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CROSSLINKING AND WATER TREEING IN POLYETHYLENE INSULATION

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ABSTRACT

The target for the present study is to analyze whether the presence of crosslinks in polyethylene influence the water tree initiation and propagation in polymer insulation materials. Combining the results of two studies – the first with crosslinks introduced via irradiation, and the second where crosslinks are introduced via peroxides, it can be concluded that crosslinking of the polyethylene chains does not affect the water tree growth but it affects the number of the initiated trees which is lower after crosslinking. This conclusion applies to both the base material and the materials containing additives.

KEYWORDS

Cable insulation, Polyethylene crosslinking, Water treeing.

INTRODUCTION

Crosslinked polyethylene (XLPE) has been extensively used in the last decades in underground transmission and distribution cables, replacing the thermoplastic low density polyethylene (LDPE) which was previously used for extruded cable insulation. The main reason was that the presence of crosslinks improved the thermal and dimensional stability. Besides its mechanical resistance and intrinsic electrical performance, another property that needs to be considered when choosing the insulating material for medium voltage (MV) power cables is its water tree resistance. Indeed ageing due to water treeing had been earlier identified as one of the main causes of MV cable insulation breakdown [1,2,3] .

In some cable constructions, the insulation material is exposed to water and this, in combination with the electrical stress, will cause water filled tree-like structures to grow. These structures, called water trees [4], degrade the dielectric properties of the insulation (e.g. reducing breakdown strength and increasing dielectric loss) and consequently limit the service life length of the cable. A question that is not fully resolved is whether the crosslinks themselves in XLPE play a role in the water treeing process. This is what we are trying to answer in this paper by using the main results of two studies that were carried out on crosslinked and non-crosslinked plaque samples.

In the first study, polyethylene crosslinking was obtained by irradiating the samples with high energy electron beams [5]. The properties of the samples, non-irradiated and irradiated, were analyzed by determining the crosslinking degree by gel fraction measurement and their oxidation profile using FTIR spectroscopy. In the second study three types of crosslinked polyethylene systems were evaluated: one containing only peroxide and the other two having, beside the peroxide, also a tree retarding additive system. The results were compared with those obtained on their thermoplastic correspondents.

EXPERIMENTAL

The samples used in both studies were circular plaques (disks) prepared from LDPE pellets. On one side of each disk small needle-like defects were introduced as initiation sites for water trees.

In the first study the material tested was LDPE without additives, referred to as material A. Two sets of samples were analyzed: *irradiated samples* – in air or in vacuum, using different doses -, and *unirradiated samples* – as reference. The samples used for water treeing were characterized by the crosslinking degree and by the oxidation level. Water trees were produced in all samples, whether irradiated or not, using the same conditions. The degradation caused by water trees was assessed by tree length measurements.

As the most common technique used for cable manufacturing is not irradiation but chemical crosslinking via peroxides [6], the second study focused on the behaviour, with respect to water treeing, of three *model material systems* A, B and C, crosslinked with peroxide. These polymer systems can be characterised as:

- a base resin of LDPE, usually used to prepare compounds for power cable insulation, which was labelled A in thermoplastic form and XLA after crosslinking with dicumyl peroxide;
- two compounds, made of the base resin A with two different chemical tree retardant additive systems, labelled B and C in thermoplastic form and XLB and XLC after crosslinking with dicumyl peroxide.

These three samples A, B and C contained antioxidant as well.

Samples

Disks of 0.5 mm thickness and 50 mm diameter were made by compression moulding from pellets of polyethylene. For the first irradiation study, pellets of LDPE without additives were pressed at 185°C and 40 bars. Afterwards, the samples were cooled in air at room temperature. For the second chemical crosslinking study, the preparation of the thermoplastic (TP) samples A, B and C was carried out as presented above. The crosslinked (XL) samples were prepared by melt pressing 20 min at 200 ^{o}C and 200 bars. The samples were cooled to room temperature, still under pressure, by a cooling rate of 15 ^{o}C/min. After crosslinking all plaques were degassed at 70 ^{o}C for 72 h to remove the crosslinking by-products. The thermoplastic samples were also heat treated using the same conditions to give a similar thermal, and hence morphological, history.

The general methods to introduce water tree initiation sites

are sandblasting or scratching of the sample surface. In the present study, in order to obtain a better repeatability and a more uniform distribution of the initiation sites, compared to the above-mentioned methods, another technique was used [7]. Small needle-like defects were introduced as initiation sites for water trees by pressing a sheet of abrasive paper (P240 grit 50 micron defect size) on one side of the sample, for 2 min at 500 bars.

Irradiation

The irradiation of the samples for the first study was performed by electron beam generated by an electron accelerator of ILU 6 type, at a dose rate of 37 MGy/h [5]. The integrated doses used in this study were 0.2, 0.4, 0.6, 0.8 and 1 MGy. First, the set of samples for irradiation was divided in two parts. Then, groups of 30 samples of one part were irradiated (at each of the above mentioned doses) in vacuum (10^{-2} Pa) and maintained in vacuum after irradiation for 30 minutes, while the samples from the other part were irradiated in air. In both cases, air and vacuum, the irradiation was performed at ambient temperature. For each dose, all 30 samples were identically irradiated.

Fourier Transform Infrared spectroscopy

A Fourier transform infrared (FTIR) spectrometer of Nicolet 510 type with an IR microscope (Spectratech IR Plane) equipped with a MCT detector cooled in liquid nitrogen were used for the first study. The IR analysis was performed on 100 μm thick slices cut along the cross section of the disk samples, the disk thickness (of 500 μm) being analyzed by 25 μm step IR mapping using a 25×400 μm^2 window (Figure 1).

This procedure was used to evaluate the oxidation from the value of carbonyl index defined as the difference between the absorbance at 1715 cm^{-1} (ketones) and the absorbance at 1850 cm^{-1} which is not sensitive to oxidation.

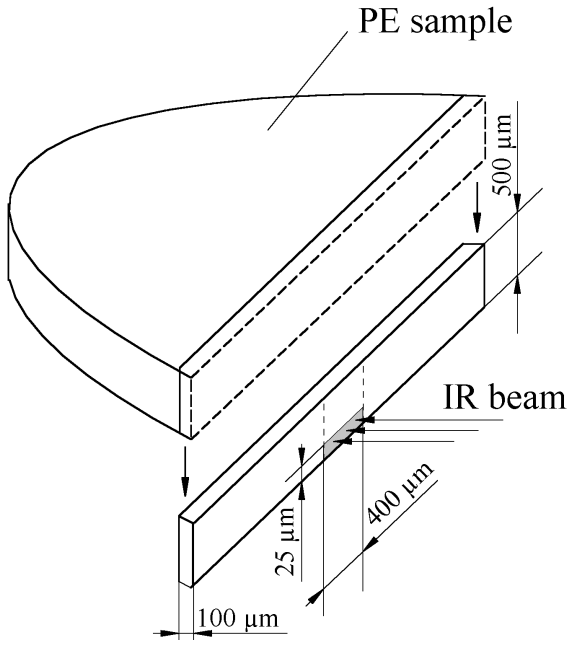

Figure 1: Slice used for FTIR mapping

Two different samples were analyzed for each dose, and for each sample two spectra per step of IR mapping were taken. Thus, the average of the four values obtained for each step is reported in the results section.

Crosslinking degree

The crosslinking degree of the unirradiated and irradiated samples was assessed by gel fraction measurements in accordance with the ASTM D2765 procedure. Thus, samples were exposed to 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 hours. The crosslinking profile of the irradiated samples was determined by measuring the gel fraction of three layers, each of them representing one third of the sample [5].

Water trees

Water trees were grown in cells (Figure 2) by fixing the sample on a polyethylene tube. 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 the samples an electric field of 4 kV/mm, 5 kHz, for 25 hours, at room temperature. Ten samples of each type were tested using these conditions.

After ageing, the samples were dyed in a rhodamine solution at 60 °C to facilitate the measurements of water tree lengths and number. Three 200 μm slices were then microtomed from each sample and optically examined (Figure 3). The trees are characterized in two ways:

Length - The lengths of all water trees from each slice were measured (Figure 3). The average length for each slice was used to determine the average water tree length L_s for each of the 10 samples.

Density – The number of trees in each slice were counted in the same manner as used for the tree lengths. These data provided the average water tree density D_s for each sample.

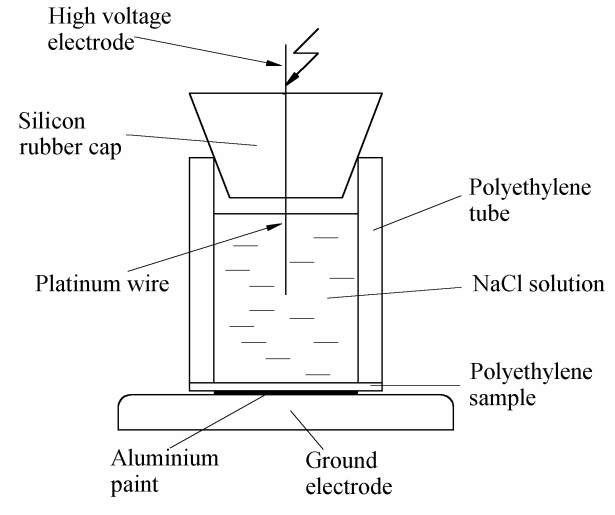

Figure 2: Cell used to grow water trees.

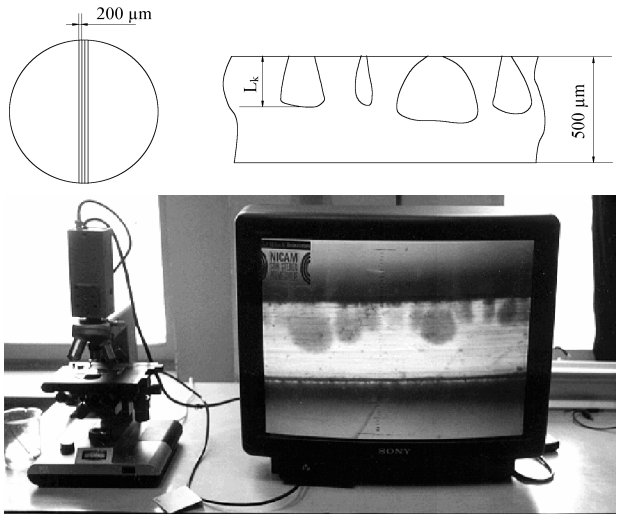

Figure 3: Upper – diagrammatic representation of water trees. Lower - setup used to measure water tree lengths and water tree densities

RESULTS AND DISCUSSION

Crosslinking by irradiation

Crosslinking analysis

Figure 4 shows the gel fraction as a function of integrated dose as resulting from the average crosslinking measurements. It can be observed that the gel fraction increases with the dose and it levels off at ~85% starting from 0.6 MGy. The evolution of the degree of crosslinking appears to be independent of the conditions used (air or vacuum) during the irradiation step. From these results, one may conclude that for obtaining the maximum crosslinking degree, a dose of 0.6 MGy is sufficient. It was also noticed that the crosslinking degree was the same in the bulk and in the surface layers of the sample [5].

Influence of crosslinking on water tree growth

The main objective of this study was to correlate the crosslinking degree with the water tree length. However, one should not neglect the fact that irradiation is also causing oxidation of polymeric materials. This is known to reduce the growth rate of water trees [8]. Therefore the irradiation experiments were carried out, besides air, in vacuum to limit the oxidation on the surface layers of the samples.

Taking into account all the above remarks, we look first at the water tree lengths (Table 1) obtained in the samples with the maximum crosslinking degree reached after an optimal exposure to radiations, and this is the case of the samples irradiated in vacuum at 0.6 MGy.

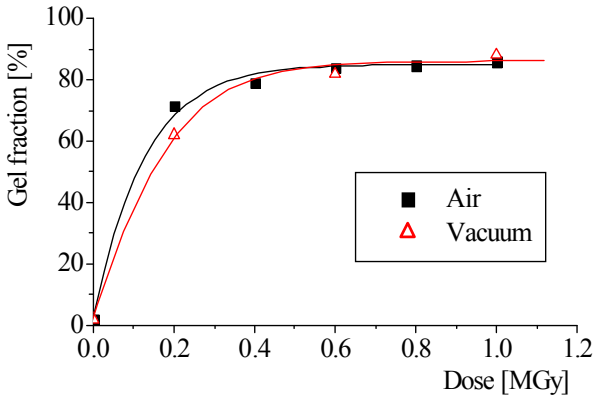

Figure 4: Gel fractions vs. the irradiation dose for samples irradiated in air and in vacuum

The results in Table 1 show that the tree lengths are almost identical in unirradiated as in irradiated samples. It appears that the crosslinking does not influence water tree growth. However, it remains to debate whether or not the oxidation could alter this result, and this aspect is discussed below.

Discussion

The oxidation profiles for samples irradiated at 0.6 MGy (in air and in vacuum) compared with that for unirradiated samples are shown in Figure 5.

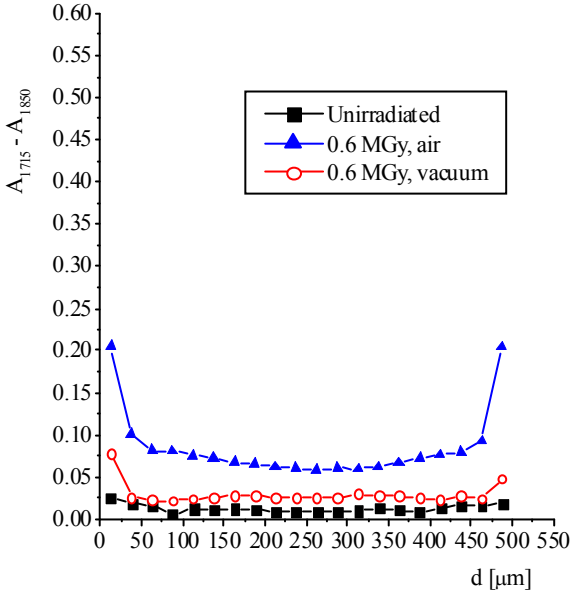

Figure 5: Oxidation profile for 0.6 MGy

Table 1

Water tree length of irradiated and unirradiated samples.

Samples	Water tree lengths of the 10 tested samples [µm]										Average length
	L_{s1}	L_{s2}	L_{s3}	L_{s4}	L_{s5}	L_{s6}	L_{s7}	L_{s8}	L_{s9}	L_{s10}	L_a
Unirradiated	281	275	282	283	255	273	259	262	262	260	269 µm ± 4%
Irradiated at 0.6 MGy (vacuum)	277	287	258	288	267	265	260	284	281	287	275 µm ± 4%

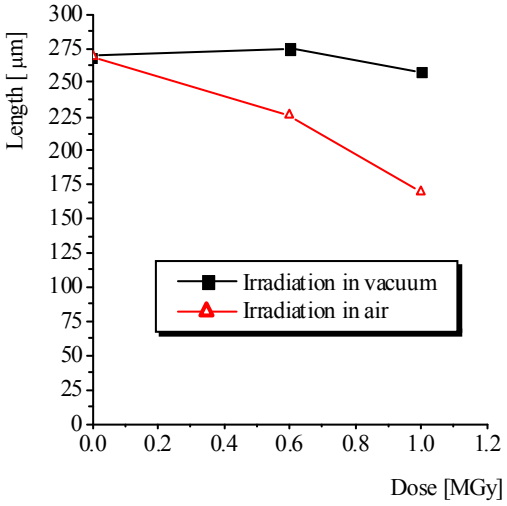

Figure 6: Water tree length vs. integrated dose

From the oxidation profiles shown in Figure 5 it can be observed that the reference samples as well as the samples irradiated in vacuum, have no significant level of oxidation over the entire thickness of the sample. Only a slight increase of the carbonyl level in a ~25 μm thick surface layer could be observed compared to the unirradiated samples. This would normally not affect the water tree initiation and propagation as the trees are initiated at the tips of the needle-like defects on a ~30-40 μm depth. Therefore, the only difference between these samples, that might influence water treeing, is the high crosslinking degree (~85%) of the samples. It can be noted in Table 1 that the water tree lengths are almost the same in reference samples (269 μm ± 4%) and in samples irradiated in vacuum (275 μm ± 4%). It appears therefore that the crosslinks introduced via irradiation does not play any role in the water tree propagation. The variations of water tree lengths with the irradiation dose, both in vacuum and in air, are shown in Figure 6.

For the samples irradiated in air (Figure 5), the level of oxidation is more significant, being ~3 times higher in the bulk compared to the reference samples. This increase is even more pronounced in the ~50 μm thick surface layer. The water tree length for the samples irradiated in air (226 μm ± 3%) is slightly smaller than in the reference samples (Figure 6), and this could be due to the oxidation that may act as a shield against water tree propagation [8]. Another conclusion is that, at the investigated conditions, the high degree of crosslinking in the irradiated samples does not influence the water tree propagation. In the samples irradiated in air, the oxidation that is introduced for 1 MGy is more important [5] (than the actual degree of crosslinking) and this could be the reason for the smaller water tree length (170 μm ± 4%) obtained for the samples irradiated in air at 1 MGy (Figure 6).

Chemical Crosslinking

Figure 7 shows the average water tree lengths (L_a) for the 6 materials evaluated in this second study. The average was computed using 10 samples in each case. The data are represented here in a non parametric (box and whisker) format. There is a clear separation of the data (see the boxes) for the material systems (A, B, C) which is not the case for the form, thermoplastic (TP) or crosslinked (XL).

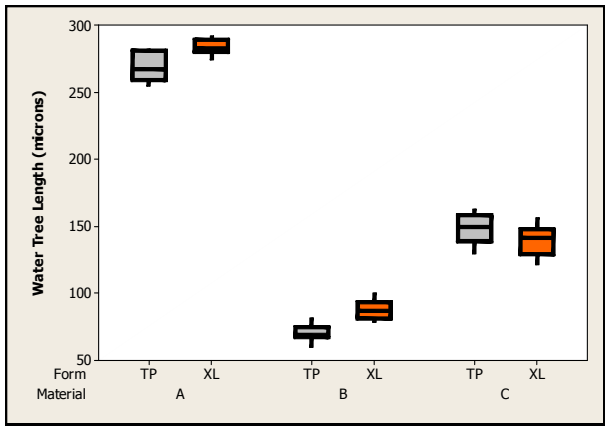

Figure 7: Mean water tree length (L_a) data, represented in a box and whisker plot – the boxes enclose 50% of the data, the whiskers 100%, the central lines represent the medians.

The optical system used is also able to determine the number of water trees that have been initiated on the surface. The water tree density data were analyzed using the Gaussian distribution and Table 2 shows the mean densities. We can see that there are both large and significant differences in the water tree density both according the form (TP or XL) and the material system (A, B or C). The small standard deviation of the means (5% to 10%) suggests that the differences are not due to differences in inception time but rather to the fact that not all the surface defects initiate water trees. This remark was confirmed by microscopic inspection. The results of the analyses for both the water tree lengths and the water tree densities are combined in Figure 8.

Discussion on water tree length

From the results in Figure 7 it can be concluded that once initiated, water trees grow at a similar speed (same lengths in these fixed time studies) in both thermoplastic and crosslinked systems. This is not so surprising if the following arguments are considered:

- Trees grow, predominantly in the amorphous regions of the polymer,
- The permanent network crosslinks are located within the amorphous regions,
- The morphology within the amorphous region is likely to be very similar between both thermoplastic and crosslinked forms since it is approximately 300 carbon atoms between the crosslinks.

Table 2

Water tree densities

Non-crosslinked samples	Mean Water Tree density [mm^{-2}]	Crosslinked samples	Mean Water Tree density [mm^{-2}]
A	16	XLA	9
B	7	XLB	2.5
C	10.5	XLC	5.5

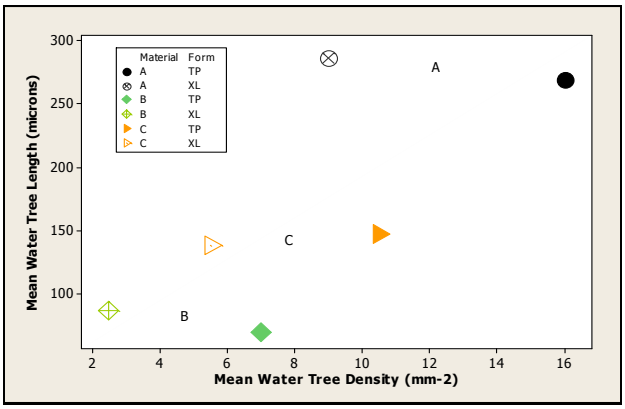

Figure 8: Mean water tree density vs. mean length for the selected *model material systems* and *form*.

Thus, on a nanometer scale it might be equally easy to perform the necessary deformations of the entangled chains to build the narrow tree channels in both *forms*, thermoplastic and crosslinked. This applies for both techniques of crosslinking, chemically or by irradiation. It is well accepted that the growth of the crystallites, as the polymer cools from the melt, is initiated in areas with no crosslinks and will also tend to exclude the additives. This leads to a concentration of the additives within the amorphous regions, representing a form of "zone refining". The different behaviour of materials B and C compared to A, with respect to water tree propagation, must be due to the polar nature of the additives used, which affect the properties of the amorphous region of the polymer.

Discussion on water tree density

The effects on tree density of the *model material systems* (A, B, C) and the *form* (thermoplastic and crosslinked) are clearly evident. The best explanation for these density effects is the modification of the tree inception processes, especially considering that not all of the defects on the surface lead to water tree inception. In the cases studied here, the *material system* and *form* combine to reduce the probability of inception. The role played by crosslinking on the probability that a defective location starts to propagate a tree can possibly be ascribed to the increase in Young's modulus in the amorphous regions as a result of the crosslinks. The initiation of microcracks at the water/polymer interface required for water tree initiation is less probable in the XL form than in the TP form and the number of water initiation sites is thereby reduced. The effect is different according to the model material system [9].

Once initiated, the formation of the water tree itself is not different in the two forms, as above discussed.

CONCLUSIONS

The results obtained using the experimental conditions in this study have not revealed any consistent influence of the irradiation crosslinking on water tree growth. This conclusion applies only to vacuum irradiated samples where, due to precautions taken, the oxidation was limited to a level very close to that of reference (unirradiated) samples.

The results of the second study has shown that both crosslinking via organic peroxides and the material system (water tree retardant additives) affect the time for water tree development in cable insulations. This time depends on initiation as well as on the growth rate.

The *material system* affects both the initiation and the growth. *Material systems* B and C require significantly longer times to grow large water trees than A.

Crosslinking as such has no effect on the growth of water trees in the three model material systems tested.

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