Water Treeing-Filled versus Unfilled Cable Insulation

Key Words: XLPE, EPR, water treeing, electro-oxidation

Electrochemical or water treeing in solid dielectric cable has been recognized for over 30 years, since first being reported in 1969 [1]. Water trees are generally observed as a dendritic pattern of water-filled microcavities in the polymer. Moreau, et al. [2] have shown that these microcavities are connected by oxidized “tracks,” probably about 0.01 µm (10 nm) wide. Water treeing is therefore best described as a self-propagating pattern of electro-oxidation. Self-propagation results from electro-oxidation of the hydrophobic polymer to a substantially more hydrophilic state which, as recognized by Zeller [3], causes condensation of moisture from the surrounding hydrophobic polymer into the hydrophilic electro-oxidized region, which results in self-propagation of the electrochemical “water” tree. Such self-propagation (water treeing) is likely to occur in any polymer that can be oxidized to a substantially more hydrophilic state, which includes a wide range of organic polymers.

Various aspects of water treeing have been reviewed in numerous previous papers [4]-[7]. The purpose of the present article is not to review the broad base of previous knowledge but to examine how the difference in propensity toward water treeing between XLPE and EPR cable insulations can be understood.

The Physical Basis of Water Treeing

Water treeing can range from predominantly electromechanical in nature to essentially electrochemical. A great deal of the early laboratory work was carried out with “water needle” configurations, which produce extremely high electric fields at the tip of a needle-shaped, water-filled cavity. The electric field at the tip was usually high enough to produce an electrical tree if the cavity were not filled with water, and the water tree grows in hours to days, rather than months to years as for a water tree grown under utility operating conditions. Dorris, et al. [8] investigated electrical signals generated by the growth of such water trees. An analysis of their data suggests that the measured electrical signals could be produced by a sudden 0.01 to 0.1 µm extension of the water tree channel. This work provides clear evidence for the growth of essentially electromechanical trees at very high fields. Such trees probably grow through (i) electrochemical damage in the tree tip region, which weakens the polymer to the point that (ii) electromechanical forces cause a sudden yielding of the polymer and extension of the tree in the range of 0.01 to 0.1 µm. Because the electric field and resulting electromechanical forces are relatively large [9], relatively little damage to the polymer in the tree tip region is required to reduce the yield stress of the polymer sufficiently that the electromechanical forces cause yielding and extension of the tree channel. For high-field, water needle-induced water trees, micro-infrared spectra of the resulting water tree indicate relatively little electro-oxidation, which progresses slowly relative to the time frame (days) in which the tree growth takes place under these high field conditions. Under long-term utility service conditions, the electric field is quite low, typically 1-3 kV/mm, as are the resulting electromechanical forces. The polymer must undergo substantial electrochemical degradation to reduce the yield stress to the point that the water tree can extend, and micro-infrared spectra of service-induced water trees show evidence of appreciable electro-oxidation in the tree region [4].

The Electrochemical Basis of Water Treeing

The electrochemical oxidation of low molecular weight hydrocarbons, such as alkanes \( \left( C_nH_{2n+2} \right) \), has been studied extensively over the past 30 years. Partial oxidation of al-
Figure 1. Chemical potential as a function of water conductivity for an ellipsoidal asperity 1000 in a background field of 5 kV/mm. For NaCl solutions, the conductivity (S/m) is about ten times the molarity. This plot is not intended to be a quantitatively accurate representation of the chemical potential for a growing water tree but simply to illustrate the general nature of the chemical potential as a function of water conductivity.

Zeller [3] took a thermodynamic view of water treeing and concluded that the water conductivity plays a very significant role. Zeller described the chemical potential that drives the electro-oxidation of water treeing as the derivative of the energy stored in the electric field with respect to the number density of ions in the water of the water tree, i.e.,

\[
\mu_w = \frac{\partial}{\partial n_i} \left( \int E^2 dV \right) = \frac{\partial W}{\partial n_i} = \frac{\partial W}{\partial \sigma_w} \frac{\partial \sigma_w}{\partial c_i} \frac{\partial c_i}{\partial n_i}
\]  

(1)

where \( E \) is the electric field, \( \epsilon_0 \) is the permittivity, \( V \) is volume, \( n_i \) is the number density of ions in the water, \( W \) is the energy stored in the electric field, \( c_i \) is the number concentration of ions in the water (number of ions divided by number of water molecules), and \( \sigma_w \) is the conductivity of the water. Note that \( \partial \sigma_w/\partial c_i \) is equal to one over the number of water molecules in the volume containing the ions. For NaCl,

\[
\frac{\partial \sigma_w}{\partial c_i} = 540 \text{ Siemens/m} \text{ at low concentrations of NaCl.}
\]  

(2)

A chemical potential, \( \mu \), greater than about 1 eV can, in theory, drive electro-oxidation although in reality a somewhat greater chemical potential is likely to be necessary. For the case of an ellipsoid of variable asperity, Zeller [3] developed an analytic formula for \( \mu \) from which we can compute the chemical potential for a large asperity (long, thin ellipsoid) as a function of water conductivity as seen in Fig. 1. The general nature of these data can be explained from the fundamental definition of the chemical potential. At very low water conductivity, a small change in the water conductivity makes negligible difference in the electric field distribution. Thus, the chemical potential will be small. For very high water conductivity, the water is a conductor, and a small change in its conductivity makes negligible difference in the electric field distribution. Thus, the chemical potential will also be small. The peak in the chemical potential occurs for intermediate water conductivity, basically when the electric field and current density in the water are 45° out of phase. This situation maximizes the change in the electric field with water conductivity and therefore maximizes the chemical potential. The chemical potential approach works especially well in interpreting water tree initiation in a homogeneous insulation system where ions are the major variable.

A large number of variables may be relevant to water tree formation and growth in filled materials, among which hydrophobicity, catalytic ion content, spatial variation in ion concentration, crystallinity, water absorption, oxidation induction time, and toughness differ the most from an un-filled material such as XLPE (Tables I and II). At best, chemical potential is a thermodynamic variable, which gives the “propensity” toward a chemical reaction. The larger the chemical potential, the more likely the reaction is to take place over a wide range of conditions. However, the chemical potential provides little guidance concerning reaction kinetics, i.e., the rate of the chemical reaction or the growth rate of the water tree.

**Water Treeing in XLPE Insulation**

As for most organic polymers, PE and XLPE meet all the requirements for water treeing, i.e., they are hydrophobic and can be oxidized to a substantially more hydrophilic state. However, polyethylene is normally very “clean,” with very low ion concentration. In a cable configuration, any water reaching the polyethylene must percolate through the semiconducting layers via the free volume
around each carbon particle. This free volume percolates (connects through the semicon) as the carbon particles must percolate in order to conduct. The carbon-filled semicon layers may act as activated charcoal filters, which tend to absorb ionic impurities from the water. Thus the water in polyethylene cable dielectric normally has too low conductivity to create the chemical potential necessary for water treeing. In other words, under normal conditions in XLPE the system operates on the low conductivity side of the peak in the chemical potential (Fig. 1), where the chemical potential is too low to cause water treeing. However, the chemical potential will increase with any increase in water conductivity, so that an ionic impurity at the dielectric-semicon interface can increase the chemical potential and cause a vented water tree.

Water trees in XLPE take the form of a series of water-filled microcavities connected by oxidized tracks [2]. While the diameter of these tracks has not been measured, they are probably in the range of 0.01 µm, which is just a “wide spot” in the path between polymer chain backbones. (This estimate is based on the consistency of a substantial number of phenomena for a channel diameter in this range. For example, the water conductivity required to produce the necessary chemical potential is a function of the channel diameter, and the reasonable range of water conductivities is known.) Thus the electro-oxidized track may consist of a slightly wider than normal path between polymer backbones with a much higher degree than normal of oxidation of the polymer, which forms the boundaries of the track. The string of water-filled cavities, which is the visible manifestation of the water tree, is probably the result of three effects, viz.: (i) Statistical effects, in that if a water tree track meets a cavity and fills it with water, the track has a much larger surface and many more possible directions in which to propagate than a track which does not meet a cavity. Thus long track growth may be associated with strings of cavities for statistical reasons; (ii) Contribution of ions within the cavities to continued water tree growth; and (iii) Substantial water flow through a tree track required to fill a cavity may enhance electro-oxidation and track formation. A source of ions is necessary to provide the water conductivity (or as an electrolyte) required for water tree growth, and ions are “consumed” as the water tree grows through attachment to the tree walls. Thus sources of ions along the growth path must promote water tree growth, and cavities normally contain ionic impurities as a result of segregation of impurities during the solidification and crystallization of the cable dielectric after extrusion. The impurities come from the surface of the pellets, which are washed with clean, but not necessarily deionized, water at the time of manufacture, and only become more dirty prior to use.

**Bowtie Trees in XLPE, Filled XLPE, and Filled EPR**

A relatively large density of short bowtie trees is characteristic of water tree growth in unfilled XLPE in comparison to filled XLPE and EPR. Table II illustrates the typical difference observed in cable insulation samples aged for eight months.

![Table](image)

**Table I. Some Chemical and Physical Properties of EPR and XLPE**

<table>
<thead>
<tr>
<th>Property</th>
<th>XLPE Insulation</th>
<th>EPR Insulation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical Structure</td>
<td>Hydrocarbon chains</td>
<td>Hydrocarbon chains</td>
</tr>
<tr>
<td>Clay Composition</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Catalyst Residue</td>
<td>Little to none</td>
<td>V. Al. etc.</td>
</tr>
<tr>
<td>Chain Branch No.</td>
<td>15-35</td>
<td>200</td>
</tr>
<tr>
<td>Length of Branches</td>
<td>2-4</td>
<td>1-4</td>
</tr>
<tr>
<td>No. avg. MW before crosslinking</td>
<td>1-4 x 10^4</td>
<td>1.5 x 10^4</td>
</tr>
<tr>
<td>Crystallinity</td>
<td>50-60%</td>
<td>5-25%</td>
</tr>
<tr>
<td>Polymer Density</td>
<td>0.91-0.93 g/cm³</td>
<td>0.85 g/cm³</td>
</tr>
<tr>
<td>Density of Cavities (curing-dependent)</td>
<td>10^3 - 10^4/cm³</td>
<td>No data</td>
</tr>
<tr>
<td>Size of cavities</td>
<td>15-30 µm</td>
<td>No data</td>
</tr>
<tr>
<td>T_g</td>
<td>-120 C</td>
<td>-60 C</td>
</tr>
<tr>
<td>T_m</td>
<td>105-110 C</td>
<td>45-65 C</td>
</tr>
<tr>
<td>Tensile Strength</td>
<td>16 MPa</td>
<td>8-12 MPa</td>
</tr>
<tr>
<td>Elongation at Break</td>
<td>500%</td>
<td>300%</td>
</tr>
<tr>
<td>Thermal Expansion (20-130°C)</td>
<td>12%</td>
<td>8%</td>
</tr>
<tr>
<td>Toughness</td>
<td>140 J/cm³</td>
<td>80 J/cm³</td>
</tr>
<tr>
<td>Hardness</td>
<td>Rigid thermoplastic</td>
<td>Soft, rubber</td>
</tr>
<tr>
<td>Dielectric constant</td>
<td>2.3</td>
<td>2.4-3</td>
</tr>
<tr>
<td>Breakdown</td>
<td>100 kV/mm</td>
<td>22-44 kV/mm</td>
</tr>
<tr>
<td>Dielectric Loss</td>
<td>10⁻⁴</td>
<td>10⁻³</td>
</tr>
</tbody>
</table>

**Table II. Bowtie Trees in XLPE, Filled XLPE and EPR Cable Insulation**

<table>
<thead>
<tr>
<th>Material</th>
<th>BT Density (mm⁻³)</th>
<th>BT Length (µm)</th>
<th>OIT (minutes)</th>
<th>Water Absorption (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>XLPE</td>
<td>&gt;28</td>
<td>90</td>
<td>33</td>
<td>17</td>
</tr>
<tr>
<td>Filled XLPE</td>
<td>4</td>
<td>180</td>
<td>&gt;180</td>
<td>260</td>
</tr>
<tr>
<td>Filled EPR</td>
<td>0.3^a</td>
<td>390</td>
<td>&gt;180</td>
<td>470</td>
</tr>
</tbody>
</table>

^a low tree density in EPR and filled XLPE is unrelated to the difficulty of detecting trees in filled insulation. With present techniques, trees with lengths as small as 10 µm can be detected with relative ease [10].
months at three times rated voltage. The EPR cable insulation has very low bowtie tree population density but relatively large average bowtie tree length. Initiation sites of bowtie trees in XLPE are associated with cavities, particle agglomerates, and flaws such as cracks. In unfilled XLPE, each “bow” is relatively spherical in nature, in contrast to the “bows” in EPR, which are longer and narrower (Fig. 2). In EPR, initiation sites are somehow associated with catalytic impurities such as iron oxides and vanadium compounds (catalyst residue).

These characteristics combine to suggest that in XLPE, bowtie trees are relatively easily initiated but grow slowly. The decreasing growth rate of bowtie trees in XLPE over time provides strong evidence that growth is limited by (i) diffusion of water into the tree and/or (ii) available ions from the cavity. Bowtie trees initiate easily and at high density in steam cured XLPE as a result of the high cavity content and segregation of ionic impurities into such cavities. In newer, dry-cured XLPE cables, the bowtie tree density is much lower as a result of the much lower density of cavities in the insulation.

In EPR, and to a lesser degree in filled XLPE, bowtie trees are difficult to initiate but once initiated appear to grow quite aggressively, probably because (i) the much greater supply of water in the insulation and diffusion rate of water through the insulation, (ii) bowtie trees in EPR tend to be initiated by sources of highly active (catalytic) ions from catalyst residues in the polymer such as vanadium [10], and (iii) low crystallinity may also contribute to rapid water tree growth in EPR. The difficulty in initiating bowtie (and vented) water trees in EPR is probably the result of three factors, (i) the greatly reduced hydrophobicity of EPR (as demonstrated by the 25 times greater water absorption in Table II) relative to unfilled XLPE, which reduces the tendency of water to condense from the bulk into an electro-oxidized region and thereby cause a self-propagating tree and (ii) the much greater ionic content of EPR, which results from ions associated with the clay filler. While this ion content contributes to a greater dielectric loss, it may also contribute to water treeing resistance by increasing the water conductivity within the dielectric to the point that a water tree normally cannot grow, especially given the more hydrophilic nature of the dielectric. In other words, the dielectric either operates on the right hand side of the peak in the chemical potential of Fig. 1 or is so hydrophilic that water tends not to condense into electro-oxidized regions. Past research has demonstrated that adding finely powdered NaCl to XLPE will render it water tree resistant. (iii) However, when highly catalytic ions such as vanadium and iron are present [10-12], they can reduce the activation energy required for electro-oxidation resulting in a region of very strong electro-oxidation which results in a sufficient reduction in hydrophobicity that a self-propagating water tree initiates from such impurities. Such a water tree grows relatively rapidly as a result of the abundance of water in the dielectric and the heavy electro-oxidation caused by the catalytic action of such ions.

The case for filled XLPE is similar to that for EPR except that the moisture absorption is less than for EPR so that the hydrophobicity is greater than for EPR. This tends to place filled XLPE between unfilled XLPE and EPR in terms of water treeing characteristics. Thus filled XLPE grows bowtie water trees less readily than unfilled XLPE but more readily than EPR. The large oxidation induction time (OIT, Table II) of the filled insulations indicates that they are relatively difficult to oxidize which may also retard water tree formation.

**Vented Trees in XLPE, and Filled XLPE and EPR**

Table III illustrates typical vented water tree growth in unfilled and filled XLPE and EPR insulation. Despite every effort to locate vented trees in EPR, vented trees are very rarely observed. The scarcity of vented trees in EPR suggests very strongly that the typical ionic impurities at the semicon- dielectric interface cannot cause sufficient electro-oxidation to generate a self-propagating tree structure given the lower hydrophobicity, greater moisture concen-
At the operating fields of distribution cables, vented water trees in XLPE (those growing from the semicon-dielectric interface) grow from ionic impurities, not from stress enhancements at the interface, because without ionic impurities at the semicon-dielectric interface, the ion concentration in the water will be too low to generate the chemical potential necessary for electro-oxidation and water tree growth. While the chemical potential increases with the square of the electric field, the typical roughness at the semicon-dielectric interface, even for older semicons, is not sufficient to generate the necessary chemical potential without a source of ionic impurities to increase the conductivity of the water. For example, experiments have been conducted in which an intentionally rough surface was created between the semicon and dielectric in a plaque configuration. Careful examination using an SEM and elemental analysis after water tree growth at moderate fields indicated an ionic impurity at the root of each water tree and no tendency of the water trees to grow from high field regions of the semicon electrodes [14,15].

### Water Tree Resistance

As is well known, TR-XLPE insulation does not stop water tree growth, it impedes water tree growth, i.e., the number and size of water trees is reduced. As is also well known to those who have worked in the field, vented water trees grow from ionic impurities at the dielectric-semicon interface [14]. The reduction in the number of water trees is probably the result of the greatly improved cleanliness of modern semicons and reduced hydrophobicity of TR-XLPE discussed below.

TR-XLPE insulation consists of XLPE with a tree retardant additive. At least some varieties of TR-XLPE dielectric contain a dispersion of hydrophilic molecular clusters in the hydrophobic matrix. One logical assumption is that the hydrophilic clusters “stop” water tree channels, i.e., when a water tree channel “hits” a tree retardant cluster, it stops propagating, probably because the hydrophilic cluster impedes condensation of water into any electro-oxidized region near it, so that the water tree cannot propagate. Based on the hypothesis that a water tree channel grows until it encounters a water tree retardant cluster, we can treat this as a mean free path problem. The tree retardant molecules represent a randomly distributed set of points in the polymer matrix which will stop a water tree, and the water tree (in the tip region) is a roughly 0.01 µm diameter channel propagating through the matrix. On this basis, we can compute the probability of a water tree channel propagating a distance, $x$, as a function of the mean distance between water tree retardant molecules, as seen in Fig. 3.

The typical mean distance between water tree retardant clusters in the polymer matrix is probably in the range of 0.2 to 0.3 µm, so that a typical water tree in TR-XLPE would grow to a length of about 0.3 to 1 mm (5% probability). This analysis provides a rational explanation and quantitative basis to estimate water tree growth in TR-XLPE insulation that is in reasonable agreement with reality.

Vented water tree channels are known to branch, and often numerous branches grow off a main branch, which is rooted at the ionic contaminant at the dielectric-semicon interface. Thus a limitation in the size of an individual branch would not necessarily stop extension of the water tree, as branches could form and extend until they hit a water tree retardant molecule, branch again, etc. The limitation in water tree growth probably comes from diffuse electro-oxidation and the high water concentration around the water tree retardant clusters after they stop a water tree channel. The water tree channel provides a supply of water, and the hydrophilic tree retardant cluster probably provides a site for diffuse electro-oxidation by creating a high water density region but suppressing water tree channel growth. Thus, the water tree grows to something like the 95-99% probability length (Fig. 3), at which point sufficient water tree channels have “hit” water tree retardant clusters to form a “surface” of diffuse wa-

![Fig. 3. Probability of a water tree channel in TR-XLPE growing a given distance as a function of the mean separation of tree retardant molecules assuming a 0.01 µm water tree channel diameter.](image)
Stability under Wet Electrical Ageing

Wet electrical ageing has differing effects on TR-XLPE and EPR dielectrics. As is well known, the ac strength of EPR cable insulation tends to drop fairly rapidly during wet electrical ageing and then level off in the range of 55 to 80% of initial strength depending on EPR formulation [17], while wet electrical ageing has less impact on the impulse strength of EPR insulations with a retained impulse breakdown strength ranging from 66% to 100% depending on EPR formulation after 48 months of field ageing under normal service conditions [17]. TR-XLPE cable shows the opposite tendency with a retained impulse strength of 50% under the same conditions [17]. However, the ac strength of TR-XLPE is nearly 100% relative to the strength of degassed, virgin TR-XLPE cable.

The above phenomena in TR-XLPE and EPR insulation can be understood on a common basis, which also explains the high reliability of EPR insulation in spite of a relatively low AC breakdown strength after wet electrical ageing.

In the case of EPR insulation, the reduction in ac strength during wet electrical ageing is probably caused by migration of water into gaps at the interface between the filler particles and the polymer. Although the filler is well treated (approximately 1 weight percent silane) to enhance adhesion to the polymer, coverage is never 100%, some “free volume” will always exist at the interface, and, in any case, some water will eventually penetrate the slane to reach the clay surface. The water in such regions will cause some diffuse electro-oxidation of the polymer, which enhances water absorption over time until a steady state is reached.

The water at the particle interfaces will polarize substantially at power frequency, which will cause some of the filler particles to “appear” to be conducting, which will increase the stress in the rest of the insulation and reduce the ac breakdown strength. However, this phenomenon occurs relatively uniformly throughout the insulation, not on an isolated basis as for water trees, with the result that it causes a predictable reduction in the ac strength of the insulation; i.e., while the mean breakdown strength drops, the variance in the breakdown strength is relatively small because this is not related to a “discrete” phenomenon which produces extreme value statistics. The result is an insulation with a relatively low but very reliable (low variance) breakdown strength. Under impulse conditions, the water at the particle interface does not have time to polarize and therefore acts as a dielectric. Thus the ac strength drops in a predictable way, but the impulse strength is less affected.

The situation in TR-XLPE involves the same phenomena but as related to the evolution of discrete water trees. As noted above, water trees will grow in TR-XLPE insulation but are limited in length by the tree retardant additive. For a water tree to grow, the small water tree channels in the tree tip (growth) region must polarize partially at power frequency. Thus under power frequency conditions, the electric field at the surface of the small, “ball-like” water tree in TR-XLPE is graded by the partial polarization of the water tree channels which provide RC grading with the result that the ac strength is little affected. However, if the water tree channels are partially polarized at power frequency, as they must be to grow, they will not polarize appreciably at the much higher frequency associated with a risetime of a standard lightning impulse. Thus under lightning impulse conditions, the small water tree channels at the boundary of the water tree act as dielectric, which exposes the larger diameter water tree trunk (typically 1 µm diameter at its base at the ionic impurity from which the water tree initiates) to the electric field. The water tree trunk looks much more like a sharp point. As well, the rapid polarization of this larger diameter channel causes a temperature rise of 10–100 °C within a few microseconds, which causes a shock wave generated by the rapid thermal expansion of the water. As is well known, the dielectric strength of insulation under tensile stress is lower than that under compressive stress, and such a shock wave near the peak of the lightning impulse could well precipitate breakdown. Because the reduction in impulse strength is associated with discrete water trees, it is likely to follow extreme value statistics, which results in greater statistical variability than does the reduction in ac strength described above for EPR insulation. However, data from field ageing indicate that the impulse strength of TR-XLPE drops to about 50% of the initial strength during the first two years of in-service ageing and then levels off [17].

Conclusions

Attempts to make XLPE increasingly resistant to water tree growth have involved additives, which decrease hydrophobicity and make the XLPE more like EPR. EPS are evolving through improved processing, clay compatibilization, etc.
reduce losses while retaining the inherent water tree resistance. Thus in the end, the two technologies appear to be moving toward the "center" from opposite ends of a spectrum (filled versus unfilled) to achieve improved cable insulation performance.

References

Steven Boggs was graduated with a B.A. from Reed College in 1968 and received his Ph.D. and M BA degrees from the University of Toronto in 1972 and 1987, respectively. He spent 12 years with the Research Division of Ontario Hydro working in the areas of soil thermal properties, partial discharge measurement, high field-induced degradation of solid dielectrics, and SF6-insulated systems. He was elected a Fellow of the IEEE for contributions to the latter field. From 1987 to 1993, he was Director of Research and Engineering at Underground Systems, Inc. He is presently Director of the Electrical Insulation Research Center and Research Professor of Materials Science, Electrical Engineering, and Physics at the University of Connecticut as well as an Adjunct Professor of Electrical Engineering at the University of Toronto.

James J. Xu holds a B.S. in Polym. Eng. from East China University of Technology (1982), an M.S. in Polymer Materials from Shanghai Jiao Tong University (1986), and a Ph.D. in Polymer Science from the University of Connecticut (1993). He was a postdoctoral research fellow at the Electrical Insulation Research Center of the University of Connecticut (1994) and since 1995 has been a senior scientist with the Phelps Dodge Wire & Cable Group.