**Periodicals of Engineering and Natural Sciences** ISSN 2303-4521
Vol. 9, No. 2, May 2021, pp.930-939

# Multiwall carbon nanotube reinforced HA/HDPE biocomposite for bone reconstruction

**Ali A. Al-allaq [1,2], Jenan S. Kashan [3], Mohamed T. El-Wakad [2,4], Ahmed M. Soliman [2]**
[1] Ministry of Higher Education and Scientific Research, Office Reconstruction and Projects ,Baghdad, Iraq
[2] Biomedical Engineering Department, Faculty of Engineering, Helwan University Cairo, Egypt
[3] Biomedical Engineering Department, University of Technology, Baghdad, Iraq
[4] Faculty of Engineering and Technology, Future University, Cairo, Egypt

## ABSTRACT

The healing of bone fractures naturally occurs without surgical intervention. Some damage and fractures in bone tissue are complex and leave remnant deformation, and this requires the use of bone replacement material. Hydroxyapatite (HA) is the main element of the bone mineral form and consider as a bioactive material which supports bone growth. Nevertheless, the HA has poor mechanical properties, such as low tensile strength. Thus the applications in bone replacement have been limited, especially in high load-bearing applications. A Carbone nanotube has newly obtained considerable concern because of their mechanical properties, potentially enhancing the bone implant's clinical efficiency. This study attempted to explain the effect of adding Multi-walled carbon nanotubes MWCNT Nanoparticles to the HDPE/HA bio-composites. Two groups of the composites samples were produced 20HA/80 HDPE and 40 HA/ 60 HDPE with adding (0.6, 1, 1.4, 2) % weights of (MWCNT) to each group. The composites were fabricated using a hot pressing technique with various pressing pressures (29, 57, 86, and 114 Mpa) at a compounding temperature of 150 C° and a holding time of 15 minutes. To evaluate samples' characteristics and performance, X-ray powder diffraction (XRD), surface topography by Field Emission Scanning Electron Microscopy (FE-SEM), tensile strength and, microhardness test were investigated. The results showed that the hybrid bio-composites demonstrated excellent structural integrity, homogeneous with the fibrous structure, and improved mechanical properties. When increasing in MWNT additions and increasing hot-press pressure, enhancing the composites' fracture strength and microhardness is beneficial. The excellent properties of hybrids bio-composite (HA/HDPE/MWCNT) samples for homogeneous fibrous structure and high mechanical properties could be applied in bone tissue engineering for bone reconstruction.

**Keywords**: Biomedical Engineering, Bone tissue engineering, Biomaterials, Bone substitute, Nanocomposite, Hard tissue

***Corresponding Author:***

Ali A. Al-allaq
Ministry of Higher Education and Scientific Research, Office Reconstruction and Projects ,Baghdad, Iraq
Biomedical Engineering Department, Faculty of Engineering, Helwan University Cairo, Egypt
E-mail: ali.martial85@gmail.com
ali.martial85@h-eng.helwan.edu.eg

## 1. Introduction

Bone is an extremely functional supporting structure of the body, described by its hardness, rigidity, repair and regeneration ability [1]. The bone bulk contains 65% mineral, 35% organic matrix, water, and cells. The bone mineral is in small crystals in plates, rods, and needles between and within the collagen fibers [2]. The hydroxyapatite (HA) is the main mineral, including constituents such as magnesium, fluoride, carbonate, strontium, and citrate combined into the crystal lattice or absorbed onto the crystal surface [2][3]. Bone diseases are pathological cases that result in the disorder of normal bone function that produces bones physically weaker by the degeneration of their structure. The bone fracture affected the normal function of bone and other disease problems encountered by the patient, such as osteoporosis, Giant cell tumors, avascular necrosis of bone, and genetic factors [4]. Bone grafting is considering one of the most methods that were used to treat bone diseases previously, which is a surgical operation that substitutes missing bone in the case of extremely complex fractures with vital health risks to the patient or fails in the healing process [5]. The main disadvantage of bone grafting

is that the harvest from the place is often extremely painful, especially after the operation and has a vital risk of increasing complications such as infection, hematoma, and nerve injury [4]. And here became the importance of using biomaterials that help heal or as bone substitutes. This case inspire the specialist in the field of biomaterials to modify a synthetic substitutes to enhance bone healing or for the replacement of the damaged bone. HA/HDPE composite considered the most suitable choice since 80s because of its structure that bio mimicking the natural bone, moreover, the superior properties like osteoconductivity, non-toxic, bioactive, and non-inflammatory make is the most biomaterials that has been use in replacement and reconstruction for damaged bone. The fragile mechanical properties for HA/HDPE composite make its applications are limited [6]. Many investigations has been done to enhance the mechanical properties of HA/HDPE system by using different reinforcements materials, such as bio inert ceramics, some of these studies investigated the enhancement of HA/HDPE composite by Nano fillers [7][8] . Recently, carbon nanotubes (CNT) are developing interest as reinforcement for HA/HDPE implants. The regular distribution of CNT in the HA/HDPE matrix, good interfacial bonding and the Nano grain size were important to increase mechanical performance with a combination of the osteoconductivity and biocompatibility [9]. Some recently studies have been attempted to apply CNT as a new method with the expectation of enhancing the mechanical properties [10][11][12]. In the present work, a hybrid Nano biocomposite of HA/HDPE reinforced with Multi-walled carbon nanotubes (MWCNTs) prepared by hot pressing technique. Effect of MWCNTs on the mechanical properties, microstructure and phase analysis has been investigated.

## 2. Materials and medthods

### 2.1. Production of the hybrid bio composite samples

Hydroxyapatite Nano powder with nodular shape, real density of (3.140 gm/cm3), particle size of 20 nm, and a purity of approximately (99%) has been supplied from MK Nano (Toronto, Canada). While the high density polyehylen powder with particle size of (5 μm) has been supplied by Right Fortune Industrial Limited (Shanghai, China).The multi-wall carbon Nanotubes were purchased from (Cheap Tubes Inc., USA)with a purity of 90%, outer Diameter is less than 8nm, inner diameter is 2-5nm, and length 10-30 μm.
The processed samples have been classified into two groups according to the compositions of (20%HA/80%HDPE) and (40%HA/60%HDPE). MWCNTs with a weight % of (0.6, 1, 1.4, and 2) has been added for both groups, and these powders were dry-mixed using ball milling. The hot pressing technique has been adopted to produce all samples using a compounding pressures of (29, 57, 86, and 114 MPa) by using (Instron 1195 series tension and compression tester) and compounding temperature of150 C° ,with The Pressing velocity was 0.5 mm/min. The hot pressing system presents in figure 1, while the sequence of sample production processes are listed in figure 2.


Figure 1. The hot Pressing System with Instron 1195 series

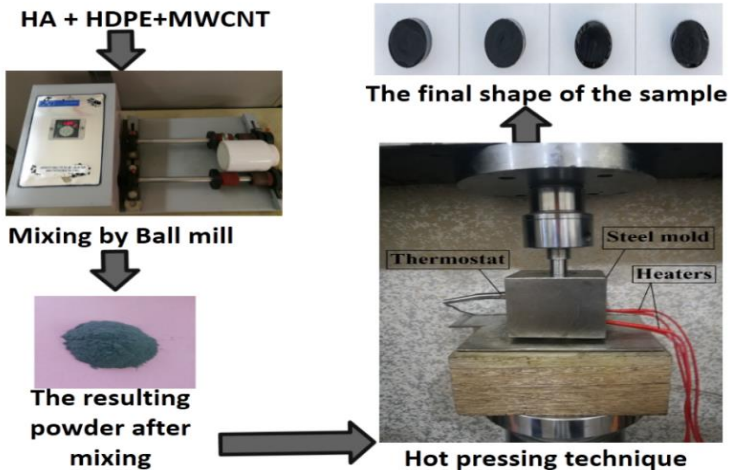



Figure 2. Fabrication process steps

### 2.2. XRD Test

X-ray powder diffraction is a nondestructive analytical technique and one of the most prospective characterization tools for identifying both inorganic and organic crystalline materials. To determine the crystal structure of the bio-composite samples (HA/HDPE/MWCNT), XRD analysis was performed by using SHIMADZU XRD 6000 with testing condition of a voltage (40kV), current (30mA), drive axis (θ -2 θ), scan speed (10.0000 deg/min ), sampling pitch ( 0.2000 deg) and preset time( 1.20 sec).

### 2.3. FE-SEM Test

The bio composite specimens' morphology was examined using a field emission scanning electron microscope (FE-SEM) (FEI Quanta 450, USA) at an accelerated voltage of (3-10) kV. The samples were coated with a thin layer of gold under vacuum to avoid heat build-up and electrostatic charging during the examination.

### 2.4. Fracture strength (diametrical compression test)

The Brazilian test, indirect tensile test and the diametral compression test are three names for one test procedure that has been used to measure the tensile strength of many types of materials such as ceramics, concrete and polymers [13]. The diametral compression test were performed for the samples to evaluate the effect of MWCNTs on the mechanical properties. All tests were carried out for samples (Diameters14.75mm, Width 7 ± 2 mm) with constant velocity rate of 0.5 mm/min, using the (Instron Tinius Olsen H50 KT machine with software Q Mat 4.53 T series), as shown in figure (3). The sample has been loaded through the diameter. The tensile strength was determined using the equation[13]:-

$$\sigma t = \frac{2P}{\pi DT}$$

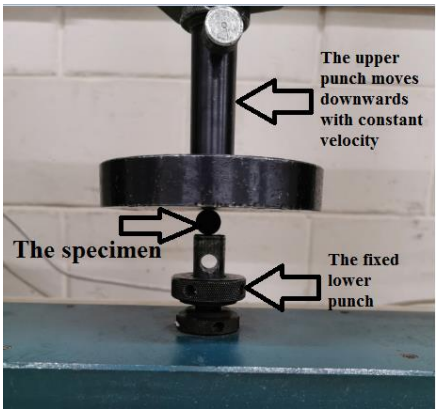



Figure 3. The sample under Brazilian test

### 2.5. Microhardness test

The Vickers microhardness test has been applied to identify hardness values for all samples prepared with varied compression pressures and compositions. Microhardness tester Digital Micro-Vickers Hardness tester TH714, (Beijing TIME High Technology Ltd., China) has been used. For this objective, a load of (25 g) was applied to the sample with a press time (15 s).

## 3. Results and discussion

### 3.1. XRD results

XRD analysis was taken out to identify various phases in the produced biocomposite samples, especially to identify the effect of MWCNTs addition on the HA/HDPE system and phase analyses for the hybrid biocomposite samples. The (Origin software 2018) has been used to represent the data in the curves form. The figure (4-a) shows the effect of different weight% of MWCNTs added to the 20HA/HDPE system, while figure (4-b) is listing this effect on the 40HA/HDPE system. It can be observed that the increasing in the weight% of MWCNT caused a slight shifting in (2θ) as listed in Tables 1 and 2 . The peaks intensity values increases incrementally with increasing the weight% of MWCNTs at most of the samples. This may be attributes to the high crystallinity of the polymeric matrix which is directly proportional to the diffraction peak intensity of XRD [14]. The Nano fillers act as a nucleation sets for the polymeric matrix , which is increased the crystalline phases in the matrix, but the increasing in weight% of the added Nano filler caused an agglomeration which is may be reduce the nucleation rate of polymeric matrix and then reduced the peak intensity. The effect of compounding pressure on the XRD results for the prepared hybrid biocomposite samples shown in (figure 5) . It can be recognized that increasing the hot pressing pressure caused a slight shifting in (2θ) this may be attributes to the high packing between the components of the biocomposite samples.

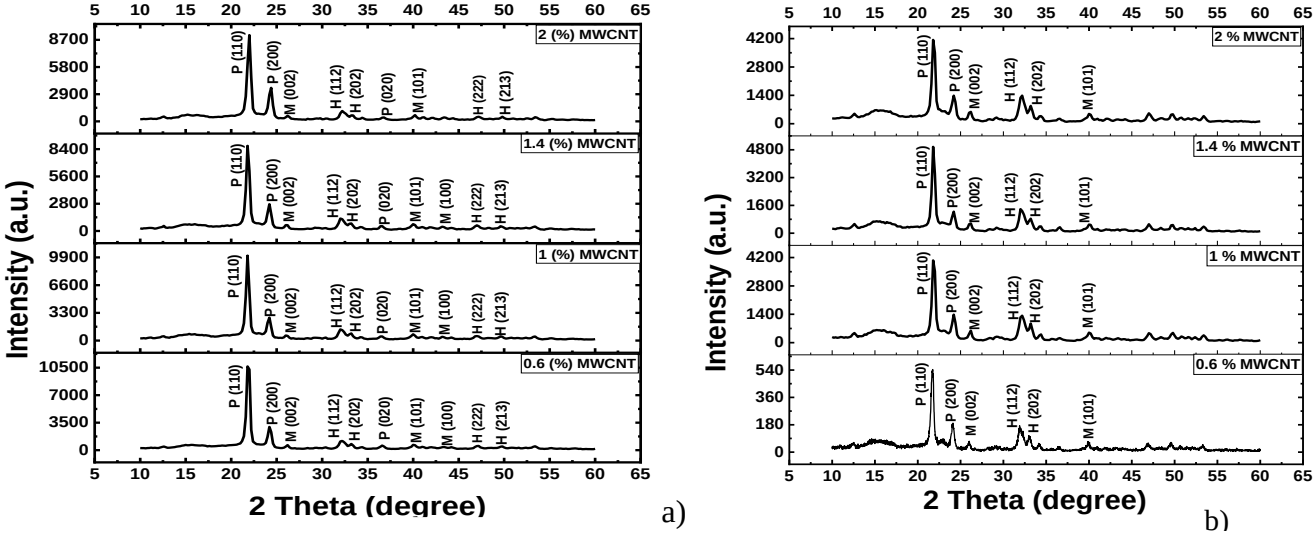



Figure 4. The XRD plots for composite materials samples with different percentage of MWCNT at a compression pressure of 29Mpa at (a) 20HA/HDPE (b) 40HA/HDPE. The abbreviation p, h and m represented HDPE, HA, MWCNT respectively.

Table 1. The effect of MWCNTs on the XRD results for 20HA/HDPE system

| Component | hkl)( | Hot-press Pressure (Mpa) | (2θ) for various Percentages of MWCNT (degree) | | | |
|---|---|---|---|---|---|---|
| | | | 0.6% | 1% | 1.4% | 2% |
| HA | 112 | 29 | 32.1098 | 32.1300 | 32.2348 | 32.3403 |
| | | 114 | 32.2773 | 32.1658 | 32.1804 | 32.2768 |
| | 202 | 29 | 33.2396 | 33.2396 | 33.2396 | 33.4394 |
| | | 114 | 33.2396 | 33.2396 | 33.2396 | 33.2396 |
| | 222 | 29 | 46.9687 | 46.9674 | 47.0137 | 47.1767 |
| | | 114 | 47.0752 | 46.9992 | 47.0396 | 47.1117 |
| | | 29 | 21.8104 | 21.8072 | 21.8735 | 22.0124 |

| | | | | | | |
|---|---|---|---|---|---|---|
| **HDPE** | **110** | **114** | 21.9140 | 21.8501 | 21.8594 | 21.9192 |
| | **200** | **29** | 24.1095 | 24.1169 | 24.2154 | 24.3680 |
| | | **114** | 24.2544 | 24.1901 | 24.2056 | 24.2748 |
| | **020** | **29** | 36.4618 | 36.5206 | 36.5517 | 36.7368 |
| | | **114** | 36.6086 | 36.5157 | 36.6229 | - |
| **MWCNT** | **002** | **29** | 26.0380 | 26.0476 | 26.1111 | 26.2391 |
| | | **114** | 26.1909 | 26.1031 | 26.0798 | 26.1374 |
| | **101** | **29** | 39.9614 | 39.9951 | 40.0335 | 40.1915 |
| | | **114** | 40.1081 | 40.0133 | 40.0312 | 40.0771 |

Table 2. The effect of MWCNTs on the XRD results for 40HA/HDPE system

| **Component** | **hkl)(** | **Hot-press Pressure (Mpa)** | **(2θ) for various Percentages of MWCNT (degree)** | | | |
|---|---|---|---|---|---|---|
| | | | **0.6%** | **1%** | **1.4%** | **2%** |
| **HA** | **112** | **29** | 32.3406 | 32.2664 | 32.2343 | 32.2259 |
| | | **114** | 32.8382 | 32.2783 | 32.2360 | 32.1333 |
| | **202** | **29** | 33.0438 | 33.2396 | 33.2396 | 33.2396 |
| | | **114** | 33.9839 | 33.2396 | 33.2396 | 33.2396 |
| | **222** | **29** | 46.8697 | 47.0542 | 47.0076 | 47.0271 |
| | | **114** | 46.6499 | 47.0439 | 47.0087 | 46.9231 |
| **HDPE** | **110** | **29** | 21.7483 | 21.9040 | 21.8783 | 21.8949 |
| | | **114** | 21.5155 | 21.9334 | 21.8795 | 21.7812 |
| | **200** | **29** | 24.1298 | 24.2244 | 24.1939 | 24.2181 |
| | | **114** | 23.8745 | 24.2788 | 24.2261 | 24.1288 |
| | **020** | **29** | 36.4766 | 36.6207 | 36.5708 | 36.5378 |
| | | **114** | 36.2833 | 36.6443 | 36.5952 | - |
| **MWCNT** | **002** | **29** | 26.0192 | 26.1750 | 26.1426 | 26.1523 |
| | | **114** | 25.7883 | 26.2020 | 26.1459 | 26.0434 |
| | **101** | **29** | 39.9289 | 40.0428 | 40.0477 | 40.0417 |
| | | **114** | 39.7274 | 40.1111 | 40.0423 | 39.9430 |

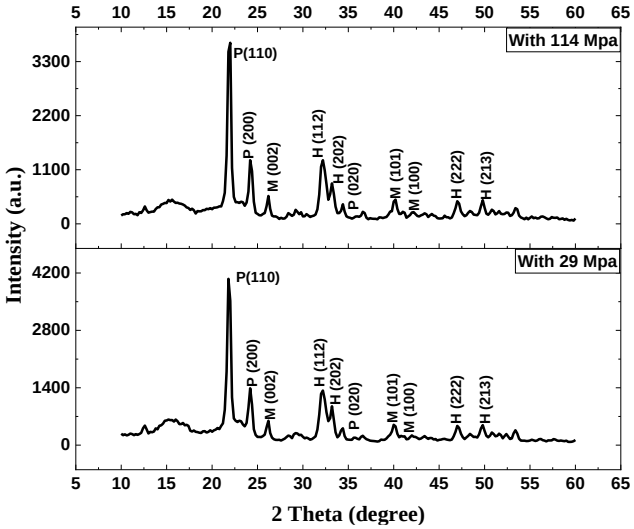
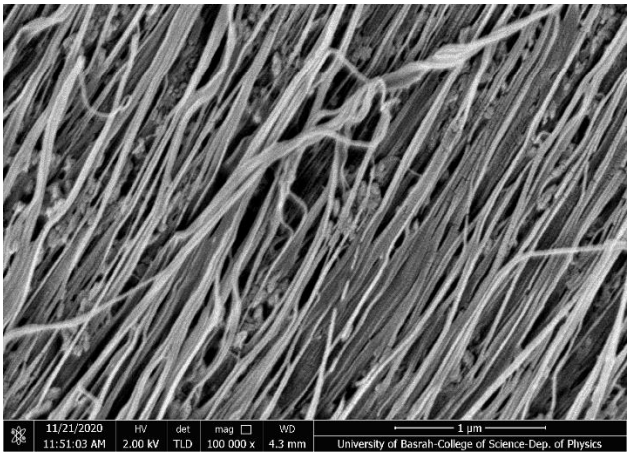



Figure 5. The XRD plots for composite materials samples that have hot pressing (29, 114) with (40% HA, HDPE) with 1% MWCNT. The abbreviation p, h and m represented HDPE, HA, MWCNT respectively

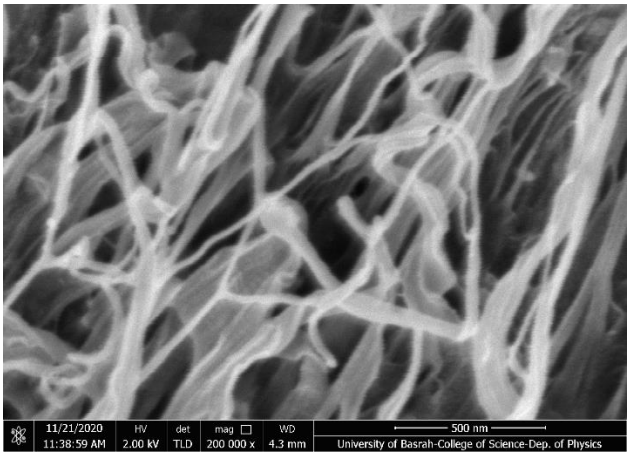
### 3.2. FE-SEM results

The surface morphologies of the presented composite samples were examined using a (FE-SEM) technique. The investigated specimens were containing various weight% of MWCNT, as shown in figure (6). The figure (7) demonstrate the effect of various pressure of the hot- pressing on the internal microstructure. The surface morphologies of samples with various conditions showed a suitable distribution of HA particles that was

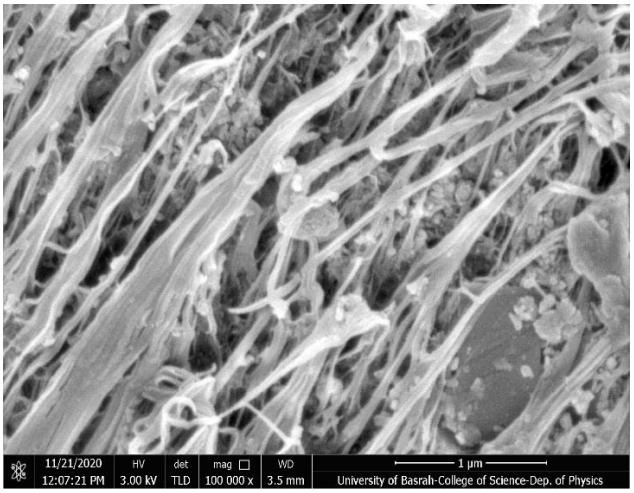
obtained in the HA/HDPE/MWCNT composites. Also, the hybrid biocomposite samples shows a bio mimicking fibroses structure just like the normal bone. So, the FE-SEM explained that the bio-composite microstructure was homogeneous with the fibrous structure like natural bone structure. Here, the effect of increasing the pressure of hot-pressing appears by reducing the size, quantity of porous and increasing the thickness of the microfiber. This leads to predict an increase in mechanical properties with increasing hot-press pressure.



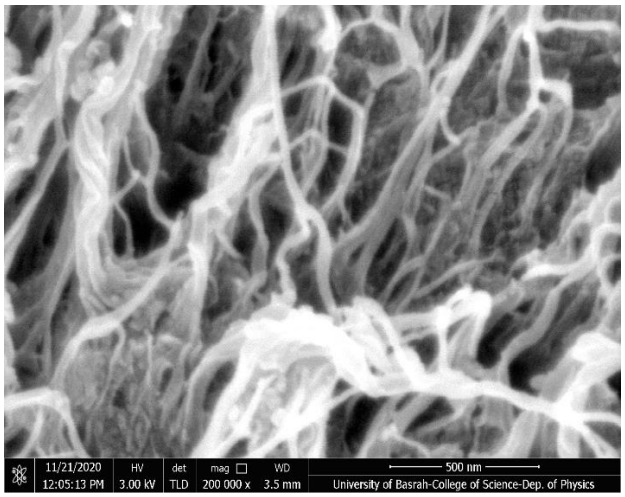

(a)



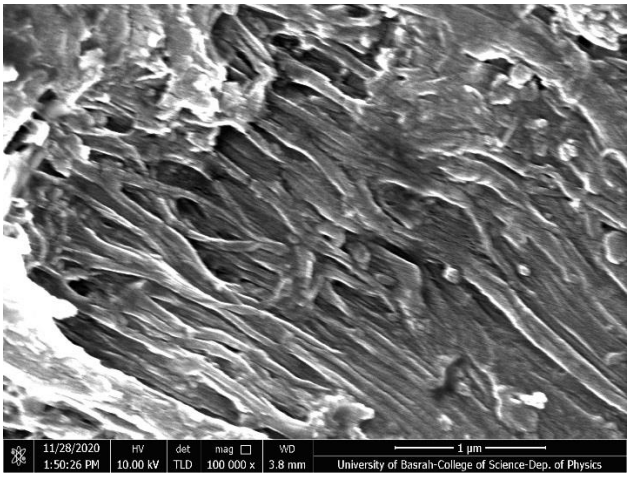

(b)



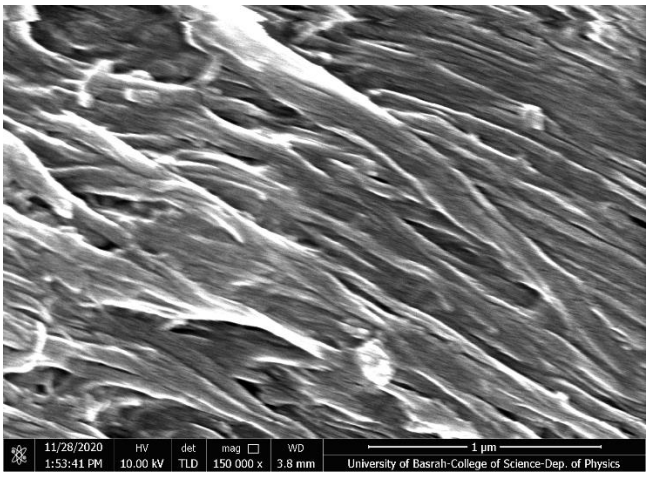

(c )



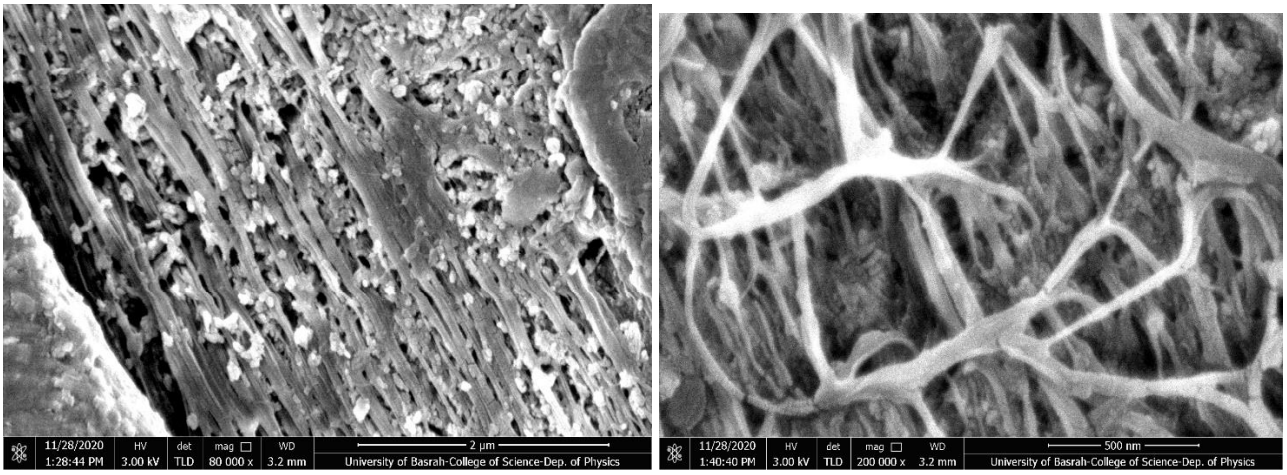

(d)




(e )

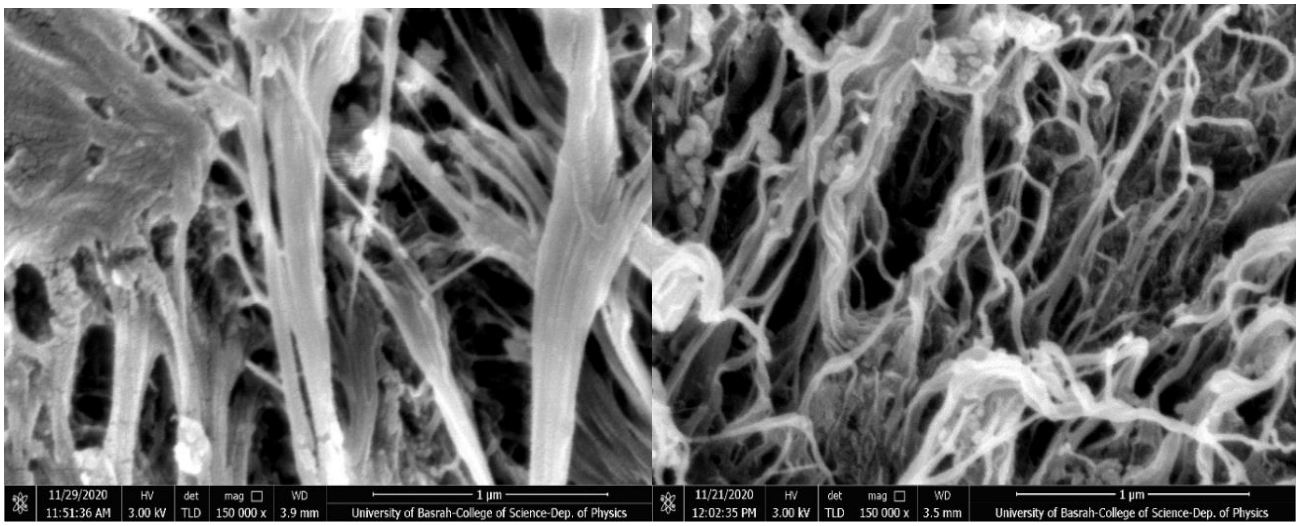



(f)




(g) (h)

Figure 6.The FE-SEM image for (40HA/ HDPE) biocomposite with various percentages of MWCN , (a, b) 0.6% MWCNT , (c, d) 1 % MWCNT, (e, f) 1.4% MWCNT , (g, h) 2% MWCNT




(a) (b)

Figure 7. The FE-SEM image of the bio-composite (40HA/60HDPE) with weight 1% of MWCNT at (a) 24 Mpa (b) 114 Mpa hot press

### 3.3. Fracture strength

The fracture strength has been measured by the Brazilian test applied to the samples. The figure (8) shows the relationships between the fracture strength and compressive Pressure (Mpa) corresponded to various MWCNT compositions. The fracture strength increased along with increasing the compressive pressure. The highest fracture strength values (148,147 Mpa) presented in the samples with composite 40HA/60HDPE, and 20HA/ 80HDPE respectively, by reinforcement of 1 % of MWCNT, at 114 Mpa hot-pressing pressure. Also, the lowest strength value (25 Mpa) was observed in composite with (20%HA/80%HDPE) with (0%) of MWCNT at (29 Mpa) compounding pressure. The collected data from the fracture strength test give an indication that the increasing in both of hot pressing pressure and the MWCNTs values caused and enhancement in the fracture strength for the produced biocomposite samples. An explanation of this improvement is in the mechanical specifications, due to the exceptional features of CNTs such as high aspect ratios and excellent intrinsic mechanical properties [15], by transferring their excellent characteristics to matrix [16]. Also, the conditions of success mechanical reinforcement in the nano-composites are the good distribution, alignment of CNT, excellent aspect ratio, and interfacial stress transfer between CNT and polymer [17]

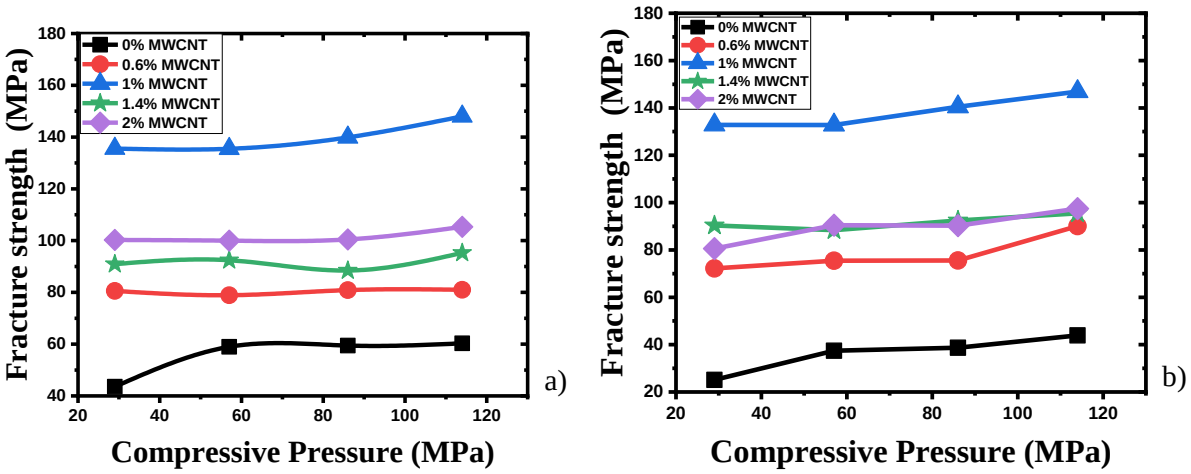



Figure8. The relationship between fracture strength and compression pressure with variations content of MWCNT for (a) 20%HA/80%HDPE group, (b) 40%HA/60%HDPE

### 3.4 Vickers microhardness

The variety of the Vickers microhardness of the prepared samples is shown in Figure (9). It can be seen that the Vickers microhardness increased with an increase in MWCNT content, and the maximum value presents when MWCNT addition was up to 2% wt. This relationship between MWCNT and increasing Vickers micro-hardness for HA and HDPE is mentioned in previous research [18][19]. The effect of the difference of hot-press pressures with various percentages of addition MWCNT to the HA/HDPE composite material is shown in figure (10). The micro-hardness values for the composite samples showed a slight increase with increasing the compressive pressure. The highest values of microhardness are recorded under (86) Mpa hot-press pressure.

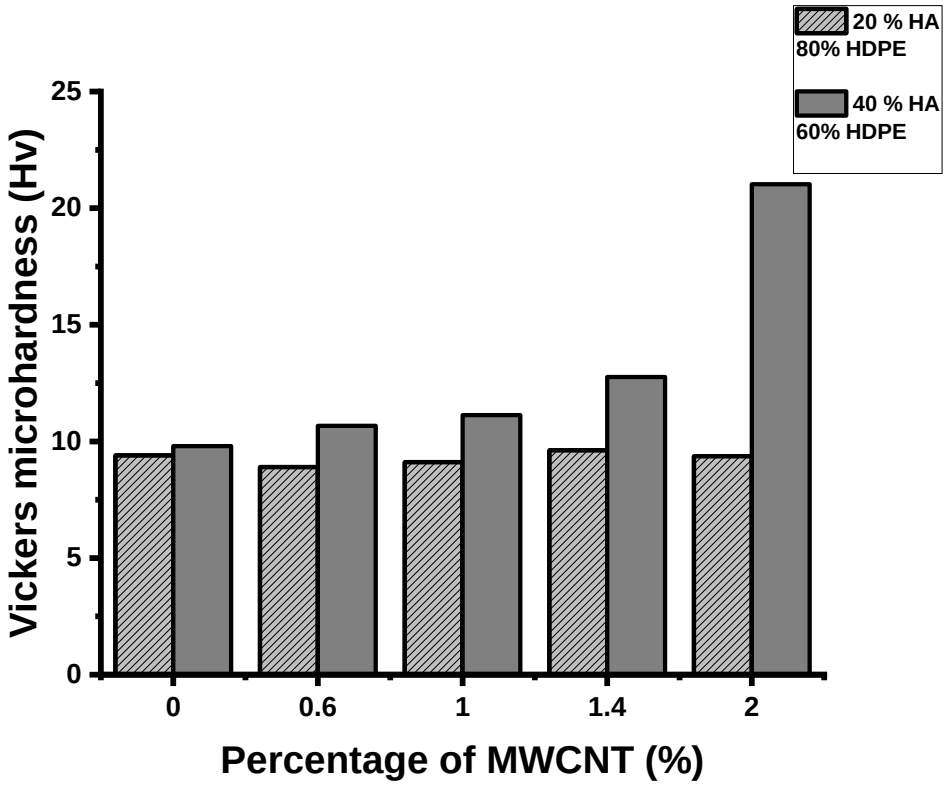



Figure 9. The variations of Vickers microhardness with different concentration of MWCNT.

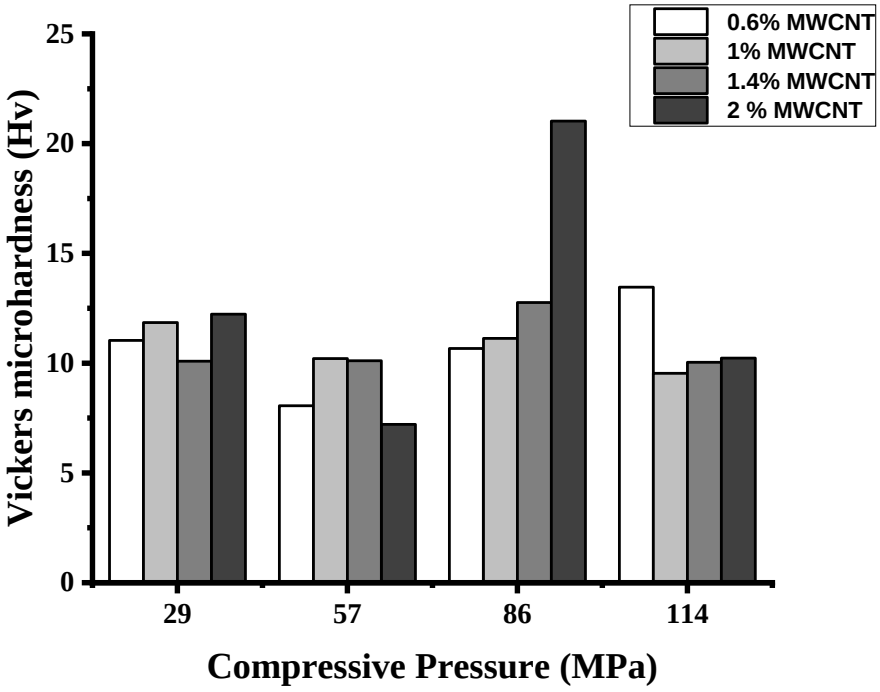



Figure 10. The relationship between compression pressure and Vickers microhardness of the bio-composite (40HA/60HDPE) with various percentages of MWCNT concentration

## 4. Conclusions

The synthesis composites (HDPE/HA) with different weight% of MWCNT were prepared using the hot pressing technique and characterizing them using several techniques. The hybrid biocomposite produced in this work shows an excellent enhancement in the mechanical properties similar to the natural bone due to the bio-mimicking structure. The MWCNTs addition and increase hot-press pressure are played a very noticeable role in this modification. The composites with 1 % weight of MWCNT at (114 Mpa) hot-press pressure exhibited the highest fracture strengths (148, 147 Mpa) with composite (40%HA/HDPE) and (20%HA/HDPE) respectively. Also, the Vickers microhardness increased with an increase in MWCNT content, the maximum value (21 Hv) marked when MWCNT addition was up to 2% weight at (86Mpa) hot-press pressure. This study's present sample features with homogenous fibrous, and high mechanical strength could be considered a promising biomaterial for bone reconstruction in the load-bearing application.

## Acknowledgments

The authors gratefully acknowledge to the Dr Mazin Auny Mahdi /college of science/ University of Basra /Iraq, for assist to complete FE-SEM examination.

## References

[1] R. S. Taichman, “Blood and bone: two tissues whose fates are intertwined to create the hematopoietic stem-cell niche,” *Blood*, vol. 105, no. 7, pp. 2631–2639, 2005.
[2] S. C. Cowin, *Bone mechanics handbook*. CRC press, 2001.
[3] R. Marcus, D. Feldman, and J. Kelsey, *Osteoporosis, Two-Volume Set*. Academic Press, 2001.
[4] M. PHILLIPS and K. JOSHI, “Bone disease,” in *Orthopaedic Bone Cements*, Elsevier, 2008, pp. 3–40.

[5] N. N. Hung, "Basic knowledge of bone grafting," *Zorzi A. Bone Grafting. Croat. InTech, Chapters*, pp. 11–38, 2012.
[6] L. Pawłowski, "Synthesis, properties and applications of hydroxyapatite," *Ind. Chem. Oxides Emerg. Appl.*, p. 311, 2018.
[7] J. S. Kashan, "Preparation and Characterization of Hydroxyapatite/Yttria Partially Stabilized Zirconia Polymeric Biocomposite." PhD thesis, UOT, 2014.
[8] J. S. Kashan, A. Jha, A. D. Thamir, and J. T. Al-Haidary, "A kinetic analysis of the melting HA/Y-PSZ/HDPE nano bio composite for hard tissue materials," *J. King Saud Univ. Sci.*, vol. 30, no. 4, pp. 286–295, 2018.
[9] Y. Akgul *et al.*, "Mechanical, tribological, and biological properties of carbon fiber/hydroxyapatite reinforced hybrid composites," *Polym. Compos.*, 2020.
[10] C. Z. Liao, K. Li, H. M. Wong, W. Y. Tong, K. W. K. Yeung, and S. C. Tjong, "Novel polypropylene biocomposites reinforced with carbon nanotubes and hydroxyapatite nanorods for bone replacements," *Mater. Sci. Eng. C*, vol. 33, no. 3, pp. 1380–1388, 2013.
[11] K. Lawton, H. Le, C. Tredwin, and R. D. Handy, "Carbon Nanotube Reinforced Hydroxyapatite Nanocomposites As Bone Implants: Nanostructure, Mechanical Strength And Biocompatibility," *Int. J. Nanomedicine*, vol. 14, p. 7947, 2019.
[12] J. Xu *et al.*, "The Application of Multi-Walled Carbon Nanotubes in Bone Tissue Repair Hybrid Scaffolds and the Effect on Cell Growth In Vitro," *Polymers (Basel).*, vol. 11, no. 2, p. 230, 2019.
[13] M. K. Fahad, "Stresses and failure in the diametral compression test," *J. Mater. Sci.*, vol. 31, no. 14, pp. 3723–3729, 1996.
[14] D. Li, L. Zhou, X. Wang, L. He, and X. Yang, "Effect of crystallinity of polyethylene with different densities on breakdown strength and conductance property," *Materials (Basel).*, vol. 12, no. 11, p. 1746, 2019.
[15] M. S. Barabashko, M. V Tkachenko, A. A. Neiman, A. N. Ponomarev, and A. E. Rezvanova, "Variation of Vickers microhardness and compression strength of the bioceramics based on hydroxyapatite by adding the multi-walled carbon nanotubes," *Appl. Nanosci.*, pp. 1–8, 2019.
[16] S. Dabees, B. Ahmed, and M. Sanad, "Experimental Design of AL2O3/MWCNT/HDPE Hybrid Nanocomposites for Hip Joint Replacement," 2020.
[17] Z. Jia, J. Zhang, C. Jia, J. Nie, and K. Chu, "Preparation and characterization of mechanical properties of carbon nanotube/45S5Bioglass composites for biologic applications," *Mater. Sci. Eng. A*, vol. 528, no. 3, pp. 1553–1557, 2011.
[18] M. Tasyurek, S. Ekinci, and M. Mirik, "Investigation of Mechanical Properties of Carbon Nanotubes/High Density Polyethylene Composites Produced by Extrusion Method," *Athens J. Technol. Eng*, vol. 2, pp. 181–192, 2015.
[19] S. Kanagaraj, F. R. Varanda, T. V Zhil'tsova, M. S. A. Oliveira, and J. A. O. Simões, "Mechanical properties of high density polyethylene/carbon nanotube composites," *Compos. Sci. Technol.*, vol. 67, no. 15–16, pp. 3071–3077, 2007.