In vitro Performance of Polymethyl–methacrylate with Ultra High Density Poly Ethylene Fiber and Nano Zirconium Oxide Particles Composite

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ABSTRACT

Background: Poly (methyl methacrylate) has been widely utilized for fabrication of dentures for many years as it has good advantages but not achieved all demands of the mechanical properties such as low transverse strength, low impact strength, low surface hardness, high water solubility and high water sorption.

Material and method: To provide bonding between ZrO_2 nanoparticles and PMMA matrix, the ZrO_2 Nano-fillers were surface-treated with a saline coupling agent. Plasma surface treatment of polyethylene (PE) fiber was done to change surface fiber by using DC- glow discharge system. For characterization of interring any functional groups, the (FTIR) spectrum were done .then the mechanical properties studied to choose the appropriate percentages to complete study.

Results: The results revealed that highly significant difference between groups in transverse strength, the highest mean value (96.1700 N/mm²) found in 2.0% polyethylene fibers and 1.5% salinized Zirconium oxide nanoparticles group, highly significant increase in impact strength (7.69 Kj/m²), surface hardness (92.35) and highly significant decrease in water sorption (0.0016 mg/cm²) and water solubility (0.0013 mg/cm²).

Conclusion: the use of saline coupling agent with ZrO_2 and oxygen plasma treatment PE fiber provided an effective procedure for getting good bonding with the PMMA matrix to give enhanced properties for the composite.

Keyword: PMMA, UHDPE, ZrO_2, FTIR, PE, oxygen plasma. **(J Bagh Coll Dentistry 2018; 30(1):5-11)**

INTRODUCTION

The material which was most widely used since 1930, for fabrication of dentures base is poly (methyl methacrylate) (1).Their mechanical properties is not perfect (2). In spite of their suitable color, it has not good strength due to its susceptibility to break when fall during use it (3). At the beginning many efforts to improve denture properties by adding metal powder filler to PMMA such as (aluminum, copper and silver) but had bad appearance (4). Another way to reinforce the PMMA by adding fibers like nylon fibers, carbon fibers, aramid fibers, and glass fibers(5). These fibers may be fracture when mixed with PMMA due to no bonding between matrix polymers. The surface of fibers must be treated with plasma or chemical to overcome this problem (6). Improving the bond between filler and matrix may be occurred when nanofillers that incorporated in PMMA treated with saline coupling agent (7,8). In this study the management of polymer done by using 2.0% oxygen plasma treatment of Polyethylene fiber alone and with different concentration of 0.5%, 1.0%, 1.5% and 2.0% nanoparticles zirconium oxide that mixed with PMMA and examine the influence of this addition on some mechanical and physical properties.

MATERIAL AND METHOD

Salination procedure (surface modification of Nano-filers (ZrO_2))

The presentation of reactive groups onto surface of fillers was accomplished by reaction of TMSPM (tri-methacryloxy propyl trimethoxy saline) silane coupling agent with zirconium oxide fillers, through the reaction of ZrO_2 Nano fillers with the silane coupling agent **(9)**. Thirty grams of Nano filler and 200ml pure Toluene were added into a flask then sonicated at ambient temperature for 20 minutes (Fig. 1). After, that, the Nano-filler and Toluene were placed into a flask equipped with magnetic stirrer at room temperature. Then 1.5g of silane (5.0% wt. to Nano-filler) was placed a drop wise by sterile syringe under quick stirrer. The flask was wrapped by Para film and this slurry was left position in flask for 2 days. The solvent (Toluene) was extracted by rotary evaporator under vacuum at 60 °C rotary 150 RPM for 30 minutes. After that the modified nano-fillers was dried in vacuum oven at 60 °C for 20 hours. Then nano-filler remained at room temperature before use as in figure 2 **(8, 9)**

The procedure of Surface treatment of polyethylene fiber with Plasma

DC- glow discharge system is a device manipulated for plasma treatment by different gases. A previous study they used oxygen for treatment of polypropylene fiber for 6 minutes (10) and 10 minutes (11). In this study the time of exposure for plasma treatment was 8 minutes and

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3 cm the distance between cathode and anode as shown in figure 3 and placed PE between anode and cathode. It supplied direct current with 30 milliamps and 400 volts as show in figure 4 and compared this condition as shown in table 1 with other conditions in previous studies each time done Fourier Transform Infrared Spectrophotometer analysis (FTIR) analysis to choose a perfect time which give changes in functional groups of the fiber surface.

Selection proper percentages of salinized ZrO_2 nanofillers and PE fiber

After salinization of ZrO_2 nanoparticles and plasma treatment of PE fiber has been accomplished and identified the active groups by FTIR, the pilot study was started to select the proper percentage of PE alone and PE with different percentages of ZrO_2 Nano fillers that will be taken in the study. 0.5%, 1.0%, 1.5% and 2.0% were used as percentages of Nano fillers, with 2.0%wt. Polyethylene fiber concentration was determined according to a previous study (12) as they found a significant improvement in impact strength when use this concentration.

Proportion and mixing ratio of acrylic resin and other materials.

The proper weight of acrylic resin powder and liquid was mixed accordance to manufacture instruction using electronic balance.

Identification of the Functional groups

Fourier Transform Infrared Spectrophotometer analysis (FTIR) is performed by spectrophotometer.

The percentage of mixing ratio 2.5/1 by wt. powder liquid ratio, the amount of addition other material decreased from powder percentage as shown in table 2. Fiber was mixed with powder by pastel and mortal and nanofillers mixed with monomer by probe sonication apparatus.

To prepare the dough, the measured ingredients were added to the monomer and polymer, the fillers were well dispersed in the monomer by ultra-sonication, by using a probe sonication apparatus (120 W, 60 KHz) for 3 minutes to break them into individual nano crystals (13). The mixing of powder and fiber was done randomly with using of mortar and pestle until homogenous mixture was obtained. The monomer with nano powder was immediately mixed with acrylic powder to reduce the possibility of particle aggregation and phase separation.

Figure 1: equipment used for surface modification of nanofillers A: probe sonication apparatus; B: magnetic stirrer.

Figure 2: Modified nanoparticles before and after dryness A: silanol containing nanoparticles; B: nanoparticles after 14 days.

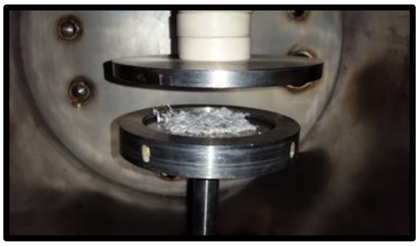

Figure 3: PE fiber between anode and cathode.

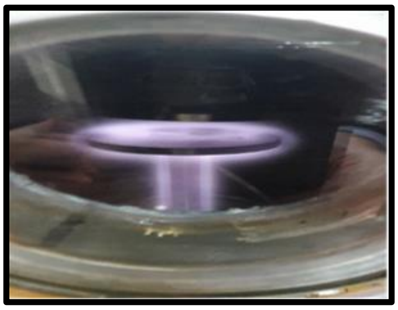

Figure 4: Plasma champer.

Table 1: The conditions of plasma Treated PE fibers in the system

Gas name	Oxygen
Gas pressure	$0.5x10^{-1}$ ml.bar
Voltage	400 V
Plasma treated time	8 minutes
Distant between anode and cathode	3 cm

Table 2: Proportion and mixing ratio of acrylic.

Groups	ZrO_2 (g)	pE Fiber (g)	Polymer (g)	Monomer (ml)
Control group	0	0	15	6
2% PE	0	0.33	14.67	6
0.5%ZrO_2 +2% pE	0.075	0.33	14.595	6
1% ZrO_2 +2% PE	0.15	0.33	14.52	6
1.5% ZrO_2 +2% PE	0.225	0.33	14.445	6
2% ZrO_2 +2% PE	0.33	0.33	14.34	6

Physical and mechanical tests to examine properties

1. Impact strength:

The samples were formed with dimensions 80mm x 10mm x 4mm **(14)** The strength of impact examination was evaluated from these steps. The samples were fixed vertically from one edge and pendulum of 5.5 Joules struck samples then impact power in Joules shows in scale readings. Izod impact strength of un notched specimens was calculated in K j/m^2.

$$\text{impact strength} = \frac{e}{B\times D} \times 1000 \quad = \text{Kj/m}^2 \ ^{(14)}$$

e: energy
D: thickness
B: width

2. Transverse strength:

Samples of acrylic resin were formed with dimensions 65 × 10 × 2.5 ±0.1 mm (15). Instron universal examination tool was used to achieve the testing samples that positioned on the flexing stand which has two equivalent arms fifty millimeter apart (Fig. 6) 50 K.J is the maximum force was directed with across tip velocity of two millimeters per minute. By a rod put in contact between arms that doing load until the sample is broken (according to the following equation)

$$T = \frac{3PL}{2bd^2} \ ^{(15)}$$

T= Transverse strength (N/ mm2)
P= maximum force exerted on samples (N)
L= distance between the supports (mm)
b= width of the samples (mm)
d= depth of the samples (mm)

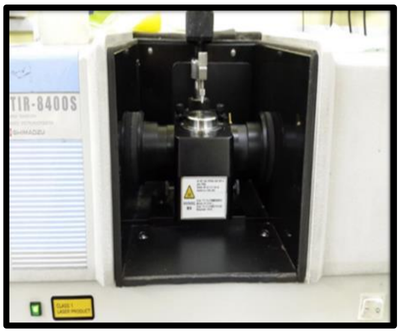

Figure 5: FTIR Shimadzu spectrophotometer.

Figure 6: Instron (examination machine for flexing test)

3. Surface hardness:

Samples of acrylic resin were formed with dimensions 65×10×2.5±0.1 mm (Shore D) durometer hardness examiner is employed to test the hardness of surface **(15)**. It was used for acrylic. The tool has spring - forced penetration (0.8mm), the penetrator is connected to scale that is graduated from up to 100 units. The method usually is force down firmly and quickly on the penetrator and give the data. Five readings were done on each specimen then the average of five data was numbered.

5. Water sorption and solubility:

Round samples were formed from plastic type with dimension (50±1.0) mm diameter and (0.5 ±0.1) mm in thickness **(15)**. The samples after finishing and polishing were put in dehydrated device containing freshly dried gel of silica. The dehydrated devise was put in an incubator at 37 ºC ± 2 ºC for 1 day after that the samples were transport to a ambient temperature for 60 minutes and electronic balance is used to weigh the sample. The procedure of weighing was repeated each 24 hours until a remained mass (M1) (conditioned mass) was arrived after 5 days, after that each round discs of all groups were immersed in distilled water for 5days at ambient temperature. Samples were eliminated from the water with tweezer rub with a warm towel to remove he humidity then shacked in the air for 30 minutes and weighed; this mass was wrote as (M2) . In order to measure the amount of water solubility, the samples were dried again in the dissector at 37°C ±2 °C and the same procedure continues as mention before in sorption test, and the obtained value represents the reconditioned mass M3. Water sorption and solubility were determined by the following formula:

Wsp= (M2-M1)/S (Wsp=water sorption, M1= conditioned mass, M2= Mass of specimen after 7 days immersion in water)

RESULTS

FTIR was done for polyethylene fiber before plasma treated and after plasma treated as seen in figure 7 and 8. FTIR test was also done to specimens of zirconium oxide nanofillers before Salination to determine absorption bands of the compound. Also other FTIR was done to zirconium oxide nanofillers after Salination to evaluate the differences in active groups, as seen in figures 9 and 10.

The characteristic for CH_2-and CH_3 occurs at 1413cm^{-1}, and groups of peaks between 1296cm^{-1} and 1166cm^{-1} can be attributed (C-O-C) stretching, the characteristic (Si-O-CH_3) stretching occurs between) 400- 470cm^{-1}.

According to the results obtained the addition of 2.0% PE fiber and 1.5% ZrO_2 nanofillers to PMMA results in greatest value of impact strength, flexural strength and hardness, and the least value in water sorption and solubility. Therefore, the decision made to take this percentages: to complete the study as present in table 3.

From these outcomes improved most properties of denture base in the group with 1.5% wt. Salinized nanoparticles ZrO_2 and 2.0% plasma treated PE fiber.

DISCUSSION

ZrO_2 was selected due to it is superior biocompatible material also because of being white is less likely to alter esthetic. Zirconium material has high refractive index, high hardness and advantages of chemical inertness, the nano-sized zirconium can be used to construct Nano composite with high hardness and improved scratch resistance. PE is hard, stiff, dimensional stable and absorbs very little of water (16).

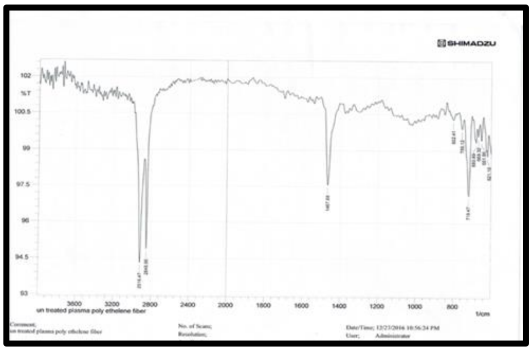

Figure 7: FTIR for PE before plasma treated

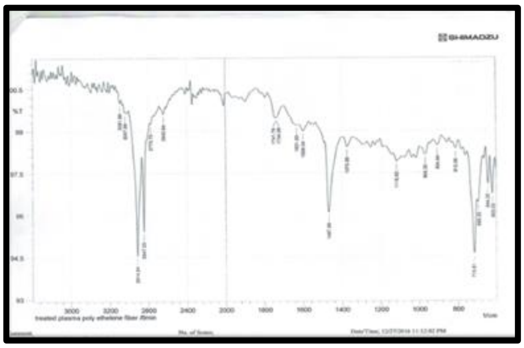

Figure 8: FTIR for PE after plasma reated

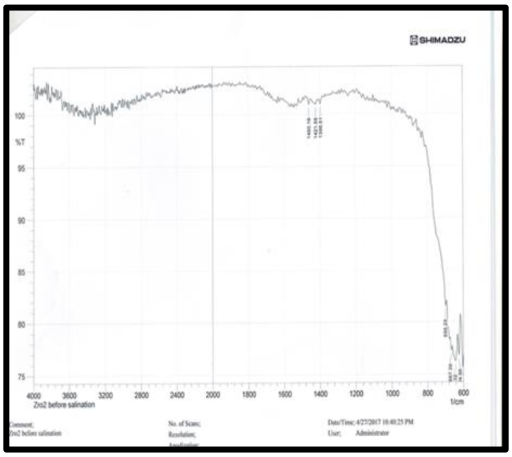

Figure 9: FTIR for nanoparticles ZrO_2 before salination

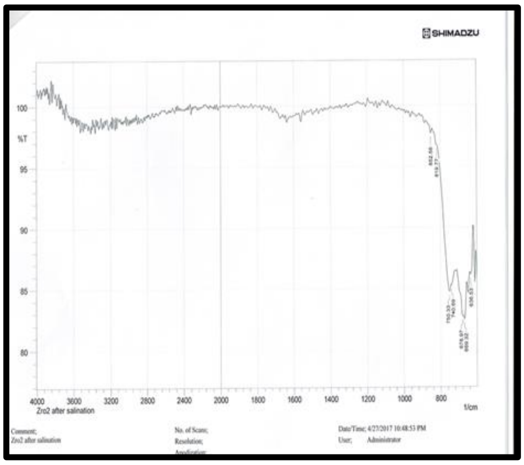

Figure 10: FTIR for nanoparticles ZrO_2after salination

Table 3 the mean readings of the five samples of each studied group of the pilot study.

Amount of PEF + nanoZrO_2	Impact test j/m^2	Hardness test No.	Transvers test N/mm^2	Water sorption mg/cm^2	Water solubility mg/cm^2
0%	4.439	82.000	90.040	0.004	0.002
2%PEF	7.083	86.133	69.200	0.004	0.001
0.5% ZrO_2 + 2%PEF	9.950	87.300	86.467	0.004	0.004
1%ZrO_2 + 2%PEF	7.417	90.667	88.500	0.003	0.003
1.5% ZrO_2 + 2%PEF	7.500	92.230	97.967	0.001	0.001
2% ZrO_2 + 2% PEF	6.367	90.300	93.950	0.003	0.002

It has highly transparent and chemical resistance. Results of this study appeared decrease in flexural strength of denture base when added 2.0% plasma treatment of PE fiber alone with PMMA in comparison with control groups (pure PMMA) the investigation of why this happened may be because of:

- Different direction of PE fiber that made little amount of fiber backing to the perpendicular force applied on it.
- Unable to moisten of fibers with resin due to space formed between its by plasma treatment that cause prohibit radical polymerization of acrylic resin which may occur with oxygen entry and residual of the monomer will increase and effect on the flexural strength **(17).**
- The effect of the plasticity oxygen plasma PE fiber may be cause decrease flexural strength **(18).**

Flexural strength increased when addition 2.0%wt. plasma treatment PE and 1.5% wt. salinized nanoparticles ZrO_2 when compared it with control groups (contents PMMA only) the interpretation of outcomes may be because of these salinized nanoparticles ZrO_2 act as a bridge factor in safety of matrix in polymer (good dispersion, and biocompatibility) (19).

The results of the study appeared raise impact strength when used 2.0 % wt. plasma treatment of PE fiber in comparison with control groups and the increase impact strength being less when used 2.0 % wt. plasma treatment fiber and 2.0%wt. salinized nanoparticles ZrO_2 in comparison with other groups which appeared raised impact strength when compared with control groups as showed in table 3 the interpretation of these results in this study may be correlate with many theories.

One of these theories that the plasma treatment of PE fiber play a significant function in increase impact strength by functional groups formed on surface of the fiber and rough surface occurred because of the plasma treatment raise fiber-matrix linking and this could be concerned prohibit the fracture generation and redirection of fracture to perform small split(fracture) between fibers it could be benefit to raise impact strength of these groups in comparison with control groups where unblocked fracture generation(20).

In fact, the plasma treatment made polar surface due to introduce functional groups on fiber surface, may get better power surface (21) which cause raise in impact strength. These results are approved with findings that studied the effect of oxygen plasma on polypropylene fiber addition (22). These results agreed due to raise in impact strength when they employed salinized Nano Al_2O_3 and plasma treatment of polypropylene fiber with heat cure of PMMA (23).

The results showed slightly raise in surface hardness when manipulated 2.0% plasma treatment of PE fiber with PMMA in comparison with control groups because of plasma treatment of PE fiber arranged closely or at the surface of composite (24). In addition to that interpretation this survey has messy directed of fiber when manipulated with heat cure resin (25). One agent causes highly significant raise in surface hardness in comparison with control groups because of used salinized nanoparticles ZrO_2 that responsible for coalescence between nanoparticles and polymer that raise linking rigidity and drive to raise resilience of Nano composite (26). From the outcomes seen in table 3 there were little lowering in water sorption when manipulated 2.0%wt. plasma treatment PE fiber with PMMA in comparison with control groups because of fibers filled voids between polymer and matrix will refuse take in water in addition to plasma treatment changed functional groups from hydrophilic to hydrophobic properties that made water out of the Nano composite but in this study appeared extremely lower in water sorption when manipulated 1.5%wt. of salinized of nanoparticles ZrO_2 and 2% plasma treatment PE in comparison with control groups to interpret this phenomena we have many routs, one of these routes the salinized nanoparticles ZrO_2 occupied micro space and micro voids that formed during polymerization of acrylic and will pull out the water out of Nano composite also the lowering in water sorption occurred because of saline coupling agent replaces hydrophilic resin, therefore reduces water imbibition than through the PMMA only(27).

The raise in percentage of ZrO_2 nanoparticles lowered water sorption and Lowering in water solubility (28). When manipulated 2.0% wt. plasma treatment of PE in comparison with control groups because of fiber has property to cross -engage happened among the addition plasma treatment of PE fiber and acrylic resin that may cause lowering the remnant monomer content following minimized dissolved of the polymer happened.

At the same figure shows lowering in water solubility when manipulated 1.5% wt. salinized nanoparticles ZrO_2 due to ZrO_2 is an insoluble in water so that addition of ZrO_2 to the composite which arrives to decline in solubility of acrylic resin (15). The lowering in water solubility by manipulation salinized ZrO_2 nanoparticles with acrylic resin. When increased the concentration of nanofillers salinized of ZrO_2 to 2.0% showed defect the properties of composite because of may be formed load by nanoparticle to matrix of composite that cause damaged and disintegration (26).

CONCLUSION

The addition of 2.0% oxygen plasma treated of polyethylene fibers with 1.5% salinized nanofillers Zirconium oxide to heat polymerized acrylic resin will get improvement in properties which are studied such as raise in flexural strength, impact strength and hardness, while reduced in water sorption and water solubility.

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الخلاصة

الخلفية: بولي مثيل ميثاأكريلات يستعمل بشكل واسع في صناعة طقم الاسنان لسنوات عديدة وله صفات جيدة لكن لايسد متطلبات الخواص الميكانيكية. تهدف هذه الدراسة الى تكوين خليط من الياف بولي الاثيلين المعالجة مع حبيبات اوكسيد الزركونيوم المعالجة ليحسن صفات قاعدة مادة طقم الاسنان.

المواد والعمل: لجعل الارتباط قوي بين حبيبات اوكسيد الزركونيوم النانوية مع مادة طقم الاسنان يجب معالجة سطحها اي الحبيبات مع سليين .هناك انواع كثيرة منها المستعمل في هذة الدراسة هو ثلاثي ميثاأكريلوكسي بروبيل تراي ميثوكسي سليين. أختير طبقا لقياس ذوبانيته مع المونمر وترابطه مع بولي مثيل ميثاأكريلات.

الجهاز المستعمل لمعالجة الياف البولي اثيليين هو نظام دي سي كلو. لتحديد مدى فعالية المجاميع الوظيفية الموجودة على سطح المواد للارتباط وتكوين اواصر تحدد بجهازالاطياف للاشعه تحت الحمراءالمتقدم.

النتائج:وصف الاواصر المتكونة على سطح المواد يتم بواسطة جهازالاطياف للاشعة تحت الحمراء المتقدم في سلاسل عندما نقارن بين قبل وبعد المعالجة بواسطة الاوكسجين لمدة ٨ دقائق وبمسافة ٣ سنتمتر توضع الالياف البولي اثيلين بين الانود والكاثود ومقارنة بين الحبيبات اوكسيد الزركونيوم النانوية المعالجة وغير المعالجة. وجد ان افضل تركيز لحبيبات اوكسيد الزركونيوم النانوية المعالجة هي واحد ونصف بالمائة واثنان بالمائة من الياف بولي اثيلين المعالجة بالبلازما مع مادة طقم الاكريل الحراري.

الاستنتاج: استخدام مادة السلين مع حبيبات الزركونيوم النانوية ومعالجة الياف بولي اثيلين بالبلازما ستعزز العملية الموثرة للحصول على ارتباط جيد مع بولي مثيل ميثاأكريلات لتعزز صفات المرغوب بها في هذا المتراكب.

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