Impact of different surface treatments and repair material reinforcement on the flexural strength of repaired PMMA denture base material

Mohammed M. GAD1, Ahmed RAHOMA2, Reem ABUALSAUD1, Ahmad M. AL-THOBITY1, Sultan AKHTAR3, Mohamed A. HELAL4 and Fahad A. AL-HARBI1

1 Department of Substitutive Dental Sciences, College of Dentistry, Imam Abdulrahman Bin Faisal University, P.O. Box 1982, Dammam 31411, Saudi Arabia
2 Department of Restorative Dental Sciences, College of Dentistry, Imam Abdulrahman Bin Faisal University, P.O. Box 1982, Dammam 31411, Saudi Arabia
3 Department of Biophysics, Institute for Research and Medical Consultations, Imam Abdulrahman Bin Faisal University, P.O. Box 1982, Dammam 31411, Saudi Arabia
4 Department of Removable Prosthodontics, Faculty of Dentistry, Al-Azhar University, Cairo, Egypt

Corresponding author, Mohammed M. GAD; E-mail: mmjad@iau.edu.sa

This study assessed the impact of surface treatments and repair resin reinforcement with zirconium oxide nano-particles (nano-ZrO2) on flexural strength (FS) of repaired denture base. A total of 320 heat-polymerized acrylic resin specimens were prepared and sectioned creating 2-mm gap. According to repair surface treatment, specimens were distributed into four groups: I) methyl methacrylate (M); II) alumina-blasted (AB); III) AB+silane coupling agent (SC); and IV) AB+ methacrylate based composite bonding agent (MA). Groups were subdivided into 4 (n=20) according to nano-ZrO2 concentration (0, 2.5, 5, 7.5 wt%). Half the specimens were thermo-cycled before testing. FS was determined by three-point bending test. Statistical analysis was done using ANOVA and Tukey-Kramer multiple comparison tests, with $p=0.05$. Alumina-blasting+(SC) or (MA) significantly increased FS of repaired specimens compared to control ($p<0.05$). All surface-treated specimens combined with nano-ZrO2 reinforced repair resin significantly increased FS.

**Keywords:** Denture repair, Surface treatment, Flexural strength, Silane coupling agent, ZrO2 nanoparticles

**INTRODUCTION**

Although polymethylmethacrylate (PMMA) resin is a common material used for denture base fabrication, it possesses some drawbacks. One of which is the low mechanical strength creating prostheses that are unable to maintain durability over a long period of time. Denture base acrylic resin is subjected to various types of masticatory forces during intra-oral function leading to fatigue. Consequently, fracture of denture bases may occur1,2. New denture fabrication is a line of treatment; but it is a time consuming and relatively expensive procedure, which motivates the clinicians to attempt repair of the broken denture2,3. Requirements of denture repair should include satisfactory strength of repair material, dimensional stability, good color match, ease of repair process, and quick procedure4,5. One of the materials that possess these requirements is the heat-polymerized acrylic resin. It demonstrates high mechanical properties; however, its use is restricted due complicated laboratory procedures which are time-consuming in addition to the risk of denture distortion by heat6,7. Therefore, auto-polymerizing repair resins are frequently used for denture base repair8,9.

Recurrent fracture of the repaired denture frequently occurs due to poor bond strength between the resin of denture base and repair resin8,9. Therefore, repair surface treatment was suggested. The interface between the original denture base resin and repair resin is considered the weakest area of denture repair7. To overcome this problem, attempts have been made to enhance the bond strength between the two resins (denture base and repair resin) using different chemical or mechanical surface modifications2,8. In addition to repair material, the repair surface design is also important as it influences the bond strength. Among butt, round, bevel, rabbet, inverse rabbet, inverse and knife edge joints, the bevel joint demonstrated the highest mechanical property in addition to its simple clinical application8,9. According to the results of previous studies, repaired acrylic resin samples of bevel shaped edge showed higher values of transverse strength as compared to repaired samples of butt shaped edge repaired under similar conditions. The geometry of 45° bevel increased the interfacial bond area and shifted the pattern of interfacial stress toward shear stress rather than the damaging tensile stress9,10.

Chemical or mechanical surface treatments of the acrylic resin base material change the surface topography or chemistry of the treated surface to better adhesion2,9. Surface conditioning increases the surface energy that results in better wetting for bonding. The chemical solvents, such as acetone, methyl methacrylate (MA), chloroform and methylene chloride are used to prepare the repair surface and change the topography to achieve good surface adhesion and improve bond strength2,3,9.

Generally, roughening the repair surfaces is an acceptable...
act to improve repair strength. A number of techniques have been applied to obtain better micromechanical retention of repaired broken dentures. These include roughening with burs or airborne-particle abrasion. In 2013, Alkurt et al., studied the effect of airborne-particle abrasion using 250-μm aluminum oxide particles and found a significant improvement in flexural strength (FS) of repaired denture base compared to chemical treatment. Also, airborne abrasion of the surface with alumina particles proved to be a promising technique in repair strength improvement due to its ability to create micro-pores significant for the process.

Bonding of repair resin matrix to intermediate wetting agent is based on the unconverted C=C double bonds. Several authors have addressed the issue of chair side repair of indirect esthetic restorations with composite and clarified the importance of silane coupling agent application following the modification of surface texture of repair surfaces. For composite repair, Tezvergil et al., proposed roughening the surface mechanically followed by the application of intermediate agent using adhesive system and/or silane. Although this method showed some positive effects on composite material repair, it is not used for PMMA denture base repair. Silane coupling agents (SC) were used to provide good adhesion through chemical bond formation between organic surfaces (resin materials) and inorganic surfaces (metal oxide particles). It is capable of improving wettability of irregular surfaces. The bonds formed between (SC) and repair resin depend on C=C. As (SC) contains C=C, additional polymerization results in strong covalent bonds between (SC) and repair resin. The application of bonding agent (MA) as an intermediate layer is also advisable. It is claimed that the bonding agent enhances the surface wettability of repair surfaces. Both agents, (SC) and (MA), penetrate the micro-pores of repair surfaces resulting in micro-mechanical interlocking.

In addition to repair surface treatment, various methods have been investigated for enhancing the strength of the repaired parts by means of metal wire, mesh, fiber and filler reinforcement of broken acrylic dentures. Nowadays, nanotechnology has invaded this field and resulted in improvement of the properties of denture repair. The addition of zirconium oxide nanoparticles (nano-ZrO2) was found to significantly improve the repair strength. Nano-ZrO2 was suggested due to its favorable properties, such as respectable surface properties, biocompatibility and biological properties. Great enhancement in the repair strength was found with nanoparticle reinforcement, depending on the application and manipulation. The addition of nano-ZrO2 to PMMA significantly improved flexural and impact strengths, and the highest values of flexural and impact strengths were observed in PMMA denture bases reinforced with 7.5 wt% nano-ZrO2. Over time with intra-oral use, denture base and auto-polymerized repair resin are exposed to a wet environment with fluctuating temperatures. It is essential, therefore, to explore whether these changes in oral temperatures would affect the mechanical properties of repaired dentures. Inclusion of thermal cycling test has been recommended as part of the testing protocol for denture base materials to simulate intra-oral conditions. Thermal cycling involves subjecting the tested materials to temperature extremes using temperature controlled water baths in a lab setting.

Finally, reports have confirmed that the most important factors affecting repair strength are reinforcement material and surface treatment in addition to repair material and method, and surface design. Even with controlled repair conditions and improved strength, the highest reported type of denture fracture was adhesive failure. Aiming to improve the bond strength of denture/repair resin interface, the present study was directed to evaluate the effect of chemical treatment using alumina blasting combined with chemical treatment using (SC) or (MA) which were not investigated before, in addition to investigating the effect of nano-ZrO2 reinforcement on the FS of repaired denture base material. Furthermore, the treated surfaces are to be assessed by means of SEM. The first null hypothesis is that the mechanical surface treatment and chemical agent application to repair surfaces will not affect the FS of repaired heat-polymerized denture base resin. The second null hypothesis is that the nano-ZrO2 addition to repair material in combination with surface treatment will not affect the strength of repaired heat-polymerized denture base resin.

MATERIALS AND METHODS

Specimens preparation
A total of 320 specimens were prepared using the following technique. According to American Dental Association Specification no. 12, custom metal molds with internal dimensions of (65×10×2.5±0.1 mm) were fabricated. Acrylic specimens were prepared using the conventional water bath technique using metal flasks. Processing of the specimens was done using water bath curing unit (KaVo Elektrotechnisches Werk, Leutkirch, Germany). The temperature was brought up from room temperature to 74°C, then increased to 100°C for 30 min. After cooling, the flask was opened and acrylic specimens were retrieved, finished using a tungsten carbide bur (HM 79GX-040 HP; Meisinger, Centennial, CO, USA) and polished using acrylic polishing bur (FINOPOL Polishers, 64830, LABOSHOP, Germany). Dimensions of the specimens were checked using a digital caliper (Extra-large LCD screen digital caliper, Neiko tool USA, China) with precision of 0.01 mm. The final polishing was accomplished using rag wheel and fine dental pumice on dental lathe.

Preparation of specimens for repair
Two lines were drawn 1 mm away on each side of the specimen center and the area between these two lines was cut using hard metal disk; creating 2-mm-gap for repair. Beveling was done by drawing a line 1 mm away from the sectioned surfaces at the top of the specimen.
and zero distance at the base. These lines were used as guides for standard bevel preparation. Identification marks were placed on both parts of the specimen to easily reassemble the pairs of each specimen (Fig. 1A–F). Specimens were distributed randomly into 4 groups depending on repair surface treatment and 4 subgroups (n=20) according to nano-ZrO₂ concentration (Table 1).

**Repair surface treatment**

The materials and their chemical structure are presented in Table 2. The bonding area on each side of repair surface was defined using a masking tape with 4.0 µm thickness. For group I, (M), forty pairs of specimens were treated using methyl methacrylate monomer for two minutes. Group II, Alumina blasting group (AB), a sandblasting machine (CEMAT-NT3, Wassermann Dental-machine, Hamburg, Germany) was used for mechanical treatment of remaining pairs of specimens using alumina particles (50 µm) under air-pressure of 380 kPa for 15 s and 10 mm distance from the nozzle and a perpendicular angle to the surface\(^{11,23}\). Following this, specimens were cleaned in an ultrasonic bath for 4 min to remove the traces of alumina particles. Group III (AB+SC), treated with AB+silane coupling agent (SC) where micro-brushes were used to apply a layer of (SC) and the specimens were left aside for one hour to insure...
Table 2  Chemical structure and composition of materials used in this study

| Material                              | Name and manufacturer                          | Compositions                                                                 |
|---------------------------------------|------------------------------------------------|-------------------------------------------------------------------------------|
| Aluminum oxide particles (Al₂O₃)      | Korox50 (Bego Bermer Goldschlagerei, Wilh. Herbst, Bremen, Germany) | O<sub>2</sub>Al<sub>2</sub>O<sub>4</sub>                                          |
| Alumina (50 µm)                       |                                                 |                                                                               |
| Silane coupling agent (SC)            | 3-(Trimethoxysilyl) propyl methacrylate (Shanghai Richem International, Shanghai, China) | H₃C<sub>12</sub>C<sub>11</sub>O<sub>5</sub>Si<sub>2</sub>OH<sub>2</sub>             |
| Methacrylate based composite bonding agent (MA) | Tetric N-Bond Universal (Ivoclar Vivadent, USA) | MDP (methacryloyloxydeyl dihydrogen phosphate); MCAP (methacrylated carboxylic acid poly); HEMA (hydroxyethyl methacrylate); D<sub>3</sub>MA (decadiol dimethacrylate); Water, ethanol, highly dispersed silicon dioxide, initiators, and stabilizers |

solvent evaporation. Group IV (AB+MA), treated with AB+methacrylate based composite bonding agent (MA), where (MA) was applied and cured for 30 s using light cure unit (LEDition, Ivoclar Vivadent, Amherst, NY, USA) of high intensity (1,500 mW/cm²) at 3 mm distance.

Silanization of ZrO₂ nanoparticles and PMMA/ZrO₂ nanocomposite preparation

The nano-ZrO₂ powder (99.9% purity, 1314-23-4, Shanghai Richem International, Shanghai, China) with average size of 40 nm (Fig. 2A) and crystalline structure (Fig. 2B) was used<sup>26</sup>. Silane coupling agent (SC) [(3-(trimethoxysilyl) propyl methacrylate (TMSPM)] (Shanghai Richem International) was used to treat nano-ZrO₂ creating reactive groups on its surface to allow for better adhesion between resin matrix and nano-ZrO₂<sup>17,25</sup>. This treatment is done by adding 0.3 g of TMSPM to 100 mL of acetone and 30 g of nano-ZrO₂. The mixture was stirred with a magnetic stirrer (Cimarec Digital Stirring Hotplates, SP131320-33Q, Thermo Scientific, Shanghai, China) for 60 min, then the solvent was eliminated using a rotary evaporator under vacuum for 30 min at 60°C and 150 rpm. Next, nano-ZrO₂ particles were heated at 120°C for 2 h then cooled to room temperature to get
the surface-treated nano-ZrO$_2$\textsuperscript{17,25,26}. To prepare PMMA/ 
ZrO$_2$ nanocomposite, the amount of treated nano-ZrO$_2$ 
particles were weighted using electronic balance (S-234, 
Denver instrument, Goettingen, Germany) to be added 
in concentrations of 2.5, 5, and 7.5 wt% of the auto-
polymerized acrylic powder (Major repair, Major Prodotti 
Dentari, Moncalieri, Italy). The PMMA/ZrO$_2$ mixtures 
were thoroughly mixed, stirred with a blender at 400 
rpm for 30 min to equally distribute nano-ZrO$_2$ within 
acrylic powder\textsuperscript{17,27}. Each group was divided into 4 sub-
groups (n=20) depending on nano-ZrO$_2$ concentrations 
(0, 2.5, 5 and 7.5 wt%, Table 1).

**Repair procedure**
Each pair of a specimen was reassembled and fixed 
into the metal mold with repair gab of 2 mm at the 
base of the specimen. According to the manufacturer’s 
recommendations, the repair material was mixed and 
packed into the repair gap with slight overfill to allow 
for compensation of polymerization shrinkage. To 
complete the polymerizer procedures, the repaired 
specimens were placed in a pressure pot for 30 min at 
2-bar pressure\textsuperscript{28}. Once the resin polymerization was 
completed, the sections of the mold were loosened and 
specimens were retrieved for finishing. The excess acrylic 
was eliminated using a tungsten carbide bur followed by 
a 600-grit abrasive paper with copious amount of water. 
A digital caliper was utilized to confirm the dimensions 
of repaired specimens (Fig. 1G, H). Half of the specimens 
were stored in distilled water at 37°C for 48±2 h. The 
remaining half was stored in distilled water at 37°C 
for four weeks then subjected to thermal stress using 
a thermal cycling machine (Thermocycler THE-1100, 
SD Mechatronik, Feldkirchen-Westerham, Germany) 
for four weeks then subjected to thermal stress using 
a thermal cycling machine (Thermocycler THE-1100, 
SD Mechatronik, Feldkirchen-Westerham, Germany) 
where they were stressed for 5,000 cycles at 5 and 55°C 
with 30-s dwell time\textsuperscript{29}.

**FS test**
Three-point bending test was employed to measure the 
FS using the universal testing machine (Instron 8871, 
Instron, Norwood, MA, USA). All specimens were 
horizontally positioned on a three-point flexural device 
keeping a distance of 50 mm between the two supports. 
At midpoint of the specimen, a load cell (50 kgf) with a 
crosshead speed of 5 mm/min was applied until specimen 
fracture occurred and the load at fracture was recorded. 
The formula $S=3WL/2bd^2$ was used for FS calculation, 
where $S$ is the FS (MPa), $W$ is the load causing specimen 
fracture (N), $L$ is the distance measured between the two 
supports, $b$ is the specimen width, and $d$ represents the 
specimen thickness\textsuperscript{9,14}.

**Statistical analysis**
SPSS-20.0 (IBM, Chicago, IL, USA) was used to 
statistically analyze the results using one-way analysis 
of variance (ANOVA). The test was run twice, once 
for the data before thermal cycling and another time 
after thermal cycling. After having significant $p$-value 
in both, pairwise comparisons were done using Tukey-
Kramer multiple-comparison test to compare the mean

of control group with the interventional groups as well 
as within interventional groups. Groups were considered 
significantly different if $p$-value was ≤0.05. ANOVA was 
used to test the overall significance of FS between all 
groups (Table 1).

**Scanning electron microscope (SEM) and transmission 
electron microscope (TEM) examination**
SEM is readily utilized to examine the surface 
morphological features of the specimens. In this study, 
the impact of repair treatments and incorporation of 
nano-ZrO$_2$ particles on the surface morphology of the 
resin base and fractured surfaces were examined using 
SEM (Inspect S50, FEI, Brno, Czech Republic). Specimens 
were mounted on metallic stubs using conductive carbon 
tape then gold coated prior to examination using a 
sputter coating machine (Q150R ES, Quorum, East 
Sussex, UK). The SEM unit was operated at 20 kV to 
capture several electronic micrographs at magnification 
of ×5,000. The representative SEM micrographs of 
specimens before repair were taken at magnification 
of ×2,000. The morphology and structure of nano-ZrO$_2$ 
particles (used in this study) were analyzed using TEM 
(Morgagni 268, FEI). More than 80 individual particles 
were measured from different TEM images to obtain a 
size histogram. The details of this analysis were described 
diselsewhere\textsuperscript{26}. To determine the nature of failure of each 
specimen, the percentage of attached repair material on 
repair surfaces was calculated. The failure is considered 
adequate if there was up to 25% of repair resin at the 
interface; cohesive if there is more than 75% of area 
fracture in the denture base resin or repair resin, while 
the mixed failure is seen when there is a cohesive and 
adequate failure combined with 25–75%.

**RESULTS**
The mean FS values, standard deviation, and statistical 
differences between surface treatments, and nano-ZrO$_2$ 
concentrations before and after thermal cycling were 
summarized in Table 3. Considering specimens without 
thermocycling treatment, and in comparison to control 
group (M), FS values of surface treatment, sandblasting, 
silane coupling agent treatment, methacrylate bonding 
agent, nano-ZrO$_2$ addition interaction were all statically 
significant ($p<0.05$). Comparing the FS of surface 
treated specimens repaired with pure repair acrylic 
resin (M, AB, SC, and MA groups) revealed significant 
differences between all unreinforced groups and (M) 
group. (SC) group significantly showed the highest 
FS value (66.45±3.43 MPa) of any unreinforced group 
compared to M (57.30±1.97 MPa), AB (61.75±3.29 MPa) 
and MA (62.05±1.72 MPa) with (AB) and (MA) being 
non-significantly different from each other. Thermal 
cycling decreased the values of all groups with significant 
differences between (TM) and all unreinforced groups 
($p<0.05$) with insignificant difference between (TAB) 
and (TSC).

Within group I, in comparison to (M), a significant 
increase in FS was found with groups (M1, M2, and
Table 3  Mean, SD, and significance of flexural strength for tested specimens before and after thermal cycling

| Nano-ZrO₂ concentration | No Thermal cycling M (Group I) | No Thermal cycling AB (Group II) | No Thermal cycling AB+ SC (Group III) | No Thermal cycling AB+ MA (Group IV) |
|--------------------------|--------------------------------|---------------------------------|---------------------------------------|--------------------------------------|
| Unreinforced             | 57.30±2.3 (M)²                | 61.75±3.3 (AB)²                | 66.45±3.4 (SC)                        | 62.05±1.7 (MA)²                      |
| 2.5%-Nano-ZrO₂           | 71.12±2.2 (M1)                | 78.36±2.5 (AB1)²              | 84.11±2a (SC1)                        | 77.74±2.9 (MA1)²                     |
| 5%-Nano-ZrO₂             | 79.62±1.6e (M2)⁴             | 84.58±2.9a (AB2)⁴            | 86.55±2.2a (SC2)                      | 82.12±1.8a (MA2)⁴                    |
| 7.5%-Nano-ZrO₂           | 81.18±1.7e (M3)⁴             | 85.79±2.3a (AB3)⁴            | 89.63±2 (SC3)                        | 84.11±1.5e (MA3)⁴                    |

²(M) Monomer; (AB) Alumina blasting; (SC) Silane coupling agent; (MA) Methyl methacrylate based composite bonding agent; (T) Thermal cycling.

*Same lowercase letters show nonsignificant differences within the surface treatment groups vertically (within respective column). While same uppercase letters identify nonsignificant differences between reinforced groups horizontally (within respective row).

Within group II, results presented a significant difference between pure repair resin and all nano-ZrO₂ concentrations, where a significant increase was reported (<0.05) for all sub-groups (AB1, AB2, and AB3). Moreover, significant differences were found between (AB1/AB2), and (AB1/AB3) with no difference between (AB2/AB3). After thermal cycling, the results showed significant increases in FS of all reinforced groups with (TAB3) showing the highest FS value (84.01±1.7 MPa).

Within group III, it was found that the FS significantly increased with all nano-ZrO₂ concentrations in comparison to pure repair resin (SC), and this increase is proportionate to the filler content. Between nano-ZrO₂ modified repair resin subgroups in group III, results showed significant differences between (SC1/SC3) and (SC2/SC3) with insignificant difference between (SC1/SC2). The heights FS value recorded for this study was reported with SC3 (89.63±2.1 MPa) followed by SC2 (86.55±2.2 MPa) and AB3 (85.79±2.3 MPa). After thermal cycling, significant differences were found between (TSC) and all reinforced groups (TSC1, TSC2, and TSC3). No significant difference was found between the latter 3 groups with the highest FS value recorded with TSC3 (81.96±1.9 MPa).

Within group IV, there were significant differences between (MA) and all other subgroups (MA1, MA2 and MA3) and between (MA1/MA2) and (MA1/MA3) with no significant difference between (MA2/MA3). After thermal cycling, significant differences were found between (TMA) and all other subgroups (TMA1, TMA2, and TMA3) while no significant difference was found between the latter 3 groups with the highest FS value recorded for TMA3 (65.69±2.4 MPa). Looking at the effect of thermal cycling for each respective group, it was found that all groups showed significant decreases in FS after thermal cycling except (AB/TAB), (AB1/TAB1), and (AB3/TAB3) (p>0.05).

The representative electronic micrographs with ×2,000 of the four surface treatments: control, air-borne particle abrasion (sandblasting), silane coupling agent, and methacrylate bonding agent before repair are shown in Fig. 3. The monomer treated specimen (Fig. 3A), showed a smooth surface while (Fig. 3B) showed several surface irregularities, hollows, and small pits produced by alumina blasting treatment. The application of silane coupling agent and methacrylate bonding agents on sandblasted surfaces resulted in them flowing into the surface irregularities and filling the created pits and fissures (Figs. 3C, D) giving a porous but smoother surface topography than sandblasting alone. Figure 4 shows the fracture surfaces of treated and repaired specimens with pure acrylic resin. The surface treated with monomer appeared smooth with flake-like sheets (Fig. 4A), while it was showing irregularities with multiple lamellae and steps due to alumina abrasion, with and without the addition of coupling agents/methacrylate bonding agent (Figs. 4B, C and D). The representative SEM images of the fractured specimens with surface treatment with the addition of nano-ZrO₂ particles are shown in Figs. 5 and 6. SEM observations of the surfaces of these groups (groups I–IV) revealed several kinds of morphological features, such as scratches, valleys, and cracks. Moreover, a number of nano-ZrO₂ particles were seen throughout the surface...
Fig. 3  Scanning electron microscopy images of the surface-treated acrylic resins before bonding at magnification of 2,000×. 
[A] control specimen (M), [B] treated with alumina abrasion (AB), [C] treated with silane coupling agent (SC), and [D] treated with composite bonding agent (MA).

Fig. 4  Scanning electron microscopy images of the fractured specimens treated with [A] monomer (M), [B] alumina abrasion (AB), [C] alumina abrasion (AB)+silane coupling agent (SC), and [D] alumina abrasion (AB)+methacrylate bonding agent (MA).
Fig. 5  Scanning electron microscopy images of the fractured specimens (group I, A–C), and treated chemically with monomer (M) and repair resin reinforced with [A] 2.5% nano-ZrO$_2$, [B] 5% nano-ZrO$_2$, and [C] 7.5% nano-ZrO$_2$; (group II, D–F) treated with alumina abrasion (AB) and repair resin reinforced with [D] 2.5% nano-ZrO$_2$, [E] 5% nano-ZrO$_2$, and [F] 7.5% nano-ZrO$_2$.

Fig. 6  Scanning electron microscopy image of the fractured specimens (group III, A–C) treated with alumina abrasion (AB)+silane coupling agent (SC) and repair resin reinforced with [A] 2.5% nano-ZrO$_2$, [B] 5% nano-ZrO$_2$, and [C] 7.5% nano-ZrO$_2$; (group IV, D–F) treated with alumina abrasion (AB)+bonding agent (MA) and repair resin reinforced with [D] 2.5% nano-ZrO$_2$, [E] 5% nano-ZrO$_2$, and [F] 7.5% nano-ZrO$_2$. 
filling spaces and voids in the resin. For specimens of groups II–IV, the nature of failures was mainly cohesive and mixed while it was mainly adhesive failure for group I (Fig. 7A). After thermal stress, a dramatic change in the nature of failure was noticed and adhesive failure was the dominant one (Fig. 7B).

DISCUSSION

The ultimate goal of denture repair is to attain durable bond strength between repair material and denture base resin, ideally matching the original strength. To restore original strength of denture base after repair, this study introduced a new method to improve the resin/repair interface through the combination of repair surface treatments with intermediate bonding agents and repair material reinforcement, and evaluated their effects on the FS. Based on the results of this study, all surface treatments as well as all concentrations of nano-ZrO₂ addition to repair material significantly increased the FS (p<0.05) of repaired acrylic resin. Therefore, both null hypotheses were rejected.

Different studies have mentioned that the repair surface treatment with monomer increased the bond strength due to changes in the surface morphology after monomer application which resulted in mechanical interlocking between the denture base resin and repair resin and consequently increased the FS. Because monomer application is widely employed as a conventional method for chemical surface treatment, it was used as a control group in this study.

The results of this study revealed an increase in FS with air-borne alumina abrasion (AB) compared to control group. In (AB) group, as the surfaces were alumina blasted using compressed air, the particles hit the surface creating high temperatures locally resulting in the transfer of kinetic energy and penetration into the repair surface, which creates micro-retentive surface textures (irregularities, fissures, cracks, and pits) and increases the surface area for bonding (Fig. 4B). Accordingly, alumina blasting showed higher FS values expressed by the nature of failure (cohesive), than that generated by monomer surface treatment (mostly

![Nature of Failure- Before Thermal Cycling](image)

![Nature of Failure- After Thermal Cycling](image)

Fig. 7 Nature of failure of fractured specimens. [A] before thermal cycling, [B] after thermal cycling.
adhesive). The results of this study come in agreement with previous studies\cite{2,3}, where the effect of mechanical surface treatment using (AB) produced significantly high repair strengths due to the increase in surface area for adhesion in addition to the interlocking of some alumina particles on the surface\cite{9}.

The results of the present study revealed that the application of (SC) on repair surface modified by (AB) increased the FS of repaired acrylic resin compared to control group. This increase may be due to the synergistic effect of (SC) through micro-mechanical interlocking and chemical bond formations. The (SC) used in this study is acetone-based type where the solvent action allowed it to penetrate the surface more and increase surface irregularities, resulting in larger bonding area. Similar to previous studies\cite{1,3,4,34,35}, using acetone as a wetting agent for repair surface treatment was found to slightly soften the surface and create a porous topography (smoother surface but with more superficial pits). Subsequently, increasing surface area and repair strength. As mentioned before, (SC), has two reactive functional groups that can react, couple, and unite different materials forming a strong bond\cite{11}.

As shown in Table 3, it is found that mechanical treatment using air-borne alumina particle abrasion and further application of (MA) increased the FS of repaired specimens. The increase may be due to the combined effect of both treatments. This finding is supported by the observation that the nature of failure was commonly cohesive, in contrast to control group. The use of free flowing bonding agent has proved to increase repair bond strength by micro-mechanical interlocking through penetration of the micropores created by (AB) of repair surfaces. The impact of bonding agents on FS is strongly related to its wetting effect and low viscosity in contrast to repair resin which has high viscosity and limited penetration capacity into the surface micro-structures\cite{36}. On the other side, is the direct chemical bond between bonding agent and repair resin\cite{19,36}. Bonding of resins is accomplished originally by covalent chemical bonds between unreacted group (C=C) of bonding agent on the surface of denture base resin and repair resin\cite{19,36} which depends on the rate of new material copolymerization with these unreacted groups\cite{36,37}. Based on the findings of this study, micro-mechanical interlocking is found to be a prime factor for increasing the repair bond strength. However, the application of bonding resin as an intermediate agent is advisable to enhance this bond.

The present study demonstrated differences in the results between (SC) and (MA). (MA) group showed lower FS values with more adhesive failures (Table 3 and Fig. 7A). Although (SC) and (MA) were applied on blasted surfaces in a similar manner using micro-brushes, the difference in the reaction of the agents may have caused this variation in results. Evaporation of the solvent in the (SC) leads to the formation of a thin layer possibly allowing for better penetration of repair resin into repair surface. Whereas, after curing of (MA), a thicker adhesive layer is formed on the treated surface which acts as an intermediate layer between resin materials (denture base and repair resin), weakening the interfacial quality and reducing the bond strength.

Comparing the effect of different concentrations of nano-ZrO$_2$ combined with the suggested adhesive techniques, FS values were higher for reinforced groups than those of pure repair resin with the same surface treatment. In agreement with previous studies, the incorporation of nano-ZrO$_2$ with repair resin resulted in a significant increase in flexural, impact, and tensile strengths of repaired acrylic denture base\cite{6,14,24}. The improvement in FS could be related to the reinforcing effect of nano-ZrO$_2$ such as; good distribution within the polymer matrix that promoted filling interstitial spaces of polymeric chains. Additionally, nano-ZrO$_2$ particles possess a property called transformation toughening, by which, nano-ZrO$_2$ transforms from the tetragonal to the monoclinic phase absorbing the energy of a crack. Also, expansion of nano-ZrO$_2$ crystals occurring in this process could place the crack under a state of compression arresting its propagation\cite{16}.

A comparison of the tested properties with and without thermal cycling for each group revealed that FS decreased significantly for all groups, except alumina blasting group (TAB). In the oral cavity, moisture contamination and thermal fluctuation facilitate absorption of water\cite{21}. Absorbed water along with the changes in temperature, may cause degradation of denture polymer\cite{20}. When water molecules penetrate the PMMA mass, they occupy inter-polymeric spaces, forcing the polymer chains apart and affecting the mechanical properties of the resin\cite{20,36}. The rate of water absorption into the resin is influenced by the polarity of PMMA mass and the diffusion of these molecules into interstitial spaces\cite{36}. Heat stress may increase water ingress into the PMMA mass due to the wide separation between polymeric chains. The absorbed water acts as a plasticizer and permits the chains to slide easily under load, decreasing the polymer’s strength\cite{20}.

A previous study observed significant decreases in FS of acrylic denture base after thermal cycling for 5,000 cycles\cite{40}. These results were in partial agreement with the current study, where a significant reduction in in FS after thermal stressing was observed. This reduction may be linked to the effects of water absorption, polymer structure, or dimensional changes of bulky repair material after thermal stress\cite{41}. In the non-thermo-cycled control groups, most of the fractures occurred at the denture base–repair resin interface (adhesive). For other groups, the failure was mainly cohesive in nature, with sporadic mixed failures. The nature of failure differed greatly among the thermo-cycled groups, where the adhesive type was more prevalent in TSC and TMA. This finding confirmed the effect of thermal stress on bond strength at the resin–repair interface. Similar results were obtained by Minami et al.\cite{35}, who reported adhesive failures in thermo-cycled repaired denture bases. The authors attributed the results to the difference in micro-integration between the denture base and the repair resin, and to the formation of micro-cracks at the
interface after thermal cycling\textsuperscript{3,4,5}. Fortunately, after thermal cycling, the groups that were treated with (AB) alone did not show a change of adhesive failure count, however, mixed failure increased, and cohesive failure decreased. On the other hand, some of (SC) treated groups and all (MA) groups showed increased number of adhesive failures after thermal cycling, which indicated the degradation of both (SC) and (MA) at the interface.

Therefore, the results of this study suggest that a combined surface treatment entailing alumina blasting followed by (SC) or (MA) works well for denture repair as pre-treatment for bonding, in addition to repair material reinforcement with nano-ZrO\(_2\). Indeed, the bond strength of auto-polymerizing resin used for the repair of dentures was favorably enhanced.

Even with the positive effects of adhesive techniques evaluated in the current study, the repair method followed did not entirely simulate the oral environment and the repaired specimens were not expose to masticatory simulated stresses. Also, the specimens tested did not resemble a definitive specimen prepared for clinical use where curvatures of the denture follow the contours of the anatomic tissues. The specimens used conformed with the ADA specification for FS testing for the sake of standardization. The length of repair area tested in this study is short, in comparison to longer fractures of an actual complete denture. Therefore, further investigations are essential to evaluate the repair bond strength under simulated clinical conditions. Moreover, further investigations with variable concentrations of nano-ZrO\(_2\), different aging procedures simulating the oral environment and various types of denture base materials are recommended.

**CONCLUSIONS**

Within the limitations of this study, the following conclusions could be drawn:
1. The most effective way to enhance the FS is the mechanical surface treatment, especially with air-borne particle abrasion - using 50 \(\mu\)m alumina particles-followed by the application of (SC) or (MA) agents.
2. The addition of nano-ZrO\(_2\) to repair resin increased the FS of repaired acrylic resin.
3. Although thermal stress affected all groups, alumina blasting alone or in combination with silane coupling agent could be considered a promising method for acrylic denture repair.

**REFERENCES**

1. Rachid RN, Powers JM, Del Bel Cury AA. Repair strength of autopolymerizing, microwave, and conventional heat-polymerized acrylic resins. J Prosthet Dent 2004; 92: 79-82.
2. Sarac SY, Sarac D, Kulunk T, Kulunk S. The effect of chemical surface treatments of different denture base resins on the shear bond strength of denture repair. J Prosthet Dent 2005; 94: 259-266.
3. Minami H, Suzuki S, Minesaki Y, Kurashige H, Tanaka T. In vitro evaluation of the influence of repairing condition of denture base resin on the bonding of autopolymerizing resins. J Prosthet Dent 2004; 91: 164-170.
4. Polyzois GL, Tarantili PA, Frangou MJ, Andreopoulos AG. Fracture force, deflection at fracture, and toughness of repaired denture resin subjected to microwave polymerization or reinforced with wire or glass fiber. J Prosthet Dent 2001; 86: 613-619.
5. Dar-Odeh NS, Harrison A, Abu-Hammad O. An evaluation of self-cured and visible light-cured denture base materials when used as a denture base repair material. J Oral Rehabil 1997; 24: 755-760.
6. Gad M, ArRejaie AS, Abdel-Halim MS, Rahoma A. The reinforcement effect of nano-zirconia on the transverse strength of repaired acrylic denture base. Int J Dent 2016: 2016: 7094056.
7. Gad MM. Evolution of denture repair and a review of new era. J Dent Sci 2017; 2: 000125.
8. Vallittu PK, Lassila VP, Lappalainen R. Wetting the repair surface with methyl methacrylate affects the transverse strength of repaired heat-polymerized resin. J Prosthet Dent 1994; 72: 659-643.
9. Alkurt M, YesliDualnum Z, Gundogdu M. Effect of repair resin type and surface treatment on the repair strength of heat-polymerized denture base resin. J Prosthet Dent 2014; 111: 71-78.
10. Vasthara A, Shetty S, Kamalanaksh Shenoy KK, Shetty MS, Parveen KA, Shetty R. Effect of different edge profile, surface treatment, and glass fiber reinforcement on the transverse strength of denture base resin repaired with autopolymerizing acrylic resin: An In vitro study. J Interdiscip Dent 2017; 7: 31-37.
11. Lucena-Martín C, González-López S, Navajas-Rodríguez de Mondelo JM. The effect of various surface treatments and bonding agents on the repaired strength of heat-treated composites. J Prosthet Dent 2001; 86: 481-488.
12. Tezvergil A, Lassila LV, Vallittu PK. Composite-composite repair bond strength: effect of different adhesion primers. J Dent 2003; 31: 521-525.
13. Della Bona A, Donassollo TA, Demeuro FF, Barrett AA, Mecholsky Jr JJ. Characterization and surface treatment effects on topography of a glass-infiltrated alumina/zirconia reinforced ceramic. Dent Mater 2007; 23: 769-775.
14. Gad MM, Rahoma A, Al-Thobity AM, ArRejaie AS. Influence of incorporation of ZrO\(_2\) nanoparticles on the repair strength of polymethyl methacrylate denture bases. Int J Nanomedicine 2016; 11: 5633-5643.
15. Ayad NM, Badawi MF, Fatah AA. Effect of reinforcement of high impact acrylic resin with micro-zirconia on some physical and mechanical properties. Rev Clin Pesq Odontol Curitiba 2008; 4: 145-151.
16. Asar NV, Albayrak H, Korkmaz T, Turkylmaiz I. Influence of various metal oxides on mechanical and physical properties of heat-cured polymethyl methacrylate denture base resins. J Adv Prosthodont 2013; 5: 241-247.
17. Ahmed MA, Ebrahim MI. Effect of zirconium oxide nano-fillers addition on the flexural strength, fracture toughness, and hardness of heat-polymerized acrylic resin. World J Nano Sci Eng 2014; 4: 50-57.
18. Shen C, Colaiazzi FA, Birns B. Strength of denture repairs as influenced by surface treatment. J Prosthet Dent 1984; 52: 844-848.
19. da Costa TR, Serrano AM, Atman AP, Loguercio AD, Reis A. Durability of composite repair using different surface treatments. J Dent 2012; 40: 513-521.
20. Silva Cde S, Machado AL, Chaves Cde A, Pavarina AC, Vergani CE. Effect of thermal cycling on denture base and autopolymerizing reline resins. J Appl Oral Sci 2013; 21: 219-224.
21. Barclay CW, Spence D, Laird WR. Intra-oral temperatures...
during function. J Oral Rehabil 2005; 32: 886-894.

22) American Dental Association Specification No 12 for denture base polymers Chicago Councilor denture materials and devices. ADA. 1975.

23) Nishigawa G, Maruo Y, Oka M, Oki K, Minagi S, Okamoto M. Plasma treatment increased shear bond strength between heat-cured acrylic resin and self-curing acrylic resin. J Oral Rehabil 2003; 30: 1081-1084.

24) Gad MM, Abualsaud R, Rahoma A, Al-Thobity AM, Al-Abidi KS, Akhtar S. Effect of zirconium oxide nanoparticles addition on the optical and tensile properties of polymethyl methacrylate denture base material. Int J Nanomedicine 2018;13: 283-292.

25) Caravaca C, Shi L, Balvay S, Rivory P, Laurenceau E, Chevolot Y, et al. Direct silanization of zirconia for increased biointegration. Acta Biomater 2016; 46: 323-335.

26) Yu W, Wang X, Tang Q, Guo M, Zhao J. Reinforcement of denture base PMMA with ZrO₂ nanotubes. J Mech Behav Biomed Mater 2014; 32: 192-197.

27) Zhang XY, Zhang XJ, Huang ZL, Zhu BS, Chen RR. Hybrid effects of zirconia nanoparticles with aluminum borate whiskers on mechanical properties of denture base resin PMMA. Dent Mater J 2014; 33: 141-146.

28) Hanna EA, Shah FK, Gebreel AA. Effect of joint surface contours on the transverse and impact strength of denture base resin repaired by various methods: an in vitro study. J Am Sci 2010; 6: 115–125.

29) Giampaolo ET, Jorge JH, Machado AL, Pavarina AC, Vergani CE. Effect of thermal cycling on microleakage between hard chairside relines and denture base acrylic resins. Gerodontology 2010; 28: 121-126.

30) Shimizu H, Ikuyama T, Hayakawa E, Tsue F, Takahashi Y. Effect of surface preparation using ethyl acetate on the repair strength of denture base resin. Acta Odontol Scand 2006; 64: 159-163.

31) Olvera N, de Rijk WG. Effect of surface treatments on the repair strength of a light-activated denture repair resin using censored data. Dent Mater 1994; 10: 122-127.

32) Anusavice KJ, Phillips BW. Phillips’ science of dental materials. 11th ed. Philadelphia: WB Saunders; 2003. p. 237-271.

33) Shimizu H, Kurtz KS, Yoshinaga M, Takahashi Y, Habu T. Effect of surface preparations on the repair strength of denture base resin. Int Chin J Dent 2002; 2: 126-133.

34) Bural C, Bayraktar G, Aydin I, Yusufoglu I, Uyumaz N, Hanzade M. Flexural properties of repaired heat-polymerising acrylic resin after wetting with monomer and acetone. Gerodontology 2010; 27: 217-223.

35) Vojdani M, Rezaei S, Zareian L. Effect of chemical surface treatments and repair material on transverse strength of repaired acrylic denture resin. Indian J Dent Res 2008; 19: 2-5.

36) Rathke A, Tymina Y, Haller B. Effect of different surface treatments on the composite-composite repair bond strength. Clin Oral Investig 2009; 13: 317-323.

37) Rodrigues SA Jr, Ferracane JL, Della Bona A. Influence of surface treatments on the bond strength of repaired resin composite restorative materials. Dent Mater 2000; 25: 442-451.

38) Lin CT, Lee SY, Tsai TY, Dong DR, Shih YH. Degradation of repaired denture base material in simulated oral fluid. J Oral Rehabil 2000; 27: 190-198.

39) Archadian N, Kawano F, Ohguri T, Ichikawa T, Matsumoto N. Flexural strength of rebased denture polymers. J Oral Rehabil 2000; 27: 690-696.

40) Machado AL, Puckett AD, Breeding LC, Wady AF, Vergani CE. Effect of thermocycling on the flexural and impact strength of urethane-based and high-impact denture base resins. Gerodontology 2012; 29: 318-323.

41) Wady AF, Machado AL, Vergani CE, Pavarina AC, Giampaolo ET. Impact strength of denture base and reline acrylic resins subjected to long-term water immersion. Braz Dent J 2011; 22: 56-61.