Effect of Water Absorption on the Compressive Strength for PMMA Nano Composites and PMMA Hybrids Nano Composites Reinforced by Different Nanoparticles Used in Dental Applications

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ABSTRACT
Poly methyl methacrylate (PMMA), are widely used as a prosthodontic denture base, the denture base materials should exhibit good mechanical properties and dimensional stability in moist environment. In the present research, efforts were made to develop the properties of PMMA resin that used for upper and lower prosthesis complete denture, by addition four different types of nanoparticles, which are fly ash, fly dust, zirconia and aluminum that added with different ratios of volume fractions of (1%, 2% and 3%) to poly methyl methacrylate (PMMA), cold cured resin (castavaria) is the new fluid resin (pour type) as a matrix. In this work, the Nano composite and hybrid Nano composite for prosthetic dentures specimens, preparation was done by using (Hand Lay-Up) method as six groups which includes: the first three groups consists of PMMA resin reinforced by fly ash , fly dust and ZrO2 nanoparticles respectively, the second three groups consists of three types of hybrid Nano composites, which includes ((PMMA:X% fly ash)+ (1%Al + 3% ZrO2 )), ((PMMA:X% fly dust)+ (1%Al + 3% ZrO2)) and ((PMMA:X%nZrO2)+(1%fly ash+3%fly dust)) respectively. As well as, the effect of water absorption was taking into consideration in this study. The compression test results show that the values of the compressive strength with and without the effect of water absorption increased with the addition of Nano powders (fly ash, fly dust, zirconia, and aluminum). Also, the results showed that the maximum values of compressive strength reach to 286.25MPa for (PMMA: 2%nZrO2) Nano composite. Whereas the maximum values of compressive strength for hybrid Nano composite reach to 270MPa for ((PMMA: 2%fly ash) + (1%Al + 3% ZrO2)) hybrid Nano composite. Moreover, the results showed that the maximum value of compressive strength under the effect of water absorption reach to 335MPa in the Nano composite material (PMMA+2% fly dust), whereas the maximum value of compressive strength under the effect of water absorption for hybrid Nano composite reach to 362MPa for ((PMMA: 2% fly dust) + (1%Al + 3% ZrO2)) hybrid Nano composite.

Keywords: Hybrid Nano Composites, Nano Composites, PMMA, Fly Ash nanoparticles, Fly Dust nanoparticles, Aluminum nanoparticles, Zirconium Oxide nanoparticles, Compressive Strength and Water Absorption.
INTRODUCTION

The most popular material has been used for the construction of dentures for many decades is the poly methyl methacrylate acrylic resin (PMMA) and it has many advantages such as accurate fit, stability in the oral environment, inexpensive equipment’s, clinical manipulation and easy laboratory and good aesthetics [1]. This material is still not enough to achieve the ideal mechanical requirements for dental applications although it is the most commonly used in dentistry for fabrication of denture bases. This problem was attributed mainly to its low plaque accumulation and low fracture resistance [2 and 3]. It was found that nearly 70% of dentures had broken within the first 3 years of their delivery in a survey to compare ten types of denture base resins. In a study [4] evaluating the denture fracture, it was reported that 29% of the repairs were because of midline fractures which were more commonly seen in the upper dentures and the rest were other types of fracture and 33% of the repairs were due to de bonded/detached teeth. Composites are multiphase materials that are chemically dissimilar and artificially made and separated by distinct interface [5]. Polymer composite materials reinforced with particles (ceramic, metal particles) can be used for various engineering applications to provide unique mechanical and physical properties with a low specific weight. In order to achieve better mechanical strength, it is usually reinforced with fillers. These fillers can be chosen as particles such as ceramic powders or fibers (aramid, carbon and glass). Ceramic particles with Small size are known to enhance the tribological and mechanical properties of polymers [6]. Fly ash, an industrial waste, because it is a mixture of oxide ceramics, it can be used as a potential filler material in polymer matrix composites. It improves the mechanical and physical properties of the composites [7]. Some researches which are accomplished in this field it’s:

Schajpal, V. K and Sood, S. B., added powders such as silver, copper and aluminum with (99.9 %) purity into PMMA acrylic resin denture base material in different volume fraction of (5%, 10%, 15%, 20% and 25 %) with average particle size of (10 µm). The addition of these metal fillers showed a decrease in the tensile strength and an increase in the compressive strength as the percentage of metal fillers increases. With the addition of these metal fillers, thermal conductivity increased progressively but did not proportionally as the metal fillers volume fraction increased [8].

Z. A. Mohd Ishak, et al, studied the effect of water absorption and Simulated Body Fluid (SBF) on the flexural properties of PMMA/HA composites for an immersion duration of 2 months. Silane coupling agent [3-methacryloxypropyltrimethoxy silane (γ-MPS)] was used in order to enhance the interfacial interaction between the PMMA and HA. It was found that flexural strength of the PMMA/HA composites after water absorption and Simulated Body Fluid (SBF) absorption was decreased due to the plasticizing effect of water molecules [9].

Chow Wen Shyang, investigated the effect of the addition of hydroxyapatite (HA) particles on the flexural properties of a heat polymerizing PMMA resin denture base. The results showed that the flexural strength, flexural strain and flexural modulus were decreased with the addition of hydroxyapatite (HA) particles [10].

Hanan Abdul, et al., studied the effect of the addition of Siwak powder in three different concentrations (3%, 5% and 7%) by weight with average particle size of 75 micro meters on the Certain Mechanical Properties of Acrylic Resin The results showed that the addition of Siwak powder with (3% and 5%) by weight to the Acrylic Resin did not greatly affect the compressive strength, tensile strength and impact strength of the Acrylic Resin in comparison to the control group, while the addition of (7 %) Siwak powder to the Acrylic Resin revealed a significant decrease in the compressive strength, tensile strength and impact strength [11]. The one recent study mentioned elsewhere, which involved the numerical study by the tensile properties analysis of the prosthetic dentures which prepared from the same of composite material maintained in the reference above, and the numerical analysis results of the finite element method shown the some agreement with the experimental results [12].
Sihama, I. S, et al., studied the effect of the addition of the micro zirconia (ZrO2) particles and nano hydroxyapatite (nHA) particles with different volume fractions of (1%, 2% and 3%) to poly methyl methacrylate (PMMA) as a matrix, woven Kevlar fiber kind (49) and woven glass fiber, it were added with a fixed volume fraction of (5%) to PMMA composites on the compression strength and fatigue strength of the composite prosthetic denture. The compression test result shows that the values of compression strength increased with increasing the volume fraction of (ZrO2 and nHA) particles for all groups’ specimens. The results showed the (PMMA- ZrO2) composite has greater values for compression strength. As well as the results shows that the maximum value of compression strength for hybrid laminated composite is obtained in hybrid laminated composite materials (PMMA- ZrO2) -5% Glass Fiber [13]. Another study about the impact strength and flexural properties for PMMA prosthetic complete denture base reinforced with zirconia micro particles and hydroxyapatite nano particles The results showed the values of impact strength decreased while, the values of most properties increase with increasing of the volume fraction of ZrO2 and hydroxyapatite particles in polymer composite materials[14].

The current work is an attempt to develop a PMMA polymer which is used in the denture base and in dental prosthesis applications. The study covers the effect of adding different Nano powders and the effect of the water absorption on the compressive strength for the PMMA Nano composites and hybrid Nano composites which use for the prosthetic denture.

Materials and Methods

Materials Used

In this research poly methyl methacrylate (PMMA) cold curing as new pour (fluid) resin type (Castavaria) has been used, provided from (Vertex – Dental Company). Table (1) shows some of the mechanical and physical properties of cold cure PMMA according to the supplied Company. Four types of nanoparticles powders were used as reinforces materials with selection volume fraction of (1%, 2% and 3%) including: the fly ash nanoparticles (nF.A) class B Obtained from the England with dark gray color, fly dust nanoparticles (nF.D) obtained from the cement plants in Kufa with Yellowish brown color. Tables (2) and (3) show the chemical composition analyses of fly ash and fly dust nanoparticle powders respectively which was used in this research, zirconium oxide nanoparticles (nZrO2) were supplied as partially stabilized particles form, which provided from (ZIRCON Company in England) and aluminum nanoparticles with dull gray color. Atomic Force Microscope (AFM) is used to measuring the average particle size of the nano powders materials, which is shown that the average diameter for each of fly ash, fly dust, ZrO2 and aluminum are (64.94nm), (84.23nm), (84.35nm) and (53.87nm) respectively. The results of particle size distribution for these nano powders are shown in Figure (1 (a, b, c and d)) respectively.

Table (1): Some Mechanical and Physical Properties of Neat PMMA Resin used in this Research According to the Company Processed (Vertex – Dental Company)

| Young’s Modulus (GPa) | Impact Resistance (KJ/m²) | Flexural Strength (MPa) | Flexural Modulus (GPa) | Water Sorption (μg/mm³) | Solubility (μg/mm³) | Water Absorptio n (%) | Density (gm/cm³) |
|----------------------|--------------------------|------------------------|------------------------|-------------------------|---------------------|----------------------|------------------|
| 1.63-3               | 8.3                      | 79                     | 2.3                    | 23.2                    | 1.8                 | 2.5                  | 1.19             |

Table (2): Chemical Composition Analyses of fly ash used in this Research

| Element Oxide | SiO2 | Al2O3 | LiO | MgO | CaO | Fe2O3 | L.O.I |
|---------------|------|-------|-----|-----|-----|-------|------|
| The weight (%)| 12.30| 3.02  | 29.30| 4.80| 38.08| 2.91  | 9.48 |
### Table (3): Chemical Composition Analyses of fly dust used in this Research

| Element | Oxide | SiO₂ | Al₂O₃ | TiO₂ | MgO | K₂O | CaO | Fe₂O₃ | Mn₂O₃ | Na₂O | P₂O₅ | L.O.I |
|---------|-------|------|-------|------|-----|-----|-----|-------|-------|------|------|------|
| The weight (%) |      | 58.2 | 27.7  | 1.4  | 0.05| 3.59| 0.84| 4.99  | 0.31  | 0.74 | 0.34 | 1.84 |

*Figure (1): Atomic Force Microscopy Test for Nano powders (a) fly ash (b) fly dust (c) Zirconium oxide and (d) aluminum.*
Preparation Methods and Curing Cycle of Test Specimens

The PMMA nano composite materials and hybrid nano composite materials specimens were prepared by using the Vertex™ - Castavaria. According to the manufacturer’s instructions of Manufacturer Company, the standard proportion in mixing ratio for cold cure PMMA resin is (1 ml) (0.95g) monomer liquid (MMA) and (1.7 g) acrylic powder (PMMA).

The Vertex acrylic Castavaria is moldable, where the liquid monomer (MMA) was placed in dry glass container, followed after that with slow addition of dry powder (PMMA) to the liquid monomer (MMA). The mixture as poured into the metallic mould cavity with maximum time about (4.5 min). After pouring completion into the metallic mould, the metallic mould was placed in the multi cure system (Ivo met) manufactured by Vertex-dental company according to the polymerization curing instructions at temperature equal to (55°C ) and pressure equal to (2.5 bar) for (30 min) in order to complete the polymerization process of the acrylic specimens. After the polymerization curing completed, the specimens were de molding to remove from the metallic mould with very smooth upper and lower surface.

Composites and Hybrid Composites Specimens

Six groups of specimens which are prepared in this research for the prosthetic denture base, includes, the first three groups, is prepared as a Nano composite specimens which divided into nine Nano composites, consists of PMMA resin reinforced by fly ash, fly dust and ZrO2 nanoparticles respectively, and the second three of groups, divided into nine specimens consists of three groups of hybrid Nano composites, which are ((PMMA: X% fly ash)+(1%Al + 3% ZrO2)), ((PMMA: X% fly dust)+(1%Al + 3%ZrO2)) and ((PMMA:nZrO2)+(1% fly ash + 3% fly dust)) respectively. According to the concentration of the reinforcement materials for all specimens of these groups are shown in the Table (4).

Table (4): PMMA Nano composite specimens and hybrid Nano composite specimens that Prepared in this research

| Nano Composite Number | Cold Cure Pure PMMA as Reference Material |
|-----------------------|------------------------------------------|
| Composite 1           | PMMA+1% nano fly ash                     |
| Composite 2           | PMMA+2% nano fly ash                     |
| Composite 3           | PMMA+3% nano fly ash                     |
| Composite 4           | PMMA+1% nano fly dust                    |
| Composite 5           | PMMA+2% nano fly dust                    |
| Composite 6           | PMMA+3% nano fly dust                    |
| Composite 7           | PMMA+1% nZrO2                            |
| Composite 8           | PMMA+2% n ZrO2                           |
| Composite 9           | PMMA+3% n ZrO2                           |

| Nano Hybrid Number    | (Matrix) %Volume Fraction of nanoParticle |
|-----------------------|------------------------------------------|
| Hybrid 1              | (PMMA+1% nano fly ash) + (1%Al and 3% ZrO2) |
| Hybrid 2              | PMMA+2% nano fly ash + (1%Al and 3% ZrO2) |
| Hybrid 3              | PMMA+3% nano fly ash + (1%Al and 3% ZrO2) |
| Hybrid 4              | PMMA+1% nano fly dust + (1%Al and 3% ZrO2) |
| Hybrid 5              | PMMA+2% nano fly dust + (1%Al and 3% ZrO2) |
| Hybrid 6              | PMMA+3% nano fly dust + (1%Al and 3% ZrO2) |
| Hybrid 7              | PMMA+1% n ZrO2 + (1%fly ash and 3% fly dust) |
| Hybrid 8              | PMMA+2% n ZrO2 + (1%fly ash and 3% fly dust) |
| Hybrid 9              | (PMMA+3% n ZrO2) + (1%fly ash and 3% fly dust) |
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Mechanical and Physical

In order to evaluate the compression properties, compressive strength under the effect of water Absorption of the PMMA Nano composite materials and PMMA hybrid Nano composite specimens of the denture prosthetic materials, Compression test and water Absorption test were performed in this research.

Compression Test

For partial or complete denture base material applications, the poly methyl methacrylate (PMMA) has suitable compressive and tensile strength [15]. According to the (ASTM D695) the compression test was performed at room temperature by using the universal tensile test machine manufactured by (Laryee Company in china), type is (WDW-50). The cross head speed was (0.2mm/min) and the load was applied gradually until the fracture of the specimen occurs [16]. According to (ADA Specification No.12, 1999), all the test specimens after preparation and polishing processes must be stored in distilled water at (37± 1℃) for 48 hr [17].

Water Absorption Test

During life period of polymer materials, much polymeric materials are susceptible to water absorption. So the water absorption leads to subjecting the material to degradation, internal stresses and instability in dimensions. Which in turn leads to the formation of crack and fracture of the denture base material [18]. The water absorption test was performed according to (ASTM D 1037-99). In this test, the specimens with dimensions 5mm width, 10mm length and 5mm thickness were soaked in distilled water at ambient temperature and limited time. At each testing time, the specimens were removed from the water, wiped with tissue paper to removed surfaced water and then weighed by using (Precision balance), manufactured by (Radwag), type is (PS 360/C/1) [19]. After reach all the specimens to the saturation state (immersion in distilled water where no change in weight occur), compression test was performed to measure the effect of water absorption on the compressive strength of PMMA, PMMA Nano composites and PMMA hybrid Nano composites.

Compression Test Results and Discussion

The compressive strength values before and after immersion in distilled water of neat PMMA resin, PMMA Nano composites and PMMA hybrid Nano composites for all samples that were fabricated in this research are presented from the Figure (2) to Figure (15) respectively. Table (5) illustrates the maximum values of compressive strength for PMMA Nano composites and PMMA hybrid Nano composites after and before immersion in distilled water (aging).

Table (5): The maximum values of compressive strength values for PMMA Nano composites and PMMA hybrid Nano composites after and before immersion in distilled water (aging)

| Material                                                   | Compressive strength before immersion in distilled water | Compressive strength after immersion in distilled water |
|------------------------------------------------------------|--------------------------------------------------------|--------------------------------------------------------|
| Pure PMMA                                                  | 250                                                    | 285                                                    |
| PMMA+2% nano fly ash                                      | 265.62                                                 | 300                                                    |
| PMMA+2% nano fly dust                                     | 268.125                                                | 335                                                    |
| PMMA+2% nZrO2                                              | 286.25                                                 | 316.25                                                 |
| PMMA: 2% nano fly ash - (1%Al +3%ZrO2)                   | 270                                                    | 315                                                    |
| PMMA: 2% nano fly dust - (1%Al +3% ZrO2)                  | 270                                                    | 362                                                    |
| PMMA: 2% n ZrO2 - (1%fly ash + 3% fly dust)               | 260                                                    | 341                                                    |
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Figure (2) shows the effect of adding various types of nanoparticles powders (fly ash, fly dust and Zirconium oxide) on the compressive strength for PMMA Nano composites before immersion in distilled water. It can be noted from this figure that the addition of the fly ash, fly dust and zirconium oxide as nanoparticles leads to increase the compressive strength of the PMMA Nano composites before immersion in distilled water and reach to maximum value at (2%) of volume fraction as comparing with neat PMMA. The reasons behind such a behavior are that the high interfacial shear strength between the PMMA matrix and nanoparticles because of the formation of supra molecular or cross-links bonding which shield or cover the nanoparticles and this in turn prevents the propagation of the cracks inside the material, as well as the propagation of the crack can be changed by good bonding between the PMMA matrix and nanoparticles [20 and 21]. Moreover, the incorporation of the brittle nanoparticles powders into the polymer matrix improves the stiffness of the composites by restricted the mobility of the matrix chains [22]. As well as good distribution of nanoparticles powders in composite materials, especially at the low concentrations of nanoparticles additives to the composites, and this it will may be reduced agglomeration of the nanoparticles, and that may lead to reduce stress concentration in composite materials near the agglomerated nanoparticles, so such small stresses are not sufficient enough to break the weak interactions at the interface [23]. Therefore, these small stresses can be easily transferred from the matrix to the brittle nanoparticles, so allowing the particles to contribute its high brittleness property to the Nano composites so, the compressive strength and compressive elastic modules increases [24]. Overtime, the formation of a strong structure of the PMMA Nano composite materials which depending on the formation of strong interfaces bonding between the reinforcing nanoparticles (fly ash, fly dust and ZrO2) and PMMA matrix, so that the resultant is Nano composite materials with strong physical bonding, therefore required high compressive stress to break it, and this lead to increasing compressive strength and compressive elastic modules [4]. On the contrary, it can be noted from the Figure (2) that the addition of the fly ash nano particles to larger than 2% ratio has no effect on the compressive strength of the PMMA composites before immersion in distilled water.

Also, from Figure (2) it is observed that the Nano composites materials reinforced with the zirconium oxide nanoparticles have the higher values of compressive strength, as compared with their counter parts of the other groups of the Nano composites materials which reinforced with fly ash and fly dust nanoparticles. The reasons behind such a behavior are that the compressive strength of the zirconium oxide higher than the compressive strength of the fly ash and fly dust, as well as have good compatibility between constituents of composite materials [4].

![Figure (2): Compressive Strength of PMMA Nano Composite Materials before Immersion in Distilled Water as a Function of volume fraction of nanoparticles (fly ash, fly dust and ZrO2) in PMMA matrix.](image-url)
Figure (3) shows the effect of adding various types of nanoparticles powders (fly ash, fly dust and Zirconium oxide) on the compressive strength for PMMA Nano composites after immersion in distilled water (for 11 day after reaching all the specimens to the saturation state where no change in gain water occurs in specimens). It can be noted from this figure that the addition of the fly ash, fly dust and zirconium oxide as nanoparticles leads to increase the compressive strength of the PMMA Nano composites after immersion in distilled water and reach to maximum value at (2%) of volume fraction as comparing with neat PMMA. The reasons behind such a behavior are related to the same reasons which mentioned in the previous item for Figure (2). Moreover, the addition of the nanoparticles powders such as fly ash, fly dust and zirconium oxide as nanoparticles leads to increasing water absorption because of the fact that the fly ash, fly dust and zirconium oxide nanoparticles replace hydrophilic PMMA resin, result in a decrease in water absorption since diffusivity of water molecules through these Nano powders is greatly lower than that through the PMMA matrix. Also, strong interfacial bonding between PMMA polymer and fly ash, fly dust and zirconium oxide nanoparticles lead to a decrease of micro voids in the PMMA Nano composite materials, and as a result of this, decreasing of water absorption and this lead to minimum volumetric expansion between the PMMA matrix and the nano powders therefore, the stress does not exceeds the strength of the inter phase region between the PMMA matrix and the nano fillers. So, de bonding not takes place between the nano powders and the PMMA matrix resulting in increase in the compressive strength of the dental PMMA Nano composite materials [9 and 25].

Also, from Figure (3) it is observed that the Nano composites materials reinforced with the fly dust nanoparticles have the higher values of compressive strength, as compared with their counter parts of the other groups of the Nano composites materials which reinforced with fly ash and zirconium oxide nanoparticles after immersion in distilled water. The reason behind such a behavior is that the chemical composition of the fly dust contain Alumina, lithium oxide and calcium oxide nanoparticles (Al2O3, LiO and CaO) as showed earlier in the Tables (2 and 3) which possess a strong ionic inter atomic bonding [21], and this gives a strong interfacial bonding between PMMA polymer and fly dust nanoparticles lead to decreases micro voids in the PMMA Nano composite materials and as a result of this, decreasing the water absorption and this leads to a minimum volumetric expansion between the PMMA matrix and the nano powders therefore, the stress not exceeds the strength of the inter phase region between the PMMA matrix and the Nano fillers. So, de bonding not takes place between the fly dust nanoparticles and the PMMA [9 and 25].

Figure (3): Compressive Strength of PMMA Nano Composite Materials after Immersion in Distilled Water as a Function of volume fraction of nanoparticles (fly ash, fly dust and ZrO2) in PMMA matrix.
Figures (4, 5 and 6) show the effect of adding various types of nanoparticles powders (fly ash, fly dust and Zirconium oxide) on the compressive strength for PMMA Nano composites after and before immersion in distilled water. It can be noted from these figures that there is a noticeable effect of water absorption on the compressive strength; it was found that there is a symmetrical behavior in the values of compressive strength of PMMA Nano composites when adding nanoparticles either before or after immersion in distilled water. Moreover, it has been observed that the compressive strength values of the pure PMMA, PMMA Nano composites after immersion in distilled water is higher than the compressive strength values of their counter parts of the pure PMMA, PMMA Nano composites before immersion in distilled water. The reasons behind such a behavior are that the immersion in distilled water leads to release and remove any residual monomer, as well as residual stresses which adversely affected on the compressive strength of the pure PMMA and PMMA Nano composites [13]. In addition, the little amount of absorbed water leads to increasing the adhesion bonding between the PMMA polymer and fly ash, fly dust and zirconium oxide Nano powders by increasing the wettability of the nanoparticles and this leads to increasing the interfacial shear strength between the PMMA matrix and nanoparticles, so that the resultant is Nano composite materials with strong physical bonding, therefore required high compressive stress to break it, therefore the compressive strength values for the pure PMMA and PMMA Nano composites after immersion in distilled water higher than the compressive strength values of their counter parts of the pure PMMA and PMMA Nano composites before immersion in distilled water [26].
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The effect of the addition of the mixture of nanoparticles powders (1% Al and 3% ZrO2) to the Nano composite materials (PMMA: X%nF.A) and (PMMA: X%nF.D), on the compressive strength for these hybrid Nona composite materials ((PMMA: X%nF.A) + (1%Al and 3% ZrO2 )) and ((PMMA: X%nF.D) +(1%Al and 3% ZrO2)) before immersion in distilled water, it was shown in Figures (7 and 8) respectively. It was noticed from these figures that the addition of the mixture of nanoparticles powders with ratio of (1%Al+3% ZrO2) to the Nano composite materials (PMMA: X%nF.A) and (PMMA: X%nF.D) respectively, leads to increase the compressive strength of the hybrid Nano composites before immersion in distilled water as comparing with their counter parts of Nano composites which are (PMMA: X%nF.A) and (PMMA: X%nF.D) of the same volume fraction of fly ash and fly dust respectively. This behavior was related to that the addition of the zirconium oxide that the compressive strength is higher than the compressive strength of the fly ash and fly dust as previously mentioned, in addition to the improvement of the mechanical properties that is associated with the addition of zirconium oxide nanoparticles [4].

Figure (6): Compressive strength of PMMA Nano Composite Materials with and without the effect of water absorption as a function of volume fraction of nano Zirconium oxide Particles in PMMA matrix.

Figure (7): Compressive strength for PMMA Nano composite and PMMA hybrid Nano composite materials before immersion in distilled water as a function of nano Fly Ash in PMMA matrix.
On the contrary, it can be noted from Figures (9) that the addition of the mixture of nanoparticles powders with ratio of (1%F.A+3%F.D) to the Nano composite materials (PMMA: X%nZrO2) leads to a decrease the compressive strength of the hybrid Nano composites (PMMA: X%nZrO2)+(1%F.A+3%F.D) before immersion in distilled water as comparing with their counter parts of Nano composites which is (PMMA: X%nZrO2) of the same volume fraction of ZrO2. The reasons behind such a behavior are that the high concentrations of the nanoparticle powders especially with fly dust leads to agglomeration and stick of these nano powders together, therefore these powders play an important role in stress concentrators. Therefore, when the compressive stress was applied on the specimen, the value of the stress concentration increases dramatically near the agglomerated nanoparticles and making the de-bonding between PMMA and fly dust, fly ash and zirconium oxide nanoparticles and this causes cracks propagate faster inside the material so that, the fracture occurs immediately [26 and 27]. Further to that a bad wettability between the nanoparticles and matrix, especially at high concentrations, so that the resultant is Nano composite material with weak physical bonding, and this required a low a compressive stress to break the sample [4].

Figure (8): Compressive strength for PMMA Nano composite and PMMA hybrid Nano composite materials before immersion in distilled water as a function of nano Fly Dust in PMMA matrix.

Figure (9): Compressive strength for PMMA Nano composite and PMMA hybrid Nano composite materials before immersion in distilled water as a function of nano Zirconium oxide in PMMA matrix.
The effect of the addition of the mixture of nanoparticles powders (1%Al and 3% ZrO2) to the Nano composite materials (PMMA: X%nF.A) and (PMMA: X%nF.D), on the compressive strength for these hybrid Nano composite materials ((PMMA: X%nF.A) + (1%Al and 3% ZrO2)) and ((PMMA: X%nF.D) +(1%Al and 3% ZrO2)) after immersion in distilled water was shown in Figures (10 and 11) respectively. It was noticed from these figures that the addition of the mixture of nanoparticles powders with ratio of (1%Al+3% ZrO2) to the Nano composite materials (PMMA: X%nF.A) and (PMMA: X%nF.D) respectively, leads to an increase in the compressive strength of the hybrid Nano composites after immersion in distilled water as comparing with their counter parts of Nano composites which are (PMMA: X%nF.A) and (PMMA: X%nF.D) of the same volume fraction of fly ash and fly dust respectively. The reasons behind such a behavior are related to the same reasons which mentioned in the previous item for Figures (7 and 8) [4]. Moreover, the high concentrations of the Nano powders leads to more fill or diminish of the open spaces and micro voids in the PMMA hybrid Nano composite materials and therefore, the water absorption by PMMA hybrid Nano composite materials is greatly lower than the PMMA Nano composite materials [4]. Also, high concentration of the Nano powders leads to more replacement of the hydrophilic PMMA hybrid Nano composite materials, and therefore, the diffusivity of water molecules through these materials is greatly lower than that through the PMMA Nano composite materials, and this leads to minimum volumetric expansion between the PMMA matrix and the Nano powders therefore, the stress does not exceeds the strength of the inter phase region between the PMMA matrix and the Nano fillers. So, de bonding not takes place between the nanoparticles and the PMMA matrix [9 and 25].

Figure (10): Compressive strength for PMMA Nano composite and PMMA hybrid Nano composite materials after immersion in distilled water as a function of Nano Fly Ash in PMMA matrix.

Figure (11): Compressive strength for PMMA Nano composite and PMMA hybrid Nano composite materials after immersion in distilled water as a function of Nano Fly Dust in PMMA matrix.
On the contrary, it can be noted from Figures (12) that the addition of the mixture of nanoparticles powders with ratio of (1%F.A+3%F.D) to the Nano composite materials (PMMA: X%nZrO2) leads to an increase the compressive strength of the hybrid Nano composites (PMMA: X%nZrO2) + (1% F.A + 3%F.D) after immersion in distilled water as comparing with their counter parts of Nano composites which is (PMMA: X%nZrO2) of the same volume fraction of ZrO2. The reasons behind such a behavior are related to the same reasons which mentioned in the previous item for Figures (3, 10 and 11) [6, 9, 21, and 25].

The effect of the addition of the mixture of nanoparticles powders (1%Al and 3% ZrO2) to the Nano composite materials (PMMA: X%nF.A) and (PMMA: X%nF.D), as well as, the addition of the mixture of nanoparticles powders with ratio of (1%F.A+3%F.D) to the Nano composite materials (PMMA: X%nZrO2) on the compressive strength for these hybrid Nano composite materials ((PMMA: X%nF.A) + (1%Al and 3% ZrO2 )), ((PMMA: X%nF.D) +(1%Al and 3% ZrO2)) and ((PMMA: X%nZrO2) + (1%F.A and 3% F.D )) after and before immersion in distilled water was shown in Figures (13, 14 and 15) respectively. It can be noted from these figures that there is a noticeable effect of water absorption on the compressive strength; it was found that there is a symmetrical behavior in the values of compressive strength of PMMA Nano composites when adding nanoparticles to it either before or after immersion in distilled water. Moreover, it has been observed that the compressive strength values of the pure PMMA, PMMA hybrid Nano composites after immersion in distilled water higher than the compressive strength values of their counter parts of the pure PMMA, PMMA hybrid Nano composites before immersion in distilled water. The reasons behind such a behavior are related to the same reasons which mentioned in the previous item for Figures (4, 5 and 6) [12 and 27].
CONCLUSIONS

In the present work, attempts were made to develop PMMA polymer which is used in the denture base and in dental prostheses applications. So the Nano composites and hybrid Nano composites with desirable properties were attended, by adding three types of Nano powders (fly ash, fly dust and ZrO₂) at the same ratio to it, as well as the effect of water absorption also studied, and it was concluded the following:

- The maximum values of the compressive strength for PMMA Nano composites and PMMA hybrid Nano composites were at 2% ratio for all nanoparticles powders which added to composites, whether before or after the absorbance test.

- The addition of ZrO₂ nanoparticles has a noticeable effect on the compressive strength before immersion in distilled water of the Nano composite prosthetic denture base specimens as compared with the fly ash and fly dust nanoparticles. Therefore, the maximum value of compressive strength increased from (250MPa) for pure PMMA to (286.25MPa) for Nano composite material (PMMA: 2%nZrO₂).

- The addition of fly dust nanoparticles has a noticeable effect on the compressive strength after immersion in distilled water of the Nano composite prosthetic denture base specimens as compared with the fly ash and ZrO₂ nanoparticles. Therefore, the maximum value
of compressive strength after immersion in distilled water increased from (285MPa) for pure PMMA to (335MPa) for Nano composite material (PMMA: 2%nDCK).

- The compressive strength values of the pure PMMA, PMMA Nano composites and PMMA hybrid Nano composites specimens after immersion in distilled water are higher than the compressive strength values of these specimens before immersion in distilled water.
- The maximum value for the compressive strength before immersion in distilled water was obtained in the hybrid Nano composite material ((PMMA: 2% fly ash) + (1%Al + 3% ZrO2)).
- The maximum value for the compressive strength after immersion in distilled water was obtained in the hybrid Nano composite material ((PMMA: 2% fly dust) + (1%Al + 3% ZrO2)).

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