ISOTHERMAL CRYSTALLIZATION KINETICS OF IRRADIATED HDPE/HA COMPOSITES WITH A STERILIZATION DOSE OF GAMMA RAY

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ABSTRACT

The objective of this work was to study the isothermal crystallization of High Density Polyethylene/Hydroxyapatite nano-composites, with 2 and 5 phr of HA, non-irradiated and irradiated with 25 kGy (sterilization dose) of ã-Ray from a ^{60}Co source at a rate of 4.8 kGy/h in air and at room temperature. The selected crystallization temperatures were 118, 117, 116 y 115 ºC. The crystallization kinetics was analyzed using the Avrami model whose parameters were optimized using a non-linear regression technique. Experimental data, as well as their simulation with the Avrami model show a clear influence of the crystallization temperature, the amount of HA added and of the applied radiation. The Avrami model satisfactorily correlates experimental data for the non-irradiated samples of pure HDPE and HDPE/HA compounds at the highest temperature of crystallization (T_c). However, as the crystallization temperature decreases, the simulated curves increasingly deviate from experimental data, specifically at the highest values of the relative crystallinity. This effect is even stronger on irradiated samples of HDPE and HDPE/HA compounds.

Keywords: Crystallization, Isothermal, HDPE, Hydroxyapatite, Irradiated, ã-Ray.

CINÉTICA DE CRISTALIZACIÓN ISOTÉRMICA DE MEZCLAS DE PEAD/HA IRRADIADAS CON UNA DOSIS DE RAYOS GAMMA PARA ESTERILIZACIÓN

RESUMEN

El objetivo de este trabajo fue estudiar la cinética de cristalización de mezclas de Polietileno de Alta Densidad (PEAD) con 2 y 5 phr de Hidroxiapatita (HA) nanométrica, no irradiadas e irradiadas con 25 kGy (dosis de esterilización) de radiación gamma proveniente de una fuente ^{60}Co, a una velocidad de 4.8 kGy/h en aire y a temperatura ambiente. Las temperaturas de cristalización elegidas fueron 118, 117, 116 y 115 ºC. La cinética de cristalización se analizó usando el modelo de Avrami con parámetros evaluados usando una técnica de regresión no linear. Los datos experimentales como también los valores simulados con el modelo de Avrami muestran una clara influencia de la temperatura de cristalización del contenido de HA en la muestra y de la cantidad de radiación aplicada. El modelo de Avrami correlaciona satisfactoriamente los datos experimentales para las muestras de PEAD y mezclas de PEAD/HA, obtenidos a la temperatura de cristalización (T_c) más elevada. Sin embargo, a medida que la temperatura de cristalización disminuye, los valores simulados por el modelo se desvían cada vez más de los datos experimentales, especialmente a valores altos de cristalinidad relativa. Se encontró que la aplicación de la radiación gamma incrementa las desviaciones.

Palabras clave: Cristalización, Isotérmica, PEAD, Hidroxiapatita, Irradiada, Rayos-ã.

INTRODUCCIÓN

Composites of polymers with ceramic fillers are considered to be a new class of very interesting materials. High-Density

Polyethylene (HDPE) usually shows low toxicity and has been recommended as a suitable material for bone tissue substitution. On the other hand, hydroxyapatite (HA) is a natural compound of bones and hence, a biocompatible

ceramic. Owing to their properties, their mixtures may have a potential use in the biomedical area. Consequently, their mechanical behavior is actually being widely studied (Sousa *et al.* 2002; Wang *et al.* 1994; Rea *et al.* 2004a, 2004b; Albano *et al.* 2006). However, it is known that mechanical properties are related to some variables, one of which could be the crystallization rate, area where the influence that the HA have on the HDPE crystallization process, is scarcely known. Besides, biomaterials could be irradiated with gamma ray with the purpose of sterilization and also with the intention of modifying structural HDPE characteristics (Albano *et al.* 2005).

The role that the polymer crystalline structure has on mechanical behaviour, specifically on tensile properties, like the Young's modulus and tensile strength, and the effect that certain kinds of radiation have on crystallinity, heighten the importance of studying the isothermal crystallization process of HDPE/HA nano-composites with 2 and 5 phr of HA, not irradiated and irradiated with a dose of 25 kGy of gamma ray at a rate of 4.8 kGy/h in air and at room temperature.

The chosen crystallization temperatures for this study were 118, 117, 116 y 115 ºC, and experimental results were correlated using the Avrami equation (Avrami, 1939):

$$1 - X(t) = \exp(-k\,t^n) \qquad (1)$$

where:

«*X(t)*» is the relative crystallinity at time «*t*», «*k*» the specific crystallization rate constant and «*n*» the Avrami exponent.

The Avrami crystallization model has been frequently used for the analysis of the isothermal and non-isothermal crystallization processes of compounds prepared mixing semi-crystalline polymers with nano-fillers. Examples are the studies done by Zhu *et al.* (2004) with mixtures of polypropylene copolymers and nano-particles of $CaCO_3$, by Qian & He (2003) with mixtures of HDPE and nano-SiO_2, and by Mucha & Królikowski (2003) with isotactic Polypropylene (iPP) and its mixtures with different fillers, one of them being a nano-clay of modified montmorrillonite with organic compounds. In this case it was found that the Avrami parameter «n» varied between 1.5 and 1.6 for the pure IPP and between 1.7 and 2.1 for the compounds, and we reached the conclusion that value of the «n» does not reflect the character of the structural growth of crystals.

EXPERIMENTAL

Composites were prepared using a pure homopolymer HDPE (MFI: 4.88g/10 min at 190 °C) and a nano-sized hydroxyapatite (20x60 nm). The HDPE/HA composites containing 2 and 5 phr of filler were made in a Haake Rheomix at 160 ºC, 90 rpm and 5 min of mixing. Compounds were then irradiated with a gamma ray source, at a dose of 25 kGy applied with a rate of 4.8 kGy/h at room temperature and in contact with atmospheric air.

The isothermal crystallization process was studied using a DSC model Mettler-Toledo 821 and nitrogen as the dragging gas. All isothermal tests were done heating a sample of HDPE, or of any of the prepared composites, at a temperature of 170 ºC which is higher than the HDPE melting point, maintaining then the temperature constant during 5 minutes in order to erase the previous thermal history, and immediately after that time cooling the samples, at the maximum rate allowed by the equipment, to the desired crystallization temperature (T_c). This temperature was maintained during the time period required to complete the crystallization process. The crystallization temperatures studied were 118, 117, 116 and 115ºC and experiments were repeated twice.

RESULTS AND DISCUSSION

Examples of crystallization isotherms obtained at 118 and 115ºC using non-irradiated samples of pure HDPE, and its composites with different amounts of HA, are shown in Figures 1 and 2 respectively. Examples using instead irradiated samples are, shown in Figures 3 and 4. It can be observed that the amount of HA added has a definite effect on the crystallization rates, which is more noticeable on experiments done at 118 ºC because, at a slower crystallization rate, the effect of other variables is more important. At the same time Figures 1 to 4 show that with increasing crystallization temperature, the time for complete crystallization increases as well. Experimental data taken at 117 and 116 ºC have an intermediate behaviour between those shown in the figures. This implies that the total crystallization time increases and crystallization rate decreases with increasing temperature T_c, which agrees with the behaviour predicted by the kinetic theory of crystallization which states that, for any increase in the crystallization temperature there will be a corresponding decrease in the value of the super-cooling («T), and hence the growth rate of crystals will decrease (Mubarak, 2000). It can also be seen that the induction time (time needed for crystallization to begin) increases with increasing T_c.

The delay in the DSC signal, observed in tests performed under isothermal conditions, cannot simply be attributed to an effect of the induction time resulting from nucleation. The apparent increase in the induction time with increasing crystallization temperatures may probably be a combined result of a slower nucleation and slower growing rates. Patkar & Jabarin (1993) reports that the behavior of the induction time with temperature is due to the decrease in

the nucleation rate as the temperature approaches the melting point. On the other hand, Kenny & Maffezzoli (1991) report that this delay is only representative of the induction time associated with the development of crystal nuclei.

The effect of the temperature on the crystallization rate of neat HDPE is clearly observed comparing the results shown in Figures 1 and 2. According to these pictures, the crystallization kinetics of HDPE is strongly affected by temperature. A qualitatively similar behavior is observed with samples of HDPE mixed with different amounts of HA, independently if experimental data belong to non-irradiated or irradiated samples (Figures 1-4).

At a temperature of 115ºC, the overall crystallization rate is very fast compared to that at 118ºC, and variations in the induction time fall almost within the order of experimental errors, making their influence in the displacement of thermograms almost imperceptible (Figures 2 and 4).
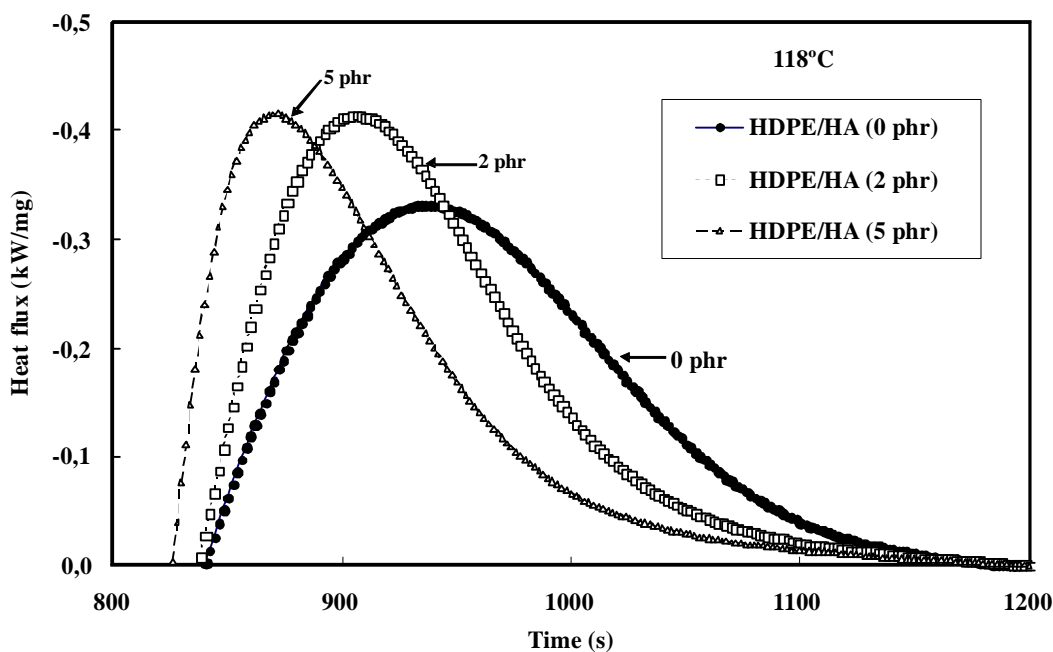
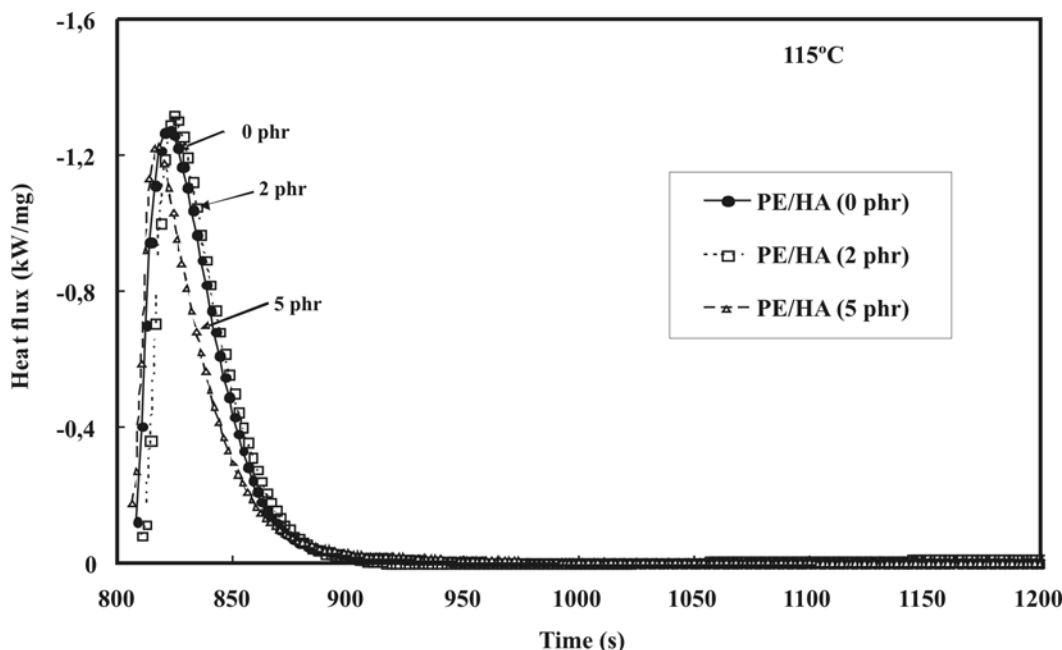**Figure 1.** DSC thermograms of non-irradiated pure HDPE and its composites with 2 and 5 phr of HA at 118ºC.

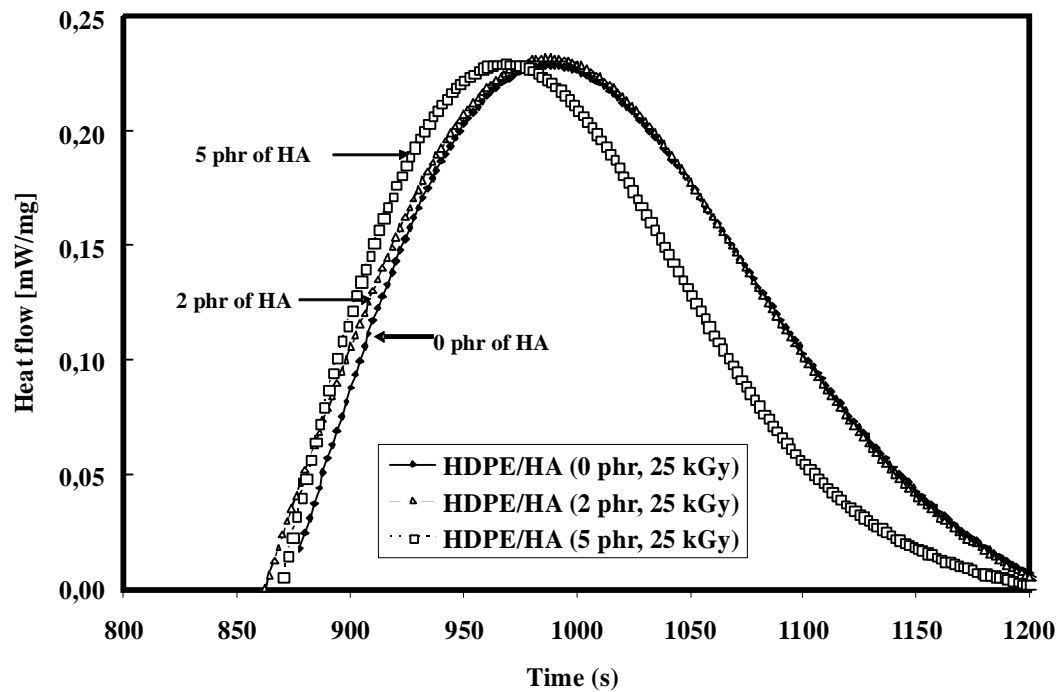**Figure 2**. The DSC thermograms of non-irradiated pure HDPE and its composites with 2 and 5 phr of HA at 115ºC.

Figure 3. DSC thermograms of irradiated samples of pure HDPE and its composites with HA at 118°C.
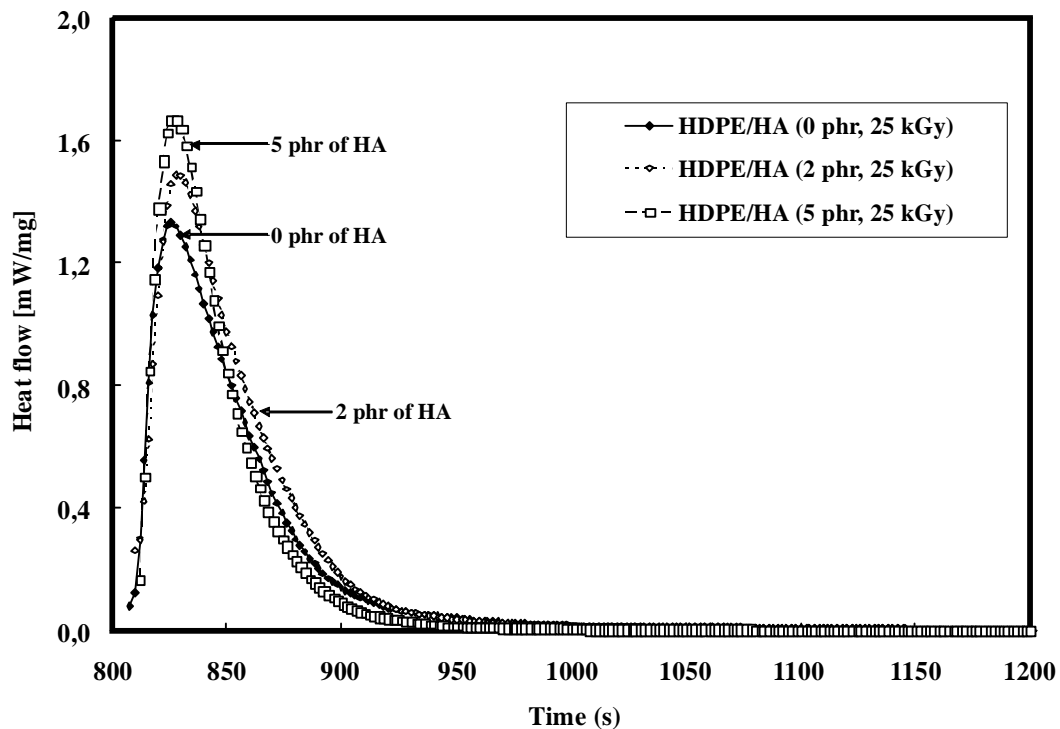

Figure 4. DSC thermograms of irradiated samples of pure HDPE and its composites with HA at 115°C.

Comparing Figure 1 with Figure 3 it can be seen that the induction time increases with irradiation, and that the crystallization rate decreases, behaviour that can be related to the degree of cross-linking produced by chain ruptures and free radicals generation by irradiation, and their recombination. The same behaviour cannot be clearly observed in Figures 2 and 4, where experimental results obtained at 115°C are shown. At this temperature the super-cooling is already high enough as to make the crystallites growth rate so fast as to make a difference of behaviour between samples almost indistinguishable.

In Figure 1, for example, thermograms for composites with 2 and 5 phr of HA appear displaced toward lower crystallization times, that is toward the left side of that for the neat HDPE, meaning that the HA used in those amounts works as a nucleation agent, accelerating in consequence the crystallization process. Comparing induction times for pure HDPE with those for composites of HDPE with HA, it is possible to conclude that the nucleation process for composites is faster than that for pure HDPE, since that the induction time decreases as the HA content increases. An increase of the nucleation rate implies also an increase in the number of nuclei per unit HDPE volume, a reduction in the spherulite size distribution, and a subsequent increase in the crystallization rate.

The effects of different content of HA on the HDPE crystallization rate are visible also in Figures 5 to 10, where the evolution of crystallization degrees with time is plotted for two different temperatures. Results for intermediate crystallization temperatures are not shown, because they give the expected intermediate results. Independently of what sample is analysed, the relative crystallinity isotherms show a sigmoid dependence with time. According to these results, the HDPE crystallization rate increases with the presence of HA, the effect being more visible at the highest crystallization temperature. Consequently it can be concluded that the relative crystallinity developed at a definite time t, decreases as the crystallization temperature increases, and that the HA acts as a nucleating agent, independently of the crystallization temperature. Xu & He

(2001) found similar results in their studies on composites of polyoxymethylene with attapulgite.

The decrease in crystallization rates by irradiation can also be seen analysing curves of relative crystallinity «X_r» versus time, like those shown in Figures 5 and 6 for pure HDPE and HDPE/HA (5phr) composites respectively at a crystallization temperature of 118ºC. It can be seen that the relative crystallinity curves for irradiated samples appear moved to the right of those corresponding to the non-irradiated ones. An increase in their «$t_{1/2}$» (time needed to reach 50% of relative crystallinity) with irradiation is then observed, confirming a decrease in their nucleation and growth rates, which is an induced effect of the chain defects generated by radiation. At the lowest crystallization temperature used in this work (115ºC) the same behaviour is observed, but differences are much smaller than those observed at 118ºC.

Experimental results were analyzed using the Avrami equation (Avrami, 1939). It was observed that results obtained using the classic linearization procedure (Martins et al. 2002; Guo et al. 2001) were not satisfactory, and was replaced by a least square regression method which allow us to process simultaneously all experimental data obtained for each sample within the explored temperature range. The method consists of minimizing the following objective function

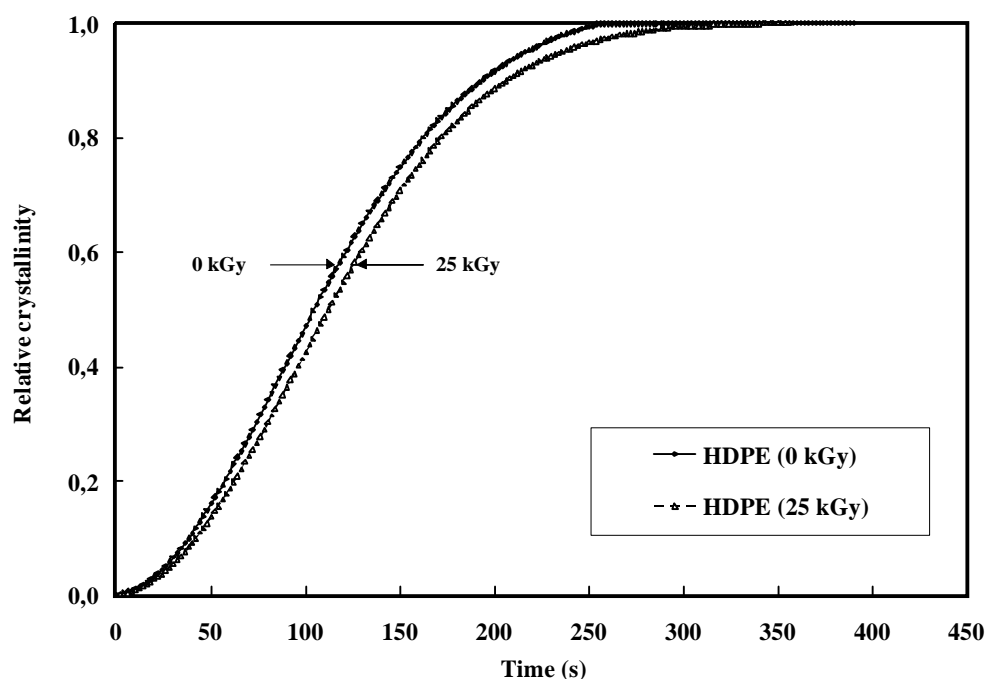$$\sum \left(\theta_{exp.} - \theta_{model} \right)^2 \qquad (2)$$

Figure 5. Experimental relative crystallinity data at 118ºC for pure not irradiated HDPE and an irradiated sample with 25 kGy of gamma radiation.
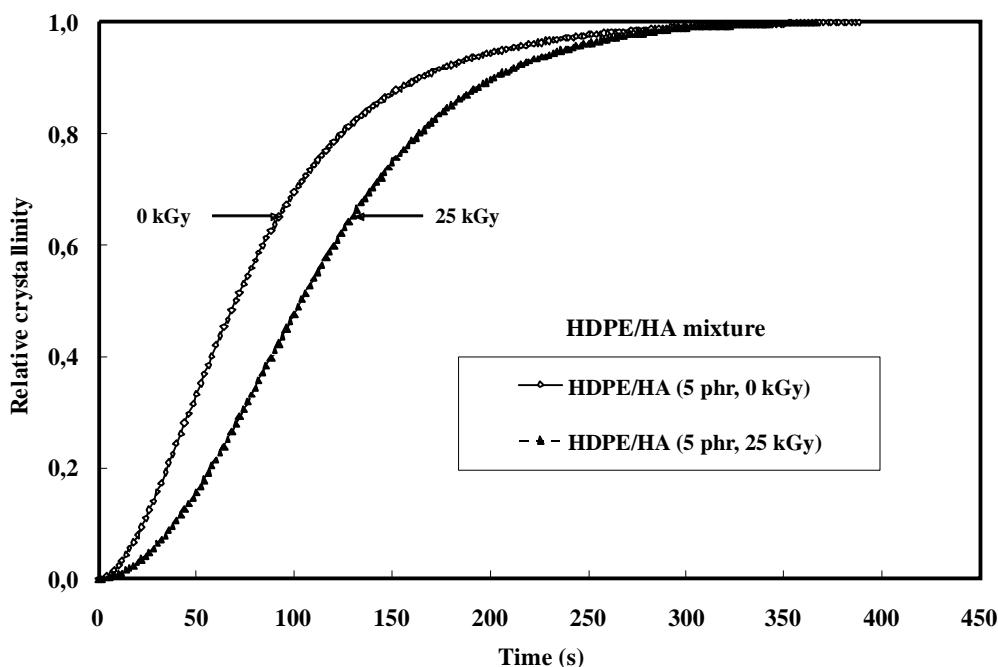
Figure 6. Experimental relative crystallinity data at 118ºC for not-irradiated and irradiated samples of the HDPE/HA (5 phr) composite.

where:

«θ_{exp}» and «θ_{model}» are the experimental and the simulated relative crystallinity respectively defined by the equation:

$$\theta = \frac{X_i}{X_{total}} \qquad (3)$$

where:

«X_i» is the absolute degree of crystallization obtained at time «t_i» and «X_{total}» the final absolute degree of crystallization. Considering the narrow temperature range used for all experiments, the parameter «n» for the Avrami equation was considered to be different for each sample but temperature independent. Instead the specific crystallization constant was assumed to follow an Arrhenius type of equation, what made it possible to make a regression against all the experimental data obtained with a given sample at all experimental crystallization temperatures. In this way the reproducibility and the experimental errors associated with the data can be statically taken in to account. As a result, the simulated curves do not always follow the experimental behavior as well as a more classical procedure will allow, but has the advantage to be a statistically a more reliable procedure to predict the composites behavior.

It was found that the parameter «n» reaches values within the range 1.5 to 1.8 for all composites, meaning a two dimensional crystals growth (like dishes) (Auer *et al*. 1994;

Krause *et al*. 1994). Similar results were obtained by Li *et al*. (2007) in their studies with compounds of polyamide-6 with multiwall carbon nano-tubes (MWNTs), finding that the value of the parameter «n» decreases from 3.8 to 1.5 with the addition of the filler.

On the contrary, when functionalized nano-tubes were used (f-MWNTs) an increase of «n» was observed. They explain this behavior suggesting the development of a 2D growth of crystals in PA6/MWNTs composites with the occurrence of a heterogeneous nucleation process. After grafting instead, the growth mechanism is suggested to change into a combination of 2D with 3D.

Day *et al*. (2006), studying the crystallization process of composites of Polylactic acid with modified nano-clay, obtained values for «n» within the range of 1.67-2.52, depending on the time that samples were maintained at 200ºC in order to erase their thermal history. Mucha & Królikowski (2003) using iPP composites with different fillers found values of «n» in the range 1.5-2.1. Zhang *et al*. (2000) working with mixtures of iPP/HDPE (30/70) observed a value of 1.46 for the parameter «n».

Low values for the Avrami exponent «n» could mean the presence of restrictions for the chains diffusion toward the nuclei giving origin to an incomplete development of crystals, or of a two dimensional growing discs. The low values for «n» obtained in our work suggest also the onset of a heterogeneous nucleation process.

To find a close relationship between the values of the exponent «n» and the kind of the crystallization process that is taking place is a complex task. Thus, for example, for the crystallization of polymer from the melt state, the literature report values from 2 to 4 (Krumme *et al.* 2004; Qian *et al.* 2003). The Avrami´s exponent «n», is defined as $n=\gamma+\lambda$, where γ represents the nucleation step: 0 for constant nucleation, i.e., when density of nucleation sites remains constant, and 1 for sporadic nucleation, and λ represents the growth step: 1 for lineal development, 2 for discs and 3 for spheres. If «n» falls within the ranges 2 to 3, the growth mechanism would be the formation of lamellae with a radial growth of a spherulitic structure. Fractional values of «n» can be explained in terms of a partial overlapping of the primary nucleation with the crystal growth.

Values for the specific crystallization rate constant evaluated using parameters obtained by regression are shown in Table 1 for all samples (non-irradiated and irradiated as well) and for all experimental crystallization temperatures. As can be seen, the value of «k» decreases with increasing temperatures showing at the same time that, the addition of 2 and 5 phr of HA causes a considerable increase in its value, meaning that the nano-particles of this compound act supplying a surface with a lower energy barrier over which chains segment can be adsorbed, increasing in this way the nucleation effect and the crystallization rate. At the same time, specific crystallization constant obtained for irradiated samples of pure HDPE or its composites with HA, reach values significantly smaller, which can be attributed to structural changes induced by radiation as explained above. Additionally, the objective functions obtained by fitting experimental data with any model, like the Avrami used in this work can, and actually does, statically confirm that the crystallization rate depend on the HA content, the amount of applied irradiation and the crystallization temperature.

Results for «θ_{exp}« and «θ_{model}» for pure HDPE and its composites with HA, irradiated or not irradiated, are shown from Figures 7 trough Figure 10. It is known that the stability of nuclei formed at the beginning of the crystallization process decreases with increasing crystallization temperatures. Hence, for crystallization temperatures of 118ºC, for example, the concentration of stable nuclei formed during the induction period is relatively small and therefore spherulites can grow to bigger sizes before touching between them, implying that the process is slower and mostly controlled by a primary crystallization mechanism. Therefore values of «θ_{model}» predicted using the Avrami model, which only take into account the primary crystallization, should reach a better agreement with experimental.

«θ_{exp}» values at 118ºC, as it is shown in figures 5, 6, 7 and 9. On composites, the amount of nuclei formed is higher than the amount formed within the lean HDPE, what justifies the behaviour observed in figure 7, but still lower when compared with results obtained at lower temperatures. Therefore the rate of crystallization of composites is something higher than the observed for the lean HDPE, but the number of spherules and their rate of growing at 118ºC is still low enough as to get the process controlled by the primary crystallization until reaching high values of relative crystallinity. Consequently for composites processed at 118ºC, the primary crystallization will still be the main crystallization mechanism and a good agreement between «θ_{model}» and «θ_{exp}» is observed (Figure 7).

Figure 8 and Figure 10 show instead that at 115ºC, the simulated values of «θ_{model}» reach a poor agreement with «θ_{exp}» for pure HDPE and for HDPE/HA composites specially for values of relative crystallinity over 80%. At 115ºC the stability and concentration of nuclei formed is much higher than those formed at 118ºC. This fact associated to a faster growing process, gets spherulites touching each other at a lower relative crystallinity giving then rise to a significant contribution of the secondary crystallization which depart from the behaviour predictable by the Avrami model. On Figure 8 is also shown an enlarged picture of the lower relative crystallinity range. It shows that due to the presence of experimental errors, there is a small deviation between

Table 1. Specific crystallization rate constant (k) for irradiated and not irradiated samples at different temperatures.

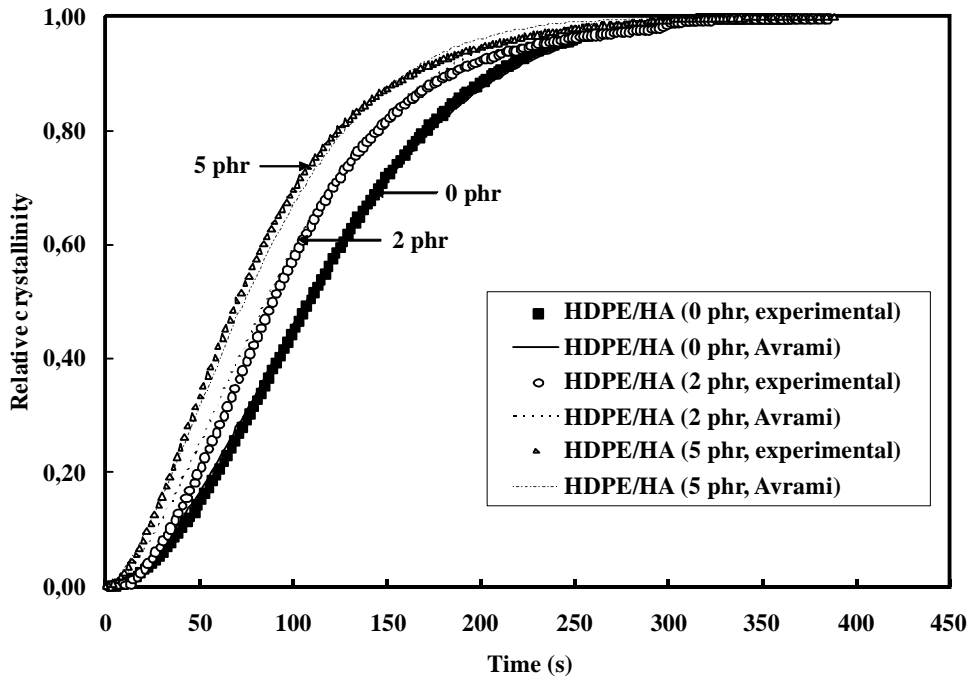| Sample	Radiation doses (kGy)	118 (ºC)	117 (ºC)	116 (ºC)	115 (ºC)
PE alone	0	0.193×10^{-3}	0.499×10^{-3}	1.292×10^{-3}	3.360×10^{-3}
	25	0.130×10^{-3}	0.287×10^{-3}	0.635×10^{-3}	1.409×10^{-3}
PE with 2 phr HA	0	0.473×10^{-3}	0.646×10^{-3}	1.856×10^{-3}	3.908×10^{-3}
	25	0.149×10^{-3}	0.329×10^{-3}	0.726×10^{-3}	1.612×10^{-3}
PE with 5 phr HA	0	0.875×10^{-3}	1.781×10^{-3}	3.635×10^{-3}	7.448×10^{-3}
	25	0.288×10^{-3}	0.426×10^{-3}	0.786×10^{-3}	1.825×10^{-3}

Figure 7. Experimental and Avrami simulated relative crystallinity at 118ºC
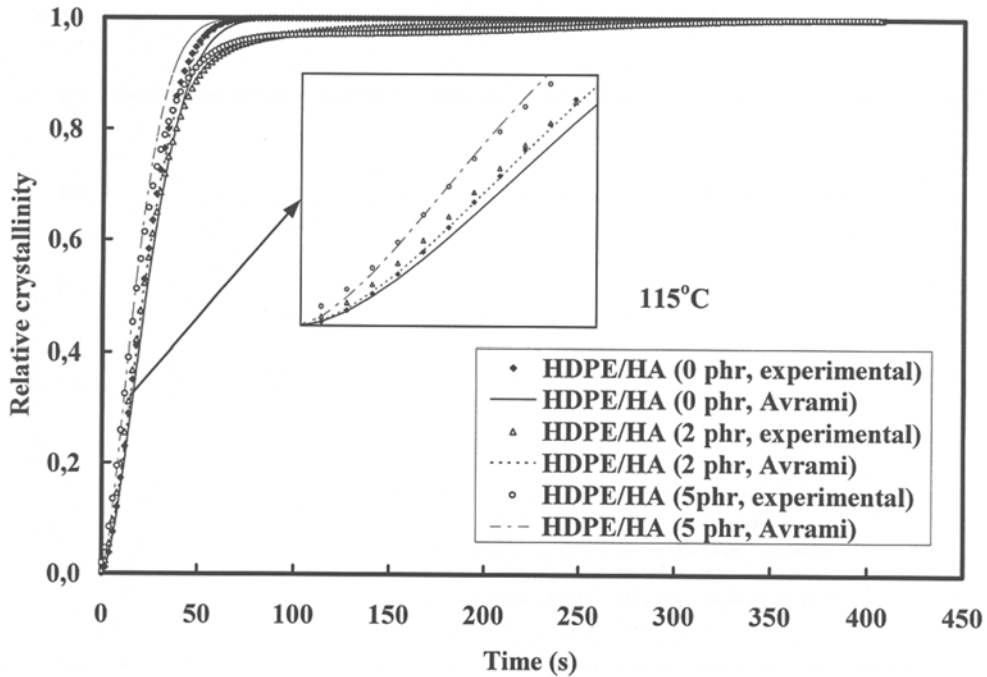for pure not irradiated HDPE and its composites with HA.

Figure 8. Experimental and Avrami simulated relative crystallinity at 115ºC
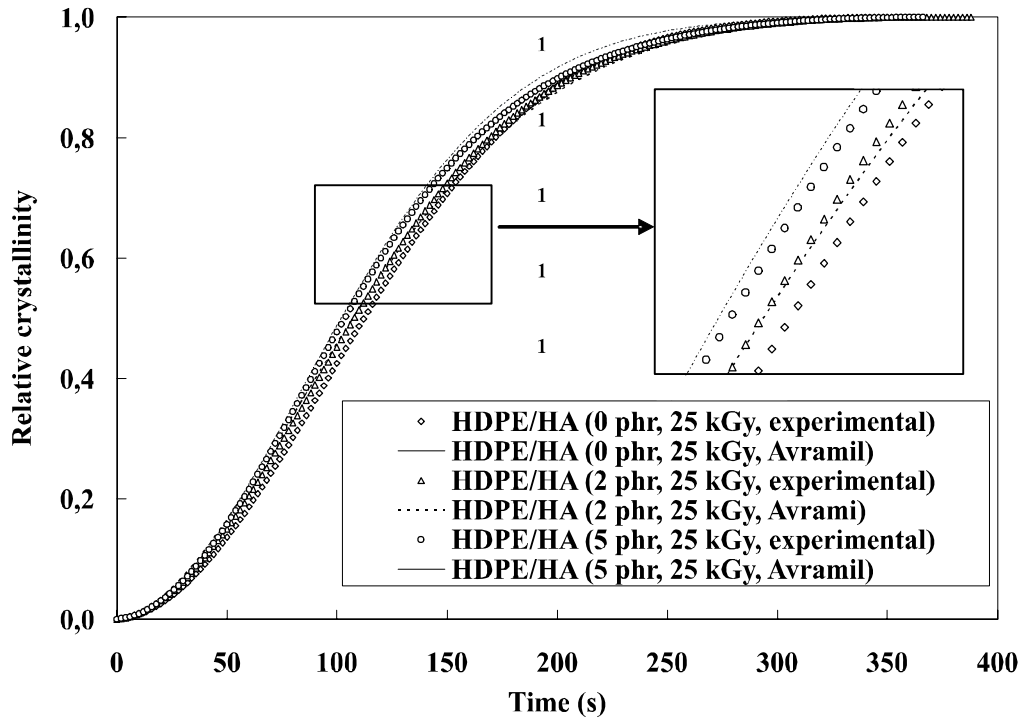for pure not irradiated HDPE and its composites with HA.

24

Figure 9. Experimental and Avrami simulated relative crystallinity at 118ºC for irradiated pure HDPE and its composites with HA.
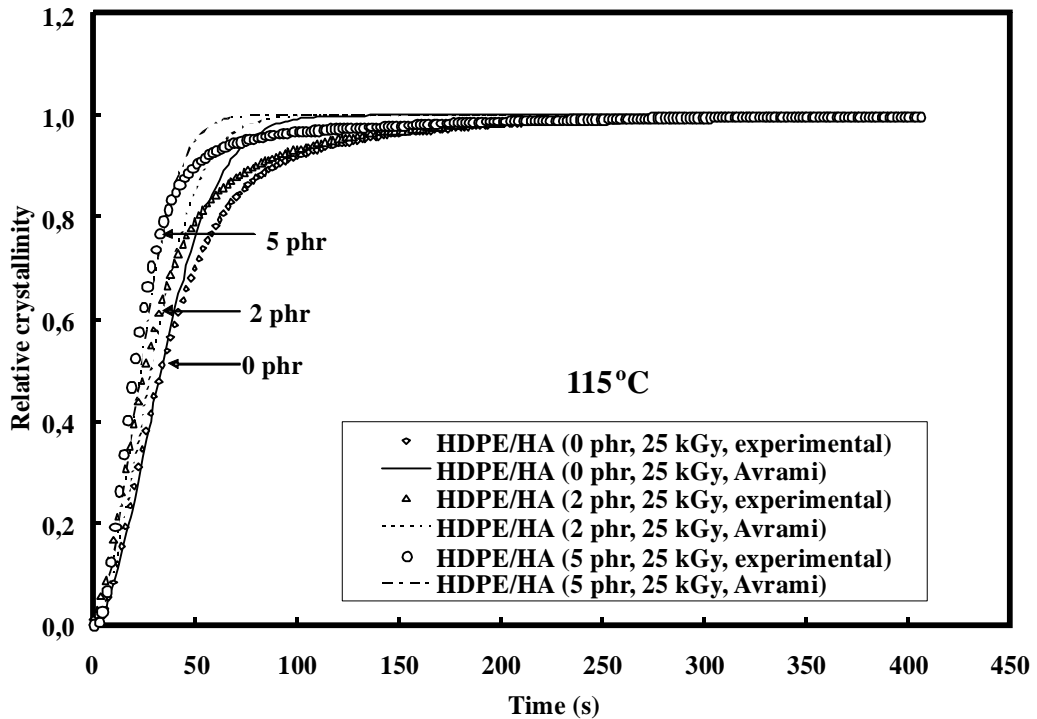

Figure 10. Experimental and Avrami simulated relative crystallinity at 115ºC for irradiated pure HDPE and its composites with HA.

experimental and predicted data, but still the correct qualitative behaviour is observed. The origin of the observed differences was already attributed to the regression procedure used, but as it was explained, the predictions are statistically more reliable.

As shown in figure 9 values of «θ_{model}» deviate lightly from «θ_{exp}» for pure irradiated HDPE at 118ºC along almost all the range of relative crystallinity. The chain defects introduced by radiation make more difficult for polymer molecules to diffuse toward the crystallization front, increasing in that

way the amount of polymer that remain amorphous, which will contribute to an increased contribution of the secondary crystallization mechanism which can develop simultaneously and/or consecutively with the primary one. However, at decreasing crystallization temperatures the rate of nucleation and the amount of nuclei formed gets higher and spherulites make contact at much smaller sizes reducing the agreement between «θ_{exp}»and «θ_{model}» to the lower range or relative crystallinity (figure 8). Defects induced by radiation make that deviation from the Avrami model appear at even lower crystallization levels.

As it can be seen in figure 9, the Avrami's equation showed also to correlate very well the experimental crystallization behaviour of irradiated compounds samples at 118ºC. This behaviour suggest that the HA enhance the rate of formation and the stability of nuclei making the crystallization process more uniform and faster, even in the presence of radiation induced defects. However the rate of crystallization is slower than the observed over not irradiated samples, and comparing figure 7 with figure 9, it seems that the slowing effect of radiation is higher on composites than in the pure HDPE, making difficult to distinguish between the relative crystallinity curves. Due to this, an amplified (5 times) central part of those curves is also shown in the figure, allowing to clearly see that the nucleation effect of HA is still present. Experimental and simulated crystallization data for irradiated compounds and lean HDPE at a temperature of 115 ºC are shown on figure 10. As it can be seen there is still an acceptable good correlation between them at the lowest end of the relative crystallinity, but increasing deviation are observed as the degree of crystallization increases. This behaviour could be explained by similar reason to those suggested for non irradiated samples. At 115ºC the amount of nuclei formed increases, spherulite sizes decreases, and as a result, their grow rate increases due to a shorter diffusion path of polymer molecules toward the crystallization front, hiding in this way the effect of induced chain defects. But as soon as spherulite gets in touch, the secondary crystallization begins and a deviation from the Avrami model is observed.

The deviations of the Avrami model from experimental values comes as a consequence of a number of reasons: 1) The model do not take into account diffusional effects that become important at the lowest temperatures; 2) The HA, being of nanometric sizes, shows a tendency to agglomerate and 3) The model do not consider the appearance of a simultaneous, or a serial secondary crystallization, that could be occurring.

Summarizing, it could be inferred that the crystals grow, the spherulite perfection, the amount of material that remain amorphous, the amount of defect produced by irradiation, and the appearance of a secondary crystallization

mechanism beside the primary one, have a high effect on the crystallization, on the absolute crystallinity obtained, and perhaps on tensile properties significant for biomedicine applications.

CONCLUSIONS

The analysis of experimental data shows that the crystallization rate of HDPE is strongly affected by factors like: a) the crystallization temperature, b) the HA content and c) the applied radiation. Decreasing crystallization temperatures translate into a rapid increase of the specific crystallization rate constant. This constant also increases with increasing amount of HA (2 and 5 phr) due to the HA nucleation effect, but it is negatively affected by radiation due to the formation of defects along the polymeric structure like cross-linking.

At a crystallization temperature of 118ºC experimental data obtained with not-irradiated samples of pure HDPE, and its composites with HA, are satisfactorily simulated with the Avrami equation, but with decreasing temperatures, increasing deviation were observed, especially for high values of relative crystallinity, attributed to the an onset of a secondary crystallization mechanism. When the pure HDPE and its composites with 2 and 5 phr of HA are irradiates with 25 kGy of gamma radiation, an increase in the deviations between «θ_{model}» and «θ_{exp}» due to the presence of defects is observed, small at 118°C but more visible at 115°C.

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