Synthesis and characterization of banana peel derived biopolymer/hydroxyapatite nanocomposite for biomedical applications

K. Kanimozhi, D. Gopi* and L. Kavitha

Abstract— The aim of this study is to prepare and characterize the novel green biopolymer/HAP nanocomposite. In this synthesis process the biopolymer derived from the peel of bananas with different concentrations were used for the synthesis of HAP nanocomposites. Fourier transform infrared spectroscopy (FTIR), X-ray diffraction analysis (XRD), scanning electron microscope (SEM) and transmission electron microscope (TEM) were used to identify the functional groups, phase structure and morphology of the as-synthesized composite. FTIR analysis confirms the COO^{-}….Ca^{2+} interaction between the as-prepared biopolymer and HAP. The nanocomposite crystal behavior and phase analysis using XRD analysis shows the formation of phase pure nanocomposite with low crystalline nature. The morphology of the as-synthesized sample was investigated using SEM and TEM analysis which demonstrates the presence of discrete particles with reduced size. Hence, the as-synthesized nanocomposite could have a potential application in the various biomedical fields.

Keywords — Nanocomposite, Banana peels, Pectin, Biomedical applications, Green synthesis.

1 INTRODUCTION

Natural bone is a composite material composed of a collagen matrix reinforced with hydroxyapatite (HAP) crystals [1]. HAP is one of the most important inorganic materials found in natural bones and teeth [2]. Hybrid organic-inorganic materials can offer great advantages because of their excellent biocompatibility and bioactivity; it has been widely used in medical, dental, as a material for damaged bones and teeth, scaffold material and drug delivery agent [3]. However, the application of pure HAP is very limited to load-bearing applications owing to its brittleness and poor mechanical properties. Introducing a polymeric component into HAP to form an organic-inorganic nanocomposite is a most commonly used method to overcome the mechanical weakness of HAP based materials. As a result, pectin is used as a polymer matrix to produce a composite because of their better biocompatibility and biodegradability [4]. Since these polysaccharides rich in carboxyl and hydroxyl groups which can promote the binding of Ca^{2+} from the solution to carboxylate ions and this initiates the apatite nucleation process. Nanocomposite materials often show an excellent balance between strength and toughness and usually possess improved characteristics compared to their individual components [5]. In the present work we have synthesized biopolymer/HAP nanocomposite using banana peels, an agricultural waste material. The banana pulp is consumed and the peels are usually discarded. This abundantly available waste material is composed of biopolymers such as pectins, cellulose and lignins. Among them, pectin is the gifted polysaccharides and is used as antimicrobial, anticoagulant, wound healing substances as well as a composite material to improve the proliferation of osteoblast. The influence of pectin concentration on the morphology, purity and the size of the as-synthesized nanocomposite were studied using various analytical techniques.

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2 MATERIALS AND NETHODS

The collected fruits were washed and separated into pulps and peels. The polymer was extracted from the peels and was used for the following synthesis procedure. 0.01 wt.% of pectin was dissolved in deionized water and stirred at 60 ºC and then 0.05 M $CaCl_2.2H_2O$ was added to the above solution and stirred for some time. Subsequently 0.03 M $(NH_4)_2HPO_4$ was added under continuous and vigorous magnetic stirring and thus yielded a white suspension. The pH of the above solution was adjusted to 9 using ammonia solution. Then the resultant precipitate was kept in a ultrasonicator and dried in a hot air oven. Finally the dried powder was washed with ethanol and double distilled water to get the as-synthesized composite. The above procedure was carried for other concentrations (0.07 and 0.15 wt.%) of pectin.

3 CHARACTERIZATION TECHNIQUES

The chemical and phase composition of the nanocomposites was determined by Fourier transform infrared spectroscopy (FTIR-Bruker Tensor 27 series spectrometer) and X-ray diffraction analysis (XRD-Rigaku, Miniflex II). The structural and morphological features of the as-synthesized nanocomposites were investigated with a scanning electron microscope (SEM, JSM-6360LV, JEOL Japan) and transmission electron microscope (TEM, JEM-2010, JEOL).

4 RESULTS AND DISCUSSION

Figure 1 illustrates the FTIR spectra of the pectin-HAP nanocomposite using different concentrations of pectin. As it is seen, three samples show the same FTIR spectra. The characteristic phosphate peaks appeared at 473, 564, 603,

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960 and 1030-1093 cm^{-1} [6]. Whereas CO^{3-} -derived peaks are appeared at 878, 1402-1460 cm^{-1}, respectively. The presence of CO^{3-} may be due to the adsorption of atmospheric CO_2 during the sample preparation.

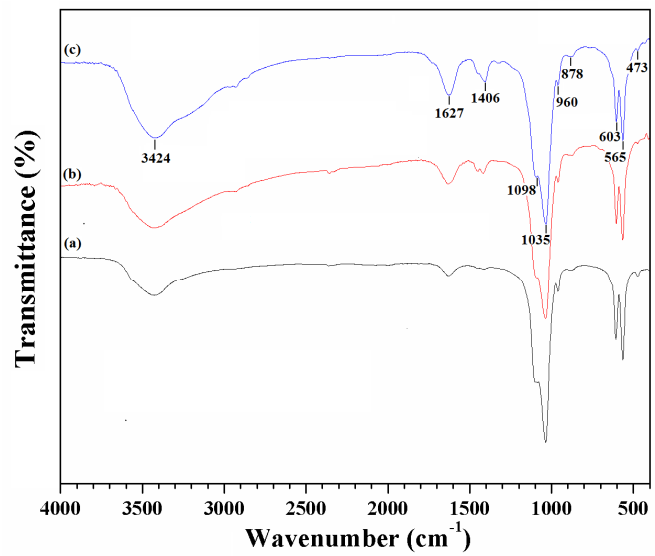

Fig. 1 FTIR spectra of nanocomposites synthesized using different concentration of pectin; (a) 0.01, (b) 0.07 and (c) 0.15 wt.%.

The broad peak appeared in the range between 3387-3435 cm^{-1} and 1635 cm^{-1} reveals the characteristic stretching mode of surface hydroxyl groups and adsorbed water molecules. In addition, the absorption peak for the composites appeared at 1627 cm^{-1}, which is $COO^{-}...Ca^{2+}$ interaction. The lattice OH absorption peak intensity increased with increasing the concentration of pectin.

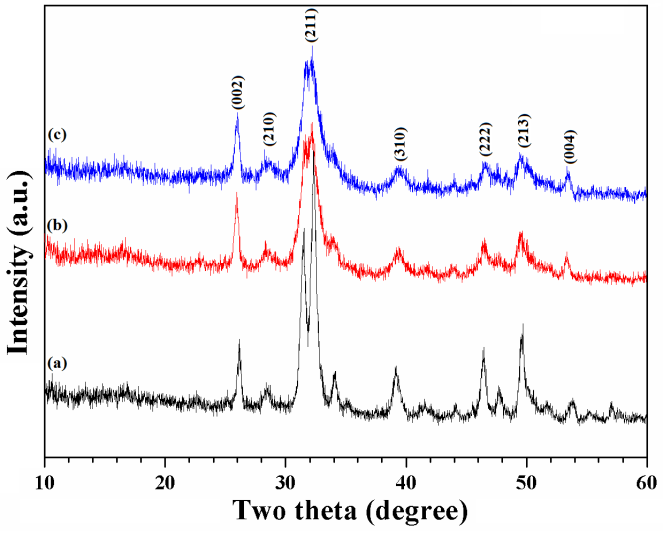

Fig. 2 XRD patterns of nanocomposites synthesized using different concentration of pectin; (a) 0.01, (b) 0.07 and (c) 0.15 wt.%.

The crystalline phase of the as-synthesized nanocomposites using different concentration of pectin was investigated by using XRD and is depicted in Fig. 2. The XRD patterns showed only the HAP crystalline phase [7], which reflected the characteristics of the (002), (210), (211), (310), (222), (213) and (004) planes. The results are in good agreement with the ICDD card No. 09-0432.

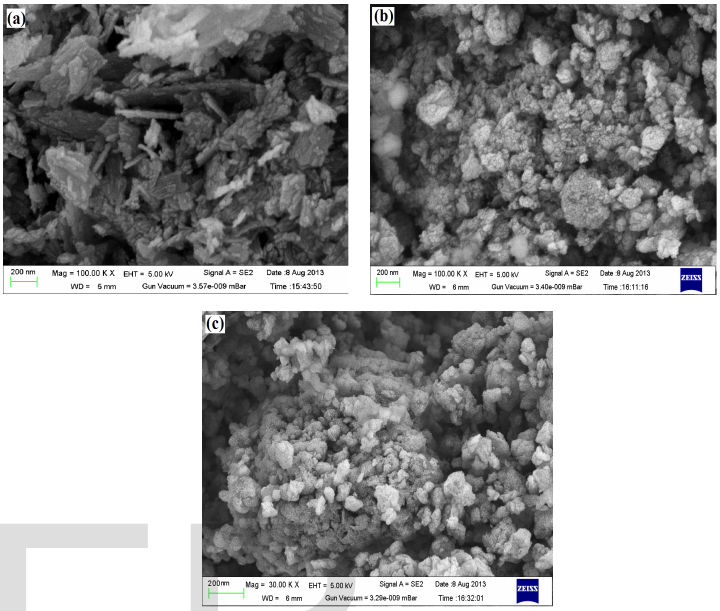

Fig. 3 SEM images of nanocomposites synthesized using different concentration of pectin; (a) 0.01, (b) 0.07 and (c) 0.15 wt.%.and (d) 45 min.

Figure 3 shows the structural morphology of the composites synthesized by different concentrations of pectin. The nanocomposite synthesized using 0.01 wt.% of pectin shows irregular aggregates of nanoparticle (**Fig. 3a**). **Figure 3b** shows the fine agglomerates of particles with regular morphology. The morphology of the nanocomposites synthesized using 0.15 wt.% of pectin shows the regular morphology of reduced size with less aggregated particles. Finally as the concentration of the biopolymer increased, the size of the nanocomposite particles decreased is evidenced in **Fig. 3c**.

The morphology of the particle is further analyzed using TEM analysis (**Fig. 4**). It is observed that the particle shows a needle like morphology with reduced size.

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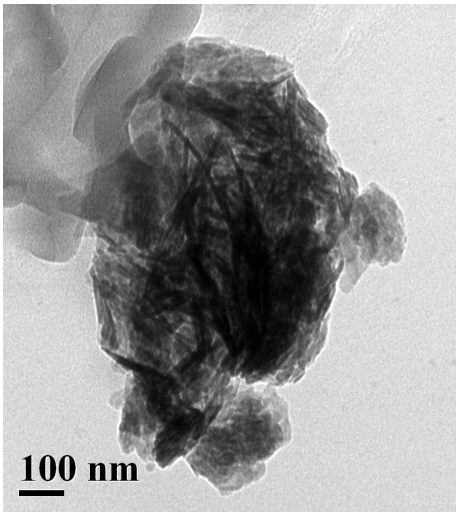

Fig. 4 TEM images of nanocomposites synthesized using 0.15 wt.% of pectin concentration.

4 CONCLUSIONS

The FTIR analysis confirms the $COO^{-}\ldots Ca^{2+}$ interaction between the biopolymer and HAP. The XRD, SEM and TEM images demonstrated that the concentration of pectin plays a major role for controlling and reducing the size of phase pure particles. This green method can be used for the synthesis of the nanocomposite which finds its application in the field of biomedicine.

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