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Reinforcement of flowable dental composites with titanium dioxide nanotubes

Manal O. Dafar[a], *Matthew W. Grol*[b], *Peter B. Canham*[a], *S. Jeffrey Dixon*[b,c,e], *Amin S. Rizkalla*[a,c,d,e,*]

[a] *Department of Medical Biophysics, Schulich School of Medicine & Dentistry, The University of Western Ontario, London, Ontario, Canada*
[b] *Department of Physiology and Pharmacology, Schulich School of Medicine & Dentistry, The University of Western Ontario, London, Ontario, Canada*
[c] *Dentistry, Schulich School of Medicine & Dentistry, The University of Western Ontario, London, Ontario, Canada*
[d] *Department of Chemical and Biochemical Engineering, Faculty of Engineering, The University of Western Ontario, London, Ontario, Canada*
[e] *Bone and Joint Institute, The University of Western Ontario, London, Ontario, Canada*

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ABSTRACT

Objectives. Flowable dental composites are used as restorative materials due to their excellent esthetics and rheology. However, they suffer from inferior mechanical properties compared to conventional composites. The aim of this study was to reinforce a flowable dental composite with TiO_2 nanotubes (n-TiO_2) and to assess the effect of n-TiO_2 surface modifications on the mechanical properties of the reinforced composite.

Methods. n-TiO_2 were synthesized using an alkaline hydrothermal process and then functionalized with silane or methacrylic acid (MA). Nanotubes were characterized by scanning and transmission electron microscopy, X-ray diffraction, energy-dispersive X-ray spectroscopy and Fourier transform infrared spectroscopy. Commercially available flowable composite (Filtek^{TM} Supreme Ultra Flowable Restorative, 3M ESPE) was reinforced with varying amounts of nanotubes (0–5 wt%). Flowability of the resulting composites was evaluated using a Gillmore needle method. Dynamic Young's modulus (E) was measured using an ultrasonic technique. Fracture toughness (K_{Ic}) was assessed using a notchless triangular prism and radiopacity was quantified. Viability of NIH/3T3 fibroblasts was evaluated following incubation on composite specimens for 24 h.

Abbreviations: ANOVA, analysis of variance; DMEM, Dulbecco's modified Eagle medium; E, dynamic Young's modulus; EDX, energy dispersive X-ray spectroscopy; FBS, fetal bovine serum; FTIR, Fourier transform infrared spectroscopy; ISO, International Organization for Standardization; K_{Ic}, fracture toughness; MA, methacrylic acid; MPTMS, 3-methacryloxypropyltrimethoxysilane; MTT, 3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide; n-TiO_2, TiO_2 nanotubes; NTP, notchless triangular prisms; OTMS, n-octyltrimethoxysilane; SD, standard deviation; SE, standard error of the mean; SEM, scanning electron microscopy; TEM, transmission electron microscopy; XRD, X-ray diffraction.

[*] *Corresponding author at*: Schulich School of Medicine & Dentistry, The University of Western Ontario, London, Ontario, Canada N6A 5C1.

E-mail address: arizkalla@eng.uwo.ca (A.S. Rizkalla).

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Results. Electron microscopy revealed a tubular morphology of n-TiO_2. All reinforced composites exhibited significantly greater values of E than unreinforced composite. Composites reinforced with 3 wt% n-TiO_2 functionalized with MA exhibited the greatest values of E and K_{Ic}. Cytotoxicity assays revealed that reinforced composites were biocompatible. Taken together, flowable composites reinforced with n-TiO_2 exhibited mechanical properties superior to those of unreinforced composite, with minimal effects on flowability and radiopacity.

Significance. n-TiO_2-reinforced flowable composites are promising materials for use in dental restorations.

1. Introduction

Although amalgam has excellent mechanical properties and longevity, it is not esthetically pleasing. Moreover, the possible release of mercury has raised concerns regarding potential adverse health effects. As a result, focus has shifted from amalgam to resin-based composites for dental restorations [1]. Conventional composites were introduced in dentistry more than 50 years ago. Since that time, many characteristics have been optimized, including filler size, to improve wear resistance and achieve highly polished surfaces [2].

More recently, flowable composites have been developed to improve handling characteristics, but mechanical properties remain inferior to those of conventional composites. It has been reported that flowable composites have 20–25% less filler content and consequently 20–30% lower modulus of elasticity [3,4]. In current practice, flowable composites are used as liners, fissure sealants and class V restorative materials. The fluidity of these composites is increased by reducing the filler content or by adding modifying agents, such as surfactants. Though no particular approach for improving mechanical properties has been found to be ‘ideal’, incorporation of TiO_2 nanotubes (n-TiO_2) into acrylic bone cement can enhance its fracture and flexural properties without significantly altering viscosity [5].

Nano-sized fillers are characterized by a high surface to volume ratio. The hollow structure of nanotubes allows interlocking with the matrix on internal and external surfaces of the tubes [6]. As a result, higher filler content can be achieved in composites, resulting in reduced polymerization shrinkage and improved mechanical properties [7]. n-TiO_2 are typically synthesized using the alkaline hydrothermal method. This method is advantageous as it produces pure-phase nanostructures in a one-step reaction that is both reproducible and cost-effective [8]. In terms of biomedical applications, n-TiO_2-modified surfaces have been used successfully to improve bone regeneration by stem cells and osseointegration of implants in animal models [9]. Moreover, nanostructured hydroxyapatite has been incorporated in root canal sealers and adhesive resins, leading to improved mechanical properties [10,11]. On the other hand, nanoparticles tend to agglomerate in their native state becoming resistant to dispersion by organic solvents. Therefore, surface modification of n-TiO_2 particles is essential to prevent agglomeration and improve compatibility with resin matrices. In this regard, silane can be used to modify the surface of inorganic fillers (including TiO_2 nanoparticles) within composite materials to improve their dispersion and bonding to the resin matrix [12–14]. The goal of the present study was to assess the effects of surface modification of n-TiO_2 on their ability to reinforce a commercially available flowable dental composite. Different weight percentages of n-TiO_2 (0–5%) were incorporated into Filtek^{TM} Supreme Ultra Flowable Restorative (3M ESPE). We investigated the dynamic Young’s modulus, fracture toughness, flowability, radiopacity and cytotoxicity of the resulting materials. We hypothesized that reinforcement of a commercial flowable dental composite with n-TiO_2 will improve its mechanical properties and that surface modification of n-TiO_2 will further enhance these effects.

2. Materials and methods

2.1. Synthesis of TiO_2 nanotubes

Titania nanotubes (n-TiO_2) were synthesized using the alkaline hydrothermal process [15]. Briefly, synthesis was started by dispersing 0.24 g strontium acetate powder in 30 mL of 10 M NaOH solution and stirring for 24 h. Next, 2 g of TiO_2 spherical nanoparticles (<100 nm particle size; Sigma–Aldrich, Oakville, ON, Canada) were added to the solution. The mixture was placed in a Teflon-lined stainless steel autoclave (Parr Instrument Company, Moline, IL, USA). This reaction was held at 160 °C for 20 h. The alkali-treated material was washed with deionized water and 0.1 N HCl until the pH dropped to 6.0. Finally, the resulting nanotubes were vacuum dried overnight and calcined at 400 °C for 2 h [16].

2.2. Functionalization of TiO_2 nanotubes

Coupling agents have functional groups to chemically link the filler and the matrix [17]. n-TiO_2 were functionalized by coating with bifunctional coupling agents, silane or methacrylic acid (MA), as described previously [5,16,18]. For functionalization with silane, n-TiO_2 was dispersed in 20 mL cyclohexane and 0.028 mL *n*-propylamine before the addition of a 10% silane mixture (7.5% 3-methacryloxypropyltrimethoxysilane, MPTMS and 2.5% n-octyltrimethoxysilane, OTMS). After 24 h under constant stirring at room temperature, the mixture was transferred to a rotary evaporator. The temperature was elevated to 95 °C for 1 h and the reaction product was dried under vacuum at 80 °C overnight [18].