

# Effect of Thermal Aging on the Electrical Properties of Crosslinked Polyethylene

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**ABSTRACT:** This article reports on the effect of thermal aging on the electrical properties of crosslinked polyethylene (XLPE) used in high voltage cables. It was shown that thermal aging modifies the electrical properties of the polymer. The degradation is accelerated when the temperature is increased. This degradation is due to a thermooxidation, followed by a loss of antioxidant, and a change in color of the material. At 80 and 100°C, the antioxidant is

practically efficacious during the aging, whereas at 120 and 140°C, it is consumed after 1500 and 1000 h, respectively, which results in an increase in the dielectric losses and a diminution in the volume resistivity. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 111: 1985–1990, 2009

**Key words:** XLPE; dielectric properties; thermal aging; degradation

## INTRODUCTION

The synthetic insulation cables are largely developed because of their advantages over the impregnated paper cables, which are at the same time economic and technical. In particular, the absence of dielectric fluid improves the exploitation. During their utilization, these cables are exposed to various stresses (electrical, thermal, mechanical, and environmental). In spite of their good properties, under separate or combined stresses, reactions of specific decomposition to each polymer will occur and degrade gradually the characteristics of the initial product. The chemical mechanisms of degradation are reactions of crosslinking between chains, oxidation, hydrolysis, etc. This degradation related to irreversible changes of the material can quickly reduce its lifetime. Thermal aging often leads to dielectric breakdown. The various mechanisms of thermal degradation were reported elsewhere.<sup>1,2</sup> The crosslinked polyethylene (XLPE) is largely used because of its excellent physical, chemical, and electrical properties.<sup>3,4</sup> Under action of various stresses, its chemical composition and physical morphology change.<sup>5,6</sup> The thermal aging of XLPE can lead to the modification of its properties: researchers highlighted a reduction in elongation at rupture and tensile strength,<sup>7</sup> an increase in the dielectric loss factor,<sup>8,9</sup> and a diminution in the resistivity.<sup>8,10</sup>

The purpose of this work is to study the effect of thermal aging on the electrical properties of XLPE used in high voltage cables.

## EXPERIMENTAL TECHNIQUES

The studied XLPE (4201 reference) is manufactured by the company UNION CARBIDE and contains an antioxidant (SANTONOX). From the mixture of the polymer resin and its various additives, plates of 2 mm thick were molded using a heated press at 180°C and under a pressure of 300 bars. Then, circular samples of 7.5-cm diameter and 2mm thick were elaborated and exposed in regulated and ventilated ovens to several temperatures: 80, 100, 120, and 140°C.

For each temperature, the variations of the dielectric loss factor, the dielectric permittivity, and the volume resistivity in function of aging time are studied. Also, the evolutions of these factors versus the temperature before and after aging are investigated.

The dielectric loss factor and the capacitance are measured with a Schering bridge (TETTEX AG) under AC voltage of 2 kV, 50 Hz, using a test cell consisting of two circular plane electrodes of 20 cm<sup>2</sup> surface. A guard electrode is used to eliminate the surface conduction effects. The electrodes are made of stainless steel. The test cell is equipped with two heating plates enabling to raise the temperature to 150°C. The temperature is measured with a platinum sensor connected to a measuring bridge of temperature (2105C type). The dielectric permittivity is calculated depending on the geometries and the measured capacitances of the samples. The scheme

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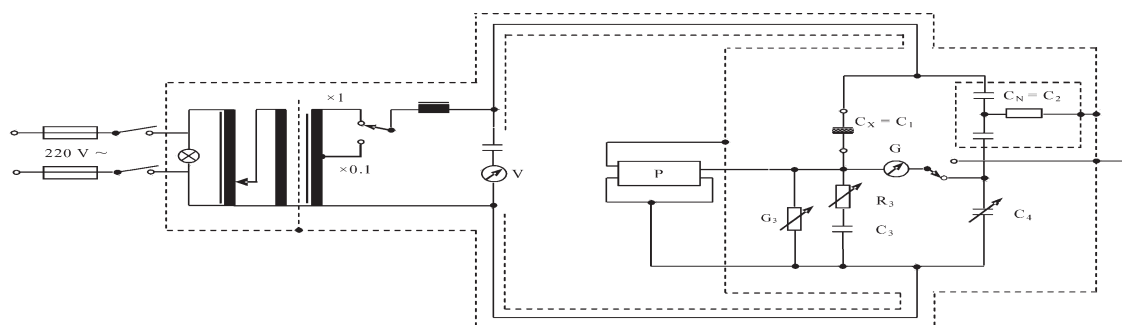


Figure 1 Scheme of Schering bridge apparatus.

of the Schering bridge apparatus is shown in Figure 1. The measurements of the volume resistivity are executed with a megohmmeter under DC voltage of 500 V. This megohmmeter is connected to the guard anode condenser of the Schering bridge apparatus. The insulation resistance is measured and the volume resistivity is derived. To have a good precision, the time of each measurement is equal to 2 min.

## RESULTS AND DISCUSSION

### Influence of aging time

#### Dielectric loss factor

Figure 2 represents the evolution of the dielectric loss factor ( $\tan \delta$ ) versus the aging time ( $t$ ). The variation can be summarized as follows:

At 80°C, the characteristic presents an irregular variation. At the beginning of aging,  $\tan \delta$  is practically invariable. From  $t = 1000$  h, the characteristic is initially increasing, presenting a peak corresponding to  $\tan \delta = 2.2 \times 10^{-3}$  at  $t = 1500$  h, then it remains constant. Beyond  $t = 2500$  h, the curve presents a second peak at  $t = 3000$  h with  $\tan \delta = 9.1 \times 10^{-4}$ , then decreases [Fig. 2(a)]. These peaks were caused by the relaxation phenomena because of the movements of macromolecular chains of the polymer (rotation, translation, vibration).

At 100°C, we notice a similar evolution. The characteristic presents three peaks corresponding to  $\tan \delta = 2.2 \times 10^{-3}$ ,  $t = 1000$  h;  $\tan \delta = 9.2 \times 10^{-4}$ ,  $t = 3000$  h; and  $\tan \delta = 4.5 \times 10^{-4}$ ,  $t = 4500$  h [Fig. 2(a)].

At 120°C, the curve is first decreasing up to a minimum at  $t = 700$  h and  $\tan \delta = 3.1 \times 10^{-4}$ , then grows [Fig. 2(b)].

At 140°C,  $\tan \delta$  is constant during the first 250 h of aging, then decreases up to a minimum corresponding to  $t = 750$  h,  $\tan \delta = 1.2 \times 10^{-4}$ , then increases quickly [Fig. 2(c)]. In this case,  $\tan \delta$  takes high values: after 1500 h, its value is  $2.2 \times 10^{-2}$ . The multiplicative factor is 10.5 com-

pared to the one before aging. We note that the values of  $\tan \delta$  are higher when the temperature is elevated.

Thermal aging intensifies the thermal agitation, which leads to a progressive reduction in viscosity expressing a weakening of the molecular bounds and an increase of the free volume. This phenomenon has like a consequence an increase in the mobility of the charge carriers and the conductivity leading to raise  $\tan \delta$ . The reduction in  $\tan \delta$  is due to the rearrangements of the molecular chains of the polymer and a diminution in the mean free path of the charge carriers, which lead to a decrease in their mobility.

#### Dielectric permittivity

Figure 3 presents the variation of the dielectric permittivity ( $\epsilon_r$ ) versus the aging time ( $t$ ).

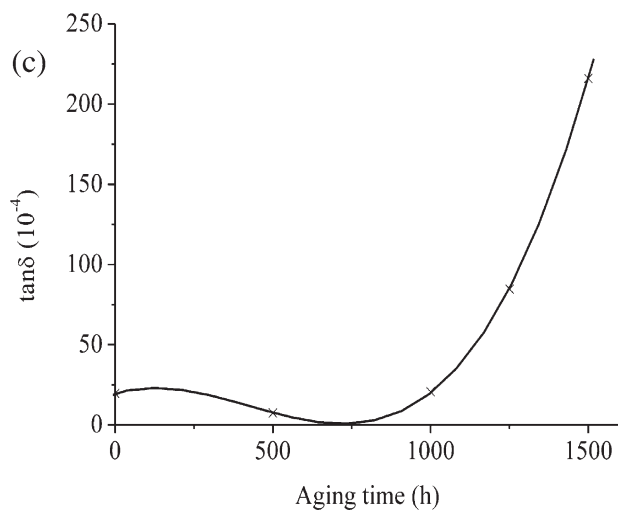
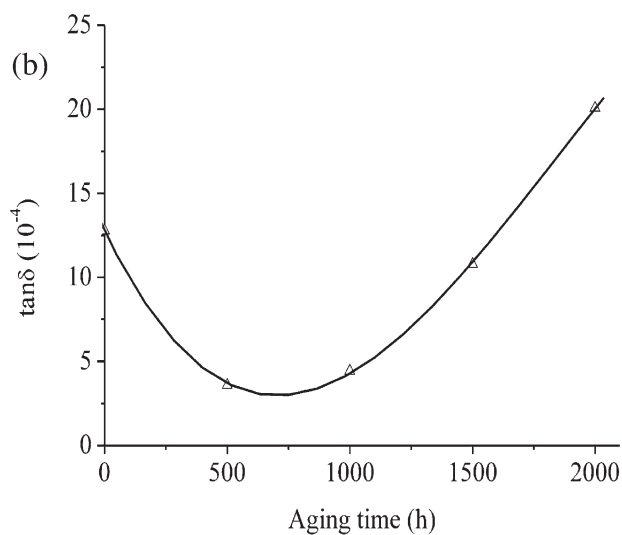
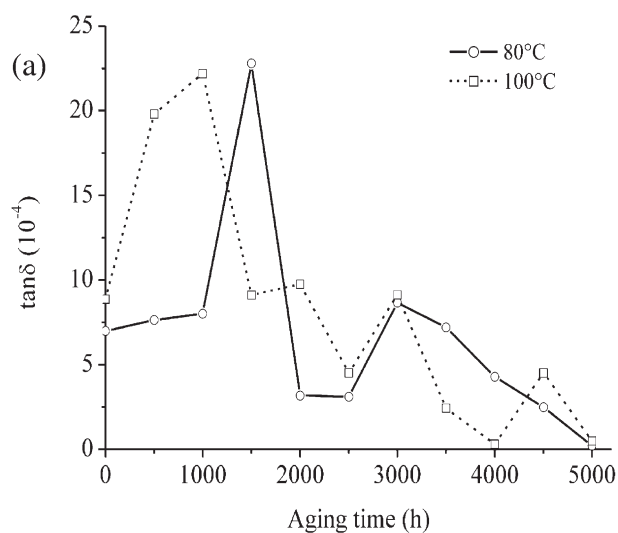
At 80°C,  $\epsilon_r$  is practically constant during the aging.

At 100°C,  $\epsilon_r$  increases lightly during the first 500 h, then remains constant.

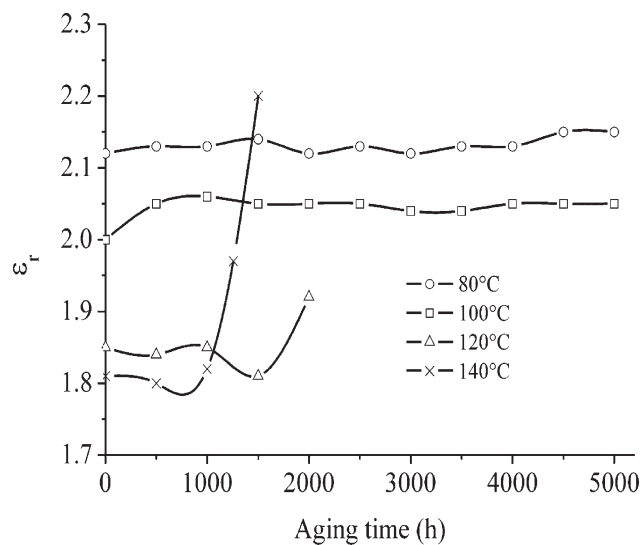
At 120°C,  $\epsilon_r$  is practically invariable during the first 1000 h. Beyond 1000 h, the curve decreases up to a minimum corresponding to  $t = 1500$  h,  $\epsilon_r = 1.81$  from which it grows.

At 140°C, during the first 800 h, the curve decreases up to a minimum at  $t = 810$  h and  $\epsilon_r = 1.78$ . Beyond this minimum,  $\epsilon_r$  grows quickly and reaches a value of 2.2.

Same interpretation can be given as previously: the increase of  $\epsilon_r$  is due to an important reduction in the viscosity leading to a significant augmentation in the conductivity, which results in a loss of the antioxidant that is possible at the temperatures of 120 and 140°C. The reduction in  $\epsilon_r$  can be explained by a rearrangement of the molecular structure of the material. The minima of the characteristics are allotted to the relaxation phenomena because of the macromolecular movements of polymer chains. Let us



**Figure 2** Variation of the dielectric loss factor versus the aging time at different temperatures (a) 80 and 100°C, (b) 120°C, and (c) 140°C.

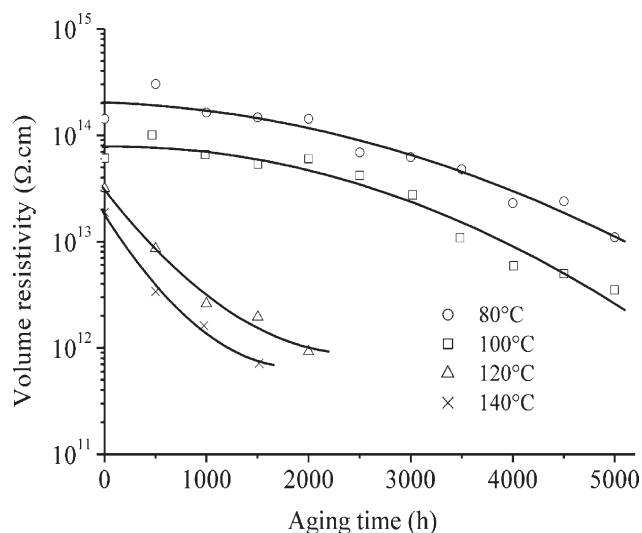


**Figure 3** Variation of the dielectric permittivity versus the aging time at different temperatures.

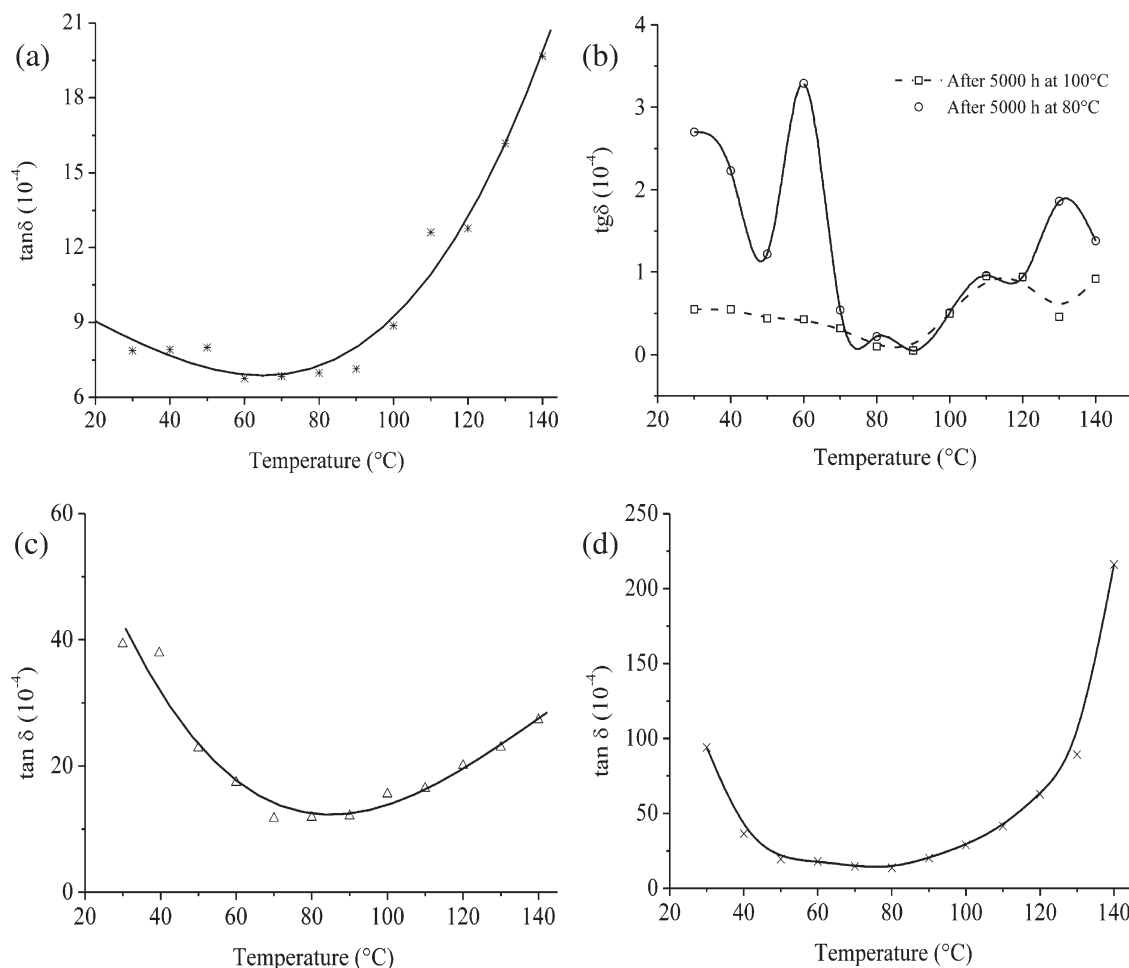
note that the low values of  $\epsilon_r$  are due to the nonpolar structure of XLPE molecule.

#### Volume resistivity

Figure 4 represents the evolution of volume resistivity ( $\rho$ ) in function of aging time. For all the temperatures,  $\rho$  decreases versus the time. We notice that more the temperature is raised, more the material degrades quickly, which is in conformity with the Arrhenius law. After the prolonged times, the molecular bonds weaken and the free volume rises. This phenomenon leads to an increase in the mobility of the charge carriers along with a reduction in the volume resistivity.



**Figure 4** Variation of the volume resistivity versus the aging time at different temperatures.



**Figure 5** Variation of the dielectric loss factor versus the temperature before and after aging (a) before aging, (b) after 5000 h at 80°C and 5000 h at 100°C, (c) after 2000 h at 120°C, and (d) after 1500 h at 140°C.

### Variations of the electrical properties versus the temperature

#### Dielectric loss factor

Figure 5 gives the evolution of  $\tan \delta$  versus the temperature ( $\theta$ ).

Before aging, the characteristic decreases up to a minimum corresponding to  $\tan \delta = 6.8 \times 10^{-4}$ ,  $\theta = 65^\circ\text{C}$ , then increases [Fig. 5(a)].

After 5000 h at 80°C, the characteristic presents several peaks at  $\theta = 60, 110, \text{ and } 130^\circ\text{C}$  corresponding to  $\tan \delta = 3.3 \times 10^{-4}, 9.6 \times 10^{-5}, 1.9 \times 10^{-4}$ , respectively [Fig. 5(b)]. After 5000 h at 100°C, the curve decreases up to a minimum corresponding to  $\tan \delta = 7 \times 10^{-6}$  and  $\theta = 85^\circ\text{C}$ , then grows and reaches a maximum for  $\theta = 110^\circ\text{C}$  and  $\tan \delta = 9.1 \times 10^{-5}$ , then decreases and grows again [Fig. 5(b)].

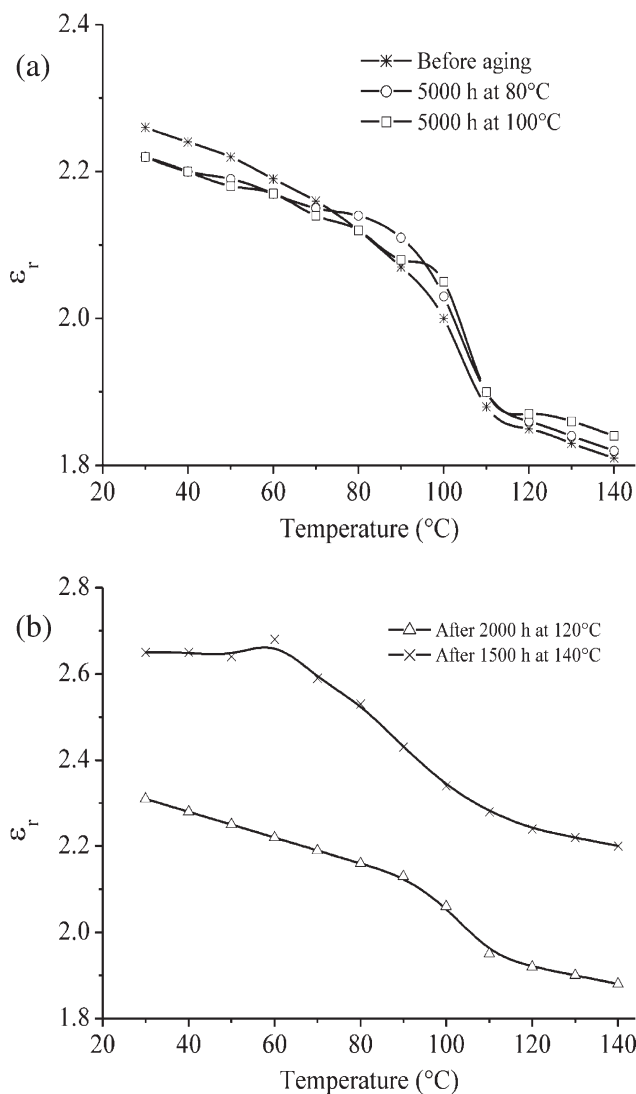
After 2000 h at 120°C, initially, the characteristic decreases up to a minimum corresponding to  $\tan \delta = 1.2 \times 10^{-3}$  and  $\theta = 87^\circ\text{C}$ , then grows [Fig. 5(c)].

After 1500 h at 140°C, the curve decreases up to a minimum at  $\theta = 78^\circ\text{C}$ , then grows. It reaches a value of  $\tan \delta = 2.2 \times 10^{-2}$  for  $\theta = 140^\circ\text{C}$ . The values of  $\tan \delta$  corresponding to the temperatures of 120 and 140°C are high.

The peaks and the minima are ascribed to the relaxation phenomena due to the movements of macromolecular chains.

#### Dielectric permittivity

Figure 6 shows the variation of  $\epsilon_r$  versus the temperature ( $\theta$ ) before and after aging. The curves, as shown in Figure 6, are decreasing and practically superposed. After 2000 h at 120°C,  $\epsilon_r$  decreases versus  $\theta$  [Fig. 6(b)]. After 1500 h at 140°C,  $\epsilon_r$  is constant at the low temperatures. Beyond 60°C, the curve decreases as shown in the Figure 6(b). Our results are in agreement with those reported elsewhere.<sup>11,12</sup>



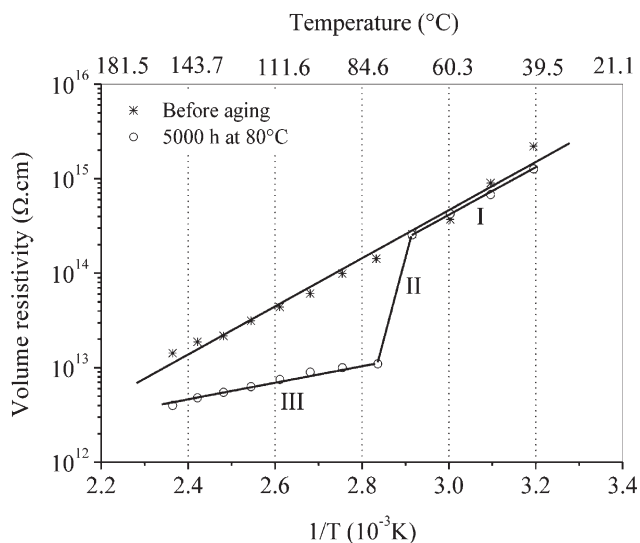
**Figure 6** Variation of the dielectric permittivity versus the temperature before and after aging (a) before aging, after 5000 h at 80°C and 5000 h at 100°C and (b) after 2000 h at 120°C and after 1500 h at 140°C.

#### Volume resistivity

Figure 7 illustrates the evolution of  $\rho$  in function of the reciprocal absolute temperature ( $1/T$ ) before aging and after 5000 h at 80°C. As one can see,  $\rho$  decreases versus the temperature. Before aging, the characteristic is a straight line and obeys the Arrhenius law. The volume resistivity of polymers is given by the following relationship<sup>13</sup>:

$$\rho = \rho_{\infty} \exp\left(\frac{-E}{RT}\right) \quad (1)$$

$\rho_{\infty}$  ( $\Omega$ ), limit of the resistivity at the infinite temperature;  $E$  ( $\text{J mol}^{-1}$ ), process activation energy;  $T$  (K), absolute temperature;  $R$ , gas constant ( $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ ).



**Figure 7** Variation of the volume resistivity versus the temperature before aging and after 5000 h at 80°C.

After aging, the characteristic is formed by three straight line segments representing a change of the degradation mechanism. From the curves corresponding to the different temperatures, the values of the activation energy are determined. Before aging, its value is 11.86 kcal/mol. In Table I, the values of the activation energy after aging are exposed. The zones of the curve (Fig. 7) are numbered from the right to the left, i.e., the low temperatures toward the high temperatures. We notice an increase in the activation energy from the zone I to the zone II, then a reduction from the zone II to the zone III. The activation energy varies in function of the aging time and the temperature. This phenomenon was reported elsewhere.<sup>14,15</sup>

#### MECHANISM OF DEGRADATION

The thermal decomposition of XLPE is due to a thermooxidation<sup>8,10</sup> accompanied by a loss of antioxidant.<sup>16</sup> At 80 and 100°C, the antioxidant is practically efficacious during the aging. At 120 and 140°C, the antioxidant is consumed after 1500 and 1000 h, respectively. During the operation of polymer reticulation, volatile products are formed in small vacuoles. During thermal aging, a part of imprisoned gases (hydrocarbons, ketones, alcohols) can be released and replaced by water, oxygen.<sup>16</sup>

**TABLE I**  
Values of the Activation Energy (kcal/mol)

Aging time	Zone I	Zone II	Zone III
5000 h at 80°C	11.40	79.68	4.55
5000 h at 100°C	11.69	77.53	3.85
2000 h at 120°C	11.06	92.58	4.18
1500 h at 140°C	3.29	32.68	—

The solubility of oxygen can be significant. The study of the effect of the thermal stress on XLPE allowed to highlight a variation of the polymer morphology (variation of the crystalline ratio to amorphous).<sup>12</sup> For high temperatures, we observed a change in color of the samples aged at 100, 120, and 140°C.

In a previous work, we studied the variation of mass loss of XLPE versus the time of aging.<sup>7</sup> We reported that the degradation of XLPE is carried out according to three phases. During the first phase, the degradation is done with a relatively significant speed. The second phase is characterized by an increase of this speed. During the third phase, a reduction speed was highlighted: the mass loss remains constant because of saturation, i.e., the antioxidant is practically completely consumed. The consequences of the XLPE degradation were reported: change in color, contracting, loss of mass, brittleness, and decrease in degree of crosslinking.<sup>7</sup>

### CONCLUSIONS

The study shows that thermal aging modifies the dielectric properties of XLPE. The degradation of the material is accelerated by the increase in temperature, which is in conformity with Arrhenius law. This degradation attributed to a thermooxidation accompanied by a loss of antioxidant is characterized by a change in color of the samples. It is shown that at 80 and 100°C, the antioxidant is effective during the aging. At 120 and 140°C, the antioxidant is completely consumed after 1500 and 1000 h, respectively, which results in an increase in the dielectric losses and a diminution in the volume resistivity. The activation energy of the process depends on the temperature and aging time, which expresses several processes of decomposition. After prolonged times at 120 and 140°C, the values of the dielectric loss factor are higher: this increase is allotted to a reduction in the viscosity. This phenomenon leads to an increase of the free volume and a raise in the mobil-

ity of the charge carriers. The reduction of the dielectric loss factor is due to a rearrangement of the material structure. The dielectric permittivity is less affected by the aging: its variations are weaker than those of the dielectric loss factor.

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