Electrical Aging of Polyurethane Under AC Voltage

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ABSTRACT: The electrical aging of polyurethane under ac voltage has been investigated using Weibull statistical analysis. It is shown that the time to breakdown characteristic (*V*-*t*) of this polymer includes three zones corresponding, respectively, to the youth defects, the statistical dispersion of the intrinsic defects, and the real aging of the polymer. The variation of slope of the *V*-*t* curve is related to the change of the degradation mechanism. This degradation is governed by the action of partial discharges according to three stages: (1) the appearance of very fast discharges within the cavities; (2) the initiation of discharges resulting of a very thin layer of oxidation products; and (3) the formation of crystals having small dimensions leading to degradation by electrical tree. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 109: 789–794, 2008

Key words: dielectric properties; failure; polyurethanes

INTRODUCTION

Because of their excellent electrical and mechanical properties as well as their availability, the polymers play an important role as solid insulating materials in the electric devices (cables, transformers, generators, motors, etc.). However, during the functioning of these devices, these materials are subjected to several kinds of stresses (temperature, electric field, radiations, etc.) which can act separately or in combination. These stresses, especially the electrical ones, became more and more important because of the development of the electrical systems which require high voltages in service, leading to the degradation in time of these polymers and thence to failures. This degradation in time of the electrical properties up to the breakdown of materials is called ''aging phenomena.'' The aging of solid dielectrics is characterized by an irreversible deterioration affecting their performances and their lifetime. The aging phenomena are also influenced by the presence of defects which can be introduced when implementing the material and/or during the manufacturing of the systems despite all the precautions one can take. These youth defects are present in the form of cavities or unsticking. The formation and evolution of these cavities were described by Bartnikas and McMahon.[1] The application of voltage can induce an important enhancement of the electric field able to produce the ionization of gas contained within the cavities, resulting in the generation of partial discharges. These discharges constitute the main cause of erosion and thus contribute to the deterioration of the insulation, i.e., to the chemical modification of material and change of the electrical and mechanical properties. Numerous works have been devoted to analyze the mechanisms of degradation by partial discharges in solid insulating materials.[2–4] It was shown that the propagation of partial discharges can lead to the deterioration of the polymer by electrical tree.[5–8] The understanding of the degradation mechanisms is fundamental for the improvement of the existing materials or the conception and development of new materials enabling to ensure the reliability of the electrical devices for a long time, let be several tens of years.

This work presents an investigation of electrical aging of polyurethane under ac voltage using Weibull statistical analysis.

EXPERIMENTAL

The samples we tested are sheaths consisting of braid of glass fiber, serving as support, covered with a polyurethane layer of class F (155°C); such sheaths are used as insulating material in the electric motors. These samples, cut out starting from coils provided by Wilhelm Hartman Company, are 4 mm in diameter, 250 mm in length, and 0.5 mm in thickness. To avoid any presence of microscopic cracks which can be the seat of partial discharges, the samples are checked under a microscope before the tests.

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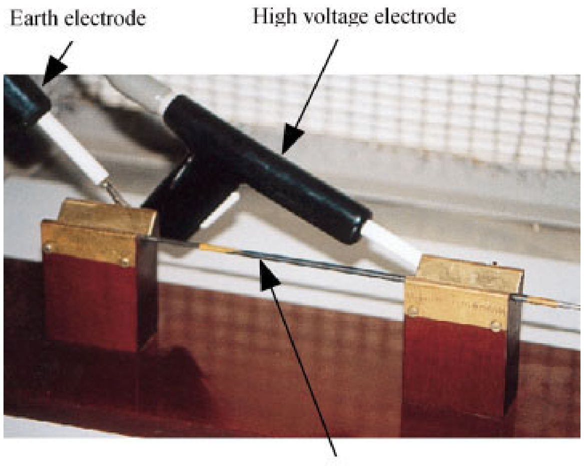

Figure 1 Photograph of experimental setup representing a polyurethane sample and the electrode connections. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

The experimental setup consists of a high voltage transformer (16 kV/50 Hz) and a support which can receive several samples, the whole being placed in a Faraday cage. A cylindrical stainless steel electrode of 500 mm length was used as a high voltage electrode. It was introduced inside each sheath. The external part of each sample was covered with a graphite layer over 200 mm length playing the role of earth electrode. The samples were deposited on a support consisting of two copper bars: the high voltage steel electrodes rest on the first bar and the layers of graphite are in contact with the earthed second bar (Fig. 1).

The tests were performed in air and at the ambient temperature on a population of 50 samples at the desired voltage. The cumulative time to breakdown is measured using a stop watch.

RESULTS AND DISCUSSION

Statistical analysis of time to breakdown

It is well known that the dielectric rupture is a random phenomenon.[9–11] Among the various statistics laws used to analyze the experimental data, the Weibull distribution[12] remains the most adapted for the dielectric rupture of solid insulating materials.[13,14] In the following we will use this kind of distribution. The cumulative probability, $P(t)$, generally used to treat the values of the time to breakdown, t, obtained from the life tests, is the two-parameter Weibull distribution. The latter is given by the mathematical expression[15]

$$P(t) = 1 - \exp\left[-\left(\frac{t}{\alpha}\right)^{\beta}\right] \tag{1}$$

where α is the scale parameter representing the time to breakdown for a probability of 63.2% and β is the shape parameter representing the slope of the straight line of Weibull plot.

The experimental data plot must be a straight line whose slope is β in the coordinate system:

$$X = \log t \tag{2}$$

and

$$Y = \log\left(\ln\frac{1}{1-P}\right) \tag{3}$$

where P is the cumulative breakdown probability.

The measured values of the time to breakdown were analyzed with the two-parameters Weibull distribution. The different steps of this method are as follows:

a. The values of the time to breakdown were classified by ascending order.
b. The cumulative breakdown probability P_i is calculated for each time t_i by using the relationship[16]

$$P_i = \frac{i}{N+1} 100\% \tag{4}$$

where N is the total number of tested samples and i is the value rank of time to breakdown t_i.
c. The experimental data ($\log t_i$, $\log(\ln 1/(1-P_i))$) were represented.
d. The best linear fit of Weibull plot was determined from the graph by an estimation based on the method of the maximum likelihood. Then both values of the scale parameter α and the shape parameter β were deduced.
e. The 90% confidence intervals were calculated by using the method described by Lawless for a Weibull distribution.[17,18] We consider the 90% confidence intervals where one takes a risk of 10% to see a spot outside belonging to the distribution.
f. The Weibull model was validated by the χ^2 test deduced from Pearson's law.[19] The principle of this test consists in testing the adjustment of an observed distribution with a theoretical distribution. Such a test was applied by Chauvet and Laurent when studying the electrical breakdown of polyethylene.[20] For that purpose, one first characterizes the distribution type of the time to breakdown by a series of N values (measures) by plotting the corresponding histogram, i.e., the distribution of the N values in k classes. Each class i of the histogram is characterized by the number of values of the time to breakdown

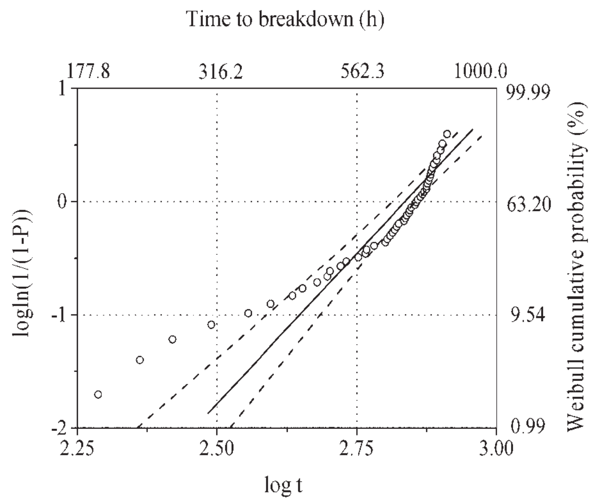

Figure 2 Weibull plot of the time data to breakdown with 90% confidence intervals at 1 kV: nominal time α (h): $650.780 < \alpha = 683.397 < 715.816$; shape parameter β: $4.242 < \beta = 5.299 < 6.256$.

N_i and the theoretical rupture probability in the center of the probability interval P_i. Thus, one calculates

$$\chi^2_{cal} = \sum_{i=1}^{i=k} \frac{(N_i - NP_i)^2}{NP_i} \tag{5}$$

Then one compares this value with $\chi^2_{v.a}$ given in tables on the χ^2 law in function of the freedom degree ν ($\nu = k - 1$) and the limit probability a (i.e., the risk).

Finally, one chooses a limit of the risk equal to 5% that one runs to refuse the hypothesis whereas it is true. In the field of reliability, the risk is normally included between 1 and 5%. The decision criterion is such as:

if $\chi^2_{cal} > \chi^2_{v.a}$, the hypothesis on the model is inferred; and
if $\chi^2_{cal} < \chi^2_{v.a}$, the hypothesis on the model is not inferred.

The different steps (i.e., from the classification of data by ascending order up to the calculation of χ^2_{cal}) were executed using a computer program developed by ''Laboratoire de Génie Electrique de Toulouse'' Group.[19,20]

Thus, one can plot the Weibull diagrams of the time to breakdown corresponding to different applied voltages as indicated in Figures 2–11. We observe that depending on the voltage, the data can be partly or totally inside the tolerance intervals we indicated by discontinuous straight lines. The values of the shape parameter vary from a distribution to another one and the width of the tolerance intervals is more important for the lower probabilities. The results of χ^2 test show that this latter is favorable (Table I).

Lifetime characteristic

The lifetime of solid insulating materials is determined from the endurance tests executed for long times of voltage application. By plotting the *V-t* characteristic giving the evolution of the applied voltage versus the time to breakdown in log–log scales, one can deduce the type of degradation of polymer (aging) according to the most used model namely the inverse power model. The latter is given by the relationship[21]

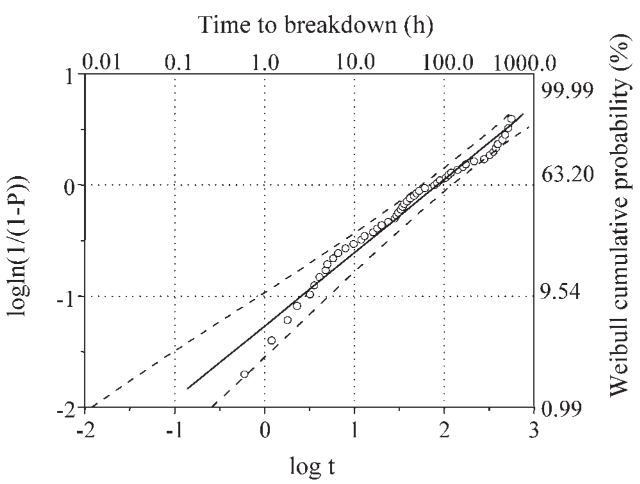

Figure 3 Weibull plot of the time data to breakdown with 90% confidence intervals at 1.2 kV: nominal time α (h): $56.500 < \alpha = 83.662 < 121.380$; shape parameter β: $0.528 < \beta = 0.668 < 0.779$.

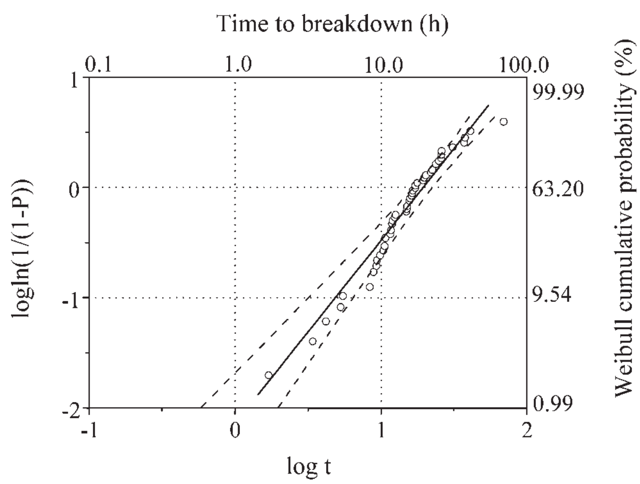

Figure 4 Weibull plot of the time data to breakdown with 90% confidence intervals at 1.5 kV: nominal time α (h): $16.653 < \alpha = 19.460 < 22.558$; shape parameter β: $1.331 < \beta = 1.663 < 1.963$.

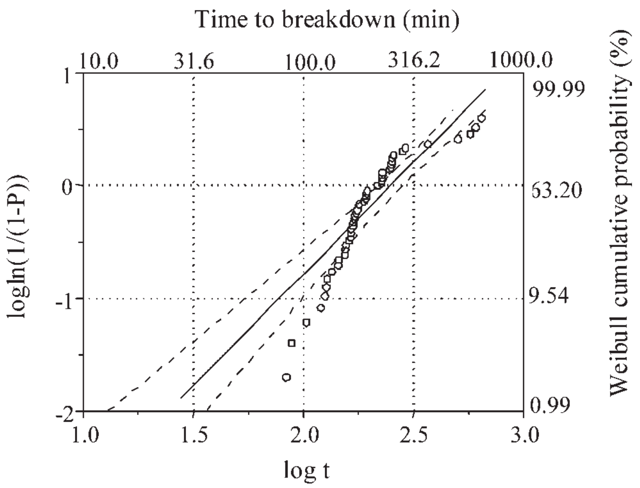

Figure 5 Weibull plot of the time data to breakdown with 90% confidence intervals at 2 kV: nominal time α (min): 219.870 < α = 250.64 < 283.783; shape parameter β: 1.584 < β = 1.978 < 2.335.

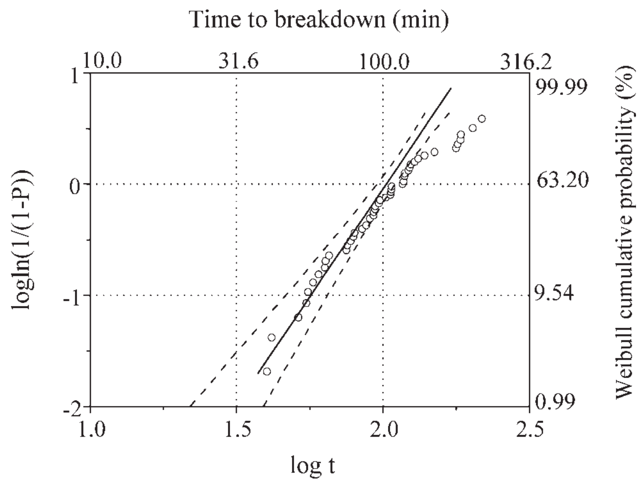

Figure 7 Weibull plot of the time data to breakdown with 90% confidence intervals at 3 kV: nominal time α (min): 95.493 < α = 102.63 < 110.178; shape parameter β: 3.045 < β = 3.890 < 4.651.

$$V^n t = k \tag{6}$$

and then

$$\log V = -\frac{1}{n}\log t + \frac{1}{n}\log k = -\frac{1}{n}\log t + k' \tag{7}$$

where t is the lifetime, V is the applied voltage, k and then k' are constants; and n is the voltage endurance constant which depends on the type of material. n is an indication of the insulation quality.

This model suppose that the lifetime curve can be approached by straight lines. Thus the slope of these latter will be equal to $(-1/n)$. Figure 12 represents the evolution of the applied voltage versus the nominal time to breakdown (63.2%) in a double logarithmic scale. We observe that this curve includes three segments of straight line (zones) where the segments 1 and 2 intersect at the point (t = 1.5 h, V = 3.5 kV) while segments 2 and 3 intersect at the point (t = 4 h, V = 2 kV). As expected, the time to breakdown is all the more important as the applied voltage is weak. Each observed zone corresponds to a given type of aging:

Zone I, characterized by n = 15.96, corresponds to the defects of youth or manufacturing which quickly occur, just after the voltage is applied. The size of these defects of extrinsic type plays a significant role. An extrinsic defect would be, for example, an impurity of abnormal size present within the dielectric. Such a statistical batch of samples with defects of big size can result of a no appropriate technology, a bad quality of basic ingredients of polymer and

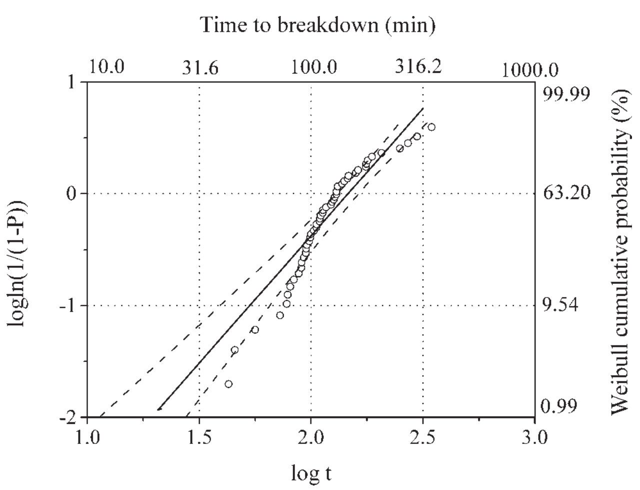

Figure 6 Weibull plot of the time data to breakdown with 90% confidence intervals at 2.5 kV: nominal time α (min): 130.688 < α = 146.43 < 163.103; shape parameter β: 1.824 < β = 2.278 < 2.690.

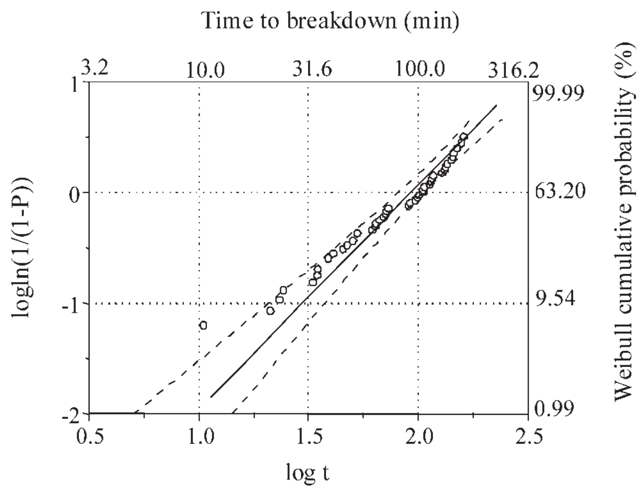

Figure 8 Weibull plot of the time data to breakdown with 90% confidence intervals at 3.5 kV: nominal time α (min): 81.196 < α = 92.74 < 105.209; shape parameter β: 1.611 < β = 2.020 < 2.388.

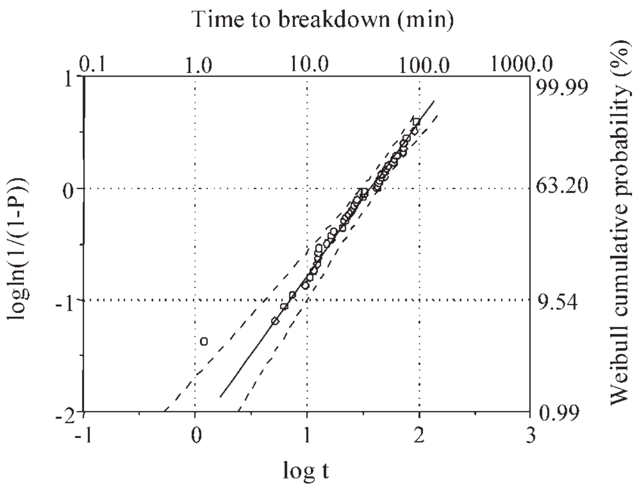

Figure 9 Weibull plot of the time data to breakdown with 90% confidence intervals at 4 kV: nominal time α (min): 5.249 < α = 7.036 < 9.290; shape parameter β: 0.708 < β = 0.884 < 1.044.

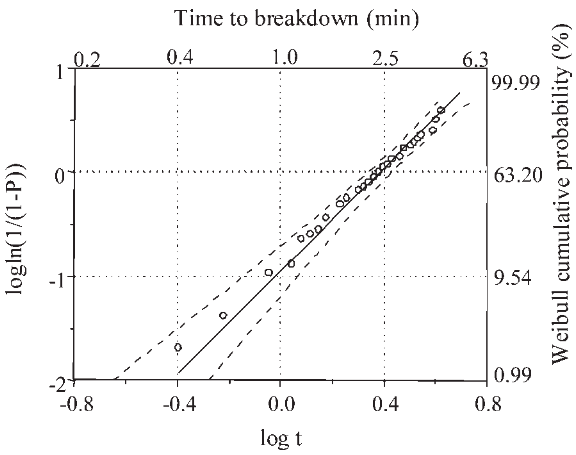

Figure 11 Weibull plot of the time data to breakdown with 90% confidence intervals at 4.5 kV: nominal time α (min): 2.193 < α = 2.435 < 2.699; shape parameter β: 1.967 < β = 2.470 < 2.926.

damages induced by mechanical stresses. In this zone, the lifetime equation can be written as

$$t = (800.45 \times 10^6)V^{-15.96} \tag{8}$$

Zone II, corresponding to $n = 1.66$, represents a statistical dispersion of the intrinsic defects of material. An intrinsic defect could be a micro-cavity because of a lack of control during the polymerization or to an interrupted reticulation during the crystallization process. Also impurities can be accidentally injected into the dielectric during the operation of extrusion. This class of defects corresponds to the micro-defects. In this case, the curve of electrical endurance is expressed, according to eq. (5), by

$$t = 12.21\ V^{-1.66} \tag{9}$$

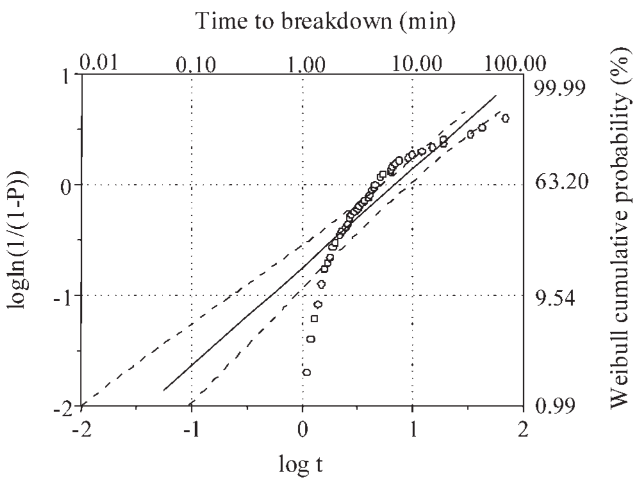

Figure 10 Weibull plot of the time data to breakdown with 90% confidence intervals at 3.8 kV: nominal time α (min): 30.721 < α = 37.31 < 44.865; shape parameter β: 1.102 < β = 1.382 < 1.634.

Zone III, for which n is equal to 7.34, expresses the real aging of the material. When the material is submitted to a prolonged action of the electric field, some of its physicochemical properties change in time leading to appearance of new defects and thence to the degradation of the dielectric strength of polymer. In that case, the electric characteristic of endurance can be written, according to eq. (5), as

$$t = 582\ V^{-7.34} \tag{10}$$

The passage from one zone to another one corresponds to a change in the mechanisms of degradation; each type of degradation is characterized by a given value of *n*. Note that the aging of polyurethane is characterized by a gaseous emission as well as a matter deposit on the steel electrode which was cleaned after each test. The presence of three and even four zones has been also observed elsewhere for other polymers.[22]

It appears from the above that the degradation mechanism of polyurethane is achieved according to three stages similarly as in other materials[23]:

TABLE I
Results of χ^2 Test

Voltage (kV)	χ^2_{cal}	$\chi^2_{v,a}$	Results
1	5.85	9.49	Favorable
1.2	6.15	9.49	Favorable
1.5	7.10	9.49	Favorable
2	9.30	9.49	Favorable
2.5	7.50	9.49	Favorable
3	0.53	9.49	Favorable
3.5	7.03	9.49	Favorable
3.8	7.12	9.49	Favorable
4	7.32	9.49	Favorable
4.5	0.823	9.49	Favorable

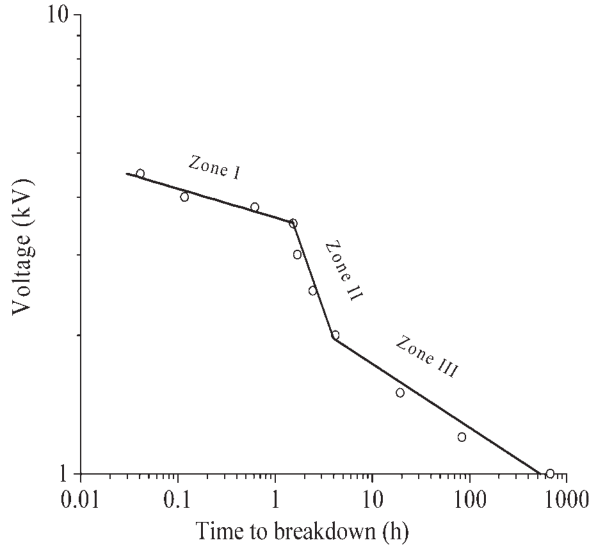

Figure 12 *V-t* characteristic of polyurethane.

1. During the first stage, very fast discharges occur within a cavity that is known as streamer-like discharges.
2. In the second stage, the discharge mechanism changes. This change is caused by a very thin layer of oxidation-products resulting from the attack of the discharge at the dielectric surface. This surface gets a substantially lower resistivity and contains appreciably more electrons in shallow traps, so that electron avalanches within the cavity can easier be formed. When this layer has been formed the discharge mechanism changes into a slower type which is known as a Townsend-like mechanism.
3. During the third stage, there is a formation of crystals. The discharges now concentrate within cavities at some of these crystals and get a character resembling to corona-discharges. At the spots where these discharges concentrate, a severe deterioration of the dielectric occurs. After some time, the discharges concentrate more and more on a few spots resulting in a severe deterioration of material and to the initiation of an electrical tree at one of these spots leading to breakdown. The increase in the number and the dimension of cavities has been also reported by Dissado and Fothergill.[13] The action of the partial discharges can lead to breakdown only if the dimension of the cavities is at least equal to 0.1 mm.[24]

CONCLUSIONS

This work shows that the time to breakdown characteristic (*V-t*) of polyurethane presents three zones corresponding, respectively, to the youth defects, the statistical dispersion of the intrinsic defects, and the real aging of the polymer. Each zone is characterized by a given value of the voltage endurance closely related to the type of polymer decomposition. This characteristic presents two angular points representing changes in the process of degradation; the latter is governed by the action of partial discharges. The mechanism of degradation is achieved according to three stages: (1) the first one is characterized by very fast discharges occurring within the cavities; (2) during the second one, the mechanism of the discharges is due to a very thin layer of oxidation products resulting of the attack of discharges at the surface of the dielectric material; and (3) the third one is characterized by the formation of crystals and the concentration of discharges within cavities at some of these crystals resulting in the initiation of electrical tree leading to a breakdown. The degradation of polymer is followed by a gas emission.

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