Emanation thermal analysis of low-density polyethylene irradiated by electron beam

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Abstract

The thermal behaviour of low-density polyethylene (LDPE) as powder and pellet have been characterised by means of the emanation thermal analysis (ETA) during heating in air. The ETA was used in the study of LDPE polymer before and after irradiation to various doses of high energy electrons. It was shown that the ETA reflects microstructure changes taking place as the result of thermal degradation and oxidation pyrolysis of the polymer samples. It was shown in the study of LDPE products, resulting after the electron-beam treatment, that the results of ETA reflect structural changes caused by the radiation over the range of absorbed doses from 0 to 20 MGy. The annealing chemical radicals produced by the electron-beam irradiation was assessed by comparing ETA curves measured during first and second heating runs. © 1998 Elsevier Science B.V.

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1. Introduction

In the emanation thermal analysis (ETA) radioactive inert gases are used as tracers of the morphology changes of solid state. The inert gas (e.g. radon) atoms released from the solids previously labelled and reflecting surface area and diffusion properties of the samples were investigated [1–5]. In this work, we have used the ETA in the study of low-density polyethylene (LDPE) irradiated by high energy electrons (0.8 MeV) to various doses. ETA curves made it possible to characterise microstructure changes taking place during oxidative pyrolysis of irradiated and unirradiated polyethylene samples

2. Experimental

2.1. Materials studied and their preparation

Chemically pure polyethylene supplied by Polymersynthesis (Russia) as high-pressure-low-density polyethylene (LDPE) was used. The degree of crystallinity was 45%, density of 0.915 g/cm^3 and the melting point 118°C. Radon isotope ^{220}Rn was used as the inert radioactive gas probe, being introduced into the sample together with its radioactive ancestors, ^{228}Th and ^{224}Ra.

Radon ^{220}Rn is formed by a spontaneous alpha radioactive decay according to the scheme $^{228}Th \rightarrow ^{224}Ra \rightarrow ^{220}Rn$. The half-life of the parent isotope ^{228}Th is high enough (1.9 years) to be considered as practically stable source of the inert gas ^{220}Rn (half-life 55.8 s). The powder of LDPE was labelled by

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impregnation by 0.1 mol ^{228}Th solution (specific radioactivity of 1 μCi/ml, i.e. 3.7×10^4 Bq/ml). To obtain a dry powder sample, the solution was evaporated at 40°C in vacuum. After evaporation of the solvent, the portion of the size 0.25 mm was separated and used for the LDPE pellets preparation. The pellets were prepared from the labelled powder by hot pressing at the temperature of 140°C and a pressure of 49 MPa. The pellets were cooled at the rate of 5°C/min at the constant external pressure of 49 MPa. The LDPE samples both powders and pellets were irradiated with accelerated electrons (energy 0.8 MeV) in thin-walled ampoules in vacuum (0.1–0.01 Pa). The absorbed dose $(1.0 \times 10^{18}$ eV/cm^3 s) was determined using a ferric sulphate dosimeter. The electron-beam doses received by the LDPE samples were 0.0064, 0.032, 0.8, and 20 MGy, respectively. A fraction of the irradiated LDPE powder with a diameter of 0.25 mm was separated from the whole sample to be characterised by thermal analysis methods.

2.2. Equipment

The simultaneous apparatus for ETA, DTA, TG and dilatometry was used [6] in order to ensure the same experimental conditions for sample characterisation by the methods used (heating and cooling rate: 4°C/min, gas medium: air, sample mass: 300 mg). In the thermal analysis equipment the samples were placed in quartz crucibles, sintered corundum powder was used as DTA reference material.

3. Results and discussion

Methods of thermal analysis (especially DTA and DSC, TG, dilatometry) have been widely used in the characterisation of the polymer materials and plastics. Therefore, the ETA results presented in this paper will be discussed comparing them with TG and dilatometry measurements carried out simultaneously with the ETA measurements.

3.1. Thermooxidative behaviour of LDPE samples as pellets and powder

The thermooxidative decomposition of polyethylene has been investigated extensively. Both isothermal and non-isothermal studies have been performed in order to determine reaction products, investigate changes in structure, molecular weight and its distribution, as well as to evaluate kinetics parameters of the decomposition process.

The thermooxidative behaviour of LDPE in the temperature range 20–600°C was described in Ref. [7]. It was demonstrated that the LDPE decomposition in air is a complex exothermic process accompanied by mass losses in the temperature range between 220° and 590°C, depending on the heating rate. At least three stages of the mass loss were reported, the effects measured by means of the Derivatograph (MOM Budapest Hungary) could not be separated even when different heating rates in the range from 5.2 to 22.4°C/min were used.

When a polymer is burned, two processes can be distinguished: one occurs in the condensed phase leading to decomposition of the polymer [5], the other takes place in the gas phase where the gaseous products are mixed and react with the oxidant. The decomposition products and their release rate from the sample provide the important information necessary for the determination of the risk connected with the ignition and subsequent burning of the polymer samples.

In this paper, the ETA was used for the first time in the characterisation of polymers and plastics. The ETA results are compared with the results of traditionally used methods (TG, DTA and dilatometry), measured simultaneously at the same experimental conditions.

3.1.1. Pelleted sample

In Fig. 1, results of ETA, TG, DTA, dilatometry and ETA obtained during heating of LDPE pellet in air in the temperature interval from 20° to 600°C are compared.

There are no changes of the sample mass during heating in the interval from 20° to 220°C (Fig. 1, curve 1). At the temperatures above 220°C two stages of the sample decomposition were determined from the thermogravimetry measurements.

From the dilatometry measurements of the pelleted sample (see Fig. 1, curve 2), the increase of the LDPE sample length in the temperature interval 20–118°C was determined. On heating to higher temperatures the melting of the sample caused the break down of the sample.
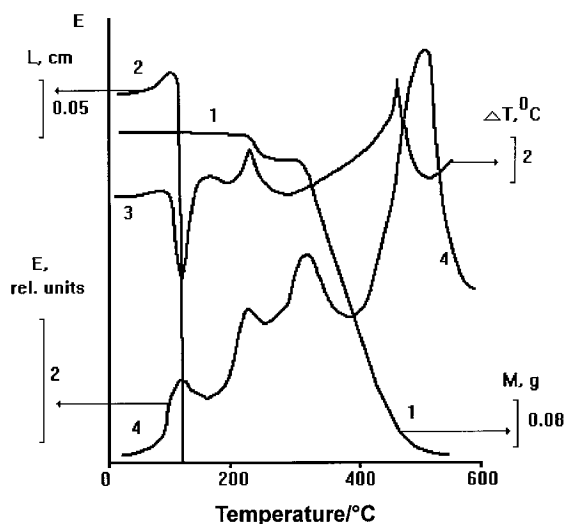
Fig. 1. Characterisation of thermal behaviour of LDPE sample (pellet) using TG, dilatometry, DTA and ETA. Heating in air at the rate of 5 K/min was used. 1, TG results; 2, Dilatometry results; 3, DTA results; 4, ETA results.

Fig. 2. Thermal behaviour of LDPE (powder). 1, DTA results; 2, ETA results; 3, Dilatometry results.

The DTA results of the pellet (see Fig. 1, curve 3) confirmed the endothermal character of the melting process (in the temperature $120\pm2°C$) and exothermal character of the thermooxidative decomposition of the sample (two exothermal effects were observed at $230\pm3°C$ and $480\pm4°C$, respectively).

On the ETA curve measured during heating of the LDPE pelleted sample four effects were observed in the temperature interval $20–600°C$ (see Fig. 1, curve 4): The first effect at $120\pm2°C$ (corresponding to melting), the second effect at $230°C$ (formation of oxygen cross links), the third effect at $320°C$ (predominantly destruction of macrochains over oxidation of side groups), and the fourth effect at $520\pm10°C$ (oxidation and sublimation of all pyrolysis products).

In the temperature interval $60–118°C$, i.e. in the temperature interval where the sample dilation took place (see curve 4, Fig. 1), the increase of radon release rate E reflected the thermally stimulated process of radon diffusion in the LDPE pellet. At the melting temperature, the decrease of the radon release rate indicated changes in the transport properties of the sample due to the heating.

During heating of the pellet to the temperatures above melting point the effects on the ETA curve
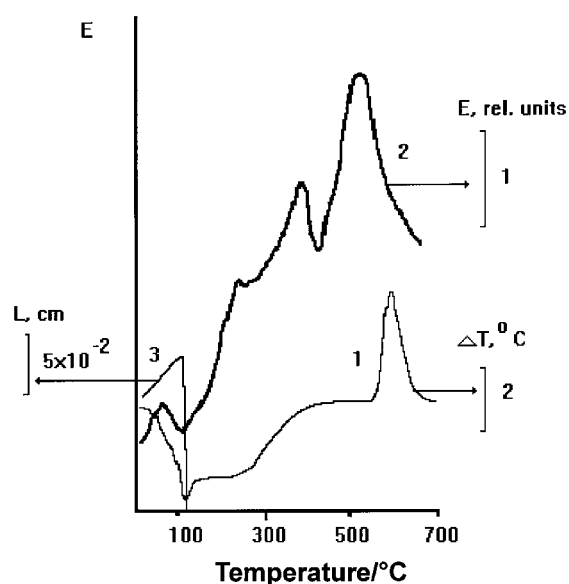
reflected changes of the molecular structure due to the destruction of the macrochains in the melt.

3.1.2. Powdered sample

DTA, ETA and dilatometry results characterising thermal behaviour of the LDPE powder are presented in Fig. 2.

DTA of the LDPE powder (see curve 1, Fig. 2) indicated clearly the melting as an endothermal effect at $120°C$ and the oxidation pyrolysis as a sharp exothermal effect peaking at $590°C$. Comparing DTA curves in Figs. 1 and 2, it became obvious that the thermal behaviour of the LDPE as powder and pellet differ, due to the differences in the mechanism of the oxidative pyrolysis (with the pelleted sample the rate of the oxidative decomposition is controlled by the diffusion of oxygen in the sample, whereas with the powdered sample the diffusion of oxygen is not important, as the air oxygen has immediate contact with the sample surface).

The temperature dependence of the radon release rate E measured by the ETA (Fig. 2, curve 2) characterises surface area and morphology changes of the LDPE samples under in situ conditions of sample heating. During heating of the powdered sample in the temperatures from $20°$ to $60°C$, the increase of E

corresponds to the radon diffusion in the intergranular space of the powdered sample and the damaged surface layers labelled with the radionuclides. In the temperature interval 60–80°C, a decrease of the E value was observed, corresponding to the annealing of the roughness of the powder grains and their agglomeration due to sintering of the powder. On heating above 80°C, the increase of E values reflected the mobility of radon atoms (atom size 0.4 nm) in the compacted sample.

In order to ascertain the surface area changes due to the sintering, the following parallel experiment was carried out with the powdered LDPE sample. The sample was heat treated in two runs: first heating from 20° to 115°C followed by the cooling and the second run heating from 20° to 140°C. The ETA results in Fig. 3 demonstrated clearly the irreversibility of the processes taking place during the first heating run.

In Fig. 2, the curve 2 indicated changes of the radon release rate of the powdered LDPE, reflecting morphology changes of the sample due to the thermo-oxidative pyrolysis. The ETA results of the powdered sample support the statement about differences in the mechanism of the thermooxidative pyrolysis of the powdered and pelleted sample. The effects on the ETA curve of the powdered sample at $250 \pm 10°C$ can be ascribed to the destruction of the weaker oxygen bonds between macromolecules and the destruction of the macrochains. The effect at $360 \pm 10°C$ reflects mor-

phology changes of the molten sample, accompanying the release of volatiles from the sample. The effect at 560°C is connected with sublimation and oxidation of all macromolecular compounds formed.

Dilatometry results measured on the LDPE powder tapped into an quartz crucible (see curve 3, Fig. 2) reflected the sample melting in a similar manner as the dilatometry curves of the pelleted sample (see curve 2, Fig. 1).

Generally, we can say that the ETA results well characterised the processes that occur in polymers during heating, especially in the measurements of hot-pressed pellets. It is well known that the crystallisation under the above described conditions leads to the formation of a surface layer consisting of narrow lamellae, oriented perpendicular to the surface. We can therefore suppose that there is no relationship between the radon release rate E and the degree of crystallinity of the polymer.

The ETA results of oxidative pyrolysis of LDPE show that the ETA permits a qualitative estimation of the regions of the formation of oxygen cross links, their destruction and oxidation. The data obtained correspond to the results of DTA and TG measured simultaneously at the same conditions of the sample heating.

3.2. Thermal analysis of LDPE samples exposed to electron-beam irradiation

It has been reported by numerous authors, e.g. [8,9] that the cross-linking macromolecules chains take place during irradiation of polyethylene. The radiation effects are based on the formation of free chemical radicals and their reaction in the polymer accompanied by the release of the gaseous products of radiolysis. The melting point of the irradiated polymer material was reported to increase. At high absorbed doses of radiation, the mechanical properties of the sample changed considerably and, finally the sample did not melt, but decomposed without melting.

DTA and mechanical testing have been used in the study of the influence of ^{60}Co gamma irradiation on the degree of crystallinity and on physicochemical properties of LDPE [10]. The crystallinity of LDPE was found to increase with gamma-radiation dose, while the specific heat decreased up to the irradiation dose of 1 MGy. The crystallite melting temperature
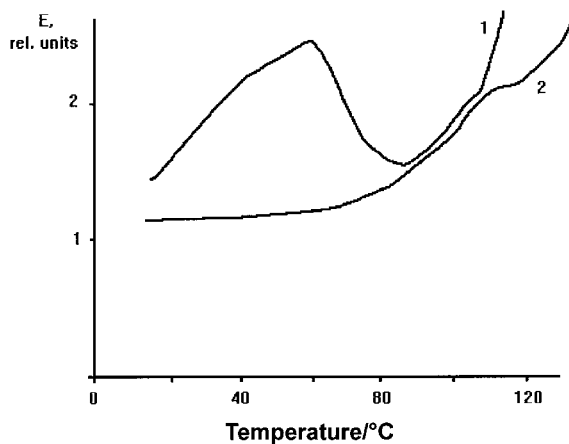

Fig. 3. Thermal behaviour of LDPE (powder) characterised by ETA during sample heating to 115°C and re-heating in air. 1, First heating run; 2, Second run heating.

did not change up to the dose of 0.1 MGy and tended to increase at higher irradiation doses. This behaviour has been interpreted as due to the folding of polyethylene from its lamellae configuration. Furthermore, the influence of irradiation was determined by the increase in chain mobility as the result of radiochemical crosslinking and by irradiation of LDPE, the chains are linked by direct chemical bonding. The crosslinking of the polymer chains is based on the recombination of such free chemical radicals to form a crosslinked network. The melting temperature of the crosslinked crystallites is shifted towards higher temperatures as the segments mobility is hindered by the crosslinks.

In this paper, we present the ETA results of LDPE samples submitted to the electron-beam irradiation (in the range of absorbed doses from 0.8 to 20 MGy). It is worth mentioning that the ETA curves of the LDPE sample after irradiation with the doses of 0.0064 and 0.032 MGy are similar to the ETA curve of the non-irradiated powdered sample (see Fig. 2, curve 2). The ETA curves of the irradiated samples are presented together with the results of dilatometry and DTA in Figs. 4 and Fig. 5, which makes the comparison of the results easy.

3.2.1. LDPE samples irradiated by the dose of 0.8 Mgy

The ETA results of this sample differ from those of non-irradiated LDPE powder. In Fig. 4, the ETA results of the irradiated sample (curve 1) are compared with the DTA (curve 2) and dilatometry results (curve 3) measured during heating in air from 20° to 600°C. The shape of the heating curves in Fig. 4 differ considerably from those for unirradiated LDPE (see Fig. 2, curve 2).

With the ETA results the maximum of radon release rate E observed at curve l at 60 ± 5°C is followed by the decrease of E values, reflecting the annealing of surface irregularities and sintering of the sample. On heating above 100°C, the E values steadily grow reflecting mobility of radon in the sample which did not melt due to the radiation treatment. The effects observed on the ETA curve can be ascribed to the morphology changes of the sample accompanying the oxidative pyrolysis (above 400°C) and destruction of the sample after thermal decomposition of the macrochains (above 500°C).
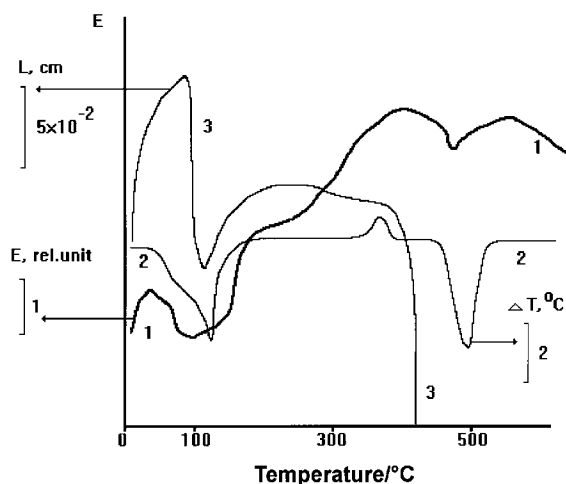

Fig. 4. Thermal behaviour of electron-beam irradiated LDPE (dose 0.8 MGy). Heating in air at the rate of 5 K/min. 1, ETA curve; 2, DTA results; 3, Dilatometry results.

The interpretation of the effects was made using the results of DTA and dilatometry simultaneously measured with the ETA (see Fig. 4, curve 2 and 3, respectively).

The DTA curve (Fig. 4, curve 2) shows the endothermal effect at 115 ± 6°C (partial melting of the sample, an exothermal effect at 360 ± 10°C, and the intense endothermal effect at 490 ± 10°C).

The dilatometry results (Fig. 4, curve 3) reflected, in the temperature interval 20–100°C, an increase of the volume of the powdered sample taped into the crucible. As expected, the partial melting of the sample began at 100°C, indicated by the dilatometry sensor as a steep decrease in the curve. However, the decrease did not continue on further heating, indicating that the sample did not melt through in the volume. We can suppose that a new quality material was formed by the heating to this temperature. The chemical radicals produced by electron irradiation in the LDPE due to their increased migration reacted with the chains, producing macrochains of the new properties, resulting in a non-fusible material. On further heating a dilation of the sample was observed in up to 200°C, above 400°C the dilatometry indicated the contraction of the sample, due to the total degradation of the sample.

In order to interpret the processes described, we have carried out additional experiments using ETA
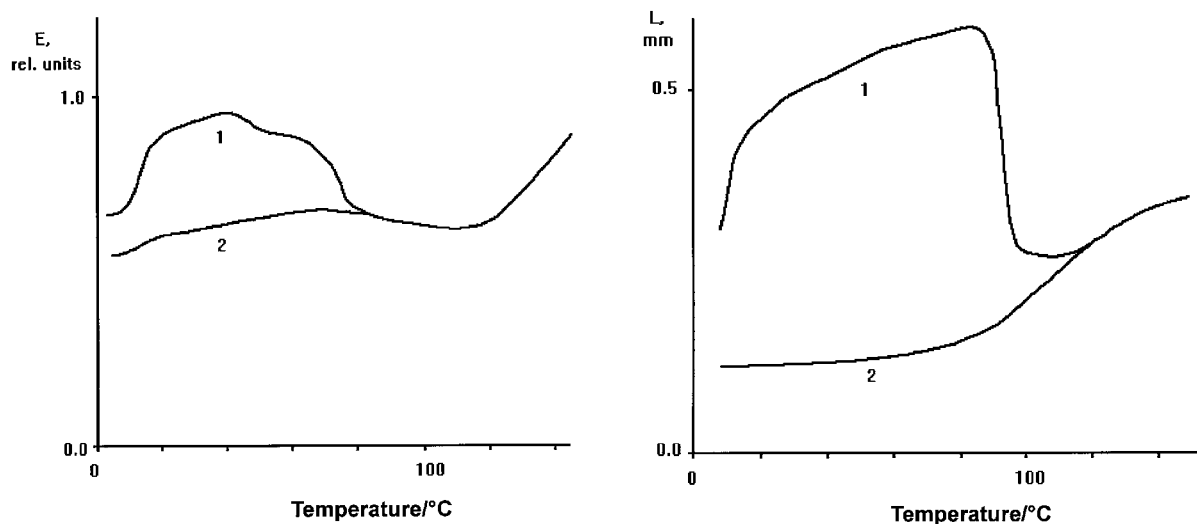
Fig. 5. Results of ETA and dilatometry of irradiated LDPE (dose 0.8 MGy). (a) ETA during first heating run to 120°C and the second run heating; (b) Dilatometry. Curve 1, First heating; Curve 2, Second run heating.

and dilatometry measurements in the following conditions: sample heating from 20° to 120°C and its subsequent cooling, re-heating of the sample from 20° to 140°C. The results are presented in Fig. 5(a) and (b). The results of the first heating are similar to the results obtained in the measurements presented in Fig. 4, curve l, which confirmed a good reproducibility of the ETA measurements.

The increase of the radon release rate in temperatures from 20° to 40°C (see Fig. 5(a), curve 1) corresponds to the diffusion of radon in the intergranual space and damages surface of the powder, whereas the decrease starting at 40°C reflected the sintering of the sample. The increase of Rn release in the temperature above 100°C reflected the mobility of radon in the new quality materials formed by the heating to this temperature. The second-run heating curve (see curve 2, Fig. 5(a)) is identical in this temperature interval, which again confirmed the reproducibility of the method. In the low-temperature interval, the E value was considerably lower during the second heating run, which confirmed the densification of the sample leaving no intergranualar space for radon diffusion.

The dilatometry sensor indicated a dilation of the taped powder in the temperature interval 20–90°C (see Fig. 5(b), curve l). At the temperatures above 90°C, the partial melting of the sample was indicated, nevertheless the dilation of the new quality material was

indicated on the heating above 100°C. The dilatometry results confirmed the densification of the sample after this first heating to 120°C, in the temperature interval 20–60°C practically no dilation was observed (curve 2, Fig. 5(b)). In the temperature intervals above 110°C, the dilatometry curve of the first and second heating runs are identical.

3.2.2. LDPE sample irradiated by the dose of 20 MGy

The ETA results (Fig. 6, curve 1) reflect the increase of radon release rate E from 20° to 60°C, followed by the decrease of E to 105°C. The smooth increase of E from 120°C to 450°C characterises the radon diffusion in the sample irradiated to the above dose. The decrease of E at 490°C is ascribed to the morphology changes accompanying the sample decomposition.

There are no maxima on the smooth DTA curve (curve 2, Fig. 6) from 20° to 450°C, (where a broad endothermal effect is observed corresponding to the thermooxidative decomposition of the sample). From the dilatometry curves (curve 3, Fig. 6), the linear expansion of the samples in the temperature interval 20–400°C was determined. The LDPE sample irradiated to this dose behaves as an non-fusible material with a definite coefficient of linear expansion and a decomposition point at 470°C.
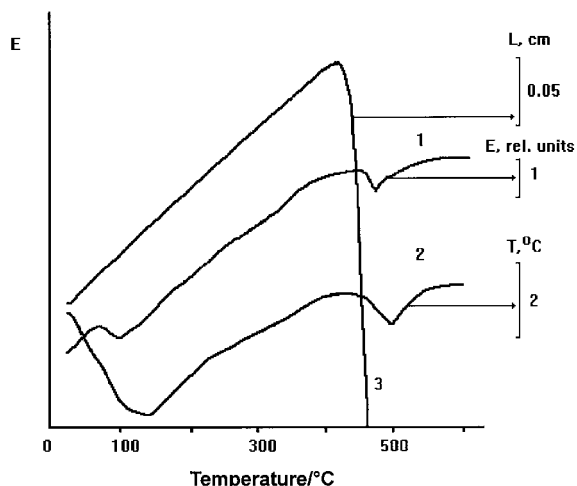
Fig. 6. Thermal behaviour of irradiated LDPE (dose 20 MGy) characterised by ETA (curve 1), DTA (curve 2) and dilatometry measurements. Heating in air at the rate of 5 K/min.

Fig. 7. Dependence of the values of radon release rate E measured at room temperature of the irradiated LDPE sample an the absorbed dose of high energy electrons.

To explain why low absorbed doses did not cause changes in the thermal behaviour of the LDPE, we have supposed that the diffusion of inert gas (radon) through the polymer depends on the disposition of small section of the chains and is controlled by their fluctuations. Therefore, it does not depend on changes in molecular weight until the polymer loses the capacity to form a film. A comparison of the ETA curves shows that within the limits of experimental error (10%), the radon release from the irradiated LDPE is independent on the degree of the cross-linking up to doses of 0.2 MGy. At higher doses the ETA curves of LDPE differ appreciably.

The increase in the solubility of radon and the decrease in radon diffusion constant, caused by radiation cross-linking leads to a decrease of radon release rate E from the polymer. On the other hand, the formation of gaseous products as a result of radiolysis (radiation decomposition) of the sample, promotes cracking and disintegration of the polymer leading to an increase of E values.

The influence of the irradiation on the radon release rate E values measured at room temperature is demonstrated in Fig. 7. The E values measured at room temperature do not change up to a dose of 0.1–0.2 MGy. For the absorbed doses of 0.2–5.0 MGy the E values decrease linearly with the absorbed doses. This linear dependence can be used for the dosimetry
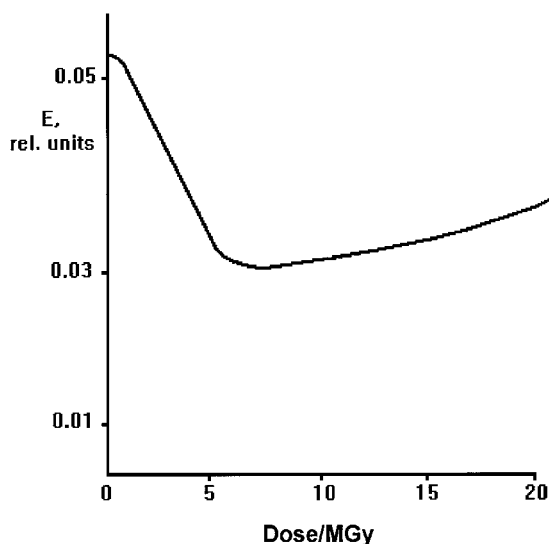
of high doses of radiation. For the absorbed doses higher than 5 MGy (up to 20 MGy) a slow increase of E values was observed.

From the freezing experiments, it followed that the increase of radon release rate E occurs as a result of the damage of the polymer structure. This results in an increase of the total surface and the appearance of microcracks. Thus, the cross-linking processes may be investigated by means of ETA directly under in-situ conditions of electron-beam irradiation up to doses of the order of several MGy.

4. Conclusions

The emanation thermal analysis was demonstrated as a tool giving additional information about morphology changes which take place during the thermooxidative pyrolysis of LDPE, associated with destruction and oxidation of the macrochains of the polymers. A good agreement of the ETA, DTA, TG and dilatometry data was obtained.

The ETA can be recommended for in-situ characterisation of the morphology changes due to the electron-beam irradiation of the LDPE over the range of absorbed doses studied (from 0.2 to 0.5 MGy). It

was found that the annealing of surfaces of powdered LDPE and annealing of chemical radicals formed by the electron-beam irradiation may be detected by comparing ETA curves measured during first and second heating runs.

The ETA will be used for characterisation of the influence of radiation treatment on morphology and changes of other polymer materials.

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