Thermochimica Acta, 227 (1993) 75–82
Elsevier Science Publishers B.V., Amsterdam

Molecular modifications and crystallization relationships for gamma-irradiated LLDPE/PA6 blends [1]

G. Spadaro [a,*], A. Valenza [a], E. Calderaro [b] and V. Brucato [a]

[a] *Dipartimento di Ingegneria Chimica dei Processi e dei Materiali, Università di Palermo, viale delle Scienze, 90128 Palermo, Italy*

[b] *Dipartimento di Ingegneria Nucleare, Università di Palermo, viale delle Scienze, 90128 Palermo, Italy*

(Received 18 January 1993; accepted 18 March 1993)

Abstract

The effects of gamma-radiation under vacuum on linear low density polyethylene/polymide-6 blends are studied and the results are compared with the effects of the same ageing treatment on the pure polymers. In particular, solubility and melt viscosity tests were performed and data are related to the crystallization behaviour of this system. The results indicate that molecular modifications of the blends can be interpreted by considering both the effect of gamma radiation on the two polymers and the presence of some interactions between the components due to radiation processing and mixing. For the thermal behaviour, the effects of irradiation on the maximum temperature rate and enthalpy of crystallization are observed and, in general, these are more marked for the minor component at high dose.

INTRODUCTION

Gamma-radiation effects on polymers have been widely investigated; they consist mainly of degradation and crosslinking phenomena, the extent of which depends on many factors, such as the chemical structure and the morphology of the polymer and the environmental irradiation conditions (temperature, presence of gas, dose rate, etc.) [1–3]. However, few studies are available in the literature concerning their effects on polymer blends [4–7], despite the increasing interest towards these "new materials" which can be used to prepare materials with selected properties by a suitable choice of polymer components [8, 9].

---

* Corresponding author.

[1] Presented at the 14th National Conference on Calorimetry and Thermal Analysis, Udine, Italy, 13–17 December 1992.

The interest in the gamma-radiation effects on polymer blends is both to know their ageing behaviour, in order to compare it with the radiation resistance of the pure polymers, and to study the possible presence of interactions between the polymer components induced by this processing.

In this work, the effects of gamma radiation under vacuum on linear low density polyethylene–polyamide-6 blends are discussed. In particular, blends with different compositions were irradiated at various doses and the molecular modifications were studied by means of solubility tests and melt viscosity, and then related to the crystallization behaviour.

EXPERIMENTAL

The materials used were a linear low density polyethylene (LLDPE) Riblene LX BF 2211 (Mw = 128 000, Mw/Mn = 4.4), manufactured by Enichem, and a polyamide 6 (PA6) ADS 40 (Mw = 62 000, Mw/Mn = 2) manufactured by SNIA.

Blending was done witha Brabender Plasticorder mod. PLE 330 at 235°C and 20 rpm for 8 min. Pure materials were subjected to the same treatment. The blend composition was 0, 10, 25, 75, 90 and 100 wt.% of LLDPE.

Before the irradiation, the samples were carefully dried under vacuum at 100°C for about 12 h; then they were sealed in glass tubes under dynamic vacuum. Unirradiated reference samples were subjected to the same thermal treatment. Irradiation was conducted under vacuum at room temperature (about 25°C) by the IGS-3, a panoramic 3000 Ci ^{60}Co irradiator [10]. The dose rate, measured by a Fricke dosimeter, was 10 kGy h^{-1}. The integrated doses were 50, 200 and 400 kGy. A variance of 5% in the dose was accepted.

Solubility tests were made with a soxhlet extractor, using formic acid and xylene, which are are typical solvents for unirradiated polyamide and unirradiated polyethylene, respectively. The polyethylene-rich blends were subjected to solubility tests in xylene before formic acid. The inverse sequence was applied to polyamide-rich blends. The LLDPE gel fractions were determined through the ratio of the weight of the insoluble fraction of LLDPE after soxhlet extraction and the weight of the same polymer before extraction. The soluble fractions in formic acid were determined by the ratio of the weight of material dissolved in the solvent and the weight of the polyamide before the extraction in formic acid.

Rheological measurements were made with a Rheometrics dynamic analyser (RDA2) used in the dynamic model with the plate geometry (R = 12.5 mm) at 240°C.

Thermal analysis was performed with a Perkin-Elmer DSC 4B. Samples were heated up to 250°C, held at this temperature for 30 min, and then cooled to 40°C. Both heating and cooling ramps were performed at

20°C min^{-1}. The temperature of the maximum crystallization rate T_c, and the crystallization enthalpies ΔH_c, were taken as the peak temperature and the area under the peak, respectively, in the specific heat-temperature plot.

RESULTS AND DISCUSSION

Gel fractions of LLDPE component are plotted against dose for all blends in Fig. 1. Irradiated pure polyethylene has a gel content ranging from about 85% at 50 kGy, up to about 95% at 400 kGy. These results agree with the literature: irradiation under vacuum of LLDPE essentially causes crosslinking according to its molecular structure which has no hindering groups attached to the main chain [1]. Similar effects are observed for the LLDPE present in the irradiated blends. In fact, the gel fractions of LLDPE component are close to the values of the pure polymer in all the compositions under the experimental conditions considered, except for the blend with a low polyethylene content (10%), which has a lower gel content. These results indicate that, in general, irradiation under vacuum of blends causes molecular modifications of the polyethylene component which are not affected by the presence of the polyamide. The only exception, 10% LLDPE blend, can be attributed to the partial solubilization of this component in the polyamide matrix, as already observed [11].

Pure polyamide is always soluble in formic acid for all the doses considered. In order to understand the molecular modifications induced by gamma radiation on this polymer, melt viscosity measurements were performed. In Fig. 2, the dynamic melt viscosity versus the angular frequency is reported for unirradiated PA6 and PA6 irradiated at 200 and

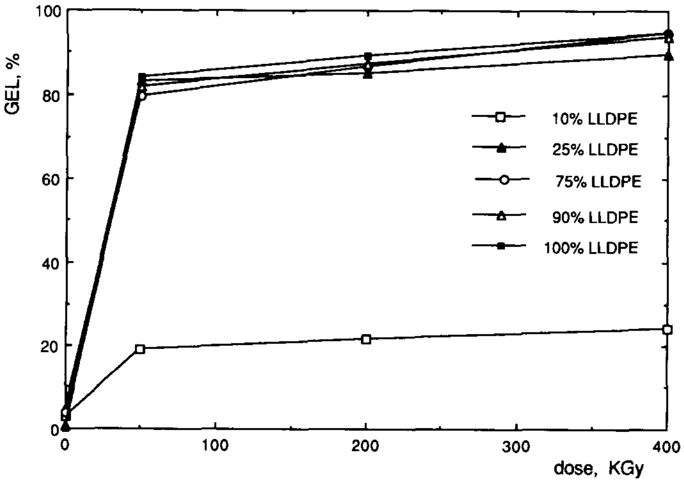

Fig. 1. Gel fractions of LLDPE component vs. dose for all blends.

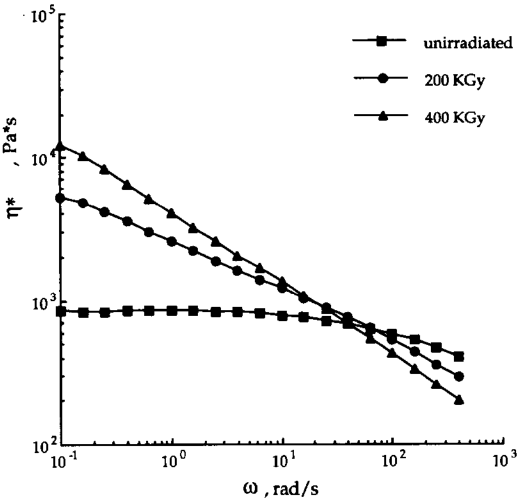

Fig. 2. Dynamic melt viscosity vs. the angular frequency for PA6.

400 kGy. A drastic change in the flow curves is observed; in particular a pronounced non-Newtonian behaviour is shown by the irradiated samples and this effect becomes more significant on increasing the dose. These results can be attributed to an increase in the molecular weight through chain branching, according to the literature [2, 12].

In Fig. 3, solubility data for the polyamide component in formic acid are reported for unirradiated and irradiated PA6 rich blends. Data for LLDPE-rich blends are not reported because of the very low weight fractions of PA6. The polyamide is always completely soluble in formic

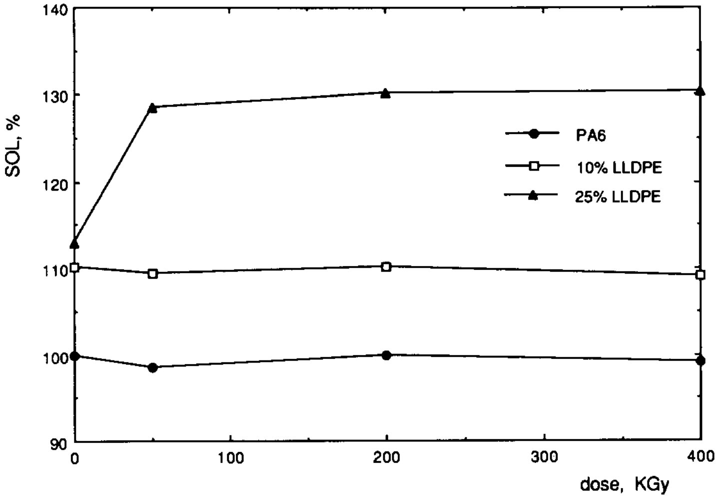

Fig. 3. Solubility data for the PA6 component vs. dose.

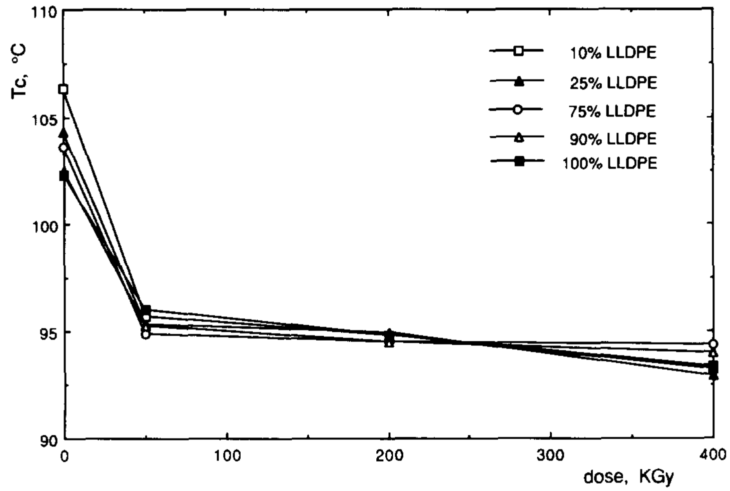

Fig. 4. Temperature of maximum crystallization rate T_c for LLDPE vs. dose.

acid; furthermore, some solubility of the polyethylene component in the same solvent is observed. This could be attributed to interactions between the two polymers, during both mixing and irradiation.

Calorimetric determinations corroborate the general behaviour outlined above. In Fig. 4 the temperatures of maximum crystallization rate T_c for LLDPE during DSC tests are plotted against the dose. For the unirradiated blends, T_c increases with polyamide content: the polyamide probably acts as a nucleating agent for polyethylene. Irradiated blends have a lower T_c of LLDPE, not significantly affected by the weight percentage of PA6. In these samples, the presence of large amounts of gel fractions, as revealed by solubility tests, hinders the crystallization kinetics.

The T_c values of the PA6 component are plotted against dose in Fig. 5. No significant differences are observed among blends of different composition for the same irradiation dose. Irradiation causes a decrease in T_c at high dose and this is consistent with the increase in branching observed in the melt viscosity tests. Data for 90% LLDPE blends are not reported, because of the uncertainty of these experimental data due to the very small crystallization peak.

Crystallization enthalpies ΔH_c for LLDPE are plotted against dose in Fig. 6. Blends with high polyethylene content (75% and 90%) and pure polymer have the same ΔH_c values, not affected by irradiation. However for the other blends, the crystallization enthalpy decreases and is lower the lower the polyethylene content and the higher the dose. This behaviour can be related to the solubility results discussed above, i.e. the crosslinking and dissolution of LLDPE in PA6 matrix.

Data relative to the ΔH_c values of the polyamide component are reported in Fig. 7. For blends with high amounts of PA6, no effect of composition or

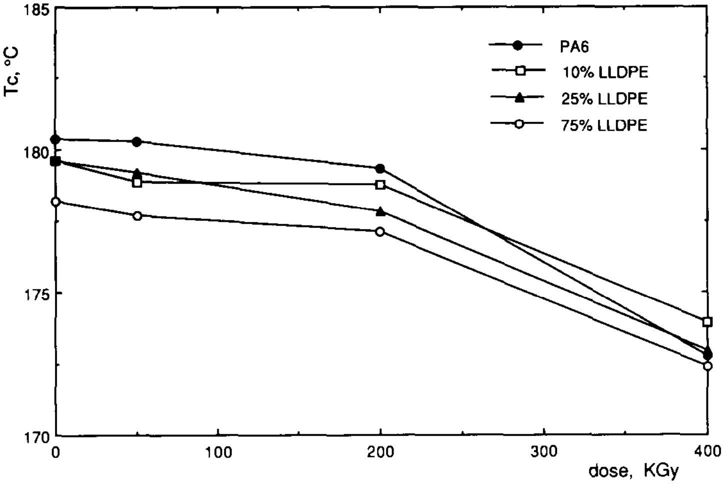

Fig. 5. Temperature of maximum crystallization rate T_c for PA6 vs. dose.

dose is observed, whereas the 75% LLDPE blend has a lower ΔH_c, which decreases on increasing the irradiation dose. This is consistent with the effects of mixing and irradiation on T_c already observed; the dispersion of polyamide in the polyethylene matrix makes its crystallization difficult, and the crosslinking of LLDPE enhances these difficulties.

Furthermore, with respect to the crystallization behaviour of LLDPE, a comparison between Figs. 4 and 6 suggests that the molecular modifications induced by gamma radiation mainly influence the kinetics of crystallization, rather than the "equilibrium" value, whereas the PA6 crystallization in 75% LLDPE blend seems to undergo the opposite effect, as revealed by a comparison of Figs. 5 and 7.

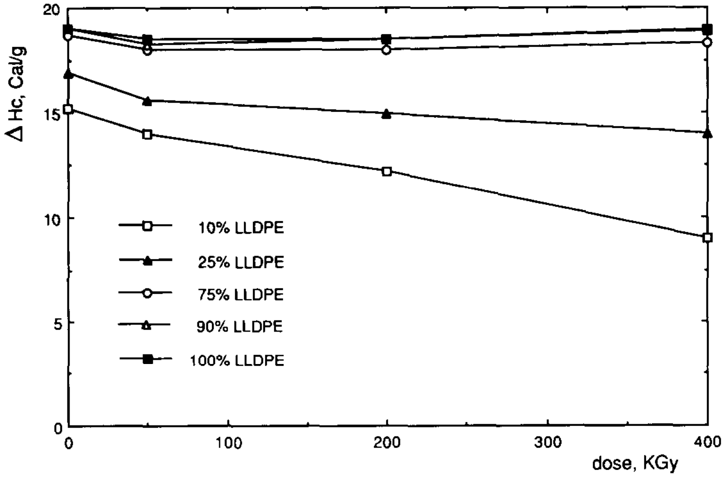

Fig. 6. Crystallization enthalpies ΔH_c for LLDPE vs. dose.

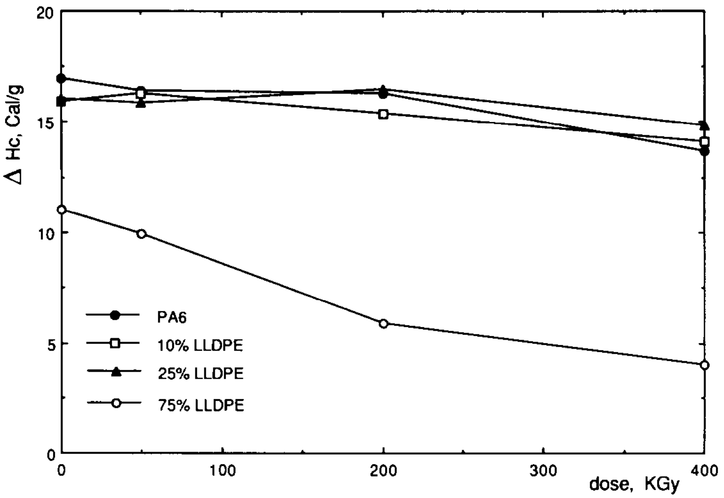

Fig. 7. Crystallization enthalpies ΔH_c for PA6 vs. dose.

CONCLUDING REMARKS

Irradiation under vacuum of LLDPE/PA6 blends at various compositions causes molecular modifications which can be related both to the effects on the pure polymers and to interactions between the two components. Also, the effects of interactions during mixing must be taken into account. Gel fractions of polyethylene indicate that this polymer, both pure and in blends, undergoes mainly crosslinking phenomena; an increase in molecular weight is observed for pure polyamide and all experimental results indicate that similar effect are always present in the blends.

For the calorimetric results, the more significant effects are usually observed for the minor component at high doses. This can be attributed to the increased difficulty of reorganization as a result of both the dispersion of the minor polymer component in the matrix for LLDPE, and the increase in molecular weight due to irradiation for PA6.

ACKNOWLEDGEMENT

This work was supported by M.U.R.S.T. 40% and 60%.

REFERENCES

1 M. Dole, The Radiation Chemistry of Macormolecules, Academic Press, New York, 1972.
2 A. Charlesby, Radiation Effects in Polymers, in A.D. Jenkins (Ed.), Polymer Science, North-Holland, Amsterdam, 1972.
3 D.W. Clegg and A.A. Collier, Irradiation Effects on Polymers, Elsevier, London, 1991.
4 L. Spenadel, Radiat. Phys. Chem., 14 (1979) 683.
5 G. Spadaro, G. Rizzo, D. Acierno and E. Calderaro, Radiat. Phys. Chem., 23 (1984) 445.

6 T. Nishi and T.K. Kwei, Polymer, 16 (1985) 285.
7 S. Thomas, B.R. Gupta and S.K. De, Polym. Degrad. Stab., 18 (1987) 189.
8 D.R. Paul and S. Newmann, Polymer Blends, Academic Press, New York, 1978.
9 L.A. Utracki, Polymer Alloys and Blends, Hanser Publishers, Munich, 1989.
10 E. Calderaro, E. Oliveri and P. Tallarita, Quaderni dell'Istituto di Applicazioni de Impianti Nucleari, Vol. 3, University of Palermo, 1980.
11 F.P. La Mantia and A. Valenza, J. Therm. Anal., 34 (1988) 491.
12 J.D. Ferry, Viscoelastic Properties of Polymers, Wiley-Interscience, New York, 3rd edn., 1980.