

Influence of the irradiation conditions on the effect of radiation on polyethylene

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Abstract: Two types of polyethylene, low density (LDPE) and high density (HDPE), as well as low density polyethylene containing an antioxidant were subjected to γ -irradiation in the presence of air and in water. The irradiated polymers were studied using IR spectrophotometric analysis. The radiation induced oxidative degradation was followed through the formation of oxygen containing groups by the development of bands in the 1850–1650 cm^{-1} region and double bonds formation by the development of bands in the 1050–850 cm^{-1} region. The crosslinking efficiency was determined by measuring the gel content by extraction with xylene. The radiation induced changes in the molecular structure, evolution of oxygen containing species and formation, of vinyl double bonds as well as of the crosslinking efficiency are discussed in terms of the properties of the polymers in an electric field of low strength.

Keywords: HDPE, LDPE, γ -irradiation, carbonyl groups, vinylene groups, *trans*-vinylene groups, crosslinking.

INTRODUCTION

The possibility of crosslinking polyethylene and many other polymers with high energy radiation, primarily fast electrons and gamma rays, has led to many useful applications (such as crosslinking of cable insulation) and to the understanding of how radiation interacts with large molecules – polymers and biopolymers and to how they can be modified beneficially.^{1,2} However, in spite of the tremendous number of investigations devoted to this topic, there still remains great interest in the study of radiation effects in polymers because radiation processing of polymeric materials is a main step in certain modern technologies.³ Moreover, the electrical performance of polymeric materials which are used widely for electrical insulation in a broad range of applications from the electric supply industry to outer space, can be compromised by their working environments and one of the most deleterious is where nuclear radiation is present.⁴

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The radiation induced ionization of a material gives rise to radicals and the subsequent alteration of the structure of the material *via* radical chemical action. High energy ionizing radiation cannot only cause alterations to the chemical structure of a polymer through mechanisms like crosslinking, chain scission, oxidation, change in the number and nature of double bonds⁵ but can also give rise to the presence of trapped charge within the material, the trapping characteristics of which may be influenced by the radiation-induced structural alterations.⁴

The aim of this study was to investigate the structural alterations of γ -irradiated polyethylene, because the extent to which a material changes structurally is an indication of the manner in which the properties of a polymer in a low strength electric field vary with dose.⁶ Due to profound influence the environment in which polyethylene is irradiated has on the consequential chemical reactions,⁷ γ -irradiation was performed in both ambient air and distilled water. This work represents a part of systematic investigations of the influence of irradiation on the electrical properties of polyethylene.⁸⁻¹⁰

EXPERIMENTAL

Materials

Two types of polyethylene were used for this study: a low density polyethylene (LDPE) Lotrene CdF 0302, 0.926 g/cm³, $T_m = 112$ °C, $M_w = 103000$, 45 % crystallinity and a high density polyethylene (HDPE) Hiplex EHM 6003, 0.969 g/cm³, $T_m = 136$ °C, $M_w = 76700$, 73 % crystallinity. A phenolic type of antioxidant, IRGANOX 1010 (purchased from Ciba-Geigy AG), was used. The low density polyethylene was mixed with the antioxidant (0.5 %) by melt blending at 150 °C and 150 rpm rotor speed for 5 min with a Rheocord Rheometer Model EU-5 equipped with a Rheomix-600 mixer. The pure polymers were treated under the same conditions as the formulation. The samples in the form of sheets of 0.3 mm thickness were prepared using a Carver press at an elevated temperature. The samples, 40 x 15 mm pieces, were fixed inside Pyrex glass tubes ($\phi = 15$ mm); for each material a half of the samples were immersed in distilled water during irradiation while the other half were kept in air.

Irradiation

Five samples of each kind (fixed in the tubes) were simultaneously irradiated at room temperature by the γ -rays of a Co⁶⁰ source at a dose rate of 9.5 kGy/h (determined by Fricke dosimeter). In order to prevent post-radiation oxidation of the samples and to allow the decay of various free radicals in the samples, the irradiated samples were annealed at 60 °C for 2 h under vacuum, before exposure to air.

Measurement of the effects

The effects observed in each specimen were:

1. Oxidative degradation *via* the formation of oxygen containing groups, by following the increase of the carbonyl group (CO) bands, and the formation of double bonds, by following the development of the C=C bands in the IR spectra of the irradiated samples, recorded using a Carl Zeiss Model 75IR Specord spectrophotometer. The precision of the IR measurement of absorption (expressed as standard deviation of the results) was approximately $s = \pm 0.005$. The scatter of the results of absorption (coefficient of variation, CoV, which is calculated by dividing the standard deviation by the mean value of the absorption) was $CoV = \pm 0.7$ % for HDPE, ± 0.6 % for LDPE and ± 0.6 % for LDPE + Aox.

2. Crosslinking – by determination of the percent gel content by Soxhlet extraction with xylol for 18 h. The extracton was performed on four samples of each kind. The weight of the samples was approximately 0.04 g.

In addition, changes in crystalline content of the samples were calculated from the IR data using equation:³

$$C(\%) = 1.2 + 15.2 D_{1894}$$

where D_{1894} is the absorbance per unit sample thickness (cm) of the crystalline band at 1894 cm^{-1} . The basic assumption which is made when determining the degree of crystallinity by the infrared method is that the optical density of a crystalline band is directly proportional to the weight fraction of the polymer that is crystalline.¹¹ It has to be noted that in the case of IR measurement it would be more correct to speak of the degree of order (the ratio of *trans* to *cis* conformation) instead of crystallinity.¹²

In general, the repeatability of a measurement is the precision expressed by the standard deviation. The precision, s_x of the crystallinity measurements derives from the sum of the relative standard deviations of the absorption, A , and the thickness, d ($s_x/x)^2 = (s_A/A)^2 + (s_d/d)^2$, ($x = D_{1894} = A_{1894}/d$). The precision of the crystallinity measurements was approximately $s_x = \pm 0.03$. The uncertainty of the crystallinity measurements derives from the uncertainty of the absorption because the relative uncertainty for d is smaller. The uncertainty of the absorption derives from the relative uncertainty of the transmission ($A_{1894} = \log T_1/T_2$). The relative uncertainties of the transmission, T_1/T_2 , standard deviation divided by the mean value of the transmission, were approximately 0.007 for HDPE, 0.006 for LDPE and 0.006 for LDPE + Aox. Multiplying the results of $D_{1894} = A_{1894}/d$ with the relative uncertainty gives the absolute uncertainty of the results (with the uncertain number being the second decimal number). This is consistent with the results obtained by Setnescu *et al.*³

RESULTS AND DISCUSSION

The analysis of IR spectra indicates significant changes in the absorption at about 1700 cm^{-1} assigned to oxidation products and also in other bands assigned to the amount of crystallinity (Fig. 1) and double bonds (Fig. 2). The data are summarized in Tables I–III.

Data on the changes in the gel content induced by the γ -irradiation in water and air are shown in Fig. 3.

The oxidation product which is readily observable with irradiated polyethylene is the carbonyl group. The increase in the amount of polar carbonyl groups with increasing absorbed dose causes modification of the dielectric properties of the polymer due to the increase in polymer polarity.¹⁰ Moreover, it is known that carbonyl groups generate shallow traps (acting both as electron and hole traps) which readily assists charge transport.¹³ It has also been reported that oxidation can enhance charge injection. It can be seen that different carbonyl containing species are formed under the action of irradiation in the presence of oxygen. The carbonyl groups are mainly ketone groups at 1718 cm^{-1} (at 1685 cm^{-1} α,β unsaturated ketones) and aldehyde groups at 1733 cm^{-1} and both are formed in the amorphous region of the polymer. Aldehyde-end groups are formed by the decomposition of peroxides and hydroperoxides formed in the polymer, or by a rearrangement of the peroxy radical intermediate, causing chain scission.¹⁴ The relative con-

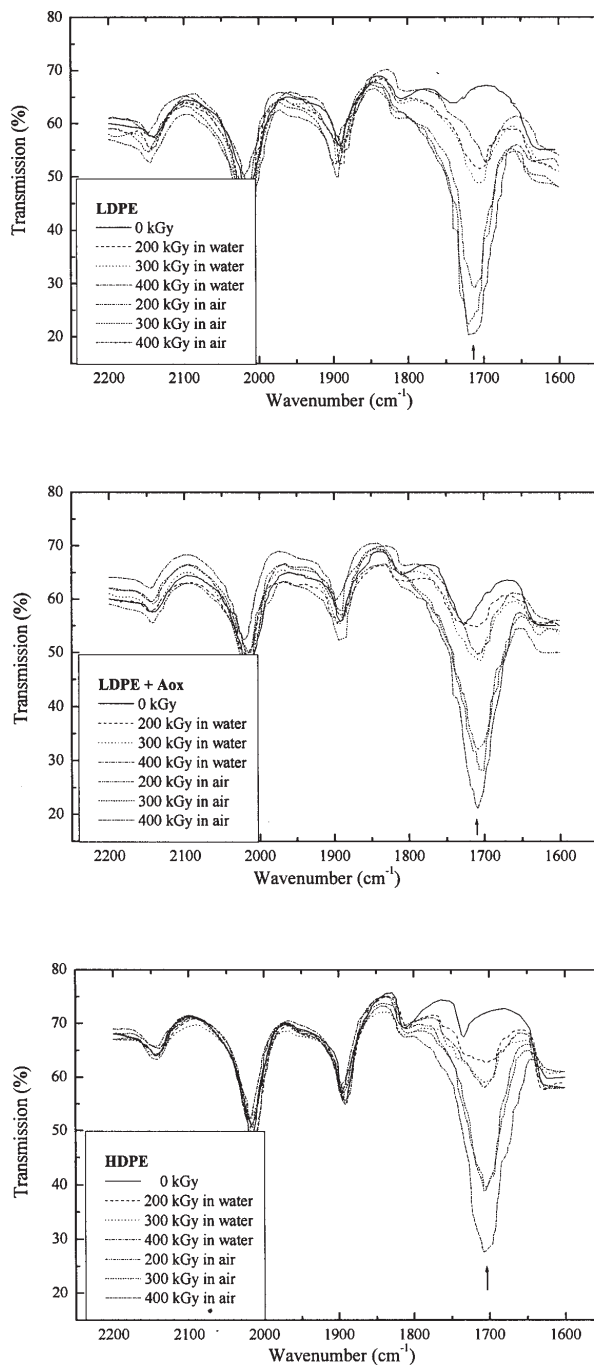


Fig. 1. IR spectra of polyethylene, LDPE sample, LDPE with antioxidant sample and HDPE sample in the 2250–1550 cm⁻¹ region.

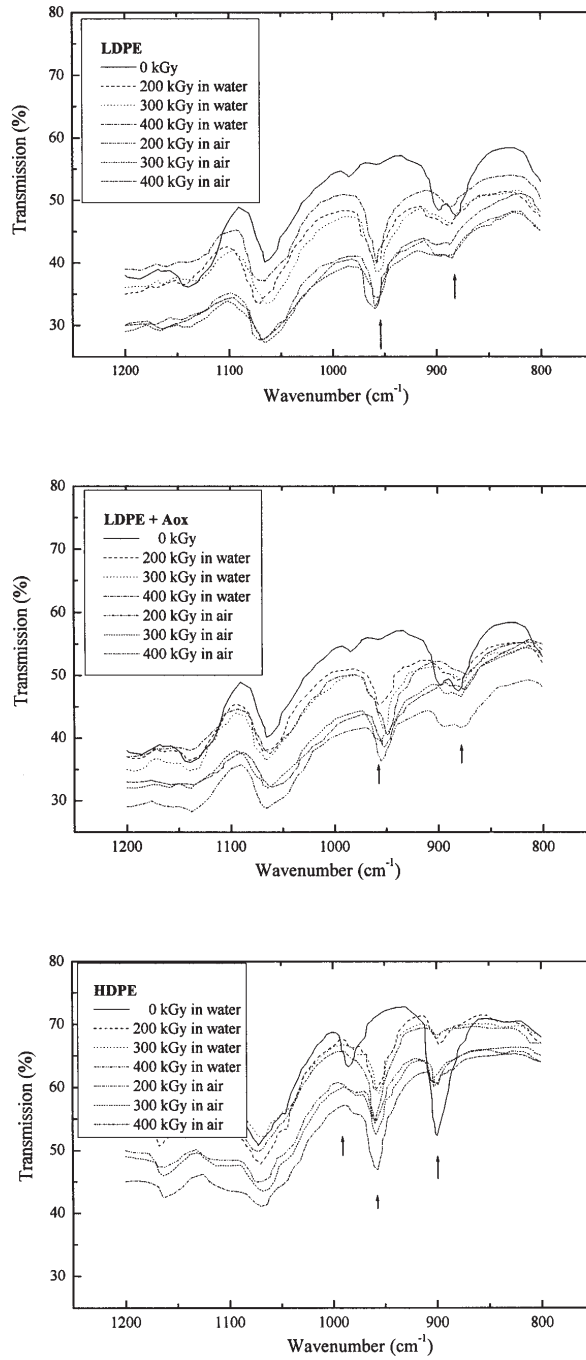


Fig. 2. IR spectra of polyethylene, LDPE sample, LDPE with antioxidant sample and HDPE samples in the 1200–850 cm⁻¹ region.

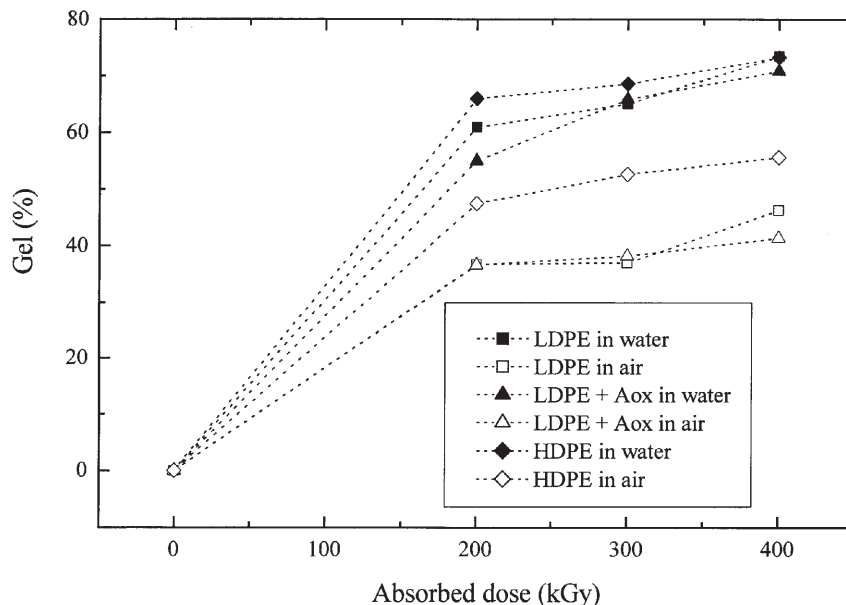


Fig. 3. Dependence of the gel content on irradiation dose.

tribution of aldehyde and ketones depends on the competition between chain scission reactions and decomposition of hydroperoxides in which water is produced. It has been reported that crosslinking and scission processes take place during free-radical mediated chain reactions in irradiated and annealed PE, even significantly under vacuum conditions.^{15,16} Acid groups, at 1705 cm^{-1} , present in the samples are formed in one reaction sequence.^{7,17} Other oxygen containing groups present in the samples have band at 1743 cm^{-1} ester-carbonyl and 1785 cm^{-1} peracid,¹⁷ as shown in Tables I–III. Ester formation in heterogeneously oxidizing systems such as polyethylene in the solid state is probably caused by condensation reactions between carboxylic acids and alcohol groups.¹⁸ From Fig. 1 and Tables I–III it is evident that the evolution of oxidation products is lower in samples irradiated in water, as was to be expected. Although the concentration of oxygen in water is about 800 times lower than in air, the chemical action of γ -irradiation on distilled water induces the generation of oxygen,¹⁹ as well as other oxidizing species, the hydroxyl radical and hydrogen peroxide,²⁰ the consequence of which is the evolution of oxygen containing groups under irradiation in water too.

It should be remembered that changes in environment induced by γ -irradiation, such as crosslinking, chain scission and double bond formation, could decrease the frequency of the carbonyl group absorption.¹⁷ Aldehydic carbonyl absorption responds to structural changes in the same manner as ketones.

The lower evolution of oxidation products in samples irradiated in water leads to higher degrees of crosslinking compared with the effects measured after irradiation in air, as shown in Fig. 3. The onset of various types of molecular motion, *e.g.*,

vibrational and re-orientational motion at the interfaces between and within crystallites (fold lamellae surfaces), the glass-to-rubber transition and the “crankshaft” motion of much shorter segments, depends on the mobility of the chain segments. The manner in which the crosslinking density (gel content) increases with absorbed dose and irradiation conditions indicates the manner in which the restriction in segment mobility due to crosslinking causes changes in the related dielectric properties, such as the increase in the temperatures of the dielectric relaxations, α, β, γ .^{9,10,21} On the other hand, electron release from the possible types of traps follows the onset of various types of molecular motion.²¹

TABLE I. Data on the changes in LDPE induced by γ -irradiation in water and air (A – absorbance, d – sample thickness)

Wavenumber cm ⁻¹	Assignment	LDPE							
		A/d in water/cm ⁻¹				A/d in air/cm ⁻¹			
		Initial	200 kGy	300 kGy	400 kGy	Initial	200 kGy	300 kGy	400 kGy
1894	Crystalline content	3.0	3.33	3.33	3.0	3.0	3.67	3.33	2.67
1785	ν_{CO} in peracids	0.45	0.0	0.0	0.0	0.45	0.26	0.48	0.89
1777	ν_{CO} in peresters or γ -lactones	0.0	0.36	0.51	0.26	0.0	0.62	1.18	1.45
1755	Anhydride	0.74	0.74	0.78	0.39	0.74	1.37	1.95	2.60
1743	ν_{CO} in esters	1.20	0.73	1.17	0.86	1.20	2.30	3.79	4.06
1733	ν_{CO} in aldehydes	1.06	1.29	1.10	1.19	1.06	3.45	10.05	9.11
1718	Ketones	0.30	2.32	2.84	1.51	0.30	8.54	13.67	15.70
1705	ν_{CO} in acid groups	0.0	2.60	3.32	2.18	0.0	8.86	11.22	14.17
1695	Carbonyl stretching	0.0	1.95	2.37	2.60	0.0	4.70	5.66	9.48
1685	α, β unsaturated ketones	0.0	0.91	1.37	1.53	0.0	2.73	2.24	5.54
993	Vinyl double bonds	0.26	0.0	0.0	0.0	0.26	0.0	0.0	0.0
965	Transvinylene double bonds	0.27	3.0	3.33	3.67	0.27	2.67	2.67	3.0
909	Vinyl double bonds	1.90	0.90	0.30	0.56	1.90	0.85	1.17	0.98
888	Vinylidene double bonds	2.44	1.49	0.90	0.14	2.44	1.35	0.51	0.50

The differences in both effects (carbonyl group content and gel content) in LDPE, LDPE+Aox and HDPE after irradiation in air are clear as shown in Tables I–III and Fig. 3.

TABLE II. Data on the changes in LDPE + Aox induced by γ -irradiation in water and in air (A – absorbance, d – sample thickness; see Table I for the assignments of the absorption bands)

LDPE with antioxidant								
Wavenumber cm ⁻¹	A/d in water/cm ⁻¹				A/d in air/cm ⁻¹			
	Initial	200 kGy	300 kGy	400 kGy	Initial	200 kGy	300 kGy	400 kGy
1894	2.70	3.10	3.10	2.77	2.70	3.23	2.57	2.20
1785	0.22	0.25	0.24	0.28	0.22	0.77	0.98	1.34
1777	0.0	0.04	0.22	0.30	0.0	0.10	1.18	1.18
1755	0.61	0.60	0.83	0.63	0.61	1.67	1.14	2.96
1743	1.40	1.47	1.70	1.56	1.40	2.74	3.27	4.23
1733	2.22	1.69	2.58	2.13	2.22	4.23	5.01	6.53
1718	2.04	1.86	3.35	3.10	2.03	7.22	8.32	12.70
1705	1.26	1.81	3.56	3.55	1.26	9.0	11.10	14.70
1695	0.79	1.25	2.15	2.86	0.79	6.93	7.76	10.60
1685	0.27	0.38	1.01	1.05	0.27	2.98	4.71	5.78
993	0.54	0.0	0.0	0.0	0.44	0.0	0.0	0.0
965	0.0	2.10	2.87	2.67	0.23	2.57	2.40	2.40
909	2.23	0.97	0.43	0.56	2.09	0.98	0.75	0.44
888	2.66	1.41	1.0	0.98	3.16	1.93	1.18	0.88

TABLE III. Data on the changes in HDPE induced by γ -irradiation in water and in air (A – absorbance, d – sample thickness; see Table I for the assignments of the absorption bands)

HDPE								
Wavenumber cm ⁻¹	A/d in water/cm ⁻¹				A/d in air/cm ⁻¹			
	Initial	200 kGy	300 kGy	400 kGy	Initial	200 kGy	300 kGy	400 kGy
1894	3.90	4.26	3.50	4.0	3.91	4.04	4.11	3.88
1785	0.41	0.56	0.37	0.62	0.41	0.63	0.60	0.95
1777	0.33	0.0	0.0	0.0	0.33	0.0	0.0	0.33
1755	0.0	0.35	0.41	0.67	0.0	0.86	0.72	1.25
1743	0.46	0.71	2.10	1.0	0.46	1.64	1.58	2.39
1733	1.29	1.36	1.26	1.56	1.29	3.86	2.76	4.48
1718	0.50	1.52	1.67	2.15	0.50	6.18	6.01	10.30
1705	0.36	1.55	1.87	2.74	0.36	8.06	7.60	12.61
1695	0.12	1.46	1.73	2.06	0.12	6.45	6.62	11.49
1685	0.0	0.62	0.48	1.03	0.0	3.04	4.08	6.15

TABLE III. Continued

Wavenumber cm ⁻¹	HDPE							
	<i>A/d</i> in water/cm ⁻¹				<i>A/d</i> in air/cm ⁻¹			
	Initial	200 kGy	300 kGy	400 kGy	Initial	200 kGy	300 kGy	400 kGy
993	1.17	0.50	0.50	0.76	1.18	0.68	0.83	0.89
965	0.0	2.39	2.61	3.84	0.0	2.54	2.88	3.81
909	4.75	1.59	1.0	0.47	4.54	1.22	1.22	0.50
888	0.0	0.48	0.24	0.12	0.0	0.76	0.51	0.27

The lower evolution of oxidation products and the larger gel content in HDPE are probably due to its higher crystallinity, Tab. IV and Fig. 3, because, in general, oxidation in polymer occurs in the amorphous phase and on the lamellae surfaces. The crystal fraction and the gel fraction are not sensitive to oxidative degradation.²² On the other hand, crosslinking, as well as scission processes under the same irradiation conditions (such as dose rate, temperature and oxygen pressure) are controlled by the structural peculiarities of the polymer. Alkyl radicals responsible for crosslinking are formed in the crystalline phase with heterogeneous spatial distribution due to specific early excitation processes. Selective bond cleavage to form alkyl radical occurs at a fold of the chain due to the higher density of the spin state in a delocalised σ -state in an extended alkane cation, *i.e.*, in the *trans-trans* conformation (crystal).^{23,24} Based on the selective alkyl radical formation on the edge of crystals, crosslinking in the crystalline state mostly occurs on the lamellae surfaces. Crosslinks that promote the higher gel content in HDPE, as shown in Fig. 3, are probably those that link crystal layers, because it has been shown that the irradiation efficiency of network formation is related to the degree of interlamellar contact.²⁵ On the other hand, these chain fold regions (lamellae surfaces) are cavity electron traps. Their amount changes in the same manner as the crystallinity content changes with absorbed dose,²¹ as shown in Table IV.

The change in crystallinity of the polyethylene samples follows as the change in the transition dipole moment which is perpendicular to the *c*-axis, as the band at 1894 cm⁻¹ suggests. This band is relatively strong in the spectrum of crystals and is a structure-dependent infrared band which is suitable for determining the state of order in polyethylene. On the other hand, the absorption at 2016 cm⁻¹ in the spectrum of the crystals is attributed to imperfect alignment, convergence of the radiation and a contribution at this frequency from defects.²⁶

The greater enhancement in the crystallinity of LDPE and LDPE+Aox with absorbed dose, as shown in Table IV, could be caused by the initial low crystallinity of this polymer due to its relatively high degree of branching, which results in an increased susceptibility to radiation-induced scission. Owing to the formation of a larger number of oxygen-containing groups (scission), the increase in crystallinity

is greater in samples irradiated in air. The initial crystallinity of HDPE was considerably higher and thus only a slight increase in crystallinity was observed after irradiation in this case, irrespective of whether the samples were irradiated in water or in air. In general, the degree of crystallinity result from the combination of two opposing effects, *i.e.*, an increase caused by chain scission and a decrease induced by both the formation of oxygen-containing groups and crosslinks on the lamellae surfaces and on the formation of double bond sites in the crystal core. A slight reduction in the crystallinity (degree of order) was observed after irradiation to higher absorbed doses (400 kGy) for all samples. The reduction was greater for samples irradiated in air.

TABLE IV. Data on the changes in crystallinity induced by γ -irradiation in water and in air

Sample	Dose/kGy	C in water/%	C in air/%
LDPE	0	46.80	46.80
	200	51.80	56.98
	300	51.80	51.80
	400	46.80	41.78
LDPE + Aox	0	42.20	34.64
	200	48.32	50.30
	300	48.32	40.26
	400	43.30	34.64
HDPE	0	60.48	60.63
	200	65.95	62.60
	300	54.40	63.67
	400	62.00	60.17

Another type of electron traps is correlated to the crystalline phase. The traps consist of imperfections in the crystallites.^{27,28} Under the action of irradiation, *trans*-vinylene double bonds are formed. Double bond sites in the crystal matrices have a trap structure because it has been established that *trans*-vinylidene bond formation, due to its coplanar configuration which is different from the tetrahedral structure of a normal repeating unit representing an area in the crystal structure, produces crystal defects.^{24,29} Increasing the number of *trans*-vinylene double bonds with absorbed dose increases the number of defects. Charge carriers trapped in deep traps such as defect within the crystalline region can feel shallow traps within the material as the result of oxidation.²⁷

The data on the appearance of unsaturated *trans*-vinylene groups at 965 cm⁻¹ is shown in Table I–III. A large fraction of the *trans*-vinylene groups are formed in

the crystalline region of polyethylene, the consequence of which is an increase in the absorption bands of all polyethylene samples at levels which are comparable with the changes in the degree of crystallinity on irradiation in water or in air, as is shown in Fig. 2 and Table I.

Other types of carbon-carbon double bond groups in polyethylene, due to out of plane C-H bending vibrations,¹⁷ absorb in the region between 1050 cm^{-1} and 850 cm^{-1} , Fig. 2. These are vinylidene double bonds (at 888 cm^{-1}), the content of which is greater in LDPE owing to the higher initial amount of branching of its chain. The diminution of the content of this type of bond with irradiation, both in water or in air, seems to be similar to the reactivity of the investigated polymers with oxygen, Tables I-III. Olefinic cation radicals are formed much more easily from branched alkanes (LDPE) than from linear ones (HDPE), because the ionization potential of a branched alkane is lower than that of a linear one and the olefinic cation is much more feasible due to the lower heat of formation (ΔH) of a branched cation.

The absorptions at 909 cm^{-1} and 993 cm^{-1} correspond to vinyl end groups.³⁰ Most of the vinyl unsaturation in PE is located in the amorphous phase, and is, relatively, very mobile.³¹ It is these properties of the vinyl groups which allow them to play an important role in crosslinking reactions. Firstly, they can directly cause crosslinking and, secondly, they can take part in radical transfer and be transformed into highly stable and mobile allyl radicals. These radicals can catalyze main chain rupture in neighboring chains by reducing the activation energy of bond rupture and take part in the oxidative degradation process. It has been established that vinyl unsaturation in HDPE is implicated in enhancing both crosslinking and void formation.³¹ The initial absorption in HDPE is considerably higher. A reduction of the amount of vinyl unsaturation after irradiation was observed in all polyethylene samples. No significant difference was observed between irradiation in water or in air, as is shown in Tables I-III.

CONCLUSION

Irradiation of polyethylene in different environments caused different alternations to the chemical structure of the polymer through different mechanisms of crosslinking, oxidation and change in the number and nature of double bonds. The difference in the extent of these effects found after irradiation in water and those irradiated in air is primarily caused by the lower concentration of oxygen in water, but also from the structural peculiarities of different types of polyethylene and the heterogeneous nature of radiation effects in polymers.

ИЗВОД

УТИЦАЈ УСЛОВА ОЗРАЧИВАЊА НА РАДИЈАЦИОНИ ЕФЕКАТ У
ПОЛИЕТИЛЕНУЗОРИЦА КАЧАРЕВИЋ-ПОПОВИЋ, ДУШАН КОСТОСКИ, ЉИЉАНА НОВАКОВИЋ, НАДА
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Два типа полиетилена, мале густине (LDPE) и велике густине (HDPE) као и полиетилен мале густине који садржи антиоксиданте су озрачивани γ -зрачењем на ваздуху и у води. Озрачени полимери су испитивани IR спектроскопском анализом. Радијационо индукована оксидативна деградација је праћена преко настанка група које садрже кисеоник у области $1850\text{--}1650\text{ cm}^{-1}$ и преко настанка двоструких веза у области $1050\text{--}850\text{ cm}^{-1}$. Ефикасност умрежавања је одређена преко садржаја гела коришћењем процедуре екстракције у ксилолу. Радијационо индуковане промене у молекулској структури, настанак група које садрже кисеоник, настанак винилних двоструких веза, као и ефикасност умрежавања су дискутоване у зависности од својстава полимера у електричним пољима мале јачине.

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