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Effect of Mica Reinforcement on the Flexural Strength and Microhardness of Polymethyl Methacrylate Denture Resin

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Abstract

Purpose: Conventional denture base polymethyl methacrylate (PMMA) is low in strength, soft, and brittle on impact. Improvements in the mechanical properties of denture base materials have been sought by adding different reinforcing phases to the PMMA matrix. The purpose of this work was to study the effects of mica reinforcement on the mechanical properties, flexural strength, and microhardness of PMMA denture base resin.

Materials and Methods: Wet ground muscovite mica and Lucitone 199 original shade denture base resin were used. Two micas were tested: W200 and P66 with average particle sizes (d50) of 131 μm and 30 μm, respectively. The mica was silane treated in a solution of 3-methacryloxypropyl trimethoxysilane, ethanol, and water, and then dried. The specimens were fabricated using the denture base resin manufacturer's instructions with a powder : liquid ratio of 21 g/10 ml and a mixing time of 30 seconds. Five treatment groups were produced with differing amounts of mica added to the PMMA denture base resin: (A) control group with 0 vol% mica, (B) 10 vol% W200 mica, (C) 20 vol% W200 mica, (D) 10 vol% P66 mica, (E) 20 vol% P66 mica. The mica replaced equal volumes of the PMMA powder component to minimize changes in viscosity. The three-point bending flexural strength specimens were $70 \times 11 \times 3$ mm^3. Seven specimens were prepared for each treatment group. The hardness specimens were prepared from the ends of the three-point bend specimens after they were broken ($N = 7$). After deflasking, the specimens were polished with 600 grit silicon carbide paper to achieve smooth surfaces. A standard three-point bending jig with a span length of 50 mm was attached to an Instron universal testing machine. The specimens were placed on the jig, and loading was carried out using a 1 mm/min crosshead speed until failure. Microhardness was measured using a Clark microhardness tester with a Knoop indenter. The load was set to 200 g and the dwell time to 15 seconds. ANOVA and Tukey tests were used for statistical analyses (Alpha $= 0.05$).

Results: The flexural strength of the control group was between 77% and 94% higher than all the mica-containing groups ($p \leq 0.05$). No significant differences were found within the four mica groups. Microhardnesses of the 20% mica groups (both fine and coarse) were 33% and 26% higher than the control ($p \leq 0.05$). The 10% mica groups had higher hardness than the control group, but the increase was not statistically significant ($p > 0.05$).

Conclusion: Mica additions to denture PMMA reduced flexural strength; however, with the specimens containing highest mica concentrations (20%), microhardness significantly increased.

Denture acrylic resin composed primarily of polymethyl methacrylate (PMMA) is the material most commonly used for the manufacture of dentures; however, the denture acrylic resin does not fulfill all the requirements in terms of mechanical properties due to its low strength, softness, and brittle behavior. Failure may be caused by uneven masticatory force or accidents.[1-4]

A study by Johnston et al[5] showed that 68% of acrylic resin dentures break within a few years after fabrication. This

is caused primarily by impact failure when the denture is accidentally dropped on a hard surface or by fatigue failure when the denture base deforms repeatedly under occlusal forces.[6]

The hardness of denture base acrylic is also important. Denture acrylic is soft enough that it can be scratched and abraded easily.[1] Improved hardness leads to greater resistance to scratching and abrasion. Abrasion by parts of the dentures rubbing against each other or from overzealous cleaning are common causes of wear of denture bases.

Several investigators have studied the properties of acrylic resin dentures reinforced with a variety of materials.[7-16] Use of both high-strength metal wires and rods has been limited because of negative effects on esthetics; in addition, the influence of metal wires on flexural fatigue resistance is minor.[7,8] Polyethylene (PE) and aramid (Kevlar) fibers have been used as strengtheners in roved, chopped strands, or in mat form, but none of these types of fiber reinforcement have found favor in clinical use. There are reports of poor adhesion of the fibers to the polymer matrix, despite the surface treatment to improve the adhesion between the fibers and the denture base polymers.[9,10] Carbon fibers are not used because they have a springy nature in handling, and their black color poses many esthetic problems.[11] Aramid fibers also have poor esthetics and are difficult to polish.[12]

In dental work, it is difficult to introduce long glass fibers into the dough of liquid MMA monomer and PMMA powder. Also, glass rods are limited to application on thin palatal areas of denture base polymer. Improper impregnation of monomer into glass fiber bundles can cause reduction in transverse strength. The absence of complete impregnation of the fiber bundles by monomer liquid (before polymerization) results in voids inside the denture.[13,14]

Micas are a group of lamellar silicate minerals distinguished by their high aspect ratio and visual glimmer. Muscovite mica, the most common type worldwide, is a hydrated silicate of potassium and aluminum and is predominately white. Muscovite mica is commonly used to reinforce thermoplastic polymers. The high aspect ratio platelet particles provide an excellent balance of mechanical, thermal, and dimensional properties when used as reinforcing filler in plastics.[15,16]

Adding mica to polymers typically increases stiffness, strength, high temperature performance, dimensional stability, scratch resistance, and acoustic damping properties and lowers coefficient of linear thermal expansion. Examples of polymers benefiting from mica addition include polypropylene, PE, thermoplastic polyolefin, polyamide, and polybutylene terephthalate. Thermosetting polymers including polyester, polyurethane, epoxy, and acrylic resin also gain enhanced performance.[17] In terms of handling and manipulation, mica allows good mold details, easy removal of mold materials, and a relatively low rise in viscosity as compared to fibrous reinforcing materials due to mica's platelet form.[18,19]

Unalan et al[20,21] evaluated the effects of four ratios of silanized mica filler and milled glass fiber on the surface hardness of a denture tooth material. They concluded that 10% mica and 10% glass added to the PMMA denture teeth exhibited the best surface hardness values. They also investigated the effect of the mica on esthetic qualities of denture teeth.

The objective of this investigation was to study the effects of mica reinforcement on the mechanical properties including flexural strength and microhardness of commercially available denture PMMA base resin. The hypothesis of this research was that the incorporation of mica would significantly improve the flexural strength and microhardness of the PMMA denture base resin.

Materials and methods

In this study, dental acrylic was reinforced with two types of mica, and each type of mica was tested at two concentration levels. The mica-reinforced acrylic specimens were compared to dental acrylic specimens without mica reinforcement.

The denture base resin used was Lucitone 199® original shade (Dentsply International Inc., York, PA). Two sizes of wet ground muscovite mica (Minelco, Inc. USA, Cincinnati, OH) were used. The average particle size (d50) for the course powder (W200) is 131 μm. For fine powder (P66) the average particle size is 30 μm.

The mica was silane treated in a solution of 2% 3-methacryloxypropyl trimethoxysilane, 94% ethanol, and 4% water. The ethanol/water mixture was first adjusted to pH 4 using acetic acid, then the silane was added. The mica was added to the solution and stirred for 5 minutes, and then the excess solution was decanted. The mica was rinsed two times with ethanol. Finally the mica dried at 23°C for 24 hours.

The specimens were fabricated using the denture base resin following the manufacturer's instructions. The powder : liquid ratio was 21 g/10 ml, and the mixing time was 30 seconds.

There were five treatment groups with differing amounts of mica added to the denture base resin: (A) control group with 0 vol% mica, (B) 10 vol% W200 mica, (C) 20 vol% W200 mica, (D) 10 vol% P66 mica, (E) 20 vol% P66 mica. To make the 10 vol% and 20 vol% mica groups (B-E), mica replaced equal volumes of the powder to minimize the changes in viscosity. The mica was then added to the monomer first and ultrasonically treated to ensure complete wetting before all components were mixed together. The mixture was covered and allowed to reach packing consistency. The time used was the point when the acrylic-mica composite started to separate cleanly from the sides of the jar and did not stick to the spatula. The mold for three-point bending specimens was fabricated as a bar-shaped mold prepared in standard denture flasks using a template measuring 70 × 11 × 3 mm^3.[18] The thickened resin was then packed into the mold using conventional denture flasks (Hanau Type, Whip-Mix Corporation, Louisville, KY) not exceeding 10 minutes of working time. The closed flask (locked by spring clamp) was cured in a water bath for 9 hours at 160°F, followed by a cooling time of 0.5 hour in water at 60°F to 80°F. The flask was bench cooled for 30 minutes and submerged in cool water for 15 minutes before deflasking.

Seven specimens were prepared for each treatment group (N = 7). A total of 35 specimens (5 groups × 7) were made. After deflasking, the specimens were then polished with 600-grit silicon carbide paper to achieve smooth edges. The tests were performed using an Instron universal testing machine (Instron Engineering Corp., Canton, MA). A standard three-point bending jig was attached to the machine. The specimens

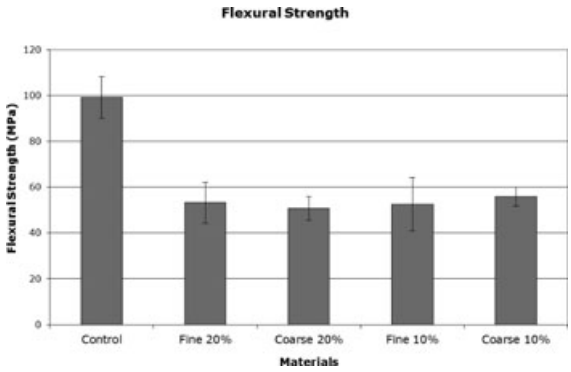

Figure 1 Average flexural strength of the control and the mica-containing denture acrylic specimens.

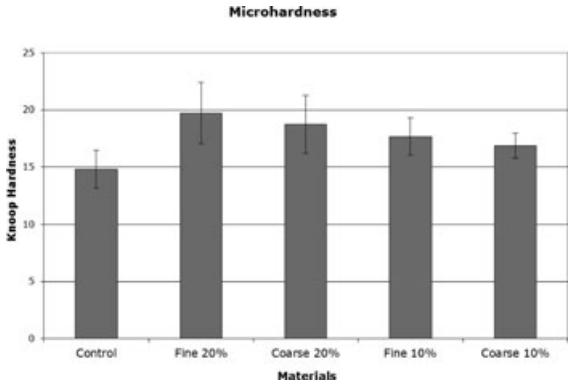

Figure 2 Average Knoop microhardness of the control and the mica-containing denture acrylic specimens.

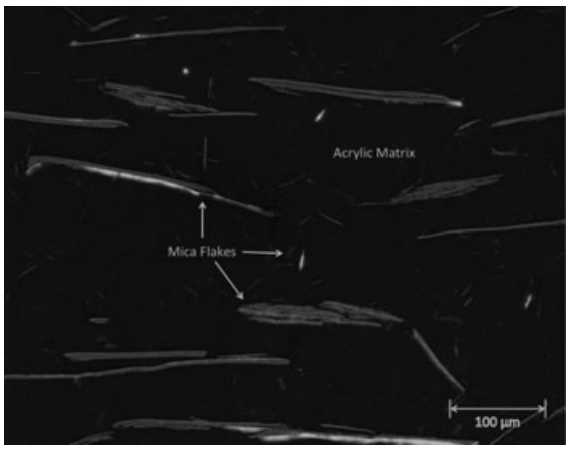

Figure 3 SEM image (200×) showing the ground and polished cross-section of a 10% coarse mica (W200) specimen. Note the orientation of the mica platelets and the delamination flaws within the platelets.

were then placed on the jig with a 50-mm span length, and the test carried out using a 1 mm/min crosshead speed until failure.

The hardness specimens were prepared from the ends of the three-point bend specimens after they had been tested (N = 7). In previous studies, the within-group standard deviations were approximately 7 MPa for flexural strength and 0.5 for microhardness.[22,23] Power calculations for flexural strength and hardness were performed for Tukey Multicomparison tests at a 5% significance level for each test. With a sample size of 7 per group for flexural strength, the study will have 80% power to detect a difference of 14.2 MPa between any two treatment combinations.[24] With a sample size 7 for the microhardness specimens, the study will have 80% power to detect a difference of 1.0 between any two treatment combinations.

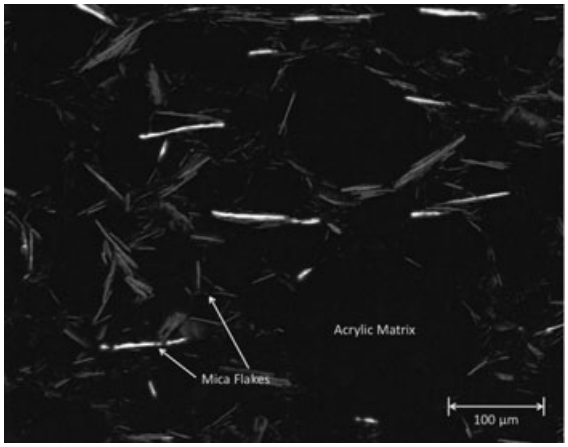

Figure 4 SEM image (200×) showing the ground and polished cross-section of a 20% fine mica (p66) specimen. The mica platelets in this specimen are smaller and more randomly oriented.

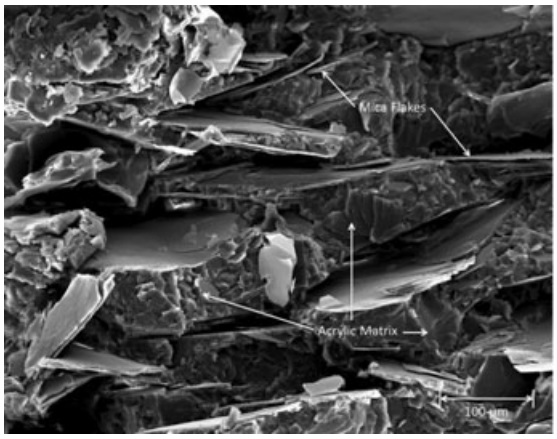

Figure 5 SEM image (200×) showing the fracture surface of a 20% coarse mica (W200) specimen. The coarse mica platelets protrude out of the surface in many locations, and there are also corresponding voids where the mica platelets have pulled out of the acrylic.

The specimens were tested using Knoop's microhardness testing machine (Clark CM-700AT, Sim-Tec Corp. Novi, MI). Three indentations were made on the surface of each specimen. The three indentations per specimen were averaged, and the average was subjected to further statistical analysis. The load of the indenter was to be set at 200 g with an indentation dwell time of 15 seconds.

Scanning electron microscopy (SEM) was used for three purposes in this study: characterizing the morphology of the mica powders, inspecting specimens for voids and other defects, and

observing fracture surfaces. A Hitachi S3200 N scanning electron microscope (Hitachi, Tokyo, Japan) was used. All specimens were sputter coated with an approximately 10-nm coating of gold to produce the necessary conductive surfaces. Images were taken of the powders to document maximum and minimum dimensions of the mica platelets. Undamaged sides of the representative specimens (one for each treatment group) were ground and polished to a 400 grit, 800 grit, and 1 μm diamond finish and viewed to determine if there were any trapped air voids. Finally, fracture surfaces of broken representative specimens were observed to characterize the fracture path through the specimen.

The effect of mica reinforcement on flexural strength and microhardness was assessed using ANOVA and Tukey tests. A 5% significance level was used for all tests. No statistics were applied to the SEM data because of its observational nature.

Results

The flexural strength of the control group was between 77% and 94% higher than the mica containing groups ($p \leq 0.05$). No significant differences were found within the four mica groups. Mean Knoop microhardnesses (HK) of the 20% mica groups were: Fine-19.7 HK and Coarse-18.7 HK. These values were 33% and 26%, respectively, significantly ($p \leq 0.05$) higher than the Control (14.8 HK). The 10% mica groups (Fine-17.6 HK; Coarse-16.9 HK) had no statistical difference from the control group ($p > 0.05$) (Figs 1, 2).

We observed what has been called "graceful fracture" during testing with the 20% coarse mica-containing specimens. The specimens would break partially and continue to hold together until the ends of the specimens were at a 50° to 90° angle and then separate completely. We believe that the mica platelets help deflect the crack propagation and prevent the catastrophic failure seen in the control group.

SEM of both control (acrylic only, no mica) and mica-containing specimens showed very low porosity. Only rare widely dispersed pores were observed; however, delaminations within the mica platelets were observed (Fig 3). Most of the larger defects appeared to be filled with the acrylic resin. In addition, there appeared to be significant debonding between the acrylic and the mica.

The orientation of the mica platelets in the acrylic was only partially oriented in the plane of the specimens. The coarse mica appeared to be somewhat more oriented than the fine mica (Figs 3 and 4).

The fracture surfaces of the acrylic specimens were relatively flat and featureless. In contrast, the mica-containing specimens showed much rougher surfaces with voids and platelets of the mica protruding from the surfaces (Fig 5).

Discussion

This study determined the effect of mica reinforcement on both the flexural strength and Knoop hardness of denture base resins. It was hypothesized that the mica reinforcement would increase both the flexural strength and the microhardness; however, only the hardness was improved. The flexural strength was lowered with the mica additions.

A number of possible reasons the flexural strength was lowered by the mica additions were proposed: (1) there was high porosity in the mica-containing specimens, (2) there were flaws within the mica, (3) the mica was poorly oriented in the acrylic resin, and (4) there was weak bonding between the mica and acrylic resin. The suggestion that porosity in the mica-containing specimens was responsible for the lower flexural strength was disproved by the SEM analysis. The ground and polished specimens showed very low porosity in the SEM images.

Flaws within the mica were observed; however, most of the larger delaminations appeared to be filled with acrylic resin. The smallest delaminations probably were not completely filled with the acrylic resin. While these flaws may have decreased the strength of the mica, many of the flakes of mica sticking out of the fracture surfaces indicate that the mica was resistant to fracture during the testing. In addition, the "graceful fracture" noted during testing supports this observation. There are many grades of mica. The wet ground mica we used is generally considered appropriate for reinforcing polymers; however, future research should also investigate the effect of more highly refined grades of mica that could have fewer internal flaws.

The mica platelets observed in SEM specimens were shown to have fairly random orientations. It would be preferred to have all the platelets oriented along the plane of the denture plate for optimal flexural strength. So, poor orientation of the mica could have contributed to the lower flexural strength observed. It might be possible to improve the orientation of the mica by rolling the acrylic into sheets during denture processing.

In observing the SEM images of the fracture surfaces, no acrylic adhering to the exposed mica flakes protruding from the surfaces was found. In addition, deep voids that probably had contained the mica before testing were observed in the acrylic. These voids appeared to have no mica adhering to the surfaces. Therefore, we can conclude that there was adhesive failure from poor bonding between the mica and acrylic resin. This poor bonding was probably the dominant cause of the low flexural strengths. In future research in mica reinforcement of acrylics, improved silane or other surface treatments should be used to improve the adhesion between the mica and acrylic.

The microhardness was increased by the mica additions—perhaps more than expected. The fairly small amounts of mica added (20%) produced 26% to 33% increases in microhardness. Probably the poor mica orientation and poor adhesion were less detrimental to the microhardness.

Conclusions

On the basis of this study the following conclusions were made:

(1) Mica additions to denture acrylic resin reduced flexural strength;
(2) The mica additions increased microhardness.

Clinical significance

Mica has been shown in this research to be useful in increasing the hardness of denture base acrylic. The mica additions were detrimental to the flexural strength of the acrylic denture base resin; however, if the poor adhesion between mica and the acrylic and the mica platelet orientation problems can be solved, mica addition to acrylic resin may become a viable method to reduce the fracture failure of dentures.

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