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Polyoxymethylene-copolymer based composites with PEG-grafted hydroxyapatite with improved thermal stability

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ABSTRACT

In this work hydroxyapatite (HAp) was chemically modified by poly(ethylene glycol) (PEG) in a grafting reaction and then incorporated into polyoxymethylene (POM) matrix using melt processing methods. The obtained POM/HAp-*g*-PEG composites for biomedical applications were investigated using FTIR, DSC, TOPEM DSC, WAXD and TG. Mechanical properties and formaldehyde release during incubation were studied, too. It was found that introduction of HAp-*g*-PEG to POM matrix has a little influence on the melting temperature as well as on degree of crystallinity. The highest degree of crystallinity and the lowest supercooling were found for POM/0.5% HAp-*g*-PEG system which suggest that HAp-*g*-PEG can act as a nucleating agent for POM crystallization process. Importantly, in the contrast to unmodified HAp, HAp grafted with PEG significantly increases the POM thermal stability—from 296 °C for POM to 326 °C for POM modified with 10% of HAp-*g*-PEG. Much smaller formaldehyde release has been recorded for composites with high HAp-*g*-PEG in comparison to POM containing unmodified HAp, lower even that for pristine POM, which is of crucial importance for biomedical applications. HAp-*g*-PEG hinders POM thermal decomposition during processing and enables to introduce high amounts of HAp without losing composite properties.

1. Introduction

Polyoxymethylene (POM) is a well-known semicrystalline thermoplastic polymer widely used in many different applications due to its excellent properties [1]. Due to its high chemical and mechanical resistance it is widely used since several decades in biomedical field in joint replacement components and other long-term bone implants [2].

POM can be easily processed by extrusion, injection moulding, drilling, tapping, etc. [3] and is characterized by good impact strength, low friction, reasonably wear-resistance, dimensional stability, and chemical resistance to solvents. Its melting point is in the range of 160–180 °C, well above usual steam autoclave temperatures during sterilization [4]. POM has negligible porosity, low moisture absorption (0.9% at saturation), and is deemed safe for food contact use [5].

In our previous paper we described POM nanocomposites with pristine hydroxyapatite (HAp) for biomedical applications [6]. However, the main problem with POM/HAp nanocomposites was significantly lower thermal stability of POM matrix after incorporation of HAp nanoparticles [7]. Generally, POM is a heat sensitive polymer due to $-CH_2-O$ bond and easily undergoes depolymerisation to formaldehyde which additionally catalyses the depolymerisation process. Additionally, POM undergo degradation in the presence of acids and bases [8]. Hydroxyapatite $Ca_{10}(PO_4)_6(OH)_2$ is the main component of animal and human bones and teeth and is broadly used in biomaterials for bone tissue regeneration, dental materials, fertilizers, and food supplements (as a source of calcium) [9]. On the other hand, HAp can be also used as a catalyst in organic chemistry since it has the unusual property of containing both acid and basic sites in a single crystal lattice [9–11]. Stoichiometric HAp with molar ratio of Ca/P 1.67 possesses mainly basic sites, while the nonstoichiometric with molar ratio of Ca/P from 1.50 to 1.65 exhibits mainly acid properties [12]. It has been shown that nonstoichiometric HAp can act as a solid acid suitable for the dehydration of ethanol to ethylene, while stoichiometric hydroxyapatite catalyses ethanol dehydrogenation to acetaldehyde [13]. Basic $OH-$ groups linked to Ca atoms were found to be the most likely basic active sites involved in catalytic reactions [14]. Based on our previous findings we postulated that POM degra-

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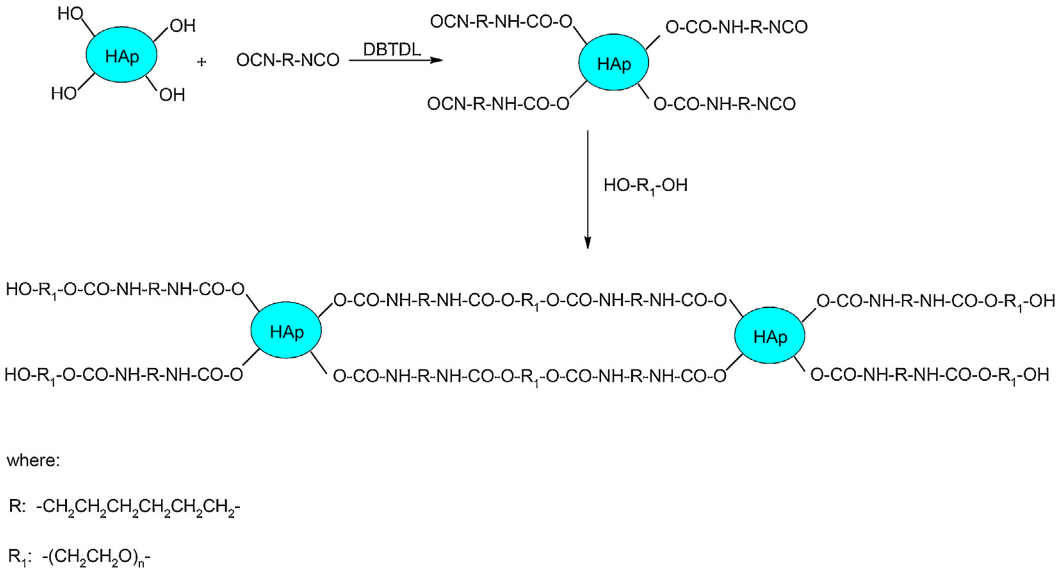

Fig. 1. PEG grafting on HAp surface using 1,6-hexamethylene diisocyanate as a coupling agent.

dation during processing in the presence of HAp nanoparticles can be catalysed on both acid and basic sites [7]. However, to check this hypothesis we decided to substitute —OH groups in HAp and then to introduce modified HAp into POM matrix. Different strategies of HAp modification by chemical grafting are available, e.g. Liu et al. [15] performed the reaction of isocyanate groups with the hydroxyl groups on the surface of HAp followed by radical polymerization in methyl methacrylate, hydroxyethyl methacrylate or butyl methacrylate. In the next work, the same group of authors prepared composites of poly(ethylene glycol-*co*-butylene terephthalate) and HAp with chemically linked by hexamethylene diisocyanate used as a coupling agent [16]. Hong et al. [17] developed method of grafting of L-lactide (LLA) through ring-opening polymerization of lactic acid onto the surface of HAp nanoparticles. Surface modification of HAp by the ring opening polymerization of γ-benzyl-L-glutamate *N*-carboxyanhydride (BLG-NCA) was also proposed to prepare poly(γ-benzyl-L-glutamate) (PBLG)-grafted HAp nanoparticles [18].

In our novel approach we grafted poly(ethylene glycol) on HAp nanoparticles surface using an aliphatic 1,6-hexamethylene diisocyanate as a coupling agent. This kind of diisocyanate is widely used in the synthesis of polyurethanes for biomedical applications as it does not contain aromatic structures that may impose toxic effects. Next, we introduced HAp-*g*-PEG to POM copolymer using melt processing methods and investigated the effect of HAp modification on selected POM/HAp-g-PEG nanocomposites properties.

2. Experimental

2.1. Materials

A commercial grade of POM copolymer (Ultraform®) with melt flow rate (MFR 190/2.16, ISO 1133) 2.6 g/10 min, was supplied by BASF (Germany). Molecular weight was determined by GPC according to ASTM D5296-05 performed at 40 °C on a VE2001 Viscotek GPC System with a RI—VE 3580 (Viscotek) detector, using a PL HFIPgel, 605 E901506 and HFIP 603 E910606 column. Average molecular weights (based on polystyrene standard) were determined as: $M_n = 8\,269$ and $M_w = 78\,565$, $M_w/M_n = 8.96$.

Stoichiometric hydroxyapatite $Ca_{10}(PO_4)_6(OH)_2$ nanopowder with a nanoparticle size below 100 nm (99% of particles) was product of nGimat Co. (Atlanta, USA). 1,6-Hexamethylene diisocyanate (HDI), poly(ethylene glycol) (PEG) with average molar mass 2000 and dibutyltin dilaurate (DBTDL) were supplied by Sigma Aldrich. Anhydrous *N*,*N*-dimethyleformamide (DMF) and methanol were products of Avantor (Poland). PEG was dried under vacuum at the temperature of 110 °C for 2 h before synthesis, while the other reagents were used as supplied.

2.2. Grafting process

The grafting of PEG chains on HAp surface was performed in a two-step procedure according to Fig. 1.

After drying at 60 °C for 24 h, 9 g of HAp nanopowder were charged to round-bottom three-necked flask together with 90 ml of dry DMF and dispersed by sonication in ultrasonic bath for 3 h at the temperature of 30 °C under nitrogen, Next, 9 μl of DBTDL catalyst was introduced to HAp dispersion in DMF and mixed using magnetic stirrer. Then, solution of 3 ml HDI in 6 ml DMF was dropped to HAp dispersion within 20 min. The dispersion was stirred with a magnetic stirrer under nitrogen. Next, the temperature was increased to 78 °C and kept for 2.5 h. In the second step, the mixture was cooled down to 40 °C and 18 g of PEG were dissolved in 18 ml DMF and dropped to the suspension for 30 min. The temperature was increased to 65 °C and the mixture was stirred for 1.5 h under nitrogen. At the end, the powder was separated in centrifugal separator at the rotary speed 4000 operating for 20 min, washed three times with ethanol and after each washing again separated in centrifugal separator. After that, the HAp-grafted (HAp-*g*-PEG) powder was dried at 40 °C for 24 h [19]. TG analysis of the obtained powder confirmed that the obtained material contains 60% of HAp and 40% of polymer and is thermally stable in the temperature of processing, i.e. 210–220 °C. FTIR analysis results are described in Section 3.

2.3. Processing of POM/HAp-g-PEG nanocomposites

POM and POM/HAp-g-PEG nanocomposites were prepared by melt processing methods. In the first stage, POM and HAp-g-PEG powder were dried for 2 h in 80 °C, and then the POM and HAp-g-PEG were mechanically mixed (0, 0.5, 1.0, 2.5, 5 and 10.0% w/w of HAp-g-PEG (calculated in relation to pure HAp) and extruded in a twin-screw extruder (HAAKE™ MiniLab Micro Compounder) at a screw speed of 50 rpm at the temperature 210 °C. Compositions