Materials Science and Engineering C 45 (2014) 359–368

Contents lists available at ScienceDirect

Materials Science and Engineering C

journal homepage: www.elsevier.com/locate/msec

Thermal cycling effect of dicalcium phosphate-reinforced composites on auto-mineralized dental resin

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ARTICLE INFO

Article history:
Received 24 January 2014
Received in revised form 11 August 2014
Accepted 16 September 2014
Available online 21 September 2014

Keywords:
Coupling agents
Particle-reinforced composites
Smart materials
Surface modifications
Transmission electron microscopy

ABSTRACT

The mineralizing capabilities of surface-modified dicalcium phosphate anhydrous (DCPA), reinforced and treated with nanocrystals and capped with silane, in composite resins were analyzed via thermal cycling. We compared two light-curable composites that were mixed at filler-to-resin mass ratios of 30/70 and 50/50. The strengths, elastic moduli, and topographical structures of the samples were determined after thermal cycling between 5 and 55 °C in deionized water for 600 and 2400 cycles. Silane-capped particles decreased the strength but enhanced the mineralizing capability of the composites. Nanocrystal-treated filler surfaces significantly increased the strength and moduli of the composites after 600 thermal cycles. However, these values declined after 2400 thermal cycles. The nanocrystal-treated filler surfaces prevented the reduction in strength before and after 2400 thermal cycles. Prior to silane capping, the nanocrystal-treated DCPA filler surfaces exhibited good mineralization capability without compromising strength. The potential for barrier generation through mineralization yielded positive effects and prevented micro-leakages.

1. Introduction

Composite resins offer excellent properties that are suitable for dental prosthetic materials. Unlike alloys, they closely match natural tooth color and do not release ions or heavy metals with contact to saliva [1]. In addition, composite resins show excellent interface adhesion owing to their flowable property, which allows them to penetrate and fit into specific sites in clinical restorations. However, repeated thermal fatigue within the oral cavity can introduce contraction/expansion stresses at the interfaces between the tooth and the restorative material, which could cause microleakages in restorative material margins, retention failure, and secondary caries [2]. Nevertheless, the addition of calcium phosphates (CaPs) can overcome these drawbacks [3–6]. Therefore, a dental resin with auto-remineralization capability upon formation and contact with the oral environment is effective in preventing recurrent dental caries and in regenerating tooth structure. CaP substances, such as hydroxyapatite (HA), α-/β-tricalcium phosphate (α-/β-TCP), and amorphous CaP (ACP), are structural prototypes of the major mineral components of tooth and bone parts [7]. The combination of ions with CaPs with low solubility product constants (K_{sp}) enhances second-phase precipitation [8–10]. A silane-modified filler of ACP has been used in composite resin to evaluate remineralizing potential; however, the strength of the composite is significantly reduced because the modified ACP filler hinders polymerization mechanisms [8,11,12]. To prevent the mineralizing ability from compromising the strength of the resin, CaPs mixed with whisker nanocrystals (>10 ratio of length to width was) are used as reinforcements for composites [13]. Numerous studies [14–17] have also used alternative strategies, such as the use of different size distributions of CaP particles [e.g., HA, tetracalcium phosphate, octacalcium phosphate, and dicalcium phosphate anhydrous (DCPA)] and varying the filler-to-matrix mass and whisker ratios to develop mineralizing dental composites and to analyze the mechanical properties and ion-releasing capabilities of the resins. Surface modification of CaP particles is important to enhance the bond between CaPs and polymer-resin matrices [18].

However, problems arise when these composite resins are used in long-term dynamic oral environments. The relatively limited amount of nanoCaP fillers (<30 wt.%) in composite resins is easily exhausted in the oral environment. Moreover, the fillers embedded in restorative matrix on the surfaces are difficult to expose [18–21]. The current research uses technology previously developed in-house, which involves capping a layer of nanocrystals and salinization with resin matrix to form a composite resin [18]. Composite resins composed of 30 and 50 wt.% modified DCPA fillers are used in the present study based on commercialized Filtek Z350 flowable resin and Filtek Z250 composite resin, respectively. To investigate

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http://dx.doi.org/10.1016/j.msec.2014.09.032
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the aging process of the composite resins, the effect of mineralization and the efficiency of silane-modified nanocrystals in composite resins during thermal cycling were evaluated. Although the thermal fatigue numbers of thermal cycling varied in large ranges depending on the applied condition and restorative sites, cycling time ranges from 100 to 12000 cycles [22–25]. Thermal cycling is generally used to simulate the temperature fluctuations that occur in the oral cavity to generate stress and to determine the changes in the properties of the prosthetic materials with age [22, 23]. To simulate oral conditions in a patient with prosthetic resins that eats three times a day, teeth were thermally cycled for three times at 5 °C/55 °C, [24]. The elapsed times after 600 and 2400 cycles were estimated to be approximately six months and two years of clinical usage, respectively. This study was designed to characterize the mechanical and mineralizing effects of DPCA nanocrystal filler with surface treatment, silanization, or a combination of both on composite resins after 600 and 2400 thermal cycles at 5 °C/55 °C. This study considered the following two hypotheses: (1) the reinforced fillers with surface-modified nanocrystals or silanization accelerate the mineralizing ability of composites after thermal cycling and (2) (null hypothesis) the reinforced fillers with surface-modified nanocrystals or silanization do not compromise composite strength.

2. Materials and methods

2.1. Preparation and characterization of composite filler

For this study, DCPA filler ($CaHPO_4$, Alfa Aesar GmbH and Co., Karlsruhe, Germany) in powder form was used, with particle size ranging from 1 μm to 3 μm and purity of 98%. The nanocrystal formation was determined during the monitored treatment in accordance with previous studies [18,21]. DCPA powder (5 g) was mixed in 40 mL of solution (constant calcium-to-phosphate atomic ratio, 2.0; pH 5.0) for 20 min at room temperature. After which, the particles were filtered, washed, dried, and observed by transmission electron microscopy (TEM) (JEM-3010, JEOL Ltd., Japan) at 200 kV. The patterns were indexed and identified by detailed measurements and compared with the Miller indices of *d* values from the Joint Committee on Powder Diffraction Standards.

2.2. Silanization

A colloidal solution containing 100 mL cyclohexane, 4% (v/v) (3-mercaptopropyl) trimethoxysilane, and 2% (v/v) *n*-propylamine (Alfa Aesar GmbH and Co., KG, Karlsruhe, Germany) was used to cap the particle surfaces. Up to 5 g of DCPA powder per batch with (w/ NP/Si) or without nanocrystal (w/ Si) modification was added to the colloidal solution with rapid agitation for 30 min at room temperature. The mixture was then heated to 60 °C. The remaining solvent was removed by drying the samples in vacuum for 2 h.

2.3. Resin compositions

The resin matrix was mainly composed of bisphenol A-diglycidyl methacrylate (Bis-GMA) and triethylene glycol dimethacrylate (TEGDMA) monomers. The free-radical polymerization initiation system contained photocurable composite resin with a light initiator camphoroquinone (CQ), an accelerator of dimethylaminoethyl methacrylate (DMAEMA), and butylated hydroxytoluene (BHT) for photostability. The chemicals used in this study were all from Sigma-Aldrich Co. (Buchs, Switzerland). The organic matrix is composed of a weight ratio of 48.975% Bis-GMA and TEGDMA, 1% CQ and DMAEMA, and approximately 0.05% BHT. The organic matrix and DCPA inorganic fillers with and without modified filler were used to form the composite resins at weight percentage ratios of filler/(filler and matrix) (30 and 50 wt.% fillers). The composite resins were prepared in a dark room and mixed with a magnetic stirrer until a colloid was formed.

2.4. Physiochemical analyses

The samples and mold dimensions used for diametric tensile strength (DTS) testing and curing procedures are shown in Fig. 1. Light curing was performed on each respective side for 40 s using a light-cure machine (Demetron Optilux 401, Kerr, USA). The samples were divided into two groups: (1) the as-prepared dried samples from curing, which were tested immediately; and (2) the wet samples, which were obtained by further immersing the cured specimen in deionized water at 37 °C beyond the initial 24 h immersion, followed by thermal cycling (600 and 2400 cycles, 5 °C/55 °C, 2 min/cycle; Long Wha Enterprise Co., Kaohsiung, Taiwan) [22]. The water baths were used to prevent ion effects and evaluate auto-mineralization. Therefore, the samples were obtained via thermal cycling testing by using the specimens immersed in pure water baths (1 g sample to 10 mL deionized water). The strength of the different specimens was immediately measured using a desktop mechanical tester (LLOYD Instruments, Tokyo, Japan) at a crosshead speed of 2.0 mm/min. The ultimate tensile strength and elastic modulus were measured from the stress–strain curves [18]. The specimens were compressed diametrically until the maximum stress was recorded or until the specimens were fractured. Compression was used to introduce tensile stress on the force application plane. The ultimate tensile strength was determined from the stress–strain curves by using the formula $DTS = 2P / \pi DT$, where P is the load applied, D is the diameter of the cylinder, and T is the thickness of the cylinder [18,26]. The elastic modulus was calculated from the inclination of the correlation line from a nearly elastic part on the proportionality of stress–strain curves by 5.0% offset deformation of the specimen [27,28].

Fifteen duplicate specimens were prepared and analyzed for each group (i.e., $n = 15$). Field-emission scanning electron microscopy (SEM) (Hitachi S-3000N, Hitachi, Tokyo, Japan) combined with energy-dispersive X-ray spectrometry (EDS; Horiba EX220, Japan) was used to study the mineralizing ability of the substances. A rough depth profile was observed near the surfaces. Surface phase analysis was conducted via X-ray diffraction (XRD-6000, Shimadzu, Japan) with Ni-filtered Cu K_α radiation at low-angle XRD mode [29].

2.5. Statistical analyses

Statistical analyses of the results were primarily performed via one-way ANOVA. Group comparisons were used to evaluate the statistical significance of the deviations in the properties of DTS and moduli among the testing groups by using JMP 9.0 software (SAS Institute, Inc., Cary, NC, USA). The results were considered statistically different at $p < 0.05$.

3. Results and discussion

3.1. Characterization of fillers

The hypothesis that fillers with surface-modified nanocrystals or silanization could accelerate the mineralizing ability of composites after thermal cycling was confirmed. The mineralizing abilities were proportional to the increase in thermal cycles. However, the null hypothesis was rejected because the DTS in the 50 wt.% filler groups decreased after 600 thermal cycles. Comparing the effects of the 600 and 2400 thermal cycles, those of increasing thermal cycles exhibited an inverse tendency with the moduli in the 30 wt.% and 50 wt.% filler groups. The effect induced by the capped nanocrystals on the DCPA surfaces is