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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

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Calcium phosphate-based biomaterials are well known for their excellent biocompatibility and bioactivity in the body [1]. However the classical low fracture toughness of synthetic hydroxyapatite has limited its use to coatings and non-load bearing applications. Carbon fibers have been trialled in previous research as a form of reinforcement especially in carbon fiber-calcium phosphate bone cement composites [2–4]. Although the addition of fibers in some cases was found to reduce the compression strength of double setting calcium phosphate cements [4], because of increased porosity, it increased toughness and tensile strength. Other studies have used the carbon fibre textile as a scaffold [5] on which to grow calcium phosphate by combined sol-gel/sintering techniques which eventually removed the fibre scaffold and left a calcium phosphate relic. In similar fashion, Zhitomirsky [6] produced porous HAP fibers by electrophoretic deposition of precipitated submicron hydroxyapatite on fibre bundles and felts followed by firing of the samples in air. Apart from this paper, however, there are few, if any papers in which direct growth from sol-gel-type derived Ca and P-containing growth media on carbon fibers has been reported. It is thus interesting to determine if some commercially available carbon fibers *per se* can stimulate the deposition of hydroxyapatite upon their surfaces. However, some sol gel-type reactions can involve the use of media in which organic solvents such as ethanol are dominant components [7] which means that the "automatic" assumption of hydroxyapatite formation from precipitation in such media cannot be taken for granted. Hence this letter represents a small fundamental study investigating whether formation of calcium-phosphate coatings by sol-gel processing on three different kinds of carbon fibre surfaces is practically achievable. At the same time, the phase of calcium phosphate formed will be investigated by infrared (IR) spectroscopy) to determine the effect of the reaction media. A potentially valuable outcome of achieving such calcium phosphate coatings on carbon fibers is the improvement of adhesion in carbon-fibre reinforced hydroxyapatite-carbon fibre composite biomedical implants by provision of a like interface.

In general, three commercially available carbon fibers were used in the deposition experiments. Two of the fibre types are: HTA (manufactured by the Tenax Company in Germany) and, T300 (manufactured by Toray from the Sofica Branch in France). Both are PAN C fibers, (i.e. polyacrylonitrile-derived fibers). The third type of C fibre is known as K13A1L, a pitch fibre of high quality used for Aerospace applications and manufactured by the Kasei Company, a predecessor of Mitsubishi Chemicals. All of the fibers in their as-received state contain a hydrocarbon compound which *sizes* the fibers (i.e. keeps the individual fibers in well-ordered bundles and prevents splaying). Before attempting any deposition, the fibers were desized by immersion in acetone and ultrasonicated to remove the hydrocarbon layer. After drying, the carbon fibers were then coated using the same reaction but by two slightly different coating procedures.

The first of the two coating methods ("Coating Method 1") involved the preparation of a calcium phosphate coating solution by the method reported by Hwang *et al.* [7]. 100 mL of 0.0385 mol L^{-1} H_3PO_4 (85% VEB Laborchemie Apolda, density 1.691–1.721 g mL^{-1}) in absolute ethanol (Merck Pro-analys) was mixed with 100 mL of 0.0647 mol L^{-1} $Ca(NO_3)_2 \cdot 4H_2O$ also in absolute ethanol. Initial mixing produced no visible reaction, however when the solution was left overnight, a cloudy solution resulted indicating precipitation of a calcium phosphate phase had occurred. HTA, T300, and K13 A1L carbon fibers were then immersed in this cloudy solution, withdrawn, excess solution removed, and the fibers dried in a 50–100 °C oven for several hours. Immersing the fibers in this already precipitated solution and drying resulted in fibers which appeared caked together. These were later characterized using a Hitachi S100 FESEM or Jeol-840 scanning electron microscope (SEM) coupled with energy dispersive X-ray analysis (EDX) (IXRF system on Hitachi S100).

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The second coating method ("Coating Method 2") involved the preparation of the calcium phosphate coating solution following the procedure as described above from $Ca(NO_3)_2.4H_2O$ and H_3PO_4 in absolute ethanol except that instead of waiting for the solution to become cloudy and then immersing the fibers, the fibers were immersed in the coating solution *immediately* after mixing of the reagents (i.e., while it was still clear) and left overnight so that calcium phosphate formation occurred on the fibers. This coating approach gave fibers that had a white coating on their surface together with settled white solid in the containing vessel. The coated fibers were taken from solution and dried for later analysis by SEM/EDX. Some of the settled solid around the fibers at the bottom of the coating vessel was also filtered off, dried, and pressed into a KBr disk for analysis by a Perkin Elmer 1000 Fourier transform infrared (FTIR) spectrometer to ascertain the identity of the calcium phosphate phase that formed on the fibers.

Fig. 1 is an SEM of a PAN C fibre coated with calcium phosphate using method 1. In general, all C fibers subjected to this coating method exhibited only very partial coatings of solid. This hence showed that Coating Method 1 was inadequate for achieving any sort of significant coating on the fibers. Figs 2a–c include the SEM micrographs for coatings on K13 A1L and HTA (PAN) C fibers prepared via Coating Method 2. The micrographs show that allowing precipitation to occur while the fibers were immersed in the reacting solution, is a better method than coating Method 1 for coating the fibers. It was evident that accumulated layers of particles had formed on the fibers often caking them (Fig. 2(a) and (b)). 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 C fibers. Handling of the dried fibers (from both Coating Methods) led to some spalling of coatings from the surface as some of the high magnification SEM micrographs of the individual fibers

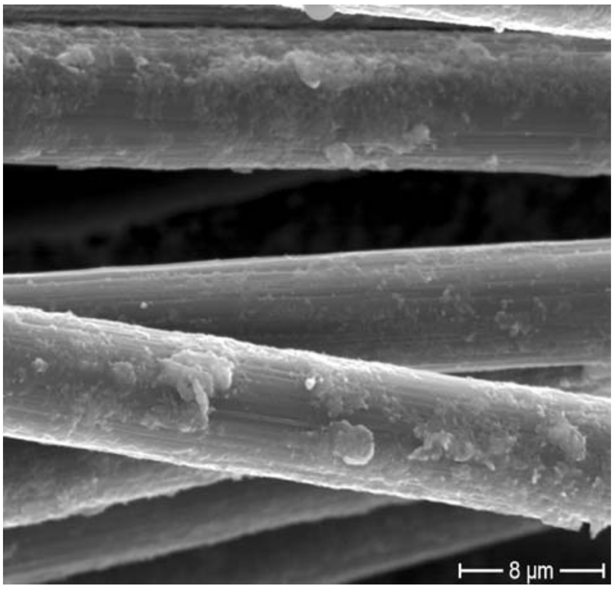
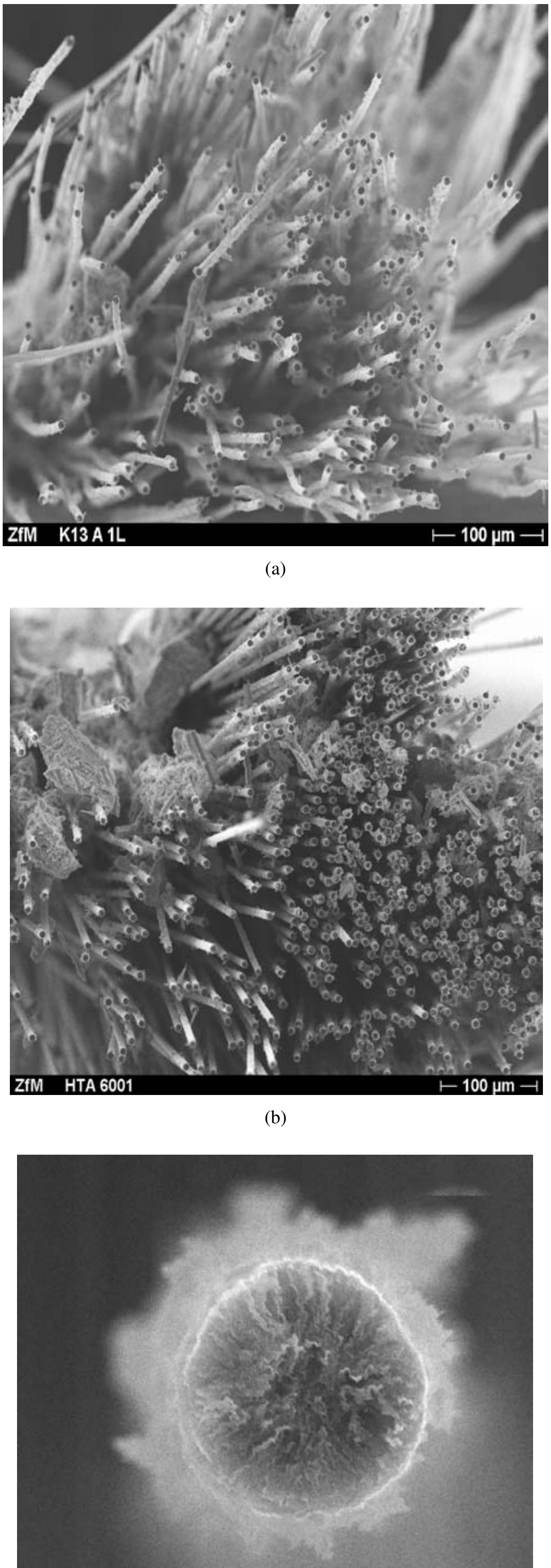


Figure 1 PAN C fibre coated with solid material generated by Coating Method 1.



(a)

(b)

(c)

Figure 2 SEM of calcium phosphate-coated K13 A1L carbon fibers using Coating Method 2. (b) SEM of calcium phosphate coated HTA fibers using Coating Method 2, and (c) High magnification SEM of K13 A1L fibre coated using Coating Method 2.

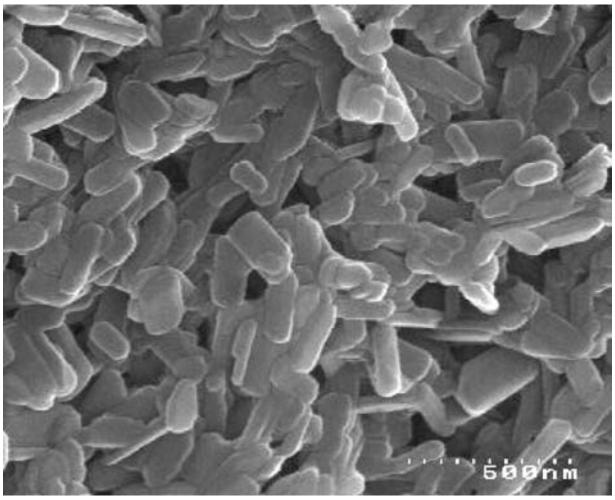


Figure 3 SEM micrograph of the white powder comprising the coatings on the C fibers and codeposited in the reaction vessel. The powdered sample is dispersed on double-sided sticky tape onto an SEM stub.

often revealed either very thin or non-uniform coatings (Fig. 2(c)). This indicated that the coatings formed by these "soft" chemical methods were not very adherent to the fibers. None of the different types of fibers tested exhibited any significant differences with respect to calcium phosphate deposition.

The IR spectrum of the KBr disk of the white solid that deposited overnight after mixing of the reagents in Coating Method 2 in absolute ethanol showed intense peaks at 1132 and 1067 cm^{-1} with weaker peaks at 998, 902, and 582 cm^{-1} (with shoulders at 564 and 526 cm^{-1} on the 582 cm^{-1} peak). The spectral pattern observed was unequivocally assigned to that of monetite ($CaHPO_4$). An intense peak also observed at 1384 cm^{-1} is due to nitrate ion from the calcium nitrate reagent. The IR spectrum revealed clearly that a non-apatitic calcium phosphate compound had formed and not hydroxyapatite as might be automatically assumed to form after prolonged overnight standing time in the reaction medium (*ca.* 12–14 hr). Monetite ($CaHPO_4$) is the anhydrous version of one well known hydroxyapatite precursor phase (i.e. brushite, $CaHPO_4{\cdot}2H_2O$) when calcium phosphates are prepared via precipitation from aqueous solution. Fig. 3, an SEM of the isolated white solid confirms this given the characteristic column-like and platey crystals expected of triclinic monetite crystals. This means that the coating of calcium phosphate on the C fibers is also monetite mixed with some contaminant calcium nitrate from the reaction media. This is reflected in random EDX sampling of the coatings which reveal values for the Ca:P mole ratio (based on atomic percentages) of >1.0 suggesting calcium enrichment in the coatings. The observation of the monetite phase shows the chemical consequence of using sol-gel-based processing techniques in media where water is not the dominant solvent. It has been well established by many researchers and in particular Eanes [8] that hydroxyapatite does not form directly when made via precipitation in aqueous solution but only via a phase transformation of a series of thermodynamically less stable (and relatively more water soluble) precursor phases. The mechanism of phase conversion essentially involves a series of dissolution-reprecipitation reactions in which the initially formed amorphous solid (known as amorphous calcium phosphate, ACP) dissolves gradually and interconverts to more crystalline phases and so on with hydroxyapatite being the ultimate end product. The dissolution-reprecipitation reaction necessarily involves water to take place otherwise further conversion does not occur (dry ACP is stable to phase conversion). For the reaction media used in the present study, the predominance of ethanol has clearly retarded this further phase conversion and produced a phase of calcium phosphate which has "stopped" at an early stage, viz., monetite. The effect of the lack of water in the reaction media is emphasized furthermore by the observation of the *anhydrous* calcium phosphate phase, monetite, rather than the more commonly observed hydrated compound, brushite ($CaHPO_4{\cdot}2H_2O$).

In conclusion, only non-uniform and weakly adherent calcium phosphate coatings form on C fibers via the sol-gel processing technique used in the present study. The most significant observation from this work is that a keen awareness of the chemistry of calcium phosphate precipitation is paramount as it is a process for which final product phases are heavily dependent on reaction conditions. If predominantly non-aqueous reaction media are to be used specifically for generating apatitic phases, it is important to thoroughly characterize the phases of calcium phosphate that are actually formed as, on occasions, non-biologically relevant phases may separate.

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