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FTIR and Raman spectra of bioceramics obtained by an innovative method

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Bioceramic coatings with defined chemical composition and structure are often needed to satisfy specific biocompatibility properties in the prosthetic field. An example is hydroxyapatite (HA) for coatings, which, according to the Standard Specifications of the ASTM, must be crystalline and have a stoichiometric molar ratio Ca/P = 1.67 with a 95% minimum amount of HA. Since the methods (plasma flame spray, ion beam sputtering, etc.) to obtain bioceramic coatings, in particular those for HA, induce changes in the chemical composition, structure and physical state of the coating, an alternative and innovative method (the so-called polymeric route) which provides bioceramic coatings under less severe conditions with controlled chemical composition and structure, was used in this work. The method was applied to the preparation not only of HA, but also, for the first time, of high-temperature-melting calcium phosphate bioactive glasses with a molar ratio $CaO/P_2O_5 = 1$ (calcium metaphosphate) and in the range 1–1.5 (calcium oligophosphates). The different phases of the process were characterized by vibrational FTIR spectra. The structure of the final glasses were also studied by Raman spectroscopy and compared with the spectra of the same products obtained by the traditional melting method.

1. Introduction

The setup of biomaterials with specific employment properties often requires the use of treatment methodologies that can modify the chemical composition, the structure and also the biocompatibility of the biomaterial itself.

A typical case is that of metals and alloys used for hip prosthesis. Although these materials have good mechanical properties, calcium phosphate (CP) coatings have different beneficial effects and in particular the ability of bonding to bone, reduction of metal corrosion product release, and enhancement of bone formation rates (osteoconduction).

Among bioceramics, hydroxyapatite (HA) is the most commonly used material. High-temperature-melting bioactive CP glasses, having a CaO/P_2O_5 molar ratio between 1.0 and 1.6, can also be suitable. Both HA and CP glasses are constituted by the same chemical elements (i.e. Ca and P) of the mineral bone component, although bioactive glasses have a different Ca/P molar ratio with respect to bone.

The most commonly used technique to apply thin bioceramic and high-temperature-melting bioactive glass coatings is plasma flame spray (PFS); this technique can, however, induce changes in the chemical composition and structure of the coating. These changes have been described in the literature as regards HA coatings [1–11], whereas the changes in CP glass coatings have not been investigated in depth.

This paper deals with coatings of hydroxyapatite (HA) and bioactive CP glasses having a CaO/P_2O_5 molar ratio between 1.0 and 1.5, and it evaluates, by means of vibrational FT-IR and Raman spectroscopies, the structural modifications undergone by biomaterials – expecially HA – owing to coating and often also to pre-coating treatments. It investigates the efficaciousness of alternative synthetic methods which could provide coatings under less severe experimental conditions, in order to avoid the above-mentioned modifications.

2. Experimental procedures

CP bioactive glasses and HA for coatings were obtained by a polymeric route [12] by hydrolysis with water of phenyldichlorophosphine (PDP) in acetone, addition of the stoichiometric amount of calcium nitrate, oxidation with air and heating at different temperatures.

Raman spectra were recorded using a Jasco R-1100 spectrometer with 488 nm radiation from a Spectra-Physics argon ion laser source. Infrared spectra were recorded with a Jasco FTIR 5300 spectrometer using the KBr pellet technique for the solid samples.

3. Results and discussion

As described in the literature, HA used as an implant material must satisfy the "Standard Specifications for

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Composition of Ceramic HA for Surgical Implants of ASTM Committee F-4 on Medical and Surgical Materials and Devices". According to these specifications, the molar ratio Ca/P has to be consistent with the stoichiometric one, i.e. 1.67, corresponding to the formula $Ca_{10}(PO_4)_6(OH)_2$; moreover X-ray quantitative analysis must show a 95% minimum amount of HA. Furthermore, HA must be crystalline because it has a very low $K_{ps}(10^{-107})$ while amorphous HA resorbs.

Nevertheless, HA can easily modify its structure and composition, since it is a member of a wider CP class (tricalcium phosphate, TCP; octacalcium phosphate, OCP; dicalcium phosphate, DCP, etc.), whose different compositions and structures can be obtained from the general formula

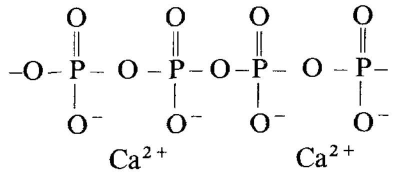
$$Ca_{10-x}(PO_4)_{6-x}(HPO_4)_x(OH)_{2-x}\cdot xH_2O \qquad (1)$$

where $0 \leq x \leq 2$

as shown in Table I.

Stoichiometric HA and OCP constitute the extremes of the formula when $x = 0$ and $x = 2$, respectively; under partial anionic substitution ($1/3\ PO_4^{3-} = OH^-$) TCP is formed, while under cationic substitution ($2H^+ = Ca^{2+}$) DCP and DCPD are obtained. Moreover, it is also possible that the crystalline phase changes into an amorphous one.

Although the transformations that CP high-temperature-melting bioactive glasses might undergo during the treatment to obtain the coating have been less amply studied, it is known that the glass with the molar ratio $CaO/P_2O_5 = 1$, calcium metaphosphate $Ca(PO_3)_2$, has a linear infinite chain structure:



$$-O-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O^-}{|}}{P}}-O-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O^-}{|}}{P}}-O-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O^-}{|}}{P}}-O-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O^-}{|}}{P}}-$$

$$Ca^{2+} \qquad\qquad Ca^{2+}$$

When the amount of basic oxides (generally alkaline and alkaline-earth oxides) increases, oligophosphate glasses are obtained, with a shorter polymeric structure, whose average chain length $\bar{n}$ (expressed as phosphorous atoms) depends on the molar ratio R, where

$$R = \frac{\text{basic oxide}}{P_2O_5} = \frac{\bar{n}+2}{\bar{n}}$$

The break-down of the linear infinite chain of the metaphosphate structure is deduced from vibrational spectra. In particular, the Raman spectra show that the increase in R leads to a decrease in the relative intensity of the $\nu_s PO_2^-$ lateral stretching modes band and to the contemporaneous appearance and successive increase in the relative intensity of the band assigned to the $\nu_s PO_3^{2-}$ terminal groups [13]. Structural modifications of these groups are to be expected when the proton substitutes the calcium ion.

Therefore, it is difficult to perfectly synthesize stoichiometric HA and CP bioactive glasses. At the same time all these compounds easily undergo several changes in their composition and structure during the formation of the coating by the PFS technique on implant metals or alloys. In particular, HA has been studied, mainly by XRD by several authors. It has been shown that this material undergoes a loss in crystallinity [4, 5, 7–10] and changes into other compounds as a consequence of the PFS. The transformation products of HA are supposed to be of different kinds, depending also on the treatment conditions, since some authors suggest the formation of oxyhydroxyapatite [3, 8, 9], while others point out that a partial decomposition of HA into α- or β-TCP [4, 7, 9, 10], into TCP or α-TCP or β-TCP and tetracalciumphosphate [2, 3, 11], into TCP or β-TCP and CaO [2, 6] can occur.

Our spectroscopic infrared measurements [14] show:

- the presence of an amorphous component (which can be highlighted by the broadening of the phosphate group band at about 1000–1100 cm^{-1});
- a partial transformation of stoichiometric and crystalline HA structure: absence of νOH and γOH typical bands; absence of $\nu_s PO_4^{3-}$ band at 960 cm^{-1}; a broad multicomponent absorbance between 1000 and 1100 cm^{-1}, which is not only due to an amorphous phase, but also to phosphate component modes which are different from those of HA and not easily discernible.

The Raman spectrum is better able to characterize the coating. Among the few Raman spectra of coatings reported in the literature [5, 9, 10], the important results obtained by Weinlaender *et al.* [5] point out the presence in the spectrum of two bands at 952 and at 964 cm^{-1}. The authors attribute one of these bands to an amorphous phase of HA, rather than to other CP, whose spectra were taken as reference. However, the implant spectra exhibited an extra band not yet identified but indicative of some structure within the sprayed amorphous phase. As an alternative hypothesis that still needs further investigation, the above-mentioned bands may be attributed to a mixture of tetracalciumphosphate (Ca/P molar ratio = 2) and α-TCP (Ca/P molar ratio = 1.5). This hypothesis is in agreement with our previous Raman study of the thermal decomposition of HA at 1300°C [13], and with the similar results, referred to above, obtained by XRD on HA coatings [3]. The high-temperature

TABLE I Main CPs originated from Equation 1

$x = 0$	HA	$Ca_{10}(PO_4)_6(OH)_2$	molar ratio Ca/P = 1.67
$x = 2$	OCP	$Ca_8(PO_4)_4(HPO_4)_2{\cdot}2H_2O$	molar ratio Ca/P = $1.\bar{3}$
$OH^- = 1/3\ PO_4^{3-}$	TCP	$Ca_3(PO_4)_2$	molar ratio Ca/P = 1.5
$Ca^{2+} = 2H^+$	DCPD DCP	$CaHPO_4{\cdot}2H_2O$ $CaHPO_4$	molar ratio Ca/P = 1.0

melting bioactive CP glasses could similarly undergo transformations in composition and structure when the PFS treatment is used. No results are reported in the literature about this subject.

Even the more recently used techniques to obtain HA coatings, i.e. ion beam sputtering, electrophoretic deposition, etc. do not seem to be able to provide coatings with the desired chemical composition and crystallinity; the latter can be obtained only after a thermal post-treatment [15]. Owing to the observations reported above, if biomaterials are to be obtained with a well-defined composition and structure, it is necessary to set up alternative methods to PFS or ion beam sputtering. Among the possible ways to achieve coatings at low temperature, other than the melting of the oxides, the two most suitable are the sol–gel method and the polymeric route.

The sol–gel method consists of the hydrolysis and thermal polycondensation of alkoxides of the corresponding elements [16]; we have used it mainly to achieve silica [17] and sodium silicate glasses [18]. Using the sol–gel method, other glasses of the systems GeO_2, Te_2O_5, Al_2O_3, TiO_2 and ZrO_2 have been prepared [19]; application to binary and ternary systems is still very limited, even if a report of the preparation of HA using this method has recently been published [20].

The polymeric route is a quite general method with wider applications than the sol–gel method and it was applied for the first time by Brendel *et al.* to obtain HA for coatings [12]. These authors succeeded in obtaining HA by hydrolysis with water of PDP in acetone, addition of the stoichiometric amount of calcium nitrate, oxidation with air, and heating at different temperatures.

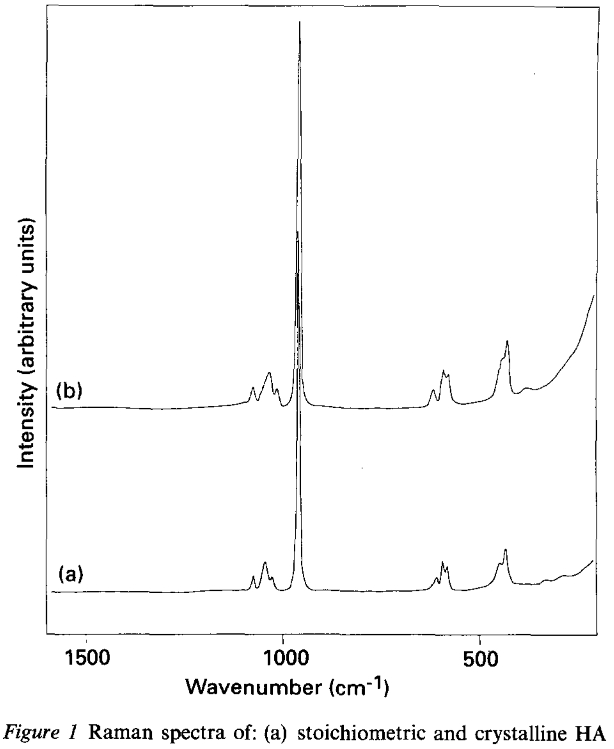


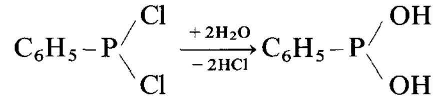
Figure 1 Raman spectra of: (a) stoichiometric and crystalline HA sample heated at 900°C, (b) HA sample obtained by the polymeric route heated at 900°C.

The different steps of the process were followed and monitored by vibrational IR spectroscopic analysis; the spectrum of the final product matches that of stoichiometric and crystalline HA.

We obtained the first Raman spectrum of HA samples synthesized by the polymeric route and, as shown in Fig. 1, it corresponds to that of stoichiometric and crystalline HA.

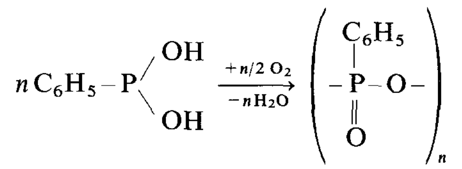
In this paper, we applied this synthetic method also to the preparation of high-temperature-melting bioactive CP glasses, calcium metaphosphate ($R = CaO/P_2O_5 = 1$) and oligophosphates ($1 \leq R \leq 1.5$). In Fig. 2 the FTIR spectra corresponding to the three significant main steps of the calcium metaphosphate preparation process are shown. The vibrational spectra highlight the transformations undergone by the starting material used to obtain the calcium metaphosphate during the following different phases of the process:

hydrolysis



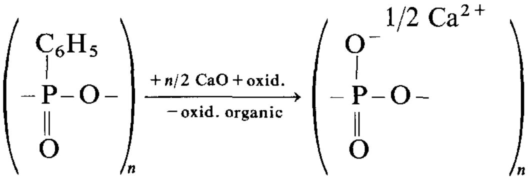
$$C_6H_5-P\begin{matrix}Cl\\Cl\end{matrix} \xrightarrow[-2HCl]{+2H_2O} C_6H_5-P\begin{matrix}OH\\OH\end{matrix} \tag{1}$$

oxidation and partial polymerization



$$n\,C_6H_5-P\begin{matrix}OH\\OH\end{matrix} \xrightarrow[-nH_2O]{+n/2\,O_2} \left(\begin{matrix}C_6H_5\\|\\-P-O-\\\|\\O\end{matrix}\right)_n \tag{2}$$

further oxidation and substitution with calcium ion



$$\left(\begin{matrix}C_6H_5\\|\\-P-O-\\\|\\O\end{matrix}\right)_n \xrightarrow[-\text{oxid. organic}]{+n/2\,CaO+\text{oxid.}} \left(\begin{matrix}O^- \quad 1/2\,Ca^{2+}\\|\\-P-O-\\\|\\O\end{matrix}\right)_n \tag{3}$$

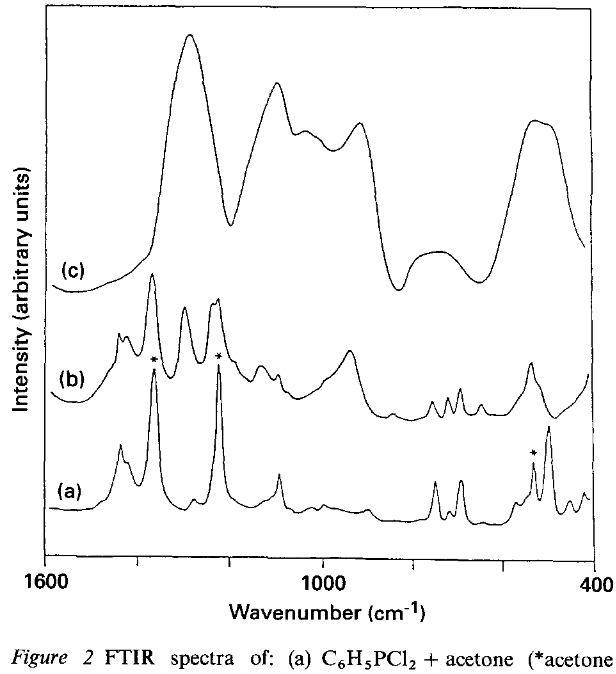


Figure 2 FTIR spectra of: (a) $C_6H_5PCl_2$ + acetone (*acetone bands); (b) $C_6H_5PCl_2$ + acetone after addition of water, $Ca(NO_3)_2$ and oxidation; (c) sample b heated at 400°C.

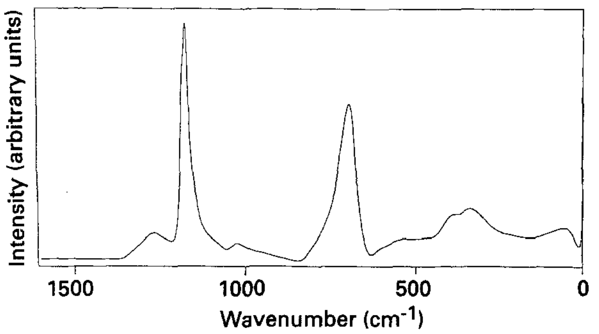


Figure 3 Raman spectrum of CP metaphosphate glass obtained by the polymeric route.

The hydrolysis is confirmed by the disappearance of the bands at 440 and 420 cm^{-1} due to P–Cl stretching modes of PDP and by the presence of a broad band at about 990 cm^{-1}, assigned to P–OH stretching modes, shown in Fig. 2b.

The oxidation and partial polymerization are demonstrated by the presence of bands at 1300 cm^{-1} (assigned to a P = O stretching mode) and at 940 cm^{-1} (due to a P–O–P stretching mode), also shown in Fig. 2b.

The further oxidation and substitution with calcium ion is confirmed in the spectrum of the final product (Fig. 2c) by the presence of bands at 1270 and 900 cm^{-1} assignable to the asymmetric stretching mode of the PO_2^- side-group of the chain and to the P–O–P asymmetric stretching mode along the chain, respectively.

In Fig. 3 only the Raman spectrum of the calcium metaphosphate final product is shown because the intermediates obtained during the different phases of the process are yellow-brown and high-quality Raman spectra could not be obtained. IR and Raman spectra of calcium oligophosphates with a molar ratio $1 \leq R \leq 1.5$ were obtained in the same way.

Both IR and Raman spectra of the final product obtained by the polymeric route are coincident with that previously described and obtained by the melting method. The only difference is that in the case of the melting, a temperature of 1300°C was necessary, whereas with the new method a much lower temperature is required.

The results of this paper clearly point out that alternative methods, in particular the polymeric route, which directly provide bioceramics and high-temperature-melting bioglass coatings, may acquire increasing interest and importance. These methods are valuable not only in the preparation of coatings with well-defined structure and composition, but also in the future development of coatings with osteoactive properties enhanced by the presence, in the basic bioceramic, of bone mineral component precursors.

Our further investigations are directed in this field.

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