VOL. 14, NO. 4, FEBRUARY 2019 ISSN 1819-6608
ARPN Journal of Engineering and Applied Sciences

www.arpnjournals.com

MODIFICATION OF SILICONE RUBBER BY ADDED PMMA AND NATURAL NANOPARTICLE USED FOR MAXILLOFACIAL PROSTHESIS APPLICATIONS

Sihama Issa Salih, Jawad Kadhim Oleiwi and Hajir Mohammed Ali
Materials Engineering Department, University of Technology, Baghdad, Iraq
E-Mail: 130005@uotechnology.edu.iq

ABSTRACT

As a result of the increased incidence cases for a maxillofacial due to accidents and cases of disease has become necessary to work on the production of alternative materials for sites damaged in this area. The particularly important bio material is silicone rubber, which is widely used in damaged maxillofacial affected areas replacement surgery. The aim of this research, prepared a nano composites materials, from polymer blend (silicone rubber: 5% PMMA) reinforced by two different type of natural nano-powders. Pomegranate Peels Powder (PPP) and Seeds powder of dates Ajwa (SPDA) with loading level (0.0, 0.1%, 0.2%, 0.3% and 0.4%). Some mechanical properties such as tensile, hardness, compression and surface roughness were test, as well as, FTIR, DSC and SEM tests were done on prepared sample. The results showed that the optimum percent of both Pomegranate Peels Powder (PPP) and Seeds powder of dates Ajwa are 0.2%, 0.3 respectively that have ideal characteristic.

Keywords: polymer blend, natural nanopowders, maxillofacial prosthesis, silicone rubber, PMMA.

1. INTRODUCTION

A prosthetic is artificial device which mimics the function of a missing body part; Prosthetic limbs are fabricated devices that provide amputees with a replacement for their missing limb, restoring some function [1]. Maxillofacial patients suffer from pains and dysfunctions also, psychological problems related with facial distortion, particularly after surgery [2]. Maxillofacial prosthetics is known as a division of prosthodontics interested with restoration and replacement of both of stomatognathic and related with facial structures by artificial substitutes that movable. It including rehabilitate parts of the body that are congenitally missing or lost due to cancer or congenital diseases [3, 4]. The main goal of maxillofacial prosthetic is the effective treatment to restore missing parts of the face; maxilla and mandible and solve the lost aesthetic look and function. [5].

In the past, maxillofacial prostheses were retained by mechanical tools (e.g. glasses), but since 1979 there is a shift towards implant-retained maxillofacial prostheses. Such prostheses are preferred by many patients over conventional maxillofacial prostheses [6]. There are many materials have been used such as polyurethane, and acrylic resins, especially maxillofacial silicone elastomer has been extremely used for manufacture facial prostheses for restoring the normal shape of patients with maxillofacial defects because of its chemical inertness, durability, easy of manipulation and coloration and biocompatibility [7]. PMMA can be successfully employed for specific types of facial defects, particularly those in which little movement occurs in the tissue bed during function (e.g. fabrication of orbital prostheses) [8].

Actually the using of silicone elastomers alone not possessing sufficient physical and mechanical properties with unsatisfactory strength and has a lack of reducing the clinical longevity of the prostheses. Thus for improving the performances of polymers and expand their application scopes, nanoparticles were incorporated into the polymer to obtain a nanocomposite [9, 10]. The usual objective for preparing a novel blend of two or more polymers is not to change the properties of the components drastically, but to capitalize on the maximum possible performance of the blend, also improved process ability, product uniformity, quick formulation changes, plant flexibility and high productivity [11, 12]. For successful nanocomposite, it is very important to be able to disperse the inorganic material throughout the polymer. If a uniform dispersion is not achieved, agglomerates of inorganic materials are found within the host polymer matrix, thus limiting improvement [13].

Nouri Al-qenae (2010) studied the physical properties of VST-50HD silicone elastomer maxillofacial material after mixed with nano alumina ceramic fiber as fillers. The results showed that there is no significant improvement of properties (tensile, tear and Shore A hardness strengths) [14]. Sara M. Zayed *et al.* (2014), Studied the effect of SiO_2 nanoparticles on the mechanical properties of A-2186 silicone elastomer that is used for extra oral maxillofacial prosthesis application. The results showed that, there is significant improvement in all mechanical properties tested, especially at 3%SiO_2 nanoparticles. In SEM test shows that no agglomeration was revealed as the SiO_2 nanoparticles loading were increased in all samples [15]. Dhuha A. Shakir and Faiza M. Abdul-Ameer (2018) developed the mechanical properties of two types of maxillofacial silicone elastomers (VST50FRTV and Cosmesil M511 HTV) by added nano-TiO_2. The results show that the incorporation of (0.25 % and 0.2 %) nanofiller increased the tear strength, tensile strength, elongation percentage, and hardness of the materials [16].

Many fruits and natural products have been analyzed for their antioxidant activity and medicinal

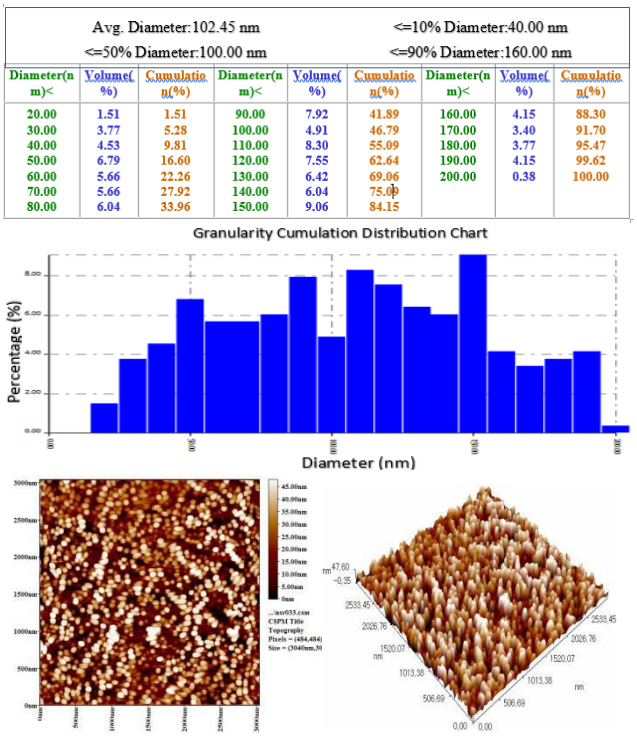
properties. The Pomegranate (Punicagranatum L.) peel have been used as a source of a traditional remedy against diarrhea, dysentery, and prevention from the development of cardiovascular disorders, hypoglycemic, antiamoebic, antibacterial, anticonvulsant, antifungal, antimalarial, and antioxidant activities anti-inflammatory and anti-parasitic [17]. One of many types of date fruits, ajwa date (Phoenix dactylifera) are unique for its medicinal properties. Ajwa dates have strong antioxidant, anticancer, anti-inflammatory, cardioprotective, nephroprotective and hepatoprotective effects, antihypertensive, antimutagenic, antifungal and antidiarrheal [18].

Maxillofacial material must be tested for different mechanical properties in order to fulfill the criteria of "ideal medical prosthetic material" and the requirement of the most suitable material. In the present study mechanical properties of polymer blend material (SR/PMMA) reinforced with two types of natural nanopowder for applications of facial and maxillofacial prostheses was studied. The polymer blends nanocomposite were characterization by the following Tensile, Hardness, Tear, Compression set, Roughness, and DSC, SEM test.

2. EXPERIMENTAL WORK

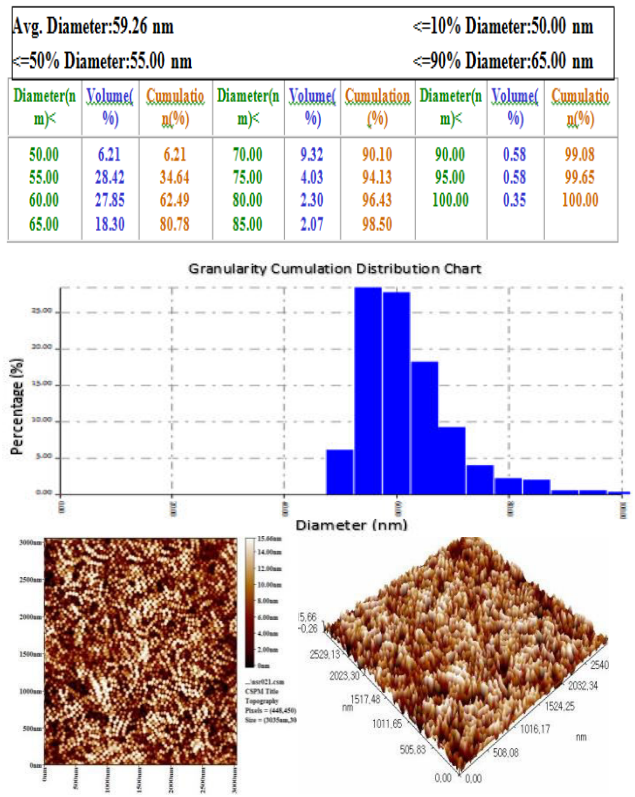
2.1 Materials used

There are two materials used to prepared binary polymer blend as matrix for composites samples include Versiltal RTV Silicone elastomertype (VST-50F) is supply from Factor II Inc., Lakeside, USA that it is consisting of two parts, one is a liquid, and another is the catalyst. polymethyl methacrylate (PMMA) is a second material of the blend which cold curing resin with Castavaria type, provided from Spofa Dental Company. The reinforcement's materials for composites samples are Pomegranate Peels Powder (PPP) taken from pomegranate fruit (Punicagranatum) which were supply from Saudi Arabia with particles size (102.45 nm). Other one is Seeds powder of dates Ajwa (SPDA) taken from date's ajwa fruit which were supply from Saudi Arabia with particles size (59.26 nm).The Atomic force microscope AFM was used to determine the average diameter of nanoparticle and its distribution. Figures (1) and (2) show the size and distribution for pomegranate peel powder and seed powder of dates ajwa nanoparticles respectively.



Diameter(nm)<	Volume(%)	Cumulation(%)	Diameter(nm)<	Volume(%)	Cumulation(%)	Diameter(nm)<	Volume(%)	Cumulation(%)
20.00	1.51	1.51	90.00	7.92	41.89	160.00	4.15	88.30
30.00	3.77	5.28	100.00	4.91	46.79	170.00	3.40	91.70
40.00	4.53	9.81	110.00	8.30	55.09	180.00	3.77	95.47
50.00	6.79	16.60	120.00	7.55	62.64	190.00	4.15	99.62
60.00	5.66	22.26	130.00	6.42	69.06	200.00	0.38	100.00
70.00	5.66	27.92	140.00	6.04	75.09			
80.00	6.04	33.96	150.00	9.06	84.15			

Figure-1. AFM test of pomegranate peels particles (Average diameter (102.45 nm)).



Diameter(nm)<	Volume(%)	Cumulation(%)	Diameter(nm)<	Volume(%)	Cumulation(%)	Diameter(nm)<	Volume(%)	Cumulation(%)
50.00	6.21	6.21	70.00	9.32	90.10	90.00	0.58	99.08
55.00	28.42	34.64	75.00	4.03	94.13	95.00	0.58	99.65
60.00	27.85	62.49	80.00	2.30	96.43	100.00	0.35	100.00
65.00	18.30	80.78	85.00	2.07	98.50			

Figure-2. AFM test of seeds powder of dates Ajwa (average diameter 59.26 nm).

2.2 Preparation method

In this work, mechanical mixing was used to prepare polymer blends composites by binary polymer

blends (SR: 5%PMMA) as a matrix material reinforced with different percentages ratios of nanoparticles (Pomegranate peels powder (PPP) and Seed powder of dates Ajwa (SPDA)) in individually form as reinforcement materials. For binary polymer blend (SR (VST-50F): 5% PMMA) were prepered in two part by mixing 95% wt from Part A of silicone rubber with 5% wt of acrylic powder (PMMA) by the vacuum mixer for 10 minutes as a part one. Then part B of silicone rubber and liquid monomer (MMA), were added to the base (part one) and mixed in the vacuum mixer for 5 minutes at speed of 360 rpm and under vacuum of (-10) bars. Then, pouring the blend into the mold. Sample were left inside the mold for 6 hour to vulcanization.For composites samples, the polymer blend (SR (VST-50F): 5% PMMA) were reinforced with different natural powders (Pomegranate peels powder (PPP) with avg. diameter (102.45 nm) and seed powder of dates Ajwa (SPDA) with avg. diameter (59.26 nm) with selected weight ratios (0, 0.1, 0.2, 0.3 and 0.4) as the Table-1 shown. Preparation of composites samples were carried out In the same practical methoed as in preparation the polymer blend sample mentioned above.

Table-1. Selected ratios of nano composites of polymeric blend.

Type	Blends		Nanopowder reinforcement %	
	SR type (VST-50F)	PMMA		
Composites	95%	5%	0.1% 0.2% 0.3% 0.4%	Pomegranate peels
	95%	5%	0.1% 0.2% 0.3% 0.4%	Seeds powder of a dates Ajwa

3. CHARACTERIZATION AND TESTING

3.1 Test methods

In order to evaluation of the tensile strength, compression strength and hardness properties for all the prepared samples, all tests were performed in according to (ADA Specification No. 12, 1999), where all the test specimens after preparation and polishing processes must be stored in distilled water at (37± 1℃) for 48 hr.

Fourier transform infrared spectrometer (FTIR) test is performed according to (ASTM E1252), made by (Bruker Optics Company, Germany), type is (TENSOR-27). FTIR was used to characterize the neat silicone rubber, and (SR/PMMA) polymer blend composites [19]. It is equipped with a room temperature DTGS detector, mid-IR source (4000 to 400) cm-1 and a KBr beam splitter.

Tensile tests, the specimens for tensile strength evaluation were cut according to ASTM D 638 [20]. In this test the universal tensile instrument, type (LARYEE) devise was used made in China. The test was conducted at velocity of (500 mm/min) at ambient temperature, tensile stress was applied till the failure of the sample and stress-strain curve was obtained. The compression test of elastomer specimens was carried in the laboratory according to the standard of elastomer compression test, ASTM D 395-03 (method B) [21]. With standard dimensions of a specimen are thickness 12.5 ± 0.5 mm and diameter 29.0 ± 0.5 mm. The hardness test of the samples was carried according the ASTM D 2240 [22], by using a device (Shore A hardness) type (Th200). In this test the specimens used must have smooth surface with thickness at least more than (3mm) and must not be exposed to mechanical vibrations, so, the specimens were made in the shape of a circular disk with dimension (thickness 6 mm - diameter 25mm). The examination occurs by work of five strikes at different places of the sample and calculated the average value of hardness.

The surface roughness test was performed by using the surface roughness tester (TR 200) device supplied with a sensor which moves linearly along the measured length. Sample was stabilized on the flat surface of machine and applying the needle of the device perpendicular to the sample and moved on the surface. For this test, the dimensions of sample are (25mm × 25mm and 3mm thick). Surface roughness was recorded for three times on different places on the surface of sample, and then the average values were recorded.

Scanning Electron Microscopy (SEM) test was used to inspect the morphology of the fracture surface for polymeric blend and nanocomposite of polymeric blend specimens at different magnification. Samples were sputter-coated with gold in device for good electric conductivity. Then take a scan for surface and fracture surface of the sample. The scanning electron microscope device of model (inspect S50). Differential Scanning Calorimetric (DSC) test is measure melting point and glass transition temperature by device which model METTLER TOLEDO (DSC 1). Through DSC test, samples with 10 mg mass were encapsulated in aluminum crucible standard 40µl and placed in the holder. Another empty aluminum crucible of the same weight was used as a reference holder. For each holder has possessed a heater and temperature sensor. The test carried out on samples each sample was scanned from an initial temperature of (-160˚) to (60˚C) with a heating rate of (10˚C/min.) followed by cooling to room temperature.

4. RESULTS AND DISCUSSIONS

4.1FTIR test

The FTIR a spectrum of neat silicone rubber (VST-50F) is shown in Figure-3. In general, the absorption peak at 2962.78 cm-1 is assigned to stretching vibration of CH_3. The absorption peak at 1413.15 cm-1 is assigned to the rocking vibration of -CH_2-. The absorption peaks at 1258.50 cm-1 and 863.93 cm-1 are assigned to bending vibration and rocking vibration of Si-CH_3. The absorption peaks at 1009.28 cm-1 are assigned to the stretching vibration of Si-O-Si on backbone of silicone rubbers. The absorption peak at 787.O8 cm-1 is assigned

to the coupling of stretching vibration of Si-C and rocking vibration of -CH_3 [23 and 24].

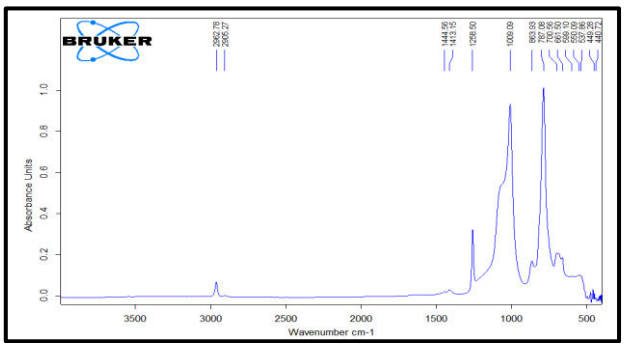


Figure-3. FTIR spectrum for neat silicone rubber (VST-50F) material.

The FTIR spectra of polymers blend (SR (VST-50F): 5% PMMA) is shown in Figure-4. It can be seen from the infrared spectrum of polymeric blend specimen; these spectra are quite similar to the FTIR spectrum of neat silicone rubbers (VST-50F) which shown in Figure (3), no other new peak or peak shifts were observed for the polymeric blend of ((silicone rubber (VST-50F): 5% PMMA) specimen. This is due to the find physical bond and absence of any cross linking and chemical reaction between constituents of polymeric blend.

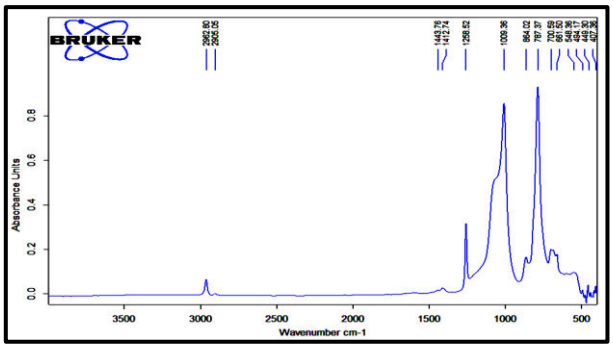


Figure-4. FTIR spectrum for polymeric blend (silicone rubber (VST-50F): 5% PMMA) specimen.

Figure-5 shows the FTIR spectrum of pomegranate peel powder (PPP). The spectrum confirmed the complex nature of these materials and proved the presence of wide variety of compounds. From this figure it can observed that the spectra for PPP showed long bandwidth 3402 cm-1 which indicates the O-H stretching band confirms the presence of alcohols compounds and carboxylic acids. The C=C stretching band of alkyne group was detected at bandwidth 2929 cm-1. The sharp mid-intense peak at 1726 cm-1 attributed to carbonyl group C=O which lead to presence of aldehydes, ketones and carboxylic acids. The moderate sharp peak at 1616 cm-1 indicates the presence of unsaturated compounds (alkenes). The band at 1338 cm-1 (CH_2 bending), related to the presence of cellulose, it can observe that the spectra of PPP is quite similar to that reported by [25 and 26].

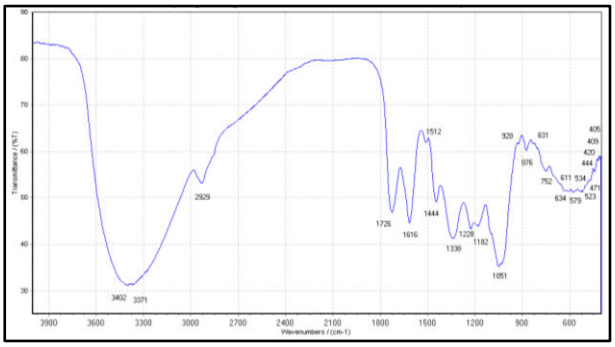


Figure-5. FTIR spectrum of pomegranate peels powder.

Figure-6 shows the FTIR spectrum of Seed powder of dates Ajwa (SPDA). From this figure it can observed that the FTIR spectrum of the Seeds powder of a dates Ajwa (SPDA) is very similar to the spectrum of pomegranate peels powder, since the two articles are from natural origin. The characteristics of the bands observed at 3431 cm -1 which indicates the O-H stretching band confirms the presence of alcohols compounds and carboxylic acids. The C=C stretching band of alkyne group was detected at bandwidth 2856 cm-1. The sharp mid-intense peak at 1743 cm-1 attributed to carbonyl group C=O The moderate sharp peak at 1624 cm-1 indicates the presence of unsaturated compounds (alkenes). The infrared spectrum of SPDA is quite similar to that reported for many different natural compounds by [26 and 27].

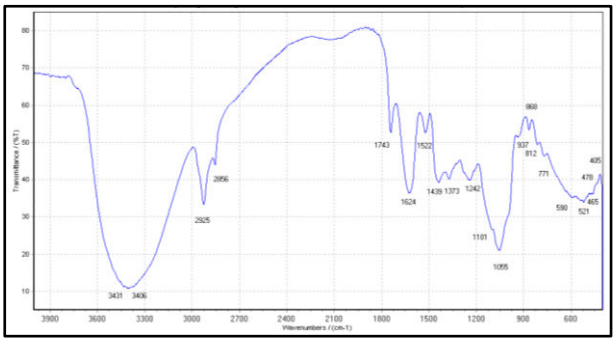


Figure-6. FTIR spectrum of Seed powder of dates Ajwa.

Figures (7), (8) show the FTIR spectra for two groups of polymeric blends nano composites, which are [(SR (VST-50F): 5% PMMA): X%PPP] and [(SR (VST-50F): 5% PMMA): X%SPDA]. It can be seen from the infrared spectrum of these group of polymeric blend composites specimens; these spectra are quite similar to the FTIR spectrum of neat SR (VST-50F) Figure-3 and polymer blend (SR (VST-50F):5% PMMA) Figure-4, no other new peak or peak shifts were observed for the polymeric blends of ((silicone rubber (VST-50F): 5% PMMA) specimens with the addition of (PPP and SPDA). This is due to the find physical bond and absence of any cross linking and chemical reaction between constituents of polymeric blends, as well as a there is no any new interaction in these specimens of polymeric blend composite.

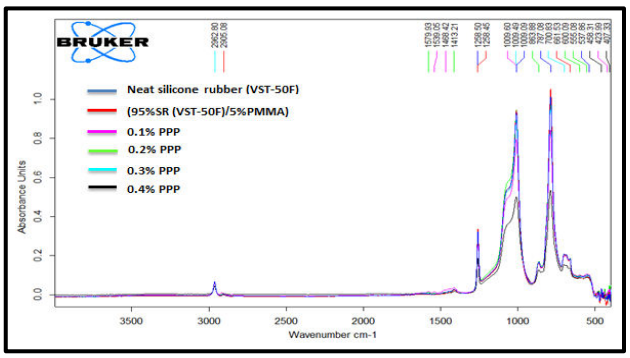


Figure-7. FTIR spectra for neat silicone rubber (VST-50F) and (95%SR (VST-50F) / 5%PMMA) polymer blend reinforced with Pomegranate peels powder (PPP).

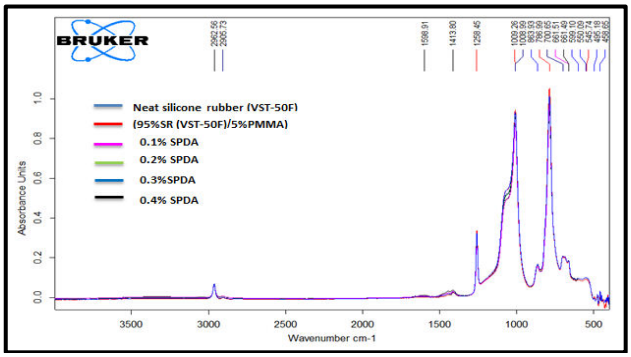


Figure-8. FTIR spectra for neat silicone rubber (VST-50F) and (95%SR (VST-50F) / 5%PMMA) polymer blend reinforced with Seed powder of dates Ajwa.

4.2 Tensile test results

The tensile strength, modulus of elasticity and elongation at break for polymeric blends (SR: 5% PMMA) reinforced with two types of natural nano powder PPP and SPDA in individually form and in different ratios (0.0, 0.1, 0.2, 0.3 and 0.4%) are show in Figures (9), (10) and (11) respectively. From these figures, it was found that the addition of natural nano powder to the base polymer blends increased tensile strength and modulus of elasticity whereas elongation at break value decreased, And the percentage of increase increases with increasing PPP and SPDA content in polymer blend composites samples, whereas the elongation percentage decrease with increasing content of these nanoparticles in base polymer blend (SR: 5% PMMA). Moreover from Figure-9 and (10), it was observed that the polymer blends nano composites ((SR (VST-50F): 5% PMMA): X% pomegranate peels powder) get the higher values of tensile strength and modulus of elasticity respectively, whereas lower values in elongation percentage Figure-11 as compared with their counter parts of the other groups polymer blend composites samples ((SR (VST-50F): 5% PMMA): X% SPDA. As well as, the results show that the highest value of tensile strength & modulus of elasticity was reach to 7.888 MPa and 1.16 MPa at 0.2% ratio of pomegranate peels powder content in composite respectively, while the highest value of tensile strength & elasticity modulus was reach to 7.3MPa and 1.09MPa at 0.3% ratio of seed powder of dates Ajwa respectively. These result related to the characteristics of natural nano powders (PPP and SPDA) which were shown a good compatibility between constituents of polymer composites at specific ratios of nano powder content in composite, as well as promote optimum dispersion of natural particles in composites [28 and 29]. From these results can be concluded that the two properties (tensile strength and modulus of elasticity) increased with increased nano powder percent, but after reach to the maximum values, then these values decrease with the increase in natural nano powder ratio in the polymer blend, but remain higher than it is of the polymer blend of the base sample. The negative effect in the tensile strength & modulus of elasticity, it may be concerning to the agglomeration of nanoparticles that occur with high concentrations, especially in areas containing clusters of added nanoparticles, So, in the high concentrations ratios, resultant is nanocomposite material with weak physical bonding between the nanoparticles and PMMA resin, and therefore, this requires low tensile stresses for the failure to occurs, which leading to lower tensile strength [30 and 31].

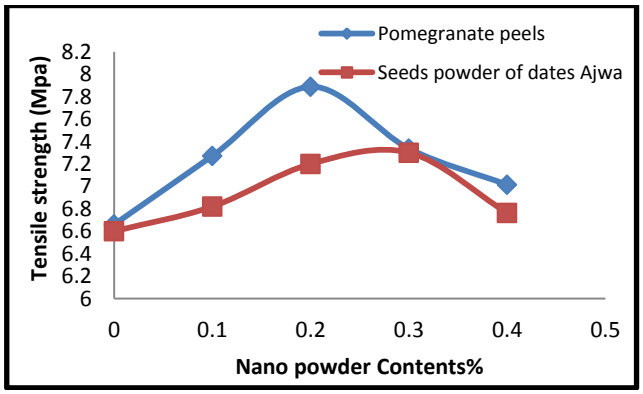


Figure-9. Tensile strength of polymer blend composite ((SR (VST-50F): 5% PMMA): X% natural nano powder) as a function of PPP and SPDA nano powders content in composites.

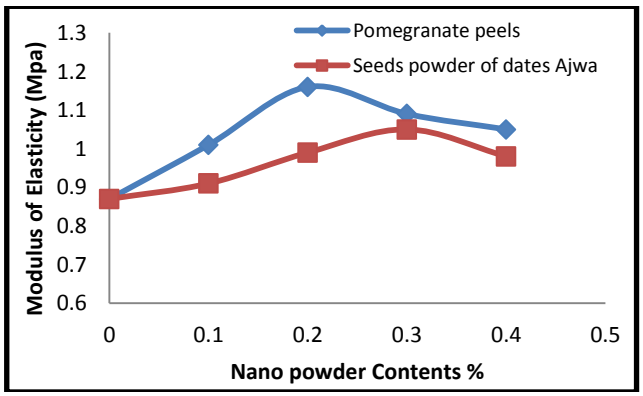


Figure-10. Modulus of elasticity of polymer blend composite ((SR (VST-50F): 5% PMMA): X% natural nano powder) as a function of PPP and SPDA nano powders content in composites.

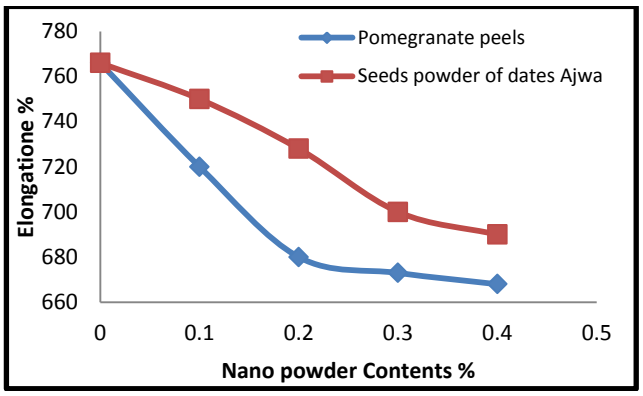


Figure-11. Elongation percentage of polymer blend composite ((SR (VST-50F): 5% PMMA): X% natural nano powder) as a function of PPP and SPDA nano powders content in composites.

4.3 Tear resistance and hardness property results

It can be noted from Figure-12 that the addition of natural nano powder to the base polymer blends increased the tear resistance and this value increase with increasing weight ratio of natural nano powder content in composite, and reach to the highest value 31.1 N/mm^2 at 0.2 % ratio of pomegranate peels powder, while for seed powder of dates Ajwa nano powder reach to the highest value 30.6 N/mm^{2}at 0.3%. After that all of them start to decline with increase nano powder content in composite but still higher than it is for the sample of the base polymer blend when ratio of natural powder content reach to 4% for the two group of composites samples. The increased in these properties may be related to the nature of consistency between the components of composite prepared, and this refer to the good compatibility between the polymer blend composites components and natural nanoparticles (PPP AND SPDA) [32]. Moreover, the incorporation of the natural nanopowders into the polymer blend improves the tear resistance of the nano composites by restricted the mobility of the matrix chains [33]. Also, the good distribution of these 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 led 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 [34].

Therefore, these small stresses can be easily transferred from the matrix to the natural nanoparticles, so allowing the particles to contribute its high strength property to the Nano composites, and thus will increase the values of tear resistance [29].

On the other side, the decreased in these values may be related to the agglomeration of nanoparticles that occur with high concentrations content in nanocomposites specimens. Furthermore, from Figure-12, it was noticed that the polymer blends nano composites ((SR (VST-50F): 5% PMMA): X% pomegranate peels powder) get the higher values of tear resistance as compared with their counterparts of the other group composites samples reinforced by seed powder of dates Ajwa.

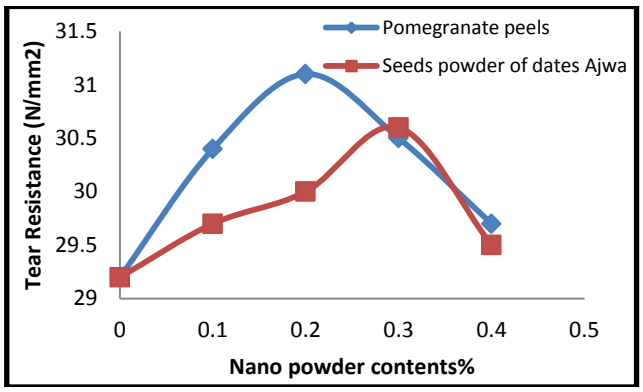


Figure-12. Tear resistance property of polymer blend composite ((SR (VST-50F): 5% PMMA): X% nano filler) as a function of (PPP, SPDA) Nano powders content in composites.

The hardness behaviors for polymeric blend composites reinforced with different ratios (0.1, 0.2, 0.3 and 0.4 %) of natural nano powder content is show in Figure-13. It was found that the hardness values slightly increased with increased two types of powders contents in nano composites. For polymer blend nano composites reinforced by pomegranate peels powder, the hardness reaches to highest values 30.5 at 0.4% PPP percent. Also, for polymer blend nano composites reinforced by seed powder of dates Ajwa, the hardness reaches to highest values 30 at 0.3% SPDA percent [31, 16].

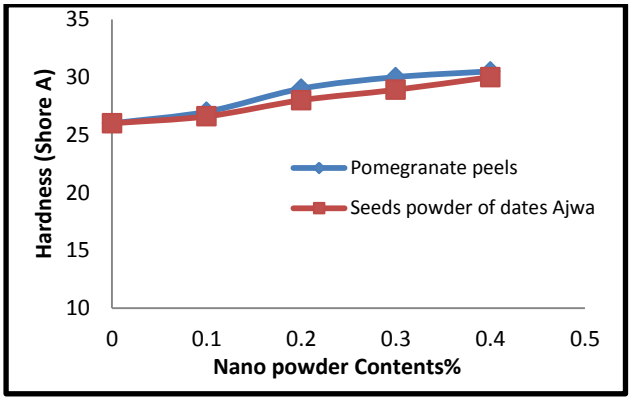


Figure-13. Shore A hardness of polymer blend composite ((SR (VST-50F): 5% PMMA): X% nanofiller) as a function of PPP or SPDA Nano powders content in composites.

4.4 Compression set property and surface roughness test results

The compression set for polymeric blends composite ((SR: 5% PMMA): X% nanopowders (PPP or SPDA) at ratios of nano powder (0, 0.1, 0.2, 0.3 and 0.4%) contents in composites, is show in Figure-14. It was found that for polymer blend nano composites reinforced by pomegranate peels powder and for polymer blend nano

composites reinforced by seed powder of dates Ajwa the compression set value decreased for nano composites ((SR: 5% PMMA): X% nanopowders) with adding nano powder as results of high strength of compatibility between the constituents of composite.

From Figure-15 which shown the relation between surface roughness as function of nano powder content in composites, it was found that for this property decreased with increased nano powder percent. This result, may be attributed to the nanoparticles are embedded inside polymeric blends matrix material (SR (VST-50F): 5% PMMA), which act as an integral part of the nano composite structure (it will be explained later when studying the morphology of the fracture surface of the samples) indicating to better interfacial adhesion between constituents of the composite material.

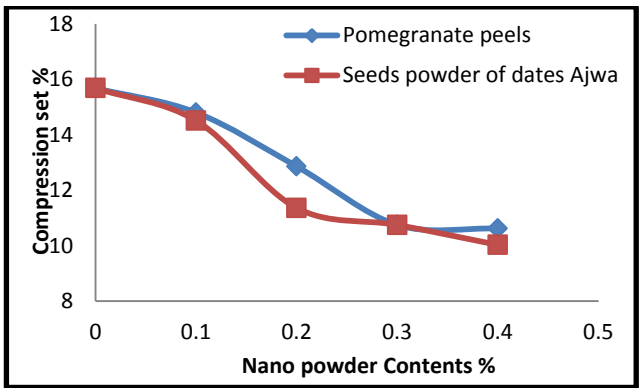


Figure-14. Compression set of polymer blend composite ((SR (VST-50F): 5% PMMA): X% nano filler) as a function of (PPP, SPDA) nano powders content in composites.

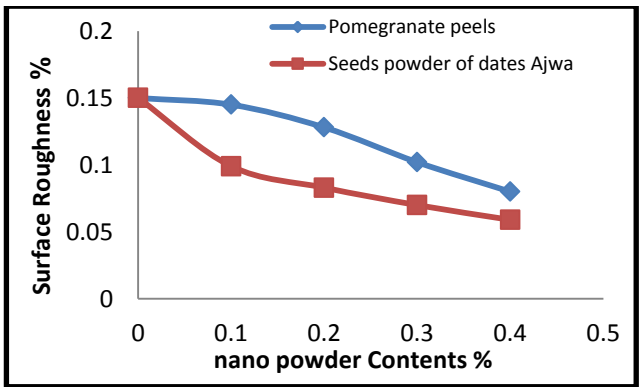


Figure-15. Shows surface roughness property of polymer blend composite ((SR (VST-50F): 5% PMMA): X% nano filler) as a function of (PPP, SPDA) Nano powders content in composites.

4.5 Scanning electron microscopy SEM test

The photographic imaging for fracture surface morphology of neat silicone rubber is show in Figure-16a at magnifications at (×5000). This images micrographs clearly illustrate homogeneous structural morphology was observed and there is no any new phase or phase separated dominants in neat silicone rubber structure. The fracture surface morphology of the prepared polymer blend ((95% SR (VST-50F): 5% PMMA) was characterized by scanning electron microscope (SEM) observations, which is shown at magnification (×3000) in Figure-16b. This photographic imaging clearly illustrates to the apparition of two distinct phases, as well as, this image showed that the polymer blend has a continuous and homogenous morphology of silicone rubber phase with a random distribution of PMMA phase, which is embedded in matrix material and dispersed as a globule's shapes in to the silicon rubber matrix. Furthermore, it can be observed that different sizes of these spherical shapes from PMMA material dispersed randomly in this matrix, which was clearly effect on the mechanical properties of the prepared polymer blend as compared with neat silicone rubber (figure 16 a).The structure morphology of nanocomposite material is influenced by several parameters, such as nature of particle, the particles shape, the particles size, particle distribution, the components ratios, the component melt viscosities and processing conditions [2].

SEM images of the polymer blend nanocomposites with natural filler (PPP, SPDA) as nanoparticle in composites which added in individually form are shown in magnification (×3000) in Figure (16 (C and d)) respectively. It was observed through microscopic imaging, that the morphology of the fracture surface of the polymer composites showed homogeneous structure for all type's composites. Moreover, through this morphology, it was noticed that most of nanoparticles are embedded inside the matrix material, which act as an integral part of the silicone rubber structure, indicating to better interfacial adhesion between constituents of composite material. And this indicated to a good compatibility between the component of silicon rubber blend and the reinforcement nanoparticles, which enhances the mechanical properties [35]. On the other hand, the scanning electron micrographs confirmed a co-continuous morphology, As well as there are small regions having smoother fracture surface, which seems to indicate better interfacial adhesion between the components of composite sample. These morphology structures are in a good agreement with other workers results [36, 37]. It was found that, by adding PPP and SPDA natural nanoparticle to polymer blend, the morphology of polymer blend nanocomposite does not changes it has structure morphology similar to morphology of polymer blend Figure16 b; However, the size of morphology structures varies, where the co-continuous morphology domains were larger in structure morphology of polymer blend (Silicone rubber: 5% PMMA) (figure 16 b) but when added 0.2% nano pomegranate peels powder and 3% Seeds powder of dates Ajwa, became smaller and more uniform (Figure-16 (c and d) respectively). It is well known that in the polymer blends, the smaller and more uniform size and distribution of dispersed phase represent an increase in the compatibility of two polymer phases. The effect of compatibility of PPP and SPDA nanoparticle was observed in Figure (16 (c and d). During mixing process, the interactions between nanoparticle and polymer blend components mainly occurred through melting of silicone

rubber and PMMA molecules, followed by wetting of molten molecules with nano particle. After mixing, polymer blend molecule melt encapsulated the surface of nanoparticles and intimate interfacial bonding was formed in nano composites as observed from the dense and solid surface especially for nano composites when reinforced by 0.2% of pomegranate peels powder [38, 39].

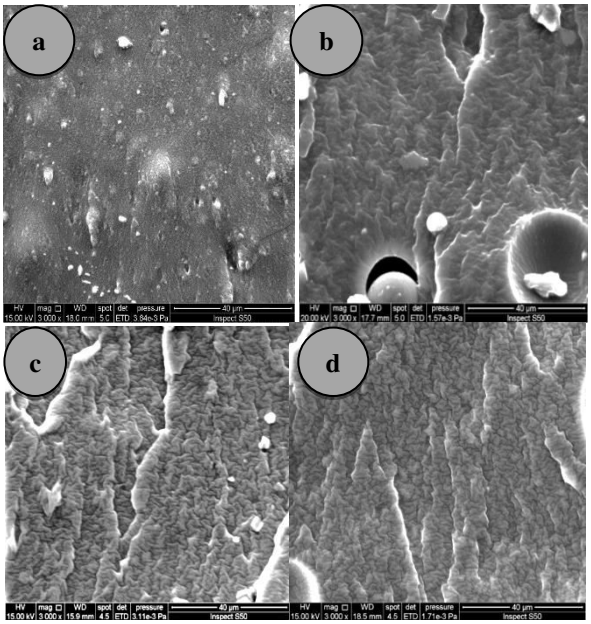


Figure-16. SEM image of fractured surface morphology for (a): Neat SR (VST-50F), (b): Polymer blend (95% SR (VST-50F):5% PMMA), (c): Nano composite (95% SR (VST-50F):5% PMMA): 2%PPP) Sample reinforced by 0.2% Pomegranate peels powder and (d): Nano composite ((95% SR (VST-50F):5% PMMA): 0.3%SPDA) Sample reinforced by 0.3% Seeds powder of dates Ajwa at 3000X Magnifications.

4.6 Differential scanning calorimeter (DSC) test

Figures (17, (a, b, c and d) show the differential scanning calorimetry traces that obtained in the temperature range from (-135 ℃ to 70 ℃) for neat silicone rubber (VST-50F SR), polymer blend (95% SR:5% PMMA), and polymer blend nano-composites for the optimal specimens which are composites specimens ((95% SR (VST-50F):5% PMMA): 0.2% Pomegranate peels powder) and ((95% SR (VST-50F):5% PMMA): 0.3% Seeds powder of dates Ajwa) respectively. from these figures, it was found that the thermal behavior of these curves is identical for all the samples that have been tested and there is nothing worthy of mention concerning with the values of Tg and Tm except very minor changes got in the values of Tg. Where, the glass transition temperature either somewhat increases or decreases depending on the type of component, its morphology the interfacial reaction and compatibility between different components and the inter crystallites distance [40, 41].

It is noticed that, in the case of neat silicone rubber (VST-50F SR) that the glass transition temperature midpoint is observed at (-122.05 ℃) (Figure-17 a). Also, it is noticed that the glass transition temperature of silicone rubber slightly increases from ((-122.05 ℃ to -121.71℃) for binary polymer blend (95% SR: 5% PMMA) Figure-17b, adding 2% PPP causes decrease this value to (-122.52℃) Figure-17 c. In Figure-17 d when adding 0.3% SPDA nanoparticle to the binary polymer blend, the Tg values also slightly increase to (-122.08), depend on the natural of nanoparticle content in polymer blend. This indicates that the polymer blend is single phase structure; this reinforces the compatibility and or miscibility of their components, with good interactions among its polymeric chains.

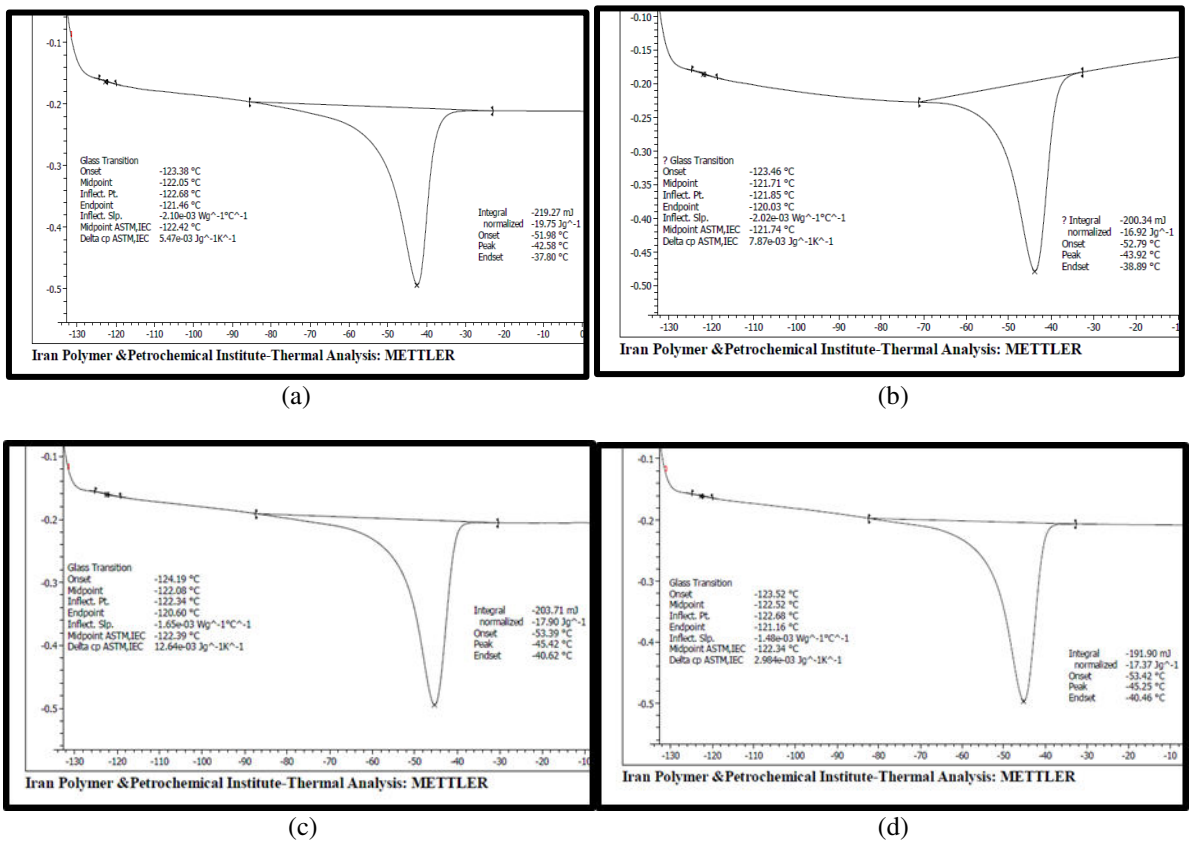


Figure-17. DSC Curves for (a): Neat SR (VST-50F), (b): Polymer blend (95% SR (VST-50F):5% PMMA), (c): Nano composite (95% SR (VST-50F):5% PMMA): 2%PPP) Sample reinforced by 0.2% Pomegranate peels powder and (d): Nano composite ((95% SR (VST-50F):5% PMMA): 0.3%SPDA) Sample reinforced by 0.3% Seeds powder of dates Ajwa.

5. CONCLUSIONS

From the test results of the prepared polymeric blend nanocomposites with natural powder, it was concluded the following:

a) The addition of nano filler to the base polymer blends increased tensile strength and modulus of elasticity with increasing PPP, SPDA in polymer blends content, whereas the elongation percentage decrease with addition these nanoparticles to base polymer blends.
b) The highest value of tensile strength & modulus at 0.2% of pomegranate peels powder are 7.888 MPa and 1.16 MPa respectively, while the highest value of tensile strength & modulus at 0.3% of seed powder of dates Ajwa are 7.3MPa and 1.09MPa respectively. In tear test, the highest value 31.1 N/mm2 at 0.2 % ratio of pomegranate peels powder, while for seed powder of dates Ajwa nano powder reach to the highest value 30.6 N/mm2 at 0.3%.
c) In SEM test, the morphology of polymer blend nanocomposite does not changes it has structure morphology similar to morphology of polymer blend. The morphology of the fracture surface of the polymer composites showed homogeneous structure for all type's composites.
d) The DSC test indicates that the polymer blend is single phase structure; this reinforces the compatibility and or miscibility of their components, with good interactions among its polymeric chains
e) The results show that the development of properties of polymeric blends (SR/PMMA) with addition PPP, SPDA, so, these can be used in the applications of facial and maxillofacial prostheses.

REFERENCES

[1] H. Hugh, W. Graham Paul and Ch. Dudley. 2011. Biomimetic Orthotic and Prosthetic Technology. North-western University Handbook, USA.

[2] Wiens JP and Wiens RL. 2000. Psychological management of the maxillofacial prosthetic patient in Taylor TD, ed, clinical maxillofacial prosthetics. Quintessence Publishing Co., Inc.: Chicago, IL.

[3] Lontz JF. 1990. State-of-the-art materials used for maxillofacial prosthetic reconstruction, Dental Clinics of North America. 34(2): 307-25.

[4] Bulbulian AH. 1965. Maxillofacial Prosthetics: Evolution and Practical Application in Patient Rehabilitation, Journal of Prosthetic Dentistry. 15(6).

[5] Mitra A, Choudhary S, Garg H, H G J. 2014. Maxillofacial prosthetic materials-an inclination towards silicones, J Clin Diagn Res. 8(12): 8-13.

[6] Raghoebar GM, Van Oort RP, Roodenburg JL, Reintsema H, Dikkers FG. 1994. Fixation of auricular prostheses by osseo integrated implants, J Invest Surg. 7(4): 283-290.

[7] Andreapoulos AG, Theopanides T. 1993. Design and properties of maxillofacial prosthetic material, Medical Device technology. 4: 20-25.

[8] Mahajan H and Gupta K. 2012. Maxillofacial Prosthetic Materials: A Literature Review.J Orofac Res 2(2): 87-90.

[9] Liu Q, Shao L, Fan H, *et al*. 2015. Characterization of maxillofacial silicone elastomer reinforced with different hollow microsphere, J Mater Sci. 50: 3976-3983.

[10] X. Sun, H. Sun, H. Li, H. Peng. 2013. Developing Polymer Composite Materials: Carbon Nanotubes or Graphene, Wiley online library. 25(37): 5153-5176.

[11] W.F. Smith and J. Hashimi. 2011. Foundation of Materials Science and Engineering, Fifth Edition, McGraw -Hill.

[12] L. Yua, K. Deana, L. Lib, L. Yu. 2006. Polymer blends and composites from renewable resources, Prog. Polym. Sci. 31, pp. 576-602.

[13] Abdulakh K. Mikitaev, Mukhamed Kh. Ligidov and Gennady E. Zaikov. 2006. Polymer, Polymer Blends, Polymer Composites and Filled Poymers: synthesis, properties and applications, Nova Science Publishers, Inc. New York.

[14] Nouri Al-qenae. 2010. Nano ceramic fiber Reinforced Silicone Maxillofacial Prosthesis, M.Sc. thesis, Indiana University, Dentistry.

[15] Sara M. Zayed, Ahmad M. Alshimy, and Amal E. Fahmy. 2014. Effect of Surface Treated Silicon Dioxide Nanoparticles on Some Mechanical Properties of Maxillofacial Silicone Elastomer, International Journal of Biomaterials, Article ID 750398, p. 7.

[16] Dhuha A. Shakirand Faiza M. Abdul-Ameer. 2018. Effect of nano-titanium oxide addition on some mechanical properties of silicone elastomers for maxillofacial prostheses. Journal of Taibah University Medical Sciences. 13(3): 281e290.

[17] Abdel-Rahim EA, El-Beltagi HS, Romela RM. 2013. White Bean seeds and Pomegranate peel and fruit seeds as hypercholesterolemic and hypolipidemic agents in albino rats. Grasas y Aceites. 64: 50-58.

[18] Janbaz K.H., Qadir M.I., Jan A., Gilani A.H. 2013. Antidiarrheal activity of methanolic extract of Tephrosiapurpurea. Acta Pol. Pharm. 79(2): 345-347.

[19] Annual Book of ASTM Standard, 2002. Standard Practice for General techniques for Obtaining Infrared Spectra for Qualitative Analysis, E 1252-98, pp. 1-11.

[20] Annual Book of ASTM Standard. 2003. Standard Test Method for Tensile Properties of Plastics. D638-87b. 09.01: 1-17.

[21] Annual Book of ASTM Standard. 2003. Standard Test Methods for Rubber Property-Compression Set. D 395-03. 14.04: 1-8.

[22] Annual Book of ASTM Standard. 2003. Standard Test Method for Plastics Properties-Durometer Hardness. D 2240-03, pp. 1-12.

[23] Xishan Wen, Xiaoqing Yuan, Lei Lan, Lu Hao, Yu Wang, Shaodong Li, Hailiang Lu1, ID and Zhenghong Bao. 2017. RTV Silicone Rubber Degradation Induced by Temperature Cycling, Energies. 10, pp. 1054-1066.

[24] Jun Feng, Qinglian Zhang, Zhengkai Tu, Wenmao Tu, Zhongmin Wanc, Mu Pan, Haining Zhang. 2014. Degradation of silicone rubbers with different hardness in various aqueous solutions. Polymer Degradation and Stability. 109, 122-128.

[25] Khairia M. Al-Qahtani. 2015. Heavy Metals Removal from Polluted Water by Activated Carbon Prepared from Pomegranate Peel. American-Eurasian J. Agric. & Environ. Sci. 15(4): 595-602.

[26] Sihama Issa Salih, Jawad Kadhim Oleiwi and Arkan Saad Mohamed. 2018. Investigation Of Mechanical Properties Of Pmma Composite Reinforced With Different Types Of Natural Powders. ARPN Journal of Engineering and Applied Sciences. 13(22).

[27] Sumaira Khalid Nauman Khalid, Rao Sanaullah Khan, Haroon Ahmed, Asif Ahmad. 2017. A review on chemistry and pharmacology of Ajwa date fruit and pit, Trends in Food Science & Technology. 63, pp. 60-69.

[28] Sihama I S, Safaa N. Alyaa H .A. and Ammar M. H. 2015. Evaluation Mechanical Properties of Polymer Composites Reinforced by different Metal Powders Eng. & Tech. Journal 33part (B) (7): 1348-1360.

[29] Sihama E. S, Jawad K. O., Alaa M. T. 2016. 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. Eng. & Tech. Journal 34-part (A) (15) pp. 2838-2835.

[30] Mohamed Ashour Ahmed and Mohamed I. Ebrahim. 2016. Effect of Zirconium Oxide Nano-Fillers Addition on Mechanical Properties of Heat-Polymerized Acrylic Resin. ALAZHAR Dental Journal. 3(1): 41-48.

[31] Annual Book of ASTM Standard. 1994. Standard Specification for Silicone Elastomer Facial Implants. F 881, May 15.

[32] Sihama E. S, Jawad K. O., Alaa M. T. 2017. Effect of Accelerated Weathering on the Compressive Strength for PMMA Nano Composites and PMMA Hybrids Nano Composites used in Dental Applications. Engineering and Technology Journal. 35-part (A) (3): 204-215.

[33] Mohamed Ashour Ahmed. 2014. 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. 4: 50-57.

[34] Jawad Kadhum Oleiwi, Farhad Mohammad Othman and Israa Faisal qhaze. 2015. A Study of Mechanical Properties of Poly Methacrylate Polymer Reinforced by Silica Particles (SiO_2). Eng. & Tech. Journal, Part (A). 33(5).

[35] Rohani Abu Bakarand M. S. Fauzi J. 2012. Natural Rubber-Grafted-Poly (Methyl Methacrylate): Influence of Coagulating Agents on Properties and Appearances, Chem. Eng. 6: 962-966.

[36] Mohammad Vaezi, Cameron Black, David M. R. Gibbs, Richard O. C. Oreffo, Mark Brady, Mohamed Moshrefi-Torbati and Shoufeng Yang. 2016. Characterization of New PEEK/HA Composites with3D HA Network Fabricated by Extrusion Freeforming, Molecules. 21(687): 2-21.

[37] Sihama Issa Salih, Fadhil Abbas, Y. Jahani and Asra Ali. 2016. Comparative Study of Fatigue properties and in vitro bioactivity and cellular responses Behavior of MWCNTs reinforced two group of polymer blend Bio-Composites for Bone Repair. Wulfenia Journal. 23(12): 283- 292.

[38] RuiMa, Luqian Weng, Lin Fang,, Zhongkuan Luo , Shenhua Song. 2012. Structure and Mechanical Performance of in Situ Synthesized Hydroxyapatite/ Polyetheretherketone Nanocomposite Materials, J. Sol-Gel Sci. Technol. 62: 52-56.

[39] Asra Ali. 2017. Fabrication and Characterization of Advanced Blend Polymer Nanocomposites for Human Bone Structural Applications, Ph.D Thesis Submitted to university of Technology / Materials Engineering.

[40] H. Teng, K. Koike, D. Zhou, Z. Satoh, Y. Koike and Y. Okamoto, 2009 "High Glass Transition Temperatures of Poly(methyl methacrylate) Prepared by Free Radical Initiators", Journal of Polymer Science Part A: Polymer Chemistry. 47(1): 315-317.

[41] T. Ramanathan, S. Stankovich, D. A. Dikin, H. Liu, H. Shen, S. T. Nguyen and L. C. Brinson. 2007. Graphitic Nano Fillers in PMMA Nano Composites-an Investigation of Particle Size and Dispersion and Their Influence on Nano Composite Properties. Journal of Polymer Science Part B: Polymer Physics. 45(15): 2097-2112.