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Morphology, thermal and mechanical properties of poly (ε-caprolactone) biocomposites reinforced with nano-hydroxyapatite decorated graphene

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GRAPHICAL ABSTRACT

Hydroxyapatite-graphene hybrids were synthesized by a hydrothermal method and incorporated into poly (ε-caprolactone) by a solvent blending method. The mechanical properties and biocompatibility of PCL nanocomposites were improved obviously.
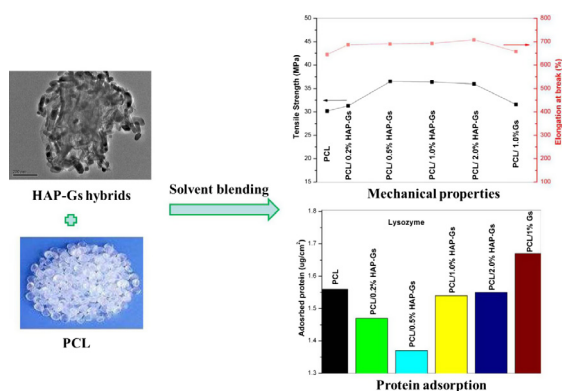
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ABSTRACT

In this work, hydroxyapatite (HAP) nanorods decorated on graphene nanosheets (HAP-Gs) was synthesized by a hydrothermal method. The structure, elemental composition and morphology of the HAP-Gs hybrids were characterized by X-ray diffraction, Fourier transform infrared and Transmission electron microscopy. Subsequently, the hybrids were incorporated into poly (ε-caprolactone) (PCL) via a solution blending method. Optical images and scanning electron microscopy observation revealed not only a well dispersion of HAP-Gs hybrids but also a strong interfacial interaction between hybrids and PCL matrix. The influence of HAP-Gs hybrids on the crystallization behavior, crystal structure, thermal stability, mechanical properties and biocompatibility of the PCL nanocomposites was investigated in detail. The results showed that the crystallization temperature of PCL was enhanced obviously, but the crystal structure was not affected by the incorporation of HAP-Gs hybrids. The mechanical properties of PCL bionanocomposites were improved obviously.

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1. Introduction

In the past few decades, the development of biodegradable polymers has attracted extensive attention owing to the environmental problems induced by the accumulation of plastic waste. As one kind of biodegradable and biocompatible aliphatic polyesters, PCL has provided a number of potential applications from agricultural usage to engineering and biomedical devices [1]. However, the further practical applications for PCL are limited by some drawbacks such as slow crystallization rate and poor mechanical properties. To overcome these difficulties, one promising alternative is to prepare nanocomposites by the combination of various types of fillers. It has been reported the incorporation of nanofillers, such as carbon nanotubes, layered silicate, polyhedral oligomeric silsesquioxanes and graphite oxide can greatly improved the physical properties of PCL with low loading [2–5]. The presence of well-dispersed nanoparticles can not only act as the anisotropic reinforcements, but also as the nucleating agents, both contributing to the improvement of mechanical and thermal properties of PCL. Moreover, filled with nanostructured particles is expected to produce new PCL based biodegradable and biocompatible composites with even unexpected properties [6].

As an emerging 2D material, graphene and its derivatives have attracted considerable attention in numerous fields due to its high surface area and chemical stability, unique electronic and outstanding mechanical properties [7–9]. The addition of graphene with very low loadings into a polymeric matrix can significantly improve the properties of polymer matrix, such as mechanical, thermal, electrical, flame retardant and gas barrier properties [10–13]. Therefore, more attention has been drawn to graphene as a potential reinforcement material in the polymer nanocomposite [14]. It has been reported that incorporation of graphene into PCL can improve the crystallization and mechanical properties [15–17]. However, it is worth noting that the homogeneous dispersion and reasonable interfacial interaction between the graphene nanosheets and polymer matrix play vital roles in the final properties of the polymer nanocomposites. But actually, polymer nanocomposites with well dispersed graphene nanosheets are hard to achieve because pristine graphene has a pronounced tendency to agglomerate and even restack in polymer matrices due to the strong van der Waals force and π-π interactions which limits its dispersion in polymer matrices [18]. Meanwhile, the formation of strong interface between graphene nanosheets and the polymer matrix is still an urgent issue that needs to be solved. Therefore, to improve and stabilize the dispersion state of graphene nanosheets in host polymers constitutes the greatest challenge in graphene based polymer nanocomposites.

HAP is well known for its unique properties such as excellent bioactivity, biocompatibility, osteoinductivity and osteoconductivity, and has been widely used as clinically available bone substitutes and implantation material [19]. However, the intrinsic brittleness, low mechanical strength and fracture toughness of pure HAP limits its further application under load-bearing conditions [20]. Therefore, the main focus of HAP research has been to improve its mechanical performance by combining it with various reinforcements such as polymers, metals and carbon nanomaterials [21–23]. However, an ideal reinforcement material would impart mechanical integrity to the composite without diminishing its bioactivity. Among these composites, PCL/ HAP composites are a strong candidate for applications as hard tissue regeneratives, in which the bioactive HAP component provides a favorable environment for cells to attach, proliferate, and differentiate, while the biodegradable PCL polymer matrix provides the required flexibility and moldability [24]. Therefore, if HAP is used as the filler for PCL, the strength of PCL might be improved to meet the clinical requirements. In return, PCL might avoid the brittleness problem of HAP.

However, HAP has a strong tendency to agglomerate in PCL matrix even at low loadings and the interfacial adhesion between HAP and the polymer matrix is poor, which will adversely affects the mechanical properties of the nanocomposites. Accordingly, it is very necessary to modify the surfaces of HAP nanoparticles as the fillers, weak agglomeration and improve the interface structure between the filler and matrix of the composite.

Recently, polymer nanocomposites based on hybrid nanofillers which comprise two or more heterogeneous nano elementary units with different properties, have been demonstrated to be a more attractive strategy with effective enhancement effects on mechanical, thermal stability, flame retardancy and thermal conductivity properties of the composites [25–31]. Moreover, it can be expected that the agglomeration of the nanoparticles and weak interfacial interaction problems in polymer nanocomposites could be solved simultaneously by using such functional hybrid nanofillers [32]. Therefore, the combination of graphene nanosheets with secondary nanomaterials integrates unique characters and functions of the two components which are not found in either of their individual components [33]. Inspired by this, it may be an efficient method to improve the crystallization, mechanical and biocompatibility properties of the PCL nanocomposites by the combining graphene and commonly used bone substitutes and implantation material (HAP). As an exfoliated two-dimensional material, graphene can be used as a perfect supporter to ameliorate the dispersion of HAP nanoparticles in the polymer matrix. In addition, the restacking of graphene nanosheets can be effectively prevented by the tightly decorated nanoparticles, which is beneficial for promoting the dispersibility of graphene in polymer matrices [28]. Therefore, integrating graphene nanosheets and HAP nanoparticles will result in the development of new composites with well dispersion, good mechanical property and excellent biocompatibility. Hydroxyapatite/graphene nanohybrids have been explored since HAP is the inorganic component of bone and offers a favorable environment for bone regeneration [34]. Nevertheless, to the best of our knowledge, there are no reports of an evaluation of their reinforcement effect in polymer nanocomposites published to date. Therefore, the target of the present study was to investigate the influence of HAP-graphene hybrids on the thermal behavior, mechanical properties and biocompatibility of PCL nanocomposites.

In present study, a hybrid graphene supported HAP (HAP-Gs) is synthesized by a facile hydrothermal method. The HAP-Gs nanohybrids are characterized by X-ray diffraction (XRD), Fourier transform infrared (FTIR) and Transmission electron microscopy (TEM). Then different weight percentages of HAP-Gs hybrids are incorporated, to obtain PCL composites via a solvent blending method and studied the influence of HAP-Gs on the morphology, thermal behavior, mechanical properties and biocompatibility of PCL nanocomposites. The research reported herein is expected to be of great interest for a better understanding of the relationship between structure and properties of polymer nanocomposites.

2. Experimental

2.1. Materials

Natural flake graphite (EG) with an average particle size of 325 mesh was supplied by Qingdao Tianhe Graphite Co., Ltd. (China). Potassium permanganate ($KMnO_4$), sodiumnitrate ($NaNO_3$), sulfuric acid (H_2SO_4, 98%), hydrogenperoxide (H_2O_2, 30% aq), hydrochloric acid (HCl, 36% aq), calcium nitrate tetrahydrate ($Ca(NO_3)_2 \cdot 4H_2O$), di-ammonium hydrogen phosphate (($NH_4)_2HPO_4$) were purchased from Sinopharm Chemical Reagent Co. All of the chemicals were of analytical grade and used as received without