



Addition of Nanohybrids Particles and Fiber to Heat Cured PMMA Denture Base Materials

Intisar J. Ismail^{1*}, Balkees M. Diya² and Farah J. Ebrahim²

¹ College of Dentistry, Al-Bayan University, Baghdad, Iraq

² Department of Applied Science, University of Technology, Baghdad, Iraq

*Corresponding e-mail: intesaralrawi@yahoo.com

ABSTRACT

This study investigated the effect of the addition of nanohybrid particles (nano lithium silicate, nanoparticles high-density polyethylene and nanoparticles zirconium oxide) with fiber reinforcement (ultra- high-density polyethylene fiber) on transverse, impact strength and surface hardness of heat cured PMMA. A total of 60 specimens were prepared, 40 specimens of each group were fabricated with dimensions of (65 × 10 × 2.5) mm to conduct the transverse strength and hardness tests, while the remaining 20 specimens of each group were fabricated with dimensions of (80 × 10 × 4) mm to perform the impact strength test. ZrO₂ nano-fillers were surface-treated with a saline coupling agent to provide bonding between ZrO₂ nanoparticles and PMMA matrix. DC-glow discharge system was utilized for plasma surface treatment to ultra-high density polyethylene fibers (UHDPE) to change fiber surface. The results showed that transverse strength and surface hardness begin to decrease after an increase in the fillers percentage and an extreme rise in the impact strength by the increasing fillers percentage in composites.

Keywords: Nanohybrid composites, Heat cured PMMA, Fiber reinforcement

INTRODUCTION

Composites structure is affected by the aesthetic, physical, mechanical properties and their clinical behavior [1]. Chemical composition of dental composite are classified into organic matrix or organic phase, inorganic matrix (filler or disperse) and organosilane or coupling agent to bond filler with the organic resin are the. This agent is a molecule with silane groups at one end (ion bond to SiO₂) and methacrylate groups at the other (covalent bond with the structure of composites affected on aesthetic, physical, mechanical properties and their clinical behavior) [1,2].

Composites like all dental materials have their own restrictions, such as cavity formalization due to polymerization contraction through the setting, which causes leakage and marginal discoloration. Though, by compression with ceramic many composites have higher wear resistance than ceramic. In addition, some of them have wear rates similar to amalgam [3].

Mechanical properties of the composite resin are affected by several factors, like light source, chemical composition, mode of photoactivation, light source and distance of emitted radiation. Compressive strength, flexural strength, and modulus strength can be affected by increasing the amount of nanocomposite inorganic filler [4].

Nanocomposites are generally of two types: nanohybrid types and nanofill types. Nanohybrids comprises of milled glass fillers along with nanoparticles in the size range of 40-50 nm. The nanofill types of composites are formed by a combination of nanomers, which are nanosized mono-dispersed, non-aggregated silica filler particles in the size range of 20-75 nm, and nanoclusters, which are agglomerations of a combination of zirconia-silica and silica nanomeric particles.

The typical “non-agglomerated” property in nanocomposites is achieved by utilizing the coating process during particle manufacturing process. This ensures even distribution of the discrete filler particles within the matrix with no clumping or sticking of particles, thus ensuring a smoother consistency and improved flow [5-6].

MATERIALS AND METHODS

Several materials used for denture base are: PMMA (Hot cure as pour type denture base materials, PMMA, MMA, Spofa Dental a. s., Czech). The mold materials are made from (di stone, pink, Bulgaria). High density polyethylene particles nano filler, (type: 10nm, particle), MPCC COM. Lithium silicate nano filler, liquid, pH=11.47, density=1.181, SiO₂=19.6%, Li₂O=2.02%, XINSEN YVANCO., ltd. Zirconium Oxide (ZrO₂) nano- filler, (type: 70-80nm, nanoparticle, 99.9%HW, china. Polyethylene fibers (ultra-high density weight, white in color) mat, Cemfiber® china. TMSPM (tri-methacryloxy propyl trimethoxy saline) silane coupling agent.

Filler Treatment and Sample Preparation

Two methods were used in filler treatment which includes:

- 1. Plasma Surface Treatment:** The treatment of ultra-high density polyethylene fibers using DC-glow discharge system was done by using a device called a DC-glow discharge system. In this study, the time of treatment of UHDP fibers was 10 minutes. The condition of the plasma system is shown in Table 1.

Table 1 Condition of plasma system

Variables	Value
Gas name	O ₂
Gas pressure	7×10^{-1} mbar
Voltage	600 Volt
Current	30 mamp
Plasma treated time	10 min
Distant between anode and cathode	4 cm

The polyethylene fibers to be treated were placed in the center of cathode assembly of the glow-discharge plasma system. The space between the electrodes was 4 cm and the voltage was set to produce enough plasma depending on the sample size. Plasma chamber was evacuated to pressure 7×10^{-1} mbar using a mechanical rotary pump when the plasma chamber evacuated the oxygen gas was introduced in the chamber. The fiber was sputter cleaned until all micro arcs disappear and uniform glow could be noticed through the chamber, as shown in Figure 1.



Figure 1 Producing plasma in the plasma chamber were the UHDP fiber between the anode and cathode

- 2. Silanation of Nanofillers (ZrO₂):** The formation of reactive groups onto the surface of the fillers was achieved by reaction of the (TMSPM) silane coupling agent with (tri- methacryloxy propyl trimethoxy saline) with zirconium oxide fillers.

Total 30 gm of nanofiller was dispersed in 200 ml of toluene by stirring with a magnetic stirrer for 20 mins into a flask

and then sonicated at ambient temperature. Then 1.5 gm of silane (5.0 wt.% to nano-filler) was applied dropwise by sterile syringe under quick stirrer. With parafilm, the flask was wrapped and for 48 hours the slurry was left positioned in the flask. Toluene was separated by rotary evaporator under vacuum at 60°C, at rotary 150 rpm for 30 minutes. Then nano-filler was kept at room temperature after use [7].

Specimens Grouping

In this study 60 specimens were prepared; according to tests used the specimens were divided to 4 groups, one for control and another for all additions (nano LiSiO₃ + nano ZrO₂ + nano HDPE + UHDPE fibers), where each subgroup contains 5 specimens to be tested.

Test Specimens General Preparation

Acrylic specimen preparation included preparation of plastic model, proportioning and mixing of the acrylic, addition of filler, packing, curing and finishing and polishing. The composites were prepared according to the percentages in Table 2.

Table 2 Polymer, monomer and fillers (nano ZrO₂, nano HDPE, nano Li₂SiO₃ and UHDPE fibers) percentages and amounts utilized in the study

Li ₂ SiO ₃ Percentage	Amount of Li ₂ SiO ₃	ZrO ₂ Percentage	Amount of ZrO ₂	HDPE Percentage	Amount of HDPE	UHPPEF Percentage	Amount of UHDPEF	Amount of PMMA	Amount of monomer
0.000	0.00 gm	0.000	0.00 gm	0.000	0.00 gm	0.000	0.00 gm	22.00 gm	10 ml
0.005	0.11gm	0.005	0.11 gm	0.010	0.22 gm	0.010	0.22 gm	21.34 gm	10 ml
0.500	0.11gm	0.010	0.22 gm	0.015	0.33 gm	0.015	0.33 gm	21.01 gm	10 ml
0.500	0.11gm	0.015	0.33 gm	0.020	0.44 gm	0.020	0.44 gm	20.68 gm	10 ml

Mechanical Tests Utilized to Examine Properties

Evaluations of the mechanical properties of the prepared monohybrid composite denture base were compared with conventional denture base (heat cure acrylic resin).

Transverse strength: The specimens used were prepared as described with dimensions (65 mm × 10 mm × 2.5 mm ± 0.2 mm). Five specimens of each concentration make a total of 20 specimens for measurements of transverse strength. All the specimens were immersed in distilled water at 37°C for 48 hours before being tested (ADA No. 12, 1999) [8].

The test was performed using a universal testing machine (WDW-200E), each specimen was positioned on the bending fixture which consists of two parallel supports (50 mm apart), the maximum load was 50 Kg and the load was applied across heads speed of 1 mm/min by a rod placed between the supports making deflection until fracture occurs. Transverse strength was calculated using the following equation:

$$T = \frac{3PL}{2bd^2} \text{ (ADA specification No. 12, 1999)}$$

Where:

T: Transverse strength (N/mm²)

P: Maximum force exerted on samples (N)

L: Distance between the supports;

b, d: The width and depth of samples (mm) respectively

Impact strength test: The specimens used were prepared as described with dimensions (80 mm × 10 mm × 4 mm ± 0.2 mm), international standard (ISO 179, 2000) for unnotched specimens [9]. Five specimens of each concentration were prepared to make a total of 20 specimens for impact strength measurements. Specimens were tested after being conditioned in distilled water at 37°C for 48 hours.

Impact strength test was conducted following the procedure is given by the ISO 179 with charpy type impact testing instrument. The specimen was supported horizontally at its ends and struck by a free-swinging pendulum which was released from a fixed height in the middle. A pendulum of 2 joules testing capacity was used. The scale reading gave

the impact energy absorbed to fracture the specimen in joules when struck by a sudden blow. The charpy impact strength of unnotched specimen was calculated in KJ/mm² as given by the following equation:

$$\text{Impact strength} = \frac{E}{b.d} \times 10^3$$

Where:

E: The impact energy in Joules

b, d: Width and thickness, respectively

Surface Hardness Test

Specimens of acrylic resin were prepared with a dimension (65 mm x 10 mm x 2.5 ± 0.1 mm) (ISO 179, 2000) for the unnotched specimen. Specimens were stored in distilled water at 37°C for 48 hours before being tested (ADA specification No. 12, 1999).

Surface hardness was determined using durometer hardness tester from type (shore D) that was fabricated by Time group INC company according to American National Standard/American Dental Association (ANS/ADA) No. 12, 1999 which is suitable for an acrylic resin material. The instrument consists of blunt-pointed indenter 0.8 mm in diameter that tapers to a cylinder 1.6 mm. The indenter is attached to a digital scale that is graduated from 0 to 100 units. The usual method is to press down firmly and quickly on the indenter and record the maximum reading as the shore "D" hardness, measurements were taken directly from the digital scale reading. About 3 measurements were done on different areas of each specimen (the same selected area of each specimen), and an average of 3 reading was calculated.

Statistical Analysis of Data

The data obtained were first entered in the computer, then tabulated and subjected to statistical evaluation. Using descriptive statistics for mean and standard deviation was then analyzed by ANOVA to study the differences between groups. All tests were performed at a significance level of 5% in SPSS version 20.0 software.

RESULTS

FTIR was done for zirconium oxide nanofillers before salinization to determine the absorption bands of the compound. Also, another FTIR was done to zirconium oxide nanofillers after salinization to evaluate the differences in active groups, as seen in Figures 2, 3.

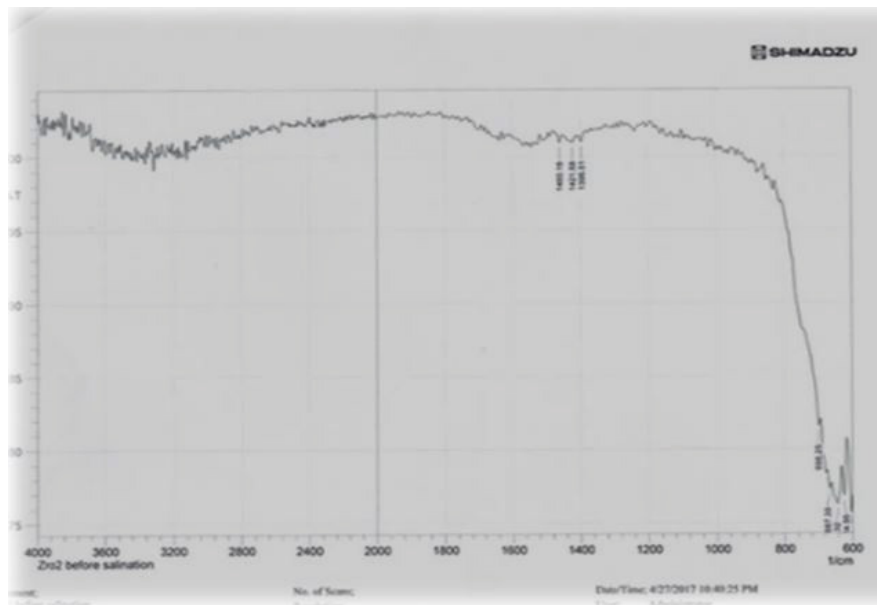


Figure 2 FTIR for nanoparticles ZrO₂ before salinization

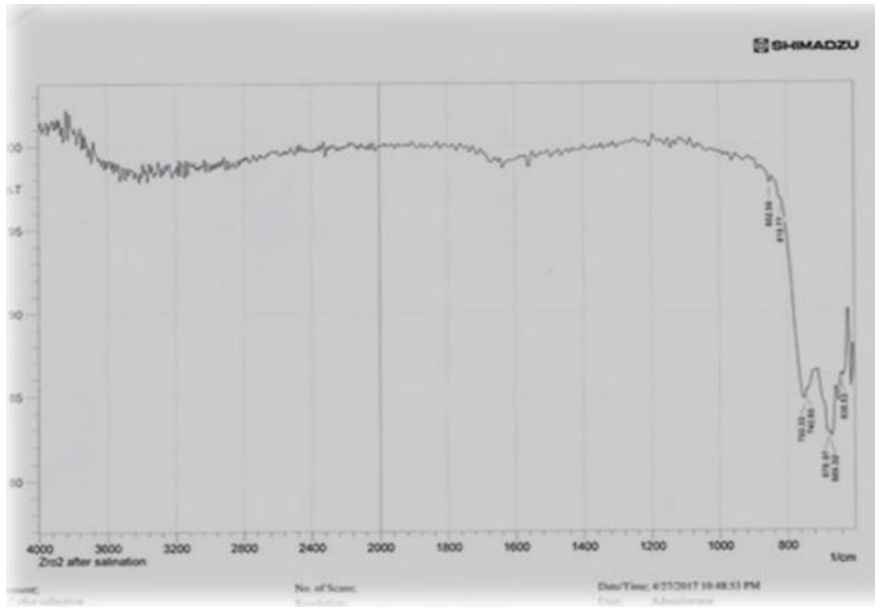


Figure 3 FTIR for nanoparticles ZrO_2 after salinization

The stretching band at 1460cm^{-1} , and for the double bond between (CH_2-CH_3) which occurred at 1396cm^{-1} with a group of two peaks between $624-700\text{cm}^{-1}$ may be caused by stretching of $(C=O)$ bond. Comparison between the Figure 4 and 5, in Figure 5 IR spectrum of the composite after increment fillers to PMMA, showed a change in shape of absorption peaks, at 3437cm^{-1} O-H stretch and H-bond also Si-OH. In 1732cm^{-1} C=O stretch, 1643.35cm^{-1} -C=C- stretch. At 1192cm^{-1} H-wag, 1086cm^{-1} Si-O-Li, while $840.96-914.26\text{cm}^{-1}$ SiO stretch.

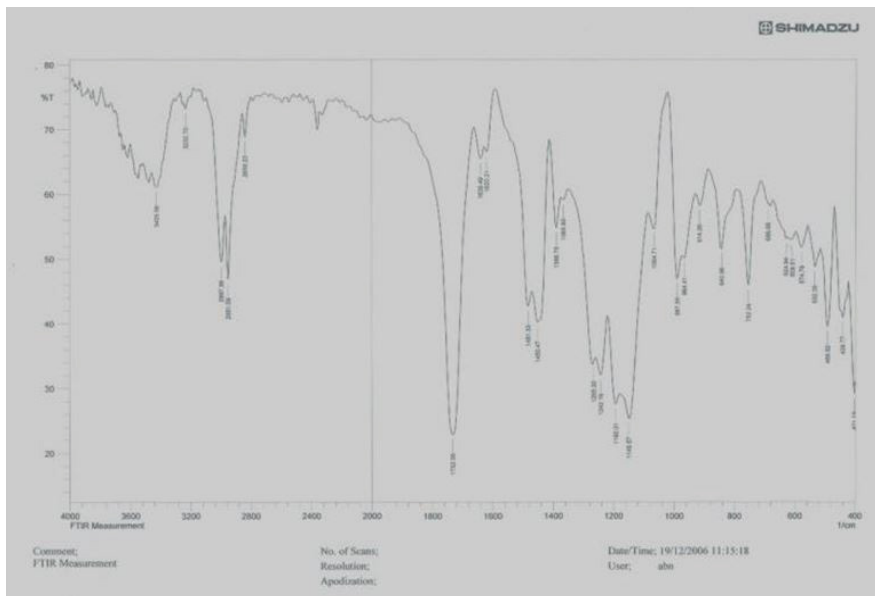


Figure 4 FTIR for control PMMA

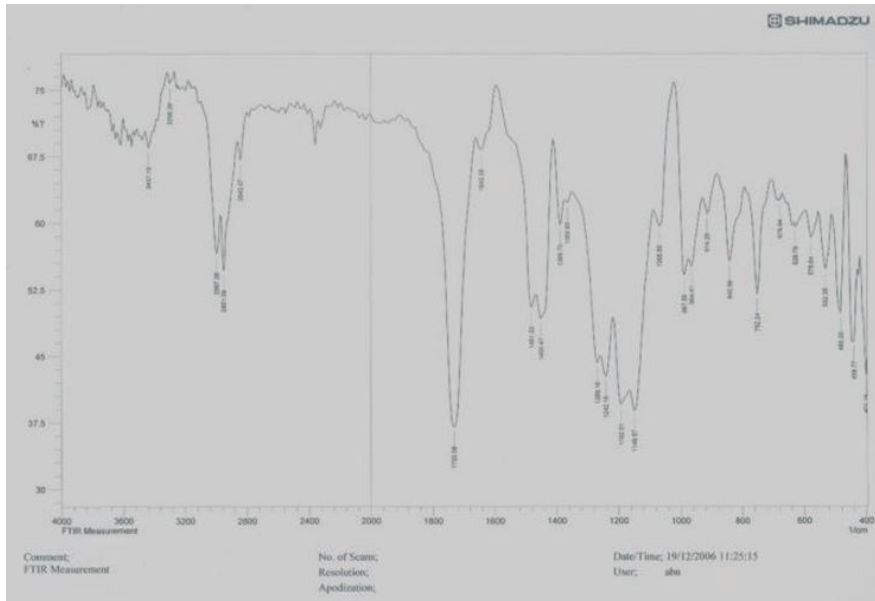


Figure 5 FTIR for composite

Mean values of transverse strength were present in Figure 6 and Table 3,4 for prepared composites specimens. The calculations revealed that the transverse strength decreased at Li_2SiO_3 (0.5%) + ZrO_2 (1.5%) + HDPE (2%) + UHDPE (2%) for composites (74.55 MPa). But it is statistically not significant when applying ANOVA test.

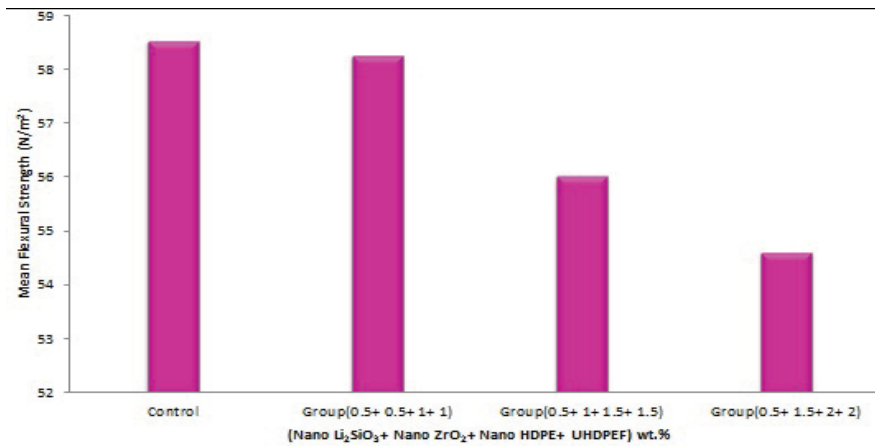


Figure 6 Bar chart represent mean value for transverse strength (MPa) of the composite contain (nano Li_2SiO_3 , nano ZrO_2 , nano HDPE particles and UHDPE fiber)

Table 3 Descriptive statistics for transverse strength (MPa) of the composite contain (nano Li_2SiO_3 , nano ZrO_2 , nano HDPE particles and UHDPE fiber)

Groups	N	Mean	Std. Deviation	Std. Error
Control	5	60.0580	8.867672	2.03060
Li_2SiO_3 (0.5%) + ZrO_2 (0.5%) + HDPE (1%) + UHDPE (1%)	5	56.6992	5.276300	2.60387
Li_2SiO_3 (0.5%) + ZrO_2 (1%) + HDPE (1.5%) + UHDPE (1.5%)	5	54.6358	4.833940	0.78291
Li_2SiO_3 (0.5%) + ZrO_2 (1.5%) + HDPE (2%) + UHDPE (2%)	5	53.9302	4.631657	0.78291

Table 4 ANOVA results for transverse strength (MPa) of the composite contain (nano Li₂SiO₃, nano ZrO₂, nano HDPE particles and UHDPE fiber)

ANOVA	Sum of Squares	df	Mean Square	F-value	Sig.
Between groups	2.306	3	0.769	0.051	0.984
Within groups	242.587	16	15.162		

For impact strength test, the results of this study indicated that, improved impact strength occurred in composite specimens at concentration fillers (0.5% Li₂SiO₃ + 1.5% ZrO₂ + 2% HDPE + 2% UHDPE fibers) (11.1980 KJ/m²) investigated in Tables 5, 6 and Figure 7.

Table 5 Descriptive statistics for Impact strength (kJ/m²) of the composite contain (nano Li₂SiO₃, nano ZrO₂, nano HDPE Particles, and UHDPE fiber)

Groups	N	Mean	Std. Deviation	Std. Error
Control	5	5.140	0.72319	0.32342
Li ₂ SiO ₃ (0.5%) + ZrO ₂ (0.5%) + HDPE (1%) + UHDPE (1%)	5	9.416	1.44412	0.64583
Li ₂ SiO ₃ (0.5%) + ZrO ₂ (1%) + HDPE (1.5%) + UHDPE (1.5%)	5	10.050	1.26590	0.56613
Li ₂ SiO ₃ (0.5%) + ZrO ₂ (1.5%) + HDPE (2%) + UHDPE (2%)	5	11.198	0.69139	0.30920

Table 6 ANOVA results for Impact strength (kJ/m²) of the composite contain (nano Li₂SiO₃, nano ZrO₂, nano HDPE particles, and UHDPE fiber)

ANOVA	Sum of Squares	df	Mean Square	F-value	Sig.
Between Groups	104.984	3	34.995	29.853	0.000
Within Groups	18.756	16	1.172		

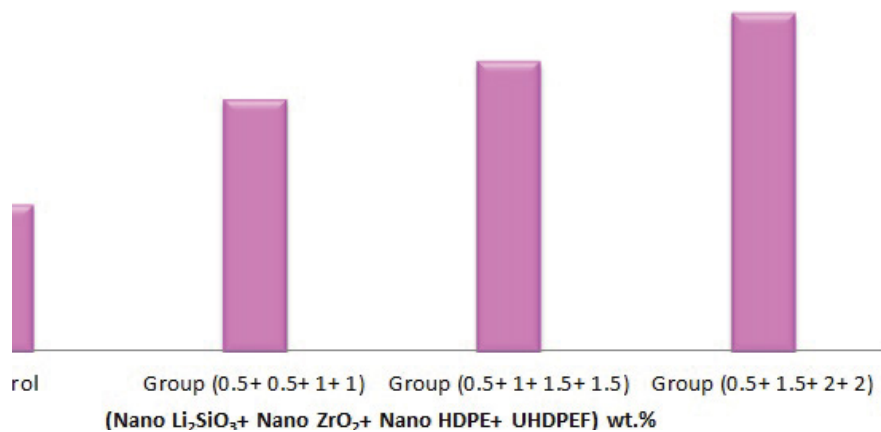


Figure 7 Bar chart represent mean value impact strength (kJ/mm²) of the composite contain (nano Li₂SiO₃, nano ZrO₂, nano HDPE particles, and UHDPE fiber)

A decrease in the surface hardness for composite specimen was prepared with (0.5% Li₂SiO₃ + 1.5% ZrO₂ + 2% HDPE+ 2% UHDPE fibers) of the mean (86.4860) when applying ANOVA test between groups (Table 7,8 and Figure 8).

Table 7 Descriptive statistics for Hardness number of the composite contain (nano Li₂SiO₃, nano ZrO₂, nano HDPE particles, and UHDPE fiber)

Groups	N	Mean	Std. Deviation	Std. Error
Control	5	81.072	1.21857	0.54496
Li ₂ SiO ₃ (0.5%) + ZrO ₂ (0.5%) + HDPE (1%) + UHDPE (1%)	5	87.496	2.15529	0.96388
Li ₂ SiO ₃ (0.5%) + ZrO ₂ (1%) + HDPE (1.5%) + UHDPE (1.5%)	5	87.218	0.67622	0.30241
Li ₂ SiO ₃ (0.5%) + ZrO ₂ (1.5%) + HDPE (2%) + UHDPE (2%)	5	86.486	0.85410	0.38196

Table 8 ANOVA test results for Hardness number of the composite contain (nano Li_2SiO_3 , nano ZrO_2 , nano HDPE particles, and UHDPE fiber)

ANOVA	Sum of Squares	df	Mean Square	F	Sig.
Between Groups	137.482	3	45.827	25.053	0.000
Within Groups	29.268	16	1.829		

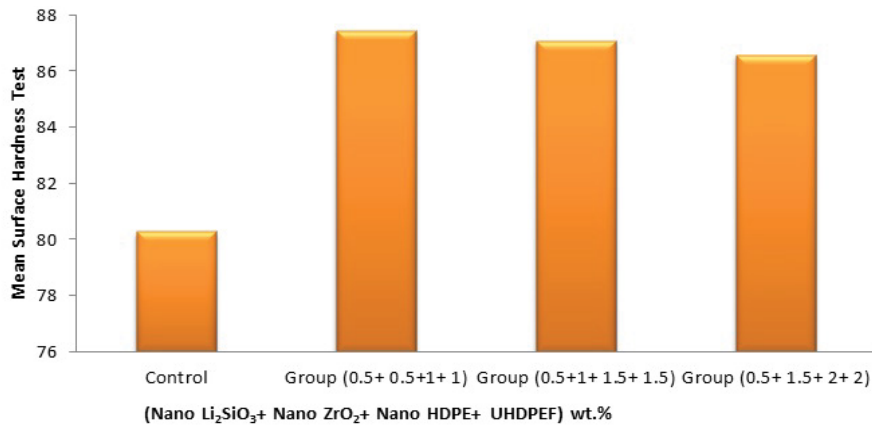


Figure 8 Bar Chart of Mean Surface Hardness of the composite contains (nano Li_2SiO_3 , nano ZrO_2 , nano HDPE particles, and UHDPE fiber)

DISCUSSION

In this study, the results showed a decrease in flexural strength by adding (0.5% Li_2SiO_3 + 1.5% nZrO_2 + 2% nHDPE particles + 2% nUHDPE fibers) to PMMA resin as illustrated in Figure 6. This can be attributed to the degree of nanoparticles dispersion in the PMMA resin matrix and the chemical composition of the commercial acrylic resin material used in the study. From this study, it can be concluded that the polar interactions between the nanoparticles and C=O of polymer matrix (weak interactions) are at adequate low concentrations that results in improved flexural strength. At higher concentrations, nanoparticles may also act as impurities of polymerization that causes a decrease in the degree of cure (DC). Hence, more amount of unreacted monomer may be left over within the matrix that results in decreasing the flexural strength [10]. The decrease in flexural strength may be related to the decrease in the cross-section of the load-bearing polymer matrix, stress concentration because of too many filler particles, changes in the modulus of elasticity of the resin and mode of crack propagation through the specimen due to an increased amount of fillers, void formation from entrapped air and moisture, incomplete wetting of the fillers by the resin, and the fact that nanoparticles act as an interfering factor in the integrity of the polymer matrix [11]. Furthermore, the decrease may be caused by the difficulty of obtaining good adhesion between polyethylene fibers and the resin matrix, or by random orientation of fibers in the specimens of most groups [12].

In Figure 7, an increase in the impact strength by adding hybrid composite (1.5% nZrO_2 particles + 0.5% nLi_2SiO_3 + 2% nHDPE particles + 2% UHDPE fibers) was observed. This is due to the increase in the filler load achieved which caused a reduction in the dimensions of the particles, along with their wide size distribution. This consequently reduces the polymerization shrinkage and increases the mechanical properties [13]. The increase may be resisted by the presence of fillers. Fillers intersect microcracks and bridge the gap between two surfaces of the crack. Under loading condition, when a crack starts to propagate, the fibers apply force opposing the crack propagation due to which the strength increases. Interface force of fiber-matrix is directly proportional to the surface area between the matrix and fiber, thus fiber concentration plays a major role in enhancing the strength quality. Fiber-matrix debonding may lower the strength and stiffness to the undamaged structural fiber reinforced polymers [14].

In Figure 8, it can be noted that the hardness increases and then starts to decrease. This is probably due to grain size effects and the reinforcement role of nanoparticles [15]. A low hardness value of a resin composite indicates poor chemical/physical bonding between the matrix and filler interface [13]. The decrease in the hardness is due to the increase in the filler ratio which causes an increase in the cluster of the nano-filled composite and causes consequently a decrease in the hardness value of the composite [16]. Further then, comparatively uniform distribution of all

phases and the lowering of interparticle distance with the matrix will result in raising the resistance of composites to indentation [17].

CONCLUSION

The addition of four different fillers to heat cured PMMA increases the impact strength, while, the transverse strength and surface hardness decreases by an increase in the percentage of fillers. There is a difference in the peak of FTIR between the control PMMA and the composites when fillers are added to PMMA.

DECLARATIONS

Conflict of Interest

The authors declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

REFERENCES

- [1] García, Adela Hervás, et al. "Composite resins. A review of the materials and clinical indications." *Medicina Oral, Patología Oral y Cirugía Bucal*, Vol. 11, No. 2, 2006, pp. 215-20.
- [2] Lyapina M., et al. "Application of nano-biomaterials in restorative dentistry." *Journal of IMAB*, Vol. 22, 2016.
- [3] Hamouda, Ibrahim M., and Hagag Abd Elkader. "Evaluation the mechanical properties of nanofilled composite resin restorative material." *Journal of Biomaterials and Nanobiotechnology*, Vol. 3, No. 2, 2012, p. 238.
- [4] Pontes, Luana Farias, et al. "Mechanical properties of nanofilled and micro hybrid composites cured by different light polymerization modes." *General Dentistry*, Vol. 61, No. 3, 2013, pp. 30-33.
- [5] Sachdeva, S., et al. "Nano-composite dental resins: An overview." *Annals of Dental Specialty*, Vol. 3, No. 2, 2015, pp. 52-55.
- [6] Jain, Atul, et al. "Evaluation of microleakage of recent nano-hybrid composites in class V restorations: An in vitro study." *International Journal of Advanced Nutritional and Health Science*, Vol. 2, No. 1, 2015, pp. 8-12.
- [7] American Dental Association. "Denture base polymers." Chicago: Council on dental materials and devices. Chicago Illinois, 1999.
- [8] Mohammed, Ahmed A., and Intisar J. Ismail. "In vitro Performance of Polymethylmethacrylate with Ultra High-Density PolyEthylene Fiber and Nano Zirconium Oxide Particles Composite." *Journal of Baghdad College of Dentistry*, Vol. 30, No. 1, 2018, pp. 5-11.
- [9] Jian-ming, Shi, et al. "Preparation of poly (methyl methacrylate)/nanometer calcium carbonate composite by in-situ emulsion polymerization." *Journal of Zhejiang University*, Vol. 5, No. 6, 2004, pp. 709-13.
- [10] Ravindranath, Sabarigirinathan C., et al. "A Comparative Study to Evaluate the Mechanical Properties of Zirconium Oxide Added Polymethyl Methacrylate by Two Different Methods at Two different Concentrations- In Vitro Study." *Analisis of International Medical and Dental Research*, Vol. 1, No. 3, 2015, pp. 161-65.
- [11] Alla, Rama Krishna, et al. "Influence of Silver Nanoparticles Incorporation on Flexural Strength of Heat-cure Acrylic Denture Base Resin Materials." *Annual Research and Review in Biology*, Vol. 17, No. 4, 2017.
- [12] Kamble, Vaibhav Deorao, Rambhau D. Parkhedkar, and Tushar Krishnarao Mowade. "The effect of different fiber reinforcements on flexural strength of provisional restorative resins: an in-vitro study." *The Journal of Advanced Prosthodontics*, Vol. 4, No. 1, 2012, pp. 1-6.
- [13] Ozsoy, Iskender, et al. "The Influence of Micro-and Nano-Filler Content on the Mechanical Properties of Epoxy Composites." *Journal of Mechanical Engineering*, Vol. 61, No. 10, 2015.
- [14] Mathew, Merin, Kamalakanth Shenoy, and K. S. Ravishankar. "Impact strength of E-glass reinforced PMMA." *Journal of Evolution of Medical and Dental Science*, Vol. 2, 2013, pp. 5971-77.
- [15] Ahmed, Mohamed Ashour, and Mohamed I. Ebrahim. "Effect of zirconium oxide nano-fillers addition on the flexural strength, fracture toughness, and hardness of heat-polymerized acrylic resin." *World Journal of Nano Science and Engineering*, Vol. 4, No. 2, 2014, p. 50.

- [16] Abdul Raheem R. H., Abdullah H. A., Ahmed S. S., “Mechanical properties of composites materials reinforced in ceramic particles.” International Conference, Berlin, Germany, 2017.
- [17] Camargo, Pedro Henrique Cury, Kestur Gundappa Satyanarayana, and Fernando Wypych. “Nanocomposites: synthesis, structure, properties and new application opportunities.” *Materials Research*, Vol. 12, No. 1, 2009, pp. 1-39.