Study of the Mechanical and Thermal Properties of PMMA/TiO$_2$ Nano Composite

S. T.Yaseen, A. Sh. Khaleel
Department of Physics Science, College of Sciences, University of Baghdad, Baghdad, Iraq.
Corresponding author email: tahasoror@yahoo.com

Abstract:-
This research investigates the effect of adding some reinforcing materials, including (nano and micro) titanium dioxide (TiO$_2$) particles with different weight fraction (0.1, 0.4, 0.7, 1, 3 and 5)% to polymethyl methacrylate (PMMA) and studying some mechanical and physical properties of composite material. Specimens of this project were prepared using (in-situ) method to form composites. Mechanical tests were performed on these specimens, including impact test, thermal conductivity was performed as a physical test. Results of this study showed that the values of impact strength were decreased when adding the (nano-micro) particles in PMMA composite materials, while the values of thermal conductivity were decreased.

Keywords: PMMA, TiO$_2$, impact test, thermal conductivity.

1. Introduction
Some materials need enhancement in their properties, so this may be achieved by combining two or more materials together to get more developed materials and that’s why composite materials were invented[1]. As the world develops, so does the need of the human body, like a need for replacing an arm, a denture, a tooth and even a valve requires special materials that are compatible and nontoxic to the human skin and human body. Polymer is more preferred in the medical field, because of its properties that are close to a certain degree to the human skin. So it became the matrix for most of the medical field materials, with the addition of reinforcements for strength [2]. Each material can have good properties, which make them suitable for biomedical applications [3]. Acrylic resins are the most widely used in dentistry applications and accepted among all denture base materials, and it was estimated that they represent (95%) of the polymer in prosthodontics applications. Poly (methyl methacrylate) is favored for its good properties such as satisfactory mechanical properties, except the impact and fatigue strength, dimensional stability, and it has high Tg temperature, the color which is similar to the human’s internal skin.

PMMA can be fabricated and processed by many methods such as casting, extrusion, injection and thermoforming method [4]. Poly methyl methacrylate (PMMA) is the most widely used of the polymers based on acrylic acid for which one trade name is "Perspex" [5]. Polymethylmethacrylate is an amorphous thermoplastic that can be delivered as clear as glass. The material is more known as "Plexiglass". It is produced by the addition polymerization of methyl methacrylate according to the reaction illustrated in figure (1) [5, 6]. The monomer, methylmethacrylate is obtained from acetone cyanhydrin by reacting it with sulphuric acid and methyl alcohol.
2. Titanium Dioxide (TiO₂)

Titanium dioxide also known as titanium(IV) oxide or Titania, is the naturally occurring oxide or titanium, with chemical formula TiO₂. When used as a pigment, it is called titanium white, Pigment white 6, or CI 77891. It is noteworthy for its wide range of applications, from paint to sunscreen to food colouring when it is given the E number E171. Titanium dioxide found naturally as the mineral rutile, anatase and brookite. Rutile, anatase and brookite all contain six coordinates titanium. Titanium dioxide is the most widely used white pigment, because of its brightness and very high refractive index (n=7), in which it is surpassed by a few other materials[8].

3. Experimental Work

3.1 Matrix Material

Poly methyl meth acrylate (self cure) has been used as a matrix material in the preparation of composite materials and manufactured by (New Stetic S.A. Cr.53 No. 50-09 Guarne, Antioquia-Colombia). This resin is pink veined color at room temperature and turns into a solid state by adding monomer, which is a transparent, colorless liquid added in the ratio of 1:2, ie, 1 g of monomer to 2 g of resin polymethyl methacrylate. This type of materials is distinguished by softer feel, low molecular weight, color stable in the long run, minimized shrinkage, stable polymerization cycle with a perfect end result, the acrylic is long pourable and model able for a long period of time [9].

3.2 Reinforcement Materials

Titanium dioxide nano and microparticles manufactured by (Cheng Du Micxy Chemical CO. Lid) were used in this research as additives, with a high purity about (99.9%). The material was tested by an atomic force microscope (AFM) carried out in Baghdad University laboratories. This test is known to give surface shape as well as for the particle size. The particles size of TiO₂ (nano) equal 53.79 nm.
3.3 Specimens Preparation

The PMMA denture base materials consist of polymer powder and monomer liquid (methyl methacrylate, PMMA).

To prepare a sample of pure resin, a certain quantity of resin (poly methyl meth acrylate) was weighed according to the size of the mold designed at 2:1 ratio (i.e., 1 ml of monomer liquid per 2 g of powder resin at its temperature). After that, they were mixed for 8 minutes to be homogenized and it is preferred to exceed this period of time because it will lead to a higher viscosity, which leads to the acceleration of the process of hardening, impeding the process of casting in the mold. The weight of different compound of reinforcement (particles of titanium dioxide (nano and micro)) and according to the required weight fraction. To prepare the composite samples, cold cure acrylic resin is moldable for a long period of time, where the mixture was mixed of liquid (MMA) and TiO2 (micro or nano) particles in the clean and dry container (glass beaker), follow after that by slow addition of dry powder (PMMA) to liquid (MMA) and TiO2 powder mixture, the final mixture was stirred at room temperature and poured with thin straight line in the center of opening glass moulds, for curing. The mixture is poured in the mold shown in the figure (1-3) (according to ASTM-D256-87) for impact test and thermal conductivity test samples with diameter (4 cm) so that the mixture is distributed to all the areas of the template continuously and add it until the mold is filled with the desired form. The castings of composite specimens after curing process stand at room temperature about (30 min) to complete the cooling and hardening of specimen. After cooling, the specimens was demould to remove from the mould carefully and cleaning.
4. Mechanical Testing

4.1 Impact strength

In Charpy test, the specimen is supported at each end and struck at the center. A large number of experimental methods have been proposed and adopted to determining the fracture of brittle and plastic fracture [10]. Impact test which is measure the fracture energy of material under the effect of stresses at a high velocity and this is the important parameter to design any structure. A material such as polymer, which has a high toughness, has high fracture energy and it is calculated using this equation:

\[ \text{I.S.} = \frac{E}{A} \]

Where I.S: impact strength in unit \((\text{kg/m}^2)\) .

E: Energy of fracture in unit (kg).

A: Cross section area in unit \((\text{m}^2)\).

The impact strength depends on the type of material, stresses system; manufacture condition, and the temperature [11].

5. Thermal Testing

5.1 Thermal conductivity

The thermal conductivity is the quantity of heat flow in unit time through a unit area of substance caused by a unit thermal gradient [12]. Lee's disk were used to calculate the coefficient of thermal conductivity (K) for the prepared samples [13].

6. Results and discussion

This section deals with the results obtained by impact and thermal tests for the prepared samples of PMMA as a matrix and TiO\(_2\) (micro and nano) as reinforcements with \((0.1, 0.4, 0.7, 1, 3, \text{ and } 5)\) %wt.
6.1 Impact Test

Figure(1-4) shows the obtained results for impact test, Impact strength values for PMMA composite specimens for prosthetic denture base materials prepared in this research are shown in the table (1), and figure (4 and 5) shows the effect of adding both types of titanium dioxide particles (nano-micro) with different weight fractions on the impact strength of PMMA matrix. This figure shows how the impact strength values change with increasing the weight fraction for both types of these particles in both groups of PMMA composite materials, because of any increasing in these particles numbers, it will act as points for localized stress concentration regions from which the failure will begin. Furthermore, the nature of these particles is brittle and weak in the ability of resistance to impact loads comparing with PMMA resin. Impact strength of the composite specimen is controlled by two elements: first, the capability of the reinforcing material to stop crack propagation by absorbing energy and the second one, poor bonding between reinforcing and matrix, which cause micro-spaces and result in crack propagation [14].

The energy needed to break the pure polyethyl methacrylate was 4.70 kJ / m², but when adding the micro particles and nano particles of titanium dioxide, the energy needed to break the composite samples increased and was higher than the impact of the addition of nanoparticles at the addition of 0.1% and reached 10.915 kg/m² was added to the micro was the highest value of the impact of the addition of the ratio of 0.4%. It reached 11.83 kg/m² and when adding other ratios start to decline because of the existence of the interfaces and agglomeration between the matrix material polyethyl methacrylate and the material added titanium dioxide (nano and micro).

**Figure 4.** The relationship between impact strength and weight percentage of titanium dioxide (TiO₂) when added:A) nano of TiO₂, B) micro of TiO₂.
Table 2. Values Impact test

| Wt % | Impact Strength KJ/m² |
|------|------------------------|
|      | PMMA/MicroTiO₂ | PMMA/Nano TiO₂ |
| 0    | 4.70             | 4.70           |
| 0.1  | 6.05             | 10.915         |
| 0.4  | 11.83            | 5.231          |
| 0.7  | 8.860            | 5.347          |
| 1    | 5.251            | 7.334          |
| 3    | 5.912            | 5.889          |
| 5    | 7.324            | 7.332          |

Figure 5. Impact Strength as a function of weight fraction

6.2 Thermal Conductivity

Thermal conductivity is a heat transfer phenomena in which the energy is transferred from one location to another because of the excitation of atoms or particles as a result of the change in the temperature of the medium.
Figure 6. The relationship between thermal conductivity and weight percentage of titanium dioxide (TiO$_2$) when added: A) nano of TiO$_2$, B) micro of TiO$_2$.

Figures (1-6), shows the effect of adding (nano-micro) TiO$_2$ particles with different weight fractions on the thermal conductivity of PMMA composite.

In Figure (6 and 7) it can be noticed the thermal conductivity values of PMMA composite specimens decrease with increasing the volume fraction of (nano-micro) TiO$_2$ particles. In addition, the presence of these particles is made to fill or diminish the spaces and voids which were inside the PMMA matrix. Finally, the result leads to facilitate the process of the increase of the thermal conductivity values of the composite specimens [15]. Thus, the thermal conductivity values decrease from (0.2692 W/m.°K) for (PMMA-pure) composite specimen to reach to the higher value of thermal conductivity (0.2248 W/m.°K) (PMMA- 3% nano-TiO$_2$) and (0.2568 W/m.°K) (PMMA- 0.7% micro-TiO$_2$).

Table 3. Values of thermal conductivity

| Wt % | Thermal Conductivity W/m.k |
|------|---------------------------|
|      | PMMA/Micro TiO$_2$ | PMMA/Nano TiO$_2$ |
| 0    | 0.2692                  | 0.2692             |
| 0.1  | 0.2234                  | 0.2210             |
| 0.4  | 0.2088                  | 0.1653             |
| 0.7  | 0.2568                  | 0.2104             |
| 1    | 0.222                   | 0.1530             |
| 3    | 0.2489                  | 0.2248             |
| 5    | 0.2049                  | 0.1492             |
7. Conclusions

According to the experimental results of PMMA denture base materials, which prepared in this research, can be the conclusions the following sentences: The addition of (nano- micro) TiO2 particles has a noticeable effect on most mechanical and physical properties of PMMA denture base materials with increasing the volume fractions of (nano- micro) particles. Some physical properties such as (thermal conductivity) of PMMA composites denture (PMMA - nano TiO2), (PMMA - micro TiO2), were increased with increasing of the volume fractions of (nano-TiO2 and micro-TiO2) particles. Some mechanical properties such as (impact strength) of PMMA composites denture (PMMA - nano TiO2), (PMMA - micro TiO2), decreased with increasing of the volume fraction of (nano-micro) TiO2 particles.

References
[1] S.L. Kakani 2004 1st ed., Age International Publishers, Ltd., London.,
[2] L.L. Hench 2002 Biomaterials 19:1423-1429.
[3] S. Ramakrishna, J. Mayer, E. Wintermantel, K.W. Leong 2001 Composites Science and Technology 61:1189-1224.,
[4] Q.A. Hamad 2017 Eng. & Tech. Journal, Part A 35 2:124-129.
[5] John, V.B. 1974 The Macmillan Press, Ltd.,
[6] Dug lukKassen, and Annette Midell 2003 Advanced Materials and Structures and their Fabrication Process", 3rd ed., narvikUniversity College Hin.,
[7] Sheldon, R.P. 1982 Applied Science Pub., London.
[8] F. Rodai, K. Hiroharu, G. Harrison, W. Pamiko 2004 J. Thin Solid Films 454:162.
[9] KennethShaw, London.,
[10] Grawford, R. J. 1987 2nd Edition, A. Weaton U. K.,
[11 ] C.Kittle 2005 Eight Edition, Professor Emeritus, University of California, Berkeley, John Wiley&Sons, Inc.,
[12 ] Johnson, D. A., Maclen, W. D., and Jacobson, R. 1997 Making & Business from Biomass in Energy, Environment, Chemicals Fiber and Material P.925 www.agroplastics.com/biomass.pdf.
[13] Jayatilaka, A. D. 1979 Applied Science London.

[14] M. Sumaila, I. Amber, and M. Bawa 2013 Asian Journal of Natural & Applied Sciences 21: 39-49.

[15] S.M. Elie 2007 M.Sc. Thesis, University of Technology, Baghdad, Iraq.