

# Influence of Thermal Aging on the Electrical Properties of Poly(vinyl chloride)

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**ABSTRACT:** This article reports on the study of the thermal aging of poly(vinyl chloride) (PVC) used in medium- and high-voltage cables. It is shown that the thermal aging leads to the degradation of the material and to the modification of its electrical properties. The degradation is all the more important and faster as the temperature is high. This degradation is attributed to a progressive evaporation of the plasticizer at the beginning of aging and to a weight

loss of stabilizer followed by a change in the color of polymer and a release of hydrochloric acid at more advanced stages of aging. It also results in a crosslinking of the material and a shrinking of samples. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 4728–4733, 2006

**Key words:** dielectric properties; poly(vinyl chloride); degradation; failure

## INTRODUCTION

Polymers used in medium- and high-voltage (HV) cables are exposed to various stresses (electrical, thermal, mechanical, environmental, ...) during their exploitation. And the mechanisms leading to the degradation of polymers and thence to the failure of cables depend upon the amplitude and the application time of each stress with regards to the others. For instance, the increase of temperature results in specific chemical reactions (the crosslinking reactions between the chains, the oxidation, the hydrolysis, ...) and irreversible changes leading to the progressive deterioration of the characteristics of initial material and thence to the shortening of its lifetime. The kinetics of degradation depends on the temperature level and the concentration of the different constituents of polymer.<sup>1,2</sup> Indeed, the thermal degradation and the speed of reaction are accelerated by the increase of temperature.<sup>3–5</sup> Several modifications of polymer structures such as change in color, reduction in volume, and brittleness have been observed.<sup>6</sup> The diffusion of products, the rise in crystallinity ratio,<sup>7,8</sup> the migration of substances out of the material (plasticizers for example), the break of chains, and loss of mass due to emissions of gases have also been pointed out.<sup>6,9,10</sup> Thermal aging can also lead to the

modifications of electrical and mechanical properties of polymers.<sup>6,8,10–12</sup>

The purpose of this work is to study the influence of thermal aging on the electrical properties of poly(vinyl chloride) (PVC) used in medium- and HV cables.

## EXPERIMENTAL

The material samples manufacturing process consists first in the mixing of poly(vinyl chloride) (PVC) resin and various additives, in the form of granulates, at 140°C to obtain a paste; the additives being the dioctyl phthalate as plasticizer, the calcium carbonate (CaCO<sub>3</sub>) as filler, and the lead stearate as stabilizer and lubricant; the weight fraction of plasticizer is 30% of the polymer. The mixture so obtained (i.e., poly(vinyl chloride) (PVC)) is cut into plate forms and then were introduced into a heated press at 160°C for 5 min to get square plates of 25 cm side and 2 mm thick; the press force is of 400 kN. The samples we tested are put into round forms, 7.5 cm in diameter and 2 mm thick, and were then cut into square plates.

To study the influence of temperature and aging on the dielectric characteristics, the samples are put within regulated and ventilated ovens at several temperatures, i.e., 80, 100, 120, and 140°C. For each of these temperatures, we investigated the dielectric loss factor,  $t_g\delta$ , the dielectric strength, the dielectric constant,  $\epsilon_r$ , (relative permittivity), and the volume resistivity,  $\rho$ , (conductivity  $\sigma = 1/\rho$ ) in function of aging time. The variation of these characteristics in

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function of temperature before and after the aging process is also analyzed.

The samples capacitances and loss tangents are measured with Schering bridge (TETTEX AG type) 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 of samples up to 150°C. The temperature is measured with a platinum sensor connected to a measuring bridge of temperature (2105 C type).

The permittivities of the samples are calculated depending on their geometries and their measured capacities and loss factors. The volume resistivity of the polymer is measured with a megohmmeter under a DC voltage of 500 V.

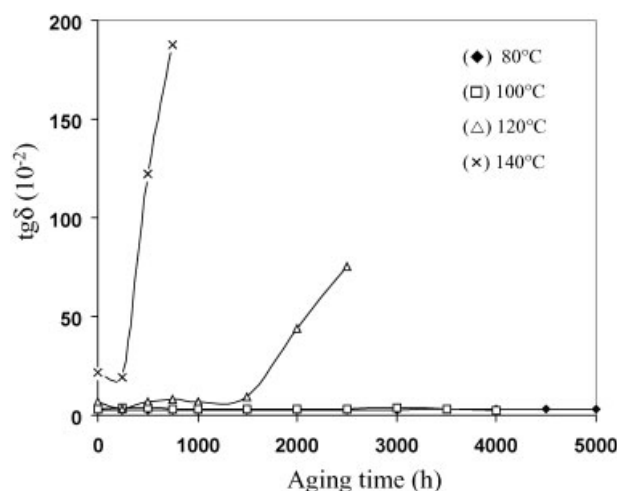
The breakdown experiments are executed on a dielectric test device (BAUR OLPRUFGERAT PGO 90 A), 90 kV, 50 Hz. The measurements are achieved at room temperature, under a quasiuniform electric field obtained with semispherical electrodes of brass, the axis of which being horizontal. The test cell containing the electrodes arrangement is filled with insulating oil ("Borak 22"). The voltage is uniformly increased with a rate of  $2.0 \pm 0.2$  kV/s and the oil is stirred during all the tests.

## RESULTS AND DISCUSSION

### Influence of aging time

#### Dielectric loss factor and dielectric constant

First, one must understand that the high values of the dielectric loss factor and the dielectric constant of the considered material are due to the polar character of PVC molecule and plasticizers. We observe generally that the increase of temperature and the aging time leads to the increase of the loss factor,  $t_g\delta$  (Fig. 1). The increase of  $t_g\delta$  is all the more important as the temperature is high. At 80 and 100°C, the variation of loss factor is not significant during the aging, whereas at higher temperatures we observe a great increase of  $t_g\delta$ . At 120°C, the dielectric loss factor remains practically constant during the first 1500 h, and then increases by one order at least of magnitude at 2500 h. At 140°C, the increase of  $t_g\delta$  is much more fast and high; it is higher than two orders of magnitude at 750 h comparing to the initial value. The increase of loss factor results in the increase of conductivity of the material. Indeed, the increase of temperature and the aging time leads to a decrease of the viscosity of the polymer resulting in an increase of the mobility of charge carriers and thence of the conductivity. The increase of tempera-



**Figure 1** Variation of the dielectric loss factor versus the aging time at different temperatures.

ture also results in the increase of the conductivity of additives.

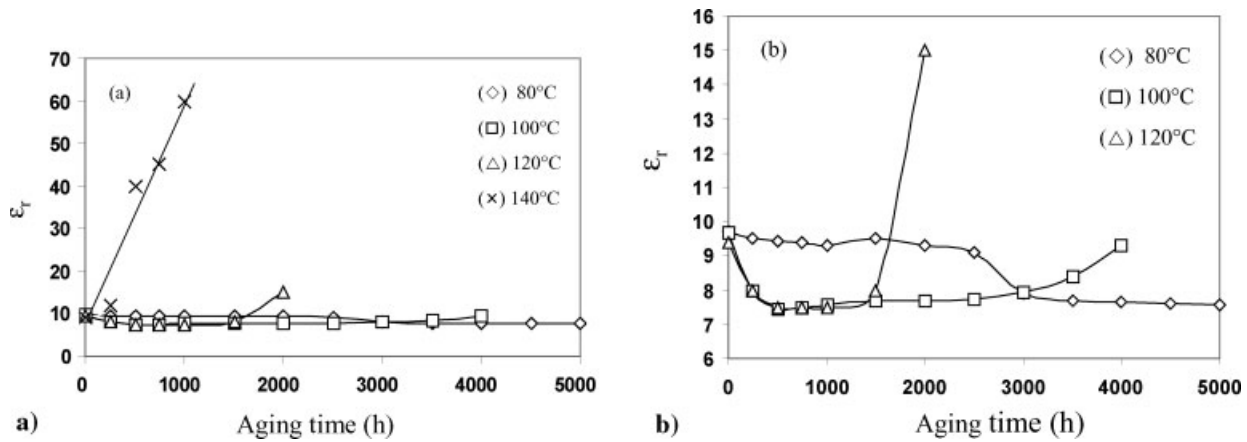
Also note that the increase of loss factor can be due to the important noxiousness of the partial discharges within the cavities, which can be introduced during the manufacturing process or generated during the aging process of insulating resulting of the evaporation of plasticizers. The partial discharges progressively lead to the erosion of the insulating material (through the erosion of the wall of cavities) and thence to its degradation.

The evolution of dielectric constant in time is not the same depending upon the temperature [Fig. 2(a,b)]:

At 140°C,  $\epsilon_r$  abruptly increases from about 9.2 to 60 after an aging time of 1000 h. As for the loss factor, this increase is due to an important decrease of the viscosity resulting in a significant decrease of resistivity (or increase of conductivity) as observed in Figure 3. The increase of conductivity also results from the dissociation and especially from the dechlorination of PVC, which is possible at this temperature.

At 120°C,  $\epsilon_r$  decreases from 9.4 to about 7.5 after 500 h and then remains somewhat constant; and over 1500 h,  $\epsilon_r$  increases in a pronounced way to reach 15 after an aging time of 2000 h. The decrease observed in the first 500 h can be explained by the rearrangement of the molecular structure of PVC; the increase of  $\epsilon_r$  beyond 1500 h is due to the relaxation phenomena.

At 100°C,  $\epsilon_r$  decreases from 9.5 to 7.5 after 500 h of aging as at 120°C, then stabilizes up to 3000 h; and beyond 3000 h,  $\epsilon_r$  increases up to about 9.4 after 4000 h. This increase is also due to the



**Figure 2** Variation of the dielectric constant versus the aging time at different temperatures (a); (b) is an extension of (a) for 80, 100, and 120°C.

slackening of bonds (relaxation), which appears after an aging time longer than that at 120°C.

At 80°C,  $\epsilon_r$  slightly decreases weakly from 9.7 to 9.1 after 2500 h of aging, then decreases rapidly up to 7.6 after 3300 h and then remains constant. This decrease is likely due to the rearrangement of molecular bonds and reticulation.

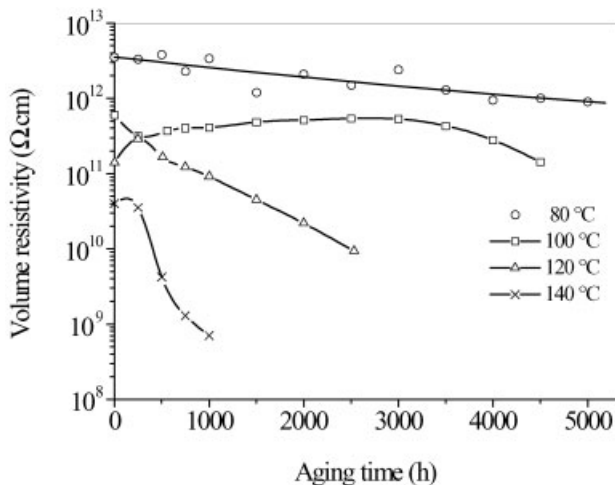
#### Volume resistivity

As concerns the volume resistivity,  $\rho$ , it generally decreases with aging time (Fig. 3). And as indicated earlier, the decrease of the resistivity (or increase of conductivity) with aging time is all the more marked as the temperature is high. For an aging time of 1000 h,  $\rho$  at 140°C is three orders of magnitudes smaller than that at 120°C. This results in the slackening of molecular bonds and the decrease of the viscosity of

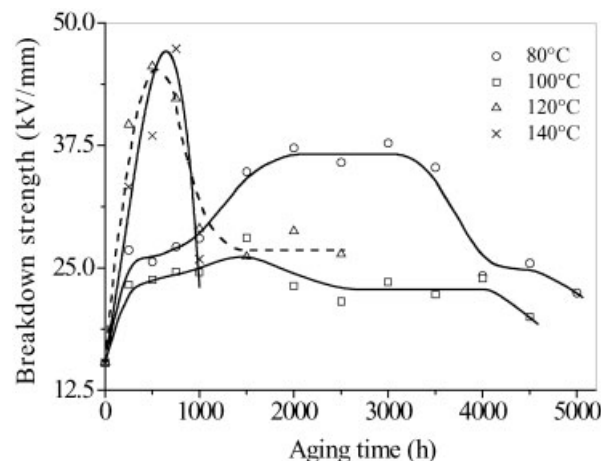
material. This effect is less marked at 80 and 100°C; the molecular bonds are slightly affected at these temperatures.

#### Dielectric strength

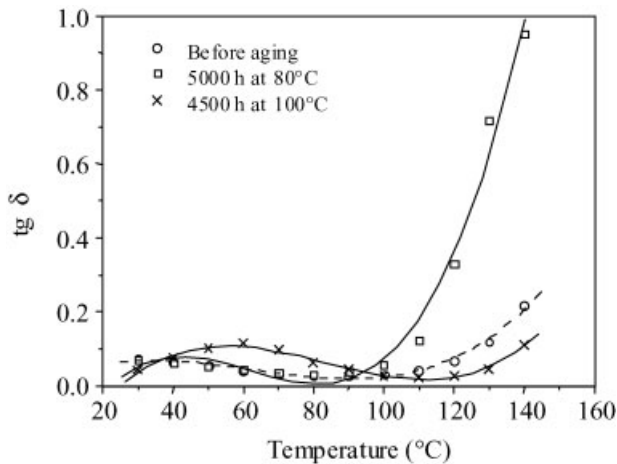
The breakdown voltage ( $V_b$ ) of the polymer versus the aging time is presented in Figure 4. The variation of  $V_b$  versus the temperature and aging time can be summarized as follows: At 80°C,  $V_b$  increases of about 146% after 2000 h, then it remains somewhat constant; after 3000 h, it progressively decreases with time. At 100°C,  $V_b$  increases of about 80% after 1500 h and then decreases; after 2000 h, it remains practically constant up to 4000 h. At 120°C and 140°C,  $V_b$  sharply increases during the first hundreds of hours (500 h and 750 h, respectively) and then rapidly decreases; the increase of  $V_b$  is of about 207% and



**Figure 3** Variation of the volume resistivity versus the aging time.



**Figure 4** Variation of the breakdown strength versus the aging time.



**Figure 5** Variation of the dielectric loss factor versus the temperature before and after aging.

220%, respectively. After an aging time of 1500 h at 120°C,  $V_b$  remains constant.

For the four investigated temperatures, we observe the same type of variation;  $V_b$  first increases and then decreases. This increase is attributed to the evaporation of plasticizers and the reticulation of polymer; it is accompanied by a deterioration of the mechanical properties, and a decrease of the density. The time necessary to reach the maximum value of  $V_b$  is all the shorter as the temperature is high. And the decrease of  $V_b$  is due to the weakening of molecular bonds, the diffusion of oxygen, which is followed by the break of C—Cl bonds and the degradation of stabilizer as well as to a decrease of resistivity. Note that the dissociation of molecules is accelerated when the temperature is high as it is the case at 140°C, for instance.

### Consequences of the material degradation

After an aging time of 750 h at 100°C, 2000 h at 120°C and 500 h at 140°C, we observed a change in the color and a shrinking of samples resulting in a decrease in the thickness and diameter of samples. The reduction of the volume of samples is 52.73% after an aging time of 4500 h at 100°C, corresponding to diminutions of 29.3% and 18.2% of thickness and diameter of samples, respectively. This shrinking is due to the evaporation of plasticizer and to the decomposition of the polymer accompanied by a release of hydrochloric acid; unsaturated hydrocarbons easy to oxidize can also be generated.

The reduction of the volume of samples is 46.72% after 2500 h at 120°C and 13.26% after 1000 h at 140°C. Note that at 140°C the samples present cracks after an aging time of 1000 h. Such an observation has been reported in a previous work.<sup>6</sup>

### Influence of temperature

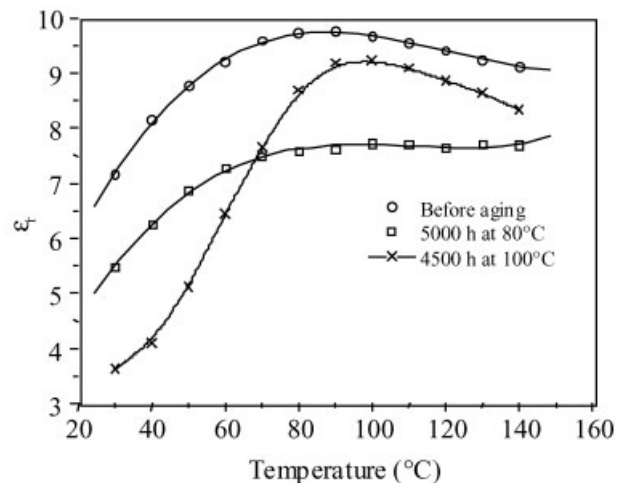
#### Dielectric loss factor and dielectric constant

Figure 5 shows the change in the electrical loss factor as a function of time before and after aging times of 5000 h at 80°C and 4500 h at 100°C. We observe that before aging  $t_g\delta$  is roughly constant up to a maximum value at 85°C, then it slowly increases. After an aging time of 4500 h at 100°C, the  $t_g\delta$  characteristic presents a peak at 60°C, which can be attributed to the relaxation phenomena, and then decreases up to a minimum at around 110°C. After the minimum, there is a rapid increase resulting of the same phenomena we evoked in the earlier section (see the first section under Results and Discussion). For an aging time of 5000 h at 80°C, we observe similar variations to those before aging with a minimum around the same temperature (i.e., at 85°C). Beyond this minimum, the increase of  $t_g\delta$  is more accentuated than before aging. This minimum is probably due to the resonance of the chains or segments of molecular structure of polymer.

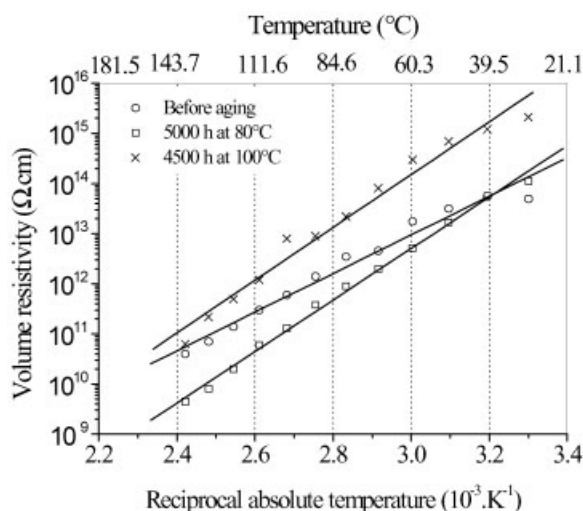
The variation of the dielectric constant versus the temperature before and after aging is shown in Figure 6. Before aging,  $\epsilon_r$  increases with temperature up to a maximum at about 90°C and then slowly decreases. After an aging of 4500 h at 100°C, we observe the same changes with a maximum at 100°C. However, after 5000 h at 80°C, the characteristic first increases, then it levels off. It appears from these characteristics that  $\epsilon_r$  is more important before aging. The increase and decrease of  $\epsilon_r$  can be explained in the same manner as given in the earlier section.

#### Volume resistivity

To well analyze the behavior of resistivity, we plot the volume resistivity versus the inverse of the abso-



**Figure 6** Variation of the dielectric constant versus the temperature before and after aging.



**Figure 7** Variation of the volume resistivity versus the temperature before and after aging.

lute temperature before and after aging times of 5000 h and 4500 h at 80 and 100°C, respectively (Fig. 7). The results show that the volume resistivity decreases linearly with temperature. These straight lines obey the Arrhenius law and so do the volume resistivity  $\rho$ .<sup>13</sup>

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

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

The activation energy,  $E$ , can be deduced from the characteristics given in Figure 7. Before aging,  $E$  is equal to 17.65 kcal/mol. After aging, the values of  $E$  are 23.53 and 24.11 kcal/mol after 5000 h at 80°C and 4500 h at 100°C, respectively. Therefore, the activation energy also varies with aging. This phenomenon is likely due to the variation of the chemical reaction rate, which is more significant after aging. This results are in good agreement with those reported elsewhere.<sup>14</sup> The fact that the activation energy is a function of aging time has also been observed by Morel et al.<sup>7</sup> in the case of polyethylene-terephthalate films.

### Degradation mechanism

PVC degradation mechanism occurs in two steps. During the first step of the aging process, the plasticizer is evaporated. The plasticizer molecule first diffuses from its initial site toward the surface. Then, a part of the plasticizer presents at the surface quickly

evaporates. At this moment, the bulk diffusion is the controlling step of the kinetics.<sup>14</sup> At 140°C, the loss of plasticizer is very fast, as reported by others.<sup>15</sup> This disappearance is followed by an evolution of the material coloration with a release of hydrochloric acid.<sup>4,15–18</sup> This phenomenon is followed by a reduction in the volume of the samples and a crosslinking of the polymer. The various studies on the mass loss of PVC versus aging time<sup>6,19,20</sup> as well as thermal degradation of nonplasticized PVC<sup>9</sup> pointed out the complexity of mechanisms implicated in the degradation of polymer. This degradation is accelerated by the presence of oxygen.<sup>9</sup> Generally, one admits that thermal aging of PVC results from simultaneous actions of heat, light, and oxygen.<sup>18</sup> Moreover, the degradation is all the faster as the temperature is high.

### CONCLUSION

This work shows that thermal aging modifies the electrical characteristics of PVC. The degradation of the material is accelerated when the temperature is increased. At the beginning of aging (i.e., the first hundreds hours), the polymer degradation is mainly due to a progressive evaporation of the plasticizer. At more advanced stages of aging, the degradation is attributed to a deterioration of stabilizer followed by a change in color of the polymer and a release of hydrochloric acid. This phenomenon also results in a crosslinking of the material and a reduction of the volume of samples. On the other hand, the volume resistivity of PVC decreases with temperature; and the activation energy varies with aging time. After long periods of aging at 120 and 140°C, the dielectric constant as well as the dielectric loss factor significantly increases taking high values enough.

### References

- Levine, I. N. *Physical Chemistry*; McGraw-Hill: New York, 1978.
- Augood, D. R. *Conference Record of 1978 IEEE International Symposium on Electrical Insulation*, June 12–14, 1978, pp 17–21.
- Paloniemi, P. *IEEE Trans Electr Insul* 1981, EI-16, 1.
- Bartnikas, R. *Engineering Dielectrics, Vol. IIB: Electrical Properties of Solid Insulating Materials: Measurement Techniques*; ASTM Special Technical Publication 926, Philadelphia, 1987.
- Carlsson, D. J.; Wiles, D. M. In *Encyclopedia of Polymer Science and Engineering*, 2nd ed.; Wiley: New York, 1986; Vol. 4, pp 630–696.
- Nedjar, M.; Boubakeur, A.; Béroual, A.; Bournane, M. *Ann Chim Sci Matér* 2003, 28, 97.
- Morel, J. F.; Dung, P. N.; Joly, J. F. *IEEE Trans Electrical Insulation* 1980, EI-15, 335.
- Bellomo, J. F.; Lebey, T.; Oraison, J. M.; Peltier, F. In *Proceedings of the 1995 IEEE 5th International Conference on Conduction and Breakdown in Solids Dielectrics*, Leicester, England, 1995; pp 442–446.

9. Braun, D. *Pure Appl Chem* 1981, 53, 549.
10. Montanari, G. C. In *Proceedings of the 2nd International Conference on Properties and Applications of Dielectrics Materials*, Beijing, China, 1988; pp 320–324.
11. Zaharescu, T.; Giuginca, M. In *Proceedings of the 1995 IEEE 5th International Conference on Conduction and Breakdown in Solids Dielectrics*, Leicester, England, 1995; pp 473–476.
12. Fournié, R. *Les isolants en électrotechnique, Essais, mécanismes de dégradation, applications industrielles*, Eyrolles ed.; 1990.
13. Dakin, T. W. *AIEE Trans* 1948, 67, 113.
14. Dalle, B.; Metzger, G.; Audouin, L.; Verdu, J. *SEE, Isolants Electriques*, Git-sur-Yvette, France, 1989, 213.
15. Metzger, G.; Paris, M. In *proceedings of the 3rd International Conference on Insulated Power Cables, JICABLE'91*, Paris-Versailles, France, pp 312–317.
16. Nass, L. I. *Encyclopedia of PVC*, Vol. 1; Marcel Decker: New York, 1976; Chapter 8.
17. Starnes, W. H., Jr. *Poly(vinyl chloride) (Mechanisms of stabilization)*, the *Polymeric Materials Encyclopedia*; CRC Press: Boca Raton, 1996.
18. Kumar, N. N. *Ageing and Stabilisation of PVC Electrical Insulation—A Review*, *Popular Plastics*; India, 1982; pp 3–9.
19. Matsusaka, K.; Tanaka, A.; Murakami, I. *Polymer* 1984, 25, 1337.
20. Audouin, L.; Verdu, J. *Thermal aging of plasticized PVC—Effect of Loss Kinetics on Plasticizer Depth Distribution*, 4th *ICPADM*, Brisbane, Australia, 1994, pp 262–265.