Influence of Morphology Effects on Electrical Properties in XLPE

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ABSTRACT: This study elucidates the influence of differences in crosslink structure and crosslink density on water tree growth, electrical tree growth, and electrical breakdown strength. One reference LDPE was compared with a LDPE containing a higher number of vinyl groups, introduced via the copolymerisation with a diene. Because of the chemical difference, the initially formed crosslink structure will be different for the materials. A range of various crosslink densities was considered for the two materials. It was found that along with a noticeable change in morphology after crosslinking, significant changes in particularly water tree growth, electrical tree growth, and electrical breakdown strength could be observed. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 121: 3483–3494, 2011

Key words: electrical trees; water trees; electrical breakdown strength; crosslinked polyethylene; insulation

INTRODUCTION

Crosslinked polyethylene (XLPE) has been used as an insulating material for power cables for half a century because of its outstanding heat deformation and electrical characteristics. A limitation is polyethylene's susceptibility to electrical degradation mechanisms, among others: water treeing, electrical treeing, and electrical breakdowns. A comprehensive treatment is given elsewhere.[1,2]

In wet environments under the action of an electric field, polyethylene is prone to water treeing. These water trees can lead to lower breakdown strength and possibly electrical failure of the insulating material. Water trees are often a precursor to the formation of electrical trees. Even nearly 40 years after the discovery of water trees, the treeing mechanisms are not yet fully understood. In 1984, Shaw and Shaw[3] summarized the knowledge about water treeing up to that time, and during the following years several authors reviewed the water treeing phenomenon.[4–6] In a review written in 1998, Ross[5] specifies four main criteria of water trees and they are as follow:

- are permanent,
- have grown in the presence of humidity and an electric field,
- have a lower electrical strength than the original polymer when wet, but which is not a short circuit or local breakdown path, and
- are substantially more hydrophilic than the original polymer.

Several mechanisms for water tree formation have been proposed, but during the past few years the prevailing view has been mainly either electrochemical, electrophysical, electromechanical, or a mixture thereof.[5,7,8] Johansson[9] recently suggested a formation of large ion–water clusters induced by an electric field, resulting in the creation of voids, in contrast to voids first induced by the electrical field and subsequently filled with water.[4,7,10]

Electrical treeing is an immensely important electrical degradation mechanism for insulating materials used in high-voltage applications. Electrical trees normally form at defects such as voids or other inclusions, where the electrical field is amplified. There are at least two stages before the tree causes an electrical failure; i.e., the inception and propagation stages. Inception of an electrical tree is recognized by a region of degeneration at a point exposed to a high divergent electric field[11,12] or by gas

discharges in a void.[13,14] The propagation step is characterized by the presence of partial discharges in gas-filled tubules.[13] Electrical trees can be conducting or nonconducting and be of branch, bush or bush-branch type.[11] Electrical breakdown only occur when a sufficient conductive path is formed between the electrodes, thus allowing a continuous current flow.[11,12]

The electrical breakdown voltage of a material is characterized by the voltage necessary for the formation of a conducting pathway that bridges the insulation. The mechanisms that lead to electrical breakdowns are complex and are in general dependent on several factors.[1,15] A difference from the electrical treeing test is that instead of inducing an amplified electrical field at a sharp point, the bulk properties of the sample are tested.

There seems to be a consensus among researchers that water treeing, electrical treeing, and electrical breakdown strength depends at least to some degree on the polymer morphology and degree of crystallinity.[12,15–19] Water trees and electrical trees are likely to grow mainly in the amorphous areas of polyethylene, either in the interstices between lamellae or in the amorphous areas between the spherulitic structures.[12,20] The morphology of a polymeric material can be altered by either addition of different stabilizing and antioxidant agents which might function as for instance nucleation points, or by a crosslinking agent like peroxide which will cause restraints of the polymer chain movements during crystallization. The latter phenomenon is thoroughly described by the authors in an earlier work.[21] The morphology can also be more or less tailor made by modification of the production parameters, for instance: annealing, quenching, and the use of different cooling rates after the crosslinking reaction. In the case of cable production, the line speed and thickness of the insulating material is also of importance for the crystallization process.

This study is a continuation of an earlier work where two LDPE materials with a difference in the crosslinking mechanism were crosslinked with increasing amounts of peroxide, thereafter thoroughly characterized. This study aims to elucidate the influence of increasing crosslinking and the resulting change in degree of crystallinity and morphology on electrical properties. The electrical properties included are water treeing, electrical treeing, and electrical breakdown strength.

EXPERIMENTAL

The experimental procedures described below present a brief overview of the equipment and methods used in the study. For a more thorough description see an earlier work.[21]

Materials

Two LDPE grades, of which one was copolymerized with a diene, were kindly supplied by Borealis AB, Sweden. The reference LDPE is denoted material A and the other LDPE with increased vinyl content, i.e., 1 vinyl/1000 Carbon, is referred to as material B. The important difference is that in material B, an immediate reaction of vinyl groups takes place during crosslinking at an early stage which gives rise to crosslinks with the preservation of the radical. Thus, less peroxide is needed to reach a high crosslink density. The ordinary crosslinking reaction, which takes place in material A, and to a less extent in material B, is here referred to as combination crosslinking. Dicumyl peroxide (DCP) was used as the crosslinking agent. The materials used in this study were unstabilized.

Sample preparation

All samples were prepared by compression molding of peroxide impregnated LDPE pellets. The amounts of peroxide for the series with increasing crosslink density were chosen to obtain as wide a distribution of crosslink densities as possible, i.e., an addition of 0–7% DCP for material A. It was found that not all peroxide was absorbed by the LDPE pellets in the case of 7% peroxide addition. This could possibly render a somewhat more inhomogeneous material. The peroxide contents in material B were adjusted to obtain similar crosslink densities as in material A. Crosslinked plaques of different thicknesses were prepared from the pellets for the subsequent electrical testing; in one step for the electrical treeing and electrical breakdown strength tests and in two steps for the water treeing test, where a plaque was thermoplastically molded in step one due to the geometry of the water tree specimens as described below. The general crosslinking procedure was composed of a compression molding cycle starting with preheating of the pellets/plaque at 120°C for 10 min, followed by compression molding at 20 bar, 120°C. After a temperature and pressure rise to 180°C and 200 bar, crosslinking took place for 10 min. Thereafter, the samples were cooled by a rate of 14°C/min. Further test descriptions are found below.

Water treeing test

All test specimens were prepared and aged according to ASTM D6097-97a.[22] During the crosslinking procedure, circular test objects with a needle formed deformation were prepared from the premolded plaque in a mold specifically designed for the water treeing test. The dimensions of a water tree specimen are given in Figure 1(a). All samples were
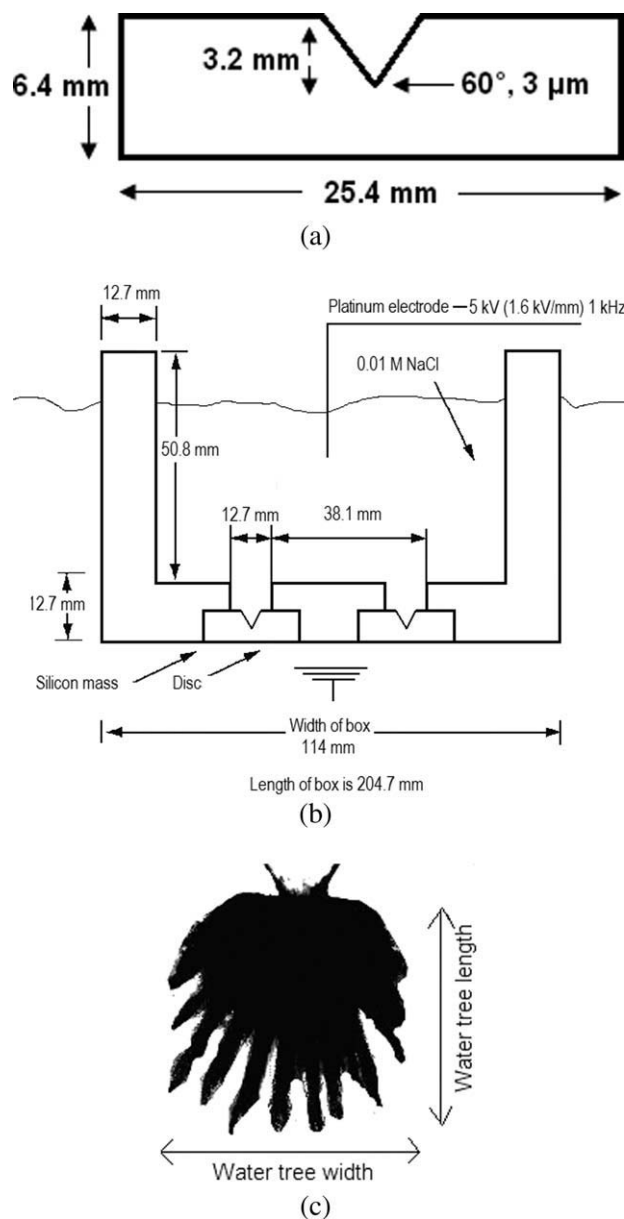
(a)

(b)

(c)

Figure 1 Dimensions of a water tree specimen (a), test setup of the water tree test (b), and definition of water tree length and water tree width (c).

degassed at 80°C for 1 week under vacuum. This treatment cause a general increase of a few percentage units in degree of crystallinity (X_c), as well as a minor rise in melt temperature (T_m), most prominent for the virgin and lightly crosslinked specimens. These changes has however not been considered in this study as the data are mainly of comparative importance.

The specimens were fixed in an insulating box and thereafter placed in a water bath filled with a 0.01M sodium chloride electrolyte. The test set-up is shown in Figure 1(b). The water trees were grown at 5 kV, 1000 Hz for 30 days at room temperature. The aged specimens were cut with a microtome to 150–

300 μm thick slices and stained with methylene blue for approximately 1 h, followed by visual analysis in a light microscope. The length and width of the water trees were measured as shown in Figure 1(c).

Water tree growth rate

A test was performed on the growth behavior of the water trees in virgin material A, material A + 2% DCP and material A + 3.5% DCP. Two to four test objects per formulation were analyzed every third or sixth day. Samples were subjected to air at the exchange of test objects.

Electrical treeing experiments

The electrical tree inception voltage test was performed according to a double-needle method. Specimens with dimensions of: 21 × 25.5 × 6 ± 0.5 mm were prepared from the compression molded plaques, and thereafter degassed in the same manner as described for the water treeing samples. Ten test objects of each material and steel needles that were supplied by Ogura Jewel Industry were placed in a needle insertion equipment. The tip of the sharp needle electrode had a radius of 5 μm, whereas the ground needle electrode with a shape of a hemisphere had a radius of 500 μm. The equipment was preheated to 125°C for 90 min, and then the needles were carefully inserted to the specimens by a spring mechanism to eliminate the risk of void formation at the needle tip. The tip to ground separation was 3.5 mm, with the exception of the densely crosslinked specimens, where the needle distance was somewhat larger. The specimens were kept in the oven for 30 min at 125°C and thereafter left to cool with an approximate rate of 15°C/h to minimize mechanical stresses by ensuring a relaxation of the polymer at the needle tip. As T_m was exceeded the samples should be in the molten state and consequently subject to at least partial recrystallization during cooling. An electrical tree test specimen is illustrated in Figure 2.
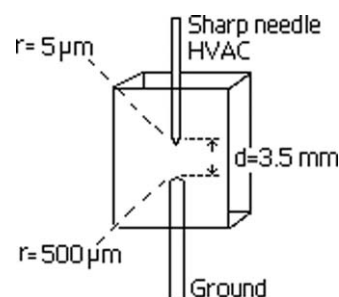

Figure 2 Specimen for electrical tree inception voltage test and electrical tree growth test.

Electrical tree inception voltage

To determine the electrical tree inception voltage, a HVAC ramp from 8 to 22 kV with a voltage rise of 0.010 kV/min and a frequency of 50 Hz was applied to up to 10 test objects simultaneously. The stop criterion for the test was set to when 15 partial discharges (PD) per second, with amplitude above around 60 pC, were detected. The stop criterion was chosen to be low enough to stop at the indication of tree inception and high enough to eliminate signal disturbances. The specimens were subsequently analyzed for the occurrence and size of trees using dark field mode in a light microscope.

Electrical tree growth

Electrical tree growth experiments were performed on samples which were prepared according to the procedure earlier, using 5 μm needles. The electrical tree growth was determined by analyses of dielectric loss and capacitance change during treeing. A technique called arbitrary waveform impedance spectroscopy (AWIS) was used to measure the dielectric response in the subpicofarad range.[23] To estimate the tree growth, a simple electric circuit model was constructed with the sole aim of describing the relationship between tree length and relative capacitance increase during treeing. Samples were subjected to an AC voltage of 16 kV, until a capacitance increase of 1 and 2%, respectively, was obtained. The electrical tree length was subsequently analyzed by the use of a light microscope. Further description are found elsewhere.[24,25] Virgin material A, material A + 2% DCP and material A + 3.5% DCP were studied.

Electrical breakdown test

The electrical breakdown test was based on IEC 60243 PT1. Thin samples were prepared during the compression molding step and were subsequently degassed for 24–36 h at 80°C in a vacuum oven. The dimensions of the samples were $50 \times 50 \times 0.3 \pm 0.05$ mm. Each specimen was immersed in Dow Corning 200 XLP silicon oil and fastened between two circular metallic electrodes with a diameter of 25 mm and a 3-mm edge radius. Each specimen was thereafter subjected to an increasing voltage (AC 50 Hz) at a ramp rate of 2 kV/s, until the specimen failed, i.e., at a current flow of 5 mA. Ten tests were performed on each batch of samples.

Characterization

Characterization was made on the crosslinked and aged water tree test object, unless stated otherwise.

A more thorough description of the characterization techniques are described in an earlier work,[21] which offers detailed characterization data on material A and material B.

Network characterization

To determine the gel content, soluble parts of the crosslinked polyethylene was extracted with boiling 1,1,1-decahydronaphtalene for 7 h. The molecular weight between crosslinks, M_c, was then calculated from the swelled weight of the crosslinked network after boiling in p-xylene for 2 h, and the Flory-Rehner equation.[26] The gel content reaches at steady state value at higher peroxide contents when the main parts of the polyethylene chains are confined in the crosslinked network. M_c continues to increase at increasing crosslinking, as more crosslinks continues to be formed in the already existing network.[21] All results are therefore presented as a function of the crosslink density; $1/M_c$.

Differential scanning calorimetry

The melt temperature (T_m) and the degree of crystallinity (X_c) were determined by differential scanning calorimetry (DSC) measurements. The samples were melted and cooled twice at a rate of 10°C/min, where the T_m and X_c values given in Table I were extracted from the second melt scan.

Morphology measurements

Samples were freeze fractured, and the amorphous parts were etched away from the surface by means of a permanganatic etchant.[21,27] The etched specimens were coated with a thin layer of gold and studied using a Leo Ultra 55 FEG scanning electron microscope (SEM) with an accelerating voltage of 2 kV at a spatial resolution of approximately 1.7 nm.

RESULTS AND DISCUSSION

The material data and the morphological structures of the two LDPEs crosslinked to increasing crosslink densities are presented in Table I and are mainly obtained from an earlier work by the authors.[21] One main object of the study was to clarify if the difference in crosslink structure and material configuration between the two materials affects the electrical degradation characteristics. The different crosslink structure in material A and material B was evaluated at a similar, fairly low crosslink density where the crosslinks in material B mainly derive from reacted vinyl groups and the crosslinks in material A mainly derive from ordinary combination crosslinking; i.e., at $1/M_c < 2.0 \times 10^{-4}$ mol/g. After further

TABLE I
T_m, X_c, and Crosslink Characteristics as a Function of DCP Content

DCP (wt %)	Gel content (%)	Crosslink density, $1/M_c \times 10^4$ (mol/g)	T_m (°C)	X_c (%)	Shape	Size (μm)
A						
0.0	0	0	111	43	Spherulites	10–14
1.0	67	1.8	108	41	Spherulites[a]	4–7
2.0	79	2.2	106	39	Spherulites[a]	4–7
3.5	87	2.7	103	38	Axialites	3–4
5.0	95	3.6	100	36	–	–
7.0	95	3.6	98	35	Random-like	1–1.5
B						
0.0	0	0	110	43	Spherulites	4–5
0.25	67	1.7	108	40	Spherulites[a]	2.5–3.5
0.5	75	1.9	105	39	Spherulites[a]	3–4.5
1.0	85	2.1	104	36	Axialites[b]	2–3
1.5	89	2.3	102	37	–	–
2.0	91	2.5	101	36	Axialites	2
7.0	97	4.0	93	33	Random-like	0.5–1

Values are obtained from the samples prepared for water treeing measurements.
[a] The spherulites are distorted to some extent.
[b] The morphology is between banded spherulites and axialites.

crosslinking the crosslinks mainly derive from combination crosslinking in both materials. In our previous study,[21] we found that there is a concurrent decrease in X_c and T_m of the materials with increasing crosslink density; therefore, all the following results are presented as a function of the crosslink density, i.e., $1/M_c$. Our morphology measurements revealed a significant change in the size and structure of the supermolecular structures with increasing crosslinking. Two SEM pictures are shown in Figure 3, where the morphology changes from consisting of well-developed spherulites in virgin material B to a structure with smaller axialites in material B + 0.5% DCP. A more thorough description of the morphology, thermal properties, and crosslink characteristics is given in our preceding work.[21]

Water tree results

Water tree length

The changes in water tree length with increasing DCP content, i.e., increasing crosslink density, for material A and material B are shown in Figure 4. This study includes an evaluation of the results earlier presented in the ISEIM'08 conference proceedings.[28] The results show a negligible change in water tree length at low crosslink densities. However, as the crosslink density increases, a significant increase in water tree length takes place. At a certain point, the water tree length decreases again. An evaluation of the effect of different crosslink structure on water tree length in the two LDPE materials show that the lengths are similar when compared at a similar, fairly low crosslink density.

As mentioned earlier, a significant morphology change takes place with increasing crosslink density, see Table I. After crosslinking with small amounts of peroxide, the spherulite size decreases and a minor disruption of the spherulitic structure occurs. However, no or only a slight change in water tree length can be observed at this initial change in morphology. As the supermolecular structure changes from being entirely spherulitic to somewhere between spherulitic and axialitic, followed by an entirely axialitic structure, the water tree length doubles. As the LDPE is crosslinked with 7% peroxide, the crosslink structure densifies distinctly to less than 3000 g/mol between the crosslinks and the morphology consists of randomly distributed lamellae stacks. At this point, the water tree length has decreased again. Although the significant increase followed by a decrease in water tree length are the most apparent changes, a minor decrease in water tree width with increasing crosslink density also occurs at the present conditions.

We have earlier learned that the spherulite size differs considerably between the two LDPE materials.[21] For the virgin materials, the spherulites in material A are two to three times the size of the spherulites in material B. With increasing crosslink density, the size of the spherulitic and axialitic structures decreases in both materials, although much more for material A, and eventually the two materials become equal in this respect. The main characteristics are similar in the two materials except that there seem to be thinner lamellae in material B at a certain crosslink density, compared to in material A.[21] The molecular weight is also somewhat higher in material B compared to material A. Despite this, no
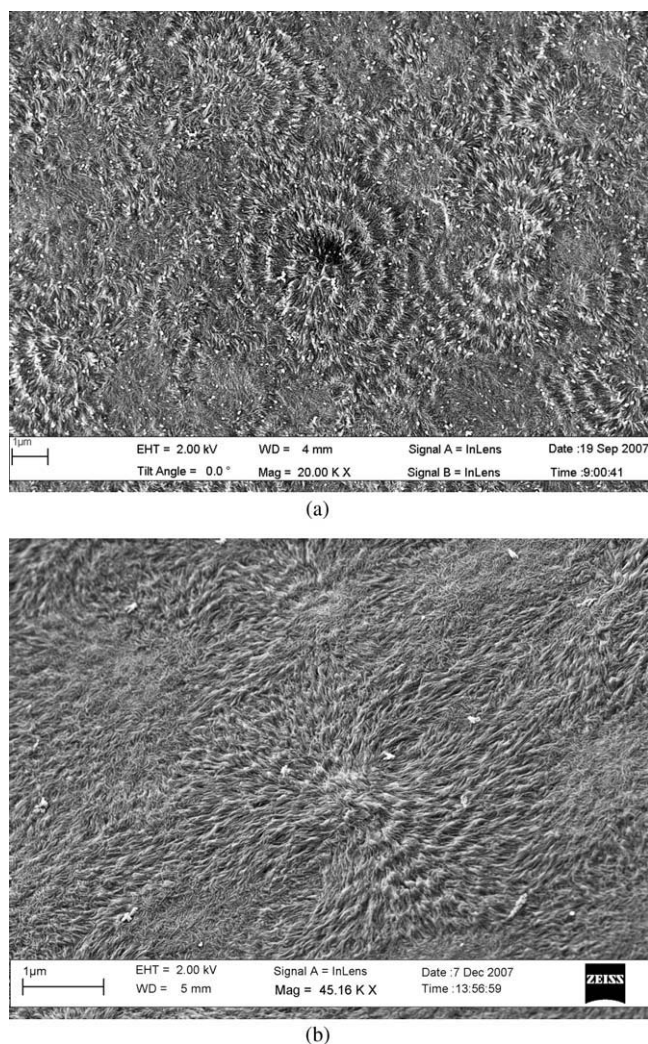
(a)

(b)

Figure 3 Scanning electron micrographs of virgin material B (to the left) and B + 0.5% DCP (to the right).

significant difference in water tree length and water tree width is observed for the virgin materials. This indicates that the spherulite size in itself has no importance for the water tree growth in the two LDPE materials.

Along with the change in water tree length, a concurrent change in water tree shape occurs. Some typical water trees in material A with increasing peroxide content are shown in Figure 5. The standard deviation in terms of water tree width is fairly large, although the main shape is relatively consistent for all test objects of each crosslink density. There is an obvious change in water tree shape from short circular trees with diffuse outer tree boundaries in virgin material A, to long pointed trees after crosslinking with 3.5% DCP, with approximately 3700 g/mol between the crosslinks (crosslink density 2.7 mol/g in Fig. 4). When the water tree length decreases again at higher peroxide contents, the trees are reminiscent in shape of those in the virgin material.

However, the tree branches are much more pointed than and not as bushy as in the virgin material. The observed tree changes correspond to the changes in morphology due to the crosslinks introduced, i.e., a transition from spherulites to axialites. In the case of axialites, they do not impinge as is normally observed for spherulites, and thus they are separated by less ordered regions with a higher amount of noncrystalline material. Several authors have come to the conclusion that the water trees grow in the amorphous parts of the polymer, that is, preferentially in the interspherulitic amorphous areas at the spherulite boundaries and to some extent within the spherulites.[6,17,18] However, other authors argue that water tree growth is most favored in the interlamellar amorphous areas within spherulites.[19] In this study, SEM images were taken from an XLPE surface obtained by freeze fracturing through the water tree, see Figure 6. The black holes are traces from the water tree penetration. Only the voids from the water trees grown perpendicular or close to perpendicular to the plane are visible, since the amorphous parts are etched away on the surface. The observed sizes of the voids are from 35 to 900 nm. The aforementioned results clearly indicate that the preferred pathway for the water trees to grow is in the interstices between spherulites/axialites, although some voids are observed in the interlamellar amorphous areas in the spherulitic structures. Fully developed spherulites most probably show a higher resistance towards water treeing, by diverting the water around the spherulite boundaries.[17] There is possibly an indication of a partial destruction of the supermolecular structures during tree growth[17,29]; however, insufficient research data are available to support this statement.

The reason for the increasing water tree growth with increasing crosslink density is likely the increase of the amorphous areas and the concurrent
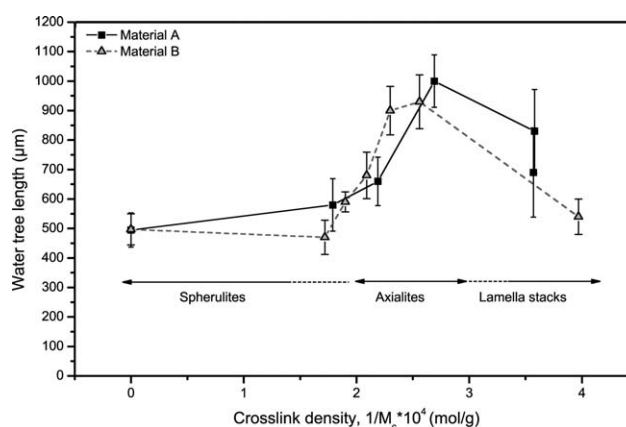

Figure 4 Water tree length for materials A and B. The major morphology for each crosslink density is indicated in the picture.

Virgin A   A+1% DCP   A+2% DCP
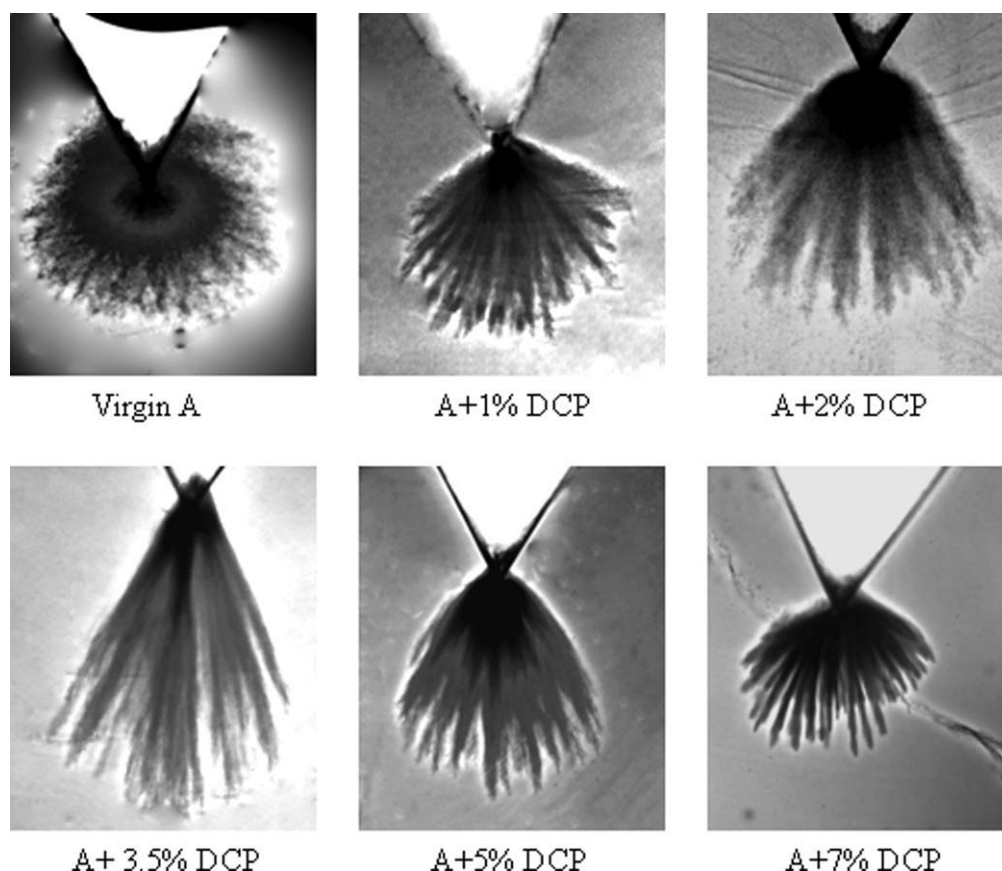
A+ 3.5% DCP   A+5% DCP   A+7% DCP

Figure 5 Changes in water tree shape for material A crosslinked with increasing peroxide content.

disruption of the morphological structures. The decrease in water tree length at higher crosslink densities is surprising, considering the continuous decrease in crystallinity and increasing degree of less ordered supermolecular structures. A plausible explanation is that the large increase in crosslink density leads to restrained chain mobility in the noncrystalline regions. It is then probable that the chains are more reluctant to move at the exposure of water molecules under an electric field.

Several previous studies that compare LDPE and XLPE[3,30,31] have shown that neither chemical nor irradiative crosslinking affects the water tree behavior. However, the peroxide crosslinked XLPE used for comparison with LDPE by for instance Ciuprina et al.[30] had a gel content of 81% and consequently it would correspond to the measure point with a crosslink density of about 2×10^{-4} as observed in Figure 4. Here we can see that only a minor change in water tree length has occurred at that crosslink density, thus their results are not *per se* conflicting with our present results. Their test object design and tree growth parameters were also different where the water trees were grown for 25 h at 4 kV/mm and 5 kHz. Most studies that compare LDPE and XLPE have to our knowledge mostly considered a reference LDPE and a standard XLPE at a certain crosslink density.

Water tree growth rate

One drawback with the water treeing test used above is that only the water tree length after aging for 30 days is obtained. However, it is interesting to see if there are any differences in the growth
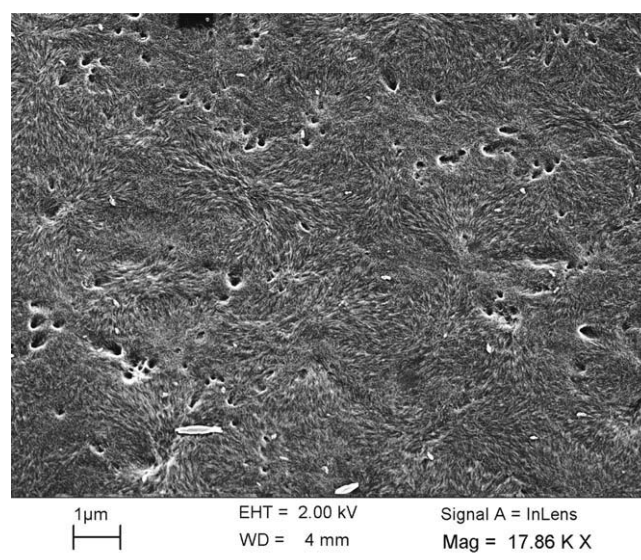

Figure 6 Holes from the water trees grown perpendicular to the plane in an XLPE specimen.
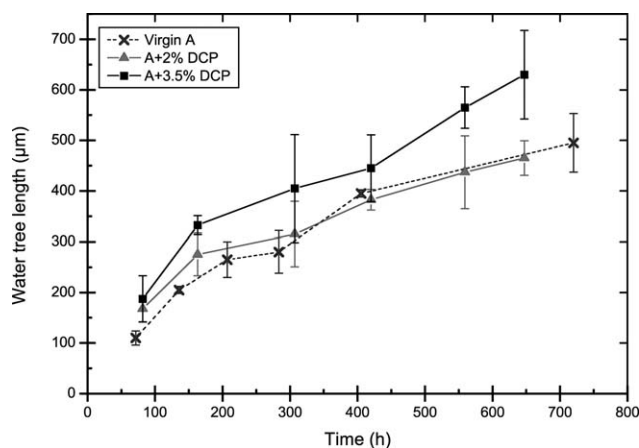
Figure 7 Water tree length as a function of time. The test run of "virgin A" is performed at a different occasion from the two other samples, with only double tests instead of quadruple number of specimens. The measure point at 720 h for "virgin A" is obtained from the previous series on water tree length.

characteristics with increasing crosslink densities. The water tree growth results for virgin A, material A + 2% DCP and material A + 3.5% DCP are illustrated in Figure 7. Since earlier obtained results show merely minor differences between the two LDPE materials, the water tree growth rate test was only performed on material A. One important observation is that the initial tree length in materials A + 2% DCP and A + 3.5% DCP after approximately 3 days of aging is about twice the length of that in the virgin material. Thus, it is obvious that already after very short aging time; the difference in material morphology is of significant importance. At this short aging time, the trees have already reached about one-fifth to one-fourth of its total length in one-tenth of the growth time, thus confirming a rapid initial tree growth. Up to approximately 170 h of aging, the trees grow with a similar rate, but after that there is a decline in growth rate for all three materials, but most obvious for virgin material A and material A + 2% DCP, while material A + 3.5% DCP continues to grow more rapidly. In general, two or three stages are involved in the water tree growth. These are the initial inception stage followed by the growth step. The third stage, where the growth rate is rapidly decelerating is not always observable.[32] Most authors agree on that the growth rate is not linear, but generally decreasing with time. Water tree growth is known to be affected by a number of operating variables, such as electric field strength, frequency, and electrolyte properties, and from the present results it can stated that morphology and degree of crystallinity are important parameter as well.

An observation on the change in tree shape along with increased aging time reveals that the initial

width for virgin material A is greater than the length in the electric field direction and that the trees are diffuse without sharp edges. After longer ageing times, the water tree growth in the field direction is increased, whereas the growth in a field perpendicular to the main electric field direction is decreased. The differences in tree shape for virgin material A are visualized in Figure 8, where the material has been aged for 3 and 30 days, respectively. Normally,
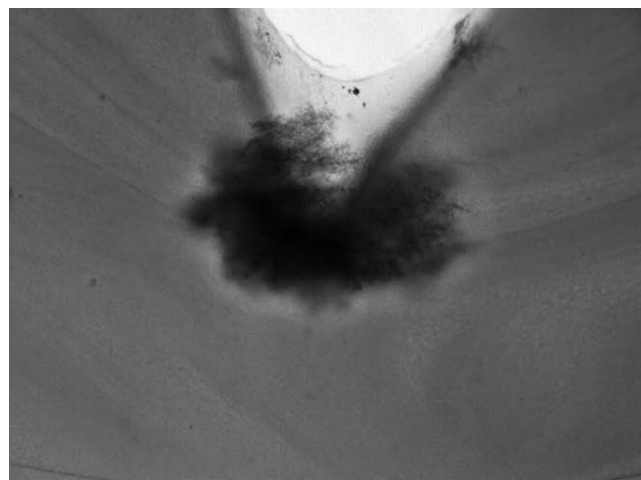
(a)
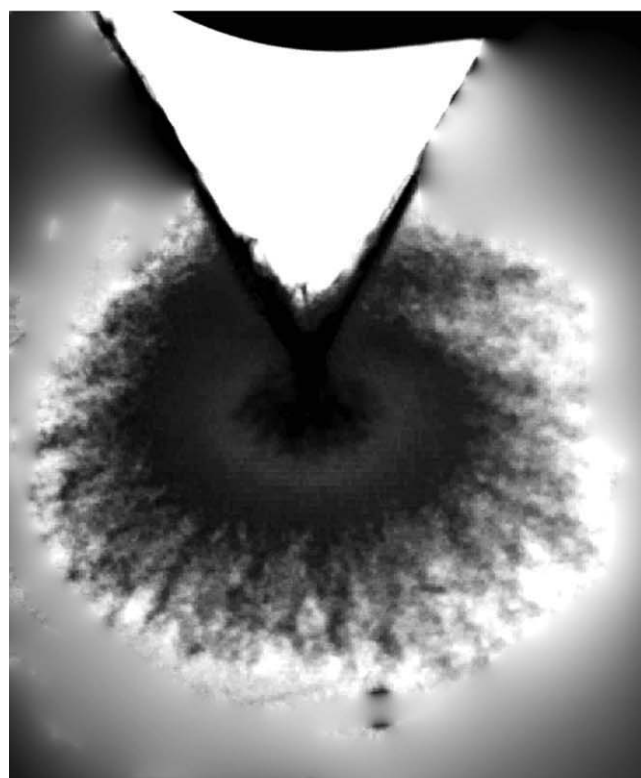
(b)

Figure 8 Water tree grown for 3 days (left) with WTL = 120 μm and WTW = 600 μm and water tree grown for 30 days (right) with WTL = 500 μm and WTW = 900 μm.

the trees in the more crosslinked materials are more frequently subject to bifurcation, i.e., the tree splits into fingers, where an increased electric field in each "finger" can cause faster water tree growth.[32] This is possibly one of the reasons for the faster growth rate in the crosslinked samples. However, at the present test conditions, multiple stops due to take out of specimens and due to operation disruptions, occurred. A difference in water tree shape compared to the previous results on water tree length was then found, where the trees in some of the crosslinked samples were much denser and wider than what was expected. A plausible reason for this ought to be the probable drying out of the tree structure during specimen exchange, where the local field would be altered at the reapplication of an electric field. However, the most critical parameter, i.e., the water tree length is only marginally diverting from previous, less faulty test runs. Consequently, it can be declared that the water tree growth trend is established already after short aging times and that the earlier discussed effects of the morphology are confirmed.

It can be stated that his way of destructive testing including repeated stops is not beneficial for testing of water tree growth rate due to the requirement of a large number of test objects and the repeated longer stops and probable drying out of the water trees. Nevertheless, it is complicated to do online measurements on an opaque polymer as polyethylene, which would otherwise be the optimal alternative.

Electrical treeing

Electrical tree inception

The electrical tree inception voltage test did not reveal any significant differences between the two LDPE materials crosslinked to increasing crosslink densities. It was found that insertion of the needles to the densely crosslinked material was problematic due to the considerable mechanical resistance in the material. Thus, the accuracy of the results could not be confirmed. Because of the design of the test, it is also probable that the polymer matrix in close proximity to the sharp needle electrode/polymer interface is likely to be considerably different to the bulk morphology, especially when the electrode has been inserted to the LDPE in the molten state.[7,33,34] A thin layer with a different morphology, referred to as the transcrystalline area, is believed to extend up to 1 μm from the surface before the bulk morphology take over.[33] Research on transcrystalline growth around cotton fibers in a polymer matrix has shown that the formation of a transcrystalline layer is favored at annealing conditions,[35] which would be close to the parameters in the needle insertion proce-

dure, where the initial slow cooling rate is about 15°C/h. Although no detection of a transcrystalline layer has been made, it is highly likely that the present electrical tree inception method is inappropriate for measurements on the effect of morphology and crosslink structure on electrical tree inception voltage, as the true morphology at the needle tip cannot be ascertained.

Electrical tree growth

In contrary to the electrical tree inception test, the electrical tree growth rates for virgin material A, material A + 2% DCP and material A + 3.5% DCP was believed to be accurate, as the bulk morphology is the determining factor of the growth rate. As the samples were not densely crosslinked, the sample preparation technique is acceptable. The results are illustrated in Figure 9. There is a significant difference between the materials, with a substantial increase in electrical tree growth rate with increasing crosslink density. These results correlate fairly well with the study on water tree growth. The propagation of an electrical tree is characterized by the presence of PD, that is; the local electric strength is exceeded and extension of channels or formation of new branches takes place.[36] Tree growth is generally divided into three categories: branch trees, bush trees, and bush-branch trees, where the last category includes several mixed structures.[37] An important difference between bush and branch trees is the considerable difference in growth rate, of which the branch-like trees grows much faster,[37] whereas the slow growing dense bush tree cause more local damage. Another distinction is that the branch tree is often conducting, while the bush tree in general is nonconducting, where the electrical activity is confined to the tree growth tips or to the electrode tip, respectively.[38] The growth patterns of the present
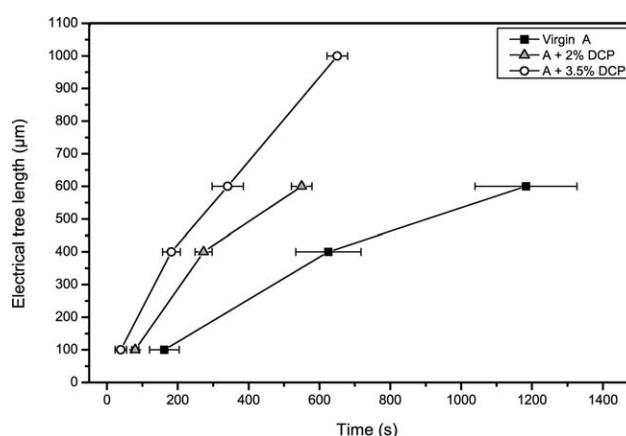
Figure 9 Electrical tree growth rates for material A with 5 μm needles. Tree lengths are calculated from the capacitance measurements.
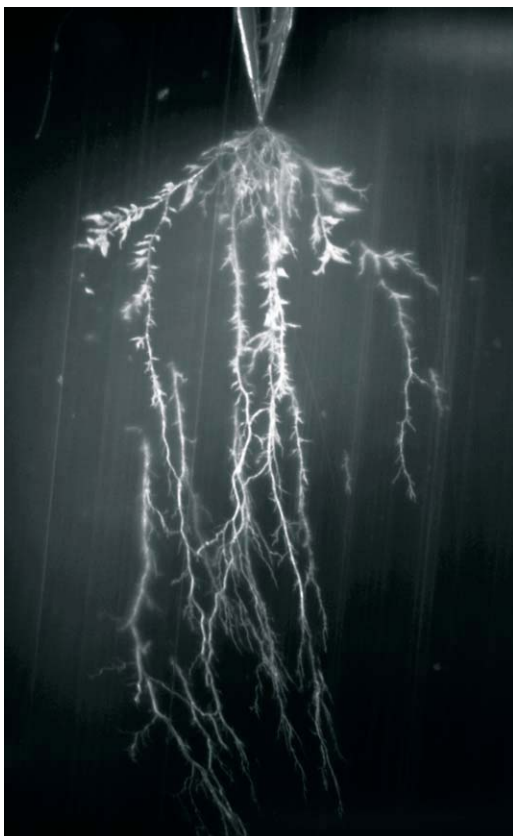
Figure 10 Typical electrical tree for A + 2% DCP, grown until a 2% capacitance increase was obtained. The length of the tree is approximately 3.2 mm. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com]

samples are typically of branch type, though it is possible that some kind of double structure appears after longer growth times.[37] A typical electrical tree that has grown until a 2% capacitance change could be measured is shown in Figure 10.

The major difference between the materials in this study can be found in the morphology, where a considerable change in supermolecular structure with increasing crosslink density and decrease in degree of crystallinity occurs. Electrical trees are known to locally seek out the weakest path, i.e., the amorphous areas of a polymer matrix. The general idea is that high density crystalline areas act as barriers for tree growth, although the morphological distribution strongly affects the tree growth as well.[12,39] Electrical trees are reported to grow easily in the weak interspherulitic boundaries between spherulites. These boundaries tends to be weaker when spherulites are large and perfect as in for instance high crystalline HDPE, which shows a high electrical tree inception voltage but a rapid subsequent growth rate.[39] Dodd et al.[12] also shows that by varying the thermal treatment and composition of polymer blends, the morphology can be more or less tailor made to obtain

enhanced dielectric strength. They found that a blend of 20% HDPE and LDPE having high crystallinity and uniformly distributed impinged spherulites shows the best electrical tree inhibiting properties. The strong influence of morphology on electrical tree growth is less pronounced at high voltages, where bush trees are typically formed.

In this study, the electrical tree growth rate increases significantly as the impinged spherulitic LDPE structure changes to a more axialitic structure, where the interspherulitic boundaries are more diffuse and containing more amorphous, less ordered material. These results correspond well to the literature and show the importance of a controlled morphology in polymers that are subject to high voltages.

Electrical breakdown strength

A noticeable decrease in electrical breakdown strength was found with increasing crosslink density as shown in Figure 11(a,b). The trend is similar at both 23°C and 90°C, but the electrical breakdown
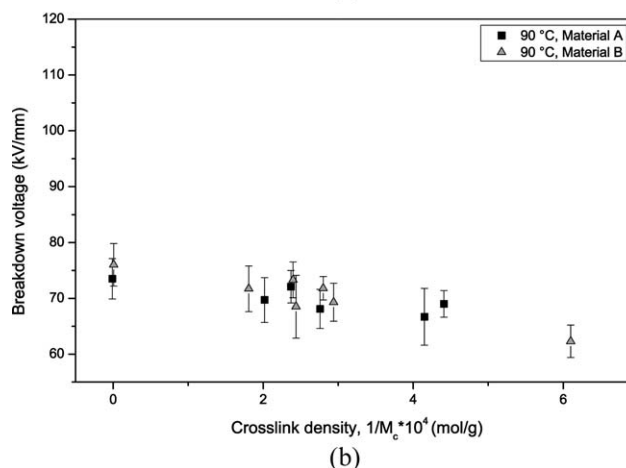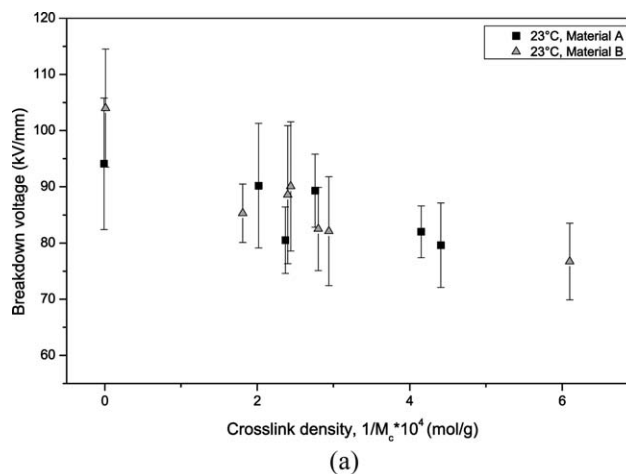

(a)

(b)

Figure 11 Electrical breakdown voltage for material A and B as a function of crosslink density for (a) 23°C and (b) 90°C.
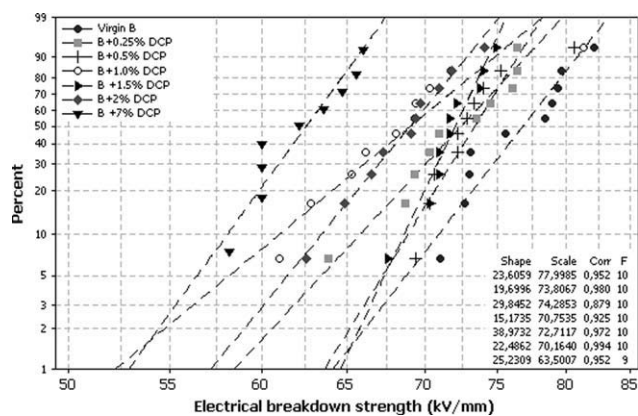
Figure 12 Electrical breakdown strength for material B at 90°C as a function of crosslinking with increasing amounts of DCP.

strength for the virgin materials at the higher temperature is substantially lower than at 23°C. The most densely crosslinked material B at 23°C contains approximately the same amount of crystalline areas as in virgin material B after being heated to 90°C, as a certain amount of crystalline lamellae in LDPE have melted at that temperature. A comparison of the crosslinked materials A and B does not reveal any major differences. However, there seem to be a deviation in electrical breakdown strength between the two virgin materials A and B, especially at 23°C, which could derive from the difference in size and perfection of the spherulites in the materials. Material B have smaller and less perfect spherulites, while the crystallinity is the same.[21] The electrical breakdown strength is reported to be strongly dependent on both degree of crystallinity and morphology.[15,16,40,41] Hosier et al.[15] report that although a high degree of crystallinity is beneficial for increasing electrical breakdown strength, it is the morphology that is critical for the change in electrical breakdown strength for chemically similar materials or blends. They found that a morphology consisting of space-filling spherulites would enhance the electrical properties most efficiently, while a morphology consisting of supermolecular structures separated by amorphous material shows a negative effect on the electrical breakdown strength. Our present results correspond well to the literature as the electrical breakdown strength decreases with decreasing degree of crystallinity and the morphology changes from impinged spherulites, via axialitic structures, to distributed lamellae in an amorphous matrix. The higher electrical breakdown strength in virgin material B, compared to virgin material A might point to a more space-filling structure of the spherulites in material B. To ensure a statistically true difference between the materials with increasing crosslink densities, a Weibull plot was constructed of material B

at 90°C (Fig. 12). The plot confirms the results from Figure 11.

CONCLUSIONS

A profound study on the effect of increasing crosslink density in two LDPE materials that were crosslinked with different mechanisms was conducted. The study was focused on water treeing, electrical treeing, and electrical breakdown strength.

The results were as follows:

- Water treeing is strongly dependent on the crosslink density, most probably due the concurrent decrease in the degree of crystallinity and change in morphology. The water tree length increases significantly up to a certain crosslink density, where it decreases again. The increase in water tree length corresponds to the change in morphology from well distributed impinged spherulites to an axialitic structure. The subsequent decrease in water tree length is believed to be due to the considerable restraint in polymer chain mobility, which would inhibit the water tree growth. The effect of different crosslink types seems to be negligible for the water treeing results.
- The water tree growth is almost linear for material A with different crosslink densities, after a rapid initial growth. A clear distinction between the materials can be seen already after 3 days of ageing.
- The electrical tree growth rate showed a considerable dependence on the crosslink density. The resulting disruption of the morphological structure is the most probable cause for the different growth rates.
- The electrical breakdown strength is primarily dependent on the resulting change in degree of crystallinity with increasing crosslink density.

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