Electrical Degradation of Polypropylene: A Study by FTIR Microspectroscopy

INTRODUCTION

Polypropylene is the dielectric mostly used in capacitors.[1] In high-voltage capacitors, it has to be impregnated with an organic liquid in order to increase the mean electric field in the dielectric up to very high values ($\sim$ 60 $V_{rms}/\mu m$).

The breakdown of such capacitors in service is attributed to a local degradation of the insulating properties of the polypropylene film,[2] but its causes remain unknown. Indeed, numerous studies are related to polymers subjected to electrical discharges in air or in an inert atmosphere (N_2, Ar),[3] but few to impregnated polymers submitted to high alternative electric fields.[4] Radicals may be formed in enhanced-field regions or on the electrodes of the capacitors. This initiation step is not yet elucidated.

Another difficulty originates from the organic liquid that may be involved in the mechanism of the polymer degradation. The radicals may be formed from its reaction at electrodes or by discharges in it. The liquid may also modify the propagation step of the polymer degradation by increasing the migration or diffusion of these radicals in the polymer.

This paper presents data obtained by infrared spectroscopy and by FTIR microscopic imaging of the degradation of polypropylene films impregnated with an organic liquid saturated with oxygen and submitted to a mean electric field of 135 $V_{rms}/\mu m$, at 80°C. These data are compared with results from photodegradation or pulse radiolysis of dilute polymer solutions.[5] A mechanism involved in the propagation of the degradation is discussed.

EXPERIMENTAL

We have studied commercial polypropylene (PP) films (Bollore Technologies Company, France), obtained by the tenter frame process. They are rough on both sides and specially made for capacitor applications. These films were sandwiched between two cylindrical duraluminum electrodes (electrode radius = 5 mm) and impregnated with an aromatic liquid mainly constituted of mono- and dibenzyltoluene M/DBT.[6] In the experiments described here, the impregnant was oxygen-saturated (relative pressure of oxygen over the liquid surface = 1.5 bar). This capacitor was tested at 80°C, 4.1 kV_{rms}, about 135 $V_{rms}/\mu m$, 50 Hz.

The dielectric strength of the PP film, 13.6 μm thick, extracted from the capacitor after electrical aging was measured in different places, under dc voltage ramp (500 V/s), at 20°C, between a plane electrode and a stainless-steel sphere, 2 mm in diameter, immersed in benzyltoluene. Measurements are made in the region of the film that was between the electrodes during aging and also outside this region.

The aged films were analyzed by FTIR spectroscopy (Nicolet infrared spectrometer with a Spectra-Tech microscope). The spectra were obtained with a 160 × 160 μm aperture. We signal-averaged 32 scans at 8 cm^{-1} resolution. Since the FTIR transmission spectra of a 13.6 μm film presented waves due to interferences, the FTIR spectroscopy study was performed with a 100 μm-thick PP film. The FTIR microscope is equipped with an MCT detector; the computer-controlled mapping stage and the corresponding software can perform a two- or a three-dimensional map for functional-group imaging. We made 160 μm steps in the x- and y-direction when moving the stage. The two-dimensional map (about 5800 spectra) was obtained in six operations. The aged films were also analyzed by scanning electron microscopy.

RESULTS AND DISCUSSION

A typical distribution of the breakdown voltage of a PP film (aged during 20 h) is shown in Figure 1. To describe
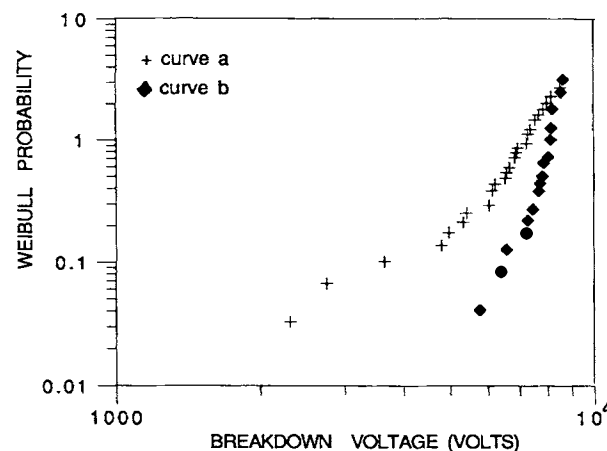
Figure 1 Statistical distribution of the breakdown voltage of an aged PP film; film thickness: 13.6 μm; number of measurements: about 50; curve a: part of the film between the electrodes during aging; curve b: part of the film outside the electrodes.

Figure 2   Mean breakdown voltage of an aged PP film in concentric rings, at different distances from the center of the electrode.

the results, we use the Weibull statistical model,[7] and relate the cumulated probability P to have breakdown at a given voltage to the applied voltage in a diagram $\mathrm{Ln}(1/1 - P)$ vs. V. The Weibull model, developed for metal-fatigue tests, is also used to represent the lifetime of elec-

trically stressed materials. Indeed, when breakdown occurs during a linear increase of the voltage with time, experimental results form a straight line in these coordinates if the mechanism of breakdown remains unchanged over the investigated voltage range. Curve b corresponds to the region of the film outside the electrodes during aging, and curve a, to the region between the electrodes. Some points have a very low breakdown voltage (< 5 kV), whereas a nonaged film breaks down at about 8.5 kV.

Such low values are measured neither on the aged film outside the electrodes nor on a nonaged impregnated film. These very low breakdown voltages are found at a distance between $R/2$ and R from the center of the electrode (R being the electrode radius) (Fig. 2). In this ring, the mean breakdown voltage is lowered by about 35% compared with the initial value. That explains why these capacitors break down after about 25 h in these conditions (4.1 $\mathrm{kV_{rms}}$).

Typical FTIR spectra for samples, 100 μm thick, aged in the same conditions during 630 h at 100 $\mathrm{V_{rms}}/\mu$m are shown in Figure 3. Two major absorption peaks develop: at 1710 $\mathrm{cm^{-1}}$ and 1018–1020 $\mathrm{cm^{-1}}$. The absorption at 1710 $\mathrm{cm^{-1}}$ has been attributed to the carboxylic acid functional group.[8,9] Shoulders at about 1720, 1750, and 1780 $\mathrm{cm^{-1}}$ indicate the simultaneous formation of ketone, ester, and
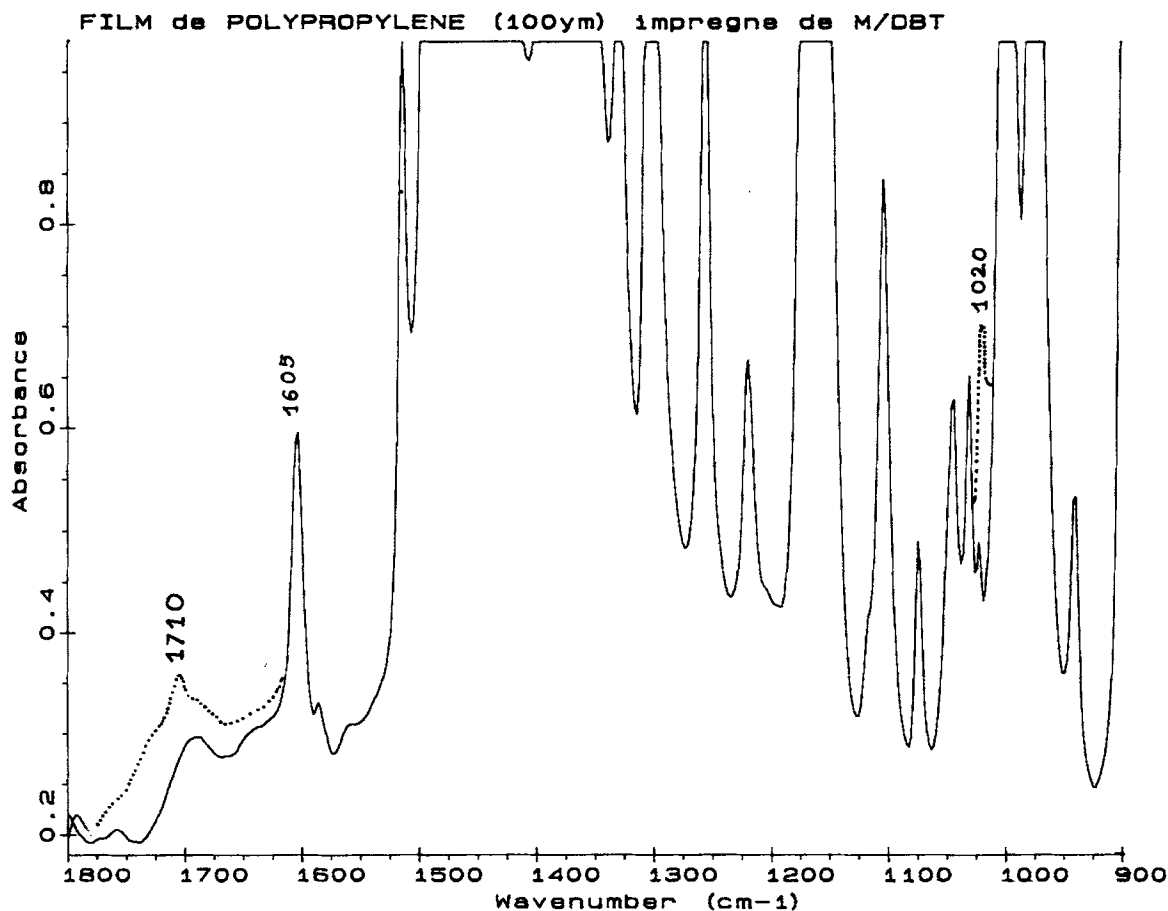
Figure 3   FTIR spectra of a 100 μm-thick PP film: (———): prior to aging; (· · · · ·): after aging at 80°C, 10 kV, 100 V/μm during 630 h.
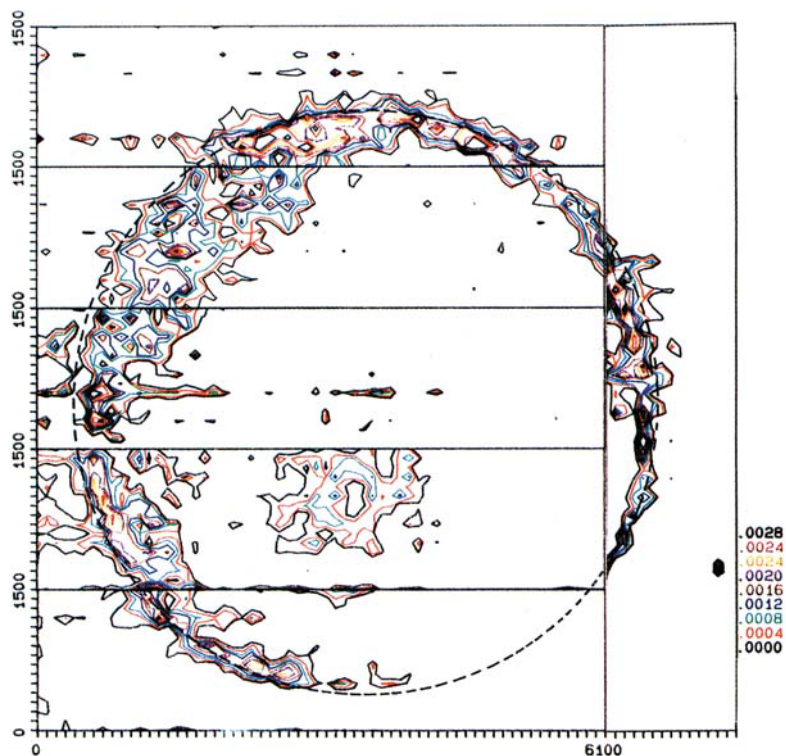
Figure 4   FTIR functional-group image based on the difference of absorption at 1710 and 1800 cm^{-1}. Representation as a contour plot. The dashed circle outlines the electrode section.
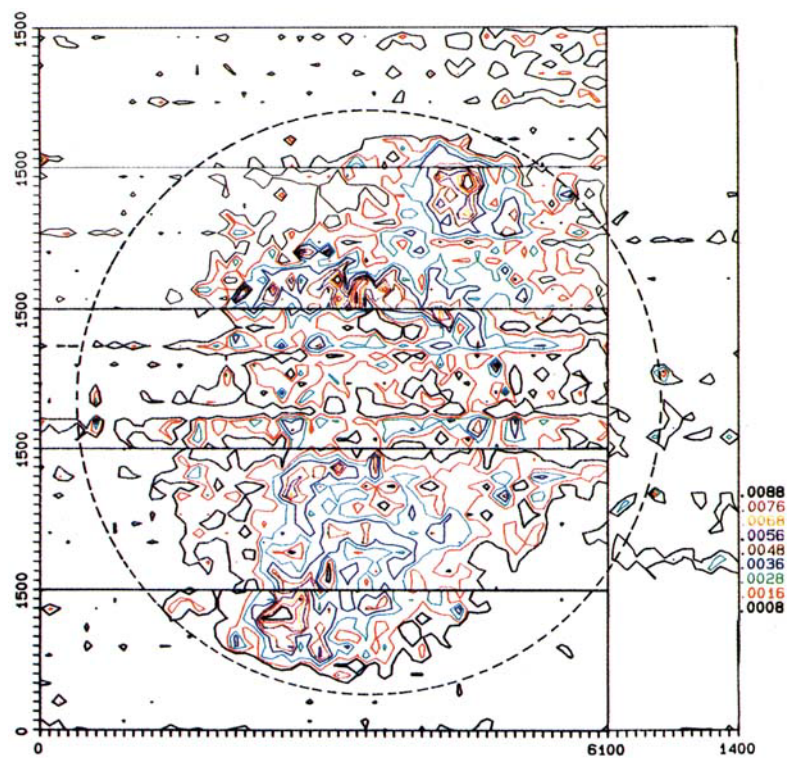

Figure 5   FTIR functional-group image based on the difference of absorption at 1020 and 1050 cm^{-1}. Representation as a contour plot.

lactone groups as previously noticed.[8] The band at 1020 cm^{-1} has been observed by Niki et al.,[10] after peroxide-initiated oxidation of atactic polypropylene at 45°C under nitrogen. They attribute it and the increase of absorption at 1100 cm^{-1} to disproportionation products of P* radicals.

In the few cases when the 1020 cm^{-1} absorption is strong, we also notice absorption peaks at about 800 cm^{-1} (—CH=CH—?) and 1150 and 1260 cm^{-1} (ether ?). But these weak absorptions were difficult to determine due to overlap with the isotactic PP bands.

Figure 4 shows a contour plot based on the peak intensity difference $A_{(1710)} - A_{(1800)}$, which corrects for varying baselines. Figure 5 shows the same type of mapping based on the intensity difference $A_{(1020)} - A_{(1050)}$.

It appears from Figures 4 and 5 that the PP film contains two distinct regions of different chemical attacks. First, in a circular region near the edge of the electrode, about 1 mm width, oxidation occurs. The reaction would be
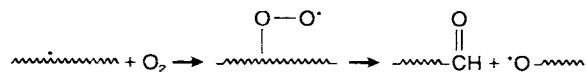
as usually proposed for polymer oxidation.[11]

The radicals reacting with oxygen are macroradicals generated upon abstraction of H atoms. This initiation step and the influence of the solvent remain to be elucidated. Since the liquid is oxygen-saturated, practically all macroradicals are converted to peroxy radicals, which further decompose and induce main-chain scission. Oxidation is not uniform. At a few points, the oxidation 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 then to its inhomogeneous attack.

Second, in the central part of the aged region, FTIR spectra can be interpreted by the mutual deactivation of macroradicals as observed in the absence of O_2.[12] Two reactions may occur: either recombination and cross-linking or radical dismutation with formation of C=C bonds. For PP, the most likely reaction is the second one.
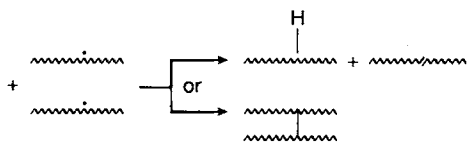
The absence of O_2 in the central part of the film between the electrodes is easy to explain, since O_2 diffuses from the edge of the electrodes toward this region and is consumed in its reaction with macroradicals.

This mechanism of the propagation of PP degradation is also confirmed by other observations. Measurements of the mean molecular weight of the polymer show that it is notably lower in the part of the film containing oxidation groups, in agreement with a scission of the macrochains. The dissolution of the smaller chains by the impregnant makes the study more difficult, since PP films extracted from the aged capacitors contain only a weak concentration of oxidization groups. The mapping of the height of

an absorption pic characteristic of the solvent (1605 cm^{-1}) shows that the liquid concentration in the PP film is lower (about 5% less) in the central region, which would be in agreement with a densification of PP by reticulation.

As a conclusion, our study explains the great influence of O_2 on the electrical aging of PP films. The lifetime of the capacitor model with 2 × 13.6 μm-thick PP films is about 25 h with O_2 saturated liquid, and more than 1500 h without O_2.[4] In our experiments, we get the two different degradations on a given film and we show the good agreement between electrical (breakdown voltage) and physicochemical measurements (FTIR spectroscopy).

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