

POLYOXYMETHYLENE HOMO- AND COPOLYMER COMPOSITES STABILIZED WITH PEG-GRAFTED HYDROXYAPATITE

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Introduction

Polyoxymethylene (POM) is a highly crystalline thermoplastic polymer. POM is mostly known for its high mechanical strength, stiffness, low friction coefficient, good chemical resistance and low water absorption [1]. There are two different kinds of polyoxymethylene, depending on production method: POM homopolymer (POM_H) and POM copolymer (POM_C). POM homopolymer crystallizes very easy and has excellent mechanical properties [2]. The main disadvantage of POM_H is its very high thermal sensitivity – autocatalytic decomposition of polymer chains occurs at elevated temperatures [3]. POM copolymer (POM_C) is produced by cationic polymerization of trioxane with the presence of comonomers, such as ethylene oxide or dioxane. It has slightly worse mechanical properties than POM_H, but its thermal resistance is higher [4].

POM has been used in heart valves replacements and orthopedic implants such as hip and knee prosthesis for years. Furthermore, POM is used in dentistry as a substitute of metals and acrylic resins in numerous prosthesis applications [5]. Now, it is proposed as a material for bone long-term implants.

Initially, POM/hydroxyapatite (HAp) nanocomposites were obtained [6]. Unfortunately, thermal stability of these composites decreased significantly even by 30°C. In our previous study, we modified HAp with poly(ethylene glycol) (PEG) 2000 (HAp-g-PEG 2000) and introduced into the POM copolymer matrix in order to improve thermal stability of POM [7]. In this work the influence of HAp-g-PEG 600 on the thermal stability of POM_H and POM_C is investigated.

Materials and Methods

Ultraform® POM copolymer (BASF, Germany) and Delrin® POM homopolymer (DuPont™, USA) were used in this work. Stoichiometric HAp nanopowder was product of nGimat Co (Atlanta, USA). 1,6-hexamethylene diisocyanate (HDI), dibutyltin dilaurate (DBTDL) and poly(ethylene glycol) (PEG) with average molar mass 600 were supplied by Sigma Aldrich. Anhydrous DMF and ethanol were products of Avantor (Poland).

Grafting process

Firstly, the HAp-g-PEG 600 filler was prepared: 9 g of HAp was dispersed in 90 ml of dry DMF. Next, 9 µl of DBTDL catalyst was introduced to HAp dispersion. Then, the solution of 6 ml HDI in 12 ml DMF was dropped to HAp. After that, the temperature was increased to 78°C and kept for 2.5h. In the second step, the mixture was cooled down to 40°C, 10.8 g PEG 600 was dissolved in DMF (1:1 w/v) and dropped to the suspension. 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 and washed three times with ethanol. After that, the HAp-g-PEG 600 powder was dried at 40°C for 24 h.

Processing

Two types of POM (POM_C and POM_H) was modified in this study. POM and POM/HAp-g-PEG 600 composites were prepared by melt processing methods. In the first stage, POM and HAp-g-PEG 600 powder were mechanically mixed (0, 0.5, 1.0, 2.5, 5.0 and 10.0% w/w of HAp-g-PEG 600) (calculated in relation to pure HAp) and extruded in a twin-screw extruder (50 rpm, 210°C). Compositions were then shaped by injection moulding method.

Thermal analysis techniques, such as DSC and TG, were used to characterise the obtained composites. FTIR spectroscopy and SEM microscopy were performed as well. Mechanical tests, in the tensile mode, were also conducted. The formaldehyde release during incubation was analysed using Schiff's reagent.

Results and Discussion

Thermal stability of POM_C and POM_C/HAp-g-PEG 600 composite was investigated with TG method (FIG. 1).

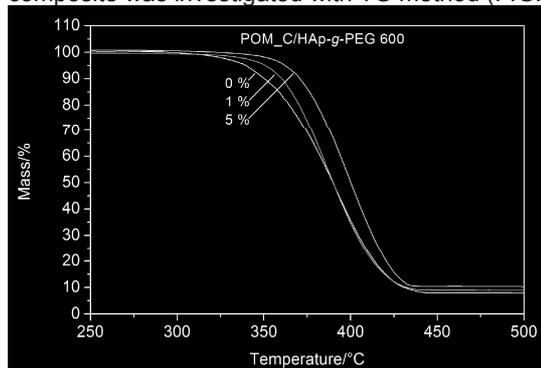


FIG. 1. TG curves of pure POM (0%) and POM/HAp-g-PEG 600 composites (1%, 5%).

HAp-g-PEG 600 contributed to the increase of thermal stability of POM from 315°C (pure POM) to 343°C (5% HAp-g-PEG 600). This effect can be explained by the decrease of the quantity of free hydroxyl groups in HAp which are able to catalyse reactions [8]. The presence of nitrogen atoms in the urethane bonds can also increase the stability of POM, as nitrogen-containing compounds such as polyamides and dicyandiamines are usually used as a heat stabilizer of POM [9]. In comparison to our previous study, the molar mass of PEG does not affect the efficiency of HAp-g-PEG thermal stabilizer.

Conclusions

The present results confirmed that incorporation of HAp-g-PEG 600 in POM matrix causes a considerable increase in POM thermal stability. Thereby, the risk of the deterioration of material properties after the polymer processing at elevated temperatures is minimized, which is crucial in the use for orthopedic applications.

Acknowledgments

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