# Reinforcement of Glass Ionomer Cement: Incorporating with Silk Fiber

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## ABSTRACT

The aim of this study was to synthesize glass ionomer-silk fiber composite and examining the effect of adding natural degummed silk fiber on the mechanical properties of glass ionomer cement (GIC). For this purpose, natural degummed silk fibers with 1 mm length and 13-16 µm diameter were added to the ceramic component of a commercial glass ionomer cement in 1, 3, and 5 wt. %. Compressive strength (CS), three-point flexural strength (FS) and diametral tensile strength (DTS) of the prepared glass ionomer-silk fiber were measured. Analysis of variance (ANOVA) was used to compare the obtained results. Moreover, SEM technique was used for the investigation of the surface morphology of the as-prepared composite and the fractured area. The results showed that the highest compressive strength, flexural strength and diametral tensile strength were obtained using 3, 3, and 5 wt. % of silk fiber, respectively. However, at 3 wt. % of silk fiber, all three measures of strength exhibited a significant increase compared to the commercial GIC. Therefore, it can be suggested that the addition of 3 wt. % silk fiber to the ceramic component of GIC is desired for dental restorations and orthopedic implant applications, where the maximum strength in all three modes of loading would be beneficial.

## 1. Introduction

Glass ionomer cements (GICs) have recently attracted increasing interest in clinical dentistry due to their excellent properties such as biocompatibility, low cytotoxicity, ability of the material for regeneration of hard tissues, low coefficient of thermal expansion, good adhesion to moist tooth structure and anticariogenic properties because of the fluoride ion release. Regarding their unique properties, GICs have many applications in dentistry as definitive restorative materials, luting cements, filling materials and fissure sealants. In spite of these desirable properties, poor mechanical strengths of the existing conventional formulations limit their high-stress applications such as class I and II restoration [1-5]. There have been many attempts to improve the mechanical properties of glass ionomer cements, including reinforcement with metal powders [6], modification with resin [7], incorporation with SiC whiskers/ short fibers [8, 9], HA and fluoroapatite nanobioceramics [10], forsterite nanoparticles [3], etc.

In recent years, several attempts have been made to incorporate fibers as agents into the composition of these materials to reinforce their physical structure for obtaining better mechanical strength and an increase in elasticity modulus. Hammouda [11] investigated the strengthening effect of glass fibers with 1 mm length and 10 µm thickness in combination with

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conventional glass ionomer restorative material. Silva et al. [12] added cellulose fibers to the GIC cement compounds and showed that the modified GIC samples had higher compressive strength, more resistance to abrasion, and higher bond strength compared to the GIC without fibers.

Silk fibers are naturally produced by various insects. Silk fibers from silkworm [Bombyx mori (B. mori)] cocoons are well-known for their magnificent mechanical properties utilized for textile production and have been successfully applied as suture materials for centuries. Due to their remarkable strength, excellent biocompatibility, and low immunogenity, silks have been employed in designing biomaterials for medical applications [13, 14].

Numerous studies regarding the addition of silk fibers to composites have shown superior strength [15-18]. The aim of the present work was to synthesize glass ionomer–silk fiber composites with different weight percentages of natural silk fiber and to assess the mechanical properties of the as-prepared samples.

## 2. Materials and methods

### 2.1. Degummed silk fiber preparation

Degummed silk fiber with 13-16 µm thickness was prepared as reported by Mobini et al. [15]. In brief, the fibroin was isolated from silkworm cocoons. Afterwards, three cocoons were boiled for 1 h in 750 mL of 0.02 M sodium carbonate solution, washed entirely with deionized water, and dried overnight. The dried degummed fibers were utilized as chopped fibers with 1 mm length. Scanning electron microscopy (SEM, Philips XL30) was used to characterize the silk fiber surface and to determine the fiber diameter.

### 2.2. Glass ionomer–silk fiber composite

Glass ionomer–silk fiber composite was prepared by adding the silk fiber with a thickness of about 13-16 µm and 1 mm length. Firstly, the silk fibers were added to the ceramic component of the commercial GIC (Fuji II, GC International, Tokyo, Japan) in 0, 1, 3, and 5 wt. %, prior to mixing with the cement liquid (polyacrylic acid). Mixing of the modified powder and polyacrylic acid was performed using a plastic spatula in accordance with the manufacturer instructions. The powder to liquid ratio was set at 2.7:1. After that, the specimens were inserted into an aluminum mold, and finally removed from the mold after 1 h.

### 2.2.1. Measurements of mechanical properties

Mechanical tests were performed on a screw-driven testing machine (Hounsfield, Model H25KS, England) with a cross-head speed of 0.5 mm/min.

Cylindrical specimens with 4±0.1 mm diameter and 6±0.1 mm height were prepared according to ISO 9917-1 standard, and their compressive strength (CS) was calculated by the following equation:

$$CS=4P/\pi d^2 \qquad (1)$$

Where P is the load at fracture (N) and d is the diameter of the cylindrical specimen (mm). In addition, diametral tensile strength (DTS) of the specimens (9±0.1 mm diameter and 4.5±0.1mm height, prepared according to ANSI/ADA 66 standard) was calculated using Eq. (2):

$$DTS=2P/\pi dt \qquad (2)$$

where P is the load at fracture (N), and d (mm) and t (mm) are the diameter and thickness of the cylindrical specimen, respectively. In order to determinate the flexural strength (FS), the specimens were prepared with dimensions of (2±0.1) × (2±0.1) × (25±2) mm3 according to ISO 4049 standard. The flexural strength in three-point bending was obtained using Eq. (3):

$$FS=3Pl/2bh^2 \qquad (3)$$

where P is the load-to-failure (N), l is the distance between the two supports (mm), and b (mm) and h (mm) are the width and depth of the specimen, respectively.

### 2.2.2. Scanning electron microscopy

The SEM technique was used to investigate the morphology of the as-prepared and fractured specimens. The specimens were sputtered with a thin gold layer.

### 2.2.3. Statistical analysis

Statistical analysis was carried out by using one-way analysis of variance (ANOVA) test with the post hoc Tukey–Kramer HSD multiple range test in order to determine the level of significance ($p < 0.05$) (SPSS v. 20 program). All values are presented as the mean ± standard deviation.

## 3. Results and Discussion

Conventional glass-ionomer cements have low mechanical properties in comparison with other restorative materials like composite resin or dental amalgam. In order to improve the strength of these materials, a dispersing agent such as different powders and fibrous reinforcements was added to the cement mixture [3, 6-12].

In this research, the effects of silk fiber as the reinforcement agent on the mechanical properties of glass ionomer cement were investigated. The mean value (standard deviation) of the measured compressive strength (CS), three-point flexural strength (FS), and diametral tensile strength (DTS) of at least 3 samples are presented in Table 1 and graphically in Fig. 1. The Two- way ANOVA tests showed a significant difference in the compressive revealed that improvement in compressive strength of the GIC was significant at 3 and 5 wt. % of the silk fibers. Furthermore, the mechanical results indicated that the compressive strength increased by 44% with increasing the concentration of silk fiber up to 3 wt. %.

Statistical analysis showed a significant difference in the flexural strength among the tested groups ($p < 0.0001$) and indicated that the increase of the flexural strength of GIC was significant at 1, 3, and 5 wt. % of silk fibers. The maximum flexural strength was obtained at 3 wt. % of the silk fiber, and enhanced about 157% as compared to the conventional GIC. Prosser et al. [19] explained that the most appropriate measure of the GIC strength is obtained with a flexural test.

**Table 1.** Means (MPa) and standard deviations of the mechanical properties of GIC containing different amounts of the silk fiber

| Silk fibers (wt. %) | Compressive strength (standard deviation) | Flexural strength (standard deviation) | Diametral tensile strength (standard deviation) |
|---|---|---|---|
| 0 | 65.28 (3.82) | 16.09 (3.36) | 7.21 (0.91) |
| 1 | 74.22 (3.19) | 39.62 (3.06) | 9.86 (0.69) |
| 3 | 94.40 (3.07) | 41.36 (2.04) | 11.62 (1.38) |
| 5 | 80.82 (2.43) | 30.33 (1.43) | 15.33 (1.28) |

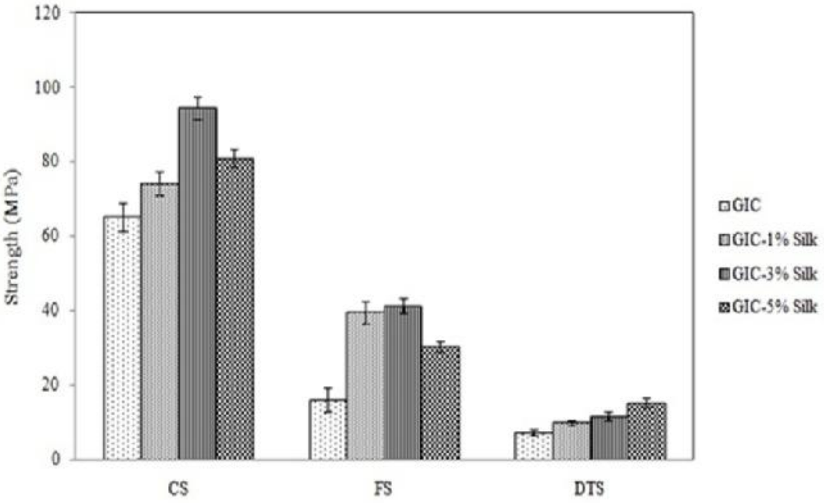

**Fig. 1.** Mechanical properties of GIC containing different contents of silk fiber. All values are presented as the mean ± standard deviation. The significance level was set at 0.05.

The strength reduction of the composites containing silk fibers more than 3 wt. % for CS and FS is caused by the reduction of the bond forces between ceramic and polymeric components of the GIC. On the other hand, reduction in the strength of the cement caused by the addition of extra silk fiber might indicate unsuitable wettability at the interface of the matrix and the filler. In this case, cracks are formed around the silk fiber, where the number of cracks is directly correlated to the silk fiber content. These cracks act as stress concentration centers and decrease the mechanical strength [3, 10, 20].

The statistical analysis of diametral tensile strength results showed that there are significant differences between DTS measurements ($p < 0.0001$) and demonstrated that betterment in diametral tensile strength of the GIC was significant at concentrations of 1 and 3 wt. % of the silk fibers. It was also found from the DTS results that the tested materials presented an increase in diametral tensile strength at around 112 % as a result of 5 % fiber loading, which is the greatest tensile strength as compared to the control sample and other composite containing 1 and 3 wt. % of the silk fibers.

Glass ionomer is one of the brittle materials with a tensile strength that is noticeably lower than the compressive strength. Such materials fail by the duplication of crack that is favored by tensile rather than compressive loading. Thus, there is a need for adding an optimal concentration of fibers to the glass ionomer cement in order to increase the tensile strength and decrease friability [11, 12]. The fibers added in this study act as crack bridging to strengthen the brittle glass ionomer restorative material.

Many studies suggested that the mechanical properties are affected by the porosity of the cement, the bonding between dispersing agents and the cement matrix, and the properties of particles dispersed through the matrix phase [21-24]. In this regard, Kobayashi et al. [8] illustrated that the length and concentration of the fibers could affect the GIC strength. The larger the aspect ratio, the better the reinforcing and crack arresting.

In general, the mechanical properties of GIC samples were significantly increased by adding silk fibers in the mixture compared to the control ones due to the significant mechanical properties and high aspect ratio of silk fibers [8, 13, 15, 25, 26]. These results suggested that the dispersed short fibers acted as a reinforcing agent for strengthening the glass-ionomer cement.

Lohbauer et al. [27] studied the ability to reinforce glass ionomer cement by short reactive glass fibers prepared from a glass frit of the system $SiO_2$– $Al_2O_3$–$CaF_2$–$Na_3AlF_6$. They concluded that using glass fibers in the GIC matrix can enhance the compression strength from 64 to 170 MPa and the flexural strength from 8.9 MPa to 15.6 MPa.

Garoushi et al. [28] experiments demonstrated that the addition of short fibers (3 mm in length) to experimental composite showed a significantly higher mechanical performance of flexural strength and compressive load- bearing capacity than the control one.

Hammouda [11] incorporated 3 wt. % and 5 wt. % of glass fibers (1 mm length and 10 μm thickness) into the glass- ionomer powder. The results indicated that fiber reinforcement increased the diametral tensile strength, hardness, flexural strength, flexural modulus, and fracture toughness of the conventional glass- ionomer restorative material.

The effect of different contents of silk fiber on mechanical properties of the conventional glass ionomer can also be related to the aforementioned fact. Accordingly, the mechanism of bonding and debonding between composite components varies and the maximum effect of silk fiber on CS, FS, and DTS occurs at different silk fiber concentrations [3]. Yli- Urpo et al. [29] examined the addition of bioactive glass (BAG) materials by 10 or 30 wt. % to the conventional cure and resin- modified GIC powders. They concluded that the compressive strength of the composites decreased with increasing the amount of BAG.

Due to the fact that fiber concentration in the composite is a critical point in the final strength of the materials, high concentration of the fibers facilitated agglutination in these cement matrices, so the matrix viscosity increased. However, increased viscosity may negatively interfere with the final properties, and hinder the handling of cement, in addition to affecting its bond to the tooth structure [12].

According to the mechanical properties measured in this paper (Table 1), the optimum amount of the silk fiber for simultaneous enhancement of CS, FS and DTS is 3 wt. %. By addition of 3 wt. % of the silk fibers to the ceramic component of GIC, mechanical properties including CS, FS and DTS increase up to 44 %, 157 % and 61 %, respectively.

Comparing the results of the previous studies [3, 8, 11, 12, 27] and the present study shows that the addition of silk fiber to the ceramic component of GIC simultaneously increases the CS, FS and DTS to the acceptable values for dentistry and orthopedic applications.

The SEM micrograph (Fig. 2) shows continuous degummed silk fibers with the average diameters of about 13-16 µm which are used as the reinforcement agents in glass ionomer cement.

Moreover, the rather homogeneous and flat surface of glass ionomer (mixture of glass ionomer powder and polymer liquid) containing 3 wt. % silk fibers dispersed randomly throughout the cementitious matrix is shown in Figs. 3a and b.

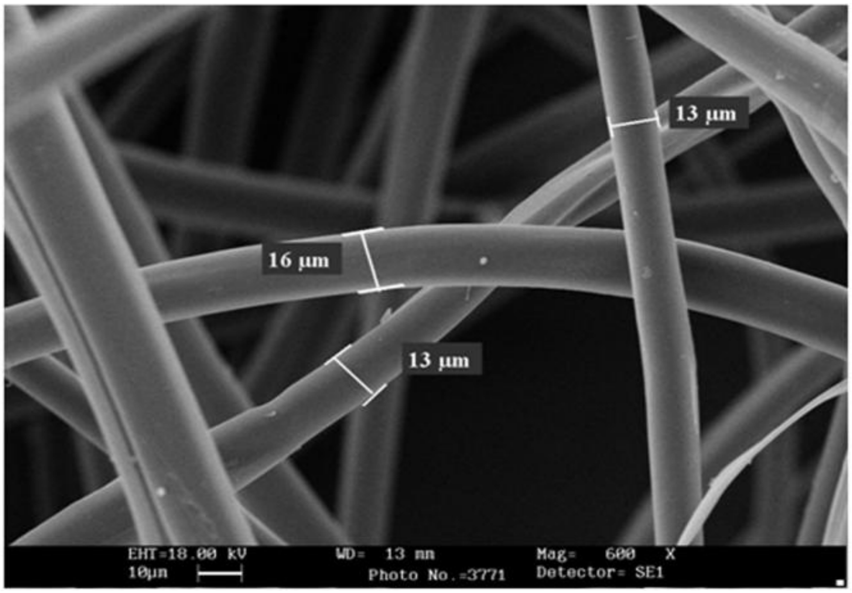

**Fig. 2.** SEM micrograph of the degummed silk fibers.

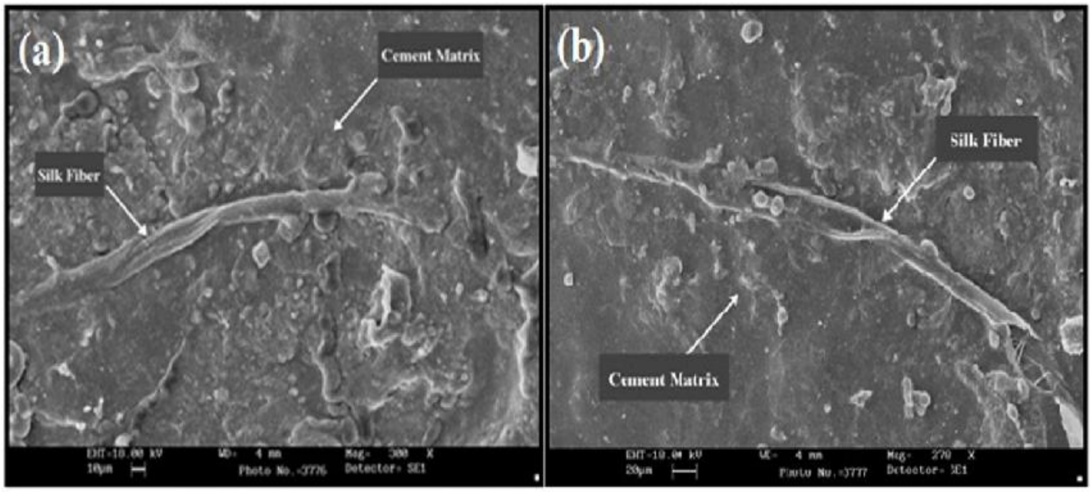

**Fig. 3.** (a) and (b) SEM micrographs of the surface morphology of reinforced glass-ionomer cement.

SEM- investigation of the fracture surface of a representative GIC specimen as the control sample showed the presence of many voids and cracks (Fig. 4a). In the fracture area of the GIC-silk fiber composite after CS measurement, in addition to the GIC particles, the fibers were clearly observed in the cementitious matrix (Fig. 4b). As can be seen, there are more cracks and voids in the fractured surface of the control sample compared to the composite one (Figs. 4a and b).

These voids are formed following the release of the glass particles from the GIC fractured surface. As a matter of fact, there is no strong bond between the glass particles and the polymeric matrix.

Xie et al. [30] deduced that a less dense surface, or rather larger amounts of voids would result in worse mechanical properties.

The silk fibers fill in the spaces between glass ionomer particles; thus, the fracture surface of the GIC sample containing silk fibers looks smoother than the control one and has less voids due to the decrease of the glass particles and debonded sites in the glass–matrix interface [31]. It has been shown that brittleness of dental materials such as cements, which failed by crack propagation, can be prevented or controlled if there are fewer voids in the structure [32].

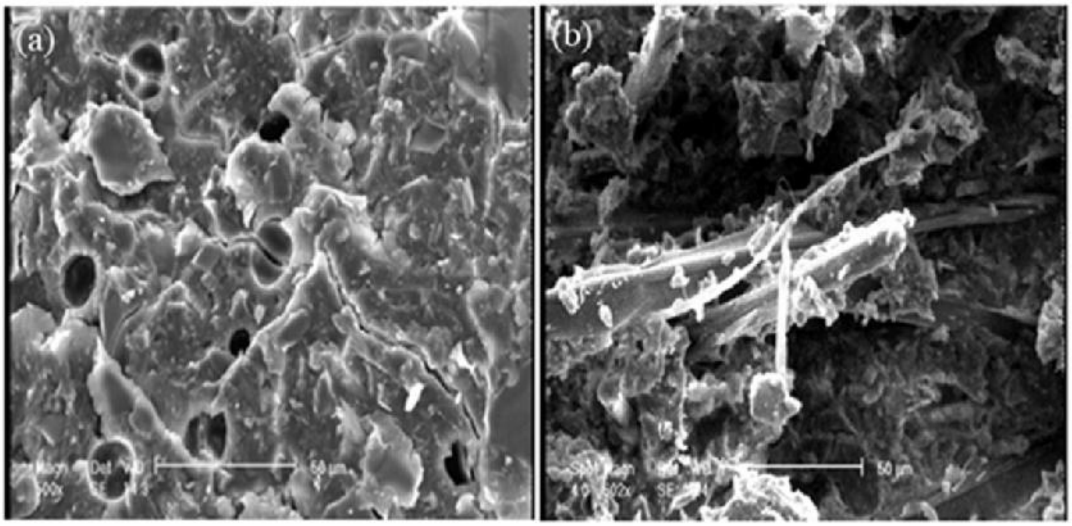

**Fig. 4.** SEM micrographs of the fractured surface of (a) the unreinforced GIC and (b) GIC-3wt. % silk fiber composite.

As can be seen from the fracture surface of 3 wt. % silk fiber-GIC composite (Fig 4. b), there is a good interfacial bond between the modified fibers and the matrix in a silk fiber-reinforced GIC composite, which may contribute to physically forming an interfacial bond between the fiber and the matrix. Lee et al. [18] examined the effect of silk fiber content on the mechanical and thermal properties of silk/poly (butylenes succinate) (PBS) bio-composites. In their study, a good adhesion between the silk fiber (with unmodified surface) and PBS matrix was found. They also suggested that desericination and/or a certain type of surface modification to enhance the fibre–matrix adhesion prior to composite processing may be necessary for further improvement of the composite properties and performances.

## 4. Conclusion

Glass ionomer– silk fiber composites were successfully synthesized with different fiber concentrations. The investigation of the mechanical properties and fractured surface illustrated that:

1- Silk fiber reinforcement significantly increased the compressive strength, flexural strength, and diametral tensile strength of the conventional glass- ionomer restorative material.

2- The GIC sample containing silk fiber shows a smoother surface and less voids than the control one.

We suggest that the composite containing 3 wt. % silk fiber is a good candidate for high stress dental and orthopedic application due to its proper mechanical properties, including the increase of CS up to around 44%, FS up to 157%, and DTS up to 61% as compared to the commercial product.

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