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CALORIMETRIC ANALYSIS OF AN ISOTACTIC POLYPROPYLENE GAMMA-IRRADIATED IN VACUUM

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Abstract

The molecular modifications induced in an isotactic polypropylene gamma-irradiated in vacuum under a complete set of experimental conditions were studied by means of calorimetric analysis. In a previous paper [1], the influence of the irradiation parameters, the total absorbed dose, *D*, and the dose rate, *I*, was analyzed and a simple kinetic model based on the rates of the main reactions occurring during irradiation, i.e. β-scission, addition to double bonds and termination, was also discussed. It is now shown how thermal analysis confirms the model forecasts and in particular the existence of the 'inversion conditions': below them the main effect is molecular degradation, while above them the main effects are chain-branching and cross linking.

Keywords: calorimetric analysis, gamma-radiation, isotactic polypropylene

Introduction

The radiation processing of polymers can be suggested as an environmentally and energetically safe way to modify their molecular structures as an alternative to other, more traditional chemical methods. In fact, the use of ionizing radiation does not need solvents or initiators at high-temperature and allows the avoidance of degradation phenomena and other side-reactions typical of polymer processing in the melt state. Moreover, the possibility of processing the polymer in the solid state in its final shape furnishes new stimulating applications to obtain materials with well-tailored properties [2, 3].

Several basic studies of gamma-radiation-induced modifications of polymers have been reported in the literature [4, 5]. It is well known that the interaction of ionizing radiation with polymers mainly causes the formation of free radicals. Their further evolution towards more stable forms can give rise to significant modifications in the irradiated materials, such as chain scission with molecular mass decrease and chain-branching with molecular mass increase up to crosslinking. Usually, all these phenomena coexist with one or more predominating, depending on the molecular structure and morphology of the polymer and the experimental irradiation conditions. These last include the total absorbed does, *D*, the dose rate, *I*, which can affect the

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concentration of the reactive species and consequently the kinetics of the involved reactions and the environment.

Among all the polymers, one of the most investigated has been polypropylene. The interest in the molecular modifications induced by gamma-rays in this material lies in its numerous applications [4–6]. In previous work [1], the response of polypropylene to gamma-radiation in vacuum was studied on the basis of a simple kinetic model. We analyzed the influence of the irradiation parameters D and I on the rates of the main reactions believed to occur during irradiation, i.e. β-scission, addition to double bonds and termination. We showed that it is possible to obtain the equation of an 'inversion curve', an implicit function of D and I, which gives the dose values enhancing chain-branching and the molecular mass increase at a fixed dose rate, and vice versa. In the previous work, the molecular modifications induced by irradiation were studied through dynamic mechanical analysis (DMA) in the melt state. Here, the possibility to analyze the effects of irradiation on the molecular structure of the irradiated polymer by means of thermal analysis is discussed, and the similarity in the responses of the calorimetric and DMA data is evidenced.

Experimental

The material used was an isotactic polypropylene (iPP), kindly supplied by Montell, with M_w=481.000 and polydispersity 6.4.

Polymer sheets were prepared from pellets by compression molding in a programmable laboratory press at 220°C for 10 min. Irradiation was performed under vacuum at room temperature (about 25°C), with the IGS-3, a panoramic 3000 Ci ^{60}Co irradiator [7]. The dose rates, measured with a PTW universal dosimeter, were in the range 0.04–5.6 kGy h^{-1} and the total absorbed doses were in the range 6–1500 kGy; a variance of 5% in the radiation absorption was accepted. As a rule, for each experiment the analysis was carried out on samples immediately after irradiation. All samples passed the time between the end of irradiation and the start of the tests in liquid nitrogen.

Dynamic-mechanical tests in the melt state were performed with a Rheometrics dynamic analyzer (RDA2), used in the dynamic mode with the plate and plate geometry (R=12.5 mm). The frequency sweep tests were carried out at 180°C and 20% strain in the range 10^{-1}–$5\cdot10^{2}$ rad s^{-1}.

Thermal analysis was carried out with a Perkin Elmer DSC-7 instrument. Samples of about 15 mg were heated up to 180°C, cooled down to room temperature and finally subjected to a second heating run. The heating and cooling rates were ±10°C min^{-1}. The reported data refer to the second heating run.

Results and discussion

It has been already shown [1] that it is possible to forecast the molecular modifications of polypropylene gamma-irradiated in vacuum on the basis of a simple kinetic model. This model is based on the assumption that the final molecular structure of the irradiated polypropylene is a result of the competition between the kinetics of the various reactions taking place during the evolution of the free radicals produced by the interactions of gamma-rays with the polymer. In particular, the main reactions, which are believed to occur significantly, are: i) β-scission; ii) addition of free radicals to double bonds; iii) termination. Both irradiation parameters *I* and *D* affect the molecular modifications of polypropylene. In particular, a molecular mass increase is favored by irradiation at low dose rates and high absorbed doses.

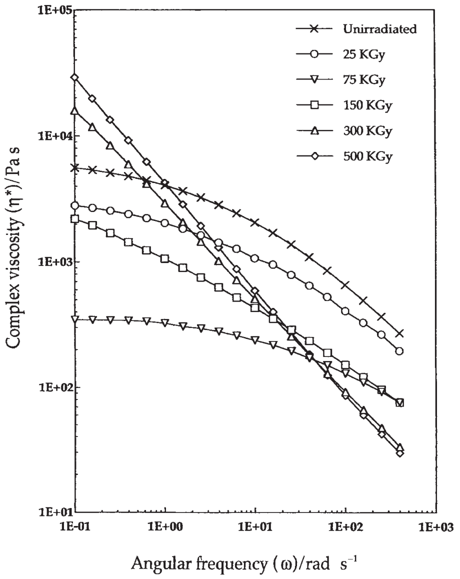

Fig. 1 Flow curves for samples irradiated at 1 kGy h^{-1} and various total doses

The effects of irradiation on the molecular structures of polymers can be studied by several methods. Previously [1], it was shown that DMA in the melt state is a very useful tool to afford a complete set of information on the complex molecular events occurring during gamma-irradiation. This is evidenced in Fig. 1, where the flow curves for samples irradiated at 1 kGy h^{-1} and various total doses are shown. In relation to the curve for the unirradiated sample, it can be observed that samples irradiated at low doses display lower complex viscosity values, and this effect in enhanced by increase of the total absorbed dose. This phenomenon can be related to the prevalence, under these irradiation conditions, of β-scission reaction, causing a molecular mass decrease, even though chain-branching reactions also occur. On increase of the total dose, a response inversion of the material to gamma-radiation is observed. In fact, the slope of the flow curve relative to that of the sample irradiated at 150 kGy becomes steeper. It is well known that this is the typical behaviour of a branched polymer close to the gel point [8].

Furthermore, for these last irradiation conditions, we cannot exclude the presence of microgels in the bulk of the polymer, even if the polymer is still completely soluble. At high absorbed doses of 300 and 500 kGy, an increase in the melt viscosity occurs, mainly at low frequencies, and the flow curves tend to become those of a strongly crosslinked polymer. Similar behaviour exhibited by the flow curves reported in Fig. 2 for samples irradiated at 5.64 kGy h^{-1} and various absorbed doses. A response inversion is also observed, but it occurs at a higher absorbed dose, in accordance with the forecasts of the model previously quoted [1]. The results to be seen in Figs 1 and 2 are confirmed by the gel extraction data presented in Table 1.

Table 1 Gel fractions for isotactic polypropylene expressed in percentage

Irradiation dose, D/kGy	I=1 kGy h^{-1}	I=5.64 kGy h^{-1}
6	–	–
12	–	–
25	0	–
50	–	0
75	–	–
150	0	0
300	0	38
500	47	55
1600	–	93

As already reported [9–12], the modifications induced in the molecular structure by irradiation can significantly affect both the ability to crystallize of a semicrystalline polymer and its final morphology. Consequently, thermal analysis can also be used to investigate the molecular effects of irradiation. Figure 3 depicts the TG relating to the second

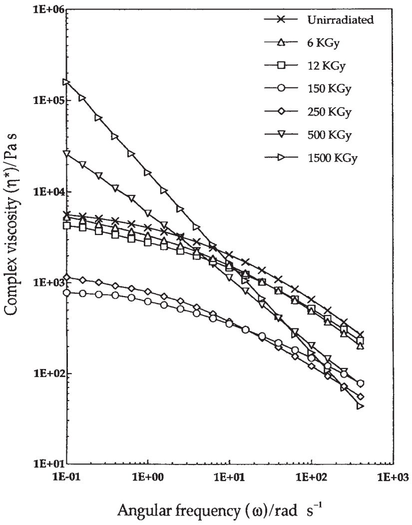

Fig. 2 Flow curves for samples irradiated at 5.64 kGy h^{-1} and various total doses

heating run of samples irradiated at 1 kGy h^{-1}. As evidenced by the flow curves, at low absorbed doses chain scission is the main effect. Double bond addiction reactions also occur, with chain-branching phenomena; this hinders the close-packing ability, giving

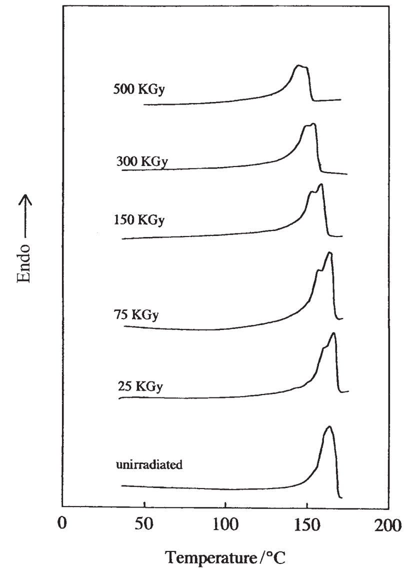

Fig. 3 DSC TG for polypropylene irradiated at 1 kGy h^{-1}

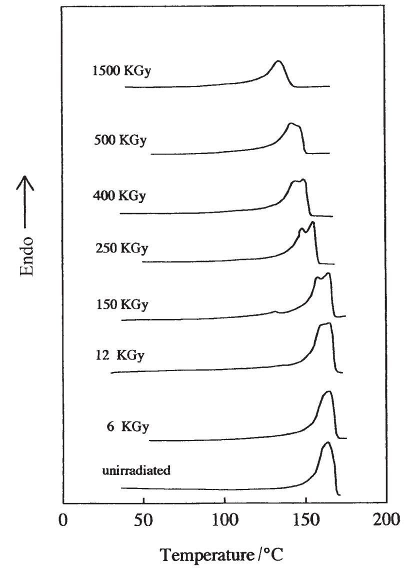

Fig. 4 DSC TG for polypropylene irradiated at 5.64 kGy h^{-1}

rise to segregation phenomena, with the formation of less regular crystalline structures characterized by an additional melting peak at lower temperature. The high-temperature peak, relative to the melting of the more regular crystals, is essentially unmodified. In contrast, the temperature of this last peak decreases for the sample irradiated at 150 kGy and this effect becomes more and more marked on increase of the total absorbed dose. For samples irradiated at high doses, the flow curves and gel extraction indicate the prevalence of chain-branching phenomena and the formation of insoluble networks. Crosslinking does not allow refolding during the heating run, giving rise to a lower melting temperature closer to the thermodynamic value for the polymer [9].

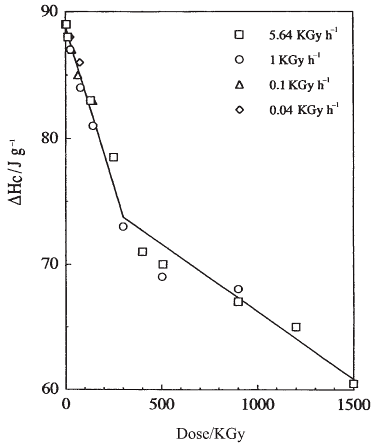

Fig. 5 Melting enthalpies as a function of the total absorbed dose

Similar results are shown by the TG reported in Fig. 4 for samples irradiated at various absorbed doses and 5.64 kGy h^{-1}. The curves present the same qualitative response to gamma-radiation. It is worth noting that the decrease in the melting temperature of the high-temperature peak occurs in correspondence of 250 kGy, according to what observed through the flow curves reported in Fig. 2, which evidence the occurrence of inversion response at higher doses observed.

Table 2 reports melting data for all irradiated samples. It can be observed that, with reference to the un-irradiated polymer, irradiation causes a generalized decrease in the melting enthalpy. This can be considered due to the occurrence of chain irregularities caused by chain-branching and cross linking. For a better understanding of the correlation of this thermal behaviour with the irradiation parameters, melting enthalpy values are reported as a function of the absorbed dose in Fig. 5. A generalized decrease in the melting enthalpy with increasing dose is observed. All the experimental data can be interpolated by two lines with different slopes, the first most likely corresponding to the irradiation conditions where crosslinking is not predominant, while for the second one crosslinking is the major effect. The cross-point between the two curves can therefore be regarded as a calorimetric means of determining the inverse response of polypropylene to gamma-radiation in vacuum.

Table 2

Dose rate, I/kGy h^{-1}	Dose, D/kGy	T_C/°C	ΔH_C/J g^{-1}	T_m/°C	ΔH_m/J g^{-1}
Unirradiated	0	109	89	163	92
0.04	25	107	88	164	84
	50	107	87	163	84
	75	106	86	161	83
0.1	12	108	88	163	84
	25	107	88	164	84
	75	107	85	161	85
	150	105	83	158	82
1	25	108	87	164	76
	75	106	84	164	76
	150	105	81	158	81
	300	103	73	153	80
	500	102	69	144	68
	900	100	68	140	67
5.6	6	108	89	164	88
	12	107	88	164	88
	150	107	83	162	86
	250	104	79	155	82
	400	100	71	149	75
	500	99	70	141	69
	900	98	67	138	65
	1200	96	65	136	62
	1500	94	60	134	58

Concluding remarks

In this work, the effects of gamma-radiation in vacuum on the molecular modifications of an iPP were studied via thermal analysis, and interpreted on the basis of a kinetic model previously reported [1]. The TG are related to the influence on the crystallization behaviour of the extent of the main reactions believed to occur during irradiation, i.e. β-scission, addition of free radicals to double bonds and termination. In particular, the presence of segregation phenomena is related to molecular degradation and chain-branching, while the decrease in the melting temperature relative to the main melting peak is related to crosslinking effects. A decrease in the melting enthalpy occurs and a new way to determine the inversion response of polypropylene to gamma-irradiation is proposed.

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