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Facile One-Step Synthesis of Calcium Phosphate/Cellulose Composite: Synthesis, Morphology, Structure and Properties

Meldin Mathew, Nathalie Lyczko, Ange Nzihou,* and Sabu Thomas*

This study focusses on reporting a facile one-step synthesis method to fabricate calcium phosphate-microcrystalline cellulose composite with an enhanced surface area. The composite preparation is done using a simple one-step method called co-precipitation method under ambient and 60 °C temperature. The calcium carbonate and orthophosphoric acid are taken, which are the two best known widely available starting materials for the synthesis of calcium phosphate. The sample is collected and taken for the drying process in an oven at 105 °C. The characterizations like XRD, SEM, BET, FTIR, TGA, and DSC of the demonstrated composites are done. From BET analysis, it can be concluded that the surface area of the demonstrated composite enhances substantially after the incorporation of the microcrystalline cellulose.

1. Introduction

The calcium phosphate has various eternal ranges of applications because of their sorption capacity, chemical-thermal stability and biocompatibility.^[1] These specifications can be used to cover the needs of many other areas, for example, protein isolation and purification, production of biocompatible ceramics, liquid chromatography,^[2] drug delivery, in catalysis, water treatment, fertilizers and pharmaceutical industry,^[3] soil remediation, etc.^[4] Thus, various work has been investigated on the synthesis of calcium phosphate such as microwave irradiation,^[5] spray drying method having controlled morphology,^[6] preparation involving hydrothermal condition,^[7] sol-gel process,^[8] precipitation in aqueous solution,^[9] emulsion route,^[10] ultrasonic freeze drying technique,^[11] preparation using templates, etc.^[12]

Among these methods, the precipitation of orthophosphate using a calcium source in an aqueous medium seems to be the major simple technique to prepare calcium phosphate powder. Even though there are different types of calcium sources are present, calcium carbonate gained a considerable attention above all due to its eco friendliness, huge availability, non-appearance of the interfering anions and cost effective, viable production from municipal and industrial wastes.^[13] The specialty of orthophosphoric acid has been studied and reported by Doan et al. and they enumerate that, orthophosphoric acid was perfect, due to its ability on the dissolution of the CaCO₃ and was the only reactant that leads to complete utilization of the starting orthophosphate group.^[14] Therefore, looking from all aspects of the CaCO₃ and the orthophosphoric acid, they are the best-known components of the calcium phosphate preparation process.

Inorganic phosphate serves a long historical background as a constituent part of the bone and teeth, it is already proposed for the bone fracture treatment.^[15] The calcium phosphate has been proved already for the effective removal of heavy metals like Pb, Zn, Cu, Co, and Cr.^[16] Moreover, the most hazardous radioactive nuclides like strontium and cesium removal studies also were conducted with modified hydroxyapatite.^[17] Different phosphate and calcium sources have been studied and reported for the preparation of calcium phosphate.^[18] The effect of stirring rate, water-solid ratio, reaction time, Ca-P ratio, etc. is important to enhance the adsorption properties in the preparation aspects and they reported with effective results.^[14,19] The relevant functioning of calcite on metal adsorption has also been analyzed.^[20] The scavenging property of phosphate and its structural specialty also has been studied and reported.^[21]

Being an abundant biomass source and biodegradable polymer, cellulose has gained considerable interest among the scientific community. Cellulose has excellent properties like good strength, high surface area, good rigidity, biocompatibility, hydrophilicity, relative thermo-stabilization, sorption capability and varying optical appearance which makes them as a promising candidate to perform in enormous applications.^[22] Especially the enormous amount of hydroxyl group present on the surface of the cellulose helps them to facilitate various surface chemistries. Physical incorporation/blending of cellulose in variant forms such as nanoparticles, gels, copolymers and membranes was also introduced to make smart composites for numerous applications. Fibrous membranes,^[23] reinforced agents,^[24] magnetic

M. Mathew, S. Thomas
School of Chemical Sciences
Mahatma Gandhi University
Kottayam, Kerala 686560, India
E-mail: sabuthomas@mgu.ac.in

N. Lyczko, A. Nzihou
Centre RAPSODEE-CNRS UMR 5302- IMT Mines Albi
Campus Jarlard, 81013, Albi, CT CEDEX 9, France
E-mail: ange.nzihou@gmail.com

S. Thomas
School of Energy Materials
Mahatma Gandhi University
Kottayam, Kerala 686560, India

devices,^[25] drug delivery,^[26] barrier films,^[27] optical media,^[28] electrical devices,^[29] thickeners,^[30] water treatment devices,^[31] stabilizers,^[32] etc., are some of the areas where cellulose are being used.

In this study, we have fabricated a calcium phosphate/cellulose composite in a facile single step process. The composite preparation was done at ambient and 60 °C. For the comparative study with composite, calcium phosphate alone also was prepared. We enhanced the surface area via microcrystalline cellulose (MCC) co-precipitation with calcium phosphate. The sample was collected and taken for the drying process in an oven at 105 °C. In order to study their behavior associated with the properties acquired, we used different characterization techniques like TGA, SEM, XRD, PSD, BET and FTIR.

2. Characterization

2.1. BET Analysis

The samples prepared at ambient and 60 °C temperature were taken for different physical, chemical and thermal analysis. The surface area analysis was done by BET study. After the outgassing step around 105 °C under high vacuum, standard nitrogen adsorption at 77k was proceeded. The isotherm obtained using Micromeritics Tristar II 3020 and with a Micromeritics 3 FLEX was used for the analysis of the sample.

2.2. FTIR Spectroscopy

The prepared samples were taken for the FTIR analysis to study the interactions of functional groups presenting in the sample prepared. The spectra were recorded using a SHIMADZU spectrometer-8400S sweeping between 4000 and 500 cm⁻¹ were used.

2.3. X-Ray Diffraction Analysis

The X-ray diffraction data were collected using a Phillips Panalytical X'pert Pro MPD diffractometer. The radiation source ray used was the copper (Cu) whose wavelength $K\alpha$ is 1.543 Å. A nickel filter was used to remove the Cu $K\beta$ ray. The apparatus operates at a voltage of 45 kV and at an intensity of 40 mA. The diffractogram was recorded from 10 to 8° in 2θ . The step size was 0.017° in 2θ and the scan step time was 29.89 s. The phase identification was carried out from the databases JCPDS and COD.

2.4. Thermal Analysis

The thermal analysis of the sample was done by using TGA/DSC apparatus SDT Q600 by TA instrument. Twenty milligram of the sample were used in each analysis and heated from room temperature to 1000 °C, with a heating rate of 5 °C min⁻¹.

2.5. SEM

For the morphological studies, the SEM analysis performed on Philips XL30 ESEM apparatus. Samples taken for the analysis were used without sputter coating and performed at 8 kV voltage.

Table 1. BET surface area of calcium phosphate and the composite.

CaP and the Composite	Prepared Condition	S_p [m ² g ⁻¹]
H ₃ PO ₄ + CaCO ₃	Ambient	2.3
H ₃ PO ₄ + (CaCO ₃ + MCC)	Ambient	11.1
H ₃ PO ₄ in CaCO ₃	60 °C	8.7
H ₃ PO ₄ in (CaCO ₃ + MCC)	60 °C	18.8

3. Result and Discussion

3.1. BET Surface Area

The surface area of calcium phosphate and the composite were measured using BET analyser. From the result, it could be concluded that, the surface area of the composite enhanced substantially, compared to calcium phosphate. It is well known that, surface area of the composite plays a vital role in the adsorption behaviour.

From **Table 1**, it is clearly understood that, the sample prepared at ambient condition showed values of 2.3 to 11.1 (m² g⁻¹) the neat calcium phosphate and MCC filled composite, respectively. The sample prepared at 60 °C also showed an increment from 8.7 to 18.8 (m² g⁻¹) upon the addition of MCC. The incorporation of the microcrystalline cellulose led to the substantial enhancement of the surface area of calcium phosphate. Moreover, from the result, it can conclude that, the influence of reaction temperature is noticeable. The reason had been studied and reported by Minh et al.^[14] According to them, the reaction temperature has a great involvement to minimize the amount of intermediate like brushite, monetite etc. Furthermore, the remaining CaCO₃ in the product was reduced. Therefore, the reaction being carried out at 60 °C led to the formation of calcium phosphate with enhanced surface area. The XRD and TGA studies were provided with supporting data by showing the reduced CaCO₃ and intermediate contents.

3.2. FTIR Spectroscopic Analysis

Figure 1 represents the IR spectrum of the calcium phosphate and composite. For all samples, spectra showed the vibrational strong peaks of PO₄³⁻ at 1018–1078 m⁻¹, 960–980 cm⁻¹, and 550–592 cm⁻¹ of hydroxyapatite phase. Medium vibrational peaks of PO₄³⁻ also were observed at 470–480 cm⁻¹ of hydroxyapatite phase.

The remaining unreacted CaCO₃ was present on 1400 cm⁻¹. A peak around 1000 cm⁻¹ was due to the tricalcium phosphate (Ca₃(PO₄)₂) formed as an intermediate during the reaction. The O-H bending peak corresponding to the dehydration of the surface moisture content was observable around 1600 cm⁻¹, which reflects in the TGA analysis as well.

The main reason for the absence of stretching peaks observed by the hydroxyl group of the cellulose was well known here due to the deposition of calcium phosphate layer on the surface of the microcrystalline cellulose during co-precipitation process. The SEM images obtained during the analysis gave strong evidence for this peak disappearance from the IR spectrum.

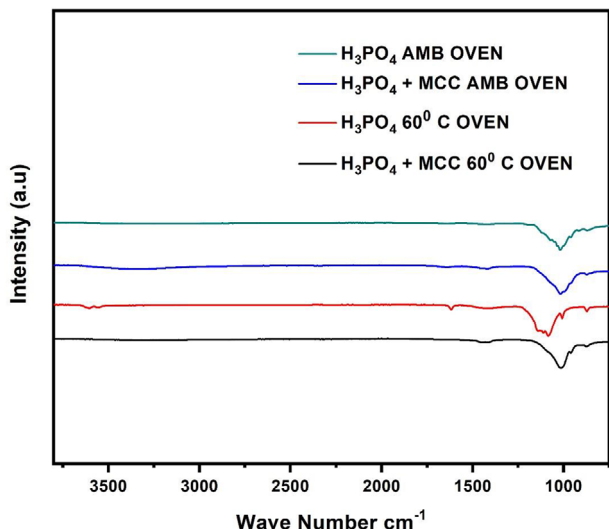


Figure 1. FTIR spectrum of calcium phosphate and the composite.

3.3. X-Ray Diffraction Analysis

The XRD pattern of the calcium phosphate prepared at ambient and 60 °C were taken (Figure 2). The calcium phosphate prepared at ambient condition showed the peaks of hydroxyapatite $2\theta = 31.7^\circ$. Other peaks of tricalcium phosphate ($\text{Ca}_3(\text{PO}_4)_2$) intermediate was appeared in the graph on $2\theta = 30.9^\circ$. The unreacted cal-

cium carbonate associated with the calcium phosphate was also present in the compound.

For the sample prepared in 60 °C shows good crystal clarity than the sample prepared in ambient condition. The peaks analogous to the hydroxyapatite are visible here on $2\theta = 25.3^\circ$, $2\theta = 31.8^\circ$ and $2\theta = 32.9^\circ$. The peaks of unreacted CaCO_3 remaining in the product is visible at $2\theta = 29.3^\circ$. The formation of calcium phosphate at 60 °C, did not show the peaks, corresponding to the intermediates due to the effect of temperature. The relevant JCPDS data are shown at the inset for the reference (CaCO_3 : ICDD 00-047-1743; $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$: ICDD: 01-073-0293; $\text{Ca}_3(\text{PO}_4)_2$ ICDD 00-032-0176).

We have analysed the XRD of the composites prepared at ambient as well as the 60 °C. We understood that both the composite and the calcium phosphate prepared alone does not show any differences in the diffraction pattern.

3.4. Thermo Gravimetric Analysis

Figure 3a shows the thermograph of the calcium phosphate and its composite prepared at ambient condition. There are three degradations for the calcium phosphate and the primary weight loss took place around 100 °C. This was due to the dehydration of the system and the weight loss is 0.7%. Second weight loss was observed in 175 °C, due to the degradation of brushite. We used the DSC graph, to study the phenomena associated with different weight losses. Here, at 175 °C, we got an endothermic peak on DSC profile, corresponding to the mass loss 1.3%. The major sharp weight loss (decomposition) between 610 °C and

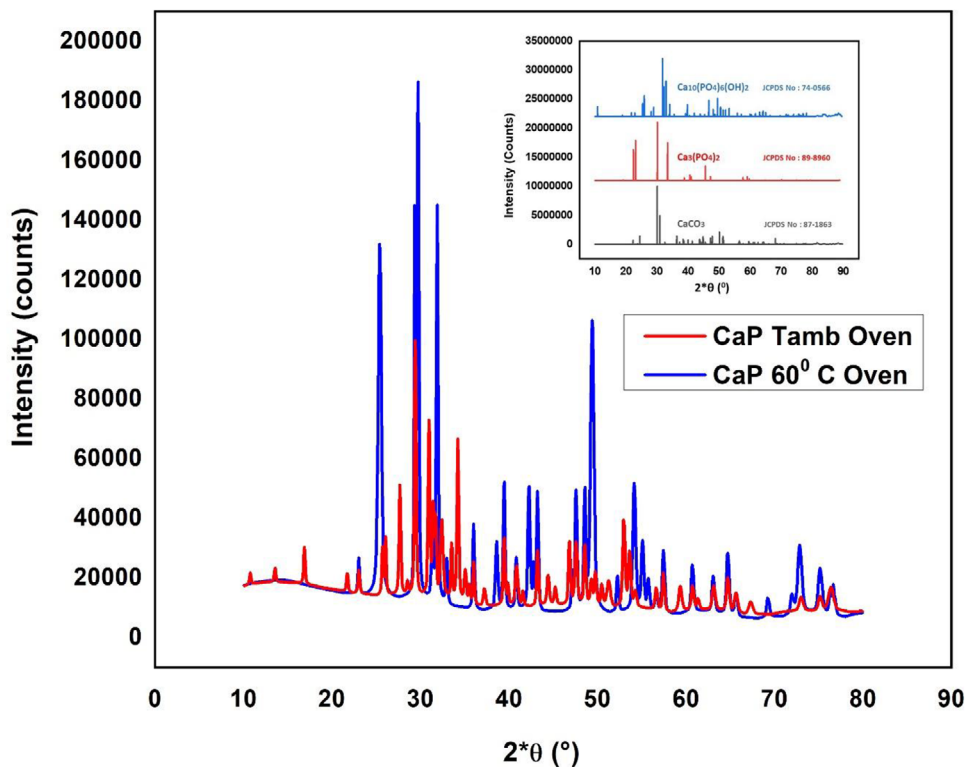


Figure 2. X-ray diffraction analysis of calcium phosphate.

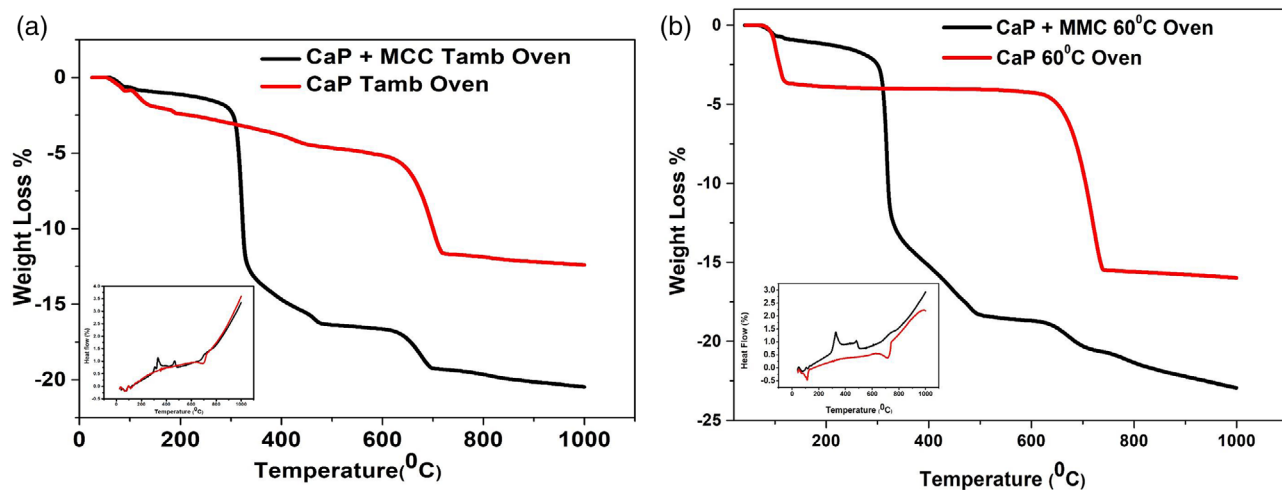


Figure 3. a) TG analysis of calcium phosphate and composite prepared in ambient temperature; b) TG analysis of calcium phosphate and composite prepared in 60 °C temperature.

720 °C could be attributed to the decarbonation in the calcium carbonate and this turns into calcium oxide and carbon dioxide ($\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$). The total weight loss was about 12.4%. For the graph of the composite prepared with microcrystalline cellulose, there are four decompositions present. The first peak was observed around 100 °C, due to the removal of surface moisture. Second peak starts around 320 °C, which belongs to the cellulose oxidation with a mass loss about 14.1%. The succeeding transition around 450 °C is due to the removal of contaminants on CaCO_3 . Thermal degradation of CaCO_3 was between 610 °C and 720 °C followed by decarbonation. Total mass loss of the system is 20.4%.

The thermograph, Figure 3b depicted the analysis of the calcium phosphate and its composite prepared at 60 °C condition. When considering the composite prepared using calcium phosphate and MCC, its primary peak near to 100 °C due to the dehydration of the surface moisture. The second peak was between 300 °C and 500 °C, corresponding to the cellulose oxidation and the weight loss was about 14.1%. Here, the corresponding exothermic peak was distinctly registered on DSC analysis. The next peak was observed at 600 °C due to the decarbonation of the CaCO_3 . For the calcium phosphate prepared at 60 °C, the primary peak was observed around 100 °C could be attributed to the dehydration of moisture content. The second peak occurred between 610 °C and 720 °C which can be due to the decarbonation of CaCO_3 with a weight loss of 11.7%. Here also, the corresponding phase transitions were clearly detectable on DSC curves with two exothermic peaks. The total mass loss of the composite and calcium phosphate was 22.9% and 15.9%, respectively.

3.5. Scanning Electron Microscopy

Figure 4a,b was the SEM images of calcium phosphate prepared at 60 °C and ambient temperatures, respectively. Here, the sheet like structure of the particle can be assigned to the presence of brushite/OCP in the product. The sample prepared under 60 °C

was more uniform and finely structured. The particle size was small and the distribution was more uniform and narrow. The high heterogenic nature of the product synthesized at ambient temperature shows varying diameter ranging up to 110 μm. In both cases, the developed flakes of calcium phosphate were assembled to give their cluster in the structure and those were spread along in the sample. Figure 4c represented the SEM images of microcrystalline cellulose. A web like appearance with self-assembled structure resulted into a spherical shaped cellulose particle with micro range.

The composite images were given on Figure 4d,f composite prepared using co-precipitation method, under SEM analysis was found as well organized form of calcium phosphate and microcrystalline cellulose. In some places, cellulose has been shown to be covered with calcium phosphate. This was understood, when the SEM was performed at high voltage. When the voltage switched from 8 to 30 kV, the cellulose was found much darker than the calcium phosphate and this was clearly depicted in Figure 4g. Therefore, a deposition of calcium phosphate layer, on the surface of the cellulose was found. In certain cases, the microcrystalline cellulose and calcium phosphate were found to be separated. In this case, secondary forces such as Vander Waals force were considerably help them to stay organized.

In order to study the enhanced surface area, due to the addition of microcrystalline cellulose into the calcium phosphate, we used particle size distribution analysis. The analysis showed that, the enhancement of the surface area was due to the decreased particle size. The sample prepared at ambient temperature showed an enhancement in surface area from 2.3 to 11.1 $\text{m}^2 \text{g}^{-1}$ due to the addition of the microcrystalline cellulose and the average particle size decreased from 60 to 4 μm. Similarly, the surface area enhanced from 8.7 to 18.8 $\text{m}^2 \text{g}^{-1}$ in the case of composite prepared at 60 °C when the average particle size decreased from 50 to 4 μm. In both cases, we observed a substantial enhancement in surface area due to the incorporation of microcrystalline cellulose. Therefore, the microcrystalline cellulose substantially improved the surface area of the resultant composite.

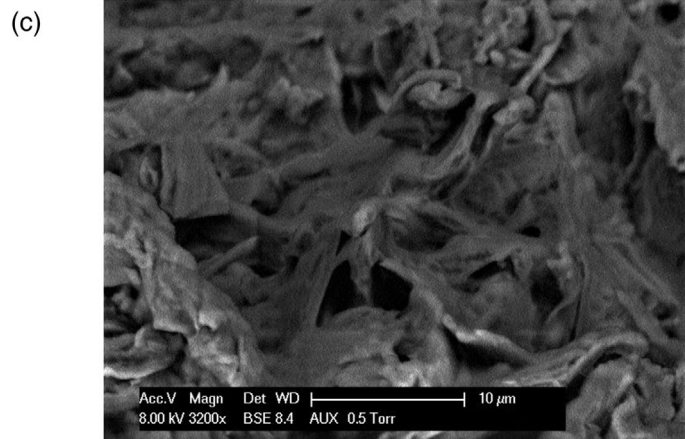
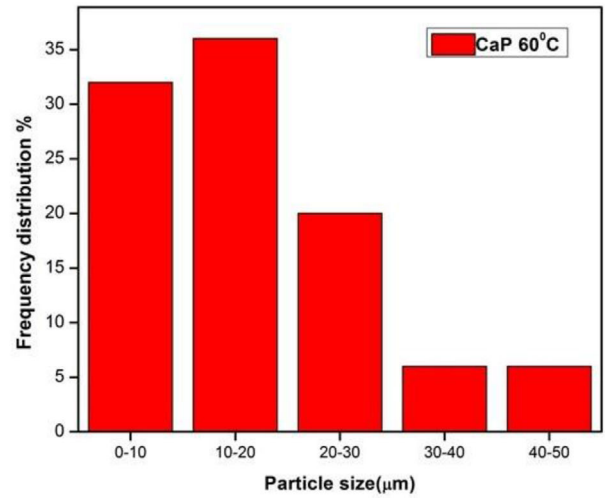
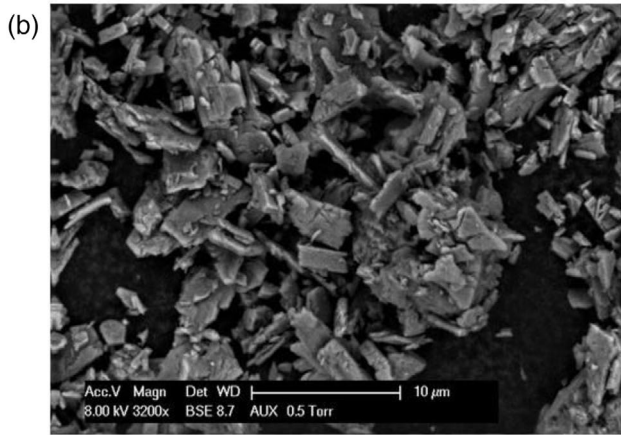
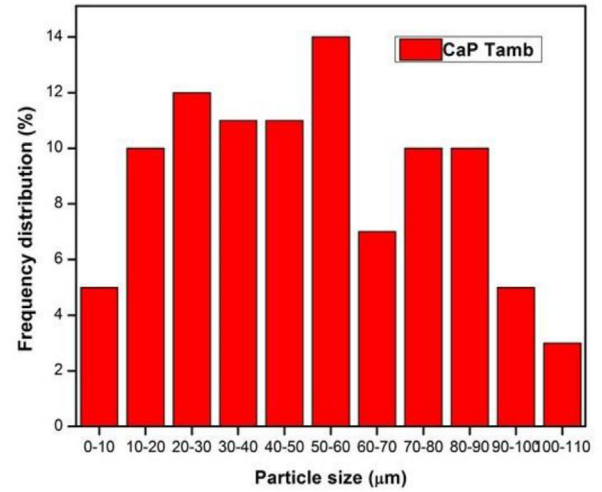
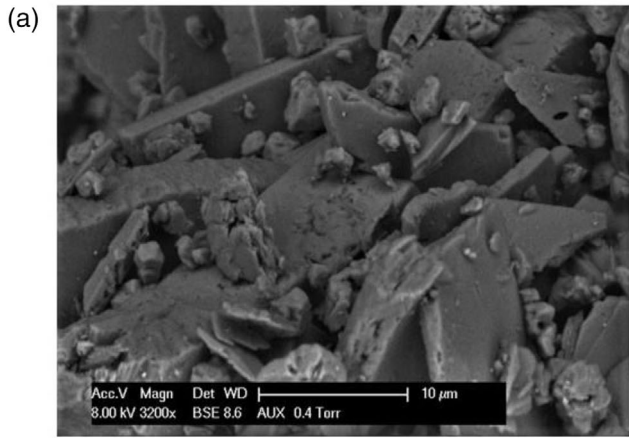


Figure 4. a) SEM analysis and particle size distribution of calcium phosphate prepared at ambient temperature. b) SEM analysis and particle size distribution of calcium phosphate prepared at 60 °C temperature. c) SEM images of microcrystalline cellulose. d) SEM analysis and particle size distribution of composite prepared at ambient temperature. f) SEM analysis and particle size distribution of composite prepared at 60 °C temperature. g) SEM analysis of the composites observed under a) 8 kV and b) 30 kV.

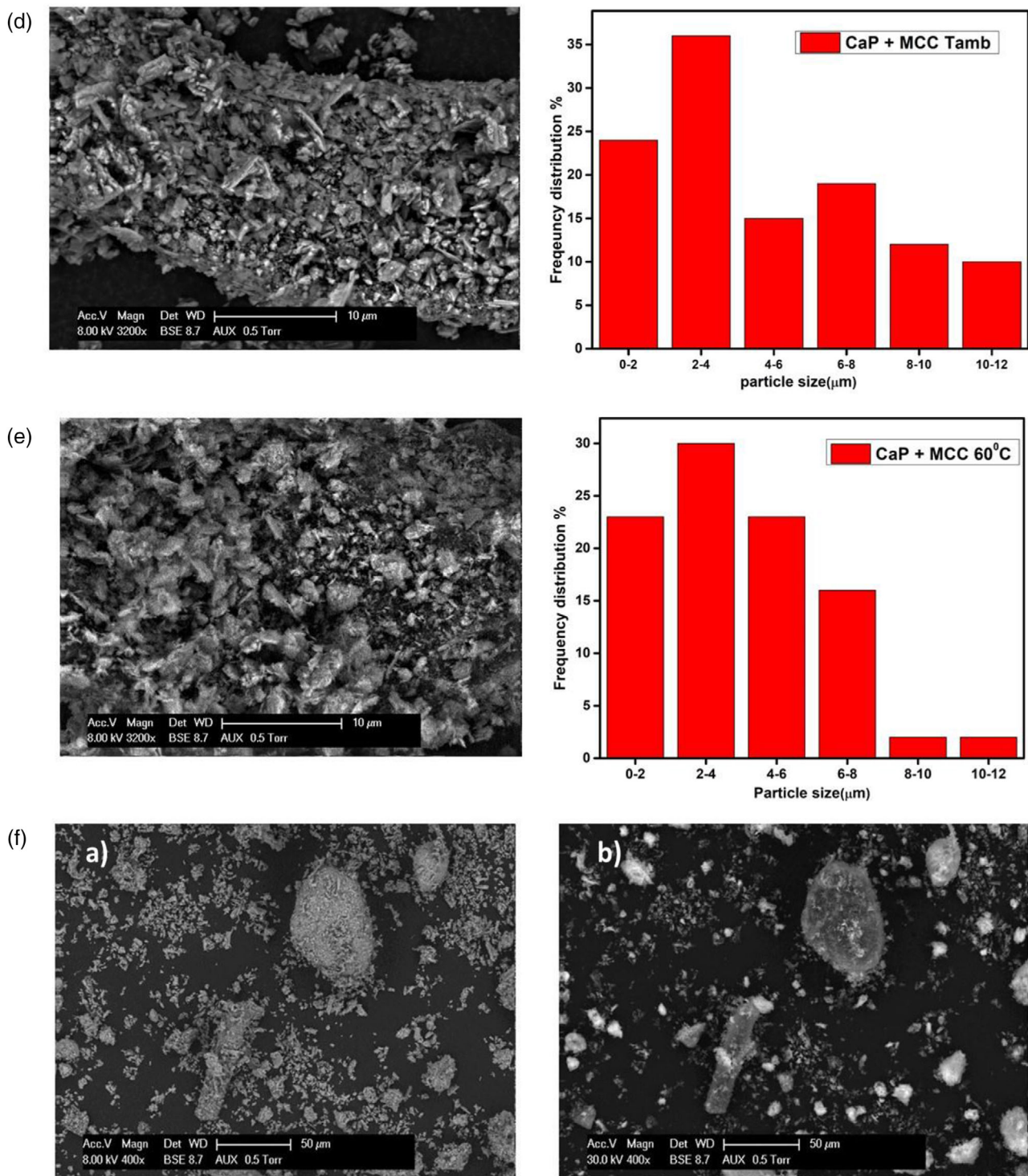


Figure 4. Continued

4. Conclusion

We have carefully performed two reaction strategies in this study at ambient and 60 °C temperature. For the incorporation of cellulose into the calcium phosphate, co-precipitation method was used. The surface area analysis of the sample

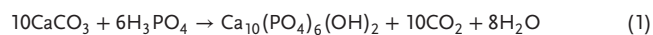
showed an enhancement with the incorporation of cellulose. Surface area of the calcium phosphate was upgraded from 2.3 (60 μm) to 11.1 m² g⁻¹ (4 μm) at ambient condition treatment, and at the 60 °C reaction, 8.7 m² g⁻¹ (50 μm) was modified to 18.8 m² g⁻¹ (4 μm). The particle size distribution studies of the composite showed that the enhanced

surface area was due to the decreased particle size in the composite.

The temperature has a strong effect on the reduction the amount of intermediate in the product formation. In 48-h reaction and at 60 °C, calcium phosphate and its composite formed with less amount of intermediate. This was supported by the X-ray diffraction studies, FTIR spectroscopy and thermal analysis. Microscopic investigation showed the cellulose-calcium phosphate interaction facilitated via either by surface coating on cellulose or by some secondary interactions like Vander Waals force.

5. Experimental Section

Calcium carbonate powder, CaCO₃ (Solvay), was chosen as the Ca source for the calcium phosphate preparation. Phosphate source was chosen for the preparation is orthophosphoric acid, H₃PO₄ (Merck). The synthesis has been done via a U form glass reactor with 2.3 L capacity and is equipped with a vertical stainless steel rotor. For each synthesis, 300 gm of calcium carbonate and 1200 mL water (corresponds to the weight ratio (L/S) of water to calcium carbonate as 4) were poured into the reactor under stirring at 400 rpm, which prevents intermediate formation like brushite, leading to good reaction rate and the better consumption of the reactant species by getting efficient contact between them. The amount of orthophosphoric acid poured into the reactor was 206.91 gm. This was corresponding to the molar ratio of calcium to phosphorus (Ca/P) which was 1.67. The reaction of calcium carbonate and phosphoric acid can be written as,



This Equation 1 represents the calcium phosphate formation in a single step reaction using aqueous medium. The temperature of the reaction was set at ambient and 60 °C for the study of 48-h reaction. Studies have shown that, 99.5% of CaCO₃ was consumed in a 48-h reaction. The formation of intermediate, like brushite (CaHPO₄·2H₂O), also could be reduced by choosing this reaction time and temperature.

The product formed after 48 h reaction made into powder by filtration of the suspension on 0.45 µm filter paper followed by a drying overnight at 105 °C.

Preparations of Calcium Phosphate/Microcrystalline Cellulose (MCC) Via Co-Precipitation Method: The co-precipitation method was employed for the preparation of calcium phosphate/microcrystalline cellulose. The cellulose microcrystalline cellulose material used is a polysaccharide composed of long chains of β (1,4) linked D-glucose units and it is purchased from Sigma Aldrich. This is used for a wide range of applications such as microfibrils, biofilms, and biodegradable composites. The surface area of this type of MCC has been reported by Vehovec et al. and it was given as 0.903 m² g⁻¹.^[33] The ease of production was the main advantage of the demonstrated technique. This method consists of simultaneous precipitation of calcium phosphate with microcrystalline cellulose. For the preparation, the microcrystalline cellulose was added to the 2.3 L U form glass reactor with water and phosphate source mixture. For the addition, 20% weight of CaCO₃: 60 gm of microcrystalline cellulose was used. The microcrystalline cellulose was added along with phosphate source into the reactor with water. After 48 h of reaction, the product was collected and dried.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

calcium phosphate, cellulose composite, differential scanning calorimetry (DSC), infrared spectroscopy, thermogravimetric analysis (TGA)

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