

# Model studies on phenolic antioxidant role in radiation- and thermally-induced accelerated degradation of electrical cable insulation

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**Abstract.** The main objective of this work was to establish a correlation between radiation- and thermally-induced changes in polyethylene and the amount of compounded phenolic antioxidant (Irganox 1035). Radiation yield of oxygen consumption, oxidative induction time and gel fraction allowed to estimate the utility of the applied experimental methods to monitor oxidative aging of the polymeric material from the standpoint of cable and wire degradation in nuclear power plants. It was found that the phenolic antioxidant not only inhibits chain oxidation but also changes the mechanisms of radical processes influencing significantly capability of polyethylene towards thermally-induced cross-linking.

**Key words:** antioxidant • radiation • degradation • aging • polyethylene • Irganox 1035

## Introduction

The polymers used as insulation and jacket materials in electric cables are susceptible to aging and to degradation processes induced by many stressors. In a nuclear power plant (NPP) service cables might be exposure to low-dose rate irradiation, elevated temperatures, humidity etc., that could significantly shorten their lifetime which, in turn, can lower the reliability of electrical power systems. The integrity of electric cables is supposed to be monitored through periodic functional testing. Therefore, a lot of research effort and activities are directed towards a better understanding of degradation phenomena, and establishing accurate methods for insulation diagnosis.

In order to improve the physical properties and to extend the lifetime of cables, their insulations contain additives hindering degradation, e.g. antioxidants, that gradually decompose during aging. Their consumption with time might cause unexpected early failures of the electric cables, what disrupts operation of electrical equipment, signal transmission and brings about considerable risk of nuclear accident. Primary phenolic antioxidant is an additive that captures and stabilizes radical centres via donating hydrogen atom from hydroxyl group to peroxy radical [8]. Alternatively, hydrogen attachment to alkyl radical regenerates macromolecule transferring active centre onto antioxidant producing phenoxy radical that might take on a quinone resonance structure. The later intermediate is capable of accepting peroxy radical limiting additionally oxidative degradation effects.

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In the reported studies the level of H-donor phenolic antioxidant, namely Irganox 1035 (IRG), in a model system was investigated. IRG is a sulphur containing primary antioxidant and heat stabilizer used for the process stabilization of wire and cable resins, particularly polyethylene [7]. Low density polyethylene (LDPE) free from any additives was doped with various concentrations of the antioxidant, subjected to accelerated radiation aging in a gamma chamber and subsequently was thermally treated at a temperature close to the melting point. A consumption of oxygen and oxidative induction time (OIT) were measured in order to estimate a relationship between absorbed doses and the depletion of antioxidant present in the material in the course of irradiation. Both methods might be utilized to predict the service lifetime of some cables installed in the reactor containment of NPPs. In the last stage of research the thermal treatment was applied to estimate the effect of two stressors, namely radiation and heating, on LDPE samples.

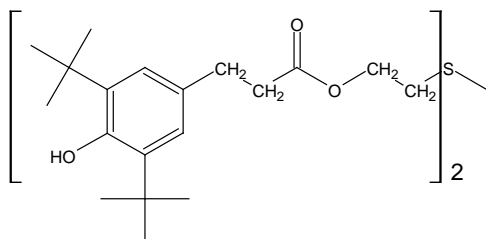
## Experimental

The studied polyethylene (LDPE) is a BASSELL ORLEN product free from any stabilizing additives of a trade name MALEN E FGNX, 23-D022 (MFI – 1.6–2.5 g/10 min, density – 0.919–0.923 g/cm<sup>3</sup>). Irganox 1035 antioxidant (melting point – 63–67°C, M = 643 g/mol) was purchased from Ciba-Geigy (Scheme 1).

The composition of polyethylene and IRG was extruded three times at an extruder screw speed of 60 rpm to ensure homogeneous distribution of the additive. A compounding procedure was performed also for the neat polyethylene to prepare material of the same thermal history as the samples containing antioxidant. A thickness of the extruded tapes was about 0.7 mm.

The samples were gamma-irradiated up to 200 kGy in a Gamma Chamber 5000 (dose rate 7.8 kGy/h) and then thermally aged at 110°C for 24 h under continuous air flow. The treatments were performed under severe conditions, far from those ones expected for NPP environment and for the accelerated ageing tests performed at the comparable surroundings. Nevertheless, such a protocol allows to estimate the contribution of radiation- and thermally-induced phenomena in polyethylene doped by an antioxidant and to determine participation of these factors in degradation of the polymeric material during nuclear accidents.

Oxidative induction time was determined using a TA Instruments differential scanning calorimeter (MDSC 2920) at a heating rate of 20 deg/min under nitrogen and subsequently oxygen atmosphere at a purge rate of 50 ml/min at 220°C.



Scheme 1. Irganox 1035.

Hydrogen emission and oxygen consumption from the space above the irradiated samples were measured by gas chromatography technique using a Shimadzu-14B apparatus equipped with thermo-conductivity detector. The carrier gas was argon of flow rate 10 mL/min. The chromatograph was attached by interface ADAM with sampling frequency of 10 Hz to a PC computer where the data were acquired by program Chromnew and processed by program Chromap.

Cross-linking yield of the radiation and thermally treated samples was evaluated by the gel fraction measurements. According to ASTM D2765 procedure, after 8 h reflux extraction of the polymeric samples with xylene, the residue was dried in a vacuum oven at 105°C to constant mass and then weighed. The average values of gel fraction were determined on the basis of two independent measurements.

## Results and discussion

Oxidative induction time parameter reveals indirectly expected service time of insulations and is supposed to be correlated with a content of antioxidant. Figure 1 shows the OIT as a function of absorbed dose for two various concentrations of Irganox, namely 0.5 and 1.0%. The parameter is below 2 min for additive-free polyethylene, both before and after irradiation. The results show instability of the polymeric material which undergoes decomposition after very short induction time. The

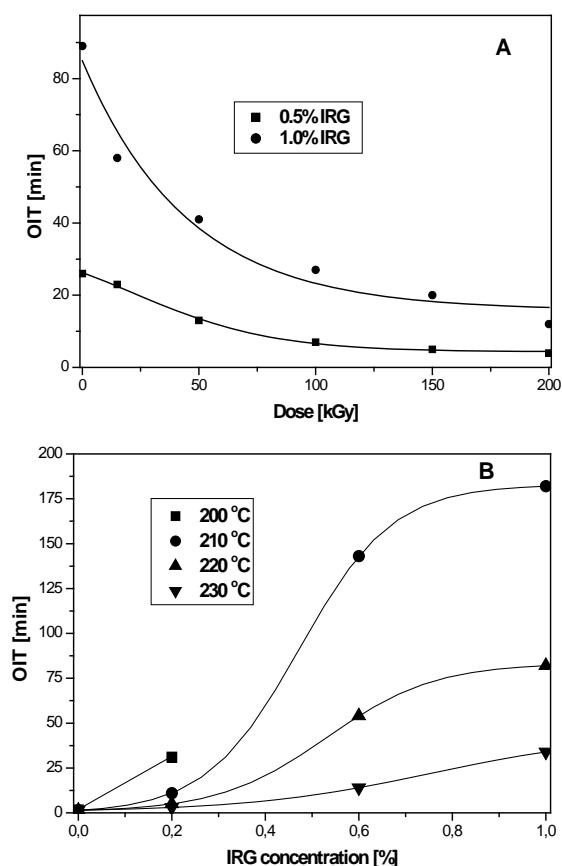
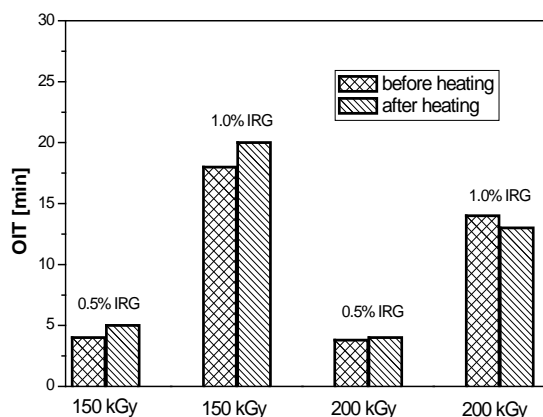


Fig. 1. Relationship between absorbed dose and OIT of LDPE doped with 0.5 and 1.0% IRG (A). OIT in a function of IRG concentration for non-irradiated LDPE at various temperatures (B).

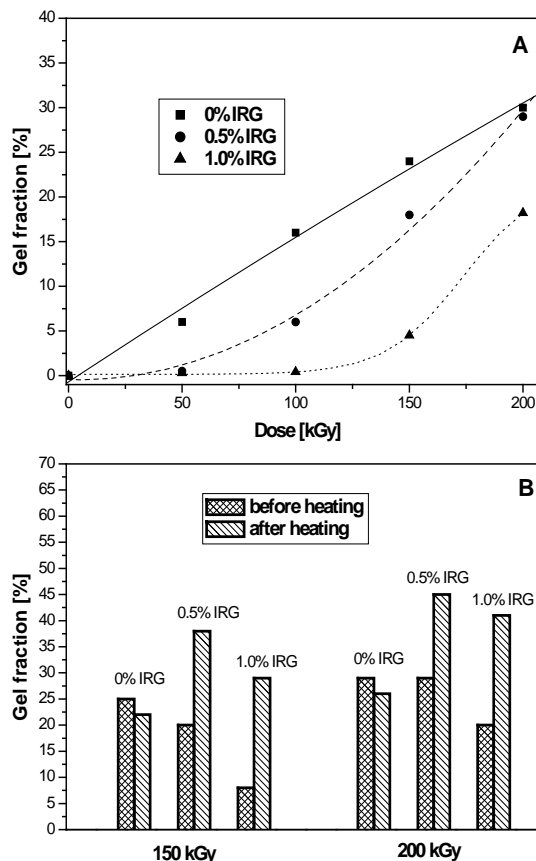
presence of 0.5 and 1.0% IRG in non-irradiated LDPE extends the values to 26 and 89 min, respectively, indicating that when the antioxidant concentration is doubled the OIT increases more than 3 times. If absorbed dose achieves 50 kGy OIT drops below 50% of the initial value at both concentrations of IRG and then gradually diminishes.

Taking into consideration the applied conditions, one might assume that radiation induced oxidation is inhomogeneous. As was confirmed by Placek *et al.* [10] and Bartonicek *et al.* [1] the LDPE sample of a thickness of 1 mm is uniformly oxidized when gamma dose rate does not exceed 0.2 kGy/h what was determined by oxygen permeability, consumption and solubility. At atmospheric pressure, the oxygen solubility in polyolefins in contact with air is 40–70 ppm over a broad temperature range [4]. Therefore, it seems that for a dose rate of 7.8 kGy/h, the decrease in antioxidant activity expressed as a reduction of OIT values, results predominantly from hydrogen transfer from the phenolic group to alkyl and peroxy radicals. Assuming that the decrease in OIT values corresponds to the changes in the amount of antioxidant, the antioxidant depletion with growing dose might be evaluated. The process is very complex as except changes in the chemical nature of IRG, its migration and evaporation must be taken into account [9]. Therefore, as it is presented in Fig. 1B, in the temperature range from 200 to 230°C oxidative induction time is a nonlinear function of the initial antioxidant concentration. It seems that 0.2% IRG is insufficient to prevent effectively LDPE against oxidative degradation as the OIT results reveal that the auto-catalytic oxidative chain reaction is not inhibited.

Upon exposure to gamma rays, some samples were kept for 24 h at 110°C, i.e. at temperature corresponding to the beginning of melting transition. Unexpectedly, OIT values did not diminish but showed trend slightly upward, Fig. 2, (except LDPE comprising 1.0% IRG irradiated with a dose of 200 kGy). Thus, instead of thermal degradation effects, a limited recovery of thermo-oxidative properties was confirmed. It seems that the observed consequences are the superposition of at least two competitive processes – (i) decomposition of the material during heating and (ii) thermally induced reorganization of the macromolecules leading to the recombination of residual radicals as well as



**Fig. 2.** OIT values for LDPE stabilized with 0.5 and 1.0% IRG, irradiated to doses of 150 and 200 kGy and subsequently heated at 110°C for 24 h.



**Fig. 3.** Gel fraction vs. absorbed doses for LDPE stabilized with IRG of various concentrations (A). Gel fraction of LDPE doped by IRG of various concentrations and irradiated with 150 and 200 kGy, before and after heating at 110°C for 24 h (B).

radicals generated via decay of peroxide groups. Two later phenomena might enhance cross-linking and subsequently improve thermo-oxidative features. The results are in accordance with Celina's *et al.* findings [3] who confirmed restoration of the mechanical properties after heating of the radiation degraded insulation. It seems that for the samples irradiated to a dose of 200 kGy the efficiency of (i) and (ii) pathways is either comparable (0.5% IRG) or thermal degradation prevails over radical combination (1.0% IRG) as a result of IRG depletion.

Gel fraction changes show that the presence of antioxidant significantly inhibits cross-linking, probably due to efficient capture of the radical centres responsible for the process, Fig. 3A. The effect depends on the IRG concentration as the gel fraction appears just over 50 kGy or 100 kGy at 0.5 and 1.0% IRG, respectively. Beyond these limits cross-linking yield increases, but still is far lower than that usually confirmed for comparable dose ranges after electron beam treatment. On the basis of the relationship one can conclude that for polyethylene comprising 0.5% IRG, the antioxidant is depleted completely at 200 kGy. Interestingly, confirmed cross-linking does not reduce the tendency towards thermo-oxidative degradation evaluated by OIT. Obviously, increasing with dose cross-linking does not lead to the reduction of induction time, but on the other hand, three dimensional network is unable to prevent the polymeric material against disintegration, especially upon IRG depletion.

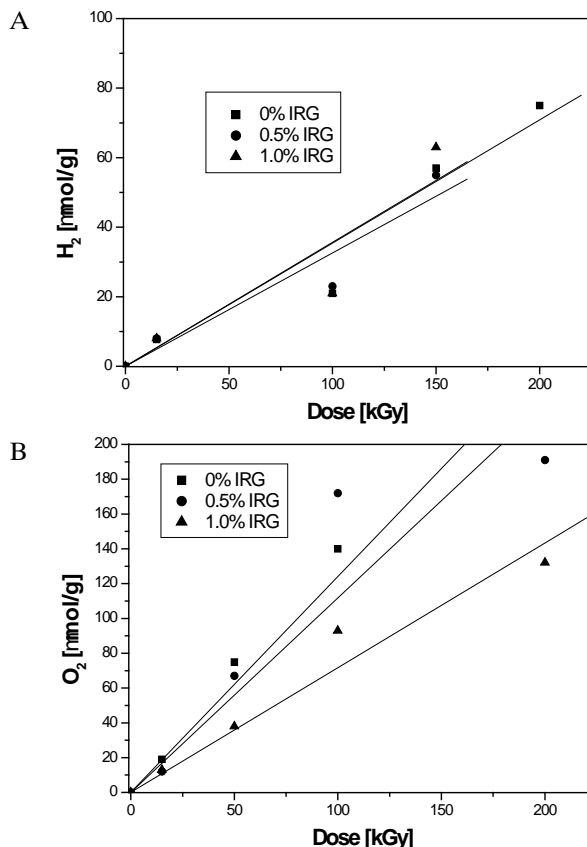
In the next stage of experiments the irradiated to 150 and 200 kGy samples were thermally treated for 24 h (Fig. 3B). At both doses, unstabilized LDPE lost about 10% gel fraction due to progressive decomposition, whereas for the materials containing antioxidant the parameter increases significantly. The role of the additive as an agent mitigating thermal decomposition in air atmosphere was confirmed in the past, however its substantial contribution to the thermally-induced formation of three-dimensional network is striking. A similar effect was found earlier at low doses by Budrugaec and Segal [2]. The increasing content of gel fraction might result from relaxation of PE structure and enhancement of interfacial zone intercepted by cross-linked amorphous phase, but the effect seems to be too strong to be caused by these phenomena.

The question arises why in the presence of IRG the yield of cross-linking process increases so considerably. Peroxy radicals formed during oxidation are converted via hydrogen transfer to stable products that upon thermolysis decay producing radical species. It should be emphasized that the decomposition of hydroperoxides at room temperature is of negligible importance, contrary to thermally activated decay that was studied and discussed in detail by Gugumus [5, 6]. He investigated kinetics of hydroperoxides decomposition during thermolysis for the samples with and without phenolic antioxidant. Homolytic scission of the peroxy bond (1) was contested by Gugumus who suggested intra or intermolecular decomposition of hydroperoxides via the mechanism (2):



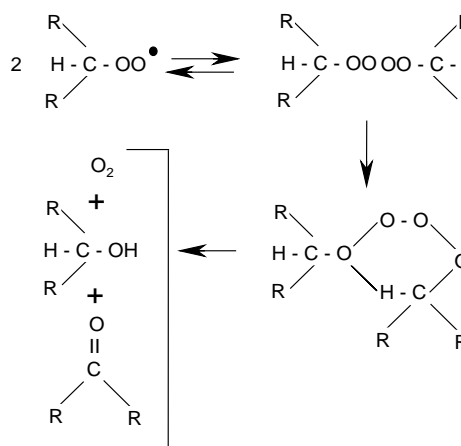
In such a case alkyl radical might participate in the formation of covalent bonds between macromolecules, whereas alkoxy radicals are prone to initiate chain scission. However, at elevated temperatures, due to increasing conformational movements the probability of reactions between alkoxy, alkyl and peroxy radicals grows significantly. Phenoxy radical present in the polyethylene doped by IRG, upon conversion to quinone resonance structure, might play a significant role in scavenging peroxy radicals – precursors of hydroperoxide.

In order to analyze more carefully the reasons of discrepancies between thermally-induced cross-linking in pure and stabilized LDPE, radiation yield of hydrogen and consumption of oxygen was assayed by gas chromatography technique (Fig. 4). The emission of hydrogen for LDPE containing 0.0, 0.5 and 1.0% IGR is comparable, thus the presence of antioxidant has not influenced the first stages of radiation-induced processes involving the cleavage of C-H bonds. Radiation yields of hydrogen  $G(\text{H}_2)$  for the studied samples were in the range of 0.33–0.36  $\mu\text{mol}/\text{J}$ . On the other hand, the uptake of oxygen decreases with increasing concentration of IRG indicating efficient inhibition of the oxidative chain reactions. The  $G(-\text{O}_2)$  values for LDPE non-stabilized and stabilized with 0.5 and 1.0% IRG are 1.24, 1.11 and 0.71  $\mu\text{mol}/\text{J}$ , respectively. The data do not support suggestion that the higher concentration of hydroperoxyl groups decomposing thermally to alkoxy and alkyl radicals results in the increase in gel fraction.



**Fig. 4.** Hydrogen emission of PE compounded with IRG at various concentrations in a function of dose (A). Oxygen uptake of LDPE compounded with IRG at various concentrations in a function of dose (B).

The results confirmed that the antioxidant is used up not only during the oxidation processes but also reacting with other radiation induced reactive species. Therefore, the background of cross-linking upon thermal treatment of irradiated LDPE must be different. It seems that in non-stabilized polymer, due to increasing contribution of peroxy radicals, tetroxides are formed via bimolecular termination between peroxy radicals (Scheme 2). The product upon transformation to a six-membered ring decomposes to alcohol, carbonyl compound and dioxygen through the Russel mechanism. Such a sequence of reactions (monomolecular decay to the stable products)



**Scheme 2.** Mechanism of bimolecular termination between peroxy radicals.

intensifies macromolecule breaking and is characteristic for non-stabilized LDPE.

On the other hand, in the presence of IRG, population of peroxy radicals is lower due to efficient relocation of hydrogen from phenolic group and consequently the dominant stable product is hydroperoxide that during heating converts to the cross-linking precursors. Decay of hydroperoxides in the presence of antioxidant and increasing contribution of tetroxides to neat LDPE seem to differentiate the thermally-induced effects.

## Conclusions

The studies revealed that accelerated aging of polymeric materials is complex and determined by many factors. The main stressors influencing cables in nuclear power plants, i.e. radiation and thermal factors, if applied one after another might lead to misleading conclusions as the oxidation products of polyethylene at temperatures close to the melting point either facilitate cross-linking or cause degradation. The rate between both phenomena is determined by the actual level of phenolic antioxidant. When irradiation is performed at elevated temperatures the effect would be different due to structural modifications of the polymeric material what involves changes in the penetration of oxygen molecules and production of peroxides. Additionally, intensification of conformational movements at higher temperatures speeds up radical recombination in the early stages of oxidation as well as accelerates competitive reaction between the radicals and antioxidant. Thus, extrapolation of the obtained results to operating conditions needs careful consideration.

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