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Comparison Between Different Syntesis Methods of PMMA/HA Using Ultrasonic Radiation

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Summary: The use of PMMA as dental and osseous cement and also in the fabrication of intraocular lenses has been widely reported. The combination of its excellent properties with those of hydroxyapatite (HA) to form a composite material, can result in very interesting properties as a biomaterial. The key is to obtain a good filler dispersion and interface bonding. Ultrasonic radiation seems to be a very versatile method for the synthesis of these materials, since the use of conventional initiators can be avoided, the filler dispersion improved and the interface interaction can be promoted. In the present work PMMA/HA composite materials were prepared by three different synthesis routes using ultrasonic radiation, in order to study the effect of the synthesis method on the final microstructure. **Method I**: *in situ* synthesis of PMMA and HA, under ultrasonic radiation by emulsion polymerization of MMA and HA precursors. **Method II**: *in situ* synthesis of HA, (from its precursors) by high frequency ultrasound in commercial PMMA solution **Method III**: *in situ* polymerization of MMA under high frequency ultrasonic radiation and adding HA to the solution and **Method IV** Mixing of hydroxyapatite nanocrystals, in different proportions, in a solution of commercial PMMA, by different periods from 10 min to 7 h, under low frequency (conventional) ultrasonic radiation, to compare the effect of high frequency and conventional ultrasound radiation. The different materials were characterized by FTIR, SEM, TEM, DRX, ^{1}H NMR and TGA. The results showed that, all the composites prepared by *in situ* synthesis showed an interaction between HA and PMMA, manifested by a bonding of the phosphate groups with the polar groups of the polymer matrix observed by FTIR. On the other hand, when the synthesis was carried out simultaneously adding HA and PMMA precursors a inhibition of the polymerization reaction of MMA was observed.

Keywords: characterization; composites; HA; PMMA; ultrasonic irradiation

Introduction

Different methods of synthesis of composites have been explored in order to improved interface interaction and therefore mechanical properties. The methods can be physical or chemical. Physical methods[1] (extrusion, mechanical mixing, etc), in general, only form weak bonding, van der Waals type that do not strongly contribute to the interface interaction. Chemical methods, on the other hand, can form stronger bonding at the interface improving the final properties of the composite.

The use of *in situ* synthesis by ultrasonic irradiation[2–4] is an alternative method of modifying the interface interaction and dispersion of the filler in the polymer matrix. This method has the advantage of avoiding the use of interface coupling agents and

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therefore looks potentially interesting for the synthesis of biomaterials. Composites of poly(methylmethacrylate) and hydroxyapatite (PMMA/HA) are very promising materials for biomedical applications, due to the high biocompatibility of both compounds. On the other hand, an adequate dispersion of the filler (HA) into the polymer matrix with a good interfacial adhesion is one of the important factors governing the final mechanical behavior of these composites.

Ultrasound comprises sonic waves with frequencies in the range of 0.001 to 104–107 MHz. When these waves are transmitted through water, cavitation takes place. During this process physical and chemical effects provide a new route for chemical reactions that are difficult or impossible to achieve under conventional conditions. The emulsion polymerization of some monomers can occur under ultrasonic irradiation, without the conventional free radical initiators.[5–7] Makino *et al*.[6] reported that water molecules were dissociated to high concentrations of $OH^\bullet$ and $H^\bullet$ radicals under this process. Therefore, different reactions occur but the exact mechanism taking place is unknown. In order to understand the different processes taking place and how synthesis variables affect the final product, PMMA/HA composite materials were prepared by four different synthesis routes using ultrasonic radiation: **Method I**: *in situ* synthesis of PMMA and HA, under ultrasonic radiation by emulsion polymerization of MMA and HA precursors. **Method II**: *in situ* synthesis of HA, (from its precursors) by high frequency ultrasound in commercial PMMA solution. **Method III**: *in situ* polymerization of MMA under high frequency ultrasonic radiation and adding previously synthesized HA to the solution under high frequency ultrasound. **Method IV** this method was used in order to compare the effect of high frequency and conventional ultrasound radiation, the mixing of hydroxyapatite nanocrystals, in different proportions, was carried in a solution of commercial PMMA, by different periods from 10 min to 7 h, under conventional ultrasonic radiation.

Experimental Part

Materials

Polymethylmethacrylate (PMMA, MD-2002) of density 0.9233 g/cm^3, and 2-butanone as solvent were used. Hydroxyapatite was synthesized using calcium hydroxide, $Ca(OH)_2$, and ammonium phosphate, $(NH_4)_2HPO_4$ as initial reagents.

Syntheses of the Composites

Composites PMMA/HA were prepared by four different methods using either MMA and hydroxyapatite precursors, MMA and previously synthesized HA or commercial PMMA and hydroxyapatite precursors, these three methods were carried out using high frequency ultrasound and a fourth method using ultrasonic agitation (conventional ultrasound) mixing commercial PMMA and HA previously synthesized. The detailed description of each method is as follows:

Method I: Composites formed by *in situ* polymerization of MMA, using SLS surfactant and *in situ* HA precursors in different wt%, under high frequency ultrasonic radiation for 1 h.

Methyl methacrylate (14% w/w MMA) analytical grade 99.8% (density: 0.943 g/cm^3) was thoroughly washed in 10% NaOH solution to remove the inhibitor agent and several times in distilled water, dried with anhydrous Na_2SO_4 and finally distilled in vacuum. The surfactant used was sodium lauryl sulphate (1.5%wt/vSLS) (MW 288,38 g/mol). The reaction was carried out in an ultrasonic generator (Fisher PG100 MSE, Mod. 150W) operating at 20 kHz, equipped with a double jacket glass vessel and a 19 mm Ti sonic wave emission probe controlled by a standard power source. Different wt% of hydroxyapatite precursors were added to obtain nominal compositions of 10, 15, 20 and 25% of hydroxyapatite in PMMA under 60 min of ultrasonic radiation.

Method II: commercial PMMA and HA synthesized *in situ* from precursors.

Commercial polymethylmethacrylate (PMMA, MD-2002, density 0.9233 g/cm^3), using 2-butanone, as solvent for PMMA was employed. Hydroxyapatite was synthesized using calcium hydroxide, $Ca(OH)_2$, and ammonium phosphate, $(NH_4)_2HPO_4$ as initial reagents. HA precursor components (calcium hydroxide and ammonium phosphate) were added in stoichiometric amounts to obtain composites with 10, 20, 30 and 40 wt% of HA. Immediately the samples underwent ultrasonic radiation for different periods (15, 25, 35 and 60 min). An ethanol/water solution (1:1) was added to precipitate the material. The solution was kept resting for 1h and then centrifuged. Composites were dried at 60 °C and weight to determine the synthesis conversion.

Method III: *in situ* polymerization of MMA under high frequency ultrasonic radiation and addition of previously synthesized HA, in concentrations of 10, 20 and 30w%.

Polymerization of MMA was carried out using an anionic surfactant (SLS, 1.5 wt/v%) as emulsifier. The water/monomer (w/m) ratio was varied from 5 to 15. Nanocrystalline Hydroxyapatite previously synthesized by co-precipitation[9] was added in different proportions to the mixture. This system was placed under ultrasonic radiation for periods of 10 to 60 min.

Method IV: the mixing of hydroxyapatite nanocrystals, in different proportions (10, 20. 30, 40 and 50%), were carried in a solution of commercial PMMA, for periods 10min, 30 min, 1 h, 2 h, 4 h and 7 h, under conventional ultrasonic radiation.

Characterization of the Composites

FT-IR spectra were recorded in a Nicolet Magna_IR 560 E.S.P. Spectrometer after 32 scans and at 2 cm^{-1} of resolution and a Perkin Elmer FTIR spectrum 100 equipment with a resolution of 0.5 cm^{-1}.

To determine the weight percentage of the synthesized hydroxyapatite thermogravimetric test (TGA) were carried out, using a SDT- Q600 TA equipment in nitrogen atmosphere and a heating rate of 10 °C/min. The microstructure was evaluated by proton nuclear magnetic resonance spectroscopy (^{1}H RMN) in a BRUKER ADVANCED 300 spectrometer, operating at 300, 13 KHz.

Transmission electron microscopy (TEM) analyses were performed using a Phillips CM10 and a JEOL 1200 microscopes, operating at 100 keV. Samples were prepared by ultramicrotomy without any further treatment. Scanning electron microscopy was carried out in a Hitachi F-S500. XRD patterns were recorded using a diffractometer (Siemens, Model D 500) in the 2θ range of 20°–60°.

Results and Discussion

Method I: *in situ* Synthesis of PMMA and HA, under Ultrasonic Radiation by Emulsion Polymerization of MMA and HA Precursors

This method consisted in the polymerization of the monomer MMA using sodium lauryl sulfate (SLS) as surfactant, and simultaneously adding the hydroxyapatite precursors: ammonium phosphate and calcium hydroxide, in different proportions. The emulsion was irradiated for 60 min.

Figure 1 shows a typical TGA thermogram of PMMA/HA composites, and Table 1 is a summary of the results of the different polymerization reactions carried out to obtain the different composites by *in situ* synthesis.

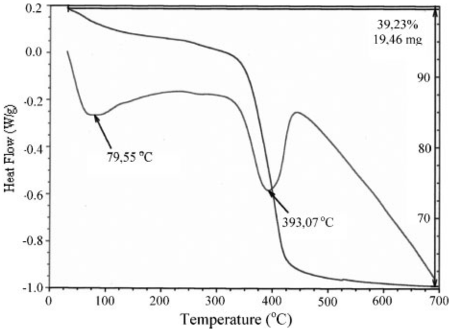


Figure 1.

TGA Thermogram of PMMA/61% HA prepared by *in situ* synthesis using 1.5% SLS and 14% MMA (60 min of ultrasonic irradiation).

Table 1.
Conversion of *in situ* synthesis of composites PMMA/HA carried out by emulsion polymerization using 1.5% wt/v of SLS and 14% v/v of MMA after 60 min of ultrasonic irradiation.

Reaction	wt%HA nominal	wt%HA obtained by TGA
1	10	70
2	15	52
3	20	84
4	25	61

This table shows that the amount (wt%) of hydroxyapatite obtained is much higher than the theoretical values. This suggest that polymerization was inhibited during the *in situ* synthesis of the composite (PMMA/ HA). The synthesis of hydroxyapatite under high frequency ultrasound is very fast, after 5 min of reaction the nanocrystals are already formed. The polymerization of MMA is a slower process, therefore, it is possible that the HA nanoparticles develop a high surface charge density acting as sites of reaction. Free radicals formed in the system can be trapped at the nanocrystals surface, decreasing the polymerization reaction. As the volume fraction of HA nanoparticles increases in the media, more free radicals are deactivated and polymerization decreases.[10] This effect is clearly observed in Table 1. A similar result was found by Xia,[11] during the *in situ* synthesis by emulsion polymerization of buthylmethacrylate and silica under high frequency ultrasonic radiation.

Figure 2 shows the FTIR spectra of two PMMA/HA composites with HA proportions of (a) 52 wt% and (b) 84 wt%.

The spectra show the characteristic PMMA vibration bands corresponding to the C-H bond (3000 y 2900 cm^{-1}) of the CH_2 groups. On the other hand the carbonyl absorption band shows a strong signal at 1734 cm^{-1} more intense in the sample with 50% HA.

Additionally, in the region 1100–1030, 960, 630–560 cm^{-1} the vibration bands of the phosphate groups are observed with high intensity, also the triplets of the methylene groups and the absorption of the C–O group are observed with very low intensity, due to the overlapping of the phosphate signal. These spectra show that a mixture between both phases is taking place, and shifts in the vibration bands of the phosphates and carbonyl groups are observed, suggesting that bonding interactions were formed under ultrasonic radiation. Figure 3 is a typical XRD pattern of the composite showing the hydroxyapatite reflections together with an amorphous background from PMMA.

Figure 4 shows a typical ^1H RMN spectrum of PMMA/HA composites prepared by *in situ* method. All spectra were very similar. The characteristic PMMA signals can be observed at: 0.83 ppm; (1.00–1.19) pmm and 1.23 ppm, attributed to syndiotactic, heterotactic and isotactic chain traiads, respectively. The microtacticity results are shown in Table 2 for some of the PMMA/HA composites, also pure PMMA synthesized under the same conditions is shown.

The polymer obtained has a structure formed by chain triads of 60% syndiotactic and 30% atactic character. Therefore, it seems that HA content does not significantly modify the polymer microstructure.

Values of the glass transition temperature of PMMA (126 °C) are in agreement with the triads formation.

Figure 5 shows the SEM secondary image electron micrograph of the composites, synthesized *in situ* with different HA content.

The morphological characteristics of these composites prepared by *in situ* synthesis can be attributed to the large amount of HA present, that due to its nanometric size has a strong tendency to form agglomerates.

Method II: *in situ* Synthesis of HA, (from its precursors) by High Frequency Ultrasound in Commercial PMMA Solution

Table 3 shows the conversion of the *in situ* synthesis of the composites PMMA/HA, obtained by this method, a good approximation with the nominal values is

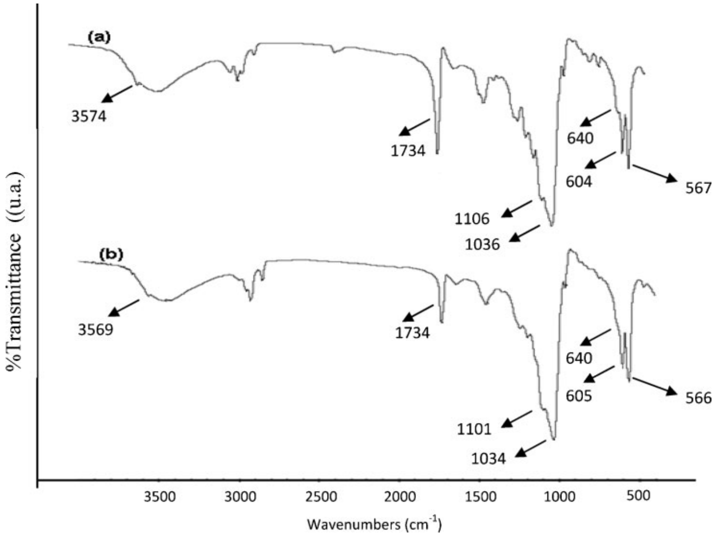


Figure 2.

FTIR of composites: (a) PMMA/52%HA (b) PMMA/84%HA prepared by simultaneous *in situ* synthesis of PMMA and HA under 60 min of ultrasonic irradiation.

observed. TGA analysis (Figure 6) was used to determine the percentage of the inorganic phase formed (HA) in the PMMA matrix, and also to confirm the conversion values obtained by calcination. In general, a good correspondence between both techniques (TGA and calcination) was obtained. The glass transition temperature for PMMA was 128 °C was in good agreement with those reported in the literature.[12]

The polarity characteristics of the polymer and the degree of miscibility of HA in the dissolved PMMA in 2-butane allowing the formation of the compound can explained these results.

Figure 7 shows a typical FTIR spectrum obtained for the different composites as-synthesized and after calcination. Figure 7a shows the spectrum of the synthesis obtained after ultrasonic irradiation for 25 min, using PMMA and HA precursors to

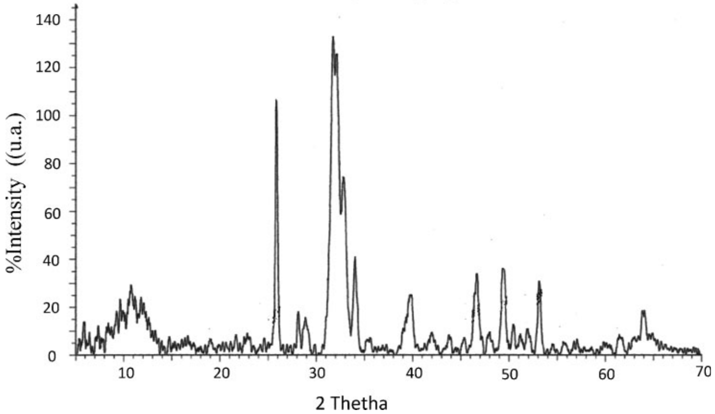


Figure 3.

XRD pattern of composite PMMA/61% HA prepared by *in situ* synthesis using 1.5 wt% of SLS and 14wt% of MMA (60 min of ultrasonic radiation).

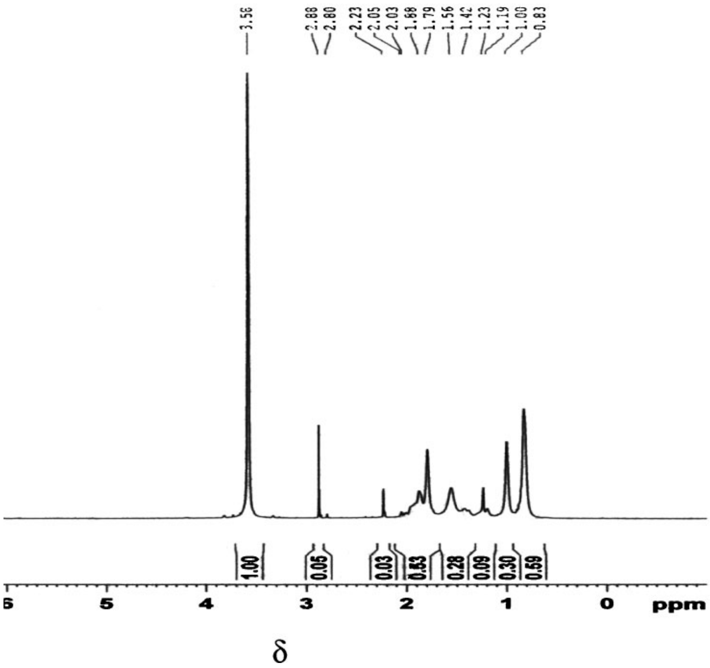


Figure 4.
^{1}H RMN spectrum of PMMA/70%HA prepared from 1.5% SLS and 14% MMA after 60 min of ultrasonic irradiation.

give a theoretical percentage of 30 wt.% of HA, in good agreement with the experimental value obtained (Table 3). The spectrum shows the PMMA vibration bands in the regions 3000–2852 cm^{-1}, 1736 cm^{-1}, 1440–1157 cm^{-1} and 1000–800 cm^{-1}, and the HA bands in the regions: 1100–1030 cm^{-1}, 960 cm^{-1} and 560–630 cm^{-1}. The spectrum of the sample after calcination (Figure 7b) shows all the bands corresponding to HA. A slight shifting is observed in the phosphate bands at 1090–1034 cm^{-1} with respect to pure synthesized HA, and also a shifting in the carbonyl groups of the composite PMMA/HA, with respect to pure PMMA (1728 cm^{-1}). This suggests an interaction between the polymer matrix and HA.

Figure 8 shows the XRD patterns of the synthesized composites confirming the formation of nanometric HA in an amorphous polymer matrix (PMMA).

The morphology of the PMMA/HA composites was analyzed by TEM. Figure 9 shows an image of the composite PMMA/30%HA, synthesized under ultrasonic for 15 min, where hydroxyapatite particles encapsulated in a thin film of PMMA are observed, forming ‘‘pockets’’ of the composite material. Also a good

Table 2.
Tacticity degree observed in PMMA/HA composites obtained by emulsion polymerization using 14% MMA and HA, under 60 min of ultrasonic irradiation.

% HA obtained	Microestructure		
	Isotactic (mm)	Atactic (rm)	Sindiotactic (rr)
61	7.22	30.93	61.85
70	8.91	27.72	63.37
0% (pure PMMA)	1.60	29.30	69.20

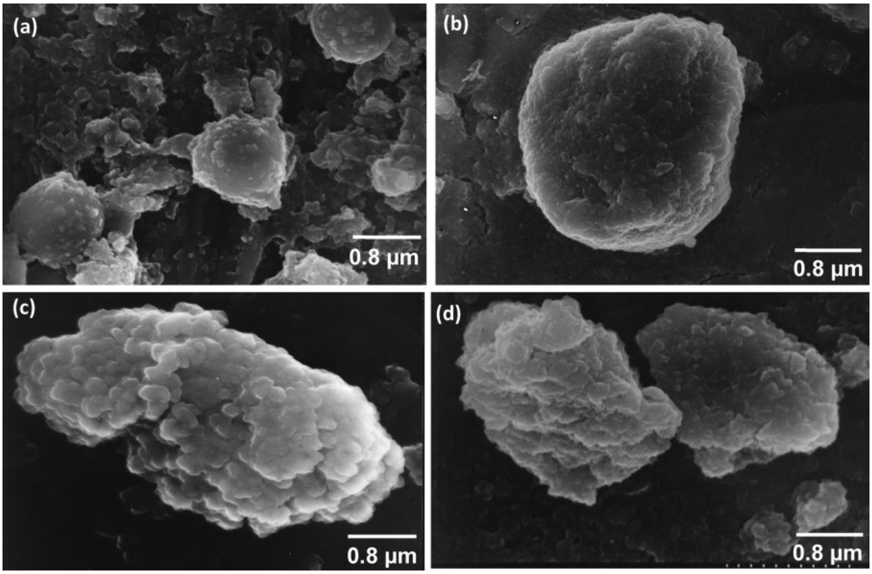


Figure 5.
Scanning electron micrographs of composites: (a) PMMA/52%HA; (b) PMMA/61%HA; (c) PMMA/70%HA; (d) PMMA/84%HA.

dispersion of HA in the polymer matrix was obtained. This behavior was characteristic for all the composites obtained by this method.

Method III: *in situ* Polymerization of MMA Under High Frequency Ultrasonic Radiation and Adding Previously Synthesized HA to the Polymer Solution

Different water/monomer ratios from 5 to 15 and polymerization periods from 10 to 60 min were employed in order to get the optimum polymerization conditions. These were: water/monomer ratio:15 and radiation time: 60 min. Figure 10 shows the FTIR for this w/m ratio and 20 wt%.HA. The vibration bands characteristic of PMMA and HA are clearly observed, also a shift in the carbonyl band and a slight shift in the phosphate bands are observed suggesting bonding interactions between both compounds.

Table 3.
Hydroxyapatite obtained from *in situ* synthesis of HA in solution of commercial PMMA under ultrasonic irradiation for different periods.

Polymer	Ultrasonic Irradiation Time (min)	% HA nominal	%HA obtained
PMMA	15	30	30
	25		26
	35		28
	15	40	39
	25		36
	35		39

TEM analysis of the composite PMMA/20%HA (Figure 11) shows a poor dispersion of HA embedded in the polymer matrix after 60 min of ultrasonic irradiation. The conversion % of PMMA was approximately 90%.

Method IV Conventional Ultrasound method

As a control experiment conventional ultrasonic mixing was carried out for different agitation periods from 10 min to 7 h. Figure 12 shows the FTIR spectrum for PMMA/30%HA, after 25 min of agitation, in this spectrum the contribution of PMMA vibration bands is very low, due to the sample heterogeneity for low mixing periods, with some parts of the sample rich in

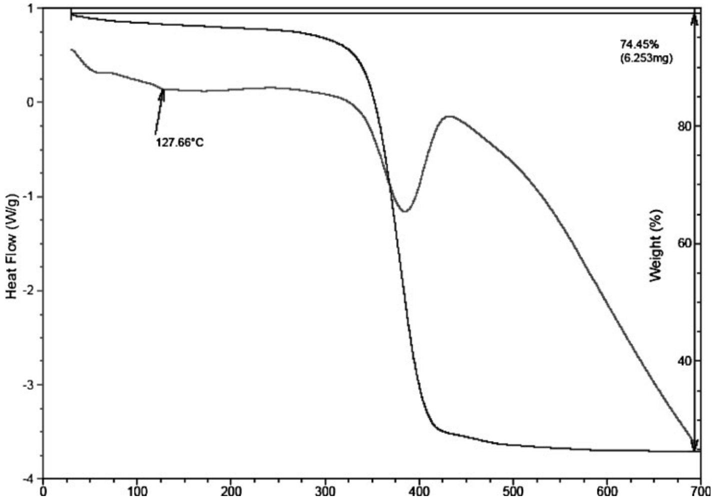


Figure 6.
TGA and DSC of PMMA/HA (30%) 25 min of ultrasonic irradiation.

PMMA and others in HA. Although no specific interaction was observed, however the HA dispersion was very dependent of the agitation period. Long agitation periods, longer than 2 h, resulted in very good dispersion. However for short agitation periods formation of agglomerates was observed. Figure 13 shows TEM images for 2, 4 and 7 h of agitation for PMMA/20%HA and PMMA/50%HA. It can be clearly observed that longer periods result in a better dispersion and as expected low

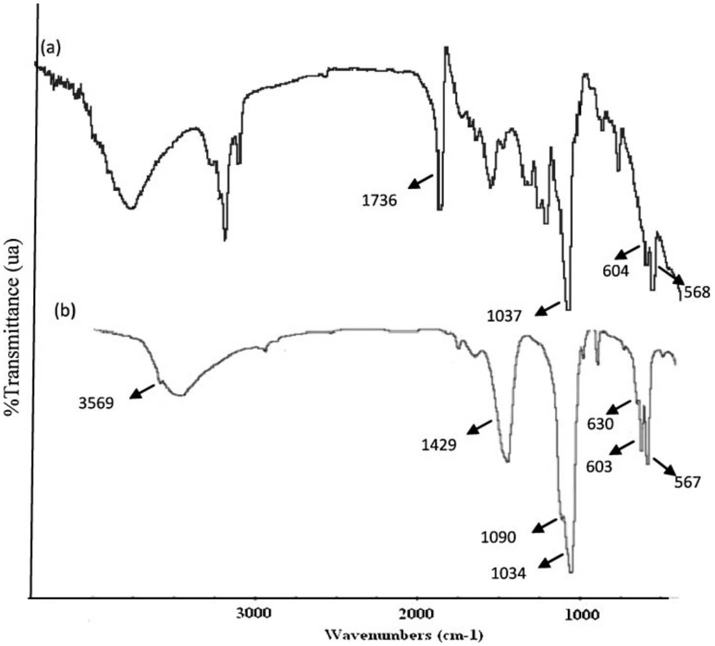


Figure 7.
FTIR spectra of: a) PMMA/30%HA 25 min of ultrasonic irradiation, b) Calcinations residue of composite.

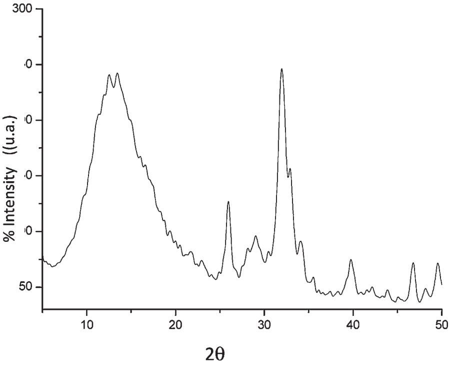


Figure 8.
XRD of PMMA/40%HA composite prepared in PMMA dissolution under 35 min of ultrasonic irradiation.

HA concentrations show better dispersion than high concentrations.

DSC experiments were carried out in these materials, in order to see if agitation time affects the glass transition temperature, showing that it remains almost constant for all periods.

Comparison of the Different Methods

A comparison between the four methods used for PMMA/HA synthesis using ultrasonic radiation is discussed in this section.

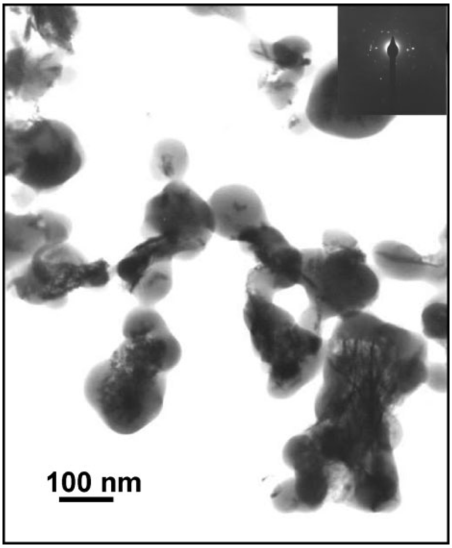


Figure 9.
Image of the composite PMMA/30%HA, after 15 min of ultrasonic irradiation.

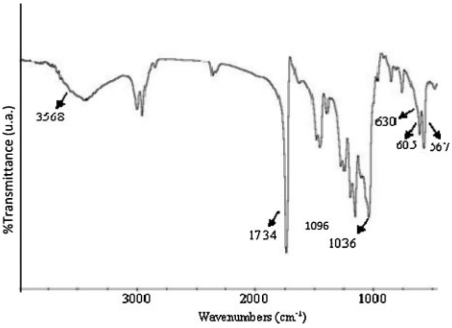


Figure 10.
FTIR spectrum of PMMA/20%HA synthesized from in situ polymerization of MMA and with previously synthesized HA (60 min of ultrasonic irradiation).

Table 4 shows a comparison of three main FTIR vibration bands corresponding to the characteristic phosphates groups of HA and the carbonyl group of PMMA. A shift in the carbonyl groups and in the phosphate groups is observed for Methods I, II and III. Figure 14 shows the comparison of the FTIR of the composites obtained by the different methods and the PMMA obtained under the same conditions. This behavior is correlated with the microstructure observed by TEM and SEM. It is obvious that an interface bonding interaction between HA and PMMA is obtained for these methods. Method IV did not show any shifts in the

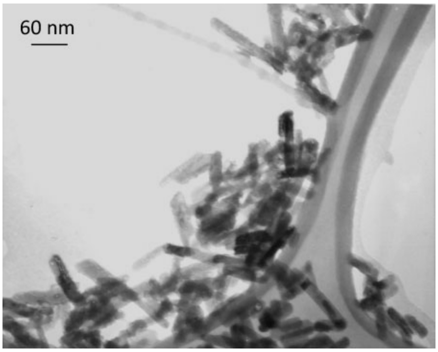


Figure 11.
TEM image of PMMA/20%HA obtained by *in situ* polymerization of MMA using a water/MMA = 15 and with previously synthesized HA after 60 min of ultrasonic irradiation.

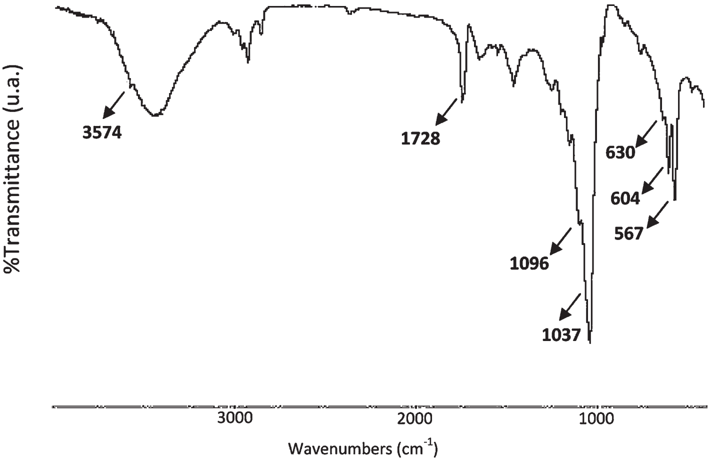


Figure 12.
FTIR of PMMA/30%HA prepared by mechanical mixing of dissolved PMMA and HA by low frequency ultrasound (25 min of agitation).

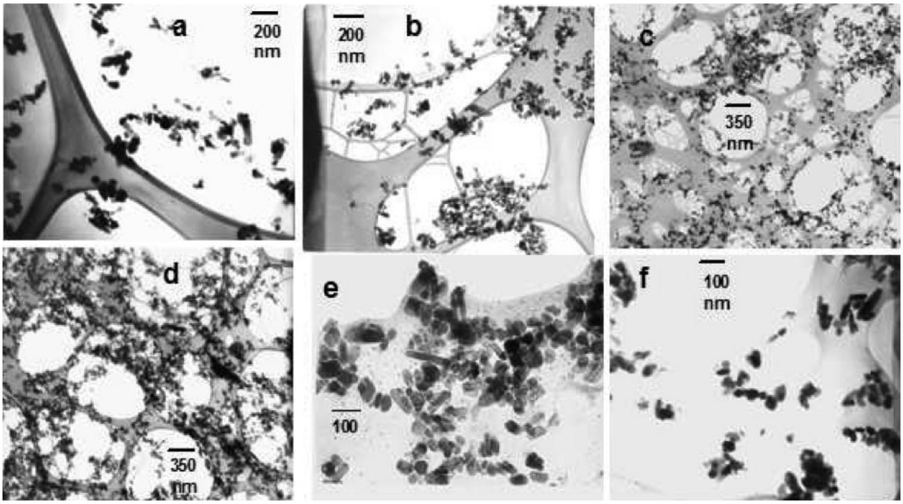


Figure 13.
PMMA/HA composites prepared by mixing PMMA and different concentrations of HA under low frequency ultrasound for different periods a) 20%HA 2 h, b) 20%HA 4 h, c) 20%HA 7 h, d) 50%HA 2 h, e) 50%HA 4 h, f) 50%HA 7 h.

Table 4.
FTIR vibration bands for PMMA/HA composites obtained by the different methods.

Material/bands	HA	PMMA	PMMA/HA	PMMA/HA	PMMA/HA	PMMA/HA
			Method I	Method II	Method III	Method IV
CO		1728	1734	1736	1734	1728
OH^{-}	3574, 630		3574, 640	3569, 630	3568, 630	3574, 630
PO^{-3}	1096, 1038		1106, 1036	1090, 1034	1098, 1036	1096, 1037
PO^{-3}	630					
	603, 568		630,604, 567	630,601, 562	630,605, 567	630, 604, 567

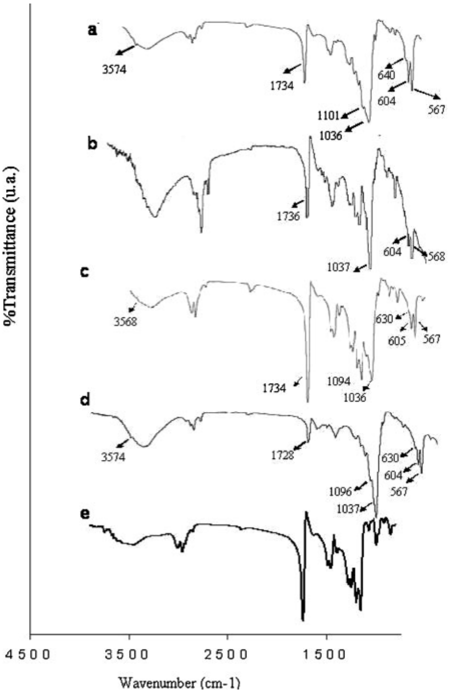


Figure 14.
FTIR of PMMA and PMMA/HA composites prepared by the different methods: a) method I, b) method II, c) method. III, and d) method IV, e) PMMA.

vibration bands of phosphates or carbonyl groups, implying that no interaction was formed between HA-PMMA. The TEM morphology is also in agreement with this observation, where only a good dispersion was evident, depending of the radiation period and HA content.

The interaction between PMMA and HA are based on the polarity characteristics of this polymer and the degree of miscibility of HA in the dissolved PMMA in 2-butane. FTIR evidenced bonding between the ester group of PMMA and the phosphates groups of HA. Different possible mechanisms could explain the interactions formed during the synthesis by the different methods used. The proposed mechanisms[13] are shown in Figure 15,16 and 17. According to the shifts of the vibration bands observed one or various mechanisms could better explain the interactions formed.

Figures 15 and 16 propose that the negative ions of HA (PO_4^{-3}, OH^-) are susceptible of reacting with the carbonyl group by a nucleophilic attack.[8] Figure 17 propose the substitution of the methoxy group of the ester of PMMA by the Ca^+ ion due to a hydrolysis reaction, this can be a consequence of the basic media generated by the ammonium hydroxide formed during the HA synthesis.

These three mechanisms could be operating simultaneously during the synthesis by methods I and II. However, in the synthesis by method III only the first

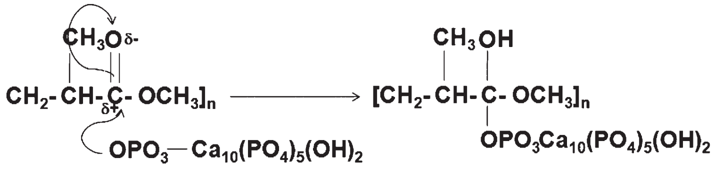


Figure 15.
Mechanisms of PMMA/HA interactions by nucleophilic addition of PO_4^{-3} group.

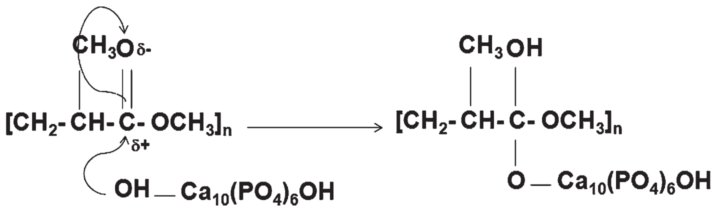
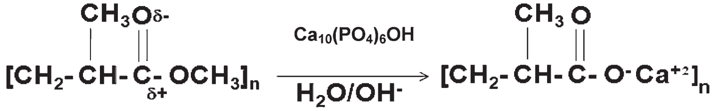


Figure 16.
Mechanisms of PMMA/HA interactions by nucleophilic addition of OH^- group.



$$\left[CH_2\text{-}\overset{CH_3}{\overset{|}{CH}}\text{-}\underset{\delta+}{\overset{O^{\delta-}}{\overset{\|}{C}}}\text{-}OCH_3\right]_n \xrightarrow[H_2O/OH^-]{Ca_{10}(PO_4)_6OH} \left[CH_2\text{-}\overset{CH_3}{\overset{|}{CH}}\text{-}\overset{O}{\overset{\|}{C}}\text{-}O^-Ca^{+2}\right]_n$$

Figure 17.
Proposed Mechanisms of PMMA/HA interactions by basic hydrolysis reaction.

two mechanisms are possible, since the conditions for a hydrolysis reaction are not given.

Conclusion

Using ultrasonic radiation is possible to establish interface interaction between PMMA and HA. Strong interactions seem to result when the synthesis is carried out by *in situ* methods either of polymerization of MMA (method I and III) or synthesis of HA (method II) or both (Method I).

When the precursors of HA are added simultaneously with the monomer, polymerization is inhibited and a composite with a very high HA concentration is obtained.

When conventional ultrasound mixing is performed no interface interactions were observed.

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