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**Research Article** 

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# Preparation and characterization of Graphene-graftedchitosan/hydroxyapatite composite

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# ABSTRACT

Nowadays graphene based composites were developed due to their unique structure and excellent properties. Present study involves the preparation of graphene grafted chitosan and hydroxyapatite (GgCH) composite through solution casting method for biomedical applications. The prepared composite was characterised by FTIR, TGA, DSC XRD and SEM analysis. The formation of GgCH composite was confirmed by FTIR and XRD studies through the shifting of peak values from Chitosan to GgCH composite due to strong interaction between the compounds (HAP, chitosan and Graphene). Thermal stability of the sample was analysed by TGA-DSC curves. The SEM images were recorded and compared with pure graphene.

Key words: Graphene, Chitosan, Hydroxyapatite, GgCH Composite, Solution casting method.

# INTRODUCTION

Chitosan, a derivative of chitin, composed of  $\alpha$ -D-glucosamine and N-acetyl glucosamine was commonly found in exoskeletons of crustacean shells and cell walls of fungi [1, 2]. Due to its properties such as biocompatibility, hypotoxicity and anti microbial activities, it has been used in the fields like biomedical, textile, drug delivery, environmental protection, food processing etc [3-5]. To use chitosan as a potential biomaterial it is essential to enhance the mechanical property and biological response of chitosan [2]. Thus hydroxyapatite and graphene material was used to improve the properties of chitosan and making it suit for tissue engineering applications.

A bioceramic, hydroxyapatite, which is an inorganic material has similar composition as that of bone and teeth mineral was extensively used as a bone implant and bone grafting material [6]. Metallic substrate coated with HAP is widely prepared, because this coating enhances the bond formation between the implant material and the tissues. However the combination of HAP and chitosan is not sufficient to overcome the brittleness and low fracture toughness compared with bone [7].

Graphene composed of  $\text{Sp}^2$  hybridized carbon atoms existing in two dimensional single layer sheets, has attracted much attention of the researcher due to its enhanced electrical, mechanical and thermal properties [8,9]. Low weight and excellent thermal stability of graphene made them suitable to act as filler/reinforcing materials with polymer [10]. The variety of graphene composites were reported for biosensor [11], wound healing [12], adsorption[13], bone tissue engineering[9] and corrosion resistance.[14]

The present study was aimed to prepare the Graphene grafted Chitosan/ Hydroxtapatite (GCH) composite. The prepared composite was characterized using FTIR, TGA, DSC, XRD and SEM analysis. The results were discussed below.

## **EXPERIMENTAL SECTION**

### Materials

Chitosan was a kind gift from Indian Sea Foods, Cochin, Kerala which is 92% deacetylated. Graphene was purchased from Nano beach, HAP was obtained from Leochem, Bangalore, Acetic acid was purchased from SD Fine Chemicals.

# Preparation of Graphene-grafted-Chitosan/Hydroxyapatite (GgCH) composite

About 1g of chitosan was weighed and dissolved in 2% acetic acid. Simultaneously 1g of HAP and 0.2g of graphene was weighed and dispersed in minimum amount of de-ionized water. The dispersed HAP and graphene was slowly added to the chitosan suspension and then the mixture was stirred for 2 hours using magnetic stirrer then the contents were transferred to the petri plates and allowed for air-drying [15].

#### Characterization

The FT-IR spectra of GgCH composite was recorded by Fourier transform infra-red spectrophotometer (FT-IR) using the Alpha Bruker FTIR Spectrophotometer in the wavelength range of  $400 - 4000 \text{cm}^{-1}$ . The X-ray diffraction pattern of the prepared sample was tested by an X-ray scattering D8 ADVANCE Diffractometer using Ni filter Cu K $\alpha$  radiation source ( $\lambda$ =0.154nm), set at scan rate = 10°C/min, using a voltage of 40kV and a current of 30 mA. The TGA study of the prepared samples was carried out using SDT Q600 V8.0 Build 95 instrument at a heating rate of 10°C per minute in nitrogen atmosphere to analyze the weight losses at different stages. The differential scanning calorimeter (DSC) was used to examine the thermal property of the blends. The measurements were performed with NETZSCH DSC 200 PC in a pan Al, pierced lid in the N<sub>2</sub> atmosphere at a heating rate of 10° K/min. The results were recorded and analyzed. The surface morphology and cross sectional morphology of the prepared composites was observed with scanning electron microscopy. For the analysis, the samples were cut into pieces of various sizes and wiped with a thin gold – palladium layer by a sputter coater unit (VG – microtech, UCK field, UK)

### **RESULTS AND DISCUSSION**

### **FT-IR Spectrometry**

FTIR spectrum of pure compound and GgCH composite was shown in Figure 1 and table 1. The C=O stretching of NHCO (amide I) and N-H bending of NH<sub>2</sub> (amide II) for pure chitosan was observed at 1624 cm<sup>-1</sup> and 1578cm<sup>-1</sup>, the same was observed at 1619 cm<sup>-1</sup> and 1516 cm<sup>-1</sup> for GgCH composite. The shifting of bands to lower values indicates the strong interaction between chitosan and graphene during grafting and also with HAP during composite formation [16-18].



Figure 1: FTIR Spectrum of (a) Chitosan; (b) HAP; (c) GgCH composite

Groups	CHITOSAN	HAP	GRAPHENE	COMPOSITE
OH str	3470	3572		~3500
N-H str	3470			~3500
C-H str	2923, 2850,		2920, 2849	2920, 2882
C-H def	1460, 1383		1461,1481	1459, 1362
N-H def	1578			1516
C=O str	1730, 624		1731, 1626	1718, 1691, 1619
C-O str	1150,040			1025
$PO_4$		1094, 1036		1025

Table. 1 FTIR values for pure chitosan, HAP, Graphene and GgCH Composite.

The C-O stretching vibrational bands of chitosan and graphene was overlapped with phosphate bands of HAP [19, 21]. Chitosan and graphene showed its C-H, C=C and C-C stretching vibrations at 2920 cm<sup>-1</sup>, 2882 cm<sup>-1</sup>, 1459 cm<sup>-1</sup>, 1362 cm<sup>-1</sup> respectively as shown in table. Figure shows a small peak of OH stretching vibration of HAP and Chitosan at 3500 cm<sup>-1</sup>. This less intense peak indicates that the OH group of both the compound was involved in weaker Hydrogen bonding.

# **XRD** studies

Figure 2 shows the XRD patterns of pure Chitosan, HAP and the prepared GgCH composite. Figure 2c shows (002) diffraction at 26° and the broadened peak at around 32° which are the diffractions of (211), (300), (202) at an angle of  $30.5^{\circ}$ ,  $31.3^{\circ}$ ,  $33^{\circ}$  respectively [22, 23]. The broadness of a peak indicates the partial demineralization of HAP and low crystalinity of the GgCH composite [22, 23, 24]. The pure chitosan shows two characteristic peaks at  $10^{\circ}$  (Crystalline structure) and  $20^{\circ}$  (amorphous structure). In GgCH composite both the peaks are shifted to  $11.95^{\circ}$  and  $26.58^{\circ}$ . The broadness of the first peak was decreased and the second peak was shifted and overlapped with grapheme (26°) and HAP (26°) peak due to the strong interaction of chitosan with HAP and Graphene[18, 25].



Figure 2: FTIR Spectrum of (a) Chitosan; (b) HAP; (c) GgCH composite

#### **Thermal Analysis**

The prepared GgCH composite was subjected to TGA and DSC Analysis. TGA thermogram of prepared GgCH composite (Figure 3) showed the various stages of decomposition. The weight loss occurred between  $30-214^{\circ}$ C showed two derivative peaks at  $45.27^{\circ}$ C and  $205.47^{\circ}$ C. The peak one indicates desorption of adsorbed water molecules and peak two indicates the release of crystalline water of HAP [26]. The weight loss occurred at this temperature is very less (7.11%) and it co-insides with FTIR spectra of the composite, confirming the existence of weaker hydrogen bonding. A major weight loss of 18.73% was observed between  $275^{\circ}$ C -  $428^{\circ}$ C, which corresponds to the degradation of the glucosamine in chitosan and it was indicated by a derivative peak of  $300^{\circ}$ C [27]. The weight loss between  $428^{\circ}$ C and  $445^{\circ}$ C attributed to the combustion of carbon present in Graphene and Chitosan [26,

28]. The decomposition of HAP was observed at  $690^{\circ}$ C shown by the DTG curve. The TGA analysis confirms the presence of all the three compounds and their decomposition temperatures. The thermal stability of the prepared composite was not increased as expected.

Figure 4a and 4b shows differential scanning colorimetry curves of Chitosan and GgCH composite. A single endothermic (Tc) and exothermic ((Tm) peak was observed in both the curves. Glass transition temperature (Tg) for pure chitosan was  $203^{\circ}$ C and for the GgCH composite was  $155^{\circ}$ C. This decrease in the Tg value of GgCH composite attributes to the modification of chitosan [29].



Figure 4: DSC thermogram of (a) Pure chitosan and (b) GgCH composite

# SEM analysis

Figure 5a and 5b shows the change in morphology upon grafting with Chitosan and HAP. It also depicts the existence of Graphene in the prepared composite shows porous nature of the composite.





Figure 5: SEM image of (a&b) GgCH composite; (c) Graphene

### CONCLUSION

Graphene grafted Chitosan and Hydroxyapatite composite was successfully prepared by solution casting method. XRD and FTIR evidenced the strong interaction among the precursors. TGA studies of the prepared GgCH composite confirms the grafting of Graphene through Hydrogen bonding with chitosan and HAP. DSC curve also showed the successful grafting and composite formation of chitosan, graphene and HAP.

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