Investigating Some Properties of Nanocomposites for Dental Restoration Materials

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Abstract

In this work, it was evaluated the wear resistance, hardness, and surface roughness values of resin-based composites that applied in dentistry as restorative materials. The resin composites were made from six types of resin matrixes (A, B, C, D, E, and F) and each one of them has contained different types and ratios of monomers as well as the inorganic nanofillers (SiO$_2$, ZrO$_2$, HA, and Al$_2$O$_3$). For each test, thirty specimens were prepared, which were classified into six groups depending on the types of the resin matrix and fillers used in the composites. The results prove that the nanocomposites that have the lowest rate of wear were the group E which was derived from the resin matrix of the group E that has monomers are (BIS-GMA, meth acrylamide, methacrylic acid, and 1-6 hexanediol methacrylate) with values range from 8.11 to 6.11 mm$^3$/mm depending on the filler type material. All prepared composites resin materials (A to F) showed an increase in their hardness values as regards the reference, group D showed the highest hardness value followed by group B while group C was the lowest. The highest mean roughness was shown in groups A and F with 0.82 and 0.79 μm respectively, while the smoother surfaces among all groups were groups B and D which had significantly fewer roughness values of 0.16 and 0.19 μm respectively.

1. Introduction

Due to their good esthetics, resin composites have recently become the most widely used materials in restorative dentistry and are made up of a polymer resin matrix, nanofillers materials as reinforcement, and coupling agents (Silane). Wear resistance is a critical factor to decide the life expectancy of the resin composites, among other mechanical properties [1-4]. During mastication, direct contact is present between the teeth with the restorations, oral parafunction, abrasive particles in brushing tooth, and chemical effects generated by food components all contribute to the deterioration of restoration materials used in the oral environment [5]. This will result in a lack of sufficient wear resistance [6]. In the oral environment, predicting the wear behavior of restorative materials is an essential clinical challenge, high wear can cause loss of the support of a posterior tooth, failure of vertical
dimension of occlusion, reduce the efficiency of masticatory, and fatigue of masticatory muscles. The restoration not only should appear good when it has installed, but also it should look good over time. Abrasive substances abrade the resin matrix and expose fillers in many circumstances, potentially increasing the roughness of composite restorations surface. The surface roughness can cause the building up of bacterial biofilm a major cause of gingival irritation leads to a rise in the risk of secondary caries [7]. Therefore, it must be mentioned the good surface characteristics of a resin composite provide the clinical longevity of a restoration [8]. As a result, the wear of composite restorative materials is identified to be dependent on the characteristics of reinforcement particles, specifically the amount and size of those particles, [9] as well as the resin composition [10]. Nano filler particles reduced the interparticle gap, resulting in less wear [11]. Effects of adhesive through two touched surfaces, fatigue, abrasion, and corrosive effects are all fundamental processes that act in different combinations depending on the qualities of the materials. The principal clinical wear mechanisms for dental resin composites have long been assumed to be abrasion and attrition [12]. Hardness is another significant metric for determining a restorative material's mechanical strength and resistance to intra-oral softening [13]. It was used to predict the material's wear behavior. It also has something to do with the ease of finishing and polishing. The relationship between a material's hardness and its wear resistance is a point of contention. [14]. The variation of hardness values between all composite restoratives surfaces can clarify the variation in the rate of wear. Consequently, it found that the wear of restorative materials is determined by some factors, especially the hardness of the restorative material [15]. Both the surface roughness value and wear affected the strength of the resultant composites that was increased with a decrease of surface roughness and has significant differences for the same surface roughness values with different directions of scratch [16]. From what was mentioned about the importance of the surface characteristics of the durability of a resin composite as clinical restoration, this study aimed to evaluate the wear resistance, hardness, and surface roughness (Ra) of prepared resin composites based on copolymer matrix to use as restorative materials.

2. Materials and Methods
2.1 Materials
The main used materials are BIS-GMA (40%) as a major monomer and 1-6 hexanediol methacrylate (20%) as crosslinked supplied by Sigma Aldrich/USA Company and other monomers are listed in Table 1. Six groups of resins were used for the production of dental composites; each matrix was prepared from four monomers named to the group of matrix monomers (A, B, C, D, E, and F).

<table>
<thead>
<tr>
<th>Groups</th>
<th>Monomers</th>
<th>Adding Ratio %</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1. 2-ethylhexylmethacrylate</td>
<td>20</td>
<td>MERCK/Germany</td>
</tr>
<tr>
<td></td>
<td>2. methylmethacrylate</td>
<td>20</td>
<td>MERCK/Germany</td>
</tr>
<tr>
<td>B</td>
<td>1. methacrylic acid</td>
<td>20</td>
<td>MERCK/Germany</td>
</tr>
<tr>
<td></td>
<td>2. methacrylate</td>
<td>20</td>
<td>MERCK/Germany</td>
</tr>
<tr>
<td>C</td>
<td>1. methacrylic acid</td>
<td>20</td>
<td>MERCK/Germany</td>
</tr>
<tr>
<td></td>
<td>2. polyethylene glycol 3500</td>
<td>20</td>
<td>MERCK/Germany</td>
</tr>
<tr>
<td>D</td>
<td>1. methacrylamide</td>
<td>20</td>
<td>MERCK/Germany</td>
</tr>
<tr>
<td></td>
<td>2. methacrylic acid</td>
<td>20</td>
<td>MERCK/Germany</td>
</tr>
<tr>
<td>E</td>
<td>1. 2-ethylhexylmethacrylate</td>
<td>20</td>
<td>Aldrich/USA</td>
</tr>
<tr>
<td></td>
<td>2. polyethylglycol</td>
<td>10</td>
<td>Aldrich/USA</td>
</tr>
<tr>
<td></td>
<td>3. bisphenoladimethacrylate</td>
<td>10</td>
<td>Aldrich/USA</td>
</tr>
<tr>
<td>F</td>
<td>1. methacrylate</td>
<td>20</td>
<td>MERCK/Germany</td>
</tr>
<tr>
<td></td>
<td>2. polyethylene glycol</td>
<td>20</td>
<td>Aldrich/USA</td>
</tr>
</tbody>
</table>

Each group was reinforced by different types of inorganic nanoparticles listed in Table 2. For each test, 30 specimens consisting of 5 specimens of every prepared composite one for unreinforced polymer and 4 for each type of the used fillers. Preparation copolymeric matrices and their nanocomposite was achieved under continuous N₂ gas flow as shown in Figure 1, the components of every group of monomers listed in Table 1, were mixed for about 90 minutes, using N₂ is to assist in removing dissolved oxygen. Then 0.4 gm of zinc oxide as an
antibacterial agent, (0.5wt %) accelerator material (DMAEMA) and 0.5wt% of camphor quinine as an initiator, were used with continuous mixing for another 20 minutes to produce matrices as a copolymer. To prepare the nanocomposites, nano-fillers (ZrO$_{2}$, SiO$_{2}$, HA, and Al$_{2}$O$_{3}$) with (2wt %) ratio, were added individually for each set of the matrix monomers mention former in Table 1. Then the same procedures used when preparing the matrices of copolymers were followed. Afterward, each of the prepared specimens was photo-cured and radiated in different positions for 60 s using an instrument of light curing (Elipar Free light 2LED, 3 M ESPE) at the intensity of 1500 mW/cm$^2$. After polymerization and previous to performing any mechanical tests, the entire specimen was kept for 48h in distilled water at 37ºC and 100% humidity.

Table 2: Nano-fillers and their particle sizes, the supplier company used in prepared composites.

<table>
<thead>
<tr>
<th>Filler Type</th>
<th>Particles Size (nm)</th>
<th>Purity%</th>
<th>Supplier Company</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zirconium Oxide</td>
<td>30-40</td>
<td>99.9</td>
<td>Skyspring Nanomaterials</td>
</tr>
<tr>
<td>Silicon Oxide</td>
<td>10-20</td>
<td>99.0</td>
<td>Skyspring Nanomaterials</td>
</tr>
<tr>
<td>HydroxyApatite</td>
<td>25</td>
<td>97.0</td>
<td>Hualanchem.Co.China</td>
</tr>
<tr>
<td>Aluminum Oxide</td>
<td>20-40</td>
<td>99.0</td>
<td>Skyspring Nanomaterials</td>
</tr>
<tr>
<td>Zinc Oxide</td>
<td></td>
<td>99.0</td>
<td>GCC</td>
</tr>
</tbody>
</table>

Figure 1: Schematic presentation and experimental of mixing system.

2.2. Methods

According to the wear test standard described in ASTM D5963-97a, the specimen has a diameter of 1 mm and a length of 2 mm [17]. Wear testing was performed on an open rotating by testing machine Pin -on- Disc. The mass loss of the tested specimens was measured by weighing way, which is the simplest method of determining the wear rate of the tested specimens. After cleaning the specimens, they were weighed by electrical balance before and after the testing process, the resultant loss in weight was applied in the formulas below to determine the rate of wear. A load of the test was a variable load in the range of (1.5 N - 6 N) and the speed and time of sliding were within the range of (0.5 m/sec. - 3.05 m/sec.), (300 sec.), respectively. The wear rate was estimated as follows [18]:

\[
K_c = \frac{V_r x}{X} \quad \text{Where} \quad V_r = \frac{\Delta m}{P_c} \quad x = V_s \times T
\]

\[
K_c = \frac{\Delta m}{P_c \times V_s \times T} = \frac{m_1 - m_2}{P_c \times V_s \times T}
\]  

Where, $K_c$ is the wear rate of composite (mm$^3$/mm), $\Delta m$: Mass loss (g), $m_1$ and $m_2$ are weights of the specimen before and after the test respectively (g), $p_c$ is the density of specimen (g /mm$^3$), $V_s$ is the sliding Speed (mm/s).
WEAR RATE VS FILLERS CONTENT

HARDNESS VS FILLERS CONTENT

Figure 2: Wear rate for hybrid nanocomposites groups (D and E) as a function of filler content (nano-hydroxyapatite) in the composite.

Figure 3: Hardness for hybrid nanocomposites groups (D and E) as a function of filler content (nano-hydroxyapatite) in the composite.
It can be noticed that the values of hardness and surface roughness properties were slightly increased with the addition of (1 wt%) of nHA for both groups of resin, these values continuously increased with increasing of the weight of (nHA) particles and can observe the maximum value of hardness (86.3 for D and 84 for E) and surface roughness (1.02µm for D and 0.76µm for E) were at (4 wt%) of hydroxyapatite. This is due to the previously reported improvement of the mechanical properties that are associated with the increasing content of fillers particles and is related to the high hardness and brittleness that have these particles as compared with the resin matrix. The wear rate has been reduced by adding the (1 wt %) of nHA for groups D and E of resin to reach the lowest value at 2wt% before its jumping to the highest value at 4wt% of nHA. In the 4wt % nanofiller ratio, these properties are significantly increased compared to the control specimens; however, the increase of wear rate and surface roughness is not desirable. Therefore, it can be concluded in this study that the best filler content must be used to achieve the high development in all mechanical properties of copolymers is exactly 2wt%.

3.2. Mechanical Test of the Nanocomposites
From the result wear rate shown in Table 1 and results in Figure 5, it was found that all copolymers (free from fillers) without fillers recorded significantly higher mean weight loss values than the nanocomposites mean values. It was observed that the tested composites, reinforced with different powders of nanoparticles, exhibited different wear rates. These results are in good agreement with other previous studies [17], which explained that these different wear rates may be attributed to the difference in material properties. Particles type, volume by weight, and distribution play a major role to keep the stability of the materials [20, 21]. In addition to the filler system, the filler–matrix coupling also has a significant power on the value of composites wear [22]. From Figure 5 it was found that the value of wear rate was decreased as the nanofillers are added; the lowest value (6.11mm/mm) was noticed at the group (E) of copolymer matrix nanocomposite that contains on SiO$_2$ nanoparticle. While the higher values were for nanocomposite that contains nano-Zirconia with the group (C) of copolymer matrix. The fact that silica particles are harder than the other filler as mentioned before that during testing responded about the high wears resistance of composites contains it. This means that the polymer reinforced with SiO$_2$ fillers has decreased the wear rate (increase abrasion wear resistance) higher than HA, ZrO$_2$, and Al$_2$O$_3$ fillers. And this depends on the compatibility between the components of the matrix material and the inorganic nano reinforcement materials. Moreover, one of the most important factors that affect the abrasions wear resistance is the interfacial properties, it depends on the extent of bonding at the reinforcing interface between the nanoparticles and the matrix material. The larger the contact area, the greater the reinforcement ratio, and this is inversely proportional to the size of the reinforcement particles. Many researchers have mentioned that silica-filled composite has been recommended instead of other filler of composite [23]. This is because of the reinforcement, which is decreased because of a breakdown at the interface of matrix reinforcement or failure in the reinforcement itself. Finally, the mechanical properties of the SiO$_2$ ceramic fillers are harder than others in nature [24].

![Figure 4: Surface roughness for hybrid nanocomposites groups (D and E) as a function of filler content (nano-hydroxyapatite) in the composite.](image-url)
The result of the hardness test in Figure 6 shows an increment of the hardness with the addition (2%wt) ratio of nanoparticles (ZrO₂, SiO₂, HA and Al₂O₃) individually in the copolymer matrix materials. The increment in hardness values is dependent on the type of both fillers and polymeric materials; the highest value of hardness was reached to (85) that seen at nanocomposite which based on copolymers of group D and reinforced by SiO₂ nanoparticle. While the lowest values were for nanocomposites that were based on copolymers of the group (A) and reinforced by Zirconia nanoparticles, as well, was noticed from Figure 6 that hydroxyapatite nanofillers had the maximum value of improvement of two groups (A and C) nanocomposites. This high hardness value of the composites was due to that the existence of particles of filler in resin matrix led to decreasing the movement of polymer chains molecular and destruction of the mobility of the dental composite matrix, especially by the addition of the filler content in nano size, this may be related to the high surface area of fillers which in contact with dental composite material and attribute to increasing the hardness [25, 26].

The difference in hardness values is also clearly observed in this figure that may be certified to the difference in both organic matrices of copolymers and filler types. The chemical composition of monomer content has an important effect on the mechanical properties of resin composites. Therefore, for the same types of filler, some monomers which participate in the composition of copolymers matrices of composite resin have been caused a
considerable enhancement in mechanical properties and led to an increase in values of hardness. Also enhances the hardness values of composites, the uniform dispersion of fillers, as well as, strong interfacial adhesion between resin/fillers must be existing [17]. Fillers are imparting the restorative materials with sufficient strength and hardness to resist the stresses and strains of the oral cavity and reach acceptable clinical longevity [28]. Other factors that affect the hardness of composite material are the nature, volume fraction, and size of the filler, as well as, the interfacial adhesion between the composite components and inorganic nanofiller, and the surface finishing [29]. The size of the filler has an impact on composite hardness, where dental composites that have been reinforced with Nanoparticles have shown high values of hardness over that free from nanofiller. Nanoparticles have a considerable increase in dental composite hardness, which have been reinforced and all used fillers were with nano size and have a dissimilar effect on the composite hardness that connected to filler type. Next, it should be noted that in the current work the highest hardness was obtained with both silica and hydroxyapatite fillers. This can be attributed to the degree of compatibility between each one of these nano-fillers and the components of the matrix material. Besides the filler content in the prepared composite which is constant in this study, and the size of particles, several factors considerably increase dental composite hardness, like: 1) Fundamental characteristics of some of the particles of the filler, like HA, SiO$_2$, and ZrO$_2$. Those particles show strong ionic interatomic bonding for conferring desirable characteristics, like a high level of hardness [30], 2) The regular Nano-particles dispersion gives a sufficient distance amongst particles, which increases the hardness and reinforcement of the composites, 3) Strong interfacial interaction between the inserted Nano-particles and polymer, and 4) Properties of filler particles that are harder show a higher level of hardness of the surface in the composites [31]. A smooth surface is important to continue on dental restorations to avoid many problems such as discoloration and change in brightness as well as to minimize the risk of secondary caries. The formation of bacterial plaque was encouraged rough surfaces, which can be harmful to periodontal health. To achieve the best clinical results, it is important to keep the composite resin surface as smooth as possible [32]. The mean surface roughness (Ra, $\mu$m) values for the composite resins are shown in Figure 7, this figure indicates that the reinforcing of matrixes with nanoparticles leads to a clear increase in surface roughness. Groups A and F showed the highest roughness values of (0.82 & 0.79) $\mu$m respectively. Groups B and D had significantly fewer roughness values (0.16 & 0.19) $\mu$m than all other groups, which created the smoother surfaces among all used resin. It was also found that the highest surface roughness was obtained with the specimen containing (ZrO$_2$) fillers rather than the specimen containing other used fillers (SiO$_2$, Al$_2$O$_3$) while the lowest value was found in composites with HA fillers.

**Figure 7:** Surface roughness of prepared composite as a function of filler type and the type of polymer blends for matrix material.

Many factors have more effect on the surface roughness property, the interaction of these factors is related to composite composition, such as type, size, shape, and distribution of fillers, in addition to the type of resin matrix, the bond efficiency at the filler/matrix interface and the degree of final cure achieved, [33]. It has been important...
to note that restoration with a Ra value of fewer than 1 μm seems to be smooth [34]. Thus, all produced resin composites in this study have optically satisfactory Ra values.

4. Conclusions
The following conclusions were obtained as a result of this study: 1) Successfully using the photopolymerization process to fabricate new dental restorative nanocomposites more than that present in markets including unique monomers and different fillers. 2) The test results showed the wear rate, hardness, and roughness values differed depending on the chemical composition of the matrix components and the kinds of inorganic nanofiller. 3) The nanocomposite that is built on a copolymer of group E containing (methacrylamide and meth acrylic acid monomers) and reinforced by silica nanoparticles showed the highest values in wear resistance (6.11mm³/mm). So, it can be the most promising material in dental restoration. 4) The highest value of hardness was (85) was nanocomposite which is based on copolymers of group D and reinforced by SiO₂ nanoparticles. 5) Nanocomposite that is based on a copolymer of groups B and D have surface roughness (0.16 & 0.19) μm values, which shows better surface roughness properties making it a more clinically suitable option for dental restorative materials.

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Conflict of Interest
There are no conflicts of interest regarding the publication of this manuscript.

References


