Assessment of some mechanical properties of PMMA/silica/zirconia nanocomposite as a denture base material

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Abstract. In this research, nanocomposites of poly(methyl methacrylate) (PMMA) and a mixture of nano silica (SiO₂) and nano zirconia (ZrO₂) were prepared in different weight percentages of the nano fillers to improve some of the properties of PMMA resin to be used as a denture base material. The nano fillers were surface modified with a coupling agent and added to the PMMA in different amounts. Impact strength, transverse strength, hardness and roughness were tested for both control and experimental groups. The results indicate that PMMA/silica/zirconia nanocomposites, prepared with 5% by weight of both types of fillers, had a slight increase in impact strength, transverse strength and hardness with only an insignificant increase in roughness. This kind of composite material may have the potential for application in dental practice.

Keywords: PMMA acrylic resin, nano silica (SiO₂), nano zirconia (ZrO₂), mechanical properties, nanomaterials.

1. Introduction

Poly(methyl methacrylate) (PMMA) is an excellent organic biocompatible polymeric material used for the construction of denture bases [1]. It was first used for denture production in 1937 and since has been the material of choice for that purpose because of its good physical and mechanical properties [2].

PMMA has various advantages including colour likenesses of the natural gum, good chemical retention with artificial teeth and ease of manipulation and repair [3]. However, PMMA possesses insufficient mechanical strength and surface hardness when used alone. It can also easily be broken during an accident with high impact force or when a patient applies high mastication forces to the denture base [4,5].

In recent years, nanotechnology has been utilised to create materials with improved mechanical and physical properties. Advanced and custom-tailored materials can be produced by integrating nanoparticles into base materials to form composite materials with unique physical and mechanical properties that cannot be attained with the base material alone. This advanced technology is used to fulfil the requirement of the intended application of base materials [6].
Several studies have investigated the properties of composites consisting of different combinations of reinforcing materials such as particles and fibres [7-10], two different types of particles [5], particles and whiskers [1] and two or three types of fibres [11]. The improvement is, in general, better with multiple rather than a single reinforcement type. The idea is that each one of the added reinforcements improves a different material property [12].

Many researchers have focused on studying organic–inorganic hybrid nanocomposite materials and comparing them with macro or microparticle filled composite material; they found that nano filled materials have better enhancements in properties than macro and micro filled materials [13,14]. Nanocomposites have properties of both inorganic (nano filler) as increased rigidity, hardness and durability and organic polymer, which has better processability and flexibility [15,16].

The simplest and most convenient way of fabricating homogeneous hybrid materials is to increase the affinity between organic polymer and inorganic filler phases. Organic–inorganic hybrid materials are generally prepared by incorporating covalent bonds [17,18] or by physical interactions to improve the compatibility between organic and inorganic phases [19,20].

A coupling agent of 3-(methacryloxy)propyl-trimethoxysilane (MPTS) was used to enhance chemical bonding of the added nano filler to the polymer base to form a composite material that has the ability to transmit external forces from the weak polymer base to the much stronger nanoparticles. The nanoparticles should be distributed uniformly within the polymer matrix to prevent the material from weakening, which would reduce the mechanical properties by forming stress concentration areas [21-23].

Silica nano powder is the most used nanomaterial in this field due to its promising and unique properties [24]. Silica nanoparticles can be used for reinforcing denture base polymer due to its rigidity and antimicrobial properties. It was found that PMMA resin incorporated with TiO<sub>2</sub>/SiO<sub>2</sub> nanoparticles showed strong antimicrobial activity against cariogenic bacteria [25].

Zirconium oxide (ZrO<sub>2</sub>) is a metal oxide that has many benefits such as high mechanical strength, toughness, stiffness, wear resistance, chemical tolerance and good thermal stability, rendering it useful for reinforcing dental materials, such as denture bases [26]. Studies have shown that superior physical and mechanical properties can be obtained when zirconia nanoparticles are incorporated into PMMA polymer [27,28]. Zirconia nano powder is a biocompatible material that has excellent toughness, resistance to physical corrosion, good mechanical strength and abrasion resistance [29].

It was found that the addition of ceramic powder containing a mixture of nano SiO<sub>2</sub>/ZrO<sub>2</sub> to PMMA improved optical properties and thermal conductivity. PMMA/SiO<sub>2</sub>/ZrO<sub>2</sub> nanocomposites have surprisingly high thermal stability while retaining excellent transparency [30].

There is no report studying the mechanical properties of PMMA/SiO<sub>2</sub>/ZrO<sub>2</sub> nanocomposites as a denture base material. The hypothesis of this study is that the mechanical properties (i.e. impact strength, transverse strength, roughness and hardness) of PMMA would be improved after the addition of nano silica/zirconia mixture.

2. Materials and methods
Heat curing poly methyl methacrylate powder (SUPERACRYLP®P PLUS, Czech Republic) and methyl methacrylate liquid monomer (SUPERACRYLP®P PLUS, Czech Republic) were used in this study as denture base material. Silicon dioxide (SiO<sub>2</sub>) nanoparticles (20 nm) (Sigma-Aldrich, Germany) and zirconium oxide (ZrO<sub>2</sub>) nanoparticles (<100 nm) (Sigma-Aldrich Germany) were used as inorganic fillers for preparing the nanocomposite. Toluene (GCC, UK) was used as a solvent, while 3-(methacryloxy)propyl-trimethoxysilane (Sigma-Aldrich, Germany) was used as a coupling agent to improve the bonding between the organic base and the inorganic filler.

A pilot study was conducted to choose the optimum nano SiO<sub>2</sub>/ZrO<sub>2</sub> weight percentages. Specimens were divided into ten groups based on the amount of nano SiO<sub>2</sub> and nano ZrO<sub>2</sub> concentrations, as shown in Table 1.
Table 1. Pilot study specimen grouping.

| Group | Percentage of nano SiO$_2$ by weight | Percentage of nano ZrO$_2$ by weight | Weight of PMMA powder | Weight of PMMA liquid |
|-------|-------------------------------------|-------------------------------------|-----------------------|-----------------------|
| Control | 0%                                | 0%                                 | 44 g                  | 20 ml                 |
| A     | 3%                                | 3%                                 | 43.12 g               | 20 ml                 |
| B     | 5%                                | 3%                                 | 42.9 g                | 20 ml                 |
| C     | 7%                                | 3%                                 | 42.68 g               | 20 ml                 |
| D     | 3%                                | 5%                                 | 42.9 g                | 20 ml                 |
| E     | 5%                                | 5%                                 | 42.68 g               | 20 ml                 |
| F     | 7%                                | 5%                                 | 42.46 g               | 20 ml                 |
| G     | 3%                                | 7%                                 | 42.68 g               | 20 ml                 |
| H     | 5%                                | 7%                                 | 42.46 g               | 20 ml                 |
| J     | 7%                                | 7%                                 | 42.24 g               | 20 ml                 |

Specimens of each pilot study group were tested for transverse strength and hardness to select an optimum group for the main study. According to the results of the pilot study, group E and the control group were selected to be tested for impact strength, transverse strength, roughness and hardness.

2.1. Salinisation of nano fillers
An amount (30 g) of each nano filler was placed in a separate container containing 200 ml of toluene each. Each container was then sonicated using an ultrasonic probe (Soniprep 150, MSE [UK] Ltd, United Kingdom) at ambient temperature for 20 minutes. After that, the mixture was placed in a magnetic stirrer (Lab SH-3, JoanLab, United Kingdom) at room temperature, and 1.5 ml of 3-(methacryloxy)propyltrimethoxysilane was added drop by drop while stirring the mixture. The mixture was then covered and left for 48 hours. After two days, the toluene was removed by a rotary evaporator (RE-801-AW2, Yamato, Japan) at a speed of 150 rpm and a temperature of 60 °C for half an hour. The nano filler was dried by a vacuum oven (OVA03100, Gallenkamp, United Kingdom) at 60 °C for 20 hours [31].

2.2. Specimens’ preparation
Eighty specimens were prepared in the main study (40 for control group and 40 for group E). Ten specimens were tested for each property (impact strength, transverse strength, roughness and hardness). Two metal bar patterns were fabricated to be used for the preparation of stone moulds. The metal pattern for the impact test had dimensions of 80 mm x 10 mm x 4 mm (length x width x thickness, respectively). While the metal pattern used for transverse strength, roughness and hardness tests had dimensions of 65 mm x 10 mm x 2.5 mm (length x width x thickness, respectively). For the control group, specimens were prepared by weighing and mixing PMMA powder and liquid according to the guidelines of the manufacturer. The moulding, packing and polymerising of PMMA were done using conventional flasking technique for dentures. For group E, specimens were prepared by first mixing 5% by weight silane-coated nano silica and 5% by weight silane-coated nano zirconia with PMMA liquid monomer, and the mixture was sonicated by an ultrasonic probe at power of 20 W and frequency of 60 kHz for three minutes to disperse the fillers into the liquid monomer [12]. The suspension of the monomer with the nano filler was instantly added to the PMMA powder and mixed for 30 seconds. Packing and polymerising was done as it was done for the specimens of the control group. Specimens of both groups were then finished, polished and kept in distilled water at 37 °C for two days.
2.3. Impact strength test
Impact strength test was performed at room temperature in accordance with ISO 179-1, 2000 and ANSI/ADA specification no.12, 2002 using Charpy type impact test instrument (Impact Tester N. 43-1, TMI, USA). The unnotched specimen was horizontally supported and struck by a free-swinging pendulum with energy of 2 joules.

Impact strength (I) was calculated in KJ/m2 using the following equation:
\[ I = \frac{E}{(bd) \times 10^3} \]
Where:
E: the absorbed energy in joules.
b: the specimen width in millimetres.
d: the specimen thickness in millimetres.

2.4. Transverse strength test
Transverse strength test was performed in accordance with ISO 1567, 1999 and ANSI/ADA specification no.12, 2002 using a universal testing machine (WDW-20, Laryee Technology Co. Ltd., China). Specimen was mounted on two parallel supports 50 mm apart for three-point bending test. The specimen was then bent using a rod located at the centre of the two support with a load of 50 kg and a speed of 1 mm/min until fracturing.

Transverse strength (σ) was calculated in MPa using the following equation:
\[ \sigma = \frac{3Fl}{2bh^2} \]
Where:
F: the maximum force applied in Newton.
l: the distance between the supports in millimetres.
b: the specimen width in millimetres.
h: the specimen height in millimetres.

2.5. Surface hardness test
Surface hardness was measured according to ISO 1567, 1999 and ANSI/ADA specification no.12, 2002 using a digital shore-D hardness durometer (HT-6510D, China). The device has a 0.8 mm diameter pointed indenter which tapers to a 1.6 mm cylinder. The indenter is connected to a digital scale. Each specimen was subjected to five indentations at different areas 10 mm apart, and the average of the five readings was calculated.

2.6. Surface roughness test
Surface roughness was measured according with ANSI/ADA specification no.12, 2002 by a profilometer (TR 220, Beijing Time High Technology Ltd., China). The profilometer has a sharp diamond-made surface analyser (stylus). The maximum distance that the stylus can travel is 11 mm. Two measurements were taken on different areas of each specimen, and the average of the two measurements was calculated.

2.7. Atomic force microscopy (AFM)
Surface topography of test specimen was examined by AFM (Solver Nano, NT-MDT SI, Ireland) to visualise the distribution of the filler in the polymer matrix and their impact on surface roughness. The thickness of the specimen should be 2 mm to be put under the scanning probe.

3. Results
The result of particle size distribution of nanoparticles was obtained by using AFM, which showed that the average diameter was 94.33 nm. The result of particle size distribution of nanoparticles of group E (5% wt. nano silica and 5% wt. nano zirconia) is shown in Figure 1 and Table 2.
Figure 1. AFM image of group E specimen (PMMA/SiO$_2$/ZrO$_2$ nanocomposites). A: two-dimensional; B: three-dimensional.

Table 2. Granularity accumulation distribution of PMMA/SiO$_2$/ZrO$_2$ nanocomposites.

| Sample: p       | Code: Sample Code |
|-----------------|-------------------|
| Line No.: linen  | Grain No.: 387    |
| Instrument: CSPM| Date: 2020-08-16  |
| Avg. Diameter: 94.33 nm | <=10% Diameter: 75.00 nm |
| <=50% Diameter: 90.00 nm | <=90% Diameter: 115.00 nm |
| Diameter (nm)   | Volume (%)        | Cumulation (%) |
| Diameter (nm)   | Volume (%)        | Cumulation (%) |
| Diameter (nm)   | Volume (%)        | Cumulation (%) |
| Diameter (nm)   | Volume (%)        | Cumulation (%) |
| Diameter (nm)   | Volume (%)        | Cumulation (%) |

| Diameter (nm) | Volume (%) | Cumulation (%) |
|----------------|------------|----------------|
| 75.00          | 4.65       | 4.65           |
| 80.00          | 15.50      | 20.16          |
| 85.00          | 13.18      | 33.33          |
| 90.00          | 13.44      | 46.77          |
| 95.00          | 11.63      | 58.40          |
| 100.00         | 8.27       | 66.67          |
| 105.00         | 9.04       | 75.71          |
| 110.00         | 8.27       | 83.98          |
| 115.00         | 5.68       | 93.80          |
| 120.00         | 4.13       | 96.38          |
| 125.00         | 2.58       | 97.42          |
| 130.00         | 1.03       | 98.71          |
| 135.00         | 1.29       | 98.97          |
| 140.00         | 0.26       | 99.48          |
| 145.00         | 0.52       | 100.00         |
| 150.00         | 0.52       |                |

Descriptive data (mean values, standard deviation, standard error) of the results of impact strengths, transverse strength, hardness and roughness test for both the control group and group E are presented in Table 3.

Table 3. Descriptive data of the study.

| Dependent variables | Control group | Group E (5% wt. nano silica and 5% wt. nano zirconia) |
|---------------------|--------------|-------------------------------------------------------|
| No.                 | mean         | SD          | SE         | No.       | mean         | SD          | SE         |
| Impact strength     | 10           | 3.7887      | .65270     | 10        | 3.8087       | 1.10942     | .35083     |
| Transverse strength | 10           | 17.1694     | 2.55035    | 10        | 17.6800     | 1.47629     | .46684     |
| Hardness            | 10           | 101.4200    | 3.35553    | 10        | 102.2000    | 1.03280     | .32660     |
| Roughness           | 10           | 3.2428      | .99449     | 10        | 3.3730      | 9.7218      | .30743     |
T-test was done to compare the differences between the mean values of control group and group E. P-value of p < 0.05 was considered significant as shown in Table 4.

|                         | Levene’s Test for Equality of Variances | t-test for Equality of Means |
|-------------------------|----------------------------------------|-----------------------------|
|                         | F          | Sig. | t  | df | Sig. (2-tailed) | Mean Difference | Std. Error Difference |
| Impact strength         | 4.988      | .038 | .049 | 18 | .961 | .02000 | .40704 |
| Transverse strength     | .974       | .337 | .548 | 18 | .590 | .51064 | .93186 |
| Hardness                | 9.316      | .007 | .703 | 18 | .491 | .78000 | 1.11024 |
| Roughness               | .042       | .839 | .296 | 18 | .770 | .13025 | .43979 |

4. Discussion
This study investigated the effect of the addition of nano silica/zirconia mixture on impact strength, transverse strength, hardness and roughness of PMMA denture base material. Surface modification of the nanoparticles was done to enhance chemical bonding between the polymer matrix and the filler phase of the material. The AFM topographic image of PMMA/SiO$_2$/ZrO$_2$ nanocomposites shows that nanoparticles were dispersed throughout the polymer matrix in a standardised way. This can be attributed to the use of an ultrasonic probe for the dispersion of the nanoparticles with the liquid monomer. Closer inspection of the image shows that the particle size of the nanocomposite is about 70–140 nm.

4.1. Impact strength test
The impact strength of the PMMA denture base is an important property to investigate as dentures can be subjected to a sudden impact force, such as an external blow to the face or dropping the denture on the floor. This property measures the amount of energy absorbed by the specimen before fracture when subjected to a sudden force [32]. The results of this study show that the impact strength values of the experimental group were higher than the control group; this could be due to high interfacial strength between the nano filler and the matrix as a result of the creation of cross-links or supra-molecular bonds covering or protecting the nano fillers, which in return prevent the spread of cracks. The proliferation of cracks may also be prevented by a strong bonding between the nano fillers and the resin matrix arising from the bonding of the functional groups on the surface of nanoparticles (created by the salinisation) and the polymer chains. Additional improvement of the mechanical properties could be due to nanoparticles filling the spaces between the polymer chains and thus filling the interstitial polymer regions to produce a heterogeneous mixture and to prevent the displacement of the polymer chain segments. In addition, nanoparticles characterised by a large specific surface area thus have the ability to dissipate energy that causes crack propagation and can hence improve impact strength [33]. This result may agree with a previous study in which a mixture of two nano fillers (ZrO$_2$-Al$_2$O$_3$) was added to PMMA, and the impact strength was improved [34].

4.2. Transverse strength test
Transverse strength is one of the mechanical properties that is particularly useful when testing denture base materials. Dentures are always subjected to three-point bending stresses during chewing and mastication, and the transverse strength test is the closest match to the forces inside the mouth. Transverse strength is composed of compression, tension and shear strength [35].

The transverse strength values of this study show that reinforced PMMA composite had higher transverse strength compared to the control group. This may be due to the good distribution of the very fine and various-sized nano fillers within the polymer that enabled them to be embedded between the
linear macromolecular chains of the polymer and fill spaces between the chains, thus limiting the segmental motions of the macromolecular chains and improving the transverse strength and rigidity of the resin.

The increase in transverse strength can also be clarified by transformation toughening; as adequate stress arises and cracking starts to propagate, a transformation phase of nano silica and zirconia depletes the energy of crack propagation. The expansion of nano SiO$_2$ and ZrO$_2$ crystals also takes place in this phase, which puts the crack under compressive stress, and crack propagation is arrested. A similar finding was reported when zirconia nano filler was added to PMMA, and a significant increase in transverse strength value was obtained [28].

Increased transverse strength may also be attributed to the transition of stress from more flexible polymer to stiffer and more stable filler particles. This result may agree with a study in which nano zirconia was added to heat curing acrylic denture base material, and transverse strength was increased with 5% by wt. nano filler loading and decreased with 7% by wt. nano filler loading [36].

4.3. Surface hardness

Hardness is described as the material’s resistance to plastic deformation and is usually calculated under an indentation charge. The current study shows that the increase in hardness of reinforced PMMA was relevant to the amount of filler loading in the polymer matrix and to the dispersion homogeneity of hard and rigid nano zirconia and nano silica within the material. The increase in hardness of the nanocomposite could also be explained by the increase in cross-linking density, which made the polymer more rigid and more resistant to penetration. The slight increase in hardness shown in this study may agree with the result obtained by another study where SiO$_2$ nanoparticles was added to PMMA in a weight percentage of 5% [37].

4.4. Surface roughness

Surface roughness provokes the adhesion and retention of Candida albicans, which is especially important in denture-induced stomatitis pathogenesis [37]. Therefore, a material should possess a smooth and polished surface so that plaque accumulation is minimised or avoided. Compared with the control group, the surface roughness of modified PMMA was insignificantly increased. This may be attributed to the difference in the particle size of the nano fillers and the acrylic denture base material as well as to the relatively high filler loading amount, which could cause the formation of some filler aggregates on the surface.

5. Conclusion

Within the limits of this study, it can be concluded that the incorporation of a mixture of nano silica and nano zirconia into PMMA denture base material can potentially increase some mechanical properties such as impact strength, transverse strength and hardness with an insignificant effect on surface roughness. To obtain such results, 5% by weight nano silica and 5% by weight nano zirconia was the optimum amount of nano fillers.

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