The Chemical Nature of Water Treeing: Theories and Evidence

James J. Xu and Steven A. Boggs
Electrical Insulation Research Center, University of Connecticut

Introduction

Water trees, first reported in 1969 [1], grow in a wide range of hydrophobic polymeric insulating materials when exposed to the combination of moisture and electrical stress. The phenomenon reduces the electrical strength of the insulation and jeopardizes the multi-billion dollar utility investment in polymeric distribution cable. As a result, water treeing has been high on the agenda of power engineers for over two decades. During this time, innumerable empirical "water treeing studies" have been carried out. These statistically-based experimental studies of water treeing as a function of growth conditions have produced a base of contradictory data that can be used to support almost any hypothesis. Only recently has the scientific community converged on an explanation of water treeing that is evolving into an ever more detailed theory, which now reaches down to the level of molecular chemistry. This article provides an overview of the present understanding.

Experimental Technique

The line of investigation that has resulted in a description of the underlying mechanism of water treeing is based on the study of chemical species produced during water treeing. Most of the data are based on microscopic Fourier transform infrared (micro-FTIR) differential spectroscopy (DS). This technique produces a high resolution infrared (IR) absorption spectrum of the difference between absorption in a treed region and a nearby untreed region. The "micro" part of micro-FTIR refers to focusing of the IR beam to microscopic dimensions so that the beam can be restricted to a treed region, while "FTIR" refers to a spectroscopic technique in which the infrared spectrum is measured using an interferometric technique followed by a Fourier transform of the resulting data to obtain the absorption spectrum. The advantages of this approach are twofold, viz., (i) the resolution depends on the distance a mirror in the FTIR spectrometer is moved during acquisition

As we "celebrate" the 25th anniversary of water treeing as a recognized phenomenon, we can take solace that understanding is now approaching a fundamental level.

of the data and (ii) data for all spectral resolution elements are acquired during the entire period of data acquisition. The latter is known as the "multiplex" advantage of FTIR and results in an increase in the signal-to-noise ratio of the resulting spectrum equal to the square root of the number of spectral resolution elements.

The investigation of the chemistry of water treeing based on micro-FTIR is complicated by ambiguities that result from the overlap of spectral features. These ambiguities are generally resolved through the use of chemical reactions that shift the IR absorption of specific species to wavelengths with less interference. For example, the carboxylate ion, with absorption in the range 1540 to 1600 cm^{-1} (wavelengths per cm), can be converted to carboxylic acid (absorption from 1707 to 1710 cm^{-1}) through exposure to hydrochloric acid. Similar "derivatization reactions" are available to confirm the identification of carboxylic acid, ketone, and other relevant species.

Relevant Data

As noted above, statistical data resulting from water treeing studies are highly variable and presumably depend on experimental conditions. Careful examination of the published literature indicates that analytical chemical data from laboratory-aged cables often differ substantially from data that result from the examination of field-aged cables. Differences between chemical data derived from laboratory and field-aged specimens are readily apparent from an examination of Table I, which summarizes carbonyl-based chemical species detected

carboxylate ions (RCOO⁻)	ketones ($R_2C=O$)	esters (RCOOR)	sulfate ions ($SO_4^=$)	Experimental Conditions	Experimental Technique	Ref.
Vented Trees						
no	no	no	yes	3.4 kV/mm, 4.6 kHz, 50 °C, 13 days, LDPE/XLPE/EPR	IR	[2], '75
no	no	no		8 kV/mm, 1 kHz, 70 °C, XLPE	FTIR	[3], '80
no	yes			4 kV/mm, 50 Hz, 2.7 years, XLPE	Micro-FTIR/DS	[4], '88
yes	yes	yes		6 kV/mm, 60 Hz, 90 °C, 8 months, XLPE/EPR	Micro-FTIR/DS	[5], '94
Vented Trees - Laboratory-aged Films						
no	yes			3 kV/mm, 1 kHz, 10 days, XLPE	FTIR/DS	[6], '83
no	yes			7 kV, 1.5 kHz, 65 °C, 13 days, needle, LDPE	Micro-FTIR/DS	[7], '90
no	no	no		10 kV/mm, 500 Hz, 25 °C, 14 days, LDPE	FTIR-IRS	[8], '91
yes	yes	yes		2-4 kV/mm, 60 Hz, 25 °C, 20 days, LDPE	FTIR-IRS	[9], '93
Vented Trees - Field-aged Cables						
yes	yes		yes	6-8 years, XLPE	FTIR/DS	[10], '87
yes	no		yes	6-8 years, XLPE	FTIR/DS	[11], '91
yes	yes		yes	XLPE	Micro-FTIR/DS	[12], '92
yes	yes	yes		XLPE		[13], '92
Bow-tie Trees - Laboratory-aged Cables						
yes	yes		yes	2.7 years, XLPE	Micro-FTIR/DS	[12], '92
yes	yes	yes	yes	6 kV/mm, 60 Hz, 90 °C, 8 months, XLPE/EPR	Micro-FTIR/DS	[5], '94
Bow-tie Trees - Field-aged Cables						
yes	yes		yes	2.7 years, XLPE	Micro-FTIR/DS	[12], '92
EPR - Bow-tie and Vented Trees, Lab-aged Cables and Slabs						
yes	yes	yes		6 kV/mm, 60 Hz, 90 °C, 8 months	Micro-FTIR	[5], '94

XLPE = cross-linked polyethylene, EPR = ethylene-propylene rubber, LDPE = low density polyethylene

in water trees by various investigators. These species are characteristic of oxidation, and the relative quantities of the various species may imply the nature of the oxidation mechanism, for example, electro-oxidation vs. thermal oxidation.

Table I indicates highly variable results for laboratory-aged samples but much more consistent data for field-aged samples for which carboxylate ions, ketones, and sulfate ions were always detected. Data are particularly variable for laboratory-aged films, which are probably the most common basis for scientific study. A more careful examination of the data would probably indicate that consistent results were largely a function of (i) adequate detection sensitivity and (ii) the use of samples with semiconducting electrodes, i.e., either high voltage distribution cables or laboratory plaques with molded electrodes of semiconducting compound. As explained in a previous article [14], the semiconducting compounds play an important part in the treeing process as a reservoir of metal ions. In addition to the semiconducting shield, other sources of metal ions include catalyst residue from polymerization, metallic contamination in the dielectric, and ground water after installation. As a result of the improved understanding of the role of semiconducting compounds and ions in water treeing, only recently have laboratory studies yielded water trees that are chemically equivalent to those found in field-aged samples [5,12], as illustrated in Fig. 1.

History of Oxidation Hypotheses for Water Treeing

Henkel and Garton

Field driven oxidation [15] was proposed as a main driving force of water treeing by Henkel [16] (1987), Garton [10] (1987), and Densley *et al.* [17] (1990). Their
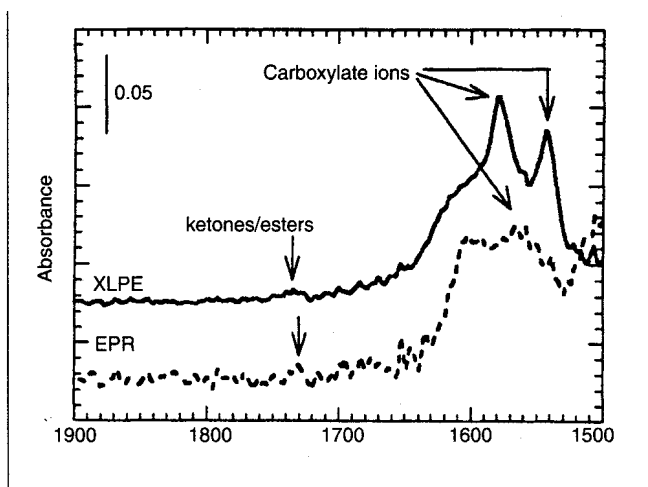
Fig. 1 Typical micro-FTIR difference spectrum of a water tree in laboratory-aged XLPE and EPR cable. Carboxylate ions cause the dominant spectral features [5]

Table II
Ionic Species in Water Treed Regions and Sites of Water Tree Initiation

Specimen	Tree Ionic Species
XLPE	$K^+, Na^+, Ca^{2+}, Al^{3+}, Mg^{2+}, Fe^{3+}, Fe^{2+}, Cu^+, Cu^{2+}, Zn^{2+}, Si^{4+}, S^{4+}, S^{6+}$
	Tree Initiation Sites
XLPE	Al, Si, O, cellulose, glass, amber, Cu, Al steel, S
Filled XLPE	Al, Si, O, Ti, Zn, Pb(S), Fe
EPR	Fe, V, Al, Si, O, Ti, Zn, Pb(S)

mechanisms involve similar sequences of free radical chemical reactions but differ in initiation processes. Garton suggested that the voids in a tree region are the locale for various catalyzed oxidative reactions. Garton believed that species such as metal ions (especially transition metal ions), sulfate ions, and carboxylate ions were responsible for the oxidative instability of a treed region, although Garton was not certain whether the oxidized species cause void formation or only become concentrated in voids after their formation. Many metal ions, especially the transition metal ions, catalyze polymer oxidation. Table II summarizes the various metal ions identified in water trees [18-27].

The initiation step proposed in Henkel's model involves an electrochemical reaction of water associated with a hydrophilic defect or contaminant. Henkel et al. noticed that water trees initiate at water-filled microvoids. He assumed that moisture accumulates on the wall of a microvoid, which results in electrolytic reactions under the influence of an electric field. This can cause the formation of hydrogen peroxide (H_2O_2, a strong oxidizing agent) and even the evolution of oxygen and hydrogen. At the polymer/water interface, electrochemical reactions, similar to the thermal oxidation catalyzed by metal ions, can also occur.

Henkel's model explores the possibility of water tree formation driven by an electrochemical process. In many ways, this hypothesis is consistent with experimental observations. For instance, water tree growth rates are lowered in high electrolyte concentrations. This is consistent with a metal ion catalyzed oxidation process in which high metal ion concentration increases the probability of intermediate species that "cancel" each other and thereby reduce the growth rate [28,29]. Henkel suggests no detailed mechanism by which molecular oxidation reactions produce tree-like defects.

Zeller

Zeller [30] (1987) suggested that electric field-induced chemical reactions cause water treeing. He estimated the local field within a water tree and showed that direct field effects, alone, cannot cause the growth of a water tree. However, the local fields are sufficiently strong to initiate an electrochemical process. Zeller referred to the observation of oxygen evolution to support the electrochemical mechanism of tree growth [31]. Zeller also tried to fill the gap between the electrochemical process and tree formation. He believed that the electrochemical reactions lead to partial oxidation of the polymer. On the basis of fundamental thermodynamic considerations, Zeller showed that if the oxidized polar groups were attached to a nonpolar hydrophobic macromolecule, phase separation would occur, i.e., water molecules dissolved in the hydrophobic polymer matrix would condense as liquid moisture in the hydrophilic region. The morphology of the water tree is then a consequence of the microphase separation in the partially oxidized polymer. Such a situation becomes self-propagating if the condensation of moisture in the oxidized region enhances the field at the tree growth front and/or the agents responsible for catalyzing the oxidation of the polymer can migrate along the oxidized paths.

Steennis

Steennis [32] (1990) developed Henkel's and Zeller's ideas that electrochemical reactions are initiated at the surface of voids where moisture accumulates and where polar groups on polymer chains cause the polymer to change from hydrophobic to hydrophilic, resulting in microphase separation (condensation of moisture out of the polymer matrix). Steennis proposed an electrochemical mechanism of water treeing in which initiation sites are located in a polar amorphous region of the polymer. Water enters the polar region if ions are pre-
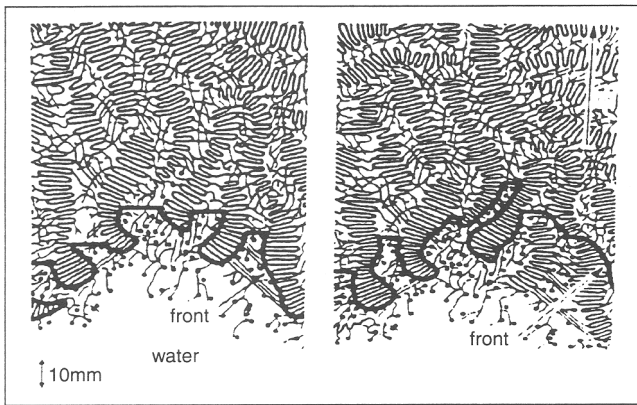
Fig. 2 Steennis's water tree model. Left: polar amorphous region and reaction front. Right: As polymer chain oxidation and scission develop, the reaction front moves into the polymer matrix

Fig. 3 (a) Carbon-carbon double bonds are oxidized by hydrogen peroxide (H2O2) to form glycols. (b) Glycols can be converted to ketones

sent. Steennis explained that polar amorphous regions can be created by scratching, pollution, or oxidation during compounding and cable manufacturing. The ionic contaminants, such as the semicon and residual catalysts, can also serve as polar sites in the amorphous region of the polymer.

In the presence of an electric field, redox reactions can take place at the interface between the water and the polymer. The redox reactions cause further deterioration of the polymer, which results in more polar structures near the water-polymer interface. This pushes the water front (see Fig. 2, left) further into the polymer (Fig. 2, right). As the front "F" moves gradually into the PE matrix, a polar path is generated.

Steennis believed that the electrolysis is possible if the voltage drop near the interface is approximately 1 volt. The charge transfer process is maintained by electrolysis, i.e., an electron given off from oxidation of a negative ion will be accepted by the polymer surface. Charge transport is maintained by capacitive current. Steennis suggested hydrogen peroxide (H2O2), an expected product of the electrolysis, may attack carbon-carbon double bonds on PE chains and produce ketones.

Steennis's model depicted a convincing connection between the electrochemical reactions and water tree formation. The several crucial assumptions in the model are in good agreement with the experimental observation. However, his speculation that oxidation starts with vinyl groups on the PE chain (Fig. 3) merits further discussion. The concentration of vinyl groups in polyethylene (about 0.3 per 1,000 carbon atoms) is so low that the oxidation of vinyl groups might not produce significant morphological changes as seen in water trees. On the other hand, the ketones that result from Steennis's model are not the dominant products in water treeing [5,12]. Thus the chemical details of Steennis's model require refinement.
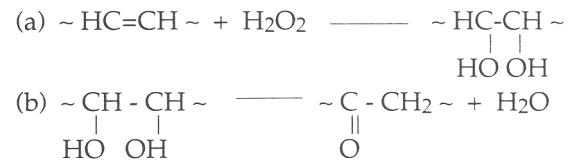
Ross

In 1992, Ross [12] proposed an advanced model of water treeing which is very similar to the Steennis model, as shown in Fig. 4. The model basically consists of a hydrophilic track through a hydrophobic amorphous region of the polymer. The tracks, similar to Steennis's tree paths, facilitate the transport of water and ions through a tree. The oxidation occurs during water tree growth. The carboxylate ions and sulfate ions are possible oxidation products. These ions are chemically or physically bonded to the polymer chain. Chain scission and the subsequent formation of voids and channels may widen the tracks and increase ion permeability, especially in the presence of an electric field. Ross stressed the presence of carboxylate ions in the treed region. He suggested that carboxylate ions can be formed through the combination of oxygen and an
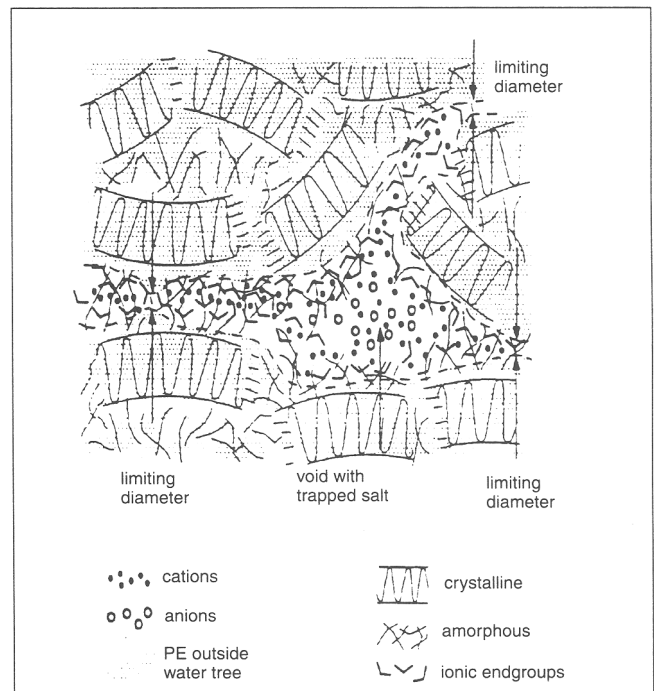

Fig. 4 In Ross's advanced water tree model, polar groups dangling on the polymer chain ends promote passage of water and ions through a newly formed water tree "track" [12]

$$\sim CH_2\text{-}CH_2\sim \; + O_2 + e^- \;\text{------}\; \text{-}C(=O)O^- \quad + \quad \bullet CH_2^-$$
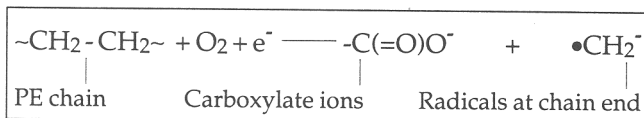
| PE chain | Carboxylate ions | Radicals at chain end |

Fig. 5 Carboxylate ions can be formed through an electrochemical oxidation of polyethylene

electron transfer reaction (Fig. 5). This was probably the first published attempt to link the observed carboxylate ions in trees to a proposed tree model, although the detailed molecular mechanism was not discussed.

Molecular Chemistry of Water Tree Formation

Oxidation

We have been discussing "oxidation" without specifying the "oxidation mode." In the water tree-related literature, "oxidation" often refers to some vague mechanism of thermal/auto oxidation and/or electrochemical reaction. Since the influence of the electric field on the oxidation process is not fully understood, "thermal oxidation" should be distinguished from "electrochemical oxidation" (electro-oxidation). The terms "thermal oxidative degradation" and "electrochemical degradation" are frequently used as synonyms, as polymer oxidation is always associated with chain scission.

Thermal Oxidation: Thermal oxidation of a polymer is a chain scission process that results from an attack by an oxidizing species at a temperature of 50-100° C. The oxidation of polyolefins such as polyethylene has a common feature, i.e., the formation of chain radicals on the polymer chain is followed by a reaction with oxygen and chain cleavage (Fig. 6). Such oxidative degradation results in the formation of C=C bonds, peroxides (~C-O-O-C~), hydroperoxides (R-O-OH), alcohols (OH) and a distribution of carbonyl species (C=O) such as ketones (R-C(=O)R), acids (R-C(=O)OH), and esters (RC(=O)OR) [31], where "R" represents a degraded polymer chain or fragments thereof.

Electro-oxidation: The detailed distribution of the end-products of electro-oxidation of polyolefins is basically unknown because of a lack of fundamental studies; however, the generation of carboxylate ions appears to be the main feature of the process [3,5, 12].

Refinements of KEMA Tree Model

The most advanced model of water tree growth is the "KEMA model" as developed by Steennis and Ross. Although the KEMA model is chemical in nature, it describes tree formation on a microscopic scale rather than on the molecular scale of chemical reactions. Thus the KEMA model requires refinements to "push" it to
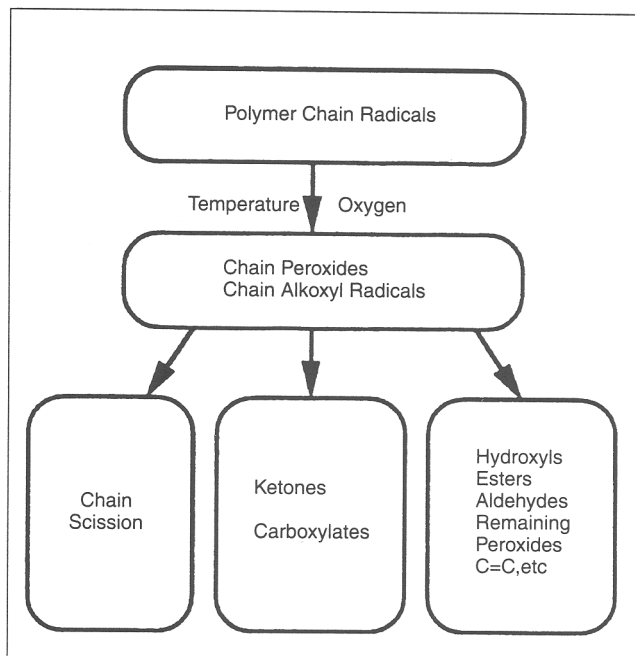

Fig. 6 A simplified scheme of thermal oxidation mechanism for polyolefins, such as polyethylene

the molecular level. An understanding at the molecular level may provide an improved basis for inhibiting the process of water treeing. Water treeing is a multistress, multiple mechanism phenomenon in which various mechanisms may predominate at different times depending on a particular set of ageing conditions. Electrochemical oxidation is clearly the most promising mechanism and is supported by many experimental observations. In a very recent report, the authors employed fluorescence microscopy to demonstrate both the existence of "tracks" connecting microvoids within the treed region, as well as the oxidation of the polymer associated with the tracks [33].

Molecular Electrochemistry of Water Treeing

A proposed electrochemical degradation mechanism should embrace all the reasonable parts of previously suggested mechanisms and explain the low concentration of ketones relative to carboxylate anions observed in water trees. Table III gives the relative production of ketones and carboxylate ions that results from possible oxidation mechanisms as determined using infrared spectroscopy. Note that "electro-oxidation" in the presence of ions and water results in a preponderance of carboxylate ions, while the other oxidation processes produce predominantly ketones. This table may be oversimplified given the lack of knowledge concerning the influence of electric fields on oxidation; however, the table provides an indication of the differences between electro-oxidation in cable systems and thermal

Table III
Distribution of Ketones and Carboxylate Ions Produced in Various Oxidation Conditions

Modes/Products	Ketones	Carboxy-lates	Carboxylic Acids
Electrical/H_2O/Ions*	0%	90-100%	0
Thermal/H_2O/Ions**	70%	30%	0
Thermal (air)***	82%	0	18%
Photo (air)***	43%	0	57%

based on ketones + carboxylate ions = 100%. *data from the treed regions of cables and slabs [5,34], **data from the oxidized PE films in aqueous salt solutions [34], ***calculated based on ref. [35]

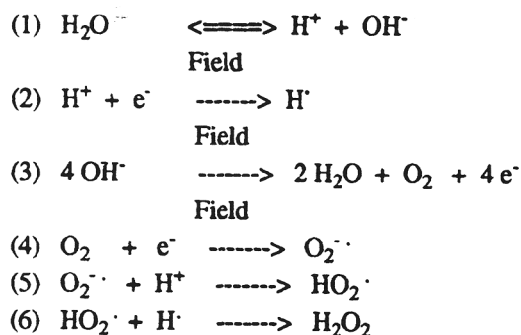Scheme 2: Electrochemical initiation of polyolefin degradation

or photo-oxidation. Charge (electron) transfer could be involved not only in the electrolysis of water to produce oxidizing agents (hydrogen peroxide and oxygen) but also through electro-oxidation of the polyolefin.

Electrochemical degradation of polyolefins associated with water treeing appears to involve five fundamental steps [34]:
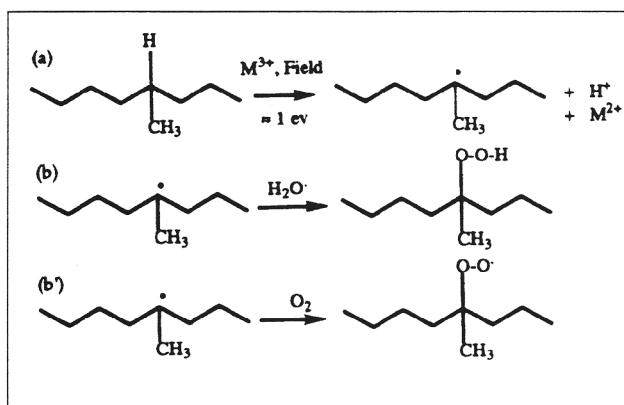
a. electrolysis of water
b. initiation of degradation
c. catalysis of degradation by metal ions
d. chain scission resulting in ketone and carboxy late ion formation
e. conversion of ketones to carboxylate ions.

(a) Electrolysis of Water (Scheme 1)

Electrolysis of water can take place at very low potentials and currents [36]. Henkel [15] suggested that an electrolytic reaction may also take place at the water-polymer interface. Electrolysis of water may take place at the water/polymer interface in the polar amorphous region. Oxygen, hydrogen peroxides and hydrogen peroxide radicals would be generated, as shown in Scheme 1. Trace amounts of oxygen may also pre-exist in water. These are oxidizing agents.

b) Initiation of Polyolefin Degradation (Scheme 2)

In the presence of an electric field and transition metal ions, the chain degradation is initiated by an electrochemical reaction to form chain radicals, as shown in Scheme 2. The ions may act as a mediator (see Scheme 2, a). Without the mediation of ions, the electrochemical potential required for the reaction is probably too high for the reaction to take place [37]. The chain radicals are highly reactive and will react with any kind of oxidizing agents to form chain peroxides and peroxide radicals (see Scheme 2, b & b'). The proposed electrochemical initiation does not exclude the possibility of the initiation via a classical thermal oxidation mode, although this would proceed very slowly under most cable operating conditions.

(c) Catalysis of Polyolefin Degradation (Scheme 3)

Polymer chain peroxides and peroxide radicals perturb adjacent carbon bonding strengths and promote further chemical reactions. O-O bonds, with bond energy less than 35 kcal/mol, are broken readily to form the chain alkoxyl radicals. Even though O-O bonds are weak, high temperatures are required for cleavage, e.g., 160-170 °C for peroxides initiated the crosslinking of LDPE. The presence of metal ions and an electric field
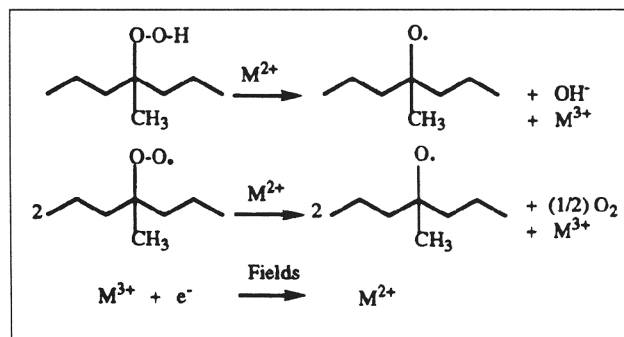
Scheme 3: Degradation catalyzed by transition metal ions

(1) H_2O $\overset{Field}{\Longleftrightarrow}$ H^+ + OH^-

(2) H^+ + e^- $\overset{Field}{\longrightarrow}$ $H^·$

(3) $4\,OH^-$ $\overset{Field}{\longrightarrow}$ $2\,H_2O$ + O_2 + $4\,e^-$

(4) O_2 + e^- $\longrightarrow$ $O_2^{-·}$

(5) $O_2^{-·}$ + H^+ $\longrightarrow$ $HO_2^·$

(6) $HO_2^·$ + $H^·$ $\longrightarrow$ H_2O_2

Scheme 1: Electrolysis of water

must lower the activation energy barrier for O-O bond cleavage. The possible reactions are shown in Scheme 3.

Note that some ions (Cu^+ / Cu^{2+}, Fe^{2+} / Fe^{3+}) can be recycled through electrochemical reactions. Therefore, the chemical species necessary for the electrochemical reactions can be recycled spontaneously.

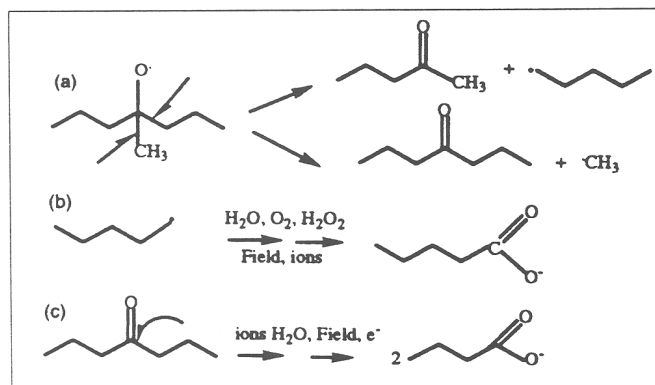### (d) Chain Scission and Ketone Formation (Scheme 4)

The chain alkoxyl radicals tend to form a stable bond by restructuring. Adjacent C-C bonds (83 kcal/mol) could be broken, leading to the formation of ketones, chain scission, and end-chain radicals. End-chain radicals would form carboxylate ions through intermediates such as aldehydes.

(e) Conversion of Ketones to Carboxylate Ions

The generation of ketones is inevitable, as demonstrated in Scheme 4. Given that carboxylate ions have a high concentration in the end products of water treeing, we suggest that ketones can be converted to carboxylate ions under the influence of an electric field and the resulting minute electric current. Low molecular aromatic ketones can be converted readily to carboxylate anions in an electro-oxidation process [38]. The conversion need not be highly efficient, only sufficient to reduce the ketone concentration to below that detectable using micro-FTIR. (Scheme IV figure)

Future Work

The study of electrochemical degradation of polymers is very challenging. Despite a few reports dealing with polar polymer systems [39-43], the electrochemical degradation of polyolefins is poorly understood. The difficulties arise from the chemically inert nature of polyolefins (e.g., PE, XLPE, and EPR) and their high resistivity, which limits the use of typical electrochemical techniques that require measurable current flow at relatively low voltage. In this context, water treeing provides a good basis for the study of electrochemical degradation of polyolefins. Although the above molecular mechanisms for water treeing are plausible, several aspects merit further investigation:

1. How does an electric field exert an influence on polyolefin oxidation? How much does electro-oxidation deviate from thermal oxidation in terms of the distribution of end-products?

2. How do transition metal ions catalyze polyolefin oxidation in the presence of an electric field?

3. Verification of the conversion of ketones to carboxylate ions in the presence of an electric field. Verify the initiation of chain degradation by an electro-chemical reaction mediated by metal ions.

4. Determine under what combination of conditions (electric fields, current flow, temperatures, and ions) does decarboxylation of a carboxylate ion take place? Why are carboxylate ions observed more frequently in field-aged cables than in laboratory-aged films and slabs? High temperatures (100 °C) and high electrochemical potentials (2.8 volts vs. Standard Hydrogen Electrode) facilitate decarboxylation reaction for oligomeric carboxylate ions.
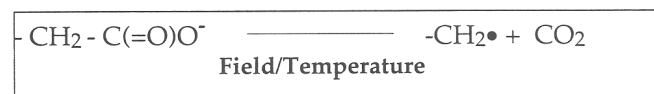
$$- CH_2 - C(=O)O^- \xrightarrow{\text{Field/Temperature}} -CH_2\bullet + CO_2$$

Fig. 7 Decarboxylation can take place as a result of elevated temperature or an appropriately high electric field
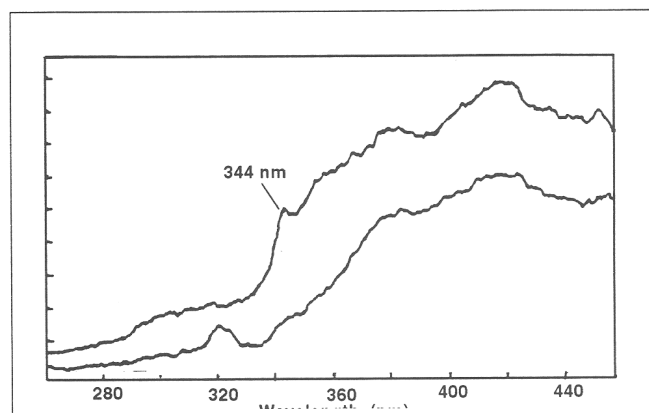

Fig. 8 Fluorescence emission spectra of 200 μm thick samples of XLPE cable dielectric [45]. The specimen that corresponds to the upper curve was aged at 6 kV/mm, 60 Hz, and 90 °C conductor temperature for 8 months. The lower curve corresponds to an unaged sample. The unstained specimens were cleaned briefly with methanol and dried. The spectra display a distinct fluorescence emission peak at 343-345 nm for the aged specimen at all excitation wavelengths from 220 nm to 250 nm. The peak has been assigned to unsaturated carbonyl species in degraded polyolefins by several authors [46,47]

Scheme 4: (a) Chain scission and ketone formation. (b) Carboxylate ion formation. (c) Conversion of ketones to carboxylate ions

5. Water trees can be observed in some EPR cables which failed prematurely, although the presence of water trees in EPR cables has not been implicated as a cause of failure. Decarboxylation can close the hydrophilic tree path for water and metal ion transport and thereby eliminate the water tree by returning the polymer to a hydrophobic state (Fig. 7). Does this contribute to the performance of EPR cables tested at high fields and temperatures [44]? (Figure 7 and 8)

6. More detailed information concerning the chemistry within water trees is needed. More sensitive spectroscopic techniques, such as micro-fluorescence spectroscopy, may be useful. To this end, the spectral assignments of micro-fluorescence need to be clarified. Conventional fluorescence spectroscopy (without microscopic accessories) can detect much lower concentrations of some organic species than micro-FTIR (Fig. 8).

Conclusion

As a result of experimental and theoretical progress over the last decade, our understanding of water treeing is approaching the molecular level at which the fundamental chemical nature of the phenomenon will be revealed. Further effort is required to complete the picture. The analytical techniques employed to date indicate that the water tree region contains a wide range of chemical species, with various forms of carbonyl and metal ions and water being dominant. Among carbonyl species, carboxylate ions are dominant, followed by trace amounts of esters and ketones. Present oxidation theories of water treeing are based on these observations and provide the best and most detailed description of the process.

The oxidation theories of water treeing discussed above describe the growth of water trees as driven by electro-oxidation of the polymer, which takes place in the direction of the local electric field and in a polar amorphous region of the polymer. As a consequence of the electro-oxidation, polymer chains are broken and a "track" or "tree path" is formed. The local electro-oxidation of the polymer along this track converts the track region from hydrophobic to hydrophilic, which results in the condensation of water molecules dispersed in the polymer matrix to form liquid water in the track. The liquid water in a track promotes the transport of ions that mediate further the electro-oxidation of the polymer at the tip of the track. Thus a track becomes self-propagating in a manner similar to the self propagation of an electrical tree or a gas breakdown channel, although on a very different time scale. Relative to the distance we have come, little work remains to gain a "complete" understanding of the molecular chemistry of water treeing. A detailed understanding of the molecular mechanism should provide bases for the development of improved inhibition of water trees.

James J. Xu is a postdoctoral research fellow at the Electrical Insulation Research Center, University of Connecticut. His professional interests center on polymer degradation and the prevention thereof (from electrical, electronic, thermal, radiation, magnetic, ultrasonic, bio, weather, and ocean-related effects). He has also worked in the area of photosensitive and photoresponsive polymers. He was graduated with a B.S. in polymer science and engineering from East China University of Chemical Technology in 1982, an M.S. in polymer materials science from Shanghai Jiao Tong University (JTU) in 1986, and a Ph.D. in polymer science from the University of Connecticut in 1993. He spent one year as a junior engineer with Shanghai Paper and Pulp Corp. and four years as a lecturer and research scientist with JTU. He has been awarded for his creative work at various points along his career, and some of his articles, poems, and speeches are kept in JTU's library. Dr. Xu's new address will be: R&D Group, BMC Industries, Inc., P.O. Box 189, Cortland, NY 13045.

Steve Boggs was graduated with a B.A. from Reed College in 1968 and Ph.D. and MBA degrees from the University of Toronto in 1972 and 1987, respectively. He spent 12 years with the Research Division of Ontario Hydro and six years as director, engineering and research with Underground Systems, Inc. He is presently research professor and associate director of the Electrical Insulation Research Center, Institute of Materials Science, University of Connecticut. His professional interests center on solid and gaseous dielectrics (primarily SF_6), although he has published in areas as diverse as the measurement of soil thermal properties and the measurement of ac losses in high temperature superconductors. He was elected a fellow of the IEEE for his contributions to the technology of SF_6 gas-insulated substations (GIS).

References

1. T. Miyashita, "Deterioration of Water-immersed Polyethylene Coated Wire by Treeing," *Proceedings 1969 IEEE-NEMA Electrical Insulation Conference*, Boston, pp. 131-135, Sept. 1969.

2. B. S. Bernstein, N. Srinivas, P. N. Lee, "Electrochemical Treeing Studies: Voltage Stress, Temperature, and Solution Penetration Effects under Accelerated Test Conditions," *1975 Annual Report Conference on Electrical Insulation and Dielectric Phenomena (CEIDP)*, pp. 296-302, 1978.

3. A. Garton, R. J. Densley and A. Bulinski, "Initial Results of a Study of Water Trees in XLPE by Infrared Spectroscopy," *IEEE Trans.* Vol. EI-15, No.6, pp. 500-501, 1980.

4. R. Ross, W. S. Geurts and J. J. Smit, "FTIR Microspectroscopy and Dielectric Analysis of Water Trees in XLPE," IEE Conference Publication Number 289, Dielectric Materials, Measurements and Applications, pp. 313-317, 1988.

5. J. J. Xu and A. Garton, "Chemical Composition of Water Trees in EPR Cable Insulations," *IEEE Trans.*, DEI-1, pp. 18-24, Feb. 1994.

6. T. Yoshimistu, H. Mitsui, S. Kenjo, and T. Nakakita, "Some Considerations on AC Water Trees in Crosslinked Polyethylene," *IEEE Trans.* EI-18, No.1, pp. 23-27, 1983.

7. J. Y. Koo, R. Bouzerara, J. T. Kim, and J. C. Filippini, "A Study of Oxidation in Water Trees using IR-microspectroscopy in Polyethylene Laboratory Models," CEIDP, pp. 494-501, 1990.

8. J. A. King, E. Cumberbatch, S. Kim, and T. Paulos, "Analysis of a New Sample Configuration for the Growth and Study of Vented Water Trees," *IEEE Trans.* EI Vol.26, No.2, pp. 285- 290, 1991.

9. J. J. Xu and A. Garton, "Water Trees in EPR Cable Insulations," *1993 Annual Report of the Conference on Electrical Insulation and Dielectric Phenomena*, IEEE Publication No. 93CH3269-8, pp. 648-652.

10. A. Garton, S. Bamji, A. Bulinski, and R.J. Densley, "Oxidation and Water Tree Formation in Service-Aged XLPE Cable Insulation," *IEEE Trans. EI*, Vol. 22, No.4, pp. 405-412,1987.

11. B. Noirhomme, J-P. Crine, A. Bulinski, and R. J. Densley, "Correlation between Chemical Group Found in Water-Tree," CEIDP. pp. 386-394, 1991.

12. R. Ross and J. J. Smit, "Composition and Growth of Water Trees in XLPE," *IEEE Trans. EI*, Vol.27, pp. 519-531, 1992.

13. W.B. Reid, L.J. Rose, V. Rose, A. Campus, C. Baker, and J. Walton, "Water Tree Degradation in Power Cable Insulation: Understanding and Prevention," IEE Sixth International Conference on Dielectric Materials, Measurements, and Applications. IEE Conf. Publication #363, p. 496-499, 1992.

14. S.A. Boggs and M.S. Mashikian, "Role of Semiconducting Compounds in Water Treeing of XLPE Cable Insulation," *IEEE Electrical Insulation Magazine*, Vol. 10, No. 1, pp. 23-27, January/February 1994.

15. L.A. Dissado and J.C. Fothergill, ed., *Electrical Degradation and Breakdown in Polymers*, Peter Peregrinus Ltd., London, pp. 74-116, 1988.

16. H. J. Henkel , N. Muller, J. Nordmann, W. Rogler, and W. Rose, "Relationship Between the Chemical Structure and the Effectiveness of Additives in Inhibiting Water-Trees," *IEEE Trans.* Vol. EI-22 No.2, pp. 157-161, 1987.

17. R.J. Densley, S.S. Bamji, A.T. Bulinski, and J.P. Crine, "Water Treeing and Polymer Oxidation," Conference Record of the 1990 International Symposium on Electrical Insulation. IEEE Publication 90-CH2727-6, pp. 178-182.

18. J. J. Xu and A. Garton, "Morphology and Chemical Composition of Water Trees in Mineral-Filled Insulations," EEIC/ICWA, pp. 579-583 Oct. 1993, Chicago.

19. C. Katz and B. S. Bernstein, "Electrochemical Treeing of Contaminants in Polyethylene and Crosslinked Polyethylene Insulation," CEIDP, pp. 307-315, 1974.

20. J. Sletbak and A. Botne, "A Study of Inception and Growth of Water Trees and Electrochemical Trees in Polyethylene and Crosslinked Polyethylene Insulations," *IEEE Trans.* , EI-12 No.6, pp. 383-389, 1977.

21. T. Uematsu, Z. Iwata, S. Irie, O. Fujii, "Bow-tie-Tree in EPR Cables after Accelerated Water Treeing Test," *IEEE Trans. Power Delivery*, Vol. 7, No.4, pp. 1667-1676, 1992.

22. S. Bamji, A. Bulinski, R.J. Densley, A. Garton and N. Shimizu, "Properties of Water Treed and Non-Treed XLPE Cable Insulation," CEIDP , pp. 141-147, 1984.

23. P. F. Hinrichsen, A. Houdayer, A. Belhadfa, J.-P. Crine, S. Pelissou, and M. Cholewa, "A Localized Trace Element Analysis of Trees in XLPE Cable Insulation by Micro-PIXE and EDX," *IEEE Trans.*, EI Vol.23, No.6, pp. 971-978, 1988.

24. A. T. Bulinski, S.S. Bamji, P. Timbrell, and R.J. Densley, "Wavelength and Energy Dispersive X-ray Studies of Contaminants in Water Treed Insulation," CEIDP, pp. 78-85. 1988. 25. P. Y. Timbrell, A. Bulinski, S. S. Bamji and R. J. Densley, "Backscattered Electron Imaging and Energy-Dispersive X-ray Studies of Water Treed Polymeric Insulation," *IEEE Trans.*, EI Vol.25, No.4 pp. 730-736, 1990.

26. A. Garton, J. H. Groeger, J. L. Henry , "Ionic Impurities in Crosslinked Polyethylene Cable Insulation," *IEEE Trans.*, EI Vol. 25, No.2, pp. 427-434, 1990.

27. M.S. Mashikian, J.H. Groeger, S. Dale, and E. Ildstad, "Role of Semiconducting Compounds in the Premature Aging of XLPE Cable Insulation," Conference Record of the 1988 International Symposium on Electrical Insulation, IEEE Publication No. 88-CH2594-0-DEI, pp. 312-320.

28. L. Reich and S.S. Stivala, *Elements of Polymeric Degradation*, McGraw-Hill, Inc., pp. 1-275. 1971.

29. W. Schnabel, *Polymer Degradation - Principles and Practical Applications*, Hanser International, 1981.

30. H. R. Zeller, "Thermodynamics of Water Treeing," *IEEE Trans.*, EI-22 No.6, pp. 677-681, 1987.

31. Y. Nitta, "A Possible Mechanism for Propagation of Water Trees from Water Electrodes," *IEEE Trans.*, EI-9 , pp.109-112, 1974.

32. a) E. F. Steennis and F. H. Kreuger, "Water Treeing in Polyethylene Cables," *IEEE Trans. IE*, Vol. 25, No.5, pp. 989-1028, 1990. (b) E.F. Steennis, "Water Treeing: The Behaviour of Water Trees in Extruded Cable Insulation," Ph.D. Dissertation, Arnheim. 1989.

33. E. Moreau, C. Mayoux, C. Laurent, and A. Boudet, "The Structure Characteristics of Water Trees in Power Cables and Laboratory Specimens," *IEEE Trans* . IE-28, No. 1, pp. 54-64. 1993.

34. J. J. Xu, "Electrochemical Degradation of Mineral-Filled Polyolefins," Ph.D. Dissertation, University of Connecticut, Storrs, CT, 1994.

35. J. Lacoste and D. J. Carlsson, "Gamma-, Photo-, and Thermally-Initiated Oxidation of Linear Low Density Polyethylene: A Quantitative Comparison of Oxidation Products," *J. Polym.Sci. Part A: Polym. Chem.*, Vol.30 493-500, 1992.

36. John O'm Bockris, and Amulya K.N. Reddy, *Modern Electrochemistry*, Vol. 2, Plenum Press, New York, 1970. pp. 1107-1391.

37. A. J. Bard and H. Lund, *Encyclopedia of Electrochemistry of the Elements*, Organic Section, Vol. XI Hydrocarbons, pp. 6-10, 1978.

38. G. Thomas, M. Chettiar, V. I. Birss, "Electrochemical Oxidation of Acidic Alberta Coal Slurries," *J. Appl. Electrochem.*, 20, 941-950, 1990.

39. A. D. Jannakoudakis, P. D. Jannakoudarkis, E. Theodoridou, J. O. Besenhard, "Electrochemical Oxidation of Carbon Fibres in Aqueous Solutions and Analysis of the Surface Oxides," *J. Appl. Electrochem.*, 20, 619-624, 1990.

40. G. Thomas, M. Chettiar, V. I. Birss, "Electrochemical Oxidation of Acidic Alberta Coal Slurries," *J. Appl. Electrochem.*, 20, 941-950, 1990.

41. A. A. Pud, "Surface Electrochemical Reactions and the Subsequent Degradation of Solid-Phase Poly (ethylene terephthalate) at a Cathode," *Polymer Degradation and Stability*, Vol. 30, pp. 181-193, 1990.

42. L. Lavielle, K. Nakajima, and J. Schults, "Influence of an Electric Field on Polar-Group Orientation and Adhesion at Poly (ethylene terephthalate) Surfaces," *J. Appl. Polymer Sci.*, Vol. 46, pp. 1045-1050, 1992.

43. J.G. Dillon, "Electrochemical Degradation of Pellethane 2363-80A and 2363-55D," *Polym. Degr. & Stab.*, 37, pp. 183-188. 1992.

44. M.D. Walton, B.S. Bernstein, J.T. Smith, III, W.A. Thue, and J.H. Groeger, "EPR-Insulated Medium Voltage Distribution Cables," IEEE PES Summer Meeting, July 1993. 93 SM 559-5 PWRD.

45. J.J. Xu. Unpublished data.

46. J. Konar and R. Ghosh, "Characterization of Oxidized LDPE by Solid State Fluorescence Spectra.," *J. Appl. Polym. Sci.*, Vol. 40. pp. 719-729, 1990.

47. N.S. Allen, J. Homer, and J.F. McKeller, "Identification of the Luminescent Species in Low Density Polyethylene," *J. of Appliy. Polym. Sci.*, Vol. 21, pp. 3145-3152, 1977.