

Investigations of Surface Degradation of High-Density Polyethylene Materials Resulting from Tracking, Using Physicochemical Analysis

R. SARATHI

Department of Electrical Engineering, Indian Institute of Technology Madras, Chennai-36, India

Received 23 April 2001; accepted 11 July 2001

ABSTRACT: In the present work tracking phenomena were studied with high-density polyethylene (HDPE) materials under dc voltage, with NH_4Cl and acid rain as contaminants. It was determined that the tracking time of the material depends on the conductivity and flow rate of the contaminant. Furthermore, physicochemical analysis by wide-angle X-ray diffraction studies, differential scanning calorimetry, and luminescence spectroscopy was carried out, whereupon it was concluded that the tracking process is a surface-degradation process. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 83: 2843–2849, 2002; DOI 10.1002/app.10260

Key words: polyethylene; tracking; surface degradation; acid rain; WAXD; DSC; luminescence spectra

INTRODUCTION

Polymers are now becoming the outdoor insulation material of choice because of their better dielectric properties and because they are lightweight and cost effective compared to porcelain insulators. Based on the performance of insulator analyzed by various means, it has been determined that most of the failure of outdoor insulation structures is the result of *tracking*,¹ a peculiar phenomenon that occurs on the surface of the insulation structure as a result of the creepage discharge from surface contamination. It varies with surface field intensity, surface current magnitude, and the state of discharge thereby induced, all of which are attributed to surface wetting and the degree of contamination. Once tracking occurs, the surface electrical insulation

property is lost completely and never recovers. To improve the reliability and performance of insulation material, the tracking phenomenon is being investigated worldwide in severe pollution conditions like acid rain.

Most of the tracking studies reported in the literature, carried out in different polymeric insulation materials, are under ac voltage.^{1,2} With the advancement of the dc power transmission system, it has become necessary to understand the tracking phenomenon, in insulation structures, under dc voltage. Polyethylene is widely used in cable insulation and as an outer jacket to all dielectric self-supporting (ADSS) optical-fiber cables worldwide.³ The uptake of water in bulk of the insulation wrapping the cable is affected by the hydrophobicity of the exterior surface. The presence of water in insulation leads to the formation of the water/electrical trees and might result in eventual failure of cables. The unaged surface of the polyethylene material is usually hydrophobic and therefore resists the formation of a continuous film of water on the surface. Un-

Correspondence to: R. Sarathi (rsarathi@mailcity.com)

Journal of Applied Polymer Science, Vol. 83, 2843–2849 (2002)
© 2002 John Wiley & Sons, Inc.

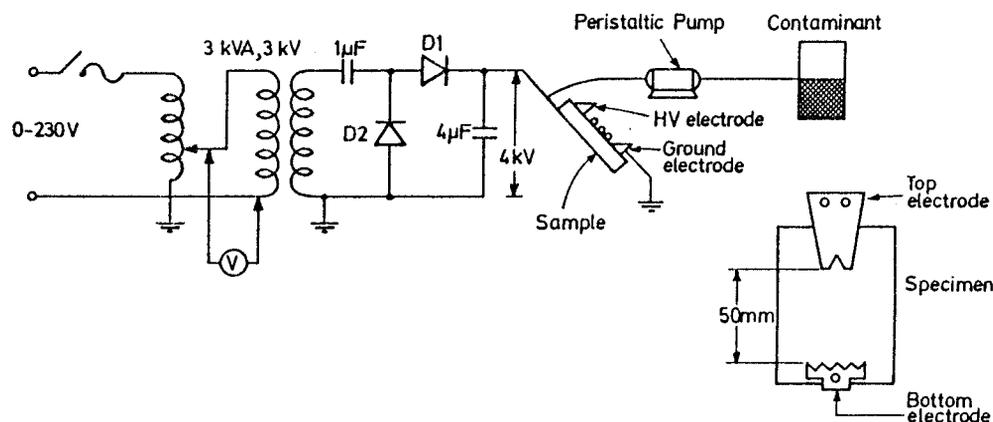


Figure 1 Experimental setup.

der wet or humid conditions and in the presence of pollutants, a gradual loss of hydrophobicity occurs, which is accelerated at higher temperatures. The formation of a continuous film of water on the surface results in the formation of leakage current followed by dry-band arcing and tracking activity on the surface, and thereby most of the optical-fiber cable envelop gets damaged because of tracking.³ Hence, there is a need for reducing the damage of the insulation material that results from tracking.

Armed with this knowledge, in the present work more care was taken to understand the tracking phenomenon in high-density polyethylene (HDPE) material (the most preferred insulation for dc voltages), by carrying out the experiment according to IEC-587,⁴ under dc voltage, with contaminants like NH_4Cl and acid rain. The influence of tracking resulting from conductivity of the contaminant and by the flow rate of the contaminant was thoroughly investigated in the present study. Mechanisms of failure attributed to tracking under dc voltages are discussed. In addition, certain physicochemical analyses, by wide-angle X-ray diffraction (WAXD), differential scanning calorimetry (DSC), and luminescence spectroscopy, were carried out to support the conclusion that the tracking process is a surface-degradation process.

EXPERIMENTAL

At the present time there is a lack of standardized test procedures to understand the behavior of polymeric insulators.⁵ Also, there is no regular test procedure to carry out a tracking test under

the dc voltage application. In the present work, the tracking test was carried out following the IEC-587 (1984) test method, which was adapted for ac voltage application.⁴ The specimen used in the present work was commercially available HDPE sheet material of 4 mm thickness. The gap distance between the top and the bottom electrode was adjusted to be 50 mm. The schematic diagram of the experimental setup and the electrode configuration used in the present work are shown in Figure 1. NH_4Cl (0.1%) and acid rain solutions were used as contaminants in the present study. The different flow rates were obtained using the control of the peristaltic pump (MICLINS pp10, India). The dc voltage (4 kV) was connected to the top electrode and the bottom electrode was solidly grounded. The tracking time was defined as the time taken by the arc to cross two-thirds of the gap (between bottom and the top electrode), from the time of application of voltage. If this time exceeds 6 h, the later duration is taken as the tracking time. The pH value of the acid rain was measured using a Digital pH meter Model DI-707 (Digital Instruments, Santa Barbara, CA) and the conductivity measured using Lutron CD-4302.

Characteristics of Acid Rain

The important characteristics of acid rain are ion ingredients, pH value, and conductivity. To understand the influence of acid rain on the performance of polymeric material, artificial acid rain was prepared in the laboratory. The investigation carried out by the Meteorology Bureau of Japan⁶ identified SO_4^{2-} , NO_3^- , Cl^- , NH_4^+ , Ca^{2+} , K^+ , Mg^{2+} , and Na^+ as the constituents of acid rain. The

composition of artificial acid rain, as shown in Table I, agrees with that of actual acid rain.⁷ The pH value of artificial acid rain is 2.0 and its conductivity was adjusted to the required value.

Physicochemical Analysis

Wide-Angle X-ray Diffraction (WAXD)

In the present work, WAXD measurement was determined by a Phillips X-ray diffractometer. A scan rate of 2°/min at 2000 cycles using Cu-K α radiation of wavelength 1.596 Å was applied. A radial scan of Bragg angle (2 θ) versus intensity was obtained with an accuracy of $\pm 0.25^\circ$ at the location of the peak.

Differential Scanning Calorimetry (DSC)

The melting behavior of the specimen was observed using Perkin-Elmer Model DSC 2C apparatus (Perkin Elmer Cetus Instruments, Norwalk, CT). The experiments were performed in a nitrogen atmosphere, at a heating rate of 10°C. Indium metal was used as the standard.

Luminescence Spectroscopy

Luminescence analysis was undertaken using a Hitachi-F4500 Spectro fluorimeter (Hitachi, Tokyo, Japan). Fluorescence spectra were obtained at ambient conditions.

The Tracking Process

Tracking is a surface-degradation phenomenon that occurs when the contaminants collect on the surface of an insulation material. When high voltage is connected to the top electrode, leakage current flows in the conductive path formed by the contaminant (between top and bottom electrode). This leakage current causes nonuniform heating of the surface, thereby forming a dry-band zone in the continuous wet film formed by the contami-

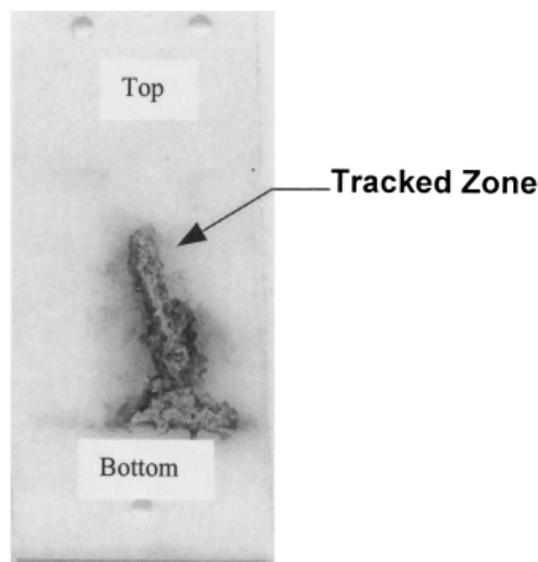


Figure 2 Tracking formed zone.

nant flow, resulting in regions of very high resistivity between the edges of the remaining wet film surface. Nearly the entire surface voltage (the applied voltage) will appear across the dry band, causing sparking across the dry band. The continuous flow of contaminant in the gap rewets the surface and the above process is repeated. The spark across the dry band results in a slow rise of surface temperature and gradual heating of the specimen. Kim et al.⁸ explained that dry-band arcing accelerates the loss of hydrophobicity and degrades the surface of the insulation material.

The high temperature of the arc in the gap as well as the high temperature attributed to the possible reaction of NH₄Cl/acid rain with the polymeric material are considered to be responsible for erosion of material followed by the tracking process. Sometimes the arc burning across the gap is extinguished by the flow of contaminants and the entire process detailed above restarts. However, over a period of time, accumulation of the contaminants in the gap permits more current to flow in the conductive path formed by the contaminant at the same applied voltage. Therefore, the entire process is accelerated so that heavy burning takes place between the electrodes, causing a carbonized path, as shown in Figure 2. This phase is identified as *failure resulting from tracking*.

RESULTS AND DISCUSSION

Figure 3 shows the variation in tracking time in HDPE material with different contaminants and

Table I Ingredients of Artificial Acid Rain Used in This Experiment (in g/2 L)

NH ₄ Cl	1.0
NaCl	2.55
KCl	0.18
MgSO ₄	1.05
CaSO ₄ · 2H ₂ O	0.90
Triton X-100	0.40
HNO ₃	0.90

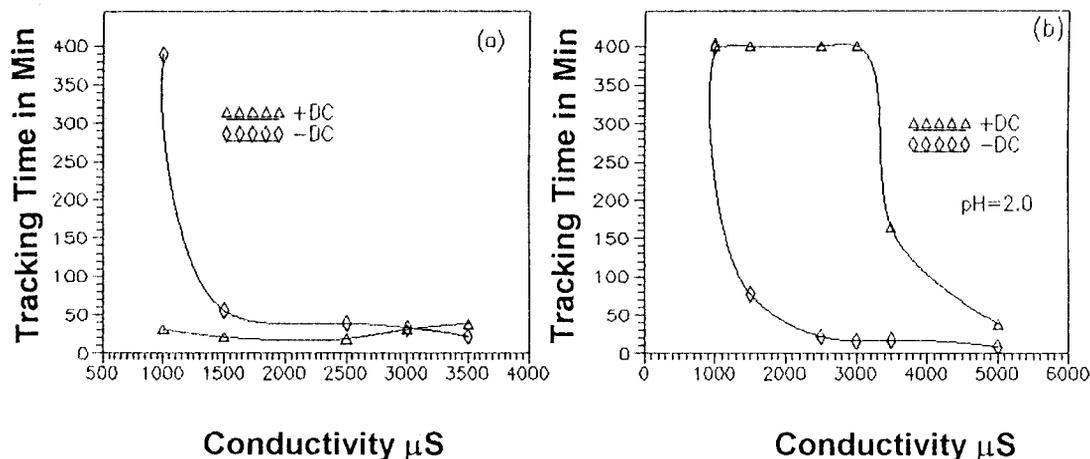


Figure 3 Variation in tracking time of HDPE material with contaminant of different rates of conductivity under dc voltages: (a) NH_4Cl ; (b) acid rain.

different rates of conductivity, under dc voltage. It is observed that, with NH_4Cl contaminant, the tracking time is less when the positive dc voltage is connected to the top electrode; this phenomenon is just opposite when the acid rain is used as contaminant. When the positive dc voltage is applied, the ion ingredients in the acid rain alter the magnitude of the leakage current flow in the surface. At lower conductivity of the acid rain, the leakage current may be too low to cause dry-band formation, arcing, and degradation of the surface of the insulation materials, thereby leading to high tracking time. It is also observed that the higher the conductivity of the contaminant, the lesser the tracking time of the specimen, irrespective of the type of polarity of the applied dc voltage. The study of tracking phenomena in epoxy resin material was carried out by Sarathi et al.,⁹ who determined that the tracking time is less under negative dc voltage at lower conductivity of the contaminant, a result that indicated that the tracking phenomenon is material dependent and influenced by the conductivity level of the contaminant. Mason et al.¹⁰ observed that the tracking inception stress is less under the positive dc voltage, the cause of which is attributed to the direction of the flow of the contaminant; these investigators explained that the positive electrode suffers from electrolyte corrosion. Hence, when the top electrode is connected to positive dc voltage, the ionic products are injected with the flowing contaminants. The additional ions can cause increased conduction, so that the dry band and intense discharges occur, leading to reduced tracking time under positive dc voltage.

Figure 4 shows the variation in the tracking time in the HDPE material, with different contaminants (of conductivity 2500 μS), with different flow rates, under dc voltage. It is observed that an increase in the flow rate of the NH_4Cl contaminant shows an increase in tracking time and, above a certain limit, a reduction in tracking time. The increase in tracking time up to a certain flow rate is ascribed to nonavailability of the contaminant in the gap to enhance the tracking process. With the acid rain as contaminant and an increase in flow rate of the contaminant, positive dc voltage does not show any variation in the tracking time, whereas under the negative dc voltage a marginal increase in time was observed. Thus, an optimized flow rate has to be identified for each contaminant, which is then used for the tracking study.

The WAXD spectrum was obtained for a virgin specimen and tracking formed zone of the HDPE specimen. Because the WAXD patterns of the tracking formed zone are formally similar to virgin samples, for brevity, only the virgin HDPE specimen spectrum is shown in Figure 5. Agarwal et al.¹¹ obtained the spectra of polyethylene showing peaks at 21.5 and 23.9°, which are the characteristics of 110 and 220 lattice planes, respectively. Similar characteristic spectra were obtained in the present work, with a shift in peak position of 0.5°. These features ought to be studied in detail. The main observation in the present work is that the WAXD obtained for the virgin and surface tracked region do not show any change in position of peaks or their splitting of peaks throughout the scan range, which indicates

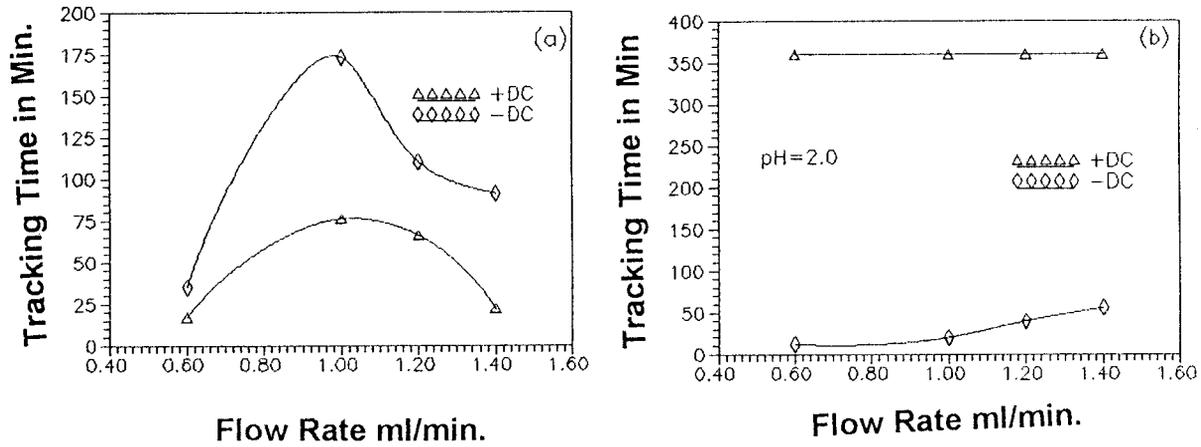


Figure 4 Variation in tracking time of HDPE material on the flow rate of contaminant under dc voltages: (a) NH_4Cl ; (b) acid rain.

that there is hardly any change (maximum of 5%) of crystallinity and no new phases are introduced in the specimen.

DSC is a measurement technique that records the energy necessary to establish a zero temperature difference between a specimen and a reference material, when two specimens are subjected to identical thermal conditions in an environment heated or cooled at a predetermined controlled rate. Figure 6 shows the DSC thermogram of HDPE

(virgin and tracking formed zone) material. The curve shows the exothermic change when heated between 30 and 300°C at 10°C/min. The peak temperature of the exothermic reaction of the virgin HDPE material is 132.3°C and, under identical conditions for the tracking formed zone material, has a peak temperature of 129.6°C with a shoulder peak at the rising part, thus confirming that the thermal characteristics of the material are altered.

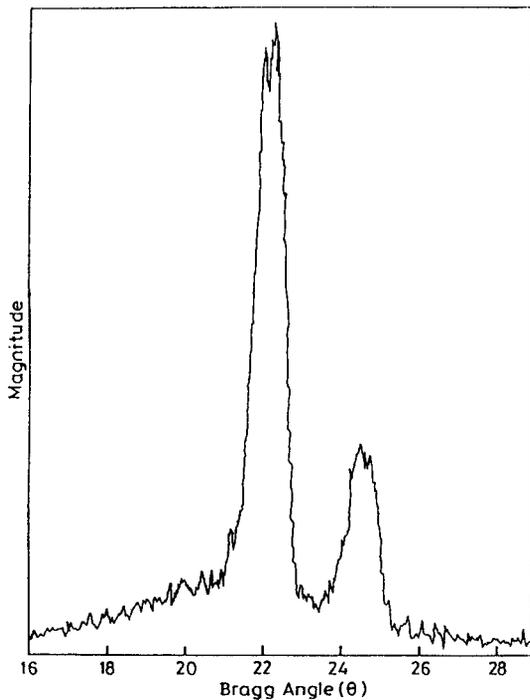


Figure 5 WAXD pattern of HDPE material.

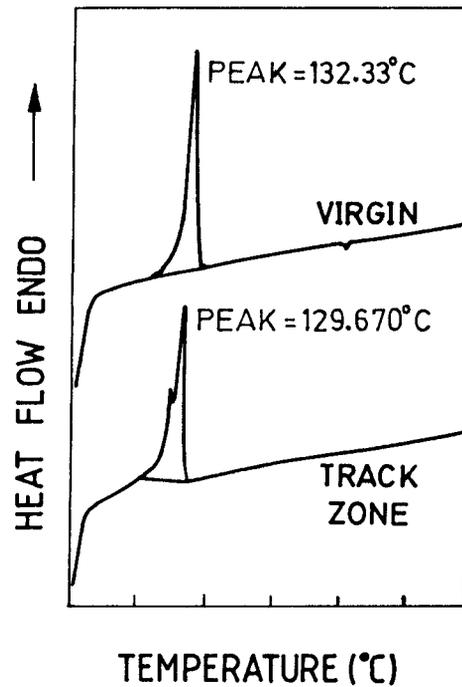


Figure 6 DSC thermogram of HDPE (virgin and tracking formed zone) material.

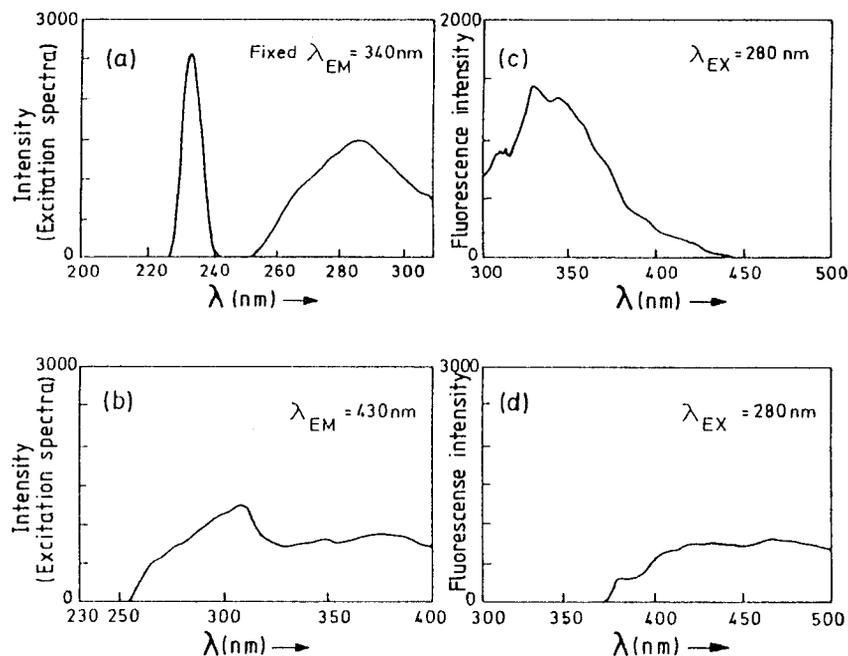


Figure 7 Luminescence spectra of HDPE material.

Figures 7(a)–7(d) show fluorescence excitation and emission spectra of HDPE material and the microtomed section of the tracking formed zone of the HDPE material. The fluorescence analysis of polyolefins now has been considered to be associated with the presence of a low level of cyclic $\alpha\beta$ -unsaturated carbonyl compounds of the enone and enal types.¹² The excitation spectra shown in Figure 7(a) were taken by exciting the emission grating at 340-nm emission band of the fluorescence emission spectra. It exhibits strong intense peaks at 230 and 285 nm. Similar characteristics were observed by Allen et al.¹² for the HDPE material. Studies were carried out with the microtomed section of the tracking formed zone material, under identical conditions, and it was confirmed that no characteristic peaks are exhibited as in the case of HDPE material, which provides clear evidence for the altered surface of the tracking zone material. Figure 7(b) shows the excitation spectra recorded for the tracking formed zone by placing the emission grating at 430 nm. Figures 7(c) and 7(d) show the emission spectra obtained for HDPE material and the tracking formed zone material, respectively. The emission spectra are different for the HDPE material and the tracking formed zone material. The characteristic peaks are observed at 330 and 344 nm for the HDPE material and, in the case of tracking formed zone material, peaks at 430 and 465 nm

are observed. This variation indicates that the tracking phenomena constitute a surface-degradation process. The increase of wavelength in the tracking zone material indicates the formation of other active species, although further detailed study is required to identify the kind of active species.

CONCLUSIONS

Positive dc voltage has a lower tracking time compared with that of negative dc voltage in the presence NH_4Cl as contaminant. The tendency is reversed with acid rain as the contaminant. An increase in flow rate of the contaminant (acid rain) shows an increase in tracking time under negative dc voltage and it is constant under positive dc voltage. With NH_4Cl contaminant, an increase in flow rate shows an increase in tracking time and, after a certain limit, a reduction in tracking time is observed.

The WAXD studies indicate that no new phase occurs in the material as a result of the tracking process. The DSC result indicates a change in melting point of the material near the tracking formed zone. In the excitation spectra, the absence of the characteristic peaks of the HDPE material at both 230 and 285 nm in the tracking formed zone material provides clear evidence for

the altered surface resulting from tracking. The fluorescence emission spectra indicate that the increase in wavelength is attributable to some active components formed in the tracking formed zone.

REFERENCES

1. Yoshimura, N.; Kumagai, S.; Du, B. *IEEE Electrical Insulation Magazine* 1997, 8.
2. Gorur, R. S.; Motesinos, J.; Vardadesikan, L.; Simmons, S.; Shah, M. *IEEE Trans Dielectrics Electrical Insulation* 1997, 4, 767.
3. Kaidanov, F.; Munteanu, R.; Sheinfain, G. *IEEE Electrical Insulation Magazine* 2000, 16.
4. IEC Publication 587. Test method for evaluating the resistance to tracking and erosion of electrical insulating materials used under severe ambient conditions, 1984.
5. Danikas, M. G. *Acta Electrotechnica Napocensis* 1999, 40, 3.
6. The Meteorology Bureau of Japan. Report of the second investigation of acid rain, Acid Rain Seminar, Tokyo, Japan, 1994.
7. Hasegawa, S.; Kumagai, S.; Wang, X.; Kobayashi, K.; Yoshimura, N. in *Proceedings of the 5th International Conference on Properties and Applications of Dielectric Materials*, Seoul, Korea, 1997; pp 754–758.
8. Kim, S. H.; Cherney, E. A.; Hackam, R. *IEEE Trans Power Delivery* 1991, 6, 1549.
9. Sarathi, R.; Sudhakar, K. in *Recent Advances in Polymers and Composites*; Mathur, G. N.; Kandpal, L. D.; Sen, A. K., Eds.; Allied Publishers: London, 2000; pp 612–616.
10. Mason, J. H.; Gleizer, H.; Sens, M. A.; Ian, A. L. Presented at Fifth International Symposium on High Voltage Engineering, Braunschweig, Germany, 1987; Paper No. 52.02.
11. Agarwal, S. L.; Tilley, G. P. *J Polym Sci* 1955, 18, 17.
12. Allen, A. S.; Edge, M.; Holdsworth, D.; Rahman, A.; Catalina, F.; Fontan, E.; Escalano, A. M.; Sibon, F. F. *Polym Degrad Stab* 2000, 67, 57.