

Effect of plate-like glass fillers on the mechanical properties of dental nanocomposites

Mojdeh Mohseni¹ · Mohammad Atai² · Alireza Sabet² · Saeed Beigi²

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Abstract In this study, glass flakes were incorporated into the spherical nanosilica component of the dental composites and its effect on the mechanical properties of these composites was investigated. To achieve a good interfacial adhesion between matrix resin and fillers, the particles were surface treated with a silane coupling agent (γ -MPS). Composites with different plate-like and spherical nanoparticle contents were prepared and their mechanical properties, including flexural strength, flexural modulus and fracture toughness were measured. The morphology of the particles and fracture surface of the composites were studied by SEM. The distribution of the flakes in the composite was also monitored using EDXA. Statistical analysis of the data was performed with ANOVA and the Tukey's post hoc test was at a significance level of 0.05. The results showed that the flexural modulus and fracture toughness of specimens were improved with increasing the glass flake content up to 15 vol % which then declined upon further increase due to the stacking of the flakes on each other. A good interfacial adhesion was observed between matrix resin and particles in the SEM micrographs. The results of this study suggest that incorporation of glass flakes into the dental composites containing spherical nanosilica particles may enhance their mechanical properties.

Keywords Dental composites · Mechanical properties · Filler morphology · Glass flake

✉ Mohammad Atai
m.atai@ippi.ac.ir

¹ Department of Biomaterials, Science and Research Branch, Islamic Azad University, Tehran, Iran

² Iran Polymer and Petrochemical Institute (IPPI), P. O. Box 14965/115, Tehran, Iran

Introduction

Resin composites are widely used in dental applications because of their good esthetic characteristics. These materials commonly consisted of 2,2 bis[4-(2-hydroxy-3-methacryloxypropoxy)-phenyl]propane (bis-GMA) and triethyleneglycol dimethacrylate (TEGDMA) as organic phases, inorganic fillers for polymer reinforcement, coupling agent and initiator/co-initiator [1, 2]. Silane coupling agents provide a strong link between matrix and filler, improving the performance of the composites where, the most commonly used silane in dental resin composite is 3-methacryloxypropyltrimethoxysilane (γ -MPS) [3, 4].

Fillers play an important role in the mechanical behavior of dental composites depending on filler content, type, shape, size, and morphology [5]. The failure of dental composites has been attributed to surface and/or bulk cracks, degradation of matrix and fillers, water uptake, and lack of sufficient mechanical properties. In this regard, it is expected to increase the dental materials performance by improvement in fracture toughness, which describes as the ability of materials to resist fracture [6].

A significant correlation between the modulus of elasticity and filler volume fraction (vol %) has been reported [7, 8]. Silica particles are the most commonly used fillers for dental composites [9, 10]. Glass flakes have recently received attention as reinforcing fillers in polymeric matrixes [11, 12]. The incorporation of the glass flakes with appropriate coupling agents have shown to enhance the mechanical properties of glass-flake-reinforced polypropylene [11]. Significant improvement in the hardness and compressive strength has been reported for the glass-flake-reinforced dental composites [12]. It has also been reported that fillers with elongated shape particles have

more resistance against crack growth compared with the ones with round-shape particles [13].

This study, therefore, with the aim of investigating of the effect of plate-like fillers on the properties of dental composites, evaluates the effect of incorporation of the glass flakes on the flexural properties and fracture toughness of an experimental dental composite containing spherical nanosilica as filler.

Experimental

Materials

2,2-Bis-[4-(methacryloxypropoxy)-phenyl]-propane (Bis-GMA), triethyleneglycol dimethacrylate (TEGDMA) as matrix resins, 3-(Trimethoxysilyl)propyl methacrylate (γ -MPS, Dynasylan[®] MEMO), and Aerosil[®] OX50 with a primary particle size of 40 nm and true density of 2.2 g cm⁻³ were obtained from Evonik (Germany). The photoinitiator system, camphorquinone (CQ) and *N*-*N*'-dimethyl aminoethyl methacrylate (DMAEMA) were purchased from Sigma-Aldrich (Germany). Nano glass flakes (GF100 nm) with an average specific surface area of 9.78 m² g⁻¹ (measured using BET method, N₂ adsorption, ChemBET 3000, Quantachrome, USA) and true density of 2.6 g cm⁻³ were obtained from Glassflake Ltd. (UK). All the solvents were of analytical grade and purchased from Merck (Germany).

Silanization of nanoparticles

To enhance interfacial adhesion between resin and inorganic particles, the surface of the filler particles was treated with γ -MPS. First, glass flake powder was washed by HCl solution for 3 h to remove any impurities and then dried. Both nanoparticles, i.e., OX50 and GF were silanized by γ -MPS. In all cases, the amount of silane was kept constant at 5 wt% with respect to the nanoparticles.

- The particles (OX50 and GF, separately), the silane, cyclohexane as solvent and *n*-propylamine as catalyst (2 wt%) were stirred in a rotary evaporator at 60 °C for 2 h. The solvent and volatile by-products were then removed at an elevated temperature using an evaporator [14]. The particles were then washed several times with cyclohexane, to remove unreacted silane, and then were dried. The silanized nanoparticles were identified by FTIR spectroscopy (Equinox 55, Bruker, Germany) using KBr pellet method. Thermogravimetric analysis of the silanized nanoparticles was also performed by TGA thermal analyzer (Mettler TG 50, Switzerland)

from room temperature to 700 °C at a heating rate of 10 °C min⁻¹ under N₂ atmosphere.

Preparation of nanocomposites

The resin matrix consisting of Bis-GMA/TEGDMA mixture (70:30 wt%) was prepared which contained CQ (0.5 wt%) and DMAEMA (0.5 wt%) as photoinitiator system. The silanized nanoparticles with different volume fractions (according to Table 1) were mixed with the resin by hand spatulation. The total volume fraction was considered constant at 33 vol %. The pastes were then inserted into the stainless steel test molds and cured using a light curing unit (Optilux 501, Kerr, USA) at an intensity of ca. 550 mW cm⁻².

Mechanical properties

The mechanical properties of the composites were measured by a universal testing machine (STM-20, Santam, Iran). Having inserted the composite paste into the test molds, the specimens were irradiated on both sides for 40 s using the light curing unit. All specimens were then stored in distilled water at 37 °C for 24 h prior to mechanical testing.

Five rectangular specimens (25 mm × 2 mm × 2 mm) were prepared for three-point bending test according to ISO 4049. The span distance of 20 mm and crosshead speed of 1 mm min⁻¹ were considered. The flexural strength (FS) was calculated using Eq. (1):

$$FS(\text{MPa}) = 3PL/2bh^2 \quad (1)$$

where *P* represents the load in Newtons exerted on the specimen, *L* is the span length in mm, *h* is the height and *b* is the width of the specimen in mm measured before testing.

To determine the fracture toughness, single-edge notch beam (SENB) specimens were prepared according to

Table 1 Volume percentages of GF and OX50 particles in the experimental composites

Specimen code	GF (vol %)*	OX50 (vol %)
5-28	5	28
10-23	10	23
15-18	15	18
20-13	20	13
25-8	25	8

The weight percent of the fillers can also be calculated using the true densities of the GF (2.6 g cm⁻³) and OX50 (2.2 g cm⁻³)

* The total content of the fillers was kept at 33 vol %

ASTM E399-05. The specimens were fabricated in steel molds with dimensions of $5 \times 2 \times 25$ mm with a razor blade providing a 2.5 mm notch in the middle of the specimens. A crosshead speed of 0.1 mm min^{-1} and a load cell of 60 N were considered for the fracture test. The fracture toughness was calculated according to the Eq. (2):

$$K_{IC} = \frac{3PL}{2BW^{3/2}} \left\{ 1.93 \left(\frac{a}{W} \right)^{1/2} - 3.07 \left(\frac{a}{W} \right)^{3/2} + 14.53 \left(\frac{a}{W} \right)^{5/2} - 25.11 \left(\frac{a}{W} \right)^{7/2} + 25.8 \left(\frac{a}{W} \right)^{9/2} \right\} \quad (2)$$

where P is the load at fracture (N), L , W , B , and a are length, width, thickness and notch length (mm), respectively. Span length was 20 mm [15]. The test results are the averages of five repeats.

Scanning electron microscopy

To study the fracture mode and interface between resin and nanoparticles, the fracture surfaces of the specimens were observed by SEM (TESCAN, VEGAII, XMU, Czech Republic). The specimens were gold coated by a sputter coater before the electron microscopy. Energy dispersive X-ray analysis (EDXA) was used to detect the distribution map of the fillers through the composites.

Statistical analysis

The results (five repeats for the mechanical properties) were analyzed and compared using one-way ANOVA and the Tukey's HSD test at a significance level of 0.05.

Results and discussion

Characterization of silanized nanoparticles

To improve the interfacial adhesion between the nanoparticles and resin matrix, coupling agents are usually used. In this study, both nanoparticles were silanized using direct condensation of γ -MPS in the presence of cyclohexane as solvent and n -propylamine as catalyst [14]. The method suggests that silane would chemically bond to nanoparticles via direct condensation of $-\text{CH}_3$ of the silane with the surface hydroxyl groups of the filler to form a covalent band [16].

The silanized nanoparticles were identified by FTIR spectroscopy. Figures 1 and 2 exhibit the FTIR spectra of the silanized and non-silanized OX50 and GF particles. The γ -MPS-grafted nanoparticles showed absorbing bands

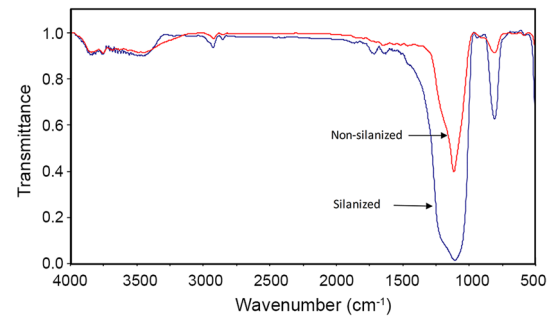


Fig. 1 FTIR of non-silanized and silanized OX50 particles

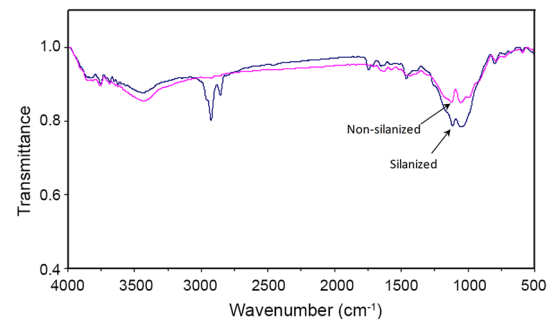


Fig. 2 FTIR of non-silanized and silanized GF particles

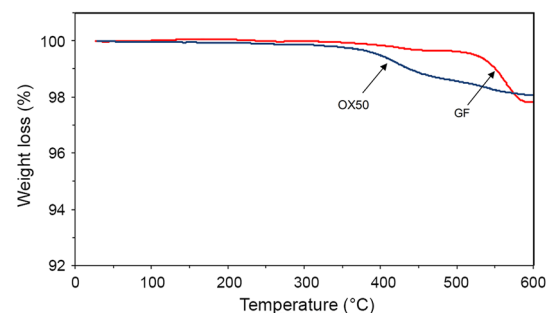


Fig. 3 TGA thermograms of silanized GF and OX50 particles

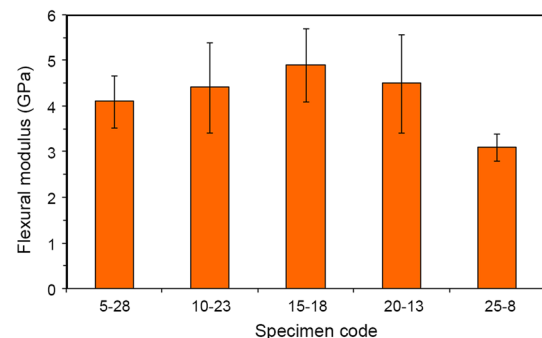


Fig. 4 Flexural modulus of the specimens with different GF contents

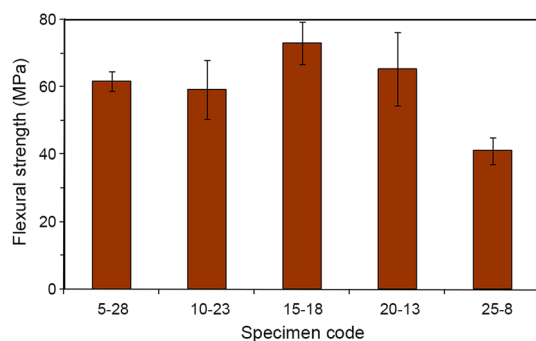


Fig. 5 Flexural strength of the specimens with different GF contents

at $\approx 1720 \text{ cm}^{-1}$ which is attributed to the carbonyl groups of γ -MPS confirming the grafting reaction [3, 17–19]. The TGA curves of the silanized OX50 and GF particles (Fig. 3) reveal the degree of grafting of 2.2 wt% for GF and 2 wt% for OX50, respectively. The weight loss between 200 and 600 °C was due to the decomposition of γ -MPS bound onto the particles, which represents silane grafting degree.

Flexural properties

The flexural modulus and strength are shown in Figs. 4 and 5. An increasing trend in the flexural modulus was observed with increasing filler content, up to 15 vol % GF ($P < 0.05$). The increase was attributed to the appropriate orientation of the flakes between the spherical particles. The properties were declined with further increase in the GF content ($P < 0.05$) due to the stacking of the GF plates on each other providing a weak path for crack growth. As Fig. 5 shows, no significant increase in the flexural strength of the GF containing specimens is observed ($P > 0.05$). Flexural strength is not only dependent on the strength of the composite ingredients, but also is strongly influenced by the quality of filler–matrix interface [20].

Fracture toughness

The ability of materials to resist fracture and crack propagation is defined as fracture toughness. As shown in Fig. 6, the fracture toughness of the specimens was enhanced with increasing the GF content up to 15 vol % ($P < 0.05$). The presence of GF between the spherical silica particles caused deviation of crack direction, which increased the energy required for fracture of the composites [13]. However, with increasing the filler fraction, a decrease in the fracture energy absorption was observed which was attributed to the stacking of the GF plates on each other providing a weak path for the propagating crack. The SEM micrographs (Fig. 7) of specimen containing 25 vol % GF shows the stacking of the GF plates.

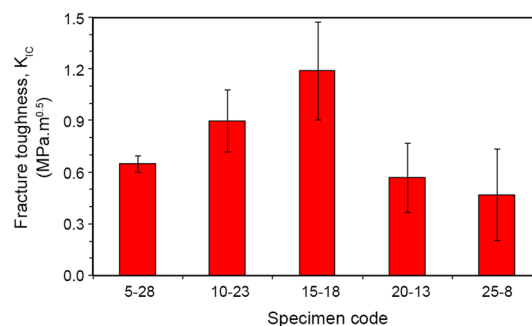


Fig. 6 Fracture toughness of the specimens with different GF contents

SEM analysis

SEM was employed to observe the cross section of the specimens. The fracture surfaces of the composite specimens reinforced with 15 and 25 vol % GF are shown in Fig. 7a, b, respectively. The micrographs demonstrate that there is a good adhesion between the resin matrix and the fillers at 15 vol % GF content and the flakes are evenly distributed between the silica nanoparticles. The random distribution of the flakes throughout the specimen thickness may prevent the propagation of the growing crack by providing a tortuous path resulting in higher fracture toughness (Fig. 6). However, at higher GF contents, the stacking of GF plates on each other along with a poor matrix–filler interface adhesion is observed in the Fig. 7b.

The parallel aligned flakes provide a straight path for the cracks to propagate through the specimen leading to a drop in the fracture toughness of the composite (Fig. 6). SEM micrographs also indicate a brittle fracture for the composites. The distribution of the GF in the composites was also monitored using Na map of EDXA (Fig. 8) which also confirmed the stacking of the flakes at higher concentrations.

Conclusion

Glass flakes were utilized to improve the mechanical properties of dental composites. The evenly distributed flakes among the spherical filler particles of the dental composites significantly improved the fracture toughness of the composite. The highest mechanical properties were observed for a dental composite sample with 15 vol % of GF. Further increase in the GF content resulted in a drop in the mechanical properties of the dental composite due to the stacking of the flakes on each other.

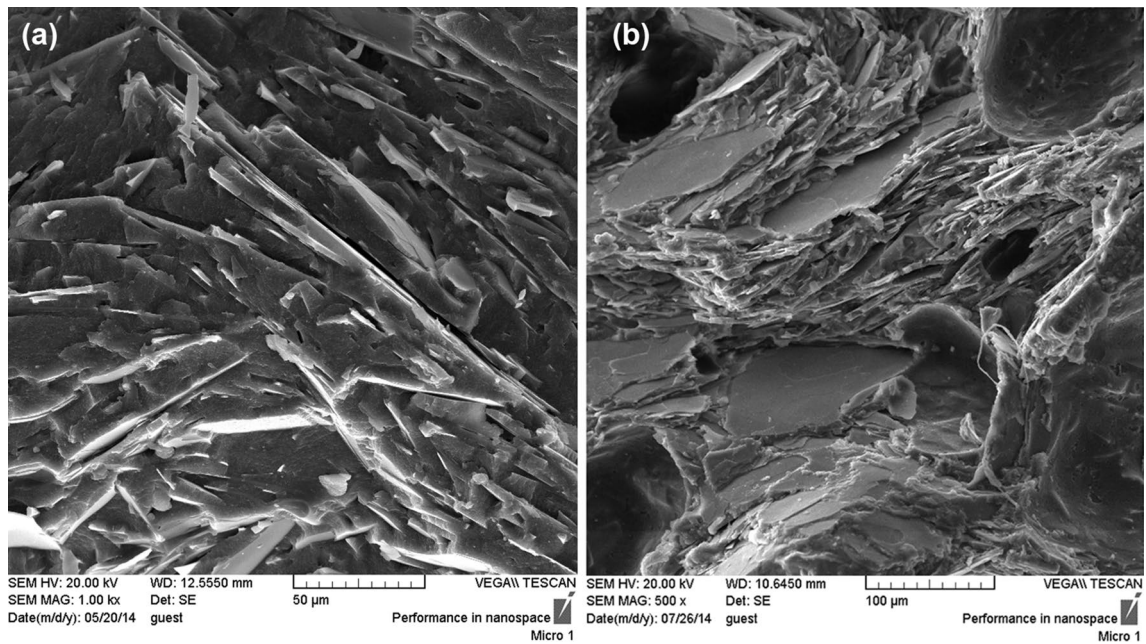


Fig. 7 SEM micrographs of the fracture surface of: **a** 15-18 and **b** 25-8 samples

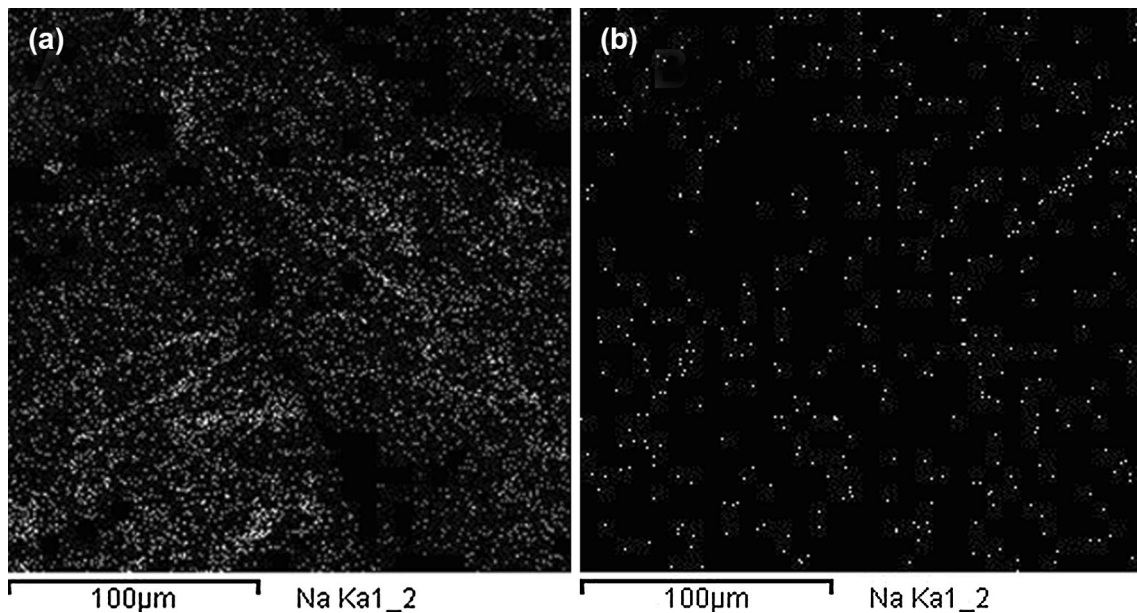


Fig. 8 EDXA Na map of the specimens: **a** 25-8 and **b** 5-28 samples

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