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AGEING DUE TO GAMMA RADIATION OF THREE LINEAR LOW-DENSITY POLYETHYLENES. SOLUBILITY AND CALORIMETRIC RESULTS

G. RIZZO[1], A. VALENZA[1], E. CALDERARO[2] and G. SPADARO[1]

[1]*Dipartimento di Ingegneria Chimica dei Processi e dei Materiali, Università di Palermo, Viale delle Scienze, 90128 Palermo (Italy)*

[2]*Dipartimento di Ingegneria Nucleare, Università di Palermo, Viale delle Scienze, 90128 Palermo (Italy)*

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ABSTRACT

Modifications induced by gamma radiation on three linear low-density polyethylenes have been studied by means of solubility and calorimetric measurements. Irradiation has been performed in air at room temperature at various integrated doses. The results indicate that the main effect is crosslinking, primarily in the amorphous regions. There were no significant differences between the three poliethylenes in the radiation dose range investigated.

INTRODUCTION

Linear low-density polyethylenes (LLDPE) are obtained by copolymerization of ethylene with olefins. In recent years, their industrial production has become substantial and they are gradually replacing conventional polyethylenes. By contrast, little is known about their response to gamma radiation [1,2].

Preliminary results for three LLDPE gamma irradiated in air over an integrated dose range are presented in this paper in an investigation of their behaviour and the identification of possible differences between them in relation to the molecular weight of the homopolymers.

In this initial stage, only bulk effects have been investigated by means of solubility and calorimetric measurements. Further work will investigate the

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depth-dependence of radiation effects as related to oxygen diffusion kinetics.

EXPERIMENTAL

The materials used were copolymers of ethylene with 1-butene (LLPB), 1-hexene (LLPH) and 1-octene (LLPO) respectively. Their physical and chemical properties [3] are shown in Table 1.

Samples were cut from sheets 1 mm thick obtained by compression moulding in a laboratory press at 180 °C and 2.5×10^{-2} GPa for 5 min. Subsequent rapid cooling was obtained by running cold water through the press platens.

Irradiation was performed at room temperature by the IGS-3, a panoramic 3000 Ci ^{60}Co irradiator. The dose rate, measured by the Fricke dosimeter, was 5.3×10^{3} Gy h^{-1}, a variance of 5% in the radiation absorption being accepted. The doses investigated were 1×10^{5}, 2.5×10^{5}, 5×10^{5}, 7.5×10^{5}, 1×10^{6} and 1.5×10^{6} Gy.

Thermal treatment for 4 days at 70 °C under vacuum was performed after irradiation. This was suggested by the well-known practice [4] of operating at very low temperature (a few dozens of K) to prevent from free radical evolving into more stable derivatives. It is reasonable to assume that this treatment substantially eliminates trapped free radicals, capable of causing oxydative degradation in the presence of air and thus modifying the properties of the materials during their measurements. The unirradiated samples were also subjected to this treatment. Furthermore, all tests were performed within 48 hours after heating to standardize the measurement procedure as much as possible.

Gel content was determined with a Soxhlet extractor. Approximately 0.3 g

TABLE 1

Physico-chemical properties of unirradiated Linear Low Density Polyethylene

Sample code	Comonomer	r/kg m^{-3}	M.F.I.	10^{-3} M_w	M_w/M_n
LLPB	1-butene	924	1.10	136	4.1
LLPH	1-hexene	921	1.09	137	3.5
LLPO	1-octene	920	0.98	122	3.7

M.F.I.: Melt Flow Index according to ASTM D1238/73 method, proc. E.

TABLE 2

Gel content in percent.

Radiation dose (Gy)	LLPB	LLPH	LLPO
0 (virgin)	0	0	0
0 (annealed)	0	0	0
1×10^5	37	44	52
2.5×10^5	66	65	69
5×10^5	75	73	75
7.5×10^5	79	77	78
1×10^6	89	87	88
1.5×10^6	84	85	84

of each sample were exposed to refluxing xylene close to its boiling point. Extraction was carried out for at least 96 hours until the sample attained constant weight.

Calorimetric tests were performed with a Perkin-Elmer DSC-4 equipped with a Perkin-Elmer Mod.3600 data acquisition system. The heating rate was 8 °C min^{-1} up to melting (1st run); the sample was then cooled at a rate of 16 °C min^{-1} down to room temperature and heated up to melting (2nd run) at a rate of 8 °C min^{-1}. Melting temperatures and enthalpies were measured in both heating runs. Reproducibilities were within ± 1 °C and ± 10% respectively.

RESULTS AND DISCUSSION

Gel fractions (Table 2) increase for all samples in function of the radiation dose. As already reported for a different LLDPE [1], this can be attributed to a significant prevalence of crosslinking with respect to degradation as an effect of irradiation. This behaviour is common to all kinds of polyethylenes, its quantitative effects depending on many parameters, such as the morphological and structural features of polymers and the environmental irradiation conditions [5-10].

Calorimetric tests have been performed on both irradiated and unirradiated samples to obtain a better understanding of the morphological and structural modifications induced by gamma radiation. Fig. 1 shows a typical DSC thermogram. The melting temperature, T_m, has been taken as the peak temperature in the specific heat-temperature plot, while the melting entalpy $\Delta_{fus}H$, has been evaluated as the area under the peak [11].

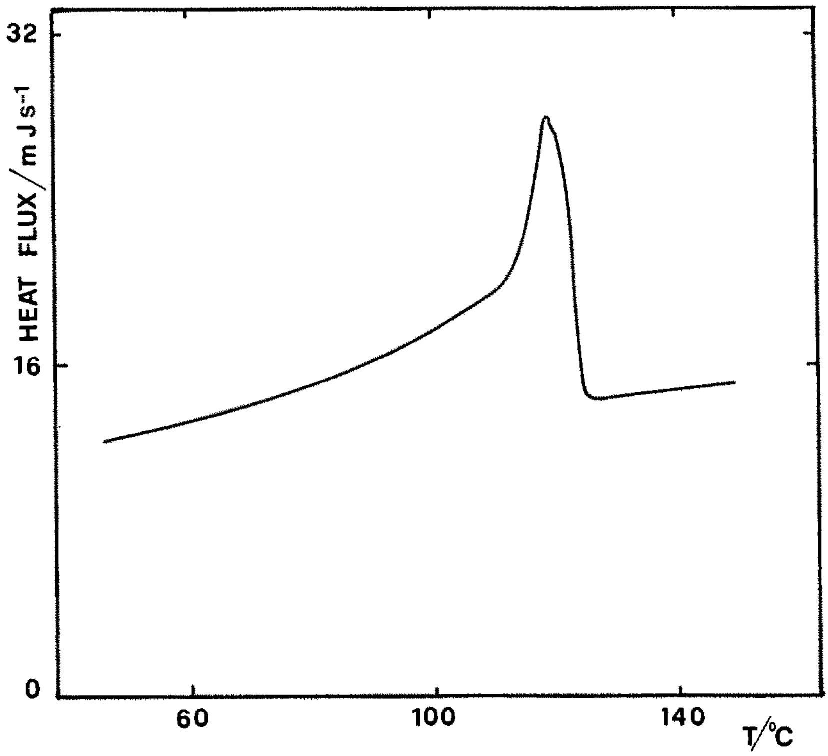

Fig. 1. Typical DSC thermogram. The sample is virgin LLPB.

The calorimetric tests results are set out in Tables 3 and 4. Comparison between virgin and annealed samples shows that thermal treatment at 70 °C for 4 days does not significantly affect T_m and $\Delta_{fus}H$ values, suggesting that no quantitative or qualitative change has taken place in polymer crystallinity.

The data in Table 3 show that melting enthalpies in the first heating run do not depend on gamma radiation. This is due to the fact that crosslinks essentially form in the amorphous regions.

The melting temperatures of irradiated samples of LLPB and LLPH in the first heating run increase at irradiation dose $1x10^5$ Gy, and then settle at a lower value for higher doses. As for LLPO, a generalized decrease of T_m is observed as an effect of irradiation. This can be interpreted by considering that the effect of crosslinking on T_m is twofold: on the one hand, it hinder chain refolding during heating in the calorimeter, thus producing a lower melting point; on the other hand, it produces a decrease in the entropy of the melt, thus increasing T_m value [5]. For LLPB and LLPH samples irradiated at 10^5 Gy, the prevailing

TABLE 3.

Melting enthalpies, $\Delta_{fus}H$, measured by DSC .

	LLPB		LLPH		LLPO	
Radiation dose / Gy	A	B	A	B	A	B
0 (virgin)	33	33	33	33	32	32
0 (annealed)	34	35	35	34	34	35
$1x10^5$	33	29	34	30	35	31
$2.5x10^5$	31	29	36	30	34	30
$5x10^5$	32	30	34	28	34	29
$7.5x10^5$	31	28	32	28	32	28
$1x10^6$	32	30	33	28	34	30
$1.5x10^6$	33	30	32	27	33	28

A: first run; B: second run. Unit: cal g^{-1}.

TABLE 4

Melting Temperatures, T_m, measured by DSC .

	LLPB		LLPH		LLPO	
Radiation dose / Gy	A	B	A	B	A	B
0 (virgin)	120	122	121	122	124	125
0 (annealed)	121	122	121	122	124	125
$1x10^5$	123	120	122	119	122	119
$2.5x10^5$	120	115	120	114	121	117
$5x10^5$	120	114	119	114	121	116
$7.5x10^5$	120	116	119	115	121	117
$1x10^6$	119	115	119	115	121	117
$1.5x10^6$	119	115	119	116	122	117

A: first run; B: second run. Unit: °C.

effect is on the entropy of the melt, whereas in all other irradiated samples it is the hindering of chain refolding. This second effect seems to become dominant on increasing the crosslinking degree, as suggested by comparison with the gel fraction data in Table 2.

In the second heating run, melting enthalpies and temperatures undergo a generalized decrease as an effect of irradiation. This can be ascribed to the presence of crosslinks, hindering the formation of crystals and deteriorating those which have formed [12,13]. At other integrated doses, the magnitude of these effects varies according to the gel fraction data in Table 2.

CONCLUDING REMARKS

The main effect of irradiation in our experiment was crosslinking. LLPB, LLPH and LLPO were not significantly different in this respect.

As a general consideration, these LLDPE undergo morphological and structural modifications similar to those reported in the literature for other more conventional polyethylenes.

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REFERENCES

1 R. Basheer and M. Dole, J. Polym. Sci., Phys., 21 (1983) 949-956.
2 R. Basheer and M. Dole, J. Polym. Sci., Phys., 21 (1983) 957-967.
3 A. Valenza, F.P. La Mantia, D. Acierno, Eur. Polym. J., in press.
4 M. Dole, The Radiation Chemistry of Macromolecules, Academic Press, London, 1972.
5 H. Jenkins and A. Keller, J. Macromol. Sci., Phys. B, 11 (1975) 301-323.
6 M. Dole and V.M. Patel, Radiat. Phys. Chem., 9 (1977) 433-444.
7 M. Dole, Polym. Plast. Technol. Eng., 13 (1979) 41-64.
8 M. Imai, Radiat. Phys. Chem., 18 (1981) 425-431.
9 T. Seguchi, S. Hashimoto, K. Arakawa, N. Hayakawa, W. Kawakami and I. Kuriyama, Radiat. Phys. Chem., 17 (1981) 195-201.
10 T. Seguchi, K. Arakawa, N. Hayakawa, Y. Watanabe and I. Kuriyama, Radiat. Phys. Chem., 19 (1982) 321-327.
11 J.A. Brydson, in A.D. Jenkins (Ed.), Polymer Science, North Publishing Company, Amsterdam, 1972.
12 D. Acierno, E. Calderaro, L. Napoli and G. Spadaro, Colloid and Polymer Sci., 261 (1983) 121-125.
13 G. Rizzo, G. Spadaro, D. Acierno and E. Calderaro, Radiat. Phys. Chem., 21 (1983) 349-353.