REVIEW

DEGRADATION PRODUCT ANALYSIS FOR POLYMERIC DIELECTRIC MATERIALS EXPOSED TO PARTIAL DISCHARGES*

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ABSTRACT

Partial discharge phenomena appear to play an important role in insulation failure, and thus the analysis of products resulting from such degradation may lead to an understanding of insulation breakdown mechanisms and more accurate determination of insulation lifetimes. Progress in the area of degradation product analysis is reviewed for solid and liquid insulating materials.

INTRODUCTION

The determination of the aging characteristics and lifetimes of electrical insulation materials is of critical importance to users of such materials. Several general approaches for predicting lifetimes have been investigated, such as time to breakdown studies, critical breakdown stress, treeing behavior, and change in the loss tangent with time. No conclusive failure mechanisms have been defined, although the damage caused by partial discharges in the voids and gaps of the insulation system appears to be of central importance. Dakin [1] suggests that careful analysis of the degradation products resulting from such damage seems to offer promise for the future elucidation of breakdown mechanisms and the accurate determination of aging rates. After a brief introduction to polymer degradation mechanisms, progress in the area of chemical degradation of polymer dielectrics due to partial discharges will be reviewed. Limited reference will also be made to the analysis of products produced in thermal degradation studies.

DEGRADATION MECHANISMS

Theories of the degradation mechanisms of polymers can be described mathematically with the object of obtaining an expression for the average size distribution of the molecules at various stages of the degradation process. The simplest model, random breakage of chain links, assumes that all links have an equal probability of breaking. If a molecule contains weak links, in addition to normal links, the expression for the size distribution of molecules during degradation depends upon the number and the distribution of weak links. In these models, the breaking of a particular link is independent of any other link breaking. This is not true when chain depolymerization occurs. Here, the degradation process consists of discrete initiation, propagation, and termination steps. An initial break occurs, forming radical species, at a particular link. Small units then break off in sequence behind this initial break. Various reactions can then occur which terminate the process. The length of chain depolymerized before termination occurs is called the kinetic chain length.

The important degradation mechanisms involving the basic principles outlined above are thermal, oxidative, radiative, mechanochemical, and chemical degradation. Only a brief description of each process will be given here, as several comprehensive works [2-4] on the subject, including complete mathematical treatments, are available.

Thermal degradation occurs in the bulk phase in the absence of other reactive species. Depolymerization is common, and if the radical species, formed thermally by the initial link breakage, tend to avoid radical transfer reactions, i.e., the kinetic chain length is large, monomer yield may be close to 100%.

Oxidative degradation also involves an initial radical forming reaction, but here the presence of molecular oxygen often results in the formation of hydroperoxide and peroxide radical species on an originally hydrocarbon substrate. For the case of n-decane oxidation [5], the hydroperoxide species result in the formation of alcohols, ketones, and acids.
Radiative degradation is divided into photolysis (photochemical radiation) and radiolysis (ionizing radiation) [2]. An example of the former is ultraviolet radiation, where relatively low levels of energy are absorbed by specific functional groups, chromophores, present in the polymer molecule. Ionizing radiation, e.g., X-ray, gamma rays, and electron beams, involves energies greater than photochemical radiation by a factor of $10^2$ to $10^8$. Whereas photolysis most often results in chain scission and monomer formation, radiolysis may cause, depending on the polymer involved, either degradation to low molecular weight species, or cross-linking.

One of the earliest studies of polymer degradation involved mechano-chemical degradation. In 1820, Hancock [6] noted that natural rubber passed through spiked rollers did not shred, but rather was transformed into a soft mass. It is now known that the polymer degraded to a lower molecular weight. In this type of degradation, the initial break is a result of applied mechanical force, and the free radicals so formed may then react with other chemical species, e.g., $\text{O}_2$, that may be present. Ultrasonic degradation [7-9,12] is often classified as a type of mechano-chemical degradation.

Finally, a large number of investigations have been undertaken [10] to determine the role of reactive chemicals in the degradation of polymers. Among the important chemical agents are $\text{NO}_2$, $\text{SO}_2$, $\text{O}_3$, acids, alkalies, and halides. As a brief example [11], $\text{NO}_2$ may react with polystyrene, removing a tertiary H atom. This results in random chain scission at the points of attack, and the formation of unsaturated terminal links and nitro and nitrite substituents.

**SOLID DIELECTRICS**

The premature failure of solid polymeric insulation systems is a serious economic and technical problem, especially in the high-voltage electrical engineering, or the formation of partial discharge channels [1]. It is often associated with the failure of solid insulating materials. Erosion of the polymer may lead to the formation of discharge channels. Wagner [13] postulated that depolymerization took place, as he observed no carbonization. Billings, et al. [14], in their study of tracking concluded that carbonization, or the formation of a conductive char, will occur under the influence of discharges in polymers where either ladder polymerization or loss of a substituent group can take place. However, polymers which do not undergo carbonization, such as polyethylene, depolymerize, and therefore erode. Such erosion is often the origin of partial discharge products. Mayou and Goldman [15], in their study of the form of partial discharges, have postulated a mechanism for erosion, and Bui Ai, et al. [16], Valdenego [17], and Aronov, et al. [18] have developed relations between the discharge energy and the volume eroded.

The three types of studies made of the degradation products of polymeric insulators involve gaseous products, solid crystalline products, and structural changes in the remaining polymeric material.

**Gaseous Degradation Products**

The simplest method of detecting gaseous decomposition products is through a change in pressure within a closed cell. Loffelmacher [19] has investigated the gas pressure evolution in partial discharge cavities in polyethylene and its influence on treeing. He noted that the gas pressure, measured optically, increases as the applied voltage increases, and that the rising gas pressure eventually interrupts the electrical discharges. McMahon and Perkins [20], in their study relating tree development in polyethylene to partial discharges, also concluded that increased gas pressure leads to corona extinction conditions; growth of the tree was impeded until the gaseous products could diffuse out of the void, reducing the pressure. However, Oliphant [21] has observed net decreases in void pressure during the long-term corona testing of epoxy resins, stating that while gaseous products are formed, their rate of formation is insufficient to compensate for the decrease in void pressure caused by the formation of nitrogen oxides and other non-volatile oxidation products. Ito, et al. [22], noted an increase in void pressure when the void was filled with nitrogen, and a pressure decrease when filled with oxygen. Mass spectrometric analysis showed $\text{H}_2\text{O}$ and $\text{CO}_2$ were formed in the oxygen-filled void. Bagirov, et al. [23], studied the volatiles evolved from polyethylene, polyvinyl chloride, and polytetrafluoroethylene by mass spectroscopy. In each case, uniaxial orientation of the polymer increased its resistance to degradation by discharges, as the amount of volatiles found was smaller.

Several other investigators have identified gaseous products, including Hawley [24], who found $\text{H}_2$, $\text{CO}_2$, and hydrocarbons evolved from a Bakelite sample in an oil-filled cell. Leroy, et al. [25], describe an electronic device for recording the total quantity of electricity corresponding to the discharges, and an instrument for the qualitative and quantitative analysis of the evolved gas mixture based on gas chromatography (GC) and infrared spectroscopy (IR). From results obtained with polyethylene, they concluded that $\text{H}_2$ was the only decay product, and heavier gases appeared only on dielectric breakdown. Stannett and Meats [26] subjected a polyethylene film to surface discharges in a variety of atmospheres, determining the time-to-breakdown and the composition of the evolved gases. The $\text{H}_2$ content, $V$, increased with time according to the relation $V = K t^{0.5}$ (where $K$ increases with discharge energy), and at breakdown was 7-15% of the total gas volume; traces of unidentified hydrocarbons were also detected. Grigor'ev, et al. [27], found $\text{H}_2$, $\text{CH}_4$, $\text{C}_2\text{H}_6$, and $\text{CO}_2$ to be evolved from low molecular weight polybutylene exposed to an electric field in air. Kammrauer and Hagedorn [28] used a gas chromatography column packed with molecular sieve 5A to determine the gaseous products of the partial discharge degradation of six polymeric insulations. The results are given in Table 1. Dear, et al. [29], have described an analytical method, based on a pre-column technique, for determining the organic compounds in the hydrogen gas used for cooling large electrical generators at a level of 1 picogram per liter.
One of the proposed mechanisms by which partial discharges erode a polymer is electron bombardment. Mitsui, et al. [30], used gas chromatography to identify the gases evolved from an acrylic sample exposed to an electron beam. They found that side chain ruptures occurred under fast discharges, and monomer generation under slow discharges. Lacoste [31] stated that the degradation mechanism is related to the energy of the discharge. He exposed polyethylene to surface discharges and found that H2 evolution increased with applied voltage. Examining the polyethylene film with infrared spectroscopy before and after exposure to discharges, he concluded that the action of the discharges was similar to electron bombardment degradation.

**Structural Changes in the Polymer**

A number of other investigators have also obtained useful information from structural analysis of the remaining polymeric material. IR spectroscopy was most commonly used, but Abasov and Kabulov [32] studied the effect of partial discharges on structure in terms of Tg, the softening or glass transition temperature. They found the discharges had no effect on the Tg of polyethylene, but for polyethylene terephthalate, there was an initial increase due to cross-linking, and a subsequent decrease, due to degradation. Among those who have employed IR spectroscopy, Blahnik and Hranikova [33] have studied the combined effect of corrosive gases and partial discharges on a polymer film, and Veisova and Predasik [34] have examined the effect of discharges in air and in steam. Oxidation of the polymer is the usual effect of discharges, as determined by IR spectroscopy. Blahnik and Hranikova [35] also studied the changes in the IR spectra of polyester and other films with time, as illustrated in Figure 1. They detected CO2, CH3, OH, NO2, NO3, and C=O, and concluded that thermal oxidative aging took place. Kajiyama [36] considered oxidative degradation of organic insulating materials using quantum mechanics, and formulated a reactivity index. The predicted order of stability was: phenolic resin > melamine resin > polyester > polybenzimidazol]; experimentally, the last mentioned was the only discrepancy from the theory.

Mayoux [37] attempted to determine the constituent parts of discharge degradation by using IR to monitor the structural changes in polyethylene due to electrons, ions, uv radiation, and electrical discharges, but concluded that the effect of partial discharges could not be explained by the superposition of these constituent effects. Benson [38] used IR to study the service aging of flexibilized epoxy resins, used in high voltage rotating electrical machines, and noted that aging was evident after only a few days of normal service. Kim and Goring [39] noted the formation of bumps on the surface of polyethylene after corona (discharge) treatment in oxygen. These microscopic bumps were dissolved by several solvents, examined by IR, and were found to contain carbonyl groups and a substantial portion of -CH2- linkages. Rossman [40] also detected carbonyl groups on the surface of polyethylene exposed to discharges, as did Hines [41], who concluded that the oxidized groups were formals and semi-formals, with a small amount of carboxylic acid. Grigor'ev, et al. [27], detected the formation of hydroperoxides, carbonyl compounds, and carboxylic acids in polybutylenes exposed to an electric field in air. Hydrogenated polybutylene was found to be more resistant to such thermal oxidative degradation.

**Solid Degradation Products**

Numerous workers have mentioned that after a period of ac stressing the partial discharges cease within the voids of the dielectric. Increased gas pressure,
resulting in corona extinction, has been postulated [20] as a cause, but short circuiting of the void due to conducting solid degradation products deposited on the wall of the void has also been mentioned. These general mechanisms are summarized in Figure 2. Oxalic and succinic acid crystals have been found by several investigators [42-48] on the discharge surfaces of polyethylene, polystyrene, and poly(ethylene terephthalate). Often, these crystals are adjacent to eroded pits on the polymer surface, as reported by Rogers [49]. Mandelcorn [50] has found that the gaseous degradation products of polymethylmethacrylate themselves break down, due to the discharges, and deposit a layer of carbon on the polymer surface. The occurrence of this in enclosed voids may suggest another mechanism for discharge cessation due to solid degradation products.

Degradation Due To Reactive Gases

The preceding studies mentioned in this review have dealt mainly with degradation caused directly by the partial discharges. However, since gas molecules are ionized by the electric field and reactive species formed in the gas phase by the discharges, it is necessary to consider the effects of these on the degradation of the polymer. Agarwal [51] states that the cause of corona degradation in air is the chemical activity of nitrogen oxides and ozone which are formed by the discharges and lead to oxidation of the polymer. Bagirov, et al. [52], have made an IR study of polyethylene degradation due to atomic oxygen formed by high voltage discharges. The atomic oxygen was formed in one chamber and then pumped into the separate sample cell. The IR spectra indicated that C-C bonds were broken and terminal aldehyde groups formed. Mayoux, et al. [53] compared the degradation of polyethylene due to partial discharges with that caused by O+, Ar+, Ne+, and He+. The effect of O+ was found by IR to be chemical, while the other ions, which do not form compounds, resulted in mechanical degradation, the degree of which depended on the mass of the ion. In another report, Mayoux and Bui Al [54] compared the degradation caused by discharges, O+ ions, electrons, and uv radiation. The oxidative deterioration produced by O+ resembled partial discharge degradation, while that caused by electrons and uv radiation did not. Antioniou, et al. [55], found that bombardment of polyethylene with O+ ions also resulted in the appearance of carbonyl groups. Bagirov, et al. [56], have studied the effect of ozone and partial discharges on the temperature dependence of the loss tangent and the dielectric constant for polyvinylidichloride films. Cooper and Prober [57] have compared the effects of oxygen corona (in which ozone is produced) and ozone alone on polyethylene. The samples exposed to the discharges exhibited a net weight loss, due to the loss of CO2, H2O, and CO, which increased linearly with exposure time, while the samples exposed only to ozone showed a net gain in weight that leveled off with time, as shown in Figure 3. This indicates that ozone alone produces only surface oxidation and no evolution of volatile degradation products; Figure 4 supports this conclusion. These results demonstrate that ozone alone is not responsible for dielectric breakdown, although it may play an important role. Finally, Rodaro, et al. [58], observed crack formation in polyethylene sheets bombarded with low energy (< 50 eV) H+ and H2+ ions. In the same report, a method is described for measuring the emission spectra of the decomposition products released from polyethylene exposed to electrical discharges.

Thermal Degradation

Degradation involving thermal processes is also important in dielectric failure. Billings, et al. [14], have suggested that partial discharges act as a heat source, and that gaseous degradation products are formed thermally. Torelli [59] has calculated the heating effect of the discharges, as have Bagirov, et al. [60], who have demonstrated that the temperature is generally insufficient for thermal breakdown, but sufficient for thermal oxidative degradation. Numerous investigations, employing a variety of methods, have been made to determine the thermal and thermal-oxidative degradation products of polymers, including the following: polyethylene [61-68], polyvinylchloride [69-74], polyethylene terephthalate [75-77], polyimides [78],...
Partial Discharges in Voids and/or Gaps

lower gas pressure

evolution

diffusion

depleted gas pressure

deposited conducting products

gaseous products

Fig. 2: Diagram of mechanisms by which discharge cessation may occur in an enclosed void.

Fig. 3: Change in weight of films exposed to discharges and ozone alone. From ref. [67] by Cooper and Prober.

epoxy resins [79, 80], and others [81-88]. In several cases [63, 71, 72, 75, 77, 78, 82, 85] the kinetics of the degradation have been investigated, either by considering the rate of product formation, rate of weight loss, or in the case of thermal oxidative aging, the rate of oxygen uptake.

LIQUID DIELECTRICS

Oils have been used extensively as insulation in transformers and oil-paper composites. The gaseous degradation products of oil insulation systems have long played an important role in fault prevention in power systems. The Buchholz relay [89] was developed in the 1920's to collect the gases evolved from transformer oil, and trip a float-activated relay before a major breakdown could occur. Analysis of the evolved gases is now widely used to indicate the type of failure, its severity, and its location [90-95].

Table 2 relates degradation mechanisms of \((\text{CH}_2)_n\) type transformer oil to temperature. Yasuda, et al. [94], have reviewed procedures for analyzing gases in transformer oil, and have discussed [95] the maintenance of power transformers by analyzing gases dissolved in the oil. Shirai, et al. [96], have studied the thermal decomposition of insulating oil by considering the thermodynamic equilibria involved in relation to the gases found dissolved in the oil. The decomposition consists of primary and secondary stages, with the former, at lower temperature, involving the evolution of saturated hydrocarbons, and the latter the evolution of \(\text{CH}_4\), \(\text{C}_2\text{H}_4\), and propylene. In a separate study, Shirai, et al. [97], found that the dehydrogenation of oil may be catalyzed in transformers by the presence of stainless steel.
TABLE 2

Degradation Mechanisms of (CH₂)n-type Transformer Oils*

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Mechanisms</th>
<th>Products</th>
</tr>
</thead>
<tbody>
<tr>
<td>no heating</td>
<td>partial discharges, resulting in random scission</td>
<td>H₂ and CH₄(1:1)</td>
</tr>
<tr>
<td>200-400°C</td>
<td>thermal oxidation and volatilization</td>
<td>H₂O, CO₂, CO</td>
</tr>
<tr>
<td>700-800°C</td>
<td>cracking</td>
<td>C₄H₄</td>
</tr>
<tr>
<td>3000°C</td>
<td>arcing, resulting in complete scission of all bonds</td>
<td>H₂ and C₂H₂</td>
</tr>
</tbody>
</table>

*information from ref. [90] by Waddington

A variety of methods have been used to identify the degradation products of transformer oil under thermal and/or electrical stressing. Thibault and Galand [98, 99] have described a method using gas chromatography for the analysis of fault gases, including hydrocarbons up to butane, and have determined the partition coefficients of these gases between the gaseous and oil phases as a function of temperature. Biacs and Takacs [100], also using gas chromatography, identified hydrocarbons up to butylene. Ishii and Namba [101] point out, however, that while CO₂, methane, CO, and ethane are commonly evolved from transformer oil in service, heavier gases are rare in appreciable amounts. Dornenburg and Gerber [102] found H₂, methane, acetylene, ethylene, and ethane by degassing the transformer oil. Oxides of carbon were also found, but were said to be due to the breakdown of wood, paper, or plastic materials present, and not the oil. Senkevich and Shtern [103], who studied discharges between electrodes in oil, reported that the quantities of H₂ and methane, as determined by gas chromatography, increased monotonically with average current. Nagel [104] has reviewed the application of mass spectroscopy to the determination of fault gases from transformer oil and resin impregnated paper insulation. Mathes [105] has discussed the formation of gaseous and wax-like products in oil-impregnated paper insulation. Several different oils were tested, in two types of cells, and a histogram of discharge count vs magnitude was integrated and recorded (monitored corona spectroscopy). Other investigations of oil-impregnated paper insulation included those by Moraru, et al. [106], who detected hydrogen evolution, and Beer, et al. [107], who found hydrogen and small hydrocarbons, and no oxides of carbon.
CONCLUSIONS

Considerable effort has been expended in determining the degradation products of dielectric materials. The important questions, still to be answered conclusively, concern the mechanisms of degradation and the degradation rate, in service. Waddington [90], for example, has related the fault gases of transformer oil to temperature-dependent mechanisms, but mere work is required in the area of solid dielectrics. Most kinetic analyses of degradation have concerned thermal stress, and in order to determine the real lifetimes of materials, such investigations need to be undertaken under conditions resembling service as closely as possible, since the effect of the electric field is clearly important. Finally, it is imperative, as pointed out by Dakin [1], that a correlation between decomposition and a functional failure condition be established.

REFERENCES


*Part XII of A Series on Lifetime Prediction of Electrically Insulating Materials

Manuscript was received 27 December 1977, in revised form 3 April 1978.
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