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Addition of mechanically processed cellulosic fibers to ionomer cement: mechanical properties

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Abstract: In this study, conventional restorative glass ionomer cement (GIC) was modified by embedding it with mechanically processed cellulose fibers. Two concentrations of fibers were weighed and agglutinated into the GIC during manipulation, yielding Experimental Groups 2 (G2; 3.62 wt% of fibers) and 3 (G3; 7.24 wt% of fibers), which were compared against a control group containing no fibers (G1). The compressive strengths and elastic modulus of the three groups, and their diametral tensile strengths and stiffness, were evaluated on a universal test machine. The compressive and diametral tensile strengths were significantly higher in G3 than in G1. Statistically significant differences in elastic modulus were also found between G2 and G1 and between G2 and G3, whereas the stiffness significantly differed between G1 and G2. The materials were then characterized by scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS). Heterogeneously shaped particles were found on the G2 and G3 surfaces, and the cement matrices were randomly interspersed with long intermingled fibers. The EDS spectra of the composites revealed the elemental compositions of the precursor materials. The physically processed cellulosic fibers (especially at the higher concentration) increased the compressive and diametral tensile strengths of the GIC, and demonstrated acceptable elastic modulus and stiffness.

Keywords: Glass Ionomer Cements; Cellulose; Compressive Strength; Tensile Strength; Microscopy, Electron.

Introduction

As a major constituent of plant cell walls, cellulose is responsible for the mechanical integrity and supporting structures of plants, and is widely exploited in industry.[1] At present, wood fibers are extensively researched for end-use applications such as composite reinforcements, and as raw materials for bioenergy and biochemical production.[2,3,4] Cellulosic fibers have been shown to increase the mechanical strength and elastic modulus of cement matrices.[5,6]

Conventional glass ionomer cement (GIC), a restorative material widely used in dental clinics, presents innumerable advantages. On account of its anti-cariogenic nature, GIC helps to remineralize the affected dentin remnant and to control caries recurrence. Moreover, unlike light activation, it is chemically activated and requires no special appliances. GIC is also biocompatible with tooth tissue; in particular, the ionomer cement bond minimizes microleakage at the tooth/restoration interface,

preventing new lesions in the treated tooth in the absence of protective materials (unless the cavity is very deep).[7] On the downside, GIC is susceptible to dehydration and abrasion, and exhibits friability, reduced translucence, and technique sensitivity.[7,8]

Cellulosic fibers were introduced to GIC by Silva *et al*.,[9] who aimed to improve the mechanical strength of this promising restorative. In suitable proportions, cellulose fibers reinforced the composite without altering the working time and final setting time of the material. The cellulosic fiber-modified GIC presented syneresis and imbibition properties, solubility and disintegration in water, and diametral tensile strength similar to conventional cement. However, the cellulose fibers increased the compressive strength and abrasion resistance of the composite, and increased the strength of bonding to dental structures. Formation of the new composite was confirmed by scanning electron microscopy.

The resistance of ionomer cements continues to be improved, and materials of various compositions have been introduced to the dental market.[10,11,12] Cellulosic fibers meet this need because they possess desirable intrinsic characteristics, such as low cost and density, specific resistance and high elastic modulus, and resistance to compression (or flattening); they are also rigid, non-abrasive, and non-toxic; are easily modified by chemical agents; and are entirely renewable, being the most abundant organic compound on the planet.[2,5,13,14]

Considering the positive properties of cellulosic fibers and their potential to improve the mechanical properties of materials used in dentistry, here, we incorporate mechanically processed cellulose fibers into conventional restorative glass ionomer cement (GIC). We evaluate the parameters of the modified GIC, namely, the compressive strength, elastic modulus, and diametral tensile strength and stiffness, and characterize the materials by scanning electron microscopy and energy dispersive X-ray spectroscopy.

Methodology

Composite Development

The cellulose fibers were obtained from eucalyptus wood and individualized in sodium hydroxide and sodium sulfide (Kraft pulping process), as described in Ferreira *et al*.[15] Next, they were bleached in a three-stage sequential process (OD(PO)) of delignification with oxygen (O), delignification with chlorine dioxide (D), and alkaline extraction with pressurized hydrogen peroxide (PO). As desired the final lightening of the fibers was approximately 80% ISO.[16] The material was stored in plastic wrapping at 6°C to prevent fungal proliferation.

To obtain the fibers, 200 ml of distilled water was added to 2.5 g of cellulosic fibers, and placed in a mixer (Ultra-turrax T 25, IKA-WERKE, Staufen, Switzerland), for 3 h at 9,500 rpm. The mixture was then oven-dried at 37°C (±1°C). The resulting sheet was cut into small pieces and maintained at 6°C until required.

Different quantities of fibers were weighed and imbibed in the GIC liquid for later agglutination with the GIC powder during manipulation, following the manufacturer's recommendations. Three experimental groups were obtained: Group 1 (G1-GIC), control; Group 2 (G2-GICMF1; GIC modified with 3.62 wt% of fibers); and Group 3 (G3-GICMF2; GIC modified with 7.24 wt% of fibers).

Evaluation of Compressive and Diametral Tensile Strength

Test specimens (ts) (n = 20) of each experimental group were prepared in a Teflon matrix of diameter 4 mm and length 8 mm. In G1, the cement was inserted into the matrix under pressure, using a specific syringe (Centrix, DFL Ind., São Paulo, Brazil) to minimize bubble formation in the body of the cement. In Groups G2 and G3, the cement was placed inside the matrix with an insertion spatula and compacted with an amalgam condenser. Once the matrix was completely filled, a polyester strip was pressed onto the cement surface to ensure adequate flow and a smooth material surface. The ts of all groups were stored for 24 h in distilled water at 37°C (±1°C) and examined in a universal test machine EZ Test (Shimadzu, Kyoto, Japan) connected to a compatible microcomputer, which was installed with operation control software.

For the compressive strength tests, the ts (n = 10) were positioned with their long axis in the vertical direction and subjected to a load cell of 200 kgf at a speed of 1 mm/min. For the diametral tensile strength test, the ts (n = 10) were positioned with their long axis in the horizontal direction and subjected to the same compressive load at 0.5 mm/min. In this test, the load was applied vertically

along the side portion of the cylindrical specimen; therefore, the tensile stress was perpendicular to the vertical plane. The compressive and diametral tensile strengths were computed by the following formulas:[17,18]

$$\textit{Compressive strength} = 4F / \pi d2$$
$$\textit{Diametrical traction tension} = 2F / \pi dl$$

where F is the fracture load, and d and / are the diameter and the length of the ts, respectively.

During the compressive strength test, the elastic modulus of the ts was computed as follows:[18]

$$\sigma/\varepsilon = (P/A) / (\Delta l/l_o)$$

where is the applied stress, is the longitudinal elastic strain of the specimen, P is the load, and A is the transverse area of the Δl and l_o are the length increase of the ts under the applied stress and the original length, respectively.

The stiffness (ε_y) was computed from the genuine elastic modulus[19] measured in the diametral tensile strength test:

$$E = 8W / \pi R (3\varepsilon_y + 3\varepsilon_x)$$

where E is the elastic modulus, and R and W are the radius and the load per unit length of the sample, respectively. ε_y and $3\varepsilon_x$ are the diameter deformations in the length and transverse directions, respectively, during the test (where the length direction is the direction of compression).

Statistical Analysis

The results of normality (Shapiro-Wilk) and homogeneity of variance (Levene) tests were submitted to analysis of variance (*ANOVA*) and Tukey *post-hoc* tests. All analyses were conducted at the $p < 0.05$ significance level.

Scanning electron microscopy and energy dispersive X-ray spectroscopy

The fibers were immersed in distilled water for 30 min under light agitation and dehydrated in increasing concentrations (50, 70, 95, and 100%) of acetone solution. The identified fibers were dried at 37°C for 12 h.

After mechanical testing, the dehydrated fiber samples and statistically significant composite samples of each group were covered with gold-palladium using a sputter coater (SC 7620, Emitech, United Kingdom). The samples were analyzed by scanning electron microscopy (SEM) (CS-3500, Shimadzu, Kyoto, Japan) and energy dispersive X-ray spectroscopy (EDS), (CS3200, Oxford, England), using 10 and 15 kV electron beams, respectively.

Results

In the compressive and diametral tensile strength tests, G1 was statistically different from G2 and G3. More specifically, the Tukey *post-hoc* test showed statistically different compression strengths between G1 and G2 ($p = 0.001$) and G1 and G3 ($p < 0.001$), and statistically different diametral tensile strengths between G1 and G2 ($p < 0.001$) and G1 and G3 ($p < 0.001$).

The ANOVA revealed statistically significant differences in the elastic moduli and stiffness among the groups. Moreover, according to the Tukey *post-hoc* test, the elastic modulus in the compressive strength test significantly differed between G2 and G1 ($p = 0.035$), and G2 and G3 ($p = 0.013$) (Table 1), while the stiffness in the diametral tensile strength test significantly differed between G1 and G2 ($p = 0.003$) (Table 2).

Table 1. Mean and standard deviation values of the compressive strength and elastic modulus, and their statistical significances.

Composite	Group	Compressive strength (MPa)			Elastic modulus (GPa)		
		Mean (DP)	*p**	*post-hoc***	Mean (DP)	*p**	*post-hoc***
GIC	G1	23.66 (8.48)		A	1.00 (1.53)		A
GICMF1	G2	40.91 (10.05)	< 0.001	B	0.78 (1.64)	0.009	B
GICMF2	G3	47.17 (8.98)		B	1.05 (2.32)		A

*ANOVA test ($p < 0.05$).
**Tukey test. Different letters (within post-hoc column) indicate significantly different results ($p < 0.05$).

Table 2. Mean and standard deviation values of the diametral tensile strength and stiffness, and their statistical significances.

Composite	Group	Diametral tensile strength (MPa)			Stiffness (Units)		
		Mean (DP)	*p**	*post-hoc***	Mean (DP)	*p**	*post-hoc***
GIC	G1	22.37 (6.04)		A	722.03 (284.11)		A
GICMF1	G2	45.55 (4.90)	< 0.001	B	281.70 (250.44)	0.005	B
GICMF2	G3	49.56 (5.03)		B	519.88 (281.51)		AB

*ANOVA test ($p < 0.05$).
**Tukey test. Different letters (in post-hoc column) indicate significantly different results ($p < 0.05$).

SEM micrographs of the cellulose fibers reveal an agglomerated aspect of elongated fibers with thin extremities (Figure 1A). Mechanical processing disrupted the well-defined cylindrical shape of these fibers, leading to intact and open fibers. Striae remained along the fiber surfaces, giving them a rough aspect (Figures 1B and 1C). The fracture areas of the representative G3 specimen present a random distribution of cellulosic fibers throughout the gelatinous matrix, in addition to load particles (Figure 1D).

The EDS spectrum of cellulose fibers presents high-intensity carbon and oxygen peaks, which are attributed to the chemical chain structure of cellulose (Figure 2A). In the EDS spectrum of the fracture area of G3, these peaks correspond to the cellulose fibers and the GIC matrix. Additional high-intensity peaks of calcium (Ca), fluorine (F), aluminum (Al), and silicon (Si) and the low-intensity barium (Ba) peak are attributed to the elemental constituents of calcium fluor-aluminum-silicate (SiO_2–Al_2O_3–CaF_2–Na_3AlF_6–$AlPO_4$) of the GIC load particles (Figure 2B).

Discussion

Glass ionomer cements are attractive materials for clinical dental use because they bond well to humid tooth structures and metals, release fluoride (an anti-cariogenic agent), are non-toxic and biocompatible, and are thermally compatible with tooth enamel due to their low heat expansion coefficients. However, because of their low mechanical strengths, conventional formulations are unsuitable for use in sites of concentrated high stress, such as posterior teeth (Classes I and II).[20]

By imbibing the cellulose fibers in the GIC liquid before agglutinating them with the powder, the fibers were successfully incorporated into the composite. Interaction between the cellulose and the restorative cement components was rendered possible by the intrinsic polarity of cellulose, which is hydrophilic in nature.[5,6]

Studies have demonstrated that cellulosic fibers increase the mechanical strength of composite materials.[6,21] In the present study, the cellulosic fibers modified the physical structure of the GICMF1 and GICMF2 composites, increasing their compressive strength. The highest improvement was observed in GICMF2. When analyzing the results, the final strength of the material was found to largely depend on the concentration of fibers in the composite. GICMF1, with lower fiber concentration, was more structurally fragile than GICMF2. A small proportion of the fibers cannot form a reinforcing network and therefore, cannot absorb the imposed rupture stresses.

Contrary to Silva *et al.*,[9] who reported no difference between ionomer cements modified by macro cellulose fibers and conventional GIC, the diametral tensile strengths of the new composites investigated in the present study were almost double those of their unmodified counterparts. We attribute this difference to the mechanical processing of the fibers in our study. The relationship between the high strength and concentrated fibers in GICMF2 is directly attributable to structural modification by the mechanical process. Glass ionomer cements are friable, which limits their utility as a restorative material in permanent teeth.[7] To reduce its friability (and increase its compressive strength), glass ionomer cement must

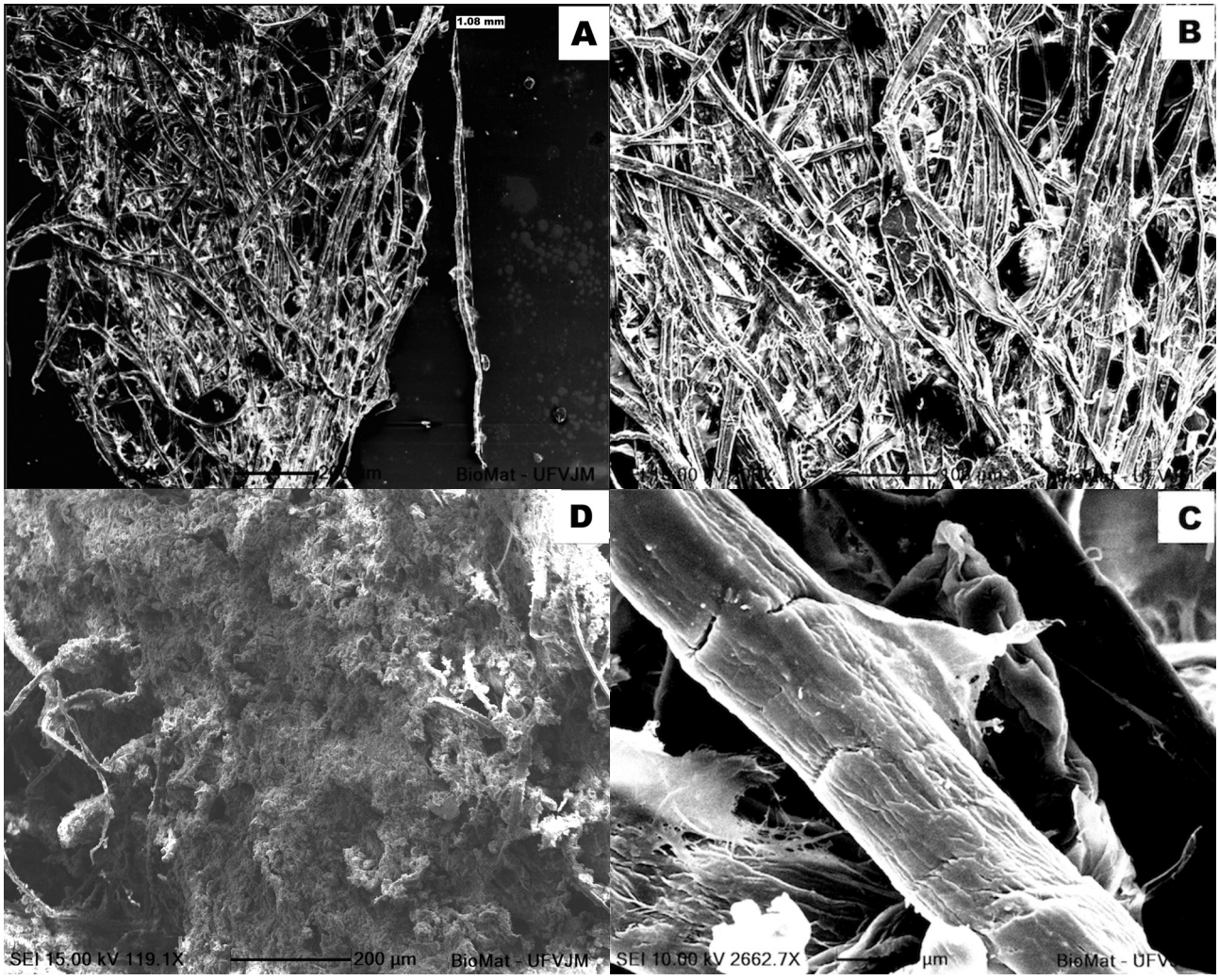

Figure 1. SEM images of the surface morphology of eucalyptus cellulose fibers after physical processing, magnified (A) ×20, (B) ×200, and (C) >×2,500; and (D) fracture area of the GICMF2 composite (×100); 10 and 15 kV; BioMat/UFVJM.

be supplemented with cellulosic fibers of the ideal size and concentration.[9] In addition, the cement must be sufficiently viscous to facilitate manipulation while preserving the capacity for wetting the dental structure, which is crucial for effective bonding.[7]

SEM is ideal for imaging and analyzing material surfaces, since it reveals features such as fracture areas,[22,23,24] whereas EDS identifies the elemental compositions of materials, particles, and contaminants on these surfaces.[22] According to the SEM/EDS characterization, the fibers were intermingled in the cement matrices of the modified composites, particularly in GICMF2, and no contaminants were observed in the EDS spectra. The species in composite microstructures have very different characteristics and can be elucidated only by multiple complementary techniques.[22,23,24] Therefore, the cements modified by cellulose fibers should also be characterized by techniques such as Fourier transformed infrared spectroscopy, which would identify the likely molecular interactions between the fibers and the ionomeric matrix and load particles.

The average length of the fibers individualized during the production process was 1.07 mm. Following the mechanical processing, some fibers were shrunk and others had only opened, maintaining their original

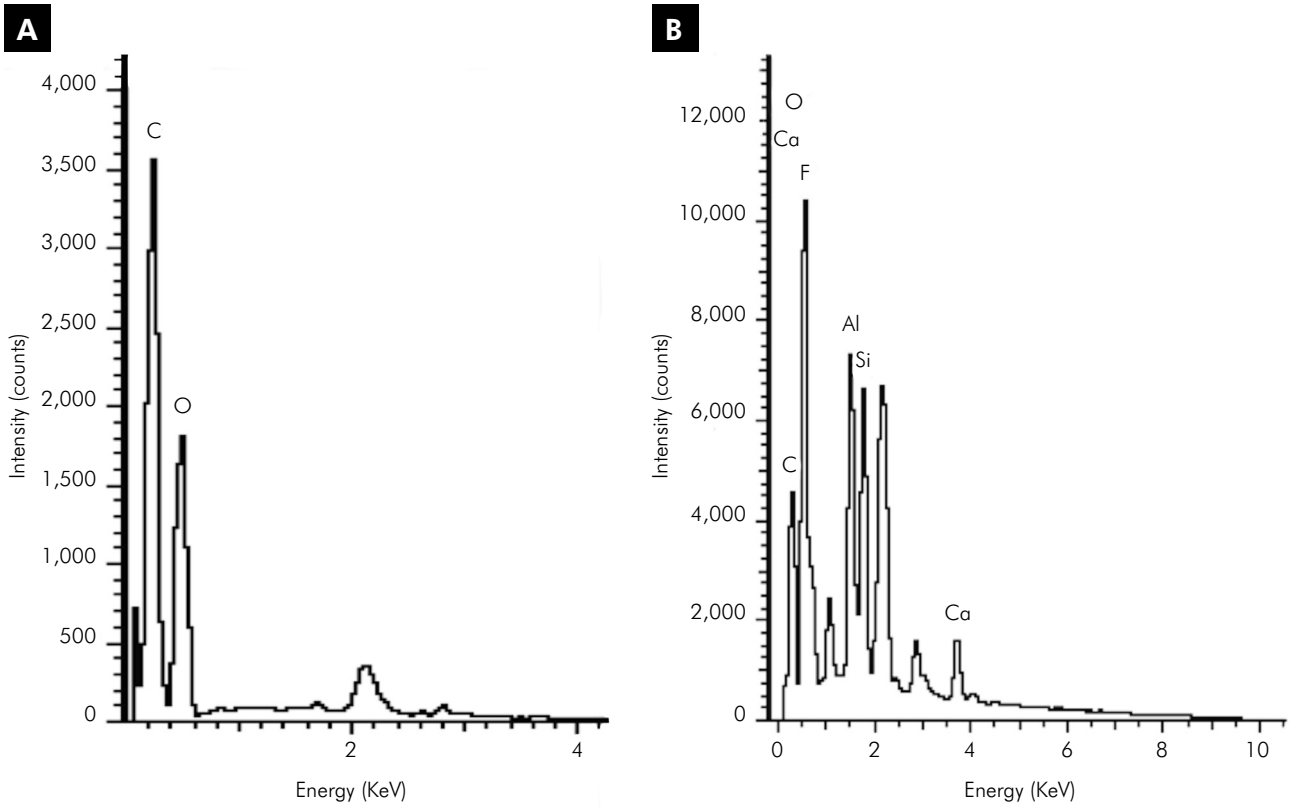

Figure 2. (A) EDS spectra of cellulose fibers (×2,500) and (B) fracture area of GICMF2 composite (×100); 10 and 15 kV; BioMat/UFVJM.

features. According to some reports, composites reinforced with unidirectional long fibers show higher tensile strength than composites reinforced with randomly arranged fibers, when tested in the longitudinal direction of the reinforcement.[25] The mechanical characteristics of fiber-reinforced composites depend not only on the material properties and fiber orientation, but also on the intensity with which an applied force is transmitted to the fibers through the matrix. In turn, the extent of this load transmittance depends on the magnitude of the interfacial bond between the fiber and matrix phases. Discontinuous or randomly organized fibers enhance the stress propagation because they increase the surface area in contact with the matrix.[26]

In this study, the cellulosic fibers were randomly oriented throughout the cement mass. Randomization is achieved by controlling the length of the cellulose fibers and properly mixing the liquid, fibers, and powder when manipulating the GIC. Decreasing the fiber size ensured a more homogeneous but still random distribution in the GIC matrix. The increased surface area of the fibers in contact with the matrix should increase the tensile strength and elastic modulus, thereby reducing the friability, of the GIC.

The elastic modulus quantifies the response of a material to an external compressive or tensile stress. In diametral tensile strength tests, the elastic modulus of enamel is approximately thrice that of dentin (82.7 GPa versus 18.6 GPa).[27] The modulus of glass ionomer cements (~11 GPa)[28] is considered to be close to that of dentin. In our study, we calculated only the ratio between the load and the transverse area, and the diameter variation in the compression direction (*i.e.*, the stiffness), during the diametral tensile strength test.[19] The diameter deformation in the transverse direction was not determined. Fiber addition significantly reduced the stiffness of the composite GICMF1 with respect to conventional GIC ($p < 0.001$), probably because of the size and random orientation of the fibers distributed at a relatively low concentration throughout the GIC matrix.

Although the stiffness of GICMF2 was also reduced, the reduction was not significant. The larger quantity of cellulosic fibers added to the GIC ensured load transfer to the fibers, diminishing the friability of GICMF2.[4]

Some of the investigations of this study might improve the quality of dental materials, particularly that of the ionomer cement. Since GICMF1 and GICMF2 demonstrated higher compressive and diametral tensile strengths than the control group, we infer that the final properties of the glass ionomer cement strongly depend on the fiber structure. Further studies will increasingly improve the mechanical strength of these promising restorative materials. By incorporating cellulose microfibers and nanofibers into ionomer cement, we hope to develop a material suitable for dental clinical use.

Conclusion

The mechanical strength of GIC was increased by adding physically processed cellulosic fibers.

The high proportion of fibers in GICMF2 was responsible for the high compressive and diametral tensile strength of this material. GICMF2 also exhibited acceptable elastic modulus and stiffness in the compressive and diametral tensile strength tests, respectively.

Morphological and elemental chemical analyses of the GICMF2 surface revealed that fibers were intermingled in the cement matrix of the composite and that no contaminants had entered the precursor materials.

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