

Investigating the Potential of Walnut Shell Powder as a Filler in PMMA Denture Bases

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ABSTRACT

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With an increasing of dental problems for aging population, there is more needing for more effective treatments to enhance the quality of denture base. Natural powders have biocompatibility characteristics and considerable mechanical properties as well as being inexpensive and eco-friendly. Poly methyl methacrylate (PMMA) is widely utilized in medical and dental field due to its high compatibility and ease of manufacturing. However, its mechanical properties are relatively weak. In current work, PMMA bio composites were reinforced with walnut shells powder of two particle sizes (25 and 150 μm) in various concentrations. Physical and mechanical properties of bio composites were investigated. SEM showed a dense and smooth bio composite morphology, indicating strong PMMA-reinforcement adhesion with no new phases. The results exhibited a considerable advancement in the mechanical properties values for all bio composite specimens as compared with neat PMMA. Specimens that strengthened with fine size from walnut shells powder exhibited enhanced properties compared with those of the coarse size for the same material. For composites reinforced with fine particles (25 μm), the maximum values for compression strength and hardness for samples strengthened with were 325.56 MPa and 86 shore-D respectively. In contrast, composites reinforced with coarse particle (150 μm) of the same material had the maximum values of 306.409 MPa and 82.2 shore-D respectively. In light of the findings, it can be concluded that adding of fine particles of walnut shells powder to neat (PMMA) resin is one of the promising substances utilized to enhance the mechanical properties for denture bases more than coarse particles.

1. INTRODUCTION

A denture is a detachable prosthetic device utilized in case of missing teeth as a hard tissue and surrounding soft tissues. Dentures are classified in two types including: partial and complete denture bases. Complete type of dentures is used in the case of losing all of the teeth, whereas the second type of dentures is used when several natural teeth exist.

The material that most widely utilized for bases of dentures is poly methyl methacrylate (PMMA) acrylic resin. It fabricated from PMMA material and it remains the mostly and oldest material used in dentistry field for manufacturing of denture bases because of its easy laboratory fabrication, inexpensive apparatus's, good esthetic, ease in finishing and polishing, chemically an environmentally stable in the oral cavity. Therefore, dentures made from PMMA were more popular and shows favorites physical and mechanical properties as compared with other kinds of polymers [1, 2]. However, PMMA exhibits several drawbacks when used alone as a denture base material, including low resistance to crack propagation, limited flexural strength and increased brittleness compared to other polymers [3].

Fracture of PMMA resin is the most common problems that occurs in denture base serving and yet remains unsolved problem for prosthodontics denture-based materials. Fracture of acrylic resin denture can happen due to impact failure outside the mouth when the denture was accidentally dropped on hard surface, or due to fatigue failure inside the mouth by refined occlusal biting force during mastication process. As a result, the denture base materials are exposed to various stress, which contribute to increase the deformations of denture base materials [4]. One of the common methods for improving the mechanical performances of dentures bases is by physical alteration for the composition of the denture base by combine strengthening fillers to the PMMA matrix like particles and fibers [5]. The additives work as barriers to prevent the crack from propagation, also, enhance both of toughness and impact strength values [6].

Tacir et al. [7] investigated the effect of adding of glass fibers as a filler material in acrylic resin as denture base. The results were referring for possibility of improving mechanical properties (flexural strength value and fracture resistance value) of heat-polymerized PMMA after incorporating this fiber.

The effect of incorporation of 5-20% from micro filler of hydroxyapatite (HA) on the mechanical and thermal properties of heat-cured PMMA resin were examined by Chow et al. [8]. Using of HA as filler materials caused increasing in the flexural modulus value for PMMA resin. On the other hand, the fracture toughness, elastic modulus values as well as glass transition temperature (T_g) of acrylic resin were also considerably influenced with this micro filler. The effectiveness of particle size and volume fraction of (SiO_2) as a strengthening material on mechanical properties for (PMMA) acrylic resin. The result of adding of these ceramic fillers showed that the values of elastic modulus, tensile strength, elongation percentage at brake, bending modulus as well as maximum shear stress of composites samples were enhanced with raising the concentration of (SiO_2) powders. On the other hand, the adding of these ceramic fillers led to a reduction in the impact strength and fracture toughness values of PMMA composites [9]. The effect of using polyester fibers as strengthening fillers incorporated in acrylic resin as denture base appliances was investigated by Gopichander et al. [10]. The result showed that samples strengthened by these fibers had improved mechanical properties (elastic modulus, compressive strength, flexural strength as well as degree of deflection) for cold and heat-cured acrylic resin.

Pentapati et al. [11], investigated the influence of addition of aluminum oxide as ceramic particles on the characteristics of a standard heat-cure (PMMA) resin. The result exhibited that addition of these ceramic oxide to the high impact heat polymerized (PMMA) resin (LUCITONE) as well as conventional heat-cured acrylic resin (DPI) with 15% by wt.% of Aluminum oxide particles improved the values of hardness and flexural strength without unfavorable effects. Somkuwar et al. [12] compared the flexural strength for PMMA resin strengthened with nanotubes of multiwalled carbon (MWCNTs) and prepared by the technique of conventional water bath and by utilizing energy of microwave. The result of this search exhibited that heat-cured (PMMA) resin without and with adding of (MWCNTs) and cured with microwave technique exhibited higher value of flexural strength than that of heat-cured fiber strengthened (PMMA) resin cured with water bath process.

Development of polymer composites fabricated from renewable raw materials (fibers or particles), has been increased considerably in the last years. There are many reasons made the composites fabricating with natural fillers were most widely used in the present time such as reducing the cost, obtain high value of strength to weight ratio, low weight and achieving considerable thermal properties. Aziz [13] evaluated the influence of adding of TiO_2 nano particles on color stability, thermal conductivity as well as impact strength values of acrylic resin cured in microwave technique as compared with the conventional cured of heat-polymerized PMMA resin. The results showed that the high-impact acrylic that cured in microwave had no effect on the thermal conductivity and color stability in comparison with water bath technique, but it reduced the impact strength value. Also, adding of 3% (TiO_2) enhanced the color stability and impact strength and without changing the value of thermal conductivity. The results revealed that adding natural particles had considerably enhanced the mechanical properties values for each type of bio composite samples as compared with pure PMMA sample. All composite samples strengthened by particles of pomegranate peels exhibited the highest properties comparing with those that strengthened with seed powder of

dates ajwa. Olewi et al. [14] studied the physical and mechanical properties (hardness, density and compression strength) of PMMA reinforced with natural particles of varying sizes and weight fractions for use in denture base applications. The results showed that the compressive strength and hardness of the PMMA composite samples improved with increasing the concentration of the filler particles. Additionally, the study showed that the density of the biocomposite samples increased as the concentration of the filler particles rose. Ahmed and Salih [15] investigated the influence of reinforcing PMMA resin as composite material with two types of nano powders: Talc particles and walnut shell particles with different particle sizes and by using three different concentrations (0.1, 0.2 and 0.3wt.%). The results showed that the Hardness shore D, modulus of elasticity as well as tensile strength properties improved with increasing the concentration of these nanoparticles, while the elongation at break value decreased as the concentration of the nanofillers increased [15].

Fouly et al. [16] studied the mechanical and tribological properties of PMMA strengthened with two different types of natural powders (corn cobs, and miswak particles) at varying weight fractions of 2.0, 4.0, 6.0, 8.0, and 10 wt.%. The results exhibited a significant improvement in the mechanical properties of PMMA composites when the concentration of both natural powders was increased, as compared to pure PMMA [16]. Sisal and coconut powder have also shown promising results in enhancing the physical properties of the PMMA composites, such as thermal conductivity and water absorption, as investigated by Hussain et al. [17].

The aim of the current study is to evaluate the effect of incorporating two different particle sizes of natural walnut shells powder on the compression, hardness and water absorption for a heat-cured PMMA used for denture base application. The choice of walnut shell powder as a filler is based on its characteristics as a biowaste material, its hard shell, good mechanical properties, availability, low cost, eco-friendliness, and strong bonding at the interfacial region between the acrylic resin matrix and walnut shell particles [18].

2. MATERIALS AND METHODS

2.1 Materials

The matrix material utilized in the current study is heat-curing poly methyl methacrylate (PMMA), as depicted in Figures 1(a) and (b). This material is reinforced with two distinct sizes of natural powder— $150\mu\text{m}$ and $25\mu\text{m}$ —derived from walnut shells particles, which serve as strengthening fillers. Four selected ratios of these fillers, namely 0.0%, 0.5%, 1%, 1.5%, and 2%, were incorporated into the heat-cure acrylic resin to fabricate composite samples intended for denture base appliances. Figures 2(a) and (b) illustrate the walnut shell powders of $150\mu\text{m}$ and $25\mu\text{m}$, respectively, which were employed in the current research.

2.2 Preparation of natural powder

As a first step, the walnut shells were washed with detergent powder and then washed in hot distilled water in get rid all mud and dust particles from them, then, these walnut shells were dried in an electric oven at (50°C) for three hours.

The dry walnut shells were crushed by the cracking machine to small grains then were ground by (porcelain mill) for several times, in each time this was done for three hours, until the grain becomes in fine size, then grinded particles are sifted to remove large particles.

Walnut shells particles that were used in this study are

crushed and sieved by passing them on a group of sieves from the largest to the smallest (600, 300, 150, 75, 53 and 25). Finally, two samples from the particles are chosen, the first one is the powder that passing from the sieve 150 micron and the second sample of powder is passing from the sieve 25 micron.



Figure 1. (a) Acrylic resin (PMMA) powder type (Veracril company) and (b) (PMMA) liquid monomer



Figure 2. The walnut shells powder used in this study where (a) microparticles size (150µm) and (b) microparticles size (25µm)

2.3 Preparation of samples

In current work, composites samples that used for dentures base appliances were fabricated manually. The procedures for the preparation of the specimens are illustrated as follows:

A total of acrylic resin samples that fabricated, were divided into three groups. The first group represent as heat cure acrylic resin (control) and both of second and third groups are bio composite specimens reinforced with walnut shells powder with selected ratios (0.5%, 1%, 1.5% and 2%) for each particle size in individually form.

A conventional flask technique was employed in the study. Firstly, standard mold cavities were prepared using wax patterns specifically designed for the flasking process. These patterns were coated with a separating material and allowed to dry. Next, Type III dental stone was mixed according to the manufacturer's instructions and poured into the lower half of the flask, embedding each wax pattern in the stone. Only half of pattern thickness was embedded in the stone at the lower part of the flask. After setting, the stone was coated again with separating material to facilitate the easy removal of samples and allowed to dry then the upper half of flask is placed and filled with stone and the lid is placed and allowed to completely set. Lastly, the flask was immersed in boiling water for five minutes to ease the wax elimination process. Once the flask was opened, the mold spaces were thoroughly cleaned with hot water to ensure that all wax debris was removed.

The control specimen was fabricated manually by adding powder to the monomer depending on the required weights of (PMMA) resin that filling the cavities of the mold depending on the company manufacturer instructions in the ratio of (3:1)

by using electronic sensitive balance, then Bio composite samples reinforced with walnut shells were fabricated depending on the required selection ratio of the reinforcing filler, by Continuously and Homogeneous mixing of acrylic powder with walnut shells powder prior adding to the monomer (MMA) to produce bio composite samples.

The mixture (acrylic resin powder and walnut shells particles), was added to the liquid (MMA) in gradually form. It was mixed for approximately for 30 sec until it was reached to dough stage and then mixture was placed and packed into the mold cavities that covered by a thin layer of a separating material and then pressed.

During packing, the acrylic dough was placed inside the mold cavity of lower half of flask and closed the upper and lower part of flask then used hydraulic press to remove the excess material. Then, the flasks were clamped for polymerizing in denture curing unit with slowly increasing of water temperature until reach 73°C and left for 1 hour. Then the temperature was raised to 100°C and the curing cycle was continued for 30 hours. After complete cooling process of the samples, all acrylic resin samples allowed to remove from the flask. The finishing process using a manual Vernier caliper for all specimens were done to ensure the accuracy of specimens' dimensions prior to testing. Figure 3 shows the sequential steps in samples preparation.

This technique offers multiple advantages over other manufacturing techniques, particularly when compared with self-curing technique. These benefits include the production of a stronger material, higher molecular weight, the elimination of residual monomers and improved color stability.

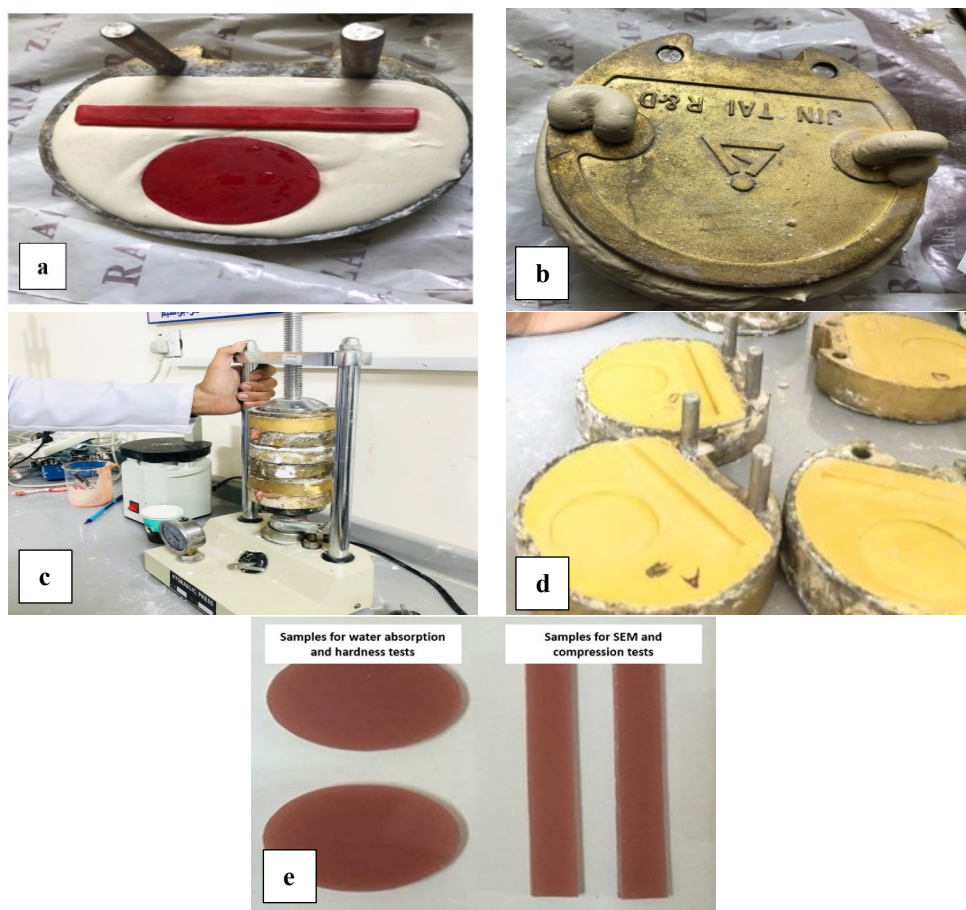


Figure 3. (a) wax elimination technique, (b) flasking process, (c) pressing the flask by hydraulic, (d) mold cavities after remove wax samples and (e) bio composites after deflasking and polishing

2.4 Mechanical and physical tests

2.4.1 Compression test

The compression test was applied to determine the compression strength value for all fabricated bio composites specimens. After complete of fabrication and finishing processes for all bio composite samples and before making any test, all of bio composite samples were immersing in the container of distill water for (48) hour at a temperature of $(37\pm 1^\circ\text{C})$ depending on (ADA specification., 1999, No.12), for ensuring from all of denture base samples were stay in conditions similar to oral cavity environment. As well as, to removing of residual monomer and reduce the residual stresses [19].

Compression strength test for bio composite samples was done depending on ASTM (D695) with utilizing the same machine that utilized in tensile properties test at a department of material engineering with across head of about 5mm/min, the fracture of specimen occur after applying compressive load in gradually form [20].

2.4.2 Hardness test

To test how well the composite can withstand mechanical stresses and abrasions during everyday use while maintaining its shape and function over time, the hardness test was performed. The hardness test for control and bio composite specimen is applied depending on ASTM (D2240). Dorumeter hardness test, type (Shore D) is used at an applied load and depressing time of measuring equal to (50 N and 15 sec) respectively. The testing zone in the surface of all samples must be smooth, also the depth of indentation measure is graduated from (0 - 100) hardness numbers. Each sample was inspected seven times in different positions, then taking the final result of the average value [20].

2.4.3 Water absorption

Water absorption can lead to dimensional changes indenture materials. Therefore, water absorption test was performed on control and bio composites to examine the effect of increasing filler content. The control and bio composite specimens were inspected in water absorption test that applied depending on (ASTM D570). The specimen in this inspection must immerse in distilled water, under certain immersed time and temperature. The specimens were entirely immersed inside a container filled by distilled water at laboratory temperature of about (23 ± 2) , then still for (one day), after that, all the samples were removed from the container. Then, all water drops on the surfaces was wiped off by utilizing dry piece of cloth, then calculating the weights with utilizing digital balance, the water absorption value was calculated with using Eq. (1) [21].

$$\text{Water absorption (\%)} = (W_s - W_d)/W_d \times 100\% \quad (1)$$

where,

W_d : weight of sample before immersion in distill water (dry).

W_s : weight of sample after immersion in distill water (for 24h).

2.4.4 Morphology test

A Scanning Electron Microscope (SEM), specifically the Tescan VEGA-SB model, was employed to examine the fracture surface morphology of the bio-micro composite specimens. Prior to the inspection, all specimens underwent

gold sputtering on their surfaces along the edges, a procedure performed uniformly for all specimens before the morphological examination.

2.5 Statistical analysis

For each test (except for SEM), four samples where tested and averaged for each particle size of filler. One-way ANOVA and t-tests were used to compare between the results across different groups. A p-value of less than 0.05 was considered statistically significant.

3. RESULTS AND DISCUSSION

3.1 Compression test

The value of compressive strength for control PMMA sample and PMMA bio composite samples strengthened with particles of walnut shells that fabricated in the current work were shown in the Figure 4.

Figure 4 shows the relation between compression strength and weight fraction content of 0.5%, 1%, 1.5% and 2% for natural fillers (walnut shells powder) which added individually with two different particle sizes, as particle reinforcement for PMMA bio composite specimens. It can be noticed that compressive strength values for all PMMA bio composite samples were enhanced by rising the concentration of natural fillers (walnut shells powder) for both of two different particle sizes (150 μm and 25 μm) as compared with control sample of PMMA acrylic resin. While this improvement was not statistically significant ($p \geq 0.05$), the steady enhancement in compressive strength across the tested concentrations suggests a potentially meaningful improvement in material performance. The improvement in the compression strength value using of walnut shells powder, may be due to good compressive strength of walnut shells particles. Also, it could be related to better interaction and adhesion between polymer matrix and this natural reinforcement, this is cause reducing of free volume in the molecular structure for polymer composites materials and as a result of this, the molecular motion of molecules in the fabricated composites samples was reduced, that results in the stiffening of the PMMA chains by impede the movement of cracks and thus exhibit a considerable resistance to compression under applied strain. Thus, walnut shells powder can be utilized as natural filling materials promising to enhance the compressive strength value of PMMA acrylic resin which used for dentures base [15, 18, 22].

Also, it can be observed from the Figure 4 that the bio composites specimens which were strengthened with a fine particle size of natural powders reinforcing material have higher compression strength values as compared with those of bio composites specimens reinforced by coarse particle sizes of the same natural material. This is may be due to the small particle size of strengthening material cause more interaction and contact regions between the natural reinforcement material and PMMA matrix material and thus, it may be led to increase in reinforcing and improvement it, and therefor increasing the mechanical properties for bio composite

material.

The highest value of compression strength among all bio composite samples reached to (325.56 MPa) at weight fraction content of 2% of walnut shells powder and particle size of (25 μ m) as compared with (270.029 MPa) for reference PMMA acrylic resin sample which has the lowest value among all the specimens.

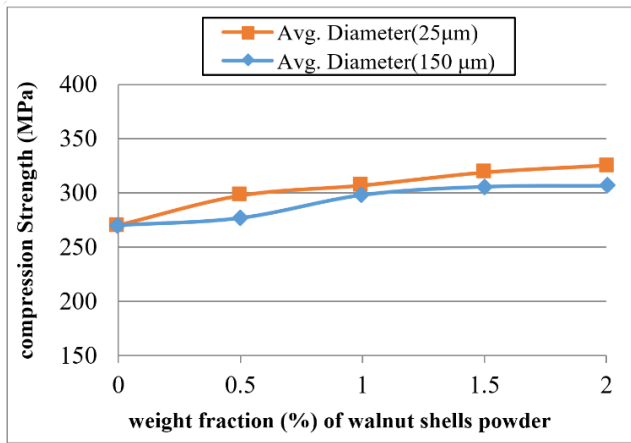


Figure 4. Compression strength of PMMA composite samples as a function of weight fraction content and a particles size of walnut shells powder

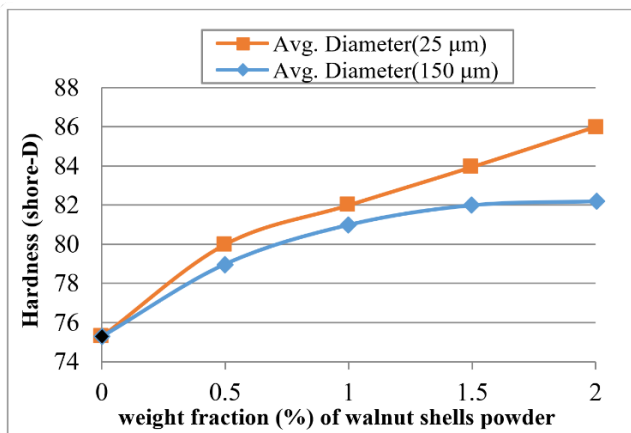


Figure 5. Hardness (shore-D) of PMMA composite specimens as a function of weight fraction content and a particles size of walnut shells powder

3.2 Hardness (shore-D) test

The values of hardness (shore-D) for reference PMMA and PMMA bio composite samples were illustrated in the Figure 5.

Figure 5 exhibited the relation between hardness and weight fraction content of (0.5%, 1%, 1.5% and 2%) of walnut shells powder which added in two different particle sizes, as a particle reinforcement for PMMA bio composite samples. It can be observed that values of hardness improved with rising in the weight fraction content for both different particle sizes of walnut shells micro particles in the (PMMA) matrix, as compared with neat PMMA (control sample). This manner may be related to the nature hardness of natural fillers (walnut shells particles) which may be a stiffer and stronger in

comparison with control PMMA specimen [15, 18]. These results are consistent with those obtained by other researchers [2].

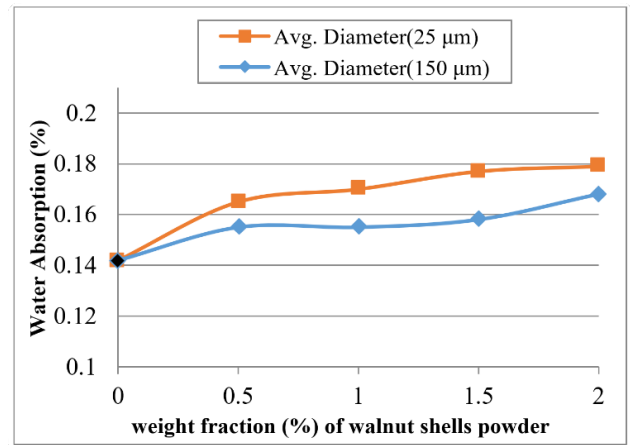


Figure 6. Water absorption (%) of PMMA composite samples as a function of weight fraction content and a particles size of walnut shells particles

Furthermore, the concept of hardness give an indication of the plastic deformation of the material can subject under the effect of external stress and so the adding of walnut shells powders will improve the hardness of material due to improve resistance to deform plastically [23, 24].

Also, it can be observed from Figure 6 that bio composite samples that strengthened with fine sizes of walnut shells particles possess higher values of hardness as compared with bio composite specimens reinforced with course sizes of the same material. This may be due to the fine size of reinforcing material, which have larger number of interaction and contact regions with PMMA matrix material and thereby, it may be led to increase in reinforcing and improvement it, and so, the mechanical properties for bio composite material will improve.

The reference PMMA specimen has a hardness value of about 75.3. The maximum value of hardness reaches to 86 for bio composite specimen that reinforced with walnut shells particles at concentration of 2% and average particle size of 25 μ m, while the highest value of hardness for all bio composite samples that strengthened with particle size of 150 μ m of the same material reaches to 82.2 at the same concentration as shown in the Figure 5. Although these differences may not reach statistical significance, the observed increases in hardness suggest a meaningful improvement in material properties, particularly for denture applications where greater hardness can improve durability and wear resistance.

3.3 Water absorption

The water absorption values for neat PMMA acrylic specimen and bio composite specimens that fabricated in the current work are seen in Figure 6.

It can be observed from Figure 6 that values of water absorption for bio composite specimens were increased with rising the concentration of natural fillers at different particle sizes as compared with the reference PMMA specimen. Also, it can be observed that there was no change in the dimensions

of the specimens, but the change in weight occurs according to the weight fraction content of the walnut shell's particles. This behavior may be related to the hydrophilic nature of walnut shells powder as natural filling materials that lead to high level of moisture absorption in PMMA matrix as result from the groups of polar hydroxides in these natural fillers.

It can be observed from the Figure 7 that bio composite samples with high weight fraction content of walnut shells

particles exhibited higher water absorption values. This behavior related to higher concentration of natural particles in bio composites specimens that lead to absorbing more water [25, 26]. This result do not align with those obtained from [27].

In addition to that, it can be noticed that the fine particle size from natural powder (walnut shells particles) of bio composite specimens has slightly higher water absorption values than the coarse particle size of the same material [26, 28].

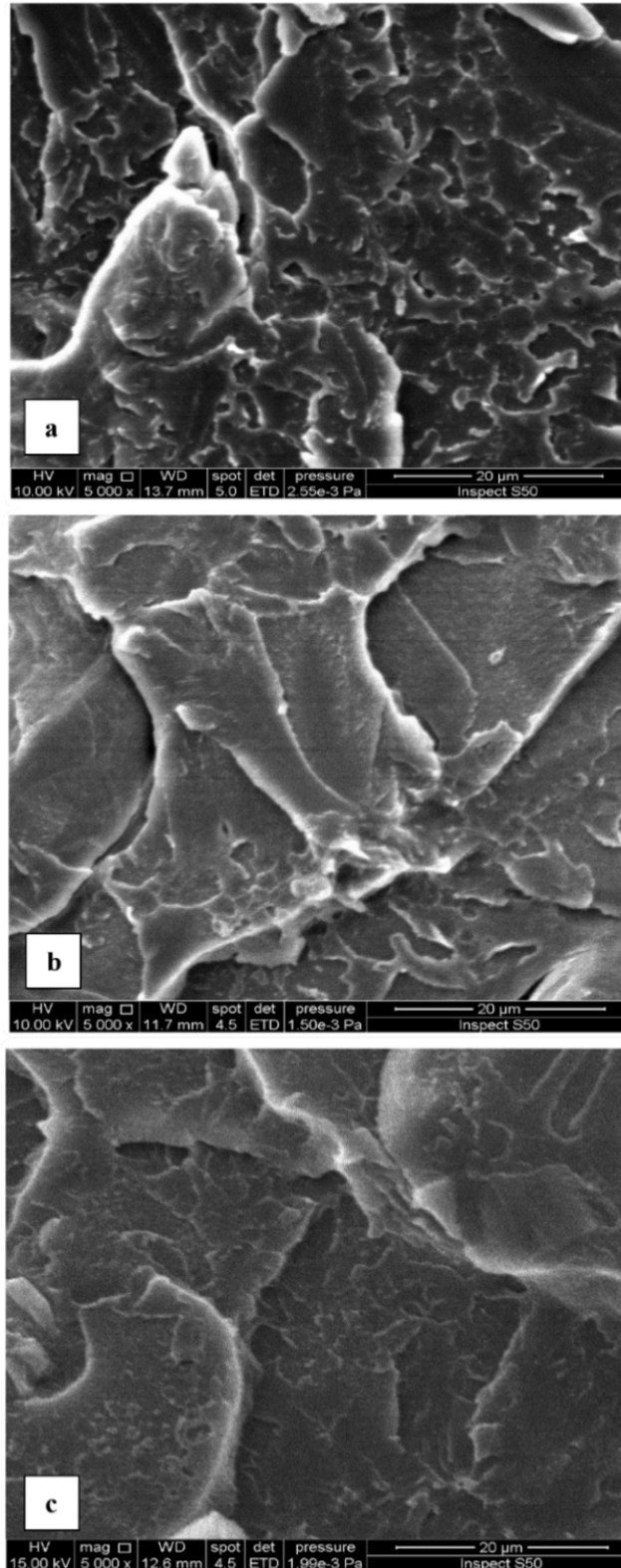


Figure 7. SEM images of fracture surface morphology for: (a) pure PMMA, (b) PMMA: x% (walnut shells particles) of 25µm particle size and (c) PMMA: x% (walnut shells particles) of 150µm particle size

The maximum value of water absorption reached to (0.179%) at weight fraction content (2%) for PMMA bio composite samples reinforced with walnut shells powder have average micro size of (25 μ m) as compared with the value of water absorption for control PMMA sample that equal (0.142%) as show in the Figure 7.

3.4 Scanning electron microscopy test

The SEM micrographs test surfaces for the surface of fracture in polymer composite materials based on several factors include the nature of polymer composite material, their components, concentration of the strengthening substances, the wettability among their components, also based on the conditions of viscosity and fabrication of the components [19, 29]. The reason behind using of the scanning electron microscopy (SEM) is to join the mechanical properties for composite samples with their microstructure. The photographic image in fracture surface morphology of reference PMMA specimen as well as the fracture surface morphology of composites specimens which reinforced with walnut shells powder (PMMA: x% (micro walnut shells particles) at magnification (x5000) are shown in the Figure 7. It can be noticed from this image, that the structural morphology of the pure PMMA structure possess in a homogenous structure with few micro porosities of free volume (Figure 7 (a)). On the other hand, the samples of bio composites possess a homogeneous and dense structural morphology which exhibited a smoother shape in the surface of fracture zone, this refers to the good interfacial adhesion between (PMMA) matrix with natural reinforcement, in addition to that, no new phase or a phase separated dominants was found in bio composites structures (Figure 7 (b) and (c)), this structural morphology appear was accepted with other researchers [30, 31]. Also, the structures of bio composite specimens explain that the increasing in the concentration of micro particles in the composite would improve the micro structures size of the fabricated composites. Add to that, the morphology of the surface in fracture zone surface exhibited good and uniform distribution of filler particles, for high and low contents of micro particle in fabricated samples, which noticed, from red lines that seen in Figure 7 (b) and (c). As well as, through this morphology, it was observed that most of micro particles (walnut shells powder) are incorporated inside the matrix material (PMMA), which represent as an integral portion of PMMA structure. Referring to better physical adhesion between PMMA material and natural filling material (walnut shells powder) leading to a good compatibility between the PMMA resin and the reinforcing material, which improve the mechanical properties of bio composite samples used for denture base appliances [32].

4. CONCLUSIONS

Depending on the obtained results from physical and mechanical tests for bio composite materials that fabricated in current work, it can be concluded that:

(1) The lowest values of compression strength, hardness and water absorption ratio are shown in the reference PMMA acrylic specimen which equal (270,029 MPa, 75.3 shore-D and 0.124%) respectively.

(2) Compression strength and hardness values improved with addition walnut shells particles for both sizes to pure

PMMA resin. Also, these values increased by increasing the concentration of micro natural fillers and they reached to the maximum amount, at 2% content of walnut shells (325.56 MPa and 86 shore-D) for particle size of 25 μ m and (306.409 MPa and 82.2 shore-D) for particle size of 150 μ m respectively.

(3) With regard to water absorption test, the results exhibit an increasing in water absorption ratio with adding walnut shells particles and the maximum value equal 179% was shown in bio composite samples that strengthened with 2% content of walnut shells powder at micro size of (25 μ m) as compared with the reference PMMA sample that has the lowest value of water absorption ratio of about 142% Compression strength and hardness values were improved with increase concentration and reducing particle size of natural fillers (walnut shells powder) and compression strength and hardness values reached to the maximum amount for bio composite samples when reinforced with walnut shells particles for both particle sizes, at 2% content of walnut shells, also the maximum values of water absorption ratio was shown in bio composite samples that strengthened with 2% content of walnut shells powder at micro size of 25 μ m.

(4) All bio composite specimens reinforced with fine particle sizes of walnut shells powder showed the highest compressive strength, hardness and water absorption ratio values as compared with those that strengthened by coarse particle sizes of the same natural fillers above.

(5) In the SEM test, specimens of bio composites possess a homogeneous and dense structural morphology which exhibited a smoother fractured surface, that refers to the better interfacial adhesion of PMMA matrix with natural reinforcement, also, no new phases were found or a phase separated dominants in bio composites structures and this mean a good compatibility between the acrylic resin and reinforcing material.

(6) It can be conclusion from the basis on the mentioned earlier, that the adding of natural fillings particles (walnut shells powder) in micro size to PMMA material is one of the promising materials in use to improve the fracture strength for denture base material.

(7) Our research demonstrated that the compressive strength and hardness values improved with increasing concentrations of natural fillers used in this study. As a result of these observations, further investigation is recommended to assess the effect of the matrix and natural reinforcing materials on other mechanical properties, such as tensile strength, impact resistance, surface roughness, wear, as well as density and thermal properties. Additionally, the impact of these natural fillers in nanoscale form on denture bases should be considered for future research to gain a more comprehensive understanding.

REFERENCES

- [1] Alla, R.K., Sajjan, S., Alluri, V.R., Ginjupalli, K., Upadhyaya, N. (2013). Influence of fiber reinforcement on the properties of denture base resins. *Scientific Research*, 4(1): 27371. <http://doi.org/10.4236/jbnb.2013.41012>
- [2] Salih, S.I., Braihi, A.J., Sadeq, H.M. (2019). The fracture toughness of heat cured acrylic-natural rubber/silicone rubber blend reinforced with pomegranate peels powder. *Journal of University of Babylon for Engineering Sciences*, 27(4): 175-184.

- <http://www.iasj.net/iasj/article/263005>.
- [3] Shahkar, L., Khachatourian, A.M., Nemati, A. (2024). Fabrication and characterization of PMMA denture base nanocomposite reinforced with hydroxyapatite and multi-walled carbon nanotubes. *Diamond and Related Materials*, 147: 111377. <https://doi.org/10.1016/j.diamond.2024.111377>
- [4] El-Sheikh, A.M., Al-Zahrani, S.B. (2006). Causes of denture fracture: A survey. *Saudi Dental Journal*, 18(3): 149-154. https://applications.emro.who.int/imemrf/sdj_2006_18_3_149.pdf.
- [5] Nejatian, T., Johnson, A., Van Noort, R. (2006). Reinforcement of denture base resin. *Advances in Science and Technology*, 49: 124-129. <https://doi.org/10.4028/www.scientific.net/AST.49.124>
- [6] Zappini, G., Kammann, A., Wachter, W. (2003). Comparison of fracture tests of denture base materials. *The Journal of Prosthetic Dentistry*, 90(6): 578-585. <https://doi.org/10.1016/j.prosdent.2003.09.008>
- [7] Tacir, I.H., Kama, J.D., Zortuk, M., Eskimez, S. (2006). Flexural properties of glass fibre reinforced acrylic resin polymers. *Australian Dental Journal*, 51(1): 52-56. <https://doi.org/10.1111/j.1834-7819.2006.tb00401.x>
- [8] Chow, W.S., Tay, H.K., Azlan, A., Ishak, Z.M. (2008). Mechanical and thermal properties of hydroxyapatite filled poly (methyl methacrylate) composites. In *Proceedings of the Polymer Processing Society 24th Annual Meeting, Salerno, Italy*, pp. 15-19.
- [9] Oleiwi, J.K., Othman, F.M., Ghaze, I.F. (2013). A study of mechanical properties of poly methacrylate polymer reinforced by silica particles (SiO₂). *Engineering and Technology Journal*, 31(15): 2925-2941. <http://www.iasj.net/iasj/download/a2b9e6eeec6002ff>.
- [10] Gopichander, N., Kumarai, K.H., Vasanthakumar, M. (2015). Effect of polyester fiber reinforcement on the mechanical properties of interim fixed partial dentures. *The Saudi Dental Journal*, 27(4): 194-200. <https://doi.org/10.1016/j.sdentj.2015.03.002>
- [11] Pentapati, L., Srinivas, K., Shankar, R., Swetha, V., Krishna, M. (2017). Effects of addition of aluminum oxide on flexural strength and hardness of acrylic resins. *IOSR-JDMS*, 16(3): 1-6.
- [12] Somkuwar, S., Mishra, S.K., Agrawal, B., Choure, R. (2017). Comparison of the flexural strength of polymethyl methacrylate resin reinforced with multiwalled carbon nanotubes and processed by conventional water bath technique and microwave polymerization. *The Journal of Indian Prosthodontic Society*, 17(4): 332-339. https://doi.org/10.4103/jips.jips_137_17
- [13] Aziz, H.K. (2018). TiO₂-nanofillers effects on some properties of highly-impact resin using different processing techniques. *The Open Dentistry Journal*, 12: 202. <https://doi.org/10.2174%2F1874210601812010202>
- [14] Oleiwi, J., Hamad, Q.A., Kadhim, N.N. (2019). Study compression, hardness and density properties of PMMA reinforced by natural powder used in denture base applications. *Engineering and Technology Journal*, 37(12A): 522-527. <https://doi.org/10.30684/etj.37.12A.5>
- [15] Ahmed, S., Salih, W. (2021). Development the mechanical properties of the acrylic resin (PMMA) by added different types of nanoparticles, used for medical applications. *Engineering and Technology Journal*, 40: 166-171. <http://doi.org/10.30684/etj.v40i1.2017>
- [16] Fouly, A., Nabhan, A., Badran, A. (2022). Mechanical and tribological characteristics of PMMA reinforced by natural materials. *Egyptian Journal of Chemistry*, 65(4): 543-553. <https://doi.org/10.21608/ejchem.2021.98063.4572>
- [17] Hussain, W.S., Oleiwi, J.K., Hamad, Q.A. (2023). Study of physical properties of bio composite based on the polymer blends used for denture base applications. *Engineering and Technology Journal*, 41(12): 1474-1487. <http://doi.org/10.30684/etj.2023.141437.1496>
- [18] Mohan, S., Panneerselvam, K. (2021). An investigation on antibacterial filler property of silver nanoparticles generated from Walnut shell powder by insitu process. *Materials Today: Proceedings*, 39: 368-372. <https://doi.org/10.1016/j.matpr.2020.07.516>
- [19] Salih, S.I., Oleiwi, J.K., Mohamed, A.S. (2018). Investigation of mechanical properties of PMMA composite reinforced with different types of natural powders. *ARNP Journal of Engineering and Applied Sciences*, 13(22): 8889-8900.
- [20] ASTM International. (2021). ASTM D2240-15 standard test methods for rubber property-durometer hardness. In *Annual Book of ASTM Standards*. <https://doi.org/10.1520/D2240-15R21>
- [21] ASTM International. (2022). ASTM D570-22 standard test method for water absorption of plastics. <https://doi.org/10.1520/D0570-22>
- [22] Ofora, P.U., Nwokoye, J.N., Ekpunobi, E.U., Okpalaunegbu, C.A., Ezeanyika, M. (2016). Effects of bamboo-corn husk as fillers on the mechanical properties in polypropylene. *International Journal of Materials Chemistry and Physics*, 2(2): 88-92. <http://repository.unizik.edu.ng/handle/123456789/498>.
- [23] Mahmood, N.Y. (2017). Studying the effect of mixture of pomegranate peel and licorice on the mechanical properties of epoxy. *Al-Nahrain Journal for Engineering Sciences*, 20(4): 871-875. <https://nahje.com/index.php/main/article/view/311>.
- [24] Kadhum, A.A.U., Mohammed, A.A. (2016). Investigation the effect of natural materials on wear and hardness properties of polymeric composite materials. *The Iraqi Journal for Mechanical and Material Engineering*, 16(4): 369-372. <http://www.iasj.net/iasj/download/40e0735ab80f2530>.
- [25] Abdullah, O.S. (2017). Experimental study to the effect of natural particles added to unsaturated polyester resin of a polymer matrix composite. *Al-Khwarizmi Engineering Journal*, 13(1): 42-49. <https://doi.org/10.22153/kej.2017.08.004>
- [26] Abd Mohammed, A., Depart, A.L.M.E. (2015). Study the thermal properties and water absorption of composite materials reinforced with data and olive seeds. *The Iraqi Journal for Mechanical and Material Engineering*, 15(2): 138-152.
- [27] Monem, Z.M.A., Hamad, Q.A., Oleiwi, J.K. (2021). DENSITY and water absorption properties of PMMA reinforced by peanut and walnut shells powders used in dental applications. *The Iraqi Journal for Mechanical and Materials Engineering*, 21(1): 46-53. <https://doi.org/10.32852/ijqfmme.v21i1.538>
- [28] Hussein, A.A., Salim, R.D., Sultan, A.A. (2011). Water absorption and mechanical properties of high-density polyethylene/egg shell composite. *Journal of Basrah*

- Researches (Sciences), 37(3A/15): 36-42.
<https://www.iasj.net/iasj/article/55026>
- [29] Cheyad, M.S. (2018). Characterization of red apple and pomegranate peels extracts as corrosion inhibitors for α Brass in Acidic media. Master's dissertation, College of Science/Al-Nahrain University.
<https://www.nahrainuniv.edu.iq/ar/node/6587>.
- [30] Salih, S.I., Braihi, A.J., Sadeq, H.M. (2020). Comparative study of some mechanical properties of nanocomposites based on the polymer's blends used for dentures base applications. Materials Research Express, 6(12): 125429. <https://doi.org/10.1088/2053-1591/ab7dfe>
- [31] Kadhim, N.N., Hamad, Q.A., Olewi, J.K. (2020). Tensile and morphological properties of PMMA composite reinforced by pistachio shell powder used in denture applications. In AIP Conference Proceedings, Baghdad, Iraq, 2213(1). AIP Publishing.
<https://doi.org/10.1063/5.0000181>
- [32] Khalid, S., Khalid, N., Khan, R.S., Ahmed, H., Ahmad, A. (2017). A review on chemistry and pharmacology of Ajwa date fruit and pit. Trends in Food Science & Technology, 63: 60-69.
<https://doi.org/10.1016/j.tifs.2017.02.009>