

Effect of an Epoxy Additive on the Electrical Aging of Impregnated Polypropylene Films

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SYNOPSIS

The lifetime of HV capacitors is drastically enhanced when epoxides are added to the liquid impregnant of the polypropylene films. The aim of this work was to understand the mechanism of action of such an additive. Aging of the dielectric was performed at a high AC field [135 MV/m]. The liquid impregnant, pure benzyltoluene or benzyltoluene with specially selected additives, was saturated with O₂ in order to accelerate PP aging. The degradation of the polypropylene films has been evaluated by the variation of their mean breakdown voltage and by FTIR microspectroscopy. The liquid impregnant has been characterized by gas chromatography. Our results show that the electrical stress enhances an oxidative degradation mechanism of the polymer and the liquid. Epoxides with two or more epoxy groups per molecule and other monomers of two or three functionalities inhibit this degradation. In the presence of such additives, electrical aging leads to the formation of a crosslinked polymeric deposit on the electrodes and the films. We attribute the good behavior of these components, and especially of epoxides in HV capacitors, to their ability to polymerize under an electrical stress and to form a protective layer that further prevents degradation. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

In power capacitors, polypropylene (PP) impregnated with an aromatic hydrocarbon withstands severe electrical, mechanical, and thermal stresses.^{1,2} Failure of these capacitors are observed and attributed to a local degradation of the insulating properties of the PP film. Our previous work on the aging of impregnated PP films submitted to a high AC electric field has shown that the electrical degradation is very similar to an oxidative one and leads to the decrease of the breakdown voltage of the polymeric films.³ The initiation step of the degradation has been attributed to the electrical stress because degradation was observed only in the electrically stressed part of the film.⁴ Radicals or ions must be created by electron exchange reactions at the electrodes. The nature of these species, the rate of their formation, and their reactivity depend

mainly on the nature and composition of the impregnant. Specific solvent effects such as their stabilization or preferential reactions with solvent molecules may also occur.⁵

Some additives to the impregnant of PP in capacitors modify this degradation process. Indeed, epoxy additives such as diglycidyl ether of bisphenol A (DGEBA) enhance the lifetime of industrial capacitors.^{6,7} We have shown that it highly increases the resistance to the degradation of the insulating materials in capacitor models;⁴ but how these epoxides operate remains unknown. When the impregnant was a polychlorinated fluid (PCB), the additive was supposed to fix the hydrochloric acid formed by ionization processes and thus to avoid the chemical attack of the dielectric and the metallic foils of the capacitors.⁸ But these additives have the same beneficial effect in capacitors impregnated with non-chlorinated liquids. This experimental observation brings up questions. First, does the epoxy group react with carboxylic acids produced by oxidation? Does it operate as an antioxidant? When ionization occurs in a capacitor, have epoxy additives any influence?

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May the epoxides undergo a polymerization or copolymerization initiated by the species produced by charge injection from the electrodes into the liquid? Indeed, graft copolymerizations of monomers onto isotactic PP induced by γ -rays or radicals (peroxides) are well known^{9,10} as well as electroinitiated polymerization of numerous monomers.¹¹⁻¹⁴ It has also been found that polyfunctional monomers are cross-linking coagents of PP.¹⁵ In a previous work we noticed that the resistance to electrical degradation of PP films was improved by the addition to the impregnant of $2 \times 10^{-2} M$ of trimethylolpropane triacrylate, a monomer of three functionalities.¹⁶

In order to clarify the role of DGEBA in HV capacitors, we have studied the influence of different monomers added to the impregnant on the degradation of PP films under high AC fields.

This article presents breakdown voltage measurements and an infrared spectroscopy analysis on aged PP films impregnated with Benzyltoluene (BT). First, we elucidate the degradation mechanism of the dielectric without additives, then we compare the stabilization effect of DGEBA, an epoxide with two epoxy groups per molecule, to that of Epoxystyrene (ES), an epoxide of only one epoxy group per molecule, and of Divinylbenzene (DVB), a monomer of two functionalities.

EXPERIMENTAL

The capacitor model consisted of impregnated PP films sandwiched between two aluminum electrodes, 8 mm in diameter (Fig. 1). The electrodes were carefully polished in order to eliminate as much as possible bumps and the resulting electric field enhancement. Their rounded edge had a curvature radius of about 200 μm . The electrodes were pushed by springs onto the polymer sheets (applied pressure = 0.2 MPa).

The PTFE cell contained 5 mL benzyltoluene (BT) introduced into the cell under vacuum.

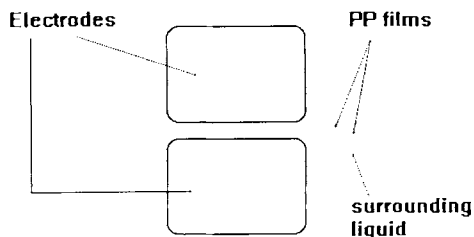
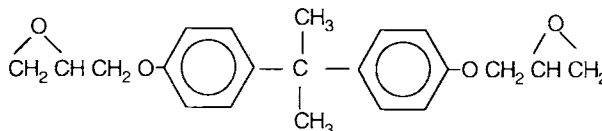


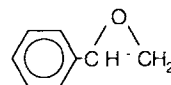
Figure 1 Schematic view of the aging cell.

BT was obtained after two distillations of a commercial blend (M/DBT) consisting mainly of monobenzyltoluene (BT), dibenzyltoluene (DBT), and tri-benzyltoluene (TBT).⁷ The purity of BT was checked by gas chromatography. The relative permittivity of BT is $\epsilon_r = 2.4$, its resistivity was $\rho = 2 \times 10^{12} \Omega\text{m}$, and its water content was about 50 ppm. The additives

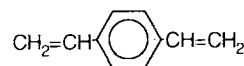
Diglycidyl ether of Bisphenol A (DGEBA),
(2 epoxy groups/molecule)



Epoxystyrene (ES), (1 epoxy group/molecule)



Divinylbenzene (DVB), (2 vinyl groups/molecule)



were of industrial grade and DVB was a mixture of isomers especially *m*- and *p*-DVB. Their concentration in BT was in the range $3 \times 10^{-2} M$ to $2 \times 10^{-1} M$.

Polymer films contained 95% isotactic PP. They were impregnated at 80°C under a static vacuum before introduction in the capacitor. The mass percent of absorbed BT in PP measured by FTIR was about $8 \pm 1\%$. For the aging studies, we used 13.6 μm thick PP films, the thickness being determined from the weight of a given surface of the film and the PP density. Its average thickness deduced from the thickness of 15 stacked films at 100 kPa pressure was 15 μm .

Aging was performed at different AC voltages, 80°C and with a 0.15 MPa O_2 pressure over the impregnating liquid. For these conditions, aging was seriously accelerated.

For breakdown voltage measurements we aged in the capacitor models two rough 13.6 μm thick PP films such as those used in industrial capacitors. The PP breakdown voltage was successively measured on both films extracted from the aged capacitors, with a DC voltage ramp (500 V/s) between a plane electrode and a stainless steel sphere, 2 mm in diameter. The whole was immersed in BT to avoid discharges before the film broke down.⁴ More than

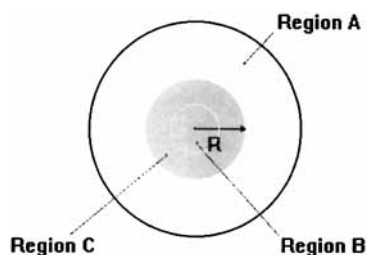


Figure 2 Aged PP film. The gray region corresponds to the part of the film aged between the electrodes.

50 measurements were performed on each film. These measurements were separated in three groups: a group corresponding to measurements on the part of the film outside the electrodes during aging (region A) and two other groups corresponding to the electrically aged part of the film: $x < R/2$ (region B) and $R/2 < x < R$ (region C), R being the electrodes radius and x the distance from the electrode axis (Fig. 2).

For the spectroscopic studies, in order to avoid the interferences in the IR spectra observed with thin samples, we aged 60 or 100 μm thick PP films at 100 $\text{MV}_{\text{rms}}/\text{m}$. Then the films were analyzed with a Nicolet FTIR spectrometer in combination with an IR-Plan Spectra-Tech microscope with a MCT detector. A two- or three-dimensional map for functional group imaging can be obtained with a computer-controlled mapping stage and the corresponding software.

RESULTS

PP Films Impregnated with Pure BT

Aging of the previously described capacitors was performed with pure BT saturated with O_2 at a pressure of 0.15 MPa over the liquid and at $T = 80^\circ\text{C}$. The applied voltage ($V_a = 4.1 \text{ kV}_{\text{rms}}$) was markedly below the inception voltage V_i of electrical discharges in the liquid. In the capacitor models, the discharge inception determined with a discharge detector having a sensitivity of 0.1 pC was found in the range 6–7 kV_{rms} . The degradation of the impregnated film was characterized by measuring the breakdown voltage (V_c) dependence on aging time and by an FTIR analysis. The deterioration of the impregnant was followed by gas chromatography. The influence of the degradation products of the liquid on the rate of degradation of the dielectric in the capacitor model was investigated, too. Some aging experiments were also performed at applied voltages higher than V_i in order to determine the differences between aging without discharges and aging under discharges.

Dielectric Strength of Aged PP Films

Aging without Discharges, at $V_a \ll V_i$

Aging was performed for lengths of time from 5 h to 400 h at $E = 135 \text{ MV}_{\text{rms}}/\text{m}$ (4.1 kV_{rms} , two 13.6 μm thick PP films).

Typical distributions of the breakdown voltage values at region A, region B, and region C of an impregnated PP film aged during 120 h are shown in Figure 3. It shows the cumulated probability P of breakdown at a given voltage versus the applied voltage: $\ln(1/1 - P)$ versus V with $P = n_j/n + 1$ (n : total number of breakdown measurements, n_j : number of detected breakdowns at $V \leq V_j$).¹⁷ The distributions in Figure 3 clearly show that the film undergoes a substantial electrical degradation under the electrode and especially in part C, which lies in the region between $R/2$ and R from the center of the electrode.

For each aged film, we determined the average V_B of about 20 values of the breakdown voltage measured in the region C of the film.

The variation of V_B with the aging time after $t_0 = 1 \text{ h}$ (Fig. 4, curve 1) follows the relation

$$V_B = V_B^0 - \alpha \log(t/t_0)$$

where $V_B^0 = 8.6 \text{ kV}$ is the mean breakdown voltage of impregnated PP films before aging. These values are found independent of the nature and the composition of the impregnant. With carefully purified BT, the capacitors broke down when the relative decrease (V_B/V_B^0) of the breakdown voltage of the

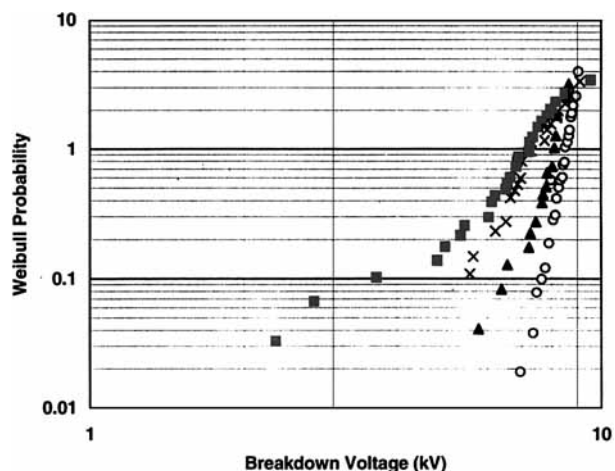


Figure 3 Statistical distribution of the breakdown voltage of a 120 h aged 13.6 μm thick PP film measured at different distances from the center of the electrodes. Region A (▲); region B (×); region C (■); before aging (○) ($E = 135 \text{ MV}_{\text{rms}} \text{ m}^{-1}$, $T = 80^\circ\text{C}$).

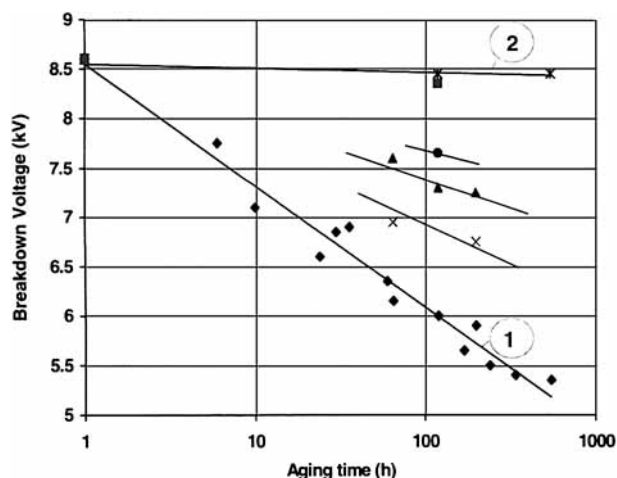


Figure 4 Breakdown voltage vs. aging time of a 13.6 μm thick PP film impregnated with BT (\blacklozenge , curve 1); $3 \times 10^{-2} M$ DGEBA in BT (\star , curve 2); $7.10^{-2} M$ ES in BT (\times); $2.10^{-1} M$ ES in BT (\bullet); $7.10^{-2} M$ DVB in BT (\blacktriangle); $2.10^{-1} M$ DVB in BT (\blacksquare). ($E = 135 \text{ MV}_{\text{rms}} \text{ m}^{-1}$, $T = 80^\circ\text{C}$).

film was about 36%; the average lifetime of the models was about 400 h. We noticed also that the breakdown voltage of an aged film was the same either after premature failure (i.e., electrical breakdown) or after intentional interruption of aging.

The Influence of Applied Voltage on Aging: Effect of Electrical Discharges

The dependence of the breakdown voltage of PP films aged during 4 h on the aging voltage (V_a) has been established. In Figure 5, the curve 1 corresponds to part C of the film under the electrodes and the curve 2 to part A of the film outside the electrodes at a distance less than 1 mm from the electrodes.

For $V_a < 6 \text{ kV}_{\text{rms}}$, no discharges were detected in the experimental arrangement. The decrease of V_B is quasi-linear in part C of the film under the electrodes (Fig. 5, curve 1) and as expected, V_B remains constant in part A (outside the electrodes).

For $V_a > 6.5 \text{ kV}_{\text{rms}}$, both positive and negative discharges were measured with a maximum apparent charge of 10 pC. By videorecording the light emitted by the discharges, we observed luminous spots mainly between the electrodes and little at the edge of the electrodes.¹⁸ These discharges led to a very fast decrease of the dielectric strength of the polymeric film, and especially in part A outside the electrodes.

Physicochemical Characterization of the Impregnant and Polymer

We successively describe the degradation caused to the impregnant and to the polymer.

Degradation of the Impregnant

Pure BT was placed at 80°C , in an open vessel. At the start of the experiment, the resistivity of pure BT was about $2 \times 10^{12} \Omega\text{m}$ and the water content about 50 ppm. During a 60-h oxidative aging, the water content of the impregnant increased from 50 ppm to more than 250 ppm, and its resistivity was reduced by a factor 5. We noticed the formation of a great number of products, especially 2-, 3-, and 4-methyl-benzophenone (Me-BP). These products were identified by gas chromatography. Their nature is consistent with the fact that the CH_2 group between the two phenyl rings is easily oxidized. The liquid oxidation started without any delay, as shown by the time dependence of 4-Me-BP concentration in the liquid (Fig. 6, curve 2).

The time dependence of the concentration of 4-Me-benzophenone can be described by the following empirical equation¹⁹:

$$c(t) = at + b \exp(t/\tau).$$

From the experimental measurements we found: $a = 0.7 \times 10^{-8} M \text{ s}^{-1}$, $b = 1.5 \times 10^{-5} M$, and $\tau = 5.5 \times 10^{-6} \text{ s}^{-1}$. Oxidation of BT in an energized capacitor model led to the formation of the same products (Fig. 6, curve 1) but the time dependence of the concentration of all the by-products was increased.

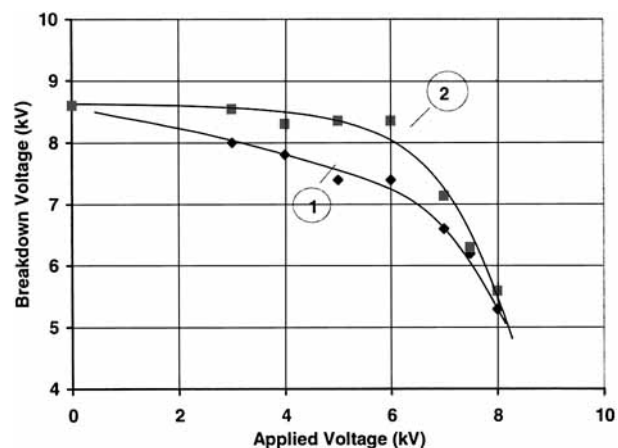


Figure 5 Breakdown voltage (V_B) of one film extracted from an aged capacitor vs. aging voltage (aging time: 4 h, capacitor with two 13.6 μm thick PP films); region C (curve 1); region A (curve 2).

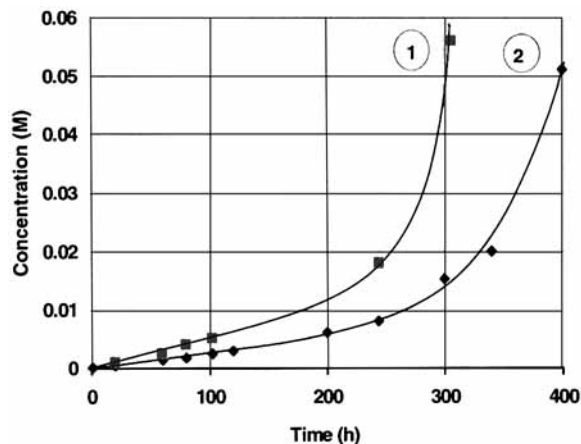


Figure 6 Time dependence of 4-Me-Benzophenone concentration after aging in a capacitor model ($E = 135 \text{ MV}_{\text{rms}} \text{ m}^{-1}$, $T = 80^\circ\text{C}$) (curve 1) and after thermal oxidation at 80°C in air (curve 2).

For 4-Me-Benzophenone, the parameters a , b , and τ were, respectively: $1.3 \times 10^{-8} \text{ M s}^{-1}$, $0.8 \times 10^{-5} \text{ M}$, and $8 \times 10^{-6} \text{ s}^{-1}$. The parameter a describing the first step of the oxidation is about twice increased in the aged capacitor. About the same effect is observed on the time constant τ . The field enhancement of the liquid oxidation is consistent with the assumption of charge-transfer reactions at the elec-

trodes creating free radicals that initiate both the liquid oxidation and the polymer degradation.³

At longer times, other products appeared and, for instance, after 450 h, an acid-base titration of the oxidized liquid indicated a $6 \cdot 10^{-4} \text{ M}$ acid concentration.

Degradation of the PP Film: An Analysis by FTIR Microspectroscopy and Mapping

A polypropylene film immersed in pure BT in an open vessel at 80°C showed no traces of oxidation even after 3000 h. Only the electrically stressed part of films aged under an AC field presented new IR absorption bands. The height of these peaks were not dependent on the aging time.

FTIR spectra for a $60 \mu\text{m}$ thick sample, aged during 280 h at $V = 6.5 \text{ kV}$, $E = 100 \text{ MV}_{\text{rms}}/\text{m}$, under 0.15 MPa O_2 and $T = 80^\circ\text{C}$ showed two major absorption bands at $\sim 1715 \text{ cm}^{-1}$ and $\sim 1020 \text{ cm}^{-1}$ (Fig. 7).

The very weak absorption band at 1710 cm^{-1} has been attributed to the carboxylic acid functional group.²⁰ Shoulders at about 1745 and 1780 cm^{-1} indicate the simultaneous formation of ester and lactone groups.^{21,22} The very strong band at 1020 cm^{-1} may be attributed to the formation of stable cyclic peroxides (A) or epoxides, i.e., (B) and (C).^{23,24}

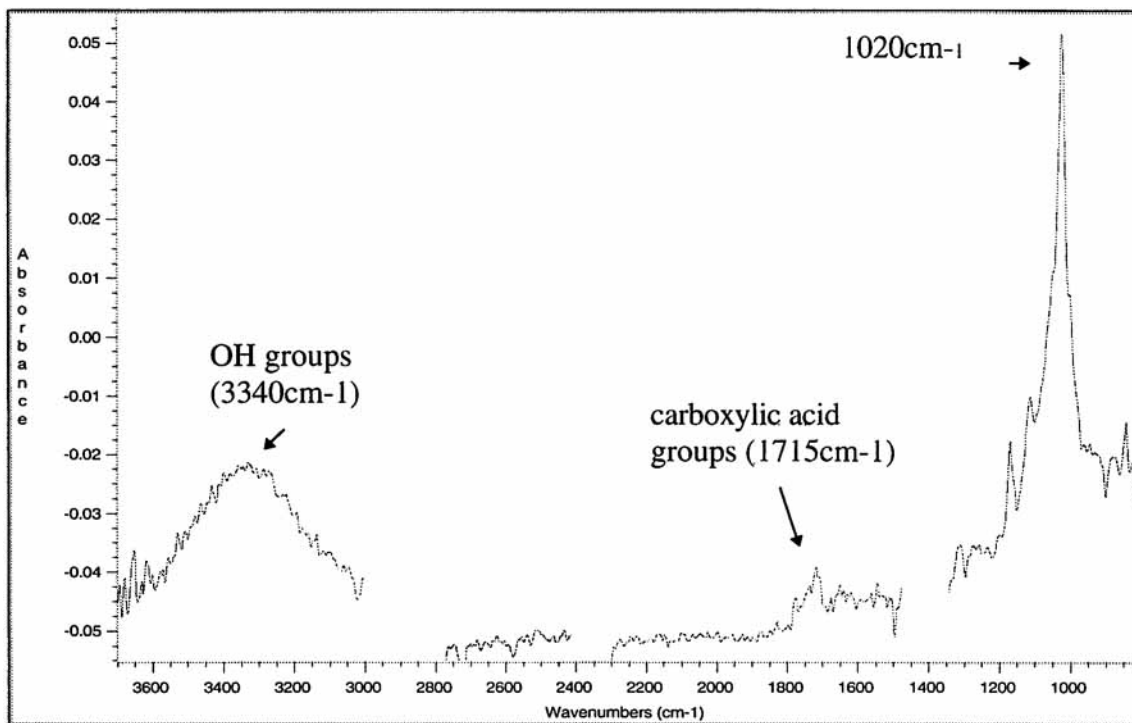


Figure 7 FTIR spectrum obtained by iterative subtraction of the spectra of region C and A of a $60 \mu\text{m}$ thick PP film aged 280 h at $100 \text{ MV}_{\text{rms}} \text{ m}^{-1}$ ($V = 6.5 \text{ kV}_{\text{rms}}$), $T = 80^\circ\text{C}$.

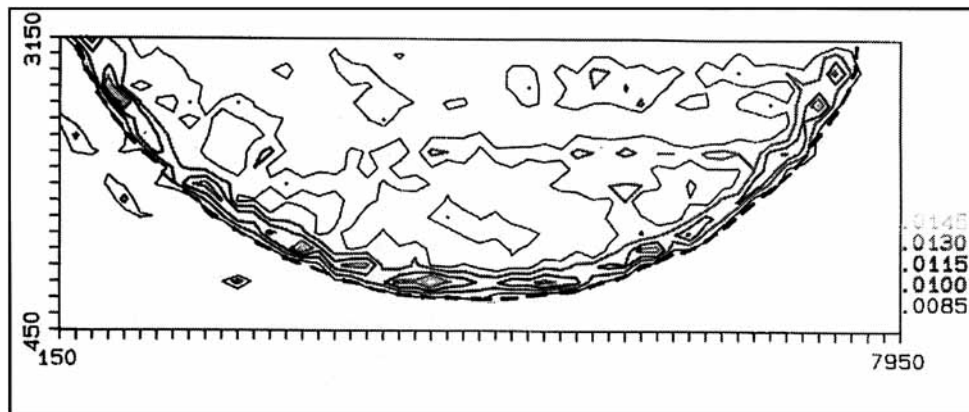
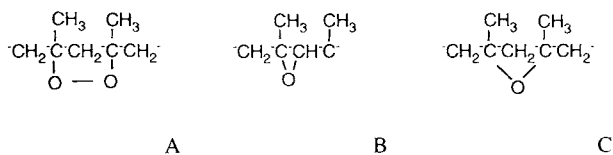


Figure 8 FTIR functional group image. Representation as a contour plot. Absorbance difference: 1710–1800 cm^{-1} (same conditions as in Fig. 7). The dashed line separates region C from region A.



In fact, it was unusual to observe on a same spectrum the absorption bands at 1710 cm^{-1} and 1020 cm^{-1} . More often a spectrum presented only one or the other of these peaks.³

Figure 8 shows a contour plot based on the $\text{C}=\text{O}$ peak intensity difference $A_{(1710)} - A_{(1800)}$, which corrects for varying baselines. Figure 9 shows the same type of mapping but based on the intensity difference $A_{(1020)} - A_{(1065)}$. The spatial resolution of the mapping was 150 μm in both directions, and the analyzed surface of the PP film was 8250 \times 315 μm^2 . The dashed circle in Figures 8 and 9 outlines the edge of the electrodes and, thus, the electrically aged

part of the film. It appears from Figures 8 and 9 that PP films undergo two distinct degradation processes:

(1) An oxidation process in a circular region near the edge of the electrode, about 1 mm wide. This oxidation is heterogeneous. At a few points, the $\text{C}=\text{O}$ peak is found twice or three times higher.

From optical observations during aging, we can attribute them to an irregular distribution of the current density over the film and to its inhomogeneous attack.

The oxidation would proceed as usually proposed for polypropylene degradation. Macroradicals generated upon abstraction of a tertiary H atom from polypropylene react with oxygen saturating the liquid. The macroradicals are converted to peroxy radicals, which further decompose and induce main chain scission and dissolution of the oxidized fragments in the impregnant.

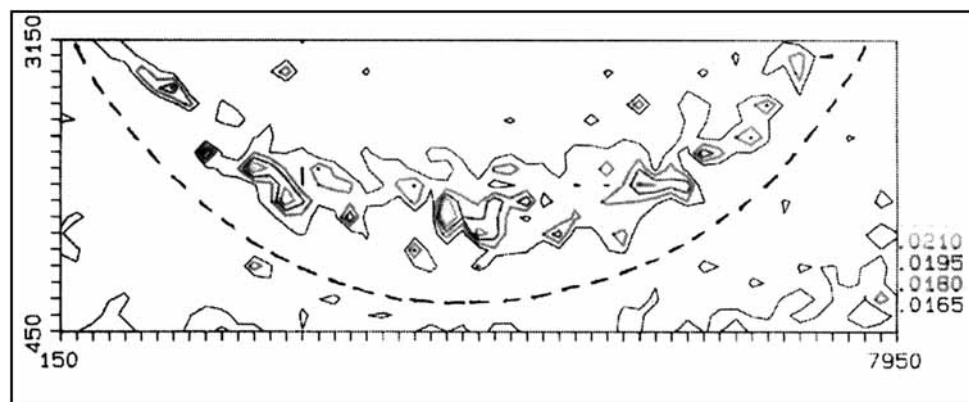


Figure 9 FTIR functional group image. Representation as a contour plot. Absorbance difference: 1020–1065 cm^{-1} (same conditions as in Fig. 7).

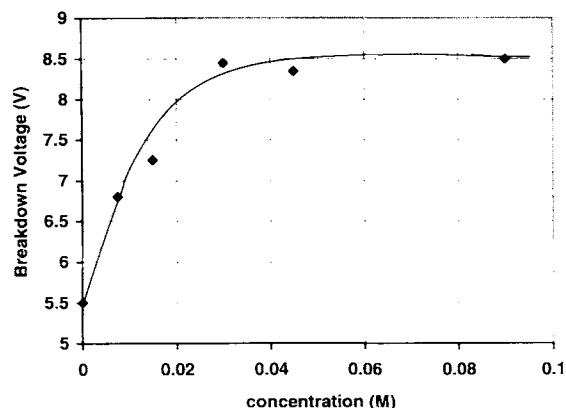
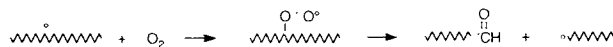


Figure 10 Breakdown voltage of PP films vs. DGEBA concentration in BT (aging time 500 h, $V = 4.1 \text{ kV}_{\text{rms}}$, $E = 135 \text{ MV}_{\text{rms}} \text{ m}^{-1}$, $T = 80^\circ\text{C}$).



Adams has suggested that the propagation of the oxidation of PP undergoes a characteristic "chain end nibbling" mechanism leading to the formation of species of low molecular weight.²⁰ The dissolution of these fragments by the impregnant makes our study more difficult, because PP films extracted from aged capacitors contain only a weak amount of oxidized groups and their concentration is not aging-time dependent.

(2) A partial oxidation of the macroradicals in a region near the center of the electrode where an O_2 deficiency allows an intra- or intermolecular recombination of radicals in neighboring positions.²³ The absence of O_2 in the central part of the film between the electrodes is easy to explain, because O_2 diffuses from the edge of the electrodes toward this region and is consumed by reactions with macroradicals.

Thus, we notice that the part of the film where the decrease of breakdown voltage is the more important, is the region where the oxidation leads to main chain scission of the macromolecules followed by dissolution of the low molecular weight fraction in the liquid. The inhomogeneity of the chemical attack shown by the FTIR spectra may explain why some capacitors broke down even if the mean breakdown voltage of the film had not significantly decreased.

STABILIZATION BY DGEBA

To analyze the stabilization of electrically stressed PP films by an epoxy additive, the films were first impregnated with DGEBA-containing BT. DGEBA is one of the epoxides used in industrial capacitors.

The films were aged either at $V_a = 4.1 \text{ kV}_{\text{rms}}$, $E = 135 \text{ MV/m}$ or at voltages higher than V_i . The objective was to determine the influence of the epoxide, either when direct charge exchange by electrode reactions occurs or when electrical discharges take place. Chemical analysis of the impregnant and the films were performed, too.

Dielectric Strength of Aged PP Films

Aging at $V_a < V_i$

For a $3 \times 10^{-2} \text{ M}$ DGEBA concentration in BT, V_B did not decrease with the time of application of the AC voltage (Fig. 4, curve 2). The DGEBA concentration dependence of the breakdown voltage of PP films submitted to an AC voltage during 500 h is shown in Figure 10. The mean lifetime of the capacitor models was not measured; it was always over 500 h.

In our experimental conditions with an O_2 -saturated impregnant, we find an optimum value of $3 \times 10^{-2} \text{ M}$ for the epoxy concentration necessary to prevent the electrical degradation of the dielectric. We notice that this concentration is nearly the same as in closed industrial devices where only traces of oxygen subsist.⁶

Aging at $V_a > V_i$

The mean lifetime of capacitor models submitted to $7.5 \text{ kV}_{\text{rms}}$ ($E = 247 \text{ MV}_{\text{rms}}/\text{m}$) versus DGEBA concentration is shown in Figure 11.

We notice that when electrical discharges occur, an epoxy additive no longer increases the electrical stability of the dielectric. On the opposite, it greatly decreases the lifetime of the capacitor models (Fig.

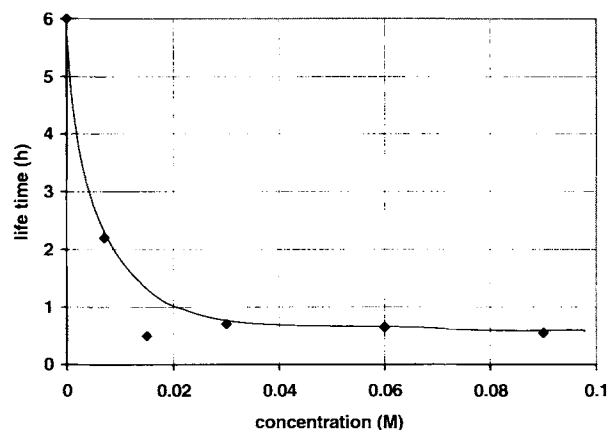


Figure 11 Mean lifetime of capacitor models vs. DGEBA concentration in BT ($V = 7.5 \text{ kV}_{\text{rms}}$, $E = 247 \text{ MV}_{\text{rms}} \text{ m}^{-1}$, $T = 80^\circ\text{C}$).

11). For instance, an aging at $V_a = 7.5 \text{ kV}_{\text{rms}}$ with a DGEBA concentration ($1.5 \times 10^{-2} \text{ M}$) in the impregnant, decreases the lifetime by a factor of 10. However, PP films extracted from these cells had nearly the same average breakdown voltage V_B as a new film.

Previous work has shown that the characteristics of the discharges changed if DGEBA was added to the impregnant¹⁸; the phase distribution of their number and their apparent charge kept the same shape but the maximum apparent charge (q_m) of the discharges recorded during 10 min might reach a value 10 times higher than in pure BT. The most probable apparent charge had the same order of magnitude or was found even slightly lower. So it appears that during the short lifetime of the capacitor models submitted to $V = 7.5 \text{ kV}$ at 80°C , the discharges cause no significant electrical degradation of the film but one more intense discharge may quickly drill the film without previous deterioration.

Physicochemical Characterization of the Aged Dielectric

Oxidation of the Impregnant

The addition of $3 \times 10^{-2} \text{ M}$ of DGEBA did not significantly change the resistivity of BT before or after aging.

During oxidative aging at 80°C in an open vessel of BT + DGEBA, we noticed the formation of the same by-products as with pure BT, but the rate of the oxidation processes were greatly enhanced,¹⁹ i.e., after a 450-h thermal aging, an acid–base titration indicated an acid concentration of 6.10^{-4} M in pure BT and of $1.5 \times 10^{-3} \text{ M}$ in BT + $3 \times 10^{-2} \text{ M}$ DGEBA. This observation shows that DGEBA does not chemically react with an organic acid. Experimental verifications by acid–base titration in organic liquids with and without DGEBA have confirmed this assertion.

We have also observed that the antioxidant Ionol has a very weak stabilization effect on the electrical aging of the dielectric.¹⁹ Furthermore, the addition of oxidation by-products to BT in capacitors from the beginning of electrical aging did not influence the aging of the dielectric. So we assume that the oxidation of the impregnant is not a determining factor in the fast decrease of the breakdown voltage of PP films under electrical, thermal, and oxidative stresses. We conclude that the stabilization effect of DGEBA cannot be attributed to an antioxidation effect; this also indicates that the epoxide has no

radical scavenging properties in these experimental conditions.

Chemical Characterization of the Aged PP Film

With 0.09 M DGEBA in the impregnant and for the same aging time as with pure BT, we observed a stronger oxidation of the electrically stressed region and an increase of the frequencies of the oxidation bands (with a maximum at 1728 cm^{-1} characteristic of carbonyl bands, instead of 1715 cm^{-1} characteristic of a carboxylic acid band) (Fig. 12). The band near 1600 cm^{-1} , which was only observed in the presence of DGEBA, must be attributed to a phenyl group resulting from a deposit of epoxide on the film. In fact, PP films that were electrically aged with an epoxy additive and washed with cyclohexane (a solvent of the aromatic impregnant) showed all the characteristic absorption bands of DGEBA aside from the epoxy functional group, which had totally disappeared (Fig. 13).

In Figure 13 we do not observe the absorption band at 1020 cm^{-1} . This band has only been observed in the absence of DGEBA and in the case of a deficiency of oxygen (Figs. 7 and 9). It has been attributed to intramolecular termination reactions of PP macroradicals.

FTIR mapping at 1250 cm^{-1} , the vibrational frequency of the aromatic ether group of the DGEBA molecule, showed a deposit of DGEBA on all the surface of the film and mainly in region C [Fig. 14(B)]. By SEM and FTIR reflexion spectroscopy, a similar deposit on the electrode surface was observed.

The comparison of mapping A with mapping B (Fig. 14) shows that the oxidation is located at the same parts of the film as the organic deposit. Thus, we assume that the oxidation bands at 1730 cm^{-1} are due to the oxidation of the polymeric deposit and not to the oxidation of the polypropylene film. Furthermore, PP oxidation leads to the formation of carboxylic acid groups with an IR absorption band at 1710 cm^{-1} and not at 1730 cm^{-1} .

Thus, the main difference in the chemical degradation of PP films impregnated with pure BT or DGEBA added BT lies in the formation of a polymeric deposit both on the film and on the electrodes. This deposit principally appears in the part of the film where aging without DGEBA is the more severe.

STABILIZATION BY EPOXYSTYRENE

As previously shown, the stabilization of electrically stressed impregnated PP films by DGEBA, an epoxy

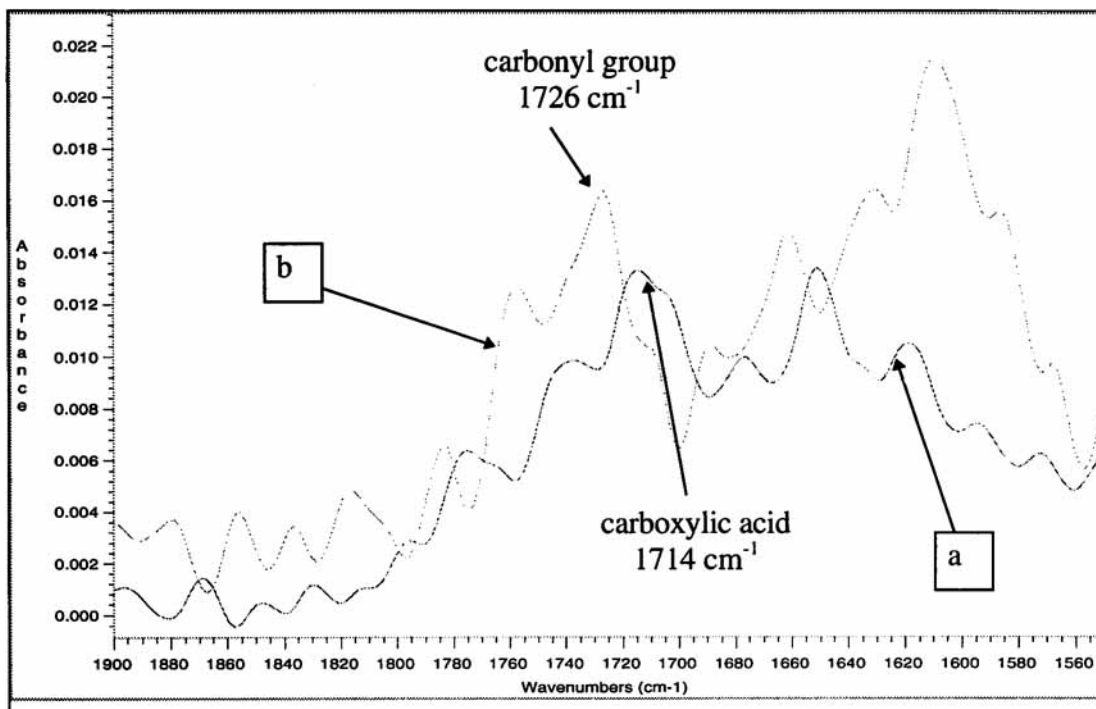


Figure 12 FTIR spectra of PP films aged 280 h ($E = 100 \text{ MV}_{\text{rms}} \text{ m}^{-1}$, $T = 80^\circ\text{C}$) impregnated with BT (a) and $9 \times 10^{-2} \text{ M}$ DGEBA in BT (b).

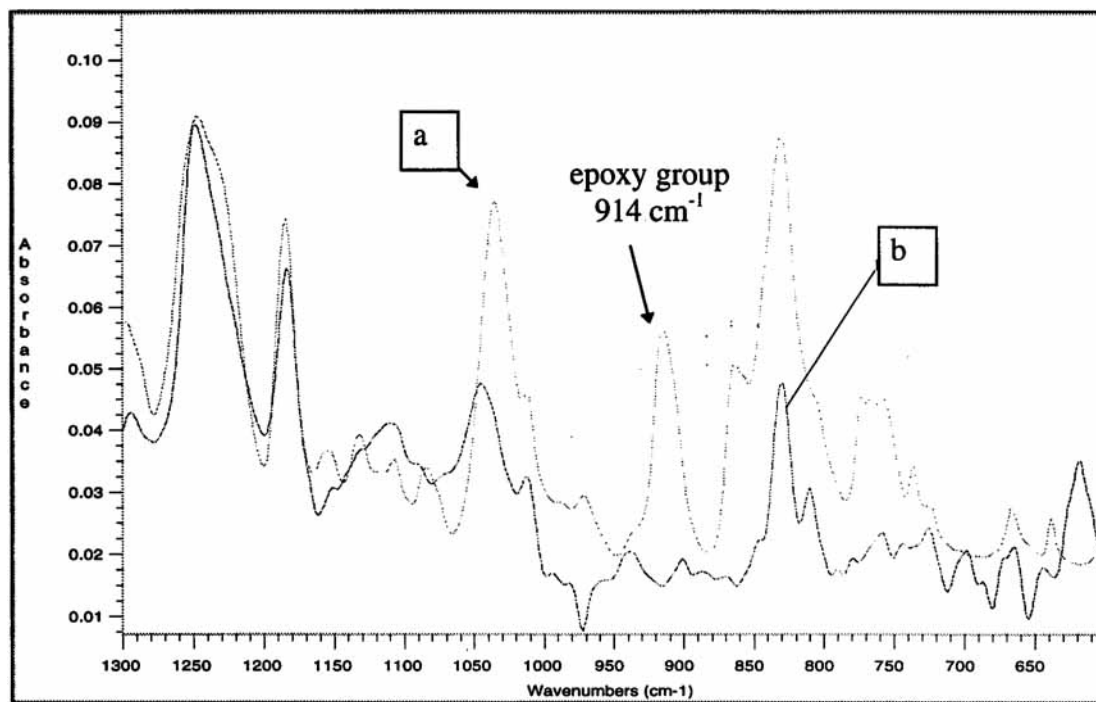


Figure 13 FTIR spectra of DGEBA (a) and of the interactive subtraction of the spectra of regions C and A of a 520-h aged PP film impregnated with $9 \times 10^{-2} \text{ M}$ DGEBA in BT (b).

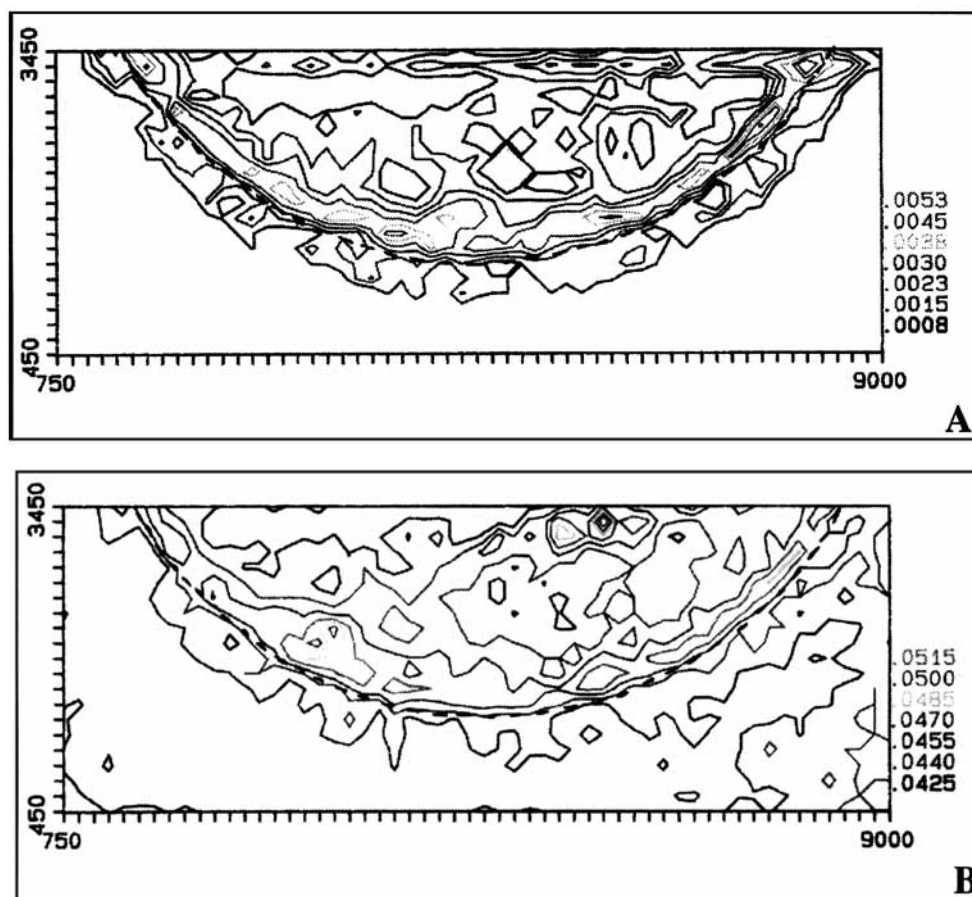


Figure 14 FTIR functional group image. Representation as a contour plot. Absorbance difference 1730–1800 cm^{-1} (A); 1250–1195 cm^{-1} (B) (same conditions as in Fig. 13).

additive of two functionalities, cannot be attributed to the neutralization of acids or the scavenging of radicals by opening of the epoxy ring as it is generally assumed. To provide another argument in order to disprove that the stabilization property of DGEBA may be attributed to a specific reactivity of the epoxy group, we have analyzed the behavior of ES added to BT.

ES has only one epoxy group per molecule unlike DGEBA, which contains two epoxy groups per molecule. On one hand, it has been shown that a monomer with only one functionality is not a good coagent of radically induced crosslinking of PP,¹⁵ and on the other hand, the opening of the epoxy ring may lead to a linear macromolecule of low molecular weight, probably dissolved in the impregnant.

Electrical Stabilization by ES

The mean breakdown voltage of a 120-h aged PP film impregnated with $7.35 \times 10^{-2} M$ ES in BT was lowered by about 20% and with 0.23 M ES in BT by

about 12% (Fig. 4). An ES concentration of $7.35 \times 10^{-2} M$ corresponds to an equivalent amount of epoxy groups and, thus, is equivalent to a DGEBA concentration of $3.7 \times 10^{-2} M$. PP impregnated with $3 \times 10^{-2} M$ DGEBA in BT had a breakdown voltage lowered by 2% after the same aging time. So, ES has a slight stabilization effect on the electrical aging of impregnated PP but by far is not so efficient than DGEBA.

Chemical Modification of the Aged PP Film

A FTIR spectrum of the region C of an aged PP film impregnated with 0.23 M ES in BT is very different from those obtained after aging with pure BT or DGEBA-containing BT. In Figure 15, we represent an interactive subtraction of the spectra of regions C and A of the aged film (curve a) and the spectrum of pure ES (curve b). The two spectra have no similarities. The spectrum obtained after interactive subtraction presents very strong and broad bands at about 1600 cm^{-1} characteristic of conjugated car-

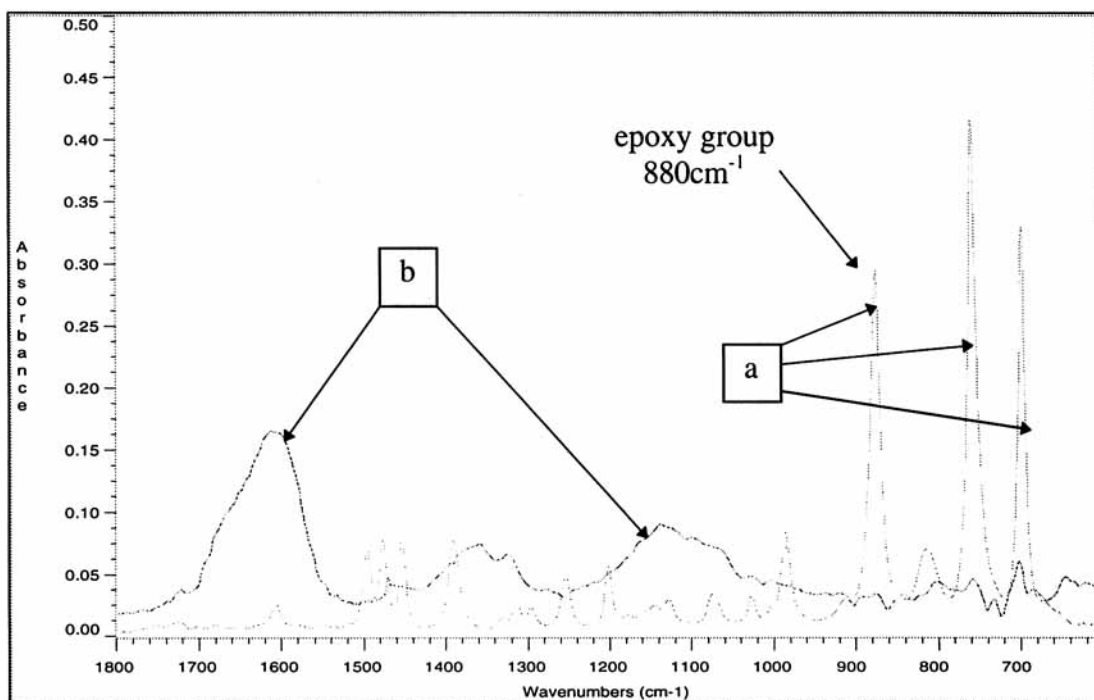


Figure 15 FTIR spectra of ES (a) and of the interactive subtraction of the spectra of regions C and A of a 120-h aged PP film impregnated with 0.2M ES in BT (b).

bonyl groups probably in the enol form. At 1130 cm^{-1} we also observe a strong and broad band characteristic of ether linkage and at about 700 cm^{-1} a weak band, which we attribute to a phenyl group. These bands were not observed in the previously described experiments with pure BT or with DGEBA-containing BT. We also notice the absence of the epoxy and benzene bands at, respectively, 880 cm^{-1} and 3000 cm^{-1} ; a very weak band at 760 cm^{-1} may be attributed to monosubstituted benzene.

All these modifications were observed after electrical aging only in the region C (Fig. 16). On one hand, the lack of the characteristic IR frequencies of phenyl groups let us assume that no significant polymerization occurred. On the other hand, the strong absorption bands at 1600 cm^{-1} and 1130 cm^{-1} , which are not observed with pure BT or DGEBA-containing BT, indicate a chemical attack of the dielectric in the electrically stressed region. The opening of the epoxy ring and even of the phenyl

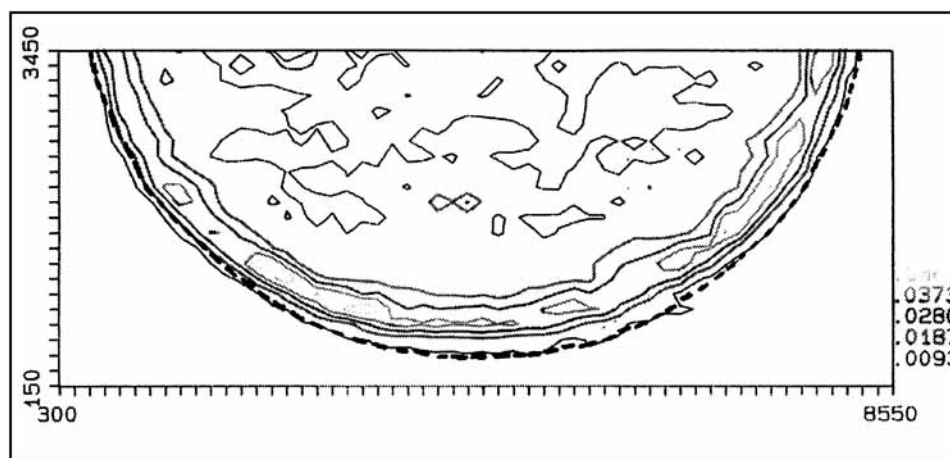


Figure 16 FTIR functional group image. Representation as a contour plot. Absorbance difference: $1615\text{--}1800\text{ cm}^{-1}$ (same conditions as in Fig. 15).

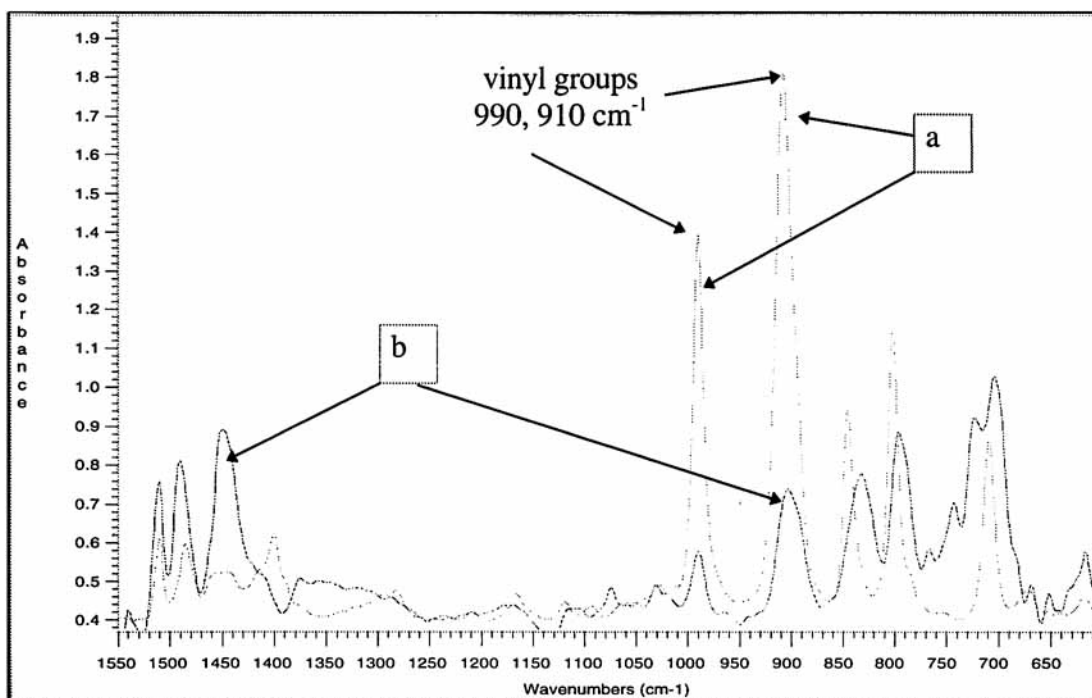


Figure 17 FTIR spectra of DVB (a) and of the interactive subtraction of the spectra of regions C and A of a 220-h aged PP film impregnated with $9 \times 10^{-2} M$ in BT (b) (same conditions as in Fig. 17).

ring may only explain the formation of ether and enol groups at the surface of the aged PP film.

These results disprove that the stabilization properties of epoxy additives in electrical devices are only due to specific properties of the epoxy group. In order to put forward another mechanism, we have analyzed the more general property of additives to undergo an electrically induced polymerization. The formation of a more or less protective layer on the PP film submitted to an electrical stress may explain the stabilization observed with DGEBA and with trimethylolpropane triacrylate.¹⁶

STABILIZATION BY DIVINYLBENZENE

The electroinitiated polymerization of commercial DVB has been studied in acetonitrile medium with an added electrolyte.¹⁴ As it can be expected from a monomer of two functionalities, a partially cross-linked white polymer was formed on the electrode after the passage of an electric current. It has also been found that DVB favors the thermally induced crosslinking of PP.¹⁰ In order to confirm the assumption that the stabilization behavior of DGEBA must be attributed to the ability of the molecule to

polymerize, we have analyzed the behavior of DVB-containing BT in the capacitor models.

Electrical Stabilization by Divinylbenzene

The mean breakdown voltage of a 120 h aged PP film impregnated with $6.7 \times 10^{-2} M$ DVB in BT was lowered by about 14% and with 0.2 M DVB in BT by about 3.5%. $3 \times 10^{-2} M$ DGEBA in BT led to a decrease of about 2% (Fig. 4). So we notice that DVB has a good stabilization effect in capacitors but at a concentration substantially higher than DGEBA.

Chemical Modification of the Aged PP Film

After a 220-h aging of a capacitor filled with 0.2 M DVB in BT, we observed the formation of a highly swollen gel around the electrodes. An extraction of BT from the gel with cyclohexane followed by drying gave a white polymer. Figure 17 (curve b) shows a FTIR spectra of this polymer. By comparison with the spectrum of pure DVB (curve a) we notice that the ratio of the intensity of the characteristic bands of substituted benzene ($3000\text{--}3050\text{ cm}^{-1}$, 1600 cm^{-1} , 1510 cm^{-1} , 830 cm^{-1} , 800 cm^{-1} , and 705 cm^{-1}) to

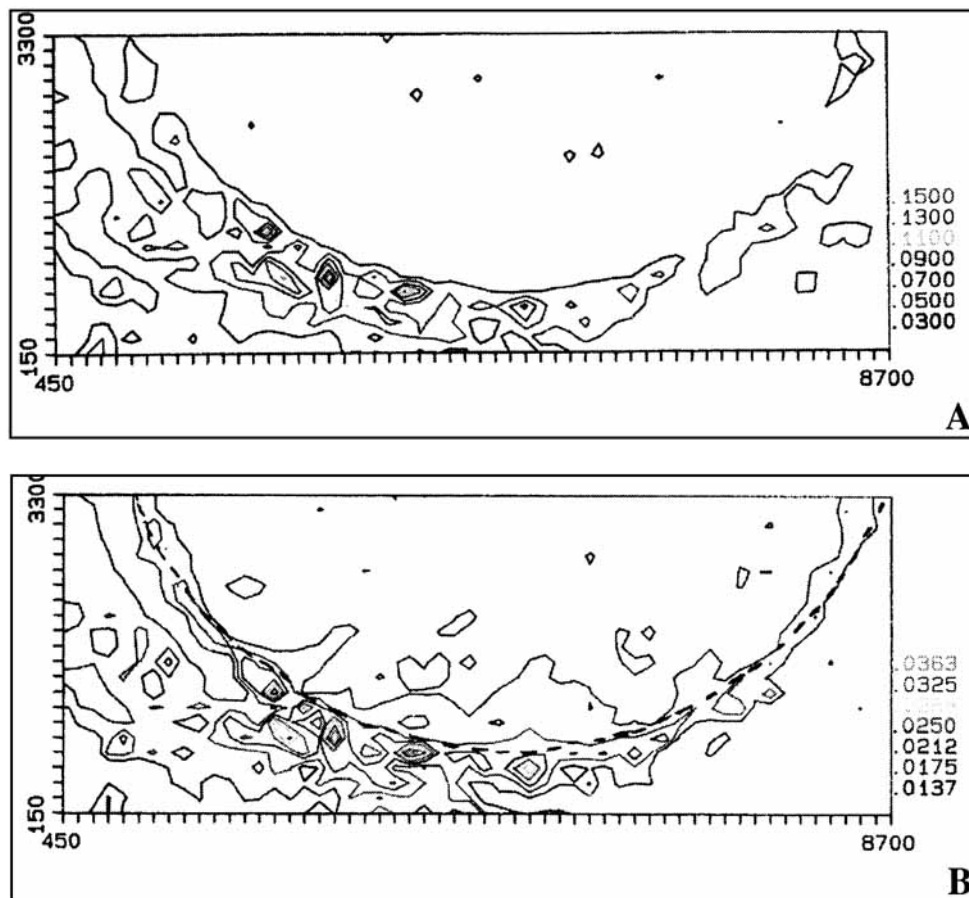


Figure 18 FTIR functional group image. Representation as a contour plot. Absorbance difference: (A) 706–639 cm^{-1} , (B) 1710–1800 cm^{-1} .

the intensity of the characteristic bands of the vinyl groups (1640 cm^{-1} , 990 cm^{-1} , 902 cm^{-1}) strongly increases. The FTIR spectrum of the polymer also presents characteristic strong bands of CH and CH_2 groups ($2930\text{--}2850\text{ cm}^{-1}$, 1446 cm^{-1}). These results are consistent with the formation of polyvinylbenzene (DVB).

However, a FTIR mapping at 710 cm^{-1} showed that this polymer was mainly formed around the electrodes but not under them [Fig. 18(A)]. The electrically initiated oxidation, too, was located outside the electrodes [Fig. 18(B)]. We conclude that the >C=O groups at 1710 cm^{-1} detected by FTIR must be attributed to an oxidation of DVB and not of PP. The absence of oxidation under the electrodes shows that oxygen cannot reach the electrically stressed region of the film. The diffusion of oxygen is greatly slowed down by the gel around the electrodes and by the oxidation of DVB. Thus, it can no further contribute to the

degradation of the PP film. The formation of a highly swollen gel likely explains why stabilization by DVB is not so efficient than by DGEBA for the same concentration.

CONCLUSION

Monomers of two or more functionalities at a concentration in the range 10^{-2} to 10^{-1} M have been added to the aromatic impregnant of PP films submitted to high AC fields. They undergo an electrically initiated polymerization. The new polymer covers both the electrodes and the PP films and prevents their electrical degradation by decreasing the kinetics of radical formation at the electrodes and the diffusion of reactive species to the film and finally by consuming these species in degradation processes that modify their own chemical structure. The efficiency of these additives in electrical devices is, of course, dependent on the physicochemical properties of the resulting

polymer. A highly swollen polymer, like that due to DVB, only slightly adheres at electrodes and films and creates a layer less protective than a strongly cross-linked polymer like that due to DGEBA, into which the impregnant cannot easily diffuse.

Thus, the stabilization effect of an epoxy additive in industrial devices must be attributed to its property to undergo an electrically initiated polymerization. The "chain end nibbling" propagation, which is characteristic of the degradation of PP,^{3,20} is inhibited by a compact layer of an epoxy polymer, which, unlike PP, does not undergo scission reactions and does not split off into small products that further dissolve in the impregnant.

An important observation is also that the addition of DGEBA markedly accelerates the failure of impregnated films when the aging AC voltage is higher than the inception voltage of discharges. As discharges are frequently observed in HV capacitors, it will be of interest to determine the exact reason of this behavior.

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