Synthesis And Characterization of Hydroxyfluorapatite Nanocomposite

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ABSTRACT

An innovative Biomimetic synthesis of novel three dimensional micro/macro porous Carboxymethyl Cellulose (CMC) - Hydroxyfluorapatite nanocomposites having four different systematically compositions has been established for its possible application in the area of synthetic bone grafting and as teeth filler in the dentistry. The nanocomposites are structurally and mechanically characterized using various techniques like scanning electron microscope (SEM), transmission electron microscope (TEM), X-ray diffraction (XRD), thermo-gravimetric analysis (TGA), and universal testing machine (UTM). The TEM analysis revealed that hydroxyfluorapatite is needlelike shaped and the crystal size in the range of 20nm-30nm. Compressive strength and elastic modulus of nanocomposite being in the range of 1.12MPa - 10MPa and 33MPa - 445MPa respectively, meet the desired range of compressive strength for synthetic graft used in trabecular bone.

Keywords: Hydroxyfluorapatite nanocomposite, SEM, TEM, XRD, UTM, TGA.

INTRODUCTION

Hydroxyapatite has been studied widely and prepared for clinical applications. In certain Applications are involving man-made bones and teeth. However, the biodegradation of Hydroxyapatite (Hap) under physiological condition makes the interface between Hydroxyapatite (Hap) and bone unstable [1-2]. Fluoridated Hydroxyapatite (FHAp), where F incompletely replaces the OH in the Hydroxyapatite, is considered as an alternative material for bone repair due to its low solubility and good biocompatibility [3]. When the pH drops below a critical level (5.5 for enamel and 6.2 for dentin), it causes the dissolution of tooth mineral (Hydroxyapatite) in a process called demineralization, when the pH is elevated by the natural buffer capacity of saliva mineral gets again incorporate into the tooth through the process of remineralization [4-5]. When the fluoride is present in oral fluid, fluorapatite rather than Hydroxyapatite forms during remineralization process. Fluoride ions (F\(^-\)) replace hydroxyl groups (OH\(^-\)) in the formation of the apatite crystal lattice. Actually the presence of fluoride increases the rate of remineralization.

2. EXPERIMENTAL PROCEDURE

2.1 Materials

Carboxymethyl Cellulose (CMC), sodium salt (pure) with an inherent viscosity of approximately 1% w/v. calcium nitrate tetra hydrate (236.15 g/mol), di-ammonium hydrogen phosphate (132.06 g/mol), sodium fluoride (41.98 g/mol).
2.2 Method
The synthesis of the hydroxyfluorapatite was done by Biomimetic method. CMC was mixed with distilled water and continuously magnetic stirred at room temperature till the whole CMC was dissolved to form a clear solution. Calcium nitrate tetra hydrate Ca (NO₃)₂.4H₂O Solution was prepared. Both the Solutions were mixed and stirred continuously, and then water and ammonia were added. It was then mixed to the solution and stir continuously. The solution was left uninterrupted for 24 hours at room temperature. Sodium fluoride (NaF) was dissolved in distilled water and mixed with the cast day prepare solution. Diammonium hydrogen phosphate (NH₄)₂HPO₄ was dissolved in distilled water and mixed with the prepared CMC solution while on continuous stirring 1:1 ratio of water and ammonia was mix with the solution and stirred continuously. The washed neutral solution was dried in the oven at 55°C. Fig 2.1 shows Biomimetic hydroxyfluorapatite.

Fig. 2.1: Biomimetic hydroxyfluorapatite

3. RESULT AND DISCUSSION
Four different percentage concentration of CMC- Hydroxyfluorapatite nanocomposite was synthesized by Biomimetic method. These composite were characterized for particle size and thermal stability by the XRD and thermo gravimetric analysis respectively. The compressive strength and micro-hardness was determined by the mechanical testing on the universal testing machine. The surface and internal morphology was studied by scanning electron microscope (SEM) and transmission electron microscope (TEM).

Sample id:
S-1= 1.5gm CMC polymer, S-2 = 2.0gm CMC polymer, S3 = 2.2gm CMC polymer, S-4 = 2.5gm CMC polymer.

3.1 XRD analysis
XRD studied of the synthesized nanocomposite, conformed the formation of fluorapatite nanoparticles in CMC.
The XRD patterns of the synthesized two nanocomposite fig.3.1 are almost similar, conform the formation of fluorapatite phase. Obtained diffraction peak could be indexed as (002), (211), (212), (113), (401), (213), (004), (214), (510), (602), and (160) characteristics peak of fluorapatite as per JCPDS file. The average crystalline size D (nm) was calculated by the following Scherer’s equation $D = \frac{k \lambda}{\beta \cos \theta}$, where k is the Scherer constant (1.84), λ is the wavelength of the radiation; β is the full width of the diffraction peak at half the maximum intensity (FWHM).
**Figure 3.1** XRD plot for hydroxyfluorapatite nanocomposite

**Table 3.1** crystalline size distribution

<table>
<thead>
<tr>
<th>Composition</th>
<th>Crystalline size of the fluorapatite</th>
</tr>
</thead>
<tbody>
<tr>
<td>(S-1)</td>
<td>42.6nm</td>
</tr>
<tr>
<td>(S-2)</td>
<td>52.5nm</td>
</tr>
</tbody>
</table>

### 3.2 Thermo gravimetric analysis (TGA)

Figure 3.2 showed the TGA thermogram of as synthesized samples. The weight loss of hydroxyfluorapatite is measured by TGA during a heating cycle from 25°C to 1200°C. The increase rate of temperature was 10°C/min.

**Figure 3.2** TGA combined plots of CMC hydroxyfluorapatite
3.3 Compressive strength of the CMC hydroxyfluorapatite nanocomposite:

Figure 3.3 showed the stress-strain diagram for the four different polymer concentrations nanocomposite. From figure 3.3 S-1 has the ultimate compressive strength of 32.7MPa, Compressive strength in elastic range is 10MPa and elastic modulus of 445MPa. S-2 has the ultimate compressive strength 20MPa; Compressive strength in elastic range of 6MPa and elastic modulus of 287MPa. S-3 has the ultimate compressive strength of 5.41MPa; compressive strength in elastic range of 3.5MPa and the elastic modulus of 120MPa. S-4 has the ultimate compressive strength of 5.27MPa; compressive strength in elastic range of 1.12MPa and the elastic modulus of 33MPa.

3.4 Morphological structure of CMC hydroxyfluorapatite nanocomposite

3.4.1 Scanning electron microscopy (SEM) analysis

SEM micrograph of the synthesized CMC hydroxyfluorapatite nanocomposite is shown in figure 3.4

![SEM micrographs of synthesized CMC hydroxyfluorapatite nanocomposite](a) (b) (c) (d)
Figure 3.4 (a) showed the SEM image at 10000x magnification for S-1, (b) showed SEM image at 10000x magnification for S-2, (c) showed SEM image at 10000x magnification for S-3, (d) showed SEM image at 10000x magnification for S-4.

From the figure 3.4 we confirmed the formation of three dimensional nanocomposites. When the concentration of CMC polymer increases the porosity of the nanocomposite also increases.

3.4.2 Transmission electron microscope (TEM) analysis:
The morphology of the sample was investigated by the transmission electron microscope. Fig. 3.5a, 3.5b represent a typical TEM image of the CMC hydroxyfluorapatite nanocomposite. From the TEM image it could be seen the agglomeration of the needlelike shaped nanocomposite of the CMC hydroxyfluorapatite. The morphological structures of the samples observed in thus study were very similar to those of mineral phase present in bone and teeth.
Figure 3.5 (c) showed the electron diffraction pattern of the CMC hydroxyfluorapatite

3.5 Discussions
The XRD graph of the sample at CMC polymer concentration 0.05% and 0.10% show that the 11 peak at d value 3.44 Å, 2.801 Å, 2.289 Å, 2.0597 Å, 1.9458 Å, 1.8366 Å, 1.72 Å, 1.5002 Å, 1.4574 Å, 1.2586 Å and 1.2374 Å representing peaks of h k l value (002), (211), (212), (113), (401), (213), (004), (214), (510), (602) and (160) confirmed the presence of the hydroxyfluorapatite in the composite.

Thermo-gravimetric analysis of the sample from 25°C to 1200°C showed that how does the weight loss with respect to change in temperature. Decomposition pattern in the range of 350°C to 650°C there is a rapid weight loss due to the decomposition of the CMC polymer. After that wt. loss occurring in the temperature range 1000°C- 1200°C may indicate release of OH- groups which substitute for some of the F ions in flourapatite.

The mechanical testing of the composite revealed that the S-1 had the ultimate compressive strength and had maximum elastic compressive strength.

The SEM image show how hydroxyfluorapatite has integrated into polymer matrix and show the agglomeration of the particle in the composite.

The TEM image shows the internal morphology of the composite. The TEM images reveals that the hydroxyfluorapatite crystals are short needlelike shaped and the crystal sizes are in the range of 20-30nm. More-ever these nano hydroxyfluorapatite/CMC samples have good dispersive properties and displayed a relatively uniform morphology.

4. CONCLUSION
We have synthesized novel Biomimetic three dimensional micro/macro porous Carboxymethyl cellulose hydroxyfluorapatite nanocomposites with four different compositions for its possible application as a synthetic bone grafting and as teeth filler in dentistry. The synthetic method involves a simple and cost effective route akin to matrix mediated biomineralization process.

From this study we conclude that:
The XRD result indicated the size of the nanoparticles between 42.6nm to 52.5nm.
The overall weight loss was continuously decreased with the temperature change obtained by the Thermo-gravimetric analysis.
The Mechanical testing conducted so far indicate the addition of the CMC polymer 2.5gm to 1.5gm has greatly improved the compressive strength of the composite. The compressive strength in the elastic range was increased from 1.12MPa to 10MPa which is very near the compressive strength of the trabecular bone.

SEM image show the CMC matrix in which fluorapatite nanoparticles are attached.
The TEM image showed that the crystals are short needlelike shaped. The crystals are in the range of 20nm to 30nm.

REFERENCES: