

Formation and Inhibition of Free Radicals in Electrically Stressed and Aged Insulating Polymers

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ABSTRACT: Previous work has shown that prebreakdown, electrical aging, and breakdown phenomena are directly associated with charge carriers injected from electrical contacts and their subsequent dissociative trapping and recombination. In addition, the energy released from each trapping or recombination event is dissipated in the breaking of the bonds of macromolecules, thus forming free radicals and new traps in the electrically stressed insulating polymers, as predicted by Kao's model. It is this gradual degradation process that leads to electrical aging and destructive breakdown. New experimental results are presented to confirm previous findings and a new approach to inhibit the degradation process by the incorporation of suitable dopants into the polymer. The concentration of free radicals in the polymer increases with an increasing electric field at a fixed stress time of 250 h and with increasing stress

time at a fixed electric field of 833 kV cm^{-1} . The concentration of free radicals is directly related to the concentration of new traps created by stress. However, when suitable dopants are incorporated, the initiation voltage for the occurrence of electrical treeing and the breakdown strength are both increased. The dopants tend to create shallow traps and have little effect on the deep trap concentration. This implies that the dopants act as free-radical scavengers that tend to satisfy the unpaired electrons of the broken bonds, which create new acceptor-like electron traps and new shallow traps. By doing so, the shallow traps screen the deep traps, thereby reducing the energy released during trapping and recombination and the probability of breaking the macromolecular bonds and causing structural degradation. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 3416–3425, 2003

INTRODUCTION

Insulating polymers, such as polypropylene (PP) and polyethylene (PE), have been widely used for wire, cable, apparatus, and system insulation. It is obvious that prebreakdown phenomena such as electrical aging and electrical treeing are important problems of industrial concern. In the past two decades, prebreakdown phenomena have been extensively studied by many investigators^{1–5} to advance the understanding of the problems involved and search for a suitable solution. Electrical aging is directly related to the change of chemical structures resulting from prolonged electrical stressing.^{6,7} Electrical treeing is actually a locally internal discharge,⁸ indicating that in the high-field region the chemical structural degradation has reached a destructive level. Thus, the degree of structural degradation can be considered as one of the possible measures of electrical aging. In our previous

article⁴ we reported that PP macromolecules decomposed into low-weight molecules or free radicals when the PP was subjected to electrical stressing at fields equal to or higher than the threshold for carrier injection from the electrical contacts. We have attributed this structural degradation process to the bombardment of hot electrons on the macromolecules. The hot electrons arise from the energy evolved from the trapping, recombination, or Auger-type process of the carriers injected from the electrical contacts that is based on Kao's model of electrical discharge and breakdown in condensed dielectric materials.⁵ In the present article we present new experimental results to confirm the formation of free radicals as the most important mechanism responsible for electrical aging. To inhibit this gradual degradation process, prolong the lifetime, and improve the stability of the polymers, we also present our approach to this problem by incorporating suitable dopants into the polymers. These dopants act as free-radical scavengers, and we hoped that these scavengers would deactivate the unpaired electrons of the broken macromolecular bonds and produce shallow traps to screen the deep traps in order to reduce the energy released from the trapping or recombination. A detailed discussion is given along with new results.

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EXPERIMENTAL

The materials used for the experimental tests were biaxially oriented PP in stretched film form (specimen thickness = 15 μm , crystallinity = 37.4%, and molecular weight > 1400) and a low-density PE (LDPE, crystallinity = 36.5%, molecular weight > 1000). The LDPE could not be stretched, and so the specimen thickness could not be made thin enough for some experiments. It was also not easy to obtain uniform PP specimens with thicknesses large enough for electrical treeing tests. Therefore, we used PP specimens for the experiments on the formation of free radicals and LDPE for the experiments involving stress-induced structural degradation. For tests involving electrical stressing, special care was taken to ensure good intimate contact between the specimen and the brass electrode before putting the epoxy resin around the edge of the electrode and to avoid any chance for the epoxy resin to contaminate the contact surface. The electrode was 2.5 cm in diameter with the edge rounded at a curvature radius of 0.5 cm. The tests were carried out in a vacuum chamber of 10^{-5} Torr to avoid any possible surface discharge. For electrical treeing tests, we used a standard nonuniform field point-plane electrode configuration.⁸ The point electrode was produced by mechanically polishing a stainless steel wire with a diameter of 5×10^{-2} cm to form a needle-shaped tip with a curvature radius of 3 μm , which was embedded into a PE block; the distance between the point and the plane was 3 μm . For electric breakdown tests we used a stainless steel sphere and plane electrode configuration that produces a quasiuniform field in the region of the shortest separation between electrodes prior to the formation of space charges. All tests were carried out at room temperature, unless otherwise stated. The experiments and results are described in the following sections. Each point of the experimental data represents the average value of at least 10 measurements on different specimens.

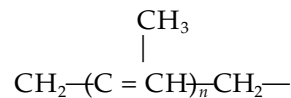
Formation of free radicals

We carried out the following experiments to investigate the formation of free radicals in electrically stressed insulating polymers.

Electron paramagnetic resonance (EPR) spectroscopy

A Varian model B-115 EPR spectrometer was used to measure the concentration of free radicals produced by electrical stressing in PP. The PP specimen was first subjected to electrical stressing at a predetermined ac field in a vacuum chamber for various stressing times and then rested after aging at room temperature for 40 h prior to the EPR measurement. Because the primary free radicals are very chemically active, as soon

as they are created they immediately react with the other surrounding radicals or molecules to form secondary radicals. Thus, the radicals that we could detect were secondary free radicals. However, the concentration of secondary radicals should be directly related to that of the primary radicals. By comparing the EPR spectrograms with that of the standard bis(1,2,2,6,6 pentamethyl-4-piperidiny) sebacate sample, it was found that the secondary radical in the PP specimens after aging was in the form



based on the absorption peaks in the EPR spectrograms.⁹ The concentration of free radicals (N_R) in PP after being subjected to electrical stressing at an ac field of 833 kV cm^{-1} as a function of the stressing time is shown in Figure 1(a) and that for a fixed stressing time of 250 h as a function of the stressing field is shown in Figure 1(b).

IR absorption spectroscopy

A Hitachi model 26-50 IR spectrometer was used to measure the IR absorption spectra for specimens before and after being subjected to ac electrical stressing at an ac field of 833 kV cm^{-1} for various stressing times. Electrical stressing causes a change in the IR absorption peaks in the range of wave numbers below 1000 cm^{-1} , indicating that the change in absorption is due to the vibration of the low-weight molecules or radicals newly formed by electrical stressing. For PP, the peak occurring at 975 cm^{-1} is attributable to the vibration of the tertiary methyl groups¹⁰ ($-\text{CH}_2-\text{CH}_3$) and the peak occurring at 841 cm^{-1} is due to the vibration of the double-bond vinyl groups¹¹ ($\text{R}_1\text{R}_2-\text{C}=\text{CH}-\text{R}_3$). If these groups represent the low-weight radicals separated from the macromolecules, then the total net absorption would reflect the total amount of free radicals formed. By defining the net absorption peak (ΔD) as the difference between the absorption after (D) and before (D_0) the specimen being subjected to electrical stressing at 833 kV cm^{-1} , then the total net absorption peak can be written as $\Delta D_T = \Delta D_{975} + \Delta D_{841}$. Figure 2 shows the ΔD_T value as a function of the stressing time for the PP specimen electrically stressed at 833 kV cm^{-1} .

Surface potential measurements

The surface potential (V_s) can be used to determine the trap concentration. We adopted the method reported earlier.⁴ We first measured the surface potential for the specimen prior to electrical stressing (V_{s0}), which should reflect the concentration of the origi-

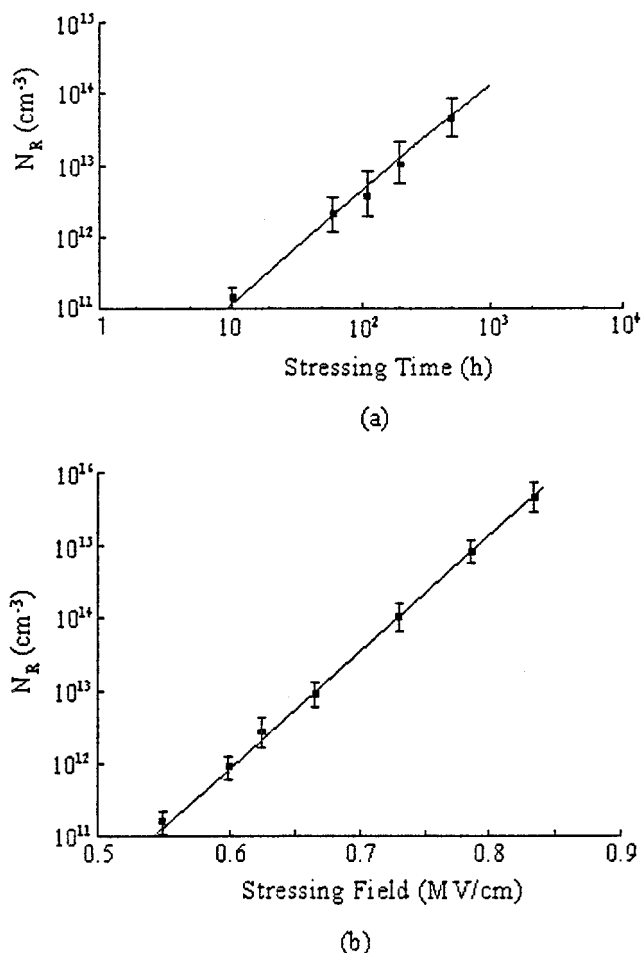


Figure 1 The concentration of free radicals (N_R) in PP specimens after being subjected to electrical stressing (a) at a fixed ac field of 833 kV cm^{-1} as a function of the stressing time and (b) for a fixed stressing time of 250 h as a function of the stressing field.

nally existing traps. After the specimen was subjected to electrical stressing, we remeasured the V_S , which should reflect the concentration of total traps, including the originally existing traps and the newly stress-created traps. Thus, the increment in surface potential ($\Delta V_S = V_S - V_{S0}$) is directly related to the concentration of the new stress-created traps. Figure 3 shows the increment of the ΔV_S value for PP after being electrically stressed at an ac field of 833 kV cm^{-1} as a function of the stressing time.

Small-angle X-ray scattering (SAXS) spectroscopy

We used a Shimadzu D/Max-TA12kW X-ray diffraction unit with a rotational target in conjunction with a model 2035 small angle scattering detector to measure the SAXS spectra. There are two major causes for small angle scattering: the boundaries between the crystalline and noncrystalline regions, and the existence of nanovoids in the specimen. In general, the SAXS due

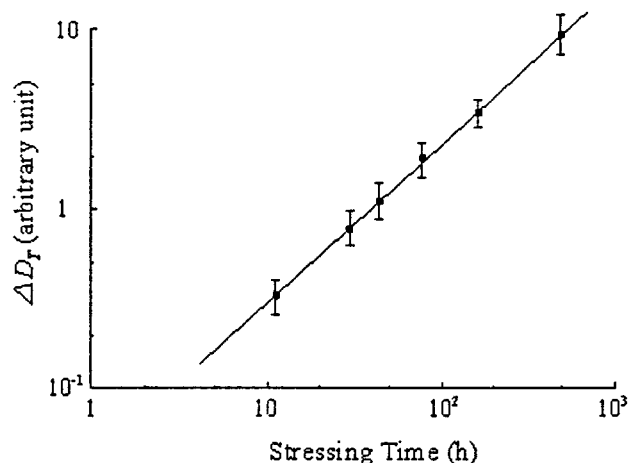


Figure 2 The total net IR absorption due to vibration of low-weight radicals in PP specimens after being subjected to electrical stressing at a fixed ac field of 833 kV cm^{-1} as a function of the stressing time.

to the second cause is much larger than that due to the first cause, so the SAXS due to the first one can be ignored.¹² Based on the analysis of the SAXS data using the standard method,^{12,13} we determined the concentration of nanovoids and the distribution of their sizes. Figure 4 presents the results for the PP after being subjected to electrical stressing at an ac field of 833 kV cm^{-1} for various stressing times.

X-ray diffraction patterns

Polymers always consist of microcrystalline regions and amorphous regions. To determine the degree of microcrystallinity in such a mixed structure, we used the method of X-ray diffraction¹⁴ with $\text{CuK}\alpha$ (accelerating voltage 40 kV and $20 \mu\text{A}$) radiation on the polymer specimen at $10^\circ < 2\theta < 25^\circ$, where θ is the Bragg angle. Figure 5 shows the X-ray diffraction intensity

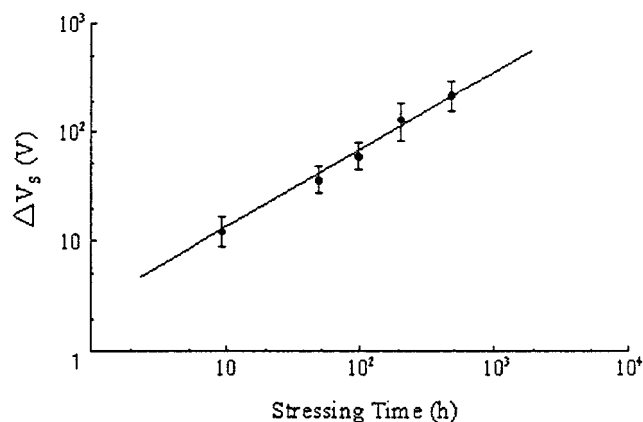


Figure 3 The increment of the surface potential for PP specimens after being electrically stressed at a fixed ac field of 833 kV cm^{-1} as a function of the stressing time.

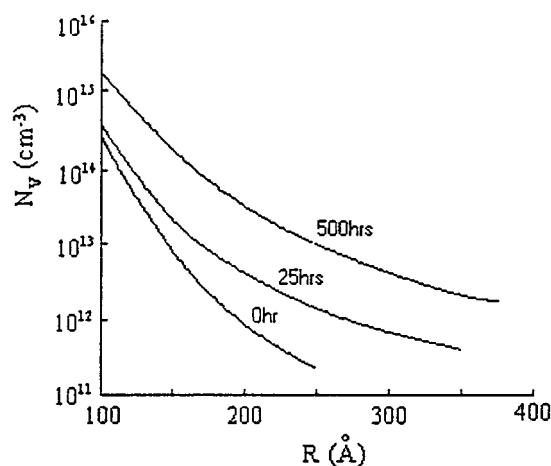


Figure 4 The concentration of nanovoids (N_v) for nanovoids of various radii (R) in PP specimens after being electrically stressed at a fixed ac field of 833 kV cm^{-1} for 0, 25, and 500 h.

for PP specimens before and after being subjected to electrical stressing at an ac field of 833 kV cm^{-1} for 25 and 500 h. The location and magnitude of the peaks correspond to the degree of microcrystallinity in the specimen. The ratio of the peak (P) to background (B) intensities (P/B) at the peaks has been chosen to characterize the degree of microcrystallinity. Thus, $P/B = 1$ means that the regions have an amorphous structure whereas $P/B > 1$ represents the degree of microcrystallinity in the regions. Table I shows the decrease in microcrystallinity with increasing stress time at a fixed stressing field of 833 kV cm^{-1} .

We also measured the effect of electrical stressing on the density of the polymer specimen and the fraction

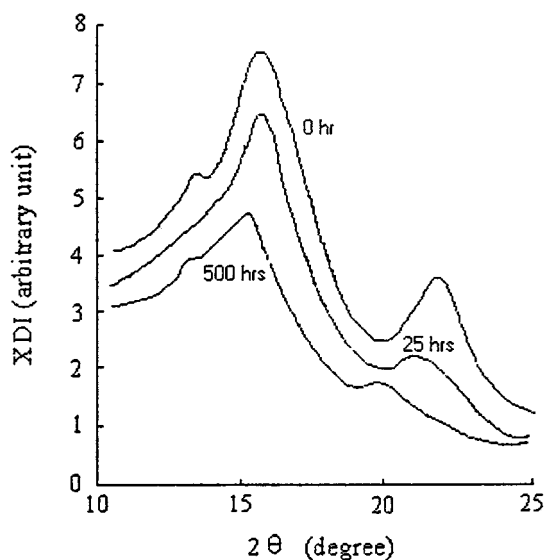


Figure 5 The X-ray diffraction intensity (XDI) as a function of the diffraction angle (2θ) for PP specimens before (0 h) and after being subjected to electrical stressing at an ac field of 833 kV cm^{-1} for 25 and 500 h.

TABLE I
Structure Parameters in Aggregate State of Polypropylene

Stressing time at 833 kV/cm	Crystallinity (%)	Density (g/cm^3)	Free volume (%)
0 h	37.4	0.8851	6.80
25 h	28.1	0.8730	9.81
500 h	26.5	0.8442	11.36

of free volume in the specimen. The latter is defined as $f = (\rho_c - \rho) / \rho_c$, where ρ_c and ρ are the densities of the material with a perfect crystalline structure and the one under investigation, respectively. Table I also shows the decrease in density and the increase in free volume with increasing stress time at a fixed stressing field of 833 kV cm^{-1} .

Electrical breakdown measurements

For these measurements, the specimen was sandwiched between a stainless steel spherical electrode with a 1-cm diameter and a polished stainless steel flat plate, which was secured in a specimen holder. Then the whole system was immersed in transformer oil to avoid possible surface discharge. The breakdown strength was measured using power-frequency ac voltages with a rise rate of 2 kV s^{-1} . At least 30 breakdowns were recorded for each electrical stressing condition, and each of the breakdown strengths is the average of about 30 measurements.

Effect of stressing field. After the PP specimens had been electrically stressed at various ac fields for 10 min and for 100 min the surface potential and breakdown strength were measured. The results are shown in Figure 6. Note that the increment of the surface potential increases but the breakdown strength decreases with an increasing stressing field.

Effect of stressing field on lifetime of polymers. For this test, each specimen was cut into two portions, one portion for the breakdown measurement and the other for the surface potential measurement. For the former measurement, the specimen was immersed in transformer oil; for the latter, we used the method reported earlier⁴ without involving transformer oil to avoid oil contamination on the specimen surface. Using these two portions of specimens, we simultaneously measured the time to breakdown at a given stressing field and the surface potential after the specimens were electrically stressed until the occurrence of destructive breakdown. The results are shown in Figure 7. It can be seen that the lifetime decreases with an increasing stressing field, but the surface potential remains practically unchanged at the time just prior to breakdown.

The experiments described above are consistent with the formation of free radicals in polymers after being subjected to electrical stressing. The changes in

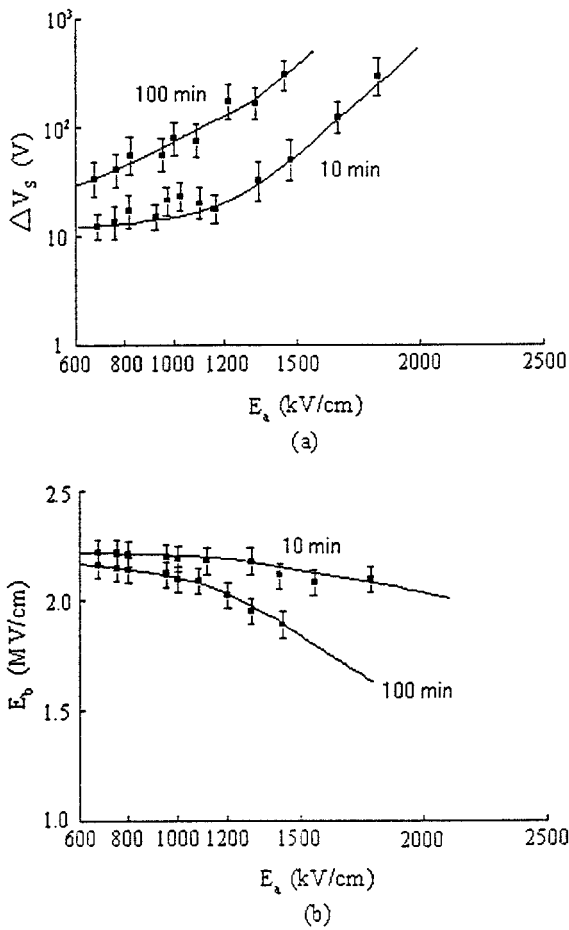


Figure 6 (a) The increment of the surface potential (V_s) and (b) the corresponding average breakdown field (E_b) as functions of the prestressing field (E_a) applied to the PP specimens for 10 and 100 min at each prestressing field.

the microcrystallinity, density, nanovoids, and breakdown strength are directly associated with the continuous decomposition of macromolecules and the formation of free radicals with stressing time. We discuss the mechanisms for its occurrence in a later section.

Inhibition of stress-induced structural degradation

Structural degradation is a direct result of the formation of free radicals. The decomposition of macromolecules to form free radicals is assumed to leave behind those broken macromolecular bonds that will act as acceptor-like traps to capture electrons. If the traps are deep traps, an energy on the order of about 4 eV may be evolved at each trapping. This energy is large enough to break the macromolecular bonds to form free radicals and hence new deep traps. That the introduction of suitable impurities into PE increases the threshold voltage for electrical tree initiation¹⁵ may be considered as being due to the creation of shallow traps to screen the deep traps in order to reduce the energy evolved during trapping.⁵ We believe this con-

cept, so we recently further studied the effects of dopants on prebreakdown and breakdown phenomena. We used dopants containing mainly phenolic hydroxyl, which is a nonsymmetrical radical needing only a small activation energy to move and react with broken macromolecular bonds to inhibit their activity. This implies that the action of the dopants tends to stabilize the disturbed region involving trapping, or recombination, in order to inhibit the broken macromolecular bonds from acting as deep electron traps. The effects of the dopants are now summarized.

Electrical treeing measurements

With a nonuniform field point-plane electrode configuration and under a high electric field, partial electrical discharge occurs first in the high-field region near the point electrode and progresses through the material, producing damage paths that look somewhat like

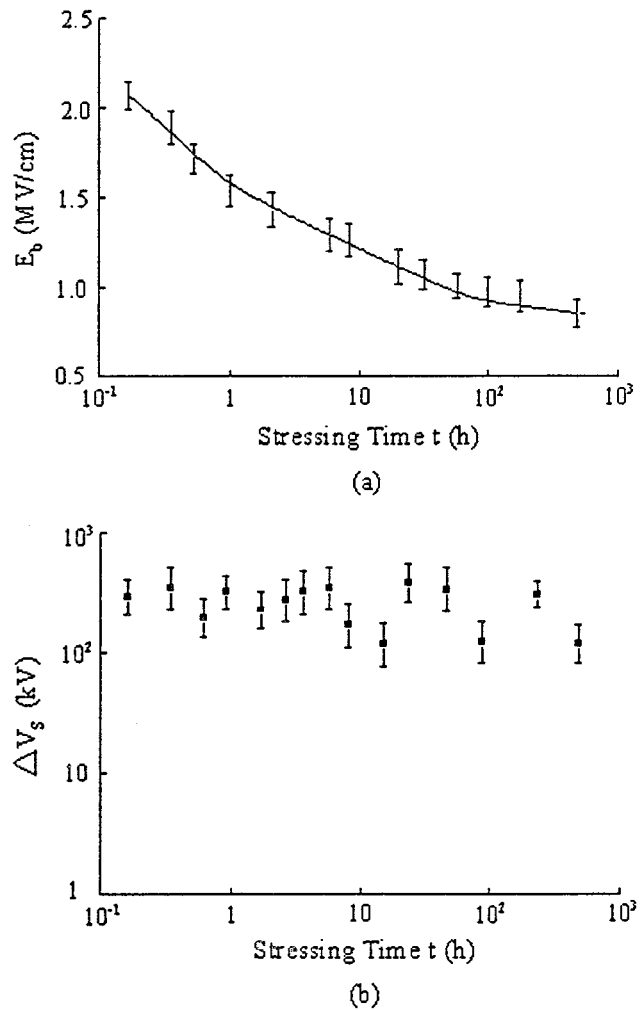


Figure 7 (a) The variation of the time to breakdown (lifetime) of PP specimens with the applied stressing field (E_b) and (b) the increment of the surface potential in PP specimens electrically stressed at various fields until the occurrence of destructive breakdown at time t .

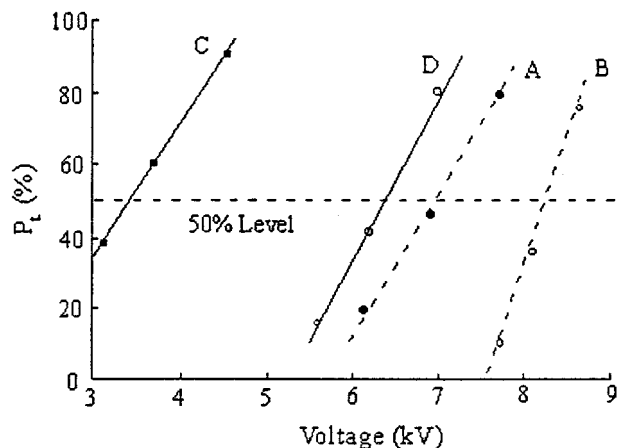


Figure 8 The percentage of PE specimens with treeing (P_t) as a function of the applied voltage. The PE specimens without dopants at room temperature (at 22°C; plot A), doped with 1% dopants at 22°C (plot B), without dopants at 80°C (plot C), and doped with 1% dopants at 80°C (plot D).

a tree. This is why this phenomenon is called electrical treeing. The voltage required to initiate the formation of a tree is referred to as the tree-initiation voltage, which is usually measured as the mean 50% initiation voltage (V_t) determined by the following procedures. The test is carried out with groups of 10 or more specimens each. Different groups are electrically stressed at different applied voltages, one group at one voltage for a period of 1 h. After the electrical stressing period, each specimen of each group is optically examined with a microscope. The percentage of the specimens that exhibit treeing (P_t) at various stressing voltages is plotted versus the applied stressing voltage as shown in Figure 8. By drawing a line at $P_t = 50\%$, the interception of this line with the plotted curve defines the mean 50% initiation voltage for electrical treeing.

Effect of temperature. It can be seen from Figure 8 that at room temperature (22°C), the mean 50% treeing initiation voltage (V_t) for PE specimens without dopants is about 6.9 kV, and it rises to 8.4 kV for the PE specimens doped with 1% dopants. At 80°C the values of V_t for PE specimens without dopants and those doped with 1% dopants are 3.5 and 6.2 kV, respectively. Although both V_t values for 80°C are lower than the corresponding values for room temperature, the percentage of the increase in V_t that is due to the incorporation of the dopants in the PE increases with increasing temperature as shown in Figure 9. We define K as the ratio of the net increase in V_t due to dopants to V_t without dopants.

Effect of dopant concentration. We also measured the V_t value for PE as a function of the concentration of dopants. The results are shown in Figure 10.

Effect of prestressing. We also studied the effect of prestressing. After prestressing the specimens at 5 kV for

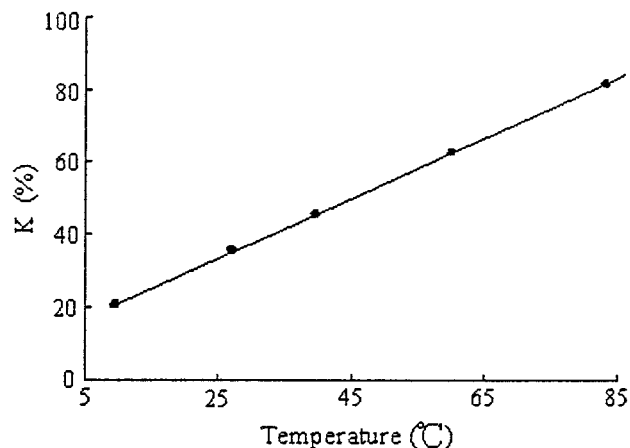


Figure 9 The percentage of increase in the mean tree initiation voltage (V_t) as a function of the temperature for PE specimens, where K is the ratio of V_t due to dopants to V_t without dopants.

48 h, we applied a stressing voltage of 9 kV and measured the percentage of the specimens with treeing as a function of the stressing time. These results were also compared with those for the specimen without prestressing as shown in Figure 11.

Electrical breakdown measurements

We used the nonuniform field point-plane electrode configuration for breakdown measurements and plotted the breakdown results on the basis of Weibull distribution statistics¹⁶ as a percentage of the cumulative probability of breakdown as a function of the stressing time at a fixed applied voltage of 10 kV. The results are shown in Figure 12. Note that the incorporation of 1% dopants into PE increases the lifetime of the polymer. We also studied the effect of prestressing. Similar to the effect of prestressing on P_t , the

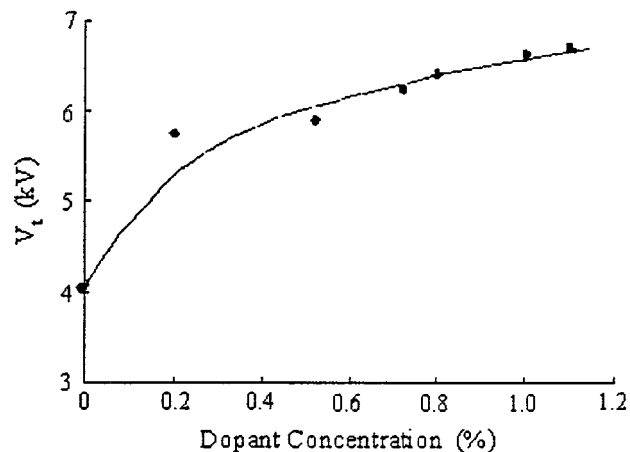


Figure 10 The mean tree initiation voltage (V_t) as a function of the dopant concentration as a percentage of the weight of the PE specimens at 80°C.

prestressing at 5 kV for 48 h tends to reduce the lifetime of the polymer without dopants but increases the lifetime for the polymer doped with 1% dopants.

RESULTS AND DISCUSSION

With regard to insulating polymers, we would immediately refer to the materials with a large energy bandgap, a large concentration of carrier traps, low carrier mobility, and a structure formed mainly by a weak bond of large macromolecules. Because of the large energy bandgap, the potential barrier height for electrons injected from the electrical contacts to the polymer is usually smaller than that for hole injection, implying that electron injection is dominant in insulating polymers under normal practical conditions.¹⁷⁻¹⁹ The nature of the bulk trapping states in polymers has been studied by several investigators.^{20,21} Their experimental results have indicated that most bulk traps are acceptor-like electron traps and donor-like hole traps. Because these traps are an acceptor-like type with a large capture cross section, the injected carriers cannot travel very far before being trapped. This is also why for low mobility insulating polymers the trapped carriers essentially lie in a narrow region close to the carrier-injecting contact.^{4,22-24} It is most likely that the electrons are injected into the polymer from the metallic cathode mainly by Fowler-Nordheim tunneling.¹⁷⁻¹⁹ These injected electrons will quickly become trapped after one or a few scatterings. According to Kao's model,⁵ a transition of an injected electron from an upper energy state (e.g., conduction bands) to a lower one (e.g., traps) due to trapping or recombination involves an energy release. This en-

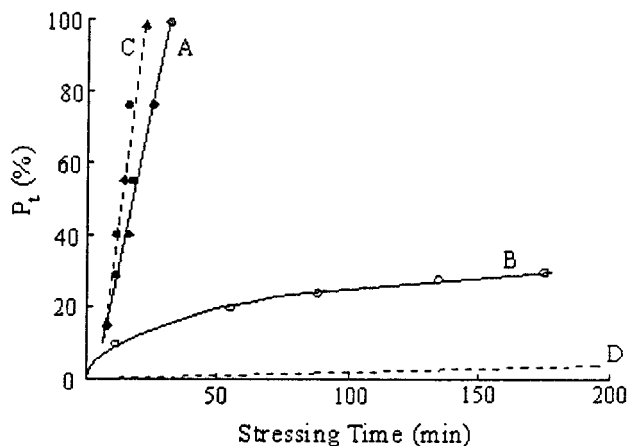


Figure 11 The percentage of PE specimens with treeing (P_t) as a function of stressing time under a fixed stressing voltage of 9 kV. The PE specimens without dopants and without prestressing (plot A), doped with 1% dopants but without prestressing (plot B), without dopants but after prestressing at 5 kV for 48 h (plot C), and doped with 1% dopants and after prestressing at 5 kV for 48 h (plot D).

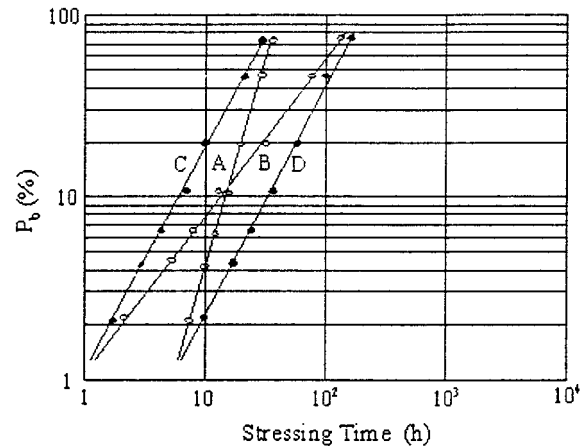
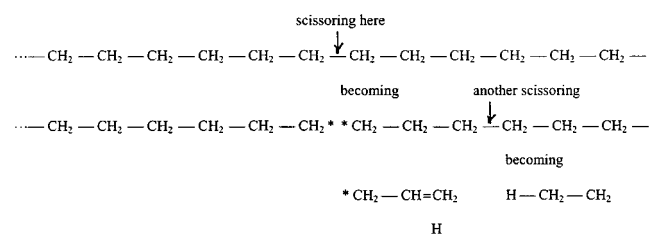


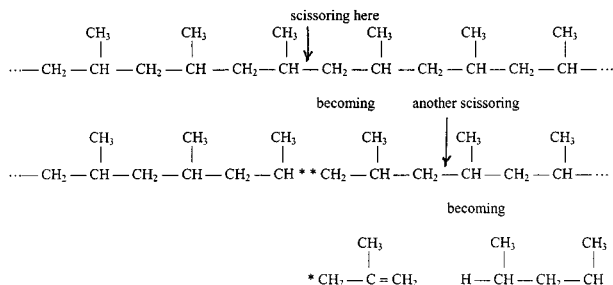
Figure 12 The percentage of cumulative probability of breakdown (P_b) as a function of the stressing time at a fixed stressing voltage of 10 kV. The PE specimens without dopants and without prestressing (plot A), with 1% dopants but without prestressing (plot B), without dopants but after prestressing at 5 kV for 48 h (plot C), and doped with 1% dopants and after prestressing at 5 kV for 48 h (plot D).

ergy, which may be on the order of 3–5 eV, is most likely dissipated in breaking the bonds of macromolecules to form free radicals. The ends of the broken bonds with unpaired electrons will act as acceptor-like traps. Kao⁵ has pointed out that the energy release due to trapping may also be transferred to another electron and make it become a hot electron via an Auger-type process and that such hot electrons would then bombard the macromolecules and decompose them, thereby causing structural degradation, formation of free radicals, and creation of new traps. Harari²⁵ has reported that electron injection into SiO₂ films at high fields results in the creation of a high density of defects close to the electron-injecting contact, which behave as electron traps. It is reasonable to think that the structural defects produced by the decomposition of macromolecules in polymers or by the breaking up of the normal structure in SiO₂ would result in the formation of new traps.

A PE molecule may be scissored off by the bombardment of a hot electron into the following radicals:



Similarly, a PP may be scissored into the following radicals:



The two broken parts have free valences in the form of unpaired electrons, which are generally identified as free radicals with an asterisk (*). These radicals readily react with other atoms, molecules, or radicals. They also act as acceptor-like electron traps to capture electrons.²⁶ The radicals formed in PP have been identified by EPR spectroscopy. Obviously, the above reactions would go on to produce more and more radicals and hence new traps when the electron injection from the electrical contact is increased by increasing the stressing field or increasing the stressing time; in other words, the number of trapping events is increased.

In our previous article⁴ we derived a formula for the relation between the concentration of newly stress-created traps (N_t), the stressing field, and the stressing time under high-field stressing conditions. This formula is given by

$$N_t = AtE_a \exp(BE_a) \quad (1)$$

where A and B are constants depending on the material structure and the potential barrier profile of the electrical contact for electron injection, E_a is the average stressing field, and t is the total stressing time. If the concentration of N_R is assumed to be proportional to the concentration of the newly stress-created traps, the relation shown in Figure 1 clearly indicates that N_R has an approximately linear relationship with the stressing time and an approximately exponential relationship with the stressing field, which are in good agreement with the theoretical prediction of eq. (1). The linear relation between the IR absorption and the stressing time shown in Figure 2 further confirms that electrical stress causes the decomposition of macromolecules to form low-weight molecules or free radicals.

In our previous article⁴ we also derived a formula to relate the concentration of the newly stress-created traps to the increment of surface potential:

$$\Delta V_s = \frac{\delta q d}{\epsilon} N_t \quad (2)$$

where δ is the thickness of the narrow region close to the electron injecting contact where the traps are filled with trapped electrons; q is the electronic charge; and

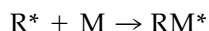
d and ϵ are the thickness and permittivity of the specimen, respectively. Figure 3 shows that the increment of the surface potential is almost linearly proportional to the stressing time at a fixed stressing field. Thus, by comparing Figures 1 and 3, we can say that the concentration of newly stress-created traps is proportional to the concentration of stress-created free radicals.

The concentration of stress-created radicals is a good indication of the degree of structural degradation that directly reflects the degree of electrical aging. Figure 4 shows that both the number and size of nanovoids increase with increasing stressing time. The large nanovoids are, in effect, the so-called low-density domains referred to by Kao.⁵ He has considered the formation of low-density domains as a necessary prelude for the occurrence of electrical discharge and breakdown, which are initiated by impact ionization. Only in low-density domains, where the electron free path is large, can impact ionization take place. Naturally, the more structural degradation there is, the smaller is the microcrystallinity as indicated in the X-ray diffraction patterns shown in Figure 5. As a result, the free volume increases and the density of the specimen decreases with increasing stressing time at a fixed stressing field of 833 kV cm⁻¹, as shown in Table I.

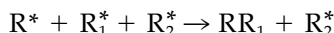
The fact that the surface potential increases with an increasing prestressing field and the breakdown strength decreases with an increasing prestressing field for a fixed prestressing time (Fig. 6) clearly indicates that the action of prestressing enhances the creation of more free radicals and therefore traps. Thus, the lifetime of an electrically stressed insulating polymer can be considered as the time required for the occurrence of destructive breakdown at a given stressing field. A typical relationship between the lifetime and the stressing field is shown in Figure 7(a). It is important to note that the surface potential due to the accumulated trapped electrons in the newly stress-created traps during the lifetime remains practically constant as shown in Figure 7(b). It can thus be concluded that the lifetime of an electrically stressed insulating polymer is the time required for the concentration of stress-created traps to reach a certain critical value, or, in other words, the time required for the size of low-density domains (i.e., nanovoids) to grow to a certain critical size to favor impact ionization inside them.

At this point the important task is to inhibit the gradual structural degradation process. On the basis of Kao's model,⁵ the major cause of this damaging process is the carrier injection from electrical contacts and the subsequent energy that evolves as a result of the carrier trapping or recombination. In our earlier article²⁷ we proposed the use of suitable emission shields to suppress carrier injection in order to reduce

the amount of injected carriers and the number of trapping events. Here we attempt to use suitable dopants to reduce the energy evolved from trapping. An electrically stressed polymer contains a larger number of molecules with free valences in the form of unpaired electrons at their endings. These unpaired electrons act as acceptor-like electron traps, which may be deep traps, depending on the structure. If a dopant can satisfy such unpaired electrons, it may serve the purpose of killing a deep trap and possibly producing a new shallow trap as described in the following. By denoting the molecule with an unpaired electron as R^* and the dopant as M , the reaction between R^* and M may be as follows:



This may kill the deep trap due to R^* and create a new shallow trap due to M^* . A dopant may also be dissociated into two new radicals, R_1^* and R_2^* , when it is dissolved into the polymer. If this is the case, we may have



In this case, R_1^* may chemically combine with R^* , leaving R_2^* to produce shallow traps. Dopants that can perform such a function would stabilize the disturbed region involving trapping, so they may be called the "stabilizers." Because they would also inhibit the activity of R^* , they may also be called the "scavengers." However, to avoid confusion, we use the term dopants.

We now describe the effects of the dopants on electrical treeing and breakdown phenomena under a nonuniform field condition. Electrical treeing has two distinct phases. The first is the tree initiation phase during which no partial discharge appears, and the second is the growth phase during which the tree propagates. It has been reported that luminescence appears during the initiation phase.^{28,29} This may indicate that low-density domains (or large size nanovoids) have been formed in the initiation stage because of the very high field at and near the point electrode tip. The appearance of luminescence indicates the occurrence of impact ionization inside the low-density domains. Xie and Kao³⁰ have reported the development of a low-density region at the point electrode tip in liquefied PE under high electric fields. Kao et al.³¹ have also found that the electrical treeing initiation voltage increases with increasing hydrostatic pressure in PE. A similar phenomenon of the effect of hydrostatic pressure has also been observed by Kao and Rashwan³² in hydrocarbon liquids, in which the brightness of the luminescence appearing at the point

electrode tip at high fields decreases with increasing hydrostatic pressure. All this experimental evidence strongly supports the formation of free radicals and hence the low-density domains that are responsible for all prebreakdown and breakdown phenomena in polymers.

Figure 8 shows that the incorporation of dopants causes an increase of the mean 50% tree initiation voltage. This can be explained as being due to the action of the dopants to suppress the formation of large-size nanovoids. The effect of temperature is just the opposite of the effect of pressure. The former helps to enlarge the size of nanovoids, whereas the latter squeezes the size of nanovoids. This is why the V_t decreases with increasing temperature for both the undoped and doped PE. However, as the dopants have already slowed down the process of forming large-size nanovoids, the effect of temperature would be more severe for the undoped specimens than for doped ones. This is why the percentage of increase in V_t that is due to the incorporation of dopants (K) increases with increasing temperature as shown in Figure 9. The value of V_t is also expected to increase with increasing dopant concentration as shown in Figure 10, but such an increase tends to become saturated. A further increase in the dopant concentration may produce a reverse effect. Prestressing for undoped specimens enhances the process of structural degradation and the formation of large-size nanovoids. This is why the P_t value increases and the percentage of specimens with breakdown (P_b) also increases with increasing stressing time at a fixed stressing field, which is shown in Figures 11 and 12. However, the effect of prestressing is different for doped specimens. In this case, prestressing may help the dopants to have more chances to suppress more deep traps and to create more shallow traps to screen the deep traps, thus reducing the energy evolved during trapping. Therefore, both P_t and P_b decrease with increasing stressing time (Figs. 11, 12).

CONCLUSIONS

All of the experimental results presented above indicate that prebreakdown phenomena in insulating polymers such as high-field electrical conduction and electrical aging are initiated by carriers injected from electrical contacts and their subsequent dissociative trapping and recombination, which leads to the formation of free radicals. This is a gradual structural degradation process. To inhibit such a harmful process, suitable dopants that act as free-radical scavengers can be used to suppress the rate of increase of stress-created deep traps or to create more shallow traps to screen the deep traps in order to reduce the energy evolved during carrier trapping and recombination. All the prebreakdown and breakdown phe-

nomena can be explained on the basis of Kao's model.⁵ The degree of electrical aging can be determined by the rate of increase in the concentration of stress-created free radicals or traps. Partial electrical discharge (or electrical treeing) or breakdown occurs when the concentration of stress-created free radicals or traps has reached a certain critical value such that low-density domains (or called nanovoids) formed in the high-field region would reach a size large enough to favor impact ionization inside them.

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