



Macromolecular Nanotechnology

Nanocomposites of TPU-PDMS blend based on chitosan wrapped hydroxyapatite nanorods

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ABSTRACT

The present investigation reports the synthesis of chitosan wrapped hydroxyapatite (CS-Hap) nanorods by coprecipitation method. 1, 3 and 5 parts of CS-Hap were introduced into TPU-PDMS (T70-P30) blend matrix and the nanocomposites were prepared by solution mixing technique. The incorporation of CS-Hap enhanced the physico-mechanical properties of the blend matrix, mainly 130% improvement in tensile strength at 5 parts of CS-Hap addition. The dispersion and distribution of the CS-Hap in TPU-PDMS matrix was confirmed using FESEM and HRTEM techniques. The storage modulus and $\tan \delta$ were improved with filler addition in all the nanocomposites. The XRD of nanocomposites reveals the intensity of crystalline planes correspond to CS-Hap was increased with filler addition and at 5 parts of CS-Hap, the crystallinity was enhanced by 40% as compared to the pristine TPU-PDMS blend. The CS-Hap promotes the thermal stability of nanocomposites due to the synergistic effect of physico-chemical interaction and superior crystallization behavior.

1. Introduction

Nowadays, hydroxyapatite is becoming the emerging material in the field of biomedical applications like tissue regeneration, bone implants, drug delivery, and self-healing, etc. [1]. The unique physico-mechanical and biological characteristics of hydroxyapatite especially in the nanoscale makes it suitable for mechanical upgradation of polymer composites for biomedical applications [2,3]. The chemical composition of hydroxyapatite ($\text{Ca}_{10}(\text{PO}_4)_2(\text{OH})_2$) similar to bone apatite and its unique biological properties such as cytocompatibility, bioactivity and hemocompatibility makes it suitable for bone related applications [4,5].

The most important parameter which differentiating the various types of consumption of hydroxyapatite by the living cells depends on the delivery medium or matrix composition and the size and shape of nanohydroxyapatite [6,7]. Generally, biocompatible, biodegradable, biostable or bioactive polymers and its blends were used for tissue engineering depending on their requirements. Addition of Hap in natural polymers like gelatin and collagen results in excellent substitutes for bone tissue engineering and exhibit enhanced biocompatibility. Owing to the higher rate of biodegradability and poor mechanical properties of these systems, synthetic biocompatible polymer matrices were pronounced over natural materials [4,8,9]. Matrices like polycaprolactone, poly (vinyl alcohol) and poly (vinylpyrrolidone) were employed in bone cartilage tissue engineering and the trend of using

synthetic biodegradable materials was also criticized due to their lower biostability and the system could not maintain the required mechanical properties after prolonged use [10–16].

The improved performance of nanocomposites of various types of nanorods and nanotubes were well studied in soft elastomer based matrices due to their unique ability to provide good dispersion [17–20]. The efficient choice of polymers and the modifications of the available matrices suitable for Hap can expand its application in the biomedical field. Polydimethylsiloxane (PDMS) elastomers reveal as the best biocompatible synthetic polymer due to its outstanding biocompatibility, biostability, higher temperature resistance and physiological inertness [21]. However, this material exhibits poor mechanical properties. This can be solved through blending process by introducing another polymer matrix. Exploration of other macromolecules with superior physico-mechanical properties leads to thermoplastic polyurethane (TPU) which possesses an established background in biomedical field especially in medical devices [18–22]. Moreover, *in-situ* synthesized TPU/Hap nanocomposites are widely used for bone and cartilage tissue engineering and the difficulty in using higher filler dosages limits its application in severe osteoporosis treatments [2,6,23,24].

The optimum dosage of Hap in polymer nanocomposites can easily enhance by the proper selection of filler characteristics. The physico-mechanical and biological properties of bioactive fillers can be controlled by tuning its shape, size and dosage [25–28]. In our previous studies, spherical nanohydroxyapatite was introduced in TPU-PDMS

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blend matrix and improvement in thermo-mechanical properties was observed due to the formation of a unique nucleated phase via proper dispersion [33]. Recent studies reveal that the rod shape possesses an intense effect on mechanical as well as biological properties compared to other shapes [30–32]. Furthermore, the high loading of bioactive agents always induce good osteo-conductivity in bone tissue engineering [33–41]. The hard segments in TPU prevent dispersion of nanoparticles at higher dosages. Hence, the higher loading of bioactive filler in TPU matrix is a challenging aspect in the preparation of bone grafts and which can overcome by incorporating soft PDMS phase [33].

The *in-situ* modifications of nanohydroxyapatite using macromolecules is an interesting method to improve its interaction with the polymer matrix and hence performance properties of the nanocomposites [42–44]. Modification of hydroxyapatite using biodegradable polymers such as polyethylene glycol, poly propylene glycol and chitosan is a novel trend and the modifier can act as a sacrificial delivery medium for Hap [19,45]. Among the various biodegradable modifiers, chitosan is a natural polymer with unique biocompatibility and antimicrobial properties [46–50].

The primary objective of the present investigation is to prepare nanocomposites of chitosan wrapped Hap (CS-Hap) and TPU-PDMS blend. This article also deals with the *in-situ* modification of nanohydroxyapatite using chitosan especially to improve the biological as well as physico-mechanical properties of the TPU-PDMS blend nanocomposites. Scrutiny of the available literature confirms that there is no report available based on the biostable matrix with optimum Hap dosage (> 4 phr) for bone and cartilage tissue engineering application. The present investigation reveals that the presence of PDMS can improve the optimum dosage of bioactive CS-Hap in the blend than the existing systems. Moreover, the incorporation of CS-Hap enhances the thermo-mechanical and crystalline characteristic of TPU-PDMS blends.

2. Experimental

2.1. Materials

An aromatic polyether-based TPU (TEXIN RxT85A) with specific gravity of 1.12 and a melt flow index of 4g/10 min at 190 °C/8.7 kg, provided by Bayer Material Science (Chennai, Tamilnadu, India) was used as the base matrix. PDMS (Siloprene) was supplied by Momentive Specialty Chemicals Inc. (India) and ethylene methyl acrylate (EMA copolymer (OPTEMA TC-120)) was purchased from M/s Exxon Chemicals Inc. Calcium nitrate ($\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$), diammonium hydrogen phosphate ($(\text{NH}_4)_2\text{HPO}_4$), and n-butanol were obtained from Sigma Aldrich (Bengaluru, India). Chitosan (molecular weight ~ 200,000, degree of deacetylation ~ 90%) was purchased from Acros Organics (Belgium). Tetrahydrofuran (THF) solvent was purchased from Merck (India).

2.2. Methods

2.2.1. Synthesis of Chitosan-wrapped Hap nanorods

Chitosan-wrapped Hap has been prepared as per the procedure reported in our previous paper with some modification [33]. The nanohydroxyapatite modification was carried out using a solution of 1.5 wt % chitosan in 1% (v/v) acetic acid solution. The nanohydroxyapatite was synthesized in the presence of chitosan acetic acid solution at a ratio of 10:1 wt% (Hap: CS). The pH of both the solutions of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and $(\text{NH}_4)_2\text{HPO}_4$, were maintained at 8 using ammonia solution. The solutions were mixed at a stoichiometric ratio of Ca to P of 1.67, subsequently stirred for 2 h at room temperature. The individual chitosan chains present in the nanoscale act as the nucleation sites for the synthesis and the long chain (high molecular weight) of chitosan promotes the crystal growth of Hap resulting rod shaped nanohydroxyapatite. In the case of chitosan wrapped nanohydroxyapatite, the superior antibacterial activity of chitosan can promote the performance

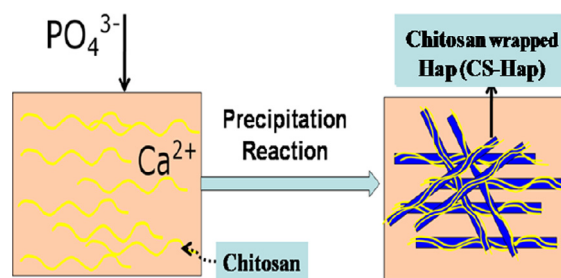
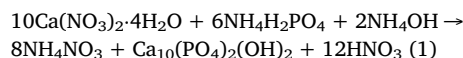


Fig. 1. Schematic diagram of preparation of Chitosan wrapped Hap.

of nanocomposites during biological application. The resultant precipitate was filtered and dried at 80 °C overnight. The chemical reaction (1) and schematic diagram (Fig. 1) represent the precipitation method used for chitosan wrapped Hap nanorod formation.



2.2.2. Preparation of nanocomposites

The compatibilized TPU–PDMS blends using EMA as compatibilizer were prepared by solution casting technique according to the procedure explained previously [51]. The uncompatibilized blends were also prepared using the same procedure in the absence of EMA. 1, 3, and 5 wt% chitosan wrapped nanohydroxyapatite (CS-Hap) dispersion in THF were prepared by sonication. The mixture was then added to the compatibilized blend solutions and mixed for 4 h at room temperature using magnetic stirrer. The mixture was then cast into a petridish and dried at 50 °C for 36 h followed by subsequent drying for 48 h under vacuum at the same temperature. The nanocomposites have been coded as Tx-PyHz, in which ‘T’, ‘P’ and ‘H’ denotes TPU, PDMS and CS-Hap nanorods and ‘x’, ‘y’ and ‘z’ are the weight proportions of TPU, PDMS and Hap nanorods respectively. For the preliminary selection of blend matrix, uncompatibilized blend nanocomposites were also prepared and coded as UTx-PyHz.

3. Characterization and testing

To confirm the successful formation of Hap nanorods and for analyzing the chemical interaction taking place in the nanocomposites, fourier transform infrared (FTIR) spectroscopy studies were carried out on a Bruker Equinox 55 spectrophotometer, at a resolution of 2 cm^{-1} , in the range of $4000\text{--}400\text{ cm}^{-1}$, and 64 scans were averaged out for each spectrum. The changes in crystallinity and crystal structure of CS-Hap and blend nanocomposites were studied using Philips X-ray diffractometer (PW1710 X-ray diffractometer) using monochromatic $\text{CuK}\alpha$ radiation (wavelength 1.5418 \AA) in the angular range of $10\text{--}80^\circ$ (2 θ) at an operating voltage of 40 kV with a beam current of 20 mA. The morphology of Hap and the dispersion of Hap in the blend matrix were analyzed with the help of high-resolution transmission electron microscopy (HRTEM). The experiment was carried out in JEM 2100, JEOL high-resolution transmission electron microscope with lanthanum hexaboride target, operating at 200 keV with an average beam current of $116\text{ }\mu\text{A}$. The surface morphology and elemental mapping of Hap was characterized using field emission scanning electron 348 microscope (FESEM), Germany (MERLIN).

The tensile properties of the blends and nanocomposites have been determined using dumbbell-shaped specimens punched out from the sheets using a hollow dumbbell cutting die (ASTM die C) and the tensile properties were measured as per ASTM D 412 using a Hounsfield H10KS universal testing machine with a cross-head speed of 500 mm min^{-1} . The average values of five specimens were reported. Dynamic mechanical properties such as storage modulus and tan delta with respect to temperature of blend and nanocomposites were

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