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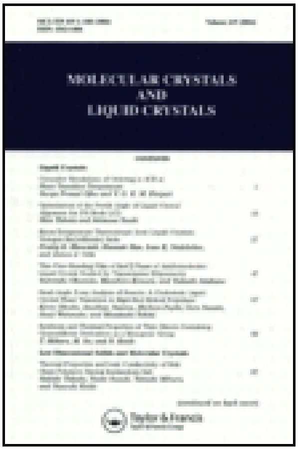

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Optimal Conditioning for the Preparation of HDPE-HA Composites in an Internal Mixer

C. Albano [a] [b] , A. Karam [a] , N. Domínguez [a] , Y. Sánchez [a] , J. Puerta [a] , R. Perera [c] & G. González [a]

[a] Centro de Química, Laboratorio de Polímeros, Instituto Venezolano de Investigaciones Científicas (IVIC), Venezuela

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

[c] Departamento de Mecánica, Universidad Simón Bolívar, Venezuela

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C. Albano
Centro de Química, Laboratorio de Polímeros, Instituto Venezolano
de Investigaciones Científicas (IVIC) and Universidad Central de
Venezuela, Facultad de Ingeniería, Escuela de
Ingeniería Química, Venezuela

A. Karam
N. Domínguez
Y. Sánchez
J. Puerta
Centro de Química, Laboratorio de Polímeros, Instituto Venezolano de
Investigaciones Científicas (IVIC), Venezuela

R. Perera
Departamento de Mecánica, Universidad Simón Bolívar, Venezuela

G. González
Centro Tecnológico, Instituto Venezolano de Investigaciones
Científicas (IVIC), Venezuela

In the last years research and development of new materials and methods for bone repairing and substitution has been a priority in the biomedicine field. HDPE/Hydroxyapatite (HA) composites have been previously used successfully for such purposes. In this study, HDPE/HA composites prepared in an internal mixer were characterized. Mixing conditions, such as temperature and mixing rate, were optimized. Results showed that high mixing rates and lower temperatures improved the filler dispersion in the polymeric matrix. At optimal conditions composites with 10, 20, 30 pph of HA were prepared and their rheological, mechanical, thermal and thermodegradative properties were determined to establish the optimum filler content. Inclusion of HA particles decreased the melt flow index. The incorporation of HA also increased the Young's Modulus and strength at break and decreased the elongation at break due to elasticity loss. Thermal properties and initial degradation temperature were not affected with the inclusion of the

Address correspondence to C. Albano, Centro de Química, Lab de Polimeros, Instituto Venezolano de Investigaciones Científicas (IVIC), Caracas 1020, Venezuela. E-mail: calbano@ivic.ve

filler but an enhancement in the activation energy was observed. A titanate coupling agent (Lica 12) was added to composites to improve the interfacial interactions. Lica 12 did not produce any variation in the mechanical and rheological behavior of composites. A slight decrease in composite crystallinity was detected for composites coupled with 0.5, 0.7 and 1.0% Lica 12. The thermal stability increased with the addition of the coupling agent.

Keywords: characterization; composites, coupling agent; high density-polyethylene; hydroxyapatite

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INTRODUCTION

Hydroxyapatite (HA) is an ideal material for hard tissue replacement, because of its similarity with bone structure and biocompatibility characteristics. It has been successfully used as coatings for hip implants and in rat femoral as well as in dental implants [1,2]. HA reinforced high-density polyethylene was introduced in the early 80's by Bonfield *et al.* as an analogue material for bone substitution [3]. It has been demonstrated that polyethylene does not produce inflammatory response in the human body. In fact, HDPE/HA composites have been satisfactorily used for orbital implants [4]. Due to the inadequate dispersion of the HA into the polymer matrix, which produces a detriment in composites mechanical performance, the objective of this work was to optimize the mixing conditions, filler content and polymer-filler interactions in high-density polyethylene (HDPE) and hydroxyapatite (HA) based composites prepared in a internal mixer. Because of the nature of the starting materials, only physical interactions occur between their surfaces, so the use of coatings or coupling agents becomes necessary to improve their compatibility. Silane coupling agents have been used successfully with this purpose but their toxicity limits their use in HA filled polyethylene for medical purposes [5–7]. Previous works show that neopentyl titanate coupling agents are not cytotoxic and are recommended as a possibility for the elaboration of implants in the biomaterials field [8,9]. Consequently, in this work a titanate coupling agent (Lica 12) was used to enhance the polymer-filler interactions.

EXPERIMENTAL

A nanometric HA suspension was prepared by a wet chemical reaction of precipitation using equimolar solutions of calcium hydroxide and

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di-amonium hydrogen phosphate reacting as shown:

$$10Ca(OH)_2 + 6(NH_4)_2HPO_4 \rightarrow Ca_{10}(PO_4)_6OH_2 + NH_4OH + 6H_2O$$

The resulting suspension was washed with de-ionized water and centrifuged in order to neutralize its pH and dried afterwards at 80°C for a period of 48 h. HA particles were then pulverized. Particles with an average size of 19.6 µm were obtained. High-density polyethylene (MFI: 4.88 g/min, Mw: 77456 g/mol) supplied by Chemical Container Andina C.A. was used for composite elaboration. Weight-average molecular weight was obtained by gel permeation chromatography (GPC) using a Waters Alliance GPCV-2000.

Composites were obtained in a HAAKE rheomix 600. Mixing conditions were optimized preparing PEAD/HA composites with 30 pph (parts per hundred) of filler content. First of all, composites were prepared at 170°C varying mixing velocity (60, 70, 80, 90 rpm) during 5 min. HDPE was melted and homogenized for 2 min before the filler addition. Afterwards, the temperature was lowered 10°C to enhance shear stress and 90 rpm was used as the rotors mixing velocity for the materials compounding. Subsequently, composites filled with 10, 20, 30 pph of HA were manufactured at optimal mixing conditions with the aim of finding the most adequate filler content. Rheological, thermal and mechanical analyses were carried out for that purpose, showing the optimal performance for composites with 20 pph of HA.

A titanate coupling agent (Lica 12) was added in 0.3, 0.5, 0.7, 1.0 wt% in relation to the weight of filler to enhance interfacial interactions between polymer matrix and HA particles. The coupling agent was dissolved in hexane and the HA's surface was then sprayed with the solution. Solvent excess was eliminated using a Heindolph rotavapor. Composites were also characterized by rheological, mechanical, thermal, thermodegradadtive and morphological studies.

Melt flow index was determined using a Ray-Ran Advanced Melt Flow System at 190°C and 2.16 kg. For mechanical evaluation, the material was compression molded into plates of 1 mm thickness using a hot press at 170°C and cut into tensile specimens according to ASTM-D 638 standard. It is important to point out that two different dimensions of tensile specimens were used in this study (type I and type IV), hence, the difference in values of mechanical properties. Tests were carried out in an Instron 4204 (type I) and an EZ-20 tensile testing machine (Type IV), at 50 mm/min. Differential scanning calorimetry (DSC) analyses were carried out in a Metter Toledo DSC822^e. A first heating process from 25–170°C at 20°C/min to erase the materials thermal history was carried out. The temperature was maintained at

170°C for 3 min and then the samples were cooled down at 10C/min. A second heating process with a rate of 10°C/min was recorded until the sample temperature reached 170°C again. Thermodegradative analyses (TGA) were performed in a Mettler Toledo TGA/SDTA 851^{e}. The sample was heated from 25 to 700°C at a rate of 10°C/min, under nitrogen atmosphere. A Phillips CM10 Transmission electron microscope (TEM) was used to analyze the microstructure of the composites. The samples were prepared by ultramicrotomy and observed without any further treatment.

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RESULTS AND DISCUSSION

The MFI values (Table 1) did not vary significantly with the increment of the mixing rate (MR) at 170°C, which was expected due to the nature of the test and that composites had same filler content. Young's modulus (E) increased slightly with the mixing rate. On the other hand, the tensile strength (σ_b) increased significantly varying from 7.12 to 13.42 MPa, which indicated an improvement in HA dispersion into the polymeric matrix. The elongation at break (ε_b) did not vary significantly. Transmission electron micrographs confirmed a better filler dispersion at higher mixing rates, showing a smaller size of the HA agglomerates (Fig. 1). Thermal and thermodegradative properties did not show considerable variations either (Table 2). Even though TEM established a better dispersion at high mixing rates, agglomerated HA particles were still appreciable by eye sight. That is why the mixing temperature (MT) was then lowered by 10°C at 90 rpm to increase the shear stress in order to break down HA agglomerates and enhance filler dispersion. As expected, the MFI values did not vary substantially because of the reasons already explained (Table 1). For mechanical characterization, type I tensile specimens were

TABLE 1 Rheological and Mechanical Properties of HDPE/HA Composites Prepared at Different Mixing Conditions

MR (rpm)	MT (°C)	MFI (g/10 min)	E (MPa)	σ_b (MPa)	ε_b (%)
60	170	2.33 ± 0.08	365 ± 44	7.12 ± 2.3	5.58 ± 1.4
70	170	2.48 ± 0.17	350 ± 23	8.99 ± 3.2	6.74 ± 1.0
80	170	2.19 ± 0.04	447 ± 27	17.90 ± 0.6	5.99 ± 0.7
90	170	2.29 ± 0.06	435 ± 48	13.42 ± 3.8	5.92 ± 0.9
90	160	2.26 ± 0.05	409 ± 25	19.16 ± 0.7	11.44 ± 0.6

MR: mixing rate; MT: mixing temperature; MFI: melt flow index; E: Young's modulus; σ_b: tensile strength; ε_b: elongation at break.

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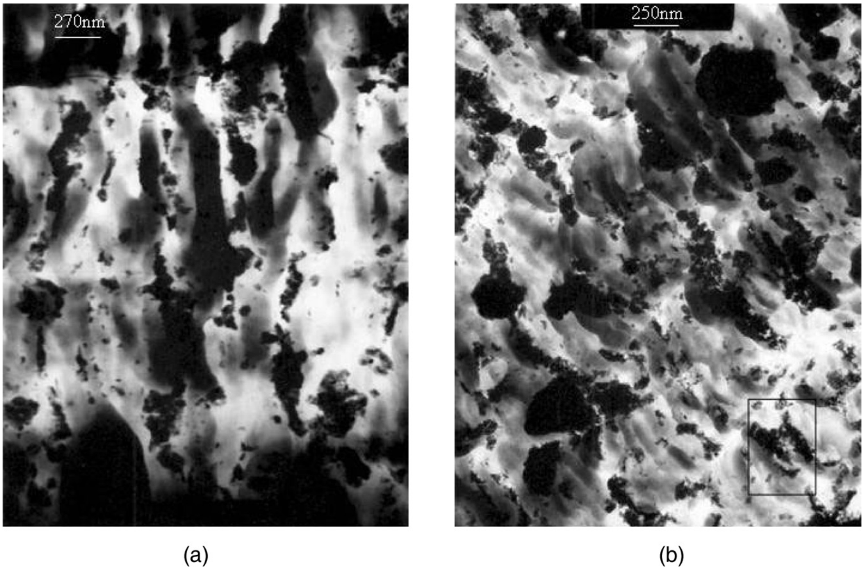

FIGURE 1 (a) Micrograph for HDPE/HA composite prepared at 170°C and 70 rpm, (b) HDPE/HA composite prepared at 170°C and 90 rpm.

employed Young's modulus did not vary with the decrease in temperature. However, a significant increase in the tensile strength and elongation at break was observed, evidencing that a tougher and more ductile material was obtained due to the improvement in filler dispersion. TEM studies confirmed the previous statement showing a significant reduction of particle agglomerates and uniformly dispersed filler in the polymer matrix (Fig. 2b).

After the mixing conditions were established at 160°C and 90 rpm, composites with 10, 20, 30 pph of HA were prepared. Tables 3 and 4

TABLE 2 Thermal, Thermogravimetric and Rheological Properties of HDPE/HA Composites Prepared at Different Mixing Conditions

MR (rpm)	MT (°C)	Tc (°C)	Tm (°C)	X (%)	Tid (°C)	Ea (kJ/mol)
60	170	112	127	61	457	309
70	170	112	127	66	453	289
80	170	112	128	60	458	309
90	170	112	127	60	459	319
90	160	113	126	60	460	315

Tc: crystallization temperature; Tm: melting temperature; X: crystallinity degree; Tid: initial decomposition temperature; Ea: activation energy.

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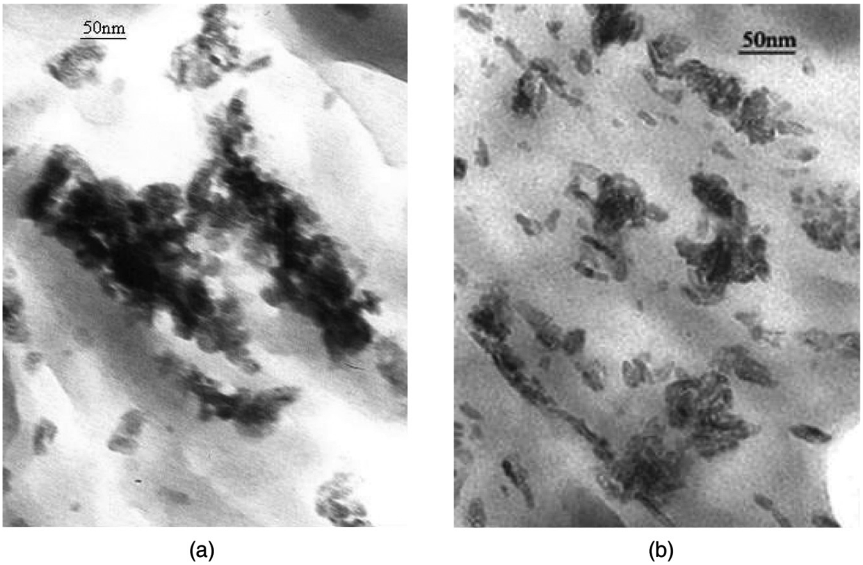

FIGURE 2 Micrographs for HDPE/HA (a) Composite prepared at 170°C and 90 rpm (zoom of Figure 1b), (b) Composite prepared at 160°C and 90 rpm.

show the results of the rheological, mechanical, thermal and thermogravimetric characterization of composites with different filler contents. The MFI values decreased with the increase in the filler content, which indicated an increase in the material's viscosity. This effect was attributed to the fact that the filler restricts the movement of the chains in the melted polymer. It is considered that for the maximum filler content, the MFI decreases too much compared to unfilled polyethylene. Type I tensile specimen were used for mechanical characterization. An enhancement in Young's modulus with filler content was appreciated signifying a rigidity gain for composites. This was also observed in an increase registered in tensile strength with

TABLE 3 Rheological and Mechanical Properties of HDPE/HA Composites with Different Filler Content

Material	MFI (g/10 min)	E (MPa)	σ_b (MPa)	ε_b (%)
HDPE	6.47 ± 0.13	301 ± 15	17.3 ± 5.7	1002.0 ± 93
HDPE/HA10pph	4.44 ± 0.11	369 ± 11	9.5 ± 1.7	46.0 ± 13.2
HDPE/HA20pph	3.27 ± 0.07	376 ± 2	17.1 ± 1.7	18.7 ± 3.2
HDPE/HA30pph	2.26 ± 0.05	409 ± 25	19.1 ± 0.7	11.4 ± 0.6

TABLE 4 Thermal and Thermogravimetric Properties of HDPE/HA Composites with Different Filler Content

Material	Tc (°C)	Tm (°C)	X%	Tid (°C)	Ea (kJ/mol)
HDPE	113	128	63	460	168
HDPE/HA10pph	113	126	65	455	231
HDPE/HA20pph	113	126	63	460	316
HDPE/HA30pph	113	126	60	460	315

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HA addition (Table 3). Good filler dispersion as a consequence of previous mixing optimization reduced possible fracture points thus increasing the energy necessary to produce the fracture in the sample.

Composites exhibited a strong decrease in elongation at break with the inclusion of HA particles into the polymer matrix, indicative of a ductile to brittle transition for high filler contents [10]. It can be explained that at higher filler contents, filler-filler interactions occur during tensile testing reducing possible elongation [11]. The more amount of filler is present; the less polymer matrix is going to suffer deformation propitiating an early sample fracture.

Thermal analyses showed that HA did not have any effects on crystallization (Tc) and melting (Tm) temperatures as well as in composites crystallinity degree (X) although a rise in Tc and in crystallinity was expected because of filler particle size [12]. Initial decomposition temperatures also did not vary with HA addition but an increase in activation energy was observed along with filler content, meaning composites gained thermal stability. This effect can be attributed to the fact that although the HA represents a discontinuity in the polymer matrix, if it is homogeneously distributed, it can delay degradation reactions. From results previously discussed 20 pph of HA was selected as optimum filler content because it exhibited an adequate mechanical performance without losing processability as MFI tests indicate, and a maximum thermal stability was obtained.

In order to improve filler-matrix interactions, a titanate coupling agent (Lica 12) was added to the system at different proportions. Tables 5 and 6 show the rheological, mechanical, thermal and thermodegradative properties of the composites prepared with Lica12. MFI values indicated that the coupling agent did not have a significant influence on the polymer's viscosity. Type IV tensile specimens were employed for the mechanical characterization of the coupled composites. Mechanical properties also did not show substantial variation with the addition of the Lica 12. Variations registered are between standard deviation's range. DSC studies showed no significant

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TABLE 5 Rheological and Mechanical Properties of HDPE/HA Composites Coupled with Lica 12

Material	MFI (g/10 min)	E (MPa)	σ_b (MPa)	ε_b (%)
HDPE/HA20 ppc	3.27 ± 0.07	1365 ± 85	18.9 ± 1.1	6.8 ± 1.7
HDPE/HA20pph Lica12 0.3%	3.63 ± 0.14	1277 ± 75	16.8 ± 2.3	7.2 ± 2.1
HDPE/HA20 pph Lica12 0.5%	3.82 ± 0.09	1338 ± 76	18.3 ± 1.2	6.7 ± 0.8
HDPE/HA20pph Lica12 0.7%	3.78 ± 0.05	1302 ± 106	18.6 ± 0.4	7.2 ± 1.2
HDPE/HA20pph Lica12 1.0%	3.75 ± 0.05	1348 ± 72	19.5 ± 1.2	6.3 ± 1.7

TABLE 6 Thermal and Thermogravimetric Properties of HDPE/HA Composites Coupled with Lica 12

Material	X (%)	Tc (°C)	Tm (°C)	Tid (°C)	Ea (kJ/mol)
HDPE/HA20pph	63	113	126	460	316
HDPE/HA20pph Lica12 0.3%	63	113	126	461	364
HDPE/HA20pph Lica12 0.5%	56	113	126	461	360
HDPE/HA20pph Lica12 0.7%	55	113	126	459	361
HDPE/HA20pph Lica12 1.0%	56	113	126	455	289

variation in crystallization and melting temperatures but a slight decrease in the crystallinity degree for composites coupled with 0.5, 0.7 and 1.0% Lica 12 was observed. This effect can be attributed to an excess of coupling agent present in the polymer matrix that interferes crystallization.

Thermogravimetric analyses showed that the addition of Lica 12 increased the thermal stability, due to an improvement in polymer-filler interactions. Lica 12 concentration did not affect thermal stability, with the exception of the composite coupled with 1.0%, whose activation energy decreased. This can be explained by the fact that there is excessive coupling agent in the polymer. On the other hand, some authors have reported that titanium is an unstable metallic center that can initiate degradation of polymer matrix [9].

CONCLUSIONS

High mixing rates and low temperatures improved the filler dispersion into the polymer matrix in an internal mixer. Optimum mixing conditions for compounding the HDPE/HA composites were 160°C and 90 rpm. An increase in filler content produced fragility in the composites, and initiated early fracture of the material. Optimal behavior was observed when HA content was 20 pph. Lica 12's presence did not affect the mechanical, thermal and rheological behavior of the composites, with exception of the crystallinity degree, which decreased slightly due to an excess of the agent. Thermal stability increased with the coupling agent, but a decrease was observed for the highest agent concentration.

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