

---

---

## **Altering Water Effect and Surface Properties of Heat Cured Poly Methyl Methacrylate by Adding Surface Treated Titanium Di Oxide Nano Particles**

Hasanen A. Alnameel

Department of Prosthetic, College of Dentistry, Basrah University, Iraq.

---

---

**Article Info:**

**-Article History:**

**-Received:** 30/4/2019

**-Accepted:** 4/7/2019

**-Available Online:** 7/2019

**Keywords:**

PMMA (heat cure acrylic), Titanium di oxide Nano-filler (TiO<sub>2</sub>), Nano technology.

**Corresponding Author:**

**Name:** Hasanen A. Alnameel

**E-mail:**

hasanen.muhsen@uobasrah.edu.iq

**Tel:** +964 7823036660

**Affiliation:**

(1) Ass. Lec. Department of Prosthetic, College of Dentistry, Basrah University, Iraq.

**Abstract**

Titanium dioxide (TiO<sub>2</sub>) is extensively used part of our regular life. It can be observed in various commonly utilized goods & customer imports for instance drugs, plastics, cosmetics, food and paper. Universally, the quantity of titanium oxide manufactured in 2009 was 4.68 million tons for that reason the tenacity of the revision is controlling the amount of change on the denture base physical features such as the heat treatment in denture processing (PMMA) through the implementation of modified outer surface titanium di oxide Nano particles. Its properties are comprised of water solubility, surface roughness, water sorption and surface hardness. The controlled TiO<sub>2</sub> powder added to heat cured acrylic material according to the main weight of PMMA in concentration of 3%, 5% and 7%, and then it's mixed regularly by engine of probe ultra-sonication. Titanium oxide Nano fillers were merged in denture based material with the help of more free radical polymerization in bulk. The nanoparticles were surface treated by a layer of trimethoxysilypropylmethacrylate (TMSPM). 120 specimens were created and separated into 3 sample sets affording to the examination (each sample sets consist of 40 samples) and each sample sets were sectioned in four subsets according to the TiO<sub>2</sub> added ratio and ultimately containing 10 samples in each subset. The tests which conducted were indentation hardness (shore D), surface roughness properties as well as water sorption and solubility. For each test four of the sub groups (one controlled and three with added Nano TiO<sub>2</sub>). Important to mention that extremely elevation in surface hardness score and roughness were detected at the ratio of 3%, 5% and 7%. Thus escalation of added TiO<sub>2</sub> nan-fillers considerably reduced the water solubility and sorption. The accumulation of the powder of TiO<sub>2</sub> nanoparticles which have been surface treated to the PMMA acrylic resin thus changing the PMMA properties for example surface rigidity and surface coarseness. In which it's increased in direct proportional relation with the raise of TiO<sub>2</sub> concentration; at the same time addition of surface treated TiO<sub>2</sub> Nano particles decrease water sorption and solubility of (PMMA) also in direct proportional relation with the raise of TiO<sub>2</sub> concentration.

---

---

## Introduction:

Regardless of the common use of acrylic resin in prosthetic dentistry the surface roughness and surface cracks are the most collective causes of failure in the cures of prosthodontic which is still an unsolved issue. To improve properties of polymers it had been strengthened by additives. Up to the present time, up to 95% dental prostheses are self-possessed of poly (methyl meth acrylate), important advantages counting its biocompatibility, properties, adequate strength and visual make it useful <sup>(1)</sup>; however, this resin inherit some flaws which used a meager power especially a worse size under exhaustion disaster intraorally wares abrasion resistance surface roughness an hardness as well as water sorption and solubility <sup>(2)</sup>. Surface treated Nano particles might be a quality material for strengthening denture based polymers as for their well acknowledged development in mechanical & physical properties and an adequate appearance as well <sup>(3)</sup>. Polymer nanotechnology characterizes a fresh view in Nano science, attracted great attention by the polymer Nano composite especially because of their unexpected hybrid properties that are consequent from the two components <sup>(4)</sup>. Modify the properties of PMMA by reinforcing surface treated TiO<sub>2</sub> to the PMMA being very important. It's a convenient technique to lessen the energy of surface, to elevate the polymer medium compatibility & scattering resemblance. Therefore, improving the polymer inorganic particle's properties by the surface alteration of an inorganic element with an organic selected material. The non-viable Nanoparticles were suffered surface dealing with saline well coupler agent and well entrenched into PMMA.<sup>(5,6)</sup> Eliminate accumulation of TiO<sub>2</sub> elements and advance its self-compatibility with organic polymer by the treatment of the TiO<sub>2</sub> nanoparticle's

surface with trimethoxysilypropyl methacrylate (TMSPM) <sup>(7,8)</sup>

## Materials and Methods:

Titanium di Oxide (TiO<sub>2</sub>) Nano filler Silanated by a layer of trimethoxysilypropylmethacrylate (TMSPM), tin foil substitute as separating media, type III hard dental stone and heat curing acrylic liquid & powder were utilized. Almost eighty samples were prepared for this research. All these specimens were distributed in two groups conferring the selected tests. These groups comprised of forty samples each while were further subdivided rendering titanium di oxide Nano filler (TiO<sub>2</sub>) concentration in four subgroups as given below:

**1-Group (A)** control group (30 specimens of acrylic resin without TiO<sub>2</sub>).

**2-Group (B)** 3% modified group (30 specimens of acrylic resin + 3% by weight TiO<sub>2</sub>)

**3-Group (C)** 5% modified group of (30 specimens of acrylic resin+5% by weight TiO<sub>2</sub>).

**4-Group (D)** 7% modified group of (30 specimens of acrylic resin + 7% by weight TiO<sub>2</sub>).

Table (1) show mixing ratio of TiO<sub>2</sub> with PMMA according to the manufacturer instruction

### Plastic model preparation:

The highly precise laser cutting machine was used to cut deferent gage (2.5 & 4mm) plastic plate in chosen dimension and shape for the construction of two plastic models Fig. (1).

1. Bar shaped samples having dimensions of length 65mm x width 10mm x thickness 2.5 ± 0.1mm were tested with Shore. D hardness test and Surface roughness test.

2. Similarly, disc dimension such as 0.5 mm thickness and 50mm diameter were utilized in water solubility & sorption tests.

#### **Mould preparation:**

Among the process of mould preparation, a conservative flasking practice was followed for complete dentures. The cold mold seal or separating medium was coated on the plastic model and dried. After that, the lower part of the metal flask was invested which was full of dental stone. All of this was mixed according to appropriate instructions of manufacturer, thus, the mixing ratio of powder to water used was 100g per 25ml. Moreover, vibration was used to release the stuck air and was left to set. Approximate insertion of the plastic model was about one half of the depth of models for easy removal after stone setting Fig.(2).

#### **Addition of Titanium di oxide Nano fillers:**

The modified Nano filler powder of  $\text{TiO}_2$  was added in four groups by weight such as the accumulation to monomers was carried out to be as 7%, 3%, 0% and 5%. For this, an electronic balance having an accuracy of 0.001 g was utilized. After adding the Nano fillers of  $\text{TiO}_2$  to monomers, the dispersion of fillers in monomers is carried out with the aid of ultra-sonication mixing type while utilizing apparatus of probe sonication (120W, 60 KHz). Thus their breakage in Nano crystals was done only in 3 minutes Fig. (3). The probability of phase separation and aggregation of particles was reduced by mixing the acrylic powder to the suspension of  $\text{TiO}_2$  Nano filler & monomers.

#### **Packing of acrylic resin:**

After indication of perfect parting of the resin from mixing glass jar or simply reaching to the dough stage, the packaging

was started. All the resin was extracted from the jar, rolled & packed into the mold which was already coated with polythene sheet and a separating medium. The flask's two portions were sealed together and a hydraulic pressure was slowly put on the flask which led the dough to even move all though the space of mould. After releasing the pressure, the flask was opened up and a sharp scalpel was used to remove all extra material. Then a second trail closure was executed. The surface of stone was coated once more with separation medium and dried. While removing the polythene sheet. Lastly, flasks two sections were closed again to obtain the intimate contact among them. I was left for five minutes under press of 20 bars and then shifted to the water bath immediately.

#### **Curing:**

The clamped flask was placed in water bath for this purpose and heat treatment was done for one and half hour at 74 °C. Thus, the increase in temperature occurred to the boiling point for thirty mins.

#### **Finishing and polishing:**

A lathe polishing machine was used to polish and finish each specimen excluding those which have to be used for test of surface roughness. All samples were removed from flasks cautiously & cleaned. Acrylic bur and W& H laboratory engine was utilized to remove the acrylic flashes. Whereas, stone bur was utilized to get a smooth surface after usage of 120 grain sand paper along with constant cooling which was provided by immersing in rubber bawl cold water. Further, specimens were polished with lathe polishing machine having ruge wheel along pumice stone and bristle brush. The surface gloss was attained with polishing swap & chamois buff. Their dimensions were calculated using a digital Vernier and polishing was achieved at low speed of

1500 rpm of the machine. A constant cooling was provided as to protect the specimens as extreme heat might distort them.

### 1- Surface hardness testing

**A-Specimen design:** The dimensions for the preparation of specimens were 65mm x 10mm x 2.5mm. To test the surface hardness, 10 specimens of each concentration along with the control made up a total of forty specimens. Before testing, all specimens were absorbed in distilled water for about 48 hours.

**B-Testing method:** a tester used to test was durometer hardness tester or also termed as Shore D hardness which was fabricated by an appropriate design of acrylic material HARTIP 3000compant. This apparatus comprised of a 1, 6 mm diameter cylinder in which a blunt pointed intender of 0.8mm diameter was present. Further this intender was attached to a 0-100 unit gradual digital scale. The normal process involved was to compress the intender quickly & firmly and noting the maximum values as Shore D hardness. All the measurements were noted directly from the digital reading scale. From the various areas (particular selected areas) of every specimen, five values were documented and calculation of the all five readings was done by taking average Fig.(4).

### 2- Surface roughness tests

**A-Test specimens:** To test the surface roughness, specimens of dimensions 65mm x 10mm x2.5mm (11) were utilized. For this purpose of roughness measurement, 10 specimens from each group while making a total of 40 specimens, were taken. All these specimens were put into distilled water before testing for about 48 hours at 37 °C.

**B-Test equipment and procedure:** the surface roughness tester known as profilometer device was utilized to observe the SiO<sub>2</sub> Nano fillers' effects of strengthening on the test surface micro geometry. This device has a sharp stylus composed of diamond or surface analyzer to find out the profile for irregularities of surface Fig.(5). The maximum 11mm of distance was traveled.

### 3- Water sorption and solubility test:

**A-Test Specimens:** plastic model of dimension 0.5 mm ± 0.1 mm thickness and 50mm ± 1 mm diameter were used for preparation of acrylic disc specimens. To measure the water solubility & sorption, 10 specimens with each concentration forming a total of 40 were utilized.

**B-Equipment and procedure:** all the specimens were dried out suing a desiccator which comprised of fresh dry silica gel Fig. (6). After that all the desiccators were kept in incubator for twenty four hours at 37°C ± 2 °C and then all specimens were placed in room temperature. Again all specimens were weighed using a digital balance of an accuracy of 0.0001 g and all the cycle was reiterated to attain a constant mass. Therefore, in 24 hours of time, all discs showed a weight loss not more than 0.5 mg. After a time period of five days, all groups showed a 'Conditioned Mass (MI)' and then these were absorbed in distilled water at 37°C ± 2°C for seven days<sup>(19)</sup>. A clean dry towel was utilized to wipe the dental tweezer and after the surety of no visible moisture tweezers were utilized to take out the discs from water. These discs were weighed after removal of one minute. All these showed a mass M<sub>2</sub> which was the disc mass subsequent to the distilled water immersion.

$$WSP=M2-M1/S$$

For the attainment of solubility value, the reconditioning of discs was done in a desiccator at a constant mass and  $37\text{ }^{\circ}\text{C} \pm 2^{\circ}\text{C}$ . Thus, at sorption test for first time, the M3 was the mass reconditioning recorded. The entire group reached at M3 in time period of five days. The solubility of each disc among the immersion was determined by equation given below:

$$WSL = M3 - M1/S$$

## Results:

**1-Surface hardness:** Table (2) indicates the standard error of means, standard deviation, means, standard deviation, maximum and minimum experimental specimen's values for measurement of hardness of surface in various TiO<sub>2</sub> Nano filler concentration.

**2-Table (2)** descriptive data of Surface hardness parameters analysis.

Thus, the uppermost mean value for group D was observed to be of 85.111 whereas, the lowest mean was detected in (Control) group A having mean of 82.711. Therefore, the means surface hardness of all 4 groups were conspired in Fig. (7).

The increase might be because of the random dispersion of Titanium di oxide (hard material) in the acrylic matrix medium. The slight upsurge of Nano composite hardness at low concentration of Nano particles will be dominated by network density. Although, the increase in Nano composite hardness at 7% & 5% may be due to the TiO<sub>2</sub> particles' accumulation on the surface of acrylic matrix.

### 3-Surface roughness

The standard error of means, standard deviations, means, specimens' maximum & minimum experimental values of surface roughness measurement at various concentration of Nano fillers.

Table (3) Surface roughness parameters analysis

It presented the highest mean value in group D which was 2.457 and lowest in group A which was 2.331. Thus, the graph of all 4 mean values have been plotted as indicated in Fig.(8).

This might be because of the reason that the variance in matrix of acrylic denture base and Titanium particles' roughness or perhaps may be due to the variations in form of particles & characteristics of microstructures.

### 4-Water sorption

The table 4 represents the means, standard error of means, standard deviation & range of experimental specimen's values which measured the water sorption in numerous concentration of Nano fillers of TiO<sub>2</sub>.

Table (4) descriptive data of Water sorption parameters (mg/cm<sup>2</sup>).

Water sorption seems to decrease in a similar manner in group B (3%) and group C (5%) concentrations of the added TiO<sub>2</sub> Nano filler (0.336), but for a limited extent. After reaching a concentration of 7% group D water sorption seems to decrease (0.304) Fig (9).

With the increase of TiO<sub>2</sub>, the water sorption value decreases. This might be due to the replacement of hydrophilic resin with TiO<sub>2</sub> percentage which results in the decrease of water uptake.

### 5-Water solubility

The standard means' error, means, standard deviation as well as min. & max. Values of specimen evaluating the solubility of water in TiO<sub>2</sub> Nano filler concentration variants.

Table (5) Water solubility parameters analysis (mg/cm<sup>2</sup>)

The greatest mean value was shown in group A having a mean of 0.015 and lowest was observed in group D as 0.011, thus, the means of all groups was plotted in Fig. (10).

These reductions can be because of the insolubility of TiO<sub>2</sub> in water as the

accumulation of TiO<sub>2</sub> to the specimen's mass performs as additive. Thus, their occurrence will further reduce the acrylic resin solubility.

### **Discussion:**

Surface coarseness of acrylic denture base considerably increased as TiO<sub>2</sub> was added. This might be because of the variance among the matrix of denture acrylic base and titanium particles roughness or perhaps ascribed to the particles' form and material micro structural characteristics variance<sup>(10, 9)</sup>. Thus, the outcomes resembled the results attained by (Nabil, et al 2011)<sup>(11)</sup> because of addition of Nano fillers to acrylic resin. A greatly significant increase indicated an increased surface hardness because of the increased percentage of TiO<sub>2</sub> powder. Which might be ascribed as the random distribution of hard material's particles (Titanium di oxide) in the matrix of acrylic media. Network density dominates a slight upsurge in Nano composite hardness at lower concentration of about 3% nanoparticles whereas, the TiO<sub>2</sub> particles' addition on acrylic matrix surface cause an increase in Nano composite hardness at 7% & 5%<sup>(12)</sup>. Our current study differed with results of Abdul Ameer<sup>(14)</sup> while same outcomes were presented by AlMomen, 2002<sup>(13)</sup>. With an upsurge in TiO<sub>2</sub> percentage, the water sorption value decreased which was because of the statement that hydrophilic resins are substituted by titanium particles. Which resulted in reduction of water uptake as the diffusion of water molecules via this material highly lowered as compared to

that of matrix<sup>(15)</sup>. This research agreed with Duraid, et al, 2012<sup>(16)</sup> who specified an increased in ZrO<sub>2</sub> Nano fillers' percentage due to water sorption decrease. A great substantial decrease was observed in the specimen's water solubility values while comprising TiO<sub>2</sub> with various percentages. This reduction might be because of the insolubility of TiO<sub>2</sub> in water, thus further addition of TiO<sub>2</sub> to the samples' mass will turn as additives and their incidence will cause reduction in acrylic resin's solubility<sup>(15)</sup>. Its outcomes were in accordance to the Duraid, et al 2012<sup>(16)</sup> who indicated a decrease in water solubility due to the increased ZrO<sub>2</sub> Nano filler's percentage.

### **Conclusions:**

Inside the boundaries of this research, the drawn conclusions are given below:

- 1- The increased percentage of TiO<sub>2</sub> caused a greatly substantial decrease in acrylic resin's water solubility & sorption.
- 2- The addition of various percentages (7%, 5% and 3%) of TiO<sub>2</sub> to heat cured acrylic resin caused a significantly increased surface hardness.

Over all conclusions from the result appear in the study the 5% reinforcement of TiO<sub>2</sub> Nano filler advisable because of the highly significant decrease in the total amount of water uptake, the significant decrease of the solubility of reinforced acrylic, non-significant increase in the roughness of the surface and finally the surface hardness was highly significant increased.



Fig. (1): Laser cutting machine (CNC).



Fig. (2): Mould preparation.



Fig. (3): Probe sonication apparatus.



Fig. (4): Durometer hardness tester.



Fig. (5): The Profilometer device.



Fig. (6): Desiccator.

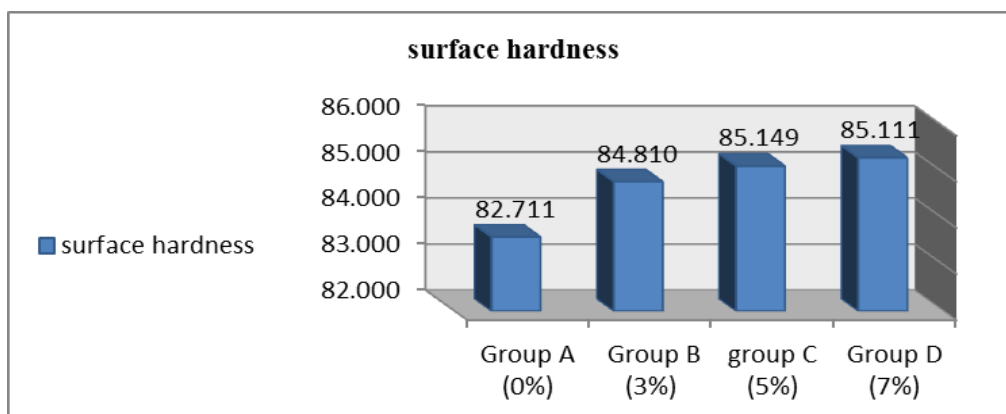


Fig. (7): Bar chart showing the mean of changes in the surface hardness.

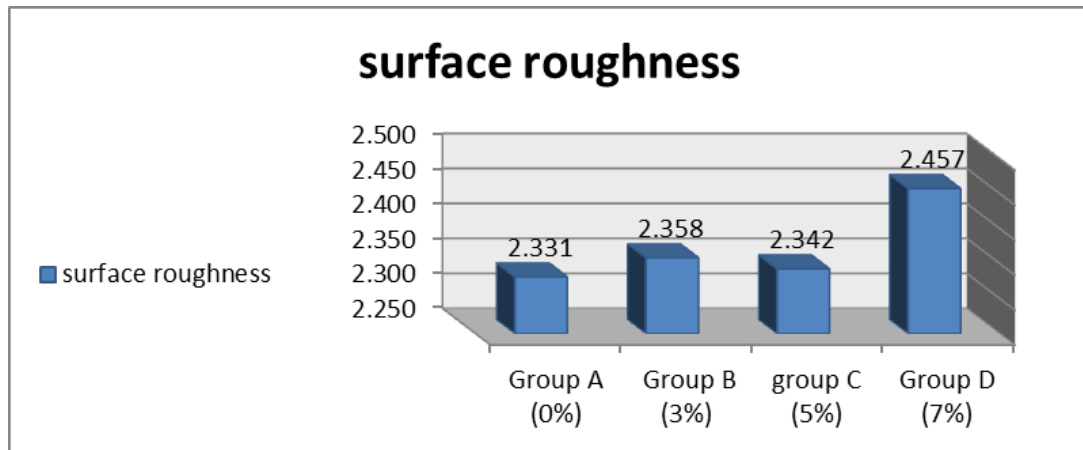


Fig. (8): Bar chart showing the mean of changes in the surface hardness..

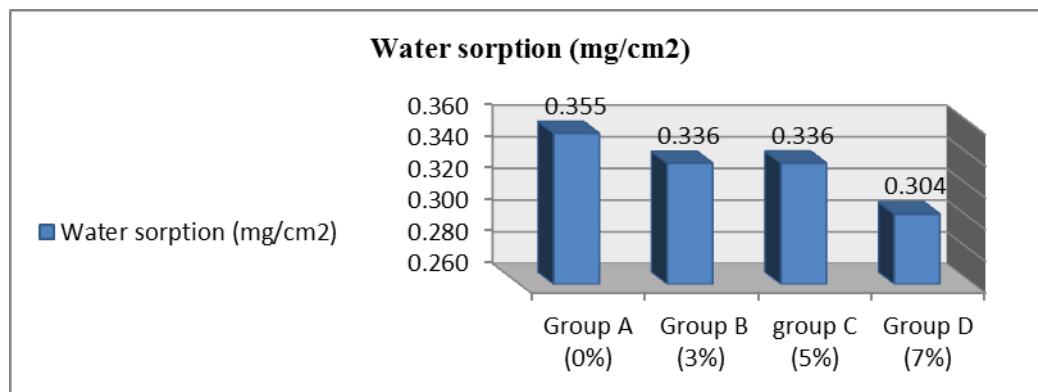


Fig. (9): Bar chart showing the mean of changes in the surface hardness.

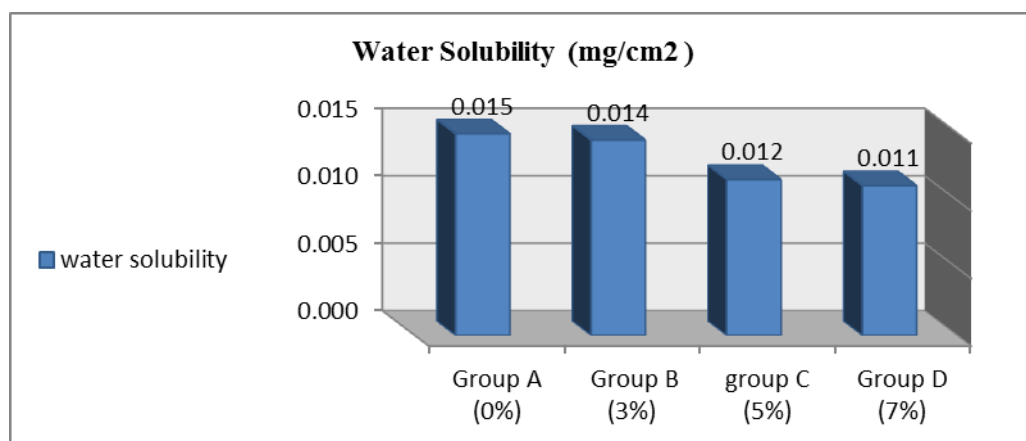


Fig. (10): Bar chart showing the mean of changes in the surface hardness.

Table (1): Mixing ratio of TiO<sub>2</sub> with PMMA according to the manufacturer instruction.

<i>TiO<sub>2</sub></i>	<i>Gram Wight</i>	<i>Polymer</i>	<i>Monomer</i>
0%	0 g	100 g	40 ml
3%	3 g	97 g	40 ml
5%	5 g	95 g	40 ml
7%	7 g	93 g	40 ml

Table (2): Descriptive data of Surface hardness parameters analysis.

	<i>Group A</i>	<i>Group B</i>	<i>Group C</i>	<i>Group D</i>	
N	10	10	10	10	
Mean	82.711	83.811	84.140	85.111	
SD	0.723	0.923	0.555	0.321	
SE	0.223	0.267	0.199	0.1	
range	Min.	81.44	82.01	83.24	84.4
	Max.	83.48	85.011	86.22	85.345

Table (3): Surface roughness parameters analysis.

	<i>Group A control</i>	<i>Group B</i>	<i>Group C</i>	<i>Group D</i>	
N	10	10	10	10	
Mean	2.331	2.358	2.342	2.457	
SD	0.01	0.031	0.001	0.007	
SE	0.003	0.009	0.003	0.002	
range	Min.	2.303	2.338	2.341	2.451
	Max.	2.337	2.41	2.344	2.471

Table (4): Descriptive data of Water sorption parameters (mg/cm<sup>2</sup>).

	<i>Group A control</i>	<i>Group B</i>	<i>Group C</i>	<i>Group D</i>	
N	10	10	10	10	
Mean	0.355	0.336	0.336	0.304	
SD	0.0001	0.005	0.001	0.004	
SE	0.0005	0.0016	0.0023	0.0013	
range	Min.	0.355	0.331	0.336	0.3
	Max.	0.356	0.348	0.338	0.311

Table (5): Water solubility parameters analysis (mg/cm<sup>2</sup>).

	<i>Group A</i>	<i>Group B</i>	<i>Group C</i>	<i>Group D</i>	
N	10	10	10	10	
Mean	0.015	0.014	0.012	0.011	
SD	0.005	0.0002	0.009	0.0001	
SE	0.0014	0.0007	0.0005	0.0002	
range	Min.	0.002	0.014	0.011	0.011
	Max.	0.017	0.015	0.012	0.011

## References

- 1-Kisin ER, Murray AR, Keane MJ, Shi XC, Schwegler-Berry D, Gorelik O, Arepalli S, Castranova V, Wallace WE, Kagan VE, Shvedova AA: Single-walled carbon nanotubes: geno- and cytotoxic effects in lung fibroblast V79 cells. *J Toxicol Environ Health A* 2007, 70: 2071–2079. 10.1080/15287390701601251
- 2-Robertson TA, Sanchez WY, and Roberts MS: Are commercially available nanoparticles safe when applied to the skin? *J Biomed Nanotechnol* 2010, 6: 452–468. 10.1166/jbn.2010.1145
- 3-EU - European Commission Recommendation on the definition of nanomaterial.
- 4-Riu J, Maroto A, Rius FX: Nano sensors in environmental analysis. *Talanta* 2006,69(2):288–301. 10.1016/j.talanta.2005.09.045
- 5-Ruth Magaye JZ, Linda B, Min D: Nontoxicity and carcinogenicity of cobalt-, nickel- and copper-based nanoparticles (Review). *Exp Ther Med* 2012, 4: 551–561.
- 6-American Conference of Governmental Industrial Hygienists (ACGIH): Threshold limit values and biological exposure indices for 1992–1993. Cincinnati: Ohio: American Conference of Governmental industrial hygienists; 1992.
- 7-Participants IRSIW: The relevance of the rat lung response to particle overload for human risk assessment: a workshop consensus report. *Inhal Toxicol* 2000, 12: 1–17.
- 8-Zhao J, Bowman L, Zhang X, Vallyathan V, Young SH, Castranova V, Ding M: Titanium dioxide (TiO<sub>2</sub>) nanoparticles induce JB6 cell apoptosis through activation of the caspase-8/Bid and mitochondrial pathways. *J Toxicol Environ Health A* 2009, 72: 1141–1149. 10.1080/15287390903091764
- 9-Sehajpal SB, Sood VK. Effect of metal filler on some physical properties of acrylic resin, *J Prosthet Dent* 1989; (61) 4: 746-51.
- 10-Khan Z.: "Soft palate obturation prostheses made with visible - light cured resin *J Prosth Dent* (1989); 62(3): p671-67.
- 11-Ihab Nabil (2012):" evaluation the effect of modified Nano filler addition on some properties of the heat cure acrylic risen denture base material" M.Sc. thesis on the college of dentistry university of Baghdad (2011)
- 12-Liu G, Li YF, Yan FY, Zhao ZX, Zhou LC, Xue QJ. Effect of Nano scale SiO<sub>2</sub> and TiO<sub>2</sub> as the fillers on the mechanical properties and aging behavior of linear low-density polyethylene/ low-density polyethylene blends. *J Polym Environ* 2005; 13:339-48.
- 13- Al-Momen MM. "Effect of reinforcement on strength and radio-opacity of acrylic denture base material", M.Sc. Thesis, University of Baghdad, college of dentistry, 2000.
- 14-Abdul Ameer. Ali.S. "Evolution of changes in some properties of acrylic denture base material due to addition of radio-opaque fillers", M.Sc. Thesis, University of Baghdad, college of dentistry, 2006.
- 15-Alam MM. Synthesis, characterization and analytical applications of a new and novel 'organic-inorganic' composite material as a cation exchanger and Cd (II) ion-selective membrane electrode: polyaniline Sn (IV) tungstoarsenate. *React Funct Polym* 2007; 55:277-90
- 16-Duraïd Mohammed (2012); the effect of Nano-ZiO<sub>2</sub> reinforcement on the mechanical properties of heat cured acrylic, M, Sc.thesis college of dentistry university of Baghdad