International Journal of Pharmacy and Biological Sciences
ISSN: 2321-3272 (Print), ISSN: 2230-7605 (Online)
IJPBS | Volume 9 | Special Issue 2 | 2019 | 263-268
| Research Article | Biological Sciences |Open Access |MCI Approved|
|UGC Approved Journal|

# A Study on Thermal Properties of F-Go Reinforced β-CD/HAp Composite

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Received: 30 Jan 2019 / Accepted: 20 Feb 2019 / Published online: 01 Apr 2019
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## Abstract
Over the past several decades, polymer composites have got a wide investigation in academics and industry because of their low cost and high performance. Composites have been advancing to their present state as fillers. For those fillers, calcium-based biomaterials, glass fiber and nanoclay are often used to strengthen the polymer matrix. Normally they do not have any functions of electrical properties, thermal stability, elasticity and mechanical strength. Nowadays carbon based fillers provide more choices with multiple functions. Especially for the graphene-based biomaterials possess the combination of excellent mechanical, thermal and electrical properties and then attract considerable attention. In addition, a reinforcement of functionalised graphene oxide improves its applications further because of the unique physical properties of graphene oxide with high charge carrier mobility, transparency, specific surface area and thermal conductivity. In the present work, we have prepared a novel β-CD-HA-f-GO composite and Fourier transform infrared spectroscopy (FT-IR) has been applied to study the occurring interactions between materials. Thermal properties of composite have been analysed by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). From the results it was concluded that the prepared composite with overall new perspectives for the development of naturally available materials with tunable functional properties of graphene oxide in combination with biomaterials possess excellent thermal stability.

**Keywords**
Polymer composites, biomaterials, fillers, functionalised graphene oxide, HAp, Cyclodextrin and thermal stability.

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## 1. INTRODUCTION
Cyclodextrins (CDs) are polysaccharide macromolecules comprising six, seven and eight D-glucose units for the respective α-, β- and γ-CDs. They have a truncated conical shape with cavity diameters of ~6–10 Å. They possess a ring-like structure with a hydrophilic exterior and a hydrophobic interior resulting from the presence of primary and secondary hydroxyl groups at the edges of the ring (C2, C3, and C6) and of apolar hydrogens and ether-like oxygen at the inside face of the ring (C3 and C5) [1]. This particular molecular arrangement allows CDs to trap or

encapsulate other compounds [2,3] commonly referred as guest molecules, becoming an important multipurpose tool. An interesting characteristic of β-CD is its ability to selectively bind various organic, inorganic, and biological guest molecules in its cavity to form host-guest inclusion complexes. [4] This prominent property has been applied in chemical, cosmetics, pharmaceutical industry, foods, and agriculture

etc. [5,6] On the other hand, hydroxyapatite (HA) is one of the major constituents of the inorganic component in human hard tissues (bones and teeth), and it is one of the most common biomaterials studied in bone tissue engineering because of its good biocompatibility. [7, 8] HAp acts as a reinforcement material in hard tissues, and is responsible for the stiffness of bone, dentin and enamel. It eventually acts as an inducing material in the formation of osteoblasts and osteoclasts, leading to bone formation and mineralization. It can form a direct chemical bond with surrounding bone and connective tissues [9] and is osteoconductive, nontoxic, non-inflammatory and non-immunogenic. [10, 11, 12, 13] However, there are some limitations in its usage because its low mechanical strength [14] and brittleness makes it hard to shape. So as to overcome the problem, the incorporation of f-graphene oxide in the β-CD/HA matrix would provide functionality and flexibility to the prepared composite. It has also been reported in a recent investigation, that Graphene Oxide (GO) has been functionalized and added with β-CD/HA polymer matrix resulted into a system adopted for various applications.

## 2. MATERIALS AND METHODS

β-Cyclodextrin (β-CD) and Hydroxyapatite were purchased from Sigma-Aldrich Co. Graphite was obtained from Molychem Chemicals Ltd. All other reagents were of analytical grade and used as received without further purification. The water used was double distilled and deionised.

### 2.1 CHARACTERIZATION

The FT-IR spectra of β-CD/HAp/f-GO composite was recorded by Fourier transform infra-red spectrophotometer (FT-IR) using the SHIMADZU FT-IR Spectrophotometer in the wavelength range of 400 – 4000 $cm^{-1}$. Thermogravimetric analysis of the prepared samples was performed using SDT Q600 V8.0 Build 95 instrument. The range of temperature used is between 20ºC to 800ºC with a heating rate of 10ºC/min under nitrogen atmosphere. 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 $N_2$ atmosphere at a heating rate of 10 °C/min.

### 2.3 PREPARATION OF GRAPHENE OXIDE

GO was synthesized from graphite powder using a modified Hummers method. 1g of graphite powder and 0.5 g of $NaNO_3$ were dissolved in 50 mL of cold 98% $H_2SO_4$ under an ice bath. After stirring of the mixture for 20 min, 4g of $KMnO_4$ was gradually added within 5 min with stirring at temperature below 20 °C. After 1 h, the reaction was continued for 30 min at 35 °C. Then, 50 mL of deionized water was slowly poured into the reaction mixture. The reaction was continued for 20 min at 98 °C, followed by further dilution of suspension to 200 mL with deionized water and subsequent addition of 5 mL 30% $H_2O_2$ for removing the residual $KMnO_4$ and $MnO_2$. The resulting mixture was then filtered and washed four times with deionized water and 5% HCl solution, respectively. The resultant GO (yield 89%) was dried under vacuum at 70 °C for 10 h.

### 2.4 FUNCTIONALISATION OF GRAPHENE OXIDE

For functionalisation, we used 10 mg of graphene oxide, 7 mg of which was added to 30 ml $H_2SO_4$ and remaining 3 mg was added to 10 ml $HNO_3$ (3:1 ratio 30 ml of $H_2SO_4$ and 10 ml of $HNO_3$). And then both were mixed together and left for 10 min, then this process was followed by centrifugation then we decanted the supernatant and repeatedly washed with distilled water until the PH is equal to 7.

### 2.5 PREPARATION OF β-CYCLODEXTRIN/HYDROXYAPATITE/F-GRAPHENE OXIDE COMPOSITE

About 0.5 g of β-Cyclodextrin was dissolved in hot water and kept aside. Then, 0.5 g of Hydroxyapatite was weighed and dispersed in minimum amount of distilled water. This dispersed HAp was slowly added to β-Cyclodextrin in hot water with constant stirring. The mixture was agitated at room temperature using ultrasonicator for 45 minutes. The homogenous solution was poured into petridish and kept for air drying.

β-cyclodextrin/Hydroxyapatite/f-graphene oxide composite was prepared by adding 0.5 g of functionalized graphene oxide to 1 g of β-cyclodextrin/Hydroxyapatite by grinding method using mortar and pestle

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## 3. RESULTS AND DISCUSSION

### 3.1 FT-IR SPECTROMETRY

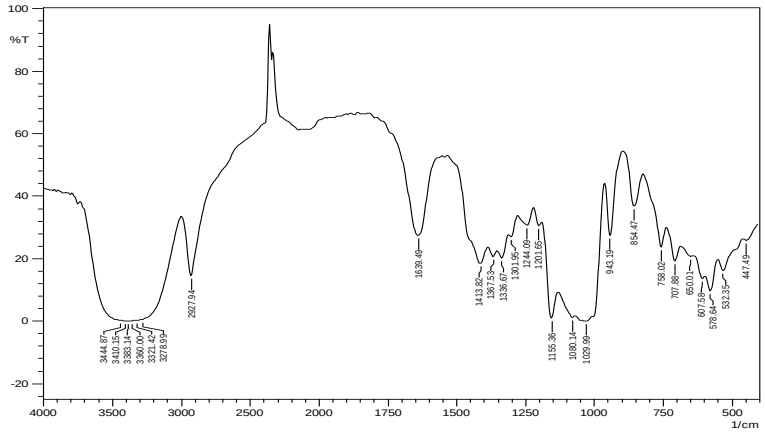


**Figure 1: FT-IR spectrum of pure β-Cyclodextrin**

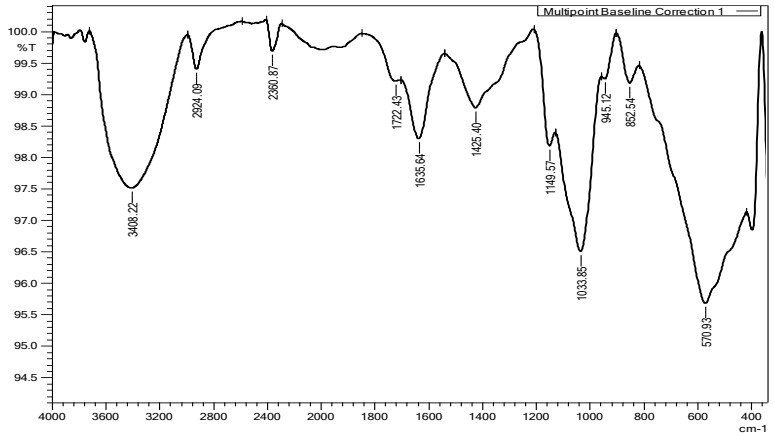


**Figure 2: FT-IR spectrum of pure β-CD/HA/f-GO Composite**

The FTIR spectral details of pure β-CD and β-CD/HAp/f-GO composite was represented in Fig.1 and Fig.2. The FT-IR spectra shows all the characteristic bands of functional groups present in the pure β-CD and β-CD/HAp/f-GO composite. The FT-IR spectrum reveals that the presence of sharp and intense band appears at 3408 $cm^{-1}$ may be due to the overlapping of O-H stretching band of β-CD with the O-H stretching band of HAp and f-GO. Because in case of pure β-CD and f-GO, there is a broad spectrum was observed. This shift in frequency range is due to the strong interaction between the hydroxyl groups present in the β-CD, HAp and f-GO which involves in the intermolecular hydrogen bonding. [15] In the composite, there is a new band appears at 2924 $cm^{-1}$, 2360 $cm^{-1}$ and 1425 $cm^{-1}$ was attributed to the phosphate group and absorbed carbonate group present in the hydroxyapatite and also for -O-H stretching vibration mode of β-CD. Both of these changes suggest that the successfull attachment of β-CD with the HAp and f-GO. The appearance of new peak at the range of 1722.43 $cm^{-1}$ corresponding to the C=O stretching vibration of carboxyl group which implies that the carboxylation of graphene oxide has been taken as well. The sharp and intense peak at 1635 $cm^{-1}$ indicates that the alkene C=C stretching and C-O/C-C stretching vibrations at 1149 $cm^{-1}$ and 1033 $cm^{-1}$. Then, intensive absorption band in 570 $cm^{-1}$ corresponds to a band characteristic to $PO_4^{3-}$

. [16] The intense peaks located at 852 $cm^{-1}$ corresponds to a band characteristic to $HPO_4^{2-}$. Thus, the FTIR spectra analysis indicated that all the three components in β-CD/HAp/f-GO composite prepared involves the expected interactions among different components.

**3.2 Thermo gravimetric analysis (TGA)**

Thermogravimetric analysis is a method of thermal analysis which deals with the measurement of changes in physical and chemical properties of materials as a function of increasing temperature (with constant heating rate), or as a function of time (with constant temperature and/or constant mass loss). The TGA and DTA curves of pure β-CD and β-CD/HAp/f-GO composite has shown in Fig.3, Fig.4 and Fig.5.

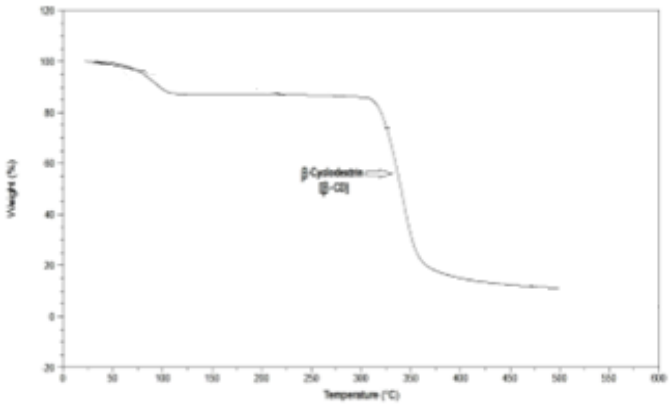


**Figure 3**:TGA thermogram of pure β-CD

The TGA thermogram of pure β-CD shows an initial weight loss peak due to loss of moisture at 93 °C and a large weight loss peak at 325 °C is due to thermal decomposition of β-CD. [17] On comparing the TGA of pure β-CD with the TGA curve of β-CD/HAp/f-GO composite, it shows the first weight losses started from room temperature to 97 °C and the second weight loss at 247 °C were observed for GO, may be due to loss of thermally unstable water molecules and loss of the labile oxygen-containing functional groups such as carboxylic, anhydride respectively. [18] Where, the composite involves two step weight loss in the range of 275-350 °C due to decomposition of β-CD in consistency with DTA curve with the total weight loss of ~ 56-57% and decomposition temperature at 600-710 °C indicating that HAp increased the thermal stability of the prepared composite which can be explained in terms of the introduction of β-CD and HAp with respect to additional OH groups leading to increased hydrogen bonding between various components present in β-CD/HAp/f-GO composite. This higher thermal stability confirming the interactions between the three components.

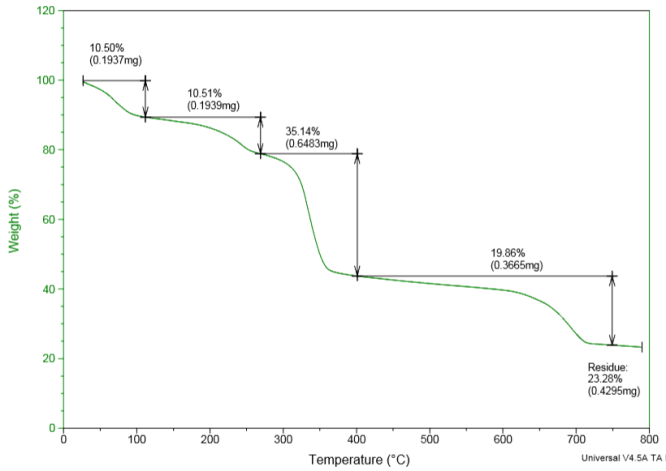


**Figure 4: TGA thermogram of β-CD/HAp/f-GO composite**

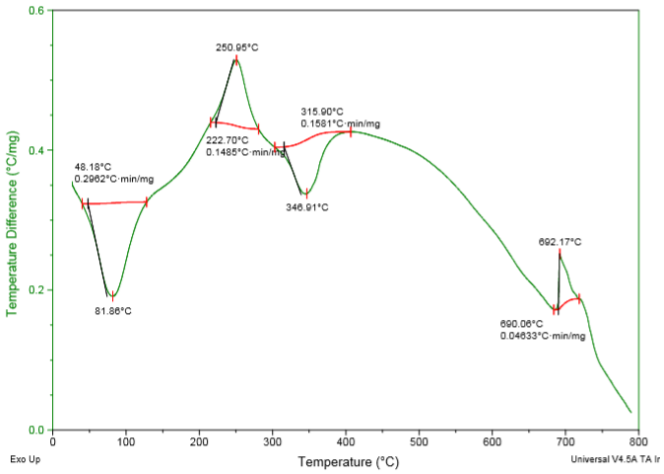


**Figure 5: DTA Curve of β-CD/HAp/f-GO composite**

### 3.3 Differential Scanning Calorimetry (DSC)

The Differential Scanning Calorimetry is a technique which involves the measurement of the difference in the amount of heat required to increase the temperature of a sample and reference as function of temperature. The DSC thermogram of the β-CD/HAp/f-GO composite is shown in fig. 5.

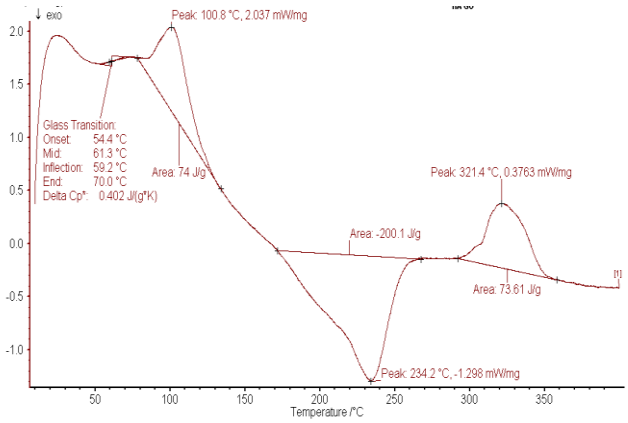


**Figure 5: DSC Curve of β-CD/HAp/f-GO composite**

The DSC curve of the β-CD/HAp/f-GO composite shows a sharp and broad endothermic peak at 100.8 °C and 321.4 °C and sharp exothermic peak at 234.2 °C which indicates the crystallization and melting process has taken place due to different polymeric components present in the composite. [19] The glass transition temperature was observed at 54.4 °C and low endothermic peak was due to loss of water and exothermic peak at 234.2 °C was observed for β-CD and 321.4 °C broad endothermic peak probably indicated the breakage of $CO_3^{2-}$ and $HPO_4^{-}$ present in the hydroxyapatite of the composite. [20]

## CONCLUSION

The β-CD/HAp/f-GO composite were successfully prepared and characterized. From the FT-IR results it was evident that, the certain new peaks were observed due to the various functional groups and intermolecular hydrogen bonding. The TGA, DSC studies clearly indicate that the prepared β-CD/HAp/f-GO composite was found to be highly thermally stable and it was evident from the higher decomposition temperature.

## REFERENCES

[1] Del Valle E. M. M., Cyclodextrins and their uses: A review. Process Biochemistry, 39 (9):1033e1046, (2004)

[2] Crini G., Review: A history of cyclodextrins. Chemical Reviews, 114(21):10940e10975. (2014)

[3] Fenyvesi E., Vikmon M.A., and Szente L., Cyclodextrins in food technology and human

nutrition: Benefits and limitations in 2012. Critical Reviews in Food Science and Nutrition, 8398:37e41, (2015)

[4] Szejtli J., Cyclodextrins and their inclusion complexes. Akademiai Kiado Budapest, 4-12, (1982)

[5] Dodziuk H., Cyclodextrins and their complexes: Chemistry, analytical methods, applications. Wiley-VCH, Weinheim, Germany (2006).

[6] Astray G., Mejuto J.C., Morales J., Rial-Otero R., and Simal-Gandara J., Factors controlling flavors binding constants to cyclodextrins and their application in foods. Food Research Internationl, 43:1212e1218, (2010)

[7] Ishihara K., Arai H., Nakabayashi N., Morita S., Furuya K., Adhesive bone cement containing hydroxyapatite particle as bone compatible filler. J Biomed Mater Res, 26:937-945, (1992)

[8] Holmes R.E., Bucholz R.W., and Mooney V., Porous hydroxyapatite as a bone-graft substitute in metaphyseal defects. J Bone Joint Surg, 68:904–911, (1986)

[9] Jones F.H., Teeth and bones: applications of surface science to dental materials and related biomaterials. Surf. Sci. Rep, 42:75-205, (2001)

[10] Jarcho M., Calcium phosphate ceramics as hard tissue prosthetics. Clin Orthop, 157:259-278, (1981)

[11] Ogiso M., Reassessment of long-term use of dense HA as dental implant:case report. J Biomed Mater Res, 43:318-320, (1998)

[12] Hench L.L., Bioceramics: from concept to clinic. J Am Ceram Soc, 74(7):1487-1510, (1991)

[13] Zhang R., Ma P.X., Polyhydroxyl acids)/hydroxyapatite porous composites for bone-tissue engineering. Preparation and morphology. J Biomed Mater Res, 44:446-455, (1991)

[14] Luna-Zaragoza D., Romero-Guzman E.R., Reyes-Gutierrez L.R., Surface and Physicochemical Characterization of Phosphates Vivianite, Fe2(PO4)3 and Hydroxyapatite, Ca5(PO4)3OH. J Miner Mater Charact Eng, 8:591–609, (2009)

[15] Tang W., Zhao J., Sha, B., Liu H., Adsorption and Drug Release Based on β-Cyclodextrin Grafted Hydroxyapatite Composite. J Appl Polym Sci, 127:2803-2808, (2013)

[16] PerezacC.A., Montelongo J., Casillas P.E., Mancilla J.R., Romero H.M., Preparation of hydroxyapatite nanoparticles facilitated by the presence of β-cyclodextrin. J Alloys Compd, 536S:S432-S436, (2012)

[17] dos Santos J. F. R., Alvarez-Lorenzo C., Silva M., Balsa L., Couceiro J., Biomaterials. 30:1348, (2009)

[18] Khan F., Baek S.H., Kim J.H., One-step and controllable bipolar doping of reduced graphene oxide using TMAH as reducing agent and doping source for field effect transistors. Carbon, 100:608, (2016)

[19] Heughebaert M., LeGeros R.Z., Gineste M., Guilhem A., Bone G., J BioMed Mater Res, 22:254, (1998)

[20] Catauro M., Bollino M., Tranquillo E., Tuffi R., Vecchio Ciprioti S., Morphological and thermal characterization of zirconia/hydroxyapatite composites prepared via sol-gel for biomedical applications. Ceramics International, 45(2):2835-2845, (2019)