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Fabrication and characterization of porous tricalcium phosphate ceramics

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Abstract

Preforms of beta tricalcium phosphate (β-TCP) ceramics were produced by using a modified slip casting technique. The slip was prepared by suspending custom-made TCP powder and PMMA beads in an aqueous medium stabilized with an acrylic deflocculant. Porous TCP ceramics were obtained by sintering the polymer-free preforms for 2 h at 1000 °C. The XRD pattern for the TCP ceramic indicated that the product was essentially pure β-TCP. SEM examination of pore size and pore size distribution revealed that the ceramic was appropriate for repair of cortical defects.

Keywords: A. Slip casting; B. Microstructure; TCP powder; Porous ceramic

1. Introduction

Bone grafts are required in orthopedic surgery for filling bone cavities, treatment of nonunion and replacement of bone lost during trauma and tumor removal. Bone defects may be filled by using autografts, allografts, synthetic bone substitutes or combinations of these materials. Currently, autogenous bone is regarded as the best material for repair of such bony defects. However, quite frequently, the advantage of an autograft is offset by its scarcity and by donor site complications. Allografts may be supplied as fresh, frozen or freeze-dried and are usually sterilized by ethylene oxide, gamma irradiation or with various organic solvents. A greater part of the strength is lost after sterilization and also there is a risk of transmittal of infectious diseases.

Synthetic bone materials can be prepared free of the shortcomings mentioned for autografts and allografts. Due to their physicochemical and biological similarities to natural bone, calcium phosphate ceramics have been used successfully in orthopedic surgery as an alternative to autogenous and allogenous bone grafts. The most remarkable property of these ceramics is their ability to bond directly to bone [1–4]. Ceramics made from synthetic tricalcium phosphate $Ca_3(PO_4)_2$ and hydroxyapatite $Ca_{10}(PO_4)_6(OH)_2$ or their combinations have been tested as bone graft substitutes with generally favorable results because of their osteoconductive characteristics [5–16]. Absence of foreign body reactions, local inflammatory response, or systemic toxicity have been reported as decisive advantages [17].

Porous β-TCP ceramic is essentially a bio-resorbable calcium phosphate. Its tissue biocompatibility is excellent and it may act as a scaffold allowing bone regeneration and ingrowth. Because of its resorbable characteristic, the porous TCP is regarded as an ideal material for bone substitutes that should degrade by advancing bone growth. Therefore, the porous structure of a synthetic bone should resemble the morphology of the natural one being replaced. In this regard, size and distribution of pores and their interconnects become quite important. Although the optimal pore diameter may depend on the location of the defect to be filled, many investigators emphasized that a minimum pore size of 100 μm is necessary for porous implant materials and the minimum size for interconnection has been specified as 20 μm [8,18–21].

The presence of micropores in the sintered material affect the bioresorption of TCP-based ceramic implants

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[22], therefore, the size and amount of macro and micro porosity must be controlled closely during manufacturing processes. A variety of possibilities exit for the fabrication of porous calcium phosphate ceramics; notable among these are in situ foaming of the ceramic slurry by a porosifier such as H_2O_2 [23], use of polymeric foams as substrates [24], and the elaborate replaminoform method introduced by White et al. [25] in 1972.

The most commonly used process for the fabrication of porous calcium phosphate ceramics utilizes uniaxial or isostatic compaction and sintering of powders that contains granules of organics such as naphthalene, polymer, etc. [10,11,19]. Despite its practical advantages, however, the pressing technique is limited to simple geometric forms and there is the problem of polymer springback which generates cracks and laminations in the pressed article.

The present study was undertaken in order to form porous TCP ceramic precursors by the slip casting process which allows us to obtain intricate green shapes by colloidal filtration. Although some HAP-based bioceramics have been produced by this technique [26] no information is available in literature on the application of slip casting in manufacturing TCP ceramics.

2. Materials and method

2.1. Synthesis of TCP powder

The TCP powder used in the present study was prepared by following the procedure established by Hayek et al. [27]. The method, which was preferred for its simplicity and higher yield in comparison to others, consisted in the precipitation of a TCP precusor from an aqueous calcium nitrate solution. A subsequent calcination step yielded phase-pure β-TCP. Starting materials for powder synthesis were reagent grade $Ca(NO_3)_2$ and $(NH_4)_2HPO_4$, both supplied by Merck. The TCP precursor was obtained by combining aliquotes of 0.3 M $Ca(NO_3)_2$ and 0.2 M $(NH_4)_2HPO_4$ in proper cationic molar proportions so that the precipitate obtained would have the specific Ca to P ratio depicted in the molecular formula of TCP.

The precipitation was carried out in a spherical glass reaction vessel fitted with ground glass joint ports for reagent admission. At the start of synthesis, 750 ml of 0.3 M calcium nitrate solution was introduced into the reaction vessel. The reactor was fitted with a tube condenser and the system was heated to 50 °C. Next, 0.2 M diammonium hydrogen phosphate solution was admixed with the hot calcium nitrate solution by dropwise addition through one of the ports. Throughout the mixing process the pH of the system was maintained between 5.5 and 6.0 with the aid of 12.5% aqueous ammonia solution. The reaction was conducted under flowing nitrogen while the contents of the vessel was stirred vigorously to eliminate any possible chemical inhomogeneity. The temperature of the reaction system was measured and kept constant with the help of a contact thermometer. Upon completion of precipitation the entire system was allowed to age for 15 h and then the colloidal TCP precursor was separated from the mother liquor by centrifugal filtration at 8000 rpm. The precursor was dried at 100 °C for 24 h before any further action.

The TCP powder was obtained through calcination of the precursor in accordance with a schedule determined by preliminary thermal analyses based on DTA and TGA. DTA traces were obtained by a Setaram Setsys TG-DTA unit on 24 mg dry precursor heated up to 1250 °C under nitrogen atmosphere at a rate of 10 °C/min. The conversion of the precursor into TCP was monitored and verified by qualitative and quantitative XRD analyses run on powder samples using a Rigaku D-MAX/B powder diffractometer with mono-chromatic CuK_α radiation. The XRD data were collected employing a step scan of $2\theta = 0.02°$ and 5 s preset time under 40 kV and 20 mA excitation.

2.2. Slip preparation

Slips were prepared at a fixed solid loading of 60 wt.% percent. DI water was used as the suspending medium for the powders. In order to enhance slip stability a commercial organic deflocculant, Dolapix PC33 (Zchimmer&Schwarz GmbH and Co., Germany) was introduced in amounts of 0.5–3 wt.%, based on the weight of the powder. During slip preparation, appropriate amounts of β-TCP powder was weighed and added slowly into the dispersant solution while the weak powder agglomerates were eliminated by ultrasonic agitation.

Rheological characteristics of slips were determined by measuring their viscosities and flow behavior by using a rotating-spindle Brookfield RV Digital Viscometer (Brookfield Engineering, Stoughton MA, USA). The small sample adapter of the viscometer permitted to determine viscosity in small volume (8 ml) slip aliquots. The flow properties of slips were determined in accordance with the procedure specified in ASTM D 2196 test. The shear rates in these measurements were varied in the interval 2.5–100 rpm of the spindle rotation.

2.3. Manufacturing porous ceramics

Porosity in the sintered ceramic was obtained through addition of polymethyl metacrylate beads (PMMA) into the slip suspension. Polymer beads, 210–250 μm in size, were mixed mechanically, and then the slip was poured into teflon rings placed on absorbent plaster blocks. The resultant cakes were dried at room temperature for 24 h. Removal of polymer from the cast pieces had to be carried out in nitrogen atmosphere in order to avoid cracks that form due to expansion of beads when heated in air. In order to impart sufficient strength, the porous green samples were fired at 1000 °C for 2 h in air. Pore size and pore size distributions in the sintered TCP ceramics were examined by SEM. Densities of the fired samples were determined by the liquid displacement technique using xylene.

3. Results and discussion

3.1. TCP powder

The thermal reactions that would occur during calcination of the TCP precursor were represented by the TGA and DTA traces shown in Fig. 1. The TGA curve revealed that the precursor would undergo weight reduction in two stages; a 6.5% loss occurred in the first stage up to 450 °C, followed by an approximate 1.6% loss up to 750 °C. The former was attributed to the evaporation of adsorbed water and ions, while the latter was linked with the endothermic event recorded in the DTA thermogram. The endothermic peak observed at 793 °C and the associated weight loss was commensurate with the following reaction which has been used to describe the conversion of a defective HAP to TCP [28]:

$$Ca_9(HPO_4)(PO_4)_5(OH) \rightarrow 3Ca_3(PO_4)_2 + H_2O \quad (1)$$

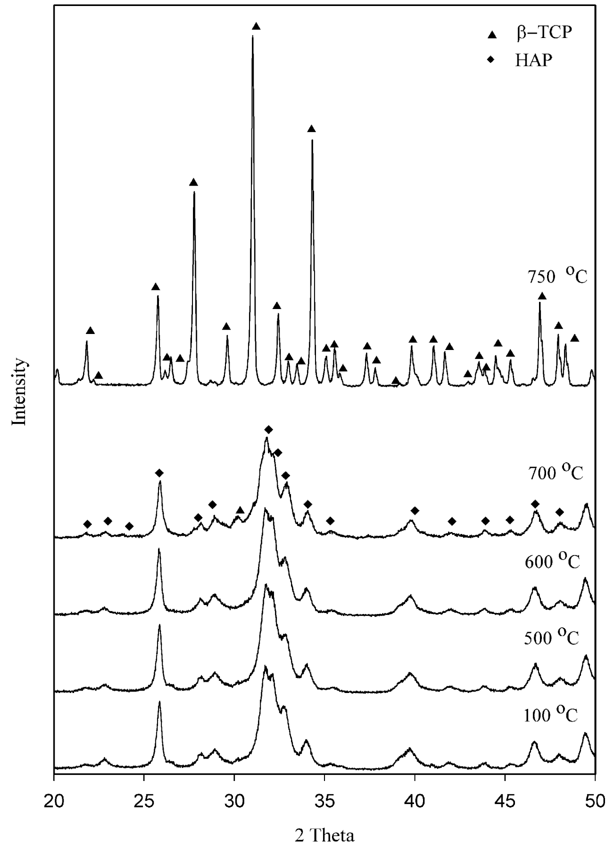


Fig. 2. Effect of temperature on the crystallization of the TCP precursor as followed by XRD.

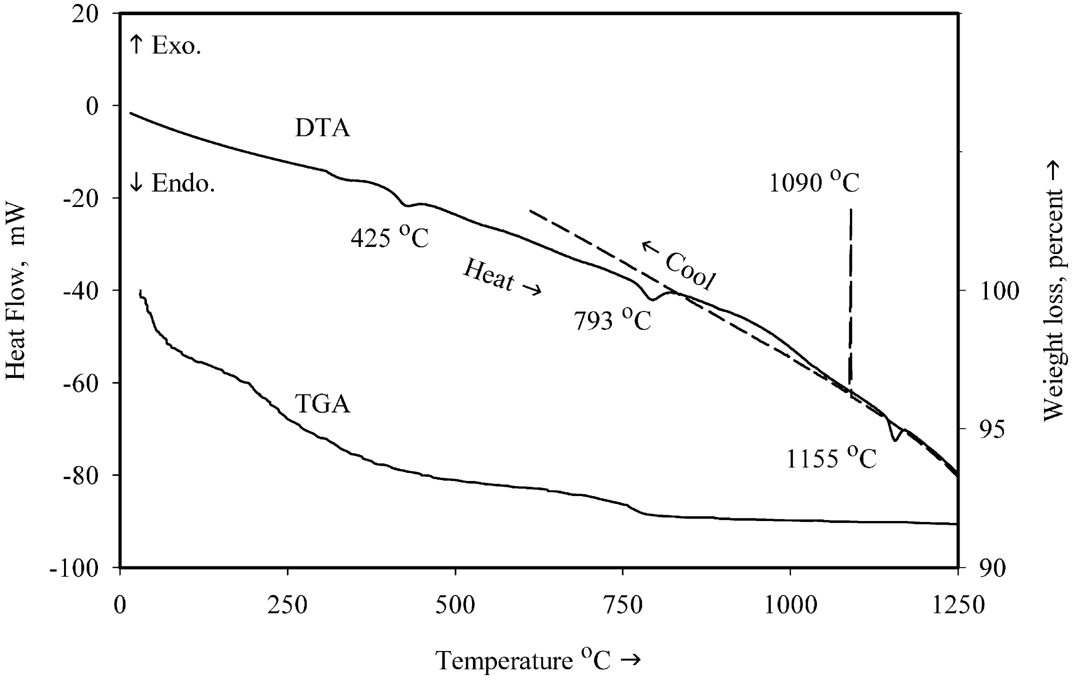


Fig. 1. The TGA and DTA traces of the TCP precursor.

The third peak in the thermogram corresponded to the well-known transformation of β-TCP to the α form. The reaction appeared to be reversible but with a certain degree of time dependence as revealed by the cooling part of the DTA trace.

In order to determine the effect of calcination temperature on the phase purity of TCP, powder XRD studies were performed on products of thermal processing of the precursor in the temperature interval 500–1200 °C. Calcination temperature was increased by 100 °C steps, and the duration at each temperature was fixed as 10 h. Figs. 2 and 3 show the XRD-patterns of calcium phosphate powders obtained by treatment of the precipitates at various temperatures. Processing temperatures lower than 750 °C was insufficient for the decomposition of defective HAP. The peaks in the diffractogram at 750 °C belongs to a fully developed β-TCP; hence 750 °C might be regarded as a proper minimum for the calcination temperature of TCP powders sythesized by the chemical techniques similar to the one described in this work.

As the thermal treatment temperature was raised towards 1200 °C, the peaks of α-TCP built up gradually. The sample calcined at 1120 °C contained only α form of the TCP. This indicated that the β-TCP produced by the chemical methods followed in the present study retained its structural stability at least up to 1100 °C. This information is important for sintering of the synthetic bone substitutes that will be made from β-TCP powders. It is known that the β to α transformation in TCP requires a significant structural rearrangement of atoms and bonds since the β and α polymorphs of TCP have different structures [29]. The increase in the molecular volume attending this transformation has adverse effects on mechanical properties.

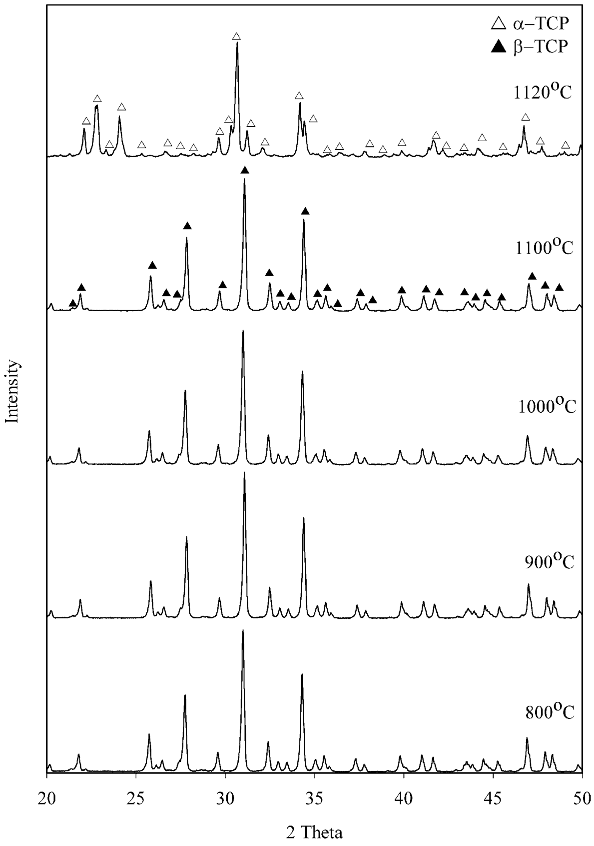


Fig. 3. XRD patterns for the TCP powder calcined at different temperature.

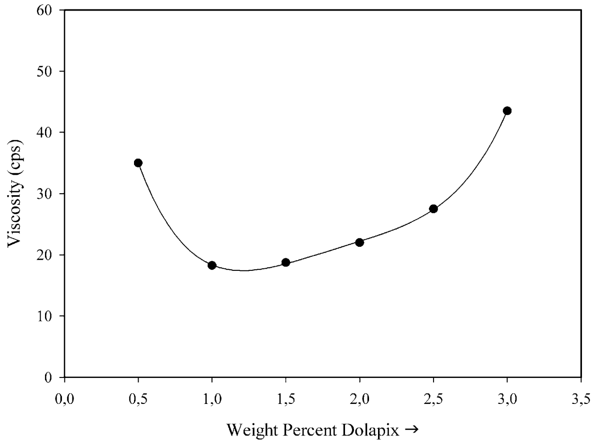


Fig. 4. Variation in the viscosity of the slurry with dispersant concentration. Solid content of the slip = 60 wt.%.

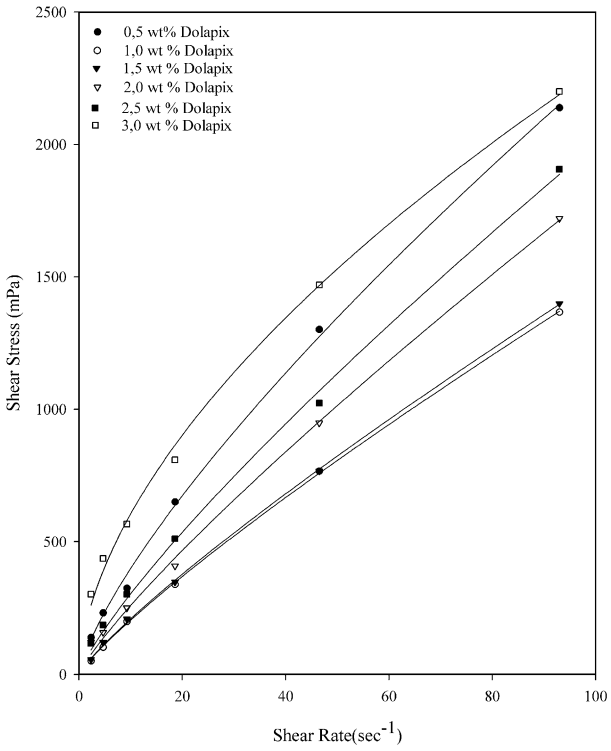
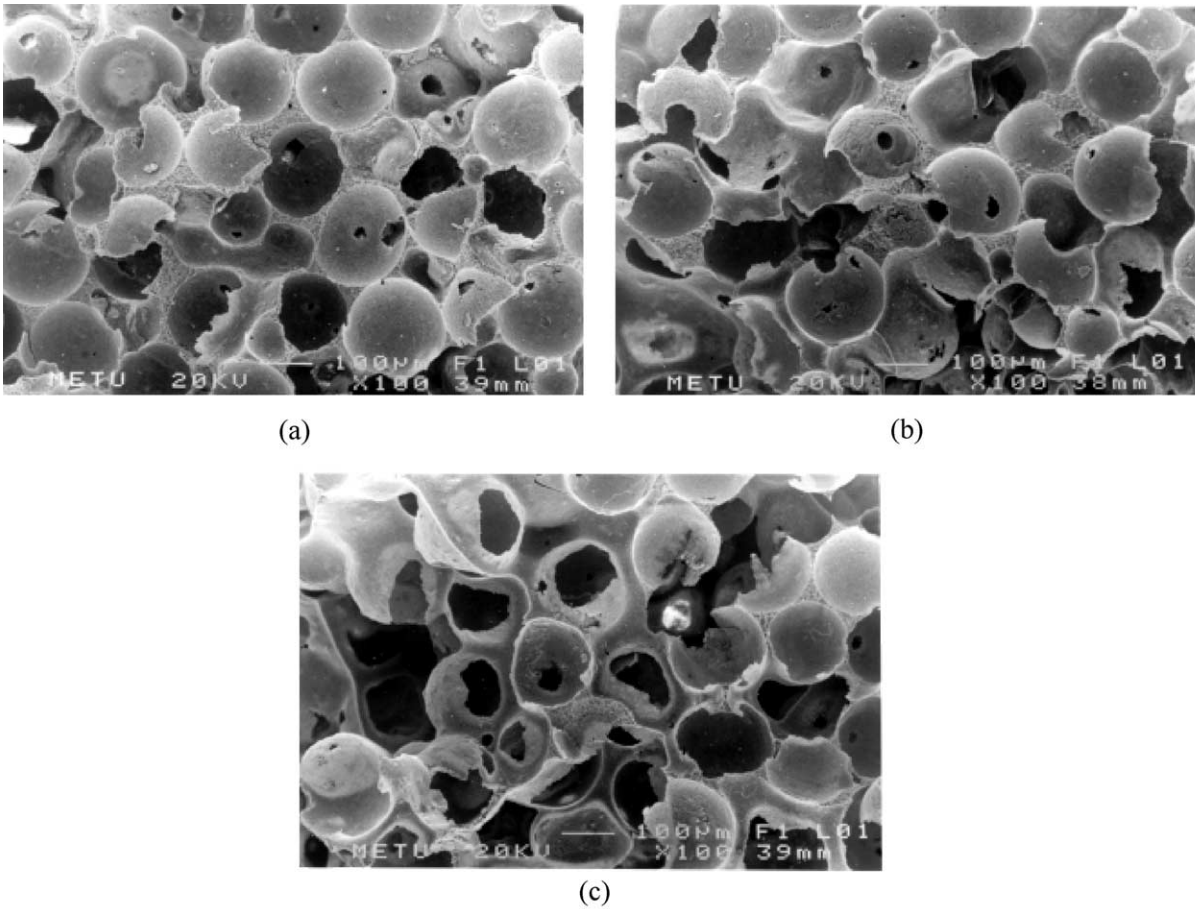


Fig. 5. Rheological behaviour of the slip with different levels of electrolyte additions. Slip containing 60 wt.% TCP powder.

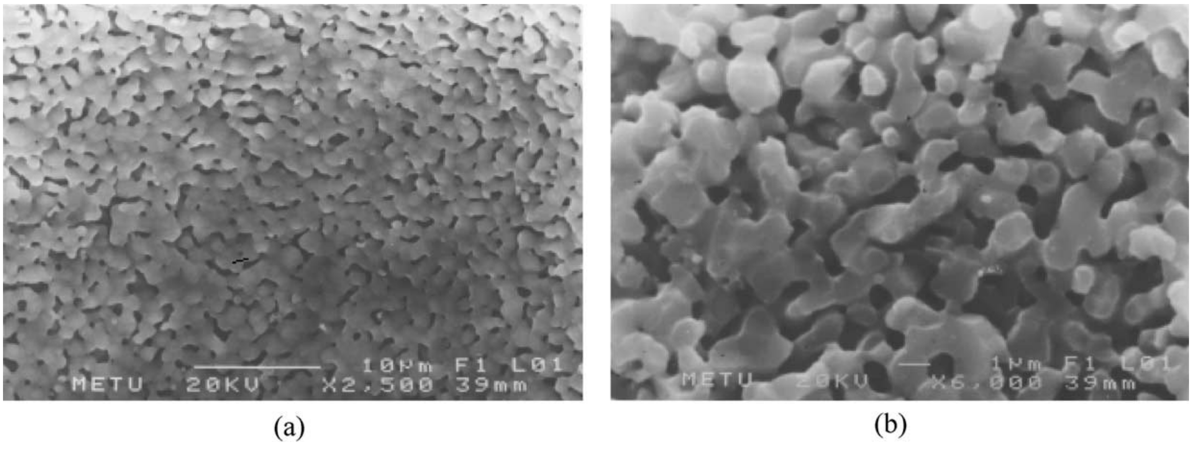
3.2. Rheology of the ceramic slips

Apparent viscosities of TCP slips with different levels of deflocculation are displayed in Fig. 4. The viscosity data were recorded at a constant shear rate of 18.6 s^{-1} corresponding to 20 rpm of spindle rotation. The viscosity curve revealed that slip could attain sufficient fluidity at 1% addition of the deflocculant by weight of powder. The flow behavior of the slip, expressed in terms of shear rate versus shear stress, is described in Fig. 5. A pseudo-plastic behavior was observed in high viscosity slips, whereas slips with low level of dispersant exhibited nearly ideal flow. These slips, which also had relatively low viscosity, were regarded suitable for slip casting.



(a) (b) (c)

Fig. 6. Morphologies of porous β-TCP ceramics. (a) Sample contains 65 vol.% porosity, (b) 75 vol.% porosity, (c) 85 vol.% porosity.



(a) (b)

Fig. 7. Microstructure porous β-TCP ceramics; (a) inside the pore X2500, (b) ceramic matrix X6000.

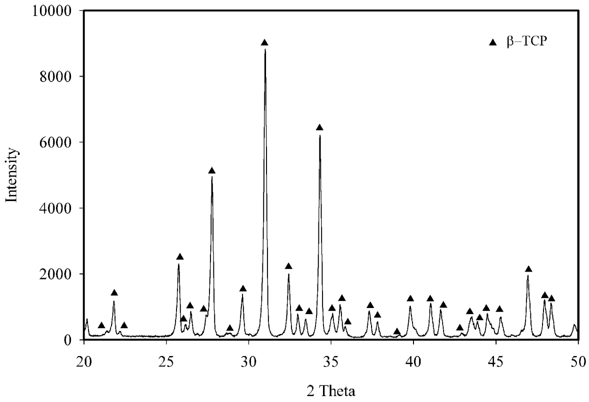


Fig. 8. XRD Pattern for the β-TCP ceramic sintered at 1000 °C.

3.3. *Microstructures of TCP ceramics*

The porous TCP ceramics were obtained upon firing the slip cast performs at 1000 °C. The sintering schedule included a special polymer removal step conducted at 600 °C. The micrographs given in Fig. 6 illustrate the change in the morphology of pore structure as the amount of the porosifier in the casting slip was increased. Micrographs show that the pore distribution was quite uniform in all samples examined under SEM, indicating the fact that polymer beads were suspended properly in the slip.

The first micrograph belongs to the ceramic which contained 65% porosity by volume. The ceramic was prepared from a casting slip which contained 70% polymer beads in the size range 210–250 μm. The average size of large pores in the sintered ceramic was around 190 μm, as determined by areal analysis of the cross section in accordance with the suggestion of Fullman [30]. Small holes at junctions of large spherical pores provided the continuity of the pore channels. The diameters of the interconnections varied between 15 and 40 μm.

Higher proportions of polymer beads in slip solids led to the development of highly porous ceramics with thinner walls. Micrographs (b) and (c) in Fig. 6 belong to the slips prepared from solids containing 75 and 85 vol.% polymer, respectively. As the amount of polymer beads was raised, the size of interconnections increased proportionately. A porosity network of this nature would allow free circulation of body fluids.

The mesoporosity in the matrix of the porous TCP ceramics fired at 1000 °C can be seen in the micrographs of Fig. 7. Apparently, the starting powder of the TCP ceramic was sub-micron in size so that a uniform and ultra-fine porosity had developed in the sintered body. Clinically, this kind of interconnective microporosity is a desirable feature since it facilitates the diffusion of calcium and phosphorus ions for mineralization [31].

4. Conclusions

In this study, a technique based on slip casting process has been developed for manufacturing porous β-TCP ceramics. PMMA beads with proper granulation were used to obtain porosity requisite for artificial bone. The pore architecture obtained was sufficient to permit ingrowth of natural bone, thus the ceramic was suitable for use in repair of cortical defects.

The typical XRD pattern of the porous β-TCP ceramic fired at 1000 °C is given in Fig. 8. Quantitative treatment of the diffraction data throught the computer code Lattice 1.4 gave the lattice dimensions a and c of the structure as $a = 1{,}043585$ nm and $c = 3{,}74358$ nm. The pattern and the lattice constants were found to be in excellent agreement with the data in JCPDS card number 9-169. Therefore, it was concluded that, the ceramic was essentially phase-pure TCP and it remained virtually unaffected from environmental contamination that could possibly accrue from processing.

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