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Thermal analysis of blends made with polyamide 6 and γ-irradiated polyethylenes[☆]

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Abstract

Blends made with a polyamide 6 and three different polyethylenes (low density, linear low density, high density) γ-irradiated in air were prepared. With reference to the corresponding blends made with the unirradiated polymers, SEM analysis showed significant modifications in the morphology. Thermal analysis indicated the absence of cocrystallization phenomena even though some effects on the calorimetric properties of the material have been observed and related to the observed modifications in the morphology.

Keywords: Blend; Irradiation; PE; Polyamide; TA

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1. Introduction

Thermal analysis can be a useful tool in the study of the structure of polymer blends. In particular, for incompatible systems, the presence of interactions between the two phases is readily detected through this experimental technique.

In previous papers [1, 2], we have discussed the thermal behaviour of polyethylene/polyamide blends γ-irradiated under vacuum. These polymers are incompatible because of the significantly different molecular structure and their resulting blends are

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"heterogeneous" with poor properties [3, 4]. Thermal analysis always reveals the presence of two crystallization peaks without cocrystallization pehnomena. However, both radiation processing and mixing induce modifications of the melting and crystallization behaviour which were related to the presence of some interactions between the two polymer components.

In order to modify the structure of these blends, we suggested the grafting of polar oxidized groups in the polyethylene chains through γ-irradiation in air [5–7]. Depending on the irradiation conditions, "compatibilization" effects with a more uniform distribution and a finer dispersion of the polyethylene particles in the polyamide matrix were sometimes observed. We attributed this effect to the presence of interactions among the oxidized groups of the polyethylene and the functional groups of the polyamide. In order to complete the study of these systems, blends made with polyamide 6 and three different polyethylenes (low density, linear low density and high density) irradiated in air at various doses were prepared and characterized through thermal analysis and scanning electron microscopy. The results obtained are related to the structural modifications induced by γ-radiation in the pure polyethylenes.

2. Experimental

The materials used were commercial polymeric samples whose main molecular characteristics, together with the code, are reported in Table 1.

Before the irradiation, 1-mm-thick polyethylene samples were prepared from pellets by compression moulding in a laboratory press. The polymer was kept at 180°C and 15 MPa for 5 min and rapidly cooled down to room temperature by cold water running through the press plates.

The irradiation was performed in air at room temperature (about 25°C) by the IGS-3 [8], a panoramic 3000 Ci ^{60}Co irradiator. The irradiation conditions were 10 and 50 kGy at 0.1 kGy h^{-1}. The dose rate was measured by a Fricke dosimeter; a variance of 5% in the radiation absorption was accepted.

All the polyethylenes were subjected to extraction in a soxhlet extractor in order to determine the presence of insoluble fractions. The samples were exposed to xylene close to its boiling point for 72 h. Gel permeation chromatography (GPC) was performed on the sol fraction of the polyethylenes by means of a Waters 150-C chromatograph at 135°C using TCB as solvent. Thermal analysis was carried out by a Perkin-Elmer

Table 1
Characteristics of the materials used

Sample code	$\bar{M}_w \times 10^3$	$\bar{M}_w/\bar{M}_n$	Trademark	Manufacturer
LLDPE	128	4.4	BF2211	ENICHEM
LDPE	108	9.8	BB2700	ENICHEM
HDPE	130	10.5	ZB5015	ENICHEM
PA6	62	2.2	ADS40	SNIA

DSC-7 instrument. The samples were heated up to 240°C and then cooled down to -10°C. Both the heating and cooling ramps were performed at 10°C min^{-1}. The crystallization temperature T_c and the crystallization enthalpy ΔH_c were taken as the peak temperature and the area under the peak, respectively.

Blends were prepared by a Brabender Plasticorder model PLE 330 at 240°C. Before mixing, the polyamide was carefully dried under vacuum. The composition was 25/75 wt/wt (polyethylene/polyamide 6) in all cases and the mixing time was 15 min. Pure materials were subjected to the same treatment.

Thermal analysis was performed as for pure polyethylenes.

SEM micrographs were obtained using a Philips scanning electron microscope. The samples, fractured under liquid nitrogen, were subjected to selective extraction of the polyethylene component by boiling xylene for 2 days, then they were coated with gold under vacuum to make them electrically conductive.

3. Results and discussion

We will first discuss the thermal behaviour of irradiated polyethylenes. Calorimetric data are reported in Table 2. For low-density polyethylene, we observe that the unirradiated LDPE and all the irradiated LDPE samples have the same T_c and ΔH_c values, whereas for LLDPE, irradiation increases the crystallization enthalpy, and for HDPE, decreases both T_c and ΔH_c.

Extraction tests performed on irradiated samples show the presence of an insoluble fraction (about 10%) in only HDPE irradiated at 50 kGy and 0.1 kGy h^{-1}. GPC analysis results are reported in Fig. 1, where Mw as a function of the dose is reported. For HDPE irradiated at 50 kGy and 0.1 kGy h^{-1}, the Mw value is relative to the soluble part of the polymer. As a general rule, the main effect of irradiation is molecular degradation and the extension of this effect varies with the nature of the polyethylene. In fact we can see a slight decrease with the dose for LDPE, while the decrease of Mw is more pronounced for the other two polyethylenes. As already shown through melt viscosity results [9], γ-radiation causes chain branching whose effects are more evident in linear polymers, such as LLDPE and HDPE, than in LDPE, perhaps due to the higher concentration of double bonds in LDPE, which minimize degradation favouring chain-addition reaction.

Table 2
Thermal analysis results of the pure materials

Irradiation condition	LDPE		LLDPE		HDPE		PA6	
	T_c/°C	ΔH_c/J g^{-1}	T_c/°C	ΔH_c/J g^{-1}	T_c/°C	ΔH_c/J g^{-1}	T_c/°C	ΔH_c/J g^{-1}
Unirradiated	98	121	98	115	117	222	189	63
10 kGy-0.1 kGy h^{-1}	98	120	98	120	116	216	–	–
50 kGy-0.1 kGy h^{-1}	98	121	97	130	114	210	–	–

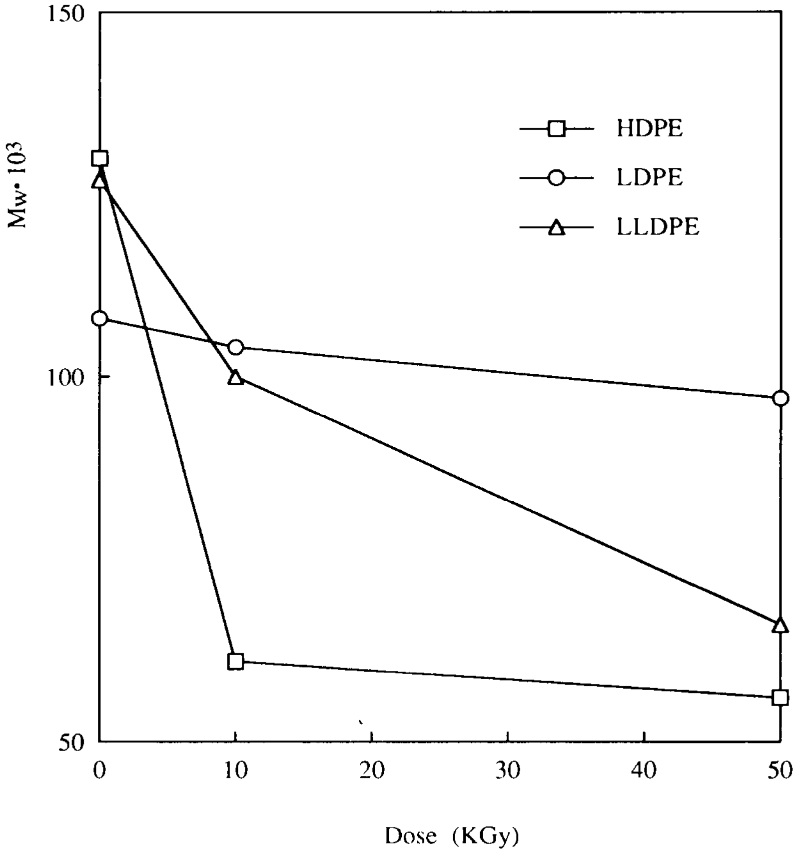

Fig. 1. Weight average molecular weight as a function of the irradiation dose for all polyethylenes.

IR analysis of microtomed samples [10] allowed us to determine the concentration of oxidized groups and their distribution along the whole thickness of the samples. Some differences among the three polyethylenes were observed. HDPE presents a higher concentration of polar groups in the external layers without oxidation effects in the bulk, whereas both LLDPE and LDPE have a more uniform distribution of oxidized groups along the sample thickness. These differences can be attributed to the higher degree of crystallinity of HDPE. Because of the low mobility, oxidized free radicals essentially evolve towards chain scission, but this effect is limited to the external layers of the irradiated samples because the oxygen diffusion coefficient is lowered by the high crystallinity. Gel extraction results are also in good agreement with oxidized group profiles. All these results suggest that, under our experimental conditions, the degradative oxidation is the main effect of irradiation, with different extents depending on the nature of the polyethylene.

We can say that the slight decrease in molecular weight observed for LDPE is in line with the constant values of T_c and ΔH_c for this irradiated polymer; furthermore we must consider that, because the high level of chain branching in the low-density polyethylene is not significantly modified by irradiation, the addition of irregular oxidized groups in the polymer chains does not really affect the crystallization ability of the chains. For irradiated LLDPE, the polar groups grafted on the main chains do not change T_c, while the lower molecular weight produces an increase in ΔH_c. Finally, for HDPE the oxidative degradation and the presence of gel decrease both T_c and the crystallization degree.

Let us discuss now the blends made with irradiated polyethylenes and PA6.

In other papers, we have shown that the oxidized polar groups grafted via γ-irradiation in the polyethylene chains can be used as interfacial active agents to "compatibilize" the polyethylene/polyamide "two-phase" system [1, 2, 9]. This is confirmed by SEM micrographs of all blends prepared with irradiated and unirradiated polyethylenes, whose boiling-xylene-etched surfaces are shown in Figs. 2–4. It should be particularly noticed that the irradiation of polyethylenes causes quite similar morphological modifications in their blends with the polyamide. The irradiated polyethylene droplets are smaller in size and more uniformly dispersed in the matrix as compared to unirradiated samples and this trend is followed with increasing dose. It must also be observed that for the blend made with HDPE irradiated at 50 kGy, even if the irradiation improves the dispersion of the two phases and reduces the size of the polyethylene droplets, their dimensions are less uniform than for other similar systems. This can be related to the higher concentration of oxidized groups in the polymer chains, which increase the interaction with the polyamide phase. So we have a more stabilized structure with HDPE droplets of reduced size. The presence of gel contributes to the less regular distribution of HDPE droplets in the matrix.

Concerning the thermal behaviour of the blends, we observe that thermograms always show two different crystallization peaks, clearly related to the crystallization of the polyamide and the polyethylene, respectively. The absence of cocrystallization phenomena is in good agreement with the "two-phase" morphology of these blends. In Tables 3–5 we report the full data for the calorimetric properties of the blends.

The crystallization temperature and enthalpy of the polyamide component are not affected by blending, whatever the nature of the polyethylene (see also Table 2).

In contrast, some effects are observed for the polyethylene component.

The crystallization temperature of HDPE in the blends, both with unirradiated and irradiated polymer, does not vary significantly with respect to T_c of the pure polyolefin. In blends made with unirradiated LDPE and LLDPE, T_c is higher than the corresponding value of the pure polymer, because of the nucleating effect of the solid polyamide. Furthermore, blends made with irradiated LLDPE show a decrease of T_c, thus indicating the presence of some interactions among the functional groups of the irradiated polyethylene and the polyamide, which hinder the crystallization process.

Comparing the crystallization enthalpy of the polyethylene component in the blends with the corresponding values of the same pure polymer reveals some differences among the three blends (see also Figs. 5–7). For LDPE/PA6 blend, ΔH_c decreases with irradiation, while for the pure polymer it is almost constant, thus indicating that the

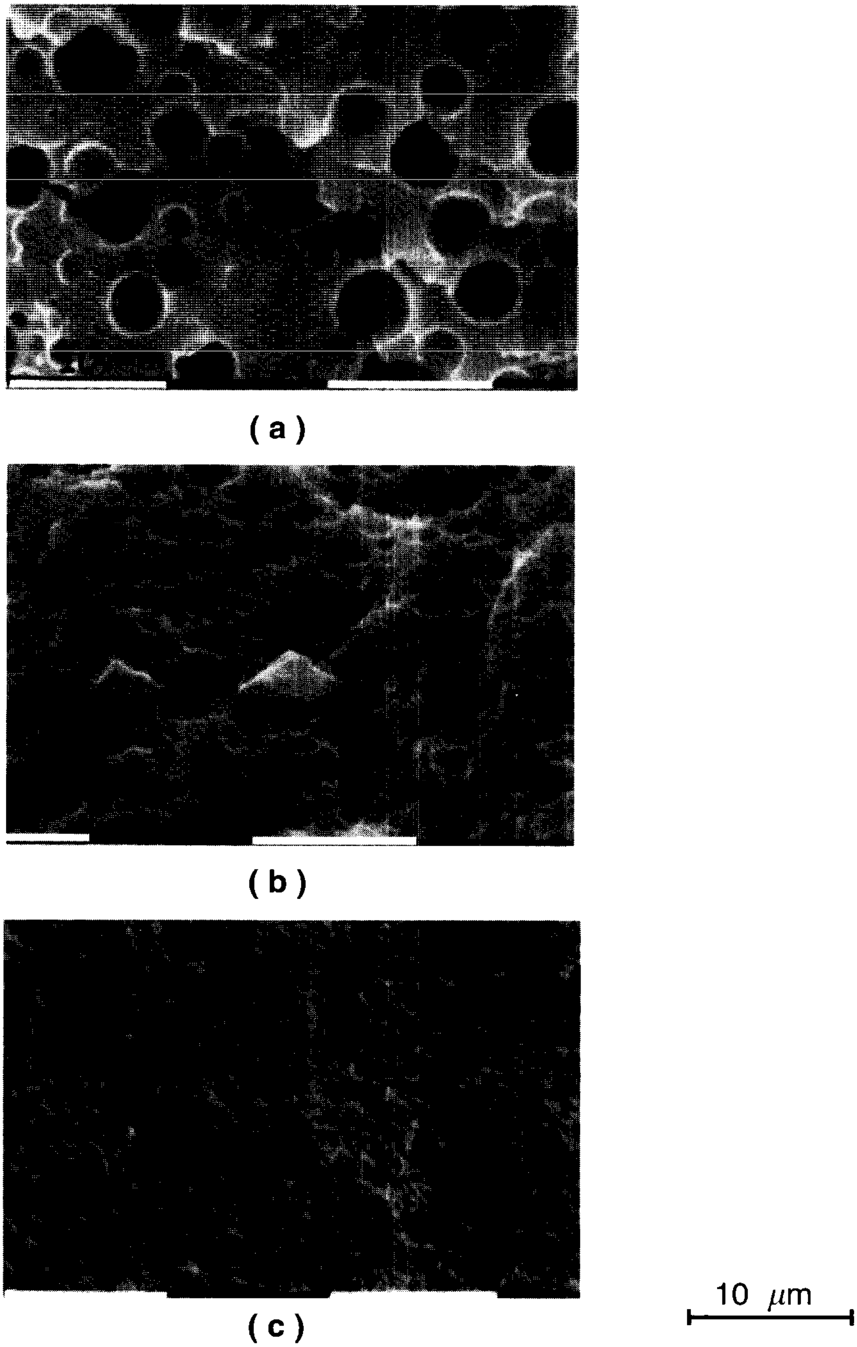

Fig. 2. SEM micrographs for LDPE/PA6 blends: (a) unirradiated polyethylene; (b) polyethylene irradiated at 10 kGy and 0.1 kGy h^{-1}; (c) polyethylene irradiated at 50 kGy and 0.1 kGy h^{-1}.

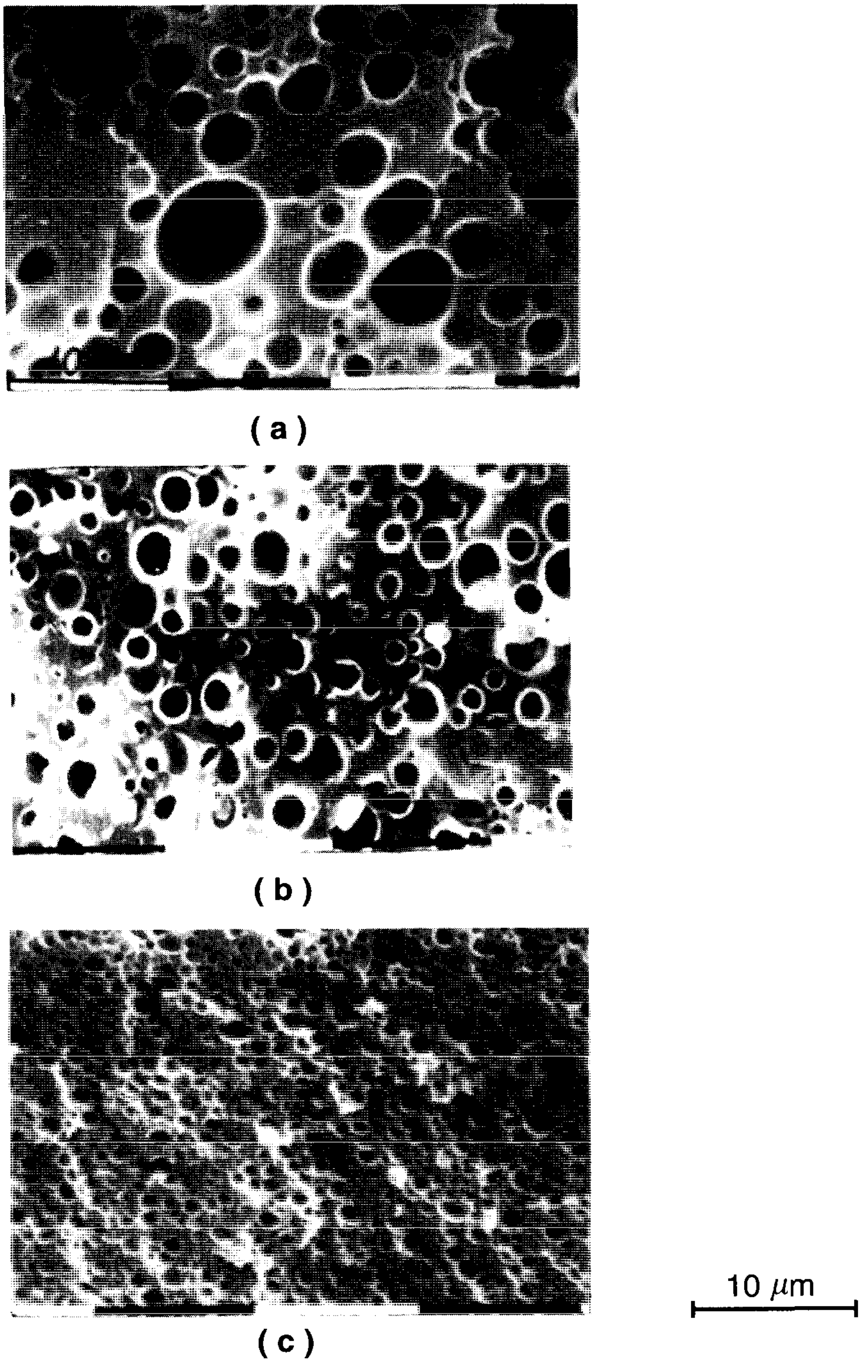

Fig. 3. SEM micrographs for LLDPE/PA6 blends: (a) unirradiated polyethylene; (b) polyethylene irradiated at 10 kGy and 0.1 kGy h^{-1}; (c) polyethylene irradiated at 50 kGy and 0.1 kGy h^{-1}.

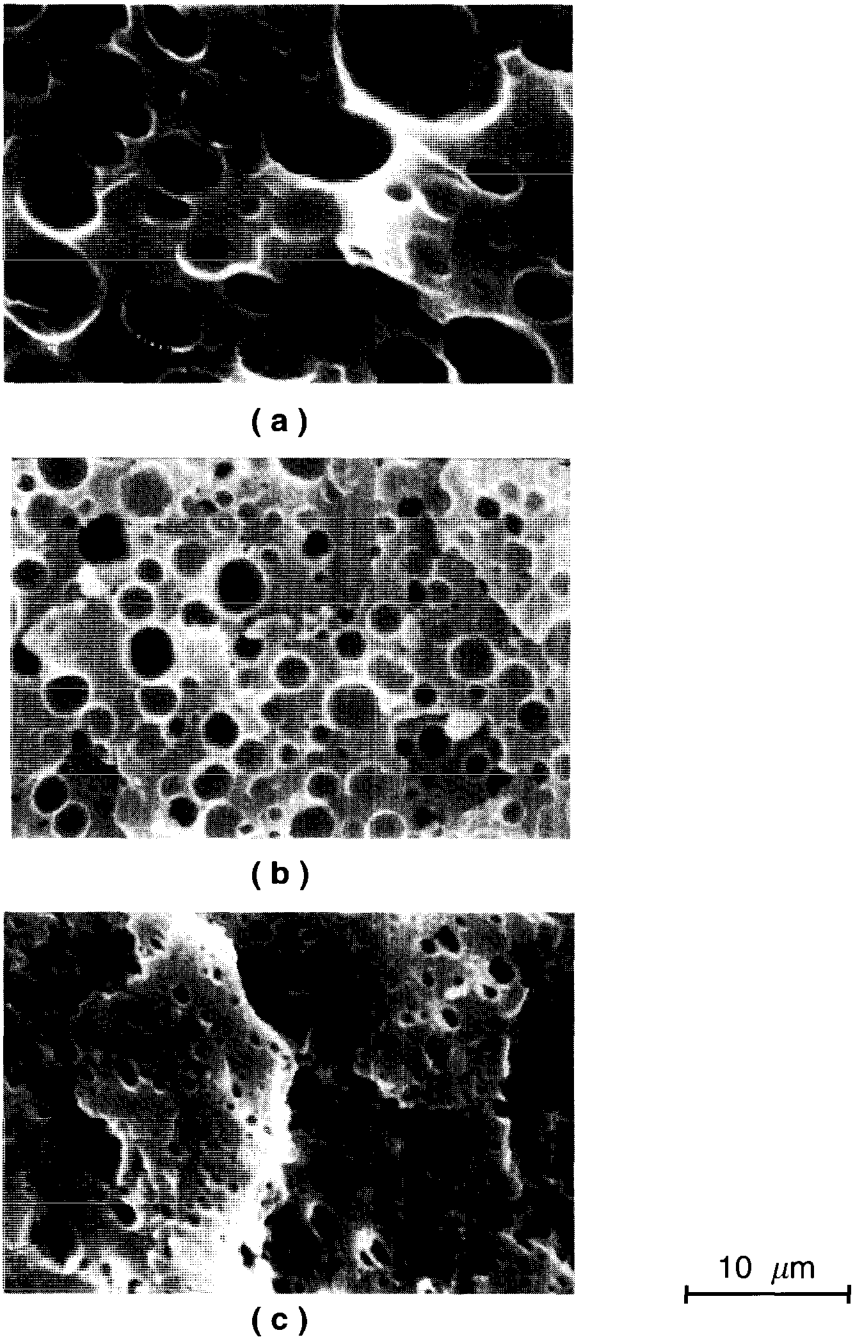

Fig. 4. SEM micrographs for HDPE/PA6 blends: (a) unirradiated polyethylene; (b) polyethylene irradiated at 10 kGy and 0.1 kGy h^{-1}; (c) polyethylene irradiated at 50 kGy and 0.1 kGy h^{-1}.

Table 3
Thermal analysis results of PA6/LDPE blends

Polyethylene irradiation condition	$T_{c,LDPE}$/°C	$\Delta H_{c,LDPE}$/J g^{-1}	$T_{c,PA6}$/°C	$\Delta H_{c,PA6}$/J g^{-1}
Unirradiated	100	120	191	62
10 kGy-0.1 kGy h^{-1}	100	115	191	60
50 kGy-0.1 kGy h^{-1}	101	90	190	63

Table 4
Thermal analysis results of PA6/LLDPE blends

Polyethylene irradiation condition	$T_{c,LLDPE}$/°C	$\Delta H_{c,LLDPE}$/J g^{-1}	$T_{c,PA6}$/°C	$\Delta H_{c,PA6}$/J g^{-1}
Unirradiated	108	110	189	62
10 kGy-0.1 kGy h^{-1}	107	113	190	63
50 kGy-0.1 kGy h^{-1}	105	116	189	66

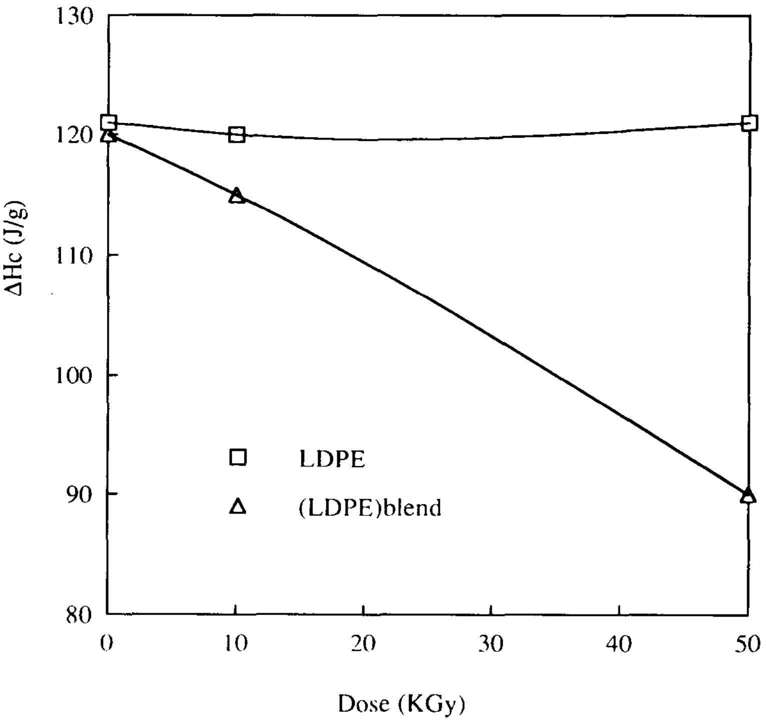

Fig. 5. Crystallization enthalpy as a function of the irradiation dose for LDPE.

Table 5
Thermal analysis results of PA6/HDPE blends

Polyethylene irradiation condition	$T_{c,HDPE}$/°C	$\Delta H_{c,HDPE}$/J g^{-1}	$T_{c,PA6}$/°C	$\Delta H_{c,PA6}$/J g^{-1}
Unirradiated	116	130	191	61
10kGy-0.1 kGy h^{-1}	117	130	191	60
50kGy-0.1 kGy h^{-1}	116	133	191	65

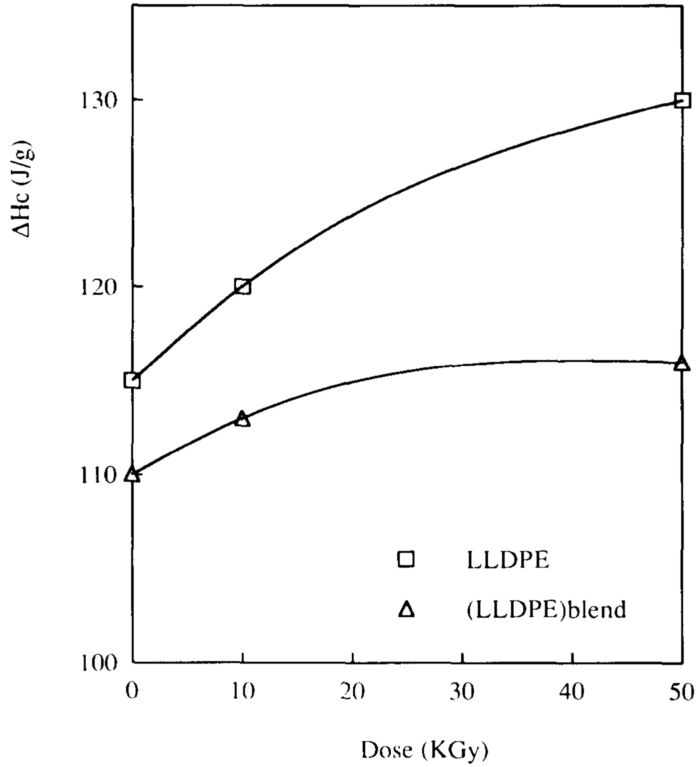

Fig. 6. Crystallization enthalpy as a function of the irradiation dose for LLDPE.

degree of crystallinity is affected by the interactions among the functional groups present in the irradiated polyethylene and the polyamide. This interaction effect is still present in LLDPE/PA6 blends (Fig. 6), reducing the increase in the melting enthalpy with irradiation, as observed for the pure polymer. Finally in HDPE/PA6 blends, we observe a strong decrease in ΔH_c with respect to the pure polymer without any increase with the irradiation; this is in agreement with the non-uniform distribution of polar groups in the irradiated samples.

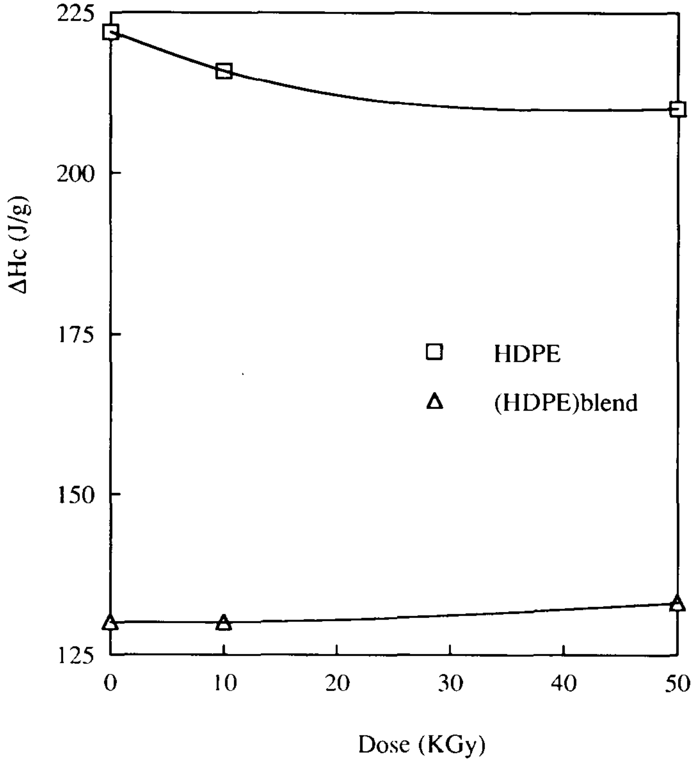

Fig. 7. Crystallization enthalpy as a function of the irradiation dose for HDPE.

4. Concluding remarks

The morphologies of blends made with polyamide 6 and polyethylene are modified by the presence of oxidized polar groups grafted to the polyethylene chains through γ-radiation in air, regardless of the polyolefin structure. In fact blends made with the irradiated polymers show a more uniform distribution and a finer dispersion of the polyethylene particles in the polyamide matrix. However, thermal analysis always indicates the absence of "true" compatibilization phenomena, at least in the crystalline phases; cocrystallization phenomena are never observed. Some effects both in the crystallization temperature and enthalpy are seen and are related to the interactions among the oxidized groups of the irradiated polyethylenes and the polyamide.

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