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WATER TREEING THEORIES - CURRENT STATUS, VIEWS AND AIMS

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INTRODUCTION

The matter of water treeing is both phenomenal in its economic impact and fascinating from scientific point of view. This is reflected in the vast number of papers that appeared since water trees were discovered in Japan. Still, the subject requires attention to maintain and increase insulation reliability. Recently, a review was performed on the understanding of water treeing up to 1997 [1]. The present paper is a condensed version of that review to which the reader be referred for further details and little over 140 references. Subsequently, this paper discusses: the term 'water treeing'; the most important properties of water trees; the main water treeing theories; countermeasures.

Definition of water treeing

The term 'water tree' was used in contrast to 'air trees' [2] refering to the ageing environment. Water trees have been identified with electrochemical trees refering to a process [3]. They are also described by their image as diffuse structures with a bush or fan-like appearance [4], being able to disappear and reappear on wetting. In polystyrene, they found non-diffuse water trees [5]. The following definition is [1] covers most findings over the past three decades:

Water trees are degradation structures in a polymer that are:
1 permanent
2 grown due to at least humidity and an electric field
3 electrically weaker than the original polymer when wet, but which are not a short circuit or local breakdown path
4 substantially more hydrophilic than the original polymer.

Point 3 and 4 still have to be quantified. The process of water treeing is a degradation phenomenon that produces water trees. The definition states that water trees are the degradation structures themselves. A string of water droplets would not be the water tree, but the inclusions and hydrophilic voids would. Also the water tree does not disappear, but it just dries out. Though it is attempted to propose a clear definition, it is not claimed that this definition will conclusively stake out the subject of water treeing.

CURRENT STATE OF UNDERSTANDING

Water in water trees

The interactions of water with the polyethylene (PE including both XLPE and LDPE) are described in [1,6]. Water is present mainly in four states: dissolved in the polymer; liquid in hydrophobic voids; liquid in hydrophilic voids or channels; liquid at hydrophilic impurities or inclusions. The amount of water in each state is temperature dependent. On cooling down, dissolved water starts to condense when its concentration equals the saturation level. Voids can then be produced, probably mainly after extrusion.

PE in contact with external (liquid) water, a "bath", will be saturated. Water in voids with hydrophobic walls will move out, because the surface energy is always higher than at the PE-bath interface. Water moves into voids with hydrophilic walls. A typical pressure built up would be .1 MPa for a 1 μm void. Dissolving species like salts trapped in voids gives a pressure up to e.g. 25 MPa with a tangential pressure of 12 MPa. Creep occurs until the pressure equals the polymer yield strength. Water trees are hydrophilic. Thus at least hydration should take place.

Important characteristics of water trees

There is a broad consensus on the most important properties of water trees. Some of them appeared in the proposed water tree definition.

Permanent and hydrophilic   Water trees can be dried, but water will enter again in a sufficiently humid environment. Drying and wetting can be carried out repeatedly. As water trees are permanent hydrophilic structures, the chemical composition seems different from the hydrophobic PE in addition to a likely change in physical structure.

Stainability   Staining methods for water trees have been developed. A dyeing method using methylene blue is recommended by Cigré [7]. Methylene blue is a redox indicator which is applied and buffered in its oxidized state to maintain a bright color. The staining is not of chemical nature, but rather a diffusion and clustering of the dye in the water tree [1].

Quantitative water content   The water content in water trees is typically about 1%, i.e. a factor 100 higher than in PE. Most of the water is in a liquid state in voids. In a needle test about 10% water was found near the needle tip [8]. This high content is due to the very high ageing stress of 60 kV/mm. More remote from the needle, the field is lower and a content of 1-2% was found. In service-aged cables lower water contents are found. In vented trees of field aged cables, infrared measurements showed .8-.92% water [9]. The water content can be increased by additional damage like boiling water trees or vacuum extraction plus rewetting.

Voids   The density of microvoids in the water tree tip is similar to that in PE [10]. A higher void density is often found for the main part of the tree. By TEM and SEM also a greater void density is found in water trees than in PE [11,3]. On the other hand, some evidence in the literature for voids is suspect: sample handling can easily produce voids in water trees by boiling and/or drying wet samples by vacuum in an exsiccator or an electron microscope. This is even used as a contrasting method [12]. Samples can be dried with a drying agent like silica gel or phosphor pentoxide. Although many voids can have been caused or enlarged by researchers, the higher density of voids in water trees is generally accepted.

Channels and tracks   The presence of elongated structures seems to differ from case to case even in one investigation [12]. The various forms of water trees in polystyrene in one experiment is a beautiful example [5]. Micro-channels as well as absence of helium permeability are found for PE [13,14,15].

The term 'channel' refers to an open duct allowing transport of water. There are however more subtle means like water hopping along hydratable sites. A string of hydrophilic footholds (e.g. trapped ions) 'woven' through the matrix would provide tracks or paths for water, i.e. the water trees [3]. The presence of nanometre tracks are indicated by TEM studies e.g. [11], dielectric measurements [9] and semi-permeability experiments [12].

Methylene blue staining of water trees often seems to reveal micro-branches. However, the same occurs if dye molecules cluster at specific endgroups or ions in nano-tracks. Such clusters can grow with other dye molecules. Not only the water tree paths are stained, but also the (sub)micron environment. A macroscopic analogon is a rope underwater looking thicker when seaweed clusters at it. Similarly, water tree nano-tracks can get a micro-channel appearance with dyeing. Though microchannels frequently occur, the main elongated structures in water trees rather seem ionic nanometre tracks than hollow (sub)micron channels.

Dielectric properties   Wet water trees have different dielectric properties than untreed PE. However, dry water trees have practically the same dielectric properties as unaged PE [16,9]. Wet water trees have an ε of 2.3 up to 3.6 [1]. With respect to tanδ, the results vary [10]. Nowadays, most agree that wet water trees have a higher tanδ, though still in the insulator range. Untreed PE has a tan$\delta \approx$.0005. Wet samples having water trees from field-aged cables had tan$\delta \approx$.002 at .01 kV/mm and tan$\delta \approx$.02 at .3 kV/mm both at 50 Hz [12]. This is still in the insulator range. The charge carriers are probably ions. The different and non-linear tanδ opens the door to diagnose cables.

The breakdown strength is reduced by sufficiently large and wet water trees [4,10]. As bow-tie trees stop after initial rapid growth whilst vented trees continue to grow, the latter control the breakdown strength on the long term [10]. However, in several cases, water trees bridged the entire insulation without causing breakdown at operating voltage [17]. A relation between the largest water tree length and breakdown strength has been reported [18,10]. In practice, breakdowns often occur with impulse voltages.

CURRENT MAIN THEORIES

The present technology and testing is based on more than one theory by lack of consensus. Though the theories tend to converge, still several theories exist:
1 electro-mechanical
2 diffusion
3 electrochemical oxidation
4 condition dependent model
These theories will be addressed in the following.

Electro-mechanical theories

Theories of water treeing by electro-mechanical forces, concern types of stress-cracking or electrically driven diffusion of water.

Cracking   An early consideration was that water treeing might be induced by supersaturation mainly. As a result, crazing of the polymer would occur both in bow-tie and vented trees. Ildstad et al. stated that Maxwell stresses could cause a pulsating compressive stress acting perpendicularly to the crack surface [19]. Particularly, internal stresses in the range of the PE yield strength might be introduced during the manufacturing process. Therefore, only small forces might be required to cause water treeing. Mechanical damage on a smaller scale resulting in microcavities has been suggested as well [20]. The idea is similar. Electrical fields in combination with water lead to mechanical forces in the material. Chain scission occurs if the resulting stresses exceed the local mechanical strength of the polymer matrix.

The theories about electromechanical forces describe realistic phenomena. However, clearcut evidence that it is the main ruling mechanism is certainly missing. Calculations by Zeller [6] and Steennis [10] for PE indicate that the mechanical stresses are much weaker than in early estimations. The expected mechanical damage in the form of cracks is rarely found. Moreover, water-filled cracks and voids in PE would still be hydrophobic.

On the other hand, electro-mechanical forces are supposed to take place to a certain extent. In needle tests, the electric field can be high enough for electromechanical deterioration [6]. In weaker materials like oils, such forces can form channels [21]. In cable insulation, high stresses can be expected from osmotic actions. Particularly for bow-tie trees starting from hydrophilic nuclei, the initial steps could be due to osmotic pressure. The role of pure osmotic pressure in degradation is already played during production, curing and cooling down of the cable. The water content of the PE in buried cables is probably lower than in freshly produced cables [1].

On the level where thermodynamic quantities are applicable, the mechanical fatigue model does not seem sufficient. It is found though that stresses can exist locally, and that much lower stresses than the yield strength can cause some local damage. The difference is that for water treeing a few local bonds may be broken, while for macroscopic fracture also the strongest bonds must be broken. When the discussion is taken at that level, the final verdict cannot be expected at this stage.

Dielectrophoresis   The theory of dielectrophoresis is more or less related to the electromechanical model. With dielectrophoresis the electric field pushes water into the polymer, but does not necessarily induce mechanical damage. Patsch et al. describe the theory of dielectrophoresis [22]. Once there is an inhomogeneous field, dipoles will move towards sites with higher electric fields. Such sites can be due to an impurity or another disturbance. Such spots are widely regarded as initiation points for bow-tie trees.

Dielectrophoresis certainly takes place. However, also from Zeller's calculations this seems not enough to cause permanent damage [6]. Like the case of the mechanical fatigue models, dielectrophoresis cannot account for the permanent hydrophilic behaviour of water trees. Therefore, the theories on the basis of pure electrophysical processes on water cannot account for water treeing. However, they can play a role in combination with diffusion theories.

Diffusion theories

The hydrophilic property of water trees indicates a change in chemical composition. One way to achieve this, is by diffusion of hydrophilic species into the insulation. Unlike surfactants and apolar solvents like pentane, hydrated ions will not penetrate PE easily. Diffusion can be driven by an electric field, which is also called electro-osmosis [3]. Diffusion of ions and contaminations has been regarded as a side effect that contaminates the water tree. In the current theory solvable species are supposed to play an important role and, moreover, the ions and other hydrophilic species are regarded to be essential parts of the water tree backbone if not be the tree itself.

There is overwhelming evidence that field driven diffusion of hydrophilic species occurs if such species are available. In their discussion of electro-osmosis, Dissado et al. note that this phenomenon would particularly take place with AC fields [3], which is in agreement with practice. Experiments also show that water trees rarely grow in the absence of such species. Cables produced with cleaner materials suffer less water tree growth usually. Particularly semiconductive shields appeared sources for ions [23]. The importance of the field is also apparent. Hydrophilic species can certainly provide the water tree with its hydrophilic character. Therefore, the ingress of ions is regarded rather instrumental to water treeing than a side effect.

However, it is also clear that ions do not only act as inert charge carriers. The chemical nature and physical properties of ions have a great impact on the growth rate of water trees. Some hydrated ions can corrosively attack polymer chains and cause a more open structure, while smaller hydrated ions may have a higher diffusion constant. Some ions can even act as inhibitors. Other processes which help producing a more open structure or hydrophilic environment should therefore be considered as well.

Electrochemical oxidation

Another theory explaining the hydrophilic nature of water trees, states that the polymer itself is (electro-) chemically modified. A range of subtheories exists on the reaction details, which are still unclear. The oxidation products can be discussed in greater detail. On the basis of those oxidation products the theory is split into a pure oxidative theory and a combined oxidation-diffusion theory.

It is also considered that oxidation could take place before [24] or after [16] the actual water tree growth. There seems to be no clear evidence for separating the water treeing process and oxidation.
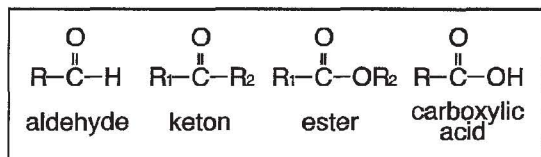
Fig.1: polar oxidation products: carbonyls

Pure oxidation   The oldest oxidation theory concerns pure oxidation. Water trees were regarded as electro-chemical trees quite early, mainly inspired by water tree properties like permanent hydrophilicity and the need of other species. The polymer turns into a polar material containing oxidation products shown in Fig.1. This provides a favourable environment for water. The oxidation can take place at void walls or develop a track through the amorphous phase with incidental void formation. Suggestions for reaction details can be found in various papers, but no specific intermediate reaction steps have been evidenced explicitly to the best of the author's knowledge. As oxidation mechanisms can be very complex, each guess seems equally valuable at this stage.

The required oxygen can have various sources, like oxygen dissolved in water [24] or electrolysis of water yielding various species among which radicals like •OH, which can oxidize PE [10]. Once radicals or ions are available, oxidation processes can take place leading to carbonyl groups in many cases.

Pure oxidation introduces polar groups which can provide the permanent hydrophilic nature of water trees, though not as effectively as hydratable ions. In contrast with practice, water treeing with distilled water at moderate stresses would seem possible owing to a pure oxidative mechanism. The need of species like catalysts or corrosive contaminants might resolve this contradiction. Still, water treeing is enhanced by many species, that are not oxidation catalysts [25]. Though support exists for hydrophilic groups attached to polymer chains [12], the oxidation products shown in Fig.1 are frequently not found in water trees. This means that the required degree of oxidation is too low to be detected or that in many cases the pure oxidative theory is not applicable. An intermediate concept could be that oxidation provides the paths while other processes also take place in parallel.

Combined oxidation and diffusion   The second oxidative mechanism is a combination of oxidation and diffusion and produces ionic groups: carboxylate groups (Fig.2). Such a group can be obtained by e.g. carboxylic acid trading its H^+-ion for a metal ion, thus becoming a carboxylate salt (group). Similarly sulphur containing antioxidants can produce sulphates. The production of ionic or salt groups requires diffusion of

metal ions in addition to oxidation. Carboxylate groups can form dimers or larger structures by sharing their metal ions. Thus nano-tracks can be formed which facilitate water transport. Carboxylate (salt) groups and sulphates are considerably more hydrophilic than the dipolar groups including carboxylic acid.
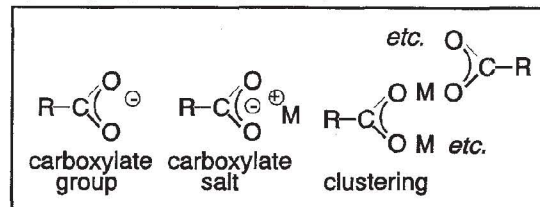

Fig. 2: carboxylate groups

In many cases carboxylate groups are found in water trees particularly in service aged cables. However, the concentration is sometimes very low and approaches the detection limit of FTIR. Good spectra and a HCl-gas test [12] are then required to evidence the carboxylate groups. In some other cases carboxylate groups are reported not to appear. This may be because the HCl-gas test had not been used, but the carboxylate content varies with the ageing conditions [26] and in certain cases carboxylate groups may not be present at detectable levels if not absent. Far less oxidation products are found generally with needle tests. It is assumed that the importance of the oxidative formation of ionic groups is reduced at high stresses and when large quantities of other hydrophilic species are available. The theory is supported by the success of reducing water tree growth with the use of cleaner materials [27,23]. The reduced supply of metal ions can become rate determining for this mechanism.

Condition dependent model

It is considered that water treeing is a complex of processes [4,13,16,26]. Certain processes can be mutually substitutable to produce a very hydrophilic environment: diffusion of ions or other hydrophilic species into the polymer; oxidation of the polymer (preferably in combination with metal ion diffusion); and oxidation of antioxidants (idem). Similarly, voids can be created by different processes involving chain scission like electro-mechanical stress and chemical reactions. Which process is dominant depends mainly on the set of ageing conditions in specific cases.

This is the core of the condition dependent model, that regards water treeing as a degradation phenomenon that produces a hydrophilic network by one or more processes that are most favourable under the whole set of ageing conditions. The model tries to relate conditions and processes. The main driving force is the electric field. The system seeks enhancement of

the permittivity by intrusion of water and the enhancement of the conductivity. Likely processes on the basis of degradation products in water trees are: oxidation because of oxidation products; (mechanical and/or chemical) chain scission because of excess voids and of carboxylate groups; diffusion because of contaminants, electrolyte and counter ions.

As for evidence, various contradicting results in the literature can be traced back to different ageing conditions like the electrical parameters, the involved chemicals, etc. This supports the idea of processes that can substitute each other to a large extent. Depending on the exact conditions, such processes can concur or compete. It is likely that changes in ageing conditions will favour one process over another [1].

The model as such is not new as it combines the various processes that seem physically likely to occur within the range of practical ageing conditions. The degradation is regarded both electrochemical and electrophysical in nature. This means that accelerated ageing studies should include some way of judging which process(es) took place and evaluate whether this is relevant to practice. This might be done with chemical analysis afterwards or with dielectric measurements during ageing. The model should not become a permit to neglect the critical analysis of mechanisms and experiments. The merit of the model is that it helps to find appropriate solutions when more than one mechanism can be active.

DISCUSSION AND CONCLUSIONS

Though the subject of water treeing is still of great concern for the reliability of cables, great progress has been made both scientifically and technologically. The success of countermeasures may be the reason why the subject draws less papers on recent conferences than in the eighties and early nineties.

Technological progress   Technology has made great progress after the identification of important key factors like humidity, cleanliness of materials and smoothness of surfaces. Water tight barriers like metal layers are used to keep the humidity low. This method is mainly applied in transmission cable for economic reasons. Swelling tape as drying agent with a PE sheath for low water permeation is an emerging method for distribution cables. The success of cleaner insulating and semiconductive materials probably due to reducing the availibility of metal ions and hydrophilic species. Care must be taken that other materials in cables will not act as sources of contaminants. Smooth surfaces with triple extrusion processes avoid electric field concentrations. Water tree retardants have been developed based on various philosophies.

Opinions   During almost thirty years of water tree awareness, many hypotheses were brought up. Clearly, even nowadays, still different opinions exist both on propagation and inception mechanisms. Part of these are undoubtedly due to different ageing conditions. The main current theories are: electromechanical (cracking and dielectrophoresis), diffusion, electrochemical oxidation (pure and combined with diffusion) and condition dependent model.

The latter model acknowledges the discrepancies of experimental findings where different processes partly compete, partly concur. At least oxidation, chain scission and diffusion are important during water tree growth. For propagation processes at service stresses particularly electro-osmosis and oxidative processes are likely to occur on the basis of chemical analyses and dielectric properties. At higher stresses as in needle tests, electro-mechanical processes become more likely.

Testing   Though most modern cables are much less susceptible to water treeing, testing remains necessary as a means of quality control. New diagnostic methods are emerging. The probable exchangeability of various water treeing processes urges to perform realistic tests. For example, high electric fields selectively promote physical processes both in cable and material tests. Acceleration can be obtained also with higher frequencies. In material tests, problems occurred with unwanted electrolyte sources like steel or brass in contact with a well defined NaCl solution [1].

Research   A problem in water tree research is of course, the slow growth of water trees in practice; i.e. typically <1 μm/day. Accelerating water treeing is usually inevitable, but care should be taken with applying severe ageing conditions. The relevancy of various processes to service ageing should be preserved and preferably evidenced. This can lead to systematic and effective countermeasures and to correct testing.

For studies of the water tree microstructure, the use of boiling or vacuum treatment is discouraged, because the morphology is changed. Samples can be dried with a drying agent. For staining, the standard methylene blue method is suitable for length measurements. To evaluate the presence of sulphates or carboxylate groups, the HCl-gas test is recommended. Particularly for low concentrations, the method is helpful.

ACKNOWLEDGEMENT

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