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Synthesis of carbonate substituted hydroxyapatite by Pechini method

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Abstract

Calcium hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$) was synthesized by Pechini method by using citric acid and ethylene glycol as a complexing agent and gelling agent. Calcium nitrate and diammonium hydrogen phosphate were taken as the source of calcium and phosphate respectively. The as-prepared precursor and calcined products were characterized by powder X-ray diffraction (XRD) for phase identification, Fourier - Transform Infrared spectroscopy (FT-IR) for functional group analysis and Thermal analyzer to check the thermal stability. Results showed that the product formed is a carbonate substituted hydroxyapatite and its thermal stability is less when compared with pure hydroxyapatite.

Keywords: Carbapatite; hydroxyapatite; pechini method; thermal analysis.

1. Introduction

Hydroxyapatite (HAp) $Ca_{10}(PO_4)_6(OH)_2$ is the major inorganic constituent present in the bone and a potential bone substitute material which finds application in the field of orthopedics and dentistry due to its excellent biocompatibility and its chemical composition being roughly equivalent to the inorganic matrix of bone (Burguera *et al.,* 2008). Upto 50 percentage of bone by weight is a modified form of hydroxyapatite, which is commonly known as bone mineral. As a component of composites, hydroxyapatite is finding uses as potential new bone replacement biomaterial (Rauschmann *et al.,* 2005). Other biomaterials such as titania, alumina, zirconia and calcium silicates have been proposed to repair bone damage but most of them don't have the ability to bond with the hard tissues directly (Kong *et al.,* 2005). Some significant properties such as bioactivity, biocompatibility and non biodegradability of hydroxyapatite is perfectly balanced, which is not possessed by any other biomaterials. In addition, hydroxyapatite finds many industrial applications in the field of catalysis (Jaoui *et al.,* 2000), chromatography (Renault *et al.,* 2006), effluent treatment (Gomez del Rio *et al.,* 2006) and sensors (Mahabole *et al.,* 2005), which drive the researchers to develop new methods to synthesis hydroxyapatite materials.

Several methodologies for the preparation and processing of hydroxyapatite bioceramics were carried out over the years. Among them, the solid-state synthesis of hydroxyapatite from oxides requires extensive mechanical mixing and lengthy thermal treatments at high temperatures. However, these processing conditions do have control over micro-structure, grain size and grain size distribution in the resulting powders.

Several wet-chemicals such as polymerized complex routes, ultrasonic irradiation (Kim & Saito, 2001), sol–gel (Bogdanoviciene *et al.,* 2006), precipitation (Mobasherpour *et al.,* 2007), microwave irradiation (Cao *et al.,* 2005), emulsion (Chen *et al.,* 2004), hydrothermal (Loo *et al.,* 2008), rapid solution combustion (Sasikumar & Vijayaraghavan*,* 2010), glowing combustion (Koppala & Swamiappan, 2015) and gel-pyrolysis (Varma & Babu, 2005) methods have been used to produce hydroxyapatite phases. Most of these methods suffer from the complexity of the procedures and are also highly time consuming. Some of these methods can produce a high quality powder, but not cost effective because of small batch production and expensive raw materials.

The Pechini method is generally used to prepare spinels and it does not require high temperature calcinations and permits good stoichiometric control as well as reproducibility. The Pechini method has first appeared in 1967 as a method of depositing dielectric films of lead and alkaline earth titanates and niobates for electrical capacitor design applications. This method was named after its inventor Maggio P. Pechini and then, the method was found to be important in the synthesis of magnetic materials, high temperature superconductors, ceramics and catalysts (Pechini, 1967).

This method consists of the formation of a polymeric resin between a metallic acid chelate and polyhydroxide alcohol by polyesterification. In this process, metal nitrates or carbonates are used as the starting materials, which avoid the problem of handling moisture-sensitive alkoxides. In addition, different cations can be mixed to the quasi-atomic level that allows precise control of the chemical composition (Taguchi *et al.*, 2008).

In the present work hydroxyapatite was synthesized by using citric acid and ethylene glycol as a gelling agent and studied the influence of gelling agent and complexing agent in the purity of the product.

2. Experimental procedure

2.1 Materials and methods

Stoichiometric amounts of powders of $Ca(NO_3)_2 4H_2O$ (99+%, AR, Rankem) $(NH_4)_2HPO_4$ (99%, AR, Merck), and Citric acid (99.7%, AR, SRL) were dissolved in demineralized water at room temperature to yield 1M stock solutions. 4 M stock solution of ethylene glycol was prepared by dissolving it in water. From the stock solution, equal volumes of the citric acid, ethylene glycol and calcium nitrate were taken in an uncovered glass beaker and stirred with a magnetic stirrer for 10 minutes at room temperature. The molar ratio of citric acid to ethylene glycol taken was 1:4 and the resultant solution was acidic (pH =1.28) to which stoichiometric volume of $(NH_4)_2HPO_4$ solution was added drop wise with the constant stirring. Throughout the process the temperature was maintained at 50°C. The resultant clear solution (pH =2.8) was stirred constantly using magnetic stirrer and the temperature was raised to 80°C and maintained for 90 min. in an uncovered glass beaker.

When the solution becomes thick white gel, the beaker was removed from the stirrer and placed inside the muffle furnace maintained at 300°C for 1 h. The gel got decomposed to form a brown precursor and the precursor obtained is calcined at 900°C for 2 h to result in the formation of hydroxyapatite.

3. Characterization

Phase identification was done using RIKAKU X-Ray Diffractometer, using Cu Kα, Ni filtered radiation. The functional groups were identified using FT-IR (Thermo Nicolet, Avatar 330 FT-IR Spectrometer, USA) studies. The thermal analysis of the precursor was carried out at a heating rate of 10 ^{0}C/min in air from room temperature to 1000 ^{0}C using Thermal Analyzer (V8.2 SDT Q600, TA Instruments, USA).

4. Results and discussion

The reaction of calcium nitrate with citric acid results in the formation of calcium citrate which is highly soluble in aqueous medium, hence the precipitation of calcium ions is prevented. When the solution was heated at 80^0 C, the carboxylate and OH functional group of citric acid and ethylene glycol molecules undergoes a polymerization reaction and resulted in a viscous gel. Figure 1 represents the formation mechanism of polymeric network gel from citric acid, ethylene glycol and Ca^{+2} (Li *et al.,* 2000). The decrease in the concentration of citric acid molecules leads to the increase in the pH of the solution. Due to the decrease in acidity, the formation of calcium phosphate is enhanced and this makes the gel to turn white.

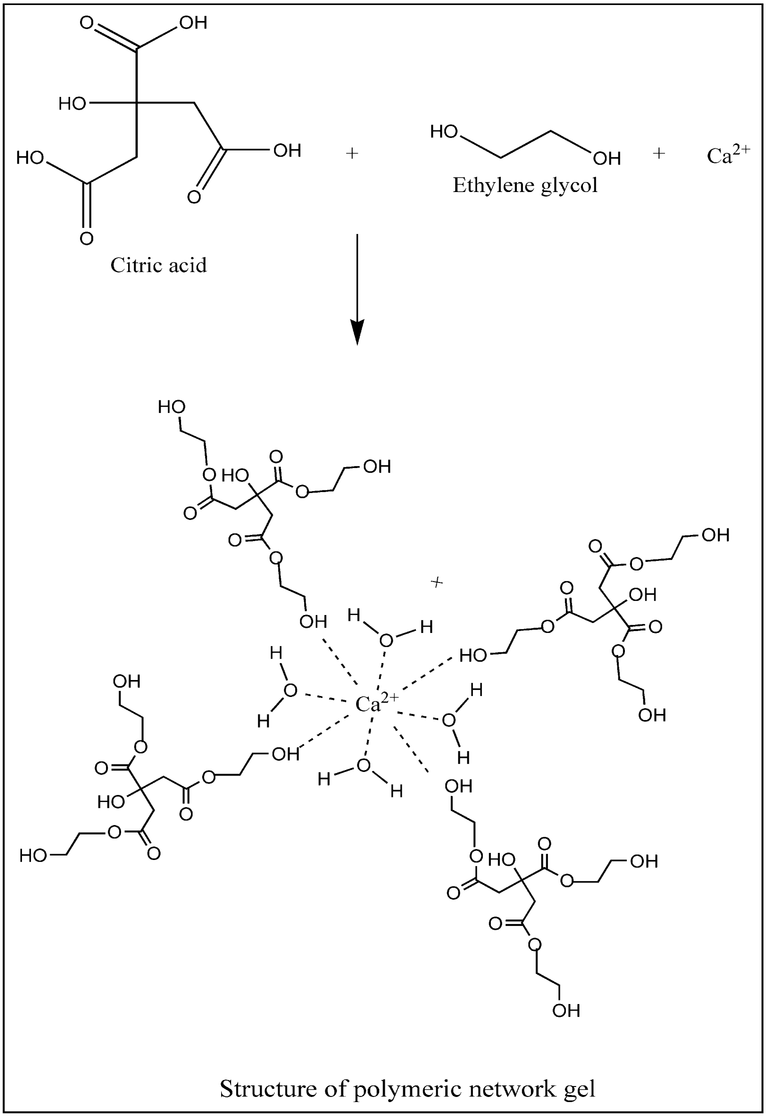

Fig. 1. Polymeric network gel formation

When the gel was decomposed at 300^0 C, the gel undergoes decomposition with a partial combustion. The presence of nitrate in the gel and atmospheric oxygen influences the partial combustion of the gel, whereas the rest of the gel undergoes decomposition by means of charring. The obtained precursor was brown in colour which indicates the incomplete combustion of the carbon network. When the precursor was calcined at 900°C for two hours, then the resultant product was white in colour, implying that the organic constituents were totally removed during calcination.

4.1 FT-IR analysis

FT-IR spectra (Fig. 2) of the resultant product shows the stretching and bending vibrations corresponding to weak OH^- bands (631 and 3571 cm^{-1}) and PO_4^{3-} (570, 601, 1044, 1089 cm^{-1}) vibrations, together with the weak bands of the CO_3^{2-} group (875, 1466 and 1680 cm^{-1}). Carbonate can substitute in $Ca_{10}(OH)_2(PO_4)_6$ on two possible anionic sites (OH^- and PO_4^{3-}), which can be distinguished by FT-IR spectroscopy. Intense peak at 1440 cm^{-1} and a less intense peak 875 cm^{-1} indicate the substitution of carbonate ions in the phosphate site and broad band at 1633 cm^{-1} indicates that OH site is also substituted with carbonate ion.

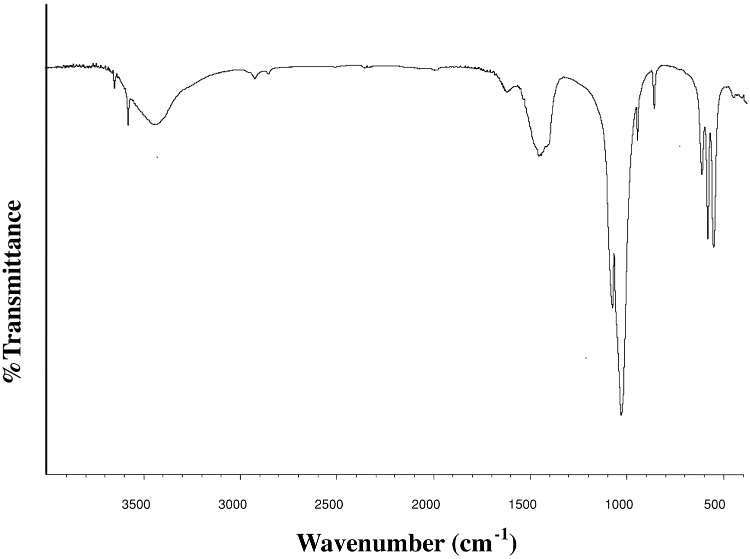

Fig. 2. FT-IR spectra of hydroxyapatite synthesized by Pechini method

4.2 XRD analysis

The obtained XRD pattern (Fig. 3) of the samples calcined at 900^0 C for two hours was well consistent with the data reported in Joint committee on powder diffraction standards (JCPDS), indicating the formation of single phase hydroxyapatite without any other calcium phosphate impurities. The refined lattice parameter values are a = 9.4053 Å and c = 6.8758 Å, which is in agreement with the JCPDS card number 009–0432. The lattice parameter values indicate that there is a shrinkage in both a and c axis indicating the substitution of carbonate ions in the crystal lattice.

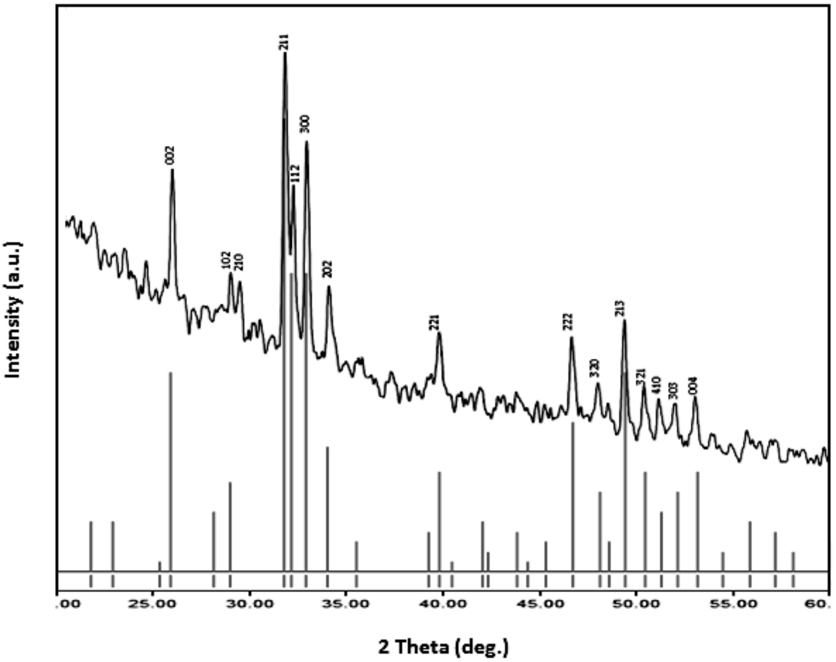

Fig. 3. XRD pattern of hydroxyapatite synthesized by Pechini method.

4.3 Thermogravimetric analysis (TGA)

TGA curve of the thermal analysis (Fig. 4) of the precursor indicates a weight loss of 8.7% between 50°C and 200°C, which may be due to the removal of water molecules from the precursor. The second weight loss of 18.5% is observed between 200°C and 600°C, which may be due to the removal of partially decomposed organic constituents present in the precursor. The third weight loss of 16.3% is observed between 600°C and 1100°C, which may be due to the decomposition of the carbonaceous substances left out in the precursor. The weight loss between 900°C and 1100°C may be due to the decomposition of carbonated hydroxyapatite due to the less thermal stability of carbonated hydroxyapatite.

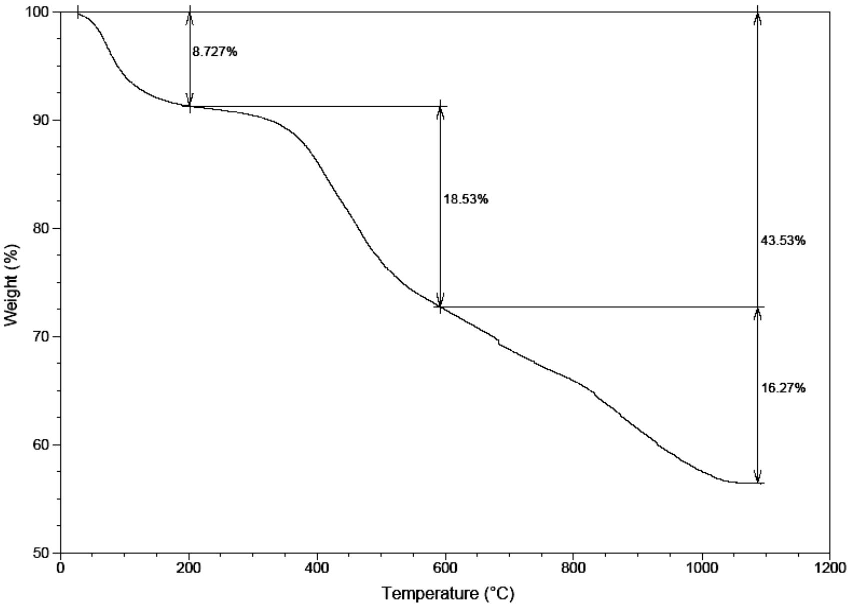

Fig. 4. TGA pattern of the precursor synthesized by Pechini method.

The decomposition of carbonated hydroxyapatites (Slosarczyk *et al.,* 2005) is due to the replacement of PO_4^{3-} ions by CO_3^{2-} ions, due to which there is a increase in Ca/P ratio, which leads to the non-stoichiometric carbonated apatites, which are thermally less stable than the pure hydroxyapatite. Hence the presence of carbonate ions in the structure lowers thermal stability of hydroxyapatite resulting in its decomposition at higher temperatures.

4.4 Differential thermal analysis (DTA)

DTA curves (Fig. 5) shows an endothermic peak between 70°C and 100°C which is due to the loss of water molecules and the broad exothermic peak obtained between 200°C and 600°C is due to the decomposition of partially decomposed organic constituents present in the precursor. The endothermic peak at 977°C may be due to the decomposition of the carbonated apatite, which is in correlation with the results of TGA analysis.

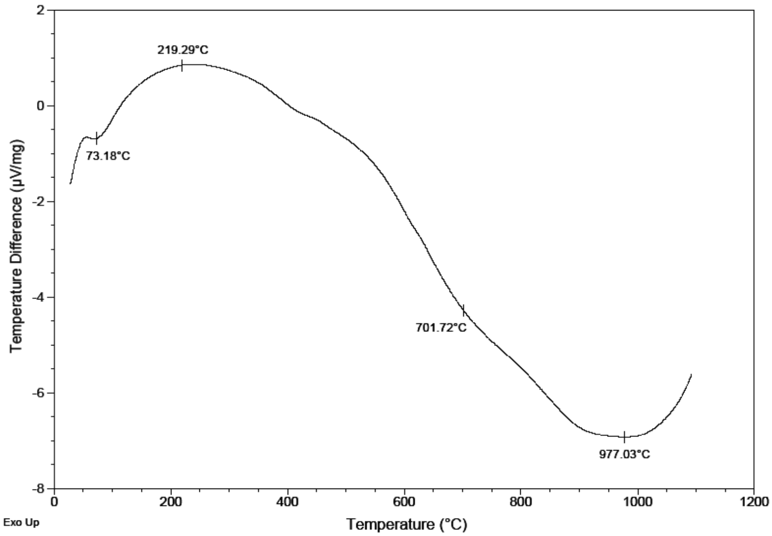

Fig. 5. DTA pattern of the precursor synthesized by Pechini method.

4.5 Differential scanning calorimetry analysis (DSC)

DSC pattern (Fig. 6) is in good agreement with the results obtained from TGA and DTA analysis, as the energy involved in the removal of water molecule, decomposition of organic substances and the decomposition of carbapatite phases is in agreement with the obtained values.

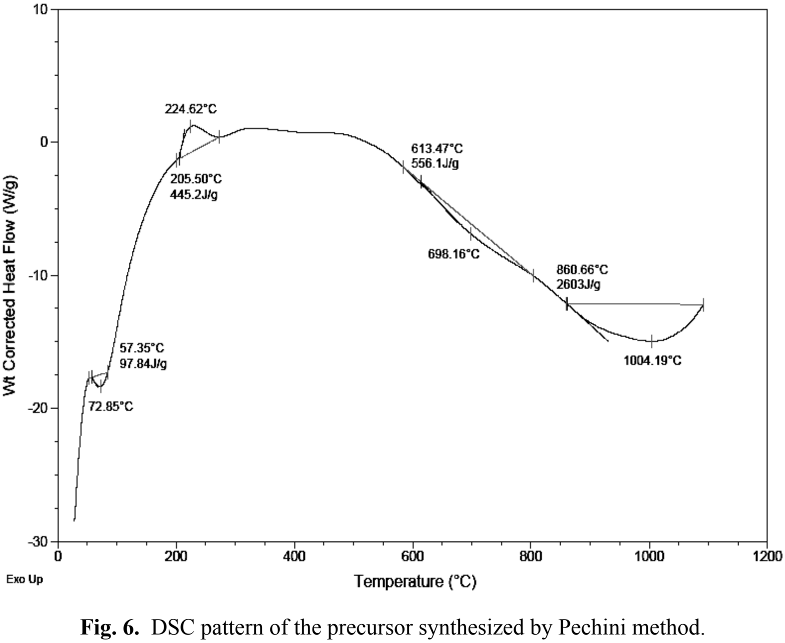

Fig. 6. DSC pattern of the precursor synthesized by Pechini method.

5. Conclusion

The present work paves a way to prepare hydroxyapatite by Pechini method, using ethylene glycol and citric acid as a complexing and gelling agent. The resultant product is found to be carbonate substituted hydroxyapatite and the substituted carbonate ions reduces the thermal stability of the prepared biomaterial. The carbonated apatites are known for its better bioactivity (Landi *et al.,* 2008) and dissolution in physiological environment hence the prepared material can be used as a temporary bone lattice, so that it will be bioresorbed allowing the generation of new bone in its place.

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تحضير هيدروكسى أباتيت مستبدل الكربونات بإستخدام طريقة بتشينى

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خلاصة

تم تحضير هيدروكسى اباتيت الكالسيوم بواسطة طريقة بتشينى باستخدام حمض الستريك والإثيلين جليكول كعامل تراكبى وعامل هلامى . اتخذت نترات الكالسيوم و فوسفات ثنائى الأمونيم الهيدروجينى كمصدر للكالسيوم والفوسفات، على التوالى. تم توصيف المصدر الأولى وكذلك الناتج الكلسينى باستخدام حيود اشعة إكس للمسحوق لتحديد الطور، وطيفية الأشعة تحت الحمراء لتحليل المجموعة المميزة، والمحلل الحرارى لإختبار الثباتية الحرارية. أثبتت النتائج أن الناتج المتكون هو هيدروكسى أباتيت مستبدل الكربونات وأن ثباتيته الحرارية أقل بالمقارنة مع الهيدروكسى أباتيت النقى.