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Fluoridated hydroxyapatite nanorods as novel fillers for improving mechanical properties of dental composite: Synthesis and application

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ABSTRACT

Fluoridated hydroxyapatite (FHA) in nanorod morphology and hexagonal cross section were synthesised via hydrothermal process using Apricot Tree Gum (ATG) as a surfactant. The synthesised FHA nanorods were then used as reinforcement in bisphenol A-glycol dimethacrylate (Bis-GMA) as base monomer of composite matrix. The FHA nanorods with different ratios were incorporated in the matrix to examine fluoride ion release and pH changes in the Simulated Body Fluid (SBF) and their mechanical properties. The resin without FHA reinforcement was used as the control sample. The Diametral Tensile Strength (DTS), Flexural Strength (FS), and Flexural Modulus (FM) of the reinforced composite were found to be higher compared to the control sample; the values increased from 34.8 to 45.4 MPa, 76.5 to 99.4 MPa, and 1.7 to 2.5 GPa, respectively. Moreover, findings revealed that the pH is reduced by releasing the fluoride ions into the SBF which can be effective for preventing secondary caries. The most optimum mechanical properties were achieved with 0.2 wt% of FHA reinforcement. The FHA nanocomposite meets the minimum standard requirements for dental applications and compared to other dental composites has advantage of preventing formation of secondary caries due to release of fluoride.

1. Introduction

Polymer based composites have been used as dental restorative materials for at least 50 years [1]. It is also known that dental composite has better aesthetic properties and safety compared to dental amalgam [2]. In terms of clinical aspects, polymer based dental composites are popular as it preserves tooth better and has a minimum risk of leakage when it is bonded only to enamel [3,4]. However, polymer based restorative materials suffer from two main aspects: (i) weakness in mechanical properties [5] and (ii) high polymerization shrinkage [6]. These weaknesses are the main reasons for the shorter lifespan of dental resin based composite (5–7 years) compared to dental amalgam (13 years) [7,8].

Recent developments in dental restorative composites involved improving aesthetic quality and its ability to bond better with the enamel surface [9,10]. In general, the restorative composites consist of a matrix which is based on polydimethacrylate monomer and a reinforcement that interacts chemically or mechanically with the matrix [11]. Bisphenol A-glycol dimethacrylate (Bis-GMA) monomer has been widely utilized as the matrix due to its low polymerization shrinkage and other desirable properties including low thermal expansion, acceptable clinical handling, and low volatility [12]. Triethylene glycol dimethacrylate (TEGDMA) is used to reduce viscosity of the Bis-GMA and eventually improve dispersion of reinforcements following dilution [13,14].

Despite recent progress in the development of dental composites, improving their mechanical properties remains a challenge. Adequate mechanical properties of dental composites such as tensile, flexural, and hardness are crucial factors that determine the composite success and must be considered before clinical use. To overcome these drawbacks, various reinforcements have been utilized such as silica, glass fiber [15–17], organic polymer fiber [18], and ceramic (SiC and Si_3N_4) whiskers [19] with reported successful enhancement of the mechanical properties for dental applications. However, these fillers did not contribute to the bioactivity of the composites and prevention of second caries [20,21].

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Specifically, calcium phosphate powders such as hydroxyapatite, amorphous calcium phosphate, and anhydrous di-calcium phosphate have been used as reinforcements [22–24]. It is well known that calcium phosphate with its precipitation and dissolution process can form a strong bonding with hard tissues such as teeth [25]. Moreover, the use of calcium phosphate in dental composites offers radio-opacity, and improvement in wear properties of the composite [14]. In spite of all these desirable properties, current composites of apatite family in form of nanoparticle need improvements in terms of mechanical properties [26]. Recently, a great attention has been concentrated on the optimization of apatite fillers in terms of size, ratio, shape, and morphology when it is utilized as reinforcement [27].

The aim of this study is to improve mechanical and biological properties of dental composites through a novel technique for fabrication of fillers, which results in the formation of nanorod shaped apatite consisting fluoride. To the best of our knowledge, this is the first attempt at synthesizing nanorod FHA with similar geometrical structure of tooth enamel to be used as composites for dental restoration. It is known that the enamel is organized in a compact regular pattern of HA which basically has a rod structure with dimensions of 33–65 nm diameter and 100–1000 nm length [28]. Gao et al. [29] analysed the nanostructure of enamel and concluded that the strength of tooth came from the geometry and nano size of these nanostructures in rod form. There are many studies on the mechanical properties of dental resin with different fillers and techniques [32–34]. However, to the best of the authors' knowledge, there is no study or evidence on the effect of FHA in nanorods structure as reinforcement of dental composites on the mechanical properties. Moreover, It is also reported by Chen et al. [33] that by using fluoride into the dental composite, fluoride would be released at the site where the pH drops, which will improve the stability of filler and prevent second caries by inhibition of bacteria metabolism. Therefore, we hypothesized that by mimicking the structure of enamel, FHA nanorods can be a promising candidate to increase the mechanical properties of dental restorative composites as well as preventing secondary caries of the teeth.

To achieve the aim of the present study, dental resin composites with FHA nanorods at different ratios are prepared and then the mechanical properties and fluoride ion release profile and its pH changes in SBF are evaluated. The X-ray diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR), Field Emission Scanning Electron Microscope (FESEM), and Transmission Electron Microscope (TEM) were applied to characterize the synthesised FHA nanorods. Moreover, the universal machine and ion chromatography were used to investigate the mechanical properties and fluoride ion release respectively.

2. Experiment

2.1. Materials

Bisphenol A glycidyl methacrylate (Bis-GMA) and Triethyleneg lycol-dimethacrylate (TEGDMA) monomers, hydroxyapatite, NaF, and I-819 (initiator) were purchased from Sigma Aldrich (Malaysia). The nitric acid and ammonium hydroxide for adjusting the pH were purchased from Merck. Apricot tree gum (Prunus Armenia) was obtained from the city of Taleghan in Iran.

3. Methods

3.1. Filler synthesis procedure

The nanorods of FHA were synthesised according to our previous work [34]. Shortly, 105 mg of HA powder with 8 mg of sodium fluoride was mixed in 100 ml of distillated water. The nitric acid was added to the suspensions until the HA and sodium fluoride powders dissolved (pH was around 2.3). The 200 mg of ATG surfactant was added to the solutions and the pH was adjusted to 10 using ammonium hydroxide. Finally, solutions were placed in autoclave under 70 °C and 1 atm hydrothermal conditions.

3.2. Preparation of the dental resin composite

Synthesised FHA nanorods with different ratios (0, 0.2, 0.4, 0.6, 0.8 wt%) were added to the mixture of BisGMA-TEGDMA (50–50 v%) and mixed by a homogeniser device for 4 h at 20,000 rpm. After dispersion of fillers into the matrix, 2% of initiator (I-819) by weight was added to the five composites. The mixing procedure was completed using an ultrasonic device to remove any air bubbles in the resin composite. The container was covered to prevent any light initiated polymerization.

3.3. Fabrication and characterization of the samples

3.3.1. Diametral tensile strength

Cylinder shape mold with dimension of 6 × 4 mm ($L \times D$) was prepared and then the composite solutions were poured into the mold. The composite samples were cured using commercial dental curing UV light device (450 nm, 1200 W) for 40 s. The compression test was carried out with a universal test machine (Instron 4206) to investigate the DTS. The diameter (D) and length (L) were measured before load P was applied. The test was conducted at the rate of 1 mm/min. According to the ADA/ANSI Specification 27 standard, mean values of three maximum loads before fracture of samples were calculated and then used in Eq. (1) to measure the DTS value.

$$\mathrm{DTS} = \frac{2P}{\pi DL} \tag{1}$$

3.3.2. Flexural strength

Composite solutions were poured into the Teflon mold with dimensions of 50 × 10 × 10 mm ($L \times T \times W$) at room temperature for flexural strength test according to the ISO 4049-2009 standard. Before the curing process, the poured resin in the mold was compressed for 30 s at 1 kg load to ensure distribution of composite inside the mold. The samples were cured for 120 s on each side using UV light (450 nm, 1200 W) device.

The cured samples were kept in a humidifier for 24 h at 37 °C before flexural test. To measure the FM and FS, the flexural test was executed with a universal test machine (Instron 4206) at room temperature. The three-point bending test was performed at a cross head rate of 0.1 mm/min. the FM and FS values estimated according to the ISO 4049 standard using following equation (Eqs. (2), and (3)):

$$\mathrm{FM} = \frac{FL^3}{4BH^3D} \times 10^{-3} \tag{2}$$

$$\mathrm{FS} = \frac{3PL}{2BH^2} \tag{3}$$

where F is load (N), L is the supports distance (mm), B and H are consequently the sample width and thickness (mm), D is the deflection at load F, and P is the maximum load (N).

3.4. Immersion test

The five composites were cured into a disk shape with 1 × 0.2 mm ($L \times D$) dimension. The SBF [35] was prepared and the composites were then sterilized by UV light and immersed into the SBF for 21 days in water bath at 37 °C. The surface area of