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Degradation of ethylene – propylene elastomers in the presence of phenolic antioxidants Part II. Oxygenated products distribution

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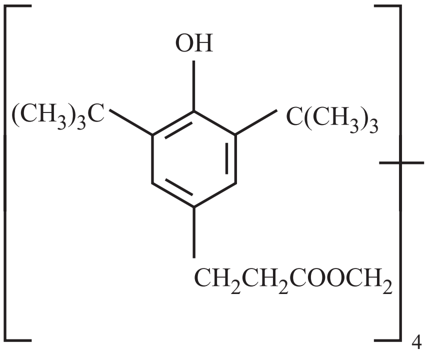
Unstabilized organic polymers degrade rapidly under the action of energy transfer, especially by exposure to high energy radiation, γ-rays or accelerated electrons [1, 2]. The stable products that can be spectroscopically measured belong to the oxygenated compounds, e.g. aldehydes, ketones, alcohols, acids, esters and so on. The formation of these products has been investigated under various conditions [3–10]. The radiation effect involves mainly oxidation of polymers in air by the reactions of molecular oxygen with free radicals. The peroxides initiate chain reactions according to the mechanism first postulated by Bolland and Gee [11] for thermal oxidation. The addition of a suitable amount of antioxidant offers higher stability against oxidation. The protection level of antioxidants depends on their ability to create sufficiently strong bonds with free radicals. The phenolic antioxidants are breaking chain stabilizers and they act especially in the previous stage of oxidation when they are not depleted. The distribution of degrading products seems to be influenced by the reactivity of antioxidants.

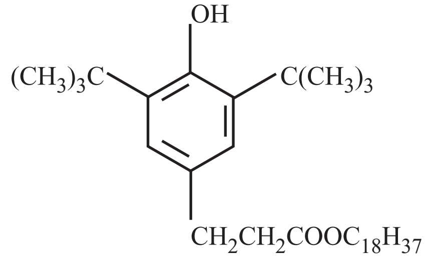
The reaction of molecular oxygen with free radicals requires a low activation energy so that this pathway is preferred when there is not a limited amount of oxygen available. The inhibition of oxidative degradation is brought about by antioxidants whose function is to retard auto-oxidation and, in general, to prolong the useful life of the host substrates. The most common stabilizers are hindered phenols that accept the unpaired electron of free radicals. At low oxygen pressure, for example in air, when diffusion feeds the inner part of the polymer with gaseous oxygen, the competition of free radicals for antioxidant or oxygen takes place. Consequently, the rate of oxidation decreases because the aroxyl radicals present a relative high stability. The distribution of oxygenated products depends on the chemical structure that free radicals attain at various stages of oxidation.

In order to study stabilization effects on γ-irradiated ethylene-propylene elastomers (EPDM and EPR), this letter reports the distribution of some of the main oxygen-containing products. Some characteristics of these rubbers have been previously presented [12]. It must be mentioned that both copolymers exhibit the same C_2/C_3 ratio (3:2), but EPDM contained 3.5% ethylidene norbornene as the third component of the terpolymer. Film specimens consisting of binary systems (polymer + antioxidant) were prepared by solvent removal of $CHCl_3$ solutions from stainless steel trays and by placing them on square glass frames for irradiation and spectrum recording.

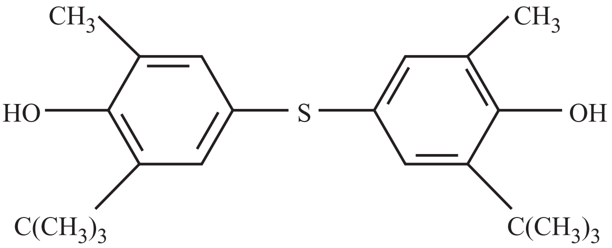
The antioxidants used in this work, AO 1 – AO 5 were produced by Ciba-Geigy and their concentration was 0.5%, achieved by the addition of stabilizers to 1% chloroform solutions



AO - 1. Irganox 1010
Tetrakis [methylene(3,5-di-*tert*-butyl-4-hydroxyhydrocinnamate)] methane



AO - 2. Irganox 1076
n-Octadecyl-3-(3′,5′-di-*tert*-butyl-4′-hydroxyphenyl)propionate



AO - 3. Santonox R
4,4′-Thiobis(2-*tert*-butyl-5-methylphenol)

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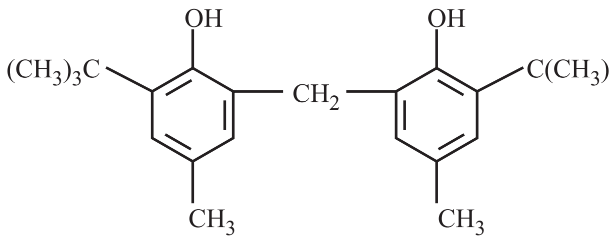
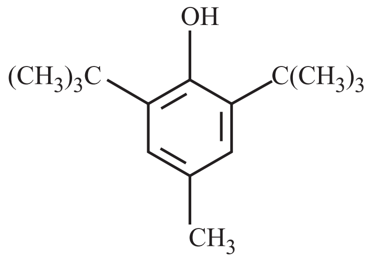


AO - 4. Cyanox 2246
2,2′-Methylenebis(4-methyl-6-*tert*-butylphenol)



AO - 5. Topanol OC
2,6′-Di-*tert*-butyl-4-methylphenol

of ethylene-propylene elastomers. The concentrations of oxygenated units were determined by IR spectroscopy at 3350 cm^{-1} (for C–OH or C–O–OH, $\varepsilon = 90\,\text{l}\,\text{mol}^{-1}\,\text{cm}^{-1}$) [13], 1744 cm^{-1} (for COOR, $\varepsilon = 590\,\text{l}\,\text{mol}^{-1}\,\text{cm}^{-1}$) [9], 1735 cm^{-1} (for aldehydes, $\varepsilon = 230\,\text{l}\,\text{mol}^{-1}\,\text{cm}^{-1}$) [9], 1724 cm^{-1} (for ketones, $\varepsilon = 320\,\text{l}\,\text{mol}\,\text{cm}^{-1}$) [9] and 1712 cm^{-1} (for acids, $\varepsilon = 710\,\text{l}\,\text{mol}^{-1}\,\text{cm}^{-1}$) [9]. IR spectra were recorded with a Specord M80 (Germany) in the wave number range 4000–1500 cm^{-1}.

Exposure of polymer samples was carried out in air inside a GAMMACELL facility provided with a ^{137}Cs source. The highest dose received by film specimens was 900 kGy. The irradiation consisted of successive exposures of 50 kGy. The intermediate IR spectra, corresponding to partial doses (multiple of 50 kGy), were recorded immediately after the end of each irradiation step.

Many studies concerning the assessment of antioxidant activities have developed the states in which stabilizers act [14, 15]. It has been stated that alkyl and alkylperoxy radicals can be deactivated by their reactions with antioxidants. The stabilizers (AO1 – AO5) used in this study are chain-breaking compounds. They can react as phenols by substitution of hydrogen with free radicals in hindered OH functionals or by addition of the radical intermediates to their quinone structures. Figs 1 to 4 support the idea of various reaction routes and their overlapping. The irregular sequence of concentration curves proves that some local factors influence differently the accumulation rate of oxidation products. It can be assumed that the stabilization activity of the tested antioxidants depends on the local concentration of radicals, the level of energy transferred during irradiation, the chemical nature of radicals (C- and O-centred free radicals) that surround the antioxidant molecule, the kind of interaction between the orbitals belonging to the antioxidant and the radical neighbours.

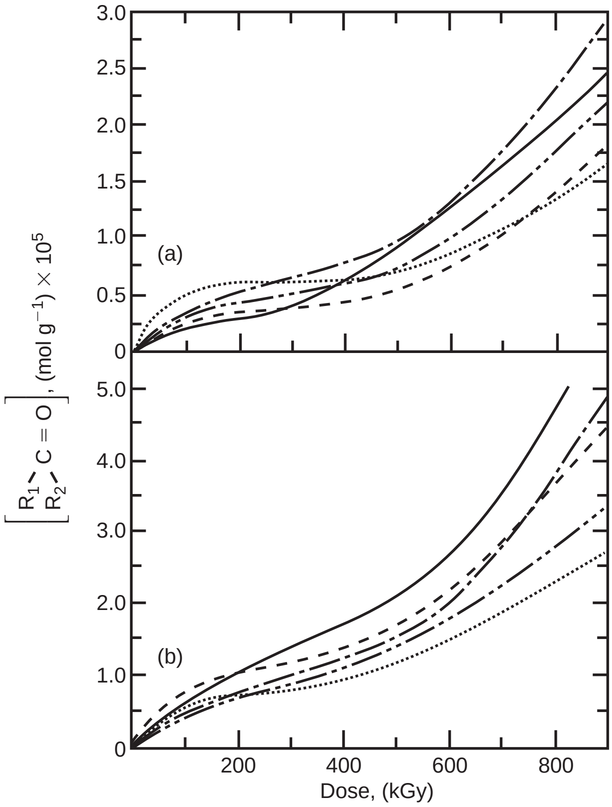


Figure 1 Plots of the ketone concentration versus dose for various stabilized elastomer systems (a) EPR, (b) EPDM; (· · · ·) Cyanox 2246; (–· ·–) Santonox R; (——) Irganox 1010; (– – –) Irganox 1076; (–·–) Topanol OC.

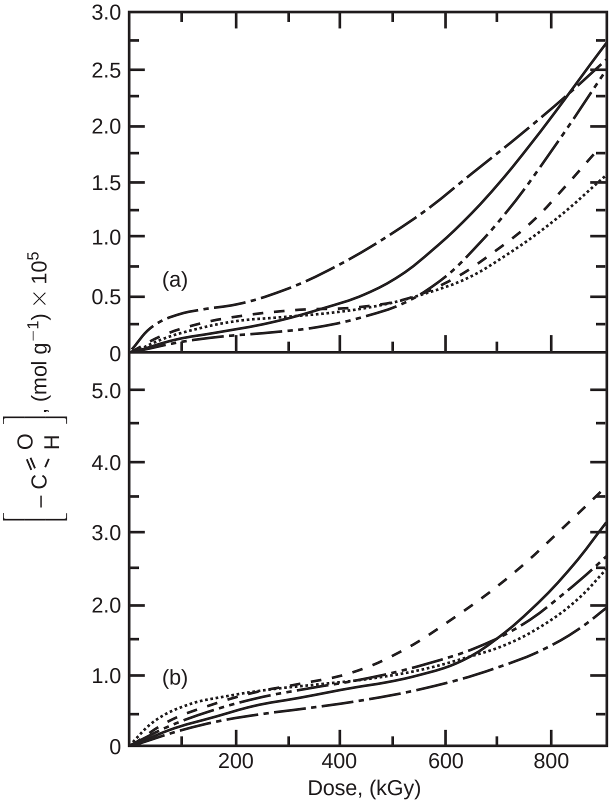


Figure 2 Plots of the aldehyde concentration versus dose for various stabilized elastomer systems (a) EPR, (b) EPDM; (· · · ·) Cyanox 2246; (–· ·–) Santonox R; (——) Irganox 1010; (– – –) Irganox 1076; (–·–) Topanol OC.

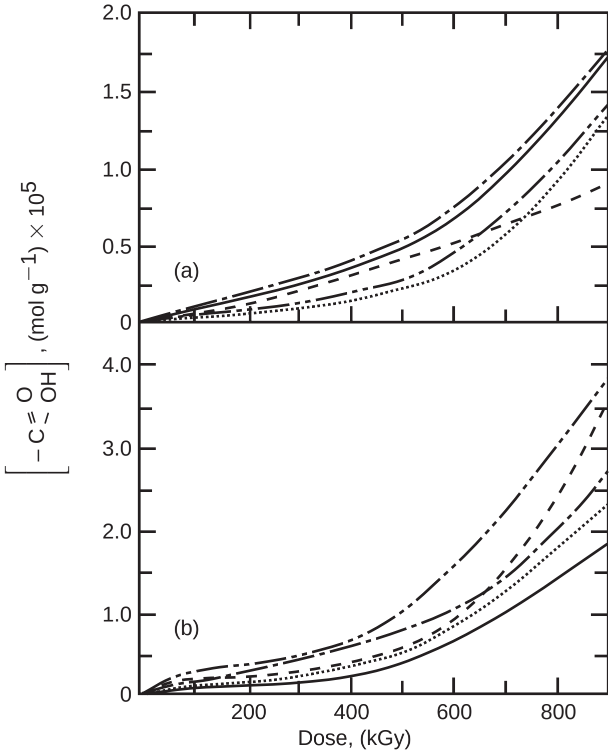


Figure 3 Plots of the acid concentration versus dose for various stabilized elastomer systems (a) EPR, (b) EPDM; (· · · ·) Cyanox 2246; (–· ·–) Santonox R; (——) Irganox 1010; (– – –) Irganox 1076; (–·–) Topanol OC.

Some main features of Figs 1 to 5 can be noted taking into account the changes in oxygenated product concentrations:

(a) The radiation stability of ethylene-propylene-diene terpolymer (EPDM) is less than the same characteristic of ethylene-propylene copolymer (EPR). This behaviour is due to the presence of ethylidene norbornene that inserts double bonds in the molecule of this elastomer;

(b) The first irradiation stage (the dose range up to 100 kGy) produces significant amounts of degradation products (alcohols, ketones and aldehydes). This means that they are produced by the reactions of free radicals with molecular oxygen dissolved in the polymer matrix. The concentration of radical intermediates is very high on the radiation tracks (inside spurs), so that the low quantity of antioxidant does not offer an efficient stability of polymers;

(c) An efficient stabilization of radiation degrading ethylene-propylene elastomers is carried out in the medium dose range (200–350 kGy), where the reaction probability of the antioxidant is significantly increased and a significant fraction of the oxidation initiators can be blocked;

(d) The similarity in the accumulation rates of ketones and aldehydes (Figs 1 and 2) emphasizes that bond cleavage occurs randomly. It is possible that the radical position migrates from the initial position along the hydrocarbon back-bone. Therefore, the proportion between aldehyde and ketone concentrations would not depend on the site of scission;

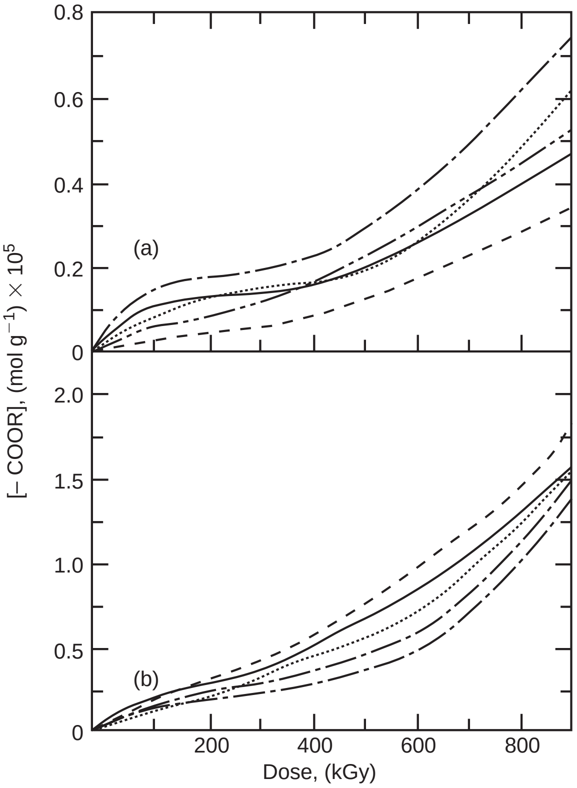


Figure 4 Plots of the ester concentration versus dose for various stabilized elastomer systems (a) EPR, (b) EPDM; (· · · ·) Cyanox 2246; (–· ·–) Santonox R; (——) Irganox 1010; (– – –) Irganox 1076; (–·–) Topanol OC.

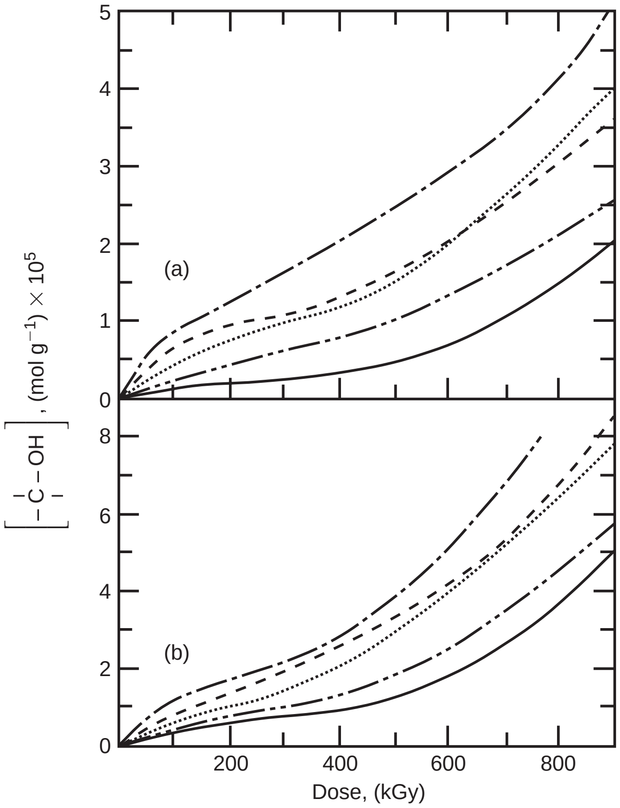


Figure 5 Plots of the alcohol concentration versus dose for various stabilized elastomer systems (a) EPR, (b) EPDM; (· · · ·) Cyanox 2246; (–· ·–) Santonox R; (——) Irganox 1010; (– – –) Irganox 1076; (–·–) Topanol OC.

(e) Antioxidants act in the first stage of oxidation when primary intermediates, peroxy and hydroperoxy radicals are formed. The lower amounts of acids (Fig. 3) and esters (Fig. 4) prove that they are preferentially formed by secondary reactions of peroxides or hydroperoxides. The scavenging of radicals (H and $R^{\cdot}$) represents the main process involved in the increase of acid or ester quantities;

(f) The relative positions of [C–OH] accumulation curves describe the order of stabilization activity. As has been pointed out in an earlier paper [10], the weakest antioxidant is Topanol OC. The increasing stabilization efficiency places the studied antioxidants in the following order:

$$\text{Topanol OC} < \text{Irganox 1076} < \text{Santonox R} < \text{Cyanox 2246} < \text{Irganox 1010}.$$

It is possible that the prepared specimens consisting of an unpurified ethylene-propylene elastomer (EPDM or EPR) and the studied phenolic antioxidant would present a synergetic effect. Thus, the simultaneous action of the protective additive (the stabilizer added during polymer manufacture to prevent material degradation on storage or processing time) and the tested antioxidant would also explain the "steady state" in oxygenated product concentrations over the dose range of 200–350 kGy. Various oxygenated products are formed directly by the action of molecular oxygen, like aldehydes, ketones or hydroperoxides. Other oxygenated products, such as acids or esters, are principally generated by $H^{\cdot}$ or $R^{\cdot}$ abstraction or by association and disproportionation of spatially close hydroperoxide groups [16].

It is clear that the distribution of oxygenated products influences the service behaviour of degrading polymer items. Electrical properties, such as volume resistivity, dielectric constant, and thermal properties, such as specific heat capacity, are largely dependent on the concentration of various degradation products. In spite of the decrease in the degradation rate, the antioxidants can determine a certain distribution of alcohols, aldehydes, ketones, acids. Moreover, the life time of any product depends on the interactions between various additives contained in polymer products.

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