POLY BIS-GMA/HA BASED HYBRID COMPOSITE MATERIALS

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În această lucrare prezentăm sinteza şi caracterizarea unor nanocompozite hibride pe bază de of poli bisfenol A glicidil metacrilat şi hidroxiapatită (poli Bis-GMA/HA) pornind de la monomerul corespunzător şi pulbere de HA. Au fost propuse două metode de polimerizare: polimerizare termică şi respectiv chimică iar materialele rezultate au fost comparate, în special din punct de vedere al comportamentului termic. Procesul de polimerizare a fost complet doar în cazul polimerizării chimice. Materialele nanocompozite hibride au fost caracterizateprin XRD, FTIR, SEM şi TEM si se confirmă compoziția şi morfologia materialelor.

In this paper we present the synthesis and characterization of poly bisphenol A glycidyl methacrylate/hydroxyapatite (poly Bis-GMA/HA) hybrid nanocomposites starting from the proper monomer and HA powder. Two polymerization methods were proposed: thermal and respectively chemical polymerization and the resulted materials were compared, especially from the point of view of thermal behaviour. The polymerization process was completed only in the case of chemical polymerization. The hybrid nanocomposite materials were characterized by XRD, FTIR, SEM and TEM that confirm the composition and morphology of the materials.

Keywords: hybrid composite materials, methacrylate, hydroxyapatite, synthesis, characterization

1. Introduction

Hydroxyapatite is one of the most used materials for hard tissue replacement because this is the main component of bones and teeth [1, 2]. Hydroxyapatite (HA) is intensively used as pure ceramic [3], coatings [4] or composite materials such as: hydroxyapatite/gelatin nanocomposites [5],

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poly(lactide-co-glycolide)/ hydroxyapatite nanocomposites [6], collagen/ hydroxyapatite (nano)composites [7], collagen- chitosan- hydroxyapatite nanocomposites [8], poly(ethylene terephthalate) / hydroxyapatite biomaterials [9] etc.

Bis-GMA (2,2-bis[p-(2'-hydroxy-3'-methacryloxypropoxy) phenyl] propane) is intensively used for dental application as filled or unfilled resins [10]. In many cases, Bis-GMA is used in association with different inorganic biocompatible components such as: alumina [11, 12], zirconia [13], silica and silicates [14], titanium dioxide [15], calcium phosphates [16], hydroxyapatite [17]. The desired properties of the composites materials can be achieved by the proper choose of the composition and processing routes; usually Bis-GMA based composite materials being obtained by chemical, photochemical or thermal curing [18-25].

Only a few papers dealing with Bis-GMA/HA composite materials were published. Mostly, these composite materials are used for cementation, the obtained results being very promising [26].

The purpose of the present work was to synthesize and characterize poly Bis-GMA/HA composite materials obtained by chemical and thermal polymerization of the Bis-GMA monomer. Also, an essential part of the present work was focussed on the study of differences induced by polymerisation methods, especially based on thermal behaviour of the two kinds of materials.

2. Materials and Methods

Hybrid polyBis-GMA/HA composite materials were obtained according to the procedure presented in Fig. 1. The polymerization of Bis-GMA was performed under chemical or thermal conditions. Benzoyl peroxide was used as initiator of the chemical polymerization of the monomer; the amount of benzoyl peroxide being of 0.5% (w/w) reported to the monomer. The thermal polymerization was done at 70^0C for ~2 h. Both hybrid materials were obtained starting from Bis-GMA and HA, the ratio of the components being 1:9 (w/w). All reagents were used as received (Sigma-Aldrich) without any purification.

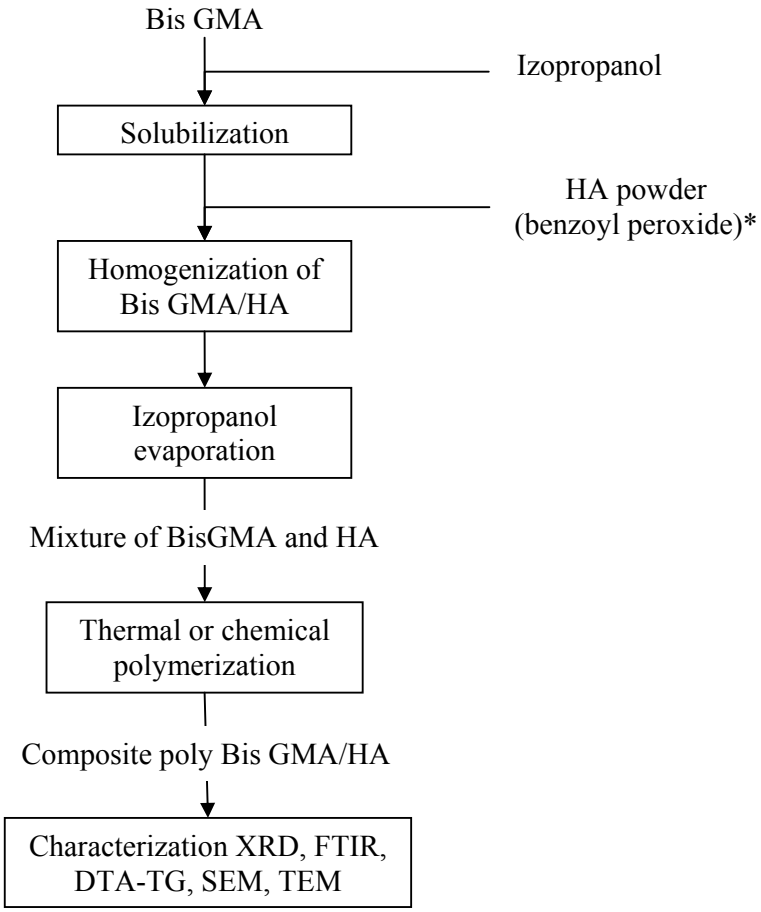
X-ray diffraction analysis was performed using a Shimadzu XRD 6000 diffractometer at room temperature, using Cu Kα radiation.

Infrared spectroscopy (Shimadzu 8400 FT-IR Spectrometer) was performed in the range of 500 – 4000 cm^{-1}, with a resolution of 2 cm^{-1}.

The differential thermal analysis (DTA) coupled with thermogravimetric analysis (TGA) was performed on a Shimadzu DTG-TA-50H, at a heating rate of 10^0C/min, in static air.

SEM images were recorded on a HITACHI S2600N electron microscope. Prior to the analysis, all samples were covered with a layer of silver by plasma sputtering.

TEM images were obtained on finely powdered samples using a Tecnai^{TM} G^2 F30 S-TWIN high resolution transmission electron microscope (HRTEM) equipped with STEM – HAADF detector, EDX and EELS. The microscope was operated in transmission mode at 300kV while TEM point resolution was 2 Å and line resolution was 1 Å. The hydroxyapatite particles were assessed by selected area electron diffraction (SAED).



* only if the polymerization occurs by chemical polymerization

Fig. 1. Synthesis scheme of the hybrid poly Bis-GMA/HA composite materials

Results and discussion

The hybrid composite materials were characterized by X-ray diffraction – XRD, Fourier transform infrared spectroscopy – FTIR, scanning electron microscopy – SEM, transmission electron microscopy – TEM and complex thermal analysis DTA-TG-DTG.

3.1 X–ray diffraction

X–ray diffraction was used to analyze the crystalline phases of the composites materials.

The most important peaks of the composite material are identified (Fig. 2). These belong to the HA (25.7; 28.9; **31.8**; 32.06; 32.98; 35.95; 39.89; 46,66; 49,29) and to the brushite (22,96; 26,64; 30,33; 34.2). The presence of brushite can be explained based on the reaction 1, phosphate anions being resulted by hydroxyapatite solubilisation and brushite formation is due to hydrogenophosphate precipitation. Based on the recorded diffractogram it can be observed a good crystallinity of the mineral phases.

$$PO_4^{3-} + H_3O^+ \underset{}{\overset{pK_{a3}=12.67}{\rightleftharpoons}} HPO_4^{2-} + H_2O \qquad (1)$$

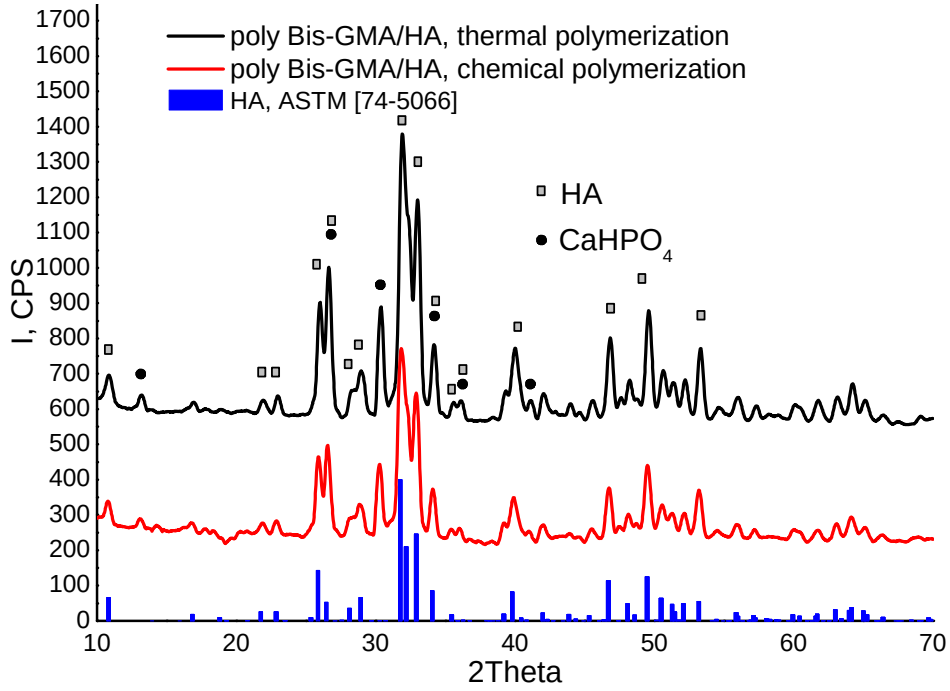


Fig. 2. X-Ray diffraction pattern of poly Bis-GMA/HA composite material obtained by thermal and respectively chemical polymerization

3.2. Infrared spectroscopy

Infrared spectroscopy is a useful tool of the composite material characterization, because it can give information even for non-crystalline phases of the composite material. The most intense absorption bands are that belonging to the phosphate groups of HA: 567, 601 and 1035 cm^{-1}. The absorption bands of the poly Bis-GMA are 1250, 1292, 1409, 1511, 1635, 1725 and 2966 cm^{-1}. The broad absorption band from 3422 cm^{-1} belong to the associated HO groups from HA, poly Bis-GMA and isopropanol while the sharp band from 3569 cm^{-1} correspond to the free hydroxyl groups of the above mentioned composites. The low intensity of the absorption bands of poly Bis-GMA can be explained based on the mixing ratio between bis-GMA and HA.

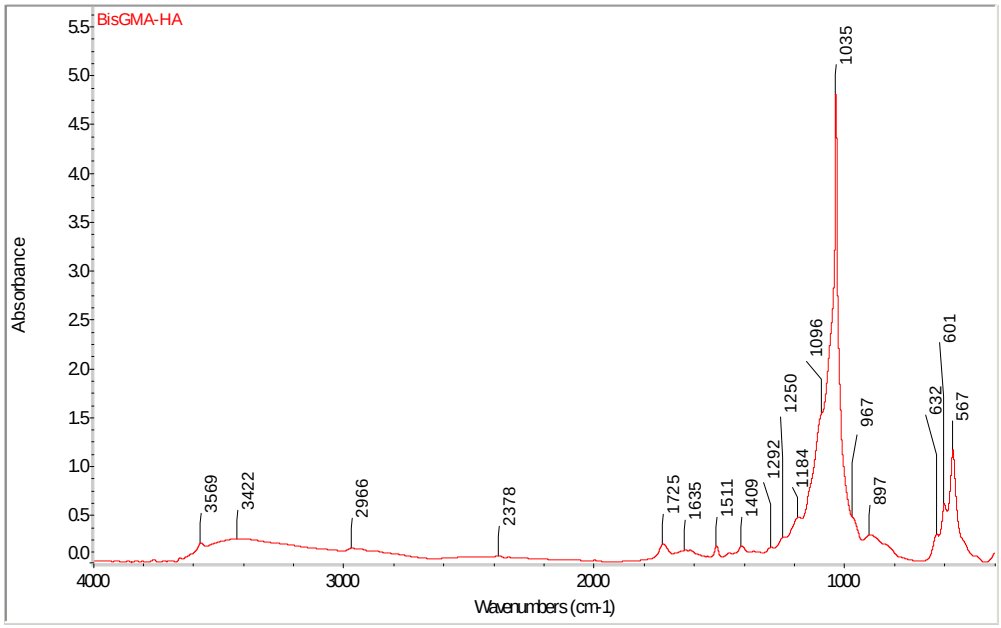


Fig. 3. Infrared spectrum of poly Bis-GMA/HA obtained by thermal polymerisation

3.3. Scanning electron microscopy

The scanning electron microscopy was used in order to visualize the morphology of the poly bis-GMA/HA composite material obtained by thermal polymerization. At low magnification (Fig. 4a, b), the SEM images prove the good homogeneity of the composite material whereas, the agglomerates and larger HA particles shape and size can be studied at higher magnification (Fig. 4c). Hydroxyapatite particles form very irregular agglomerates from the point of view of shape and size.

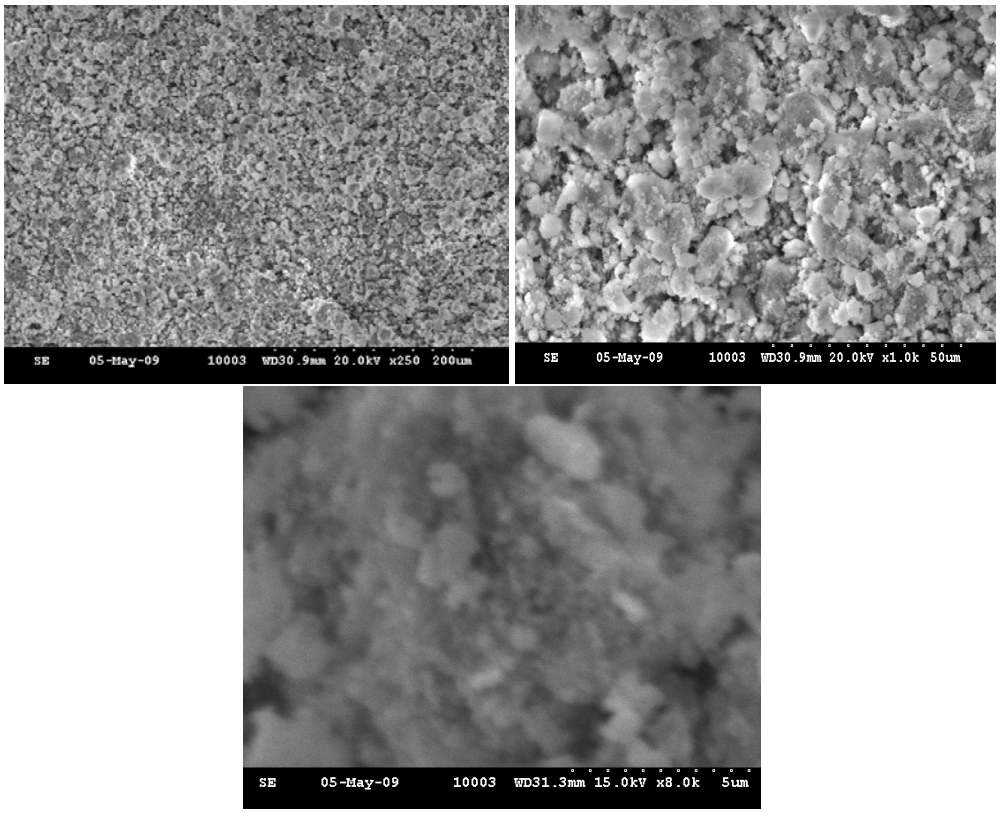


Fig. 4. SEM images of poly Bis-GMA/HA composite material obtained by thermal polymerisation at 70^0C

3.4. Transmission electron microscopy

TEM and HRTEM images were recorded in order to obtain higher magnification and to study the morphology of the agglomerates. Based on the TEM images, it can be seen that the agglomerates are composed mainly by spherical, quasispherical and rod like particles. The rod like morphology is induced by the polymer, due to the presence of $–C_6H_4–CH_2–C_6H_4–$ groups. TEM images are also a useful tool to determine the particles size. Based on the average size determined by SEM, the composite material can be considered as a true hybrid nanocomposite. At high resolution, the main crystallization planes of hydroxyapatite can be identified, for instance [210] and [211].

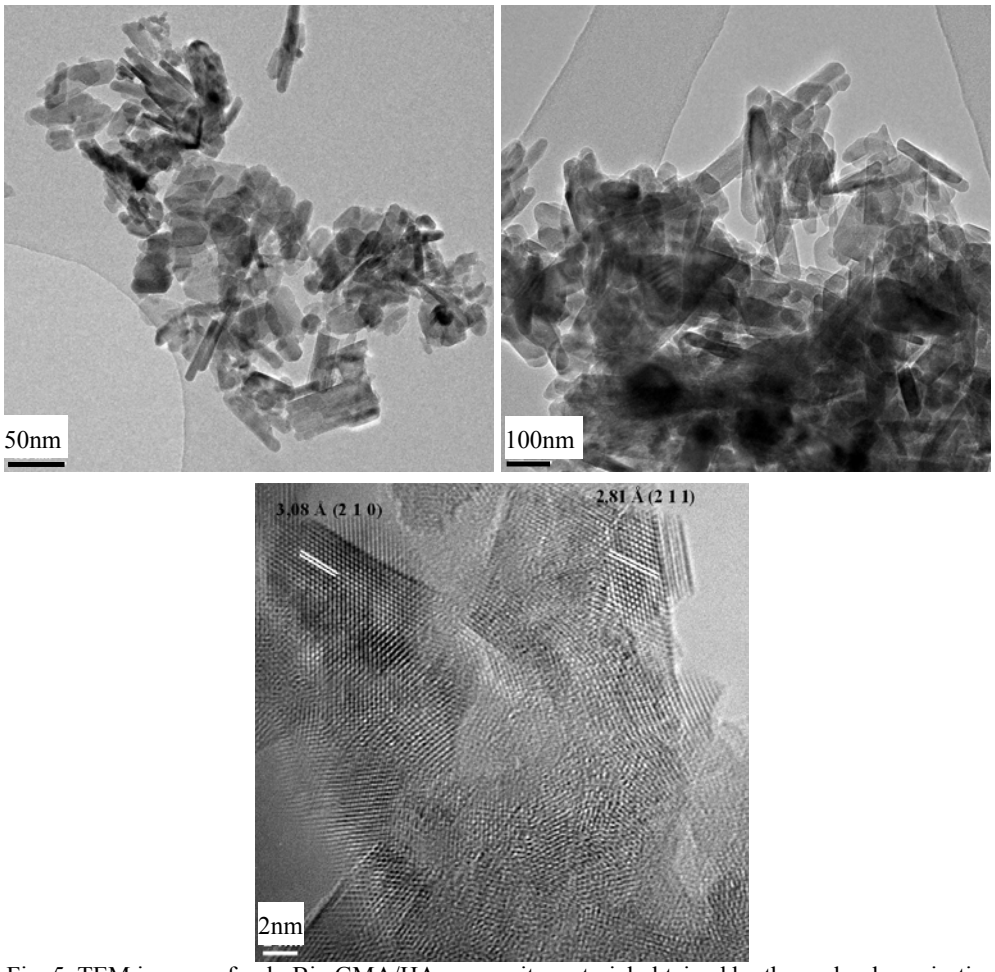


Fig. 5. TEM images of poly Bis-GMA/HA composite material obtained by thermal polymerisation at 70 ^{0}C

3.5. Thermal analysis

The thermal behaviour of the poly Bis-GMA composite materials is slightly influenced by the polymerization method. The use of benzoyl peroxide leads to a better polymerization of the Bis-GMA, which can be proved by the absence of the effect at 340^{0}C (on DTA curve), but also by the absence of the peak (on DTG curve) at 210^{0}C, respectively. The presence of these peaks is a proof that Bis-GMA is left unpolymerized and also partially polymerized Bis-GMA. The endothermic effect at 210^{0}C, accompanied by a mass loss on TG curve corresponds to the degradation of the Bis-GMA. In both cases, the mass loss between ~200 and 450 ^{0}C of about 10% correspond to the polymer degradation.

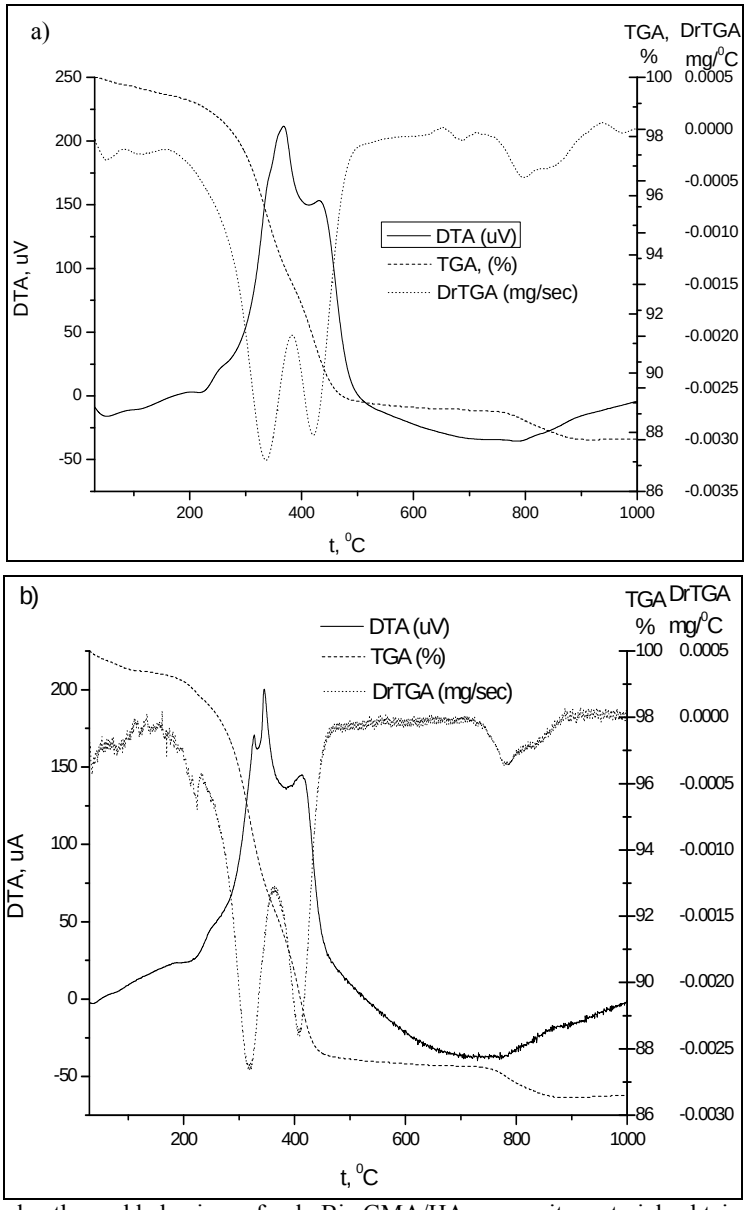


Fig. 6. Complex thermal behaviour of poly Bis-GMA/HA composite materials obtained by a) chemical and b) thermal polymerization

4. Conclusions

This paper presents two synthesis methods of poly Bis-GMA/HA hybrid composite materials starting from Bis-GMA and HA powder. It can be concluded, the use of benzoyl peroxide improve the polymerization process of Bis-GMA, based on the complex thermal analysis.

The TEM images showed that the obtained hybrid materials are true nanocomposite, the polymer having rod-like morphology with 100-150 nm length and 15-25 nm diameter; the rod-like morphology being induced by the presence of the poly Bis-GMA.

The obtained poly Bis-GMA/HA composite materials have potential applications in orthopaedics and dentistry as filling or cementation materials.

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