

Investigation of Hardness and Flexural Properties of PMMA Nano Composites and PMMA Hybrids Nano Composites Reinforced by Different Nano Particles Materials used in Dental Applications

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ABSTRACT

Poly methyl methacrylate (PMMA), widely used as a prosthodontic denture base, the denture base materials should exhibit good mechanical properties and dimensional stability in moist environment. In the present research, efforts are made to develop the properties of PMMA resin that used for upper and lower prosthesis complete denture, by addition four different types of nanoparticles, which are fly ash, fly dust, zirconia and aluminum that added with different ratios of volume fractions of (1%, 2% and 3%) to poly methyl methacrylate (PMMA), cold cured resin (castavaria) is the new fluid resin (pour type) as a matrix. In this work, the Nano composite and hybrid Nano composite for prosthetic dentures specimens, preparation was done by using (Hand Lay-Up) method as six groups which includes: the first three groups consists of PMMA resin reinforced by fly ash, fly dust and ZrO₂ nanoparticles respectively, the second three groups consists of three types of hybrid Nano composites, which includes ((PMMA: X% nF.A) + (1%Al + 3% ZrO₂)), ((PMMA: X% nD.A) + (1%Al + 3% ZrO₂)) and ((PMMA - X%nZrO₂) + (1%F.A + 3%F.D)) respectively. The hardness and flexural tests results show that the values of the hardness, flexural strength, Maximum shear stress and flexural modules increased and with the addition of Nano powders (fly ash, fly dust, zirconia, and aluminum). And the results showed that the maximum values of hardness reach to (84.166) for ((PMMA: 3%nZrO₂) + (1%F.A + 3%F.D)) hybrid Nano composite, whereas the maximum values of hardness for Nano composite reach to (83.333) for (PMMA: 3%nZrO₂) Nano composite. Also, the results showed that the maximum values of flexural strength and Maximum shear stress reaches to (101MPa) and (2.4738MPa) respectively for (PMMA: 2%nF.D) Nano composite. Moreover, the results showed that the maximum values of flexural modules reaches to (13.95GPa) for ((PMMA: 3% nF.A) + (1%Al + 3%ZrO₂)) hybrid Nano composite, whereas the maximum values of flexural modules for Nano composite reach to (12GPa) for (PMMA-3%nZrO₂) Nano composite.

Keywords: Hybrid Nano Composites, Nano Composites, PMMA, Fly Ash nanoparticles, Fly Dust nanoparticles, Aluminum nanoparticles, Zirconium Oxide nanoparticles, Hardness and Flexural Strength.

INTRODUCTION

A biomaterial can be defined as any synthetic or natural material that is used to replace or restore function to a body tissue and is continuously or intermittently in contact with body fluids [1]. Complete or partial Denture base material represented one type of biomaterials that must be have good mechanical properties such as stiffness, toughness, hardness and resistance to wear and abrasion, and good thermal properties such as thermal conductivity, thermal diffusivity, and Dimensional stability for example should not expand, tissue compatibility (non-toxic or allergic), Color stability, good chemical stability, in addition to esthetical pleasing and use in the oral cavity [2]. In dentistry applications, the most widely used polymeric material is Poly methyl metha crylate (PMMA) Acrylic resin which is a thermoplastic polymer majority used for denture bases and orthodontic devices [3]. Particulate composite materials consisting of polymer resin as matrix and particles as reinforcement phase. The particles in these composites are smaller than in large particles strengthened composites. The particle diameter is typically on the order of a nano meter. In this case, the particles carry a major portion of the load. The particles are used to increase the modulus and decrease the ductility of the matrix. Particle reinforced composites are much easier and less costly than making fiber reinforced composites. Polymer composite materials reinforced with particles (ceramic, metal particles) can be used for various engineering applications to provide unique mechanical and physical properties with a low specific weight. In order to achieve better mechanical strength, it is usually reinforced with ceramic powders or fibers (aramid, carbon and glass). Ceramic particles with small size are known to enhance the tribological and mechanical properties of polymers [4]. Fly ash, an industrial waste, can be used as a potential filler material in polymer matrix composites because it is a mixture of oxide ceramics. It improves the physical and mechanical properties of the composites [5]. Some researches which are accomplished in this field it's:-

Chow Wen Shyang, studied the effect of the addition of hydroxyapatite (HA) particles on the flexural properties of a heat polymerizing PMMA denture base resin. The results showed that the flexural modulus, flexural strain and flexural strength of PMMA/HA composites were decreased with the addition of hydroxyapatite (HA) particles [6].

Mohamed Ashour Ahmed, investigated the effect of the addition of zirconium oxide (ZrO₂) Nano powder with different weight fraction on the some mechanical properties of heat-polymerized acrylic resin. The results showed that significantly increased the fracture toughness, hardness and flexural strength of heat-polymerized acrylic resin, and the best mechanical properties were achieved by adding 7%wt ZrO₂ [7].

Intisar J. Ismail et. al., studied the effect of the addition of surface treated Alumina (Al₂O₃) Nano particles in three different percentages (1wt%, 2wt% and 3wt %) on some physical and mechanical properties of heat cured poly methyl meth acrylate denture base material. The results showed that the addition of 1wt% and 2wt% Al₂O₃ to heat cured PMMA denture base material increases transverse strength, while a significant reduction occurred in transverse strength at the percentage of 3%. In addition, a significant increase in surface hardness and non-significant differences in surface roughness were observed for all percentages. [8].

H. K. Hameed, investigated the effect of the addition of silanized zirconium oxide (ZrO₂) Nano powder to acrylic resin cured by autoclave. The results showed that the addition of silanized Zirconium oxide improved transverse and impact strength of denture base Nano composite reinforced with 5% weight fraction of Nano- ZrO₂, also, the results showed slightly increases the surface roughness; hardness and the apparent porosity also decrease by addition of Nano ZrO₂ weight fraction increase [9].

S.I. Salih et al., investigated the comparative study of the flexural properties and impact strength for PMMA prosthetic complete denture base reinforced by different particles. The result showed the flexural properties increased with increasing of the volume fraction of (nHA) and (ZrO₂) particles in polymer composite, while, the impact strength decreased [10]. The one recent study mentioned elsewhere, which involved the numerical study by the tensile properties

analysis of the prosthetic dentures which prepared from the same of composite material maintained in the reference above, and the numerical analysis results of the finite element method shown the some agreement with the experimental results [11].

The objective of the current work is attempts to develop a PMMA polymer which is used in the denture base and in dental prosthesis applications. Through study the effect of adding different nanoparticles powders on the hardness and flexural properties for the PMMA Nano composites, as well as the PMMA hybrid Nano composites which use for the dental prosthesis applications.

Materials and Methods

Materials Used

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

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

Young's Modulus (GPa)	Impact Resistance (KJ/m ²)	Flexural Strength (MPa)	Flexural Modulus (GPa)	Water Sorption (µg/mm ³)	Solubility (µg/mm ³)	Water Absorption (%)	Density (gm/cm ³)				
Element	SiO ₂	Al ₂ O ₃	TiO ₂	MgO	K ₂ O	CaO	Fe ₂ O ₃	Mn ₂ O ₃	Na ₂ O	P ₂ O ₃	L.O.I
Oxide	8.3		79	2.3		3.2	1.8		2.5		1.19
The weight (%)	58.2	27.7	1.4	0.05	3.59	0.84	4.99	0.31	0.74	0.34	1.84

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

Table (3): Chemical Composition Analyses of fly dust used in this Research

Element Oxide	SiO ₂	Al ₂ O ₃	LiO	MgO	CaO	Fe ₂ O ₃	L.O.I
The weight (%)	12.30	3.02	29.30	4.80	38.08	2.91	9.48

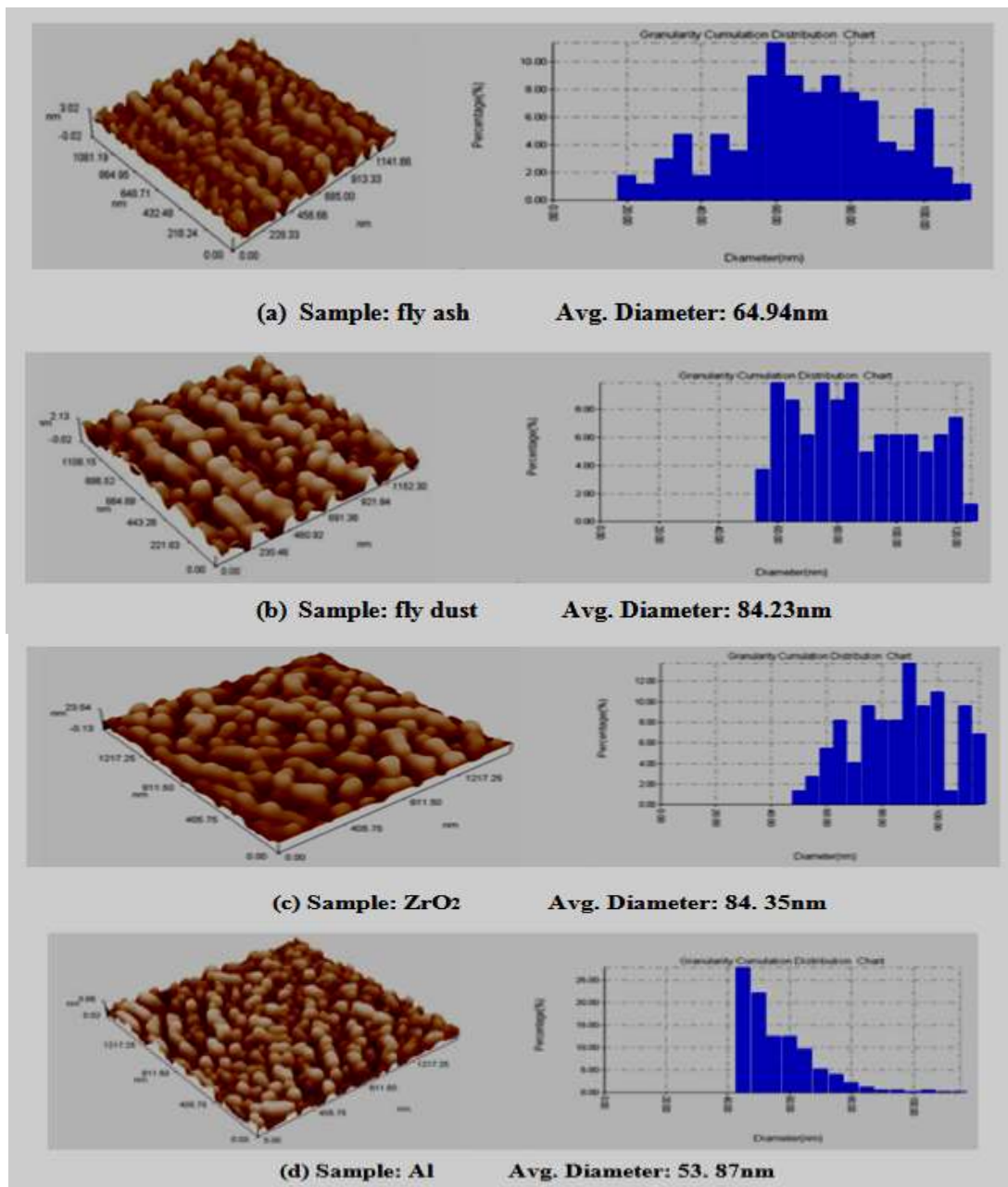


Figure (1): Atomic Force Microscopy Test for Nano Powders (a) Fly ash (b) Fly dust (c) Zirconium oxide and (d) aluminum

Preparation Methods and Curing Cycle of Test Specimens

The PMMA Nano composite materials and hybrid Nano composite materials specimens were prepared by using the Vertex™ - Castavaria. According to the manufacturer's instructions of Manufacturer Company, the standard proportion in mixing ratio for cold cure PMMA resin is (1 ml) (0.95g) monomer liquid (MMA) and (1.7 g) acrylic powder (PMMA). The Vertex acrylic Castavaria is moldable, where the liquid monomer (MMA) was placed in dry glass container, followed after that with slow addition of dry powder (PMMA) to the liquid monomer (MMA). The mixture as poured into the metallic mould cavity with maximum time about (4.5 min). After pouring completion into the metallic mould, the metallic mould was placed in the multi cure system (Ivo met) manufactured by Vertex-dental company according to the polymerization curing instructions at temperature equal to (55°C) and pressure equal to (2.5

bar) for (30 min) in order to complete the polymerization process of the acrylic specimens. After the polymerization curing completed, the specimens were de molding to remove from the metallic mould with very smooth upper and lower surface.

Composites and Hybrid Composites Specimens

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

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

Material	
Cold Cure Pure PMMA as Reference Material	
Nano Composite Number	Matrix+%Volume Fraction of nanoParticle
Nano Composite 1	PMMA+1% nano fly ash
Nano Composite 2	PMMA+2% nano fly ash
Nano Composite 3	PMMA+3% nano fly ash
Nano Composite 4	PMMA+1% nano fly dust
Nano Composite 5	PMMA+2% nano fly dust
Nano Composite 6	PMMA+3% nano fly dust
Nano Composite 7	PMMA+1% nZrO2
Nano Composite 8	PMMA+2% n ZrO2
Nano Composite 9	PMMA+3% n ZrO2
Hybrid Nano Composite Number	(Matrix) +%Volume Fraction of nanoParticle
Hybrid Nano Composite 1	(PMMA+1% nano fly ash)+ (1%Al and 3% ZrO2)
Hybrid Nano Composite 2	(PMMA+2% nano fly ash)+ (1%Al and 3% ZrO2)
Hybrid Nano Composite 3	(PMMA+3% nano fly ash)+ (1%Al and 3% ZrO2)
Hybrid Nano Composite 4	(PMMA+1% nano fly dust)+ (1%Al and 3% ZrO2)
Hybrid Nano Composite 5	(PMMA+2% nano fly dust)+ (1%Al and 3% ZrO2)
Hybrid Nano Composite 6	(PMMA+3% nano fly dust)+ (1%Al and 3% ZrO2)
Hybrid Nano Composite 7	(PMMA +1% n ZrO2)+ (1%fly ash and 3% fly dust)
Hybrid Nano Composite 8	(PMMA+2% n ZrO2)+ (1%fly ash and 3% fly dust)
Hybrid Nano Composite 9	(PMMA+3% n ZrO2)+ (1%fly ash and 3% fly dust)

Mechanical Testing

In order to evaluation of the hardness and flexural properties of the PMMA Nano composite and PMMA hybrid Nano composite of the denture prosthetic materials, hardness and flexural tests were performed in this research. According to (ADA Specification No.12, 1999), all the test specimens after preparation and polishing processes must be stored in distilled water at (37± 1°C) for 48 hr [12].

Hardness Test

Hardness is the property of a solid material which can be defined as the surface resistance of the material to penetration, wear, and scratching. The value of hardness can be used to predict the strength, structure coherence and the wear resistance of the dental materials. Hardness test is depending on the many factors such as temperature, intermolecular bonds, structure like cross-link in the chains, volume fraction of particles reinforcement and particle size [13]. According to the (ASTM D2240) the hardness test was performed at room temperature by using the Dorometer 3120 hardness test device, type is (Shore D), manufactured in USA. The applied load was nearly equal to the 50 N. The depressing time of measuring was nearly equal to the (5sec). All the specimens which had dimensions 5mm thickness and 42mm diameter were tested 3 times at different positions at the same time and the average values were taken [14].

Flexural Test

The denture base materials are subjected to the many and complex stresses such as compressive stress at the denture base interior surface (upper surface), Maximum shear stress at the denture base interface and tensile stress at the external surface (lower surface). The flexural test was performed according to the international standard (ISO 178, 2003) at room temperature by using the universal tensile test machine manufactured by (Laryee Company in china); type is (WDW-50). The strain rate (cross head speed) was (0.5mm/min) and the load (5KN) was applied gradually until the fracture of the specimen occurs [15]. The flexural strength, flexural modulus and Maximum Shear stress can be calculated from the following equations: [16].

$$\begin{aligned} \sigma &= \frac{F \cdot L}{W \cdot H^2} \dots(1) \\ E_f &= \frac{F \cdot L^3}{W \cdot H^3 \cdot \delta} \dots(2) \\ \tau_{max} &= \frac{F}{W \cdot H} \end{aligned}$$

Where:

σ : Flexural strength (MPa). E_f : Flexural modulus (GPa). δ : the beam deflection when a force F is applied. τ_{max} : Maximum shear stress (MPa). F: the fracture load (N). L: the distance between the two supported points. W: the specimen width (mm). H: the specimen thickness (mm).

Mechanical Tests Results and Discussion
Results and Discussion of Hardness Behavior

The hardness values of pure PMMA, PMMA Nano composite and PMMA hybrid Nano composite materials for all samples that were prepared in this research are presented in the Figure (2) , Figure (3), Figure (4) and Figure (5), respectively.

Figure (2) shows the effect of adding various types of nanoparticles powders (fly ash, fly dust and Zirconium oxide) on the hardness for PMMA Nano composites. It can be noted from this figure that the hardness increased with increasing of the volume fractions of (fly ash, fly dust and zirconium oxide) nanoparticles in the PMMA Nano composites as comparing with pure PMMA. The reasons behind such a behavior are that the formation of the strong supra molecular bonding or cross-links bonding between the matrix and the nanoparticles which shield or cover the Nano fillers, thus the interface can transfer pressure which in turn lead to increase the hardness, also the resistance strength of PMMA polymer to the plastic deformation through restricted the movement of the polymer chains along the stress direction by the (fly ash, fly dust and zirconium oxide) nanoparticles (formation of harder surface) leads to increase the hardness.[17 and 18].

Also, it observe from Figure (2) that the Nano composites materials reinforced with the zirconium oxide nanoparticles have the higher values of hardness, as compared with their counter parts of the other groups of the Nano composites materials which reinforced with fly ash and fly dust nanoparticles. The reason behind such a behavior is that the improvement of the mechanical properties that is associated with the addition of zirconium oxide nanoparticles, as well as has good compatibility between constituents of composite materials [19].

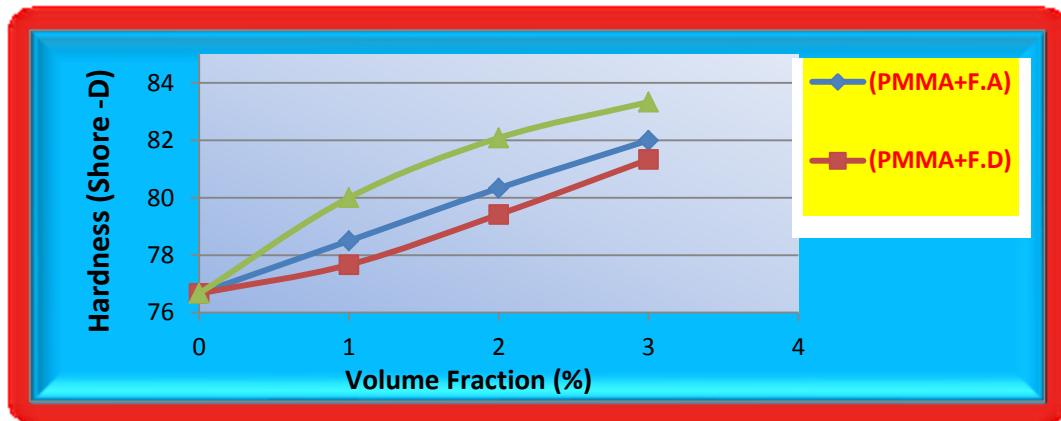


Figure (2): Hardness of PMMA Nano Composite Materials as a Function of volume fraction of nanoparticles (F.A, F.D and ZrO2) in PMMA matrix.

The effect of the addition of the mixture of nanoparticles powders (1%Al and 3% ZrO2) to the Nano composite materials (PMMA: X%F.A) and (PMMA: X%F.D), as well as the addition of the mixture of nanoparticles powders (1%F.A+3%F.D) to the Nano composite materials (PMMA: X%ZrO2), on the hardness for the product hybrid Nano composite materials ((PMMA: X%F.A) + (1%Al and 3% ZrO2)), ((PMMA: X%F.D)+(1%Al and 3%ZrO2)) and ((PMMA: X% ZrO2)+(1%F.A and 3% F.D)), it was show in Figures (3, 4, and 5) respectively. It was noticed from Figures (3 and 4) that the addition of the mixture of nanoparticles powders with ratio of (1%Al+3% ZrO2) to the Nano composite materials (PMMA: X%F.A) and (PMMA: X%F.D) respectively leads to increase the hardness of the product of hybrid Nano composites as comparing with their counter parts of the matrix of Nano composites which are (PMMA: X%F.A) and (PMMA: X%F.D) of the same volume fraction ratio of fly ash and fly dust. This behavior was related to that the improvement of the mechanical properties that is associated with the addition of zirconium oxide nanoparticles as previously mentioned [19].

On the contrary, it can be noted in Figure (5) that the addition of the mixture of nanoparticles powders with ratio of (1%F.A+3%F.D) to the Nano composite materials (PMMA: X%ZrO2) lead to increase the hardness of the product of hybrid Nano composites as comparing with its counter part of the matrix of Nano composites which is (PMMA: X%ZrO2) of the same volume fraction ratio of zirconium oxide. The reason behind such a behavior is that the addition of the fly ash and fly dust in which the chemical composition of the fly ash contain alumina nanoparticles (Al2O3) and fly dust contain lithium oxide and calcium oxide nanoparticles (LiO and CaO) as showed earlier in the Tables (2 and 3) which possesses strong ionic inter atomic bonding, giving rise to the hardness of the product of hybrid Nano composite materials [20].

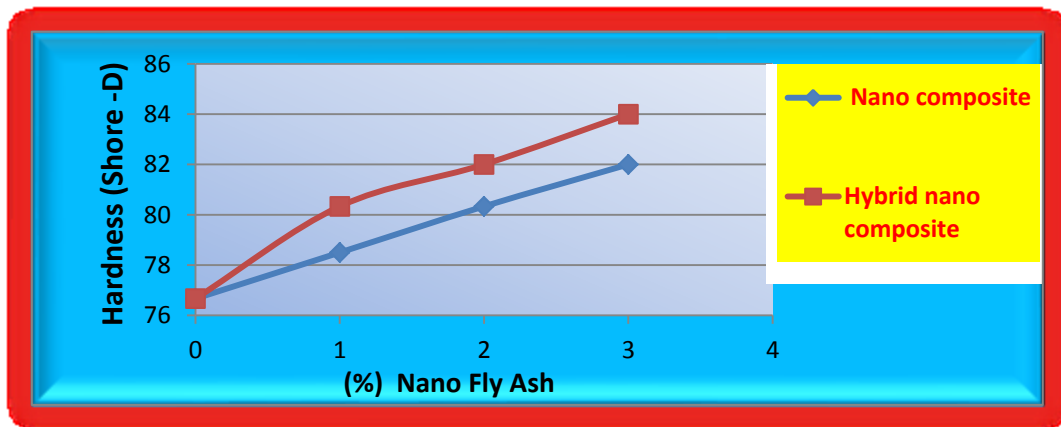


Figure (3): Hardness of PMMA Hybrid Nano Composite Materials as a Function of volume fraction of Fly Ash nanoparticles in PMMA Composites.

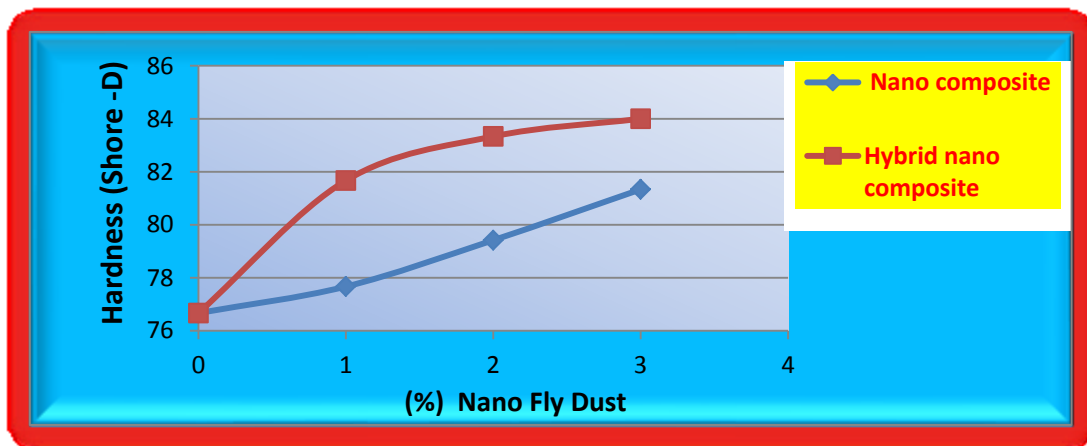


Figure (4): Hardness of PMMA Hybrid Nano Composite Materials as a Function of volume fraction of Fly Dust nanoparticles in PMMA Composites.

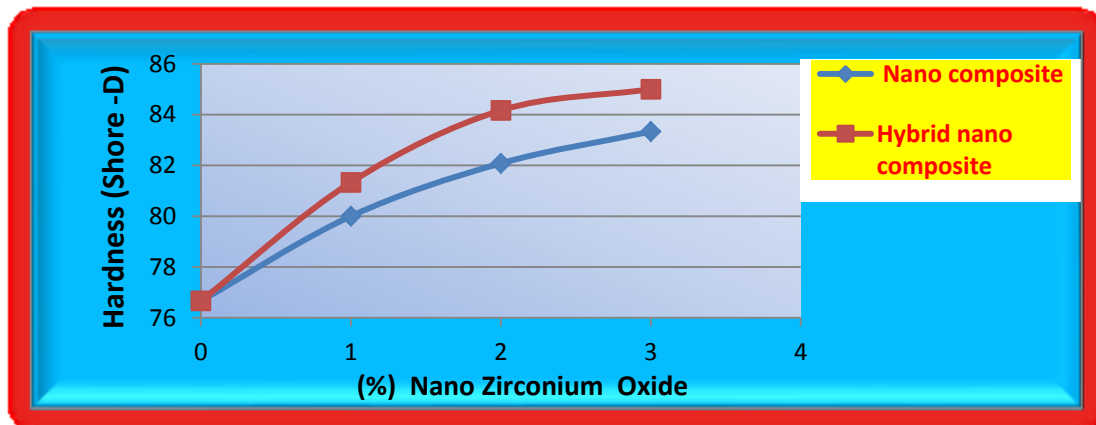


Figure (5): Hardness of PMMA Hybrid Nano Composite Materials as a Function of volume fraction of Zirconium Oxide nanoparticles in PMMA Composites.

Results and Discussion of Flexural Test

flexural strength, Maximum shear stress and flexural modules values of pure PMMA, PMMA Nano composite and PMMA hybrid Nano composite materials for all samples that were prepared in this research are presented from the Figure (6) to Figure (17) respectively.

Figure (6), Figure (7) and Figure (8) shows the effect of adding various types of nanoparticles powders (fly ash, fly dust and zirconium oxide) on the flexural strength, Maximum shear stress and flexural modulus for PMMA Nano composites. It can be noted from these figures that the addition of the fly ash, fly dust and zirconia nanoparticles powders leads to increase the flexural strength and Maximum shear stress as well as flexural modulus of the PMMA Nano composites, moreover it can be observed from Figures (6, 7 and 8), that flexural strength and Maximum shear stress reach to maximum value at (2%) ratio of volume fraction as comparing with pure PMMA, whereas flexural modulus, was increased with all ratios of the volume fraction of the nanoparticles content in the Nano composites. The reasons behind such a behavior are that the high interfacial shear strength between the PMMA matrix and nanoparticles because of the formation of supra molecular or cross-links bonding which shield or cover the nanoparticles and this in turn prevent the propagation of the cracks inside the material, as well as the propagation of the crack can be changed by good bonding between the PMMA matrix and nanoparticles [19 and 20]. Also, the increase in the flexural strength might be because of the high modulus of elasticity of the strengthening material compared with that of the PMMA matrix material [21]. Moreover, the incorporation of the hard nanoparticles into the polymer matrix improves the stiffness of the Nano composites by restricted the mobility of the matrix chains [22]. Also, the good distribution of nanoparticles especially at the low percentages of nanoparticles additives to the Nano composites materials, and this will reduce agglomeration of the nanoparticles and that may be lead to reduce stress concentration in Nano composite materials near the agglomerated nanoparticles and such small stresses are not sufficient enough to break the weak interactions at the interface [7]. Therefore, these small stresses can be easily transferred from the matrix to the hard nanoparticles, so allowing the particles to contribute its high flexural property to the Nano composites, and thus will increase the values of each of the flexural strength and flexural modulus as well as Maximum shear stress [23]. Overtime, the formation of a strong structure of the PMMA Nano composite materials which depending on the formation of strong interfaces bonding between the reinforcing nanoparticles (F.A, F.D and ZrO₂) and PMMA material, so that the resultant is Nano composite materials with strong physical bonding, therefore required high flexural and shear stress to break it and this lead to increasing flexural strength, flexural modulus and maximum shear stress [19]. On the contrary, it can be noted from the Figures (6 and 7) that the addition of the zirconia nanoparticles leads to decrease the flexural strength and Maximum shear stress of the PMMA Nano composites as comparing with pure PMMA. The reasons behind such a behavior are that the agglomeration and stick of the zirconium oxide Nano powder together, so on this powder plays an important role in stress concentrators. So, when the flexural and shear stress was applied on the specimen, the value of the stress concentration increases dramatically near the agglomerated nanoparticles and making the de bonding between PMMA and zirconium oxide nanoparticles and this cause cracks propagate faster inside the material so that, the fracture occurs immediately [24 and 25]. Furthermore, the bad wettability between zirconia nanoparticles and PMMA matrix especially at high concentrations, so that the resultant is composite material with weak physical bonding, therefore required low flexural and shear stress to break it [19].

Furthermore, it observes from Figures (6 and 7) that the Nano composites materials which is reinforced with the fly dust nanoparticles have the higher values of flexural strength and Maximum shear stress, as compared with their counter parts of the other groups of the Nano composites materials which reinforced with fly ash and zirconia nanoparticles. The reasons behind such a behavior are related to the same reasons which mentioned in the previous item for Figure (5) [20]. Whereas it can be seen from Figure (4) that the Nano composites materials which is reinforced with the zirconia nanoparticles have the higher values of flexural modulus as compared with their counter parts of the other groups of the Nano composites materials which reinforced with fly ash and fly dust nanoparticles. The reasons behind such a behavior are related to the same reasons which mentioned in the previous item for Figures (3 and 4) [19].

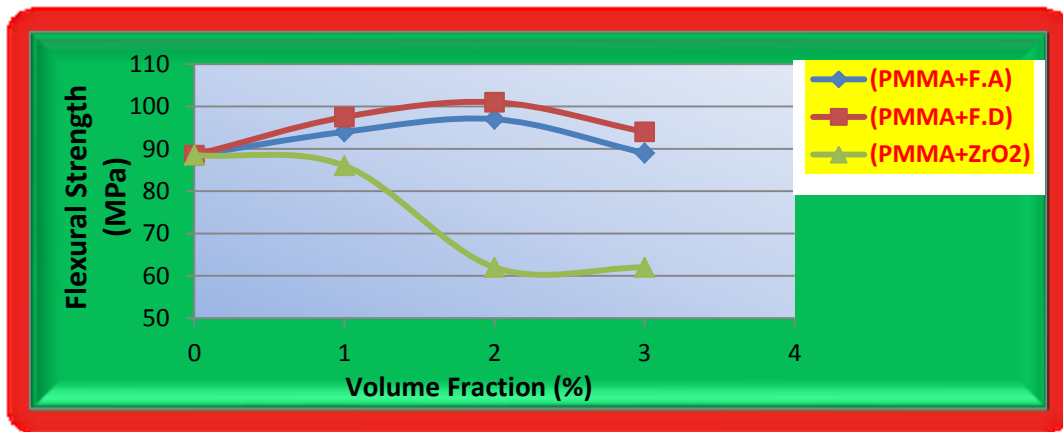


Figure (6): Flexural Strength of PMMA Nano Composite Materials as a Function of volume fraction of nanoparticles (F.A, F.D and ZrO2) in PMMA matrix.

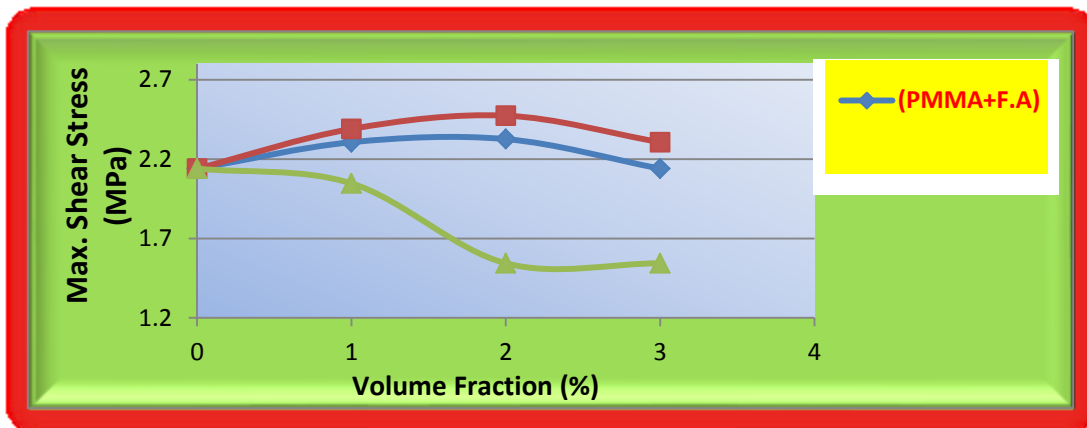


Figure (7): Max. Shear Stress of PMMA Nano Composite Materials as a Function of volume fraction of nanoparticles (F.A, F.D and ZrO2) in PMMA matrix.

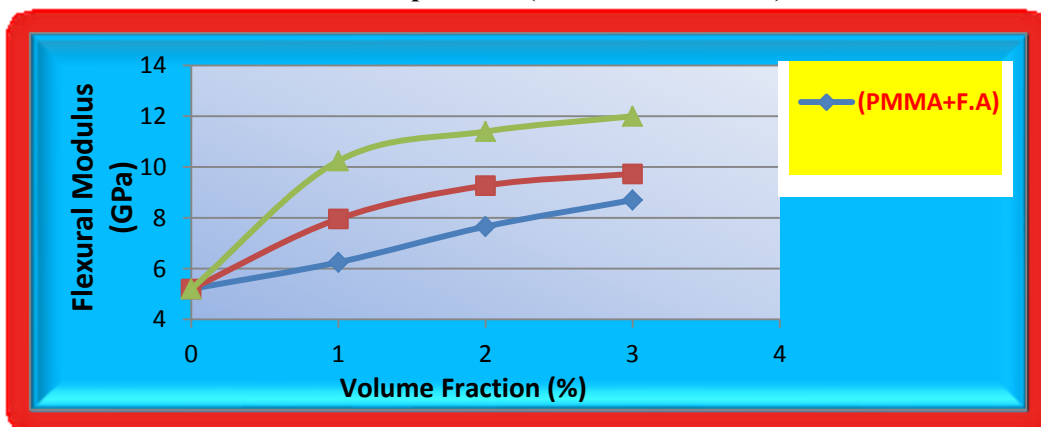


Figure (8): Flexural Modules of PMMA Nano Composite Materials as a Function of volume fraction of nanoparticles (F.A, F.D and ZrO2) in PMMA matrix.

The effect of the addition of the mixture of nanoparticles powders (1%Al and 3%ZrO2) to the Nano composite materials (PMMA: X%nF.A) and (PMMA: X%nF.D), as well as the addition of the mixture of nanoparticles powders (1%F.A+3%F.D) to the Nano composite materials (PMMA: X%n ZrO2), on the flexural strength, Maximum shear stress and flexural modulus for the product hybrid Nano composites it was show in Figures (9, 10 and 11), (12, 13 and 14) and (15, 16 and 17) respectively. It was noticed from Figures (9, 10 and 11) and (12, 13 and 14)

that the addition of the mixture of nanoparticles powders with ratio of (1%Al+3% ZrO2) to the Nano composite materials (PMMA: X%nF.A) and (PMMA: X%nF.D) respectively, leads to increase the flexural modules and decrease the flexural strength and Maximum shear stress of the product of hybrids Nano composites as comparing with their counter parts of Nano composites which are (PMMA: X%nF.A) and (PMMA: X%nF.D) of the same volume ratio of fly ash and fly dust. The reasons behind increasing the flexural modules are related to the same reasons which mentioned in the previous item for Figures (3 and 4) [19]. And, the reasons behind decreasing the flexural strength and Maximum shear stress are related to the same reasons which mentioned in the previous item for Figures (6 and 7) [19, 23 and 24]. On the contrary, it can be noted from Figures (15, 16 and 17) that the addition of the mixture of nanoparticles powders with ratio of (1%F.A+3%F.D) to the Nano composite materials (PMMA: X%nZrO2) leads to increase the flexural strength and Maximum shear stress as well as the flexural modules of the product of hybrids Nano composites as comparing with its counter parts of Nano composites which is (PMMA: X%nZrO2) especially at 2% and 3% ratio of the volume fraction for zirconia content in the Nano composite. The reasons behind such a behavior are related to the same reasons which mentioned in the previous item for Figure (5) [20].

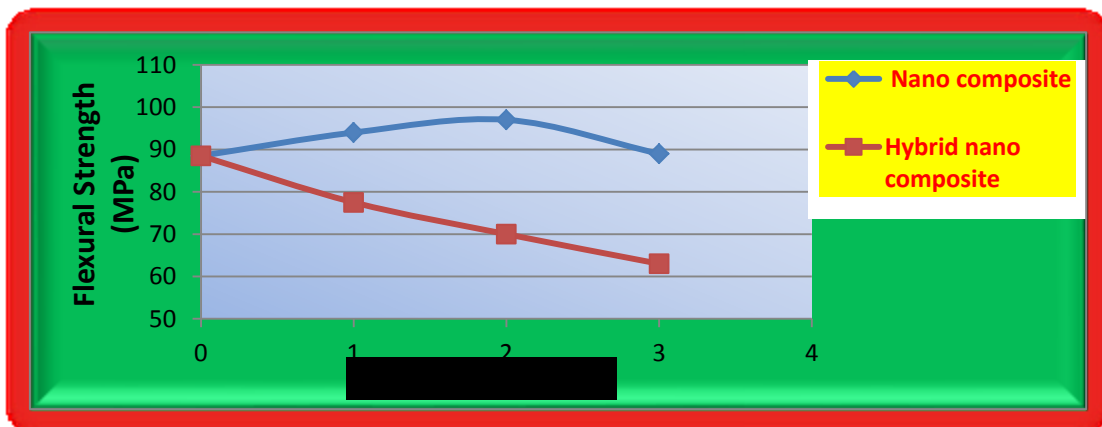


Figure (9): Flexural Strength of PMMA Hybrid Nano Composite Materials as a Function of volume fraction of Fly Ash nanoparticles in PMMA Composites.

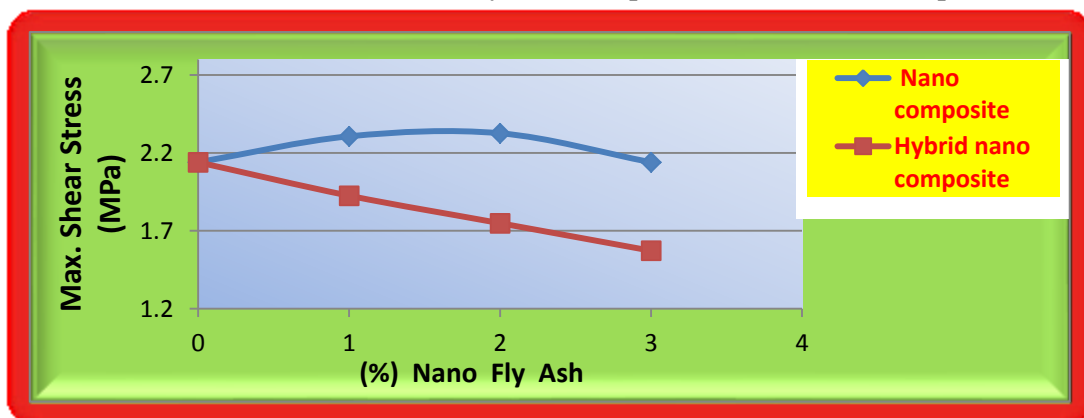


Figure (10): Maximum Shear Stress of PMMA Hybrid Nano Composite Materials as a Function of volume fraction of Fly Ash nanoparticles in PMMA Composites.

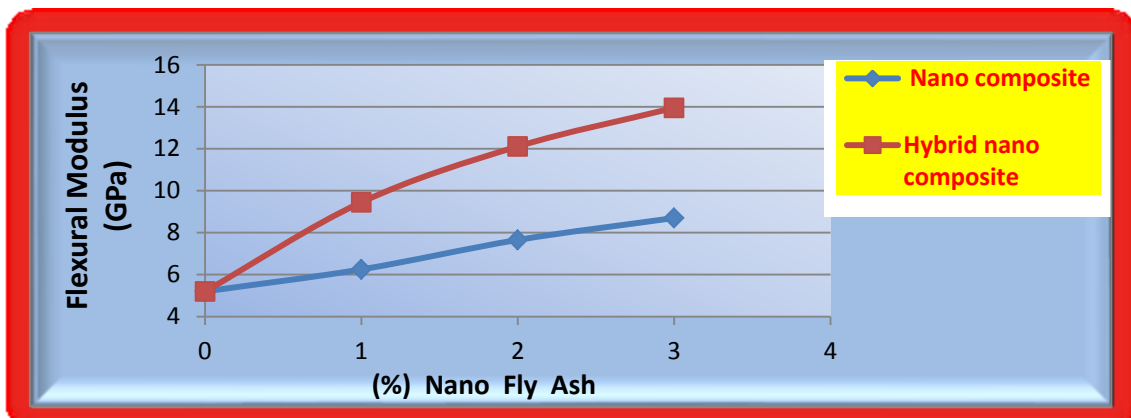


Figure (11): Flexural Modules of PMMA Hybrid Nano Composite Materials as a Function of volume fraction of Fly Ash nanoparticles in PMMA Composites.

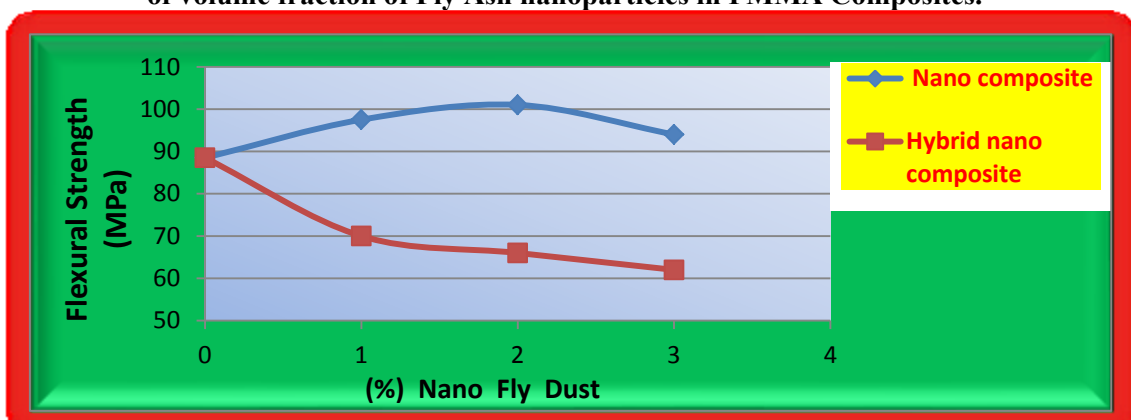


Figure (12): Flexural Strength of PMMA Hybrid Nano Composite Materials as a Function of volume fraction of Fly Dust nanoparticles in PMMA Composites.

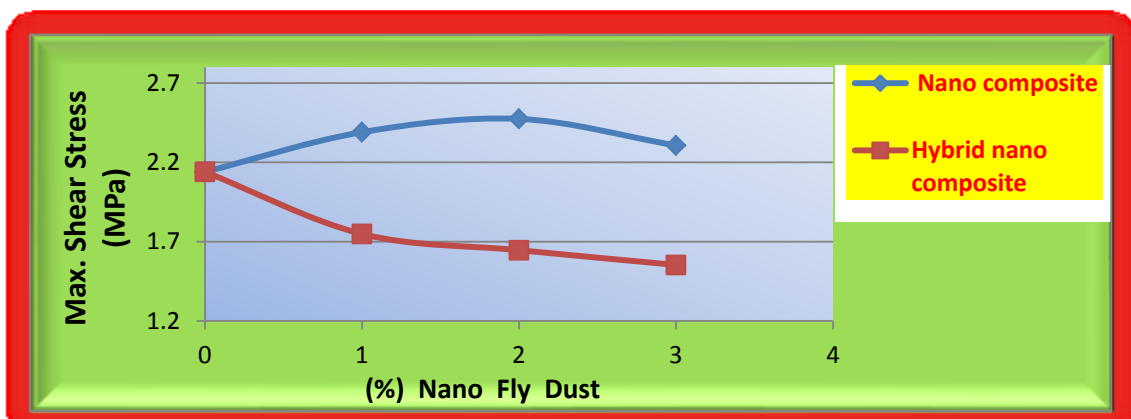


Figure (13): Maximum Shear Stress of PMMA Hybrid Nano Composite Materials as a Function of volume fraction of Fly Dust nanoparticles in PMMA Composites.

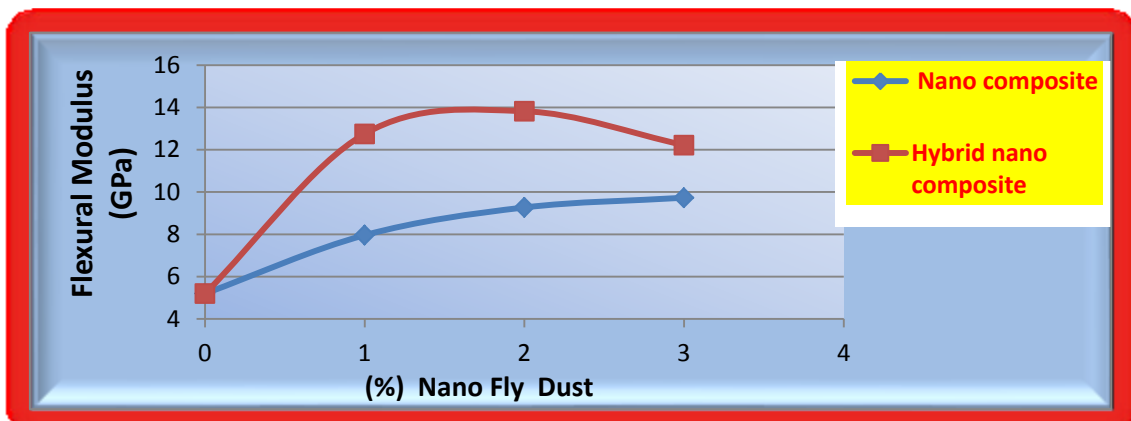


Figure (14): Flexural Modules of PMMA Hybrid Nano Composite Materials as a Function of volume fraction of Fly Dust nanoparticles in PMMA Composites.

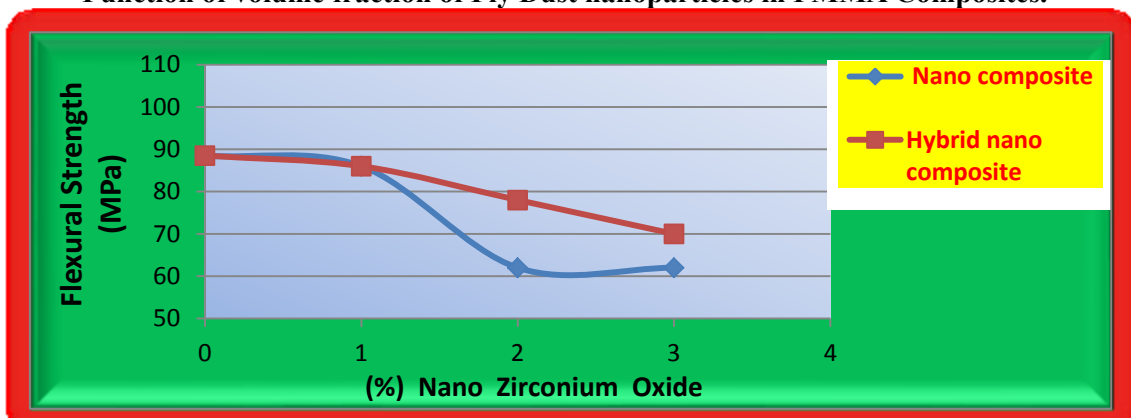


Figure (15): Flexural Strength of PMMA Hybrid Nano Composite Materials as a Function of volume fraction of Zirconium Oxide nanoparticles in PMMA Composites.

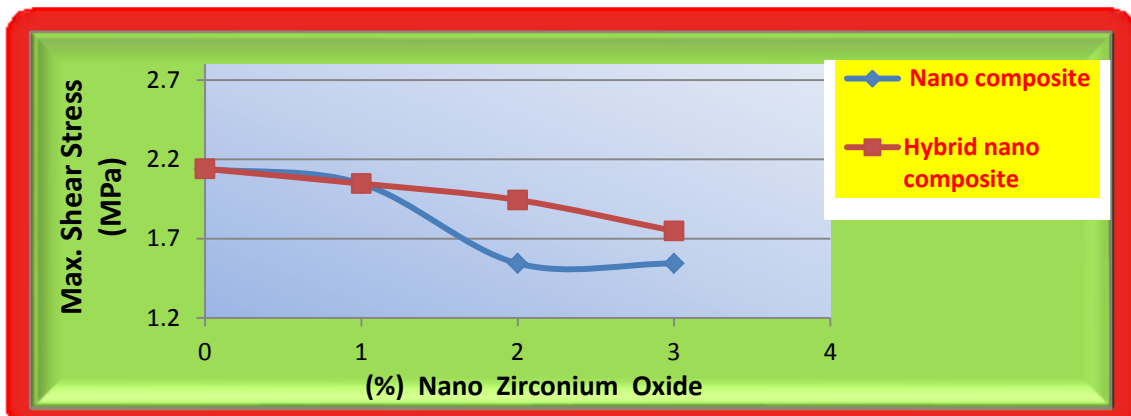


Figure (16): Maximum Shear Stress of PMMA Hybrid Nano Composite Materials as a Function of volume fraction of Zirconium Oxide nanoparticles in PMMA Composites.

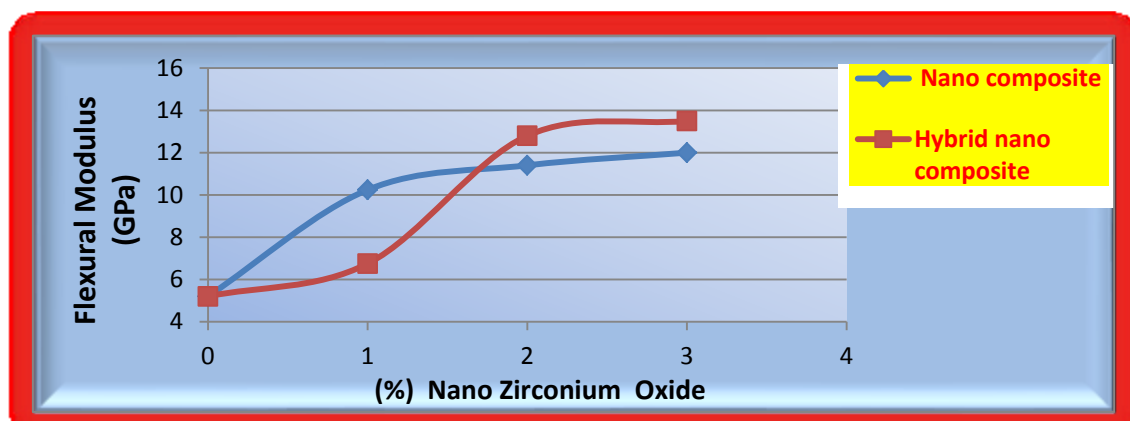


Figure (17): Flexural Modules of PMMA Hybrid Nano Composite Materials as a Function of volume fraction of Zirconium Oxide nanoparticles in PMMA Composites.

CONCLUSIONS

In the present work, attempts are made to development PMMA polymer which is used in the denture base and in dental prostheses applications. So the Nano composites and hybrid Nano composites with desirable properties were attended, by adding three types of nanoparticle powders (fly ash, fly dust and ZrO_2) at the same ratio to it, and it was concluded the following:-

- The mechanical properties such as (hardness and flexural modules) increased with increasing of the volume fractions of (fly ash, fly dust and zirconium oxide) nanoparticles in the PMMA Nano composites and PMMA hybrid Nano composites.
- The mechanical properties such as (flexural strength and Maximum shear stress) increased with the addition low concentrations of (fly ash, fly dust and zirconium oxide) nanoparticles and decreased with the addition high concentrations to larger than 2% of the all nanoparticles to the PMMA Nano composites and PMMA hybrid Nano composites.
- The addition of ZrO_2 nanoparticles has a noticeable effect on the hardness and flexural modules of the Nano composite and hybrid Nano composite prosthetic denture base specimens as compared with the F.A and F.D nanoparticles.
- The addition of F.D and F.A nanoparticles has a noticeable effect on the flexural strength and Maximum shear stress the Nano composite and hybrid Nano composite prosthetic denture base specimens as compared with the ZrO_2 nanoparticles.
- In the current work, the maximum values for hardness (84.166) was obtained in the hybrid Nano composite material ((PMMA : 3% $nZrO_2$)+(1%F.A + 3%F.D)), the maximum values for the flexural strength and Maximum shear stress (101MPa), (2.474MPa) respectively, were obtained in the Nano composite material (PMMA:2% nF.D), the maximum value for the flexural modules (13.95MPa) was obtained in the hybrid Nano composite material ((PMMA : 3% nF.A) + (1%Al + 3% ZrO_2)).

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