

The Effect Of Nano-Hydroxyapatite On Some Mechanical Properties Of Polyethylene Glycol-Carnauba Wax Composite.

Randa K. Hussain

Physics Department, College of Science Al-Mustansyriyah University, Baghdad, Iraq.

Natheer N. Mahmoud

Ministry of Science and Technology, Baghdad, Iraq.

Corresponding author, Email :ahmed_naji_abd@yahoo.com

Abstract—Structure and mechanical properties of PEG-Carnauba wax/nano-HAP composites were studied. XRD analysis proved a nano-HAP particle formation in range 9.5nm, and XRD of composite SEM results showed a crack in composites at using high HAP concentration. The strength in compression and tensile strength decreased with filler increasing, as well as the ultimate stress show a decreasing in both of composite and tensile. The modulus of elasticity obtained by compression and tensile have higher values at 1%wt of HAP to reach (706.75 MPa) and (32.95 N) respectively

Keywords—Bone tissue, HAP, Compression, tensile, nanocomposite.

1. Introduction

Bone has unique mechanical properties, it is one of the body's hardest materials and a natural composite material consisting of both solid phases and fluid, described as a connective tissue, Bone tissue able to repair itself and adapt to changing environmental stresses[1]. Unfortunately, this hard components "bones" may be destroyed or ill because of accidents or diseases, this leads to looking for substitution tissues very close to building structure of natural tissues, has the same performance, and nontoxic when implemented in human body. Many suggestions of synthesis a nanocomposite were successful to be the artificial tissues of this a bioactive material is one which when used as an artificial tissue makes a chemical bond with the natural tissue thus strengthening the implants. Bone implants should possess good biocompatibility, biostability and mechanical properties similar to those of human cortical bones. Nano Hydroxyapatite (nano-HAP) is one of major

constituent elements of the human body it is found in 60% of bones[2]. HAP can be summarized with three important key words bone compatibilities, high absorptivity, and unique ion exchangeability and have widely applied as biomedical materials, including such uses as bioactive coatings, soft tissue repairs, drug/protein/gene loading and delivery systems[3]. Nano-HAP still cannot be used as a stand-alone material for load bearing implants, it can be used as a filler to enhance the biocompatibility and mechanical strength of polymers. The nanocomposite that synthesis for bone engineering is basically consists of polymer as matrix like polyamides (PAs) [4], polyethylene (PE) [5], poly(vinyl chloride) (PVC)[6], poly(ethylene terephthalate) (PET)[7], poly(ether ether ketone) (PEEK)[8], poly(glycolic acid) (PGA)[6] and their copolymers (PLGA) [9]. In this search, the structural and mechanical properties were studied for PEG-Carnauba wax /nano-HAP 5555 composite at room temperature. The polymer used is polyethylene glycol of 8000 molecular weight, mixed with 10% weight ratio Carnauba wax as a matrix, the filler is used with (1%, 3%, 5%) weight ratio.

2. Materials and methods

a. Materials

The material required diammonium hydrogen phosphate $(\text{NH}_4)_2\text{HPO}_4$ and Calcium nitrate $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ obtained from Merck (Russian)

and PEG (8000 MW) from (India). Deionized Water was used as the solvent and Carnauba wax (U.S.A.).

b.Methods.

i.Synthesis of nano-HAP.

They have several methods were used to produce the nano crystalline HAP. One of these methods is done by direct synthesis from Ca^+ and PO_4^{-3} sources this is know a wet chemical technique (aqueous based solvent) . In this method a 0.5M of diammonium hydrogen phosphate $(\text{NH}_4)_2\text{HPO}_4$ solution in 75ml of deionized water is slowly added to 0.5M Calcium nitrate $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ solution in 75ml of deionized water of under continues stirring the total volume 150ml. The pH was adjusted within 10 to 11 by addition ammonia solution NH_4OH (28%). The reaction was allowed to proceed for 24 hr with constant stirring , The resulting white precipitate was washed thoroughly three times with deionized water and oven dried at about 50°C overnight.

2.2.2 Synthesis of HAP/PEG-carnauba wax nanocomposites

Nanocomposite have been prepared by melt PEG with Carnauba wax in beaker using stirrer for the mixing process to obtain more homogeneous solution thick with temperature 80°C , then adding nano-HAP with using ultrasonic waves to aiding dispersion of the filler and creating a more homogenous solution thick than casting method in molds is used to preparation the specimens.

3-Results and discussion

3.1XRD analysis

The structure of the samples were analyzed by X-ray diffraction (XRD) using a device of the model (Shimadzu XRD-6000 / Japan) with $\text{Cu-K}\alpha 1$ radiation ($\lambda = 1.5406 \text{ \AA}$), the XRD pattern of nano-HAP particle is shown in figure (1); the peaks are broadening which means that the particle size are very small, that lies in range of (9.5-22)nm. The HAP pattern has eight principle peaks appear corresponding to Miller indices (002), (210), (211), (300), (310), (203), (213), and (004) within range (10-80) degree (2 θ). This

is very close to (ICDD 09-0432), the crystalline hydroxyapatite (P63/m) belonging to the hexagonal symmetry, it is matching well with an articles[10] and [11].

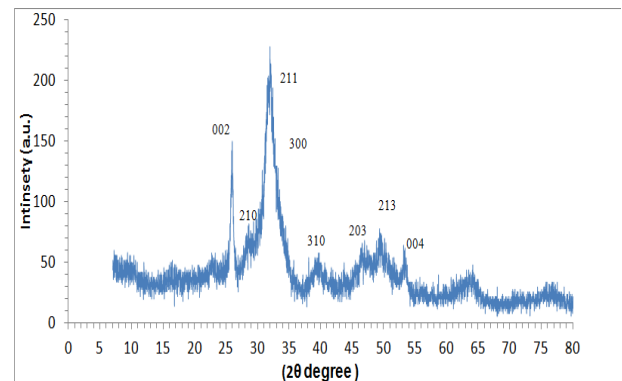


Fig.(1) XRD of nano-HAP by starting chemicals ions aqueous based solvent in room temperature

Figure (2) illustrated the XRD of PEG-carnauba wax with nano-HAP composite with ratio (1% and 5%)wt , it is seems that the diffraction of PEG tended to cover the reflection of nano-HAP and Carnauba wax, therefore, a strong reflections at 2θ of 19.203° , 23.324° were observed . Table (1) summarized the values of d-space, intensity, and FWHM of PEG-Carnauba wax/nano-HAP composite from, table it is clear that the decreasing of d-space and intensity with increasing weight ratio of HAP powder, but FWHM is increasing as HAP content increasing.

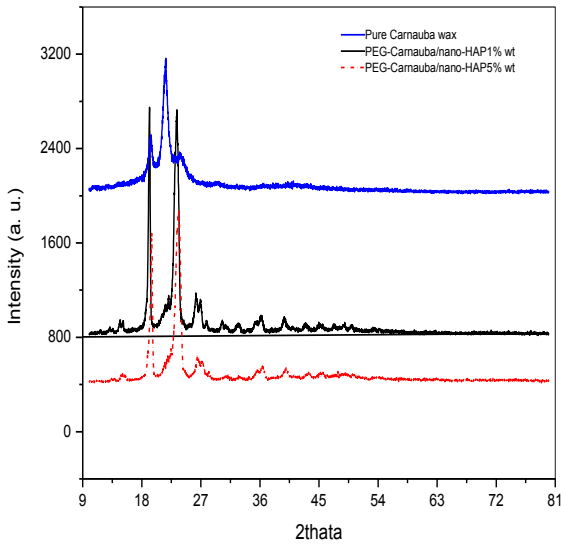


Fig.(2) XRD patterns of PEG-carnauba wax with HAP nanoparticles compsite (1wt% , 5wt%).

Table(1) PEG-carnauba wax/nano-HAP composite with deferent weight ratio.

PEG – Carnauba wax (wt)	Nano-HAP %wt	2θ (dig)	d-space (nm)	FWHM (degree)	Intensity (a.u.)
(90% - 10%)	1 %	19.203	0.462	0.300	1227
		23.324	0.381	0.770	1162
	5%	19.494	0.455	0.564	600
		23.571	0.377	0.905	917

crystallite size was calculated by the equation (Debye-Scherrer) equation (1) ,which is used to calculate the particle size for each sample [12]:

$$D = \frac{0.89 \lambda}{\beta \cos \theta} \quad (1)$$

Where crystallite size (D), λ is the wavelength of CuK α , β the full width at half maximum (FWHM) in radian and θ the diffraction angle (degree).

Table (2) introduce the crystallite size of PEG-Carnauba wax /nano-HAP it is found that the 1%wt HAP content has higher crystal size than 5% wt.

Table(2) The crystallite size of PEG-carnauba wax /nano-HAP composite in ratio.

PEG-carnauba wax /nano-HAP				
HAP wt%	2θ (degree)	FWHM (degree)	D (nm)	D _{avrg} (nm)
1 %	19.203	0.300	26.8564	18.6975
	23.324	0.770	10.5385	
5%	19.494	0.564	14.2890	11.6270
	23.571	0.905	8.9650	

3.2-The Scanning electron microscopy SEM

The morphology of the HAP nanocrystals is rod-like shape. The particle size of rod like HAP which is about (20-30)nm in width and (55-65)nm in length small rod-like and it is agglomerated particles, as show figure (3). Figures (4) and (5) show the SEM of PEG polymer with carnauba wax composite with nano-HAP in (1% and 5%)wt weight percentage respectively. It seems that the nano-HAP is covered by the PEG polymer matrix, making it more difficult to distinguish between the PEG polymer and the HAP particles. SEM micrographs show that the particles of HAP uniformly distributed within the polymer, and they can see increasing cracks when increasing the concentration of nano-HAP, Which affects the physical properties like (compression , tensile and impact).

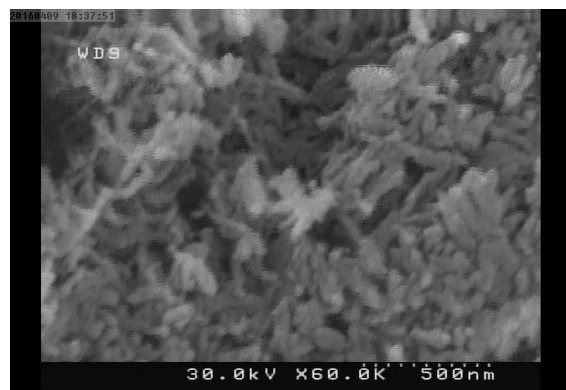


Fig.(3) SEM micrograph of HAP powders at 37° C.

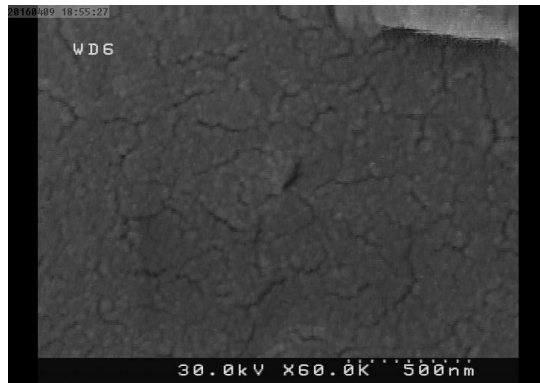


Fig.(4) SEM micrograph of PEG-Carnauba wax/HAP 1 wt% nanocomposite.

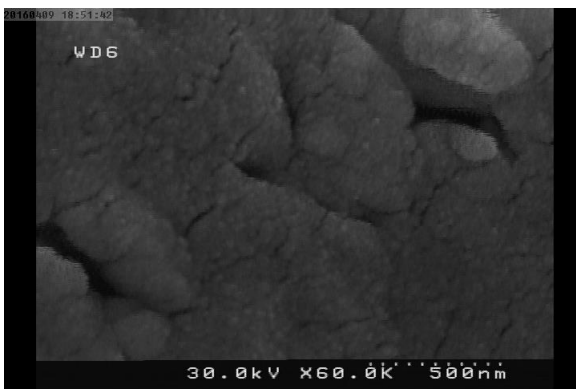


Fig.(5) SEM micrograph of PEG-Carnauba wax/HAP 5wt% nanocomposite.

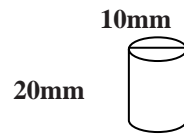


Fig. (6) standar schematic Diagram and dimensions of compression test.

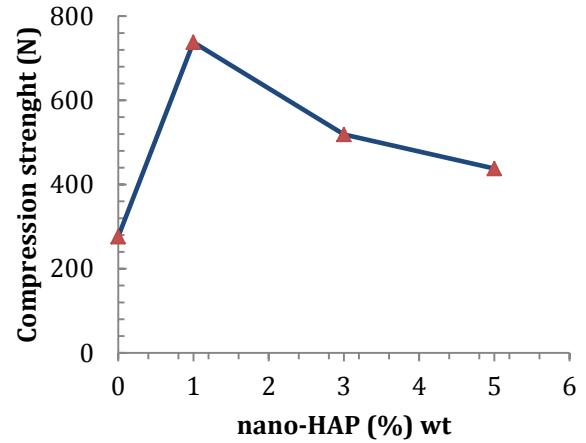


Fig.(7) Compression strength of PEG-Carnauba wax/nano-HAP.

this leads to lowed of material ability to resists the stress as increasing filler content, i.e. the ultimate stress is decreasing with nano-HAP weight ratio, that is illustrated in figure(8).

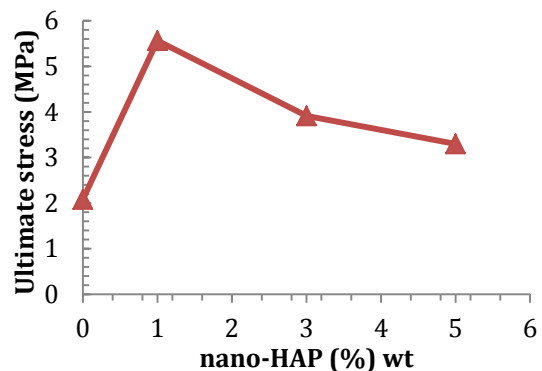


Fig.(8) Ultimate stress of PEG-Carnauba wax/nano-HAP.

4-Mechanical properties

Basically bones to compression, tensile, and impact loads. In this search the mechanical properties of PEG-Carnauba wax/HAP are related to them.

4.1 Compression strength

According to ASTM (D695) the samples were prepared in formed dimensions as in figure(6). The strength of compression applied to samples is decreased by increasing of filler content, as shown in figure (7). The nano-HAP powder acquired material resistant to compression, but more amount of HAP makes material brittle which means less resistance to compression.

4.2 Curve of stress – strain compression

The stress-strain relationship of a material is provide a valuable information about its mechanical properties..

Figure(9) show the nano-HAP effect on stress-strain relationship when filler of PEG-Carnauba wax matrix at (90%-10%)wt in room temperature. The maximum stress is decreased as nano-HAP weight ratio increasing , two regions

appear in stress-strain curves, the elastic region and the plastic region. In elastic region, the relation between stress and strain is linearly, which is from it could calculated compression elastic modulus. Materials become higher elasticity when using 1%wt of HAP, but is loose it elasticity if the filler of nano-HAP increased to 3% and 5%wt comparing to matrix elasticity. This results compatible with results in figures (7) and (8). Table (4) provides the elastic modulus of PEG-Carnauba wax and PEG-Carnauba wax/HAP composites.

According to table (4) the elastic modulus is (377 MPa) for PEG-Carnauba wax, this value decreased when that matrix is reinforced by nano-HAP to 3% and 5%wt.

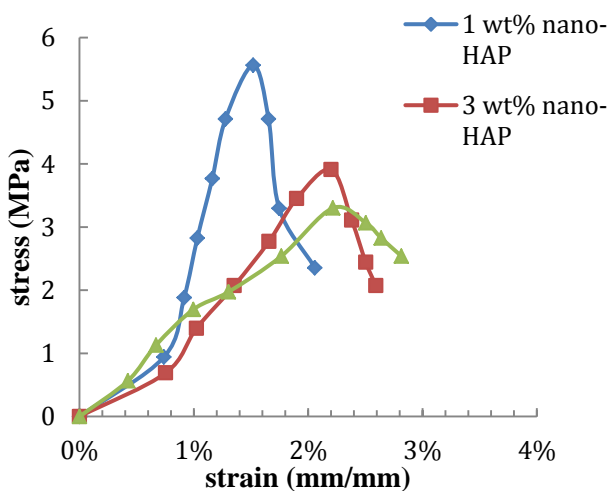


Fig.(9) Stress-strain Compression for PEG-Carnauba wax/nano-HAP.

Table(4) Elastic modulus values for PEG-Carnauba wax/nano-HAP composite.

PEG-carnauba wax (wt%)	nano-HAP wt%	E-modulus (MPa)
90% - 10%	0	377
	1	706.75
	3	275.8
	5	235.67

The highest E-modulus values is gives at (1%wt) nano-HAP comparing with (3wt%, 5wt%). This indicted that rises of higher compression of strength values have higher

resistance against compression loading. That may be due to the distribution of nano-HAP effects where the agglomeration may be happen for nano-HAP at (3wt%, 5wt%) which decreases resistant compressive strength. These agglomeration makes cracks that appears in SEM results.

Aspect ratio, the specific area (surface area to volume ratio) of nano particles have a high surface area compare the volume ,therefore a good dispersion of nanofillers into the polymer matrix is extremely difficult to disperse the nanoparticles uniformly in the polymer matrix due to the Van der Waal forces between particles and the high surface energy. Large agglomerations of nanoparticles can be viewed as defects inside the matrix, which negatively affects the mechanical properties [13].

4.3 Tensile test

According to ASTM (D638) the samples were prepared in formed dimensions as in figure(10). Effect of HAP content ratio on tensile strength and ultimate stress is introduced in figures(11) and (12) respectively. The higher tensile strength is obtained at 1%wt of HAP, which gives material a sharply increased of resistance to tensile lead comparing of matrix. More amount of HAP filler makes material weak to resist to the applied tensile load, as shown in figure(11). The same behavior happened for ultimate stress, where the peak is lies at 1%wt of HAP, as appears in figure (12).

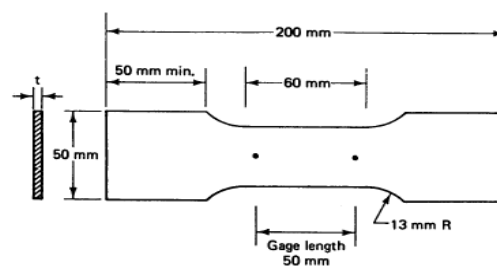


Fig.(10) Stander schematic diagram and dimensions of tensile test.

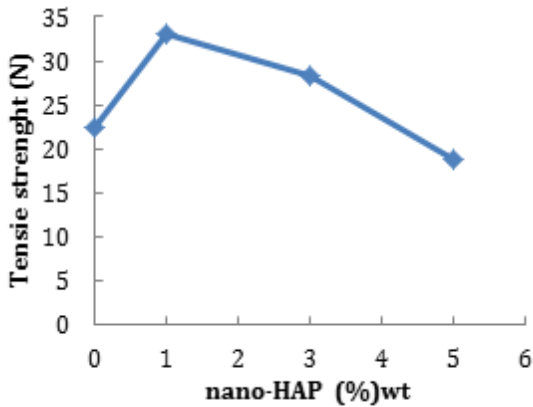


Fig.(11) Tensile strength for PEG-Carnauba wax/nano-HAP.

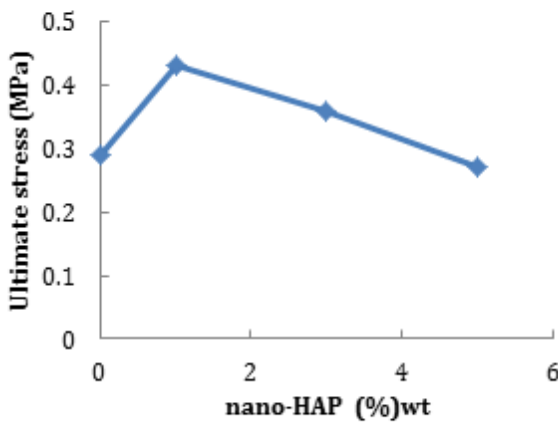


Fig.(12) Ultimate stress (MPa) for PEG-Carnauba wax/nano-HAP.

The tensile elastic modulus values of elasticity calculated from figure (12) are listed in table (5).

Table(5) the tensile elastic modulus values for PEG-Carnauba wax/nano-HAP composite.

PEG-carnauba wax (wt)	nano-HAP (% wt.	Tensile E-modulus (MPa)
90% - 10%	0	5.67
	1	18.09
	3	10.68
	5	7.08

The best weight ratio of nano-HAP were added to matrix of PEG-Carnauba wax is 1% wt. where it is observed that nano-HAP is enhanced the elasticity of PEG-Carnauba wax polymer, it is

increased from 5.67MPa to be 18.09MPa for 1% wt ratio of nano-HAP.

It is found that small additions of nano-HAP significantly affect on tensile strength, where the highest values of all enumerated parameters were obtained at the lowest contents of nano-HAP (1wt%); the values of tensile strength and stress decreased with increasing content of nano-HAP powder (> 1%) with PEG8000-Carnauba wax in different ratio. This distinct reinforcement of tensile strength properties for nanocomposites modified with small amount of HAP nanofiller suggests that there is some interaction between nanoparticles and polymer matrix. Similar behavior is obtained in case of other ceramic nanoparticles [14] that is used to modify of polymer matrix. This is compatible with [15] which suggested that mechanical properties of the nanocomposite are affected by dispersion of nanoparticles and their interaction with polymer matrix.

The results showed that low contents of nano-HAP (1 wt%) used with the polymer matrix can increase the tensile strength. But for higher nano particle content the nano-HAP will create a weak link with the polymer, thus increasing applied loading will leads to break bonding of the nanoparticle-polymer composite and displays very low plastic deformation compared to other materials and become brittle. Where the high nanoparticle contents in the specimen cause their embrittlement because are more difficult to disperse uniformly, therefore they create a weak zone in the form of voids (defect) or agglomerate nanoparticl (the Van der Waal forces between particles) and decrease the tensile strength, stress and E-modulus.

5 Conclusions

PEG-Carnauba wax is an acceptable to be the matrix of HAP particle to analog the bone tissue studies. The best HAP content is 1%wt, which has the better mechanical properties. Increasing HAP content in composite many formed a cracks that affect an mechanical properties.

6 References

- [1]. Miao, X., D.M. Tan, J. Li, Y. Xiao, and R. Crawford, *Mechanical and biological properties of hydroxyapatite/ tricalcium phosphate scaffolds coated with poly(lactic-co-glycolic acid)*, Acta Biomater, **4**(3), p. 638-45, 2008.
- [2]. Liu, C., *Collagen–hydroxyapatite composite scaffolds for tissue engineering*, p. 211-234, 2015.
- [3]. Mucalo, M., *Hydroxyapatite (HAp) for Biomedical Applications*. Woodhead Publishing Series in Biomaterials, Elsevier, p i-iii, 2015.
- [4]. KAI, L., *Fabrication and Characterization of Polymer - Hydrox-yapatite Nanocomposites for Bone Tissue Engineering*, Department of Physics and Materials Science, City University of Hong Kong, Hong Kong, p 201, 2010.
- [5]. Pielichowska, K. and S. Blazewicz, *Bioactive polymer/ hydroxyapatite (nano) composites for bone tissue regeneration*, in *Biopolymers*. Springer, 2010, p. 97-207.
- [6]. Feldman, D., *Polymer nanocomposites in medicine*, Journal of Macromolecular Science, Part A, **53**(1), p. 55-62, 2016.
- [7]. Chen, C., H. Li, C. Guo, and S. Chen, *Preparation and in vitro evaluation of a biomimetic nanoscale calcium phosphate coating on a polyethylene terephthalate artificial ligament*, Experimental and Therapeutic Medicine, **12**(1), p. 302-306, 2016.
- [8]. Najeeb, S., Z. Khurshid, J.P. Matinlinna, F. Siddiqui, M.Z. Nassani, and K. Baroudi, *Nanomodified peek dental implants: Bioactive composites and surface modification—A review*, Int. J. Dent, **2015**, p. 381759, 2015.
- [9]. Takeoka, Y., M. Hayashi, N. Sugiyama, M. Yoshizawa-Fujita, M. Aizawa, and M. Rikukawa, *In situ preparation of poly(l-lactic acid-co-glycolic acid)/ hydroxyapatite composites as artificial bone materials*, Polymer Journal, **47**(2), p. 164-170, 2015.
- [10]. Barabás, R., M. Czikó, I. Dékány, L. Bizo, and E. Bogy, *Comparative study of particle size analysis of hydroxyapatite-based nanomaterials*, Chemical Papers, **67**(11), p. 1414-1423, 2013.
- [11]. Alobeedallah, H., J.L. Ellis, R. Rohanzadeh, H. Coster, and F. Dehghani, *Preparation of nanostructured hydro-xyapatite in organic solvents for clinical applications*, Trends Biomater. Artif. Organs, **25**, p. 12-19, 2011.
- [12]. Langford, J.I. and D. Louer, *Powder diffraction*, Reports on Progress in Physics, **59**(2), p. 131, 1996.
- [13]. Jackson, M.J. and J.S. Morrell, *Machining with nanomaterials*, Springer, 2009.
- [14]. Fuad, M., H. Hanim, R. Zarina, Z.M. Ishak, and A. Hassan, *Polypropylene /calcium carbonate nano-composites -effects of processing techniques and maleated polypropylene compatibiliser*, eXPRESS Polymer Letters, **4**(10), p. 611-620, 2010.
- [15]. Mammeri, F., E. Le Bourhis, L. Rozes, and C. Sanchez, *Mechanical properties of hybrid organic–inorganic materials*, Journal of materials chemistry, **15** (35-36), p. 3787-3811, 2005.