PREPARATION AND CHARACTERIZATION OF POLYOXYMETHYLENE/ FUNCTIONALIZED HYDROXY-APATITE NANOCOMPOSITES

KLAUDIA KRÓL-MORKISZ*, KINGA PIELICHOWSKA

DEPARTMENT OF BIOMATERIALS AND COMPOSITES,
FACULTY OF MATERIALS SCIENCE AND CERAMICS,
AGH UNIVERSITY OF SCIENCE AND TECHNOLOGY, POLAND
*E-MAIL: KLAUDIAK@AGH.EDU.PL

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Introduction

Polyoxymethylene (POM) is one of an engineering thermoplastic polymers that is characterized by excellent mechanical properties, low friction coefficient and high chemical resistance to most solvents (1). POM is commonly used to replace metal and glass parts in automotive industry, industrial and medical equipment, consumer goods and parts of domestic appliances (2). It is usually manufactured by the copolymerization of trioxane with cyclic ethers and processed by extrusion and injection moulding methods (3). However, the biggest disadvantage of POM is its poor thermal stability. In elevated temperature it readily undergoes thermal decomposition. Furthermore, POM tends to follow an "unzipping" process with emission of formaldehyde molecules (4). Formaldehyde presence limits the range of application of POM in medicine in particular. To improved the thermal endurance of POM, a functionalized hydroxyapatite as a new kind of thermal stabilizer was applied.

Materials and Methods

POM copolymer (Ultraform®, BASF) was used as a composite matrix. Hydroxyapatite (HA, nGimat Co) in the shape of nanopowder was functionalized with poly(ethylene glycol) (PEG 2000, Sigma Aldrich). 1,6-hexamethylene diisocyanate (HDI) as a coupling agent, and dibutyltin dilaurate (DBTDL) as a catalyst were used (both form Sigma Aldrich). Anhydrous N,N-dimethylformamide (DMF, Avantor) was used as a solvent of the functionalization reaction. HA/HDI/PEG molar ratio was 1:2:1.

Grafting process of HA-g-PEG

HA/DMF (9 g/90 ml) was dispersed using sonication. Then, 9 µl of DBTDL catalyst was introduced to HA dispersion. Next, HDI/DMF (6 g/12 ml) solution was dropped to HA dispersion. The mixture was heated up to 80°C using magnetic stirrer and it was kept in this temperature for 1.5 h. After cooling down, PEG/DMF (36 g/36 ml) was dropped to the suspension and the system was heated up to 65°C and stirred in this temperature for 1.5 h. Finally, the powder was separated in centrifugal separator and washed three times with ethanol. After that, the HA-*g*-PEG powder was dried at 40°C for 24 h.

Processing of POM/HA-g-PEG composites

In the first stage, POM and HA-*g*-PEG powder were mechanically mixed (0, 0.5, 1.0, 2.5, 5.0 and 10.0% w/w of HA-*g*-PEG) (calculated in relation to pure HA). Then, composites were compounded in a twin-screw extruder (50 rpm, 210°C) and shaped by injection moulding method (210°C, 10 Bar). The composites were characterized using DSC and TG methods. FTIR and XRD analyses were also performed. The mechanical strength was measured using tensile test. SEM was applied to investigate the surface morphology of fractured specimens. The formaldehyde release during incubation was assessed using Schiff's reagent.

Results and Discussion

FTIR spectroscopy proved the urethane bond formation presence between –OH from HA and –NCO groups. SEM observations (FIG. 1) showed high cohesion between POM matrix (2) and the HA-*g*-PEG additive (1). DSC analysis confirmed that HA-*g*-PEG additive does not affect the crystallinity of POM relevantly, but supercooling of POM composites was lower, even by 4°C (for 10% HA-*g*-PEG content), compared with pristine POM. Most importantly, as can be seen in FIG. 2, the thermal stability of modified POM was increased up to 16.5°C (for 5% HA-g-PEG). Using the Schiff's test, the small amount of formaldehyde, comparable with distilled water, was detected in all samples. Mechanical tests exhibited some decrease in tensile strength from 70 MPa to 60 MPa for 10% of HA-*g*-PEG contents.

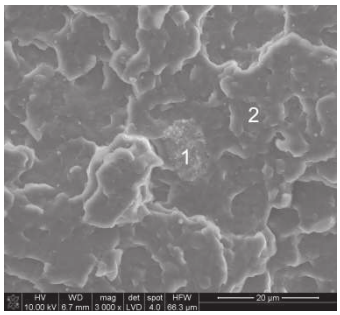

FIG. 1. SEM microphotographs for POM/ 1% HA-g-PEG nanocomposites

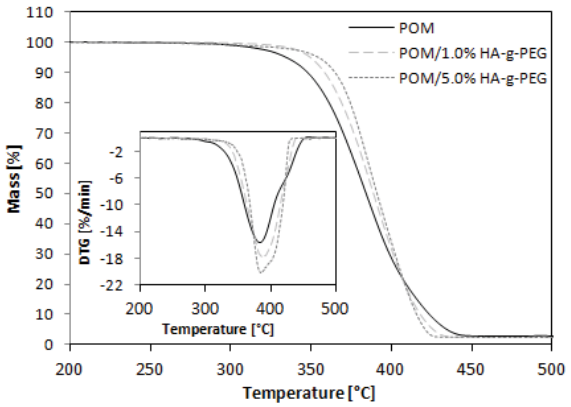

FIG. 2. TG/DTG curves of POM/HA-*g*-PEG composites (0%, 1%, 5%).

Conclusions

In this study, polyoxymethylene/functionalized HA composites with improved thermal stability were obtained. High mechanical properties and good stability of modified POM make this polymer material a great candidate as a material that can be used in many orthopedic applications.

Acknowledgments

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