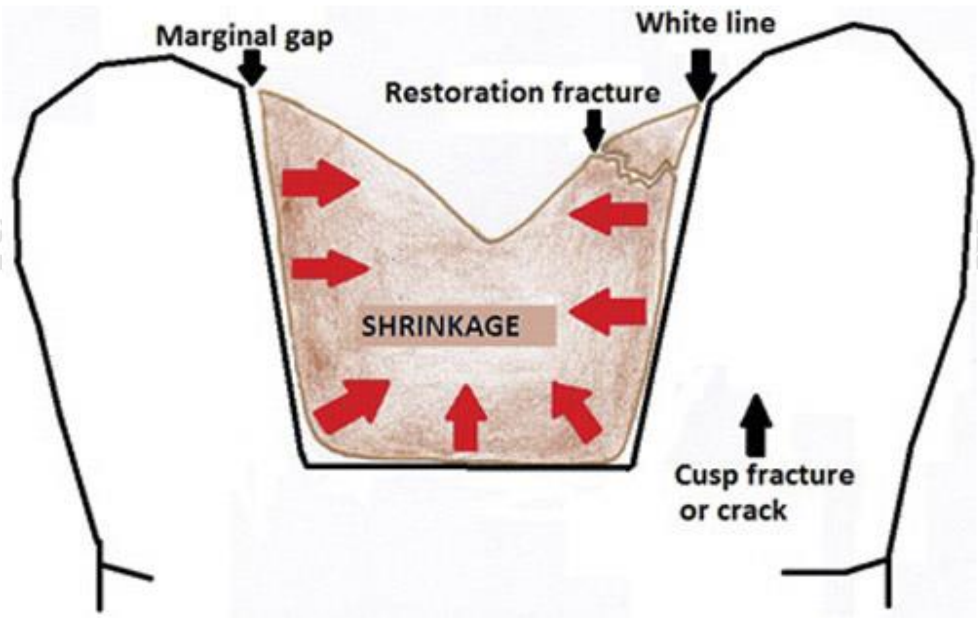

Figure 1.1. Polymerisation Shrinkage of the Dental Composites. Adapted from Djustiana, Greviana, Faza, & Sunarso, 2018

Hydroxyapatite (HA) is one of the constituent that present in either human bones or teeth. HA as a form of calcium phosphate is the main biomineral component in enamel and dentine, and it also has been explored as dental filler. As the main mineral component of hard dental tissues, hydroxyapatite (HA) is responsible for their hardness and other mechanical properties (Lezaja et al., 2013). Currently, most of the HA materials used in biomedical applications were synthesized through chemical routes which reported to be expensive due to the high cost of raw materials. In addition, synthetic HA has very low degradable properties which would inhibit the growth of new bone tissue (Jongwattanapisan et al., 2011). However, HA from natural sources reported have better and more crystallised than synthetic HA (Boutinguiza et al., 2012; Mezahi et al., 2011). Besides that, extraction process of natural HA from bio-waste is biologically safe, no chemicals needed and more economical due to cheaper raw materials.

In the laboratory, HA is prepared through dry methods, wet method or high-temperature process and diverse structures (sphere, nanorods, fibers, flowers, etc.) are produce from these methods (Sadat-Shojai, Khorasani, Dinpanah-Khoshdargi, & Jamshidi, 2013). But, HA also found in agricultural waste also known as natural sources namely eggshell, bovine bone, fish bone and scales (Abdulrahman et al., 2014; Zainol et al., 2012; Mezahi, Oudadesse, Harabi, Gal, & Cathelineau, 2011). Thus, it is helping in controlling solid waste and obtaining value added products. Mezahi et al. (2011) reported that the natural HA more crystalline than synthetic HA and the properties obtained are similar in composition to the calcium and phosphate components of our natural bones and teeth. Therefore, natural HA is promising to use as filler in dental composites.

In this study, the use of hydroxyapatite from the fish scales in fabricating dental composites is a big challenge. It perhaps could contribute to the effort in enhancing composite filling materials performance, such as the potential to improve the mechanical properties and overcome biological concerns. Chronic inflammation in pulp tissues and the healing process are examples of biological problems.

1.2 Problem Statement

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 aesthetic restoration that matches the colour of natural teeth, the ability to bond to tooth tissues and ease of use compared to dental amalgams and dental ceramics (Liu et al., 2015; Lezaja et al., 2013). 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 polymerisation shrinkage (Chen et al., 2011).

This organic resin when used unfilled for the restoration of teeth shows poor wear resistance (Sideridou et al., 2002). This can be improved by the incorporation of inorganic fillers; it will provide better mechanical properties due to the higher strength and stiffness of the filler particles (Chadda et al., 2016). Nowadays, researchers are focusing their attention on the improvement of the physical and mechanical properties of an inorganic filler because the major obstacle in composites are directly caused by the filler itself (Habib, Wang, Wang, Zhu, & Zhu, 2015). According to Guo et al. (2010), a large number of fillers play an essential role in the mechanical and biological properties of resin composites. Furthermore, the current commercially-used composites in dentistry applications are lack of hydroxyapatite (HA) content which is a natural component of dental enamel and dentine. HA, as a form of calcium phosphate shows high bioactivity and able to release the calcium and phosphorus ions which provide the remineralisation of teeth (Okulus, Buchwald, Szybowicz, & Voelkel, 2014).

Remineralisation of dental resin composite will improve marginal adaptation between restorations and teeth, as well as delay bacterial accumulation and penetration, and also halting a potentially recurrent caries (Liu, Jiang, Zhang, & Zhu, 2014; Peters, Bresciani, Barata, & Fagundes, 2010). The addition of inorganic bioactive filler such as hydroxyapatite from natural sources can thus change the degradation behavior of resin-based dental materials by enhancing the mechanical properties as well as reducing toxicity in composite resins (Chadda et al., 2016). Besides, this inorganic material of HA is less expensive than commonly used glass fillers, helping in controlling solid waste and obtaining value-added products.

The advantages of natural HA make it more worthy use as inorganic filler in dental resin composites compared to synthetic hydroxyapatite. However, the characteristics of low fracture toughness, poor tensile strength, stiffness and brittleness of HA exclude itself to employ as a load-bearing implants (Ozmen & Akin, 2012; White & Best, 2007; Bakar et al., 2003). Therefore, it is necessary to improve the mechanical properties and bioactivity of HA for long term applications by adding a second phase of silica particles (Calabrese et al., 2016; Chadda et al., 2016; Liu et al., 2014; Chen et al., 2011).

According to Samuel et al. (2009), addition of silica tends to improve the abrasion resistance, hydrolytic stability, and shrinkage of restorative composite resins. The hydroxyapatite and silica-based composite resins used in the previous study were not found to be cytotoxic, which is in close agreement with the Chadda et al. (2016). Silica is commonly used as fillers in dental resin composites for reinforcement and enhanced radiopacity. The incorporation of silicon into the apatite structure to form "bioglass" will increase bioactivity. This is due to the presence of the silinol group (Si–OH) that enhances the apatite phase formation at the implant tissue interface (Lung et al., 2016; Jongwattanapisan et al., 2011).

1.3 Significance of the Study

Study on developing new dental filling materials are very challenging and demanding as it has several variables that need to be fulfilled following certain standards. Therefore, physical and mechanical properties are the variables that play important roles in this study achieving better dental filling material with a value-added feature. Restoring a damaged tooth with enhanced properties helps in extending the lifespan of composite resin restorations. Thus, working on filler modifications such as optimization of filler content, filler packing and development of hybrid fillers have been identified as effective approaches to improve the performance of dental composite resins (Wang et al., 2016).

Although several studies have reported on the combined properties of hydroxyapatite and silica, to our knowledge, none has characterised and evaluated the reinforcing effects of natural hydroxyapatite (NHA) on organic resins. NHA which extracted from natural sources such as fish scales have abundant of calcium phosphate and could be used as an economic source for HA synthesis. This biowaste conversion considered as one of the benefits for solid waste management, as well as reduced environmental impact. Besides, this inorganic material of NHA is much cheaper than other inorganic fillers and has better features compared to synthetic, such as exhibited larger cell adhesion, proliferation, and differentiation of cells (Pon-On et al., 2016). In the present study, it was anticipated that the incorporation of NHA could significantly enhance both mechanical properties and biocompatibility, which might eventually extend the life of composite resin restorations. The aim of this study was to evaluate the influence of natural hydroxyapatite and silica as filler incorporation in resin-based dental composites.

This study is important in understanding the properties of hydroxyapatite-silica as the inorganic fillers with various mass fractions and its reinforcing effect on organic matrix phase which could potentially be used for the prevention of dental caries by reducing the polymerisation shrinkage and improving mechanical properties. It is expected that the silica particles may fill the voids present between HA particles, subsequently enhance the filler packing density by making the resin composite harder and stronger, and further improve the hardness of the composite (Liu et al., 2014). Besides, some filler are being investigated and developed with more advanced functions including bioactivity and antibacterial compound release such as remineralisation and fluoride release (Wiegand, Buchalla, & Attin, 2007). Composites with these features will probably be commercialized in the future.

1.4 Objectives of Study

The objectives of the study are as follows:

i) To prepare resin-based composites using NHA as inorganic filler at a different ratio
ii) To characterise the physical and mechanical properties of resin-based dental composites
iii) To evaluate the degree of conversion and water sorption of the composite materials