PROPERTIES OF POLYOXYMETHYLENE COMPOSITES WITH FUNCTIONALIZED HYDROXYAPATITE

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Introduction

Polyoxymethylene (POM) belongs to the class of the thermoplastic polymers showing an excellent endurance, good mechanical properties and wear resistance [1]. However, low thermal stability and resistance to UV radiation limits POM range of applications. From the biomedical applications' point of view it is important to improve POM resistance to higher temperatures, due to the sterilization process. Some bioactive additives introduced to POM catalyse its decomposition during melt processing under elevated temperatures [2]. In the previous studies it has been found that addition of functionalized hydroxyapatite leads to increase of POM thermal stability [3]. In the presented study hydroxyapatite with controlled nanoparticles size and shape was functionalized with poly(ethylene glycol) (PEG) of average molar mass 2000, and the influence of HAp-g-PEG on POM composite properties was investigated.

Materials and Methods

Hydroxyapatite with needle like shape and particle size of 60 nm were used. Functionalized hydroxyapatite was obtained by grafting of poly(ethylene glycol) using 1,6-hexamethylene diisocyanate as a coupling agent. The obtained HAp-g-PEG was introduced into the polyoxymethylene matrix using the extrusion methods and shaped by injection moulding.
Obtained POM/HAp-g-PEG composites were tested using infrared spectroscopy (FTIR), thermogravimetry (TG) and differential scanning calorimetric (DSC). The degree of crystallinity and crystallization rate were calculated on the basis of DSC curves obtained under isothermal conditions.

Results and Discussion

The effects of PEG grafting on hydroxyapatite were confirmed by FTIR results. The absorption bands at 3200-3450 cm^{-1} confirmed formation of urethane groups (FIG. 1). A decrease in the intensity of absorption band at 3571 cm^{-1} , arising from hydroxyl group in HAp, and the presence of new bands in the characteristic ranges for urethane groups, confirm the successful PEG grafting on the surface of HAp. Thermogravimetry analysis shows that obtained HAp-g-PEG contained 30% of organic phase. From TG data of POM/HAp-g-PEG composites, it can be seen that the addition of HAp-g-PEG increased the thermal stability of the composites from 274°C for pure POM to 327°C for POM with 0.5% of HAp-g-PEG.
The analysis of DSC curves did not show any significant differences between unmodified polymer and composite with HAp-g-PEG.
An endothermal peak of POM melting was observed at 165°C. Melting point and crystallization temperature of nanocomposites were determined from DSC curves. The degree of crystallinity was calculated based on DSC results. For unmodified polymer, degree of crystallinity was ca. 49% and with the increase HAp-g-PEG concentration, degree of crystallinity slightly decreased to 44% for POM with 5% of HAp-g-PEG.
From isothermal DSC results the relative crystallinity was calculated (FIG. 2) and next Avrami coefficient and rate of crystallization were determined (FIG. 3). It was observed that the time of crystallization increases with the increase of crystallization temperature.

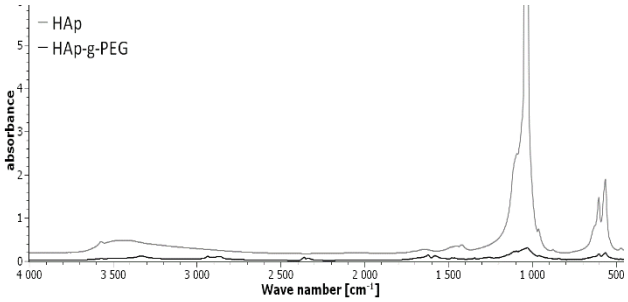

FIG. 1. FT-IR spectrum of HAp and HAp-g-PEG.

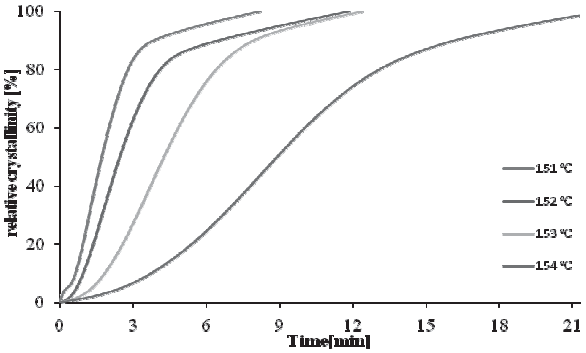

FIG. 2. Relative crystallinity as a function of crystallization time of nanocomposite POM/5%HAp-g-PEG.

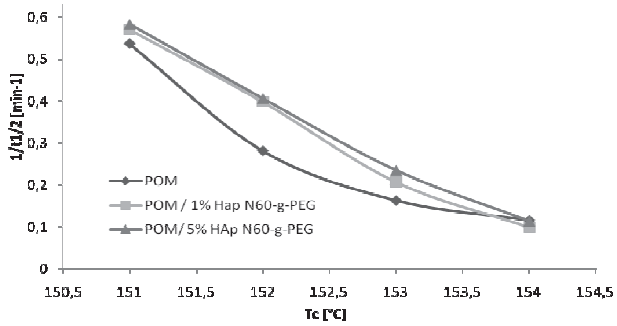

FIG. 3. Total crystallization rate as a function of crystallization temperature for POM and nanocomposites POM/HApN60-g-PEG.

Conclusions

Based on the presented results it can be concluded that the addition of HAp-g-PEG significantly improves the thermal stability of polyoxymethylene (increase of 50°C for 0.5% of the additive concentration). No significant effect of the additive on the properties such as rate and degree of crystallization, crystallization temperature and melting point was observed.

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