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Dental glass ionomer cement reinforced by cellulose microfibers and cellulose nanocrystals

Rafael M. Silva [a,b], Fabiano V. Pereira [c,*], Felipe A.P. Mota [b], Evandro Watanabe [d], Suelleng M.C.S. Soares [a], Maria Helena Santos [a,b]

[a] Departamento de Odontologia, Universidade Federal do Vale do Jequitinhonha e Mucuri, UFVJM, Diamantina CEP: 39100-000, MG, Brazil
[b] Centro Avançado de Avaliação e Desenvolvimento de Biomateriais, BioMat, Universidade Federal do Vale do Jequitinhonha e Mucuri, UFVJM, Diamantina CEP: 39100-000, MG, Brazil
[c] Departamento de Química, Universidade Federal de Minas Gerais, UFMG, Belo Horizonte CEP: 31270-901, MG, Brazil
[d] Departamento de Odontologia Restauradora, Faculdade de Odontologia de Ribeirão Preto, USP, Ribeirão Preto CEP: 14040-904, SP, Brazil

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ABSTRACT

The aim of this work was to evaluate if the addition of cellulose microfibers (CmF) or cellulose nanocrystals (CNC) would improve the mechanical properties of a commercial dental glass ionomer cement (GIC). Different amounts of CmF and CNC were previously prepared and then added to reinforce the GIC matrix while it was being manipulated. Test specimens with various concentrations of CmF or CNC in their total masses were fabricated and submitted to mechanical tests (to evaluate their compressive and diametral tensile strength, modulus, surface microhardness and wear resistance) and characterized by scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS), transmission electron microscopy (TEM) and Fourier transform infrared spectroscopy (FTIR). The incorporation of CmF in the GIC matrix did not greatly improve the mechanical properties of GIC. However, the addition of a small amount of CNC in the GIC led to significant improvements in all of the mechanical properties evaluated: compressive strength (increased up to 110% compared with the control group), elastic modulus increased by 161%, diametral tensile strength increased by 53%, and the mass loss decreased from 10.95 to 3.87%. Because the composites presented a considerable increase in mechanical properties, the modification of the conventional GIC with CNC can represent a new and promising dental restorative material.

1. Introduction

Glass ionomer cement (GIC) is frequently used in restorative dentistry and its properties have been constantly improved because of its significant flexibility in clinical applications. In the contemporary world economic scenario, GIC cement has been indicated by international bodies as the definitive restorative material for low-income populations, because of its favorable clinical performance [1–3]. In the last few years, the volume of scientific investigations involving GIC has become more relevant [4,5]. In addition, in spite of presenting some desirable properties, such as biocompatibility, good adhesion to dental hard tissue and the possibility to release fluoride, some deficiencies of GIC still need to be overcome. These drawbacks are mainly related to the mechanical properties of this material, such as wear resistance and compressive and diametral tensile strength. For this purpose, new GIC formulations are being developed in the literature, with a focus on their mechanical properties, leading to the possibility of a greater demand for these cements in the dental clinic [6,7].

Cellulosic fibers have been studied for several years, with the goal of incorporating them into materials, mainly polymers, as a reinforcing agent. Studies have described significant improvements in the mechanical properties of these materials, generally in proportion to the concentration of fiber additions [8,9].

Silva et al. [10], described the use of cellulosic fibers to enhance the mechanical properties of dental restorative materials. The cellulosic ..fibers were obtained by a sodium hydroxide and sodium sulfide treatment from eucalyptus wood obtaining tangle of fibers with approximately 1 mm in size. Different amounts of eucalyptus fibers have been added as a reinforcing agent to conventional GIC. The authors found that the addition of the ideal proportion of fibers to GIC did not interfere with its working and setting times, solubility, disintegration in water, and diametral tensile strength, which remained similar to those of the conventional GIC. However, an increase in compressive strength, abrasion resistance, and bond strength to dental structure were observed.

The great development in nanotechnology studies, combined with the need for sustainable development, has made the use of cellulose attractive, due to its renewable capacity, abundance as a raw material, lack of toxicity, low density and low thermal expansion [11]. In this context, the use of nanocellulose, or cellulose nanocrystals (CNC) as a new

* Corresponding author.
E-mail address: fabianovp@ufmg.br (F.V. Pereira).

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renewable nanomaterial to reinforce materials has attracted significant attention during the last few years [11,12]. The CNC are highly crystalline rod-like nanostructures obtained from cellulose and present excellent mechanical properties. They can be obtained by controlled acid hydrolysis of any natural source of cellulose and present an average dimension of approximately 100–250 nm in length and 5–15 nm in diameter. The acid hydrolysis readily destroys the amorphous regions of cellulose, leaving the crystalline segments intact and leading to the formation of single crystals of high-purity [11]. Because of their mechanical properties, the CNC have been studied as reinforcement elements in different polymer matrixes [12,13]. Because of their renewable nature, low cost, low density, high specific mechanical properties and nonabrasive nature, which allow for easy processing, the CNC present numerous advantages compared with inorganic fillers, which are commonly used to reinforce different polymers [11–13].

Considering that renewable and bio-based nanocomposites are the next generation of materials for the future [12], the mechanical deficiencies of the GIC, and the originality of the study of the application of CNC in a dental restorative material, our aim was to modify conventional GIC with CNC in order to enhance the mechanical properties of the neat GIC material. We also used CmF to prepare different composites with GIC in order to compare the mechanical reinforcements promoted by both cellulosic particles. For statistical analysis purposes, the null hypothesis used was that the mechanical properties of the modified GIC (GIC composites) were not different from that of the non-modified GIC, and in all cases the cut off for null hypothesis rejection was set at 5%.

2. Materials and methods

2.1. Materials

2.1.1. Preparation of cellulose microfibers and cellulose nanocrystals

The cellulose microfibers (CmF) were prepared from kraft eucalyptus cellulose pulp. Briefly, 6 g of cellulose fibers was mixed with 250 ml of 37% hydrochloric acid and submitted to strong mechanical stirring for 2 h. The suspension was then heated to 50 °C for 3 h under magnetic stirring. The mixture was cooled to ambient temperature for 1 h, filtered, washed and sonicated. The final material was freeze-dried and kept in a refrigerator.

For the preparation of the CNC, eucalyptus cellulose pulp was hydrolyzed using sulfuric acid, as described in the literature, [14,15], with minor modifications. Cellulose pulp was added to a solution of 64 wt% of sulfuric acid under strong mechanical stirring. The hydrolysis was performed at 50 °C for 40 min. The suspension containing the CNC was diluted twice and washed three times with deionized water by means of centrifugation. Dialysis against deionized water was performed until the dispersion attained pH ~7. The suspension was submitted to ultrasonification for 5 min in order to completely disperse the CNC. The final concentration of CNC in aqueous suspension was approximately 10 mg/ml.

2.1.2. Sample preparation

CmF were weighted and added to the GIC matrix of a conventional glass ionomer brand (Vidrion R, SS White, Brazil), in three different concentrations. Thus, we obtained three different experimental groups: G1: GICCmF 3.5%; G2: GICCmF 6.7% and G3: GICCmF 9.8%. A control group (CG) of GIC without CmF was also prepared.

To prepare the GIC composites modified with CNC (GICCNC), the CNC were firstly added to the liquid of GIC in five different concentrations, sonicated for 2 min for complete homogenization and then incorporated to the GIC powder, respecting the powder:liquid ratio of 1:1, and manually manipulated in accordance with the manufacturer's recommendations. Test specimens (ts) were then fabricated, and five experimental groups were obtained: G01: GICCNC 1%; G02: GICCNC 0.8%; G03: GICCNC 0.6%; G04: GICCNC 0.4% and G05: GICCNC 0.2%.

2.2. Methods

2.2.1. Sample calculation

To determine the sample size (n), the comparison of means formula was used. The level of significance (Zα) and statistical power (Zβ) were considered 95% and 80%, respectively. The difference (D) to be detected among groups was stipulated at 16. The value referring to the standard deviation (sd = 11.49) was obtained after a pilot study. To this value, 20% was added to predict eventual losses. Thus, the minimum to be investigated became 9.69.

2.2.2. Compressive strength, diametral tensile strength and modulus of elasticity evaluations

Twenty test specimens (ts) of each of the experimental groups were prepared in a Teflon matrix 4 mm in diameter and 6 mm long, according to standard ISO 9917-1:2007 [16]. To fabricate the ts of the CG, the GIC was manipulated and inserted with a syringe in a Teflon matrix (mold) under pressure. In the preparation of ts for the other groups, the cement was inserted in the mold with an insertion spatula and compacted with the aid of an amalgam condenser. After completely filling the Teflon matrix, a polyester strip was pressed onto it with a 500 g weight, until its net setting time was attained (time necessary to a needle fails to make a complete circular indentation in the cement), [16] in order to obtain adequate flow and surface smoothness. After 24 h of storage in distilled water at 37 °C (±1 °C), the 10 ts of each group were submitted to the compressive strength and diametral tensile strength tests in a universal test machine (EZ Test, Shimadzu, Kyoto, Japan) with a load cell of 200 kgf, at a speed of 1 mm/min for the former test and 0.5 mm/min for the latter. The long axis of the ts was in the vertical position for the compressive strength test and in the horizontal position for the diametral tensile strength test. The compressive and diametral tensile strength were computed by formulas [17].

$$\textit{Compressive strength}\ (\mathrm{MPa}) = \frac{4F}{\pi d^2}$$

$$\textit{Diametral traction tension}(\mathrm{MPa}) = \frac{2F}{\pi d l}$$

where: F = fracture load, d = diameter, and l = length.

The modulus of elasticity of the ts was also computed, while performing the diametral tensile strength test by equation [17]:

$$E(\mathrm{MPa}) = \frac{\sigma}{\varepsilon} = \frac{\left({}^{P}/_{A}\right)}{\left({}^{\Delta l}/_{l_o}\right)}$$

where: E = modulus of elasticity, P = load, A = transverse area, Δl = increase in length, and l_o = original length.

2.2.3. Surface microhardness assessment

The surfaces of the ts (with 5 mm in diameter and 3 mm in deep) were polished with a grinder and metallographic polishing machine (Model PLFDV, Fortel, São Paulo, SP, Brazil), using a sequence of 320, 400 and 600 grain abrasive papers. Each ts was submitted to five impressions on its surface, with a distance of 0.2 mm between each indentation, by means of a pyramidal diamond tip, with a load of 300 gf for 15 s. The Vickers Hardness Number (VHN) was calculated as the mean of the five readouts taken.

2.2.4. Wear resistance assessment

The test specimens measuring 4 × 8 mm (n = 10) were stored in distilled water at temperature of 37 °C for 14 days. After drying for 12 h at ambient temperature, the ts were weighted, and mounted on an appropriate device with a capacity for six ts, on 800 grain abrasive paper in a metallographic polishing machine. The ts were submitted to an abrasion wear test cycle, using a load of 100 g at a speed of