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Characteristic of polypropylene nanocomposite material reinforcement with hydroxyapatite for bone replacement

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ABSTRACT

Purpose: Human bone suffered some degeneration due to age and accidents; therefore, there are many interests in the prepared synthetic bone with properties nearer to natural bone. The present study prepared a nanocomposite of polypropylene reinforced with different weight fraction of Nano hydroxyapatite (HAp) to be used as a bone replacement with good biological properties that enhanced the growth of osteoplastic cells and enhance the prevention of clots and coagulates creation.

Design/methodology/approach: Nanocomposite from polypropylene reinforced with different weight fraction of Hydroxyapatite (HAp) (1,2 and 3) % prepared by first dispersion Nano hydroxyapatite insolvent and then mixing with a pellet of polypropylene by the twin-screw extrusion process, the current research study the surface properties (atomic force microscopy (AFM), contact angle test) Moreover, it studied the characteristics of prepared nanocomposite materials (Differential Scanning Calorimetry (DSC), Field Emission-Scanning Electron Microscopy (FE-SEM) and Fourier Transform Infrared (FTIR)).

Findings: The AFM results show the surface roughness decreased with increasing content of HAp, which diminished the chance of creation clots and coagulates on it. The contact angle results referred to polypropylene behaviour transformed from hydrophobic to hydrophilic with addition HAp that permission to grow the osteoplastic cell on it, so the healing process is accelerated. Moreover, the FE-SEM images revealed uniform distribution and good bonding between polypropylene and Hydroxyapatite. The thermal properties were measured by the DSC test showed the melting temperature, and the enthalpy of melting (indicated to increase the crystalline structure per cent) are increased with increasing the percentage of Hydroxyapatite.

Research limitations/implications: This research studied the characteristics of nanocomposite materials prepared by three steps (dispersion by ultrasonic device, manually mixed and melting and mixing by twin extruder) which can be used as a bone replacement. However, the main limitation was the uniform distribution of nano-hydroxyapatite within the matrix. In a further study, the cytotoxic test can be tested to study the effect of prepared nanocomposite on living cells' growth.

Practical implications: The interest object is how to connect among different properties to prepared bone replacement with good properties and biocompatibility that made able to stimulate the growth and healing process.

Originality/value: The nano-hydroxyapatite is a biomaterial that has a composition similar to the natural mineral phase of the bone and does not have any negative effect, which enhanced the growth of osteoplastic cells and decreased the clots and coagulates creation; therefore, nano-hydroxyapatite is used to decrease the surface roughness which decreased the chance of coagulation creation and to enhance the hydrophilic properties.

Keywords: Polypropylene, Hydroxyapatite, Osteoplastic cells, Surface roughness, Contact angle, Wettability, Bone replacement, Clots and coagulates creation

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BIOMEDICAL AND DENTAL ENGINEERING AND MATERIALS

1. Introduction

The bone is one of the essential organs in the human body that plays an animated role in organizing the muscles to achieve numerous activities and react to environmental variations, also providing mechanical maintenance and keeping the tissues inside the body, hematopoiesis, and mineral loading [1-4]. Besides, it can organize the muscles to achieve numerous activities and react to environmental variations. Though a bone has a certain ability for revival and self-healing [1,5], big segmental bone imperfections caused by critical shock, growth resection, cancer, or inherited illnesses can only be restored by bone implanting. There was a growing mandate for that termed bone-implant replacements at latest times, [6]. In the United States, over 2000000 surgical procedures are proceeding yearly to healing injured or broken bones by implanting. Figure 1 showed the structure of natural bone. A normal bone is contained from organic and inorganic ingredients [1], where collagen fibres are the organic ingredients [7]. The primarily calcium (Ca) and phosphorus (P) in the crystals of Hydroxyapatite (HA), besides the other elements such as sodium (Na) and potassium (K) are the inorganic ingredients. The structure of natural bone was considered a multi-scale structure that can be conformed from cortical and cancellous bone [1].

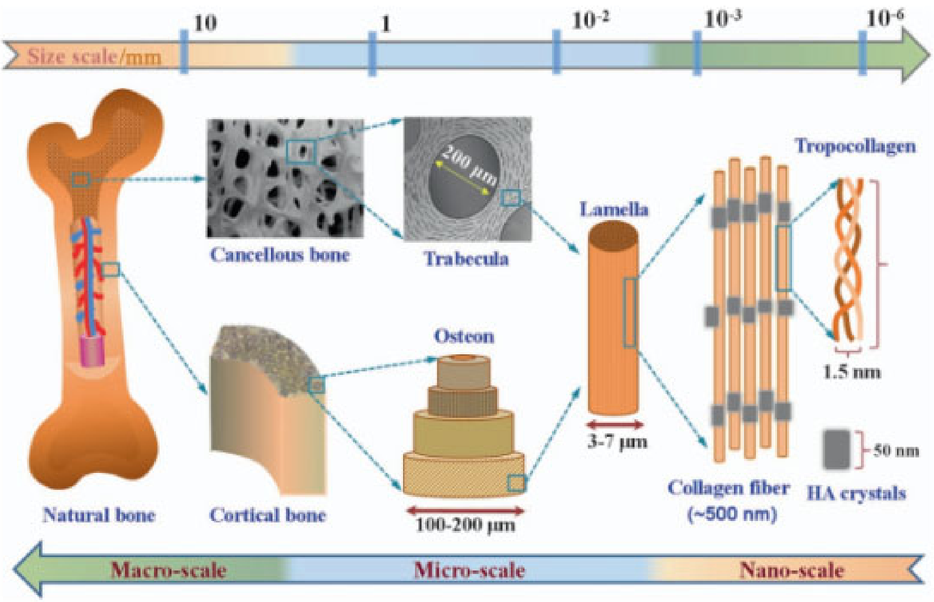

Fig. 1. The chemical composition and multi-scale structure of natural bone [1]

The greatest orthopaedic implants are made of metallic constituents, comprising stainless steel, cobalt-chromium, and titanium-based alloys, due to their high mechanical strength and good ductility. But their Young modulus surpassed that of human bones, which generates a stress shielding effect of the adjacent bone tissue, leading to carry a higher amount of the implant's applied weight. Subsequently, the failure resulted from the resorption and loosening process of the metallic implant. Furthermore, at 37°C, the human body fluids with 0.9 w.t % sodium chloride are antagonistic to metallic materials that are subject to corrosion and cause liberating metallic ions that prompt inflammation, allergically, and cytotoxic reaction [8]. Due to its lightweight, ease of fabrication, and relatively low cost of polymers, it posse a suitable application in the biomedical field [9]. Their tensile stress and modulus can be checked by reinforced with fillers at micrometre sizes [8,10]. Therefore, composite technology is an active method for manufacturing bone grafting from polymer with favourite mechanical features.

Polypropylene (PP) is a biocompatible and bio-stable polymer [11], and it is stronger and stiffer compare with polyethene PE. For bioactive composites, polypropylene seems a proper matrix than PE. It shows better mechanical properties in case of fatigue and at elevated temperatures, it is less detrimental to the deterioration of mechanical properties, which are an essential property for bone grafts, because implants must provide adequate mechanical properties at body temperature (37°C) and withstand millions of charge-discharge cycles. Conversely, the study of polypropylene composites reinforced by hydroxyapatite has been very incomplete and nonsystematic [12]. Mid all bioactive bio-ceramics, hydroxyapatite HAp is the greatest material studied for hard-tissue replacement and growth due to its close likeness to the main inorganic constituent of normal bone and outstanding bio-compatibility and bio-activity (i.e., good osteoconductivity) [11,13]. As HAp is a weak bio-ceramic, it cannot be employed alone as a load-bearing bio-material. Though, with its desired osteoconductivity, hydroxyapatite HAp has been widely employed as coatings on metal grafts and as the bioactive reinforcement phase in biomedical composites [11,14,15]. The connection and growth of osteoblasts are pointedly improved on the surface of nHA fillers. Besides, by the addition of nHA particles, the content of filler in thermoplastic polymers can be extremely decreased. At the same per cent of the filler, the Nano-Hydroxyapatite/polymer nanocomposites display superior mechanical properties compared with conventional micro-hydroxyapatite/polymer composites. Nano-hydroxyapatite offers excellent biocompatibility, biodegradability, and osteoconductive and osteoinductive properties [16,17] and has been broadly used for numerous biomedical uses.

In the current study, the nanocomposite materials of polypropylene reinforced with different nano-hydroxyapatite weight fractions (1,2 and 3) nHAp % were prepared to use as a bone replacement. The objective of HAp used to support mechanical, thermal, and surface properties of polypropylene, enhance the growth of osteoblastic cells, and avoid the creation of clots and coagulates on the surface of bone replacement.

2. Materials and experimental procedures

2.1. Materials and methods

Nanopowder of Hydroxyapatite (HAp) with model MH-HAP04 and particle size 20 nm are acquired from N&R INDUSTRIES, INC. HAp is weighted according to the per cent of addition tabulated in Table 1 and dispersed in acetone using the ultra-sonication device for 20 min. After that, the pellet of polypropylene (PP) is added gradually and manually mixed for 15 min, and then the mixture is dry by oven at temperature 80°C for 30 min to evaluate the acetone. Then the mixture is melted and remixed by a twin extruder. Extruder reigns' temperature is 130°C and 155°C to obtain a sheet of composite materials with a uniform dispersion of hydroxyapatite within polypropylene.

Table 1.
Weight Fraction of Nanocomposite Materials

Nanocomposite Material	The Percent of (PP) w.t%	The Percent of (HAp) w.t%
Neat PP	100	0
PP / 1% HAp	99	1
PP / 2% HAp	98	2
PP / 3% HAp	97	3

2.2. Properties measurement

Fourier Transformation Spectroscopy (FTIR)

The test of FTIR was achieved by using Fourier transform infrared spectrometer type IR Affinity-1. The test was carried out to study the nature of the interaction between the nano-hydroxyapatite and polypropylene and the shifting of the bands due to the additional reinforcement phase.

Differential Scanning Calorimetry measurements (DSC)

The test was carried out according to ASTM (D3418-03) under the atmosphere of nitrogen gas, the samples of prepared nanocomposite materials were placed in aluminium pans with the weight of (8-10) ± 0.5 mg and heating with a heat rate of 10°C / min from 25 °C to 250°C.

Atomic Force Microscopy (AFM Test)

The AFM test is used to study and analyze the interaction between the probe and the surface of prepared materials and provide a three-dimensional image of the topography of the sample's surface.

Field Emission-Scanning Electron Microscopy (FE-SEM Measurement)

The FE-SEM measurement was used to study the fracture surface, the distribution, and the nature of adhesion of hydroxyapatite nanoparticles within the matrix. The samples are spluttered by gold to improve the samples' electrical conductivity to obtain pictures of the sample's surface.

Contact Angle Test

The test was carried out by using the device, SL 200C - Optical Dynamic I Static Interfacial Tensiometer & Contact Angle Meter. The aim of this test is to study the effect of the nano-hydroxyapatite on the wettability of polypropylene which predicted the formation of a clot on the surface of the implant.

3. Results and discussion

3.1. FTIR measurements

The FTIR spectrometer test is a means to study the effect of reinforcement materials on the chemical structure of polymer (polypropylene), the band value, and its change due to addition nanomaterials (hydroxyapatite) shown in Figure 2 and tabulated in Table 2. The bands of neat polypropylene (PP) shown in Table 2 correspond with the value of bands in literature [18]. Figure (2) revealed the transmission band at 808.17 cm^{-1}, 840.96 cm^{-1}, 972.12 cm^{-1}, and 997.20 cm^{-1}, 1166.93 cm^{-1}, 2868.15 cm^{-1} and 2914.22, which are C-C stretching, C-H rocking, CH_3 rocking and C-C stretching, C-H wagging and CH_3 rocking, CH_3 stretching, and CH_2 asymmetrical stretching, respectively do not change with the addition of the hydroxyapatite. While the CH_3 symmetrical bending bands at 1369.46 and 1452.40 cm^{-1} were shifted to 1369.82 and 1454.33 cm^{-1} respectively, and the CH_3 asymmetrical stretching band at 2953.02 cm^{-1} was shifted to 2949.16 cm^{-1}. Moreover, it is indicated that no chemical bond is created, but the shifting process that happened in some transmission bands indicated the uniform dispersion of nanoparticles (HAp) within the polymer and good bonding between them [19].

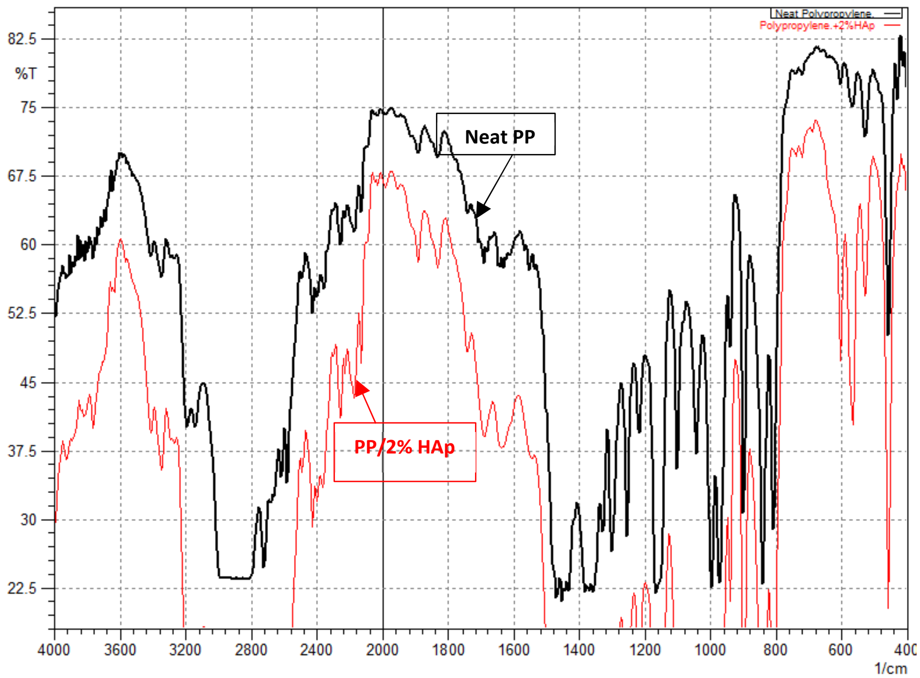

Fig. 2. FTIR Spectrum of Polypropylene Composite Materials as a Function of HAp%

Table 2.
The Transmission Bands of IR Spectrum for Polypropylene Composite Materials

Type of bond	PP standard [18]	Neat PP	PP+2% HAp
C-C stretching	808	808.17	808.17
C-H rocking	840	840.96	840.96
CH_3 rocking C-C stretching	973	972.12	972.12
CH_3 rocking C-C stretching	996	997.20	997.20
C-H wagging CH_3 rocking	1166	1166.93	1166.93
CH_3 symmetrical bending	1376 1456	1369.46 1452.40	1369.82 1454.33
CH_3 stretching	2870	2868.15	2868.15
CH_2 asymmetrical stretching	2920	2914.44	2914.44
CH_3 asymmetrical stretching	2950	2953.02	2949.16

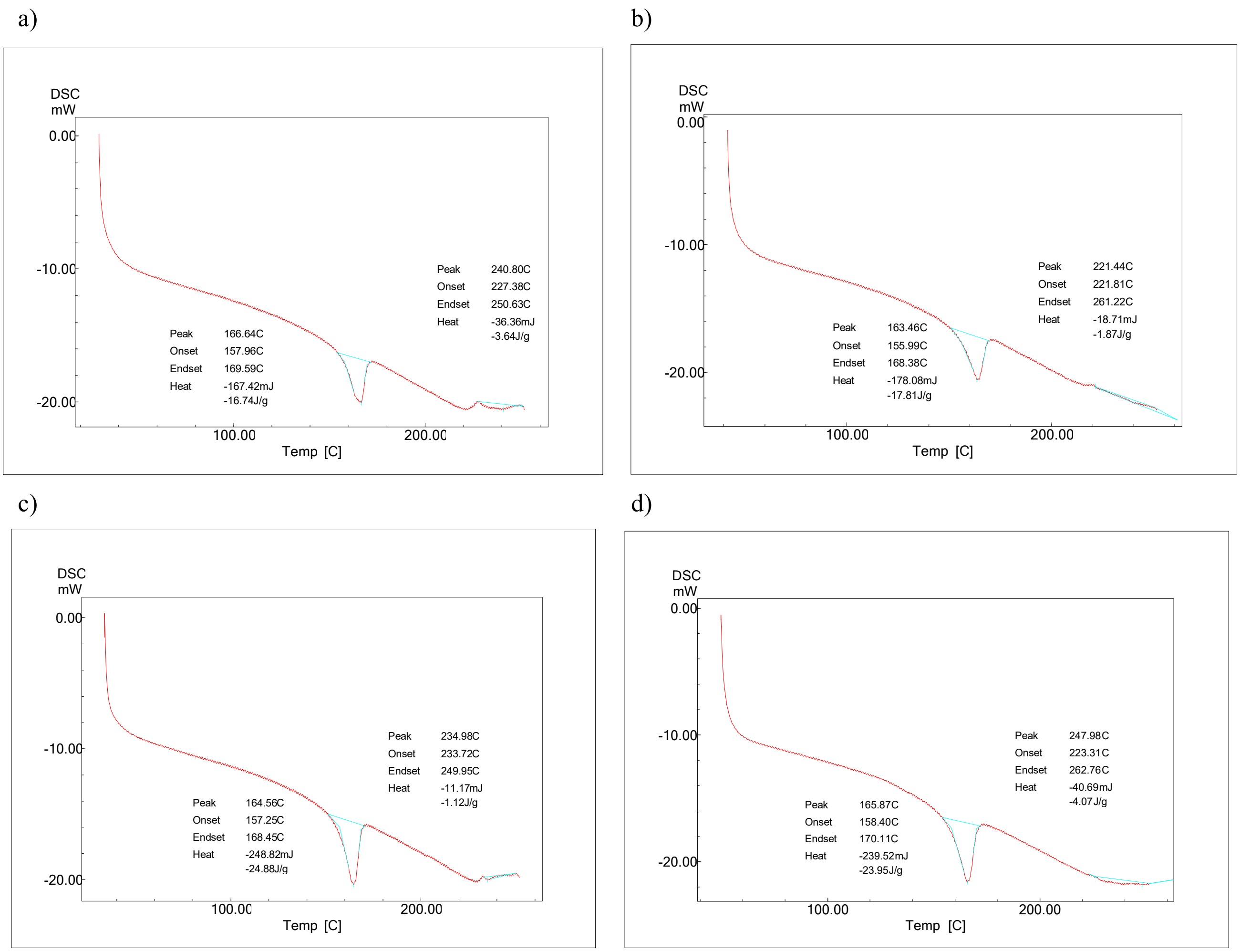

Fig. 3. DSC measurement of melting cycle for nanocomposite materials as a function of HAp: a) neat PP, b) PP/1%HAp, c) PP/2%Hap, d) PP/3%HAp

3.2. DSC measurements

The Differential Scanning Calorimetry (DSC) analysis of the melting endotherm cycle 25-250°C for nanocomposite materials is revealed in Figure 3. The melting temperature and its range (onset and ends) are increased with increasing the weight fraction of Hydroxyapatite (HAp) due to the good thermal properties of HAp [21]. Moreover, the enthalpy of the heating cycle (ΔH_m) increased with increasing the percentage of HAp, which indicates good dispersion of hydroxyapatite within the matrix (PP) and increases the ratio of crystalline that needed more heat to melt the crystalline structure [22]. The degradation temperature which appeared in the curve was increased with increasing the percentage of hydroxyapatite that proved the thermal stability of nanocomposite increase with increasing the content of hydroxyapatite.

3.3. AFM measurements

The results of AFM show the surface roughness (Roughness Average and Root Mean Square) is decreased with increased the weight fraction of nano-hydroxyapatite (HAp) as illustrated in Table 3 due to the nanoparticles fill the voids in the surface of the matrix and also attributed to the uniform distribution of HAp within polypropylene (PP). These results can help avoid creating clots on synthetic bone and permit the growth of the osteoblastic cells on it [20,21].

Table 3.
The Surface Roughness of Nanocomposite Materials as a function of HAp

Nanocomposite Materials	S_a (Roughness Average) nm	S_q (Root Mean Square) nm
Neat PP	13.4	16.7
PP+1%HAp	4.65	5.88
PP+2%HAp	4.5	5.72
PP+3%HAp	1.1	1.39

Figure 4 shows the three-dimension topography of nanocomposite surfaces which revealed a uniform distribution of hills within the matrix. These hills' height decreased with increasing hydroxyapatite (HAp) ratio, which enhance and correspond with surface roughness results [20].

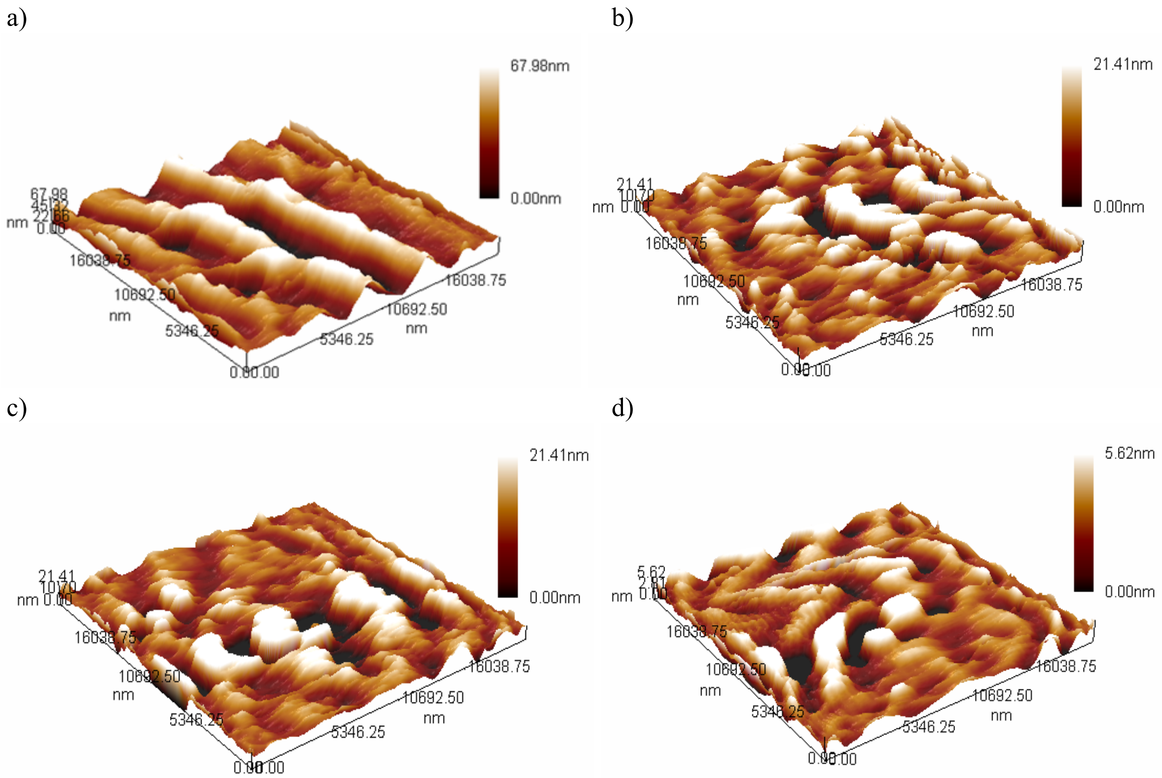

Figure (4) three-dimension topography of nanocomposite materials as a function of hydroxyapatite (HAp): a) neat PP, b) PP/1%HAp, c) PP/2%Hap, d) PP/3%HAp

3.4. FE-SEM measurements

Figure 5 shown the images micrograph of fracture surface for nanocomposite materials reinforced with (1, 2 and 3) w.t % of HAp at magnification 5, 10 and 25 kx, which revealed a good dispersion of hydroxyapatite and embedded within the polypropylene and also show good wettability and interfacial bonding between HAp and polypropylene [23]. Moreover, images showed that the fracture surface was free from voids and defects, and the distribution of hydroxyapatite within polypropylene is similar to the distribution of the nanoparticles in PP reported in the literature [8]

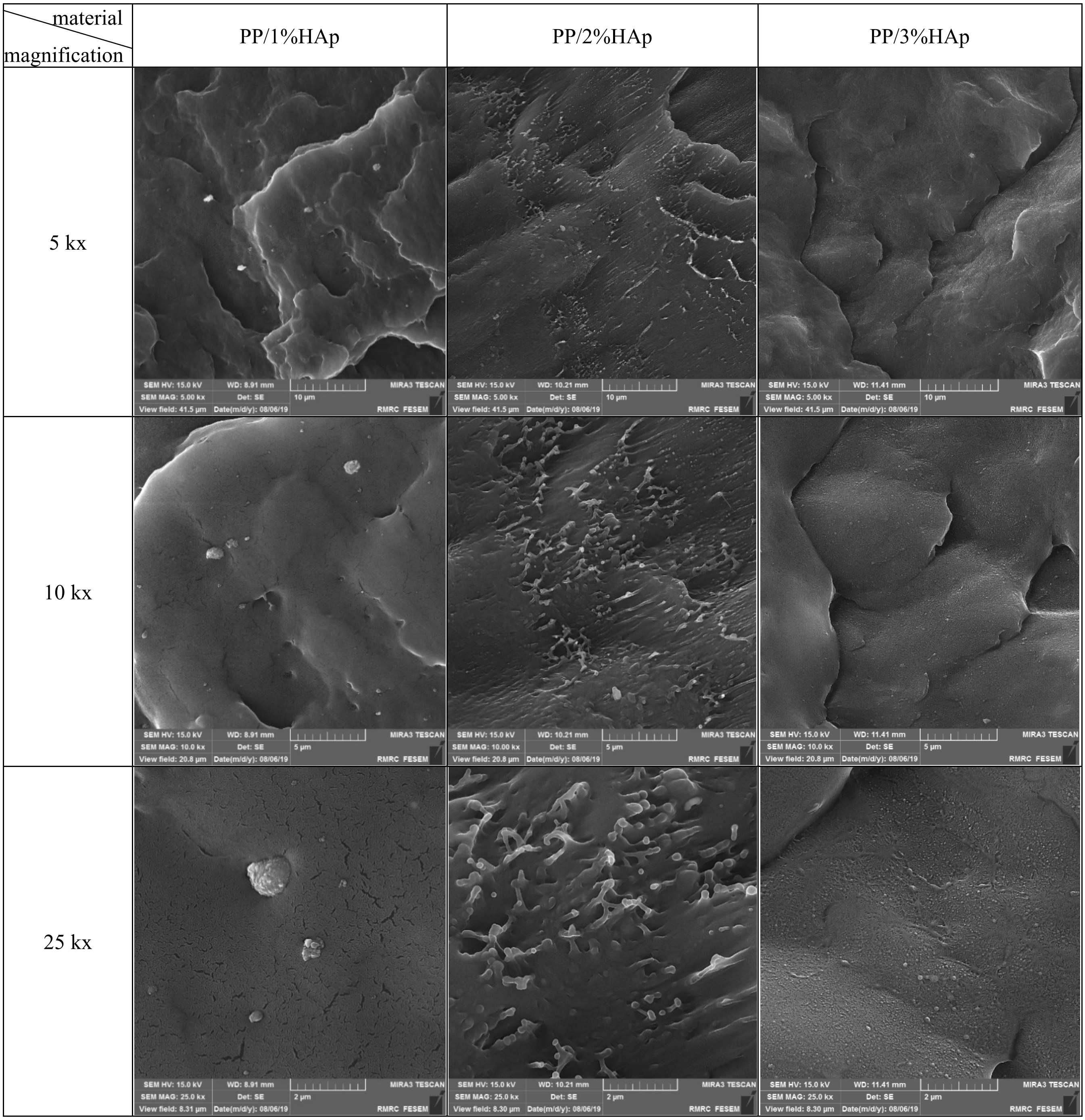

Fig. 5. FE-SEM of a fracture surface of nanocomposite reinforced by different weight fraction of HAp

The uniform distribution of HAp in polypropylene returned to the methodology of the preparation process considered in the present work – dispersion of HAp in acetone by ultrasonic and melt mixture of polypropylene and HAp by twin-screw extruder.

3.5. Contact angle measurements

Figure 6 show the contact angle analysis by the circle fitting method between the water drop and the surface of the nanocomposite. As revealed in Table 4, the contact angle (CA) decreased with increased the weight fraction of Hydroxyapatite (HAp)%, which develop the wettability (became more hydrophilic) that enhances the growth of the osteoblastic cells on the synthetic bone (nanocomposite material) [22].

The contact angle (CA) of nanocomposite materials decreased with the time 0, 60 and 180 sec but still more stable (low diminish in contact angle) compare with pure polypropylene, such as at 2 %HAp, the contact angle (CA) is 82.056°, 75.421°, 68.925° at the time 0, 60 and 180 sec respectively. In contrast, the CA of neat polypropylene is 85.827°, 76.531°, 35.498° at the time 0, 60 and 180 sec, respectively, which decreases the probability of creation coagulates and clots on the surface of synthetic bone.

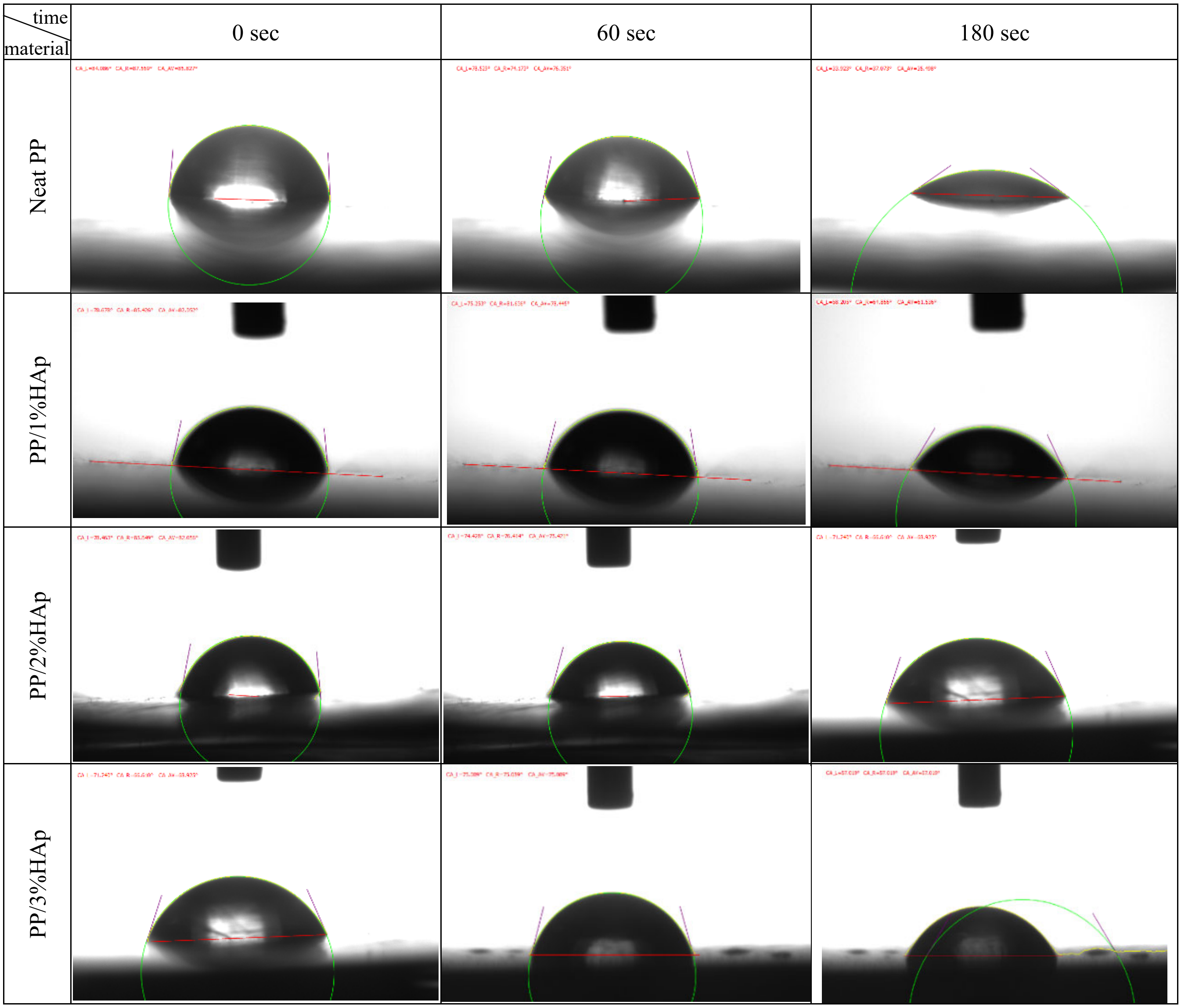

Fig. 6. The contact angle for composite material as a function for hydroxyapatite HAp

Table 4.
The contact angle for nanocomposite materials as a function of hydroxyapatite HAp

Nanocomposite Material	Contact Angle, °	Time, sec
Neat PP	85.827	0
	76.531	60
	35.498	180
PP+ 1% HAp	82.052	0
	78.445	60
	61.536	180
PP+ 2% HAp	82.056	0
	75.421	60
	68.925	180
PP+ 3% HAp	77.934	0
	75.089	60
	57.019	180

4. Conclusions

The goal of using the hydroxyapatite as a filler in polypropylene is to enhance the growth of osteoblastic cells and decrease the chance of clots or coagulates creation by increase the wettability (decreased CA) and decrease the surface roughness. Moreover, the FE-SEM revealed the homogenous distribution of HAp and good bonding and embedded with polypropylene. The FTIR results referred to no chemical bond create but referred to shifting in the transmission bond due to the polymer's uniformed distribution of HAp. Finally, the DSC results referred to improve thermal properties, increase the melting temperature and the enthalpy of melting, which referred to enhance the crystalline structure of nanocomposite materials.

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