Tensile and morphological properties of PMMA composite reinforced by Pistachio Shell powder used in denture applications

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Abstract. The purpose of this research is to investigate the effect of Pistachio Shell powder on some properties of (heat-cure) PMMA acrylic resin that’s popularly used as denture base material, where this natural powder had been added in different weight fraction (3, 6, 9, and 12 wt. %) and different average particle size (53 μm, 106 μm, 150 μm, and 212 μm). Tensile and SEM test had been studied, the results where statistically analyzed by using SPSS (one-way ANOVA) program to evaluate the mean value and show the significant difference for each particle size. The results were as the following: the tensile strength and elongation percentage were dropped with increasing the weight the weight of Pistachio Shell powder, while the Young’s modulus had been increased with increasing the weight fraction of Pistachio Shell powder and reached its maximum value at (12 wt. %) of average particle size (53 μm). SEM results show that the smoothness of fractured surface will increase and that is suggesting a brittle to semi ductile transformation.

INTRODUCTION

Polymeric materials represent important material in the dentistry field because of their special characteristics allow it a wide range of medical applications which are not available in other types of materials, today and since 1930 poly (methyl methacrylate) (PMMA) is the most commonly used polymeric material in the fabrication of the denture base materials [1, 2]. Although, its advantages those are represented in the simplicity of molding and repairing, inexpensive if compared with metal- base denture and excellent aesthetic appearance, but the main drawbacks of PMMA are presented in its poor mechanical properties especially the low toughness [3, 4].

Therefore, this research was done to develop the dental restorative material by using natural powder as reinforcing material, and trying to evaluate whether the natural powder can enhance the strength and modulus of denture base resins. W. Abbas et. al., (2010), they study the effect of adding of (low cost materials biocompatible antibiotic materials) Genuine Nigella sativa and Thyme as oil to heat cure acrylic resin in different weight fraction by (0.5, 1, 1.5, and 2 wt.%), and estimate the changes that may occur to transverse strength, indentation hardness, color property, residual monomer, dimensional accuracy, porosity, measurement of IR spectra, and anti–microbial–sensitivity test. The results of this study illustrated that there was a significant difference (S) where (P= 0.05). And there were an increasing in transverse strength and hardness of the denture base materials, no porosities, an increase in residual monomer elution at 1st day [5].

J. Xu et. al.,(2011), the influence of adding of short sisal fiber to auto- polymerized denture base resin had been investigated in this study, where sisal fiber used by different weight fraction of (2.5, 5, 7.5, 10.0 wt.%) with fiber length of (2mm), the results of untreated (UT) and silane treated (ST) sisal fiber had been compared. The results showed that flexural modulus is increased with increasing sisal fiber content, also sisal fiber concentrations lower than (10 wt. %) caused decreasing in flexural strength of denture base resin, but denture base resin reinforced by
H. A. Khalaf, (2013), was tried to enhance the mechanical properties of denture base resin PMMA (tensile strength, impact strength and transvers strength) by reinforcing it with Siwak powder with average particle size of (75μm) in different concentration of (3%, 5% and 7%) by weight, the results indicated that the addition of Siwak powder in low concentration (3% and 5%) to heat polymerized denture base acrylic resin did not affect greatly the mechanical properties, while the addition of (7%) Siwak powder showed a significant decline in tensile strength, impact strength and compressive strength in comparison to the control group [7].

EXPERIMENTAL PART

The Pistachio Shell which is used as cellulose agricultural waste materials, was used as reinforcing material in the present study, in different average particle size of (53μm, 106μm, 150μm and 212μm), and different weight fraction of (3, 6, 9 and 12 wt. %), this powder has been added to PMMA acrylic resin to produce bio composite specimens of prosthetic denture. The natural powder was chemically treated by alkali solution consist of 5% (w/v) of (NaOH) in distilled water, at room temperature (25°C) [8, 9]. The bio composite specimens of tensile test had been designed according to the international standard (ASTM D638) [10], the test was carried out at room temperature by using universal tensile machine type (LARYEE) in the laboratory of Materials Engineering Department-University of Technology-Iraq.

RESULTS AND DISCUSSION

Tensile Test

Tensile Strength

Fig. 1 represents the tensile strength test results graphically for PMMA samples before and after reinforcing with Pistachio Shell powder. The results were be as the following: there were a decreasing in tensile strength values of PMMA composite as the weight fraction of Pistachio Shell powder is increased, this behavior may be resulted from that, Pistachio Shell Powder cannot minimize the slip of PMMA chains, furthermore, the lack of wettability of the particles which is resulting from the higher Pistachio Shell powder loading, which in turn resulted in reducing the adhesion between the matrix and reinforcing powder, and this in turn will result in decreasing the tensile strength [11, 12].

![Fig. 1. The Relationship between Tensile Strength of PMMA Composite and Weight Fraction of Pistachio Shell Powders at Different average Particle Size.](image-url)
The results were statistically analyzed by using one-way ANOVA SPSS, where table (1) represents the descriptive statistics (Mean, Std. Deviation, Std. Error, Minimum, Maximum) and one-way ANOVA (p value between groups)) for tensile strength test, the statistical results showed that, neat PMMA has mean value greatest than the others, also the lowest value was obtained at the specimen reinforced by 12\%wt. of average particle size 212\μm, the groups of average particle size of 53\μm and 150\μm have significant difference (S) (p>0.01), while the groups of average particle size of 106\μm and 212\μm showed very high significant difference(VHS) (p≤0.001).

TABLE1. Represent Descriptive Statistics and one-way ANOVA of Tensile Strength Results.

| Groups | N  | Mean | Std. Deviation | Std. Error | Minimum | Maximum | P-value between groups |
|--------|----|------|----------------|------------|---------|---------|-----------------------|
| A53    | 3  | 65   | 1.732          | 1.000      | 63      | 66      | .021 (S)              |
| 3\%    | 3  | 62   | 3.000          | 1.732      | 59      | 65      |                       |
| 6\%    | 3  | 61   | 3.606          | 2.082      | 57      | 64      |                       |
| 9\%    | 3  | 58   | 2.646          | 1.528      | 55      | 60      |                       |
| 12\%   | 3  | 56   | 2.646          | 1.528      | 53      | 58      |                       |
| A106   | 3  | 65   | 1.732          | 1.000      | 63      | 66      | .001 (VHS)            |
| 3\%    | 3  | 60   | 2.7839         | 1.6073     | 58      | 63      |                       |
| 6\%    | 3  | 59   | 3.4641         | 2.0000     | 55      | 61      |                       |
| 9\%    | 3  | 54   | 4.5826         | 2.6458     | 50      | 59      |                       |
| 12\%   | 3  | 48   | 3.0000         | 1.7321     | 45      | 51      |                       |
| A150   | 3  | 65   | 1.7321         | 1.0000     | 63      | 66      | .015 (S)              |
| 3\%    | 3  | 59   | 2.1794         | 1.2983     | 57      | 61      |                       |
| 6\%    | 3  | 57   | 3.1225         | 1.8028     | 54      | 60      |                       |
| 9\%    | 3  | 56   | 3.1225         | 1.8028     | 53      | 59      |                       |
| 12\%   | 3  | 54   | 4.5826         | 2.6458     | 49      | 58      |                       |
| A212   | 3  | 65   | 1.7321         | 1.0000     | 63      | 66      | .000 (VHS)            |
| 3\%    | 3  | 52   | 3.9686         | 2.2913     | 48      | 55.5    |                       |
| 6\%    | 3  | 48   | 3.7749         | 2.1794     | 44.5    | 52.0    |                       |
| 9\%    | 3  | 47   | 4.3589         | 2.5166     | 42.0    | 50.0    |                       |
| 12\%   | 3  | 43   | 4.3589         | 2.5166     | 38.0    | 46.0    |                       |

Modulus of Elasticity

The variation of modulus of elasticity for PMMA and PMMA composite specimens those are prepared in this study is presented in the fig.(2), from this fig. it can be noticed how the modulus of elasticity values increased with increasing the weight fraction of Pistachio Shell powder, this is may be resulted from the truth that the used powder have stiffness and modulus of elasticity higher than the neat material itself, and because of this, the total composites stiffness will increase, also this behavior gives an indication that the modulus of elasticity is not depending on the matrix-particles bonding properties [11,13]. In addition the fig. showed that the finest particle size enhance the modulus of elasticity higher than the coarser one, this is due to that the fine particles prevent the slipping of the matrix chains and they are demanding additional force to bend them in tight space among particles as comparison with large particle [14].

FIGURE 2. The Relationship between Modulus of Elasticity of PMMA Composite and Weight Fraction of Pistachio Shell Powders at Different Particle Size.
Table (2) represents descriptive statistics (Mean, Std. Deviation, Std. Error, Minimum, Maximum and one-way ANOVA (p value between groups) for Modulus of elasticity, the statistical results showed that the neat PMMA has mean value lowest than the others, also the highest value was obtained at the specimen reinforced by 12%wt. of average particle size (53μm), the average particle size of (53μm) group has high significant difference (HS) (p>0.001), while the other groups have non- significant difference (NS) (p>0.05).

**TABLE 2.** Represent Descriptive Statistics and one-way ANOVA for Modulus of Elasticity Results.

| Groups | N  | Mean   | Std. Deviation | Std. Error | Minimum | Maximum | P-value between groups |
|--------|----|--------|----------------|------------|---------|---------|------------------------|
| A53    | 3  | 1.0262 | .0938638       | .0541923   | .9643   | 1.1342  | .009 (HS)              |
| 3%     | 3  | 1.1942 | .1452546       | .0838628   | 1.0293  | 1.3032  |                        |
| 6%     | 3  | 1.2843 | .0217559       | .0125608   | 1.2617  | 1.3051  |                        |
| 9%     | 3  | 1.2941 | .0723050       | .0417453   | 1.2125  | 1.3502  |                        |
| 12%    | 3  | 1.3525 | .0590250       | .0345977   | 1.2835  | 1.3915  |                        |
| A106   | 3  | 1.0262 | .0938638       | .0541923   | .9643   | 1.1342  | .121 (NS)              |
| 3%     | 3  | 1.1492 | .1799336       | .1038847   | .9915   | 1.3452  |                        |
| 6%     | 3  | 1.1902 | .0661481       | .0381906   | 1.1139  | 1.2314  |                        |
| 9%     | 3  | 1.2255 | .0951787       | .0549515   | 1.1225  | 1.3102  |                        |
| 12%    | 3  | 1.2991 | .0988384       | .0570644   | 1.1932  | 1.3889  |                        |
| A150   | 3  | 1.0262 | .09386378      | .05419228  | .96430  | 1.13420 | .089 (NS)              |
| 3%     | 3  | 1.10903| .10181741      | .05878431  | 1.03479 | 1.22510 |                        |
| 6%     | 3  | 1.1352 | .03086470      | .01781975  | 1.11050 | 1.16980 |                        |
| 9%     | 3  | 1.15975| .05827214      | .03364344  | 1.11415 | 1.22540 |                        |
| 12%    | 3  | 1.2704 | .13566299      | .07999915  | 1.11610 | 1.38420 |                        |
| A212   | 3  | 1.0262 | .09386378      | .05419228  | .96430  | 1.13420 | .206 (NS)              |
| 3%     | 3  | 1.05623| .06587288      | .03803172  | 1.01360 | 1.13210 |                        |
| 6%     | 3  | 1.09508| .03253031      | .01878138  | 1.06654 | 1.13050 |                        |
| 9%     | 3  | 1.10812| .04730346      | .02731086  | 1.05360 | 1.13826 |                        |
| 12%    | 3  | 1.16225| .07799934      | .04503294  | 1.10123 | 1.25013 |                        |

Elongation Percentage

The values of elongation percentage for PMMA and all the composite specimens that prepared in the current study are shown in fig. (3), which is illustrating the relationship between elongation percentage and the weight fraction of Pistachio Shell powder, it can be noticed the decreasing in the elongation percentage as compared with the neat PMMA. The reason behind this behavior is that, because of the use of brittle powder the brittleness of the composite will increase, so the elongation at break will decrease [15], also, it may be result from the entering of the powder particles between the resin chains, which is playing the role of restricting the chains motion so, the slipping of these chains will decrease and leading to decreasing the plastic deformation, then the elongation percentage will decrease [16, 17, 18], In addition the figure showed that the finest particle size enhance the modulus of elasticity higher than the coarser one, this is due to that the fine particles prevent the slipping of the matrix chains and they are demanding additional force to bend them in tight space among particles as comparison with large particle [14].
FIGURE 3. The Relationship between Elongation of PMMA Composite and Weight Fraction of Pistachio Shell Powder at Different Average Particle Size.

Table (3) represents descriptive statistics (Mean, Std. Deviation, Std. Error, Minimum, Maximum and one-way ANOVA (p value between groups)) for elongation percentage, the statistically results showed that the neat PMMA has mean value lowest than the others, also the lowest value was obtained at the specimen reinforced by 12% wt. of average particle size 212 μm, all groups have been shown very high significant difference (VHS) (p ≤ 0.001) as compared with neat PMMA.

| Groups | N | Mean | Std. Deviation | Std. Error | Minimum | Maximum | P-value between groups |
|--------|---|------|----------------|------------|---------|---------|------------------------|
| A53    | 0 | 3    | 5.1667         | .2635969   | 4.8793  | 5.3972  | .000 (VHS)             |
| 3%     | 3 | 4.12 | .1589959       | .0917963   | 3.9987  | 4.3000  |
| 6%     | 3 | 3.53 | .3692371       | .2131791   | 3.1260  | 3.8500  |
| 9%     | 3 | 2.81 | .376308        | .2157159   | 2.4700  | 3.2100  |
| 12%    | 3 | 2.28 | .2644560       | .1526838   | 1.9870  | 2.5010  |
| A106   | 0 | 3    | 5.1667         | .2635969   | 4.8793  | 5.3972  | .000 (VHS)             |
| 3%     | 3 | 4    | .2645751       | .1527525   | 3.7000  | 4.2000  |
| 6%     | 3 | 3.24 | .4077389       | .2354082   | 2.9810  | 3.7100  |
| 9%     | 3 | 2.71 | .4044750       | .2335237   | 2.2500  | 3.0100  |
| 12%    | 3 | 2.1  | .2981610       | .1721434   | 1.8500  | 2.4300  |
| A150   | 0 | 3    | 5.1667         | .26359687  | 4.87930 | 5.39720 | .000 (VHS)             |
| 3%     | 3 | 3.75 | .38314488      | .22120880  | 3.31000 | 4.01000 |
| 6%     | 3 | 3.13 | .27823192      | .16063727  | 2.95800 | 3.45100 |
| 9%     | 3 | 2.51 | .30876633      | .17827787  | 2.15700 | 2.73000 |
| 12%    | 3 | 2.01 | .19150196      | .11056371  | 1.89300 | 2.23100 |
| A212   | 0 | 3    | 5.1667         | .26359687  | 4.87930 | 5.39720 | .000 (VHS)             |
| 3%     | 3 | 3.23 | .47117300      | .27203186  | 2.91800 | 3.77200 |
| 6%     | 3 | 2.53 | .32241155      | .19008770  | 2.33000 | 2.91000 |
| 9%     | 3 | 2.1  | .20663978      | .11930353  | 1.91000 | 2.32000 |
| 12%    | 3 | 1.55 | .20663978      | .11930353  | 1.38000 | 1.78000 |

Morphological Test (SEM)

Scanning electron microscopy (SEM) test was done in order to match the mechanical behavior and the fracture surface morphology of neat PMMA and PMMA composite specimens, that is reinforced with the Pistachio Shell powder at different average particle size of (53μm, 106μm, 150μm and 212μm) and weight fraction of (12% wt.), for the fractured specimens of tensile test. The test was done at different magnification for each one of these specimens (500x and 1000x) as shown in figs. (4, 5, 6, 7 and 8) respectively.
The morphology of polymeric composite strongly depends on some of factors such as the processing conditions, particle size, components nature and components ratios. Fig. (4) Shows the fracture morphology of neat PMMA at different magnifications (500x and 1000x), which is appeared as a brittle failure of homogenous material.

![Fracture morphology of neat PMMA at different magnifications](image)

**FIGURE 4.** Represents SEM Image of Fractured Surface for Neat PMMA at Different Magnification (a) 500x and (b) 1000x.

The fracture surface morphology of PMMA composite specimens reinforced with Pistachio Shell powder of different average particle size in PMMA matrix at different magnification (500x and 1000x) are illustrated in figs. [(5a,b), (6 a,b), (7 a,b) and (8 a,b)] respectively.

![Fracture surface morphology of PMMA composite specimens](image)

**FIGURE 5.** Represents SEM Image of PMMA Composite Reinforced with (12%wt.) Pistachio Shell Powder of Average Particle size of (53μm) at Different Magnification (a) 500x and (b) 1000x.

![Fracture surface morphology of PMMA composite specimens](image)

**FIGURE 6.** Represents SEM Image of PMMA Composite Reinforced with (12%wt.) Pistachio Shell Powder of Average Particle size of (106μm) at Different Magnification (a) 500x and (b) 1000x.
FIGURE 7. Represents SEM Image of PMMA Composite Reinforced with (12%wt.) Pistachio Shell powder of Average Particle size of (150μm) at Different Magnification (a) 500x and (b) 1000x.

FIGURE 8. Represents SEM Image of PMMA Composite Reinforced with (12%wt.) Pistachio Shell powder of Average Particle size of (212μm) at Different Magnification (a) 500x and (b) 1000x.

From these figs. it can be noticed a smoother fracture surface morphology and semi continuous morphology also shows good distribution of the powder in PMMA matrix. There is a remarkable difference in the behavior of the fracture surface morphology of neat PMMA compared with the PMMA composite reinforced with Pistachio Shell powder of different average particle size, where the smoothness will increase and that is suggesting a brittle to semi ductile transformation, the dispersion of Pistachio Shell particles is relatively good and the particles embedded in the matrix and became part of it, so there is a uniform dispersion through the entire PMMA matrix that is resulting from the strong interfacial and interaction between the PMMA matrix and Pistachio Shell powder in the composite specimens. Also, from these figs. it can be noticed that, there is not density gradients in the cross sections analyses of the composite specimens, while showing in all cases a homogenous microstructure. Also observations in these composite materials exhibited a good compatibility between the PMMA matrix and reinforcing material (Pistachio Shell) powder. Furthermore, from these figs. it wasn’t found any attributes to craze formation or crack growth inside the PMMA matrix [19].

CONCLUSION

1- The tensile strength, elongation percentage were decreased with increasing the weight fraction of Pistachio Shell powder in PMMA resin. The lowest values of them were obtained at (12wt.%) and at average particle size of (212μm)
2- The modulus of elasticity will be increased with increasing the weight fraction of Pistachio Shell powder in PMMA resin, and the highest value was obtained at (12%wt.) at average particle size of (53μm).
3- The morphological test results showed a brittle to semi ductile transformation, where the smoothness of the composite specimens will increase when the PMMA reinforcing with Pistachio Shell powder, also there is not density gradients in the cross sections analyses of the composite specimens.

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