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Role of temperature during ageing under gamma irradiation of filled EPDM – Consequences on mechanical properties

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Abstract:

The consequences of the combined effect of gamma irradiation and temperature on the mechanical properties of an EPDM, unfilled or filled with ATH or silica fillers are studied. All the degradation processes occurring during irradiation at 25°C are largely accelerated at 80°C. This is mainly due to the thermal activation of the chemical reactions involved during irradiation. This conclusion is true whether the materials are filled or unfilled and whatever the filler size (micronic for ATH and nanoscopic for silica). Moreover, the specific effect of the filler on the degradation mechanisms are also thermally activated: the acceleration of the degradation by the ATH fillers presence, already reported for irradiation at 25°C, seems also effective at 80°C. And in the case of silica filled EPDM, the creation of strong filler-matrix bonds is also thermally activated and therefore enables this material to keep its integrity at high irradiation dose.

Keywords: Rubber – Irradiation – Mechanical properties

INTRODUCTION

Rubber composites are sometimes used in environments, for instance, in nuclear power plants, where they may be exposed to high-energy radiation and heat. It is well known that irradiation and heat, depending on their level, can lead to the degradation of these materials and therefore shorten their lifetime. However the effect of the combination of both on the degradation of elastomers has only been the topic of very few studies, which have, for instance, measured the evolution during ageing of ultimate elongation [1, 2, 3], of the dynamic viscosity [4], or of the concentration in oxidation products [5]. All these works evidenced that the rate of increase in carbonyl concentration and the rate of decrease in ultimate elongation of ethylene-propylene elastomer (EPR) submitted to the combination of heat and radiation are much higher than the sum of the rates obtained for each ageing condition.

This synergistic effect can be generally attributed to different factors. First, the chemical reactions involved in polymer degradation are thermally activated. Particularly, a temperature increase promotes the decomposition of hydroperoxides created by irradiation, which enables the formation of additional radicals. Taking into account this decomposition, Colin et al. [5] have developed a kinetic model to predict the lifetime of unstabilized and unfilled polyethylene exposed to gamma-irradiation and temperature in air, which is in good agreement with the experimental results collected in the literature. But others approaches have been used as time-temperature superposition to take into account the combined effect of temperature and irradiation [1, 7]

Besides, in the case of semi-crystalline material, the dependence on temperature of their crystallinity must also be taken into account to explain this synergy. Due to the weak permeability of oxygen in crystallites [7, 8], such materials, when they are irradiated above

their melting temperature, are more likely to be sensitive to radiations than when they are irradiated in their semi-crystalline state [9, 10, 11]

For instance, a study of the irradiation of an EPDM at room temperature and at 80°C [12] has highlighted substantial differences between ageing conditions, because 80°C is above the melting temperature of a substantial fraction of small crystallites.

Moreover, a return below the melting temperature after irradiation above the melting temperature can promote a reorganization of the semi-crystalline microstructure of the material and explain the preservation of its mechanical properties [13]. The crystallization of the chain cut during ageing can even lead to supplementary crystallization called chemi-crystallization, which can even improve the material mechanical properties.

Thus, many complex phenomena are involved in an ageing combining heat and irradiation of semi-crystalline polymers. Moreover these phenomena are very dependent on the initial studied material, in particular its crystallinity, its melting temperature, and its chemical nature... To our knowledge, literature is limited on this topic, especially about the consequences of ageing on the mechanical properties. Thus the purpose of this paper is to study the consequences of the combined effect of irradiation and temperature on the mechanical properties of an unfilled EPDM. As the studied semi-crystalline EPDM (with 10-15% of crystallinity ratio) has a large melting temperature domain, between 20°C and 60°C, the chosen irradiation temperature is 80°C i.e. above the melting temperature of its crystallites. The consequences of this ageing process will be compared to those obtained after irradiation at 25°C [14, 15]. Moreover for most of EPDM applications, fillers are introduced to improve their properties. In previous studies [7, 14, 16, 17], EPDM rubbers with and without fillers (ATH or silica) have been aged by gamma irradiation at room temperature under oxygen atmosphere. It was found that even if the polymer phase is degraded by the

same degradation mechanisms, the filler presence induces particular phenomena. In the case of silica filled EPDM, an acceleration of the degradation kinetic has been evidenced as well as a modification of the silica surface, and crosslinking reactions between filler and matrix at high irradiation dose. It was also noticed an acceleration of the degradation process in ATH filled EPDM by the presence of ATH. This leads to a peculiar evolution of the mechanical properties of this material compared to the one found with unfilled EPDM: a more rapid decrease in the elastic modulus and an increase in the strain at break attributed to filler-matrix decohesion mechanisms promoted by the polymer degradation in the close vicinity of the filler surface. In this paper, the same materials, silica filled EPDM and ATH filled EPDM, are studied after ageing under gamma irradiation at 80°C in oxygen atmosphere. In addition, for a better comprehension of the degradation mechanisms, a thermal-oxidation campaign at 80°C is also performed. The consequences of the three ageing methods - thermal ageing at 80°C, irradiation at 25°C and irradiation at 80°C - on the mechanical properties - are then compared.

EXPERIMENTAL

Materials

The EPDM elastomer (Nordel IP NDR 3722 P from Dow Chemical Company) is made of 70% ethylene, 29.5% propylene and 0.5% ENB (Ethyl Norbonene) and the crosslinking agent is the dicumyl peroxide (Perkadox BC-FF from Akzo Nobel). EPDM is reinforced with ATH [16] (Apyral 40 CD from NABALTEC) or silica [17] (ULTRASIL VN3 from DEGUSSA). The filler ratio in the ATH filled EPDM studied is equal to 150 phr (150 g per 100 g of EPDM, this corresponds to a weight fraction of 60%, and a volume fraction of 35%) and the filler ratio in silica filled EPDM is equal to 50 phr (i.e. 33 wt% and of 17 vol%). The different

formulations are given in Table 1. The samples are processed as follows: the matrix is introduced in the internal mixer and mixed for 2 minutes, then the fillers are introduced. After 5 minutes of mixing, peroxide is added: the mixing is then performed for 10 min, at low temperature (80°C). Then a mixing is performed in an external mixer (cylinders) for 10 min still at 80°C. Then, the compound is pressed as 1-mm-thick films, at 170 °C to promote crosslinking reaction. The curing time (t_{98} at 170°C) is previously estimated from torque measurement performed with a MOSANTO analyser; it is the time needed to obtain 98% of the maximum torque ; it is chosen equal to 10 min for unfilled EPDM and ATH filled EPDM, and to 5 minutes for silica filled EPDM. In the previous study [17], it has been shown that the polymer phase of this composite is slightly less crosslinked than the unfilled material.

Ageing conditions

E-CR, E-ATHU and E-SiU samples (for unfilled EPDM, EPDM filled with ATH and silica respectively) are exposed to γ -radiation of a ^{60}Co source at a dose rate of 1 kGy/h in an oxygen atmosphere:

- At room temperature (the water temperature of the pool was around 18°C) for doses 50, 165, 300, 510 kGy. At this temperature, these materials are semi-crystalline with a cristallinity ratio of ca. 11% [14, 16, 17].
- At 80°C for doses 50, 165 kGy and 300 kGy. At this temperature, the materials are above their melting temperature; therefore, they are totally amorphous. At 300 kGy, E-CR and E-150ATHU samples was totally degraded. Conversely, E-SiU materials could be characterized. But unfortunately, theses samples were polluted by the other degraded materials. That is why, the characterization above 165kGy for all samples has not be possible..

For comparison, all the samples have been also thermally aged at 80°C in ventilated oven during 50h, 165h and 300h.

Afterwards, all samples were stored under vacuum at about 22°C. The samples will be named hereafter E-CR-YYYY-XXXX, E-SiU-YYYY-XXXX and E-ATHU-YYYY-XXXX; YYYY represents the ageing conditions: IR25 for irradiation at 25°C, IR80 for irradiation at 80°C and T80 for thermal ageing at 80°C, XXXX is the irradiation dose or the ageing time.

IR spectroscopy

Analyses by IR spectroscopy are performed in order to evaluate the oxidation of the materials. Firstly, changes in carbonyl concentration were followed by a Thermo Nicolet Nexus FT-IR spectrophotometer with the technique Attenuated Total Reflectance (ATR) accessory using 32 scans and a resolution of 4 cm⁻¹. IR spectroscopy in the transmission mode could not be used because the samples are absorbing. Secondly, oxidation (carbonyl) profiles were deduced from IR-microspectroscopy using a Continuum microscope coupled to a Nexus Nicolet optical bench (32 scans, resolution of 4 cm⁻¹). A slice of sample, of about 40 µm, was cut by cryo-microtomy in the thickness direction. Then IR spectra were measured on this slice every 50 µm to have an oxidation profile along the sample thickness. These analysis were conducted in CNEP - Centre National d'Evaluation de Photoprotection – Clermont Ferrand (France).

Swelling in xylene

Swelling measurement is a useful technique to characterize the network degradation. In the case of unfilled rubber, the swelling restriction is due to crosslinks connecting the polymer chains, which avoid their extension and their diffusion. Because of the filler-rubber interactions, the addition of fillers is equivalent to the introduction of additional crosslinks, which perturb the polymer swelling. Samples with an initial mass M_i are introduced in xylene

at room temperature for 8 days to achieve the swelling equilibrium, and then the materials with a swelled mass M_s are dried under vacuum at 60°C during 1 day and finally weighted to obtain the dried mass M_d . Note that it was checked that uncrosslinked EPDM is totally soluble in xylene at room temperature, which means that the crystallites are also soluble in xylene. In the case of the composites, TGA (TGA F3 apparatus from Netzch) enables to estimate the filler weight ratio ε_i in the initial sample and the filler weight ratio ε_d in the dried sample after swelling. Therefore, the swelling ratio Q and the polymer soluble fraction F_p (%) can be evaluated from the following relations:

$$Q = 1 + \frac{\rho_{polymer}}{\rho_{xylene}} \frac{M_s - M_d}{M_d (1 - \varepsilon_d)} \quad (1)$$

$$F_p = \frac{(1 - \varepsilon_i)M_i - (1 - \varepsilon_d)M_d}{(1 - \varepsilon_i)M_i} \quad (2)$$

For E-ATHU samples, for the irradiation doses tested, ε_d and ε_i are found equal, suggesting that the sol fractions do not contain fillers. For E-SiU materials, at low dose, given the low sol fraction measured for this material, the difference found between ε_d and ε_i is within the experimental uncertainties. However, at high irradiation dose, actually for total sol fractions above 20%, it is found that ε_d is clearly lower than ε_i , meaning that the sol fractions contain a significant amount of fillers.

Extensive use has been made of the kinetic theory of rubber elasticity and the Flory-Rhener network theory of swelling to estimate the degree of crosslinking in crosslinked rubbers. The success of these techniques with unfilled elastomers makes highly desirable their extension to the technologically important filler-reinforced rubbers. Unfortunately, the introduction of rigid filler particles into the network leads to some serious theoretical and practical complications. The most basic of these is the inability of the network to undergo deformations

which are affine with the sample dimensions. For this reason, we did not use swelling measurements to calculate crosslink densities.

Tensile tests

Tensile tests are performed on an MTS device equipped with a temperature controlled chamber. Experiments are conducted at 80°C with a true strain rate 0.01 s⁻¹. 80°C is above the materials melting temperature. An image processing acquisition system (Apollor VideoTraction System) is used to obtain the true stress – true strain curve. The samples are dumbbell-shaped with dimensions 20 x 4 x 1 mm³. For one type of samples, three specimens are tested; on figures only one test is reported, but the average stresses and strains at break calculated from the three tests are given in a separated table. Note that the rupture has not been reached for the E-SiU samples. The elastic modulus E is calculated as the slope of the linear initial portion of the curve.

RESULTS AND DISCUSSIONS

Homogeneity of the degradation process

After irradiation or thermal ageing of EPDM, an increase in absorbance in the hydroxyl absorption region (3800-3000 cm⁻¹) was observed [17] corresponding to the formation of alcohols, acids and hydroperoxides. The formation of carbonyl band can be evidenced by an absorption maximum at 1713 cm⁻¹ accompanied by several shoulders around 1785, 1755, 1740, and 1695 cm⁻¹[17]. The measurements by IR spectroscopy (ATR) have shown that in the case of filled EPDM, the same oxidation products are created. For all materials (unfilled and filled), an increase in hydroxyl and carbonyl absorption regions can be observed with an increasing irradiation dose, but it is not possible to quantify these products by ATR and thus to compare the oxidation level of the different elastomers. Indeed, the IR depth penetration

and the number of reflections can be influenced by the presence of fillers. Moreover, scattering phenomena can occur.

However, the use of IR - microspectroscopy on sample slice can provide the oxidation product distribution within the sample thickness. The variations in absorbance at 1713 cm^{-1} are chosen for this characterisation. Figure 1 presents the oxidation profiles of E-CR, E-SiU and E-ATHU irradiated at room temperature at 510 kGy, irradiated at 80°C at 165 kGy, and aged at 80°C during 300h. The oxidation profiles are flat for thermal ageing at 80°C , indicating an homogeneous oxidation within the sample thickness. For E-CR and E-ATHU sample, the profile is kept quasi-flat whatever the irradiation conditions. In the case of silica filled EPDM, the oxidation profile is slightly more heterogeneous than that observed for others materials, but this heterogeneity level can be considered relatively low: actually the variation is below 15 %.

Consequences of the different ageing conditions on the E-CR rubber

Thermal ageing at 80°C

Figure 2 presents the evolution of the elastic modulus measured at 80°C and of the swelling ratio Q of E-CR submitted to thermal ageing at 80°C , as a function of the ageing time. The swelling ratio Q decreases with an increasing time whereas the elastic modulus increases. As reported in Table 2, no evolution of the polymer soluble fraction F_p is evidenced. All these results indicate that E-CR is submitted to a crosslinking phenomenon. This is in agreement with the evolution of the large strain behaviour at 80°C (cf. Figures 3 and 4): an increase in the stress level at a given strain is observed as well as a decrease in the strain at break. Thus chain scission does not occur at this temperature for time below 300h. This is in agreement

with Kelidj which found that the induction period for a classical unstabilized and unfilled PE aged at 80°C is around 300h [19]. Note that in this study, this induction period is evaluated by the measurement of oxidation products concentration estimated by IR spectroscopy and not like in our case by mechanical measurements. Note also that in our case, peroxide added in the formulation is largely in excess compared to the ENB proportion (0.5 %) and the exposition of the material at 80°C can promote the decomposition of residual peroxide (still present after material processing) and additional crosslinking reactions.

Irradiation at 25°C

Consequences of irradiation at 25°C have already been discussed in a previous paper [14]. Between 0 and 50 kGy, a competition between crosslinking and chain scissions takes place. Then, after 50 kGy, chain scissions become the main degradation process. This leads to a decrease in the elastic modulus and in the strain at break with an increasing irradiation. Moreover, the network architecture of the material becomes very irregular. After degradation, the network contains more and more weakened zones, which deteriorate the material ultimate properties. Given the distributed character of the chain lengths, the elongation at break is likely controlled by the shortest chains which percolate through all samples whereas the increase in the average length of the active chains control the material modulus.

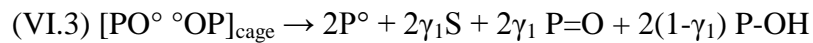
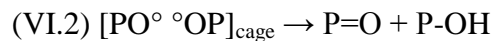
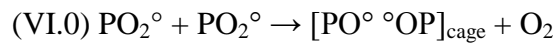
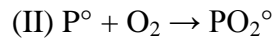
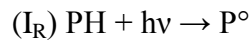
Irradiation at 80°C

The evolutions of swelling ratio and of the elastic modulus at 80°C during irradiation at 80°C are compared to data obtained for irradiation at 25°C in figure 2. For irradiation at 80°C, like in the case of irradiation at 25°C, an increase in the irradiation dose leads to an increase in the swelling ratio. Thus, in both irradiation conditions, the preponderant phenomenon occurring

in the studied material is chain scissions. The only difference is that the degradation is much faster in the case of irradiation at 80°C, so that conversely to E-CR-IR25-510, E-CR-IR80-300 is totally soluble in xylene, i.e. totally degraded.

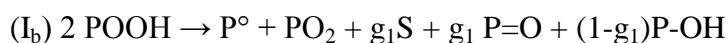
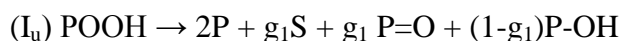
Several explanations to these results can be given. During irradiation at 80°C, E-CR is above its melting temperature and is therefore totally amorphous. As the major part of degradation is assumed to take place in the amorphous region of semi-crystalline materials, E-CR may be more sensitive to radiation, when its crystalline phase is molten. However, given the low crystallinity ratio of the studied EPDM, around 11%, it can be considered that this is not the key explanation of our results.

The radio-oxidation and the radio-thermo-oxidation of polyethylene have been studied by Kelidj et al. [8, 19]. The complete radio-oxidation mechanism proposed by Kelidj et al. [19] is the following:



where γ_1 is the yield of carbonyl build-up in the non-terminating process and S the scission products. All these reactions are thermally activated, which means that a temperature increase should accelerate the degradation process.

Moreover, during thermal ageing, hydroperoxides can be decomposed by an unimolecular and bimolecular mechanism, to induce the formation of radical species, following the reactions [8, 19]:



where g_1 is the yield of carbonyl build-up in the non-terminating process and S the scission products. Consequently, when the material is irradiated at high temperature, these two additional initiation reactions must be added to the radio oxidation mechanisms and we can observe that the number of chain scissions due to these reactions is an increasing function of temperature. Thus, heat during irradiation leads to a much faster increase in radical concentration and therefore also accelerates the degradation mechanisms.

The evolution of the mechanical properties during irradiation at 80°C is similar to the one observed with irradiation at room temperature (see figures 3 and 4). During ageing under irradiation at 80°C a decrease in the strain at break and in the elastic modulus with the irradiation dose is observed. As expected, the modulus decrease is much faster than when irradiation is performed at 25°C. Moreover, the decrease in elongation at break is faster than the decrease in modulus, so that E-CR-IR80-165 has a much lower strain at break than E-CR-IR25-510 in spite of their close modulus. Since it has been previously shown that the thermal ageing at 80°C induces a crosslinking phenomenon, it seems reasonable to think that such crosslinking also occurs during irradiation at 80°C. This process is of course less important than the scission mechanism. If one considers that the chain scissions induced by irradiation are independent on the crosslinking mechanism, then they occur at 80°C on a material effectively more crosslinked than the material kept at 25°C. This explains the lower elongation at break of the materials irradiated at 80°C.

The fastest degradation observed when irradiation is performed at 80°C can be quantitatively estimated from the sol fraction data. To do so, the Charlesby's approach is used [20, 21]. It gives a simple expression relating the sol fraction F_p to the irradiation dose. As shown in

previous paper [14], when the main occurring process is chain scissions, this expression can be simplified as :

$$F_p + \sqrt{F_p} = \frac{G_s w D}{q_f} + \frac{1}{q_f u_1} \quad \text{with} \quad u_1 = \overline{M}_n / w \quad (7)$$

where D is the radiation dose. In this relation, the proportion of crosslinked monomer q_f is constant. Moreover, $G_s w D$ represents the chain scission kinetic with G_s the chain scission yield. Here it is made the assumption that this kinetic is proportional to the irradiation dose (like Charlesby [20, 21] did in his work). \overline{M}_n and w are the average number molar weight and the molar mass of the polymer unit, respectively. Such approach has been previously used for E-CR material irradiated at 25°C. In this case, q_f value was estimated from the extrapolated elastic modulus of E-CR at 0 kGy. It was found equal to 0.015. As shown in figure 5, the experimental evolution of $F_p + \sqrt{F_p}$ versus irradiation dose for E-CR is in good agreement with relation (7). The value of G_s of E-CR deduced from the fit was found equal to 5.2×10^{-7} mol/J. The same approach is used for irradiation at 80°C, assuming that the crosslinking phenomenon observed during thermal ageing at 80°C is negligible compared to the phenomenon of chain scission occurring during irradiation at 80°C. This assumption is reasonable since the modulus evolution of E-CR-T80 shows an increase of a factor of ca. 15% whereas the modulus decrease is of about 80%. This assumption is also confirmed by the fact that the fit is again very satisfactory (see Figure 5). Taking the same value of q_f used for irradiation at 25°C, It is found a value of G_s around 3×10^{-6} mol/J. This is ca. 6 times the value of G_s found for irradiation at 25°C. Note that an account for the q_f evolution (i.e. a slight increase of this parameter induced by a crosslinking phenomenon), would lead to a factor even higher. Thus, the thermal activation of the degradation mechanisms and in particular of the decomposition of hydroperoxides induced by gamma radiation is very important.

Consequences of the different ageing conditions on the E-ATHU rubber

Thermal ageing at 80°C

The influence of ageing on the degradation kinetic of E-ATHU is now explored. The thermal ageing at 80°C is firstly considered. The swelling ratio Q (cf. Figure 6) and the soluble fraction F_p (cf. Table 2) of E-ATHU are stable up to 300 h, whereas the elastic modulus is stable up to 165 h and then slightly decreases. Thus the crosslinking phenomenon observed for the unfilled matrix is not noticeable for E-ATHU. Moreover the large strain behavior at 80°C (cf. Figures 8 and 9) shows an increase in the strain at break with an increasing ageing time. Therefore, it seems that the crosslinking phenomenon observed for the unfilled matrix is not activated and a slight degradation process has taken place. Such inactivation of the crosslinking reactions may be explained by adsorption of residual peroxide on ATH surface. On the other hand, thermal ageing at 80°C might lead to a release of free water from the filler which might promote the matrix degradation mechanisms. This is supported by the strain at break increase of E-ATHU with the time of thermal ageing, which suggests the occurrence of chain scission mechanism inducing filler-matrix decohesion.

Irradiation at 25°C

As evidenced in a previous study [16], the degradation kinetic during gamma-irradiation at 25°C of ATH filled EPDM is activated by the filler presence. In fact, this filler has free bound water at its surface and different articles report filler degradation under gamma or electronic radiation[22, 23]. In the case of ATH, this degradation leads especially to their dehydration and the formation of radicals. These supplementary radicals might be at the origin of the observed accelerated degradation in the composite. As thermal ageing, the matrix degradation

is probably promoted by the release of free water from fillers [16]. The use of the equation (7) led to the conclusion that the presence of ATH increases by a factor 1.5 the scission yield, which is found equal to 3.7×10^{-6} mol/J. Our assumption is that the presence of an important proportion of fillers induces the formation of supplementary radicals. This particular phenomenon has consequences on the evolutions of the mechanical properties: it induces filler-matrix decohesion and cavitation processes during tensile tests performed at 80°C, and therefore lead to higher strain at break.

Irradiation at 80°C

Like during irradiation at 25°C, E-ATHU is mainly submitted to chain scissions during irradiation at 80°C. This is evidenced by an increase in swelling ratio Q (cf. Figure 6) and in soluble fraction F_p (cf. Table 2), as well as a decrease in the elastic modulus at 80°C with increasing irradiation dose (cf. Figure 7). The more rapid evolutions of Q , F_p and of the modulus indicate the thermal activation of the degradation.

The ratio of the elastic modulus (measured at 80°C) of E-150ATHU by the one of E-CR decreases from 3.5 to 1.8 from 0 to 165 kGy for irradiation at 80°C. Considering that there is no reason for a modification of the reinforcement factor by the fillers (since the microstructure and the filler mechanical properties are constant during irradiation), this suggests that the introduction of fillers induces a more rapid polymer degradation. Such result was also found for irradiation at 25°C.

The same approach used for E-ATHU material irradiated at 25°C is applied to estimate the activation of the degradation by the increase in temperature of irradiation. Assuming again that q_f is constant and equal 0.015 and that chain scissions are the predominant events occurring after 50 kGy (cf. Figure 5), a new value of G_s can be estimated for irradiation at

80°C. However, as the fit is only deduced from two data, such estimation must be used with caution. Actually, the radiation dose at which the material becomes totally soluble is necessarily between 165kGy and 300kGy. This means that the deduced from the fit is an underestimation. G_s is found 1-1.25 times the value estimated for E-CR submitted to the same ageing conditions and 5-6 times the value estimated for E-ATHU aged by irradiation at 25°C. Thus, the important thermal activation of the degradation processes induced by irradiation is confirmed for E-ATHU; moreover, the influence of an important proportion of ATH fillers on the degradation kinetic is also evidenced (since the factor 1-1.25 is an underestimation).

The consequences of ageing by irradiation at 80°C on the large strain behavior measured at 80°C are presented in figures 8 and 9. From 0 to 50 kGy, the curve evolution is similar to the one observed for irradiation performed at 25°C: a decrease in stress level at given strain and an increase in the strain at break are observed. But after 50 kGy, the strain at break strongly decreases. This behavior is still coherent with the facts observed for irradiation at 25°C: the ATH presence enables a larger strain at break in irradiated filled EPDM compared to unfilled EPDM.

Consequences of the different ageing conditions on the E-SiU rubber

Thermal ageing at 80°C

The evolution of the swelling ratio Q of E-SiU samples as a function of time is presented in figure 10. The extracted ratios are given in table 2. Thermal ageing at 80°C leads to a decrease in the swelling ratio Q with ageing time. Thus crosslinking takes place during thermo-oxidation at 80°C like in the case of the unfilled polymer. But the Q decrease for the silica filled material is more important since it leads to the same value at high dose although it

begins from a higher value in the unaged state (Indeed, for processing reason, E-SiU is initially slightly less crosslinked than E-CR [17]). This suggests that the crosslinking process is more important in E-SiU, probably because the material is initially farther from its maximum possible crosslinking density. This important crosslinking process is confirmed by the evolution of the elastic modulus at 80°C (cf. Figure 11) and by the tensile tests at 80°C (cf. Figure 12), which show a significant increase in the stress levels with ageing time.

Irradiation at 25°C

As reported in reference [17], because the polymer phase of this composite is less crosslinked, irradiation at 25°C, leads also to a slight crosslinking phenomenon at the beginning of irradiation. However, after 50 kGy, the main occurring process is chain scission. This process is promoted by silica. But the consequences of such acceleration of chain scission are less dramatic than in the case of ATH filled EPDM since the silica filler network remains mechanically efficient (the E-SiU-510-80 modulus is still high and around 8 MPa). Note that the presence of the filler network prevents any use of the Christensen and Lo model, since the fillers cannot be seen as individual particles. Moreover, the degradation of silica under gamma irradiation [24, 25] promotes the formation of filler-matrix interactions whose the presence is evidenced at high irradiation doses (above 300 kGy), by a decrease in the swelling ratio (cf; Figure 10), and a stabilization of the sol fraction (cf. table 2).

Irradiation at 80°C

Swelling ratio and polymer sol fraction F_p of the E-SiU samples irradiated at 80°C are presented in figure 10 and Table 2 respectively. F_p increases with the radiation dose much more rapidly than when irradiation is performed at 25°C. Thus, the thermal activation of the scission mechanism is evidenced. However, the swelling ratio Q is quite stable with radiation

dose. This might be due to crosslinking reactions promoted by the filler presence and likely forming covalent bonds at the filler/matrix interface.

Concerning the mechanical properties, the elastic modulus at 80°C of E-SiU rubber irradiated at 80°C decreases from 14 MPa down to 6 MPa, i.e. down to a modulus value lower than the one of E-SiU-IR25-510. Thus at low strains the higher degradation of polymer phase is visible and is in agreement with the sol fraction results. However the large strain behavior at 80°C (Figure 7) shows a very strong hardening in agreement with the swelling measurement. Therefore, the filler network limits the consequences of material degradation, this network being reinforced by the formation of strong filler-matrix bonds. In addition, these bonds are formed earlier than when irradiation is performed at 25°C. This suggests that this crosslinking process is also thermally activated. This has for consequences that conversely to E-CR and E-ATHU irradiated at 80°C, the silica filled rubber keeps its integrity at 300 kGy.

CONCLUSIONS

An increase in the temperature of irradiation has very strong consequences on the degradation process of the studied materials. All the mechanisms occurring during irradiation at 25°C are largely accelerated at 80°C. Thus the unfilled material shows much faster chain scission process, and therefore a much faster decrease in its mechanical properties. The melting of the polymer crystallites cannot explain such acceleration which is actually mainly due to the thermal activation of the chemical reactions occurring during irradiation and to the thermal decomposition of the hydroperoxides.

This conclusion can be similar in the case of filled materials, whatever the filler type : micronic for ATH and nanoscopic for silica. Moreover, the specific effects of the filler in the degradation processes are also thermally activated. The acceleration of the polymer degradation by the ATH fillers evaluated in the case of irradiation at 25°C seems also

effective at 80°C, but the activation determined for irradiation at 80°C is more important than the one evaluated for irradiation at 25°C. And in addition in the case of silica filled EPDM, the creation of strong filler-matrix bonds, already reported for irradiation at 25°C, are also thermally activated and therefore enables to this material to keep its integrity at high irradiation dose.

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