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Polyethylene crosslinking and water treeing

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Abstract

Water tree resistance of crosslinked polyethylene (XLPE) and of low density polyethylene (LDPE) were compared in order to elucidate whether the crosslinking influences or not, the water tree propagation in polymer insulation. To avoid possible errors due to by-products from chemical crosslinking, this study used irradiation crosslinked polyethylene. Irradiation conditions (high dose rate, vacuum) were carefully chosen in order to minimize the errors due to concomitant oxidation. The results obtained indicate that there is no significant difference caused by crosslinking, between water treeing lengths in XLPE and LDPE. © 2001 Published by Elsevier Science Ltd.

Keywords: Polyethylene crosslinking; Water trees; Cable insulation

1. Introduction

Over the last 20 years crosslinked polyethylene (XLPE) has progressively replaced low-density polyethylene (LDPE) in extruded cable insulation. This was due to the fact that XLPE has better mechanical characteristics at high temperatures.

Polyethylene was the first polymer used on a very large scale for the synthetic insulation of underground cables. The first cable insulation was made of LDPE, but XLPE is now by far the most widely employed. Both materials are excellent insulators, and the reason for the choice of XLPE essentially comes from the fact that it keeps adequate mechanical properties at temperatures for which LDPE gets too soft. Thus, the use of XLPE allows the cable to withstand temporary overload conditions during which the temperature of the insulation may rise above the melting point of polyethylene: an uncrosslinked polymer would flow away from the conductor under these conditions causing the cable to fail.

Mechanical resistance is just one of the many polymer properties to be considered in choosing a material for cable insulation. A very important property for polymer-insulated power cables is the water tree resistance of the material. In medium voltage (MV) cables, the main cause for the insulation breakdown is the aging due to water treeing [1].

Most MV polymer-insulated cables are laid in an underground environment and they are not really water tight. Water from the soil can slowly diffuse through the protective layers of the cable and, finally, come into contact with the insulating polymer and fill the small defects, such as microvoids or microcracks which pre-exist or are formed at the interface between the insulation and the semiconducting shield. In this region water and ionic impurities are subjected to an alternating electric field, which leads to the penetration of water into the polymer by complex mechanisms, which are not yet entirely elucidated [2].

Cross-sections of the damaged insulation show tree-like or bush-like structures, which are called water trees. More detailed investigations show that water trees are made of water-filled microcavities — of dimensions of the order of 1 μm or less — having an organized structure related to the orientation of the electric field in the vicinity of the initiating defect, and influenced by the morphology of the polymer [3].

Due to the importance of water treeing as a cause of insulation breakdown, it was of interest to compare the water tree resistance of XLPE and of LDPE. The first laboratory tests showed a clear difference between the two materials, the water trees grown after a given time being much shorter in XLPE than in LDPE [4,5]. The observed difference could be due to a difference in morphology between the two materials since it is known that morphology strongly influences water treeing [6], or to the action of chemical by-products, since polyethylene crosslinking is

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generally obtained from a chemical reaction. It was shown that acetophenone, which is one of the decomposition by-products of the peroxide used for this reaction, is a water tree inhibitor. In fact, if acetophenone and the other by-products are extracted from XLPE by vacuum heating, the water tree resistance of XLPE decreases. Experiments performed on two samples of the same base polymer, one of them being crosslinked and degassed, failed to show any difference in growth kinetics of water trees in the two samples [7]. It was concluded that better water treeing resistance of XLPE was really due to the effects of the reaction by-products and it was assumed that the differences in morphology between XLPE and LDPE did not influence the propagation of water trees. The large dispersion of the water tree lengths observed in [7] has, however, led us to speculate if a better accuracy would have revealed a certain difference in tree growth kinetics between XLPE and LDPE. Although to our knowledge, there is no published data on the subject, a doubt still remains, and in industry crosslinking is itself thought to endow water tree resistance.

In order to clarify the question, we propose a different approach: since studies with chemically crosslinked polyethylene are liable to errors due to by-products, we have performed studies on irradiation crosslinked polyethylene. Water trees were grown in compression moulded disks of polyethylene, either untreated or electron irradiated. We discuss the results from accurate crosslinking and oxidation level measurements and from considerations on polymer morphology.

2. Experimental

The samples used in this study were moulded disks made of LDPE. On one face of each disk small needle-like defects were created, serving as initiation sites for water trees. Two sets of samples were analyzed: irradiated samples — in air or in vacuum, at different doses and unirradiated samples — as reference for the present study. The structure of the samples used for water treeing was characterized by the crosslinking degree and by the oxidation level. Water trees were produced in all samples (irradiated or not) under the same conditions, the degradation due to water trees being then assessed by tree length measurements.

2.1. Samples

Disks of 0.5 mm thickness and 50 mm diameter were made by compression moulding from pellets of LDPE without additives, manufactured by Borealis Company. The pellets were pressed at 185°C and 10^5 N in a Carver press (model 2696) using a pattern with 12 holes of 50 mm diameter and 0.5 mm thickness (Fig. 1). Afterwards, the samples were cooled in air at room temperature. In order to obtain identical samples, the quantity of pellets used in each hole of the pattern was set by taking into account the hole volume and the density of polyethylene as given by the polyethylene manufacturer.

Two of the methods generally used to create water tree initiation sites are sandblasting [8] or scratching [9] the sample surface. For this study, in order to obtain a better reproducibility than those obtained by the above-mentioned methods, and a uniform distribution of the initiation sites, we used another method [10], needle-like defects being created by pressing a sheet of abrasive paper (P240) on one face of the sample, for 2 min at 50 MPa.

2.2. Irradiation

Irradiation was performed at SC Electrostatica of Bucharest, using an electron beam generated by an electron accelerator of ILU 6 type, at a dose rate of 37 MGy/h. 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 separated into two parts. Then, groups of 30 samples of one part were irradiated (at each of the above doses) in vacuum (10^{-2} Pa) and maintained in vacuum after irradiation for 30 min, while the samples from the other part were irradiated in ambient air. In both cases, air and vacuum, the irradiation was performed at room temperature. For each dose, all 30 samples were identically irradiated.

2.3. FTIR spectroscopy

A Fourier transform infrared spectrometer of Nicolet 510 type with an IR microscope (Spectratech IR Plane) equipped with a MCT detector cooled in liquid nitrogen was used for this study. The spectra were carried out on slices of 100 μm thickness cut along the cross section of the disk samples, the disk thickness (of 500 μm) being analyzed by 25 μm step IR cartography using a 25×400 μm^2 window (Fig. 2). This procedure was used to evaluate the oxidation from the value of carbonyl index defined as the difference between the

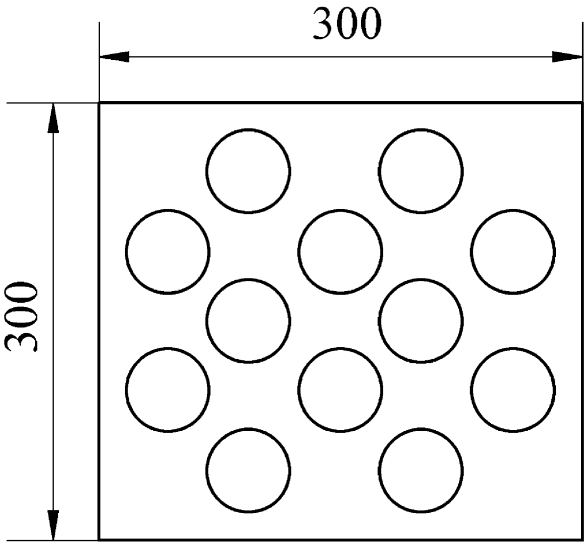

Fig. 1. Pattern used to manufacture the samples.

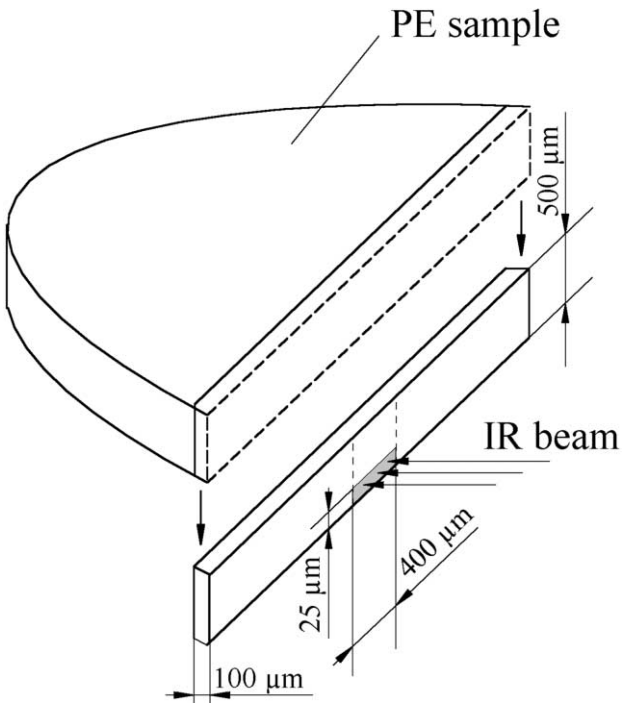

Fig. 2. Slice used for FTIR cartography.

absorbance at 1715 cm^{-1} (ketones) and the absorbance at 1850 cm^{-1}, which is not sensitive to oxidation. Two different samples were analyzed for each dose, and for each sample two spectra per step of IR cartography were taken. Thus, the average of the four values obtained for each step is presented in Section 3.

2.4. Degree of crosslinking

The degree of crosslinking 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 h.

Two types of measurements were performed: an average crosslinking degree of the sample (for all doses) and a crosslinking profile of the sample (only for 1 MGy). The crosslinking profile of a sample was determined by measuring the gel fraction of three layers, each of them representing one third of the sample (Fig. 3). Since it was

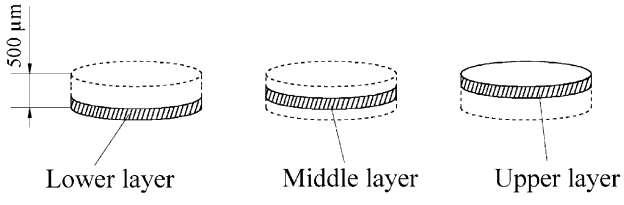

Fig. 3. Layers for the crosslinking profile.

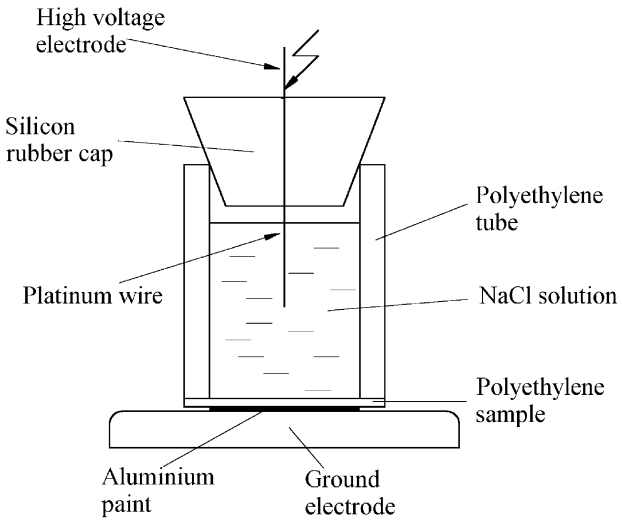

Fig. 4. Cell used to produce water trees.

very difficult to microtome the disk sample into three equal parts, we used an abrasive paper to eliminate two thirds of material from the sample, keeping either the upper, the middle or the lower layer, as shown in Fig. 3.

2.5. Water trees

Water trees were grown in cells (Fig. 4) realized by sticking the sample on a polyethylene tube, using LOCTITE 401 after 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 connecting the HV electrode to a 2 kV, 5 kHz supply for 25 h. Hence, during tree growth, the electric field across the polymer was 4 MV/m.

The samples were then dyed in order to facilitate the measurements of water tree lengths. The samples were detached and introduced in a rhodamine solution at 60°C where they were maintained for 3 days. Afterwards, three slices of 200 μm thickness were microtomed from each sample (Fig. 5(a)), and the lengths of all water trees from each slice were measured using the experimental setup shown in Fig. 6. The average length L_a for a sample was determined as the average of the water trees lengths L_k measured on the three slices of the sample (Fig. 5(b)).

Ten irradiated samples of each dose and 10 unirradiated samples were tested by the procedure described above.

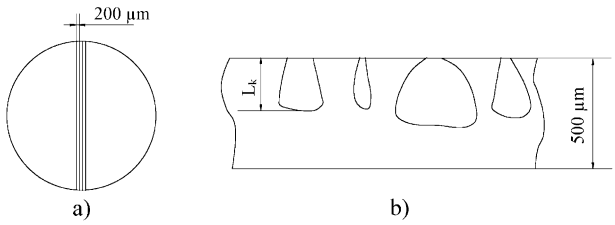

Fig. 5. (a) Slices for measuring water trees dimensions; (b) Water tree length L_k as measured on a slice.

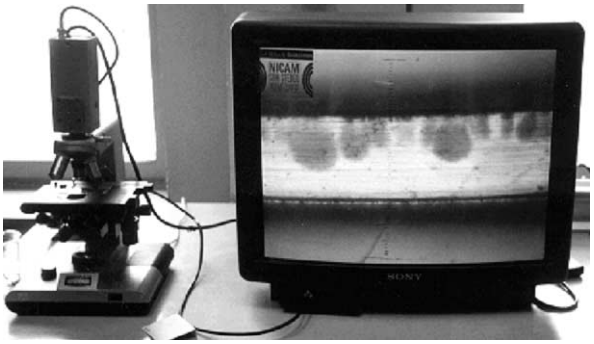

Fig. 6. Setup used to measure water tree lengths.

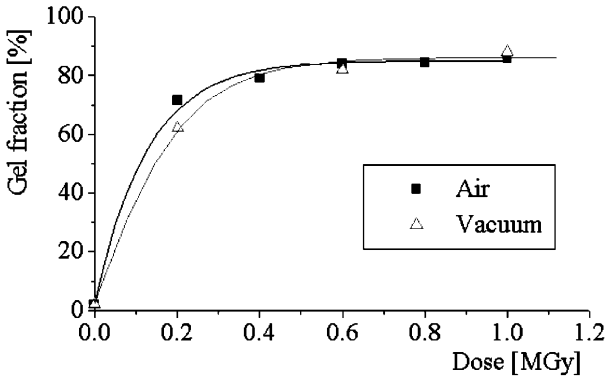

Fig. 7. Gel fractions vs. the irradiation dose for samples irradiated in air and in vacuum.

3. Results and discussion

3.1. Crosslinking analysis

Using the results of average crosslinking measurements, Fig. 7 shows a plot of the gel fraction as a function of integrated dose. It can be observed that the gel fraction increases with the dose reaching a limit of ~85% at ~0.6 MGy. This behavior appears to be independent of the conditions of irradiation (air or vacuum). From these results, one may conclude that for obtaining the maximum crosslinking degree, a dose of 0.6 MGy is sufficient. The crosslinking profile in the depth of the sample, carried out for 1 MGy, reveals that the degree of crosslinking is the same in the bulk as in the surface layers of the sample. Moreover, this value is nearly the same as that obtained from the average crosslinking measurements, the difference being less than 3.5%.

3.2. Influence of crosslinking on water tree growth

For the present study the crosslinking is the main irradiation effect we are interested in, but it cannot be neglected that, generally, an oxidation coexists. Starting from this, to limit the oxidation as much as possible, we chose a high dose rate irradiation source (electron beam), instead of a low rate one (as γ rays) which usually leads to some oxidation along with the crosslinking. On the other hand, it is well known that at high dose rates, like the one used in this study, the oxidation is limited to the surface layers of the samples, whereas in the bulk the prevailing effect is crosslinking [11]. Moreover, if the irradiation is performed in vacuum, even the oxidation in the surface layers could be considerably reduced. Taking all these factors into account, 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.

Thus, from the results shown in Table 1 it can be observed that the tree lengths are almost the same in unirradiated as in irradiated samples, and so 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 analyzed in the following discussion.

3.3. Discussion

The oxidation profiles for samples irradiated to 0.6 MGy (in air and in vacuum) and for unirradiated samples are shown in Fig. 8, and a similar comparison for samples irradiated to 1 MGy. are shown in Fig. 9. Water tree lengths for reference samples and for samples irradiated at 0.6 MGy and at 1 MGy, both in vacuum and in air, are shown in Fig. 10.

First, we compare the samples irradiated at 0.6 MGy, in vacuum and in air, with the reference (unirradiated) samples. From the oxidation profiles shown in Fig. 8 it can be observed that the reference samples show no significant level of oxidation over the entire thickness of the sample. The samples irradiated in vacuum also show no significant oxidation, except for a slight amount in the surface layer (~10 μm). It should be noted that the trees start from the tips of the needle-shaped defects at a depth of a ~30–40 μm. Consequently, slight oxidation up to a depth of ~25 μm would not be expected to affect tree propagation. Therefore, the only difference between these samples, that

Table 1
Measurements of water tree length

Samples	Water tree lengths of the 10 tested samples (μm)										Average length, L
	L_{a1}	L_{a2}	L_{a3}	L_{a4}	L_{a5}	L_{a6}	L_{a7}	L_{a8}	L_{a9}	L_{a10}	
Unirradiated	281	275	282	283	255	273	259	262	262	260	269 μm±3.57%
Irradiated at 0.6 MGy (vacuum)	277	287	258	288	267	265	260	284	281	287	275 μm±3.78%

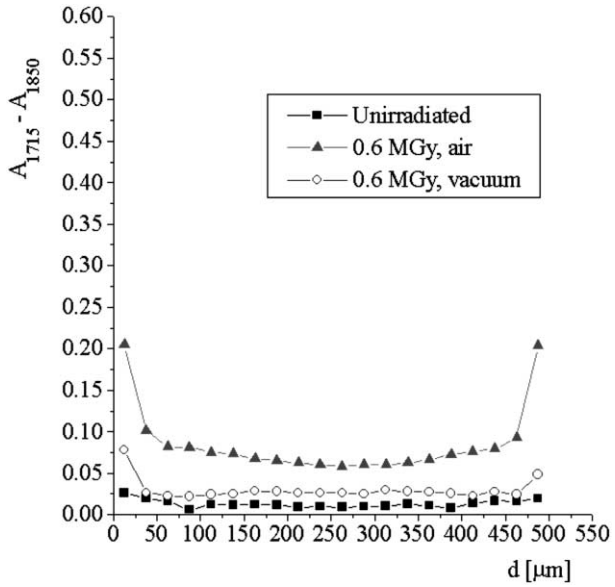

Fig. 8. Oxidation profile for 0.6 MGy.

might influence water treeing, is the high crosslinking degree (gel content ~85%) of the samples irradiated in vacuum. Looking now at the water tree lengths (Fig. 10), one can observe that they are almost the same in reference samples (269 μm ± 3.6%) and in samples irradiated in vacuum (275 μm ± 3.8%), and it appears that the crosslinking does not play any role in the water tree propagation. For the samples irradiated in air, the level of oxidation is more significant, being ~3 times bigger in the bulk than in reference samples, this increase becoming even more important in the ~50 μm thick surface layers. The water tree length for the samples irradiated in air (226 μm ± 2.5%) is slightly smaller than in reference samples, and this could be due to the oxidation that may act as a shield against water tree propagation [8].

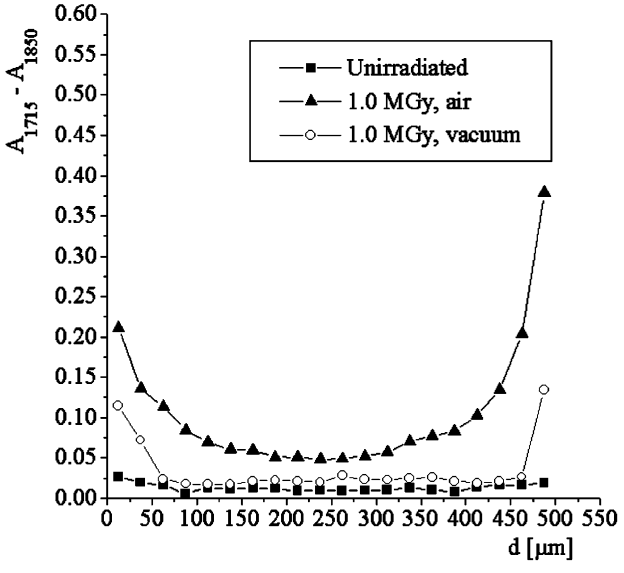

Fig. 9. Oxidation profile for 1.0 MGy.

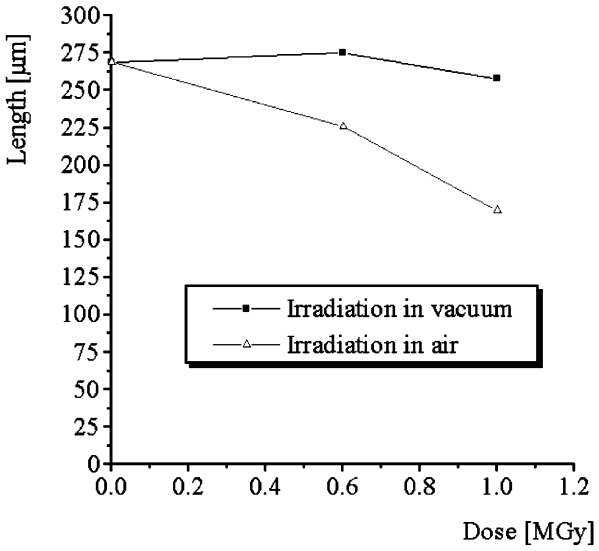

Fig. 10. Water tree length vs. integrated dose.

The results obtained for the samples irradiated at 1 MGy confirm this pattern of behaviour. Thus the oxidation profiles shown in Fig. 9 show that there is no significant oxidation both for the unirradiated reference samples and for the samples irradiated in vacuum, apart from a very slight increase of the oxidation near to surface. So, the water tree length (Fig. 10) in the samples irradiated in vacuum (258 μm ± 4.5%) being nearly the same as for reference samples (269 μm ± 3.6%), one may conclude that, in our conditions, the high level of crosslinking of the irradiated samples does not influence the water tree propagation. In the samples irradiated in air, the oxidation obtained for 1 MGy is again significant as for the 0.6 MGy irradiated samples, but with the surface oxidation this time extending to ~100 μm. This could be the reason for the small water tree length (170 μm ± 4%) obtained for the samples irradiated in air at 1 MGy.

4. Conclusions

The growth rate of water trees in thermoplastic and electron beam crosslinked polyethylene was determined with good accuracy. The results obtained in our experimental conditions 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. Our results are in agreement with a previous work in which water trees were grown in chemically crosslinked polyethylene from which the by-products of the decomposition reaction was previously eliminated. We conclude that polyethylene crosslinking does not create any network able to hinder the migration of water through the polymer under the action of the electric field.

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