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Dielectric and mechanical spectroscopies for the study of thermal and radiochemical ageing of polymers

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Abstract

Thermal and/or radiochemical ageing of polymer has been extensively studied by thermal, FTIR, UV or static mechanical analysis. The aim of this work was to make a parallel study of dynamic mechanical and dielectrical properties of EPDM elastomers, and to present the possibility of using such methods for studying ageing. These analyses reflect not only the molecular dynamic, but also through dielectric spectroscopy the chemical evolution due to modification of dipolar species. Changes in the main relaxation peak, both in mechanical and dielectrical spectra, allow the degradation to be quantified.

1. Introduction

The thermal and/or radiochemical ageing tests reveal the existence of competition between crosslinking and chain scissions and between oxidative and non oxidative reactions. This is characteristic of an oxygen-diffusion-controlled process which depends on oxygen permeability of polymer, dose rate and sample thickness [1–8]. In some cases, other processes like plasticizer migration or hydrogen chloride release can be revealed [9–11]. On the other hand, dielectric and viscoelastic spectroscopies have been widely used to understand the molecular dynamics of polymer chains or networks in relation to the chemical structures or morphologies [12,13]. Our investigations were mainly focused on dynamic mechanical and dielectric behaviour of filled and crosslinked rubber compounds, with the aim to analyse the ageing of such polymers and establish relationship with more classical techniques. As some examples of these possibilities, this work presents the results of the ageing characterization of EPDM elastomers, which are widely used as electrical insulators in electrotechnic industries.

2. Experimental

2.1. Materials and processing of samples

A neat polymer and two industrial compounds were examined. The pure polymer (sample A) was an uncrosslinked, unfilled and unstabilized ethylene propylene hexadiene 1-4 terpolymer supplied by Dupont de Nemours under the trade name Nordel 2722. From this polymer, an industrial rubber (sample B) was manufactured and supplied by Pirelli under the trade name EPR 1321. This material was crosslinked, filled and stabilized. A third sample type

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Table 1
Compositions of materials and samples

Ingredients	Sample types		
	A	B	C
Nordel 2722	X	X	X
Fillers (carbon black, kaolin...)	O	X	O
Vulcanizing agents	O	X	X
Stabilisers	O	X	O
Processing oils	O	X	X

(sample C) was crosslinked but unfilled and unstabilized.

The compositions of these differents samples are summarized in Table 1.

Rubber samples were processed by compression molding in the form of sheets of 2 mm and films of 100 μm thickness.

2.2. Thermal exposure

For all experiments exposure to thermal ageing was carried out in ventilated ovens regulated at ± 1°C in the temperature range (90–135°C) for crosslinked samples (B and C).

The thermal ageing of sample A was conducted only at 180°C.

2.3. Radiochemical exposure

Irradiations with a ^{60}Co source were carried out in air, in nitrogen (non oxidative conditions) and at 0.5 and 1 atm. oxygen partial pressures. Irradiations were conducted at 50 and 90°C in air, and at 50°C in nitrogen and oxygen. Integrated doses were between 5 and 100 kGy with dose rates between 10 to 2500 Gy/h.

2.4. Dynamic Mechanical Analysis (DMA)

Viscoelastic measurements of both storage shear modulus (G') and mechanical loss tangent ($\tan \delta$) were performed on a TA Instruments DMA 983 viscoelasticimeter. Experiments were carried out in a combined shear-flexion mode over a temperature range of − 150 to 100°C with a programmed heating rate of 3°C/min.

All experiments were performed on 30 × 12 mm rectangular and 2 mm thick rods at the frequency of 1 Hz. The general procedure was to cool the sample to − 150°C, tighten and hold it for 10 min at this temperature, and then record measurements during warming up.

2.5. Dielectric measurements

A DEA 2970 from TA Instruments with parallel plate sensors was used to measure both permittivity (ϵ') and dielectric $\tan \delta$. The procedure was the same as for dynamic mechanical measurements, but using 100 μm thick films with a 2°C/min heating rate under nitrogen flow. Since this method allows the use of a wide range of frequencies, it was possible to record measurements at fourteen frequencies between 1 Hz and 100 kHz.

In complement to these experiments, thermal analysis, FTIR spectroscopy and swelling tests of these materials were performed to complete our results.

3. Results

3.1. Unaged neat polymer and compounds

Viscoelastic properties (G' and $\tan \delta$) for ethylene propylene rubbers (EPR) are illustrated in Fig. 1 and Fig. 2. Three phenomena can be observed: (1) a subglass transition at − 120°C (β relaxation); (2) the

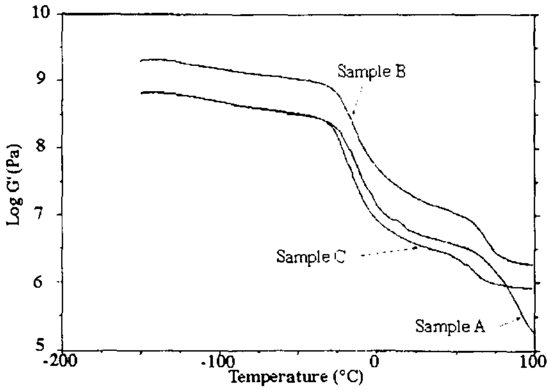

Fig. 1. Storage modulus versus temperature of ethylene-propylene-hexadiene-1,4 based rubbers. Frequency 1 Hz; heating rate 3°C min^{-1}.

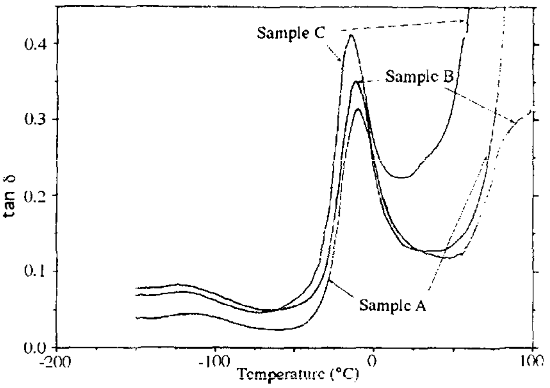

Fig. 2. Mechanical loss tangent versus temperature of ethylene-propylene-hexadiene-1,4 based rubbers.

glass rubber transition at −15°C (α relaxation) and (3) melting of crystalline entities around 50°C.

The main difference between the neat polymers and vulcanized forms is the level of rubbery state above 50°C due to crosslinks. Another important fact is the increase of the storage modulus over the full temperature range, due to the mechanical reinforcement of fillers (sample B).

Dielectric analysis (Fig. 3) in the same temperature range is characteristic of insulating materials, the dielectric losses are below 5×10^{-3} in accordance with the low polarity of the polymer chain. EPDM (sample A) gave a flat spectrum within the precision limit of our equipment. We can notice the increase of α relaxation for unstabilized sample C probably due to oxidative reaction during the processing. Introduction of fillers gives some additional conduction phenomena which are superimposed on the dipolar relaxation especially at high temperature.

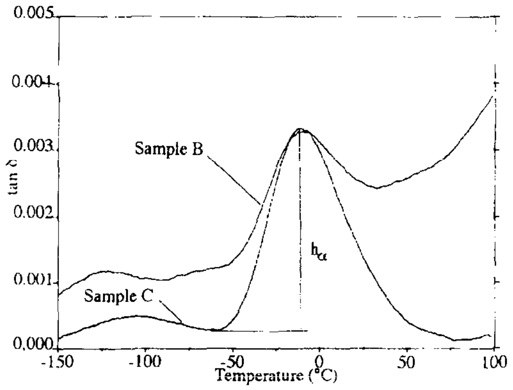

Fig. 3. Dielectric losses versus temperature of EPDM based rubbers. Frequency 1000 Hz; heating rate 2°C min^{-1}.

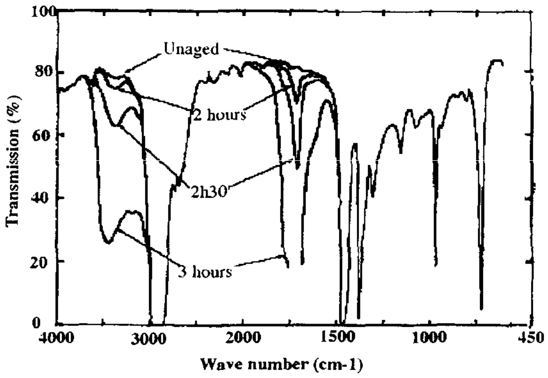

Fig. 4. FTIR spectra of sample A films before and after thermal exposure (180°C).

3.2. Thermally aged samples

Examples of IR spectra of pure polymer before and after thermal exposure (180°C) are shown in Fig. 4. As expected for hydrocarbonated polymers, bands appear for the -OH stretching (3300 cm^{-1}) and the $>C=O$ stretching (1720 cm^{-1}) after an induction period corresponding approximately to two hours at 180°C [9].

Dielectric measurements were performed on the same samples. The results are illustrated in Fig. 5. A dielectric relaxation appears between −15 and

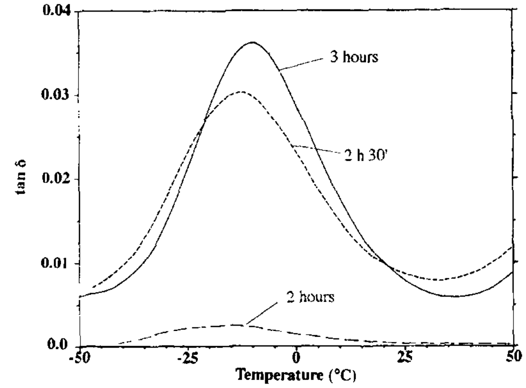

Fig. 5. Dielectric tan δ versus temperature for pure polymer thermally aged at 180°C (sample A). Frequency 1000 Hz; heating rate 2°C min^{-1}.

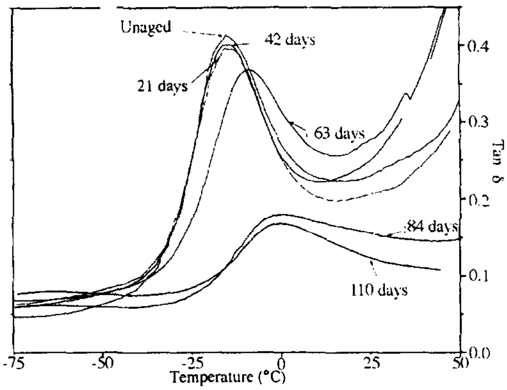

Fig. 6. Effects of thermal ageing at 135°C on mechanical tan δ spectra for unfilled material (sample C). Frequency 1 Hz; heating rate 3°C min^{-1}.

– 10°C (1000 Hz), and increases in height and width with the exposure time. This main relaxation has an activation energy of about 170 ± 10 kJ.mol^{-1}.

The influence of thermal exposure is illustrated in Fig. 6 and Fig. 7 for unfilled material (sample C), and in Fig. 8 and Fig. 9 for industrial rubber (sample B). Both mechanical and dielectrical properties are modified. For unfilled samples, two important changes occur during ageing in mechanical damping, namely a decrease of the α relaxation peak height with ageing after an induction period (~ 50 days at 135°C), and a shift of all the tan δ spectra to higher temperatures. It can be seen in dielectric loss (tan δ) spectra that after the same induction period the α relaxation peak height increases.

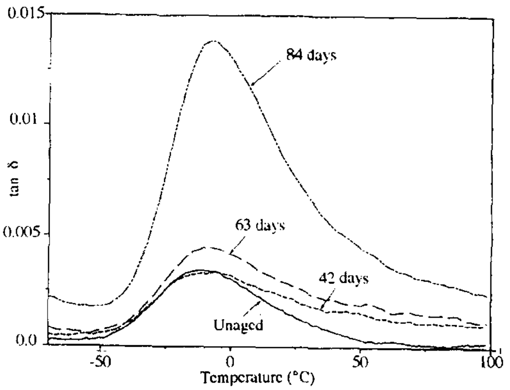

Fig. 7. Effects of thermal ageing at 135°C on dielectric tan δ for unfilled material (sample C). Frequency 1000 Hz; heating rate 2°C min^{-1}.

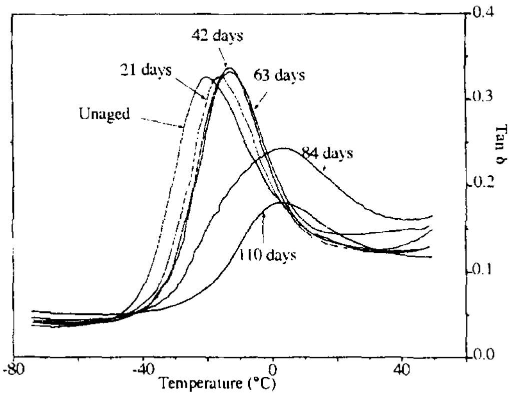

Fig. 8. Effects of thermal ageing at 135°C on mechanical tan δ spectra for industrial rubber (sample B). Frequency 1 Hz; heating rate 3°C min^{-1}.

For industrial rubber (filled and stabilized), the same behaviour is observed. However for mechanical and dielectrical spectra, it can be seen that the induction period is more prolonged (~ 63 days at 135°C), and during this period the α mechanical relaxation is shifted to higher temperatures. In addition, for the same ageing time, these effects are less important than for the unfilled material.

Results have also been reported for two other ageing temperatures, 110 and 125°C. As expected, the lower the ageing temperature, the longer it takes for ageing effect to appear. In order to characterize these effects, we have chosen to measure the dielectric α relaxation peak height (h_α shown in Fig. 3) for sample B. The results are presented in Fig. 10.

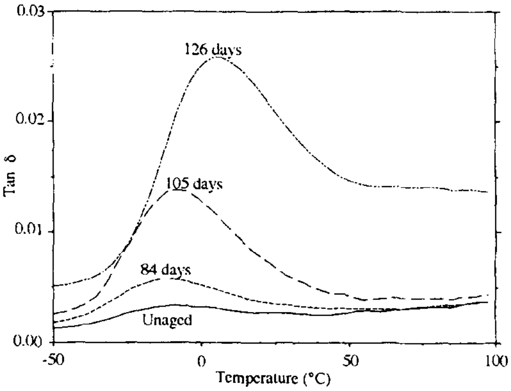

Fig. 9. Effects of thermal ageing at 135°C on dielectric tan δ for industrial rubber (sample B). Frequency 1000 Hz; heating rate 2°C min^{-1}.

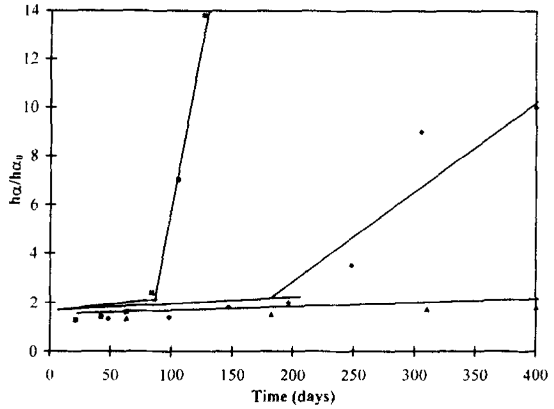

Fig. 10. Dependence of dielectric α relaxation peak on ageing time for various temperatures: Sample B (1000 Hz).

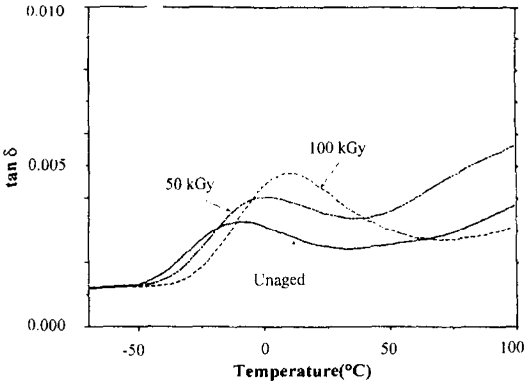

Fig. 12. Effects of radiochemical ageing at 1 bar O_2 pressure (100 Gy.h^{-1}) on dielectric tan δ for industrial rubber (sample B). Frequency 1000 Hz; heating rate 2°C min^{-1}.

3.3. Irradiated samples

First of all, it must be pointed out that (1) for every radiochemical ageing condition, samples B and C show the same behaviour through mechanical and dielectrical spectroscopies, and (2) significant effects on mechanical and dielectrical properties are obvious only for doses above 50 kGy.

Concerning the influence of oxidative conditions, no significant difference could be observed as a function of oxygen partial pressure (Fig. 11) on mechanical spectra. For every oxygen pressure condition, α relaxation peak is shifted to higher temperature over ~ 8°C. The same behaviour is observed on dielectrical spectra, however sensibility to dose is visible as soon as 50 kGy (Fig. 12) on sample irradiated under 1 atm oxygen pressure.

Concerning irradiation at elevated temperature (90°C), α mechanical relaxation shift is detectable, even for very low doses, i.e. 10 kGy (Fig. 13). Besides, no more evolution could be noted on dielectrical spectra regarding irradiation at low temperature (50°C). In order to separate radiochemical effects from thermal ones, we present in Fig. 14 and Fig. 15 superimposed spectra of thermally aged and radiochemically aged samples for the same temperature and approximately same duration. On thick materials, i.e. mechanical spectroscopy samples, γ irradiation seems to accelerate thermal ageing effects, as indicated by the shift of α relaxation to higher temperatures. However, contrarily to thermally aged

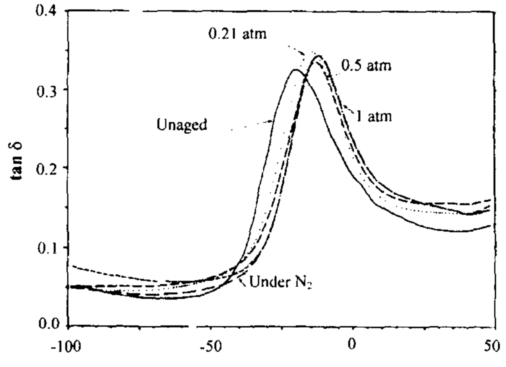

Fig. 11. Effect of O_2 pressure and irradiation (100 kGy at 100 Gy.h^{-1}) on mechanical spectra of industrial rubber (sample B). Frequency 1 Hz; heating rate 3°C min^{-1}.

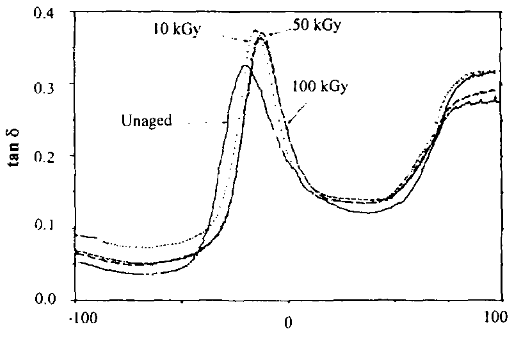

Fig. 13. Effects of radiochemical ageing at 90°C (100 Gy.h^{-1}) on mechanical tan δ for industrial rubber (sample B). Frequency 1 Hz; heating rate 3°C min^{-1}.

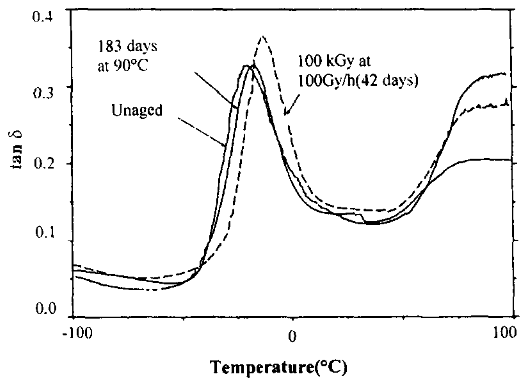

Fig. 14. Effects of thermal and radiochemical ageing at 90°C on mechanical tan δ for industrial rubber (sample B). Frequency 1 Hz; heating rate 3°C min^{-1}.

samples behaviour, there is no decrease of peak height, but an increase.

4. Discussion

4.1. Thermal ageing

As demonstrated by Figs. 5, 7 and 9, ageing of ethylene-propylene- hexadiene terpolymer is obviously a gradual oxidation of the macromolecular main chain. Some authors have investigated these processes with precision [8,14]. The originality of our work is to show such effects by a non-conventional technique such as dielectrical measurement. In fact, this method allows the detection of molecular dynamics through dipolar labelling [12]. In the particular case of non polar insulating polymers, such as polyethylene or polypropylene, the very low value of tan δ is difficult to measure with conventional system, except for slightly oxidized polymers [15,16]. This was the case for our aged material. The gradual appearance of oxidized functions induces an increase of α dielectric relaxation [17], in relation with the number and the mobility of dipoles.

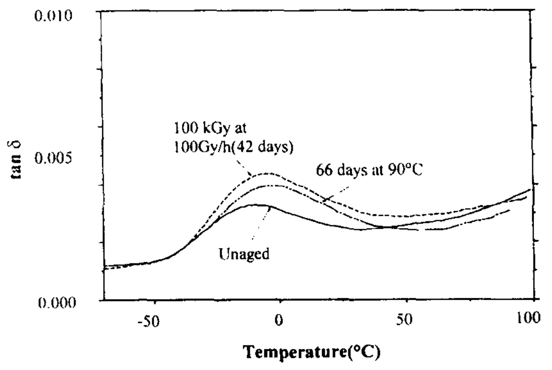

Fig. 15. Effects of thermal and radiochemical ageing at 90°C on dielectrical tan δ for industrial rubber (sample B). Frequency 1000 Hz; heating rate 2°C min^{-1}.

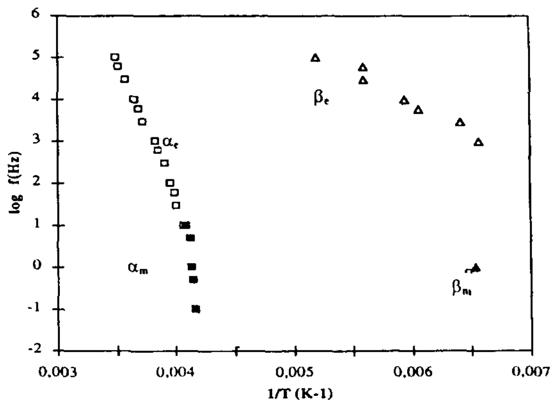

Fig. 16. Relaxation map of industrial rubber (sample B).

In the case of crosslinked materials (samples B and C), the vulcanizing system and particularly the processing of samples, induce oxidation which allows the detection of dielectric relaxation, even on unaged materials. As in the case of pure polymer, this relaxation increases with ageing.

Results obtained from dynamic mechanical analysis allow us to complete this interpretation. First, it has to be pointed out that, in our case, α mechanical and α dielectrical relaxations have the same origin, i.e. cooperative molecular motions of the main chain. The relaxation map (Fig. 16) of the industrial rubber (sample B) shows the reliability of these data. According to Fig. 9, few changes are noticed in mechanical relaxation at low ageing times. Similarly, after the induction period which is in accordance with the result of Gueguen [18] by thermogravimetric analysis, the dielectric relaxation increases (Fig. 10). According to the decrease of molecular mobility observed in the mechanical spectra, the increase of dielectric losses is in accordance with an oxidation process. This assumption is confirmed by the increase of oxidation bands in the IR spectra and relationship with α relaxation (Fig. 17).

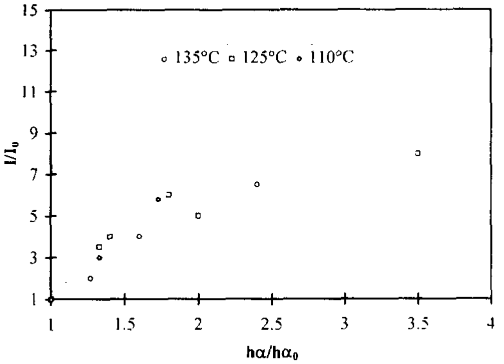

Fig. 17. Correlation between α dielectric relaxation and oxydation (FTIR absorption at 1730 cm^{-1}).

It is noteworthy that for long time in accelerated ageing (more than 63 d at 135°C, for example), it is more difficult to compare dynamic mechanical and dielectrical results. It can be assumed that the 100 μm thick films (used for dielectrical measurements) are submitted to an aerobic degradation oxygen can diffuse through the sample. On the contrary, during ageing of thick samples (used in mechanical measurements), oxygen is consumed in the upper layers of the sample. In the bulk, crosslinking due to anaerobic degradation occurred. Crosslinks decrease molecular mobility, and then decrease α mechanical process and shift it to higher temperature. The competition between crosslinking and oxidation is related to the diffusion controlled inhomogeneous oxidation [19]. But the whole behaviour of thick samples, under mechanical characterization, is essentially the bulk one.

4.2. Radiochemical ageing

It is manifest that, within the explored temperature and dose ranges, and at the applied dose rate, radiochemical ageing effects are less important than thermal ageing ones. This is essentially due to integrated doses examined in this study, which are too low to give significant changes on dynamic properties [8,20–22]. However Figs. 14 and 15 show a real additional effect of γ irradiation on EPDM compounds, probably a preponderance of irradiation on temperature. According to thermal ageing, the shift of α mechanical relaxation to higher temperatures (Figs. 11 and 13) can be related to crosslinking. On the other hand, the increase of dielectric losses, especially on α relaxation (Fig. 12), is in accordance with an oxidation process, probably oxidizing scissions. But FTIR spectra show that this oxidation process is weak, even for a higher dose (100 kGy).

In our case, the ageing process seems to be typically a competition between chain scissions and crosslinking. It is noteworthy that such a competition, due to the limited diffusion of oxygen, always exists under thermal and radiochemical stresses for elastomers [8,22,23]. According to previous discussion on thermal ageing, dynamic mechanical and dielectrical results are difficult to compare because of different extents of the diffusion of oxygen. But regarding mechanical spectra (Fig. 14), it can be assumed that the same ageing process occurred under thermal and radiochemical stresses, and there is probably oxidizing scissions and crosslinking profiles in the sample thickness. As radiochemical ageing influences dynamic mechanical and dielectric properties, a microscopic approach of such techniques [24,25] could be more appropriate.

5. Conclusion

Thermal and radiochemical ageing of elastomers used as insulating material in cable industries has been studied by mechanical and dielectrical spectrometries.

It has been observed that both dynamic and dielectric properties are influenced by thermal and/or radiochemical degradation. Experimental results allow us to draw the following conclusions for EPDM materials: (1) thermal ageing is characterized by an induction period followed by a thermoxidative process; (2) in spite of weak effects in our dose and dose rate ranges, radiochemical ageing is characterized by competition between chain scissions and crosslinking; (3) dynamic mechanical properties seem to be more sensitive to long term ageing effects, i.e. crosslinking for thick materials and (4) dielectric loss is a very convenient method for detecting the early steps of degradation, mainly oxidation.

Acknowledgements

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