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Thermal analysis studies using oscillation DSC to determine changes in LD ethene/butene copolymer induced by gamma radiation treatment [☆]

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Abstract

A polymeric material is used in one part of a container for an eye-drop solution. The material is sterilized by ionizing radiation. The effect of exposure to different doses was studied by thermal analysis. The technique used is called oscillating DSC. The DSC signal can be separated into two components, reflecting reversible reactions and non-reversible reactions respectively. The sum of these two components makes up the conventional DSC signal. The conventional DSC signal showed no variation in the enthalpy for a melting reaction. However, the two components showed very clear changes, which could be correlated to dose. The most significant changes were found in the non-reversible component during heating of the samples.

Keywords: Butene; Copolymer; DSC; Gamma irradiation; MDSC; ODSC; Polymer

1. Introduction

A polymeric material consisting of an ethene–butene (less than 10% butene) copolymer including some additives is used in one part of a container for an eye-drop solution. This part is sterilized by ionizing radiation. The effects on the

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polymeric material of exposure to different doses and different storage conditions (temperature and humidity) were studied by thermal analysis. The aim of the study was to evaluate how well DSC could provide information that could be correlated to dose and storage conditions.

2. Experimental

2.1. The material

The copolymer contains small amounts of antioxidant Irganox 1076, zinc stearate, calcium carbonate and titanium oxide. The additives were blended with the copolymer, and this blend was melted and formed into components by injection moulding.

The container components were irradiated in air by a Co-gamma source to a certain dose. Directly after irradiation, they were exposed to controlled storage parameters (humidity and temperature). They were kept under these conditions for 15 months. For each combination of dose and storing condition, duplicate samples were prepared and run in parallel.

2.2. Sample preparation

The samples for thermal analysis were cut to a suitable shape. Cylindrical samples with a diameter of 4 mm and a height of 1.5–2 mm were used. The sample weight was in the range 8–12 mg. After cutting, the samples were stored in plastic vials (Eppendorf) until analysed by DSC.

Table 1 shows the conditions and dose levels used, and the samples were named accordingly. Because duplicate samples were prepared, the two samples from group LL, for example, were also identified by a number, LL1 and LL2.

Table 1
Sample denomination, storing conditions and dose

Sample	Temperature in °C	Humidity in % rel	Dose in kGy
LL	+8	amb	30
LH	+8	amb	90
HL	+50	amb	30
HH	+50	amb	90
MM	+30	75	60
LO	+20	amb	0

The first letter of the sample indicates temperature and the second is dose: H, high; M, medium; L, low; O, none.

Table 2
Temperature programs

Step	Heating rate in °C min ⁻¹	Frequency in Hz	Amplitude in °C	Program name
1	10	0.02	5	A
1	5	0.02	3	B
2	-5	0.02	5	C
3	10	0.02	5	D
3	5	0.02	3	E

2.3. Thermal analysis

For the DSC measurements, a Seiko Instrument DSC 220C with automatic cooling was used. The instrument was equipped with software to perform oscillating DSC (controlling the effect to the furnace, and analysing the resulting DSC signal).

In oscillating DSC (called ODSC), the normally linear heating ramp is overlaid with an oscillating function, defined by a frequency and an amplitude, to produce a sine-wave-shaped temperature versus time function. Using Fourier mathematics, the DSC signal is then split up into two components, one reflecting non-reversible events, the other reversible events. The sum of these two makes up the total (conventional) DSC curve. Usually, the frequency ranges between 0.01 and 0.05 Hz, and the amplitude is 1–10°C.

The following DSC parameters were used: the samples were enclosed in an aluminium pan with a crimp cover, and an empty pan was used as a reference. The DSC cell was purged with 80 ml min⁻¹ N₂(g).

The temperature program was as follows: the samples were first quickly cooled to -130°C, without collecting data. After stabilizing at this temperature, they were heated to 180°C, again cooled to -130°C and again heated to 180°C. This made it possible to collect data from each sample from the first melting (step 1), the subsequent cooling (step 2) and also a second melting (step 3). The heating rate, frequency and amplitude used in the different steps are shown in Table 2.

2.4. Statistical evaluation

A multiple linear regression [1] was used to correlate the thermal analysis results to dose and storing temperature. This was done with the computer program Codex (SumIT, Sweden).

3. Results

In the first tests, samples of denomination HH and non-irradiated reference material were run according to programs A + D (Fig. 1), and also B + E. The

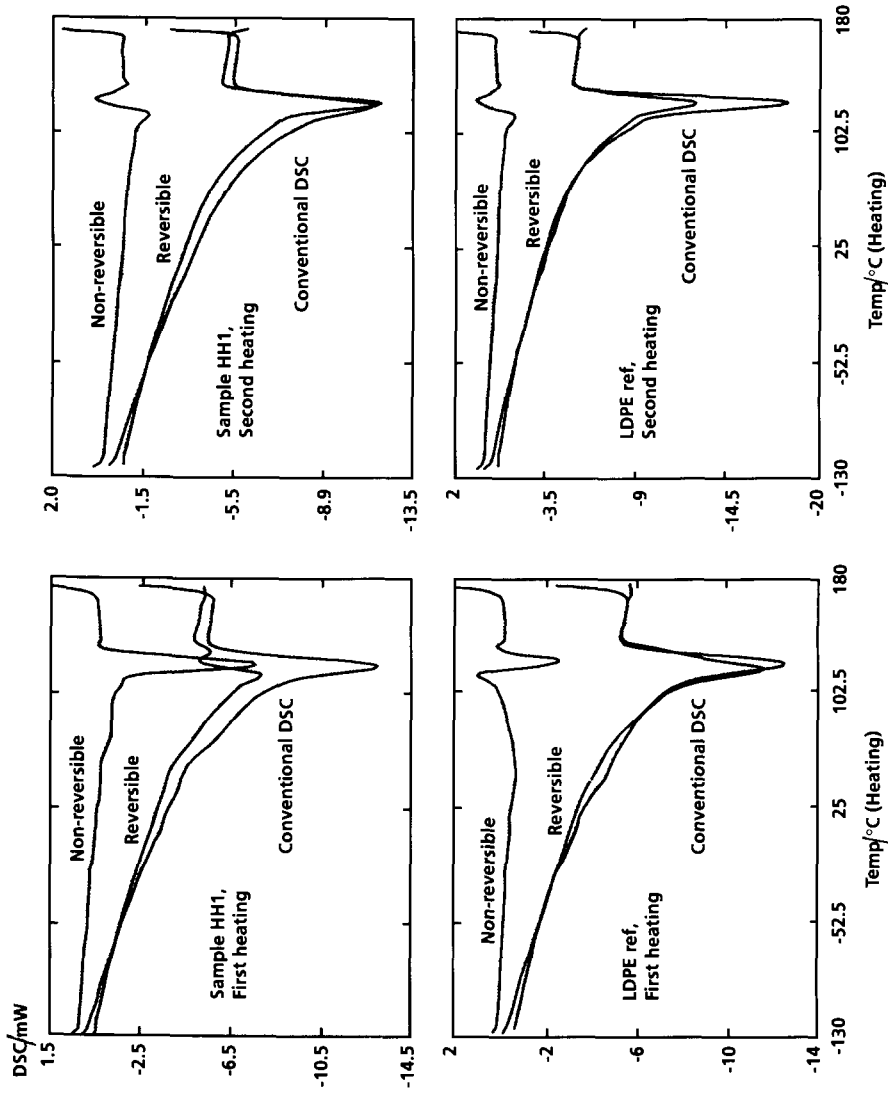


Fig. 1. DSC signal components, non-reversible and reversible, and the sum of these (the conventional DSC curve) are shown for samples HH and Reference, respectively, during the first and second heating according to temperature programs A and D (see Experimental section for details). All sample weights are normalized to 10 mg.

results show significant differences between sample HH and the reference material, with both programs A and B. For one sample, the differences between A and D, and B and E, respectively, reflect the expected difference due to reversible and non-reversible reactions.

After the initial studies of samples HH and reference material, it was decided to run the 6 samples in Table 1 using programs A and C.

Before looking at the detailed study of the non-reversible component, which was found to be the most powerful in differentiating between dose levels and storing conditions, conventional DSC and the reversible component during program A will be briefly described.

In Fig. 2, the conventional DSC curves are overlaid. The integrated endothermal peak enthalpy shows a difference of only 4.7% between the highest and lowest values. This is a variation that can be expected from the DSC equipment alone, and does not carry any significant information. In the temperature range 31.8–137.8°C, the mean enthalpy was found to be 139.1 mJ mg^{-1} , with a standard deviation s of 2 mJ mg^{-1} . The peak minimum temperature was found to be 121.5°C with a standard deviation of 0.8°C.

All irradiated samples show a double peak in the reversible component, see Fig. 3. The average peak minimum temperatures for the two peaks for 12 samples are 116.4°C ($s = 1.4^\circ\text{C}$) and 131.3°C ($s = 3.5^\circ\text{C}$), respectively.

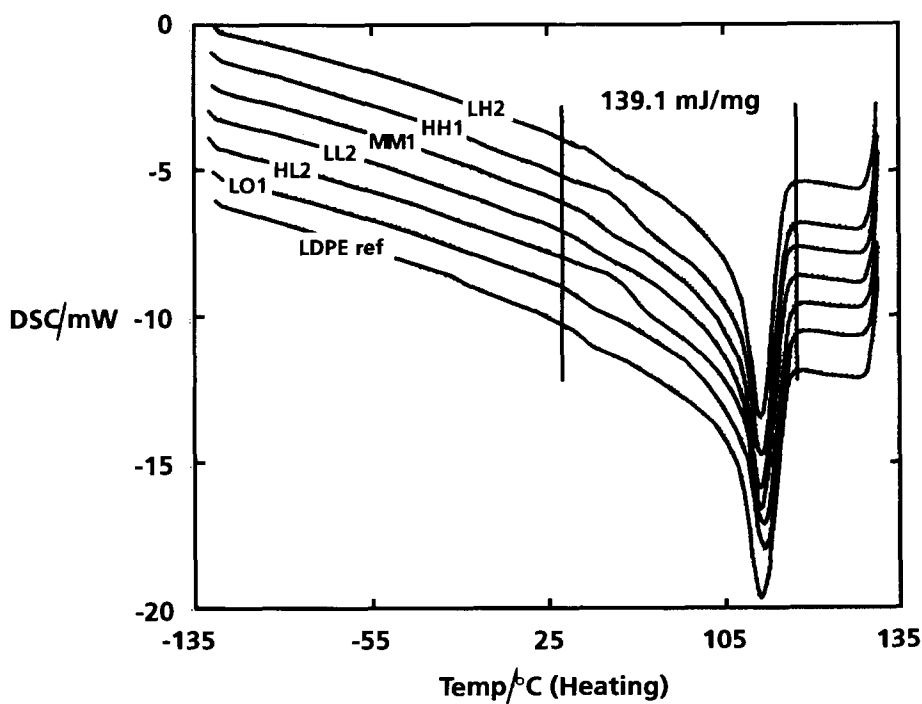


Fig. 2. Conventional DSC curves showing the endothermal melting during the first heating. Heating rate $10^\circ\text{C min}^{-1}$, amplitude 5°C and frequency 0.02 Hz . All sample weights are normalized to 10 mg.

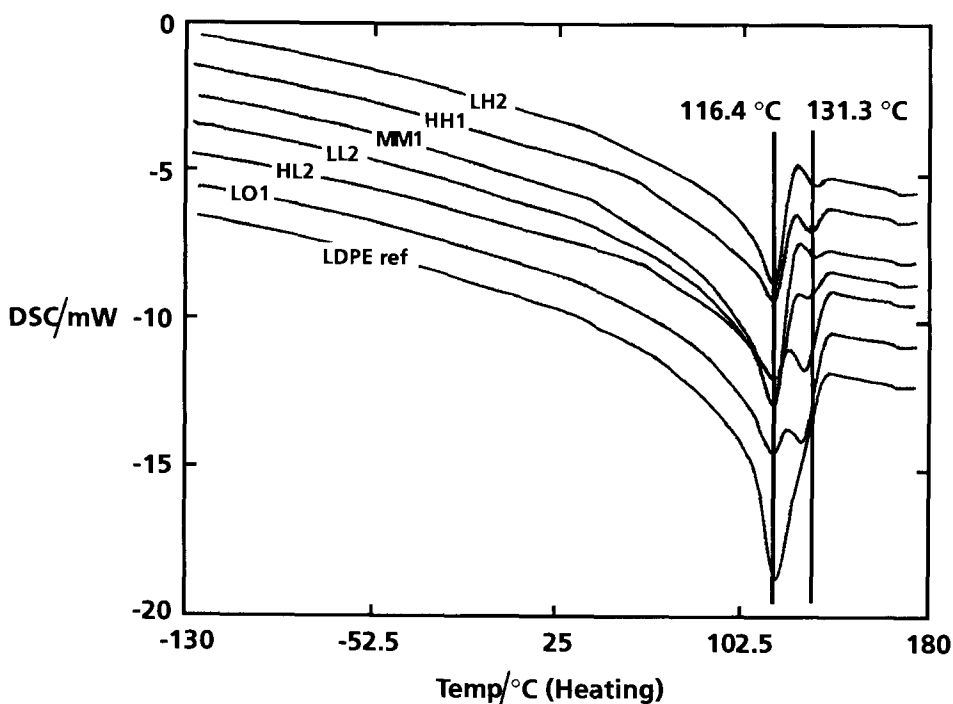


Fig. 3. The reversible components, during the first heating, showing double peaks for all irradiated samples. Heating rate $10^{\circ}\text{C min}^{-1}$, amplitude 5°C and frequency 0.02 Hz . All sample weights are normalized to 10 mg.

3.1. The non-reversible component

From the conventional DSC signal (Fig. 2), a glass transition is apparent in the region $30\text{--}65^{\circ}\text{C}$ in program A (and B). However, by studying the two components that make up this conventional DSC signal, it is clearly seen that this change comes from the non-reversible component alone. Comparing the non-reversible components from the first and second heating (Fig. 1), it is obvious that this reaction is non-reversible.

The position of the inflection point in the non-reversible component in program A has been used for the statistical evaluation of this work, and is denoted "inflection point", see Table 3. Only the mid point was used, but the size of the step could probably be of interest, Fig. 4.

A second characteristic in the non-reversible component, which strongly correlates to sample treatment, is the endothermic "melting" peak in program A (and B). This peak was evaluated in two ways: as an integrated peak area, giving an enthalpy in mJ mg^{-1} , and also as a difference in DSC signal between the peak minimum and the baseline after the peak. (The thermograms were normalized to 10 mg sample weight in this case.) Both these measures were used in the statistical

Table 3
Mid point values of the inflection point

Sample	Mid point temperature in °C	Sample	Mid point temperature in °C	Sample	Mid point temperature in °C
HH1	65.5	LH1	49.2	LL1	41.1
HH2	63.1	LH2	52.9	LL	41.0
HL1	63.6	MM1	50.4	LO1	40.7
HL2	62.6	MM2	48.7	LO2	38.6

evaluation (denoted enthalpy and DSC signal difference). The endothermic peak in the non-reversible component is the most obvious feature correlating to the received dose. Evaluated as enthalpy, the result is given in Table 4. Evaluated as the difference in DSC signal between peak minimum and baseline, the result is given in Table 5. Note that the figures are listed in descending order, as is the dose order.

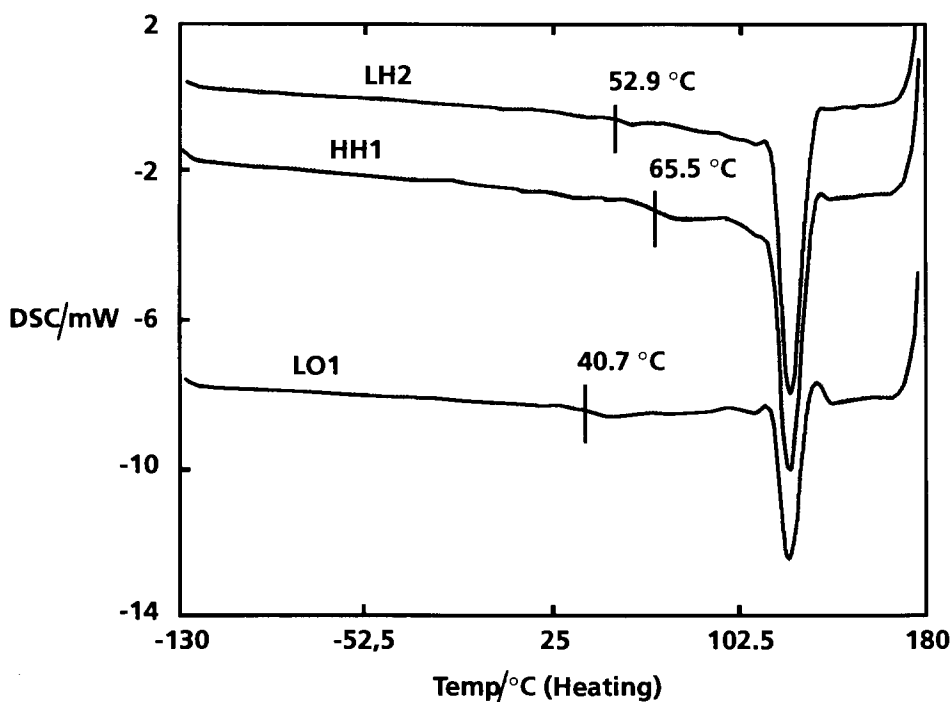


Fig. 4. The non-reversible component for samples LH, HH and LO, showing the inflection point and the endothermic peak. Heating rate $10^{\circ}\text{C min}^{-1}$, amplitude 5°C and frequency 0.02 Hz . All sample weights are normalized to 10 mg.

Table 4
Endothermal enthalpy for the non-reversible component

Sample	ΔH in mJ mg^{-1}	Sample	ΔH in mJ mg^{-1}	Sample	ΔH in mJ mg^{-1}
HH1	41.5	LH1	41.0	LL1	33.7
HH2	37.6	LH2	43.0	LL2	36.1
HL1	29.6	MM1	37.8	LO1	24.9
HL2	31.6	MM2	43.3	LO2	22.3
LDPE	19.2				

3.2. Reversible component during cooling

A very striking, continuous change in the appearance of the reversible component during cooling (program C) is observed (Fig. 5). On the high-temperature side, an endothermal reaction is shown for sample LO. It changes to an exotherm, and then the DSC signal returns to the baseline. The shape changes from sample LO to sample HH. When looking from the high-temperature side and with increasing dose, the first endotherm (C) decreases and disappears, the exotherm (B) diminishes, but a second endotherm (A) starts forming at lower temperatures. Table 6 gives the peak maximum/minimum to baseline difference for the DSC signal for the samples. Each value in this table is an average of 2–3 samples of the same type.

3.3. Time differences

The results in Table 5 were all obtained within a few days after opening the vials containing the pieces. New analyses were performed four days later (Table 7), after exposure to normal room conditions. Comparison of the DSC signal differences shows a decrease in the total level (compare LH2 in Table 6 to LH1 in Table 7, etc). However, the correlation between values and dose still remains in all cases except one.

A new set of analyses was performed after another 17–18 d, and again the same two parameters were evaluated. The result showed that the inflection point was less affected by the time that had elapsed than the DSC signal difference. In the DSC signal difference (Table 8), three samples now show values which are much lower

Table 5
DSC signal difference and dose order

Sample	Signal diff. in μW	Storing temperature	Dose
LH2	7657	L	H
HH1	7360	H	H
MM2	7163	M	M
LL2	6304	L	L
HL2	5800	H	L
LO1	4299	L	O
LDPE	2714	–	–

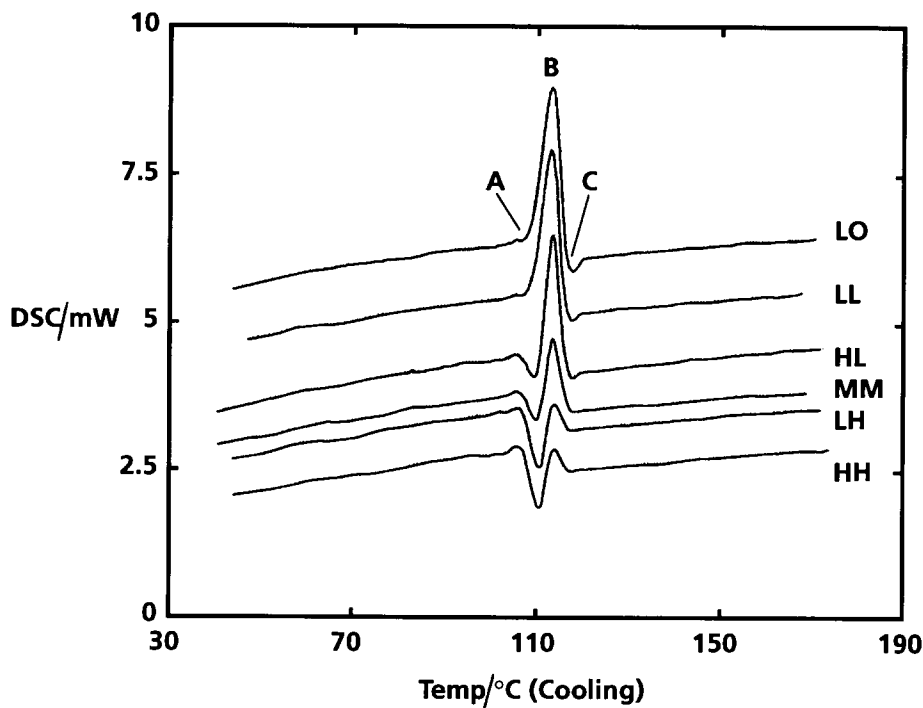


Fig. 5. The reversible component during cooling. Cooling rate $5^{\circ}\text{C min}^{-1}$, amplitude 5°C and frequency 0.02 Hz . All sample weights are normalized to 10 mg .

than expected from the correlation with dose, as found earlier. It is worth noting that all three belong to the high-dose group.

According to these results, there seems to be a large influence on the enthalpy peaks due to time elapsed between runs, evaluated as the DSC signal difference, for samples with a high dose. The effect on the inflection point is much less. This influence was discovered during the analysis, hence handling of the samples was not controlled in this respect.

Table 6

DSC signal differences in μW for peaks in the reversible component during cooling. The peaks are indicated in Fig. 5

Sample	Peak A	Peak B	Peak C
HH	1185	-464	0
LH	935	-467	0
MM	360	-1376	40
HL	167	-1934	77
LL	30	-2553	135
LO	0	-2457	307
LDPE (ref)	0	-4299	129

Table 7
DSC signal difference and dose order after sample exposure to ambient conditions

Sample	Signal diff. in μW	Storing temperature	Dose
LH1	6795	L	H
HH2	(6253)	H	H
MM1	6461	M	M
LL1	5605	L	L
HL1	5135	H	L
LO2	4108	L	O

Table 8
DSC signal difference in μW for the group analysed 17–18 d after the first group

Sample	Signal diff.	Sample	Signal diff.
LH2	7037	HL2	5940
LH1	3950	LL2	5456
HH2	<i>5854</i>	LL1	4962
HH1	<i>3811</i>	LO2	3173
MM1	6773	LDPE	1765
MM2	6690		

The italicized values are much lower than expected from the correlation with dose.

3.4. Statistical correlations

The endothermal enthalpy in the non-reversible DSC component and the DSC signal difference show very similar regression coefficients. The latter is given in Fig. 6. Both show very high correlation with the dose received by the sample. There is a weak negative correlation with storage temperature, and almost no correlation with the combined effect of dose and storing temperature.

The inflection point (Fig. 7) in the non-reversible DSC component shows a strong positive correlation with the storing temperature, a positive correlation with dose and a small negative correlation with the combined parameter, storing temperature and dose.

The reversible component also correlates strongly with dose during cooling, Fig. 8. The first peak (from the high-temperature side) correlates negatively, and the two following positively, with dose. The correlations with storing temperature and with the interaction of the two parameters are much lower.

4. Discussion

It is very clear that the oscillating DSC technique can differentiate the effects of dose level and storing conditions of the polymeric samples. In the literature, many

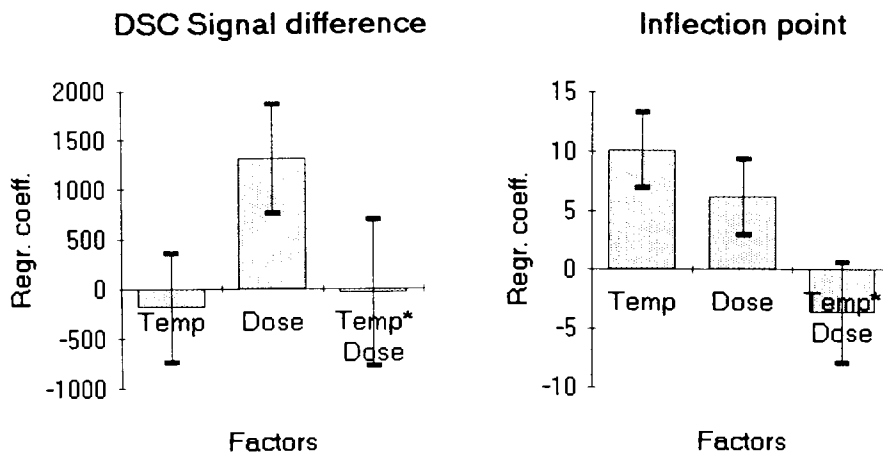


Fig. 6 (left). Regression coefficients for the DSC signal difference.

Fig. 7 (right). Regression coefficients for the parameter inflection point.

papers describe the effects of irradiation, both gamma rays and electrons, on HD and LD polyethylene. The predominant effects are chain scission and crosslinking. The most common thermal techniques to analyse changes are dynamic mechanical analysis and DSC. The mechanical properties of elongation and tensile strength are measured. Generally, polyethylene becomes stiffer and more brittle due to irradiation.

The effects of irradiation are dependent on dose, temperature, atmosphere, degree of crystallinity, crystal size distribution and imperfections [2]. Some effects also depend on dose rate [3].

The enthalpy of fusion from a DSC measurement is used as a measure of crystallinity, and values from 288 mJ mg^{-1} [4] to 278 mJ mg^{-1} [5] are used to correspond to 100% crystalline PE material. This would give a crystallinity of about 50% for the material used in this investigation. In Ref. [6] it was found that the enthalpy of fusion did not change significantly within the range 52–526 kGy, and in Ref. [4] a dose of less than 2 MGy was not found to change the enthalpy of fusion (2.5 MGy in Ref. [7]). In this work, very clear effects can be distinguished in material containing antioxidant, even at the level of 30 kGy. This is due to the increased sensitivity of oscillating DSC, and also to the fact that reversible and non-reversible events can now be separated.

During irradiation in air (or pure oxygen), free radicals are formed that very quickly react with oxygen to form carbonyl groups [3,8], metastable peroxides and hydroperoxy groups [3,8,9], and methyl groups [8]. These reactions lead to chain scission in the amorphous regions [10]. During irradiation in vacuum, these free radicals remain until the material is subjected to air (or other reactive atmospheres).

Chain scission in the amorphous regions leads to an increased mobility of the molecules, and this allows the polymer to crystallize further [9]. It is not clear if this takes place immediately, or when the temperature is raised. Many authors find large

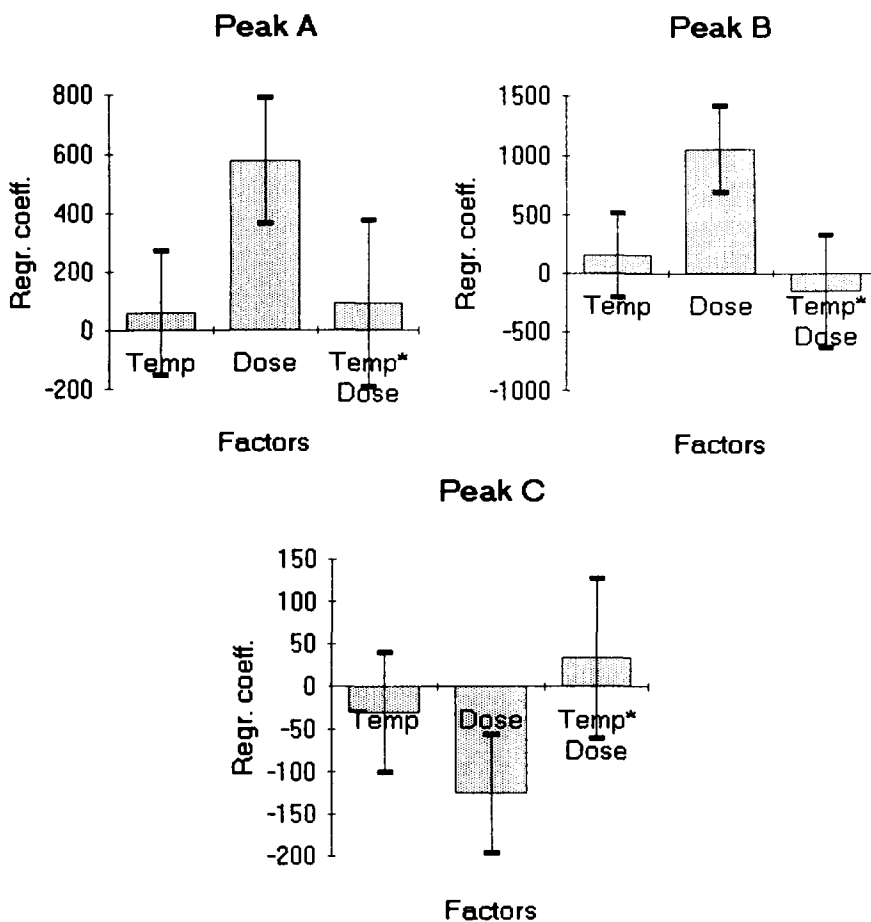


Fig. 8. Regression coefficients for the parameters A, B and C.

differences in crystallinity (enthalpy of fusion) between the first and second melting [7].

Many authors [11] describe the oxidation degradation to be superficial. This means that it just takes place in a skin zone of the polymer, a few hundred microns deep at the most. The depth is inversely proportional to dose rate.

The second dominating effect due to irradiation is crosslinking. This takes place in the amorphous regions [9], and also between and within the crystalline regions. In both cases it leads to higher strength and lower elongation at break [8,12]. Crosslinks formed during irradiation are not destroyed during melting of the polymer.

The addition of antioxidants like Irganox reduces the formation of free radicals during irradiation, and thereby also the reactions with oxygen. The effects were also found to be dependent on dose only, not on dose rate [3].

In this investigation, the polymeric components were irradiated in air, and then stored under different conditions until preparation for the ODSC analysis. According to the cited literature [3,8,9,10], chain scission in the material and reactions between free radicals and oxygen must have taken place, forming carbonyl groups, metastable peroxides, hydroperoxy groups and methyl groups. When heated in nitrogen in the DSC, reactions involving these new groups may have resulted in the inflection point and the endothermal peak in the non-reversible component. In a second run, they have disappeared, and the thermograms are similar to the one obtained on unirradiated reference material. Also, on exposure to ambient conditions, some of these reactions happen slowly, which could explain why these ODSC characteristics are detected at a smaller magnitude after some time at ambient conditions.

It is obvious from the results of this work that some effects of irradiation remain even after the large melting, endothermal reaction. This is shown by the very consistent cooling thermograms. When the polyethylene–butadiene copolymer is heated to 180°C, large aggregates of molecule chains are still intact. The characteristics of these aggregates, such as the number of crosslinks, are governed by the radiation and determine the cooling reactions, and are reflected in the reversible DSC component.

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