Chemical Crosslinking of Polyethylene and its Effect on Water Tree Initiation and Propagation

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Abstract
The water tree resistance of chemically crosslinked polyethylene and of low density polyethylene were compared in order to elucidate whether the crosslinking itself influences or not the water tree characteristics of polymeric cable insulation materials. For this purpose, water trees were grown in compression moulded disks, obtained from pellets of either thermoplastic or chemically crosslinked polyethylene. Three types of crosslinked polyethylene were evaluated: one containing only peroxide (XLA) and two others having, besides peroxide, a tree retarding additive system (XLB and XLC), and the results were compared with those obtained on their thermoplastic correspondents (A, B and C). Results were determined for both Water Tree Propagation and Water Tree Initiation. The results obtained for Water Tree Propagation indicate that there is generally a large difference between the types (A, B & C) yet only small difference between thermoplastic and crosslinked samples. However for two cases (A & B) these small differences between crosslinking are statistically significant. The complementary Water Tree Initiation results show both large and significant differences between material types and the crosslinking.

Index Terms — Cross linked polyethylene insulation, water trees, cable insulation.

1 INTRODUCTION
During the last decades crosslinked polyethylene (XLPE) has been extensively used as extruded cable insulation in underground transmission and distribution cables, replacing low density polyethylene (LDPE) which was previously used. The main reason for the change was that crosslinking improved the thermal and the dimensional stability, especially at elevated temperatures. Besides the mechanical resistance and electrical performance, another property that needs to be considered when choosing the insulating material for medium voltage (MV) power cables is the water tree resistance. Indeed ageing due to water treeing had been earlier identified as one of the main cause of MV cable insulation breakdown [1]. Therefore the question is if the crosslinking itself plays a role in water treeing in polyethylene insulation? It is indeed widely accepted that XLPE is outperforming the thermoplastic LDPE technology in the electrical cable distribution networks.

In our first study [2] the crosslinking of the polyethylene was obtained by irradiating the samples with high energy electron beams. The results showed no difference with respect to the growth of water trees between thermoplastic polyethylene and irradiation-crosslinked polyethylene. The conclusion was that the crosslinking network, created by irradiation, did not prevent the propagation of water trees.

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Since the most common technique used today for XLPE cable insulation manufacturing is not irradiation but chemical crosslinking, it was of interest to perform a similar study using different chemically crosslinkable compounds designed for cable insulation. The chemical crosslinking using dicumyl peroxide has been extensively studied and it has been shown that by-products originating from decomposition of the peroxide, in this case acetophenone, influence the propagation of water trees, thus introducing an additional parameter which has to be taken into consideration [3]. Experiments which were performed about twenty years ago on samples where the by-products have been removed did not reveal any difference concerning the growth of water trees between thermoplastic and crosslinked materials [4]. However, the large dispersion of the water tree lengths observed by de Bellet and al. in 1987 has led us to question if a better accuracy, presently available, could reveal a difference between XLPE and LDPE with respect to water tree growth kinetics.

The materials used in this study were three polyethylenes designed for use as insulation of MV cables. One sample was a base polymer containing only dicumyl peroxide to avoid the possible influence of any other components on water treeing other than that of polymer crosslinking. Then two different compounds based on the same polymer but containing additionally a tree retardant additive, intended to reduce the number and the size of water trees, were included as well.

2 EXPERIMENTAL

2.1 MATERIALS

The water treeing tests were performed on samples provided by Borealis AB. All materials for the samples in thermoplastic form, labelled A, B and C, were based on low density polyethylene (LDPE) prepared by the high pressure polymerization process usually used to manufacture compounds for power cable insulation and they all had a Melt Flow Rate (2.16 kg) (MFR2) of 2 g/10 min.

The material A contained no further additives.

The materials B and C were based on material A and contained antioxidant to impart thermo-oxidative ageing protection during cable manufacture and service life. These samples also contain different water tree retardant additive systems (one for B and another for C), both of polar nature.

Many studies have been conducted on the effect of peroxide crosslinking on a number of important properties of cable insulations [5-7]. In keeping with these studies, the samples labelled XLA, XLB and XLC were obtained from the materials A, B and C, respectively, by crosslinking using 2% wt of dicumyl peroxide. These levels provide very comparable performance with insulations used for a range of power cables [7].

2.2 SAMPLE PREPARATION

Disks of 0.5 mm thickness and 50 mm diameter were press moulded from pellets of polyethylene, in a CARVER press (model 2696) using a mould with 12 holes of 50 mm diameter and 0.5 mm thickness (Figure 1). The thermoplastic polyethylene pellets of (A) were pressed 5 min at 150 °C and 40 bar and afterwards, the samples were cooled in air at room temperature. The crosslinkable polyethylene pellets (used for obtaining XLA) were pressed 14 min at 195 °C and 4 MPa (40 bar) and then the cooling was made with a rate of 15 °C/min. In order to obtain identical samples, the quantity of pellets used in each hole of the pattern was set by taking into account the whole volume and the density of polyethylene.

After manufacturing, the crosslinked samples were degassed in vacuum at 90 °C for 72 h.

The sample preparation for the thermoplastic samples B and C was performed in a somewhat different way compared to the description above. The mould used for pressing was preheated at 130 °C for 10 min. Then the pellets were pressed into a plaque of 0.6 - 0.65 mm thickness at 130 °C, 2 min at 2 MPa (20 bar) and 5 min at 10 MPa (100 bar) followed by cooling to room temperature at a cooling rate of 15 °C/min. For the preparation of the crosslinked samples XLB and XLC the mould was preheated for 10 min. Then the pellets were pressed into a plaque of 0.6 - 0.65 mm thickness using the following conditions: 2 min at 130 °C and 2 MPa (20 bar) followed by 20 min at 200 °C and 10 MPa (100 bar) and then cooling to room temperature at a cooling rate of 15 °C/min.

Five plaques were prepared of each formulation. After manufacturing the crosslinked samples were heat treated in an oven at 90 °C, no vacuum, for 72 h to remove the peroxide decomposition products. The level after heat treatment of dicumyl peroxide, acetophenone, cumyl alcohol, alpha methyl styrene and cumene were all found to be below 10 ppm. Also the thermoplastic samples were heat treated in the same way in order to have the same thermal history in all the samples. The purpose of the heat treatment was to remove the crosslinking byproducts that are known to have large influence on the treeing [8]. The conditions used in this experiment do not significantly affect the insulation morphology as they are considerably below those employed in cable manufacture. Furthermore, any small effect that may be present due to the heat treatment is excluded from the experiment by applying the same conditions to all of the tested samples. Initially there were some concerns that the temperatures and times employed for the degassing of the samples might induce some morphological change that would affect the electrical performance of the insulations. Confirmation of the fact that this is not true comes from the

![Figure 1. Pattern used to manufacture the samples.](Image 368x501 to 520x639)
inspection of data obtained from experiments where selected crystallization and annealing conditions were applied to a similar type of LDPE to that discussed in this paper [9]. These experiments show that the conditions used here for degassing only effect the breakdown strength by 3% and these changes are not statistically significant due to the inherent scatter in breakdown tests. It is important to note that the results reported in the present paper display large and more significant changes than can be attributed to any morphological changes.

The crosslinking degree was assessed by gel fraction measurements in accordance to the ASTM D2765 procedure by refluxing xylene close to its boiling point, and the extraction was carried out until the insoluble gel reached a constant weight. The extraction time was of at least 96 h.

2.3 WATER TREES

To compare the water tree resistance of polymeric materials, it is critical to grow water trees under well defined conditions which include: (a) a defect at the water-polymer interface which amplifies the electric field, (b) an ac electric field, (c) an ionic solution. For consistency of the results, the shape of the defect, the frequency and amplitude of the voltage and the concentration of the ionic solution have to be well defined and consistent. As defects acting as initiation sites for water trees, small needle-like imprints, were created on one side of the compression moulded sample, by pressing a sheet of abrasive paper (P240 type with an average particle size smaller than 25 μm) for 2 min at 50 MPa (500 bar) at room temperature.

The images in Figure 2 show the typical distribution of defects achieved for each of the tested samples. Inspection of the images shows that the initiation sites are evenly (in separation and size) on the surface of the samples. Figure 3 gives the concentrations of the initiating defects in a Box and Whisker format, segregated for the three material types, both thermoplastic and crosslinked versions. The median defect contribution for this approach is expected to lie within the range (set by the lower and upper quartiles) 100 to 140 defects per mm². Analysis of the data (Kruskal Wallis test) shows that there is no significant difference between the material types (Figure 3a) however, the same analysis shows that the thermoplastic versions have 25% more initiation sites than the crosslinked versions (Figure 3b) and it also confirms that this difference is statistically significant. Consequently one would expect the thermoplastic samples to contain 25% more initiated water trees.

Figure 2. Defects acting as initiation sites for water trees, created on samples by pressing a sheet of abrasive paper before water tree tests.
In our experiments, water trees were grown in cells (Figure 4) arranged by fixing the sample on a polyethylene tube using LOCTITE 401 in combination with an adequate surface treatment. The electrolyte was a NaCl solution of concentration $c = 0.1$ mol/l. Groups of five cells were fixed in a cell-holder and water trees were grown by applying a voltage of 2 kV at a frequency of 5 kHz for 25 h at room temperature.

After ageing the samples were detached and dyed in a rhodamine solution at 60 °C for 3 days to facilitate the measurements of the water tree lengths. Three slices of 200 μm thickness were microtomed from each sample (Figure 5a), and the lengths of all water trees from each slice were measured using the experimental setup shown in Figure 6. The average length $L_{ai}$ for each sample was determined as the average of the water trees lengths $L_k$ measured on the three slices of the sample (Figure 5b). The number of trees in each slice was counted to determine the water tree density on the sample surface.

Ten samples of each type were tested according to the procedure described above.

### 3 RESULTS AND DISCUSSION

Table 1 gives the average water tree lengths $L_{ai}$ obtained from each of the ten samples tested for each material, the average length of the ten average tree lengths, and the measured crosslinking degree.

![Figure 4](image-url)  
**Figure 4.** Cell used to produce water trees.

![Figure 5](image-url)  
**Figure 5.** (a) Slices for measuring water trees dimensions. (b) Water tree length $L_k$ as measured on a slice.

![Figure 6](image-url)  
**Figure 6.** Setup used to measure water tree lengths and water tree densities.

#### 3.1 RESULT ACCURACY

To evaluate the accuracy of the measurements both the scattering between samples and the uncertainty on the measurements of the water tree lengths need to be considered. In fact, the scattering in the $L_{ai}$ values is very small, in the order of 3%. Based on this finding it was decided to consider the measurement error on the length values as well. Among the different sources of error, the depth and the shape of the water tree initiation sites as well as the determination of the water tree front could be mentioned. The last one is by far the most important and the scatter in the length measurements can be estimated to be in the range between 10 and 15%, depending on the type of material used. It has been observed that different types of materials give rise to trees that are more or less marked. Finally, it was concluded that each material can be characterized by the average length $L$ affected by an overall uncertainty of less than ±15%, which is a lower value than the previous work on this subject [4]. Figure 7 gives the distribution of the individual average water tree lengths for different material types and crosslinking conditions.

![Figure 3](image-url)  
**Figure 3.** Concentration of defect sites estimated from images shown in Figure 2, represented in a box and whisker plot – the boxes enclose 50% of the data, the whiskers 100%, the central lines represent the medians: (a) materials A, B and C - both forms, (b) crosslinked and thermoplastic - all materials.
### 3.2 INFLUENCE OF CROSSLINKING ON WATER TREE GROWTH

A detailed discussion of the statistical tests is outside the scope of this paper and will be dealt with elsewhere. Nevertheless, inspection of Table 1 and Figure 7 shows three very interesting features. Firstly, these data confirm the results published in earlier studies, by de Bellet et al [4], generated under other conditions and with a lower accuracy, and they are also in agreement with the findings in our previous study where water trees were grown in irradiation crosslinked polyethylene [2].

The second feature is the large and significant differences between the lengths of water trees grown in the three types of materials, irrespective of the state of crosslinking.

Finally, and somewhat surprisingly, the differences in tree length that can be ascribed to the crosslinking are small. Yet in two of the cases (A & B) these small differences in crosslinking are significant, namely the scatter within the lengths are smaller than the differences between the crosslinking states.

One explanation for this third observation could be that a polyethylene crosslinked to 80-85% gel has a network density, i.e. a molecular weight between crosslinks, in the range of 5000-6000 g/mol.

During peroxide crosslinking of polyethylene, the radicals generated from the decomposed peroxide abstract hydrogen atoms from the polyethylene chain forming macroradicals. When two macroradicals combine a crosslink is formed. However, several authors have suggested that during crosslinking the entanglements naturally present in a polymer melt become trapped to different degrees (so-called physical crosslinks) by the chemical crosslinks thereby contributing to the network density. It has been reported that in the network formed in crosslinked low density polyethylene, around 1/3 of the crosslinks originate from chemical crosslinks and around 2/3 from physical crosslinks [10]. Thus the number of chemical crosslinks is not large and therefore this could be the explanation for the small difference observed on the water tree growth rate between thermoplastic and chemically crosslinked samples, at the investigated degree of crosslinking.

Our work also shows that materials B and C which contain additives, e.g. antioxidants and water tree retardant substances, have a degree of crosslinking that is essentially the same as in the reference material XLA, indicating that the additives have only a minor influence on the crosslinked network.

### 3.3 INFLUENCE OF CROSSLINKING ON WATER TREE DENSITY

In addition to water tree growth, the same samples yielded information concerning the behavior of different materials with respect to water tree initiation.

### Table 1. Water tree lengths and crosslinking degree for the tested materials.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Crosslinking degree [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0</td>
</tr>
<tr>
<td>XLA</td>
<td>81</td>
</tr>
<tr>
<td>B</td>
<td>0</td>
</tr>
<tr>
<td>XLB</td>
<td>84</td>
</tr>
<tr>
<td>C</td>
<td>0</td>
</tr>
<tr>
<td>XLC</td>
<td>81.5</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Water tree lengths of the ten tested samples [μm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>L_{a1}</td>
</tr>
<tr>
<td>---------</td>
</tr>
<tr>
<td>A</td>
</tr>
<tr>
<td>XLA</td>
</tr>
<tr>
<td>B</td>
</tr>
<tr>
<td>XLB</td>
</tr>
<tr>
<td>C</td>
</tr>
<tr>
<td>XLC</td>
</tr>
</tbody>
</table>

### Table 2. Surface densities of water trees in tested materials.

<table>
<thead>
<tr>
<th>Non-crosslinked samples</th>
<th>Water tree density [mm(^{-2})]</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>16</td>
</tr>
<tr>
<td>B</td>
<td>7</td>
</tr>
<tr>
<td>C</td>
<td>10.5</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Crosslinked samples</th>
<th>Water tree density [mm(^{-2})]</th>
</tr>
</thead>
<tbody>
<tr>
<td>XLA</td>
<td>9</td>
</tr>
<tr>
<td>XLB</td>
<td>2.5</td>
</tr>
<tr>
<td>XLC</td>
<td>5.5</td>
</tr>
</tbody>
</table>

Figure 7. Mean water tree length (L_{a}) data, represented in a box and whisker plot – the boxes enclose 50% of the data, the whiskers 100%, the central lines represent the medians.
trees were grown in irradiation crosslinked polyethylene. It is plausible that the crosslinked network formed in the polyethylene was not able to hinder the migration of water through the polymer under the action of the electric field, thereby the water tree growth was not influenced once initiated.

One may conclude that crosslinking itself does not influence the water tree propagation but it plays a role in the water tree initiation due to the better stress-cracking resistance of crosslinked materials. We assume that different additives added to polyethylene influence the initiation in different ways according to the nature of additives.

4 CONCLUSIONS

The results obtained under our experimental conditions have shown no large influence of the chemical crosslinking on water tree propagation, for the range of water tree lengths smaller than 300 microns, in the tested materials. This is in agreement with the results of a previous work in which water trees were grown in irradiation crosslinked polyethylene. It is plausible that the crosslinked network formed in the polyethylene was not able to hinder the migration of water through the polymer under the action of the electric field, thereby the water tree growth was not influenced once initiated.

REFERENCES


Florin Ciuprina (M’93) was born in Galati, Romania, in 1965. He received the M.Sc. and Ph.D. degrees in electrical engineering from the University Politehnica of Bucharest (UPB) in 1989 and 1997, respectively. Since 1991 he has been with UPB, Faculty of Electrical Engineering, working as an assistant professor, lecturer, associate professor and, presently, Professor of Electrical Materials. His research activity have been developed mainly at Electrical Materials Laboratory (ELMAT) from UPB, but also at Laboratoire d’Electrostatique et de Matériaux Diélectriques (LEMD) – CNRS Grenoble, France, during several research visits between 1995 and 2007. His main research fields include water treeing in cable insulation, ageing and conduction phenomena in polymers and electrical properties of nanodielectrics. He authored/co-authored several scientific publications and communications.
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