Crosslinking on ageing of elastomers: I. Photoageing of EPDM monitored by gel, swelling and DSC measurements

Mohamed Baba *, Jean-Luc Gardette, Jacques Lacoste

Laboratoire de Photochimie Moléculaire et Macromoléculaire, UMR CNRS 6505, ENS Chimie de Clermont-Ferrand, Université Blaise Pascal, F-63177 Aubière Cedex, France

Abstract

The crosslinking reactions occurring during the photo-oxidation of EPDM have been examined by measuring changes in gel fraction, degree of swelling and freezing point by Differential Scanning Calorimetry. The correlation with the variation of the carbonyl index showed that the crosslinking process was very efficient (similar to that obtained by peroxide vulcanization) and occurred at the very early stages of the photo-oxidation. Gel fraction measurements showed that chain scissions were detected as soon as the formation of oxidation photoproducts could be observed by infrared analysis of the oxidied polymer. © 1998 Elsevier Science Ltd. All rights reserved.

1. Introduction

Polymers containing unsaturated groups, such as conventional dienic elastomers or EPDM are well known for their potential for vulcanization (both by sulfur and peroxides) but have only limited resistance to oxidation even in weathering or low temperature storage [1].

Because both reactions (oxidation and crosslinking) involve radical processes, crosslinking reactions can occur on the same time scale as oxidation. The conventional analytical techniques such as FTIR spectrometry used for the evaluation of the chemical changes that occur in polymeric materials upon ageing are not efficient enough to detect the crosslinking reactions of the matrix.

The aim of this series of papers is to explore the potential of specific techniques such as thermal or rheometric analyses to detect physical changes in polymers submitted to oxidation in exposure conditions representative of natural ageing ($T \leq 60°C$, $\lambda \geq 300$ nm). The physical changes observed in the polymeric materials are correlated with the oxidation followed by FTIR spectroscopy.

This first paper is devoted to the study of the behavior of an Ethylene Propylene Diene Monomer (EPDM) terpolymer.

The crosslinking is followed by conventional gel and swelling measurements but also by Differential Scanning Calorimetry (DSC). In this last case, the freezing temperature of cyclohexane (a swelling solvent) was measured at different times of exposure to ageing and at different degrees of crosslinking resulting from a peroxide vulcanization.

2. Experimental

Ethylene Propylene Diene Monomer (EPDM) was based on 5-ethylidene-2-norbornene (VISTALON 7500-EXXON). The molar contents determined by ^{1}H NMR at 400 MHz (BRUKER AC-400) were 60.0/37.3/and 2.7 mol% respectively. SEC analysis (WATERS 150C) performed in 1,3,5-trichlorobenzene at 135° gave 45×10^3, 535×10^3 and 12 for $\bar{M}_n$, $\bar{M}_p$ and PDI, respectively. The polymer was precipitated in methanol to remove additives. Films (ca. 100 μm) were prepared by moulding in an electrically heated laboratory press at 145°C and 19 MPa for 1 min.

Photo-oxidations were performed in a polychromatic set up based on the conventional accelerating device SEPAP [2] but modified in such a way that photo-oxidation can be performed at temperature as low as 35°C. The instrument already described elsewere [3] contains only one medium pressure mercury lamp filtered with a borosilicate envelope (MAZDA MA 400)

* Corresponding author. Tel.: +33-473407161; fax: +33-473407095; e-mail: baba@cicsun.univ-bpdermont.ft
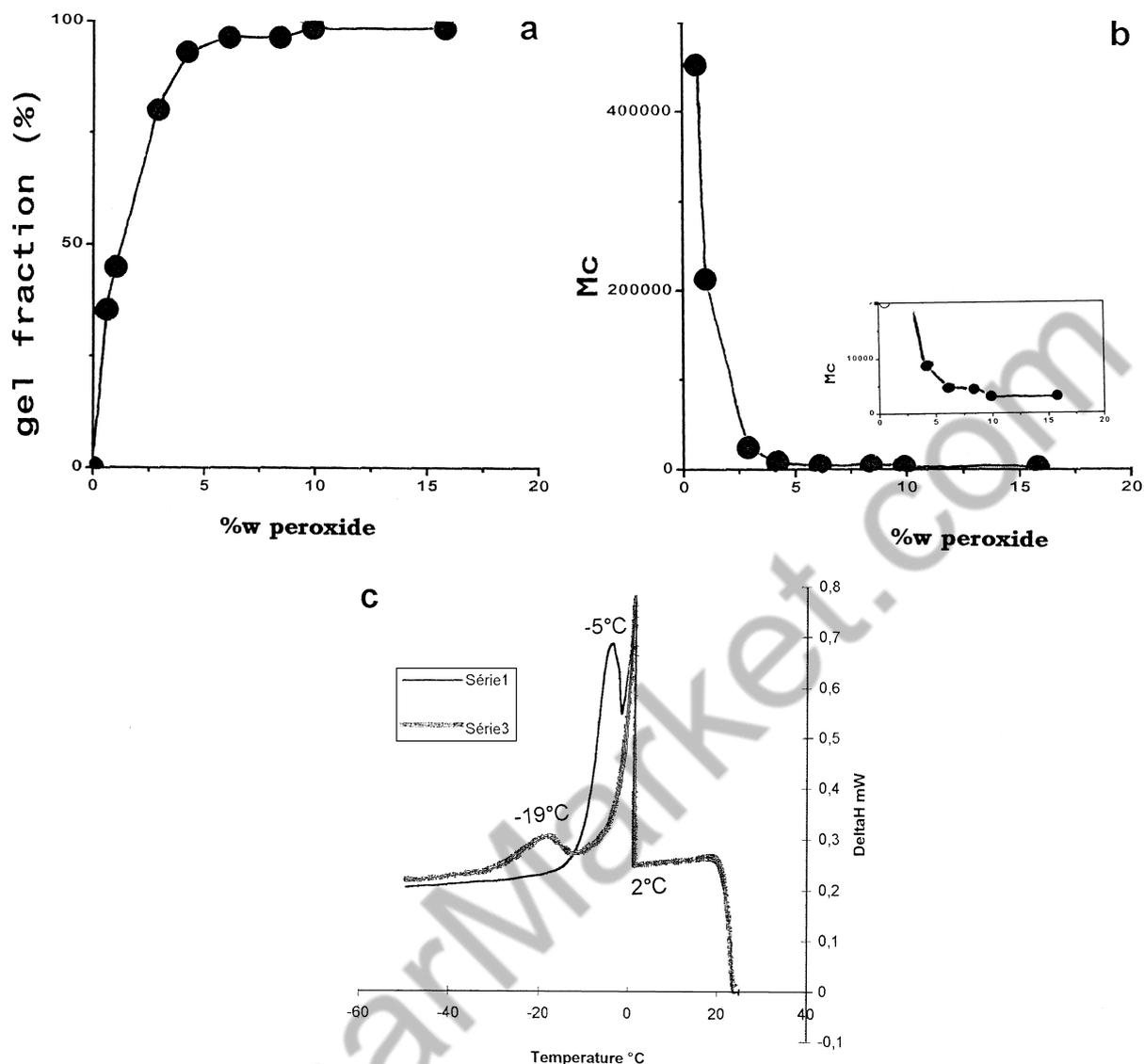
Fig. 1. Gel fraction (a), M_c (b) and cyclohexane freezing temperature (c) (series 1: 5%w peroxide, series 2: 10%w peroxide) changes upon peroxide (DCP) vulcanization of EPDM.

Some experiments were also performed in the absence of oxygen (photolysis experiments). For that, the EPDM film was placed in a borosilicate tube that was then flushed with nitrogen and sealed off.

For comparison, a few EPDM films were chemically crosslinked with dicumyl peroxide (DCP). DCP was introduced by dissolution of both EPDM and DCP in cyclohexane. The solvent was then evaporated under vacuum.

EPDM containing DCP were pressed between the plates of a heating press maintained at 145°C, 19 MPa. Residual DCP and its decomposition products were then removed by washing samples with acetone. Two series of samples were prepared, in the first case different contents of DCP were used with the same heating (curing) time (10 min), in the second case only one

content of DCP was used (4.2%w) but the heating time was varied from 0 to 60 min.

The gel fractions (G_F) were determined by weighing polymer samples before and after a soxlhet extraction in cyclohexane, typically carried out for 24 h with about two siphonings per min.

$$G_F = \frac{M_{insoluble}}{M_{initial}}$$

The Equilibrium Degrees of Swelling (DE_E) were measured by comparing weights of samples before (M_0) and after (M_s) swelling[1] according to the relationship

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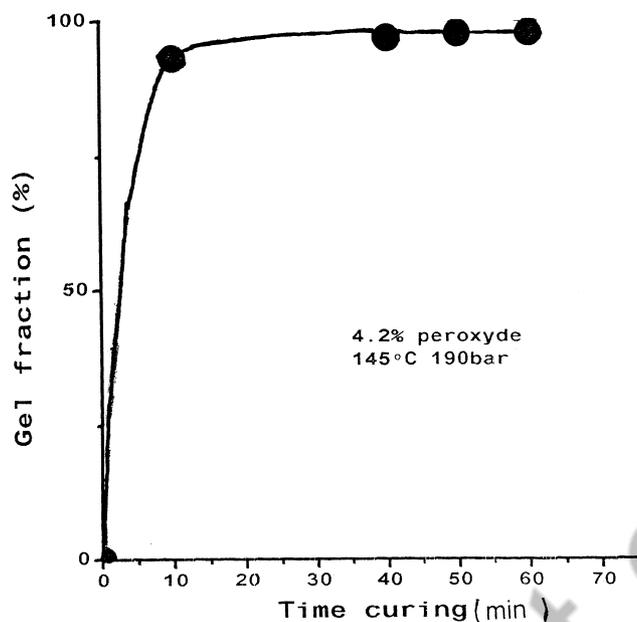[1] The swelling was performed by leaving samples in an excess of cyclohexane for 6 h to reach equilibrium.

Fig. 2. Influence of the curing time on the gel fraction changes on peroxide (DCP) vulcanization of EPDM.

$$DS_E = 1 + \frac{d_c}{d_s}\left[\frac{M_s}{M_0} - 1\right]$$

where d_s and d_c are the densities of cyclohexane and crosslinked EPDM, respectively.

DS_E values were converted into M_c (molecular weight between crosslinks) by using the Flory–Rehner equation [4]

$$M_c = \frac{d_c V_0\left(DS_E^{-1/3} - \frac{1}{2}DS_E^{-1}\right)}{\ln(1 - DS_E^{-1}) + DS_E^{-1} + \chi DS_E^{-2}}$$

with V_0, the molar volume of cyclohexane (107.7) and χ the interaction parameter EPDM/cyclohexane (0.32) [5].

The calorimetric method consisted in measuring the freezing point of cyclohexane (contained in swollen samples) by decreasing the temperature in a DSC instrument (METTLER DSC 30) typically 10°C per minute from 20 to −30°C. The freezing point decreases as the crosslinking level increases. This phenomenon, following Raoult's law, is described in detail in Refs [6,7].

The oxidation level in photo-aged samples was followed by FTIR spectroscopy (Nicolet Impact 400 spectrometer, Omnic Software). According to the mechanism of EPDM ageing formerly reported [8–11], the oxidation was measured at 1715 cm^{-1}, in a band corresponding to the formation of carbonyl functional groups (ketones, acids,...).

3. Results and discussion

3.1. EPDM vulcanization by peroxide

The aim of this part was both to validate the calorimetric technique by a systematic comparison with usual methods such as gel fraction and equilibrium swelling degree and to determine the order of magnitude of the crosslinking level for a further comparison with that occurring upon ageing.

3.1.1. Influence of DCP content

The variations of both gel fraction and M_C values with the DCP content are reported in Fig. 1(a) and (b). It is shown that, in these experimental conditions (100 μm film, 145°C, 19 MPa for 10 min) the degree of crosslinking is maximum for 7–9%w of DCP. In the same experimental conditions, a significant decrease of the freezing point of cyclohexane is observed for samples crosslinked with 1 and 10%w DCP (curve C). Values such as −5.2 and −19.4°C were measured respectively and have to be compared with +2.5°C, the value for the free solvent. However this analysis has to be considered as qualitative only as the value at the peak maximum is slightly dependent of the amount of solvent present in the polymer network [12]. The onset temperature[2] will be more significant but unfortunately cannot be determined with sufficient precision in this case. Nevertheless, one may expect that the evolution of crosslinking which

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[2] Extrapolated from tangent.

can be followed by this technique as 10%w of DCP can be considered as a maximum value according G_F and M_C measurements [see Fig. 1(a) and (b)].

3.1.2. Influence of curing time

The curve is shown on Fig. 2 for gel fraction analysis. The results of Fig. 2 show that, in our experimental conditions (4.2%w DCP, 145°C, 19 MPa), a basic network is completed after 10–15 min. This justifies the curing time of 10 min chosen for the study of the influence of DCP content.

3.1.3. EPDM vulcanization upon oxidation

The modifications of G_F, M_C and T_F upon exposure in the SEPAP chamber are reported on Fig. 3. From the

gel fraction and swelling degree changes, it appears that crosslinking occurs in the first stages of the irradiation. For longer exposure times, the values are changing in an opposite way and a maximum value for 30 h can be clearly observed in the case of G_F measurements [Fig. 3(a)], while a minimum value can be suggested for the same exposure time in the case of swelling measurements. This result indicated that chain scissions occurr upon photo-oxidation.

In photo-oxidation, chain scissions result from Norrish reactions of ketonic functional groups or from (scissions of alkoxy radicals formed by decomposition of EPDM peroxides resulting from the oxidation of the polypropylene [13–15].
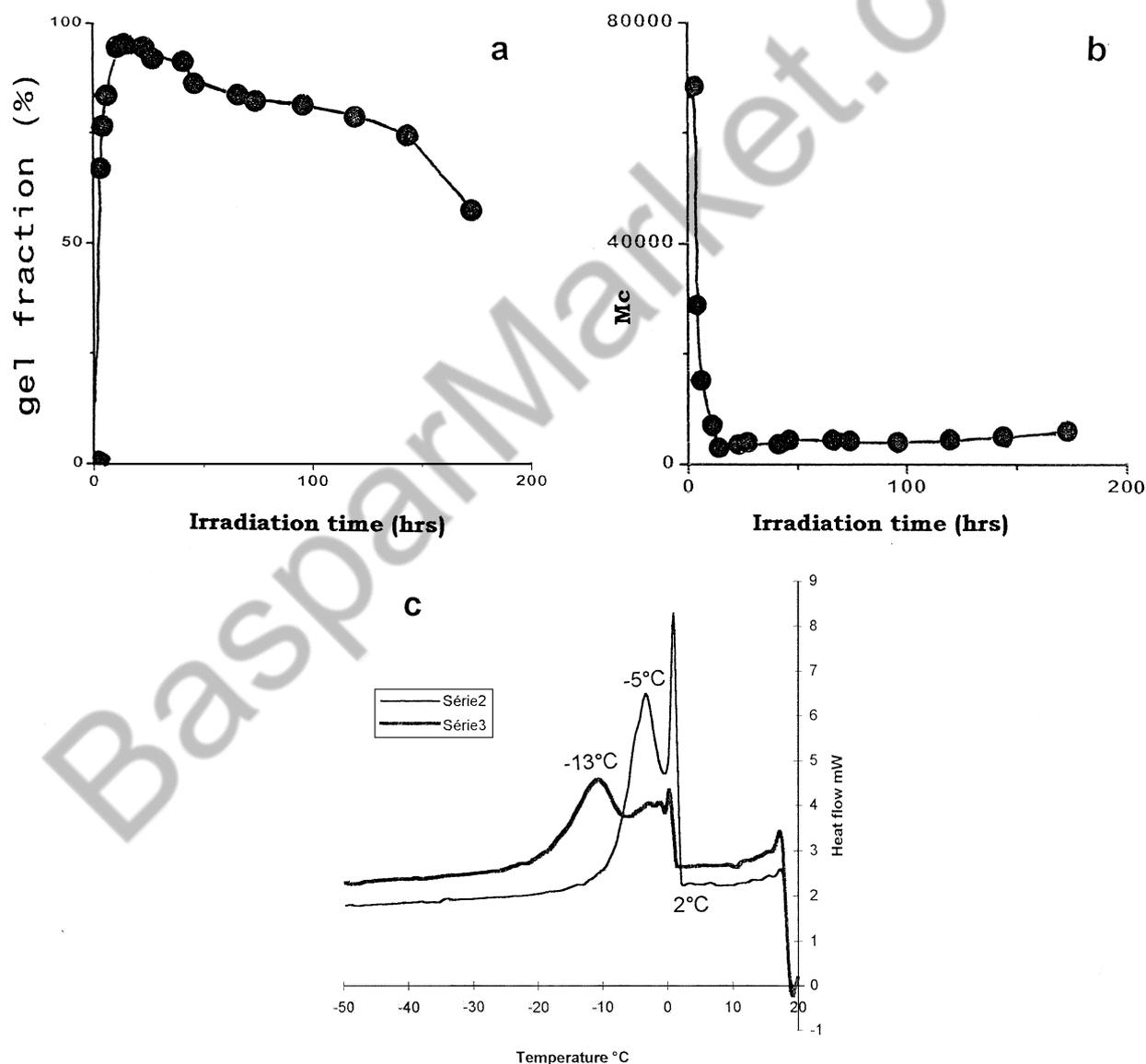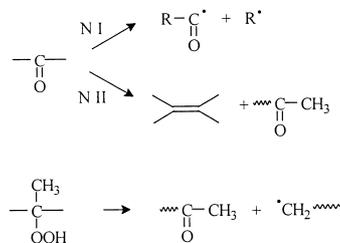

Fig. 3. Gel fraction (a), M_c (b) and cyclohexane freezing temperature (c) (series 2: 204 min, series 3: 293 min) changes in EPDM photo-oxidation at $\lambda \geq 300$ nm.

$$\begin{array}{c} \overset{|}{\underset{|}{-C-}} \\ \parallel \\ O \end{array} \quad \begin{array}{c} \overset{N\,I}{\nearrow} \quad R-\overset{\bullet}{C}\underset{\parallel}{-}O + R^{\bullet} \\ \\ \overset{N\,II}{\searrow} \quad \text{~~~}C= + \text{~~~}\overset{}{\underset{\parallel}{C}}-CH_3 \\ \qquad\qquad\qquad O \end{array}$$

$$\begin{array}{c} CH_3 \\ \overset{|}{-C-} \\ \overset{|}{OOH} \end{array} \longrightarrow \text{~~~}\overset{}{\underset{\parallel}{C}}-CH_3 + {}^{\bullet}CH_2\text{~~~}$$

DSC measurements are here again sensitive to the crosslinking process. Fig. 3(c) suggests that the EPDM sample is more crosslinked after 293 min than for 204 min but the measurement is not sensitive enough to detect, as for G_F and M_C analysis, the irradiation time from which chain scissions become predominant. The formation of oxidation products determined by FTIR at 1715 cm^{-1} is plotted on Fig. 4 together with G_F changes upon exposure at $\lambda > 300$ nm. The crosslinking process appears to be very fast comparatively with oxidation. This result suggests that recombination of radicals can precede the chain oxidation

$$RH \longrightarrow R^{\bullet} \begin{array}{c} \overset{x\,2}{\nearrow} \quad R-R \\ \\ \underset{O_2}{\searrow} \quad ROO^{\bullet} \longrightarrow ROOH \longrightarrow \begin{array}{l}\text{carbonylated and}\\\text{hydroxylated products}\end{array} \end{array}$$
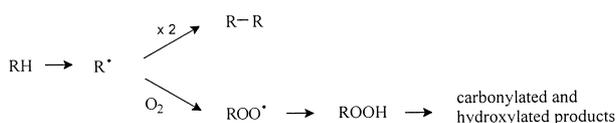
Fig. 4 also shows that chain scissions (corresponding to the maximum on the G_F curve) start immediately after the formation of the first carbonylated products, which confirms the hypothesis that chain scissions are correlated with oxidation processes.

When oxygen is removed no carbonyl products are detected but conversely a small increase in G_F is
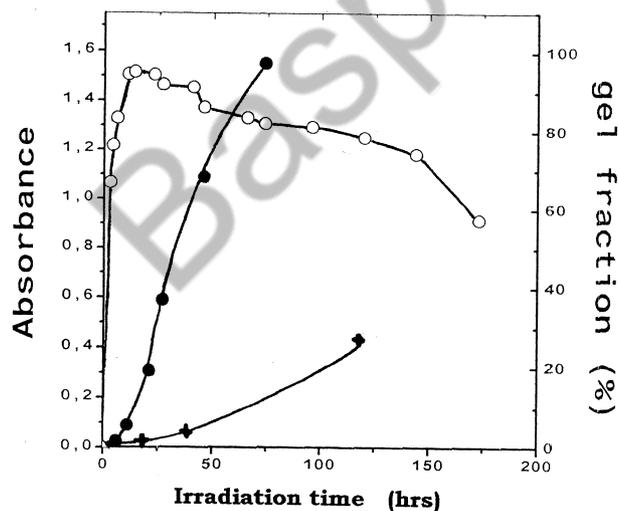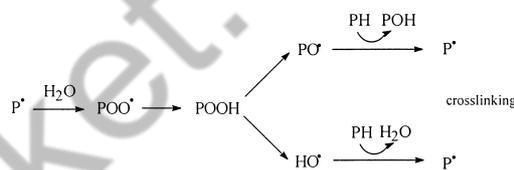

Fig. 4. Evolution of gel fraction (○) and carbonyl index (●) values in photo-oxidation at $\lambda \geq 300$ nm and effect of the absence of oxygen on G_F values (+).

observed. This suggests that the radicals needed for the crosslinking process are formed by UV irradiation of EPDM.

In such a polymer, which cannot absorb UV light of wavelengths longer than 300 nm, the initiation of oxidation is usually attributed to chromophoric impurities such as residual hydroperoxides resulting from the polymer processing [16]. Our results suggest that crosslinking irradiation in the absence of oxygen could result from the photolysis of the chromophoric impurities.

$$ROOH \xrightarrow[hv]{PH} P^{\bullet} \rightarrow \text{crosslinking}$$
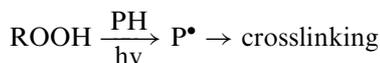
When oxygen is present, a chain reaction occurs that is initiated by decomposition of hydroperoxides and the crosslinking process is accelerated as show on Fig. 4.

$$P^{\bullet} \xrightarrow{H_2O} POO^{\bullet} \longrightarrow POOH \begin{array}{c} \overset{PH\ POH}{\nearrow} PO^{\bullet} \longrightarrow P^{\bullet} \\ \\ \underset{PH\ H_2O}{\searrow} HO^{\bullet} \longrightarrow P^{\bullet} \end{array} \quad \text{crosslinking}$$

In the same way, the higher the crosslinking level, the smaller the amount of oxygen which penetrates into thepolymer matrix: this results in a decrease of the oxidation rate, that can even reach zero, as reported in several papers concerning various dienic elastomers such as EPDM, [10] BR [17], SBR [18] or NBR [19]. Then the crosslinking process can be considered as protecting these polymers from an extended oxidation. As a result of the intrinsic reactivity of this polymer, oxidation starts very fast, but is limited only to the outer layers of the sample.

It can be concluded from our experiments that crosslinking reactions occur at the very beginning of the oxidation of dienic elastomers and can be revealed by suitable methods involving gel, swelling and freezing temperature (DSC) reasurements. Among these, DSC has the advantage of being very fast and easy to perform but unfortunately it not sensitive enough to detect small changes in the polymer network such as chain breaking following the oxidation process.

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