

# ACETAL POLYMERS MODIFIED WITH HYBRID INORGANIC-ORGANIC HYDROXYAPATITE-BASED SYSTEMS

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## Introduction

Acetal polymers, also known as polyoxymethylene (POM) or polyacetals, are formaldehyde-based engineering thermoplastic polymers apply in a broad range of applications because of their improved properties [1]. They have been used in different areas including automotive and mechanical industry, electronics, consumer goods but also in the production of elements of medical devices and drug delivery systems [2-3]. However, the using of POM as biomaterial is limited due to a lack of bioactivity and poor thermal stability. Considering the upper limitations, the composites made of POM matrix and the hybrid, inorganic-organic hydroxyapatite-based filler (HAp-*g*-PEG) with improved thermal stability, bioactivity and the hybrid filler dispersion in POM matrix, were prepared and investigated in this study.

## Materials and Methods

POM copolymer (POM\_C, Ultraform®, BASF) and POM homopolymer (POM\_H, Delrin®, DuPont) were used as a composites matrix. Hydroxyapatite (HAp, nGimat) in the shape of nanopowder was functionalized with poly(ethylene glycol) (PEG, Sigma Aldrich) of three average molar mass of 600, 2000 and 6000. 1,6-hexamethylene diisocyanate (HDI) was used as a coupling agent. In consequence, the hybrid, inorganic-organic fillers of HAp-HDI-PEG (HAp-*g*-PEG) intended to POM composites were synthesized.

The dispersion of fillers in the polymer matrix was observed using transmission electron microscopy (TEM). Thermal degradation, the kinetics of thermal degradation and gaseous degradation products of composites were analyzed using thermogravimetry (TG), Friedman method and multiple non-linear regression (Netzsch Thermokinetics). Identification of degradation products was performed using TG-FTIR/MS technique. Bioactivity of composites was confirmed by scanning electron microscope (SEM) with energy dispersive X-ray spectroscopy (EDX) after incubation in simulated body fluid (SBF).

## Results and Discussion

The TEM micrographs of POM\_C and POM\_C/HAp-*g*-PEG composites are shown in FIG. 1. The hybrid HAp-*g*-PEG particles, in the form of connected nanospheres, are well dispersed in the POM matrix. This is possible because a hybrid material exhibits a higher affinity to polymer matrix in comparison to inorganic nanoparticles. The mechanism and kinetics of thermal degradation investigations of POM/HAp-*g*-PEG materials shown a strong increase in thermal stability. For pristine POM, one-stage degradation mechanism with autocatalysis was observed. While for composite materials, an additional of *n*-th order reactions or *n*-dimensional nucleation (Avrami-Erofeev equation) were observed.

From TG-FTIR/MS results, it was found that the main degradation product for POM and POM/HAp-*g*-PEG composites is formaldehyde and the amount of other degradation products is lower in comparison to unmodified POM. This method also confirmed the thermal stability increase in comparison to pure POM.

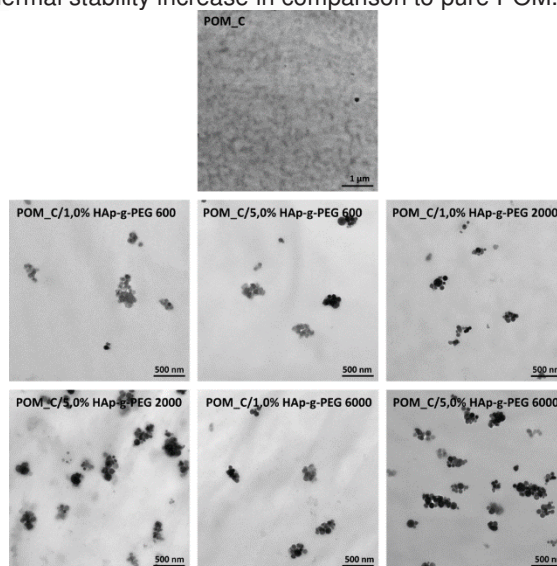


FIG. 1. TEM micrographs of POM\_C/HAp-*g*-PEG composites.

As can be seen in FIG. 2, a thick layer of apatite was formed on the POM composites surface after 21 days incubation in SBF. It confirmed that POM/HAp-*g*-PEG materials have a great potential for the *in vivo* bone bioactivity.

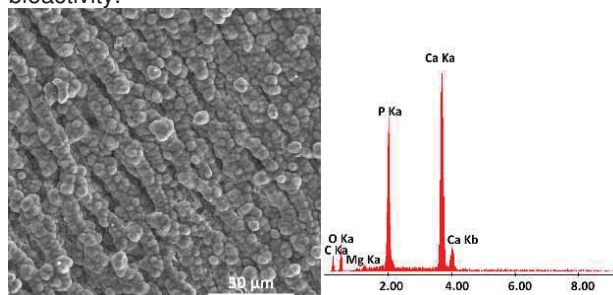


FIG. 2. SEM/EDX result for POM\_C/5,0% HAp-*g*-PEG 2000 after incubation in SBF.

## Conclusions

The chemical modification of HAp nanoparticles with PEG provides good, homogenous dispersion of filler within the POM matrix. The HAp-*g*-PEG additives affected the POM degradation mechanisms, as a result the thermal stability of POM/HAp-*g*-PEG composites was improved. The presence of HAp particles in HAp-*g*-PEG additive improved bioactivity of composites that can be considered for orthopedic applications.

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## References

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