

## Coating of Carbon Fibers with Calcium Phosphate by Sol-Gel Method

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### ABSTRACT

Sol-gel technique has been used to coat carbon fibers with calcium phosphate to improve the esthetic of black carbon fibers as it's biocompatible. To improve bonding between carbon fibers and prepared calcium phosphate powders, the surface of carbon fibers has been treated with para-aminobenzoic acid. The structural tests include: (SEM, XRD, AFM and FTIR). The morphology of the coating layers has been examined by scanning electron microscope (SEM). The crystallized phase composition of coatings has been identified by x-ray diffractometry (XRD). The grain size of dried and heat treated calcium phosphate coat has been estimated by atomic force microscope (AFM) and fourier transform – infrared spectroscopy (FTIR) analysis which support and verify the x-ray diffraction findings.

**Keywords:** calcium phosphate; carbon fiber; coating of carbon fibers; sol-gel.

### تغطية الياف الكربون بفوسفات الكالسيوم بطريقة المحلول الجيلاتيني

#### الخلاصة:

أستخدمت تقنية المحلول الجيلاتيني لتغطية الياف الكربون بفوسفات الكالسيوم، لتحسين جمالية الياف الكربون الاسود ولكونها مادة متوافقة حيويًا. لتحسين الترابط بين الياف الكربون و مسحوق فوسفات الكالسيوم المحضر، تم معالجة سطح الياف الكربون بحامض البارامينو بنزويك (para-aminobenzoic acid). تتضمن الاختبارات التركيبية (المجهر الماسح الالكتروني (SEM) و حيود الاشعة السينية (XRD) و مجهر القوة الذرية (AFM) ومطيافية الاشعة تحت الحمراء (FTIR)). مورفولوجية طبقات التغطية فحصت باستخدام (SEM). تركيب الطور المتبلور للتغطية تم تمييزه باستخدام (XRD). الحجم الحبيبي لطبقة فوسفات الكالسيوم المجففة والمعاملة حراريا تم تقديره باستخدام (AFM). ونتائج ال (XRD) دعمت بالتحاليل الطيفية للاشعة تحت الحمراء (FTIR).

### INTRODUCTION

Calcium phosphates have been widely studied for bone replacement, dental defect filling, bone tissue engineering and drug delivery applications due to their excellent biocompatibility and bioactivity.

Hydroxyapatite [ $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ ] was the most stable calcium phosphate salt. Hydroxyapatite is an inorganic compound which is a non-toxic bioactive ceramics and synthetic HAP particles were similar to the inorganic part of human bones and teeth in chemical composition and size and they were especially studied for biomaterials as reinforcement of polymer and coating of material. The preparation of HAP phases could be done by a number of novel methodologies such as solution processes, hydrothermal systems, bio-mimetic systems, sol-gel methods and so on [1,2,3].

Among the alternative methods, sol-gel synthesis of CaP powders has been recently attracted much attention due to their many advantages, which include high product purity, homogeneous molecular mixing and low processing temperature. The sol-gel process method requires a strict pH control, vigorous agitation and takes long time for hydrolysis [4].

Coatings are necessary to provide various degrees of protection. All coatings—whether used for corrosion protection, to provide good aesthetics or a pleasing appearance, or for any other purpose—will contain a film-forming material. This material may be organic or inorganic and, after application, may form a hard, impervious film, a soft porous film, or combinations in between [5]. There are different processes of coating includes physical and chemical vapor deposition techniques, thermal and plasma spraying, surface modification by directed energy techniques such as ion, electron and laser beams, thermo-chemical treatment, wet chemical and electrochemical processes such as plating, sol-gel coating, anodization, plasma electrolytic oxidation, etc. [6].

The sol-gel process is considered to be the most practical method in recent years for preparing chemically homogeneous coatings and powders with a variety of useful applications such as coating materials, adsorbents, catalysts, and biosensor, or for chemical separation [7].

Carbon fibers have good mechanical properties but poor aesthetic, therefore black carbon fibers have been coated with calcium phosphate by sol-gel method to hide the black color.

### **Experimental materials**

The materials used for coating carbon fibers are Phosphoric acid ( $\text{H}_3\text{PO}_4$ , Riedel-de Haën, ortho-Phosphorsäure 85%, chem. resin, DAB, Ph. Franç), Calcium nitrite ( $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ , Chem supply, south Australian), Absolute alcohol (GCC, Ethanol,  $\text{C}_2\text{H}_6\text{O}$ , Assay 99.99%, U.K.), and Ammonium Hydroxide (GCC, ANALYT REAGENT, Ammonia solution,  $\text{NH}_4\text{OH}$ , Assay 25%, U.K.).

### **Samples Preparation**

Carbon fibers were cut to 5mm long. Chopped carbon fibers were used, which randomly oriented in denture base is a simple preparation and gives isotropic properties to the composite.

#### **Carbon fibers were divided into two groups:**

##### **Group I:** Untreated chopped carbon fibers (UTCF)

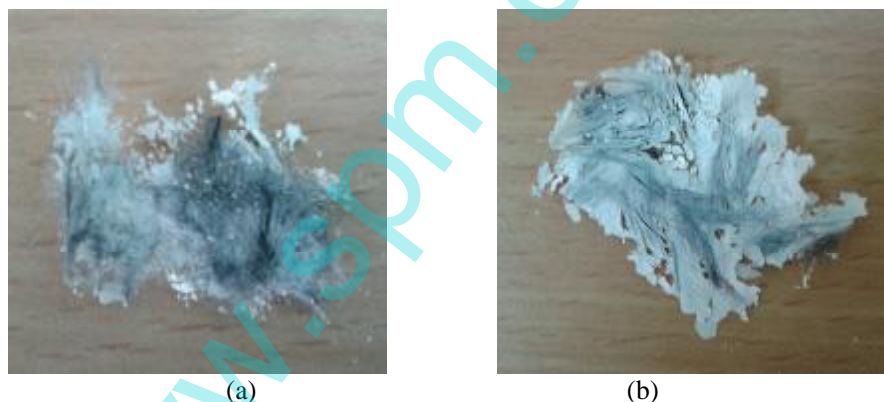
Chopped fibers were immersed into ethanol for 15 min for riddance from oxidation and to remove it from impurities, then the fibers were filtered by filtering paper to riddance from excess ethanol, and then dried in an oven at  $60^\circ\text{C}$  for about 60 min to clearing off from remains ethanol.

##### **Group II:** Treated carbon fibers (TCF)

Chopped carbon fibers were washed with ethanol as above, and then immersed into 2% (mass fraction) para-aminobenzoic acid solutions at 37 °C for 5 h. Subsequently, these fibers called modified carbon fibers were rinsed with distilled water and alcohol in sequence, and then dried in an oven at 70 °C for about 5h.

**Two procedures were used for carbon fibers coating they are illustrated as follow:**

- 1) The coating method involved the preparation of calcium phosphate coatings solution by the method reported by Michael et al. [8]. 100mL of 0.00585mol L<sup>-1</sup> H<sub>3</sub>PO<sub>4</sub> in absolute ethanol was mixed on magnetic stirrer for 5h, and 100mL of 0.01755mol L<sup>-1</sup> Ca(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O was also mixed for 5h on magnetic stirrer in absolute ethanol. And then mixed two individual solutions together. Initial mixing shows no visible reaction, the solution still stirred until a cloudy solution resulted indicating of a calcium phosphate material had occurred. Ammonia was added to the cloudy solution and stirred till a constant PH=10 in order to produce the gel. The untreated and treated fibers were immersed separately in the coating solution immediately and left overnight so that calcium phosphate formation occurred on the fibers. This coatings approach gave fibers a white coating on their surface together with settled white solid in the containing vessel, then dried in an oven at 65 °C for 5h, and then heat treated in argon atmosphere. The resulted fibers are shown below in Figures (1) a and b.



**Figure (1) coated carbon fibers – without adding HAP.**

(a) Untreated carbon fibers.

(b) Treated carbon fibers.

- 2) The coating method involved the preparation of calcium phosphate coating solution as described above from Ca(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O and H<sub>3</sub>PO<sub>4</sub> in absolute ethanol, waiting until become cloudy solution, then added ammonia to adjust PH to 10, and then added HAP powders to the solution (0.3 gm HAP for 100mL of cloudy solution). And then follow the same steps above. (For treated and untreated fibers). The resulted fibers are shown below in Figure (2) a and b. Figure (3) show the chart of calcium phosphate preparation by sol-gel method.



Figure (2) Coated carbon fibers – with adding HAP.  
 (a) Untreated carbon fibers.  
 (b) Treated carbon fibers.

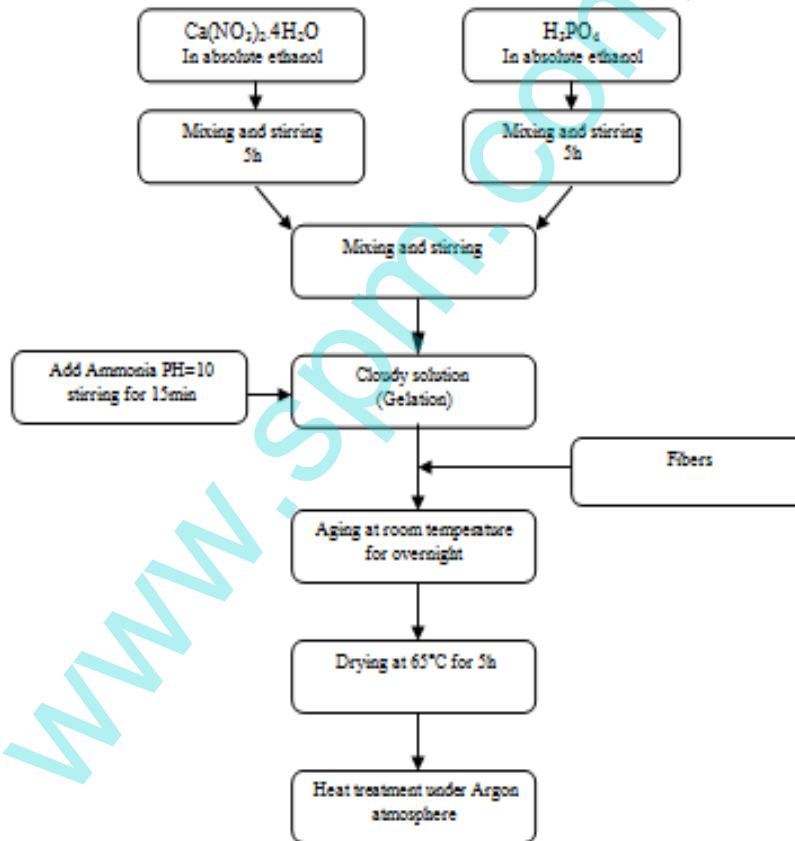


Figure (3) flow chart of calcium phosphate preparation by the sol-gel method.

### Scanning Electron Microscopy (SEM)

Morphological and microstructural features of the samples (calcium phosphate coat on the fibers substrate) were investigated by scanning electron microscopy (SEM) type (VEGA TE SCAN). A typical accelerating voltage of 20 KV was used for secondary electron imaging (SEI) of 1500 nm thickness Au coated samples.

### X-ray Diffraction (XRD)

The phase purity and the levels of crystallinity of (the rest CaP powders in vessel from sol-gel precipitation on carbon fibers) were studied by X-ray diffraction (XRD). X-ray diffraction measurement has been done according to joint committee on powder diffraction standards (JCPDS) card. A  $\text{CuK}_\alpha$  tube with radiation of wavelength  $\lambda=1.5406\text{\AA}$  operated at 40 kV and 20 mA was used for the generation of x-rays, scanning speed 5 deg/min, scan mode: continuous scan).

### Atomic Force Microscopy (AFM)

Atomic force microscopy used to measure size, granularity, accumulation, distribution, and roughness average in nano-meter or even in sub nano level. Scanning probe microscope (CSPM-5000) as instrument was used to measure grain size of calcium phosphate coating.

### Fourier Transform-Infrared (FTIR)

Fourier transform-infrared spectroscopy (FTIR) from (SHIMADZO IRFFINITY) was used in the wave number range of  $400\text{-}4000\text{ cm}^{-1}$  to support and/or verify the XRD findings, to differentiate between varying levels of relative crystallinity, and to provide evidence of ionic substitution. Experimental spectra of solid samples were obtained by preparing KBr pellets with a 3:100 "sample (CaP powder) to KBr" ratio.

## Results and Discussion

The chopped carbon fibers (treated and untreated) were used as a substrate to deposit the prepared calcium phosphate by using sol-gel method. Scanning electron microscopic analysis for coatings of carbon fibers surface was imaged. In general all coated carbon fibers exhibited good deposition and distribution of CaP coating on the surface of carbon fibers. Attachment of CaP coating on the fiber surface is quite evident in both cases as shown in Figure (4) and Figure (5). In case of untreated coated carbon fibers, it was distinct that accumulated layers of calcium phosphate formed on the fibers. This may have involved some combination of nucleation and growth, though it is plain that the bulk of the coating formed by simple settling of precipitated particles on the carbon fibers [8]. The high magnification SEM micrographs of the untreated carbon fibers showed smooth and uniform coatings. Figure (5) a, b, c and d show the morphologies of CaP coat on treated carbon fibers. It can be seen that the CaP coating grew homogenously and the adhesion between fibers and CaP coat expected better than untreated coated carbon fibers. The reason for such adherence is coming from the para-aminobenzoic acid functional group that has been installed in the carbon fibers, the creation of a large functional group concentration on fiber surfaces is essential in order to induce the growth of CaP coatings on fibers through interfacial chemical bonding. The higher the density of functional surface groups was, the larger the possibility of surface reactions could be; as a result, the interfacial chemical bonding strength of coatings to fiber surfaces could be promoted [9]. Surface of untreated coated carbon fibers seems to be smoother more than treated coated fibers as shown in Figure (4) and Figure (5). The nucleation and growth centers, agglomerations and seeding of CaP coat in treated coated fibers much more

than untreated coated fibers, because of the etching effect of para-aminobenzoic acid. That is, the fiber surface becomes rougher in the form of cracks. It is believed that the increased fiber roughness should promote the mechanical interlocking effect between the fiber and the coating, this explanation agrees with Tao et al [10].

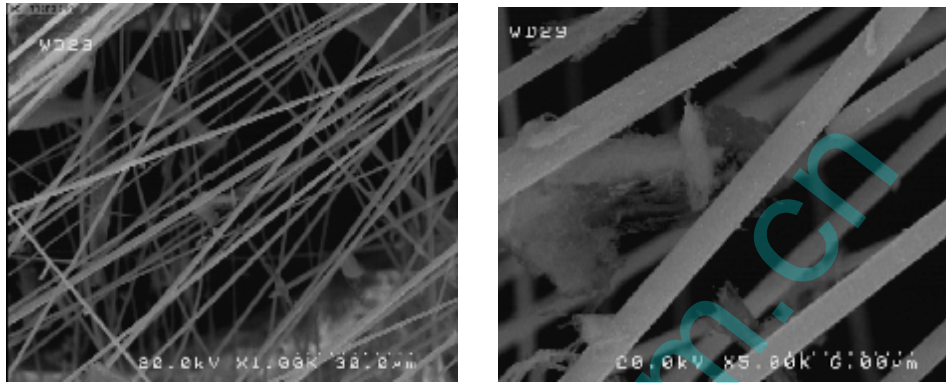


Figure (4) SEM of calcium phosphate coating on untreated carbon fibers.

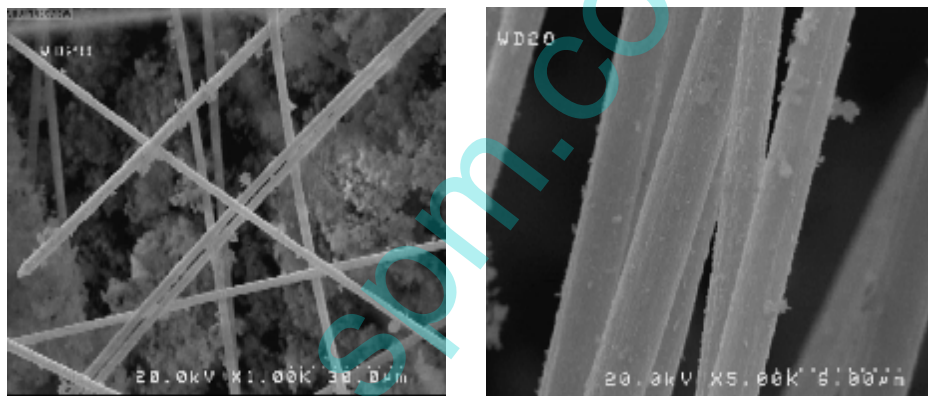


Figure (5) SEM of calcium phosphate coating on treated carbon fibers by para-aminobenzoic acid.

The XRD patterns of the synthesized calcium phosphate powder grown on the carbon fibers are presented in Figure (6) and Figure (7). All the powders have indicated the formation of an apatite phase. All charts obtained from XRD analysis was polycrystalline, as a result to adding  $\text{NH}_4\text{OH}$  to cloudy solution [11].

Figure (6) a and b show the x-ray diffraction patterns of the coatings before heat treatment. It has been shown that HAP ( $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$ ) is the main phase of CaP powders on (untreated and treated carbon fibers), and  $\beta$  - CaP ( $\text{Ca}_2\text{P}_2\text{O}_7$ ) as minor phase. Whereas after the heat treatment,  $\beta$  - CaP appearance as major phase as shown in Figure (7) a and b.

XRD shows HAP as major phase and  $\beta$  - CaP as minor phase in case of HAP addition within coating material, before heat treatment as shown in Figure (6) c, while  $\beta$  - CaP as major phase and HAP as minor phase after heat treatment as shown in Figure (7) c.



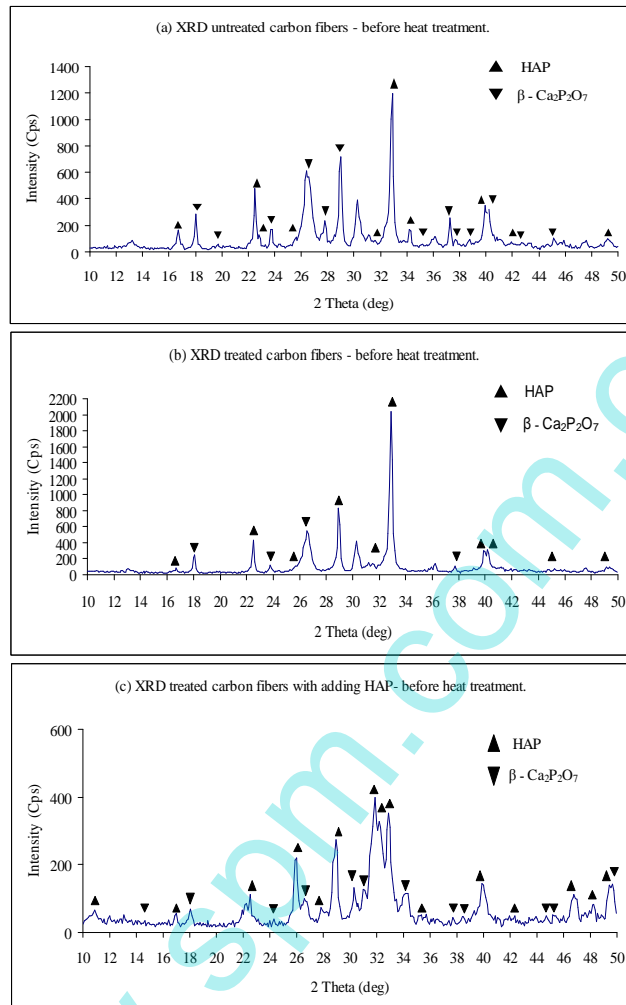
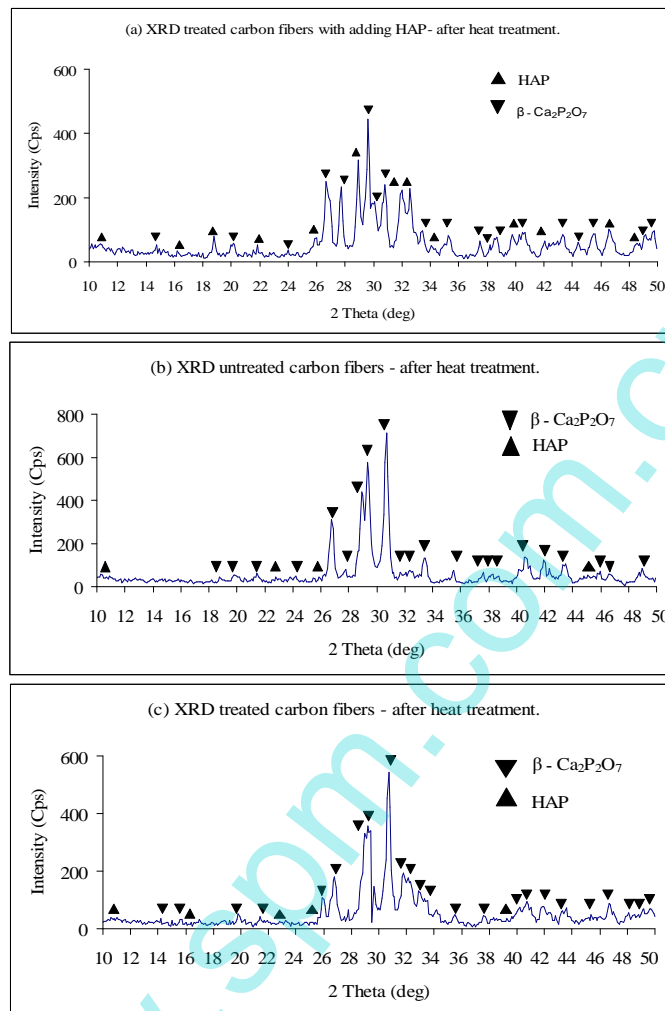


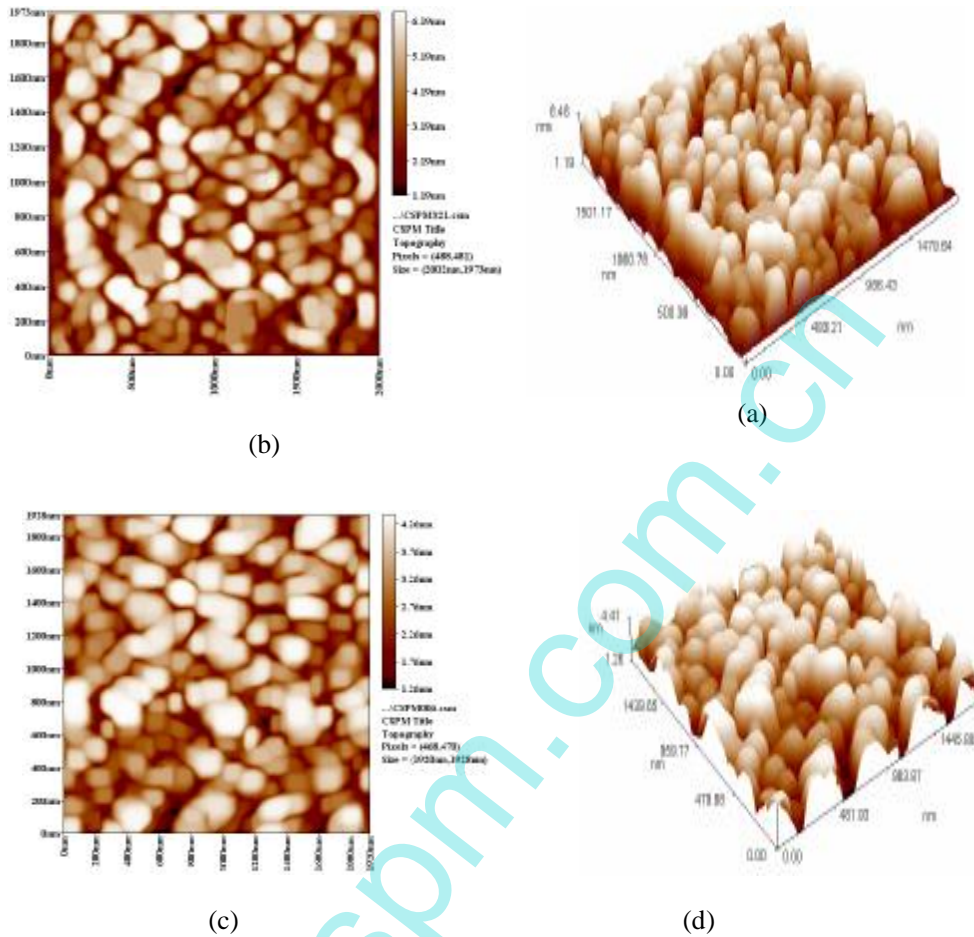
Figure (6) XRD pattern of CaP powders before heat treatment.



**Figure (7) XRD pattern of CaP powders after heat treatment.**

Atomic Force Microscopy (AFM) provides nanometer-scale information about surface structure. Figure (8) shows the morphology of the CaP coat on carbon fibers, prepared by sol-gel method. The obtained CaP particles size agree with the particle size range of sol-gel method ( $<1\mu\text{m}$ ) (i.e. within nanoparticles range). After heat treatment the evaporation of water and remove impurities led to agglomeration of CaP particles on the surface of fibers, as shown in Figure (8) c and d. The deposited particles size on the surface of carbon fibers in ambient (116.81 nm) before heat treatment and in ambient (93.42 nm) after heat treatment.





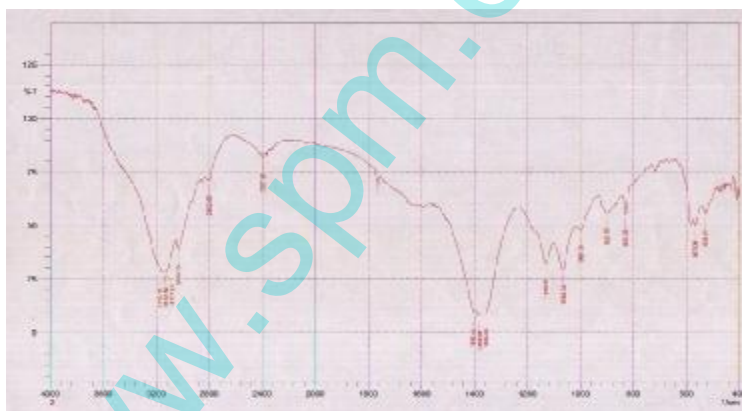
(a) (b) (c) (d)  
**Figure (8) 2D & 3D AFM image for CaP coat**  
**(a,b) before heat treatment.**  
**(c,d) after heat treatment.**

In the Fourier Transform-Infrared (FTIR) spectra shown in Figure (9) the spectrum of CaP powder of untreated carbon fibers before heat treatment shows two clear peaks in  $501.51\text{cm}^{-1}$  and  $580.59\text{cm}^{-1}$  represent  $(\text{PO}_4^{3-})$  peaks of HAP ( $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$ ) materials, this result similar to the literature data [12], and two peaks at  $496\text{cm}^{-1}$  and  $727\text{cm}^{-1}$  correspond to  $\beta - \text{CaP}$  ( $\text{Ca}_2\text{P}_2\text{O}_7$ ) absorption bands. This obtained result confirms with XRD findings.



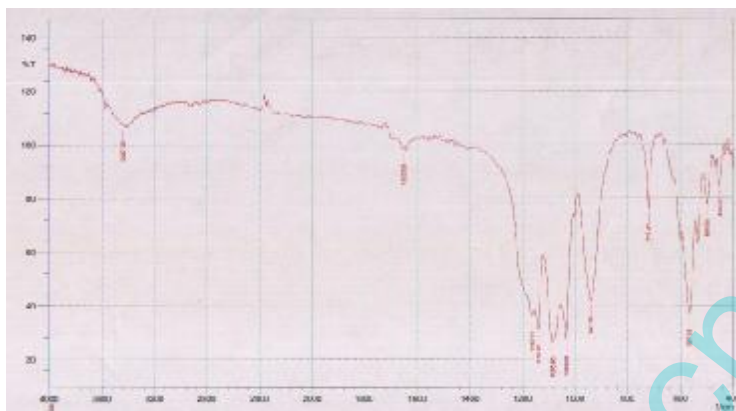
**Figure (9) FTIR spectrums of CaP powder-untreated carbon fibers before heat treatment.**

The FTIR spectrum of the CaP powder of treated carbon fibers before heat treatment is shown in Figure (10). The peak at  $567.09\text{cm}^{-1}$  represents  $(\text{PO}_4^{3-})$  of HAP material, and the peaks group in the range of  $900\text{-}1200\text{cm}^{-1}$  represent the stretching mode of  $(\text{PO}_4^{3-})$  group of HAP material. While at  $496\text{cm}^{-1}$ ,  $727\text{cm}^{-1}$  and  $1130.32\text{cm}^{-1}$  represent  $\beta$  – CaP absorption band. These results support obtained results from XRD.



**Figure (10) FTIR spectrum of CaP powder- treated carbon fibers before heat treatment.**

The characteristic broad and weak absorption bands at  $3437.26\text{cm}^{-1}$  and  $1653.05\text{cm}^{-1}$  are attributed to adsorbed water, as shown in Figure (11). Very clear peaks at  $499.58\text{cm}^{-1}$ ,  $721.40\text{cm}^{-1}$ ,  $1139.97\text{cm}^{-1}$ , and  $1163.11\text{cm}^{-1}$  correspond  $\beta$  – CaP absorption bands. HAP peaks appear at  $567.09\text{cm}^{-1}$  and  $1085.96\text{cm}^{-1}$  represent  $(\text{PO}_4^{3-})$  group. These findings confirm obtained results of XRD.



**Figure (11) FTIR spectrums of CaP powder-treated carbon fibers after heat treatment.**

It is obvious from the XRD pattern for both the CaP powder - treated and untreated carbon fibers before heat treatment, the intensity of the peaks under analysis for components (CaP and HAP) is lower than that of treated carbon fibers. Moreover FTIR spectrum for mentioned powders are denoted that the absorption peaks of group determined for the later is more clear than that of former one, so the FTIR and XRD analysis are coincide for each powder, this means more intensity in XRD pattern, more clear absorption band revealed and vice versa. The treatment of carbon fibers by para-aminobenzoic acid is accelerated the crystal growth rate and the functional groups on fibers acted as nucleation center for CaP crystal growth [9], as mentioned in SEM examination.

## CONCLUSIONS

In this study, the color of black carbon fiber was hidden successfully, by sol-gel coating technique. Treating carbon fibers with para-aminobenzoic acid improved the adhesion between fibers and CaP material. The results of FTIR spectrum confirmed that results obtained from XRD, morphological of coating on carbon fibers by CaP was good and clarified by images of SEM, and grain size of the CaP coat within nano range of sol-gel method was clarified by AFM.

## REFERENCES

- [1]Tao Yan, Dong Wei, Xianpeng Zheng, Xiaodong Xin, Nuo Zhang, Dan Wu, Liangguo Yan, He Li, Bin Du,Qin Wei, "A Facile Fabrication of Hydroxyapatite in Vitro Using Polymer Fasciculus as Biotemplate Carrier", Adv. Mat. Lett., Vol.1 ,No.2, PP 106 – 113, 2010.
- [2]Peih-Jeng Jiang, "Application of Calcium Phosphate Based Gels for Encapsulation of Therapeutic Molecules", Department of Chemical Engineering, PH.D Thesis, the University of Birmingham, UK, 2010.
- [3]Sakshijain, "Processing of Hydroxyapatite by Biomimetic Process", Department of Ceramic Engineering, Bachelor Thesis, the National Institute of Technology, Rourkela, India, 2010.
- [4]M. Rajkumar, N. Meenakshi Sundaram, V. Rajendran, "Preparation of Size Controlled, Stoichiometric and Bioresorbable Hydroxyapatite Nanorod by Varying

Initial pH, Ca/P Ratio and Sintering Temperature", Digest Journal of Nanomaterials and Biostructures , Vol. 6, No 1, PP 169 – 179, 2011.

[5] Gilbert Gedeon, "Engineering and Design Painting: New Construction and Maintenance", Manual No. 1110-2-3400, Continuing Education and Development, Inc., Washington, 1995.

[6] Krishna Seshan, "Handbook of Thin-Film Deposition Processes and Techniques Principles, Methods, Equipment and Applications", Second Edition, William Andrew Publishing, California, 2002.

[7] Murat Akarsu, Hikmet Sayilkan, Şadiye Şener, Funda Sayilkan, Ertuğrul Arpaç, "Sol-Gel Derived Zirconium Oxide Adsorbent Powder: Removal from Aqueous Solution of Phenol and P-Chlorophenol", Turkish Journal of Chemistry, Vol. 27, No. 4, PP 477- 486, 2003.

[8] Michael R. Mucalo, "Deposition of Calcium Phosphate on Carbon Fibers using Sol-Gel Based Reactions: The Consequences of Using Predominantly Organic Solvents on the Ultimate Phase of Calcium Phosphate Formed", Journal of Materials Science, Vol. 40, Issue 9-10, PP 2671-2673, 2005.

[9] Huang Su-ping, Zhou Ke-chao, Li Zhi-you, "Preparation and Mechanism of Calcium Phosphate Coatings on Chemical Modified Carbon Fibers by Biom mineralization", Transactions of Nonferrous Metals Society of China, Vol. 18, No. 1, PP 162-166, 2008.

[10] Tao Ke, Huang su ping, Zhou Ke chao, "Influence of Surface Treatment of Carbon Fibers on Electrochemical Crystallization of Calcium Phosphate", J Cent. South Univ. Technol., Vol. 12, No. 2, PP 113-116, 2005.

[11] M.P. Ferraz, F.J. Monteiro, C.M. Manuel, "Hydroxyapatite Nanoparticles: A Review of Preparation Methodologies", Journal of Applied Biomaterials & Biomechanics, Vol. 2, No. 2, PP 74-80, 2004.

[12] Bahman Nirhadi, Behzad Mehdikhani, Nayereh Askari, "Synthesis of Nano-Sized  $\beta$ - TCP via Wet Precipitation", Processing and Application of Ceramics, Vol. 5, No. 4, PP 193-198, 2011.