Enhanced dielectric AC breakdown strength of polyethylene using voltage stabilizing additives

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Utveckling av polyetens elektriska isolerande egenskaper

Populärvetenskaplig sammanfattning

När el distribueras via högspänningskablar går mycket av energin förlorad via läckströmmar i det isolerade materialet. Däremot om el distribueras med lägre strömstyrka och med högre spänning kan läckförlusterna minskar, vilket i sin tur ställer högre krav på isolationsegenskaperna. Denna uppsats visar ett mycket lovande tillvägagångsätt om att öka isolationsstyrkan i polyeten med särskilda additiv.

Läckförlusterna kan minska eftersom läckströmsförlusterna är proportionella mot strömstyrkan i kvadrat. Samma effekt kan också uppnås om spänningsnivån höjs eftersom effekten, P, är ekvivalent med produkten av strömmen, I, och spänningen, V, (P=I*V). Det finns för tillfället ett behov av att öka spänningsnivån i högspänningsomvandling och distribution, i syfte att kunna överföra elkraft mer energieffektivt. Högspännings likströmskablar (HVAC) används framförallt och består av tvinnade koppartrådar täckta av skyddade höljen samt en isolator, ett tjockt isolationsmaterial bestående av polyeten. För att kunna öka spänningsnivån i HVAC-kablar måste isolationsegenskaperna i polyeten förbättras vilket kan uppnås med addition av organiska aromatiska föreningar, spänningsstabiliserande tillsatser.

Syftet med detta projekt är att undersöka hur den dielektriska genomslagsstyrkan i polyeten förbättras av nya typer av spänningsstabiliserande tillsatser som innehåller långa alkylkedjor och erhåller särskilda fysikaliska egenskaper. Dessa strukturer och egenskaper har i publikationer visat lovande resultat. De utvalda additiven blandades med polyeten i särskilda viktkoncentrationer med hjälp av en Brabender mixer. Därefter pressades de till en specifik tjocklek och slutligen testades genomslagsstyrkan på fjorton bitar per pressad platta i högspänning-växelströmstillstånd. Resultaten utvärderades med hjälp av Weibullfördelningar och jämfördes med en ren polyetenreferens tillverkad vid samma tillfälle.

Alla additiv gav vid minst en given koncentration en viss förbättring i genomslagstyrka relativt referensen. Additiv D1 gav upphov till den generellt bästa förbättringen, 0,2 wt% samt 0,5 wt% genererade en ökning på 7,5 % respektive 8,2 % i dielektrisk genomslagsstyrka. Varför tidigare publikationer har genererat betydligt högre ökningar tros bero på projektets referens som redan erhöll starka isolationsegenskaper vilket kan har gjort det svårt att öka genomslagsstyrkan i materialet ytterligare. Eventuellt är de förbättringar i avseende på den nedbrytningsmekanism detta projekt har fokuserat på, snabb lavinartad nedbrytning, inte jämförbar med den nedbrytningsmekanism, elektriska träd, som tidigare publikationer framförallt har undersökt. Däremot kunde det konstateras att metodens tillförlitlighet var lovande och den Rogowski-formade elektroden genererade en smal distribution av resultat.

Abstract

There is currently a need to increase the voltage level in high voltage transmission and distribution systems in order to transmit power in a more efficient way. However, the insulation of the conductor in high voltage alternating current (HVAC) cables needs to be improved in order to withstand these high voltages. One approach to enhance the dielectric breakdown strength, i.e. the threshold value before the insulator becomes conductive, of polymer insulation materials is to use organic molecules with aromatic structures.

The aim for this investigation was to increase the dielectric breakdown strength for polyethylene with nine different aromatic additives. The additives where chosen according to physical properties and alkyl chains attached to its aromatic core. The additives where mixed at a certain weight concentration with polyethylene in a Brabender mixer, pressed to a certain thickness and fourteen pieces from these pressed plates where tested with AC breakdown. The result where evaluated with Weibull distribution statistics and compared with polyethylene references that was prepared likewise at the same occasions. Although all the additives showed at some concentration an increase relative to the reference, the concentration of 0,2wt% and 0,5wt% of additive D1 resulted in the highest overall increase in breakdown strength, 7,5% and 8,2% respectively. It was suggested that the relative small increases compared to the published data might be due to the reference's already excellent insulation properties. The deviated results may also indicate that the enhancements in electrical treeing resistance are not comparable with enhancements in dielectric breakdown strength. However, it was concluded that the reliability of the method was promising and that the Rogowski-shaped electrode generated trustworthy and narrow distributions of results.

List of Acronyms

HVAC	High voltage alternating current	OM	Optical microscopy
PE	Polyethylene	SEM	Scanning electron microscopy
LDPE	Low density polyethylene	FTIR	Fourier-transform infra-red
XLPE or PEX	Crosslinked polyethylene	DSC	Differential scanning calometry
HDPE	High density polyethylene	VSA	Voltage stabilizing additive
BD	Breakdown	DBS	Dielectric breakdown strength

Table of Contents

1. Introduction

Electrical power can be transferred either by alternating current (AC) or direct current (DC). In the late 1800s a debate emerged regarding the best transferring way. Tomas Edison was pushing for DC, but lost "the war of currents" against AC's supporters Nikola Tesla and George Westinghouse, primarily due to the inconvenient way of transferring DC currents to lower voltage. However, DC is still necessary for connecting asynchronous AC grids and for long-distance transmissions.

During the transmission of AC and DC, losses mainly occur due to Joule heating, i.e. the resistivity of the material cause heat. This phenomenon can be described by Joule's first law and the amount of heat released is proportional to the square of the current.

$$Heat = RI^2t$$

Where R is the resistance, I is the current and t is the time. According to Ohm's law, the same power can be transmitted at lower currents but with a higher voltage. The current dependent losses can therefore be decreased significantly[1].

$$P = V * I$$

Consequently, there is currently a need to increase the voltage level in high voltage transmission and distribution systems in order to transmit power in a more efficient way. But the insulation material needs to withstand these high voltages. It is thus desirable to develop insulation materials with excellent dielectrical, thermal, and mechanical properties, combined with a life time of 30 years or more. One approach to enhance the dielectric breakdown strength, i.e. a threshold value before it becomes conductive, of polymer insulation materials is to use organic molecules with aromatic structures. They are able to quenching the energy of the energetic electrons responsible for the breakdown mechanisms.

1.1. Aim of the thesis

The aim of this master thesis is to investigate the effects of various organic aromatic additives on the dielectric breakdown strength of polyethylene under high voltage alternate current (HVAC) conditions. It will start with a literature study where a hypothesis will be formulated of how to enhance the dielectric breakdown strength (DBS). According to this hypothesis certain organic additives will be selected and compounded into polyethylene with a Brabender mixer. The dielectric breakdown strength of the materials will be tested, correlated to the thickness of the sample and evaluated with Weibull distribution statistics. Before the investigation begins, the right electrodes in the AC-breakdown machine will be evaluated. There will also be an investigation in the beginning regarding the factors that might influence the DBS in order to make sure that any enhancements in DBS are mainly due to the additives. Impulse testing will also be carried out on a selected material to get additional understanding. Finally, the results and the analysis will evaluate the validity of the hypothesis and suggestions for further work.

1.2. High voltage power cables

The European Union has announced a massive expansion of the existing European power grid (presently containing 300.000 km of routes) and the installation of 43.000 km of new transmission lines until 2030. Approximately 75% of these will be high voltage alternating current (HVAC) lines[2]. However, in a 100-km long 132 kV HVAC submarine cable up to 5% of the transmitted power is lost[3]. As mentioned earlier, the efficiency of power transmission scales with the transmission voltage. The quality of electrical insulation materials is critical for many high voltage applications and becomes increasingly important with the increased need for power transmission. Electrical,

thermal and thermo-mechanical degradation of the insulation layer are major factors that can lead to failure of HVAC cables during operation. Further improvements of insulation materials are thus required[2].

HVAC power cables are used to transmit large amounts of electrical power. It consists of a conducting core, either copper or aluminum, which is surrounded by several protective layers, see **Figure 1**. The conductor (A) cannot consist of massive metal, since it needs to be flexible. Instead it consists of many thin wires wired to a massive wire which makes it more mobile[4]. On the other hand it results in an uneven surface to the insulation layer, which is why a thin semiconducting layer, consisting of a thermoplastic filled with carbon black, (B) needs to surround the conductor. The purpose is to even out the heterogeneous electric field and to provide a void-free interface between the conductor (A) and the insulation material (C). The insulation material usually consist of a cross-linked polyethylene (XLPE), characterized by low electrical conductivity, low dielectric losses, high dielectric strength and sufficient form of stability at the operating temperature, up to 90 ˚C. The other semiconducting layer (D) again provides a homogenous electric field distribution between insulation and the outer reinforcing jacket (E) .HVAC insulation is subjected to many types of stress during its operational lifetime, which is commonly around 50 years[7].
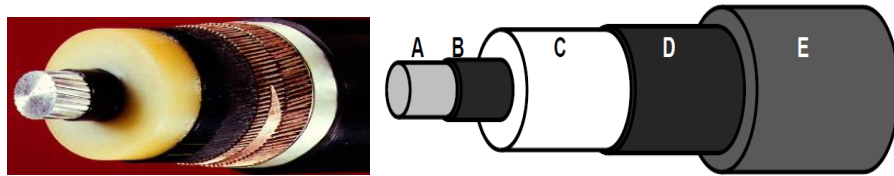
Figure 1 *HVAC cable (left) and a schematic drawing of a high voltage cable (right) comprising (A) a central conducting core that is surrounded by (B) a semiconducting shield, (C) an insulation layer of e.g. polyethylene, (D) a semiconducting shield surrounded by a conducting screen and (E) an outer jacket.*

To form the insulation layer (C), consisting of low density polyethylene (LDPE), and the electrically conducting compound (B) to the metallic core, cable extrusion coating is performed in a continuous process. The polyethylene is later cross-linked by free radicals, e.g. by thermal decomposition of dicumyl peroxide (DCP), in order to withstand the rather high operating temperature of a HVAC cable[5]. Therefore, this thesis is initially focused on the same processing sequence, which is most relevant from an industrial perspective; stabilizing additive is added prior to LDPE cross-linking process.

1.3.   Polymeric insulation materials

The first material that really improved the quality of the insulator was introduced by the 1930s and was made of synthetic polymer. This polymer revolutionized the insulator due to the low cost, high corrosion resistance and magnificent physical properties. However, the physical understanding of the polymers electrical breakdown mechanism or long term degradation, such as water diffusion, was not fully understood. In the early 1960s, polyethylene (PE) turned up to be a suitable candidate for these problems, primarily due to its hydrophobic properties. Although PE solved many problems, new insulation failures started to emerge and once again breakdowns due to water occurred, but now in a new form called water treeing. These trees appeared since water diffused into the defects that are present in the polymer and degraded the polymer. Water treeing is a type of erosion breakdown, i.e. polymer defects leads to local partial discharges which degrade the polymer over time[1]. Today, the failure mechanisms behind water treeing are understood. The aim of this thesis is to evaluate various types of additives which can increase the breakdown strength of LDPE.

2. Theory

2.1. Structure of polyethylene

Polyethylene was first made in 1933, but the production did not grow until films began to be made in 1952. Nowadays, polyethylene is the most common synthetic polymer with a worldwide annual production of around 80 million tons, where the majority is used for packaging.

PE is a semicrystalline polymer, i.e. it consists of a vast number of thin crystals, the crystalline lamella, which are separated by amorphous layers, the amorphous regions. These lamella are ordered in a superstructure of so-called spherulites or axialites, see **Figure 2**. The growth of a crystalline lamella is initiated from a nucleation site; either by heterogeneous nucleation, where impurities or residual crystalline polymers act as nucleation sites, or by the more rare heterogeneous nucleation, where collision of chain segments could lead to a cluster from which growth could proceed. The growth of the spherulite is stopped by contact with another growing spherulite.
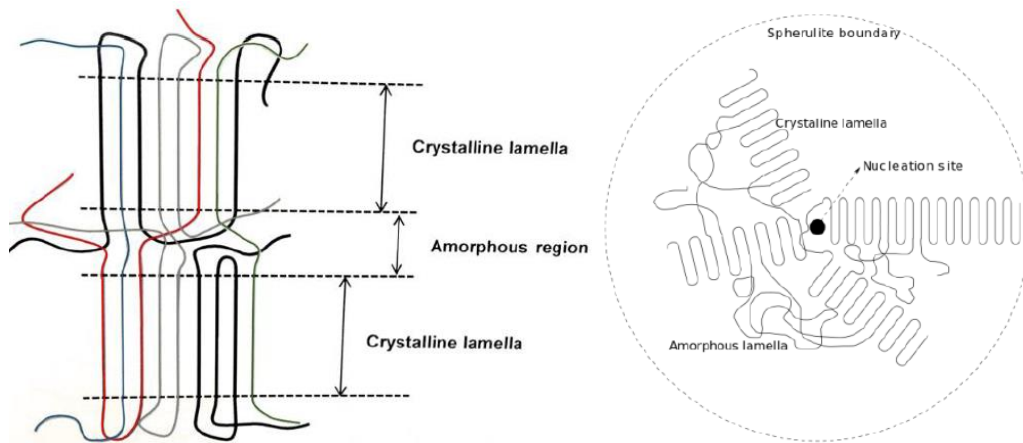
Figure 2 *Schematic picture of PE's microstructure, a) Depicts the two different regions b) Depicts a spherulite.*

The lamellar thickness is an important microstructural parameter and has for example a strong impact on the electrical properties. The size of individual lamellae is determined in part by the chain configuration, e.g. branching, but also the thermal history of the material. The lamellar region is constructed in a regular pattern, called the unit cell. Each chain is stretched in a planar zigzag formation and placed along each other. The unit cell is described as orthorhombic with 27 % of free space and consists of two complete chains, see **Figure 3**[6, 7].
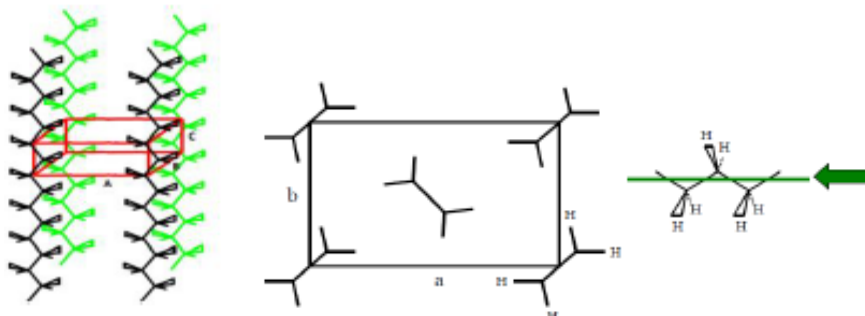
Figure 3 *The unit cell of the crystalline lamella seen from different angels. The unit distance a is 7.4 Å, b is 4.9 Å and c is 2.6 Å.*

Although PE consist of a simple monomer structure (-CH$_2$-CH$_2$-) $_n$, its properties varies strongly by molecular weight, branching and processing conditions. High density polyethylene (HDPE) and linear low density polyethylene (LLDPE) are produced by Ziegler-Natta catalyst, meanwhile low density polyethylene (LDPE) is produced in stirred autoclaves or long tubular reactors at high pressure (120-300MPa) without a metal catalyst . All these major types of PE are depicted in **Figure 4**, including the cross-linked version of LDPE (XLPE). [7] HDPE is characterized by linear polymers, not branched, which results in high density (ρ=950-997 kg/m^3), high melting point and thus high crystallinity. LDPE is, on the other hand, characterized by branched polymers with thus lower densities (ρ=910-940 kg/m^3), lower melting point and lower crystallinity. HDPE is commonly not used for HV power transmission cables due to the high modulus of the material, resulting in too large bending radius. The operating temperature for HVAC cables is typically around 90 ˚C and it can be significantly higher in case of overvoltages, for example, caused by a lightning strike[8]. Consequently LDPE needs to be cross-linked (XLPE) in order to withstand these high temperatures. Cross-linked polyethylene (XLPE) is the most widely used insulation material for high voltage cables[6]. Permittivity is a measure of how an electric field affects, and is affected by, a dielectric medium, and it is needless to say relatively low for XLPE[9].
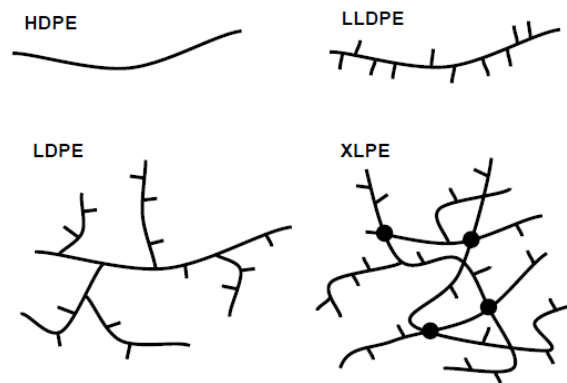

Figure 4 *Schematic pictures of four common types of polyethylene. The black lines represent hydrocarbon chains and the large dots indicate crosslinks*

2.1.1. Antioxidants in polyethylene

Polyethylene is sensitive to oxidation at room temperature. To prevent this, antioxidants are dissolved in polyethylene's matrix which prevent oxidation by effectively capturing radicals and thus prolonging the service life. There are two different types of antioxidants, primary and secondary, that are used in combination. Primary antioxidants, such as hindered phenols and aromatic amines, are designed to eliminate the propagating peroxy and alkoxy radicals before they attack the polymer. Secondary antioxidants are designed to stop the autocatalytic chain propagation by decomposing the hydroperoxide. Antioxidants reduce the peroxide radicals which are supposed to crosslink the LDPE to XLPE. But on the other hand they also crosslink to the polymer chains which is important[10], see **Figure 5**. The antioxidants must be chosen carefully depending on which crosslinking species that one might choose. Phenolic antioxidants, for instance, are claimed to interfere more with peroxide cures than amine antioxidants[11].

The diffusion coefficient for antioxidants is quiet high[10,12], and it is not very dependent on either the temperature or the molecular weight. Even antioxidants with long alkyl chains attached to the core possess high diffusion coefficients. However the desorption is very dependent on temperature and molecular weight. The concentration of antioxidants depends on what kind of environment the polyethylene will be exposed to. In HVAC cables for instance relative low content of antioxidant, such as Santonox®, is needed since it is a closed system. The right relation between antioxidant and crosslinking-species must also be chosen[10,13-14].

Furthermore, the choice and concentration of antioxidant can actually affect the insulation properties [15] which will be discussed later on.
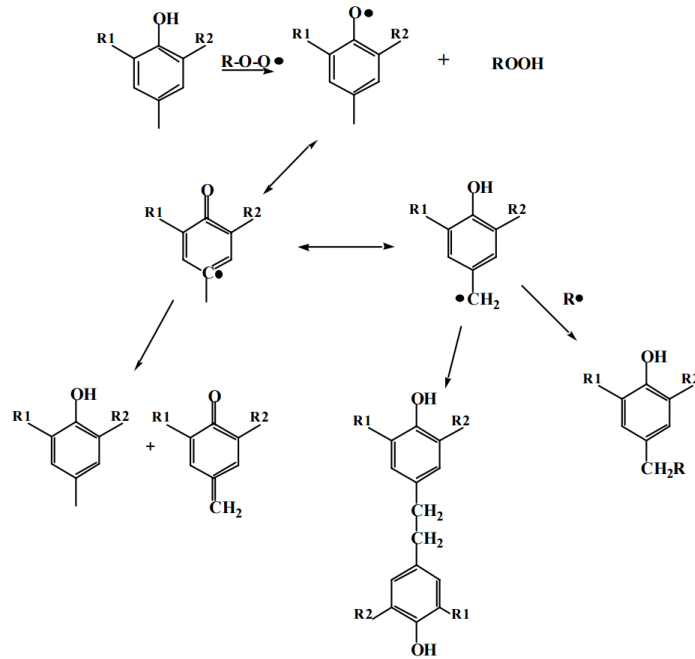

Figure 5 *Reactions of hindered phenols with peroxide leading to crosslinking of polyethylene*

2.2. Breakdown mechanisms

When a polymer is exposed to too high voltage, an irreversible failure emerges and the polymer becomes electrically conductive. This threshold field, an insulation material can withstand before collapse, is called dielectric breakdown strength (DBS). The theoretical value of the DBS is higher than the experimental value since the DBS is dependent on many parameters such as temperature, polarity, morphology, thickness and defects[16]. The DBS for intrinsic failures can be regarded as the required field to promote electrons from the valence band to the conduction band. The intrinsic DBS is thus a material property and is considered to be very difficult to reach during experiments[17].

The three major breakdown mechanisms for polymers are avalanche, thermal and electromechanical breakdown. Although avalanche breakdown is dived into three subclasses fast avalanches, erosion breakdown and water treeing, only fast avalanches is considered as a short term breakdown. Erosion breakdown and water treeing leads to the phenomena called treeing and degrades the material over time until failures occurs. Meanwhile fast avalanches, thermal and electromechanical breakdown occurs rapidly and leads to a dielectric breakdown, see **Figure 6** and **Table 1**. In the case of treeing the applied voltage is below the DBS of the material and conducting path arises slowly over longer time during lower applied voltages[6 16 -18].

Usually there is one dominating mechanism when failure occurs, but combinations are also common. In this thesis work only fast breakdowns in ambient temperature will be primarily present; fast avalanche and thermal breakdown. This is due to the fact that the AC- machine will have relative high ramp rate until breakdown occurs and it will operate at room temperature. Introducing additives to polyethylene under AC condition cause both thermal breakdown (motion and rotation of the additives) and fast avalanche breakdown (degradation of polyethylene). More information about the possible mechanisms can be found in reference 18.
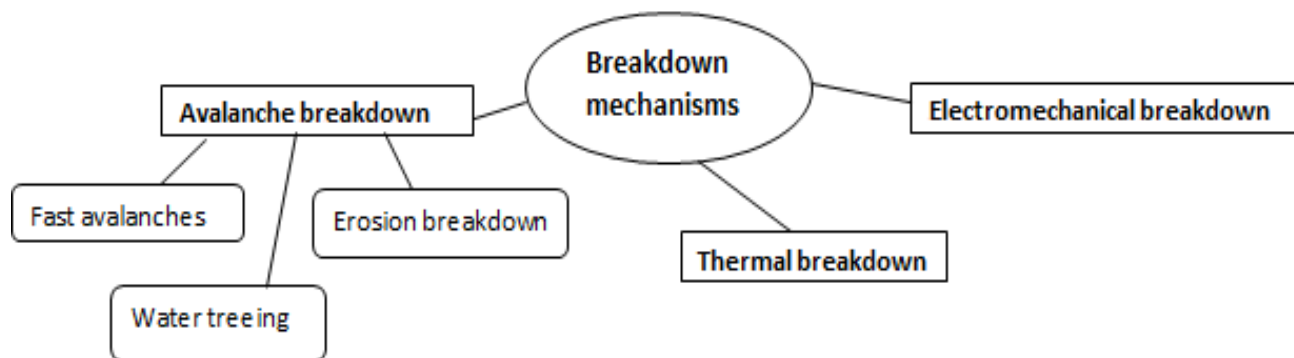
Figure 6 *The most important breakdown mechanism for polyethylene*

Table 1 *The most important breakdown mechanisms for polyethylene and their corresponding characteristics[6]*

	Fast avalanches	Thermal breakdown	Electromechanical breakdown	Erosion breakdown	Water treeing
Duration of the breakdown process	1ns - 1µs	0.7 µs - 1ms	1µs - 1ms	10 ms - 10years	Hours- years
Mechanism	Dielectric breakdown	Dielectric breakdown	Dielectric breakdown	Treeing	Treeing
Optimal conditions	Low T	Low T <T< High T	High T	Low voltage over time	Presence of water

2.3. Enhanced dielectric breakdown strength (DBS)

Dielectric breakdown in polymeric insulating materials is complex since it depends on many different factors, such as chemical composition, morphology, chemical impurities, voltage waveform, temperature, electrode shape, etc. The factors that enhance dielectric strength will be discussed here below. More information regarding the effects can be found in reference 6.

2.3.1. Morphology

The effect of polyethylene's morphology on DBS will be discussed roughly here below. Tacticity may also affect the DBS, depending on which breakdown mechanism is dominant[19], but it is left out in this thesis since only polyethylene is investigated. The crosslinking tacticity of antioxidants is neither considered.

2.3.1.1. Crystallinity

The electron mean free path is the distance an electron can travel before it collides with a polymer chain. The distance is correlated to the energy of the electron, i.e. the electron accelerates to higher energies and ionizes easier the C-C bonds in the polymer chain when the distance, the free volume, increases. Increased crystallinity, thus, decreases the DBS when avalanche breakdown is dominant since the electron mean free path increases, unless the number of spherulites doesn't change. However, this is not the case for higher temperature when electromechanical breakdown is dominant, since increased crystallinity increases the mechanical strength of the polymer. It is thus important to know which mechanism that is mostly dominant in the intended application in order to enhance the DBS[16].

2.3.1.2. Spherulites

The weakest path in the material is between the boundaries of the spherulites, the interspherulitic region[20]. This is explained by the fact that particularly impurities are expelled into the spherulite boundaries and thus creating a weaker path. Kolesov et al.[22] demonstrated that an increase in spherulite size from 77 µm to 350 µm decreased the

DBS by 77%. Further increases in size did not really affect the DBS. It was suggested that smaller spherulite sizes tend to improve the DBS since they generate higher tortuosity for the electrons which disturbs their acceleration. Yan et al.[21] found that a decrease in lamellar thickness from 15 to 10 nm lowers the tree initiation voltage of LDPE and HDPE by about 50%[21], which also supports Kolesov's theory. The number of spherulites is of course also very important. The number and size of the spherulite is dependent on nucleation sites, molecular weight and cooling temperature. Kolesov also investigated the effect of molecular weight on the DBS. It was concluded that an increase in molecular weight of PE creates smaller spherulites, due to branching, which generates a higher DBS[22].

2.3.1.3. Thickness

The thickness of polyethylene samples has a large impact on DBS. Karlsson et al.[18] investigated the effect of different polyethylene plates pressed, prepared exactly the same, with a thickness between 350-500 µm. It was concluded that lower DBS was obtained for thicker samples. The explanation for this finding was that thicker samples contain more defects which thus reduce the DBS. Artabauer[23], on the other hand, related it to the length of the mean free path in the free volume for thicker samples. It is more probable to find free volumes, the volume which is not occupied by polymer chains, in thicker samples. Hence, the probability of avalanche initiation increases with thickness which results in a reduction of the DBS[23].

2.3.1.4. Crosslinking

In order for the cable to withstand the high operating temperature of HVAC cables, LDPE needs to be cross-linked. Special peroxides are most commonly used since they are able to decompose at a temperature above the melting temperature of PE and below the temperature of material degradation, which enables a melt process without gel formation and without material deterioration. Dicumyl peroxide (DCP) is most commonly used for LDPE cable insulation. During the reaction, by-products such as acetophenone, cumyl alcohol and methane are formed which influence the electrical properties, see **Figure 7**. The by-products need to be removed by degassing which is a time consuming process[7]. However, acetophenone increases DBS significantly which will be discussed later on.
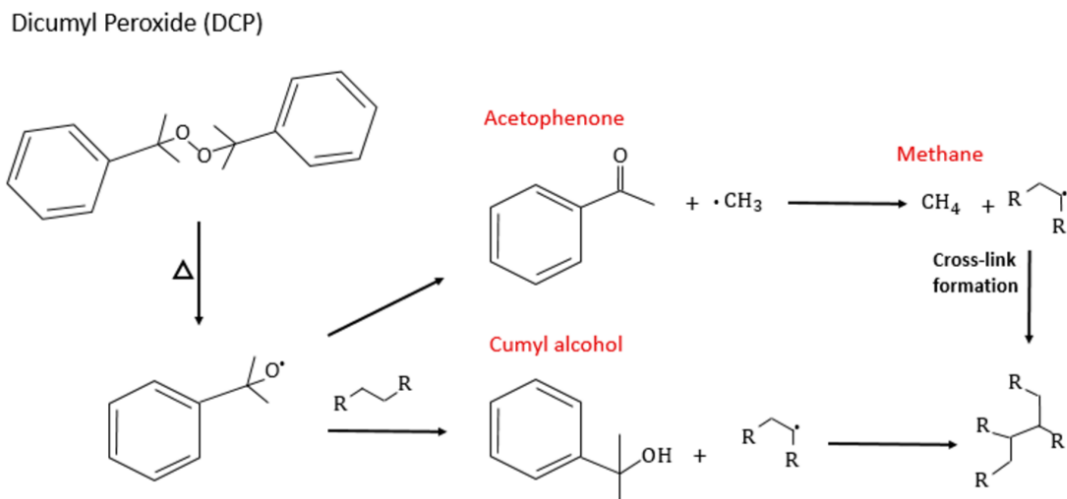

Figure 7 *The decomposition of dicumyl peroxide (DCP) which initiates polyethylene cross-linking and disturbing by-products indicated with red labels. The figure is reused from reference 7.*

2.3.2. Defects

Air voids are easily left in the material during the molding process. The dielectric strength for air is lower (~3kV/mm) than that of a solid insulator and as a consequence of that discharges are likely to occur. This is due to the mean free path of electrons being much longer in gases than in solids which is dependent on the pressure of

the gas. The gas filled voids inside the polymer can thus be ionized at lower voltages and initiate an avalanche of energetic electrons which will lead to dielectric breakdown. Paschen made experiments on breakdown voltages in gases and found a relationship which he named Paschen's law, which says that the minimum voltage, V_g, to cause a spark between two electrodes depends on the product of the length of the gap, l, and the density of the gas, ρ. In **Figure 8** Paschen's law for air is shown. The breakdown field increases very steeply towards smaller gaps at constant pressure from the minimum voltage required for breakdown, which is regardless of gap or density. In short, the smaller the bubbles are in the compact insulator the less interfering of the electric field[18, 24-25].
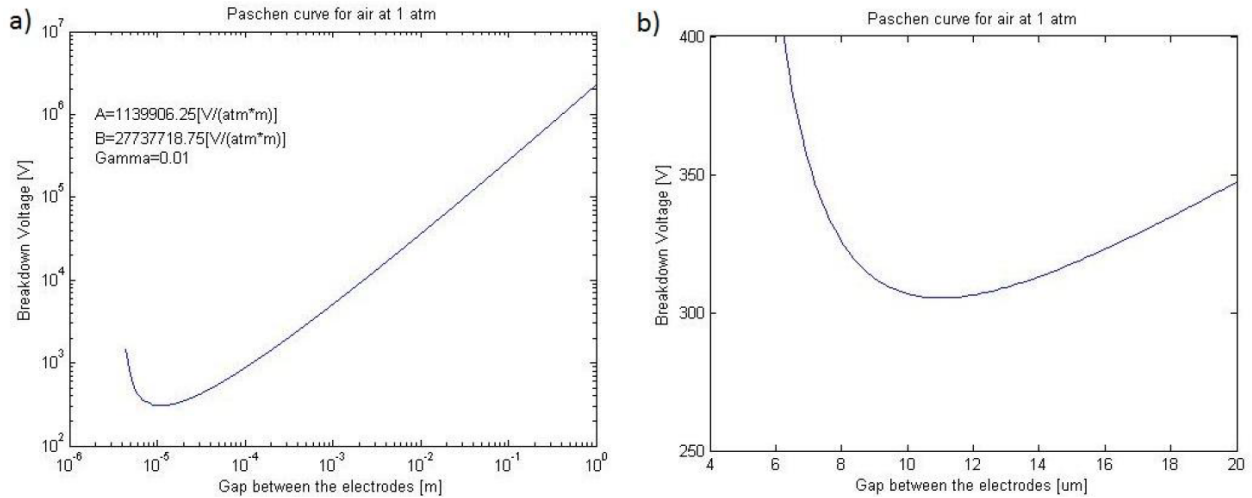
Figure 8 *Two different plots of Paschen's law, which calculates the breakdown voltages for air at atmospheric pressure as a function of the distance between the electrodes. The values of the constants A and B are for air, gamma is for aluminum electrodes and are taken from reference. a) is a logarithmic plot from micrometer to meter and b) plots the interval around the minimum breakdown voltage in micrometer. These diagrams are reused from reference 18.*

2.3.3. Nanoparticles

Many investigations regarding enhancing dielectric breakdown strength by nano particles have been reported[26-29]. The large surface area of the nanoparticles is one of the reasons why they have emerged into this new field. A large fraction of the polymer are thus in close contact to the particles and these adjacent polymers exhibits different properties, such as electrical properties, than the ordinary polymer matrix[26]. The interaction zone around the particles could be "quasi-conductive" regions which partially overlaps in the nanocomposites[27]. These overlapped interface regions thus may allow charge dissipation, which in turn, could be expected to improve the dielectric breakdown strength and voltage endurance characteristics. The enhanced DBS could also be due to a scattering mechanism or to a change in the space charge distribution. However, both increased and decreased DBS have been reported, the dispersion of the nano fillers is for instance very crucial. If the particles agglomerate they can behave as micro sized fillers. Too big fillers can act as defects in the dielectric and locally distort the electric field. When the dielectric is applied under AC conditions, the difference in permittivity between the polymer matrix and filler can become too large[16,28-29].

Although both size of the particles and homogenous dispersion is important, another important technique to hinder the agglomeration of nanoparticles is to attach compatible polymer brushes onto the nanoparticles. The agglomeration is mainly driven by the high surface energy of the particles and the nano particles reduce their energy by forming clusters. Organic coatings mitigate the attraction between the particles. Coating on nano particles have resulted in enhanced DBS compared to uncoated particles. The coating can be polar or nonpolar[16,18].

2.3.4. Antioxidants

As discussed in the introduction, antioxidants need to be dissolved in PE in order to protect the polymers from degradation by oxidation. These compounds typically consist of aromatic groups and thus affect the conduction. Goshowaki[15] and his coworkers concluded four important facts about antioxidants' influence on electrical conduction in LDPE and XLPE. First of all, it was confirmed that under high-electric field, greater conduction current flows in XLPE than in LDPE. The leakage current flowing in XLPE is dependent on type and amount of antioxidant, particularly antioxidants containing sulfur, such as Santonox®. The antioxidants may also work as charge traps for charged particles moving through XLPE. Besides that they also have some effect on the crystallinity[15].

Olsson et al.[30] also investigated the effects of antioxidants. LDPE was aged in air 80 ˚C with the initial concentration of 0.14 wt% Santonox® in the beginning of the experiment. The amount of antioxidant decreased exponentially and finally reached a concentration of 0,06wt% Santonox after 800 hours. The breakdown tree inception voltage had decreased with about 20% after 800 hours of ageing. It was suggested that the antioxidant may, by modifying the material's conductivity, modify electric field distribution in the vicinity of the wire electrode and consequently the conditions for tree inception[30].

3. Voltage stabilizing additives

A hot electron is known as an electron that gains enough kinetic energy under an electric field to cause breakdown. In particularly, a hot electron may collide with an atom and as a result a bound electron is knocked out, creating a new carrier, see **Figure 9**. If a chain reaction forms during this process, the carrier concentration increases rapidly, resulting in the electron avalanche effect and the properties of the insulating material is lost. This phenomenon is known as electric breakdown. If the electron avalanche mentioned above is limited to a local area, the carbon-carbon bond of the polyethylene chain will be attacked, either by initiating a partial degradation known as electric treeing or by a rapid degradation known as fast avalanche breakdown[7,31].

Figure 9 *The electric breakdown mechanism of polyethylene*

Voltage stabilizing additives (VSA) have the ability to dispose of these hot electrons in such a way that the polymer matrix is left unharmed. In short, they increase the dielectric strength of an insulation material. They can dispose these electrons in different mechanism which will be discussed here below. During the last decade many different classes of voltage stabilizer have been proposed for both AC and DC applications, among these are polycyclic aromatic hydrocarbons, aromatic dyes[6,7,32].

3.1. Properties of voltage stabilizing additives

In order to exhibit voltage stabilizing properties, certain properties need to be fulfilled. In particular, some of these properties must exhibit certain values in order to hinder degradation of the polymer from bombarding electrons, which is equal to the required energy to break a carbon-carbon bond, roughly 3.6 eV. Except this criteria, it needs to be compatible with the polymer matrix and the environment as well as being environmentally friendly in case of migration to the nature.

3.1.1. Ionization potential

Ionization potential (IP) is defined as the minimum required amount of energy to remove an electron form the molecule to infinity and thereby creating a cationic radical. However the geometry of the cation's ground state can occasionally be optimized. Thus, there are vertical and adiabatic ionization potentials, IP_v and IP_a respectively, where the vertical energy, v, is based on the geometry of the neutral molecule while a represents the adiabatic energy from the optimized structure, see **Equation 1 & 2** [7,47]. Consequently it is defined as:

$$IP_v = E_{cation} - E_{neutral} \approx E_{HOMO} \text{ **Equation 1**}$$

$$IP_a = E_{cation}{}^+ - E_{neutral} \qquad \text{**Equation 2**}$$

However IP_a is approximately the same as IP_v, and thus referred to IP. Aromatic compounds usually exhibit a lower IP compared to PE and thus they are more susceptible to ionize as if a hot electron interfere an adjacent polymer chain. Additionally, the released electron from the ionization and the incoming electron have now significantly lower kinetic energy which reduces the probability of causing further ionization. The formed cationic radical will eventually recombine with an adjacent electron. Except from that mechanism, the lower IP of the aromatic compound can also cause quenching of adjacent PE radical, from which an electron transfer emerges from the PE

16

to the aromatic compound, both mechanisms can be seen in **Figure 10** [6]**.** The IP could significantly be reduced by attaching strong electron donating groups, such as amines and hydroxyl groups [33].
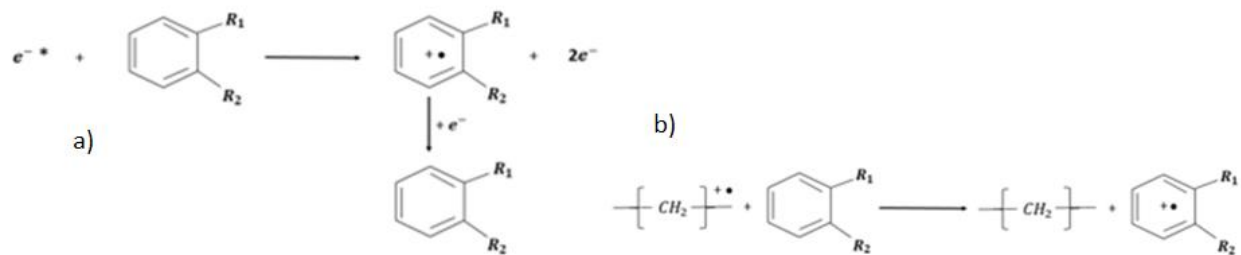

Figure 10 *Two possible mechanisms due to the lower ionization potential of VSA compared to polyethylene, where e⁻ * denotes a hot electron .a) Hot electron interfering with a stabilizing additive. b) The quenching mechanism of a stabilizing additive. The figure is altered from reference 7.*

3.1.2. Electron affinity

Electron affinity (*EA*) is defined as the amount of energy released when an electron is added to a molecule or atom. It indicates how susceptible an atom or molecule is to absorb an electron. A molecule that has a large positive value of EA is called an electron acceptor whereas an electron donor exhibits a negative EA. It is a complicated function of the electronic structure and some molecules exhibit negative EA, such as benzene. The susceptibility is determined by certain functional groups, either electron withdrawing groups, such as nitro groups, aldehydes, esters carboxylic acids etc. which increase the EA or electron donating groups, such as amines and hydroxyl groups, which decrease the EA. As for the IP, there is a vertical and adiabatic EA, EA_v and EA_a respectively. Although one would expect that molecules with the high electron affinity will perform well as voltage stabilizing additive i.e. trap electrons, Kisin et al.[34] showed that in fact only EA_a is correlated to the enhancement of the DBS in combination with a certain IP[34]. Worth mentioning also is that Johansson concluded in her PhD that the efficiency of voltage stabilizer, such as benzil- thiaxanthone- fullerene- and melamine-types, with respect to tree initiation voltage was found to depend more on the EA of the molecules rather than on their IP[35].

The proposed mechanism correlated to the EA is called the electron scavenging mechanism. The aromatic stabilizer absorbs the hot electron and gains thereby more energy which is afterwards released as radiation and it becomes an anionic radical. It can then undergo three different mechanism; a) it can donate one electron to an adjacent cationic polymer chain which neutralize them both, b) it can donate one electron to a positively charged stabilizer which also neutralize them both or c) a hot electron could collide with it which neutralize the stabilizer and releases two electron with less kinetic energy, see **Figure 11.**
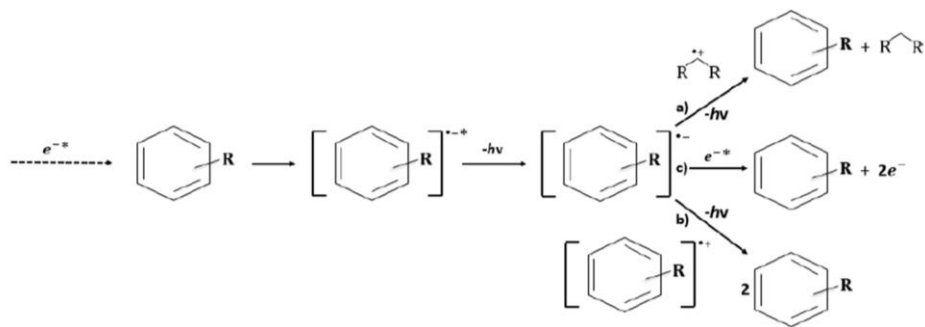

Figure 11 *Possible electron scavenging mechanism for voltage stabilizing additives, where e⁻ * denotes a hot electron. a) The stabilizer reacts with a positively charged polymer chain; b) The stabilizer reacts with a positively charged stabilizer and c) The stabilizer interferes with another hot electron. The figure is adapted from reference 7.*

3.1.3. Excitation energy

Excitation energy, (*Ex*) in a molecule is defined as the minimum amount of energy required to excite an electron from the lowest, E_{LUMO}, to the highest occupied molecular orbital, E_{HOMO}, i.e. the electron remains within the molecule and thus the charge of the molecule remains.

Stabilizing additives have optimal excitation energies that result in a mechanism where the incoming hot electron excites the stabilizer to a higher state. The hot electron emits considerable amounts of kinetic energy which reduces the risk of polymer degradation. The stabilizer will eventually relax to its ground state by phosphorescent light, see **Figure 12.** As already mentioned, the required amount of energy to degrade a PE chain is equal to the amount of energy to break a carbon-carbon bond, 3.6 eV. Consequently, the probability for the mechanism described above increases if the Ex of the voltage stabilizer is below 3.6 eV[6,7].
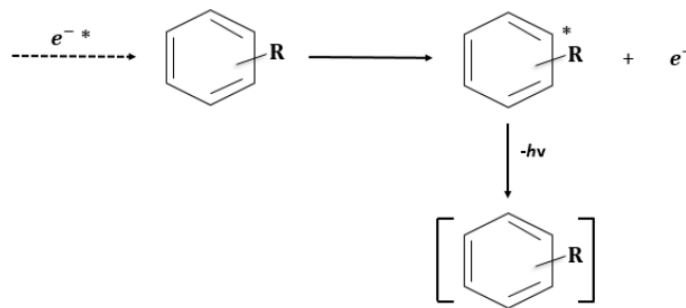
Figure 12 *The possible mechanism due to the relative low excitation energy of the voltage stabilizer. The figure is adapted from reference 7.*

3.1.4. Solubility

Except the important properties of actual interaction with the hot electrons, it is easy to forget the solubility of the additive in the actual polymer matrix. There are numerous promising additives mentioned in the literature, however, very little is discussed regarding the additives compatibility with the matrix. Additives that are not soluble tend to agglomerate and/or migrate to the surface, which obviously decreases the effect in terms of dielectric strength[6]. The additives that do dissolve in the matrix tend to be present in the amorphous region and not in the crystalline region[36].

In order to increase the solubility of the additive in polyolefines, several articles suggest additives with alkyl chains attached to the aromatic core showing promising features. The diffusion rate of the stabilizer through the polyethylene matrix decreases since the chains act as anchors. Hjertberg et al.[37], for instance, attached different length of alkoxy chains to different stabilizers and found that by increasing the length from C_4 to C_8 the migration decreased significantly, nearly 80%. However, longer chains didn't affect the migration further and Jarvid et al[33], who attached different lengths of alkyl chains onto benzil-additives, even found that chains longer then C_{12} actually begun to decrease the efficiency of the stabilizers[32]. Thus, an optimal length needs to be found. But as mentioned earlier, even bigger molecules with long alkyl chains tends exhibit a rather high diffusion coefficient in LDPE.

An interesting alternative is to covalently bind the additives to the polymer chains, an interesting example will be discussed later in the section of publications.

3.1.5. Thermal properties

As mentioned in the introduction, LDPE is later cross-linked to form XLPE by heat in order to dissociate the peroxides and form radicals. The voltage stabilizing additives are supposed to be introduced into the PE matrix prior to the crosslinking since it facilitates the production of a HVAC cable. So the VSA needs to be stable during the

crosslinking process. Additionally, the vapour pressure of the additives is important since it determines the migration. Thirdly, the operating temperature could be up to 90 ˚C, which also stresses the essentialness of the additives' thermal properties[33].

Longer alkyl chains are advantageous from a processing perspective since they significantly reduce the melting temperature[33].

3.1.6. Polarity

The attraction of dipoles could increase the probability of thermal breakdown; the polarity of the stabilizer should be minimum. But it could also be compensated, once again, by the length of the side chain which thereby could decrease the dielectrophoresis. Bulky molecules don't have the time to rotate when the field is alternating quickly[33].

3.1.7. Long term stability

The long term stability of a cable containing VSA still remains unclear. The diffusion coefficient could be rather high even for larger molecules[10] such as VSAs. On the other hand, a HVAC cable is in a closed system and equilibrium between the XLPE and the adjacent semiconductors may emerge. The life time of HVAC cable is approximately 50 years[7] and thus the VSA migration needs only to fulfil this time interval.

3.1.8. Concentration

The concentration of the additives is definitely crucial. No effect will be seen for too low concentrations and the insulation properties will be lost for too high concentrations. If the concentration is above 1.5 wt% the performance gradually decreases[7]. The concentration of additive should be correlated to the concentration of aromatic groups, since these are the ones that give rise to the stabilizing mechanisms.

3.2. Relevant additives reported in the literature

Here below are some interesting publications regarding some promising VSA.

3.2.1. Benzil

Jarvid et al[38] tested seven different benzil-type voltage stabilizers in electrical tree inhibition experiments under HVAC conditions (50 Hz, ramp rate of 0.5 kV/s up to 75 kV)[39] and all of the investigated additives substantially enhanced the dielectric strength of the insulating material at a concentration of only 10 mmol kg^{-1}, corresponding to approximately 0,3wt% and a concentration of aromatic groups of 0.15 wt%. The VSA was added to LDPE, prior to the crosslinking process, and was later measured to the reference of XLPE. It was shown, by a combination of differential scanning calometry (DSC) and small-angle x-ray scattering (SAXS), that the additives only had a minor effect on the crystallinity as well as the lamellar thickness. Accordingly, the increased field required to initiate electrical trees was entirely due to the additives. The best result was obtained from the benzil compound containing methyl groups linked to the benzil core via ester or tertiary amine groups and it gave rise to an improvement in dielectric strength of over 70 % compared to neat XLPE. This additive had no long alkyl chains attached to it, see **Figure 13**.

The attached chains to the benzil-core had the benefit of decreasing the vapor pressure compared to neat benzil and it significantly improved the thermal properties with less than 1% weight loss up to at least 190˚C. The side-chain length could also explain how the rate of dielectrophoresis decreases with increased alkyl sidechain length. Although these statements are mentioned regarding the attached chains, the actual migration of additives is not

further mentioned. The shortest alkyl chain gave the highest DBS but it is assumed to have the highest migration rate[38].
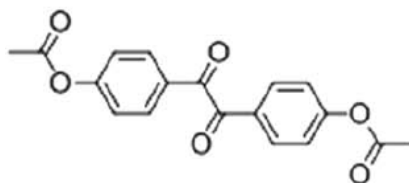
These papers inspired Zhang et al.[31] to investigate the relationship between the electrical character of voltage stabilizers and their molecular structures, and the mechanism of PE electrical breakdown strength increments at atomic and molecular levels. A systematic investigation on the tailored side-chain architecture of benzil voltage stabilizers for enhanced dielectric strength of XLPE was made. They conclude that benzil-molecules with heteroatom (O, N and S) can: 1) effectively trap hot electrons (larger electronegativity) and thus reduce the kinetic energy which is correlated to C-C bond energy breakage; 2) dissipate the energy from hot electrons to isomerization reactions (the energy of these reactions are lower than C-C bond energy); 3) prevent the bombarding of C-C bonds (lower $E_{HOMO} - E_{LUMO}$).[31]

3.2.2. Acetophenone

Acetophenone is a by-product from the crosslinking of PE, see **Figure 14**. It is known to have an effect on the electrical insulation properties of XLPE[40-43], and there are reports that show rises in AC insulation breakdown voltage for XLPE as well as reduce the electrical strength for coated acetophenone LDPE surfaces, spatial charge distribution[41]. Andrews et al.[42] investigated the effects of acetophenone on AC breakdown on degassed XLPE and found that 1,15 wt.% acetophenone increased the AC breakdown strength by 32%. It was suggested that acetophenone filled the voids present in the polymer. But this improvement was reduced with time since these small molecules migrate quite fast[42].

Zhang et al.[43] investigated the mechanisms of the valence bond isomerization of acetophenone and the effect of acetophenone on the AC breakdown strength. It was determined that the valence bond isomerization of acetophenone was the formation a Hückel structure, as it had the lowest overall potential energy barrier. They also experimented on proper amounts of acetophenone and 1 wt%, corresponding to 0.7wt% aromatic groups, led to a 50% increase of the AC breakdown strength of XLPE under treeing conditions[43].
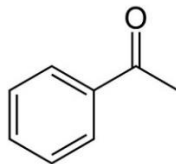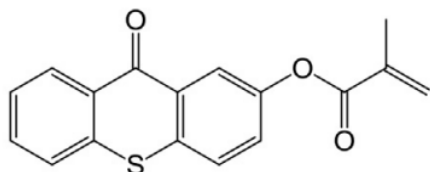

Figure 14 *The molecular structure of acetophenone*

3.2.3. Thioxanthone

Jarvid et al[2] further investigated thioxanthones based on their promising ionization potentials, previous reports on photoactivity and structural similarities to benziles. Once again the DBS was investigated with additives in XLPE under the same electrical tree initiation conditions[33] as the test for benzil compounds. Both thermal analysis, small angel X-ray scattering and gel content measurements indicated that the additives had no significant effect on the

molecular structure and gel fraction of XLPE. The highest increase in electrical tree initiation field was obtained for an addition of 0,3wt%, corresponding to 0,15 wt% aromatic groups, of 9-oxo-9H-thioxanthen-2yl- methacrylate, **Figure 15,** which increased the required field for breakdown with 55% compared to a reference XLPE. This compound contained electron-withdrawing methacrylate- functionality. They also found a trend towards increasing stabilizing effect with decreasing triplet-state lifetime of the thioxanthones. They suggested that it implies the stabilizing mechanism for these compounds is more related to impact excitation than to impact ionization[32]. Overall, the thioxanthone voltage stabilizers was not as efficient voltage stabilizers as the benzil derivates.

Figure 15 *The molecular structure of the most promising thioxanthone form Jarvid et al.[2] investigation, called 9-oxo-9H-thioxanthen-2yl- methacrylate.*

3.2.4. Fullerenes

Jarvid et al.[44] also investigated fullerenes as a VSA in polyethylene, see **Figure 16**. It was claimed that, on a molar basis, fullerenes are the most efficient voltage stabilizers that have been identified to published date of the article, 2015. As in many other investigations of Jarvid and his coworkers[5,7, 32-33], the initial focus was adding the VSA prior to the LDPE cross-linking which is most relevant from an industrial perspective. Consequently the VSA's influence on cross-linking was investigated and it was concluded that the gel content had increased compared to neat XLPE. It was proposed that these VSA participate in the crosslinking reaction and covalently bind to polyethylene. The quantity of the VSA was also measured with FT-IR spectroscopy before and after the crosslinking, and it revealed a slight decrease in the signal, which suggests that the VSA is modified during the reaction. However, as previously discussed in this thesis, aromatic compounds have a tendency to act as VSA. Although, these new compounds could possibly migrate to the surface, the intact VSA covalently bonded to the polyethylene's backbone which is a considerable advantage since it strongly reduces the risk of additive migration during the lifetime of a HVAC cable. The difference in lamellar thickness compared to neat XLPE was low according to the DSC. As a result it was concluded that any changes in dielectric strength is not caused by changes in polyethylene microstructure[44]. Finally, the electrical tree initiation test[39] resulted in a 15% increase in DBS for 1 mmol kg $^{-1}$ C_{60} and an even higher improvement of 26% was for PCBM [44]. These concentrations are related to 0,07wt% of C_{60} and 0,09wt% of PCBM and since these compounds almost entirely consist aromatic groups, these concentration also resembles 0,07 wt% and 0,09 wt% aromatic groups respectively. However, it is very important to stress that the fullerenes that do not covalently bound to the polymers could migrate and/or agglomerate, as well as the products from the destroyed fullerenes.
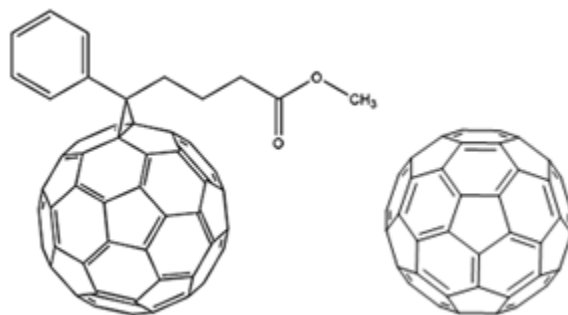
Figure 16 *The molecular structure of PCBM (left) and fullerene (right).*

3.3. Patents

Some VSA have been patented and here below are some recent patents related to these compounds are discussed.

3.3.1. Borealis

Borealis Ag published a patent[45] called "*Polyolefin composition for medium/high/extra high voltage cables comprising benzil-type voltage stabilizer*" in June 2015 which was related to Jarvid et al.[38] promising article about the different benzyl compounds described earlier. As a reference they used pellets of a LDPE called Supercure™ LS4201S, supplied by Borealis, Sweden, which is prepared by high pressure polymerization and has a density of 0.922 g/cm^3 (ISO1872-2/ISO1183-2), MFR2 (ISO 1133, load 2.16 kg, at 190° C.) of 2 g/10 min. The reference polymer was in a form of pellets and contained dicumyl peroxide as the cross-linking agent.

The pellets were grind to a fine powder in a Retsch grinder with a 500 micrometer sieve and the voltage stabilizing additives was later impregnated by a proper organic solvent for one hour while agitated every 15 minutes. The solvents were removed by rotary evaporation and vacuum oven until a dry powder was received. The powder was then molded into plaques with a thickness of 6 mm according to a specific press program, which can be seen in the Appendix. The pressed plaques was afterwards degassed at 1 atm at 90° C. for 4 days and then cut into 25.5 mm×21 mm×6 mm plates. Since electric treeing was tested, sharp needles was used as electrode and inserted into the plaque from opposite sides on each of the 21 mm×6 mm surfaces, as detailed in "ASTM D3756-97 (2004) "Standard Test Method for Evaluation of Resistance to Electrical Breakdown by Treeing in Solid Dielectric Materials Using Diverging Fields," E. Series, Ed., ed: ASTM International, 2004. They were inserted slowly under 120˚C until they were 3,5mm apart. The electrical treeing was performed under room temperature. The voltage was increased with a rate of 10V/min, starting at 8 kV and to a maximum level of 22 kV. A partial discharge detector shut off the high voltage upon detecting any discharge. A microscope was also used to give additional understanding and the results was analyzed by a 2nd parameter Weibull statistics. The final results are depicted in **Table 2**.

Table 2 *The results from the Borealis patent[46]. n: number of tested samples, Susp.: number of suspended samples, α and β scale and shape parameter respectively, obtained from Weibull statistics, TIV: tree inception voltage, ΔkV: difference in voltage between the reference and the example MVS: molal voltage stabilisation.*

	n	Susp.	α	β	TIV [kV]	ΔkV	MVS [kVkg/mol]
Reference	20	3	12.9	5.1	12.9	-	-
Example 3	10	5	21.7	2.8	21.7	8.7	1442
Example 4	10	6	29.8	2.7	29.8	16.9	2639
Example 5	10	4	18.2	2.9	18.2	5.3	1036

3.3.2. DOW

The Dow Global Technologies Ll. recently filed in a patent called "*Voltage-stabilized polymeric compositions*" and it concerns three suitable VSA, see **Figure 17**. It was claimed that these enhanced the DBS of LDPE with over 20%, and one of with over 35%, see **Figure 17**. As a reference they used a LDPE called DMX-446 from The Dow Chemical Company, Midland, MI, USA, which has density of 0.92 g/cc and a melt index of 2.0 g/10 min. The additives were melt-compounded into this reference by a Brabender mixer with a 60 rpm at 200˚C during 10 minutes. The polymer melt were removed from the mixer and compression molded in a special press-program (350 bar for 5 min at 200 °C, then 830 bar for 5 min at 200 °C, then 1400 bar for 5 min at 200 °C). The pressed plate was later cut into 4"x 4"x 0.25" pieces for evaluation of electrical properties. To get a fair distribution, standard error and time for 10 pieces were tested by AC breakdown for each sample.

The AC breakdown strength measurements was performed by utilizing needles with a tip radius of 1 μιη (=0.5-mm diameter, 1.5-inch length) and a large flat copper plate. For each test a staircase step ramp method (1 kV every 30 minutes) was used to increase in applied voltage up to a maximum 15 kV available voltage or until a breakdown was detected. The procedure was similar to the ATSM D3756-97, a well-known method. The characteristic breakdown strength for the ten values was calculated by a 2- parameter Weibull failure distribution model[46].
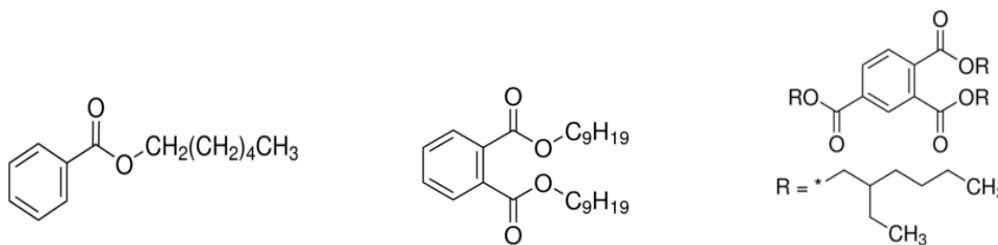
Figure 17 *The molecular structure of Dow Global Technologies Ll's molecules for their intended patent. The compound to the right gave rise to the highest increase, 37%.*

3.4. Conclusion concerning stabilizing additives

First of all, the additives need to be sufficient compatible with the polymer matrix in order for the additives to be homogenously distributed until the AC breakdown test. Long alkyl chains enhance the solubility and reduce the diffusion. Furthermore, a long alkyl chain is also of important since it reduces the effect of thermal breakdown during the AC breakdown test. Ideally, the additives would be cross-linked to polyethylene, otherwise they will diffuse, and because of that the effect of thermal breakdown is reduced. Consequently, it is desirable to resemble this crosslinking by just adding a longer alkyl chain to the aromatic core. When a suitable additive is found, the design of the additive can be slightly changed by introducing suitable crosslinking groups if the migration will be too significant. However, long alkyl chains reduce the effect of thermal breakdown but it could also enhance the effect of thermal breakdown if the VSA are cross-linked to polyethylene. Additionally Jarvid et al.[33] suggested chains longer than C_{12} could decrease the effect of the VSAs. With these hypotheses in mind, not too long alkyl chain need to be attached to the aromatic core.

Second of all, certain physical properties seem to be very important in order for the hot electrons not to attack the C-C bond (3.6eV). The right ionization potential (IP), electron affinity (EA) and excitation energy (E_{HOMO}–E_{LUMO}) are crucial. Many articles suggest that [2,7, 10, 47] the value of IP is not as important as EA and the excitation energy. Small differences E_{HOMO}–E_{LUMO} and high EA are beneficial for achieving high voltage stabilizing efficiency[7, 47]. Effective voltage stabilizers typically have a difference in E_{HOMO}–E_{LUMO} around 3,6eV and adiabatic electron affinities of ~0.5-3.5eV[7]. Molecules that fulfill these properties were assembled by an ABB employee who used the density
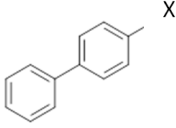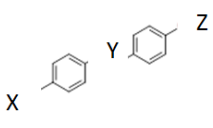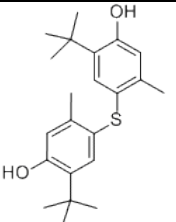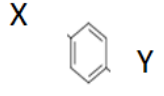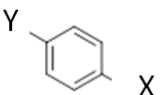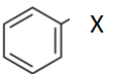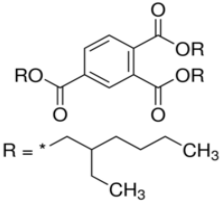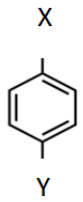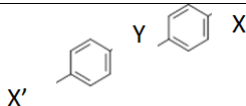
functional method (DFT modeling)[48], which is a well-known method for modeling molecular orbital energy levels and determine physical properties of VSA[31-34, 40].

Thirdly, there seems to be no clear correlation regarding the chemical species in the molecular structure. However, the optimum concentration should be relative small. Since the effect seems to depend on many parameters, such as how dispersed the additives are and number of aromatic groups in the additive's molecular structure, each additive seems to exhibit a unique optimum concentration. Approximately the concentrations should be around 0,3wt% or an aromatic concentration of 0,15wt%.

3.4.1. Chosen additives

DFT modeling gathered numerous molecules that fulfilled the physical properties (IP, EA and Ex). These were then reduced to the ones that fulfilled the other required properties mentioned above and the chosen additives are listed in **Table 3**. The antioxidant, Santonox was also chosen despite its less suitable physical properties, since it affects the DBS and it has the favorable ability to cross-link to polyethylene.

Table 3 *The additives that were tested where X, Y and Z stands for various attached groups.*

Structure	Shortening	Structure	Shortening
	A1		C2
	Santonox®		C3
	B1		D1
	DOW1		D2
	C1		

4. Experimental

The experimental procedure was inspired by DOW Global Technologies Ll's patent[46] and earlier investigations[6,18] performed by ABB. Although it was similar to DOW's method, the AC breakdown test was considerably different. This method was focused on fast avalanche breakdown and not treeing. Furthermore the references are different and no information regarding their reference, LDPE DMX-446, could be found.

4.1. Used chemicals

The used LDPE pellets has a density of 0.92 g/cm3 and a melt mass flow rate (190oC/2.16 kg) of 2.0 g/10 min and it contained antioxidants.

The additives used in this report are listen in **Table 3** and were provided by Sigma Aldrich or Alfa Aesar, all having a purity >98 %. All the additives had at least one aromatic core with various attached groups to it.

The samples that were aged were washed with ethanol and cyclohexane before the AC breakdown test. Mylar films, trademark owned by Dupont Tejjin films for a specific family of Polyethylene Terephthalate (PET), was used in the press.

4.2. Sample preparation

This preparation method involves three important steps and any failures in these will lead to unclear results. To detect any faulty measurements, a LDPE reference was always tested together with the additives. This technique also made in possible to really detect the increase in breakdown strength of an additive at that particularly preparation condition.

4.2.1. Brabender mixer

The Brabender mixer (Brabender® OHG Duisburg) was used to mix the additives into LDPE. The mixer was always carefully cleaned with a brush and the wiped off with ethanol before it was switched on. It was then run with an rpm of 30 and at 130˚C. In order to clean it further, around 80g of LDPE was firstly run during approximately 5 minutes. Then the reference of 100g of LDPE was run, during exactly 10 minutes from when a complete melt was formed, before it was removed and cut into smaller pieces with a scissor. LDPE with different concentration of additives was prepared likewise, the additives was added slowly at time 0 when a melt was formed, until everything was added. The concentrations were correlated to related weight concentration of aromatic groups.

4.2.2. Press

The reference and the additives was pressed in a hot press (Servitec Polystat 300S), into thin films in order to remove as much defects as possible and create the same crystallization conditions. The amount of 37g was placed in-between polished steel plates covered by two Mylar films and compression molded at a specific press program, see Appendix. A distance square in steel of 0.5mm and two Mylar films of 0.075 mm each were used to reach the desired thickness of 400 μm in the middle of the plate. Unfortunately, the machine could not obtain a homogenous pressure, see **Figure 18,** and thus the thickness varied between 280-500 μm.
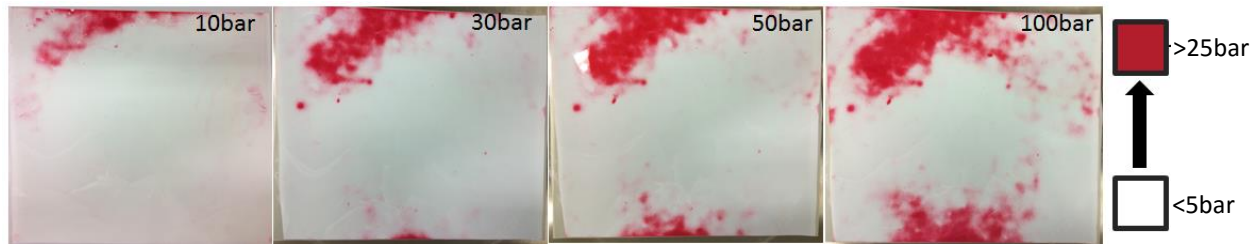
Figure 18 *Pressure test preformed at 10 bar, 30 bar, 50 bar and 100 bar on the used press machine. The test was performed in room temperature with the duration of 3 minutes. Increase intensity of red color indicate higher pressure due to a pressure indicator, maximum intensity indicate that the area was subjected to over 25 bar.*

The samples were directly after the press cut into square plates of 50x50mm and run in the AC Breakdown machine. It is important to test the samples immediately after the press in order to make sure no antioxidants or additives had migrated to the surface. Since the thickness of these plates varied a lot, fourteen of those plates were chosen according to the right thickness interval between 360-440 μm. As described earlier, a narrow distribution of samples thickness is important.

4.3. AC Breakdown test

In order to test the dielectric breakdown strength a BA 100 breakdown analyzer from B2 was used. It creates a field over two electrodes where the sample is placed in-between, see **Figure 19**. The sample is gently squeezed in between the electrodes in order to not compress the sample and not favor breakdown at a certain area. All the measurements was done by IEC 60243-1 standard, but with the exception of the electrode geometry. It is used for determination of short-time electric strength of solid insulating materials at power frequencies, that is, those between 48 Hz and 62 Hz. It does not consider the testing of liquids and gases, although these are specified and used as impregnates or surrounding media for the solid insulating materials being tested[49]. In order to force the breakdown through the sample, Castrol oil, with a dielectric constant of 4.5 at 26˚C, was used as the surrounding medium. The AC had a frequency of 50 Hz and the ramp rate was 0,5kV/s until a breakdown occurred. The samples were always tested with every other LDPE reference at same occasion which was prepared equally. The oil was always changed after either 3 occasions of the same additive or when a new additive was introduced. Since carbon is created from the breakdown, carbon residue had to be removed to the corners. The creation of carbon made it usually possible to detect a black dot in the sample. The thickness at this breakdown spot was measured with a thickness meter with a precision of one micrometer. If a breakdown spot was not observed, the breakdown spot was assumed to be found in the middle of the sample and, thus, the thickness of four different spots close to the middle, was measured instead.

4.3.1. Electrodes

The electric field over the electrodes depends on the shape of the electrodes. A curved electrode, mushroom shaped, creates a homogenous field but on the other hand it has a small connection to the sample. Flat shaped electrode has a large connection to the sample, but the sharp edges create a heterogenic field which favors breakdowns at the edges[50]. Rogowski electrodes, however, is a mix of flat and mushroom shaped electrodes. It has a specially designed smooth shape to minimize the electric field at its' ends, see **Figure 19.** It creates a more homogenous electric field[51] compared to flat electrodes, and can thus generate higher breakdown values. The three different electrodes was accordingly tested in order to find the most suitable electrode.

Figure 19 *The oil bath in the BA 100 breakdown analyzer with different electrodes that could be used to test different materials DBS with AC breakdown; Mushroom shaped electrode (left), Flat shaped electrode (middle) and Rogowski shaped electrode (right). The Rogowski shaped electrode geometry was used for AC breakdown tests and the Mushroom shaped geometry was used for Lighting impulse tests*

4.4. Lightning impulse test

Overvoltages caused by lightning strikes are common in HV transmission systems, which can be simulated in a high voltage laboratory. It is thus interesting to perform light impulse tests. Light impulse testing test the samples during a quick impulse of AC. The impulse is so quick that the only mechanism that can break the material is fast avalanche breakdown. A positive pulse with a rise time of 1 µs and 50µs decline period was given to the sample starting at 50 kV, following with a gradual increase of 5 kV until breakdown occurred. Since the brass sticks, that the electrodes are mounted on, were slightly tilted for the impulse testing cell, the mushroom shaped electrode was needed. Mushroom shaped electrodes were used[6].

4.5. Characterization methods

Earlier investigations performed by Jabri et al.[6] quantified the concentrations of different additives with FT-IR and the result indicated that Brabender mixed homogeneously and the intended concentration was valid upon testing for additives with similar properties. [6]

4.5.1. Microscopy

Impurities and air bubbles was detected by optical microscopy (OM) (Olympus AX70) and by a more precise microscopy, scanning electron microscopy (SEM) (EVO MA15), which utilizes electron beams to create an image of the surface. OM was also an easy method for determine any migration of the additives to the surface. Migration could also be detected by the eye.

4.5.2. Differential Scanning Calorimetry

Differential Scanning Calorimetry (DSC) is a thermal analytical technique which measures the difference in amount of energy required to increase the temperature between a material and a reference material with a well-defined heat capacity. The sample and the reference have the same temperature always and the temperature increases linearly as a function of time. The method is excellent to determine the crystallinity of a polymer and to determine if the additives have any effect on the crystallinity. This investigation used a Mettler Toledo DSC at a heating/cooling range of 10 °C/ min under nitrogen atmosphere. Additionally, DSC was also used to check how homogenous the cooling rate was in the press machine.

4.6. Evaluation of breakdown results

The results from the AC BD tests were evaluated by the Weibull distribution, a continuous probability distribution of extreme values. It is the most frequently used technique in characterizing failures in solid insulators. It is based on the probability of failure of a chain with *n* links being equal to the probability of failure in its weakest link. From that assumption, the Weibull distribution function P(x) is given, see **Equation 3**.

$$P(x) = \begin{cases} 1 - e^{\left(\frac{x-c}{\alpha}\right)^{\beta}} & for\ x \geq 0 \\ 0 & for\ x < 0 \end{cases} \quad \textbf{Equation 3}$$

Equation 3 is a cumulative distribution function, giving the probability for failure to occur at value X≤x. The α-parameter is the scale parameter and refers to the 63.2% probability for the failure to occur analogous to the mean of the Gaussian distribution, i.e. P(x) =63.2% if x=α. The scale parameter is the most convenient to use in order to evaluate the VSA efficiency since it is not influenced significantly by lone extreme values and is therefore a more reliable statistic[52], especially when using small data sets as in this case. The β-parameter, known as the shape parameter, refers to the form of the distribution which is correlated to the slope of the linear regression through the samples. The higher the shape parameter, the less scattering is obtained between the samples and the slope of the linear regression becomes steepened. A high shape factor is important since a higher value of breakdown, at low probability of failures, increases. The c-parameter refers to a threshold value below which P(x) =0. However the physical reason for the use of this parameter it is not clear and as in many other cases the c-parameter is here set to zero. Consequently, a "2-parameter Weibull distribution" was used.

In order to plot the results, the measurement data is sorted in increasing order. Then a cumulative failure probability P(*i,n*), approaching P(x), should be assigned to a discrete value, where *i* stand for the rank of the ordered data point and *n* for the total number of measurements. A superior approximation for the cumulative probabilities is given by the median rank approximation[53], see **Equation 4.**

$$P(i,n) = \frac{i-0,3}{n+0,4} \quad \textbf{Equation 4}$$

In short, the breakdown will always occur at the weakest point in LDPE. All the samples will be ranked in an increasing order where each number will correspond to a certain probability of failure, depending on how many samples that will be tested. In this investigation fourteen samples were mostly tested.

5. Results and discussion

5.1. Effect of electrode

As discussed in the experimental section, different electrodes generate different breakdown strength. The scale factor increases with a smaller active area since the probability of encountering a defect becomes smaller. Due to the same reason the shape factor reduces for smaller active areas. As a first step of the thesis, three different brass electrodes where tested in order to evaluate the most suitable shape for further experiments. The results in **Figure 20**, entails, as Kulkarni[50] also observed, mushroom shaped electrodes with an active are of 20 mm^2, to be less favorable compared to flat electrodes since it scatters the most and gives the highest breakdown strength. The flat electrode had an active area of 491 mm^2 and was gently grounded and polished before use. It exhibits lower breakdown strength due to the probability of encountering a defect in the material is higher and, as mentioned in the theory, defects act as active centers for breakdowns. From that clarification, the larger surface area will also provide a narrow distribution since the breakdown will always occur in the weakest point in-between the electrodes. The low scatter makes it more accurate to determine significant changes in AC breakdown strength between different materials. The Rogowski electrode creates a more homogenous field, and thus it gives higher breakdown values than flat-shaped electrodes. However it is not as homogenous as mushroom shaped electrode. Consequently, the results in **Figure 20** indicate that the Rogowski electrode, with an active area of 314 mm^2, gives breakdown values in-between flat- and mushroom shaped electrode with a narrow distribution, shape factor of 21,3. Thus, it is the most suitable choice of electrode for further experiments. The results from the reference LDPE that was tested with flat shaped electrodes, are also in line with previous work[6] performed with the same preparation method, this is also further proved by another test with flat shaped electrodes which can be found in the Appendix. The conditions for this method have consequently not changed significantly during the last year. The Rogowski electrode was also gently grounded and polished but unfortunately after this test.
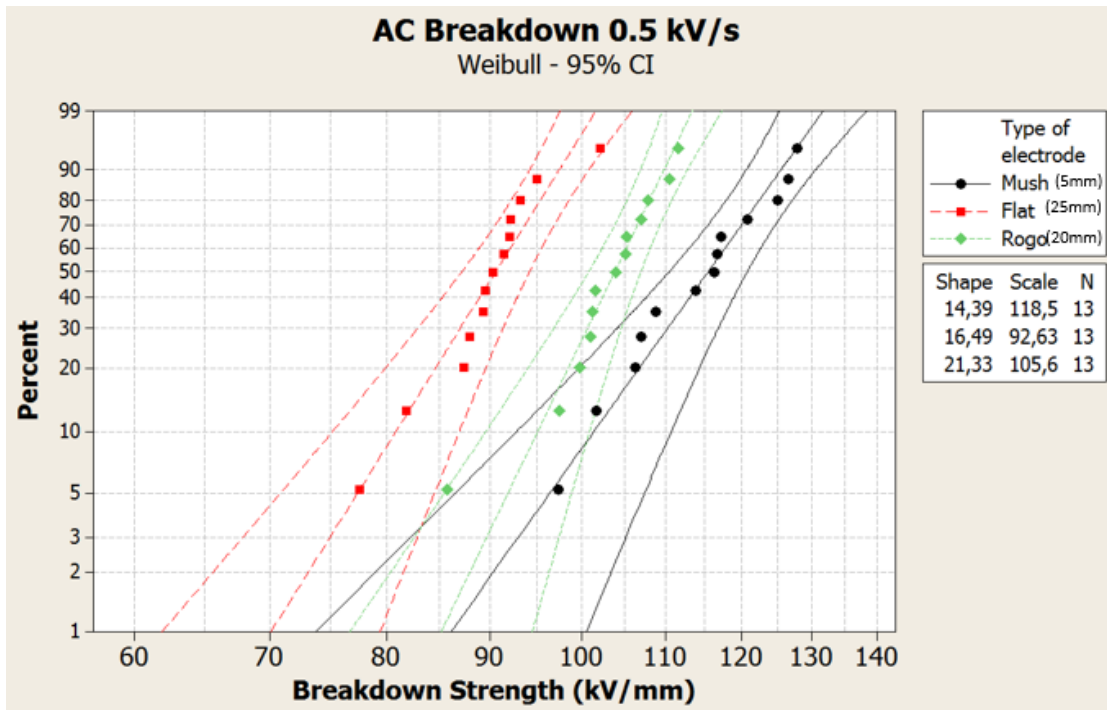

Figure 20 *A Weibull plot with 95% confidence interval with the results from the LDPE reference with different geometries of electrodes with their corresponding diameter of their active area. N indicates number of samples and high values of Shape indicate a narrow probability distribution. All the samples were pressed at 200bar.*

5.2. Effect of sample preparation

As a second step in the thesis, defects in the pressed LDPE plates were investigated. This was important to investigate in order to make sure any enhancement of DBS is mainly due to the intended effect of VSA and not VSA's interaction with defects. The additives might migrate towards air bubbles, fill them and thus increase the DBS by absorbing the electrons before they accelerate in the air bubbles as Andrews et al.[42] indicated. Additionally, larger air bubbles reduce the breakdown strength according to Paschen's law. One might possibly think that the pressure in the sample preparation could be increased to remove these bubbles. Consequently a microscopy investigation was firstly made on the amount of air bubbles and impurities in the samples. Neat LDPE was prepared, as always, in the Brabender and pressed at two different pressures, 200bar and 350bar. It was concluded that no clear difference could be seen in either OM or SEM, see **Figure 21, 22 & 23**. The microscopes did not reveal any major impurities neither did it reveal any large air voids i.e. > 1- 2 µm in diameter. It was thus concluded both the Brabender and press-machine works fine in those aspects. No major differences could either be seen in the Weibull plot, see **Figure 24**. However since the press machine did not press homogenously, 350bar was considered as the suitable pressure for further experiments.
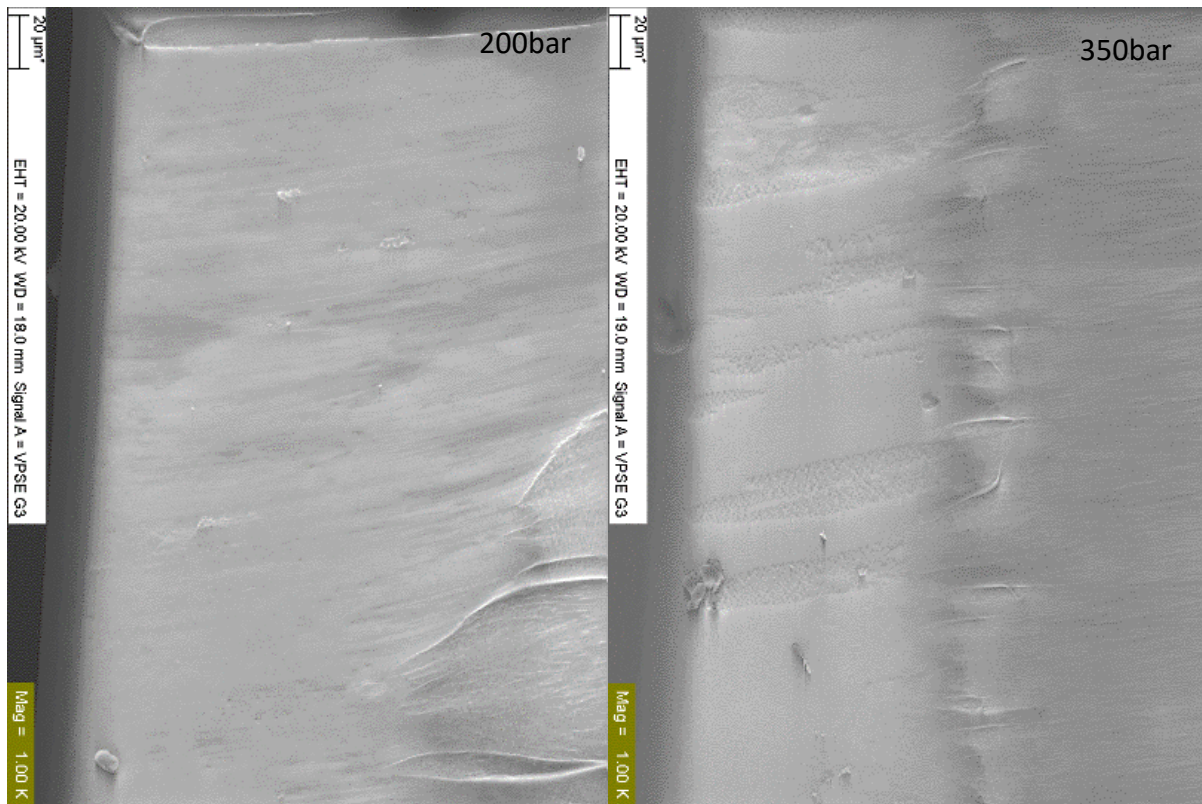

Figure 21 *SEM cross section pictures, scale 20 µm, of LDPE pressed at 200bar and 350bar different pressures. No major differences could be seen*
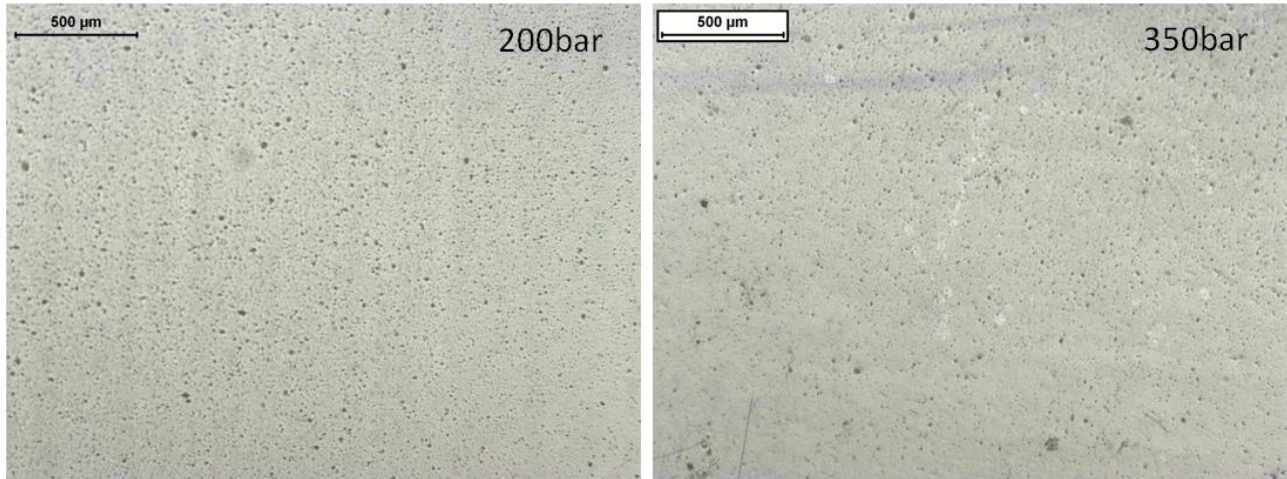
Figure 22 *OM surface pictures, scale 500µm, of LDPE pressed at 200bar and 350bar. No major differences could be seen. The majority black dots, in the pictures below, depict the spherulites of PE. No particular difference could be seen in these images.*
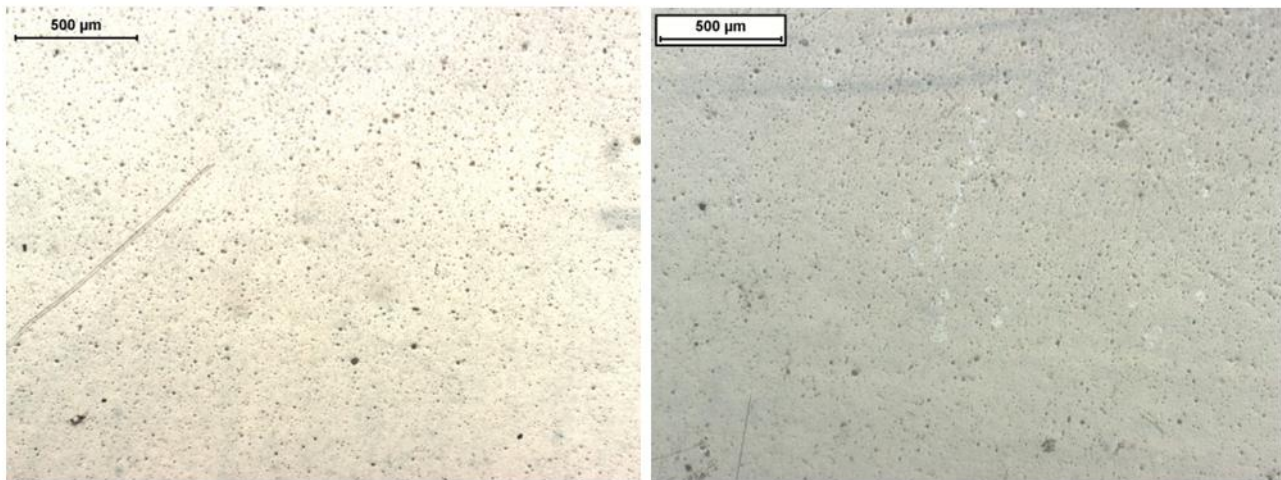
Figure 23 *Microscope pictures of LDPE at different locations pressed at 350bar after 6 days, the majority black dots depicts the spherulites of PE. No particularly difference could be detected between the different locations*
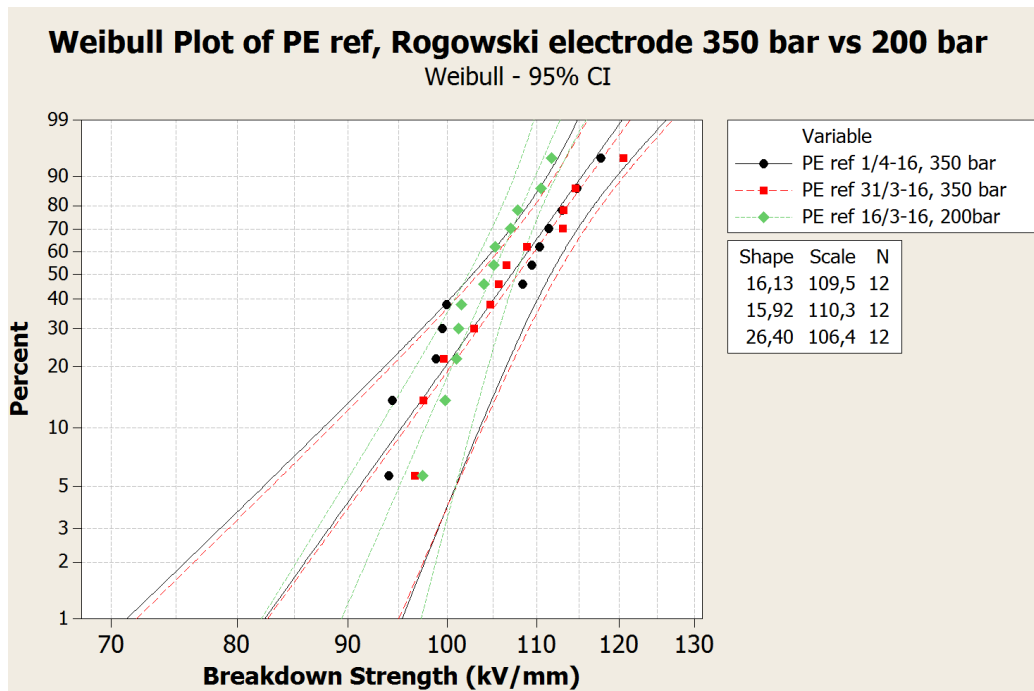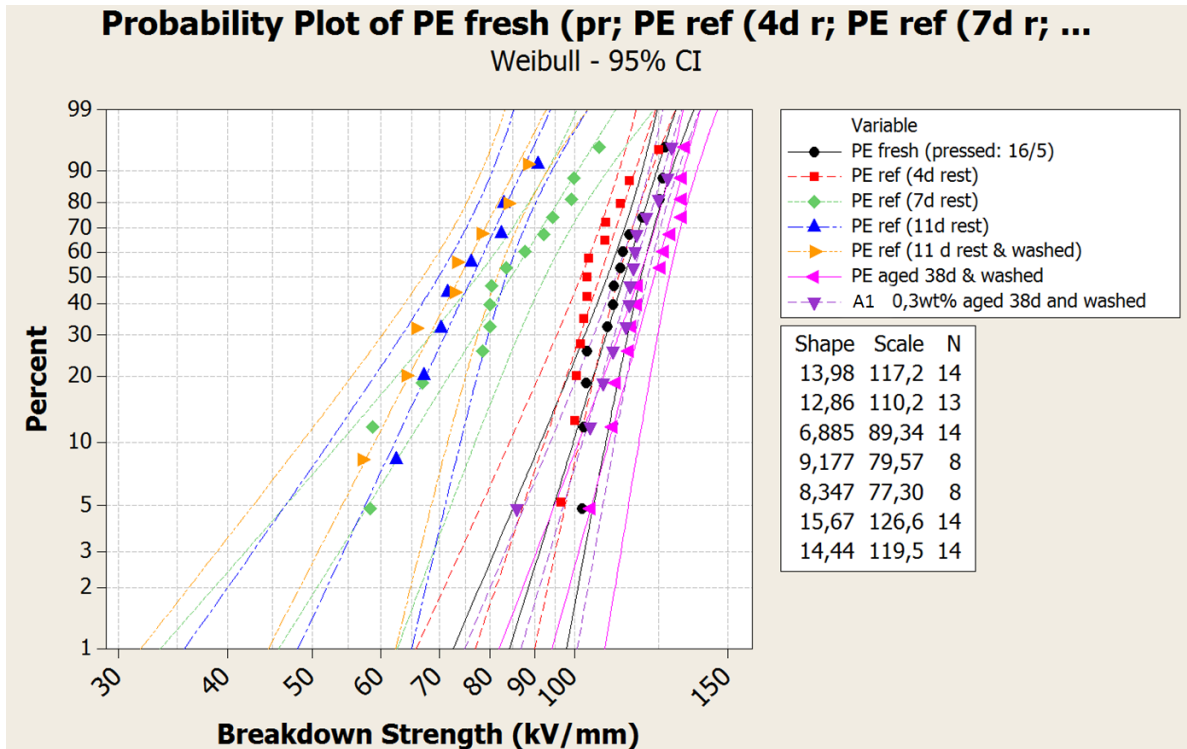
Figure 24 *Weibull plot with 95% confidence interval of LDPE references pressed both at 200bar or 350bar and tested with the Rogowski-shaped electrode. N stands for number of samples*

5.3. LDPE ageing

As mentioned in the section Theory, the antioxidant Santonox® impacts the breakdown strength. The amount of Santonox® was, however, not known. To test how much impact the Santonox® could have in our LDPE with unknown concentration, some polyethylene plates were pressed and aged during a different amount of days in Mylar films in room temperature. In **Figure 25** one could easily see the strong impact time has on the breakdown strength. It was believed that the significant decrease could depend on the Santonox® that had migrated to the surface on the samples. However this hypothesis was rejected since the reference that had been aged eleven days showed basically the same result as the reference that had been aged the same amount of days but was carefully rinsed during one minute, first using ethanol and thereafter cyclohexane. Surprisingly, the samples that had been aged 38 days in Mylar films, exactly like the others, showed an increase of 10%, for both the reference and for the LDPE containing the additive A1. These ambiguous results were probably due to the diffusion of oligomers and carbonyl compounds from the Mylar film. This hypothesis was further investigated with a new ageing condition. Now, the pressed plates was not covered in Mylar films but instead hanged in room temperature air. By comparing the results from the new ageing conditions in **Figure 26** with the results in **Figure 25,** it is clearly indicated that the Mylar-films can affect the DBS. In short, the time did not have as significant affect when the samples were not in contact with Mylar-films. The slight decreases in DBS are most likely due to the migration of Santonox®. The results also indicate that Mylar-films might not be a suitable to use in the press. However, since only the relative increase in DBS were to be tested the effect of the Mylar-films was assumed to not affect the end results, by assuming that the compounds migrating from the Mylar-film into the samples did not interact with the VSA.
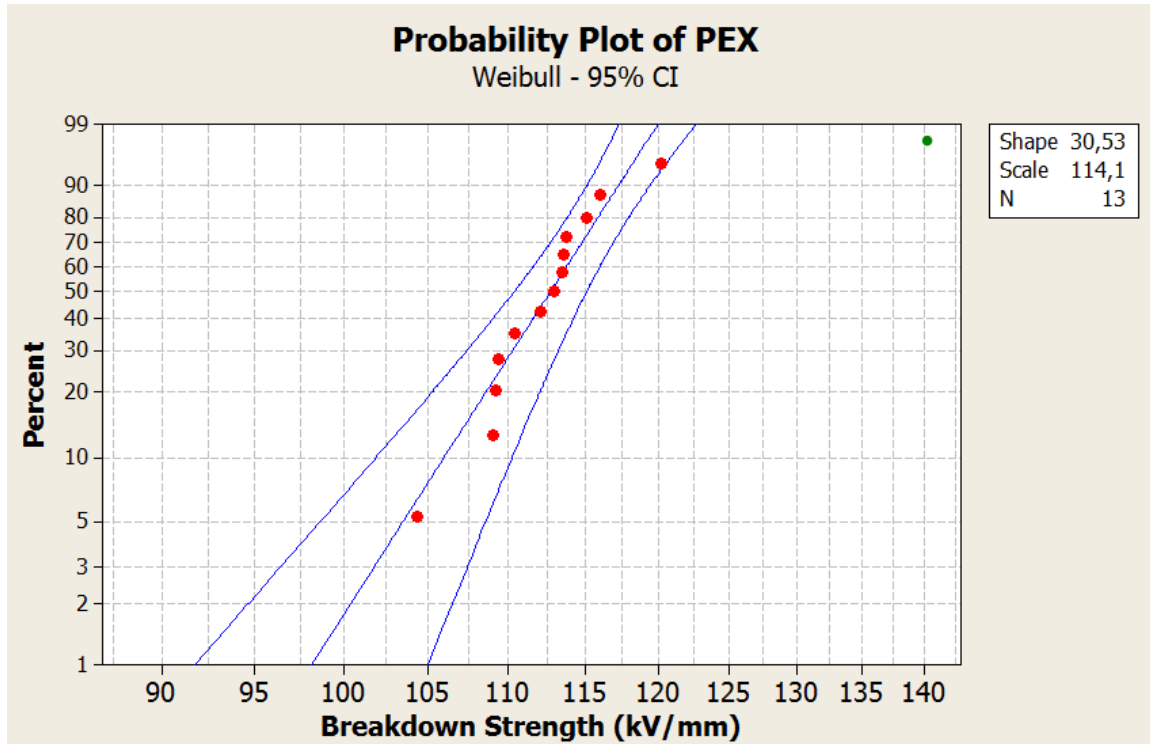
Figure 25 *Weibull plot with 95 % confidence interval of the reference polyethylene and the additive A1 aged between Mylar-films different amount of days. "Washed" means that the samples where rinsed with ethanol and cyclohexane, one minute respectively. N stands for number of samples*
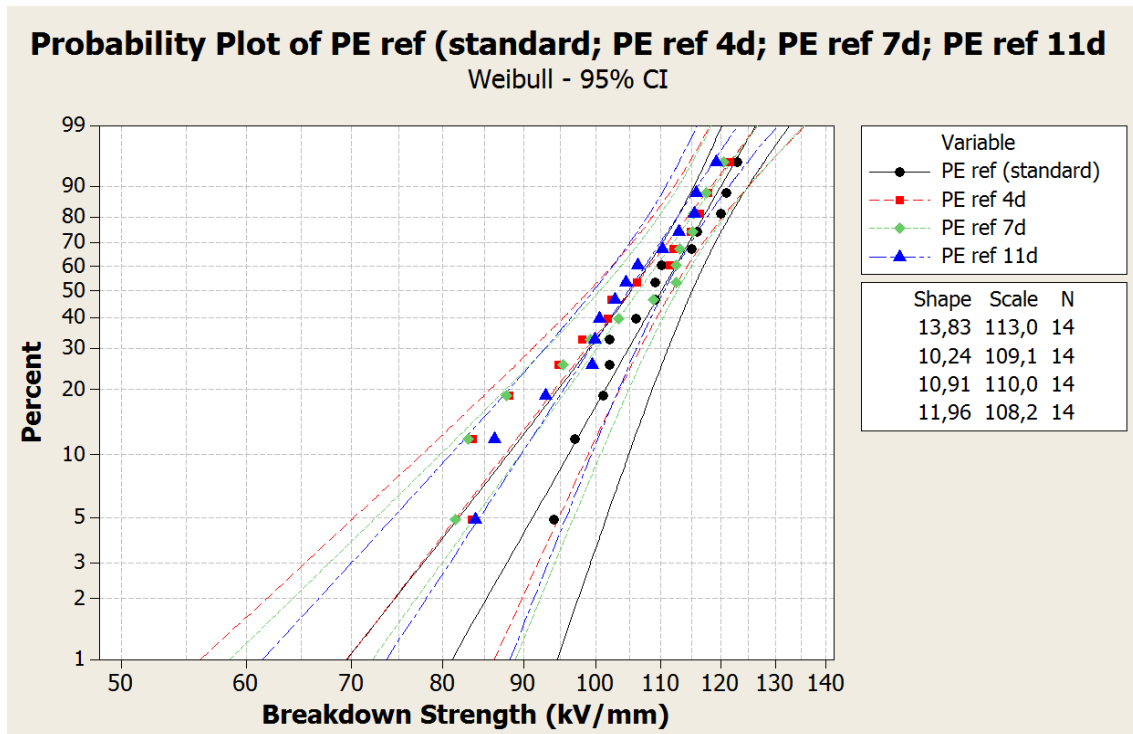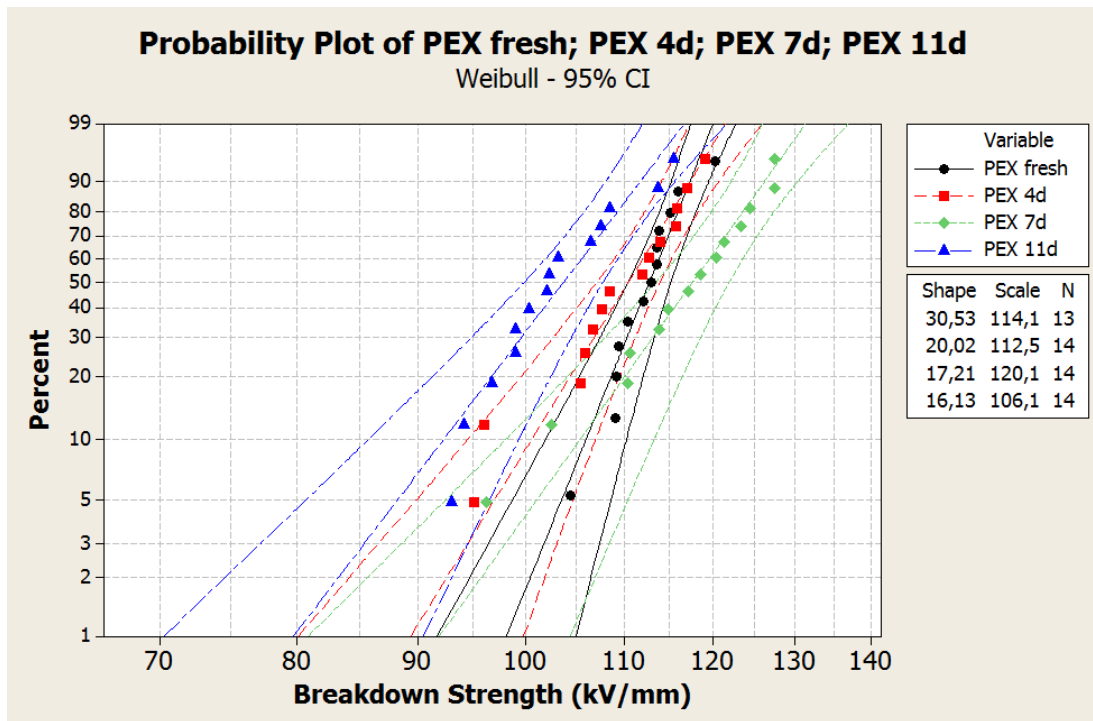

Figure 26 *Weibull plot with 95 % confidence interval of the reference polyethylene aged different amounts of days by hanging in room temperature air. N stands for number of samples*

5.4. LDPE in comparison to XLPE

Olsson et al.[30] tested an XLPE which gave basically the same breakdown strength as our ordinary LDPE . XLPE should only increase the breakdown strength slightly by reducing the impact of thermal breakdown of attached antioxidant and by the by-products from the crosslinking process. The additives that were tested would, thus, probably give the same result for LDPE as for XLPE (PEX), when the byproducts had left. The results, in **Figure 27 & 28**, from the same ageing condition as LDPE (hanged in room temperature air) indicate that the PEX roughly gets down to the same breakdown strength as LDPE. In short, a LDPE reference could be used instead of a XLPE reference since the same end results would be given. A XLPE reference would be much more complicated to use since one must here also consider the diffusion of the decomposition products of the peroxide.

Figure 27 *Weibull plot with 95 % confidence interval of XLPE. The green dot was left out since it was considered to be an extreme value; it increases the scale by a factor of 4kV/mm and reduces the shape by a factor of 20. N stands for number of samples*

Figure 28 *Weibull plot with 95 % confidence interval of XLPE aged by hanging in room temperature air during different amounts of days. The samples that were aged where washed with ethanol and cyclohexane, one minute respectively, which generated a cleaned surface. N stands for number of samples*

## 5.5.   Variation within the polyethylene references

The reliability of the method could be determined by comparing the references. However, it was realized in the beginning that the antioxidant Santonox® in the LDPE had migrated out from the pellets inside the LDPE-bag and may have fallen down. Antioxidants have, as discussed, a well-known effect on the breakdown strength[30]. Consequently it was believed that the result from the reference could depend on where the pellets in the bag where taken. To avoid these deviations, the LDPE-bag was shaken. The result of this can be seen in **Table 4** and in the Appendix, where some of the references are gathered before and after the shake. No clear variation could be seen in the scale factor, but the shape factor increased slightly after the shake. The distribution of Santonox® becomes more homogenously distributed and all the pellets get the same amount of Santonox® on the surface. Santonox® on the surface of the pellets is, however, not a problem since it gets incorporated in the polymer matrix during the mixing process. This shake made sure that the results would not depend on where the pellets where taken.

Variation between the experiments may also be due to how thoroughly the Brabender was cleaned between the experiments. Black soot could be found in the Brabender after use and it was believed be due to burned antioxidants. This soot could be whiped of with tissue and ethanol but the importance running the Brabender with LDPE afterwards can be seen in the Appendix. Deviation may also be due to heterogeneously electric field between the Rogowski electrodes or just by the fact that the weakest link in the material may be very random, extreme values can change both the scale and shape factor significantly.

Table 4 *A compilations of Weibull statistics of LDPE references preformed before and after the bag was shaken. The reference where tested in the order from the oldest (before) to the newest (after). All the references where tested with 14 square plates with a thickness of 360-440µm. The shake had some effect on the shape factor, ß.*

	Shape factor, β	Scale factor, α (kV/mm)
Before the bag was shaken	8,6	111,6
	9,6	105,6
	10,1	116,5
After the bag was shaken	18,5	111,5
	16,6	112,6
	16,1	117,2
	14,6	115,3
	15,4	113,9
	18,6	115,0
	15,4	112,4
	18,4	115,4
	14,0	117,2
	18,3	109,7
	11,4	112,4
	17,0	116,5

The mean value for the scale factor and the shape factor after the bag was shaken was established to 114.5kV/mm and 16,4 respectively, see **Figure 29**. The standard deviation for the scale factor and the shape factor after the bag was shaken was established to 2.0kV/mm and 1.7, respectively, see **Figure 29.** The reliability of this method was acceptable.
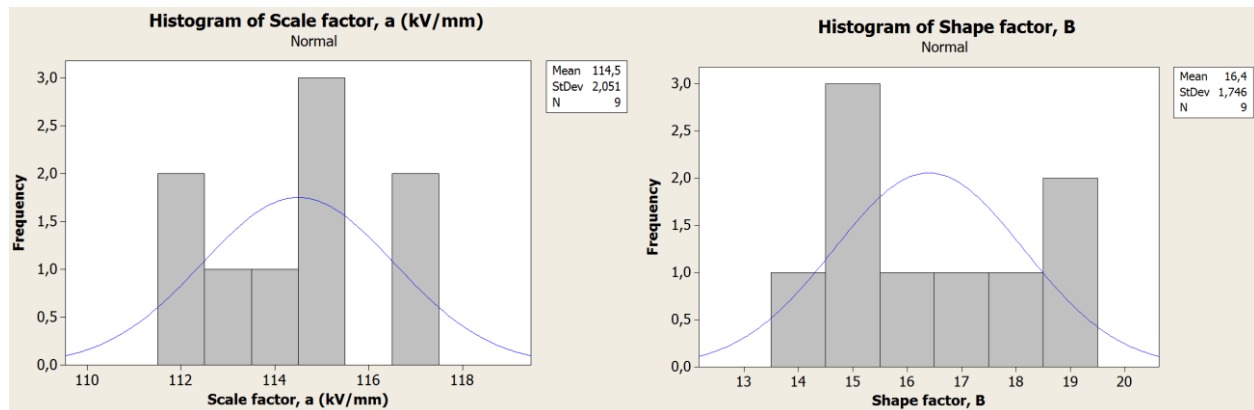

Figure 29 *Histogram plots of all the scale and shape factors obtained from the Weibull distribution of the polyethylene references after the bag was shaken. The mean value for the scale factor and the shape factor was established to 114,5kV/mm and 16,4, respectively. The standard deviation for the scale factor and the shape factor was established to 2,0kV/mm and 1,7, respectively.*

5.6. Effect on crystallinity

The variations of the results could perhaps depend on the disproportional cooling rate at the pressed metal plates in the press machine. The DSC analysis in **Figure 30** indicated, however, a homogenously distributed cooling rate in the press machine. The crystallinity of a sample from a corner (3 cm from the sides) and from middle gave principally the same values. Surely, the corners can deviate from each other, but this investigation showed the deviation was most likely small. Two samples taken from the middle exactly beside each other also resulted in the same crystallinity, which can be seen in the Appendix. The crystallinity of a LDPE pressed plate was determined to 47 % ±1 % and the melting temperature to 114˚C. The sudden increase at 175˚C for the LDPE sample, taken from the middle, was explained by impurities.

Furthermore, it was important to investigate if the crystallinity was affected by additives. The largest additive C3 with a relative high concentration was tested and the result indicated no effect. This further verifies the intended effect of the additives.
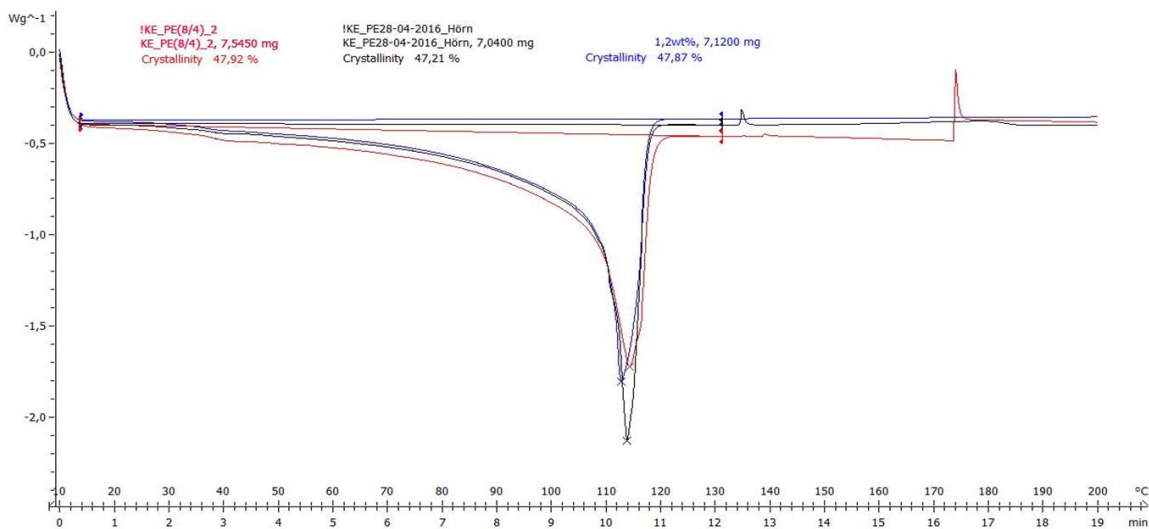
Figure 30 *A differential scanning calometry (DSC) plot of two samples of LDPE (red lines resemble a sample taken from the middle and black lines resemble a sample taken from the corner) and a sample of LDPE containing 1,2 wt% of the additive C3 taken from the corner is resembled by blue lines . The normalized weight effect (W/g) is plotted to temperature (˚C) and time (min).*

5.7. Results of the additives

First of all, all the samples that were tested had a clear and homogenous appearance in all cases which indicates a homogenous distribution of the voltage stabilizers. Previous investigations performed by ABB have quantified the concentrations which also indicated homogenous distribution upon testing[6]. However, almost all the additives, no matter concentration, had migrated within the duration of the thesis (4 months). This could easily be detected by the eye and images from the OM microscope clearly demonstrate this as well. **Figure 31** clearly shows migration of the additive A1, which was one of the additives that migrated the fastest. This finding also correlates with the diffusion coefficients and calculations of large molecules found in the literature[10]. Consequently these are not good alternatives for a HVAC cable. However, as previously discussed, it might be possible to adjust the molecular structure of the additive so it might be able crosslink to polyethylene, which obviously hinders the diffusion. On the other hand, adjusting the structure probably change the physical properties. Still, the additives reduced the impact of thermal breakdown due to alkyl chains and thus resembled a cross-linked scenario.

Figure 31 *Microscope pictures of LDPE containing 0.3 wt% of the additive A1 (initial) at different locations after 4 days. The pictures clearly prove agglomeration and migration of A1 as well as different locations have different spots of additive agglomeration.*

Worth mentioning is that, even though the concentration was correlated to the same weight concentration of aromatic groups, the aromatic groups are more dispersed in polyethylene for those compounds that contains less aromatic groups in their molecular structure. It was, however, believed this was a better choice of comparison in this case than the comparison of weight percent. All the results from the Weibull plots of the references and the additives are listed in **Table 5**, the corresponding Weibull plots can be seen in the Appendix, and a concluding graph can be seen under the comparison section.

Table 5 *The best results achieved. The corresponding weight concentration of aromatic groups is left out due to confidential reasons.   *Indicate less than 14 samples were tested, ᴹ indicate the mean value of the reference*

| Additive	Conc. (wt %)	Scale factor of the reference (kV/mm)	Scale factor of the additive (kV/mm)	Relative increase in Scale factor (%)	Shape factor of the reference	Shape factor of the additive	Relative increase in Shape factor (%)
A1	0,05	108,6*	111,3*	+2,5	17,6	27,1*	+54
	0,2	112,4	114,6	+2,0	15,4	14,1	-8
	0,3	111,0*	118,1	+6,4	9,4*	13,9	+48
	0,8	115,4	117,2	+1,6	18,4	11,6	-37
	1,0	114,7	112,8	-1,7	9,5	14,3	+51
	1,6	115,4	114,3	-1,0	18,4	15,7	-15
Santonox	0,3	115,3	114,6	0	14,6	24,4	+67
	0,5		117,0	+1,4		17,6	+21
B1	0,1	111,6	117,1	+4,9	8,6	11,2	+30
	0,3	114,1ᴹ	116,8	+2	16,2ᴹ	26,7	+65
	0,4	105,6	122,0	+15,5	9,6	14,3	+49
DOW1	0,2	116,5	112,7	-3,2	17,0	16,1	-5
	0,7		117,5	+0,9		17,3	+2
C1	0,2	116,5	114,8	+1,7	10,1	16,3	+61
	0,3	112,6	119,6	+6,2	16,6	17,1	+3
	0,5	111,5	117,1	+5,0	18,5	22,2	+20
	1,6		115,7	+3,3		23,9	+29
C2	0,3	117,2	116,3	-1,0	16,1	14,7	-9
	0,5		112,0	-4,4		16,6	+3
C3	0,7	113,9	118,8	+4,3	15,4	12,9	-16
	1,2		109,6	-3,8		19,3	+25
D1	0,2	109,7	118,0	+7,5	18,3	14,8	-19
	0,5		118,5	+8,2		17,5	-4
D2	0,2	112,4	111,0	-1,2	11,4	19,7	+73
	0,6		115,0	+2,2		16,1	+41

5.7.1. Additives with short alkyl chains

5.7.1.1. The additive A1

The first additive, A1, was interesting to investigate since it was the cheapest and for that reason it was tested the most. However this compound did not increase the DBS significantly for AC breakdown tests. Neither did it increase the breakdown strength for impulse test, see **Figure 32,** which indicates that thermal breakdown is not significant for the AC breakdown test at least for this compound. Furthermore as mentioned earlier, it migrated relativy fast. However the results in **Figure 33** from the same ageing condition as LDPE, hanged in room temperature air, suggest that migration does not affect the DBS significantly. It can thus be concluded that this additive is not suitable as a voltage stabilizing additive for increasing the breakdown strength for polyethylene in a HVAC cable.
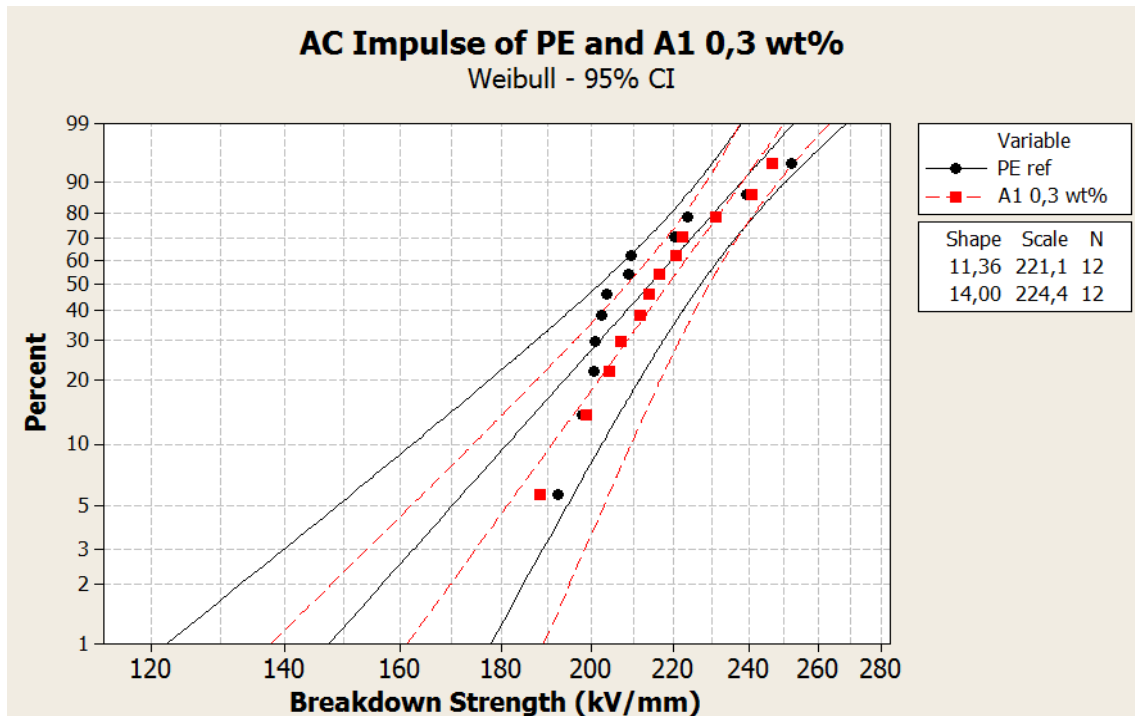
Figure 32 *Impulse test, Weibull plot with 95 % confidence interval of the reference polyethylene and the additive A1. The addition of 0,3 wt% A1 to polyethylene resulted in a 1,5% increase in breakdown strength. N stands for number of samples.*
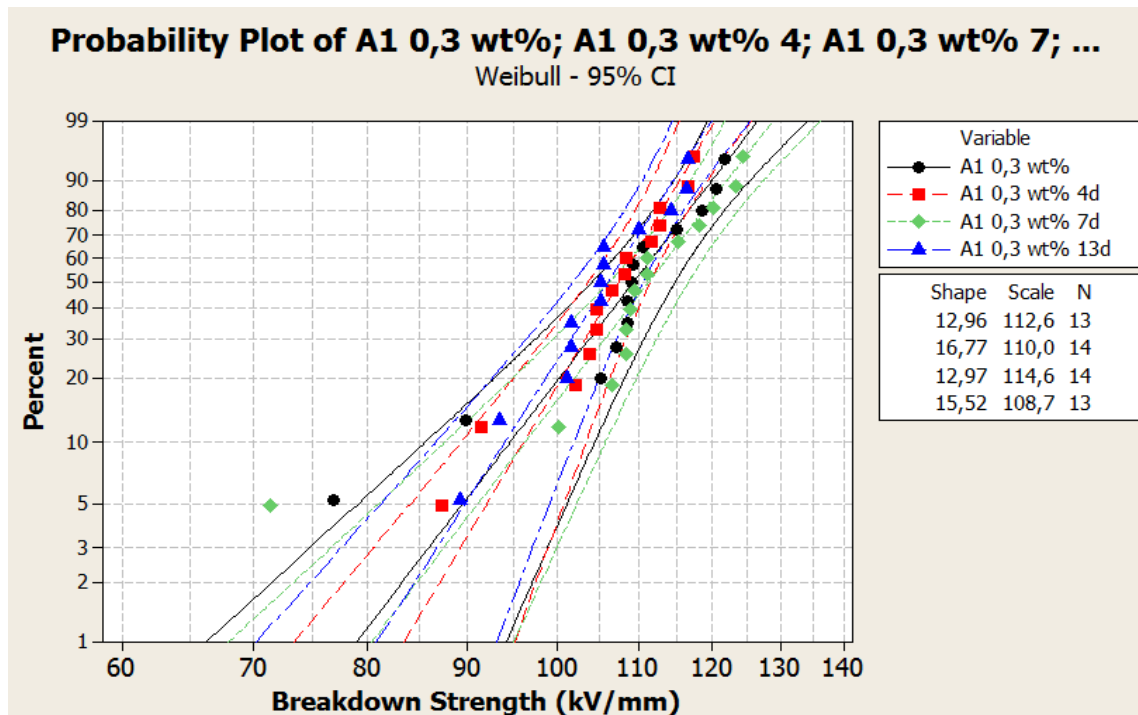
Figure 33 *Weibull plot with 95 % confidence interval of polyethylene containing 0,3 wt% of the additive A1 aged by hanging in room temperature air different amounts of days. The samples that were aged where washed with ethanol and cyclohexane, one minute respectively, which generated a cleaned surface. N stands for number of samples.*

5.7.1.2. The antioxidant Santonox®

Since it is known that Santonox® increases the DBS in LDPE and it also has the favorable ability to crosslink, this additive was also tested. It did not, however, exhibit as promising physical properties as the other additives, but still it had some short alkyl chains attached to its core. Santonox did, unfortunately, not cause any increases in DBS and it migrated at least as fast as the additive A1. The additives with the shortest chains, thus, migrated the fastest.

5.7.2. Additives with intermediate alkyl chains

5.7.2.1. The additive B1

The second additive, B1, generated the highest increase in breakdown strength of 16% with a concentration of 0,4wt%. However the main reason behind this large increase was the low scale factor of the PE ref and it was tested before the PE pellets were homogenized by shaking the container.. A similar concentration of 0,3wt% did not result in any significant increase which also indicates that the increase of 16% was unreliable. Furthermore, this additive contained chloride and was corrosive which could degrade PE. No clear migration could be seen, but objects that was in touch with the LDPE contained B1- plates resulted in a discoloring and the plates smelled. As for the additive A1, a simple ageing test, where the samples hanged in air in room temperature, also reveals migration or degradation since the BD decreases over time until it gets down to LDPE reference values, see **Figure 34**.
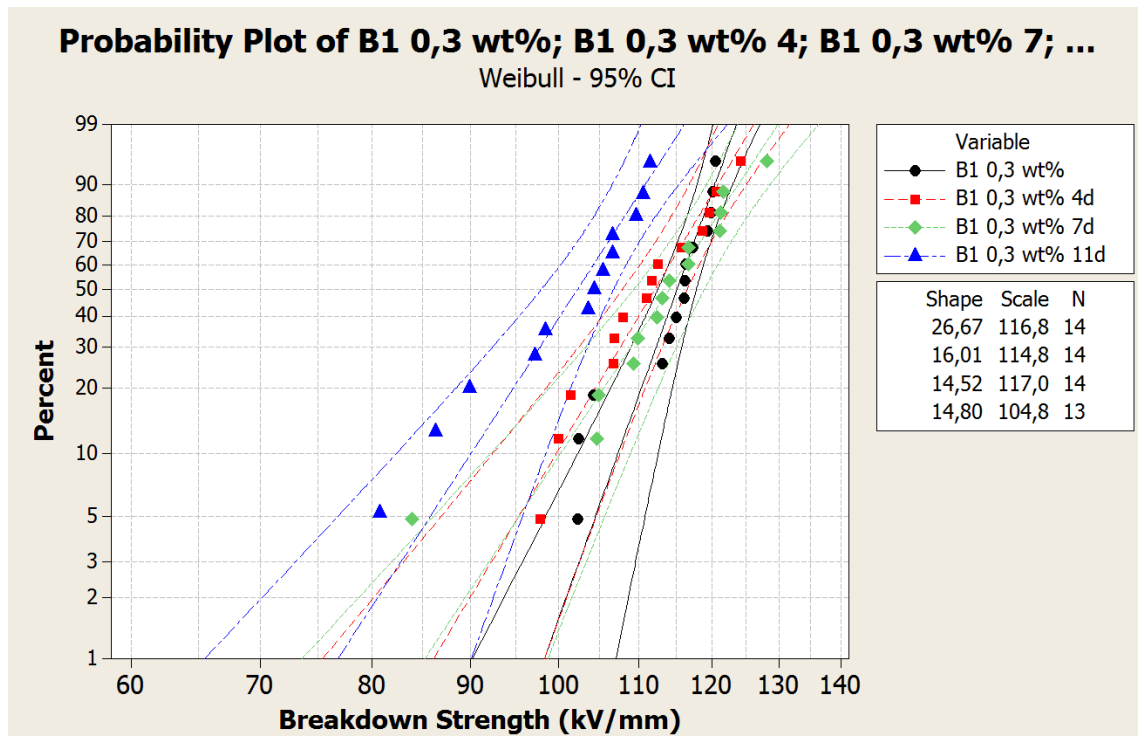
Figure 34 *Weibull plot with 95 % confidence interval of polyethylene containing 0,3 wt% of the additive B1 aged by hanging in room temperature air different amounts of days. The samples that were aged where washed with ethanol and cyclohexane, one minute respectively, which generated a cleaned surface, before the test. N stands for number of samples.*

5.7.2.2.   The additive DOW1

It was especially interesting to test DOW Chemical Company's best additive that they claim in their patent to increase the required electrical field for treeing by >35%. In this investigation this additive did not show any effect in DBS. Neither did it increase the shape factor significantly. In that aspect, this additive is not suitable as a stabilizing additive for HVAC cables. And it also shows that the enhancements in electrical treeing resistance may not be comparable with increases in DBS. However, their large increase in electrical treeing resistance might be due to their reference has worse insulation properties which may be easier to increase.

5.7.3.   Similar additives with intermediate alkyl chains

5.7.3.1.   The additive C1

The additive C1 showed at first some promising result since the increase in DBS was fairly high between large concentration intervals. However, when the results from two concentrations were being reproduced, no clear increase in DBS could be seen, see **Figure 17** in Appendix. These ambiguous results further demonstrated that the increases are within the LDPE reference confidence interval. Furthermore, C1 clearly migrated.

5.7.3.2.   The additive C2

C2 was an additive that was almost identical to the additive C1. Nonetheless, it showed no significant increase as C1. But it was not believed, however, that the differences were due to the slight change in molecular structure. It was more reasonable to believe it was in the confidence interval as C1 and by coincidence it showed a lower increase. Consequently, neither the additive C1 nor the additive C2 causes significant increases in DBS. No migration differences could either be seen between these two additives.

5.7.3.3.   The additive C3
The additive C3 had large anchors attached to its aromatic core. Because of that, C3 migrated the slowest and no clear migration could be seen within the duration of the thesis. On the other hand, it did not generate any significant increases in DBS and thus not investigated further.

5.7.4.   Additives with long alkyl chains

5.7.4.1.   The additive D1
The molecular structure of the additive D1 also showed promising migration properties as additive C3. It also generated the second highest increase in DBS, 8,2% and the highest overall increases in DBS, 7,5% and 8,2%, which are outside of the LDPE reference confidence interval. Although the additive decreased the shape factor slightly, this additive was considered as the best additive.

5.7.4.2.   The additive D2
The additive D2 had a molecular structure different from the other additives. It also consisted of long carbon chains and thus, no clear migration could be seen. However, no significant increases in DBS could be seen either. The shape factor did, on the other hand, increase significantly and perhaps it may be due to its favorable compatibility properties with PE. The additives with the longest alkyl chain exhibit the slowest migration rate.

5.8.   Comparison
The general trend is that all the additives at a certain concentration have some positive effect on both the breakdown strength of the LDPE reference and the shape factor. However most of the increases in breakdown strength are within the reference 95% confidence interval and thus not considered as significant increases. As mentioned earlier, reproduction of some results also indicate an uncertainty in the results. Most of the additives also increase the shape factor which is at least as important as the scale factor. However since one sample alone in the Weibull plot can influence the shape factor remarkably it is hard to compare the increases. The increases may indicate that the additives tend to reduce the effect of defects. In **Figure 36** the relative changes in DBS are plotted against the weight concentration.
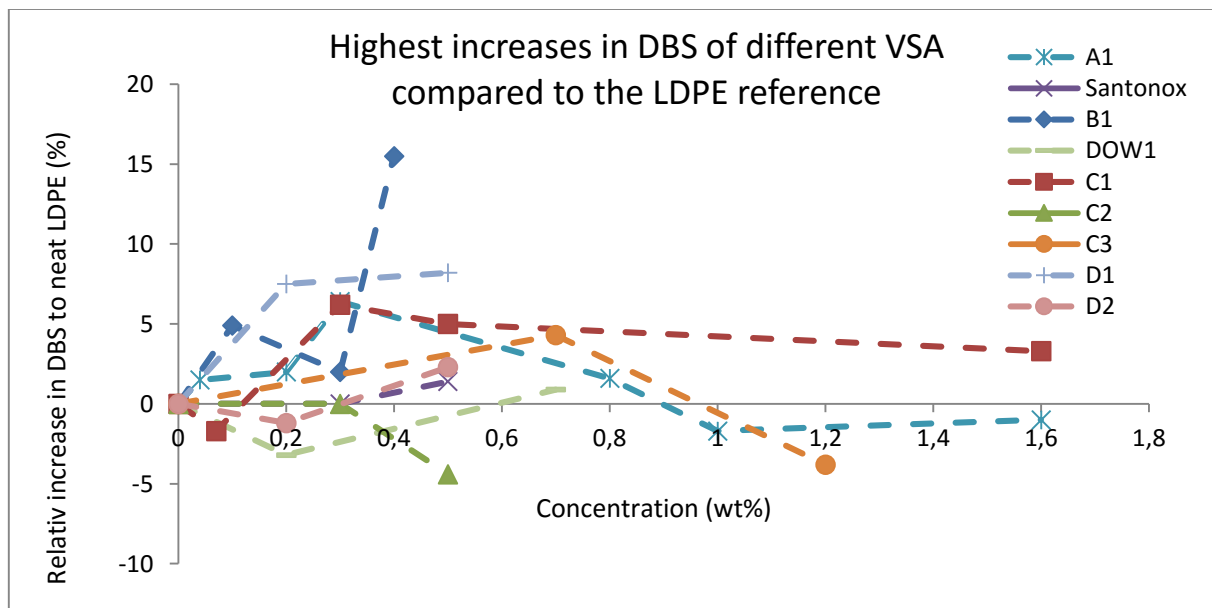

Figure 35 *Highest increases in DBS of different VSA compared to neat LDPE plotted against concentration (wt %).*

Unfortunately, no clear trends or correlations could be drawn from these results. However, the results indicated as many other publications that the optimum concentrations seem to be found below 1wt%. The results also indicated that the compounds with longer alkyl chains exhibit slower migration rate towards the surface of the plates.

5.9. Hypothesis

The relativly low increases in DBS of the tested additives might be due to our LDPE reference already having excellent properties. Previous publications might have used references that contain many defects such as air bubbles and thus it may be easier to see significant increases for materials with worse insulation properties. Furthermore, it may be too difficult to compare the enhancement in electrical treeing resistance, which most of the publications has investigated, with these enhancements in DBS. Additive DOW1 gave not as significant increases as the patent from DOW Global Technologis Ll claims for instance. The mechanisms behind the breakdowns are different.

6. Conclusion

A screening investigation was performed where nine different voltage stabilizing additives where tested according to breakdown strength in AC conditions compared to a reference LDPE. No major impurities or defects could be detected by the microscopes, OM and SEM, and the variations between the references were small. It was thus concluded this was a reliable method and that any enhancement in dielectric breakdown strength was mainly due to the intended stabilizing mechanisms. Rogowski-shaped electrodes also gave rise to this reliability.

Although this rather new promising approach, of attaching alkyl chains to aromatic core of the voltage stabilizer, that was tested, most of the tested additives did not increase the breakdown strength significantly. These alkyl chains were supposed to reduce the impact of thermal breakdown. However, only additive D1, with the concentrations of 0,2wt% and 0,5wt%, generated an significant increase, of 7,5% and 8,2% respectively, in breakdown strength compared to the polyethylene reference, tested at the same occasion. The attached alkyl chains were also supposed to increase the compatibility with the polymer matrix, and reduce the diffusion. However most of the additives tended to migrate after the tests within 4 months. Nonetheless, the additives with the longest alkyl chains exhibit the slowest migration rate. The low increases and the migrations might be due to our LDPE reference's excellent insulation properties. Moreover, perhaps enhancements in electrical treeing resistance is not comparable with enhancements in dielectric breakdown strength. Still, this investigation indicated as many other articles that voltage stabilizing additives could increase the breakdown strength for low density polyethylene and the concentration of additives should be small for the enhancements.

7. Further work

- Test pure LDPE and pure LDPE containing additives
- Add crosslinking species to the VSA molecular structure
- Investigate how the VSA reacts with the DCP- radicals when LDPE is cross-linked
- Evaluate more additives that increase electrical treeing with this method
- Investigate the long-term stability such as equilibrium with the adjacent semiconductors

8. Acknowledgments

9. References

[1] A. Gustafsson, 1993, "*Degradation of polyethylene and styrene polymers in electrical fields*", Department of Polymer Technology Stockholm.

[2] M. Jarvid, 2014, "Thioxanthone derivatives as stabilizers against electrical breakdown in cross-linked polyethylene for high voltage cable applications" , Polymer Degradation and Stability, Vol. 112, pp. 63-69

[3] N. Barberis Negra, J. Todorovic, T. Ackermann, 2006 "*Loss evaluation of HVAC and HVDC transmission solutions for large offshore wind farms*" Electric Power Systems Research, Vol. 76, pp. 916–927

[4] Interview with Fredrik Sahlén , ABB employee, 08-04-2016, ABB CRC Västerås

[5] M. Jarvid, A. Johansson, V. Englund, A. Lundin, S. Gubanski, 2015 "*A New Application Area for Fullerenes: Voltage Stabilizers for Power Cable Insulation*", Advanced Materials, Vol. 27, pp. 897-902

[6] Jabri ,Z., 2015, "*Investigation of the dielectric breakdown strength of LDPE*" Teknisk- Naturvetenskaplig Fakultet, Uppsala University.

[7] M. Jarvid, 2014 "*Voltage Stabilizers: From Design to Synthesis, Processing and Electrical Characterization*" Department of Chemical and Biological Engineering Chalmers, University of Technology

[8] International Electrotechnical Commission (IEC) Standard 62067:2011, 2nd ed. 2011 IEC, Geneva, Switzerland.

[9] Wikipedia, Online access 2016-03-30, https://en.wikipedia.org/wiki/Relative_permittivity

[10] K. Möller, T. Gevert, 1996, "*A Solid-state Investigation of the Desorption/Evaporation of Hindered Phenols from Low Density Polyethylene Using FTIR and UV Spectroscopy with Integrating Sphere: The Effect of Molecular Size on the Desorption*" Journal of Applied Polymer Science, Vol. 61, pp. 1149-1162.

[11] X. Zhang, H. Yang, Y. Song, Q. Zheng, 2012, "*Assessment of Hindered Phenol Antioxidants on Processing Stability of Peroxide-Cure LDPE by Rheology and DSC Analysis*", Journal of Applied Polymer Science, Vol. 126, pp. 939–946

[12] C.O. Olsson, X. Chen, A.R. Mantsch, L. Hu, S-M- Gubanski and J. Blennow, 2013, "*Electrical Treeing Behavior of DC and Thermally Aged Polyethylenes Utilizing Wire-Plane Electrode Geometries*" IEEE Transactions on Dielectrics & Electrical Insulation Vol. 21, pp. 45-52

[13] Interview with Carl Olof Olsson, ABB employee, 12-04-2016, ABB CRC Västerås

[14] M. Lundbäck, 2005, "*Long-term performance of polyolefins in different environments including chlorinated water: Antioxidant consumption and migration, and polymer degradation*" PhD thesis, Kungliga Tekniska Högskolan

[15] M. Goshowaki, Iori Endoh, K. Noguchi, U. Kawabe, Y. Sekii, 2007, " *Influence of antioxidants on electrical conduction in LDPE and XLPE*", Journal of Electrostatics Vol. 65 pp. 551–554

[16] T. Krentz, H. Hillborg, "*Literature survey: Enhancing dielectric breakdown strength of solid polymer insulation*", ABB Technical Report, SECRC/PT/TR-2013/210.

[17] S. Ying, S.Boggs , R. Ramprasad, 2015 "*The Effect of Dipole Scattering on Intrinsic Breakdown Strength of Polymers*" IEEE Transactions on Dielectrics and Electrical Insulation Vol. 22, pp. 495-502

[18] M. Karlsson, 2014 "*Investigation of the dielectric breakdown strength of polymer nanocomposites*", Teknisk-Naturvetenskaplig Fakultet, Uppsala University.

[19] M. Ieda, 1980, "*Dielectric Breakdown Process of Polymers*", IEEE Transactions on Electrical Insulation*, Vol. 15, pp. 206-224.

[20] M. Roy, J.K. Nelson, R.K. MacCrone, L.S. Schadler, 2005, "*Polymer Nanocomposite Dielectrics – The Role of the Interface*", IEEE Transactions on Dielectrics and Electrical Insulation, Vol. 12, pp. 629-643

[21] P. Yan , Y. Zhou , N. Yoshimura, 1999 , Proceeding of the Institute of Electrostatics Japan, Vol. 23 , pp. 319.

[22] S.N. Kolesov, 1979, "*The supermolecular structure and electrical properties of polymeric materials*," Polymer Science U.S.S.R, Vol. 21, pp. 1993-2000.

[23] J. Artbauer, 1996, "*Electric strength of polymers*", Journal of Physics D: Applied Physics, Vol. 29, pp. 446.

[24] T. Blythe, D. Bloor, 2005, "*Electrical Properties of Polymers"* Second Edition, Cambridge University Press, pp. 195-197,

[25] E. Husain, R. S. Nema, 1982,"*Analysis of paschen curves for air, N2 and SF6 using the Townsend breakdown equation"* IEEE transactions on electrical insulation, Vol. 17, pp. 350-353.

[26] D. Liu, A.M. Pourrahimi, L.K.H. Pallon, C. Cobo Sanchez, R.T. Olsson, M.S. Hedenqvist, L. Fogelstrom, E. Malmström, U.W. Gedde, 2016 "*Interactions between a phenolic antioxidant, moisture, peroxide and crosslinking by-products with metal oxide nanoparticles in branched polyethylene*" Polymer Degradation and Stability, Vol. 125, pp. 21-32

[27] T. J. Lewis, 1994 "*Nanometric Dielectrics*", IEEE Transactions on Dielectrics and Electrical Insulation, Vol.1, pp. 812-25

[28] D. Ma, T.A Hugener, R.W Siegel, A. Christerson, E. Mårtensson, C. Önneby, L. S Schadler, 2005, "*Influence of nanoparticle surface modification on the electrical behavior of polyethylene nanocomposites*", Nanotechnology, Vol. 16, pp. 724–731

[29] J. K. Nelson, 2010, "*Backgrounds, principles and promise of nanodielectrics*", in: J. K. Nelson (Ed), Dielectric polymer nanocomposites, Springer US

[30] C.O. Olsson, X. Chen, A.R. Mantsch, L. Hu, S-M- Gubanski and J. Blennow, 2013, "*Electrical Treeing Behavior of DC and Thermally Aged Polyethylenes Utilizing Wire-Plane Electrode Geometries*" IEEE Transactions on Dielectrics and Electrical Insulation, Vol. 21, pp. 45-52

[31] H. Zhang, Y. Shang, H. Zhao, X. Wang, B. Hana, Z. Li, 2016 "*Theoretical study on the tailored side-chain architecture of benzil-like voltage stabilizers for enhanced dielectric strength of cross-linked polyethylene"* RSC Adv., Vol. 6, pp. 11618–11630

[32] M. Jarvid, 2014 "*Thioxanthone derivatives as stabilizers against electrical breakdown in cross-linked polyethylene for high voltage cable applications*" Polymer Degradation and Stability, Vol. 112, pp. 63-69

[33] M. Jarvid, A. Johansson, V. Englund, A. Lundin, S. Gubanski, 2014, *"Tailored Side-Chain Architecture of Benzil Voltage Stabilizers for Enhanced Dielectric Strength of Cross-Linked Polyethylene"* Journal of Polymer Science, Part B: Polymer Physics, Vol. 52, pp. 1047–1054.

[34] S. Kisin, J. Doelder, R.F. Eaton, P.J. Caronia, 2008 "*Quantum mechanical criteria for choosing appropriate voltage stabilization additives for polyethylene*", Polymer Degradation and Stability, Vol. 94, pp. 171–175

[35] A. Johansson, 2015, "*Characterizing Resistance to Electrical Treeing in New XLPE-Based Materials for High-Voltage Cables"*, Department of Materials and Manufacturing Technology, Chalmers University of Technology

[36] A. Marin, 1998, "*Additives Solubility in Polymers"* International Journal of Polymeric Materials, Vol. 42, pp. 125-163.

[37] V. Englund, T. Hjertberg, S. Gubanski, R. Huuva, 2008, "*Voltage stabilizers for improving the electrical treeing resistance of XLPE*" International Symposium on Electrical Insulating Materials, pp. 566-569

[38] M. Jarvid, A. Johansson, V. Englund, A. Lundin, S. Gubanski, 2014, *"Tailored Side-Chain Architecture of Benzil Voltage Stabilizers for Enhanced Dielectric Strength of Cross-Linked Polyethylene"* Journal of Polymer Science, Part B: Polymer Physics, Vol. 52, pp. 1047–1054

[39] M. Jarvid, A. Johansson, J. Blennow, M. Andersson, S. Gubanski, 2013 "*Evaluation of the Performance of Several Object Types for Electrical Treeing Experiments"* IEEE Transactions on Dielectrics and Electrical Insulation Vol. 20, pp. 1712–1719.

[40] Z. Yang, H. Zhang, H. Zhao, B. Han, 2015, *"Trap Mechanism Based on Frontier Molecular Orbitals of Additives in Polyethylene Insulators: A Theoretical Study and Molecular Design Strategy"*, International Journal of Quantum Chemistry 2015, Vol. 115, pp. 1483–1489

[41] H. Mitsumoto, M. Nagao, M. Fukuma and N. Hozumi, 2002 *"High-Field Electrical Properties under AC Voltage Application in Acetophenone-Coated LDPE Film"* Electrical Engineering in Japan, Vol. 142, pp. 1-7

[42] T. Adrews, R.N. Hampton, A. Smedberg, D. Wald, V. Waschk, W. Weissenberg, 2006, "*The role of degassing in XLPE power cable manufacture*", IEEE Electrical Insulation Magazine, Vol. 22, pp. 5-16.

[43] H. Zhang, Y. Shang, H. Zhao, B. Han, Z. Li, 2014, *"Study of the effect of valence bond isomerizations on electrical breakdown by adding acetophenone to polyethylene as voltage stabilizers"* Elsevier B.V. Computational and Theoretical Chemistry, Vol. 1062 pp. 99–104

[44] M. Jarvid, A. Johansson, R. Kroon, J.M. Bjuggren, H. Wutzel, V. Englund, S. Gubanski, M.R. Andersson, C. Müller, 2015 *"A New Application Area for Fullerenes: Voltage Stabilizers for Power Cable Insulation"*, Advanced Materials, vol. 27, pp. 897-902

[45] C. Müller, M. Jarvid, A. Johansson, J. Mattiasson Bjuggren, M. Andersson, S. Gubanski, V. Englund, "*Polyolefin composition for medium/high/extra high voltage cables comprising benzil-type voltage stabilizer"* EP 2886595 A1, 24 June 2015.

[46] V. TOMER, T. J. Person, D.M. Welsh, M. T. Bernius "*Voltage-stabilized polymeric compositions*" US 20160096950 31 Dec 2014

[47] M. Jarvid, A. Johansson, V. Englund, A. Lundin, S. Gubanski 2015 *"High electron affinity: a guiding criterion for voltage stabilizing design"* Journal of Materials Chemistry, Vol. 3, pp. 7273-7286

[48] DFT calculations preformed by Joakim Jämbeck, ABB employee, 03-2016, ABB CRC Västerås

[49] CEI IEC 60243-1, Second edition 1998-01, International Standard, Electrical strength of insulating materials, International Electrotechnical Commission

[50] M. Hanai, T. Nakamoto, H. Ikeda, 2007, "*Dielectric Breakdown Characteristics of an Insulator with a Sharp Edge in SF6 Gas under Lightning Impulse Voltage"*, IEEE Transactions on Dielectrics and Electrical Insulation Vol. 14, pp. 321-327

[51] Quickfield, Online access 2016-03-20 http://www.quickfield.com/advanced/rogowski_electrodes.htm

[52] Jarvid, M., Johansson, A., Englund, V., Gubanski, S., and Andersson M. R., 2012, "*Electrical Tree Inhibition by Voltage Stabilizers*", Annual Repot Conference on Electrical Insulation and Dielectric Phenomena, pp. 605–608.

[53] Laihonen. S. J., 2005, "*Polypropylene: Morphology, Defects and Electrical breakdown*", Doctoral Thesis on Polymer Technology KTH Chemical Science and Engineering, Chapter 4, p4-1 -4-6

Appendix

Table 1 *The press program used in this investigation for compounding LDPE with its corresponding time (min), temperature (˚C) and pressure (bar).*

Temperature time (min)	Temperature (˚C)	Pressure time (min)	Pressure (bar)
9	120	9	20
7	130	2	100
7	130	12	350
2	130	2	350
11	40	11	350

Table 2 *The press program used in this investigation for compounding XLPE with its corresponding time (min), temperature (˚C) and pressure (bar).*

Temperature time (min)	Temperature (˚C)	Pressure time (min)	Pressure (bar)
7	130	7	20
10	180	10	200
15	180	15	200
10	70	10	200

Table 3 *The press program used for Borealis patent for compounding XLPE with its corresponding time (min), temperature (˚C) and pressure (bar).*

Temperature time (min)	Temperature (˚C)	Pressure time (min)	Pressure (kN)
6	130	3	2
15	180	18	200
30	25		
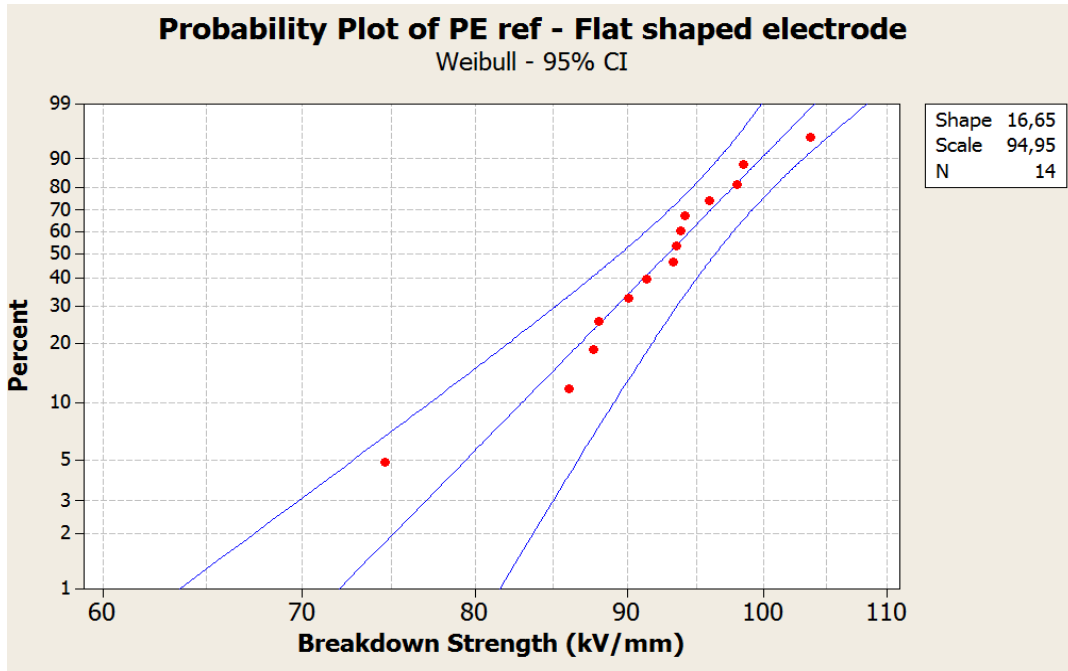
Figure 1 *Weibull plot with 95 % confidence interval of the reference polyethylene pressed at 350bar and tested with flat shaped electrodes. The results are in correlation with previous work[6] performed by ABB. N stands for number of samples.*
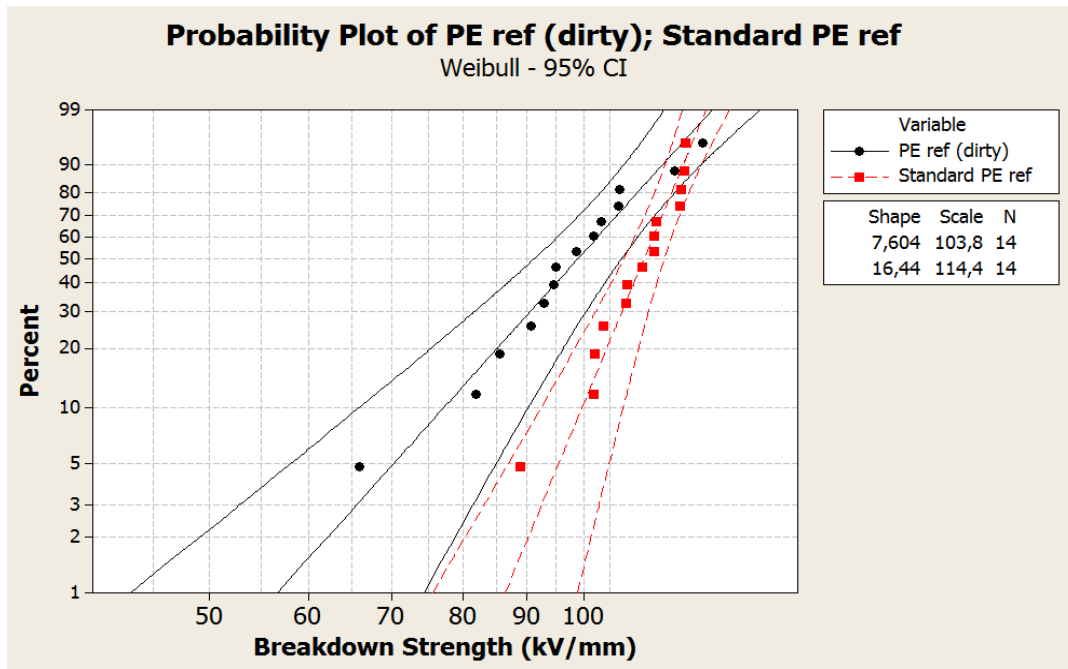
Figure 2 *Weibull plot with 95 % confidence interval of a reference polyethylene after the Brabender was cleaned with ethanol (PE ref (dirty)) and a standard reference (Standard PE ref). The results indicate the Brabender is not completely cleaned after the cleaning procedure with ethanol and thus a reference polyethylene needs to be run afterwards before the materials could be run. N stands for number of samples.*
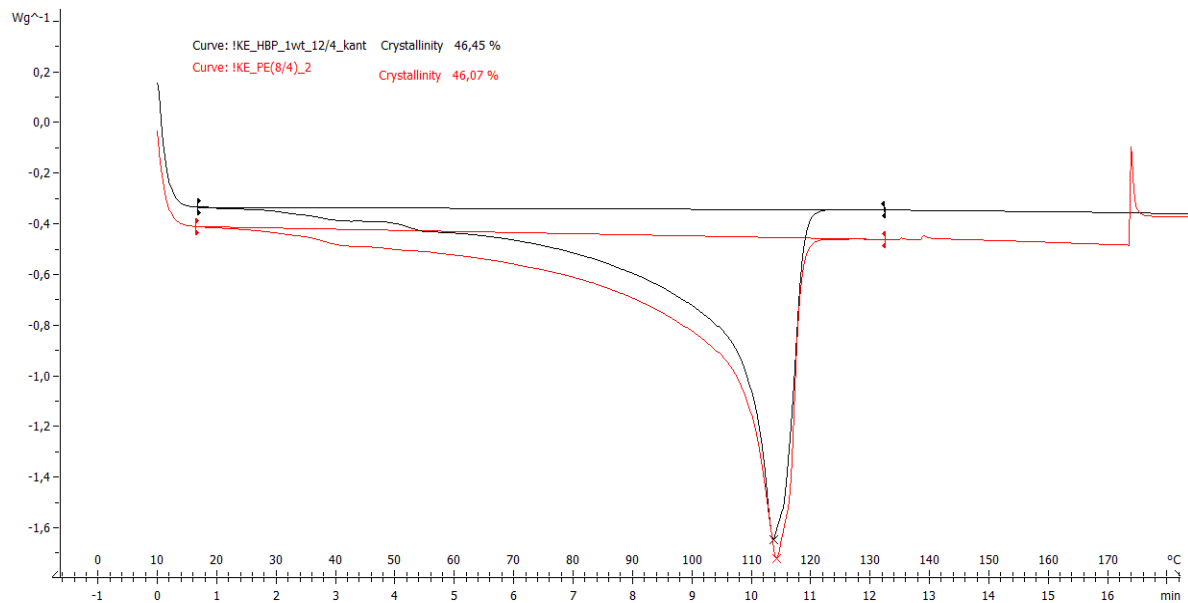
Figure Fel! Endast huvuddokument. *A differential scanning calometry (DSC) plot of two samples of LDPE (red lines resemble a sample taken from the middle and black lines resemble a sample taken adjacent to that sample). The normalized weight effect (W/g) is plotted to temperature (˚C) and time (min). The results indicates a fair reliability of the DSC machine.*

Weibull plots for the additive A1
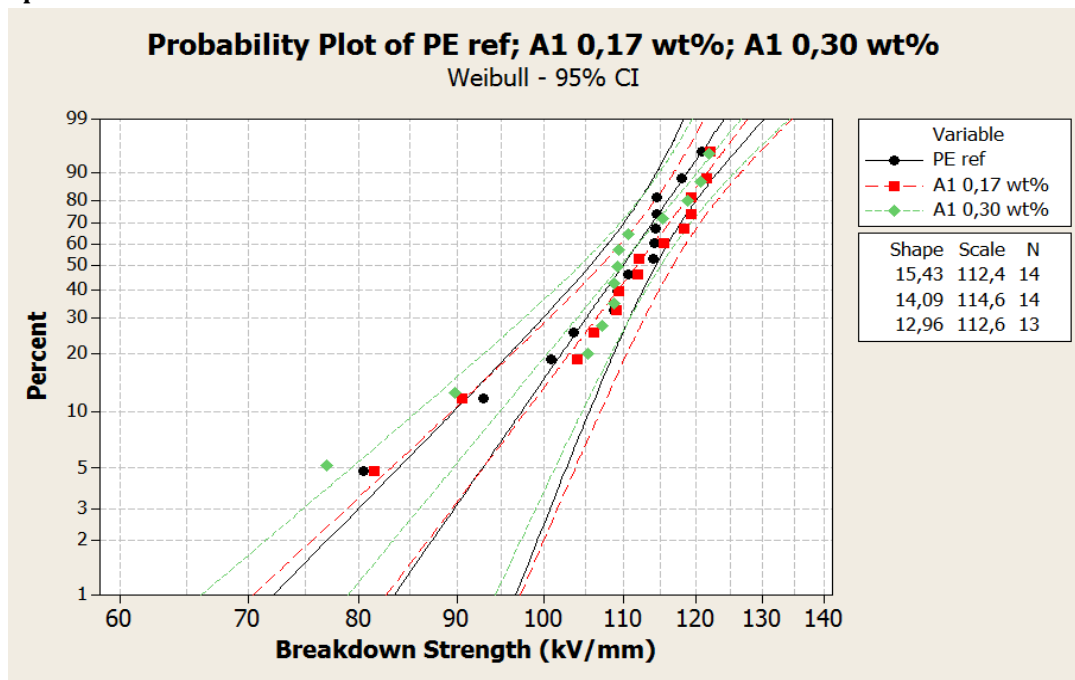
Figure 3 *Weibull plot with 95 % confidence interval of the reference polyethylene and the additive A1 in polyethylene. The addition of 0,17 and 0,3 wt% of the additive A1 to polyethylene resulted not in an increase in breakdown strength. N stands for number of samples.*
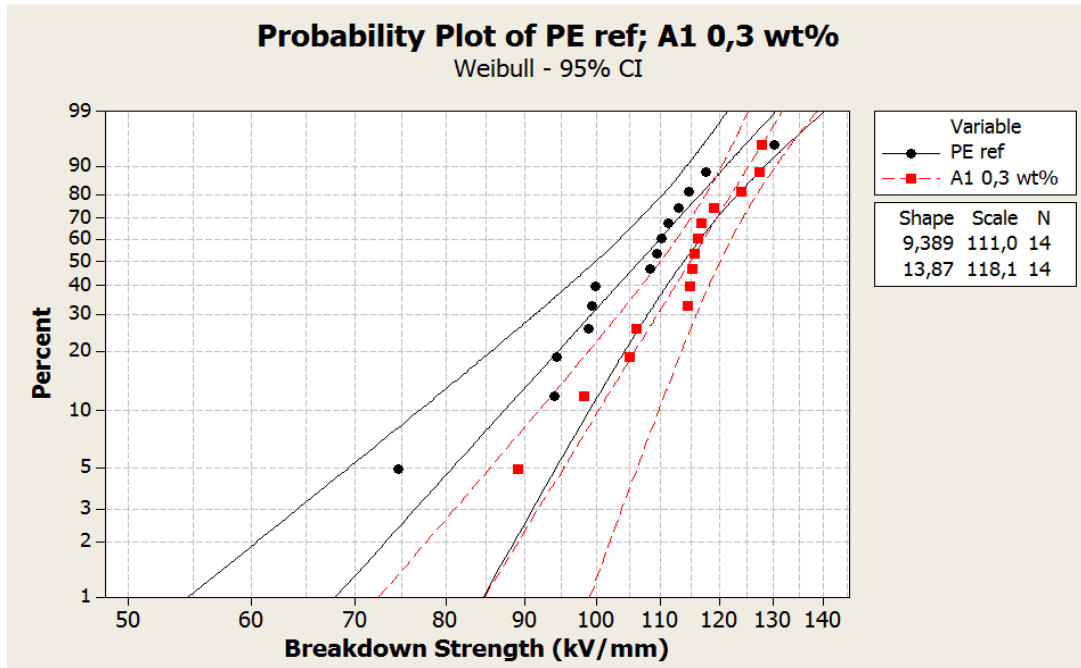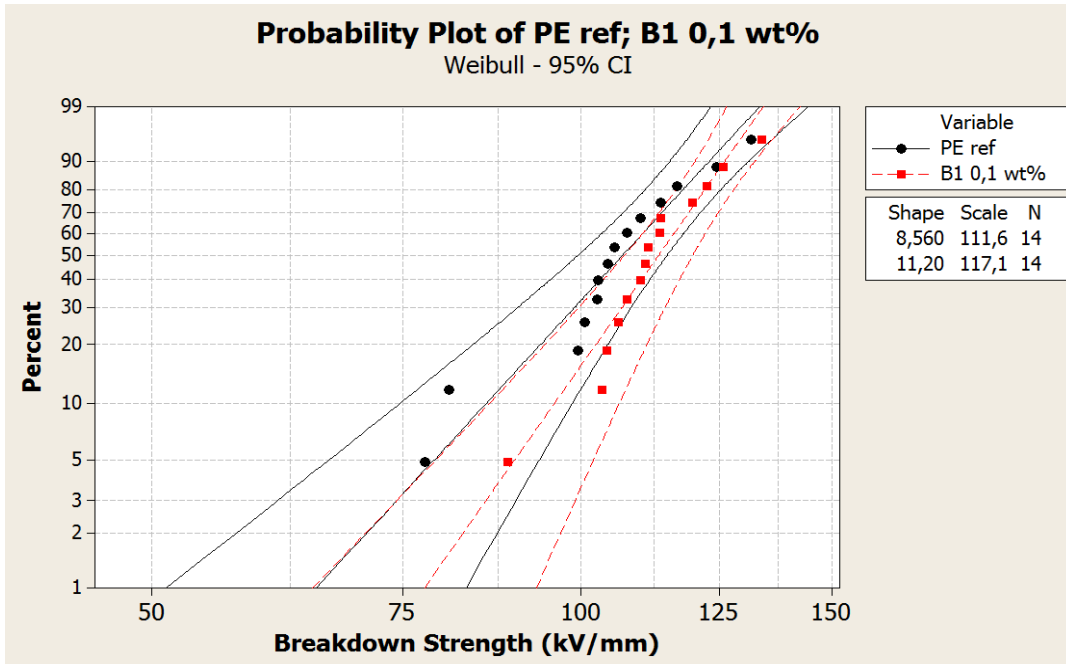
Figure 4 *Weibull plot with 95 % confidence interval of the reference polyethylene and 0,3 wt% A1 in polyethylene. The addition of 0,3 wt% of the additive A1 to polyethylene resulted in a 6% increase in breakdown strength. N stands for number of samples.*
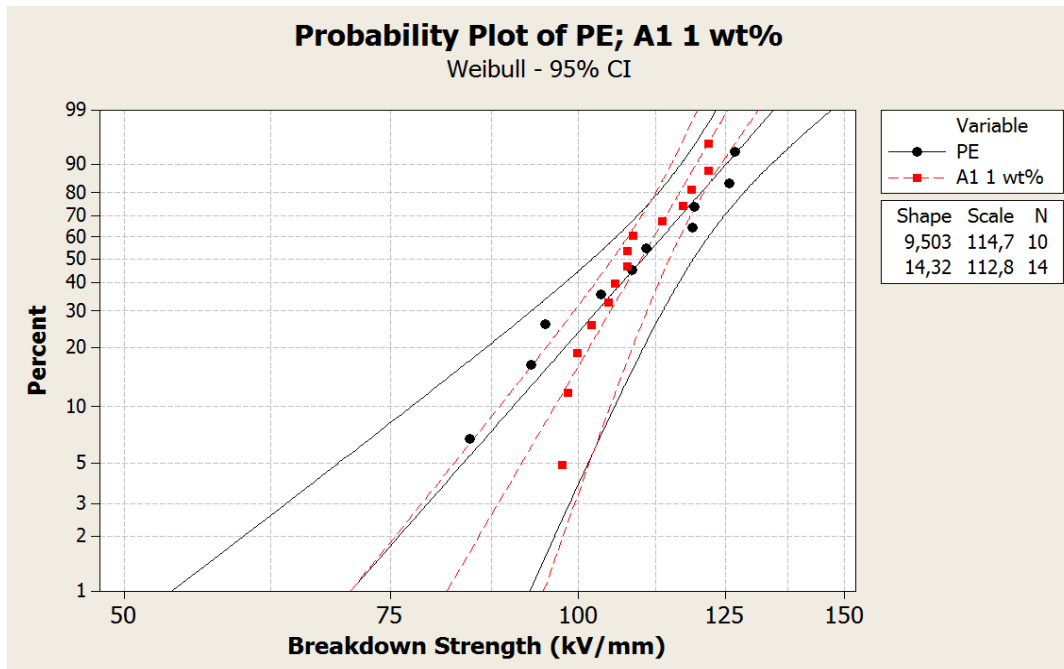
Figure 5 *Weibull plot with 95 % confidence interval of the reference polyethylene and 1 wt% A1 in polyethylene. The addition of 1 wt% of the additive A1 to polyethylene resulted not in an increase in breakdown strength. N stands for number of samples.*
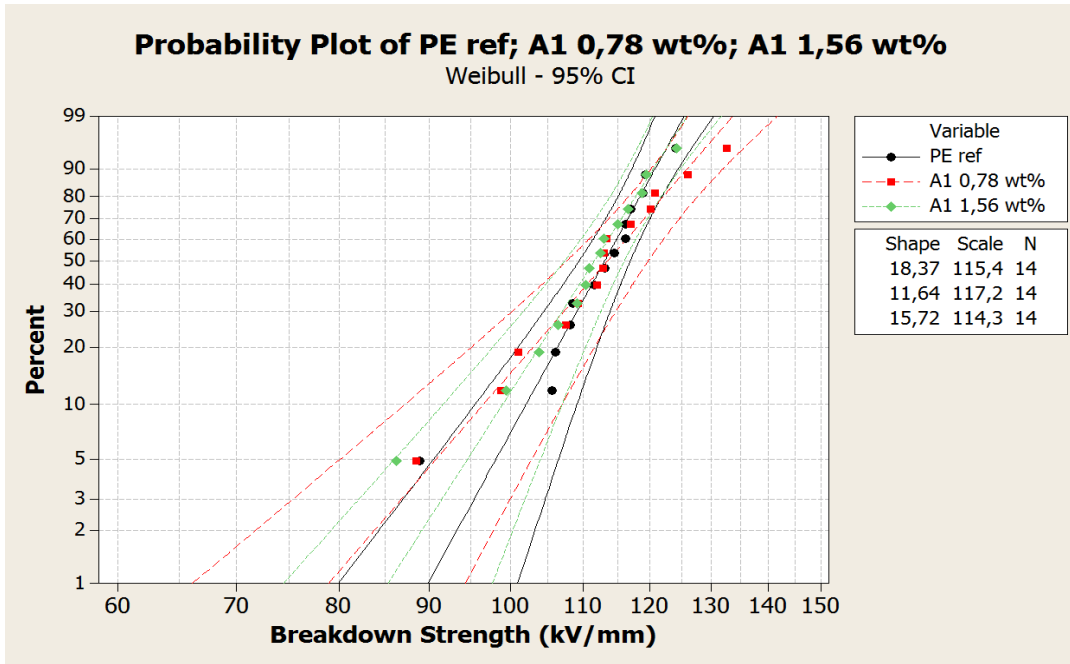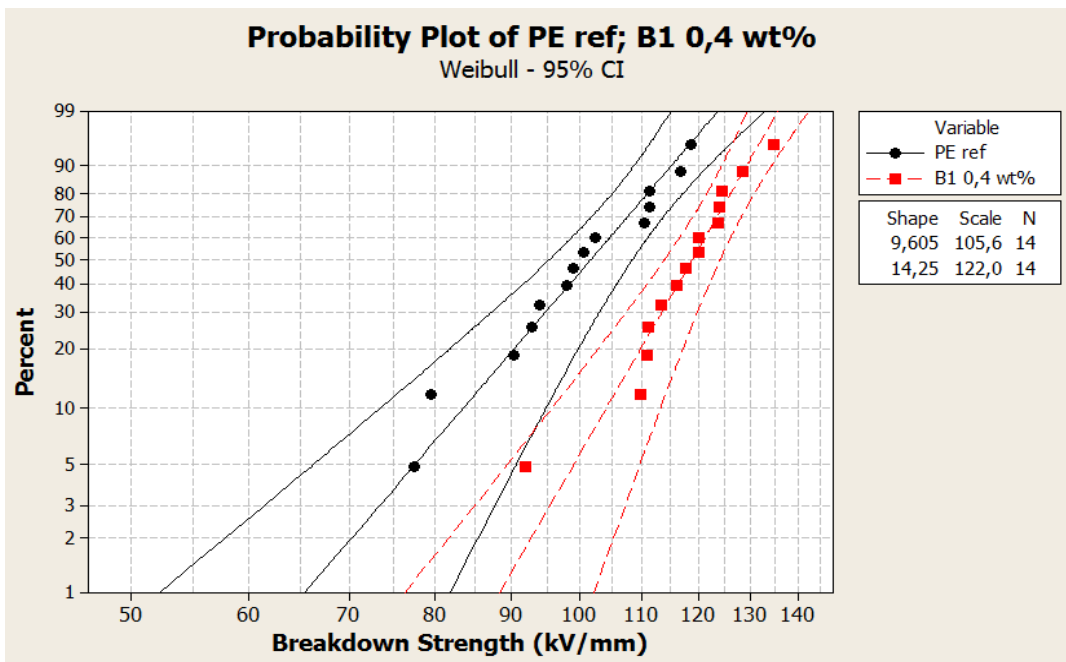
Figure 6 *Weibull plot with 95 % confidence interval of the reference polyethylene and the additive A1 in polyethylene. The addition of 0,8 and 1,6 wt% of the additive A1 to polyethylene resulted not in an increase in breakdown strength. N stands for number of samples.*
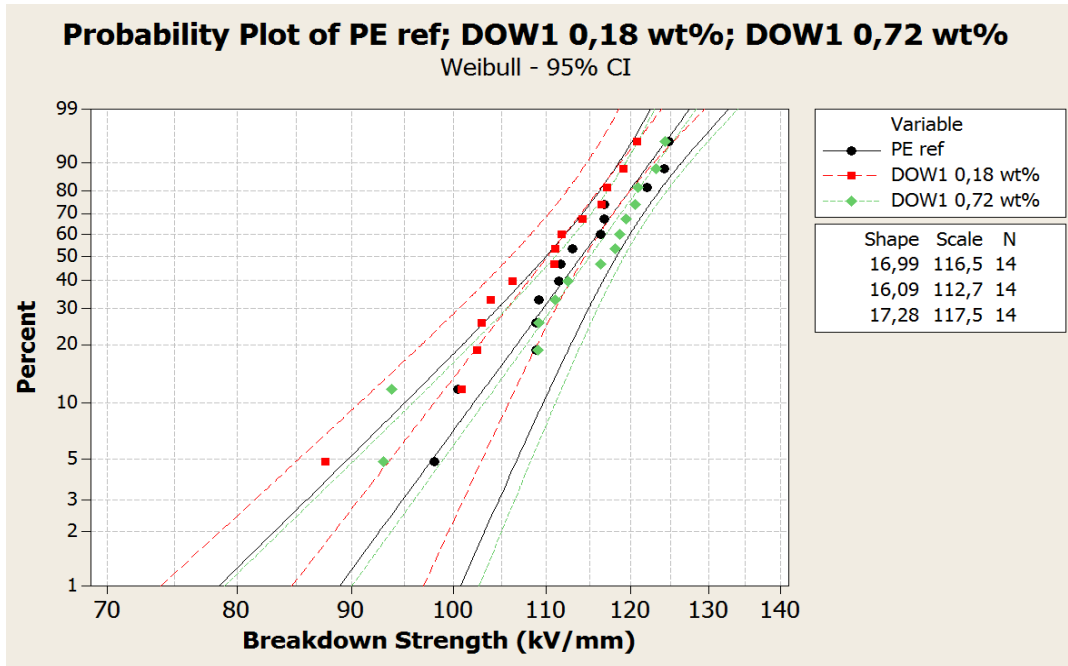
Weibull plots for the Santonox®
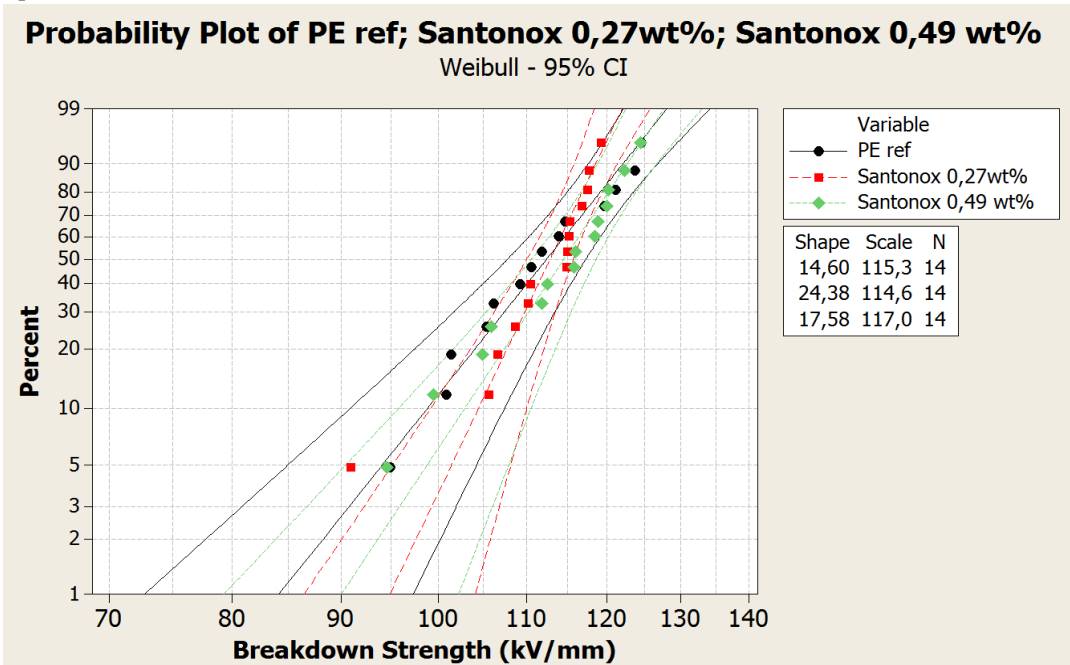
Figure 7 *Weibull plot with 95 % confidence interval of the reference polyethylene and the antioxidant Santonox in polyethylene. The addition of 0,3 and 0,5 wt% of Santonox, which corresponds to 0,1 and 0,2 wt% respectively of aromatic groups, to polyethylene resulted not in an increase in breakdown strength. N stands for number of samples.*

Figure 7 *Weibull plot with 95 % confidence interval of the reference polyethylene and 0,1 wt% B1 in polyethylene. The addition of 0,1 wt% of the additive B1 to polyethylene resulted not in an increase in breakdown strength. N stands for number of samples.*

Figure 8 *Weibull plot with 95 % confidence interval of the reference polyethylene and 0,4 wt% B1 in polyethylene. The addition of 0,4 wt% of the additive B1 to polyethylene resulted not in an increase in breakdown strength. N stands for number of samples.*

Weibull plots for the additive DOW1

Figure 9 *Weibull plot with 95 % confidence interval of the reference polyethylene and additive DOW1 in polyethylene. The addition of 0,2 and 0,7 wt% of DOW1, which corresponds to 0,03 and 0,1 wt% respectively of aromatic groups, to polyethylene resulted not in any significant increase in breakdown strength. N stands for number of samples.*

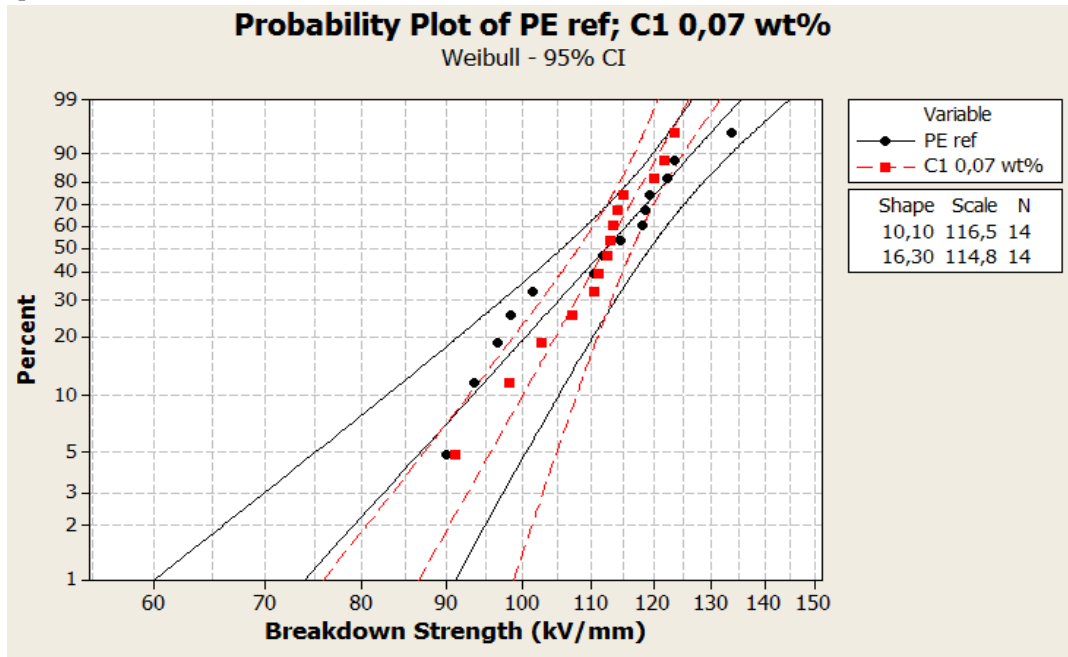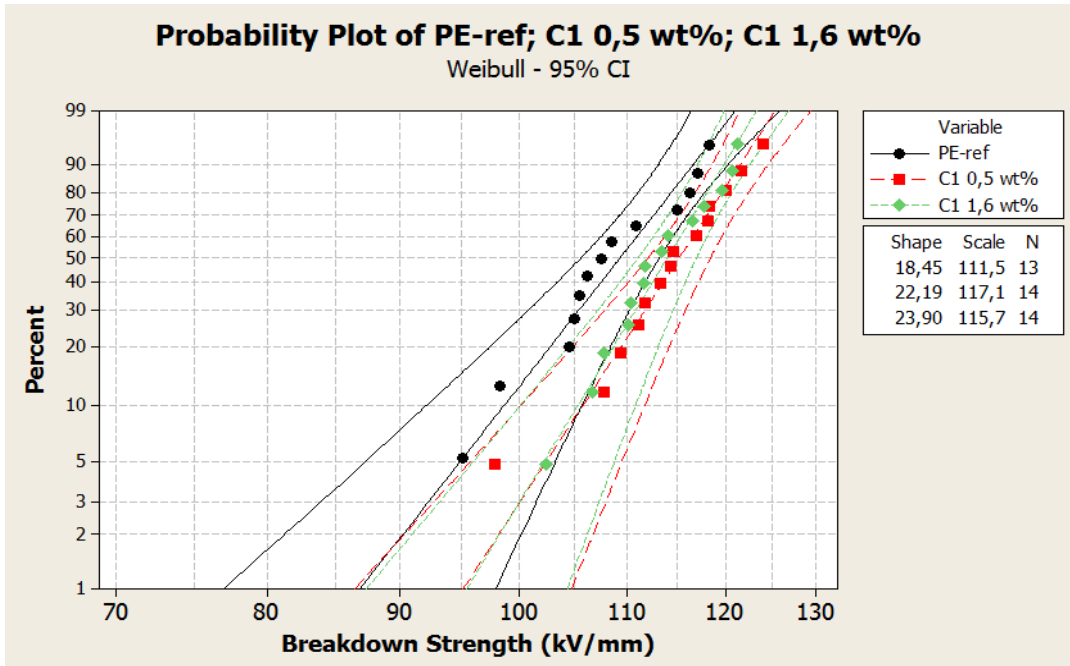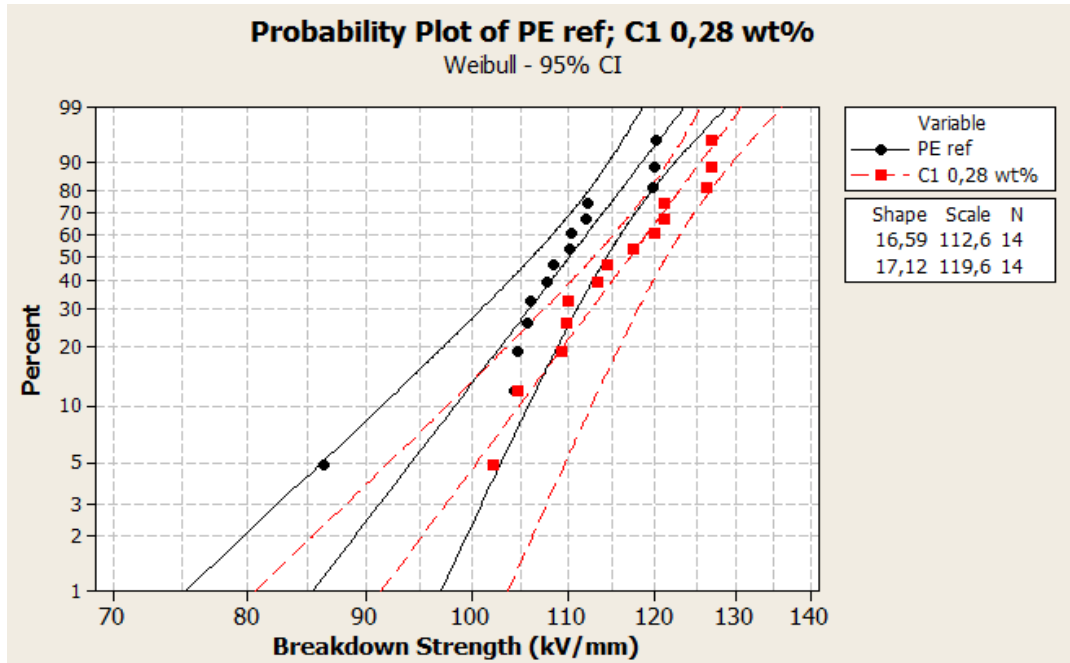**Weibull plots for the additive C1**

Figure 10 *Weibull plot with 95 % confidence interval of the reference polyethylene and C1 in polyethylene. The addition of 0,07 wt% of the additive C1 to polyethylene resulted not in an increase in breakdown strength. N stands for number of samples.*

Figure 11 *Weibull plot with 95 % confidence interval of the reference polyethylene and C1 in polyethylene. The addition of 0,5wt% and 1,6 wt% C1 to polyethylene resulted in a slight increase in breakdown strength. The reference had a value at 55kV/mm but it was considered as an extreme value; it reduced the scale factor by 2 and the shape factor by 7, and it was therefore left out. N stands for number of samples.*

Figure 12 *Weibull plot with 95 % confidence interval of the reference polyethylene and C1 in polyethylene. The addition of 0,3 wt% C1 to polyethylene resulted in an 6% increase in breakdown strength. N stands for number of samples.*
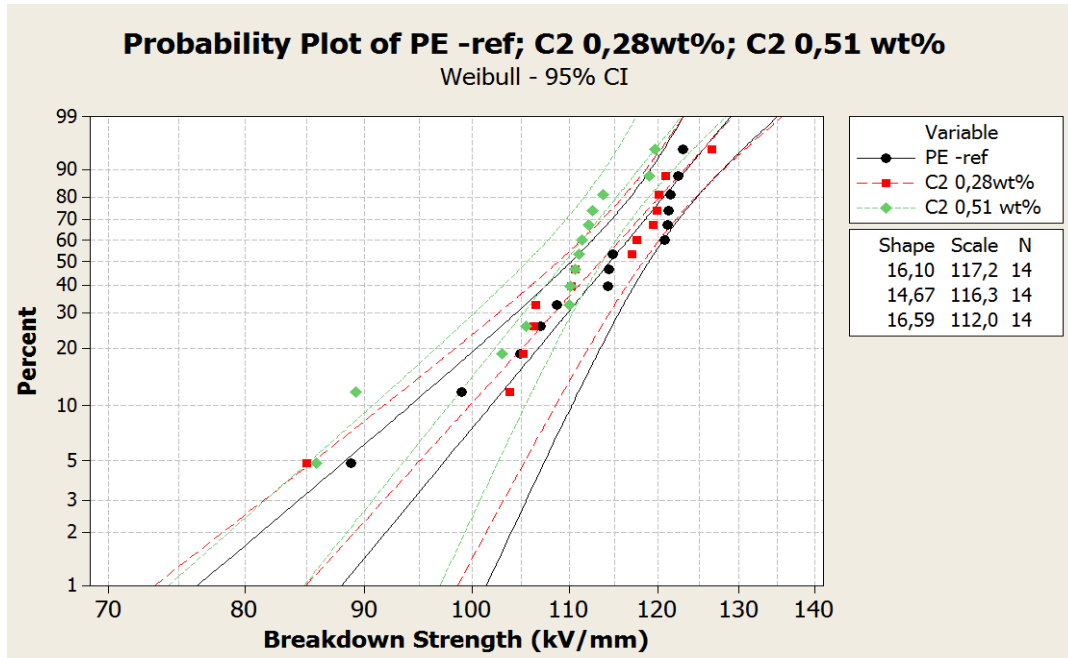
Weibull plots for the additive C2

Figure 13 *Weibull plot with 95 % confidence interval of the reference polyethylene and C2in polyethylene. The addition of 0,3 and 0,5 wt% of C2 respectively of aromatic groups, to polyethylene resulted not in an increase in breakdown strength. N stands for number of samples.*
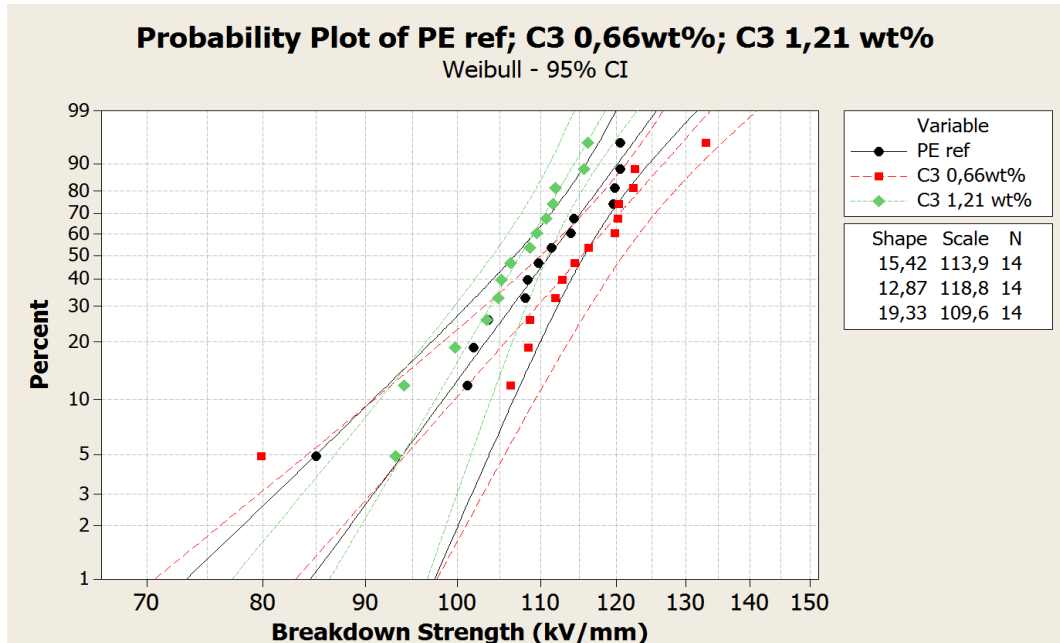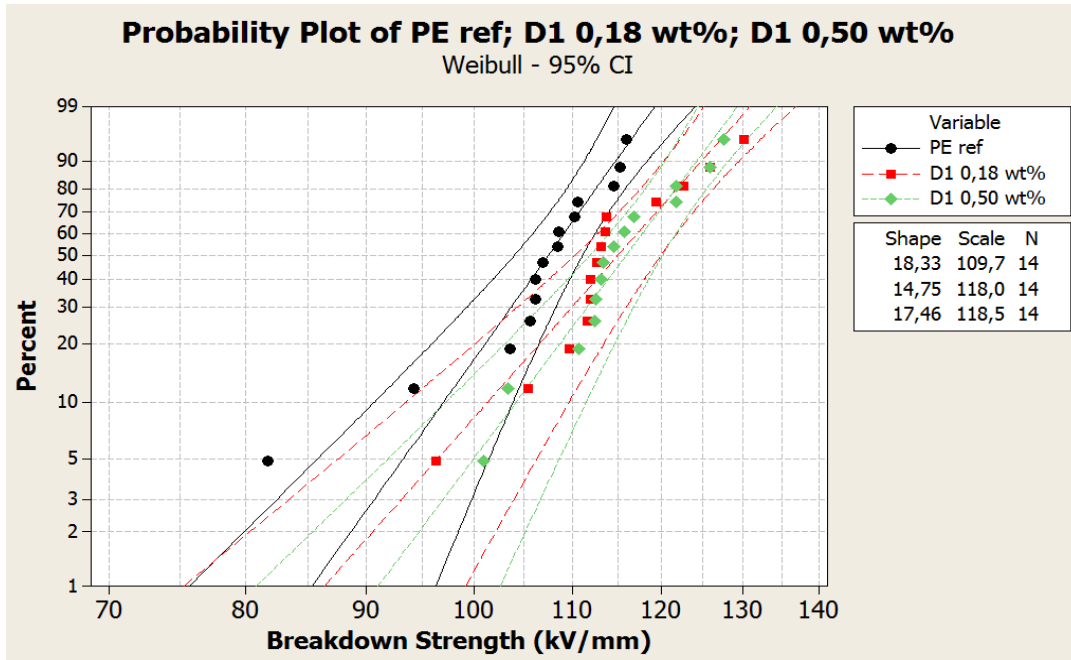
Weibull plots for the additive C3

Figure 14 *Weibull plot with 95 % confidence interval of the reference polyethylene and the additive C3 in polyethylene. The addition of 0,7 and 1,2 wt% of C3 to polyethylene resulted not in any significant increase in breakdown strength. N stands for number of samples.*
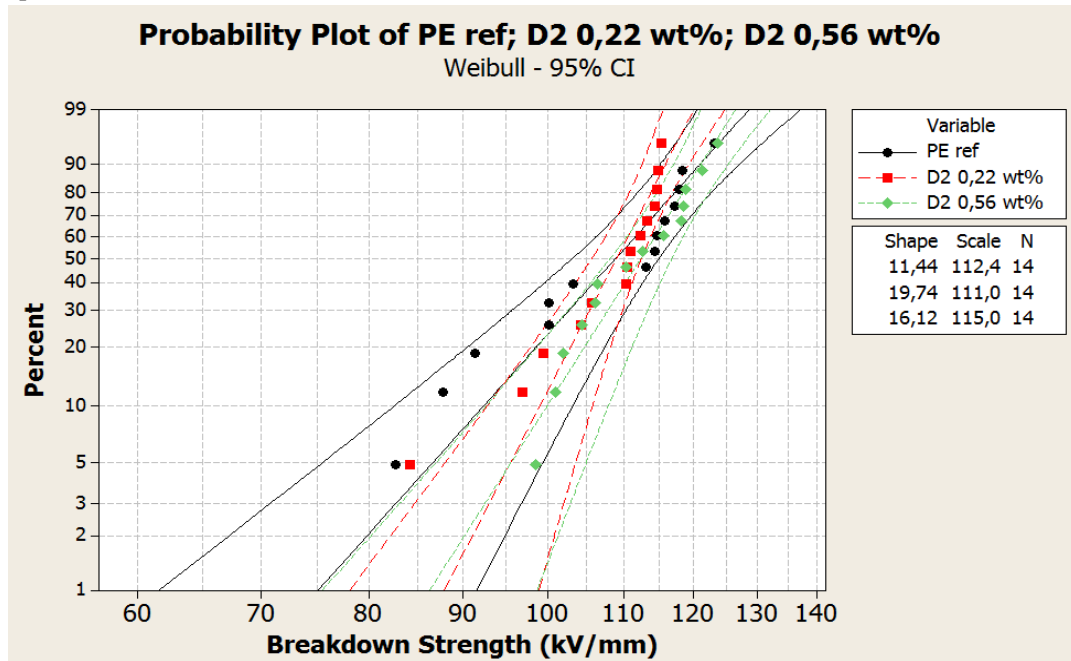
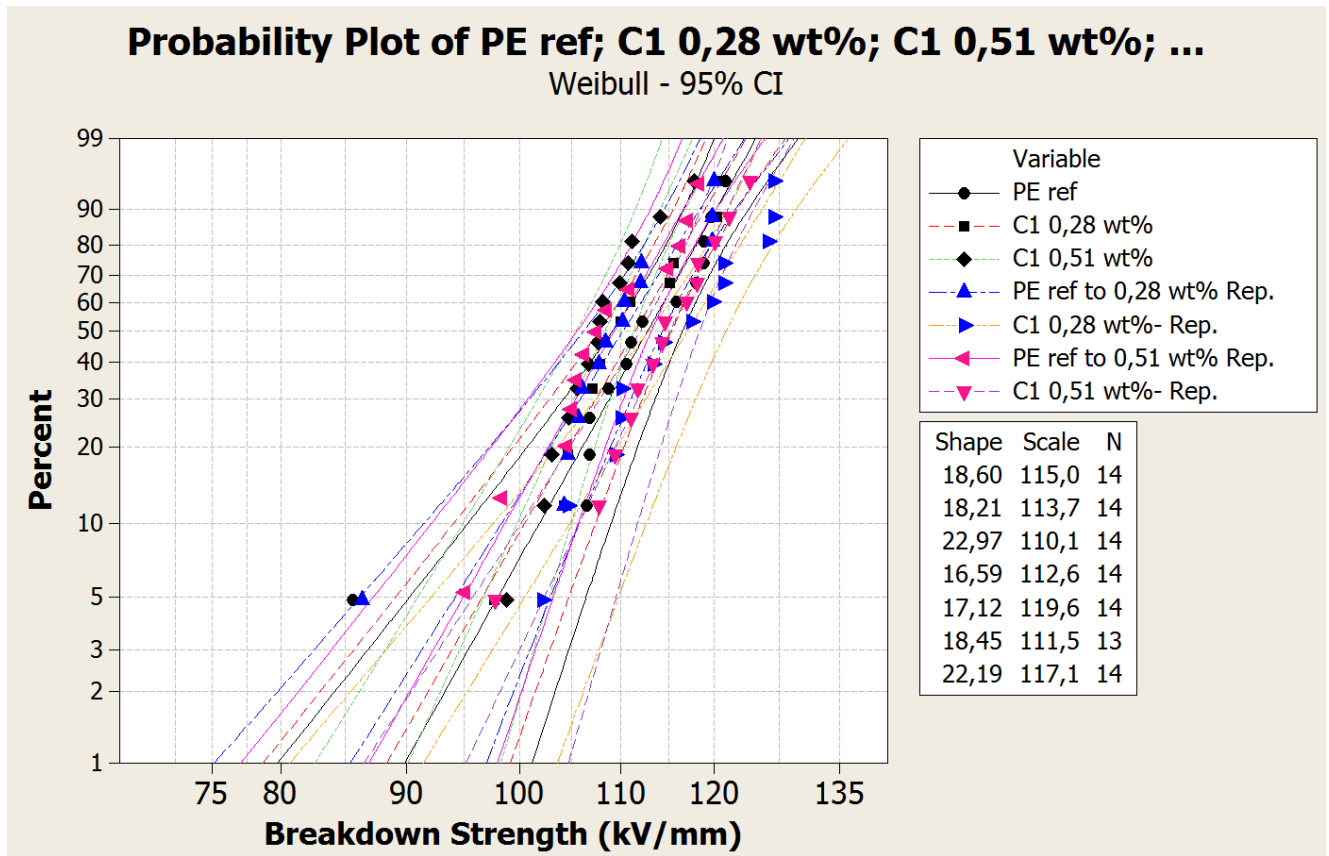**Weibull plots for the additive D1**

Figure 15 *Weibull plot with 95 % confidence interval of the reference polyethylene and additive D1 in polyethylene. The addition of 0,2 and 0,5 wt% of D1 to polyethylene resulted a significant increase in breakdown strength, 7,5% and 8,2% respectively. N stands for number of samples.*

Weibull plots for the additive D2

Figure 16 *Weibull plot with 95 % confidence interval of the reference polyethylene and additive D2 in polyethylene. The addition of 0,2 and 0,6 wt% of the additive D2 to polyethylene resulted not in any significant increase in breakdown strength. N stands for number of samples.*

Figure 17 *Weibull plot with 95 % confidence interval of polyethylene containing 0,3wt% and 0,5 wt% of the additive C1. The shape and scale factor belongs to the variables in numerical order. Rep. stands for reproduced test after a few weeks. The Weibull plots indicate ambiguous results. N stands for number of samples.*