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HA/HDPE Reinforced with MWCNTs for Bone Reconstruction and Replacement Application

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Abstracts: *The objective of this study is to demonstrate how the effect of adding multi-walled carbon nanotubes (MWCNTs) nanoparticles to the (Hydroxyapatite /High-density polyethylene) bio-composites. In this investigation, the samples with various percentages of (MWCNTs) were fabricated by a hot-press technique. The morphological characteristics, roughness of the surface and thermal properties of the bio-composite samples (HA/HDPE/MWCNTs) were investigated. The excellent homo-geneous distribution of the internal fibrous network and microstructure arrangements were among the most prominent characteristics obtained through FE-SEM and AFM examinations. The degree of crystallinity showed that the (MWCNTs) additives enhance by an increase of approximately (35%), compared with pure sample (without addition MWCNTs). Based on the experimental results obtained, the fabrication of the presented bio-composites sample exhibited the excellent characteristics that make them promising material for biomedical application as a substitute material for hard tissue likes bone reconstruction.*

Keywords*: Bone tissue engineering, biomaterials, Hot-press technique, MWCNTs, hydroxyapatite, HDPE, hard tissue*

1. Introduction

Diseases of the skeletal system are a serious health condition that directly affects patients' quality of life. In most cases, the treatment of bone deficiency requires an extensive amount of bone graft. Bone grafting is one of the most ordinarily used medical techniques to increase bone regeneration in orthopaedic surgery. This technique has many limitations and risks on the patient so the evolution of artificial bone and use as substitute materials that do not affect healthy tissue such as bacterial or viral risk to the patients and can be provided at any time, in any amount [1,2]. Calcium phosphate bioceramics have been vastly used as synthetic bone replace materials for orthopaedic and dental treatments [3]. Between these ceramics, special consideration has been given to hydroxyapatite (HA) nanoparticle ($Ca_{10}(PO_4)_6(OH)_2$) base mineral constituent of human bones and teeth because of its excellent bioactivity and biocompatibility [4]. Nevertheless, the Hydroxyapatite has poor mechanical features such as low tensile strength and brittleness; thus, the clinical treatments have been limited in long-bone injuries or high load-bearing [5]. Polymers have beneficial in scaffold purpose applications due to their lightweight, less inflammation, ease of fabrication, excellent biocompatibility and moderately low cost. Some polymers can act as the natural collagen in natural bone, such as HDPE [6]. Many researchers have attempted to improve hydroxyapatite's mechanical properties by using reinforced materials to match the natural bone specifications, with parallel studies to investigate bioactivity level [7]. The carbon nanotube has large aspect ratios, extremely high surface areas and signally high mechanical strength. The thermal and electrical conductivities approach those of copper, and the tensile strength of carbon nanotube is 100 times higher than that of metal like steel. These extraordinary features nanotubes good candidates as fillers in various ceramics and polymers to achieve desirable properties. Due to the exceptional chemical and physical features of CNTs, there are particular problems correlated with their toxicity, especially at

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the human pulmonary system, which is a primary route of exposure. It can be expected that combining polymeric materials with CNTs will modify the surface characteristics of CNTs, which could modify their toxicity without affecting their particular characteristics and potential for use in future applications [8]. The (CNT) can be classified into either single-walled carbon nanotube (SWCNT), and multi-walled carbon nanotube (MWCNT), this classification depending on its preparation method [9].

The inclusion of CNT in a ceramic matrix as composite will improve mechanical features, exhibit composite possessing high stiffness, increase toughness, and provide extra absorption energy compared with the single-phase ceramic material. Additionally, no obvious chemical reaction between CNT and HA has been identified, and the physical crosslink with a high value of hardness and modulus obtained [10]. Also, The CNT like MWCNT have a feature to increases the interfacial interaction between the polymer matrix and MWCNT due to its chemical functionalization. This feature improves the adhesion of the MWCNT in the polymers and various organic solvents. Also, improves dispersion and reduces the tendency to agglomerate. The improved interactions between a polymer matrix and MWCNT administer the load-transfer from the polymer to the nanotubes and, therefore, improve the reinforcement efficiency [11]. SWCNT and MWCNTs have the same features. However, the multilayer of MWCNTs, the outer layers, can exhibit high tensile strength features and shield the inner carbon nanotubes from chemical interactions with outside substances, that do not present in SWCNTs exist slightly [12]. The hot pressing method can be made familiar to the final shape without allowance having to be made for sintering shrinkage, and a great deal of time-consuming and costly grinding is avoided. Fine-grained, dense material production results in a signed improvement in the physical properties of hot-pressed material as corresponded with sintered samples [13]. So the hot pressing technique has the many advantages in fabrication processes and has beneficial properties for the bone substitute. Many investigations have strived to improve hydroxyapatite's mechanical features by using reinforced materials to match natural bone properties, with parallel investigations the bioactivity level. Bonfield and coworkers made the first idea of compatible implant material for bone replacement by using the mixing technique to prepared composites material from various natural and synthetic hydroxyapatite powder and polyethene [14]. This research group were continued to improve composites for the highest mechanical performance and bioactivity materials for bone substitute [15, 16]. Several studied have attempted to apply CNT as a new method to the expectation of improving the mechanical properties of polyethene [17] and hydroxyapatite [18]. For bone tissue engineering, many studies have concluded that the use of hydroxyapatite with polyethene [19, 20] and CNT [21] provides excellent results in mechanical and biocompatibility properties. To the best of our knowledge, there has been no experimental investigation at using (HDPE/ HA /MWCNTs) together by applying the hot-press technique to form bio-composites material promising for bone substitute. This work aims to investigate the enhancement additions of MWCNTs into (HA, HDPE) bio-composite on the microstructure, morphology and thermal properties.

2. Materials and methods

2.1. Production of the hybrid bio composite samples

With particle size (5μm), the HDPE Powder has been purchased from Right Fortune Industrial Limited (Shanghai, China). The MWCNT that have purity 90% were provided from (Cheap Tubes Inc., USA). The HA nanoparticles were taken from M.K. Nano (Toronto, Canada). With the particle size of 20nm, the approximately powder purity was 99% and the density of (3.140gm/cm^3). Our previous research studied the biocomposite (40%HA/60%HDPE) with various (%) weights of MWCNTs [22]. In this investigation, the composition of (20%HA/80%HDPE) was chosen with addition (0, 0.6, 1, 1.4, 2) percentages of MWCNTs. The hot pressing technique for composite shaping has been employed to fabricate all specimens. The pressure is applied hydraulically using (Instron 1195), and heating is produced externally using external heaters. The mould was heated to 150^{o}C and held at this temperature for 15 min. The melt pressure value was used (29 MPa) for samples moulded, Figure 1 shows a summary of the sample fabrication process.

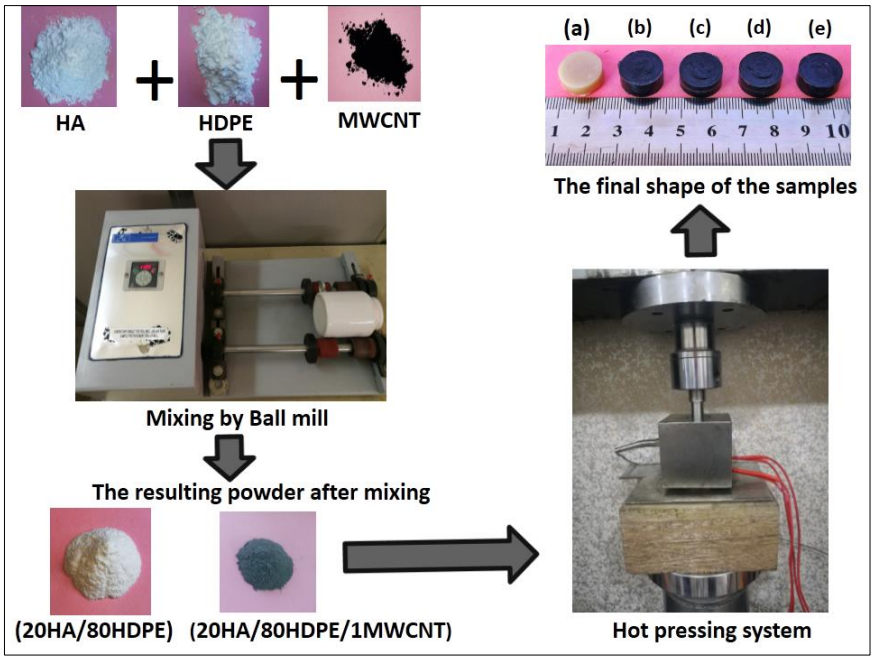


Figure 1. Steps of fabrication process, the (a, b, c, d, e) refers the samples with (0, 0.6, 1, 1.4, 2) %MWCNTs, respectively

2.2. Materials characterization techniques

2.2.1. Fourier transform infrared spectroscopy (FTIR)

Fourier transform infrared spectroscopy is a technique widely used to recognize the functional groups in the materials (solid, liquid, gas) by applying the beam of infrared radiations. Fourier transform infrared (FTIR) spectra were determined using the range of 4000-500 cm^{-1} with a resolution of 0.5 cm^{-1}. Samples were tested directly without the need to prepare any procedure that commonly use in powder specimen

2.2.2. Morphological examination

2.2.2.1. Field emission scanning electron microscopy (FESEM)

The composite material specimens' morphology was examined using a Field Emission Scanning Electron Microscopy (FESEM) at an accelerated voltage of (3-10) kV. At College of Science/ University of Basra /Iraq. The composite specimen is coated with a thin layer of gold under vacuum before the FESEM investigation to avoid heat build-up and electrostatic charging during the examination. The composite specimen is coated with a thin layer of gold under vacuum before the FESEM investigation to avoid heat build-up and electrostatic charging during the examination.

2.2.2.2. Atomic force microscopy (AFM)

The atomic force microscope (Ntegra NT-MDT, Russia) was used to investigate the surface topography (surface roughness and particles size). The resulting images were processed by using the Nova™ software. The examination was performed under ambient conditions by applying a tapping mode.

2.2.3. Thermal properties (differential scanning calorimetry (DSC))

The DSC furnace is an isolated container provided with a heat flux plate with a thermopile to calculate the thermocouples related and heat flow to both the reference and sample containers. A Differential Scanning Calorimeter (DSC-60 /Shimadzu/ Japan). The scanning method was applied to determine the melting and crystallization point for all the biocomposite samples. A sample mass (about

5 mg) was sealed in aluminium pans then heated at a constant degree rate (5°C /min) in the temperature range (25-180°C) and cooling rate (10°C/min).

3. Results and discussions

3.1. FTIR results

The FTIR is an effective technique to mark the existence of functional groups**.** Figure 2a shown the transmittance of FTIR peaks of the fabricated composite powders and the final form of the sample with (0 and 1) % adding the weight of MWCNTs. The FTIR spectra of the hydroxyapatite (HA) at (3566 and 624) cm^{-1} belong to the vibration of the hydroxyl (O-H) group. The peak at 1421 cm^{-1} represents CO_3^{-2}. The bands at (1001, 1039 and 1093) cm^{-1} characterize phosphate stretching vibration, and the bands recognized at (615, 559) cm^{-1} are due to the phosphate being in vibration. The spectrum of HDPE, peaks at (721 and 1465) cm^{-1} are recognized, which correspond to the rocking and bending vibrations of C-H, respectively. The two peaks are shown at about (2850 and 2918) cm^{-1} assigned to asymmetric and symmetric C-H stretching, respectively, as reported in [23]. In the composite of HA/ HDPE, the transmittance peaks at (667, 981, 1253, 2320, 2347 and 2726) cm^{-1} have been characterized in the pure sample (without addition MWCNTs). The reason for the different bonds between fabricated composite powders and the final form of the sample is the success of the mixing and fabrication method so that new bonds appeared that overcame the individual bonds.

While Figure 2b shown the FTIR spectrums results of samples with 20HA /80HDPE, with various adding (% weight) of MWCNTs. The spectra of the samples (0.6%, 1%, and 1.4%) weights of MWCNT show the presence of bonds; approximately the same characteristic bands appeared in pure samples (0% MWCNTs), indicating that the nanocomposite was significantly more stable. The peaks corresponding to the MWCNTs were not apparent obviously to be expected because of the low concentrations of MWCNT compared to other compounds (HA/HDPE). Except for the C-H bond at peaks 2917 cm^{-1} (±40 cm^{-1}) was remarked in samples after adding % weights of MWCNTs. This bond is expected from the presence of MWCNTs, as reported in [18]. The FTIR analysis of the sample with (1)% of MWCNTs shows typical bands at (3560.59 to 3795.91) cm^{-1} that corresponds to the stretching mode of the OH group (hydrogen-bonded), other strong bands at (2316.51and 2345.44) cm^{-1} also correspond to O=C=O stretching (carbon dioxide).The band at 1730.51cm^{-1} belongs to the C=O stretch. The band 977.91cm^{-1} is for the C=C bending, which belongs to the alkenes functional group, while $(PO4)^{-3}$ bend presents at 570.93cm^{-1}. The values of phosphate bands have been detected, confirming an apatite structure [24]. Almost the same peaks have been reported of the absorbance spectrum for the same samples, with differences in the intensity value due to the different densities for the components. Due to present the cross-linking bonds, the FTIR result indicated that HA/HDPE and MWCNTs were strongly adapted as composite materials.

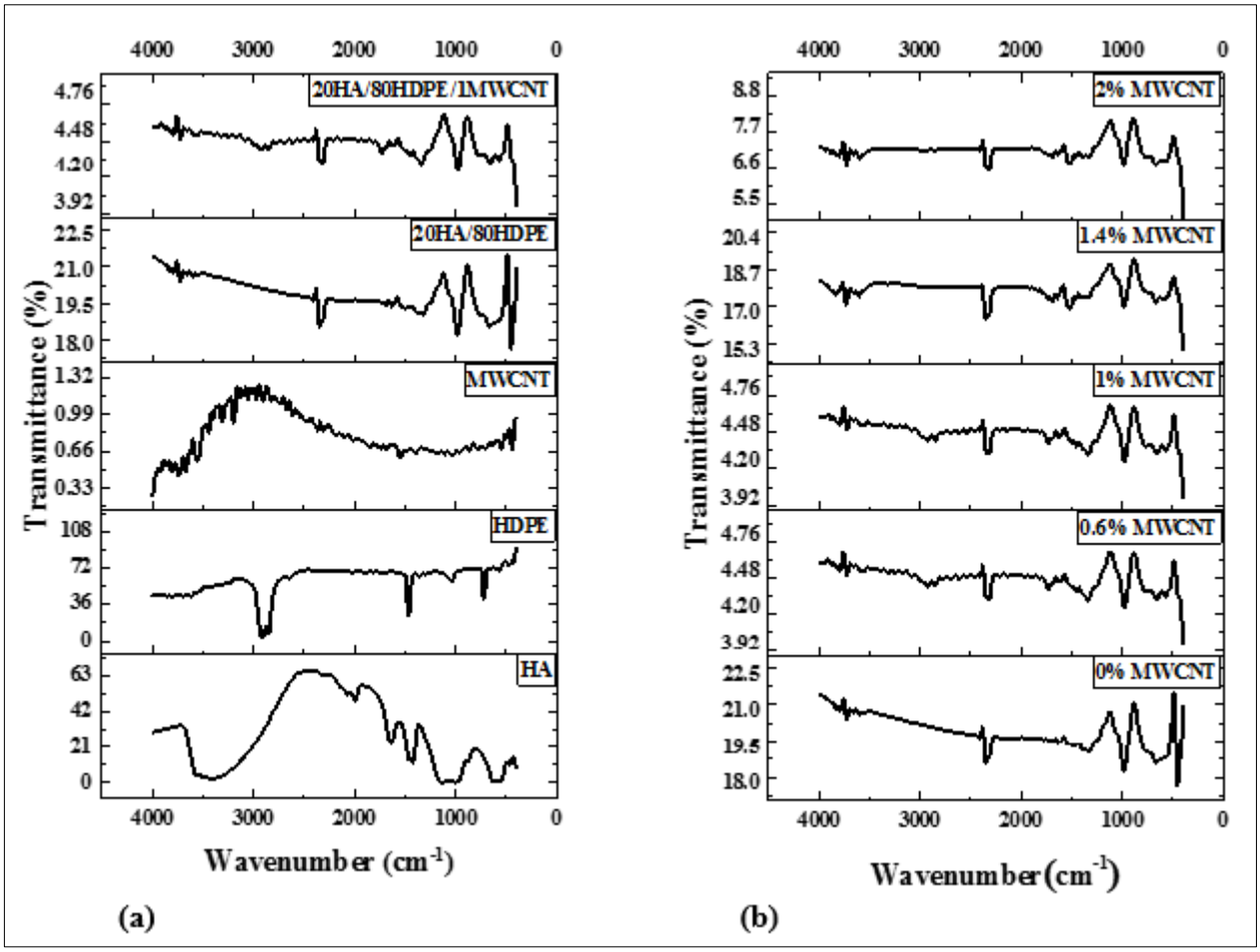
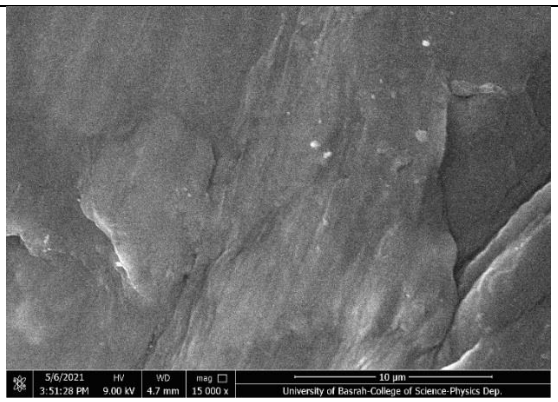


Figure 2. The FTIR absorption results of a) (HA, HDPE, MWCNTs) pure powder and samples with 20HA /80HDPE with (0, 1) % of MWCNTs, b) 20HA/80HDPE composite materials samples with various percentages of MWCNTs concentration

3.2. FE-SEM results

The surface morphologies of the presented composite samples were examined using a (FE-SEM) technique. The investigated specimens were containing various weight % of MWCNTS, as shown in Figure 3. The surface morphologies of samples with various conditions showed a suitable distribution of HA particles that was obtained in the HA/HDPE/MWCNTS composites. Also, the MWCNTSs have distributed homogeneously and adhesion between the HDPE matrix and HA particles. The addition of MWCNTs (up to 2%) improved the composite's fibrous structure compared with a sample with a (0 %) weight MWCNTSs. The process procedure that was performed during the fabrication of the samples like a ball mill method and hot- press technique resulted in a result successful as reasonable distribution of HA and MWCNTs with HDPE particles was achieved in the composite. The hybrid biocomposite samples shows a bio mimicking fibroses structure just like the normal bone. So, the FE-SEM explained that the bio-composite microstructure was homogeneous with the fibrous structure like natural bone structure. As reported in [25] explained, the rough material surface could support the wetting effect and increase the contact area between the cells to facilitate cell adhesion and material surface. Accordingly the FESEM analysis of the morphological structure of presented samples in this investigation exhibits that they are proper for a bone substitute material.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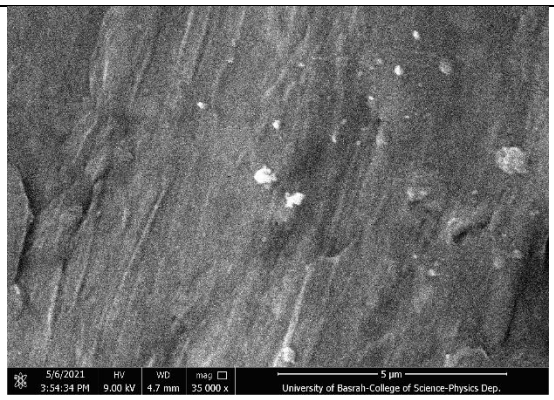
(a)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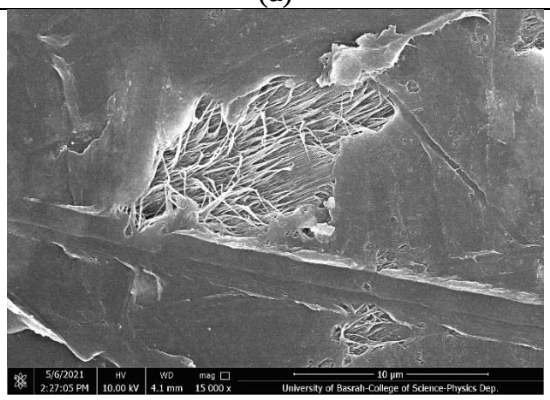
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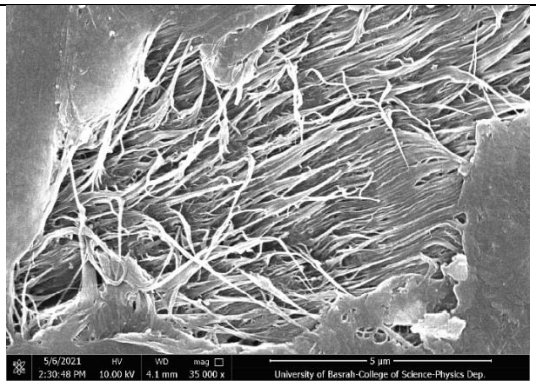
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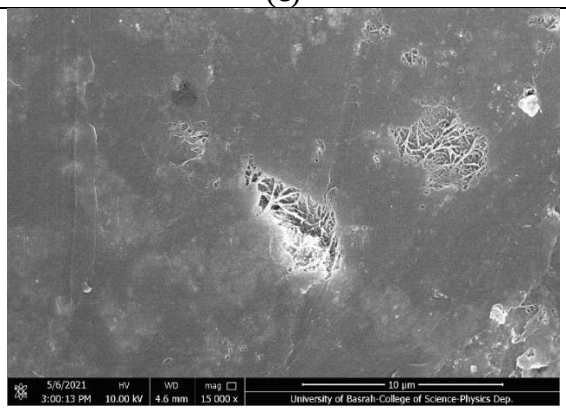
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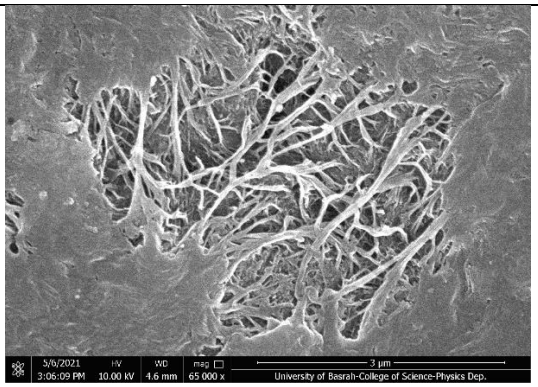
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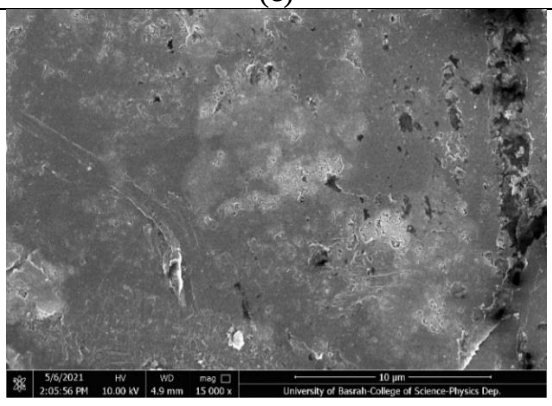
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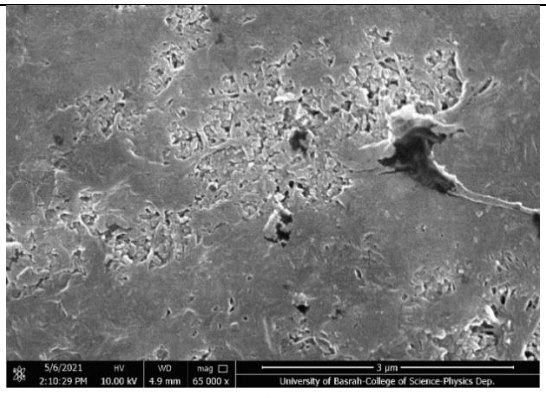
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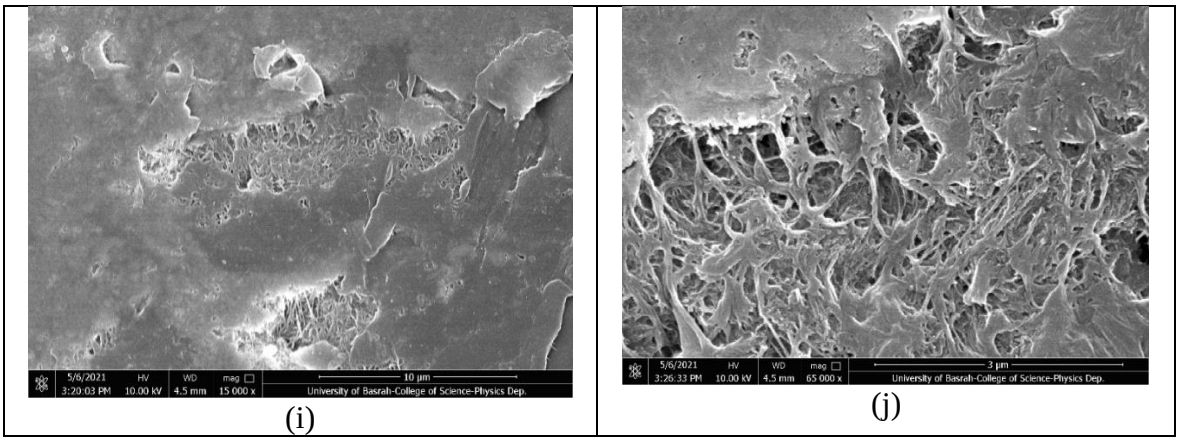
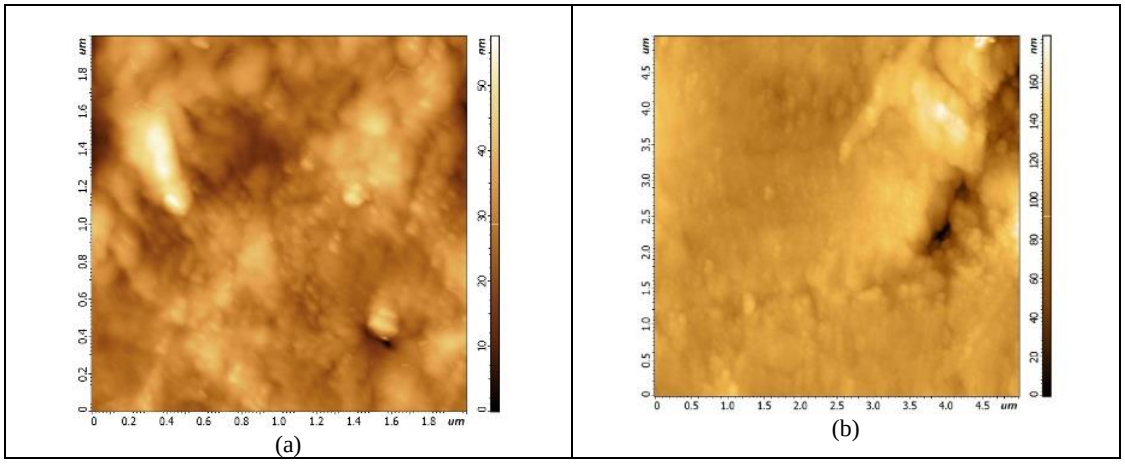


(i) (j)

Figure 3. The FE-SEM image for (20HA/80 HDPE) biocomposite with various percentages of MWCNTs, (a, b) 0% MWCNTs, (c, d) 0.6 % MWCNTs, (e, f) 1% MWCNTs, (g, h) 1.4% MWCNT, (i, j) 2% MWCNTs

3.3. AFM results

In order to recognize the surface morphology of the sample, the surface characterization was evaluated by AFM. Figure 4 shows the microstructure for 20HA/80HDPE with different adding percentages of MWCNTs. The sample microstructure indicates a homogeneous distribution, and interconnections between the HA and MWCNTs nanoparticles within the HDPE matrix contribute a good explanation for the enhancement of mechanical properties resultant. This figure shows that the fibrous structure increases with an increases percentage content of MWCNTs and HA due to excellent nanofillers particle distribution within the HDPE matrix. The surface topography by AFM 3D images recorded the samples 20HA/80HDPE with different adding percentages of MWCNTs and their granularity accumulation distribution shows in Figure 5. Table 1 listed the differences in the roughness of the sample's surface with various compositions the maximum degree of roughness equal (7.025 nm) at 0.6 % MWCNTs. The roughness of the sample surface has a significant effect on the increase in differentiation and cell proliferation [26, 27].



(a) (b)

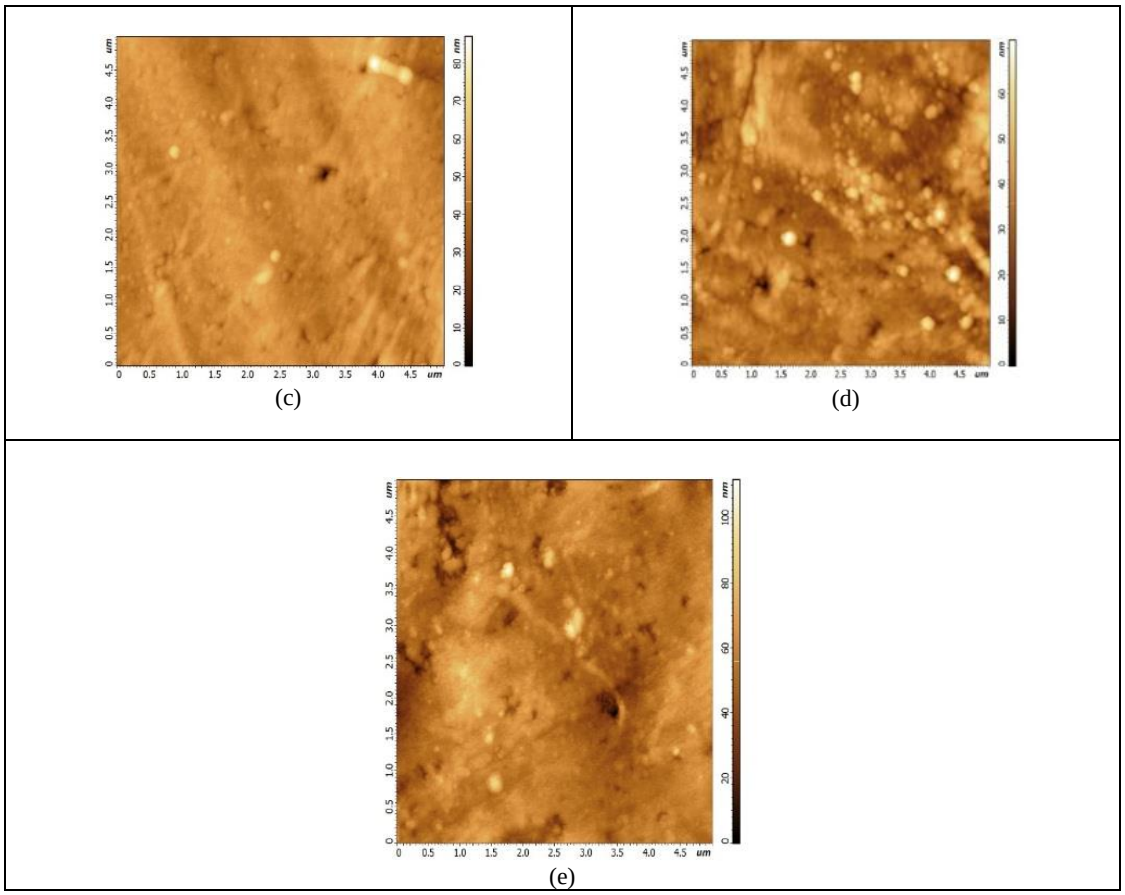
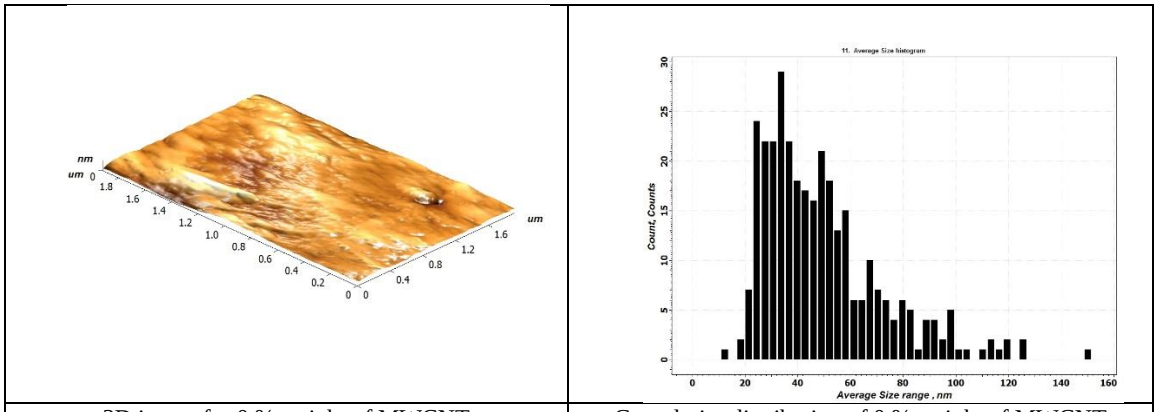
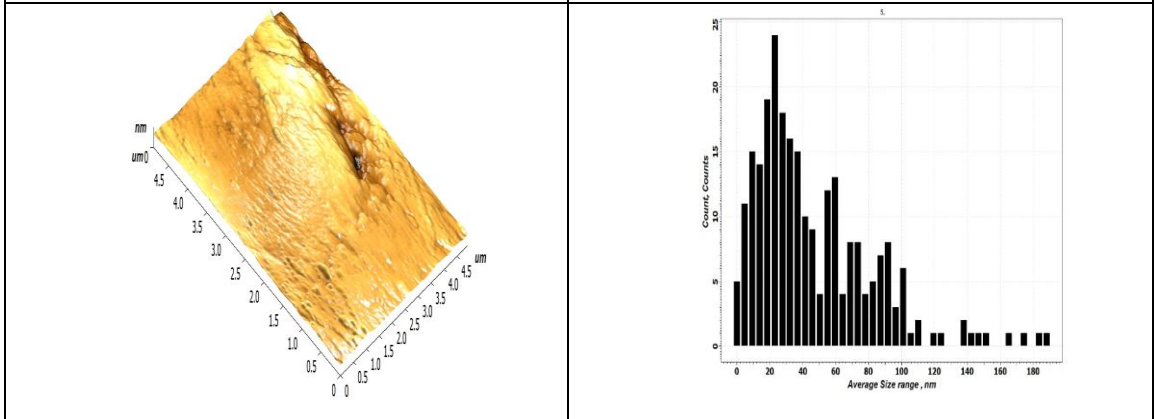


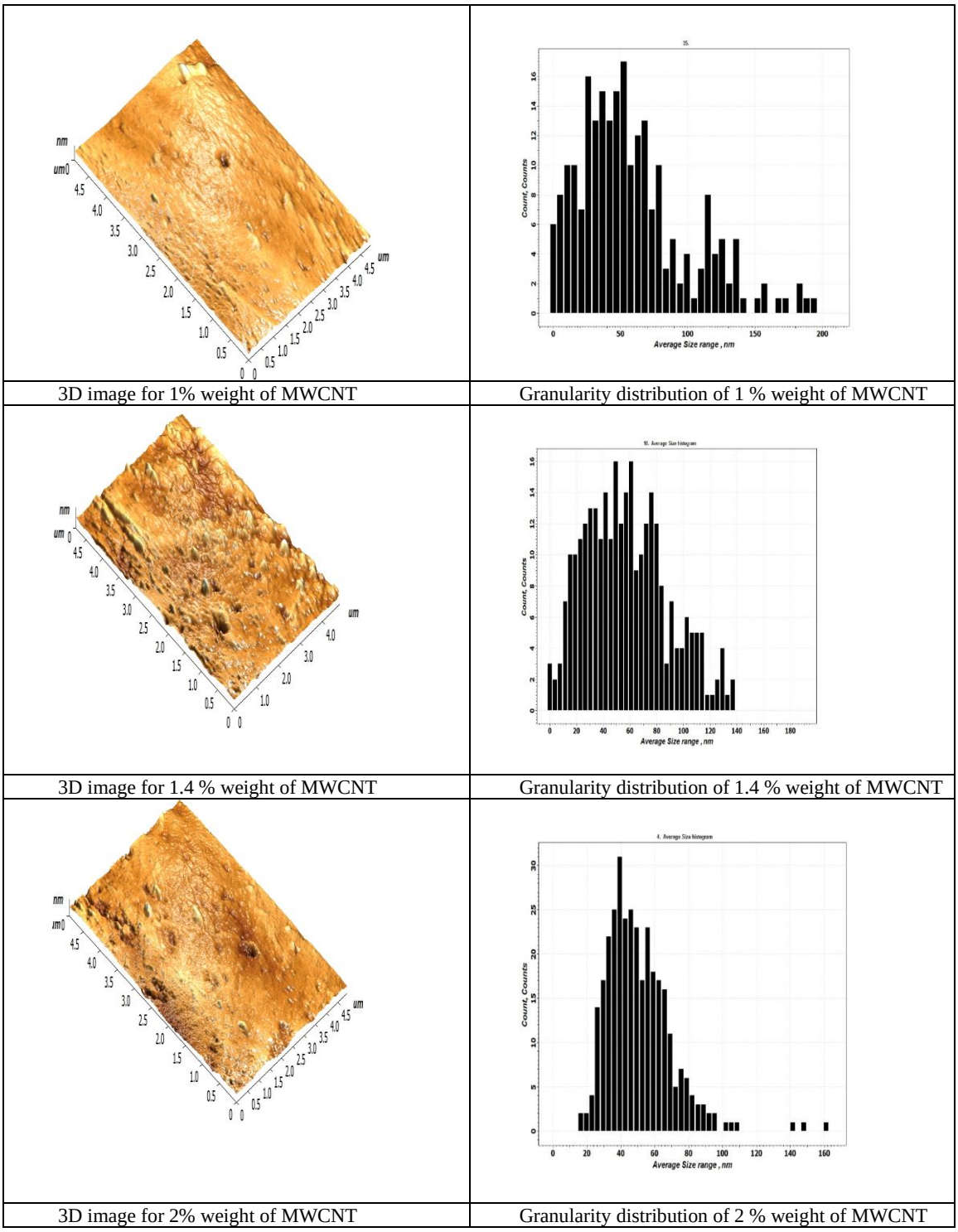
Figure 4. The AFM 2D images for (a) 0% (b) 0.6 % (c) 1% (d) 1.4% (e) 2% weights of MWCNs



3D image for 0 % weight of MWCNT | Granularity distribution of 0 % weight of MWCNT



3D image for 0.6 % weight of MWCNT | Granularity distribution of 0.6 % weight of MWCNT



3D image for 1% weight of MWCNT	Granularity distribution of 1 % weight of MWCNT
3D image for 1.4 % weight of MWCNT	Granularity distribution of 1.4 % weight of MWCNT
3D image for 2% weight of MWCNT	Granularity distribution of 2 % weight of MWCNT

Figure 5. The AFM 3D images and their granularity accumulation distribution for (20HA/80HDPE) at different % weight of MWCNTs

Table 1. AFM parameters (Peak-peak distance, roughness average, and Root mean square (RMS) roughness) for samples with various (%) weights of MWCNTs

Weight of MWCNTs (%)	Peak-peak (nm)	Roughness average (nm)	RMS roughness (nm)
0	57.520	4.896	6.514
0.6	106.55	7.025	10.359
1	31.103	2.525	3.276
1.4	57.776	3.719	5.438
2	70.936	4.050	6.016

3.4. DSC results

Figure 6 shows the DSC curve for sample (20 HA / 80 HDPE/0.6 MWCNTs) with exhibited the value of melting peak temperature, crystallization peak temperature, melting enthalpy and crystallization enthalpy. Figure 7 exhibits the DSC curve for samples explains the effect of adding MWCNT in different percentages. The thermal behavior for the heat and cooling of nanocomposites (HA/HDPE) with various MWCNTs percentage (wt. %) are summarized in Table 2. The degree of crystallinity increased from (53.5% to 73%) for (0 and 2 % wt.) of MWCNTs, respectively, for 20HA/80% HDPE composites. These results exhibited MWCNTs performance as nucleating agents, and previous investigations also report this [28, 29]. On the other hand, when the increased addition of the MWCNTs, the fillers began to block the polymer macromolecular mobilization chains and inhibit macromolecular parts from getting the arrangement of crystal structures [30]. The mechanical properties of polymers increase significantly with an increase in the degree of crystallinity [31]. The thermal stability can be strongly enhanced by adding nanofillers such as MWCNTs, which can be deactivated by the free radicals [32].

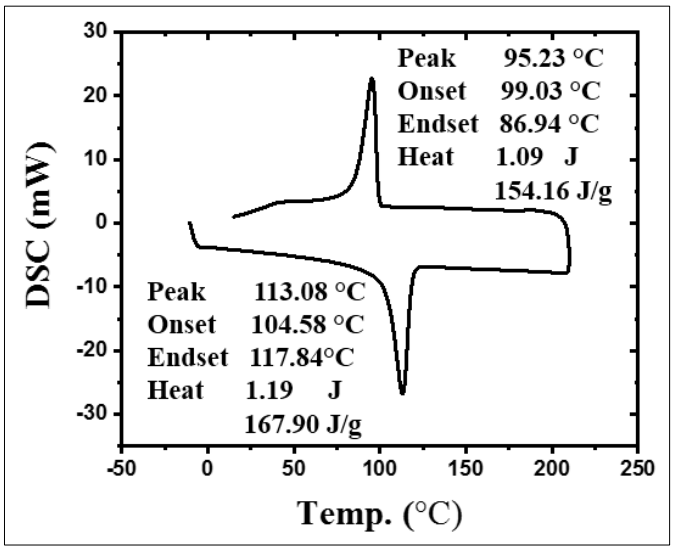


Figure 6. Heat-cool process of a specimen of (20 HA/80HDPE/0.6 MWCNTs) by using DSC

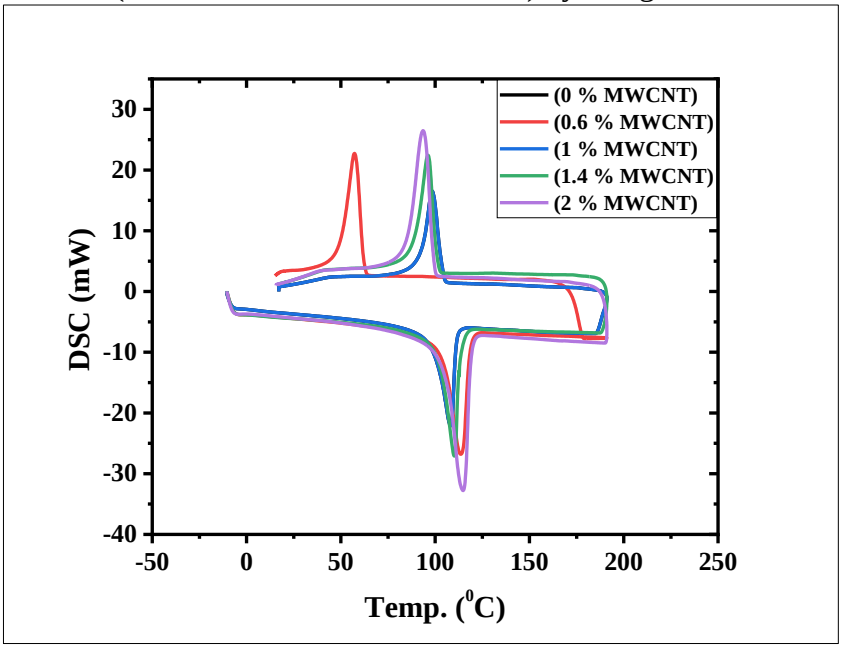


Figure 7. The DSC curves for (20HA/80HDPE) composite recorded with various (%) weights of MWCNTs

Table 2. Summary of the thermal data for DSC curves properties with different percentages (% weight) of (HA/HDPE/MWCNT) biocomposite. T_m - melting peak temperature, T_o - Onset temperature, T_e - Endset temperature, ΔH_m - melting enthalpy, T_c - crystallization peak temperature, ΔH_c - crystallization enthalpy, X_c - degree of crystallinity

Specimen group (% MWCNT)	Melting stage (°C)			ΔH_m (J/g)	Cooling stage (°C)			ΔH_c (J/g)	X_C (%)
	(T_m)	(T_o)	(T_e)		(T_c)	(T_o)	(T_e)		
0	112	105	117	155	94	100	86	164	54
0.6	113	104	118	168	95	99	87	154	58
1	113	104	117	181	95	99	85	181	62
1.4	112	104	116	205	95	99	86	206	71
2	113	105	118	214	95	100	86	205	73

4. Conclusions

The hot-pressing technique was used to fabricate the biocomposite samples (HA/HDPE) with various amounts of MWCNTs in the present study. The FTIR investigation exhibited the existence of bonding types and functional groups for the biocomposite samples. The FESEM and AFM diagnosis of the sample surface revealed a homogeneous, good distribution of the components' microstructure arrangements and improvement in the roughness of the sample surface. This indicates the best achievement of the sample preparation and fabrication method. The typical fibres shape, similar to the construction of bone tissue, was shown in FESEM examination. The hybrid biocomposite produced shows an excellent enhancement in the mechanical properties with an increased addition % weight of MWCNTs as reported in our previous study [33]. The results confirmed that the addition of the MWCNTs had improved the mechanical properties of biocomposite due to the increased crystallinity as exhibited in DSC results. The individual characteristics of the presented samples in this research with homogenous fibrous shape and high mechanical properties could be used as reconstruction materials for hard tissue.

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