



# In situ construction of pompon-like hydroxyapatite hybrid via interfacial self-assembly in polypropylene matrix



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## ABSTRACT

This work reports on a one-pot in situ epitaxial growth strategy to prepare a pompon-like hydroxyapatite (HA) hybrid that demonstrates a good interfacial interaction by mechanical interlocking with polypropylene (PP) melts, resulting in improved mechanical performance. The formation process involves the preferred adsorption of dissolved WBG molecules (a rare earth compound) at the polydopamine-modified HA particle–polymer melt interface, followed by in situ epitaxial growth of the thorn-like branches. The branch size and density depend on the nucleation and diffusion of the WBG molecules, and can be adjusted by the heating temperature, cooling rate, WBG concentration, etc. The concept that the mechanical interlocking of pompon-like WBG–HA hybridized with a PP matrix can improve the interfacial interaction was successfully realized, as indicated by the mechanical performance of PP/HA composites with pompon-like structures outperforming the conventional PP/HA composites up to an increase of 45% in impact strength.

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## 1. Introduction

The incorporation of inorganic fillers into a polymer matrix can endow the latter with new functionalities and higher performance, which has attracted great interest in the scientific and industrial communities over the past few decades [1–3]. Hydroxyapatite (HA), a calcium phosphate, has a similar structure to the mineral component of human bone. Many investigations show that, when HA particles are introduced into a polymer matrix, the obtained composites can possess promising biocompatibility and bioactivity [4,5]. Ignjatovic implanted a polylactide/HA composite into mice and reported on the good cell adhesion on the surface [6]. The pioneering work of Wang indicated that polymer/HA composites had potential applications for bone fixation and repair [7]. Kouhi successfully adopted an electrospinning method to fabricate poly(3-hydroxybutyrate-co-3-hydroxyvalerate) containing HA/bredigite (50/50) nanofibers with a high ability for apatite formation, which is potentially suitable as desired scaffolds for bone regeneration applications [8]. Tang also confirmed that the presence of HA particles can promote bone growth [9]. Among

synthesized polymers, polypropylene (PP) exhibits a biologically inert, good performance in fatigue and less mechanical strength reduction at elevated temperatures, which is very important for applications in the human body, so that PP/HA composites have been considered as good materials for bone substitution [10,11]. However, the poor interaction between PP and HA reduces the mechanical performance of the resulting composite material, especially the impact strength, thereby limiting the load-bearing applications of the composite [12].

Common routines for improving interfacial interactions between the two immiscible components can be divided into two main categories: the surface modification of inorganic particles or the introduction of a compatibilizer with bifunctional groups. In this way, interfacial tension is reduced and the compatibilization is enhanced. For example, Albooyeh introduced maleic anhydride-grafted polypropylene and preferentially located it at the interfacial region to bridge the PP matrix and HA and to promote interfacial interaction [13]. Younesi grafted a silane coupling agent onto the surface of HA and prepared PP/HA composites, resulting in excellent interfacial properties [14].

Besides decreasing the interfacial tension, the design and optimization of inorganic fillers mechanically interlocking with the polymer matrix is another approach to improve the interfacial

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interaction [15,16]. Accordingly, many inorganic fillers with special topological structures have been developed, such as bamboo-like silica fibers [17], tetrapodal-shaped ZnO microparticles [18], and shish-kebab carbon nanotubes (CNTs) [19]. Recently, inspired by tree roots which are pulled out with great difficulty due to the mechanical interlocking of the root branch with the surrounding soil, some root-like fibers have been constructed [20–22]. Tamrakar controlled the nucleation and growth of CNTs on the surface of glass fibers (GFs) via electrophoretic deposition to prepare the branched fiber and improve the interfacial strength between the fiber and epoxy resin [23]. Wang grafted CNTs onto carbon fibers by a chemical grafting method to promote the interfacial load transfer from the polymer matrix to the reinforcing fiber [24]. Our group also prepared root-like GFs by controlling the interfacial diffusion and self-assembly of organic molecules in PP melts, solving the interfacial problems of polymer composites [25]. The previous studies focused on the design and control of the topological structure of one-dimensional fibers; however, to our knowledge, the preparation of pompon-like particles with mechanical interlocking has not been reported due to the increased difficulty of attaching the thorn-like fibers onto the small surface. Obviously, this is a promising and challenging research field, which induces us to further extend the idea of interfacial molecular self-assembly in the reinforcing fiber to zero-dimensional particles and tailor the topological structures for an enhanced interfacial interaction.

In this study, a kind of rare earth compound (WBG) that can dissolve in PP melts and self-assemble upon cooling [26,27] was chosen to prepare pompon-like HA. To increase the diffusion and deposition of WBG molecules on the surface of the HA, polydopamine layers, which can form hydrogen bonding with WBG [25], were first coated onto the surface of the HA at room temperature via dopamine oxidation. Then, the nucleation and growth of the self-assembling molecules were investigated at the surface of the HA in the PP melt, and its dependence on the temperature, cooling rate, and concentration were also systematically studied. The in situ formation mechanism of HA particles with some thorns composed of self-assembling molecules in PP melts was proposed. Finally, to prove that the mechanical interlocking improves the interfacial interaction, the mechanical strengths of the PP/HA composites with thorn-like structures and conventional PP/HA composites were also studied for comparison.

## 2. Experiment

### 2.1. Materials

A commercially available isotactic PP resin (trade name: T30S) was provided by the Dushanzi Petroleum Corporation (Xinjiang, China). The rare-earth compound (trade name: WBG-II), a kind of dimetal complex of lanthanum and calcium with dicarboxylic acid and amide-type ligands, was purchased from Guangdong Weilina, Inc. (Guangdong, China). It has a general formula of  $\text{Ca}_x\text{La}_{1-x}(-\text{LIG1})_m(\text{LIG2})_n$ , where  $x$  and  $1-x$  are the proportions of  $\text{Ca}^{2+}$  and  $\text{La}^{3+}$  ions in the complex, respectively, and LIG1 and LIG2 correspond to dicarboxylic acid and amide-type ligand with coordination numbers of  $m$  and  $n$ , respectively [28]. HA powders were purchased from Nanjing Duly Biotech Co., Ltd. (Nanjing, China). Dopamine was provided by the Aoduofuni Biological Technology Co. (Nanjing, China). Tris(hydroxymethyl) aminomethane (Tris) was provided by the Chengdu Kelong Chemical Reagent Factory (Chengdu, China).

### 2.2. Sample preparation

PP/WBG blends with different concentrations of WBG (0.1, 0.3,

0.5, and 1 wt%) were melt-compounded in a co-rotating twin screw extruder at 180 °C and then were used to investigate the dissolution and self-assembly of WBG in the polymer melts.

In order to promote WBG molecules diffusing onto the HA, modified HA with a few-nanometer thickness of the coated polydopamine layer was prepared [25,29]. HA powders and 200 mg of dopamine were added to 50 mL of diluted tris solution. The mixture was stirred rapidly for 6 h at room temperature. The modified HA samples were washed with acetone and dried, which is hereafter named as P-HA.

PP samples containing 0.3% WBG and P-HA were extruded in a co-rotating twin screw extruder and then were subsequently injection-molded for mechanical measurement. The processing temperature was 240 °C. In this study, the concentration of P-HA in the PP matrix was 10 wt%. For comparison purposes, PP/HA composites were also prepared under the same processing conditions.

### 2.3. Characterization

#### 2.3.1. Polarized light microscopy (PLM)

First, the dissolution and self-assembly processes of WBG in PP melts were observed by PLM (Leica DM2500P) connected to a hot stage (Linkam THMS600, Linkam Scientific Instruments, Ltd., UK). Next, the modified HA powders were imbedded into two pre-prepared WBG-containing PP films and then were placed in the sample holder. The samples were heated to different temperatures at a rate of 50 °C/min, held at the temperature for 5 min, and then cooled down at different rates. The self-assembly process of the WBG molecules on the surface of the P-HA samples was recorded by a PixelINK camera (PL-A662).

#### 2.3.2. Surface energy measurements

HA, PP, and WBG powders were pressed into thin sheets under a 12 MPa pressure at room temperature, and their surface energies were measured using a DSA30 drop shape analyzer (Hamburg, Germany).

#### 2.3.3. Mechanical property test

The impact strength was measured on an izod machine PIT501J (Shenzhen Wance Testing Machine Co., Ltd.). The depth of the V-notch was 2 mm. The tested values of five samples were averaged.

#### 2.3.4. Scanning electron microscope (SEM) observation

After the samples were impact-tested, the fracture surfaces were gold-sputtered and investigated by an FEI Inspect F-SEM instrument with an acceleration voltage of 20 kV.

## 3. Results and discussion

The dissolution of the WBG molecules in the PP melt is a prerequisite for controlling the self-assembly of the former in the interfacial region between the HA particles and the polymer matrix. PLM was first adopted to investigate the dissolving behaviors of WBG as a function of temperature and concentration. Typical photographs of PP with 0.5% WBG during the heating and cooling process are shown in Fig. 1a–c. Dot-like WBG distributed in PP melts at the low temperature of 180 °C was observed; with increasing temperature, the WBG particles disappeared and homogenous melts formed. During the cooling process, WBG reappeared in the form of dendritic crystals. The dendritic structure can be an indicator of WBG being completely dissolved in the PP melts. Otherwise, only dot-like or fibrous WBG can be generated as a result of the non- or partial dissolution [26]. Accordingly, the completely dissolving temperatures of WBG in the PP melts are summarized in Fig. 1d. A positive correlation between the

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