Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

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Version of record first published: 31 Jan 2007

To cite this article: C. Albano, A. Karam, G. González, N. Domínguez & Y. Sánchez (2006): Study of Gamma Radiation Effect on PMMA/HA Composites Prepared by Solution, Molecular Crystals and Liquid Crystals, 448:1, 243/[845]-249/[851]

To link to this article: http://dx.doi.org/10.1080/15421400500403283

Mol. Cryst. Liq. Cryst., Vol. 448, pp. 243/[845]–249/[851], 2006

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400500403283

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Research and development of new materials and methods for bone repair and substitution is today one priority in bone defects treatment. PMMA is the current standard for cement held prostheses, providing immediate structural support, being inert as well as compatible. In this study, PMMA/Hydroxyapatite (HA) composites prepared by solution and gamma irradiated were characterized. Inclusion of HA particles caused a decrease in Melt Flow Index while radiation originated an increase in this parameter as a consequence of a strong degradation. Filler provided an increase in Young Modulus and a decrease in strength and elongation at break due to elasticity loss. On the other hand, radiation caused a decrease in composites mechanical properties. Initial decomposition temperatures increased with filler content and low doses radiation. At higher doses, a decrease was noticed due to degradation. HA showed a stabilizing effect, the activation energy of filled irradiated and non irradiated materials were higher than unfilled ones.

Keywords: characterization; composites; gamma radiation; hydroxyapatite; PMMA

The authors would like to thank Msc. Pablo Joskowicz from PDVSA Intevep for supporting the mechanical and MFI essays.

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INTRODUCTION

Poly(methyl methacrylate) (PMMA) bone cement is one of the popular bone repairing materials for bone fixation joints. Significant problems on the PMMA bone cement are caused by looses of adhesion at the interface between bone and the cement, since the cement does not show bone bonding. Mechanical characteristics have been a problem with PMMA cements; polymers produced by mixing the cement phases are usually brittle, and have poor fatigue life [1].

The prerequisite for an artificial material to show bone bonding is the formation of a biologically active bone-like apatite layer on its surface when implanted in the body [2]. The addition of small amounts of particulated materials, such as hydroxyapatite (HA), offers the possibility of strengthening, without affecting stress distribution. HA can lend bioactivity to composite materials; however, the extent of this activity is dependent of the volume of HA incorporated.

The sterilization of medical supplies is now mainly being performed by gamma radiation. When PMMA is exposed to radiation, its chemical and physical structure is modified [3]. In the present work, PMMA/HA composites, irradiated at different doses were characterized through mechanical, rheological, thermodegradative and morphological essays.

MATERIALS AND METHODS

A commercial polymethylmethacrylate (PMMA) was used. Hydroxyapatite was synthesized via precipitation methods at room temperature. The synthesis was carried out from an aqueous suspension of calcium hydroxide ($Ca(OH)_2$) and solution of di-ammonium hydrogen phosphate ($(NH_4)_2HPO_4$). The products were thoroughly washed to neutral pH and dried at 75°C for 48 h.

The PMMA/HA composites were prepared by solution in chloroform. The procedure followed was: the polymer was dissolved in chloroform at room temperature under continue agitation, then the HA was added maintaining the agitation for 20 min in order to get a better dispersion of the filler. After this time, hexane was added to precipitate the composite. The precipitate was filtered and washed with n-hexane to eliminate the chloroform. The same procedure was utilized for the polymer without filler.

Different fractions of HA were used, i.e., 10, 20 and 30 wt%. The probes were molded by compression and cut according to ASTM-638 norm. Specimens, probes and pellets, were irradiated with γ-rays from a ^{60}Cobalt source in air at a doses rate of 4.8 kGy/h at room

temperature. Integral doses were in the 0–100 kGy range. They were 0, 10, 25 and 100 kGy.

Melt Flow Index (MFI) measurements were made from the irradiated pellets and from non-irradiated pellets of the PMMA and composites PMMA with HA for comparison. A Ray Ran Advanced Melt Flow Systems with a weight of 5 kg was used at 230°C. Gel content was determined for unfilled irradiated PMMA by Soxhlet extraction with chloroform for 24 hours.

The mechanical properties of irradiated and non-irradiated composites were carried out in an Instron Tensile Tester Machine (model 4204). Each experimental point represents an average of at least seven samples tested under identical conditions.

Differential scanning calorimetric measurements were performed to study the glass transition temperatures of the materials using a Metler Toledo DSC 821. A single heat was recorded from 25 to 250°C at 20°C/min, using nitrogen as a dragging gas.

The activation energy (Ea) and initial decomposition temperatures (T_{id}) were obtained from thermograms taken with a Thermogravimetric Analyzer (Mettler Toledo TGA851) under the following conditions: heating rate 20°C/min up to 700°C in a nitrogen atmosphere. The McCallum-Tanner method was used to determine these kinetic parameters [4].

RESULTS AND DISCUSSIONS

Table 1 shows Melt Flow Index of irradiated and unirradiated PMMA/HA composites. MFI tended to decrease with filler content as a consequence in polymeric chains movement restriction imposed by solid particles. On the other hand, radiation induced chain scission of PMMA causing a strong increase on MFI when radiations dose was augmented. This phenomenon was observed even at low doses, but it can be observed that for composites the increase is minor, so it is possible to say that HA is slowing down the polymer degradative process.

TABLE 1 Melt Flow Index of PMMA/HA Composites at Different Radiation Doses

HA content (%)	0 kGy	10 kGy	25 kGy	100 kGy
0	6.74 ± 0.37	7.16 ± 0.17	14.57 ± 0.18	44.02 ± 3.72
10	2.01 ± 0.14	3.17 ± 0.10	6.58 ± 0.21	25.07 ± 0.38
20	1.43 ± 0.04	3.08 ± 0.09	4.49 ± 0.23	17.27 ± 0.44
30	0.97 ± 0.03	1.61 ± 0.05	2.94 ± 0.26	10.47 ± 0.24

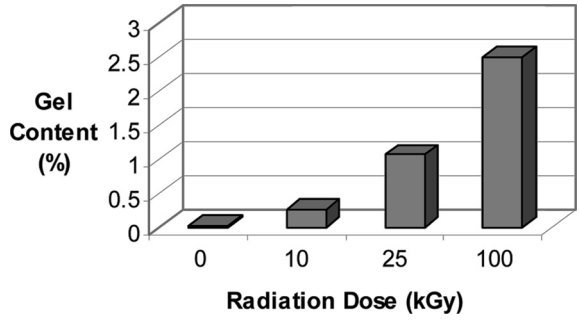

FIGURE 1 Crosslinking degree of irradiated PMMA.

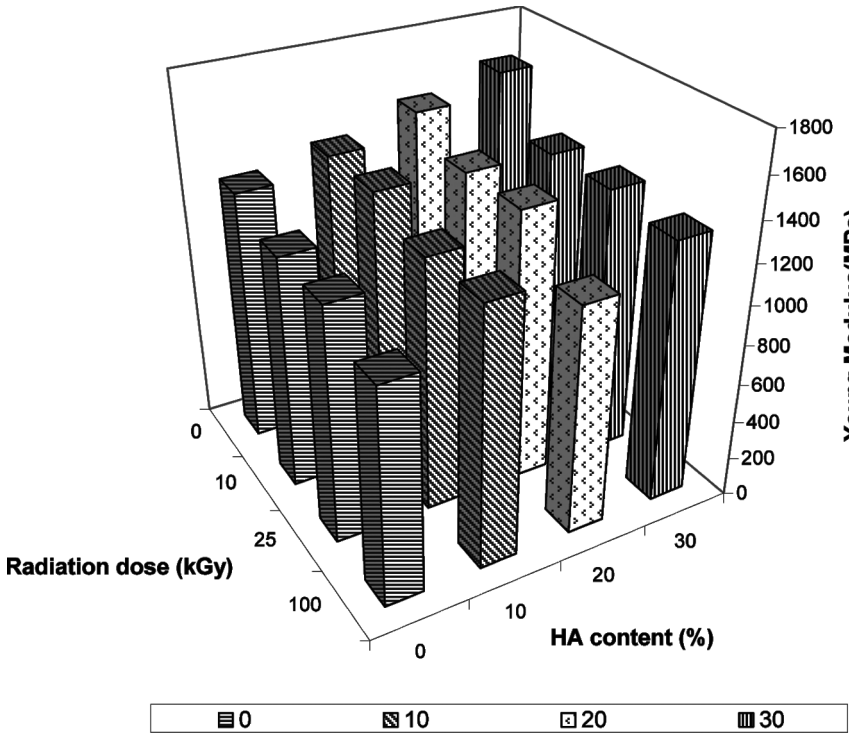

FIGURE 2 Radiation effect on composite's Young Modulus.

TABLE 2 Radiation Effect on the Mechanical Properties in PMMA/HA Composites Break Point

	Stress at break (MPa)				Elongation at break (%)			
HA content (%)	0 kGy	10 kGy	25 kGy	100 kGy	0 kGy	10 kGy	25 kGy	100 kGy
0	89.98 ± 9.37	85.47 ± 5.98	75.02 ± 1.71	35.40 ± 2.16	9.19 ± 0.52	10.34 ± 0.68	8.02 ± 0.42	3.98 ± 0.22
10	49.03 ± 4.60	55.97 ± 4.01	50.58 ± 3.94	42.49 ± 4.92	4.14 ± 0.20	5.43 ± 0.80	5.23 ± 0.39	4.10 ± 0.36
20	49.53 ± 4.13	43.18 ± 1.55	43.98 ± 2.65	39.59 ± 2.79	3.84 ± 0.20	4.17 ± 0.59	4.16 ± 0.48	4.31 ± 0.25
30	51.68 ± 3.20	37.30 ± 1.90	40.43 ± 1.33	39.82 ± 2.41	3.83 ± 0.30	3.87 ± 0.77	3.33 ± 0.24	3.79 ± 0.38

Gel content measurement (Fig. 1) showed that there were crosslinking reactions in PMMA, but very small degree was reached. Miguez *et al.* reported a tough decrease in average molecular weight of irradiated PMMA when exposed at low doses [3].

Young Modulus (Fig. 2) increased with HA inclusion, meaning that composite became tougher. Instead, radiation decreased this parameter as a consequence of polymer degradation. Is possible to observe that HA exerted a stabilizing effect on polymer, because loss of Young Modulus was minor in filled materials.

Strength and elongation at break values are shown in Table 2. These two parameters showed similar behavior, in which HA content caused a decrease as a consequence of diminution in materials elasticity. Unfilled PMMA exposed to radiation suffered a strong degradation reflected in an abrupt decrease of these parameters, while filled material also tended to decrease but in lower proportion, exerting HA a stabilizing effect.

Typical DSC curves obtained from the PMMA composites, before and after irradiation, are depicted in Figure 3. Neither filler content (Fig. 3a) nor radiation (Fig. 3b) caused significant variations of polymer glass transition temperatures, remaining in 101°C for all studied composites.

In Table 3 are presented thermodegradative parameters of PMMA/HA composites. For non irradiated composites, initial decomposition temperature slightly increased with filler content; this confirmed the stabilizing effect observed in the other properties. A small decrease was observed at 30% HA probably due to agglomerates formed for excessive filler content, which accelerates the decomposition process. When radiation dose was increased, unfilled PMMA

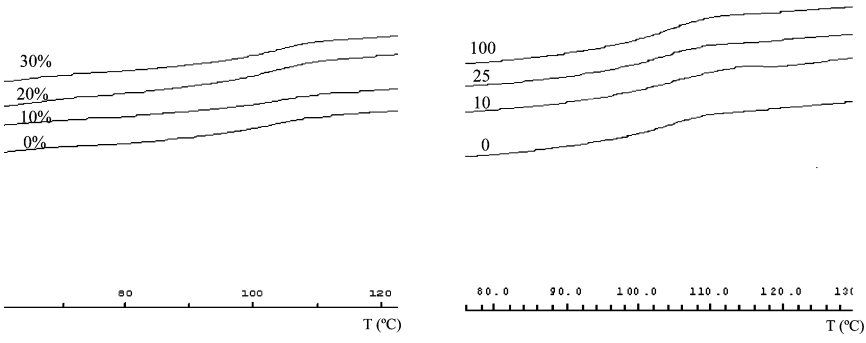

FIGURE 3 Calorimetric curves. (a) Effect of filler content at 0 kGy, (b) Effect of radiation for unfilled PMMA.

TABLE 3 Thermodegradative Parameters of PMMA/HA Composites

	Initial decomposition temperature (°C)				Activation energy (kJ/mol)			
HA content (%)	0 kGy	10 kGy	25 kGy	100 kGy	0 kGy	10 kGy	25 kGy	100 kGy
0	341	344	345	330	210	165	148	90
10	345	350	352	351	207	194	195	182
20	349	355	349	349	220	197	193	167
30	343	346	345	347	218	168	176	170

Tid decreased indicating degradation of the polymer. Instead, PMMA/HA composites did not show significant variations in initial decomposition temperature.

Activation energy tended to increase with HA inclusion, which indicates that HA conferred thermal stability to the materials. But when materials are exposed to gamma radiation, thermal stability decreases drastically for unfilled PMMA and composites also tended to decrease but in slight way, confirming the previous results.

CONCLUSIONS

The results indicated that including HA in PMMA matrix improved the thermal stability. Additionally, HA caused an increase in toughness and elasticity loss and improved thermal stability.

On the other hand, gamma radiation induced chain scission and a small crosslinking in PMMA. This degradation affected the mechanical and thermal behavior, especially for unfilled materials. Composites also suffered degradation but HA showed to exert a stabilizing effect.

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