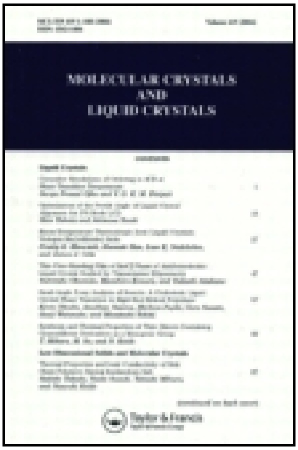

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Composites Based on ?-Ray Irradiated HDPE and HA

A. Karam [a], Sánchez [a], N. Domínguez [a], G. González [a], C. Albano∗ [a b], J. Reyes [a b] & P. Reyes-Turcu [c]

[a] Polymer Laboratory, Chemistry Center, and Materials Laboratory, Technology Center, Venezuelan Institute for Scientific Research (IVIC), Caracas, Venezuela

[b] Escuela de Ingeniería Química, Universidad Central de Venezuela, Caracas, Venezuela

[c] Universitatea "Politehnica", Bucaresti, Bucaresti, Romania

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COMPOSITES BASED ON γ-RAY IRRADIATED HDPE AND HA

A. Karam, Y. Sánchez, N. Domínguez, and G. González
Polymer Laboratory, Chemistry Center, and Materials Laboratory, Technology Center, Venezuelan Institute for Scientific Research (IVIC), Aptdo. 21827, Caracas 1020-A, Venezuela

C. Albano and J. Reyes*
Polymer Laboratory, Chemistry Center, and Materials Laboratory, Technology Center, Venezuelan Institute for Scientific Research (IVIC), Aptdo. 21827, Caracas 1020-A, Venezuela
and
Universidad Central de Venezuela, Facultad de Ingeniería, Escuela de Ingeniería Química, Caracas 1041-A, Venezuela

P. Reyes-Turcu
Universitatea "Politehnica" Bucaresti, Bucaresti, Romania

The evaluation of the mechanical and thermal behavior of composites (γ-HDPE-HA) based on gamma ray irradiated high density polyethylene (γ-HDPE) and hydroxyapatite (HA) showed an increase in the Young modulus values. This was attributed to the radiation effect and also to the HA addition. The tensile strength values were found in the range of those materials suitable for applications in the biomedicine field. The activation energy values allow estimating the optimum volume fraction of HA in the γ-HDPE to avoid detrimental properties in biomedicine applications of the γ-HDPE-HA composites.

INTRODUCTION

High Density polyethylene (HDPE) usually shows low toxicity and has been recommended as a suitable material for bone tissue substitution [1,2]. Wang *et al.* [3] and Di Silvio [4] studied composite materials based on PE filled with HA, which showed appropriate hardness, rigidity as well as high biocompatibility for tissue replacement.

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*Corresponding author. E-mail: calbano@ivic.ve

The interfacial adhesion between the polymer and HA is one of the important factors that governs the mechanical behavior of these composites. The interface control is a difficult task; one of the methods employed is the use of coupling agents. Sousa *et al.* [5] studied HDPE-HA composites containing zirconate and titanate coupling agents. However, these additives may have detrimental effects on the biocompatibility properties of the material. The objective of the present work was to study the mechanical, thermal and thermodegradative behavior of γ-HDPE-HA and non-irradiated (HDPE-HA) composites.

EXPERIMENTAL

The synthesis of HA [6] was carried out via precipitation at room temperature from an aqueous solution of $Ca(OH)_2$ and $(NH_4)_2HPO_4$. The products were thoroughly washed to neutral pH and dried at 75°C for 48 h.

The synthesis of the HDPE was carried out using a metallocene precatalyst (Cp_2ZrCl_2), which allows the synthesis of high density polymers with a narrow distribution of molecular weights. Methylaluminoxane (P-MAO) was used as cocatalyst. The reaction conditions were $T = 30°C$, $P = 3$ bar, bar, stirring = 500 rpm, the Al/Metal ratio = 500. At these conditions have been reported [7] that metallocenes showed high catalytic activity (60.900 kgPE/mol Zr. H). An amount of Irganox (0.3 wt%) was added to the HDPE and then the material was irradiated with γ-rays using a dose of 25 kGy and a dose rate of 5 kGy/h at room temperature in air atmosphere. γ-HDPE-HA composites were prepared by initially mixing irradiated HDPE and HA in a mixer (WAB) at room temperature for 2 h. Different volume fractions of HA were used, i.e., 10, 20 and 30 wt%. These mixtures were processed in a mini piston extruder with a temperature profile of 180–190°C. The mechanical properties of irradiated and non-irradiated HDPE and γ-HDPE-HA were carried out in an Instron Tensile Tester Machine (model 4204). Each experimental point represents an average of at least five samples tested under identical conditions. Differential scanning calorimetric measurements were performed to study the crystallization and melting behavior of the materials using a Metler Toledo DSC 821. Two tests were carried out for each sample using Nitrogen as a dragging gas. The first cooling and the second heating thermograms (after a common thermal history) were recorded at 10 K/min. Melt flow index measurements were made in a Davenport 3/80 plastometer using a weight of 5 Kgf at 190°C. FTIR spectra were taken from irradiated and non-irradiated HDPE in a Nicolet Magna-IR 750 spectrometer. The activation energy (Ea) and the order of reaction (n) were obtained from thermograms taken with a Thermogravimetric Analyzer (Mettler Toledo TGA851) under the following conditions: heating rate 10°C /min up to T = 773°K in a nitrogen atmosphere. The McCallum-Tanner method was used to determine these kinetic parameters [8].

RESULTS AND DISCUSSION

The effect of γ-rays over PE, the irradiated and non-irradiated HDPE were analyzed by FTIR (Fig. 1). As can be seen in the Figure 1 an increase is observed in the interval 1650–1800 cm^{-1} for the γ-HDPE, which can be attributed to carbonyl groups (C=O). The presence of this group confirms that degradation processes are taken place in polymeric matrix. The band at 964 cm^{-1} can be assigned to the trans-vinylene group (trans-RCH=CHR), which increase with the absorbed dose. While a light decrease at 909 cm^{-1} corresponding to terminal vinyl groups, indicating the formation of cross-linking or long branched chains. The mechanical properties (MFI, tensile strength σ_B, Young module E and the elongation at break ε_B) of the HDPE, γ-HDPE and composites are showed in the Table 1 A. The MFI value for HDPE indicates the formation of a polymer with high molecular weight (0.0177 dg/min). This value decreases with the increase of HA (20%) content in the polymer indicating a raise in the viscosity of the material composites due to the rigid filler. For the γ-HDPE and γ-HDPE-HA composites its MFI could not determinate because of their high viscosities produced by crosslinking reactions and/or ramifications in the irradiated HDPE.

In the case of Young module, when the HDPE is submitted at low doses to gamma irradiation (25 kGy) shows a decrease. On the other hand, an increase in this property is observed when the amount of HA was added. Under the same conditions described above, the elongation at break of these materials decreases very rapidly. This is due to the behavior of the HDPE under irradiation gamma and to the fact that HA is rigid filler. The tensile strength of the non-irradiated HDPE shows a decrease with HA content because of the stress concentration at the interface. While for the γ-HDPE this effect produces an increase of this mechanical property.

The mechanical behavior can be explained based on the destruction of the crystalline region in the polymer, which act as ‘physical crosslinking’. This kind of crosslinking has a greater effect on the tensile strength and Young module than the chemical crosslinking produced. These results are in agreement with the mechanical behavior indicated by Chapiro [9]. For HA content greater than 30% a higher decrease on the tensile strength occurs probably because to the major quantity of agglomerates, which act as cracks activators.

In the Table 1B can be seen the results for the activation energy (Ea), the order of the reaction (n) and the initial decomposition temperature

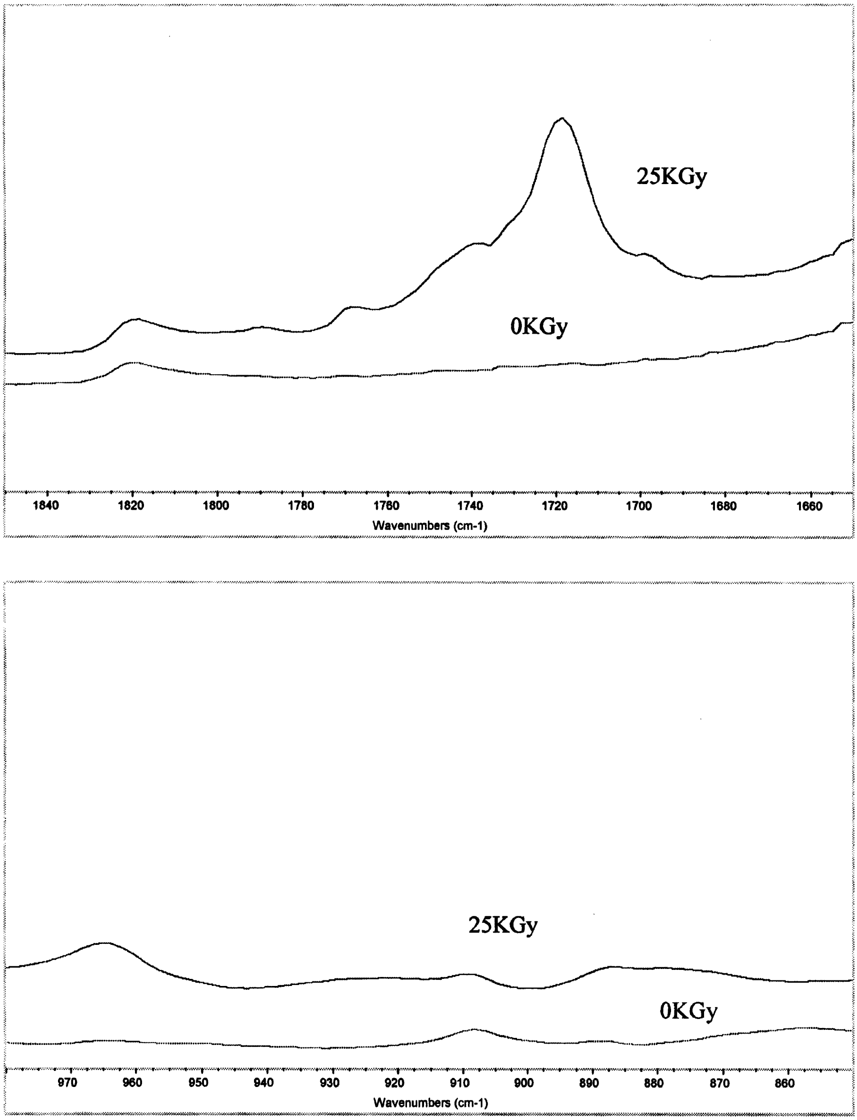

FIGURE 1 FTIR of unirradiated and irradiated HDPE.

(Ti). This is the maximum temperature of the operating conditions for the elaboration of the composites to avoid degradation process. The Ti values indicate that the gamma irradiation affects the degradation process. The γ-HDPE shows lower Ti values than the non-irradiated HDPE, because it becoming less stable and therefore allowing rapid decomposition. Also, HA

TABLE 1 MFI, Mechanical, Thermodegradative and Thermal Behavior of the Samples

A)

Samples	MFI (dg/min)	σ_B (MPa)	E (MPa)	ε_B
HDPE	0.0177	6.5 ± 0.9	420 ± 40	603 ± 44
γ-HDPE	*	11.3 ± 1.1	325 ± 41	199 ± 10
HDPE-HA (20%)	0.0692	1.3 ± 0.6	438 ± 47	25 ± 11
γ-HDPE-HA (10%)	*	6.4 ± 1.4	450 ± 30	56 ± 18
γ-HDPE-HA (20%)	*	4.7 ± 1.1	473 ± 25	52 ± 10
γ-HDPE-HA (30%)	*	3.1 ± 0.8	530 ± 30	54 ± 13

B)

Samples	n (-)	Ti (°C)	Ea (KJ/mol)
HDPE	1.2	432	456
γ-HDPE	0.9	406	293
HDPE-HA (20%)	1.3	443	572
γ-HDPE-HA (10%)	1.2	429	440
γ-HDPE-HA (20%)	1.2	428	412
γ-HDPE-HA (30%)	1.2	419	393

C)

Samples	Tm (°C)	ΔH_c (J/g)	Tc (°C)	Xc (%)
HDPE	137	207	115	85
γ-HDPE	136	182	113	75
HDPE-HA (20%)	136	241	116	99
γ-HDPE-HA (10%)	136	139	115	57
γ-HDPE-HA (20%)	135	194	113	79
γ-HDPE-HA (30%)	134	211	115	87

*The MFI of these samples could not determinate.

addition decreases the initial temperature of degradation and as a consequence accelerates decomposition. This process is more pronounced in the γ-HDPE-HA composites due to both effects are operating.

The kinetic values showed that the activation energy Ea for the HDPE-HA (80–20) is higher than the γ-HDPE/HA (80–20). Therefore, irradiation affects the sample reducing its stability. The order of the reaction for all the samples studied is around 1.2, indicating a complex mechanism of degradation.

Comparing the values of the thermal properties obtained by DSC (Table 1 C) for HDPE and γ-HDPE a decrease in Tc and crystallinity were observed. This is due to the degradative process present in the polymer as a result of radiation.

The polymer with 20% HA shows an increment in crystallinity indicating the nucleating effect of the filler. Additionally, for higher HA content an increase in the degree of crystallinity of the irradiated HDPE-HA mixture is observed, due to the degradation effect of radiation on the polymer.

CONCLUSIONS

The decrease in the crystallization temperature is due to the degradation effects that suffer the polymer with irradiation. HA increases the crystallinity of the irradiated HDPE, but not higher than the HDPE-HA composite due to the radiation effect on the polymer. The decrease in Ti as well as in Ea indicated a decrease in thermal stability of these materials. The behavior of the Young module and the tensile strength can sustain a possible application of these materials for biomedical applications.

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