# Radiochemical ageing of ethylene-propylene-diene elastomers. 4. Evaluation of some anti-oxidants.

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# Radiochemical ageing of ethylene–propylene–diene elastomers. 4. Evaluation of some anti-oxidants

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## Abstract

The preceding papers of this series were devoted to the identification and quantification of the main chemical changes resulting from the radiochemical ageing of EPDM (77.9% ethylene, 21.4% propylene, 0.7% diene) and EPR (76.6% ethylene, 23.4% propylene) films irradiated under oxygen atmosphere using $^{60}$Co γ-rays. It was shown that two processes are involved in the EPDM radio-oxidation. The random γ-radiolysis of the polymer provides a constant source of macro-alkyl radicals that are likely to initiate a selective oxidation of the polymer through free-radicals reactions involving the abstraction of labile hydrogen atoms. In the present paper, infrared spectroscopy has been used to study the γ-degradation of EPDM cross-linked with dicumyl peroxide and/or stabilised with two types of anti-oxidants (hindered phenol or amine-type). The results show that the anti-oxidants are not efficient in preventing oxidation. To understand the lack of efficiency of the stabilisers, the impacts of the various formulations on the rate of degradation of EPDM against chain oxidation involved in thermal and UV ageing were also studied.
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*Keywords:* Radiochemical ageing; EPDM; Stabilisation; Radio-oxidation; Infrared spectroscopy

## 1. Introduction

The modifications of the structure and properties of polymers resulting from exposure to ionising radiation has attracted much interest. The present study, developed in a series of articles, concerns the radiative ageing of EPDM copolymers which are composed of ethylene (PE), propylene (PP) and diene monomer (5-ethylidene-2-norbornene (ENB)). The aim is to propose mechanisms accounting for the main routes of EPDM degradation. Irradiations were carried out both in the presence and in the absence of oxygen, and the comparison with EPR containing the same ethylene/propylene ratio than

EPDM were made to assess the importance of the diene moiety and the involvement of oxygen.

The first paper focused on the modifications of the chemical structure of EPDM (77.9% ethylene, 21.4% propylene, 0.7% diene) and EPR (76.6% ethylene, 23.4% propylene) under argon atmosphere [1]. Irradiation of EPDM and EPR was shown to generate *trans*-vinylene, vinyl, vinylidene and diene unsaturation, with similar radiochemical yields for both polymers. Degradation was shown to also involve cross-linking and production of hydrogen. The presence of the diene, the double bonds of which are consumed with a high radiochemical yield, contributes to the increase in rate and intermolecular bridge density. Mechanisms were proposed to account for the main routes of EPDM degradation. In particular, it was shown that the depletion of unsaturation, which

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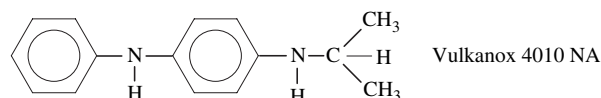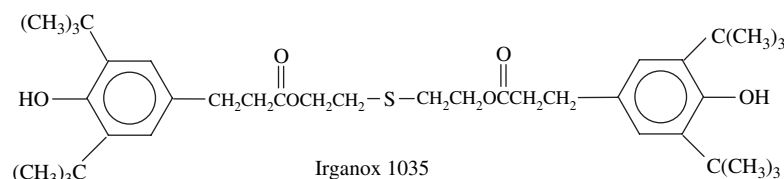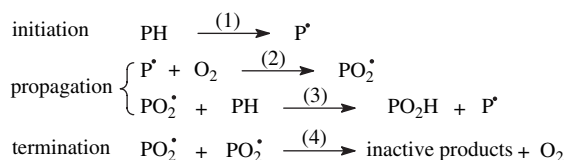*E-mail address:* luc.gardette@univ-bpclermont.fr (J.-L. Gardette).

cannot result from unselective direct radiolysis, involves addition by macro-radicals formed in the EPDM radiolysis.

In paper 2 [2], the chemical changes occurring in EPDM and EPR films γ-irradiated under oxygen atmosphere were identified and quantified using a combination of IR analysis, derivatisation reactions and iodometric titration. The extent of cross-linking was evaluated by gel fraction methods.

On the basis of these experimental results, mechanisms accounting for EPDM γ-degradation under oxygen atmosphere were proposed in paper 3 [3]. Discussion took also into account complementary experimental results showing the instability of hydroperoxide groups under γ-radiation. It was shown that radio-oxidation involves two concomitant processes. As the interaction of high energy radiation with matter is unselective, the irradiation of EPDM (77.9% ethylene) mainly involves C—H bond scissions of the ethylene units. Radicals resulting from the direct effects of radiation are likely to initiate a chain oxidation process. It was shown that the methylene groups in an α-position to the double bonds of the ENB are the most oxidisable site and that saturation reactions of the ENB moieties cause the cross-linking of EPDM films.
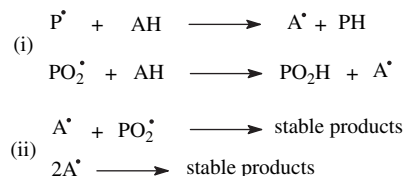
The present paper reports some recent results and obtained ion stabilisation of EPDM to radiochemical ageing. The EPDM samples were vulcanised with dicumyl peroxide and/or stabilised with hindered phenol or amine-type anti-oxidant. In order to verify the efficiency of the stabilisers against chain oxidation, the impact of the various formulations on the oxidation rate of EPDM induced by UV-light or by temperature was also studied.

Thermo-oxidation, photo-oxidation and γ-irradiation involve a chain-oxidation process whose common points can be described according to [4]:

$$\text{initiation} \quad PH \xrightarrow{\;(1)\;} P^\bullet$$
$$\text{propagation} \begin{cases} P^\bullet + O_2 \xrightarrow{\;(2)\;} PO_2^\bullet \\ PO_2^\bullet + PH \xrightarrow{\;(3)\;} PO_2H + P^\bullet \end{cases}$$
$$\text{termination} \quad PO_2^\bullet + PO_2^\bullet \xrightarrow{\;(4)\;} \text{inactive products} + O_2$$

The main differences between the processes lie in the initiation step and in the hydroperoxide decomposition. It is generally admitted that photo- and thermo-oxidation starts on the ENB moiety before reaching the ethylene—propylene units [5,6]. The thermal and photochemical degradation of hydroperoxides involves the scission of the O—O bonds [7].

It is briefly recalled that anti-oxidants (AH) prevent by chain transfer (i) or termination (ii) the propagation reactions [7] in any oxidation process (UV, thermal or radiation initiated), according to:

$$(i) \quad \begin{array}{l} P^\bullet + AH \longrightarrow A^\bullet + PH \\ PO_2^\bullet + AH \longrightarrow PO_2H + A^\bullet \end{array}$$
$$(ii) \quad \begin{array}{l} A^\bullet + PO_2^\bullet \longrightarrow \text{stable products} \\ 2A^\bullet \longrightarrow \text{stable products} \end{array}$$

The present paper reports a study of the behaviour of various formulations under conditions of oxidation initiated by UV-light, temperature or γ-radiations. The objective is to compare the efficiency of the anti-oxidant in stabilising EPDM against these various conditions of degradation.

## 2. Experimental

Ethylene—propylene—diene monomer (EPDM), based on 5-ethylidene-2-norbornene (ENB), was supplied by Dupont under the trade name NORDEL IP 3725. The molar composition of EPDM determined by solid state ^{13}C NMR was 77.9% ethylene, 21.4% propylene, 0.7% diene. Various formulations of EPDM were processed: a pure gum (EPDM), an elastomer cross-linked agent with dicumyl peroxide (Aldrich) and an elastomer stabilised with two types of anti-oxidants: a hindered phenol (Irganox 1035, Ciba-Geigy) and an amine-type anti-oxidant (Vulkanox 4010 NA, Bayer). A detailed description of the samples is given in Table 1.



Irganox 1035



Vulkanox 4010 NA

Table 1
Composition of the EPDM compounds

| Sample code | Cross-linking agent | Irganox 1035 (phenolic AO) | Vulkanox 4010 NA (amine-type AO) |
|---|---|---|---|
| Additive-free EPDM 9 | – | – | – |
| EPDM 9 | – | – | – |
| EPDM 10 | 3 | – | – |
| EPDM 11 | 3 | 0.1 | – |
| EPDM 12 | 3 | – | 1 |
| EPDM 13 | – | 0.1 | – |

Concentrations are expressed in wt%.

All the EPDM samples contained processing anti-oxidants, which can be characterised by a UV absorption band at 280 nm with a shoulder around 230 nm. The remaining processing anti-oxidants were removed from the pure gum (EPDM 9) by Soxhlet extraction with methanol for 24 h. The sample was then vacuum dried for 24 h. This sample, which contains no residual processing anti-oxidants, is referred as "additive-free EPDM 9" in Table 1.

EPDM films (approximately 100 μm thickness) were prepared by compression moulding between PTFE-coated glass sheets at 200 bar in an electrically heated laboratory press at 180 °C for 10 min. Films were then stored in a vacuum oven for 10 min at 100 °C.

Radiochemical ageing was performed at Arc-Nucléart (CEA/Grenoble, France). Gamma irradiation was delivered by $^{60}$Co γ-sources. Samples were irradiated in a watertight container, at doses between 5 and 455 kGy, dose rate being 1 kGy/h, with an oxygen flow of 0.5 L/min at 20 °C.

Thermal oxidation was performed at 100 °C in an oven ventilated by natural convection. Photo-oxidation was performed in a polychromatic set-up based on the conventional accelerating device SEPAP [8] but modified in such a way that photo-oxidation can be performed at 35 °C. The instrument already described [9] elsewhere contains only one medium pressure mercury lamp filtered with a borosilicate envelope (Mazda MA 400).

The changes in several typical functions and the decrease of the double bond content in EPDM were followed by infrared spectroscopy with a Nicolet Magna-IR 760 FTIR spectrophotometer (32 scans summation, nominal resolution of 4 cm$^{-1}$). Changes in the UV–vis spectra were followed with a Shimadzu UV-2101PC spectrophotometer equipped with an integrating sphere.

Total peroxide species (hydroperoxides and peroxides) were titrated using the iodometric method [10,11].

## 3. Experimental results

### 3.1. Radio-oxidation

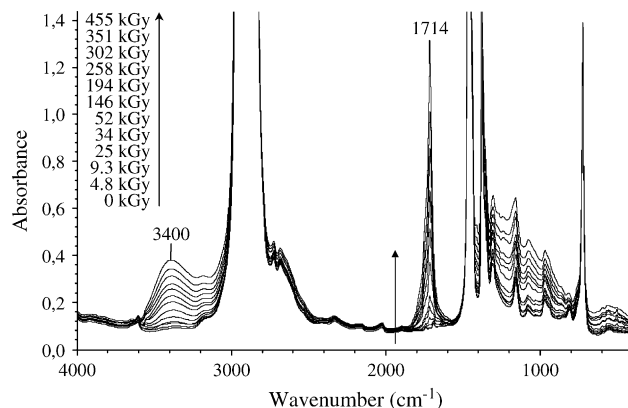Radio-oxidation of EPDM leads to notable modifications in the IR and UV–vis spectra of the samples.



Fig. 1. IR spectral changes during γ-irradiation under oxygen atmosphere of additive-free EPDM 9 film.

The oxidation products formed by γ-irradiation of additive-free EPDM 9 were characterised by IR spectroscopy. The results obtained are shown in Fig. 1: the development of a broad band in the hydroxyl absorption region centred at 3400 cm$^{-1}$ is observed and in the carbonyl region the formation of a carbonyl band with an absorption maximum at 1714 cm$^{-1}$.

Focussing on these two regions of the FTIR region (see paper 2 [2]) showed several shoulders to the main absorption bands. This indicated that radio-oxidation produces a complex mixture of different products. The products were identified by combining IR analysis with chemical derivatisation reactions.

The maximum around 3400 cm$^{-1}$ was attributed to hydrogen bonded –OH stretch of alcohols, hydroperoxides and carboxylic acids. The maxima at 3600 and 3553 cm$^{-1}$ were, respectively, attributed to isolated OH stretch of alcohols and hydroperoxides. In parallel one observed a progressive decrease in the intensity of the $\nu$(C=H) absorption band at 3040 cm$^{-1}$, which suggested the disappearance of the double bond of the termonomer ENB.

The appearance of a band with an absorption maximum at 1714 cm$^{-1}$ accompanied by several shoulders around 1785, 1755, 1740 and 1695 cm$^{-1}$ was observed during radio-oxidation. Saturated ketones (1725–1718 cm$^{-1}$) and carboxylic acids (1755 and 1718–1710 cm$^{-1}$) were the main carbonyl products formed. The formation of esters (1740 cm$^{-1}$) and γ-lactones (1785 cm$^{-1}$) was shown to occur in lower concentrations. At weak conversion degree, unsaturated structures were observed to be formed: unsaturated ketones at 1685 cm$^{-1}$ and unsaturated acids, identified by SF$_4$ treatments, around 1700 cm$^{-1}$.

In the region corresponding to the out of plane vibration of the C–H bond linked to unsaturation, one observed a progressive decrease in the γ(C–H) absorbance at 808 cm$^{-1}$, indicating therefore the progressive disappearance of the diene double bonds throughout radio-oxidation.

The γ-irradiation of stabilised EPDM caused the same modification in the IR spectra as those observed for additive-free EPDM 9 but with a different rate. As an example, the change of the IR spectra of EPDM 12 is reported in Fig. 2.

The formation rates of carbonyl products measured at 1714 $cm^{-1}$ and of hydroxyl products measured at 3400 $cm^{-1}$ during γ-oxidation of EPDM are shown in Fig. 3A and B. The curves corresponding to the consumption of the double bond (808 $cm^{-1}$) of the ENB as a function of the dose are plotted in Fig. 3C.

The kinetic curves given in Fig. 3 show that the curing has no effect on the oxidation and that the anti-oxidants do not prevent the oxidation of EPDM. It is only in the case of EPDM 12, cured and stabilised with Vulkanox at 1%, that a stabilising effect can be observed, the rate of accumulation of the final oxidation products as well as the rate of consumption of the double bonds are reduced. A short induction period, before the oxidation starts is observed, below 25 kGy.

The EPDM 12 formulation has been studied in more detail because the high concentration of anti-oxidant used (1%) permits the evaluation by IR spectroscopy of the stability of the additive.

Figs. 4A and 5A show the modifications of the spectra in the C=O domain in the case of EPDM 12 and in the case of additive-free EPDM 9, limited to a dose of 52 kGy. In order to better characterise these modifications, the spectra obtained by subtraction of the initial spectrum from the spectra recorded after each irradiation dose are also presented (Figs. 4B and 5B).

Comparison of these figures shows that the envelope of the carbonyl absorption does not has the same shape for additive-free EPDM 9 and EPDM 12. It can be noted that the decrease in the double bond contents (absorption band at 1685 $cm^{-1}$) occurs at a lower rate in the case of EPDM 12.

The formation of the oxidation products is accompanied by the consumption of the anti-oxidant as shown by
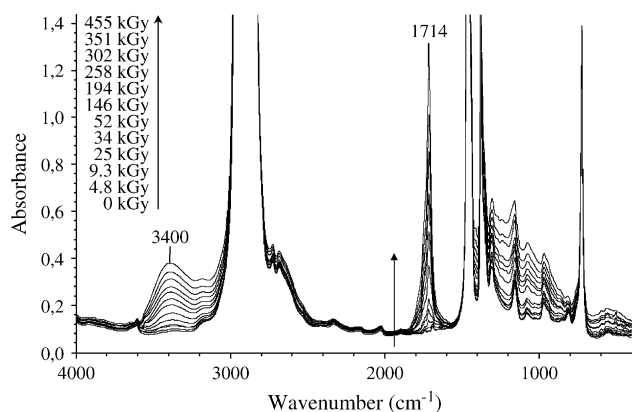


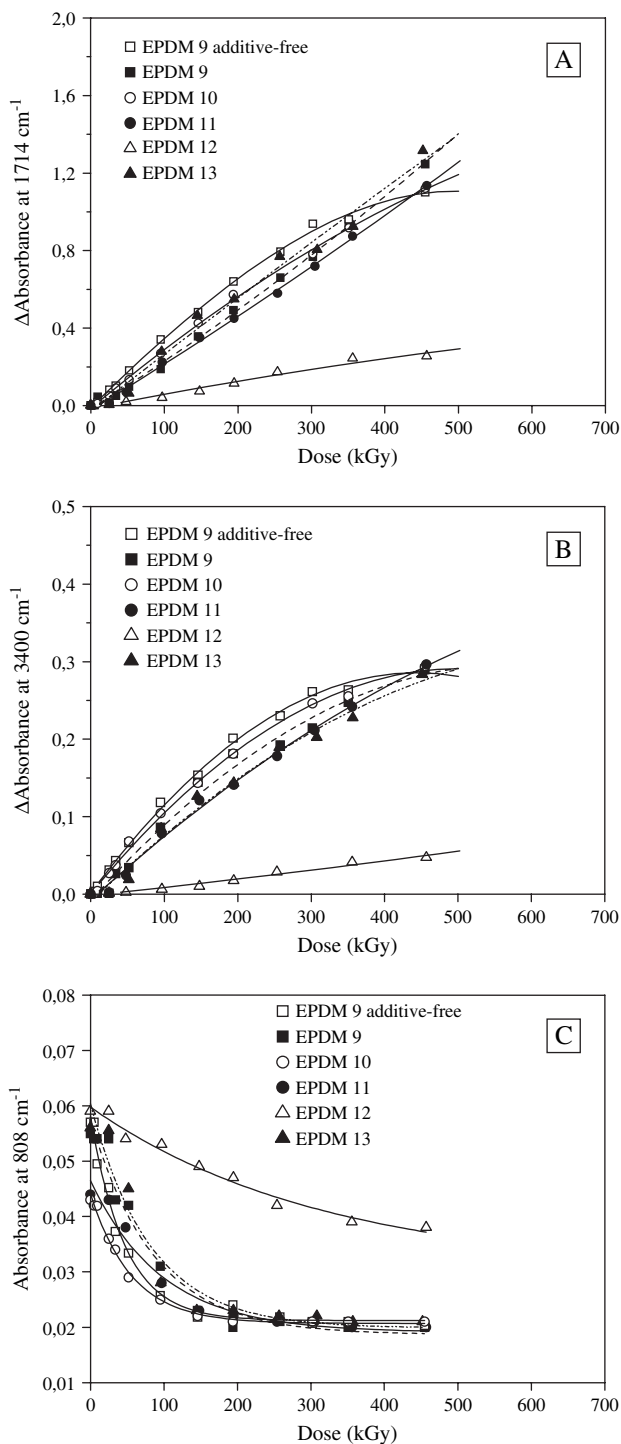Fig. 2. IR spectral changes during γ-irradiation under oxygen atmosphere of EPDM 12 film.



Fig. 3. Increase in the absorbance at 1714 (A) and 3400 $cm^{-1}$ (B) as a function of the dose for various formulations of EPDM films γ-irradiated under oxygen atmosphere. (C) Decay in the absorbance at 808 $cm^{-1}$ for various formulations of EPDM films γ-irradiated under oxygen atmosphere.

the progressive disappearance of the absorption bands at 1613, 1598, 1512 and 1496 $cm^{-1}$. Fig. 6 shows the kinetic curves of oxidation and loss of additives in the case of EPDM 12. It can be observed that both the consumption
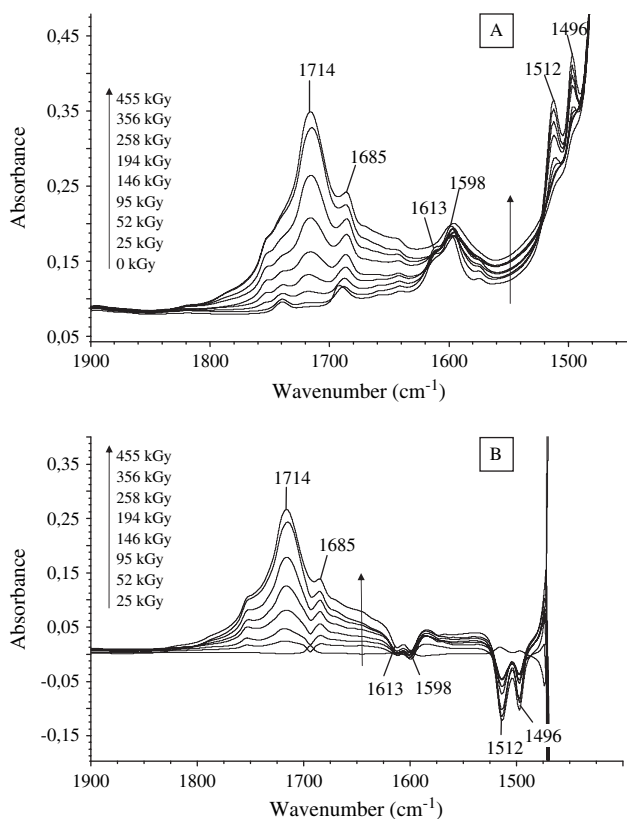
Fig. 4. IR spectral changes in 1900–1500 cm$^{-1}$ region of EPDM 12 film γ-irradiated under oxygen atmosphere. (A) Direct spectra, (B) subtraction (irradiated – initial).
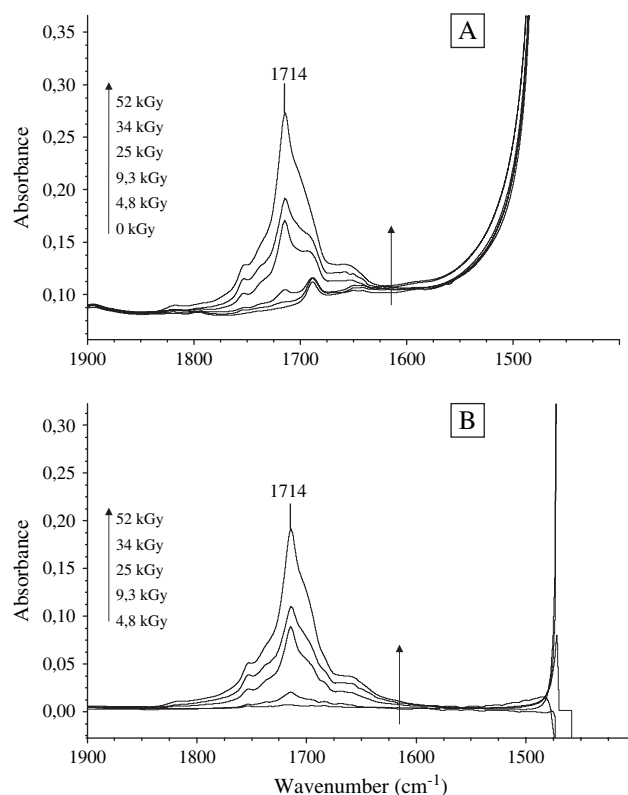


Fig. 5. IR spectral changes in 1900–1500 cm$^{-1}$ region of additives-free EPDM 9 film γ-irradiated under oxygen atmosphere. (A) Direct spectra, (B) subtraction (irradiated – initial).

of the anti-oxidant and the formation of oxidative species are progressive all through the exposure.

Fig. 7 compares the rates of formation of the peroxide species (hydroperoxides and peroxides) for additive-free EPDM 9 and EPDM 12 films. The anti-oxidant is observed to be efficient in reducing the accumulation rate of peroxide species. A ratio of about 10 can be measured.

### 3.2. Thermo-oxidation and photo-oxidation

There are many similarities between the modifications of the IR spectra provoked by radio-, photo- and thermo-oxidation:

— The shapes of the hydroxyl absorption bands are the same in the three oxidative conditions. One observes the formation of an absorption band with a maximum centred at 3400 cm$^{-1}$ accompanied by two shoulders around 3600 and 3553 cm$^{-1}$.
— In the 1000–800 cm$^{-1}$ region, the progressive decrease of the absorbance at 808 cm$^{-1}$ indicates that the diene double bonds are saturated throughout oxidation.
— The carbonyl absorption bands that appear reveal the presence of the same maxima or shoulders as reported above at 1788, 1732 and 1714 cm$^{-1}$.

Ketones and carboxylic acids, responsible for the absorption maximum at 1714 cm$^{-1}$, are the main oxidation products in the three conditions of ageing.

However, a detailed analysis shows that differences exist. First, the accumulation of esters (1740 cm$^{-1}$) is favoured in thermo-oxidation, and photo-oxidation shows that high amounts of α,β-unsaturated carbonyl groups (ketones and acids at 1685 cm$^{-1}$) are formed.
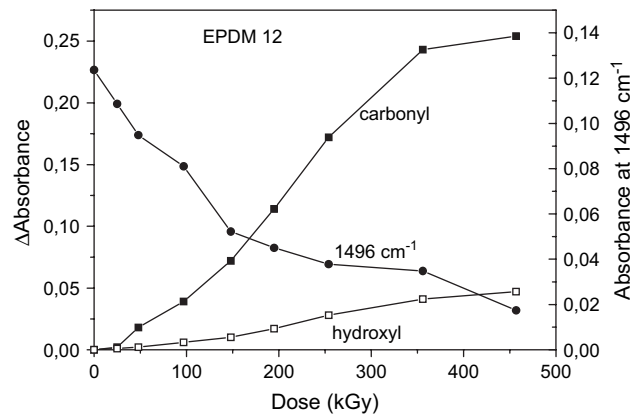


Fig. 6. Increase in the absorbance at 1714 and 3400 cm$^{-1}$ and decay in the absorbance at 1496 cm$^{-1}$ for EPDM 12 formulation of as a function of the dose.
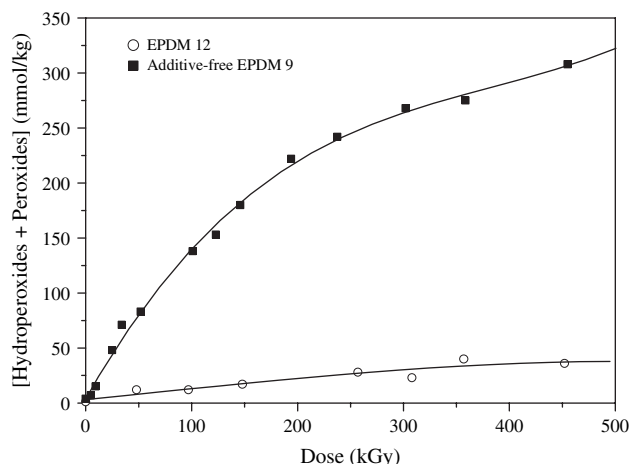
Fig. 7. Effect of the Vulkanox anti-oxidant on the peroxidic species concentration.



Fig. 8. Increase in the absorbance at 1714 cm$^{-1}$ as a function of thermo-oxidation duration at 100 °C for various formulations of EPDM films.

Second, when EPDM is stabilised by anti-oxidant or cross-linked, thermo-oxidation involves two steps:

– At low conversion one observes the development of a carbonyl absorption band centred at 1732 cm$^{-1}$, whereas no hydroxyl groups and no maximum at 1714 cm$^{-1}$ characteristic of the oxidation of the ethylene and propylene unit are formed and no consumption of the ENB double bonds is observed. This indicates that within the first period, it is the oxidation of the norbornene sites that occurs without attack of the double bonds (cross-linking).
– Then saturated ketones and carboxylic acids, responsible for the absorption at 1714 cm$^{-1}$, rapidly become the main oxidation products. The formation of these products indicates the oxidation of ethylene and propylene units. During this second period, the double bonds disappear and hydroxyl groups are formed.

The formation rates of carbonyl products measured at 1714 cm$^{-1}$ throughout thermo-oxidation of the various formulations are shown in Fig. 8.

From Fig. 8, it clearly appears that EPDM thermo-oxidation can be efficiently inhibited by anti-oxidants, with a notable induction period. Irganox and Vulkanox provide high stability. Cross-linking EPDM slightly decreases the efficiency of Irganox.

The formation rates of carbonyl products measured at 1714 cm$^{-1}$ throughout photo-oxidation of the various formulations are shown in Fig. 9.

From curves drawn on Fig. 9, it is apparent that none of the additive systems causes a reduction in the formation rate of oxidation products. Some of the stabiliser systems even increase the initial rate of oxidation. If one gives a particular attention to the EPDM 12 formulation, it can be checked that the first
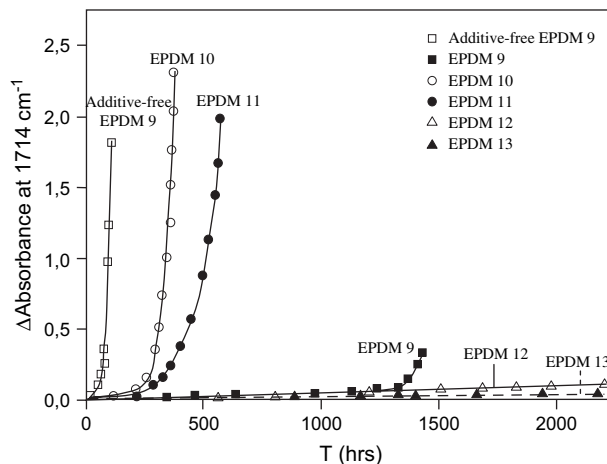
five hours of exposure provoked the elimination of this anti-oxidant. This strongly suggests that the anti-oxidant photodegradation is likely to induce the polymer photo-oxidation.

## 4. Discussion

Oxidation of polymers induced by UV-light, temperature or γ-radiation results in chain scission, cross-linking and formation of oxygen-containing functional groups. The stabilisers role is to retard these oxidation processes. Oxidation prevention involves the scavenging of free-radical intermediates (P$^{•}$ and PO$_2^{•}$ radicals) and in some cases can also involve in the reduction of radicals formation.

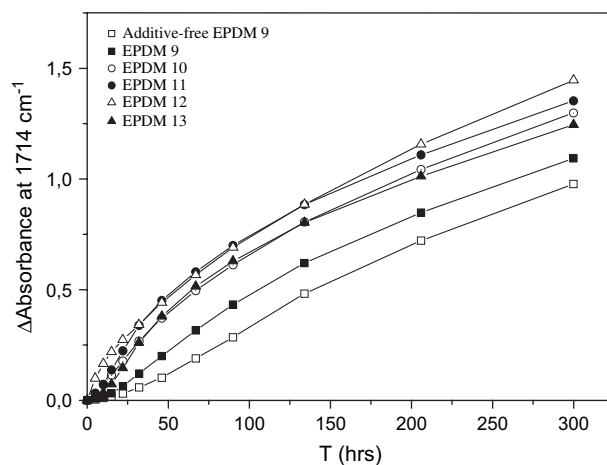Conventional anti-oxidants are highly efficient against EPDM thermal oxidation and provoke long



Fig. 9. Increase in the absorbance at 1714 cm$^{-1}$ as a function of photo-oxidation duration for various formulations of EPDM films.

induction periods. In the case of EPDM, the most oxidisable sites are the norbornene moieties. The oxidation of these groups is not easily inhibited by the anti-oxidants. However, oxidation of the norbornene sites has only minor consequences due to the low diene content (0.7% diene). Ethylene and propylene sites are less oxidisable than the norbornene units and the propagation of the chain oxidation reactions involving these units can be efficiently inhibited by anti-oxidant. The oxidation of EPDM is indeed strongly reduced in the case of EPDM 12 and EPDM 13 formulations.

In contrast, in condition of UV-light induced oxidation, anti-oxidants do not protect the polymer against oxidation. The inefficiency of the anti-oxidants results from two antagonist effects: due to their aromatic structure, anti-oxidants can absorb the incident UV light. The photochemical reactions which are in turn induced provoke the formation of radical species that are likely to initiate the polymer photo-oxidation by hydrogen abstraction from the macromolecular backbone. At the same time, anti-oxidants are likely to scavenge the PO$^{\bullet}$ and POO$^{\bullet}$ radicals which are formed. Their overall efficiency is the average of these two antagonistic effects, initiation of chain oxidation reactions and anti-oxidant effects. For these reasons, anti-oxidants must be protected by UV-absorbers in order to prevent them from absorbing UV-light [4,7].

Degradation of EPDM exposed to γ-rays was shown to result both from random direct radiation effects (C–H scissions caused directly by radiation reaction) and from the selective oxidative chain reactions [3]. As the effect of high-energy radiation on matter results from random interaction with the electrons [12,13], additives present in small concentrations do not directly absorb the energy. It was therefore expected that anti-oxidants would be stable and efficient to stop the chain oxidation process. Unfortunately, our results indicate that only the formulation based on Vulkanox shows a stabilising effect which is however very weak and with a very short induction period. In addition, the loss of the aromatic infrared absorption bands revealed degradation of the anti-oxidant. In order to understand the lack of efficiency of the anti-oxidants to protect EPDM against the γ-initiated oxidation, the following points have to be taken into account.

In the present experimental conditions, the rate formation of the oxidation products in additive-free EPDM 9 is about 10 times higher in thermo-oxidation than in γ-irradiation (compare Figs. 3A and 8, considering that the dose rate is 1 kGy/h). This result is confirmed by the determination of the decomposition of hydroperoxides. For an EPDM film γ-irradiated at a 351 kGy dose, a total disappearance of the hydroperoxides can be obtained only after 30 h of thermolysis at 100 °C whilst a 300 kGy dose is not sufficient to provoke the decomposition of these products [2,3].

- There are very strong differences between the initiation steps that are involved in the three ageing types: initiation is selective in thermo-oxidation and photo-oxidation, but statistical in γ-irradiation. The initiation step in γ-irradiation mainly involves the ethylene sites (77.9% ethylene). The concentration of radical species which are formed is largely too important to be stopped by the anti-oxidant even used at concentration 1%.
- Another reason for the lack of efficiency of anti-oxidants results from the fact that they can be degraded during γ-irradiation, as observed by the loss of aromatic absorption bands. Part of this degradation is due to their anti-oxidant activity, which involves reactions with free-radicals intermediates. After hydrogen transfer to the peroxy radical, the phenoxy form of the anti-oxidant in the mesomeric form could give a quinone-type product [14–17]. But this proposal does not permit understanding the difference in efficiency between thermal and γ-oxidation. The anti-oxidants disappearance could also result from their degradation by the deposited energy, even if this interaction is not direct as in UV-degradation. Whilst thermo-oxidation and photo-oxidation only involves radical species, excited states and charged species such as ionic intermediates and electrons also account for γ-irradiation [18]. Aromatic rings are known to act as 'energy sinks' as they are able to trap charged species and quench the excited states [19]. Consequently to the excitation of the electrons of the macromolecular chains, transfer of the excitation energy (before scission of the main chain) to the aromatic additive may occur [20]. When the excitation energy is dissipated to heat, the additive constitutes a protecting agent ("anti-rad") able to prevent the radical formation resulting from direct radiation effects. In the EPDM case, energy transfer to additives is likely to be achieved, which results in the degradation of the chemical structure of the additive.

Results obtained with EPDM are in agreement with previous results obtained with polypropylene showing that the presence of residual "conventional" anti-oxidants induced the γ-degradation of the matrix [21].

As in the case of UV-degradation, an efficient stabilisation against γ-irradiation should take into account a rate of decrease in radical formation and should minimise the anti-oxidant degradation by the use of high concentration of aromatic molecules acting similarly with energy transfer and dissipation. Compounds like anthracene, biphenyl or aromatic polyimides, which were found to be effective "anti-rads" [22,23], should be used in combination with classical anti-oxidants.

## 5. Conclusion

The oxidation rate of EPDM can be efficiently reduced by anti-oxidants in thermo-oxidation conditions. In photo-oxidation conditions, anti-oxidants can induce the EPDM degradation because they are not protected by UV-absorbers. In γ-irradiation conditions, anti-oxidants are rapidly consumed and only the amine-type formulation at 1% is observed to display a limited stability, with a very short induction period (25 kGy) before the oxidation starts.

A more effective stabilisation system should involve the incorporation of two types of stabilisers in the polymer. For this purpose a parallel could be made between photo-oxidation and radio-oxidation. In photodegradation, a strong synergistic effect can be observed in the case of mixtures of UV-absorber and anti-oxidant. By analogy, a synergistic effect is expected between an ''anti-rad'' and an anti-oxidant. In the case of EPDM, fused-ring aromatics of anthracene-type (also called ''anti-rads'') could be added to the amine-type formulation. Whilst anti-oxidants are active on the propagation of the chain oxidation reactions, ''anti-rads'' are efficient against the initiation step. The effects of these stabilisers are thought to be an energy transfer of radiation from polymer to the aromatic compound, producing a delocalisation of the energy which is then changed to thermal energy. Meanwhile, the introduction of anti-oxidant and ''anti-rad'' could cause complex chemical reactions: the mixture of stabilisers could have synergistic effects or in contrast antagonism between the components could occur. Therefore, complementary studies have to be carried on.

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