

RHEOLOGY OF TRICALCIUM PHOSPHATE (β -TCP) SUSPENSIONS

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Reliable bioceramics are needed to implement the high requirements that living tissues demand. This work focuses on the processing steps necessary to manufacture advanced ceramics that can be used as resorbable medical devices. The most used biomaterials are based on hydroxyapatite (HA) and tri calcium phosphate (TCP). Beta-TCP was obtained by sintering in solid state reaction from raw materials of p.a. grade ($\text{CaCO}_3 / \text{NH}_4\text{H}_2\text{PO}_4$). This compound was marked out, as unique phase, by x-ray diffraction, infrared and SEM analyses. From β -TCP powder, aqueous suspensions with Arabic gum (A.G.), sodium-carboxymethylcellulose (Na-CMC) and polyvinyl alcohol (PVA) as dispersing, stabilizing, and binding agents were prepared, respectively. Elaborated suspensions were tested from the point of view of volume weight, pH and rheological behaviour at pouring in plaster mould. The preliminary results are promising for preparation of the β -TCP aqueous suspensions with the selected additives.

INTRODUCTION

Calcium phosphate powders used for suspensions preparation can be obtained by non-conventional methods (sol-gel, coprecipitation), reactions in solid state and hydrothermal treatment, as well. The preparation technique has a significant influence on the powder morphology, specific surface area, stoichiometry and crystallinity. Therefore, the control over all synthesis conditions is decisive to obtain reproducible results.¹ The dispersive medium can be the distilled water or deionised water.

Aqueous suspensions are used for shaping through pouring in plaster moulds. A successful shaping from these requires relative concentrated and well non-agglomerated suspensions.

To obtain the dispersed suspensions with high content of solids, it is necessary to study different factors that influence their stability and rheological characteristics, such as: characteristics of the dispersion medium, disperser type and its amount, powder characteristics (specific surface area, chemical composition and particle-size distribution of the powder particles), suspension preparing time.

The surface properties have a decisive role regarding the dispersing behaviour in the water. To

obtain these suspensions, the complex interfacial reactions among the dispersion medium (solvent), disperser, powders and additives have to be taken into account.

The preparation of the aqueous suspensions is based on the control of the inter-particle forces by modifying the reactivity at the solid-liquid interface.² These forces are attractive and repulsive ones. The Van der Waals attractive forces lead to the slight agglomerations of the particles that can be destroyed and dispersed by the repulsion forces.

The repulsive forces between particles can be promoted by one or both of the following methods: control of the surface load by adjustment of pH medium or by adsorption of dispersers (electrolytes) upon the powder particle surface (electrostatic stabilization); steric separation of the particles individually by adsorption of polymers with high neutral chain or loaded upon the particle surface (steric stabilization or electrosteric).^{3,4}

An important property of the aqueous suspensions (colloids) is the rheological behaviour. The rheological measurements are able to monitor the changes of the flow behaviour as a response to an applied force. The viscosity of the suspensions is dependent on the applied shear stress, τ , and the

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shear rate, $\dot{\gamma}$. The flow behaviour depends on the composition and stability of the suspensions.

Due to the fact that in the literature data there are only few pieces of information about the aqueous suspensions of β -TCP and their rheological characterization, respectively, the purpose of this paper is to obtain β -TCP aqueous suspensions with different additives and to evaluate them from rheological point of view.

RESULTS AND DISCUSSION

β -TCP powder

The β -TCP powder prepared in the experimental conditions presented further was characterised from structural and morphological point of view.

The XRD pattern is shown in Fig. 1.

The pattern shows an excellent agreement with the published JCPDS files for β -TCP.

The FTIR spectrum of tricalcium phosphate sample is shown in Fig. 2.

The range of $800 - 1200 \text{ cm}^{-1}$ exhibits a wide absorption band typical of tetrahedral anions XO_4^{n-} , in particular, PO_4^{3-} . FTIR analysis demonstrated PO_4^{3-} adsorption peaks around $1040\text{-}1122$; 610 , and 551 cm^{-1} attributable to β -TCP. ^{5, 6} FTIR spectrum of sintered beta-tricalcium phosphate showed typical spectrum for TCP material. The characteristic phosphate peaks for β -TCP at wave numbers of $1122,5$ - $1045,3$; $609,5$ and $551,6 \text{ cm}^{-1}$ were present. The band at position of $1436,9 \text{ cm}^{-1}$ is probably from carbonate, which is commonly found in both synthetic TCP and natural bone. ⁷

SEM micrograph of pure β -TCP powder, sintered at 1150°C for two hours, is shown in Fig. 3.

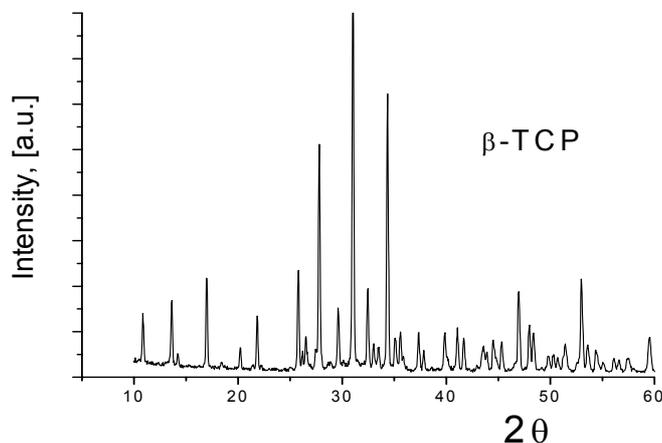


Fig. 1 – XRD pattern of the β -TCP powder, sintered at $1150^\circ\text{C}/2\text{h}$.

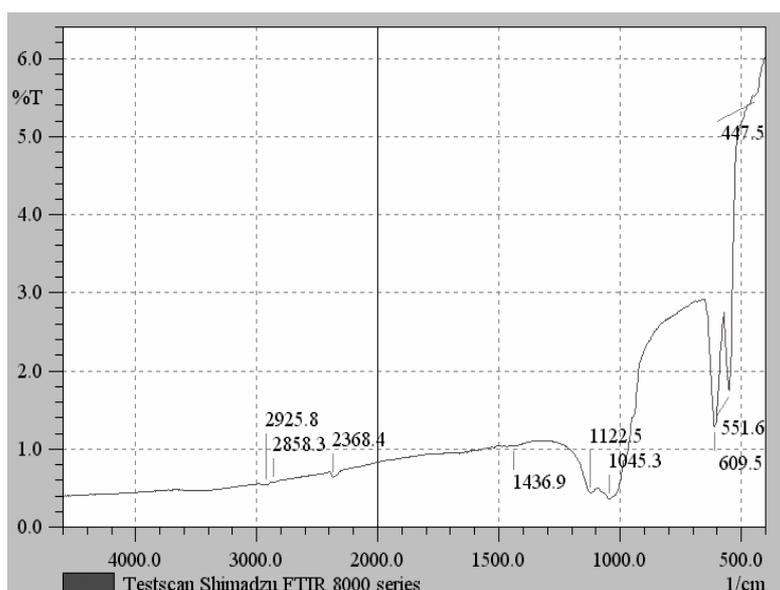


Fig. 2 – IR spectrum of the β -TCP powder, sintered at 1150°C for 2h.

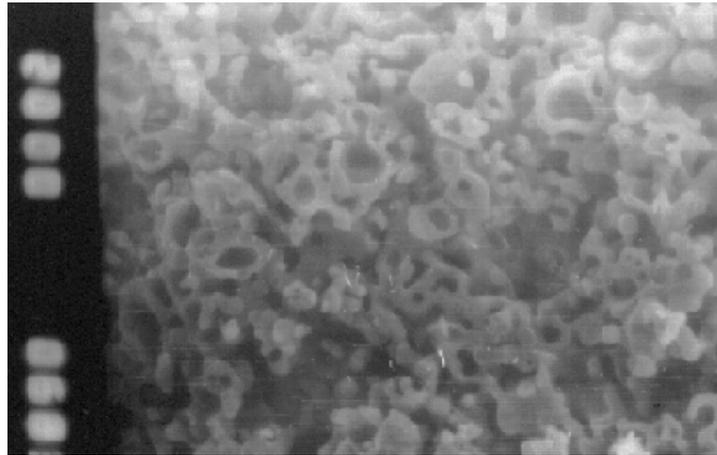


Fig. 3 – SEM micrograph for β -TCP powder, sintered at 1150 °C for 2h, (X 2.000).

The SEM pictures gave insight into the ceramic structure with respect to porosity, pore structure, pore and crystal size and their variations. Fig. 3 shows the variation in pore size, shape and distribution which is caused by the manufacturing process. The ceramic has an interconnecting pore system with pores of sizes 0.1-3 μm similar to the natural structure of bone.⁷ The size of the β -TCP crystals ranges from 1 to 7 μm .

Figs. 1, 2 and 3 show the obtained β -TCP powder as unique phase, after sintering at 1150 °C for 2h.

β -TCP suspension

The investigated properties of the beta-tricalcium phosphate suspensions are shown in Table 1.

Table 1

Properties of the prepared suspensions

Sample	Volume weight [g/L]	pH	T [°C]	$\eta \dot{\gamma}^{-1} = 100 \text{ s}^{-1}$ [mPa .s]
TCP-1	1600	7.15	24.0	395.35
TCP-2	1707	12.53	27.0	436.80
TCP-3	1586	12.50	24.7	191.02

The suspensions present high volume weights. The pH values (measured with pH-conductometer Denver Model 220) are in a low basic domain for the sample with A.G., Na-CMC and PVA as additives (TCP-1) and much more basic for the samples with the highest quantity of Na-CMC and PVA (TCP-2) and only with Na-CMC (TCP-3). They seem well homogenized, flow well and were poured well on the plaster plate and in different plaster moulds.

The rheological behaviour of the samples is shown in Figs. 4 and 5.

The best fit for measured rheological data was obtained with the Cross model according to equation:

$$\eta = \eta_{\alpha} + \frac{\eta_0 - \eta_{\alpha}}{1 + \left(\frac{\dot{\gamma}}{\dot{\gamma}_b}\right)^n} \quad (1)$$

where: η – viscosity [mPa·s]

η_0 – zero shear viscosity [mPa·s]

η_{∞} – infinite shear viscosity [mPa·s]

$\dot{\gamma}$ – shear rate [s^{-1}]

$1/\dot{\gamma}_b$ – Cross time ratio

n – Cross rate constant

The suspensions exhibit a non-Newtonian behaviour of pseudoplastic (shear thinning) type (Fig.4). TCP-3 suspension presents only slight non-Newtonian behaviour in comparison to the TCP-1 and TCP-2 suspensions. TCP-2 sample shows higher tendency of particles agglomeration comparatively to the other ones, fact observed also by the shear rate domain (0-350 s^{-1}) and viscosity value (Table 2). It seems that the Na-CMC with PVA mixture lead to the increase of the viscosity value due to the particles agglomeration comparing to the TCP-3 sample in which only Na-CMC was used.

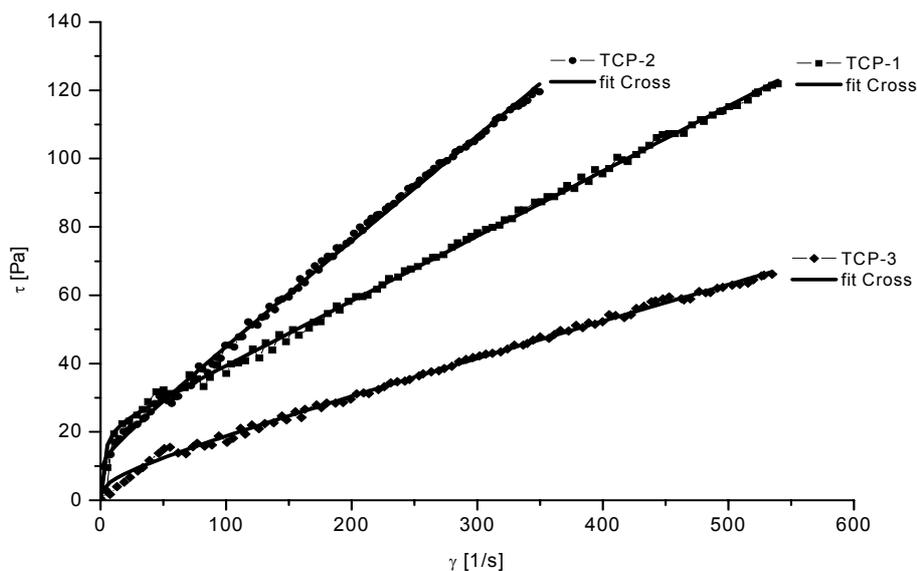


Fig. 4 – The flow behaviour for the beta-tricalcium phosphate suspensions.

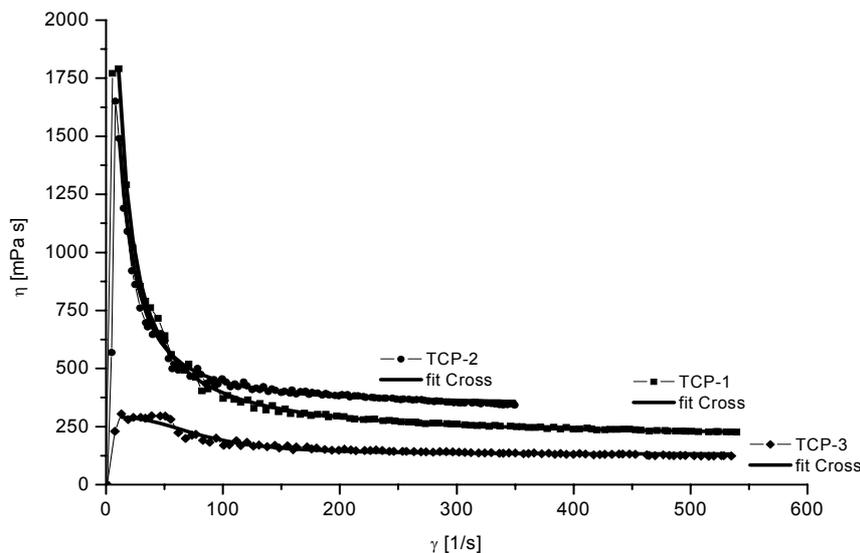
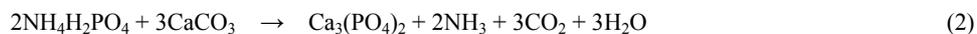


Fig. 5 – Viscosity curves for the beta-tricalcium phosphate suspensions.

The preliminary results are promising as far as beta-TCP powder preparation as aqueous suspensions in view to casting mould is concerned. Also, the used additives for dispersing/stabilizing suspensions carried out their role, although they were not reported in the literature. As a consequence of this preliminary study, it can be concluded that the investigations related to the suspensions of beta-TCP with the studied additives could be continued.

EXPERIMENTAL

Beta-tricalcium phosphate obtained from raw materials of advanced grade like $\text{NH}_4\text{H}_2\text{PO}_4$ and CaCO_3 , respectively, (Merck quality) was used in the experiments. The tricalcium phosphate has been prepared through the classic sintering in solid phase according to the reaction:



The raw materials dosed to the compound stoichiometry were wet homogenized, in planetary mills, ethanol medium. The dried material was calcinated at $900\text{ }^\circ\text{C}$ for 2 hours, when

the formation of the tricalcium phosphate (TCP) begins, and then it was sintered at $1150\text{ }^\circ\text{C}$ / 2 hours to finish the formation of the stoichiometric beta-TCP compound. The

chemical composition and the morphology of the powder investigated by X-ray diffraction analysis (XRD), infrared spectroscopy (IR) and scanning electron microscopy (SEM), was used to emphasize the obtained beta-TCP compound as a unique phase. The crystal structure analysis, mineralogical composition and lattice parameter determinations was carried out using a X-ray powder diffractometer, Bruker-AXS, D8 ADVANCE with CuK radiation.

Infrared spectroscopy (IR) of powders was performed with a Testscan SHIMADZU FTIR, 800 series, spectrometer using a KBr pellet technique. Approximately 2 mg of sample and approximately 300 mg of KBr were ground and pressed in a

7.5 mm diameter die at ~90 MPa for 1 minute to produce uniform discs for analysis.

Microcrystalline structure was analysed with electron-scan microscope SEM, Hitachi S-2600N.

To obtain the aqueous suspensions, the beta-TCP powder was homogenized with distilled water by manual and magnetic agitation (30 min). As deflocculants, stabilizers and binders the following compounds were used: Arabic gum (A.G.), sodium-carboxymethylcellulose (Na-CMC), polyvinyl alcohol (PVA).

The composition of the suspensions is presented in Table 2.

Table 2

Composition of the prepared suspensions

Sample	Suspension [%]		Additives [wt.%]		
	Solid [wt.%]	Distilled water [wt.%]	Na-CMC	A.G.	PVA
TCP-1	49.10	50.90	1.64	5.00	0.68
TCP-2	51.60	48.40	5.00	-	0.80
TCP-3	48.81	51.18	3.00	-	-

All obtained suspensions were characterized from point of view of the volume weight, pH and flow behaviour. The initial pH values were measured using pH-conductometer Denver Model 220. Rheoviscosimetric measurements were carried out using rotational HAAKE VT® 550 viscometer at different shear rates (0 – 541 s⁻¹) at room temperature. The data were analyzed with RheoWin v. 2.0 software and plotted with Origin 5.0 software.

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