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Preparation and characterization of calcium phosphate-poly(vinyl phosphonic acid) composites

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Composites of calcium phosphates and the calcium salt of a biomedical polymer were prepared *in situ* by hot-pressing particulate mixtures of poly (vinyl phosphonic acid) (PVPA) and tetracalcium phosphate $Ca_4(PO_4)_2O$, or TetCP) at different temperatures, pressures, and time periods. The objective was to establish whether PVPA could react with TetCP (Ca/P ratio of 2.0) to form a calcium salt, and thereby decrease the available Ca/P ratio 1.67 to facilitate hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$ or HAp) formation. The effects of varying the bulk composition, temperature (to 300 °C), pressure (to 690 MPa) and time (to 60 min) on the reaction between TetCP and PVPA were studied using X-ray diffraction, infra-red spectroscopy and scanning electron microscopy techniques. Results showed that the conversion of TetCP into HAp increased with compaction time as temperature and/or pressure were increased. Formation of anhydrous dicalcium phosphate ($CaHPO_4$, or DCPA) was also observed. Complete conversion of TetCP to HAp was achieved in composites pressed at 250 °C and 415 MPa for 30 min.

1. Introduction

Tetracalcium phosphate (TetCP) is the only calcium phosphate more basic than hydroxyapatite (HAp). Because of the Ca/P ratio difference between HAp and TetCP [1], complete TetCP hydration produces HAp and calcium hydroxide according to Equation 1

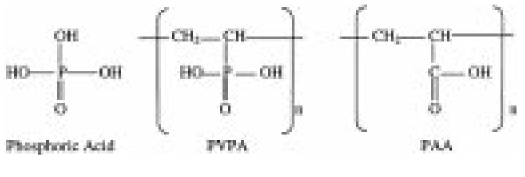
$$3Ca_4(PO_4)_2O + 3H_2O \longrightarrow Ca_{10}(PO_4)_6(OH)_2 + 2Ca(OH)_2 \qquad (1)$$

Recently, it was demonstrated that the presence of a poly(alkenoic acid), such as poly(acrylic acid) (PAA), influences TetCP hydrolysis [2]. The carboxylic acid groups in this polymer react with TetCP via an acid-base reaction forming a Ca salt of the acid

$$\text{TetCP} + \text{PAA} \longrightarrow \text{HAp} + \text{Ca(PAA)} \qquad (2)$$

Consequently, a biocomposite in which HAp crystals were embedded in a network of the Ca salt of the polymer was produced.

Poly(vinyl phosphonic acid), PVPA, is an acidic polyelectrolyte analogous to poly(alkenoic acids) [3], that contain acid functional groups similar to those of phosphoric acid [4]:



Moreover, poly(phosphonic acid)s are stronger polyacids than poly(carboxylic acids)s [5]. Cements formed from the reaction between PVPA and aluminosilicate glasses have been investigated for use as dental cementing materials which are analogous to the glass polyalkenoate cements [6].

The nature of the functional group in PVPA enables it to form highly cross-linked structures rather than in-chain di salts [7]. In the former, the phosphonate groups are intermolecular and bonds to cations forming these cross-links. In the latter, the phosphonate groups are intramolecular and two attached to a single polymer molecule coordinate to a calcium ion in the set structure [7]. Based on the ability of phosphonate ions to exchange with the phosphate ions on hydroxyapatite crystals [8], a polymeric compound that carries multiple phosphonate ions is expected to have a higher affinity for the HAp surface because the polymer can simultaneously attach itself to many sites [9]. In this respect, ^{32}P-polyphosphonated polyethylene forms a strong, practically irreversible, monolayer on tooth enamel surface [10].

A companion study has shown that TetCP reacts to initially form DCPA and the salt of the polymer. DCPA then reacts with the remaining TetCP to form HAp [11].

The objective of the present study was to determine the extent of TetCP hydrolysis in presence of PVPA and the characteristics of the resultant composites depending on the processing variables of reaction time, temperature, and pressure. Thus, powder mixtures were hot-pressed at

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elevated temperatures and pressures in a solid state process that resembles those used in powder metallurgy. The composites produced were characterized for their compositions using X-ray diffraction (XRD) and Fourier-transform infra-red (FTIR). Microstructures were observed by scanning electron microscopy (SEM). Mechanical properties were measured by the diametrical compression test.

2. Experimental work

2.1. Synthesis of $Ca_4(PO_4)_2O$

$CaCO_3$ (OSRAM Sylvania, Towanda, PA) and $Ca(H_2PO_4)_2 \cdot H_2O \cdot$ (MCPM) (FMC corporation, Philadelphia, PA) were mixed in a molar ratio of 3 : 1 and milled in n-Heptane for 16 h. The resultant slurry was then filtered, dried at room temperature for 24 h and assessed by XRD analysis for absence of the MCPM, formation of $Ca(H_2PO_4)_2$, and the presence of $CaCO_3$. The powder mixture was then fired at 1310 °C in air for 2 h, and rapidly quenched to room temperature. The fired product was ground by hand, then milled in a Sweco mill for 24 h, and examined for phase purity as $Ca_4(PO_4)_2O$ using XRD and FTIR. The $Ca_4(PO_4)_2O$ powder produced was kept under vacuum to avoid hydrolysis.

2.2. Composite formation

PVPA (Polyscience, Inc.) and TetCP powders in a TetCP-to-PVPA ratio of 1.5 were thoroughly mixed then placed in a stainless steel mold with a 0.5 inch diameter cavity. The mold was wrapped with a heating tape (Thermolyne Brisk Heat), and powders were hot-pressed at different temperatures, pressures and times using a Carver hot-press. During the heating process, pressure was released 5–6 times before the maximum temperature was attained to expel the water vapor produced during reaction. At the end of each experiment, the assembly was cooled while the maximum pressure of the experiment was still applied. After room temperature was reached, the composite was removed, ground by a mortar and pestle to be characterized for its composition and microstructure.

2.3. Characterization of the composites

XRD analyzes were performed using an automated diffractometer (Scintag, Inc., Sunnyvale, CA), with a step size of 0.02°, a scan rate of 2° per min, and a scan range from 20° to 40° 2θ. A single beam infra-red spectrometer (FTIR) (MB100, Bornem/Hartmann & Braun, Quebec City, Canada) was used, and spectra were obtained over the wave number range of 400–4000 cm^{-1} at a resolution of 3 cm^{-1}. The KBr (Spectroscopic grade, Aldrich Chemical, Milwaukee, WI) drifts technique was used with a KBr/sample ratio of 100 : 1. Microstructural development was observed using a conventional dual-stage SEM (XL-200, Philips).

2.4. Measurement of mechanical properties

The fracture strengths of the composites were determined using the diametral compression test [12]. Testing was performed using an automated Instron machine at a crosshead speed of 0.05 cm/min. A right circular disk is compressed diametrically between two flat plates. The maximum tensile stress is developed normal to the loading direction across the loading diameter. The maximum tensile strength, which occurs on the dimetral plane between loading points, given by $\sigma = 2P/Dt$, where P is the load, D is the specimen diameter, t is its thickness. A pad of a soft material was inserted between the hard plates and the specimen to help reduce the high compressive stresses at the loading lines.

3. Results and discussion

Fig. 1 shows the XRD pattern of a sample prepared at 300 °C and 140 MPa for 60 min. Compared with the diffraction pattern of TetCP, there were almost no changes in the diffraction pattern after hot-pressing under these conditions. However, the variation in the relative intensities of the peaks at $2\theta : 29.3$ and 29.9° when compared to those at 31.9, 32.2 and 32.9° and the existence of another peak at $2\theta : 26.1°$ indicate that a small amount of HAp might have formed. Moreover, the presence of the peaks at $2\theta : 26.5$, 26.7 and 30.5° may also indicate the presence of a small amount of DCPA ($CaHPO_4$). Thus, at a pressure of 140 MPa, reaction starts to take place very slowly. However, this pressure is not sufficient for the reaction to continue until completion.

Fig. 2 shows XRD patterns of samples hot-pressed for 30 min at 250 °C at various pressures. It can be seen that the main phase formed at all pressures was HAp. $CaHPO_4$ (DCPA) was also detected in the samples prepared at 275, 550 and 690 MPa. Reaction at 415 MPa appears to form essentially phase-pure HAp. The presence of DCPA in these samples was consistent with SEM observations. Fig. 3 shows SEM micrographs of the fractured surface of a sample hot-pressed at 250 °C, 275 and 550 MPa for 30 min. HAp, large irregularly-shaped features and DCPA crystallites $\sim 2\ \mu m$ in length can be observed. These results indicate that reaction can take place leading to complete formation of HAp at 415 MPa. However, at excessive pressures, complete reaction does not occur.

The FTIR spectra of these samples shown in Fig. 4 illustrate the bands at 931 cm^{-1} (assigned to the

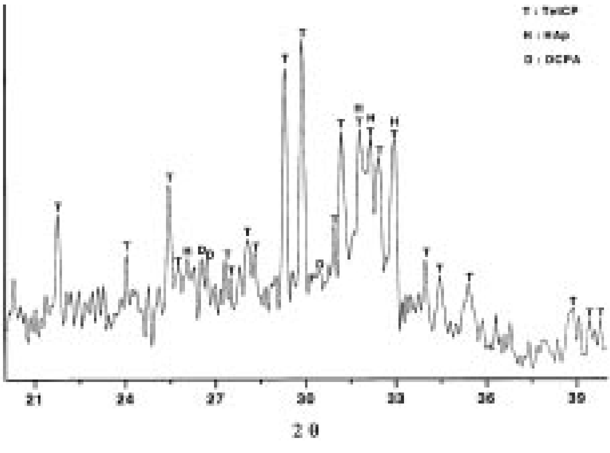
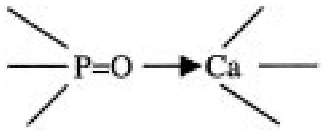


Figure 1 XRD pattern of sample hot-pressed for 60 min at 300 °C, and 140 MPa.

symmetric vibration of P-O of PVPA) decreased to 907 cm^{-1} while the band at 984 cm^{-1} (assigned to the asymmetric vibration of P-O of PVPA) [4] disappeared as pressure was increased. Such changes are attributed to salt formation [4]. In addition, a new band appeared at 1054 cm^{-1}. This has been assigned to the polyphosphonate salt [4] indicating the interaction involves bonding of Ca ions with the P-O^{-} ions of the polymer. The orthophosphate (PO_4^{3-}) group in both HAp and TetCP absorb strongly in the range of 1090–960 cm^{-1}. Therefore, an overlap is expected between the PO_4^{3-} and the salt bands. Another band at 1173 cm^{-1} is assigned to the phosphonyl group (P═O) of PVPA. This band continued to exist with diminished intensities in all samples after hot-pressing indicating that some P═O bond character is retained in the polysalts formed. It has been claimed [4] that the shift in the P═O band to lower values is indicative of an interaction of the type



However, no shift in this band was observed indicating an interaction of this type does not occur. Moreover, the OH band at 3408 cm^{-1} of the acid disappeared indicating salt formation causes complete deprotonization. Finally, the two bands at 601 and 566 cm^{-1} characteristic of apatites were found in all samples.

Building on the above results, samples were hot-pressed for 30 min at 275 MPa and different temperatures. The XRD patterns of these samples are shown in Fig. 5 and clearly indicate that HAp formed as the main phase at all temperatures. However, the crystallinity of the HAp varied with temperature. Crystallinity increased with increasing temperature from 250 to 275 °C then decreased again at 300 °C. At 300 °C, TetCP was still detected in the XRD pattern. A minor amount of DCPA was also detected. Fig. 6 shows the microstructure of the composite prepared at 275 MPa, 300 °C for 30 min; these three phases can be observed. TetCP is present as dark, irregularly shaped grains, HAp as agglomerates of crystals while DCPA appears as collections of rod-like crystallites [13]. Thus, as with overcompaction (Fig. 2), reaction at an excessively high temperature is also limited.

Prior results showed the reaction between TetCP and PVPA to take place via the following mechanism: the polymer starts to flow when its T_g is reached, surrounding the TetCP particles. Reaction initiates at the interfacial zone between them forming calcium polyphosphonate salt and DCPA according to Equation 3

$$\text{TetCP} + \text{PVPA} \longrightarrow \text{Ca-PVPA} + \text{DCPA} + [\text{TetCP}] \quad (3)$$

where [TetCP] = unreacted TetCP.

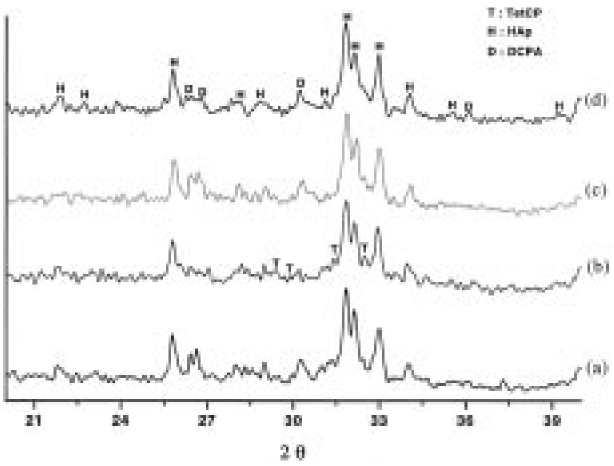
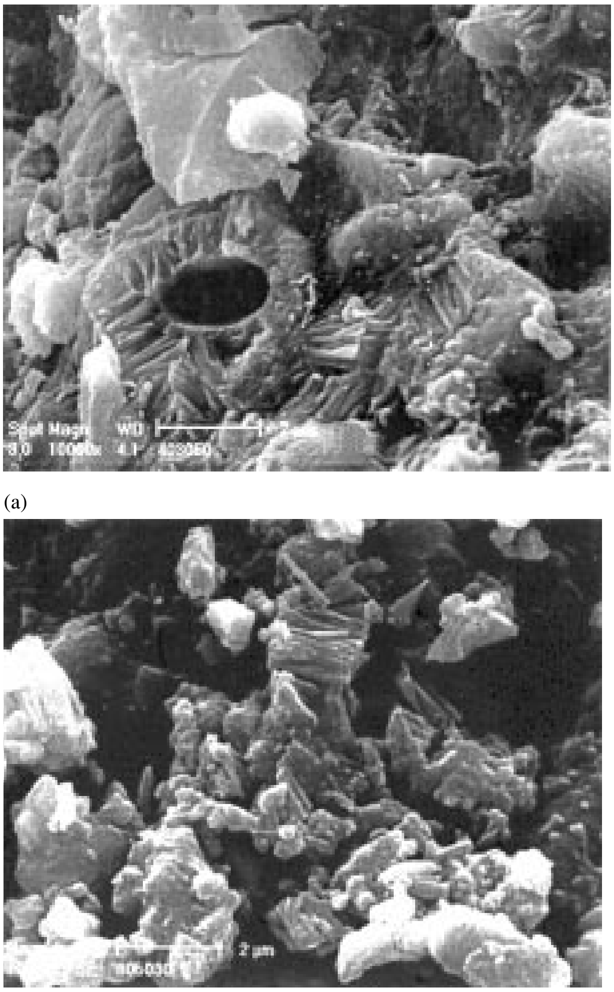


Figure 2 XRD patterns of samples hot-pressed for 30 min at 250 °C, and (a): 275, (b) 415, (c) 550, and (d) 690 MPa.

The formation of the salt is expected to take place very rapidly as soon as reaction starts based on the site binding of Ca^{2+} ions with PVPA [14]. Formation of the salt was confirmed with the FTIR results based on the absence of the bands at 984 and 3408 cm^{-1} in Fig. 4 that are assigned to the undissociated acid. Therefore, although it was not possible to assign bands characteristic to DCPA in the FTIR spectra of all samples, the FTIR results confirmed the formation of HAp and polyphosphonate salt in these samples. The presence of H_2O promotes the reaction between DCPA and TetCP forming HAp according to Equation 4

$$2CaHPO_4 + 2Ca_4(PO_4)_2 \xrightarrow{H_2O} Ca_{10}(PO_4)_6(OH)_2 \quad (4)$$

The presence of DCPA in small amounts with HAp in those samples hot-pressed for 30 min at 250 °C, and 275,



(a)

(b)

Figure 3 SEM micrographs of samples hot-pressed for 30 min at 250 °C, and (a) 275 and (b) 550 MPa.

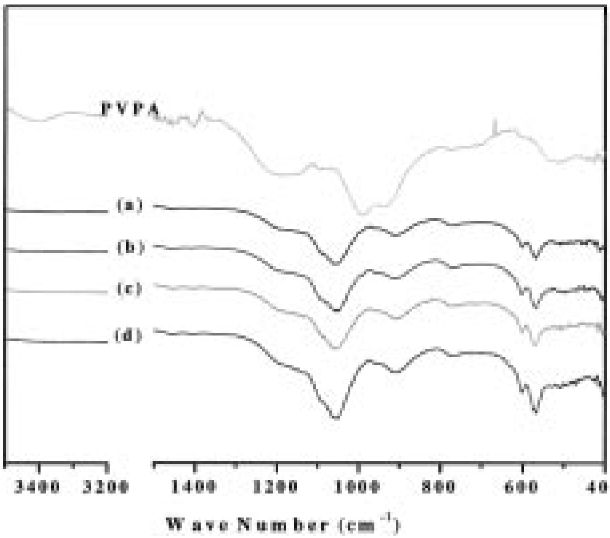


Figure 4 FTIR spectra of samples hot-pressed for 30 min at 250 °C and (a) 275, (b) 415, (c) 550 and (d) 690 MPa.

550 or 690 MPa indicates that TetCP is consumed [15] according to Equation 5

$$(2+x)\mathrm{CaHPO_4} + 2\mathrm{Ca_4(PO_{42}O} \longrightarrow \mathrm{Ca_{10}(PO_4)_6(OH)_2} + x\mathrm{CaHPO_4} \qquad (5)$$

This was confirmed by the absence of TetCP diffraction peaks in these samples. The presence of essentially phase pure HAp in sample b in Fig. 2 indicates that reactions 3 and 4 occurred resulting in HAp and Ca polyphosphonate salt.

Fig. 7 shows the XRD patterns of samples hot-pressed for different times at 275 MPa, 250 °C, and Fig. 8 compares the SEM micrographs of the samples hot-pressed for 10 and 60 min. Small amounts of TetCP and DCPA were detected in the sample heat treated for 10 min indicating incomplete reaction between them. However, heat treating for longer times resulted in the formation of only two phases. HAp was predominant with a minor amount of DCPA. The presence of DCPA regardless of the duration of heat treatment is consistent with the observation that conversion of TetCP to HAp involves the formation of DCPA as an intermediate [11].

Figure 6 SEM micrograph of sample hot-pressed for 30 min at 300 °C, and 275 MPa.

Fig. 9 shows the tensile strengths of samples hot-pressed for 30 min and 250 °C at different pressures. All samples exhibited brittle fracture. The presence of DCPA as a second phase accompanying HAp enhanced the mechanical properties as shown in samples hot-pressed at 275 and 550 MPa. On the other hand, the presence of HAp as the predominant or single phase lowered the mechanical properties. The strengths of the present composites are inferior to those observed in our previous study of HAp-acrylate compolymer composites where a maximum tensile strength of 81 MPa was achieved by compaction at 300 °C, 415 MPa for 30 min. The origin of the difference is attributable to the following reasons:

(a) Presence of micro-cracks, as seen in Fig. 8 (a) and (b).

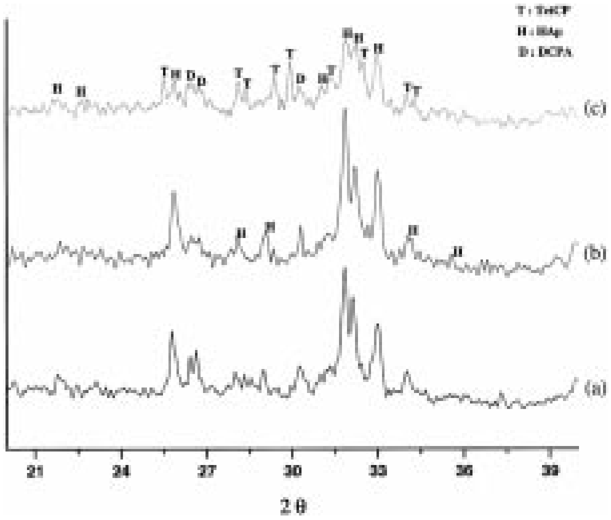


Figure 5 XRD patterns of samples hot-pressed for 30 min at 275 MPa and (a) 250, (b) 275 and (c) 300 °C.

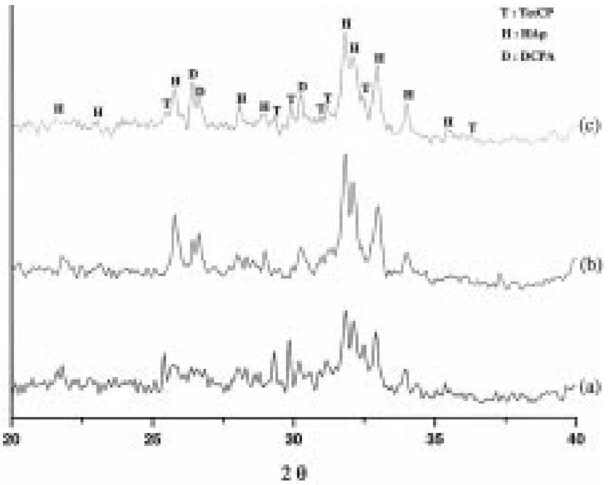
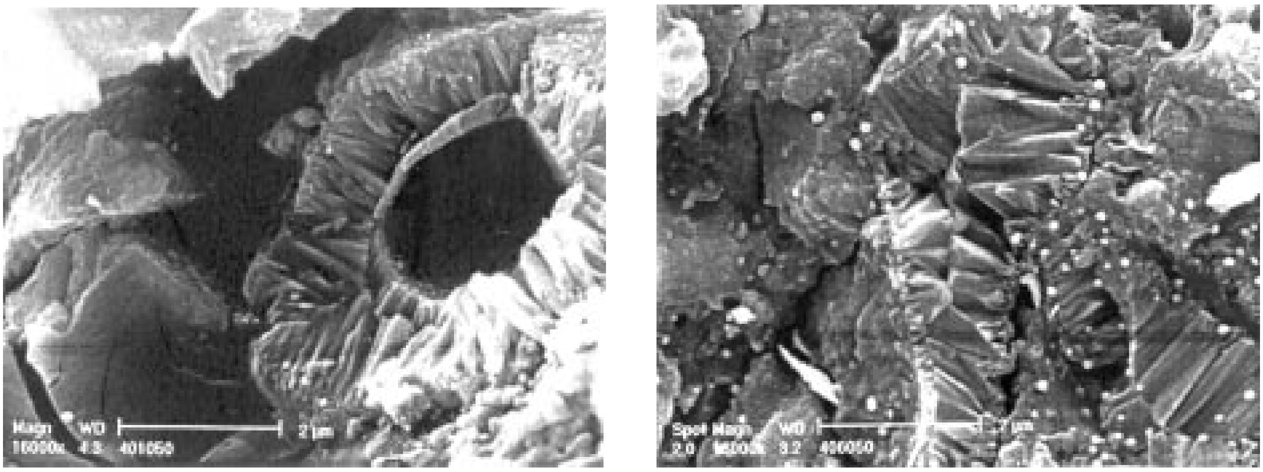


Figure 7 XRD patterns of samples hot-pressed at 275 MPa, and 250 °C for (a) 10, (b) 30 and (c) 60 min.



(a) (b)

Figure 8 SEM micrographs of samples hot-pressed at 250 °C, and 275 MPa for (a) 10, and (b) 60 min.

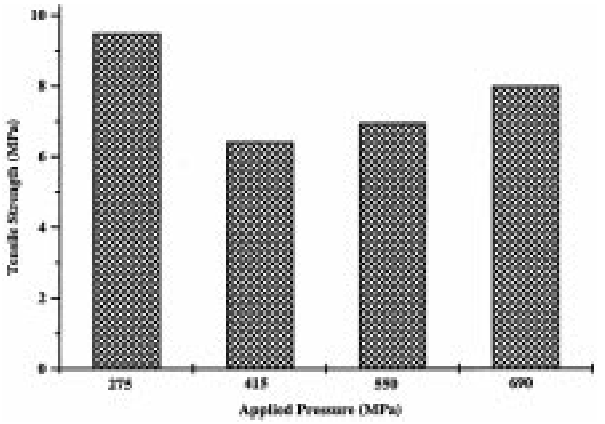


Figure 9 Tensile strength of composites prepared at 250 °C for 30 min and different pressures.

(b) The presence of a high proportion of the polymer (~30 wt %).

(c) The relatively low molecular weight of PVPA as compared to that of the acrylate copolymer previously investigated [2].

4. Summary

A solid-state acid-base reaction takes place between a basic inorganic solid (TetCP) and an acidic polymer (PVPA) when a mixture of these reactants is compacted at elevated temperatures. The reaction initiates with the formation of DCPA and a Ca salt of poly(vinyl phosphonic acid). In the presence of H_2O, DCPA reacts with the unreacted TetCP forming HAp. The extent of HAp formation increased with pressure or time as observed by XRD, FTIR and SEM. However, at 300 °C, reaction became very slow and unreacted TetCP was detected along with HAp and DCPA. Highest tensile strengths were observed in samples hot-pressed at 275 MPa, 250 °C and 30 min, whereas almost phase-pure HAp was only observed for samples hot-pressed at 415 MPa, 250 °C for 30 min. At higher pressures, tensile strength values decreased as micro-cracks formed.

Acknowledgment

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