

INFLUENCE OF ANTIBACTERIAL COPPER GLASS PARTICLES ON SURFACE AND MECHANICAL PROPERTIES OF FLOWABLE COMPOSITES

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ABSTRACT

Copper oxide containing phosphate glasses showed an antibacterial action against *streptococcus sanguis*, *streptococcus mutans* and *staphylococcus epidermidis*. This study aimed to investigate the effect of adding copper glass particles (0- 25 wt%) into flowable composites (Filtek Z350XT flowable and Fusio liquid dentin dental flowable) to induce antibacterial properties. Surface (contact angle and Vicker hardness number) and mechanical (flexure strength, strain and modulus) properties of modified composites have been tested throughout this study; the antibacterial action will be tested in the future. The results showed that both surface and mechanical properties were dependent on the original composite as well as the added filler content. Lower contact angles, indicating higher wettability of the composites, observed with the higher loading of copper glass particles in both resin composites; this high wettability was obvious with Fusio flowable composites. This would be beneficial in bacterial adhesion to the composite surface and hence the expected antibacterial activity of copper glass against the adherent bacteria during biofilm formation. Surface hardness was not negatively affected by adding copper glass particles, except at higher loading levels (25 wt%) particularly when added to Z350 composites. This could indicate that the copper glass at low wt% had no adverse effect on monomer conversion. Generally, the rigidity (indicated by flexure modulus) and strain % of both composites were not affected by the presence of copper glass particles. Finally, it can be concluded that addition of low wt% of copper glass particles (up to 10 wt%) could provide a restorative material with antibacterial action without compromising their surface and mechanical properties. Addition of high wt% of copper glass to Fusio flowable in particular could be beneficial in producing a more hydrophilic material that could potentially encourage bacterial adhesion and hence a significant antibacterial action of copper glass against adherent bacteria will be expected.

INTRODUCTION

The ultimate goal of restorative dentistry is to replace damaged dental tissues for restoring function

and esthetics as well as to prevent the recurrent decays of restored tissues. The most widely used esthetic direct restorative resin materials in current decades are satisfying the first goal, but they are

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mostly bioinert to prevent the recurrent decays⁽¹⁾. This has therefore been documented as the main cause of failure in resin restorations⁽²⁾.

Two main mechanisms are needed to prevent secondary caries; suppressing biofilm acids and promoting remineralization⁽¹⁾. Researchers are diligent to modify the current resin restorative materials with antibacterial elements to prevent caries under dental restorations at the same time to allow for hard tissue remineralization without the need of several materials application. For this purpose, bioactive resins with anti-caries properties were developed and a new generation of bioactive/therapeutic materials has been introduced⁽¹⁾. Several materials with antibacterial actions were considered as modifiers for dental restorative materials^(1,3-11). Examples of these materials include zinc methacrylate monomer, silver particle, titanium dioxide, calcium phosphate, zinc oxide and copper oxide.

Silver particles known to have antimicrobial activity against *Escherichia coli* and *Streptococcus mutans* were added to resins in previous investigations^(1,6). The silver nano-particles greatly reduced biofilm growth without negatively affecting the material's color and bond strength. Incorporation of calcium phosphate particles with antibacterial activity into resins released calcium and phosphate ions and re-mineralized carious lesions⁽¹²⁾. However, composites containing calcium phosphate particles were mechanically weak and cannot be handled as a restorative materials⁽¹⁾.

Fluoride is a dual element, that can inhibit bacterial metabolism and enhance tooth remineralization⁽¹⁾. Topical fluoride application will provide remineralization of infected and affected dental tissues with the antibacterial action when applied as a glass ionomer restoration; this bacterial inhibition will diminish if fluoride is incorporated in resin based restorations⁽¹³⁾. Regardless of the antibacterial action of fluoride, it was not proven

that fluoride releasing restorative materials will reduce the incidence of recurrent caries⁽¹⁴⁾.

In several investigations^(7,15), Copper oxide (CuO) delivered by phosphate based glass fibers, showed antibacterial action against *streptococcus sanguis*, the main cariogenic bacteria *streptococcus mutans*⁽¹⁶⁾ and *staphylococcus epidermidis*. Furthermore, CuO particles were proved to be more potent against *streptococcus mutans*, compared to zinc oxide particles as confirmed by Ramazanzadeh *et al*⁽⁷⁾. Therefore, adding CuO particles to restorative materials may lower the risk of bacterial accumulation on restorative materials and then reducing the potential of recurrent decays in restored teeth.

Incorporation of bioactive elements into dental resins are still within its experimental stage and it needs further investigations. The influence of added antibacterial elements into resin materials on surface and mechanical properties is an essential factor to determine the applicability of these restorative materials. Therefore, the aim of the present study was to evaluate the effect of adding copper glass particles to flowable composites on contact angle, surface hardness, flexure strength and modulus.

MATERIALS AND METHODS

Composite materials used in the present study (Filtek Z350 XT flowable, Fusio Liquid dentin) are presented in table 1. The filler used in this study was copper containing phosphate based glass particles of approximately 60- 200 mm in diameter. These particles have the composition of 50 mol% P₂O₅, 30 mol% CaO, 10 mol% NaO and 10 mol% Cu⁽¹⁵⁾. Copper glass was added at 0, 1, 5, 10 and 25 wt % to each composite material; this resulted in 10 experimental groups, 5 groups (n=3 for each group) for each composite material. Samples were coded as Z350, 1% Cu Z350, 5%Cu Z350, 10% Cu Z350 and 25% Cu Z350. Fus, 1%Cu Fus, 5%Cu Fus, 10%Cu Fus, 25%Cu Fus.

TABLE (1) Details of restorative resin materials used in the study.

Resin material	Manufacturer	Composition	Filler loading
Filtek Z350 XT flowable composite	3M ESPE	Organic: bis-GMA, UDMA, TEGDMA, and bis-EMA(6) resins, In-organic: a combination of silica, zirconia, and zirconia/silica cluster filler	78.5% by weight 63.3% by volume
Fusio Liquid dentin dental flowable composite	PENTRON	Organic: UDMA, TEGDMA, HEMA, 4-MET, In-organic: Silane treated barium glass, Silica.	65% by weight 52% by volume

Contact Angle Measurements

Discs of 10 mm diameter and 2 mm height were prepared using a split Teflon mold (n=3). Experimental materials were backed into the Teflon mold and sandwiched between two celluloid strips and glass slides. Samples were then light cured from each side for 20 seconds using LED light (3M ELEBAR) with a wave length range between 430-480 nm and light intensity of 1200Mw/cm². Three samples from each composition were subjected to wettability measurement using a drop shape analyzer (Kruss). Contact angle was performed using distilled water as the test liquid. Drop Shape Analysis [DSA4] software was used to measure the contact angle.

Vickers Hardness Number

Discs of 10 mm diameter and 2 mm height were prepared using a split Teflon mold (n=3) as described above. Vickers hardness numbers were determined using a micro-hardness tester (Micromet 6040, Buehler, USA) under a load of 100 g and dwell time of 10 seconds. Three readings were recorded for each surface; the hardness number was presented as the average of these readings. Relative hardness (ratio of bottom to top hardness) for each experimental group was also recorded.

Three-point Bending Test

Thirty specimens were prepared (n=3 for

each composition), by backing composite into a rectangular split Teflon mold (2x2x25 mm³) according to ISO 4049 specification for polymer-based restorations ⁽¹⁷⁾. Molds with composite materials were sandwiched between two celluloid strip and glass slides and tightened at both ends using paper clamps. Each specimen was then subjected to 4 overlapping 40 seconds curing cycles from one side. The cured specimen was then removed from the mold; excess materials were removed with a sharp scalpel. The prepared specimens were then stored for 24 hours in dry container at room temperature (22°C±1) prior to testing. Before flexure testing, dimension of each specimen was determined with a micrometer accurate to 0.01 mm. The three-point bending test was carried out using the Instron testing machine (Instron 5944, USA) with a span of 20 mm at a crosshead speed of 0.25mm/ min and 2 KN load. The flexure strength (MPa), modulus (GPa) and strain at break (%) were measured using Bluehill 3 software.

Statistical Analysis

The data were collected and analyzed using one-way ANOVA and Tukey's post hoc test to delineate areas of significance. Data collection and analysis was done using SPSS (Version 20.0, IBM, and New York, USA).

RESULTS

Contact Angle Measurements

One way ANOVA test of contact angle mean values and standard deviations revealed a significant difference between groups ($p < 0.001$). There was no significant difference in contact angle tested with distilled water between Z350 flowable composite groups modified with 0%, 1%, 5% and 10% copper glass particle (85 ± 6 , $86 \pm$, 84 ± 1 and 81 ± 7 , respectively) ($P > 0.05$). However, 25% copper glass modified Z350 composite showed a significantly lower contact angle (71 ± 8) compared to the Z350 group modified with 1% copper glass particles ($p = 0.038$) – Fig. 1.

On the other hand, 10% and 25% copper glass modified Fusio liquid dentin composite, had a statistically significant lower contact angle (61 ± 5 , 65 ± 5) compared to 0%, 1%, and 5% copper glass modified Fusio composite groups (77 ± 4 , 79 ± 1 , 77 ± 6) ($p < 0.05$) – Fig. 1.

Comparing the two composite materials revealed that 10% and 25% copper glass modified Fusio liquid dentin composite had a statistically significant lower contact angle values compared to all other experimental groups ($p < 0.05$) - Fig. 1

Vicker Hardness Number

Regarding surface hardness, a significant difference between experimental groups of Z350 ($p < 0.05$) were observed. However, all groups of Fusio composite material surface hardness was not affected significantly by adding copper glass particles (42 ± 5 , 38 ± 6 , 43.5 ± 3 , 37 ± 1 and 35 ± 2 , respectively) ($p > 0.05$). Z350 groups surface hardness showed that, adding 25% copper glass to Z350 composite resulted in a significantly lower surface hardness (31 ± 1) compared to the 0%, 1%, 5% and 10% copper glass modified groups of Z350 composite materials (47 ± 1 , 43.5 ± 0.1 , 41 ± 2 and 55.5 ± 14) ($p < 0.05$) – Fig. 2

Mean values of relative hardness were not affected significantly in both materials after adding the experimental amounts of copper particles ($p = 0.233$) – Fig. (3)

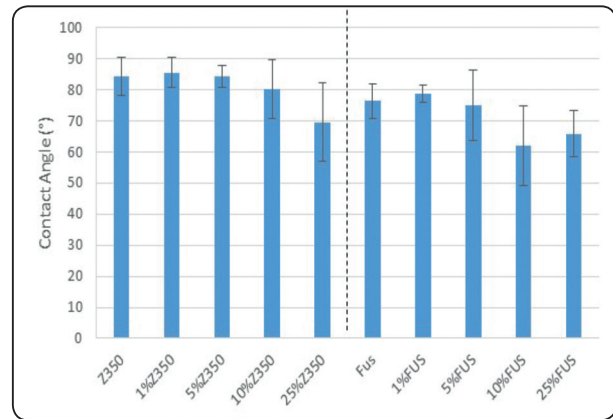


Fig. (1) Contact angle (°) of tested materials.

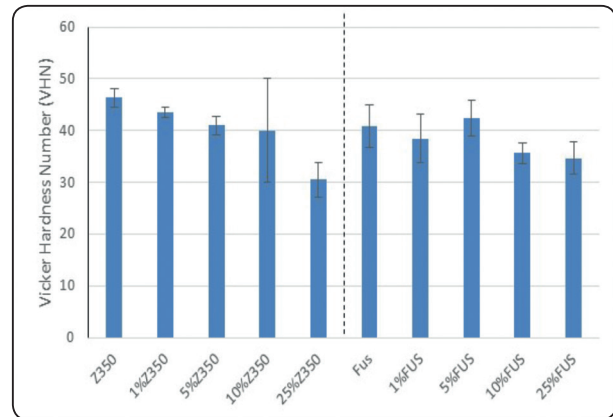


Fig. (2) Vicker hardness number of tested materials.

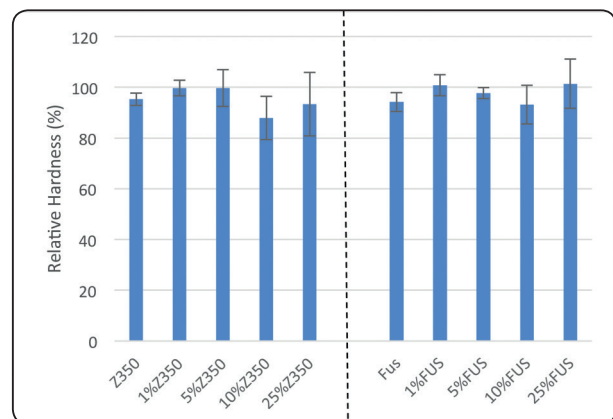


Fig. (3) Relative hardness (%) hardness of tested materials.

Three-point Bending Test

Analysis of the mean strain (%) values showed that the addition of copper glass produced no significant change in strain % of Z350 flowable composites. On the contrary, a significant reduction was observed in strain % of Fusio flowable composites – Fig. 4.

Analysis of mean flexure strength values showed a significant difference between different experimental groups ($p < 0.05$). Z350 experimental groups showed a significant drop in flexure strength after adding 1% copper glass compared to the 0% copper glass modified Z350 ($p < 0.05$). In addition, the 5%, 10% and 25% copper glass modified Z350 groups (61 ± 4 , 49 ± 11 and 39 ± 7 MPa respectively) were significantly lower than the 0% and 1% copper glass-modified Z350 (112 ± 5 and 76 ± 19 MPa respectively) ($p < 0.05$) – Fig. 4.

Different results were observed in Fusio experimental groups, in which 10% and 25% copper glass modified Fusio (65 ± 9 and 60 ± 2 MPa respectively) had a statistically significant drop in flexure strength compared to 0%, 1% and 5% copper glass modified Fusio material (99 ± 11 , 74 ± 14 and 71 ± 7 MPa respectively) ($p < 0.5$), while there was no significant difference between the former three experimental groups ($p > 0.05$) - Fig. 4.

Analysis of modulus of elasticity mean values showed a significant difference between groups ($p < 0.5$). 25% copper glass modified Z350 (3.3 ± 1 Gpa) was significantly lower than the 0%, 1%, 5%, and 10% copper glass modified Z350 experimental groups (6 ± 0.7 , 5 ± 0.5 , 5 ± 0.6 and 6 ± 0.5 GPa respectively) ($p < 0.05$). On the other hand, there was no significant difference in modulus values between 0%, 1% 5%, 10% and 25% copper glass modified Fusio composite materials (6 ± 0.5 , 6 ± 0.2 , 7 ± 0.5 , 7 ± 0.5 , 6 ± 0.5 Gpa respectively) ($p > 0.05$) – Fig. 4.

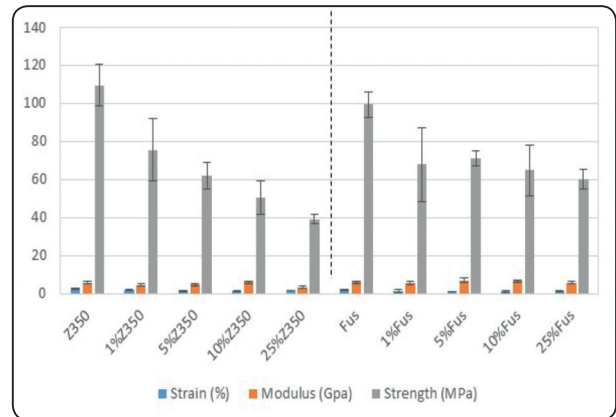


Fig. (4) Flexure strain (%), strength (MPa) and Modulus (GPa) of tested materials.

DISCUSSION

Several investigations examined the influence of copper glass particles as antibacterial/ anticariogenic element when added to dental resin materials^(3-5,7). In an old study by Bapna *et al* (1988), copper oxide was not effective as antibacterial agent against *streptococcus mutans* when compared to silver compounds⁽⁵⁾. However in a more recent study⁽⁴⁾, the application of copper modified varnish had anticariogenic effects to root surfaces treated with this varnish when compared to the negative control that received no treatment. In another study by Argueta-figueroa *et al*⁽³⁾, the incorporation of copper nanoparticles into the orthodontic resin adhesives showed a bacteriocidal effect against *S. aureus*, *E. coli* and *S. mutans*.

In the present study, copper glass particles were added to two types of flowable composites to induce the antibacterial action, but this study aimed to investigate the influence of copper glass particles on the surface and mechanical properties of dental resins. Testing the antibacterial action of these composites however will be carried out in the future.

Results of the present work showed that, the effect of copper glass particles depends on the type of composites to which this filler was added as well

as the percent of the added particles. Fusio liquid dentin, used as a self-adhesive dentin replacement material, showed promising results with lower loading levels of copper glass particles. The hardness was not negatively affected by adding the copper glass particles. However, the flexure strength was only significantly reduced when copper glass particles were added at high percentage (10% and 25 wt %). At this high level of copper glass, the wettability was significantly increased; at low level of filler loading (1% and 5 wt %), however, the flexure strength and wettability were not significantly affected. There was no reduction in flexure modulus at any copper glass loading levels.

However, for Filtek Z350 flowable composite, addition of copper glass particles resulted in a significant drop in flexure strength at all loading levels of copper glass. The reduction in flexure modulus and hardness was only observed with the highest filler loading (25 wt%). The wettability however was significantly increased at 25 wt% filler addition.

Therefore, copper glass modification of Fusio liquid dentin at 1% and 5% loading level may result in a restorative bacteriostatic material that can be clinically applied without compromising the material's surface or mechanical properties. On the contrary, adding copper glass particles to Z350 composite resulted in a significant drop in flexure strength even at the lowest amount. This might be inferred to the lower filler content of Fusio liquid dentin (65% by weight) compared to the filler loading of Z350 (78.5 % by weight), that permitted the addition of copper glass up to 10 wt% without reducing the mechanical or surface properties of Fusio Liquid dentin.

Relative hardness as an indication of degree of monomer conversion ^(18,19) 2- and 3-mm thick samples of three types of resin composite: an anterior microfill, an anterior hybrid and a posterior hybrid, all having differing filler size and loading

but similar shade (A2 was not affected by adding copper glass particles in both materials at all loading levels. This might indicate that the addition of copper glass particles did not affect the penetration of light beam within the resin material. Therefore the degree of monomer conversion was not affected by the presence of copper glass particles.

Results of the present work showed that, higher loading levels of added particles will compromise all tested mechanical and surface properties in both tested materials. These results coincide with other investigation ⁽²⁰⁾ in which the incorporation of zinc oxide antibacterial particles into the resin matrix of flowable composite enhanced its mechanical property in low percentages up to a threshold beyond which, more added particles negatively affected the mechanical properties.

This might be explained as the higher loading with the antibacterial particles will result in reduction of the amount of the main bulk of the composite material and increasing flaws and defects within the material deteriorating the surface and mechanical properties.

CONCLUSION

- 1- The influence of copper glass particles on surface and mechanical properties of flowable composite materials is material dependent.
- 2- Wettability of tested composites, as indicated by the contact angle, was not significantly affected by the addition of copper glass except only at 25 wt% that produced relatively more hydrophilic materials. Hydrophilic restorative materials could be beneficial in helping bacterial adhesion and hence a more antibacterial action could be produced by the incorporated copper glass.
- 3- Surface hardness was only significantly reduced by adding 25 wt% copper glass particles to Z350 composites. This indicated that copper

glass particles at low wt% had no adverse effect on degree of monomer conversion.

- 4- Addition of copper glass produced a significant reduction in flexure strength of Z350 flowable composites, but this reduction was only observed particularly with Fusio flowable composites when copper glass was added at high wt% (10 & 25).
- 5- Addition of copper glass produced no significant change in strain % of Z350 flowable composites. On the contrary, a significant reduction was observed in strain % of Fusio flowable composites.
- 6- Addition of copper glass produced no significant change in modulus of both Z350 and Fusio flowable composites.
- 7- Finally, it can be concluded that addition of low wt% of copper glass particles (up to 10 wt%) could provide a restorative material with antibacterial action without compromising their surface and mechanical properties. Addition of high wt% of copper glass to Fusio flowable in particular could be beneficial in producing a more hydrophilic material that could potentially encourage bacterial adhesion and hence a significant antibacterial action of copper glass against adherent bacteria will be expected.

ACKNOWLEDGMENT

The author would like to acknowledge with gratitude Prof. Ensanya A. Abou Neel for providing the copper glass particles used in the present work, and for her advice and efforts during the conduction and writing of this research. The author would also like to acknowledge the “Advanced Technology Dental Research Laboratory” at King Abdulaziz University, Faculty of Dentistry.

CONFLICT OF INTEREST

The author declares that there is no conflict of interest regarding the publication of this paper.

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