

# Synthesis and Characterization of Nano hydroxyapatite with Polyurethane Nano Composite

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**Abstract-** In this study, a new kind of nano hydroxyapatite (nHAp) / polyurethane (PU) nano composite were fabricated for potential use in teeth and bone tissue engineering. Nano hydroxyapatite was successfully synthesized by wet chemical precipitation method. In this work, hydroxyapatite/polyurethane nano composites were synthesized and characterization of the compound were done by using Fourier transform infrared (FTIR), X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive spectrum (EDS).

**Index Terms-** FTIR, XRD, SEM, EDS, Polyurethane (PU).

## I. INTRODUCTION

Hydroxyapatite(HAp) is a major mineral component of bone and teeth[1]. HAp is biocompatible with the human organism. It is capable of integrating biological compound into bone tissue. HAp with the chemical formula  $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ , has been studied to repair bone defect or restore bone tissue functionality[2]. Various methods have been tried for the preparation of HAp either from natural sources (coral or bone) through wet chemical synthesis [3, 4]. The bioceramic has been widely used in dental materials. It can also be used as bone substituent materials due to its excellent biocompatibility, bioactivity, and non-toxicity, non-inflammatory nature [5]. HAp is manufactured in many forms and can be prepared as a dense ceramic [6], powder [7], ceramic coating [8], or porous ceramic [9] as required for the particular applications.

In recent years, much research has been carried out towards the development of applications. The small amounts of other materials such as carbon, nitrogen, iron, and another element are incorporated along with HAp to prepare the biomaterials. This biomaterials are widely used to repair, fill, extend and reconstruct deranged bone tissue and can also be used in soft tissue. HAp can also be manufactured synthetically by using number of different methods. The process for the preparation of hydroxyapatite and other calcium phosphate powder may be classified in synthesis from manual bone or coral. It can also be synthesized by reactions in solid state [10], co-precipitation [11,12],hydrothermal method[13], sol-gel.process[14], microwave processing[15].

Polymeric materials have been used in medical and surgical applications. This paper has shown to improve the performance of polyurethane along with HAp for medical applications in addition to the usage of Polyurethane to be used in formulation of industrial, foot ware, cable & wire, tube, paint, film and sheet [16]. The requirement of specific materials differ according to the nature of the application and there fore different techniques

have been used in modifying and fabricating different compositions to achieve exact requirements for clinical use. Polyurethane is a versatile class of polymers and is one of the most interesting classes of synthetic elastomer with unique properties that are used in a broad range of applications due to their excellent physical properties and relatively good biocompatibility [17]. However, during the commercial process, the studies found that the prepolymer i.e., two step process yielded polyurethane was insoluble in common organic solvent at room temperature but are easily moldable. In contrast the one-step process with the same formulation generally produced soluble polyurethane. A great deal of attention has been given to the synthesis morphology, chemical and mechanical properties of this family of materials [18]. Polyurethane is of good physical strength, abrasion resistance, water resistance, fatigue life and biocompatible character. Research on polyurethane has focused on its potential application as a facial prosthesis in dentistry, based on its inherent environmental stability, high tear resistance and low modulus without strength and elongation.

## II. MATERIAL AND METHOD

### Material

Material used in this study were: calcium hydroxide ( $\text{Ca}(\text{OH})_2$ ) and ammonium dihydrogen phosphate( $(\text{NH}_4)_2\text{H}_2\text{PO}_4$ ) obtained from Merck(India) and polyurethane purchased from Sigma Aldrich. Doubly distilled water, ethanol and N,N-dimethylformamide (DMF) was used as the solvent.

### Method

#### Synthesis of nano Hap

Nano HAp was synthesized by following a modified wet chemical precipitation method. At  $33^\circ\text{C}$ , 7.48g of  $(\text{Ca}(\text{OH})_2)$  was first dissolved in a 100 ml volume of an ethanol-water mixture (50:50%, v/v) and was stirred for 3hrs. A solution of 6.7g  $(\text{NH}_4)_2\text{H}_2\text{PO}_4$  was dissolved in 100 ml volume water and then added to the  $(\text{Ca}(\text{OH})_2)$  solution over a period of 24hrs. The PH of the slurry was measured digitally during to the precipitation reaction, reaching a final value of PH as 11.

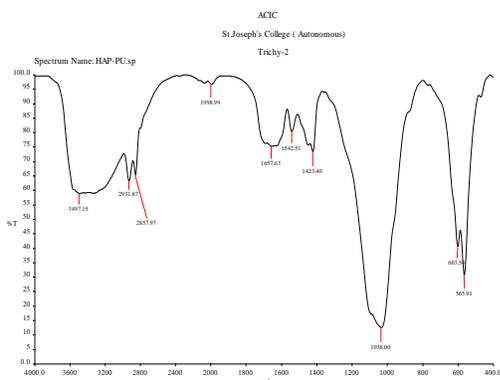
#### Synthesis of PU/Hap nano composites

Polyurethane was dissolved in N,N-dimethylformamide(DMF) solvent. After it was homogeneously dissolved in DMF nano hydroxyapatite powder was added to the parent solution. The PU / HAp solution was subjected to microwave exposure for initiating nano synthesis process under heat treatment.

### III. RESULTS AND DISCUSSION

#### FTIR

The Fourier transform infrared (FTIR) investigations were carried out using PERKIN ELEMER spectrometer in the range of  $400\text{ cm}^{-1}$  to  $4000\text{ cm}^{-1}$ . The functional groups were identified using the peak assignments. A strong peak at  $3497.15\text{ cm}^{-1}$  was assigned to the O-H stretching in alcohol group. The strong band at  $2931.87\text{ cm}^{-1}$  was assigned to C-H stretching alkane group. The band  $\text{C}\equiv\text{C}$  which usually occurred at  $1998.99\text{ cm}^{-1}$ . The strong peak at  $1657.63\text{ cm}^{-1}$  revealed the stretching vibration of C=O urea group. The strong peak at  $1542.51\text{ cm}^{-1}$  was attributed to the N-O stretching nitro group. The medium weak and multiple band appeared at  $1423.40\text{ cm}^{-1}$  had shown alkyl halide C-F and C-Cl stretching respectively. The alkyl halide stretching at  $565.91\text{ cm}^{-1}$  was also observed

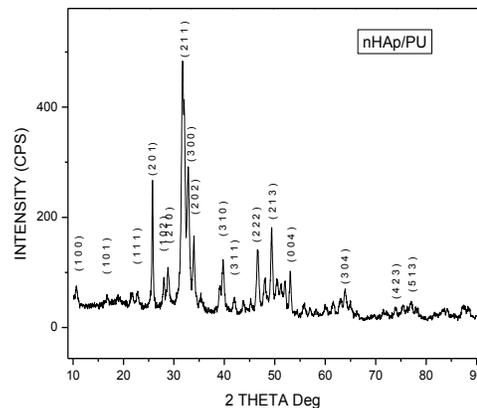


**Figure 1: FTIR spectrum of nHAp/PU**

#### XRD

The XRD patterns of nHAp and PU nanocomposite were taken. The observed diffraction peaks were identified by standard JCPDS (file no. 09-0432) file and were assigned as crystalline HAp. Well defined Bragg peaks were obtained at specific  $2\theta$  angles indicating that nanoparticle was ordered. The diffraction peaks, particularly in the planes 201, 211, 300, 222, and 213 are high and narrow implying that the HAp crystallines well. The crystalline size of the pure HAp/PU nano composite was calculated using Scherrer's formula. The structure of the samples was analyzed by X-ray diffraction (XRD) using a RIGAKU X-ray diffractometer. The  $\text{Cu K}\alpha$   $\lambda = 0.15418\text{ nm}$  was used as a target material for X-ray source. The Scherrer formula is  $X_s = K\lambda/(\beta_m \cos\theta)$

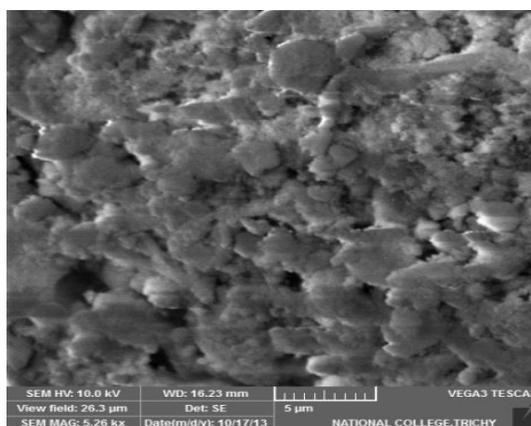
Where  $X_s$  is the mean crystallite size in nm,  $K$  is the constant taken for HAp as  $0.89\lambda$ ,  $\lambda$  is the X-ray wavelength ( $0.154\text{ nm}$ ),  $\theta$  is the diffraction angle, and  $\beta_m$  is the full width at half maximum for the diffraction peak under consideration.

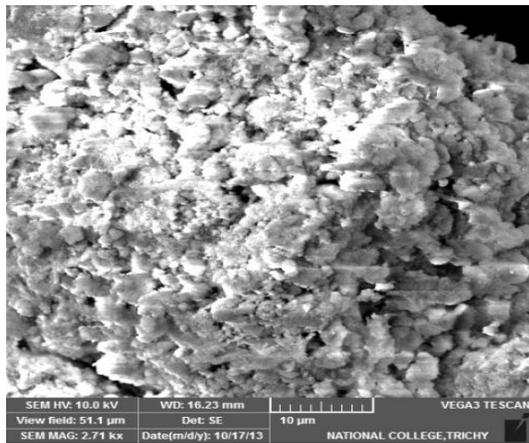


**Figure 2: XRD pattern of nHAp/PU**

#### SEM

The microstructure of pure and nHAp/PU is shown in figure 3. The presence of well-distributed macroporous through and microporous within the pore walls can be seen on the figure. The size, morphology, and interconnectivity of pores determine the ability of the nutrient diffusion, metabolic product delivery, cell attachment, tissue in growth and angiogenesis. With increase of mineral content, porosity and pore average size decreases, and well thickness increases slightly. It seems that the closed pores are formed in the samples containing higher nHAp content. Moreover, the SEM images showed that nHAp powder homogeneously dispersed in the pore wall as well in the pore surface. The porosity of pure nHAp 50% and PU 50% samples were identified approximately. The pores are regular, uniformly distributed, and interconnected with average pore size ranging  $5\text{ }\mu\text{m}$  to  $10\text{ }\mu\text{m}$  which are suitable architecture for application in bone tissue engineering.

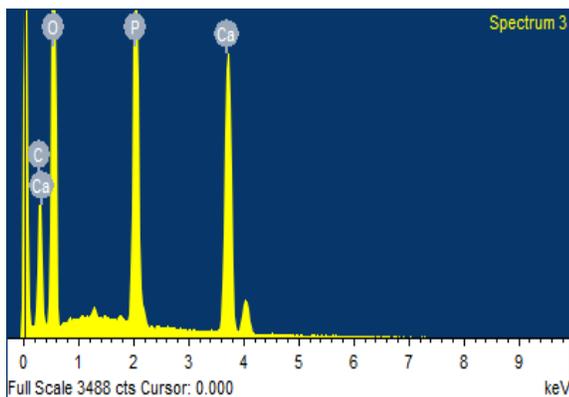




**Figure 3: SEM image of nHAp/PU microsphere particle at different magnifications.**

#### EDS

The energy dispersive spectrum(EDS) of nanoHAp/PU is given figure4. Energy peaks correspond to the various elements in the are also observed. The characteristic peaks for C, O, Ca and P were observed at 1.263 keV respectively. The atomic percentage of C, O, Ca and P are focused to be 15.54%, 59.25%, 10.47% and 14.75% respectively. So the EDS conform the presence of Ca/P nanoparticle.



**Figure 4: EDS of nHAp/PU**

#### IV. CONCLUSION

According to the results, nHAp/PU nanocomposites synthesis using a wet chemical precipitation method is feasible for synthesized nanocomposite with homogeneous composition. Composites showed satisfactory mechanical properties giving the possibility for using them as both structural substitute and regeneration element of bone in future application due to low biodegradability and acceptable elastic module. In addition, the results conformed as well as the composite with high nHAp/PU contents increase apatite formation growing. The data suggest that the method utilized in this work can be successfully synthesized by hydroxyapatite on polyurethane substrate.

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