

# Thermal degradation and stabilization of HVDC power cable insulation materials based on polypropylene

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M.Sc. Thesis in Chemical Engineering

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Åbo Akademi University 2022

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## Abstract

Most modern extruded high voltage cables use cross-linked polyethylene (XLPE) as the insulation. Unfortunately, XLPE also presents a major barrier to material recycling and environmental pollution reduction. Polypropylene-based polymers may have the potential for recyclable thermoplastic cable insulation application because of their high melting temperatures, and adjustable mechanical and electrical properties. This work aimed at evaluating the long-term thermal stability (LTTS) efficacy of various antioxidants and its combinations such as BASF Irgastab, Lowinox Fast XI, Irganox B 215, Songnox 11B and Songnox 2124 at different loading levels for isotactic polypropylene cable insulation materials. The different antioxidants were blended with Hiflex CA 7800 in an extruder, pelletized and then injection-moulded to dog bone specimens. The prepared specimens of Hiflex CA 7800A polypropylene with antioxidants were subjected to oven-aging at 150 °C up to 33 days in a circulating air oven. The effects of thermo-oxidative aging at different time intervals were investigated by monitoring changes by thermal analysis (oxidative induction times and onset of thermal degradation), morphological and chemical compositions (degree of crystallinity and degradation products by

FTIR) and mechanical (tensile strength) and rheological properties (mass flow index). BASF Irgastab and Lowinox Fast XL showed very poor performance in comparison to other stabilizer formulations. This can be attributed to the fact that BASF Irgastab and Lowinox Fast XL have been originally design for stabilization of XLPE insulation and not polypropylene insulations, per se. All HIFEX samples containing 0.2 wt% of stabilizers showed strong thermo-oxidative degradation at the end of oven ageing experiments. In general, 0.2 wt% loading was inferior to 0.4 wt% both in case of IRGANOX B 215 and Songnox 11B. At 0.2%, loading Songnox 11B was somewhat better than Irganox B 215, whereas at 0.4% loading no difference could be noted.

No significant difference between using 1:1 and 1:3 ratio between primary and secondary antioxidant could be detected under these experimental conditions. Overall, IRGANOX B 215 (0.4%), Songnox 11 B (0.4%) and Songnox 2124 (0.5%) performed very well in all the tests. Overall, Songnox 2124 outperformed all other stabilizer combinations and it showed extraordinarily high performance, e.g., in the OIT test, and it was also among the best in class in all other stabilization efficacy evaluation tests for polypropylene performed in this master's thesis work.

## 1.1 Introduction

In recent years, the interest in extruded HVDC cables has grown since modern power plants demand green and renewable energy sources that require long distance and large capacity HVDC cable power transmissions [1].

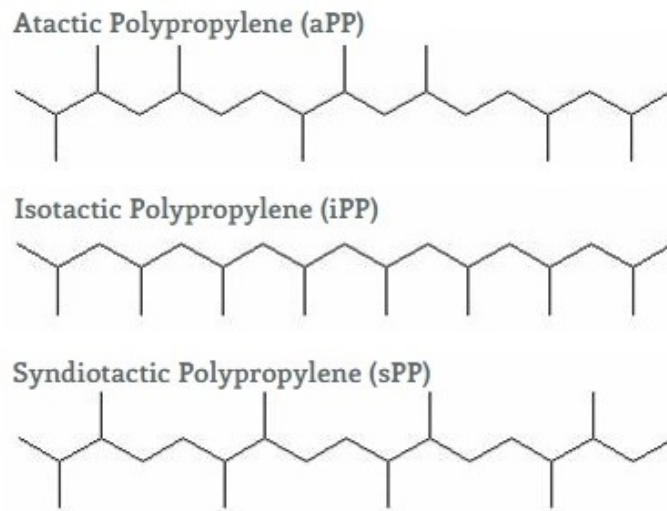
For example, the global offshore wind industry had a record year in 2019 with 6.1 GW of new additions and total cumulative capacity has passed 29 GW, representing 4.5 percent of total cumulative capacity. In addition, the next decade could see a 10-fold increase of offshore wind power capacity and wide-scale electrification [2].

In the future, we could utilize wind power from Antarctica and the North Pole, and also solar power from the equator to solve the problem of asymmetric power generation and consumption. HVDC power transmission technology is an ideal solution to increase the capacity. For example, the  $\pm 1100$  kV DC allows a transmission distance of 5000 km and a capacity of 12 GW, which well covers the demand to interconnect the power grids of different countries and even different continents to ensure safe and reliable supply of global energy [3].

The most frequently used transmission channel for HVDC transmission systems are overhead transmission lines. However, overhead transmission lines have their complications. Overhead lines clutter the landscapes and have a negative impact on the environment and the population in its proximity. Furthermore, it is becoming more difficult to find routes of overhead transmission lines for hydropower station output and the power access to big cities. Offshore wind power cannot be transferred to shore by overhead lines. That is why long undersea or underground transmission lines have the advantages of reduced environmental impact. Additionally, they are also safer and have a lower failure rate than overhead lines [3].

## 2.1 XLPE vs PP

Currently, the majority of HVDC cables utilize cross-linked polyethylene (XLPE) as the insulation material. The cross-linking process makes XLPE a thermoset material that is difficult to recycle, and the cross-linking and degassing processes in cable manufacturing also cause high energy consumption and formation of undesired polar byproducts such as water and benzyl alcohol. Considering this, XLPE cannot completely meet the requirements of modern power systems in terms of cable recyclability and manufacturing costs. That is why polypropylene insulation has drawn great attention in modern power systems, because it has some important qualities, for example that it is easy to recycle, it is cheap and it can be manufactured without the cross-linking process and associated byproducts. The improvement of thermo-mechanical property enables XLPE-insulated cables to continuously operate at a maximum temperature of 90 °C and even withstand 200 °C for a couple of seconds in case of short circuits.[4]



*Figure 1 The different structures of polypropylene*

PP is a thermoplastic polymer used in a wide variety of applications and it is produced via chain-growth polymerization from the monomer propylene. There are many asymmetric carbon atoms in its main molecular chain. According to the different arrangements of methyl groups on the main molecular chain, there are three different stereostructures of PP. Polypropylene can be categorized as atactic polypropylene (a-PP), syndiotactic polypropylene (s-PP) and isotactic polypropylene (i-PP). In the case of atactic polypropylene, the methyl group (-CH<sub>3</sub>) is randomly aligned, alternating (alternating) for syndiotactic polypropylene and evenly for isotactic polypropylene. This has an impact on the crystallinity (amorphous or semi-crystalline) and the thermal properties. i-PP and s-PP are semi-crystalline materials with melting temperatures of about 165 and 135 °C, respectively, while a-PP is amorphous [1].

The s-PP has a limited availability and, therefore, it is considerably more expensive at present than i-PP. In general, i-PP has a high melting temperature and excellent electrical properties, such as high electrical resistivity, low dielectric constant and low dielectric loss. Therefore, a logical question is why is i-PP not being used in large quantities as insulating material for cables? Firstly, the mechanical properties limit the application of i-PP in cables, since it suffers from high stiffness, brittleness at especially low temperatures and low thermos-oxidative stability. Secondly, the breakdown strength of i-PP is relatively low. Breakdown strength is the voltage when an electrical insulating material suddenly becomes an electrical conductor and electric current flows through it. This is caused by space charge accumulation due to the large spherulite size. The space charge accumulation causes electric field distortion and contributes to the breakdown of the insulation material, which decreases the service life of the HVDC power cable.

The deficiencies of i-PP materials can be circumvented by using either random or heterophasic polypropylene. These PP-based copolymers simultaneously exhibit high mechanical flexibility with good electrical properties. Therefore, PP copolymers containing up to 10 wt% of ethylene offer more optimal properties for use as insulating materials than i-PP [1].

## 3.1 History

Alternating current (AC) power cables were widely used earlier, because they were easier to maintain and had lower power losses than direct current (DC) cables. HVAC turned out not to be the most effective way of transferring power and rapidly HVDC became the more popular choice. The technological advancements to the modern HVDC cables and transmission systems were made in 1930 in Sweden by ASEA, now known as ABB. The first HVDC subsea cable was put into use in 1954, named Gotland 1. This was a 98 km 100 kV and 20 MW system between mainland Sweden and Gotland. This marked the beginning of the modern era of HVDC and the basic concept has remained essentially the same since.

Gotland 1 was a mass-impregnated (MI) cable, meaning the insulation was made of lapped paper that was impregnated with a high viscous compound. MI HVDC cables are reliable and are the most used cables for submarine applications. Their weakness is that they are poorly suited for land applications. At this point, MI HVDC cables were the preferred choice; however, after the first polymer extruded cable appeared, people realized their future potential. Thereafter, scientists have been developing and refining different polymer combinations and searching for the optimal additives packages for the polymeric insulation materials. In 1999, a new link was built in Gotland using an 80 kV extruded HVDC cable system having cross-linked polyethylene insulation. Three years later, ABB also installed the Murray link in Western Australia, and it became the longest land-based HVDC cable in the world at 180 km long [5].

Extruded cables are on par or even succeeded the MI cables. XLPE cables are mechanically more robust and simpler to install, because that the jointing process is much simpler for XLPE cables. This is especially noticeable on land where about one joint every 1-2 km is needed, so XLPE cables are more popular for land cables. The range of MI cables is around 600 kV with a power rating of 1100 MW, giving a power transmission capacity of 2200 MW in bi-pole configuration. The range of XLPE cables is about at 525 kV with a power rating up to 2,600MW.



Thus, we could ask ourselves why XLPE cables are not more popular than MI cables. The reason is that MI cables have been proven to be reliable and have been in use longer. The critical factor is that the big organization and investor behind the big projects, like NordLink (between Norway and Germany) and the North Sea Link (between Norway and the UK), want as little risk as possible. Consequently, MI cables with their long and proven track record are deemed a safer investment than the somewhat unproven XLPE cables. [6]

### 4.1 Structure of HVDC cables

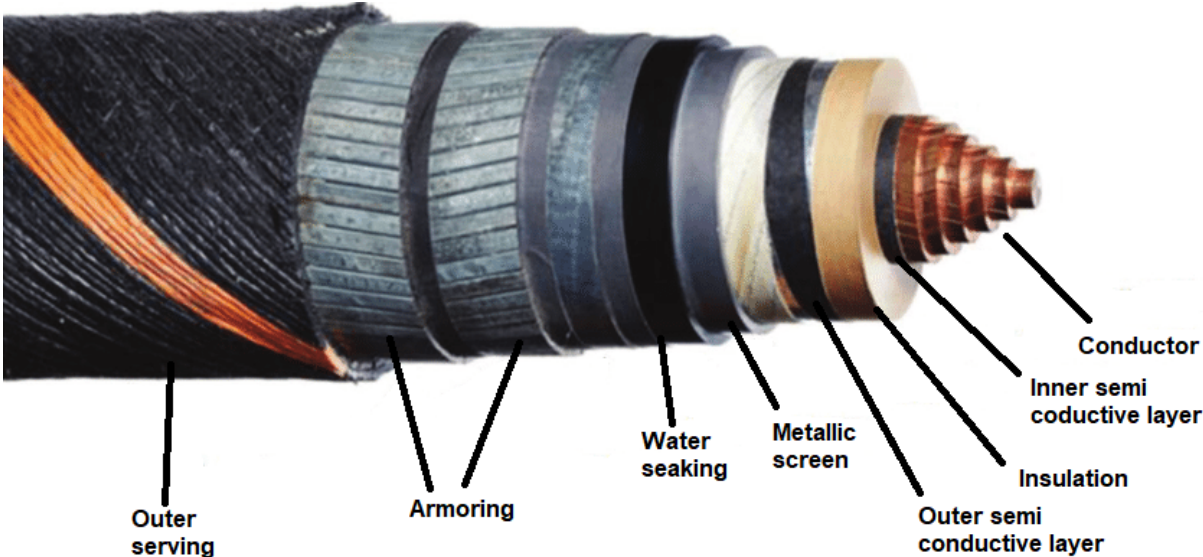


Figure 2 Submarine HVDC cross-section

### 4.2 Conductor

Copper is the first choice of metal for conductors with highest electrical conductivity rating of all non-precious metals. Copper dominates underground systems because its higher volumetric electrical and thermal conductivities compared to other conductors. These beneficial properties for copper conductors conserve space, minimize power loss, and maintain lower cable temperatures. [7]

Next choice is Aluminum, which is lighter and cheaper. Aluminum is often used instead of copper in overhead transmission lines due to its lighter weight and lower cost. It can also be used in deep undersea cables that are below 400m. If the conductor is stranded, it looks like a metallic rope made from metallic strings and if it is profiled it is made of bigger and flatter wires. Stranded is more flexible and thus easier to install, while profiled is stiffer but has better protection against longitudinal water penetration. [7]

### 4.3 Inner semi conductive layer

Surrounding the conductor is a very thin layer of semiconductive compound that is supposed to maintain a uniform electric field around the core. It adheres the conductor to the insulation and smoothens out surface irregularities, as the conductor is not an even surface and air pockets are detrimental. This is usually achieved by using the same material as the insulation and dispersing carbon black into the polymer matrix. Homogenous carbon black dispersion is important for good thermal stability and reducing or eliminating space charges. [7]

### 4.4 Outer semi conductive layer

Between the inner and outer semiconductors is the insulation that have already been described earlier. Outer semi conductive layer has the same general purpose has the inner layer, which is to create a smooth surface and distribute the electrical field equally across the surface against the metal screen. The outer layer is often made of the same material as the insulation but impregnated with carbon black particles. The compounds used in the outer layer can be different from the inner. [7]

## 4.5 Metallic screen

The electrostatic metallic screen is the only layer with the specific task of withstanding voltage. It is applied on the insulation layer and further contributing to the radial field. The screening strengthens the cable mechanically and accomplishes a safety action of providing a low resistance path to short circuit. This is to avoid sort circuiting to the soil. There are two types of screening: the first is metal wires usually made of copper under a thin continues metallic sheath often made of aluminum. The wires are for short circuits and the sheath is to create a barrier against moisture. The second type is a continuous metal sheath usually made of aluminum, copper, or lead. The sheath is either an extruded layer with corrugated shape or a metallic foil bent in a cylindrical shape. The sheath must still ensure that the cable has good flexibility for transportation and laying. [7]

## 4.6 Water sealing

Hygroscopic powders are dispersed in stranded conductors, while hygroscopic tapes are wound on both stranded conductors and on metallic screens. In case of damage to the protective thermoplastic over sheath the hydroscopic tapes prevent longitudinal water propagation over the metallic screen. [7]

# 5.1 AC vs DC

HVDC transmission system consists of three basic parts: 1) converter station to convert AC to DC, 2) transmission cable and 3) second converter station to convert back to AC. The difference is that HVDC needs terminal stations that use thyristor or IGBTs based converters for conversion between high & low DC voltage. HVAC do not need these expensive converters only a transformer, which makes HVAC cheaper for short distances. HVDC is usually preferred to be used for transmitting power over 600 km, this number will fluctuate as many different factors come to play. AC is used a lot for domestic and industrial purposes but is rare for long transmission lines. That is why the first transmission systems were based on AC-types because they were cheaper, more stable than DC -types and the need for long lines were low. There are pros and cons to both systems, and it depends on several factors what is more viable and economical for a project. [8]

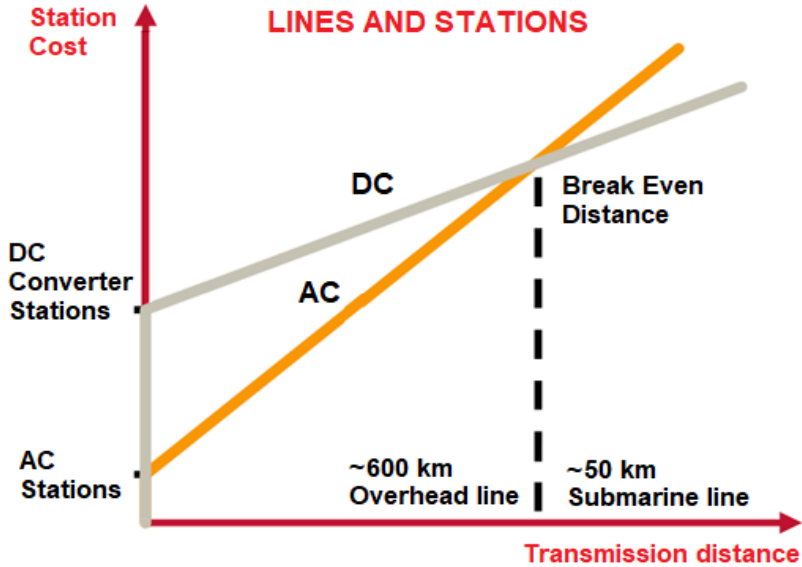


Figure 3 HVDC vs HVAC

AC cables alternate their polarity this means that AC-systems continuously change direction. This will take its toll and make AC-systems worse than DC at transmitting over long ranges. The cables functions like capacitors and the power only comes through when it is loaded. AC-systems must load up the cable every half cycle which means energy goes to waste charging the cable. That is not a problem for DC-systems where the electricity does not change directions, so once the cable it charged, and it will output all the energy after that with minimal losses. [8]

When two or more AC-cable lie parallel to each other, the magnetic field of one cable will induce longitudinal localized electric current, called an eddy current, to the adjacent wires. This alters the overall distribution of the current flowing through the cables in such a way that the current is concentrated in areas of the conductor farthest away from the nearby cable carrying current in the same direction. Since the current is concentrated in a smaller area the resistance will increase in the nearby cables. This phenomenon is called the proximity effect and it increases with frequency; at high frequencies the resistance of an AC-circuit can easily exceed ten times when compared to its DC counterpart. [8]

# 6.1 Degradation mechanisms

Polymers undergo thermal-oxidative degradation when exposed to heat, light or oxygen. This will change the structure of polymers in a significant way and dramatically affect the service life and properties of the polymer. To negate these changes antioxidants must be added to the polymer to prevent premature failure and it is the only way changes can be partially inhibited or slowed down. Stress and exposure to elements in the environment increase the rate of polymer deterioration. All polymers will eventually experience some type of degradation during their service life such as mechano-degradation, thermal oxidation, photo oxidation or ozone degradation. This degradation will lower the polymer's mechanical properties due to changes in the molecular weight, molecular weight distribution and chemical composition of the polymer chains. Polymer chains will break via so-called chain scissions, which leads to softening of the polymer. Some more changes are embrittlement caused by chain hardening, cracking, charring, color changes and a general reduction in many of the desirable physical properties.

[9]

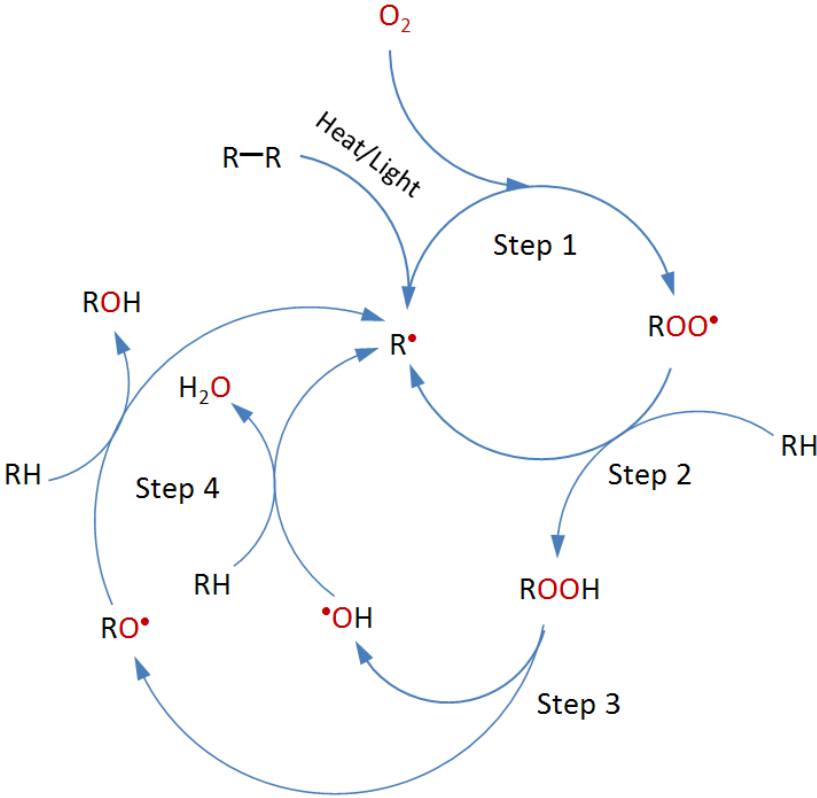


Figure 4 Polymer Degradation Cycle

## 6.2 Initiation

The initiation in the first phase of the oxidative degradation is typically started by the formation of free radicals ( $R^*$ ). The radicals are either formed by hydrogen abstraction or by homolytic scission of a carbon-carbon bond. This can occur during polymerization, processing or service. [10]

## 6.3 Propagation

The propagation is the second phase and involves several reactions. The first step is when atmospheric oxygen molecules ( $O_2$ ) react with free radicals to form a peroxy radical ( $ROO^*$ ). The peroxy radical further reacts with a hydrogen atom from another polymer and abstracts it to form an unstable hydrogen peroxide ( $ROOH$ ). The unstable molecule then immediately decomposes through homolytic cleavage and splits into two new free radicals, which are alkoxy ( $RO^*$ ) and hydroxyl ( $^*OH$ ) radicals. These two molecules then also abstract labile hydrogen atoms from other polymer chains. Because each hydro peroxide can generate two new free radicals, the process can accelerate depending how easy it is to abstract hydrogen from the other polymer chains. How quickly the free radicals undergo termination also affects the speed at which the propagation mechanism occurs. [10]

## 6.4 Termination

The third phase is termination and its reaction progress by recombination of two radicals or by disproportionation/hydrogen abstraction. These two reactions always occur but can be deaccelerated by the addition of stabilizers. Recombination of two chain radicals results in an increase of the molecular weight and cross-linking density. The result of these changes is that the polymers become more brittle and cracked, which is the opposite of chain scission where the molecular weight decreases instead, causing the polymer to become softer and to a reduction in mechanical properties. The condition and the type of polymer determine which of these termination processes are dominant. Polymers with less active double bonds, for example polybutadiene and polychloroprene, are more likely to endure embrittlement caused by cross-linkage than polymers with short alkyl side groups like polypropylene, polybutylene and unsaturated rubbers like natural rubber. [10]

## 7.1 Antioxidants

Polymer properties will change over time when used in applications where it is subjected to long-term exposure to radiation, excessive heat, high electric fields and/or corrosive environments. Polymer insulations for HVDC cables are exposed to at least two of these elements and, therefore, finding a good antioxidant package is critical for long-term cable durability. Changes are the results of oxidative degradation caused by free radicals which are formed through hydrogen abstraction or homolytic scission of carbon-carbon bonds when polymers are exposed to heat, oxygen, ozone or light.



These changes have a large impact on long-term service life and properties of the polymer. The properties tends to deteriorate the physical & mechanical properties, molecular weight will decrease and melt flow index will increase due to  $\beta$ -scissions in the case of polypropylene, discoloration of polymer takes place due to oxidation, and thermal stability characteristics of the polymer decrease. These changes can be partially inhibited or delayed by the addition of suitable antioxidants. The mechanism, by which a polymeric material undergoes autoxidation involves a free radical chain reaction. PP has a tertiary proton in every monomer unit, which makes it very vulnerable to this free radical mediated chain degradation. [11]

## 7.2 Phenolic primary antioxidants

Antioxidants may work through single or combined mechanisms and based on their activity, they have been categorized into primary and secondary antioxidants. Primary antioxidants react rapidly and interrupt the primary oxidation cycle by removing the propagating peroxy, alkoxy and hydroxy radicals and are, therefore, called "Radical Scavengers" or "Chain-breaking" antioxidants. To specify, these mainly phenolic antioxidants donate hydrogen to the free radicals which convert them into hydroperoxides by electron transfer of an electron and proton from the phenolic moiety to the peroxy radical.

Common commercially used primary antioxidants are sterically hindered phenols and aromatic amines. They are available in various molecular sizes, structures, and functionalities. Sterically hindered phenols are the most extensively used antioxidants, they have high radical scavenge efficacy for oxygen centered radical and, therefore, provide both short-term and long-term stabilization for polymeric materials. Sterically hindered phenols can be classified according to the substituent pattern in 2-, 4- and 6-positions, into fully or partially sterically hindered phenolic antioxidants. The efficacy of the sterically hindered phenolic antioxidants is largely determined by the content of phenolic moieties and the molecular weight of the phenolic antioxidants.

Studies have shown that for polypropylene subjected to circulating air oven aging at 135 °C and 149 °C the best results have been obtained with pentaerythritol Tetrakis[3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate] type of phenolic antioxidants. In recent years, it has also been shown that the bio-active form of vitamin E,  $\alpha$ -tocopherol, is an extremely effective antioxidant for polypropylene, especially during polymer processing at high temperatures. In addition, aromatic amines have been found to be the very efficient primary antioxidants, but their shortcomings are discoloration and less favorable toxicological profiles than sterically hindered phenols have in general. However, aromatic amines may also exhibit favorable antiozonant and metal ion deactivating properties. [12]

### 7.3 Secondary antioxidants

The most important mechanism of secondary antioxidants is the non-radical hydroperoxide decomposition. Therefore, they are sometimes referred to as “peroxide scavengers”. They decompose hydroperoxides into nonreactive products and, therefore, interrupt the second oxidative cycle by preventing or inhibiting the generation of free radicals such as peroxy, alkoxy and hydroxyl radicals. Using both primary and secondary antioxidants leads to a strong synergistic effect against oxidation, since both oxidation cycles are effectively suppressed [12]

The most significant classes of secondary antioxidants are phosphite esters and organosulfur compounds. Arylphosphites reduce hydroperoxides to alcohols and are themselves oxidized to the corresponding phosphates (therefore, the consumption of trivalent organophosphorus secondary antioxidants can be monitored by analyzing the extent of phosphate formation). The efficacy of aryl phosphite is a compromise between peroxy scavenging and hydrolytic stability. The peroxy radical efficacy increases with less sterically bulky aryl substituents, whereas the hydrolytic stability again decreases at the same time. Thiosynergists decompose molecules of hydroperoxide catalytically, whereby one antioxidant molecule destroys several hydroperoxides. This is done by transforming them into the corresponding alcohols and are themselves transformed to sulfoxides and sulfones [12]

## 7.4 Factors Determining antioxidant selection

Several factors need to be considered, when selecting antioxidants (AOs) for various polymers. In many cases, a compromise between desired performance and additive costs need to be made. Here are some additional considerations:

Application requirements and what type of stresses the polymer will be subjected to during production, service life and disposal. AO is for processing/melt stabilization or long-term heat stability need to be taken into account. What are the safety requirements, is the polymer in direct contact with e.g., food or subjected to extractive media like in hot water pipes, etc. What is the temperature profile during polymer processing and overall conditions during service life itself?

The plastic additive structures need to be different for various polymer types such as PP, LDPE, PA or PET, since the underlying degradation mechanisms are polymer structure dependent. In order to avoid polymer degradation during polymer processing various process stabilizers need to be added depending on the processing method (.e.g. injection, blow molding, extrusion).

One needs also to pay attention to the possible interactions between the AO and other additives in the polymer. Will the different additives react with each other and will the interaction be synergistic or antagonistic?

Will the physical (liquid, granules, concentrate) form of the AO impact on the production processes, compatibility with the polymer matrix and migration tendency? [11]

## 8.1 Materials

Table 1 shows the different polymer and antioxidant combinations that have been evaluated in this study. Most of the antioxidants were in powder form except Songnox 2124, which was originally in granular form and it was prior to melt mixing with polypropylene grinded to powder. Whereas, antioxidants denoted BASF IrgaStab Cable KV10 and Lowinox FAST XL were liquids.

Sample nro	Polypropylene grade	Antioxidant	Loading of Antioxidant
1.	Hiflex CA 7800 A	Irganox B 215 (Blend of Irganox 1010 (33%) and Irganox 168 (66%))	0.2 wt%
2.	Hiflex CA 7800 A	Irganox B 215 (Blend of Irganox 1010 (33%) and Irganox 168 (66%))	0.4 wt%
3.	Hiflex CA 7800 A	Songnox 11B (Blend of Irganox 1010 (50%) and Irganox 168 (50%))	0.2 wt%
4.	Hiflex CA 7800 A	Songnox 11B (Blend of Irganox 1010 (50%) and Irganox 168 (50%))	0.4 wt%
5.	Hiflex CA 7800 A	Songnox 2124 + Songnox 168	Songnox 2124 (0.4 wt%) + Songnox 168 (0.1wt%)
6.	Moplen RP215 (75 wt%) & Hiflex CA7441A (25 wt%)	Songnox 11B	0.4 wt%
7.	Hiflex CA 7800 A	BASF IrgaStab Cable KV10	0.2 wt%
8.	Hiflex CA 7800 A	Lowinox FAST XL	0.2 wt%

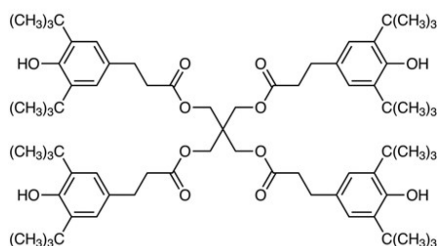


Figure 5 Irganox 1010

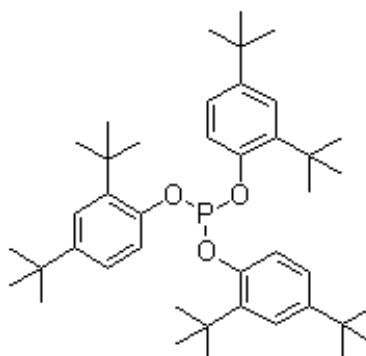


Figure 6 Irganox 168

## 8.2 Preparation of the Samples

The antioxidants were mixed into the polymer by using a twin-screw lab extruder at Turun AMK. The extrusion parameters and heat profile were chosen from the extruder manufacturers recommendations for this polypropylene grade and then slightly modified in order to get a nice and uniform polymer strand. The amount of powder antioxidant was measured up by the amount of mass the hopper pushes into the screw per minute. It was then continuously fed into the screw before zone 1. The hot polymer strand was air cooled on a conveyor and then granulated by a pelletizer at the end. Detailed view of the parameters and heat profile can be seen below:

Extrusion parameter	Speed
Motor speed	37 rpm
Hopper feed speed	20 rpm
Air cooling conveyer belt	240 rpm
Drawing machine	3 rpm
Pelletizer	11 rpm

Heatprofile in °C										
Zones	1	2	3	4	5	6	7	8	9	10 die
Temperature	180	185	190	190	200	210	210	210	210	195 190

*Table 1 Heat profile of the extruder*

Thereafter granulates were injection molded to tensile test bars for mechanical properties testing. Tensile test bars were placed in an air forced oven at 150 °C for thermal aging in accordance to standard ISO 527-1. The samples were taken out at time intervals to monitor changes caused by thermal oxidative degradation. Samples were in room temperature for at least 16h before any analysis was conducted. Some of the samples had to be frozen down due to time concerns. The frozen samples were taken out 24h hours and kept at room temperature before further sample analyzes were made. The samples were taken out at the following intervals: 3, 6, 9, 12, 15, 21, 27, 33 days of oven aging.

## 9.1 Methods

### 9.2 Tensile

The ability to resist breaking under tensile stress is one of the most important and widely measured properties of materials used in any applications. It is very important to know the basic mechanical properties of the polymer before its application in its service environment, basically how much it can be stretched, how much it can be bent, how hard or soft it is, and how it behaves after repeated stress. Molecular weight, cross-linking and crystallinity are a few properties that affect the tensile strength of polymers [16].

Tensile strength is the highest stress required to break the sample by stretching it and ultimate strength is defined as the maximum stress that a material can withstand before failure. Tensile strength can be defined as the magnitude of force applied along the sample, which is divided by the cross-sectional area of the sample in a direction perpendicular to the applied force. Stress is the force per unit area of a material, therefore:  
Tensile Stress (Mpa) = Force (N) / Cross-sectional Area (A)

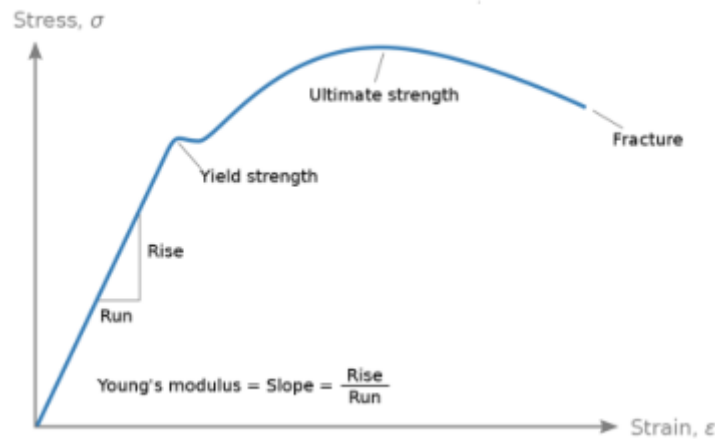


Figure 7 Tensile strength curve

An object or medium under stress becomes deformed. The quantity that describes this deformation is called strain which can be measured as the change in length. Ultimate elongation is important for any kind of material. It is nothing more than the amount the sample can be stretched before it breaks. The greater the stress, the greater the strain, however the relation between strain and stress does not need to be linear. Only when stress is sufficiently low is the deformation it causes in direct proportion to the stress value. The proportionality constant in this relation is called Young's modulus. The yield strength is defined as the maximum stress a material can withstand without undergoing permanent deformation. [16]

To measure the tensile strength of the polymer samples, the instrument Lloyd Instruments LR 30k was used. This machine simply clamps each end of the sample, then it stretches the sample. While it is stretching the sample, it measures the amount of force (F) that it is exerting and the length that the clamps have moved. Tensile tests were made on the sample test bars and the machine gave a strength curve from which the elongation at break, ultimate strength, yield strength and Young modulus could be calculated. 5 parallel test dog bone type of specimens were tested for each of the seven samples that were retrieved at different time intervals. Average values were calculated from the 5 parallel test specimens. In case of technical errors during mechanical testing of specimens they were excluded from the calculations. The rate of increase in clamp distance was 25mm/min. [16]

The measurement of the sample dog bone can be seen from figure 6. Young’s modulus was calculated with the formula:

$$E = \frac{FL_0}{A\Delta L}$$

Where E is the Young's modulus, F is the force exerted on an object under tension, A is the actual cross-sectional area, ΔL is the amount by which the length of the object changes and L<sub>0</sub> is the original length of the object. [16]

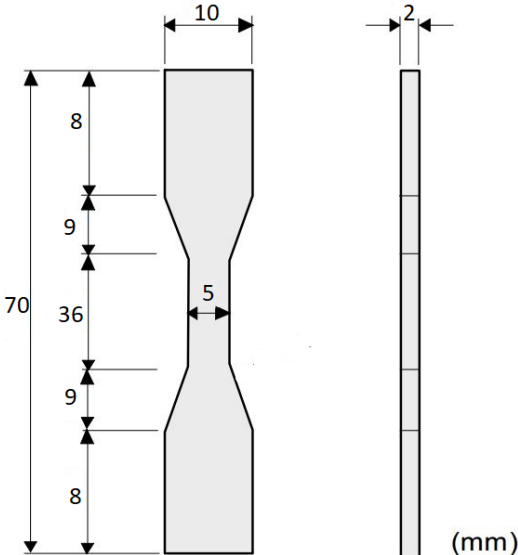


Figure 8 Dimension of the sample dog bones



### 9.3 Melt Flow Index - MFI

Melt flow index (MFI), melt flow rate (MFR), or melt index (MI) are the same type of tests, which are determined under different test conditions, and they are used for measuring melt viscosity under a constant load and a low shear rate. Melt Flow Index is defined as the weight of the polymer (g) that moves under 10 minutes through a capillary of a specific diameter and length, caused by pressure applied through a deadweight under prescribed temperature conditions. Starting with a clean barrel, the polymer is added and packed into the barrel with the plunger or piston. After a specified heating period of polymer melt or soften resin, a weight is placed on the piston, and the molten polymer is forced through the die. Higher melt flow index correlates with a lower viscosity polymer. As the polymer viscosity decreases, the flow per unit time increases. [17]

MFI measurements need a very strict control of all variables such as temperature, loading, timing, sample collection and weighing, although the test is simple as such. Three MFI measurements were conducted on each polymer. The produced strings were weighted to the nearest 0.001 g and their average mass was calculated. The first cutoff and any samples containing bubbles were discarded. The granules were aged in an oven, in the same conditions as the dog bones, but on petri dishes. The granules were then taken out of the oven after 7, 14, 21 and 27 days. They were kept at room temperature for 24 h before determination of MFI. The temperature in the cylinder was maintained at 230 °C for 15 min before loading the polymer granules into the cylinder. A weight of 2.16 kg was used during the experiment and 4 g of polymer granules was loaded into the barrel. The unloaded piston was inserted and after 5 min the weight was added.

## 9.4 Thermogravimetric analysis - TGA

TGA can be used to analyze the thermal, thermo-oxidative stabilities (the oxygen absorption rate of the material), and in some cases the composition (e.g. filler content, polymer resin content, amount of solvent) of the samples. TGA studies the changes in weight of the samples while increasing or decreasing the temperature in a controlled environment. For our samples we are interested in thermal stability of the polymers. The thermogravimetric curve provides the decomposition temperature profile of the propylene copolymer containing different set of stabilizers. The upper limit of the thermal stability for the material is often defined by the onset of mass loss. Some extensive degradation can occur before detectable changes occur in the mass of the sample.

Dog bones that were aged 0, 15 and 33 days were analyzed with TGA in this study. Samples that were used in the TGA analysis were cut from the middle of the aged dog bone ends by using a knife. The cut pieces were placed in alumina sample holders with an average weight of 10 mg. The following method was performed under nitrogen gas flowing at 100ml/min into the chamber. The onset temperature was taken from the Trios program and 10% and 90% weight loss temperatures was manually calculated. [18]

## 9.5 Differential scanning calorimetry - DSC

Differential scanning calorimetry is one of the most used thermal analysis techniques, and it can be used to study the melting of a crystalline polymer or its glass transition. This provides qualitative and quantitative information about endothermic and exothermic processes or change in heat capacity. The concept of the DSC is to obtain information on thermal change in the sample by heating or cooling it alongside an inert reference. The sample and the reference are in a cell, where the temperature sensors are located. Two identical measuring sensors are used for the sample and the reference. The difference in responses between those signals represents thermal change, which is free from diverse thermal effects, while both sensors are affected equally. This allows for high sensitivity in measurements in a controlled environment. [20]

Polymer chains have high mobility above glass transition temperature. As the temperature rises, the polymer chains have enough energy to form ordered arrangements and undergo crystallization. Recrystallization occurs after the polymer has melted and is cooled down, and the polymer chains are free to align themselves in an ordered arrangement once again. The degree of crystallinity ( $\chi_c$ ) was calculated using the formula

$$\frac{\Delta H_{m1} + \Delta H_{m2}}{\Delta H_{m^{100}}} * 100\% = \chi_c$$

$\Delta H_{m1}$  and  $\Delta H_{m2}$  are the observed heating fusion for the sample from the heating cycle.  $\Delta H_{m^{100}}$  is the heat required to melt a sample with a crystallinity of 100%, which is 170 J/g according to Lanyi, F et al. [19]

## 9.6 Fourier transform infrared spectrometry - FTIR

Since the early 1950s, IR spectroscopy has been a powerful tool for the identification of organic materials. In the past, spectra were recorded using the so-called dispersive technique, i.e., with grating-type or prism instruments. In the last decades, Fourier transform infrared (FTIR) spectrometers have become increasingly more available for routine laboratory work. The development of FTIR has introduced a popular method for the quantitative analysis of complex mixtures, as well as for the investigation of surface and interfacial phenomena. [21]

Infrared spectroscopy is an old and familiar technique for polymer characterization. It is based on the absorption of radiation in the infrared frequency range due to the molecular vibrations of the functional groups contained in the polymer chain. A device called an interferometer is used to record information about a material placed in the IR beam. [21]

The spectra were measured at the middle of the end parts of the dog bone. Some of the top layer of the dog bones was scraped off with a surgical knife to obtain a clean surface. One sample was run two times and compared to obtain a consistent result. The IR-spectra were measured between  $4000\text{ cm}^{-1}$  and  $700\text{ cm}^{-1}$

## 9.7 Oxidative induction time - OIT

TA Instruments DSC 250 was used for measuring the oxidative induction time (OIT). The aim of the OIT measurement is to assess the stability of the polymer blends and the resistance to oxidative decomposition. The longer the PP resists oxidation the greater OIT. Tzero Aluminum pans were used, without a lid so the samples are in contact with Oxygen. The samples were prepared by chopping identical samples from the tips of the tensile strength bars. The mass and shape of the sample affect the OIT measurements, so these parameters were kept as similar as possible.  $2,5 \pm 0,1\text{ mg}$  was the mass of the samples [22]. The method that was used:

- 1) Equilibrate at  $50^{\circ}\text{C}$
- 2) Ramp  $20^{\circ}\text{C}/\text{min}$  to  $210^{\circ}\text{C}$
- 3) Isothermal for 5 min
- 4) Select gas: 2 ( $\text{N}_2 \rightarrow \text{O}_2$ )
- 5) Abort next segment if  $\text{W/g} > 1.0$

stops the measurement when the energy of the oxidation is higher than  $1\text{ W/g}$

- 6) Isothermal for 200 min

# 10.1 Results

## 10.2 Ultimate elongation

The Lloyd Instruments LR 30k is designed primarily for measuring mechanical properties of metals and their alloys, i.e., it is ideal for testing applications up to 30 kN. This means the accuracy of testing less strong materials, such as conventional polymers, is not optimal. Nevertheless, the instrument can be used for measuring mechanical properties of polypropylene. All samples except for the reference had higher ultimate elongation after 3 days of aging. Between aging for 3 and 21 days, there were no drastic changes in the sample elongations, apart from the reference which failed already after 15 days. After aging for 21 to 33 days, we can observe a significant decline in the elongation in many of the samples. It is clear that the degradation has been quite severe and the antioxidants may start to be close to depletion after 21 days of aging. The polymer chains have undergone b-scission reaction whereby the polymer chains have fragmented and, thereby, the molecular weight has decreased considerably. The decrease of molecular weight has an immediate negative impact on mechanical properties and service life. [13]

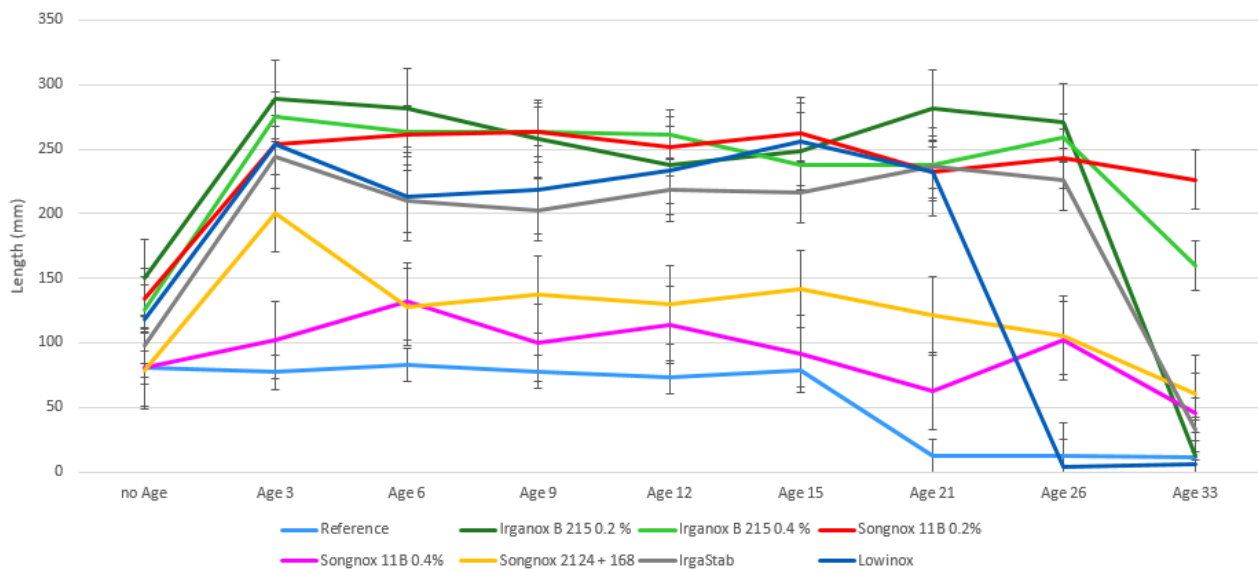


Figure 9 Ultimate elongation

### 10.3 Ultimate Strength

As we can see from Figure 10, the reference started to fail after 15 days and Lowinox after 21 days. These were the two worst performing samples, whereas the rest of the samples show similar behaviour up to 21 days of aging. Irganox B 215 0.4%, Songnox 11B 0.4% and Songnox 2124 + 168 had the best performances. Irganox B 215 0.2%, Songnox 11B 0.2% and IrgaStab did not perform as well as the top three. As could be anticipated, the decline of ultimate strengths was in proportion less than recorded decreases in elongation at different aging times. [14].

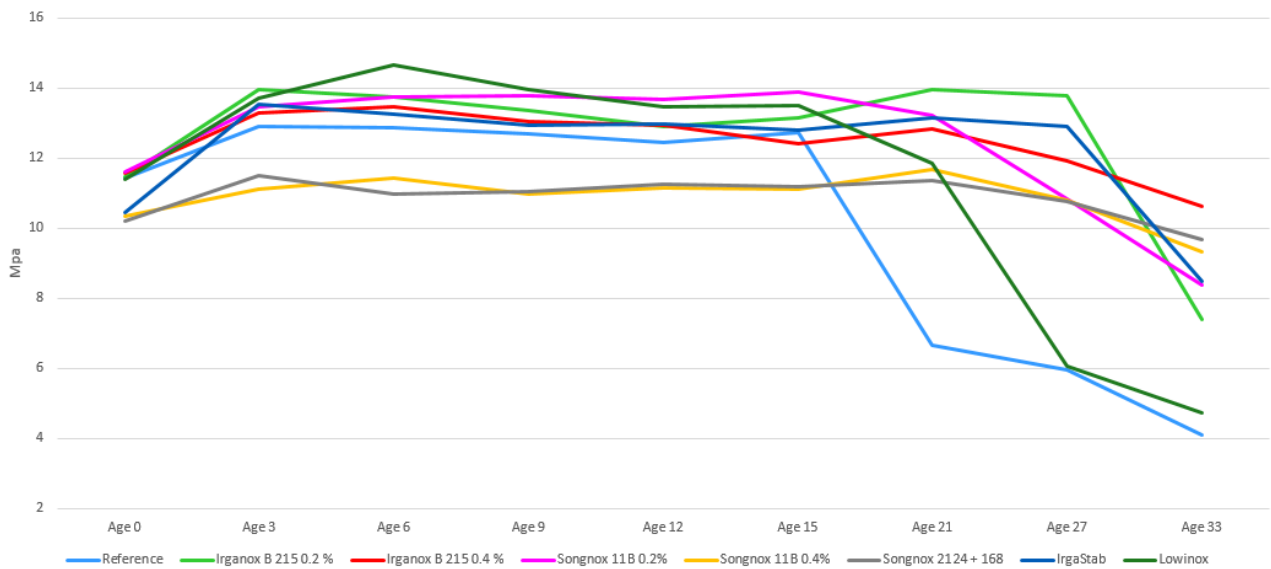


Figure 10 Ultimate Strength

## 10.4 Yield Strength and Young Modulus

From both the plots of yield strength and Young's modulus, we can clearly see that half of the polymer samples failed drastically, while propylene copolymer samples containing Irganox B 215 0.4%, Songnox 11B 0.2%, Songnox 11B 0.4% or Songnox 2124 + 168 did not show signs of drastic failure even after 33 days. The strength curves did not differ much until abrupt failure occurred. The reference was the worst, as it has only basic stabilization made by the producer. Irgastab and Lowinox also showed a poor performance. The tensile strength properties did not differ much until sudden and strong drops in strength were recorded. When PP is exposed to high temperatures in the presence oxygen, the phenolic antioxidants act as radical scavengers by reacting with the formed oxygen-centered radicals formed during oxidation of polypropylene chains, whereas the secondary antioxidants based on phosphite or thiosynergists transform hydroperoxides into nonradical species. After prolonged thermal aging, both the primary phenolic and secondary antioxidants of phosphite start to be consumed, whereby changes in the molecular weight start to become severe. At this point, the antioxidants can no longer effectively delay or inhibit polymer degradation. At the beginning of thermo-oxidative degradation of polypropylene, the highest molecular weight chains have the highest likelihood of being broken via chain  $\beta$ -scission. These high molecular weight polymer chains are known to be important for maintaining high yield strength, Young's modulus and elongation at break values. In general, PP which is a ductile material, becomes brittle as the molecular weight starts to decline and this is then also reflected in the deterioration of all measured strength values. [15]

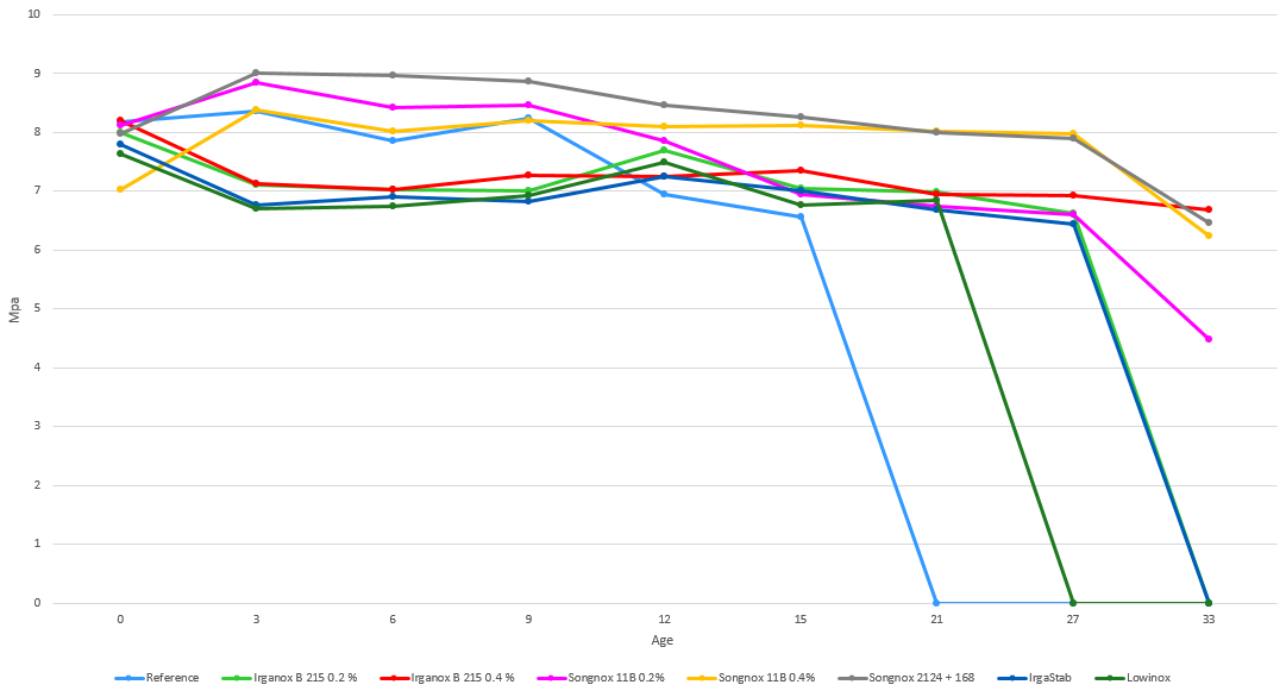


Figure 11 Yield Strength

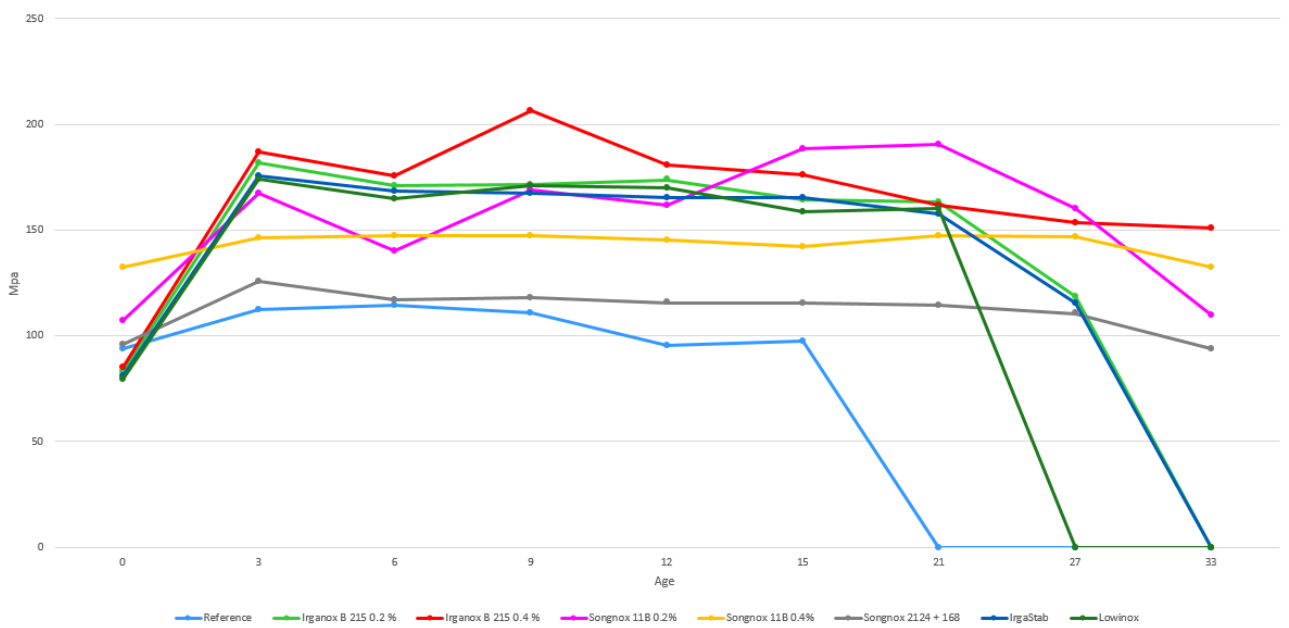


Figure 12 Young Modulus



## 10.5 Melt flow index (MFI)

From the graph, we can see that the efficacy of the various antioxidant packages was similar until 21 days of oven aging after which the melt flow index started to gradually increase. As anticipated, changes in the MFI value were first observed for the reference sample, whereas after 27 days of oven aging IrgaStab, Lowinox and Irganox B 215 at 0.2% loading also showed a decrease in protective performance, as the melt flow index started to increase. Irganox B 215 0.4%, Songnox 11B 0.2% and Songnox 11B 0.4% showed a sharper increase in their viscosity. Songnox 2124 + 168 exhibited the lowest change in MFI values in this series of experiments. [23]

Comparing the MFI graph to the tensile strength graphs, we can see similar trends. Irganox B 215 0.4%, Songnox 2124 + 168, Songnox 11B 0.4% and Songnox 11B 0.2% performed well in both tests showing that the antioxidants protect the propylene copolymer against thermal and oxidative degradation better than the rest of the antioxidant tested. The abrupt decrease of tensile strength could be observed after 27 days of oven aging and, at the same time, an increase of MFI values was noted. If the MFI values had been determined after 33 days of aging, the MFI values would surely have spiked upwards even more. [23]

One of the most important properties affecting viscosity is the polymer's molecular weight or, in other words, the chain length. The increase in MFI is a sign of chain scission. This decreases viscosity, as the shorter chains are less entangled and slip past each other during deformation more easily than high molecular weight chains. This change in molecular weight is also reflected in decreased tensile strength values. [23].

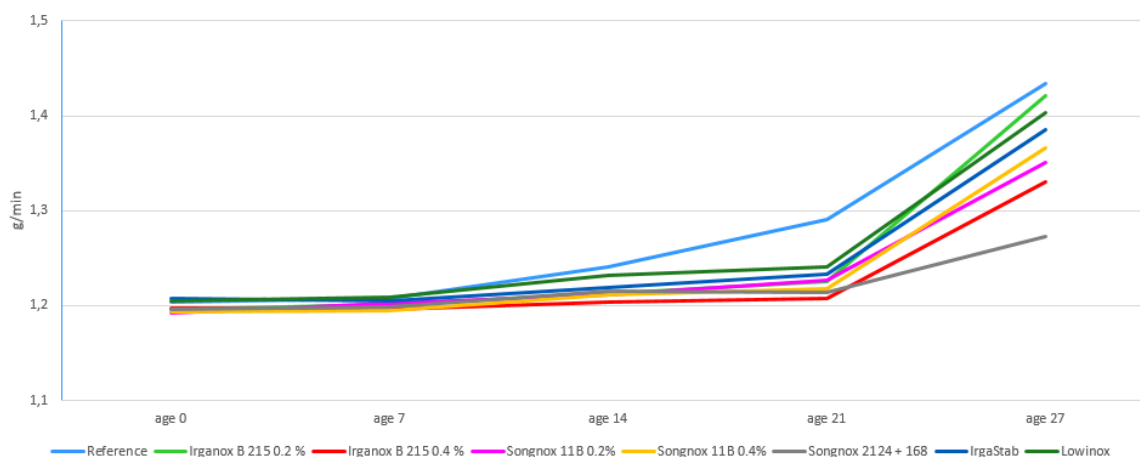


Figure 13 Melt Flow Index

## 10.6 TGA

As expected, the reference sample had the lowest thermal stabilities after oven aging and it exhibited the lowest onset decomposition temperatures, as seen in Table 3. Lowinox, Irgastab and Irganox B 215 0.2% showed poor stability, which is also in line with the other degradation monitoring experiments. In contrast, Songnox 2124 + 168, Irganox B 215 0.4%, Songnox 11B 0.4%, Songnox 11B 0.2% had the highest thermal stabilities. The onset of mass loss often defines the upper limit of thermal stability of the polymeric material. However, it should be noted that extensive degradation of polymer may already take place before the point at which detectable changes in mass loss occurs. The degradation of PP under N<sub>2</sub> atmosphere is due to chain scission and subsequent chain fragmentation. The shorter chains are more prone to thermal degradation than longer chains. The increased melt flow index is due to lowering of molecular weight and, thereby, reflected in decreased thermo-oxidative stability. [18]

## 10.7 DSC

All samples had lower crystallinities after being aged for 33 days except for the sample containing 0.4% of Irganox B 215 (see Table 2) The crystallinity increases when the polymer chains are split, as the smaller chains have better mobility to rearrange themselves than the longer chains. From the other experiments, this is shown to be happening across the samples. This can explain Irganox B 215:s increase in crystallinity. The other samples have been so degraded that their crystallinity has fallen lower. Here we also see the trend continue, as the same samples fail more than the others. [14]

## 10.8 FTIR

All of the samples were the same at day 0 graph 1 and showed little change until the end. From graph 2 and graph 3, at day 33 we can see changes that occur in the structure of the samples the best. The group that consists of Irganox B 215 0.4%, Songnox 0.4% and Songnox 2124 + 168 performed almost identically, only differentiating a little at  $3200\text{ cm}^{-1}$ . The peak at  $3200\text{ cm}^{-1}$  is a broad hydroxyl signal and at around  $1700\text{--}1760\text{ cm}^{-1}$  is a carbonyl group. As explained in the degradation mechanisms earlier, these groups are formed during the oxidative degradation process. Peaks from the graphs explained:  $1640\text{ cm}^{-1}$  are C=C double bonds which are also found in degradation products  $2858\text{--}2972\text{ cm}^{-1}$  are CH, CH<sub>2</sub> and CH<sub>3</sub> bonds,  $1460\text{ cm}^{-1}$  scissions in the polymer chain and  $1375\text{ cm}^{-1}$  methyl scission from main chain. For the rest of the samples, we can clearly see a higher overall absorbance for the functional groups containing oxygen. This is a sign of severe degradation of thermal oxidation. The reference, Lowinox and Irganox B215 0.2% shows a peak at  $1100\text{ cm}^{-1}$  which is from a C-O bond found in Alkoxy and other degradation products. From the other experiments, we can clearly see that higher amount of degradation products equals poorer performance. [24]

## 10.9 OIT

Songnox 2124 + 168 performed extremely well in the OIT tests having twice the durability compared to the next best time after 3 days of aging, i.e. 128 min as shown in Table 4 and Table 5. Then OIT dropped to 42 min, possibly because one of the antioxidants in the blend had been partially consumed after 6 days. Thus, the phosphite denoted Songnox 168 (secondary antioxidant) had been consumed after 3 days. However, the oxygen induction time remained very high even after 33 days of oven in comparison to all other sample formulations tested in this series. The high thermo-oxidative stability provided by Songnox 2124 + 168 was reflected in its good performance in all other tests evaluating the effects of aging. Songnox 11B 0.4% and Irganox B215 0.4% had good performances, which was to be expected as they had more antioxidants than Songnox 11B 0.2% and Irganox B215 0.2%. It has been well documented that the OIT increases linearly with the amount of phenolic stabilizers. The sample formulations having OIT > 1 min have little to none of the original antioxidants left, which can be seen in their overall poor efficacy in preventing undesired changes of polymer properties after oven aging. FTIR spectra showed that Irganox B215 0.2% and Lowinox exhibited high amounts of oxidation products (C=O) from thermo-oxidative degradation, which is also in line with low recorded OIT values. [25]

## 11.1 Conclusion

In this work, a series of antioxidant formulations' effectiveness for propylene copolymers intended to be used as insulation materials for HVDC cables has been evaluated by subjecting the polymer samples to forced-air oven aging at 150 °C with subsequent periodical monitoring of changes in polymer properties. Thus, changes in visual appearance (yellowing), mechanical properties (e.g., tensile strength and elongation), chemical composition (FTIR), thermal properties (TGA/DSC, onset of thermal oxidation) and thermo-oxidative stability (OIT by DSC) have been monitored periodically after oven aging up to 33 days. The experimental results reveal that the effectiveness of the eight selected antioxidant formulations at different concentration was significant and, thereby, the antioxidant formulations could be ranked. The lowest antioxidant efficacy was measured for the Lowinox and Irgastab samples which both showed very poor resistance to thermo-oxidative degradation. The poor performance of these two antioxidants can be attributed to the fact that they have been designed for XLPE cable insulations and not for stabilization of polypropylene. In this case, the antioxidants Lowinox and Irgastab should not be very effective radical scavengers in order not to prevent the desired cross-linking of LDPE during cable production. This feature explains the poor performance for polypropylene, since effective radical scavenging is essential for preventing degradation of polypropylene.

As could be anticipated in the case of Irganox B215 and Songnox 11 B, the results indicate that an antioxidant concentration of 0.2% is inferior to 0.4%. Songnox 11 B exhibited somewhat better performance than Irganox B215 at 0.2%, whereas no significant difference could be detected at 0.4%. In general, it seems that 0.2% concentration of antioxidant in polypropylene insulation material would lead to premature failure of HVDC cables. No pronounced difference between using a ratio of 1:1 or 1:3 of primary phenolic antioxidant to secondary phosphite antioxidant could be observed under these experimental conditions of oven aging. Thus, Irganox B 215 (a blend of 33% of Irganox 1010 33% and 66.6% of Irganox 168) and Songnox 11B (a blend of Irganox 1010 50% and Irganox 168 50%) exhibited similar efficacies of inhibiting autoxidation of polypropylene. Moreover, 0.4% of Irganox B215, 0.4% of Songnox 11B and Songnox 2124 + 168 were among the three best in class based on all individual monitoring tests used for assessing antioxidant efficacy as stabilizer for polypropylene. Songnox 2124 + 168 clearly outperformed all other antioxidant formulations in the OIT tests and it also gave among the best results in all other monitoring tests of polypropylene stabilization efficacy. In conclusion, Songnox 2124 + 168 showed the greatest potential as stabilizer for propylene copolymer in this study and further testing in pilot scale production of HVDC cables is recommended.

## 11.2 Future research and outlook

Recent progress in technology has made syndiotactic polypropylene (s-PP) commercially more accessible and its properties have been found to be superior to isotactic polypropylene (i-PP) as an insulating material for electrical high voltage cables. In contrast to i-PP, s-PP has the flexibility necessary for cable insulation. Moreover, the degradation induced by the copper cored of s-PP is less severe compared to i-PP. Owing to s-PP unique steric configuration (helix and zi-zag conformation), it possesses superior mechanical characteristics and electrical strength in comparison to i-PP. These beneficial features can be attributed to its morphology and small amount of spherulite phase. The recent study has even shown that s-PP can outperform XLPE and it lacks the weaknesses of conventional i-PP. Therefore, it could be a very interesting alternative as insulation material for the next generation of HVDC cables. [26]

Poly(3-hexylthiophene) P3HT is a widely studied conducting polymer that has gained much attention recently in different fields of electronics, photovoltaics and thermoelectrics. P3HT is found to be a highly effective conductivity-reducing additive. Repurposing conjugated polymers as an additive for polyolefins, rather than employing them as the active material in optoelectronic devices, may considerably enhance the scope of this promising class of materials. By adding very small amounts of P3HT, five parts per million to polyethylene, the electrical conductivity was lowered up to three times. It can be predicted that further optimization of the molecular weight and regioregularity of P3HT will result in an even stronger reduction of conductivity and, thus, enhanced electrical insulation of cable. The manufacturing of a 100 km long cable with a 6 cm wide conducting core surrounded by a 3 cm thick insulation layer would only require about 4 kg of P3HT, assuming  $c_{P3HT} = 0.0005 \text{ wt\%}$ . [27]

## 12.1 Summary in Swedish – Svensk sammanfattning

### Termisk degradering av kabelisolering baserat på polypropen

De flesta extruderade högspänningskablar använder tvärbunden polyeten (XLPE) som isolationsmaterial. Tyvärr är XLPE inte miljövänligt och bidrar inte till en grönare framtid. Polymerer baserade på polypropen har potential att vara miljövänligare och mera återanvändbara lösningar. Dessa polymerer är termoplaster med hög smältpunkt och reglerbara mekaniska och elektriska egenskaper. Målet med detta arbete är att utvärdera olika antioxidanter och deras koncentrationers potential att fungera som stabilisatorer i en isostatisk polypropenblandning. Prover av Hiflex CA 7800A-polypropen med stabilisatorerna lades i en ugn i 33 dagar. Påverkan av termisk degradering analyserades under olika tidsintervall med olika metoder: DSC, TGA, FTIR och dragtest. En koncentration med 0,2 wt% är sämre än en koncentration med 0,4 wt% och ingen skillnad upptäcktes mellan 1:1- och 1:3-förhållandena av primära och sekundära antioxidanter. Irganox B215 (0,4 %), Songnox 11B (0,4 %) and Songnox 2124 + 168 presterade bra i alla experiment och har potential för att studeras vidare.

Polymerer genomgår termiskoxidativ nedbrytning när de utsätts för värme, ljus eller syre. Detta kommer att förändra strukturen hos polymeren på ett betydande sätt och drastiskt påverka polymerens livslängd och egenskaper. För att motverka dessa förändringar måste antioxidanter tillsättas i polymeren för att förhindra tidig nedbrytning, och det är det enda sättet som förändringar delvis kan hindras eller bromsas. Alla polymerer kommer så småningom att uppleva någon typ av nedbrytning under sin livslängd, såsom mekanisk nedbrytning, termisk oxidation, fotonoxidation eller ozonnedbrytning. Denna nedbrytning kommer att sänka polymerens mekaniska egenskaper på grund av förändringar i polymerkedjornas molekylvikt, molekylviktsfördelning och kemiska sammansättning. Polymerkedjor kommer att gå sönder via så kallade kedjeklippningar, vilket leder till att polymeren mjuknar upp. Ytterligare några förändringar är sprödhet orsakad av kedjehärdning, sprickbildning, förkolning, färgförändringar och en generell minskning av många av de önskvärda fysikaliska egenskaperna. [16]

Inledningen är den första fasen och början av den oxidativa nedbrytningen som vanligtvis startas av bildningen av fria radikaler ( $R^*$ ). Radikalerna bildas antingen genom väteabstraktion eller genom homolytisk klyvning av en kol-kolbindning. Detta kan inträffa under polymerisation, bearbetning eller användning. [10]

Förökningen är den andra fasen och involverar flera reaktioner. Det första steget är när atmosfäriska syremolekyler ( $O_2$ ) reagerar med fria radikaler för att bilda en peroxiradikal ( $ROO^*$ ). Peroxiradikalen reagerar vidare med en väteatom från en annan polymer och bildar en instabil väteperoxid ( $ROOH$ ). Den instabila molekylen sönderdelas sedan omedelbart genom homolytisk klyvning och delas upp i två nya fria radikaler som är alkoxi ( $RO^*$ ) och hydroxyl ( $^*OH$ ). Eftersom varje hydroperoxid kan generera två nya fria radikaler, kan processen accelerera beroende på hur lätt det är att reagera med väte från de andra polymerkedjorna. [10]

Den tredje fasen är avbrytningen, vilket innebär väteabstraktion eller rekombination av två radikaler. Dessa två reaktioner inträffar alltid men kan bromsas genom tillsats av stabilisatorer. Rekombination av tvåkedjeradikaler resulterar i en ökning av molekylvikten och densiteten. Resultatet av dessa förändringar är att polymererna blir mer spröda och spricker. Det är motsatsen till kedjeklyvning där molekylvikten istället minskar, vilket gör att polymeren blir mjukare och minskar de mekaniska egenskaperna.



Det beror på tillståndet och polymersorten vilka av dessa processer som är dominerande. Polypropen har större sannolikhet att genomgå kedjeklyvning. [17]

Antioxidanter kan fungera genom enkla eller kombinerade mekanismer, och baserat på deras aktivitet har de kategoriserats i primära och sekundära antioxidant. Primära antioxidant reagerar snabbt och avbryter den primära oxidationscykeln genom att ta bort de förökande peroxi-, alkoxi- och hydroxiradikalerna och kallas därför kedjebrytande antioxidant. Allmänna kommersiella primära antioxidant är vanligtvis steriskt hindrade fenoler och aromatiska aminer. De finns i olika molekylstorlekar, strukturer och funktionaliteter. Steriskt hindrade fenoler är de mest använda antioxidanterna, de har hög radikalfångande effekt för att reagera med syrecenterade radikaler och ger därför både kort- och långtidsstabilisering för polymera material. Dessutom har aromatiska aminer visat sig vara mycket effektiva primära antioxidant, men deras negativa sidor är missfärgning och mindre gynnsamma toxikologiska profiler än de som steriskt hindrade fenoler har i allmänhet. [18]

Sekundära antioxidanters viktigaste mekanism är icke-radikal hydroperoxid nedbrytning. De bryter ner hydroperoxider till icke-reaktiva produkter och avbryter därför den andra oxidativa cykeln genom att förhindra eller hämma genereringen av fria radikaler såsom peroxi-, alkoxi- och hydroxylradikaler. Användningen av både primära och sekundära antioxidant leder till en stark effekt mot oxidation, eftersom båda oxidationscyklerna effektivt attackeras. De viktigaste klasserna av sekundära antioxidant är fosfitestrar och organiska svavelföreningar. Arylfosfiter reducerar hydroperoxider till alkoholer och oxideras själva till motsvarande fosfater. Effektiviteten av arylfosfit är en kompromiss mellan peroxiavlägsnande och hydrolytisk stabilitet. Peroxiradikaleffektiviteten ökar med mindre steriskt stora arylsubstituent, medan den hydrolytiska stabiliteten samtidigt minskar. [18]

Antioxidanterna blandades in i polymererna med hjälp av en dubbelskruvad labbextruder vid Turun AMK. Extruderingsparametrarna och värmeprofilen valdes från extrudertillverkarens rekommendationer för denna polypropen kvalitet och modifierades sedan något för att få en snygg och enhetlig polymersträng. Mängden antioxidantpulver mättes upp som mängden massa vilken skruven tar in per minut. Den matades sedan kontinuerligt in i skruven före zon 1. Den varma polymersträngen luftkyldes på rullande

band och granulerades sedan med en stränggranulator vid slutet. Därefter formsprutades granulaten till provstavar för testning av mekaniska egenskaper. Provstavarna placerades i en torrluftugn i 150 °C för termisk åldring i enligt standarden ISO 527-1. Proverna togs ut med tidsintervall för att övervaka förändringar orsakade av termiskoxidativ nedbrytning. Proverna var i rumstemperatur i minst 16 timmar innan någon analys utfördes. En del av proverna fick frysas ner på grund av tidsskäl. Det frysta provet togs ut 24 timmar före och hölls vid rumstemperatur innan ytterligare provanalyser gjordes. Proverna togs ut med följande intervaller: 3, 6, 9, 12, 15, 21, 27 och 33 dagars ugnsföråldring.

Lloyd Instruments LR 30k är designat primärt för att mäta mekaniska egenskaper hos metaller och dess legeringar, d.v.s. den är idealisk för att testa upp till 30 kN. Detta innebär att den inte är optimal att testa noggrannheten i mindre starka material som konventionella polymerer. Instrumentet kan ändå användas för att mäta mekaniska egenskaper hos polypropen. Efter föråldring i 21 till 33 dagar kan vi observera en signifikant minskning av förlängningen i många av proverna. Mellan 3 och 21 dagars föråldrande skedde inga drastiska förändringar i provets förlängningar, förutom referensen som hade blivit skört redan efter 15 dagar. Det är tydligt att nedbrytningen har varit kraftig och antioxidanterna börjar att ta slut efter 21 dagars föråldrande. Polymerkedjorna har genomgått en b-skärningsreaktion varvid polymerkedjorna har fragmenterats och därigenom har molekylvikten minskat avsevärt. Minskningen av molekylvikten har en omedelbar negativ inverkan på mekaniska egenskaper och livslängd. [16]

Smältindex (MFI) är ett test som används för att mäta smältviskositet under konstant belastning och låga skjuvhastigheter. Smältindex definieras som vikten av polymeren som under 10 minuter trycks genom en kapillär med en specifik diameter och längd, genom att applicera en vikt under specifika temperaturförhållanden. Högre smältindex korrelerar med en polymer med lägre viskositet. Granulerna åldrades i torrluftugnen under samma förhållanden som dragproverna, men på petriskål. Granulerna togs sedan ut vid 7, 14, 21 och 27 dagar. De hölls vid rumstemperatur i 24 timmar före mätning av MFI. Temperaturen i cylindern hölls vid 230°C under 15 minuter innan polymergranulerna sattes in i cylindern. En vikt på 2,16 kg användes under experimentet och 4 g polymer laddades i cylindern. Tyngden sattes på kolven efter 5 minuter för att säkra homogen smältning. [17]

Termogravimetrisk Analys (TGA) studerar provens viktförändringar samtidigt som temperaturen ökas eller sänks i en kontrollerad miljö. För våra prover är vi intresserade av deras termiska stabilitet. Den termogravimetriska kurvan ger sönderdelningsprofilen för proverna som innehåller olika uppsättningar av stabilisatorer. Proven som hade åldrats 0, 15 och 33 dagar analyserades med TGA i denna studie. Proverna som användes i TGA-analysen skars från mitten av de åldrade dragproven med hjälp av en kniv. De skurna bitarna med en medelvikt på 10 mg placerades i en aluminiumoxid-provhållare. Följande metod utfördes under kvävgas som strömmade med 100 ml/min in i kammaren. Onset-temperaturen togs från Trios-programmet och 10 % och 90 % viktminskningstemperaturer beräknades manuellt. [18]

Differentiell svepkalorimetri (DSC) är en av de mest populära termiska analysteknikerna och den kan användas för att studera smältningen av kristallina polymerer eller deras glasövergång. Detta ger kvalitativ och kvantitativ information om endotermiska och exoterma processer eller förändringar i värmekapaciteten. Idén med DSC är att erhålla information om termisk förändring i provet genom att värma eller kyla det tillsammans med en inert referens. Skillnaderna i signalerna man får från dessa representerar den termiska förändringen. [20]

Graden av kristallinitet beräknades med formeln:

$$\frac{\Delta H_{m1} + \Delta H_{m2}}{\Delta H_{m^{100}}} * 100\% = \chi_c$$

$\Delta H_{m1}$  och  $\Delta H_{m2}$  är den observerade entalpiförändringen för provet från uppvärmningscykeln.  $\Delta H_{m^{100}}$  är värmeenergin som krävs för att smälta en 100 % kristallint prov, som är 170 J/g enligt Lanyi, F et al. [19]

Infraröd spektroskopi är en gammal och välkänd teknik för polymerkaraktärisering. Den är baserad på absorptionen av strålning i det infraröda frekvensområdet på grund av molekylära vibrationer hos de funktionella grupperna som finns i polymerkedjan. Med FTIR spektroskopi kan man analysera många olika ämnen förutsatt att de har molekylstrukturer som interagerar med infrarött ljus i vågtalsområdet 400–4000  $\text{cm}^{-1}$ . Spektran mättes i mitten av den tjockare delen av dragprovet. En del av det översta lagret av dragprovet skrapades bort med en kirurgisk kniv för att få en ren yta. Analysen kördes två gånger per prov och jämfördes för att få ett jämt resultat. IR-spektra mättes mellan 4000  $\text{cm}^{-1}$  och 700  $\text{cm}^{-1}$ . [21]

TA Instruments DSC 250 användes för att mäta den oxidativa induktionstiden (OIT). Syftet med OIT-mätningen är att bedöma polymerblandningarnas stabilitet och motståndskraften mot oxidativ nedbrytning. Ju längre polymeren motstår oxidation desto högre OIT. Tzero Aluminiumpannor användes, utan lock så att proverna är i kontakt med syre. Proverna framställdes genom att klippa provbitar från spetsarna på dragproverna. Provets massa och form påverkar OIT-mätningarna, så dessa parametrar hölls så lika som möjligt.  $2,5 \pm 0,1$  mg var provernas massa [22]. Metoden som användes:

- 1) Jämvikt vid 50°C
- 2) Öka 20°C/min till 210°C
- 3) Isotermisk i 5 min
- 4) Välj gas: 2 (N<sub>2</sub> -> O<sub>2</sub>)
- 5) Avbryt nästa segment om W/g > 1,0

stoppas mätningen när energin för oxidationen är högre än 1 W/g

- 6) Isotermisk i 200 min

Antioxidanterna med de sämsta resultaten var Lowinox- och Irgastab-proven, som båda visade mycket dålig resistens mot termooxidativ nedbrytning. De dåliga prestationerna för dessa antioxidanter kan bero på att de är tillverkade för XLPE-kabelisoler-ring och inte för att stabilisera polypropen. I tillverkning av XLPE behöver inte antioxidanterna Lowinox och Irgastab vara särskilt effektiva radikalfångare, för att inte förhindra den önskade tvärbindingen av LDPE under kabeltillverkning. Detta förklarar den dåliga prestationen i polypropen, eftersom effektivt radikalbindande är väsentlig för att förhindra nedbrytning av polypropen. I fallet med Irganox B215 och Songnox 11 B indikerar resultaten att antioxidantkoncentrationen på 0,2 % är sämre än 0,4 %, vilket är ganska självklart. Songnox 11 B uppvisade något bättre prestation än Irganox B215 vid 0,2 %, medan ingen signifikant skillnad upptäcktes vid 0,4 %. Generellt sett verkar det som att 0,2 % koncentration av antioxidanter i polypropenisoleringsmaterial skulle leda till förtidig nedbrytning av HVDC-kablar.

Ingen signifikant skillnad syntes mellan att använda ett förhållande på 1:1 eller 1:3 av primär fenoliskantioxidant till sekundär fosfitantioxidant under dessa experimentella förhållanden. De vill säga Irganox B 215 (en blandning av 33 % av Irganox 1010 och 66,6 % av Irganox 168) och Songnox 11B (en blandning av Irganox 1010 (50 %) och Irganox 168 (50 %)) uppvisade liknande stabilisationsförmåga. Dessutom var 0,4 % av Irganox B215, 0,4 % av Songnox 11B och Songnox 2124 + 168 de tre bästa stabilatorerna, baserat på alla tester som användes för att bedöma antioxidanternas effektivitet som stabilisatorer för polypropen. Songnox 2124 + 168 överträffade tydligt alla andra antioxidantblandningar i OIT-testerna och den hade också bland de bästa resultaten i alla andra tester av stabiliseringseffektivitet. Sammanfattningsvis visade Songnox 2124 + 168 ha den största potentialen som stabilisator för propylensampolymer i denna studie men ytterligare testning i pilotskalig produktion av HVDC-kablar rekommenderas.

## 13.1 References

- [1] Zhou, Y., Peng, S., Hu, J. and He, J., 2017. Polymeric insulation materials for HVDC cables: Development, challenges and future perspective. *IEEE Transactions on Dielectrics and Electrical Insulation*, 24(3), pp.1308-1318. (Zhou, Peng, Hu and He, 2017)
- [2] Lee, J. and Zhao, F., 2020. *Global Wind Report 2019*. [online] Gwec.net. Available at: <[https://gwec.net/wp-content/uploads/2020/08/Annual-Wind-Report\\_2019\\_digital\\_final\\_2r.pdf](https://gwec.net/wp-content/uploads/2020/08/Annual-Wind-Report_2019_digital_final_2r.pdf)> [Accessed 25 January 2021]. (Lee and Zhao, 2020)
- [3] Zhou, Y., Yuan, C., Li, Q., Wang, Q. and He, J., 2018. Recyclable insulation material for HVDC cables in Global Energy Interconnection. *Global Energy Interconnection*, 1(4), pp.520-526. (Zhou et al., 2018)
- [4] Huang, X., Fan, Y., Zhang, J. and Jiang, P., 2017. Polypropylene based thermoplastic polymers for potential recyclable HVDC cable insulation applications. *IEEE Transactions on Dielectrics and Electrical Insulation*, 24(3), pp.1446-1456. (Huang, Fan, Zhang and Jiang, 2017)
- [5] Library.e.abb.com. 2014. ABB review: Special Report 60 years of HVDC. [online] Available at: <[https://library.e.abb.com/public/aff841e25d8986b5c1257d380045703f/140818%20ABB%20SR%2060%20years%20of%20HVDC\\_72dpi.pdf](https://library.e.abb.com/public/aff841e25d8986b5c1257d380045703f/140818%20ABB%20SR%2060%20years%20of%20HVDC_72dpi.pdf)>.
- [6] Sanden, B., 2021. Why mass-impregnated cables remain the solution for long-distance HVDC. [online] Nsenergybusiness.com. Available at: <<https://www.nsenenergybusiness.com/features/mass-impregnated-cables/>> [Accessed 26 April 2022].
- [7] Mazzanti, G. and Marzinotto, M., 2013. *Extruded Cables for High-Voltage Direct-Current Transmission: Advances in Research and Development*. 1st ed. WILEY, pp.11-41.
- [8] Kalair, A., Abas, N. and Khan, N., 2016. Comparative study of HVAC and HVDC transmission systems. *Renewable and Sustainable Energy Reviews*, 59, pp.1653-1675.
- [9] Al-Malaika, S., 1997. *Reactive Modifiers for Polymers*. 1st ed. Springer Dordrecht, pp.266-302.
- [10] Rabek, J., 1975. Chapter 4 Oxidative Degradation of Polymers. *Degradation of Polymers*, pp.425-538.
- [11] Polymerdatabase.com. 2021. Antioxidants. [online] Available at: <<https://polymerdatabase.com/polymer%20chemistry/Antioxidants.html>> [Accessed 28 April 2021].

- [12] Allen, N. and Edge, M., 1993. *Fundamentals of Polymer Degradation and Stabilization*. 1st ed. Springer Dordrecht.
- [13] Speight, J., 2020. *Handbook of industrial hydrocarbon processes*. 2nd ed. Gulf Professional Publishing: SCITUS ACADEMICS LLC, pp.597-649.
- [14] Gensler, R., Plummer, C., Kausch, H., Kramer, E., Pauquet, J. and Zweifel, H., 2000. Thermo-oxidative degradation of isotactic polypropylene at high temperatures: phenolic antioxidants versus HAS. *Polymer Degradation and Stability*, 67(2), pp.195-208.
- [15] da Costa, H., Ramos, V. and de Oliveira, M., 2007. Degradation of polypropylene (PP) during multiple extrusions: Thermal analysis, mechanical properties and analysis of variance. *Polymer Testing*, 26(5), pp.676-684.
- [16] Davis, J., 2005. *Tensile testing*. 2nd ed. Materials Park, Ohio: ASM International, pp.1-28,137-152.
- [17] Shenoy, A. and Saini, D., 1986. Melt flow index: More than just a quality control rheological parameter. Part I. *Advances in Polymer Technology*, 6(1), pp.1-19.
- [18] Ng, H., Saidi, N., Omar, F., Ramesh, K., Ramesh, S. and Bashir, S., 2018. Thermogravimetric Analysis of Polymers. *Encyclopedia of Polymer Science and Technology*, pp.1-29.
- [19] Lanyi, F., Wenzke, N., Kaschta, J. and Schubert, D., 2019. On the Determination of the Enthalpy of Fusion of  $\alpha$ -Crystalline Isotactic Polypropylene Using Differential Scanning Calorimetry, X-Ray Diffraction, and Fourier-Transform Infrared Spectroscopy: An Old Story Revisited. *Advanced Engineering Materials*, 22(9), p.1900796.
- [20] Menczel, J. and Prime, B., 2022. *Thermal Analysis of Polymers: Fundamentals and Applications*. 1st ed. Wiley, pp.18-37.
- [21] Mohamed, M., Jaafar, J., Ismail, A., Othman, M. and Rahman, M., 2017. Fourier Transform Infrared (FTIR) Spectroscopy. *Membrane Characterization*, pp.3-11.
- [22] Holappa, A., 2009. Evaluation of properties of melt processed thermoplastics.
- [23] da Costa, H., Ramos, V. and Rocha, M., 2005. Rheological properties of polypropylene during multiple extrusion. *Polymer Testing*, 24(1), pp.86-93.
- [24] Celina, M., Ottesen, D., Gillen, K. and Clough, R., 1997. FTIR emission spectroscopy applied to polymer degradation. *Polymer Degradation and Stability*, 58(1-2), pp.15-31.
- [25] Richaud, E., 2013. Kinetic modelling of phenols consumption during polyethylene thermal oxidation. *European Polymer Journal*, 49(8), pp.2223-2232.

[26] Yoshino, K., Demura, T., Kawahigashi, M., Miyashita, Y., Kurahashi, K. and Matsuda, Y., 2003. Application of a novel polypropylene to the insulation of an electric power cable. *Electrical Engineering in Japan*, 146(1), pp.18-26.

[27] Pourrahimi, A., Kumara, S., Palmieri, F., Yu, L., Lund, A., Hammarström, T., Hagstrand, P., Scheblykin, I., Fabiani, D., Xu, X. and Müller, C., 2021. Repurposing Poly(3-hexylthiophene) as a Conductivity-Reducing Additive for Polyethylene-Based High-Voltage Insulation. *Advanced Materials*, 33(27), p.2100714.

## 14.1 Appendix

Sample	Aged Days	Crystallization		Melting 1		Melting 2		Crystallinity $\chi_c$
		$\Delta H_c$ (J/g)	$T_p$ (°C)	$\Delta H_{m1}$ (J/g)	$T_p$ (°C)	$\Delta H_{m2}$ (J/g)	$T_p$ (°C)	
Reference	0	71.795	113.66	52.921	126.47	13.851	163.07	39.3 %
	33	36.874	110.93	15.336	124.35	10.202	162.53	15.0 %
Irganox B 215 0.2 %	0	72.261	112.11	47.052	126.46	13.572	164.16	35.7 %
	33	38.519	109.18	14.99	123.26	10.1	162.37	14.8 %
Irganox B 215 0.4 %	0	72.778	111.95	43.787	123.57	15.223	164.12	34.7 %
	33	89.799	113.66	64.413	126.81	19.624	163.8	49.4 %
Songnox 11B 0.2%	0	83.417	112.06	52.888	126.65	14.112	164.21	39.4 %
	33	60.337	110.14	38.603	124.39	11.716	163.49	29.6 %
Songnox 11B 0.4%	0	79.075	112.14	58.059	126.72	15.036	164.06	43.0 %
	33	74.826	112.17	52.482	126.52	13.101	164.03	38.6 %
Songnox 2124 + 168	0	79.215	112.03	57.364	126.72	16.187	164.14	43.3 %
	33	76.434	113.84	51.782	126.86	14.462	164.19	39.0 %
IrgaStab	0	78.645	111.94	55.145	126.83	16.82	164.03	42.3 %
	33	30.958	110	11.943	123.74	12.968	162.17	14.7 %
Lowinox	0	67.9942	112.28	44.2	126.48	12.822	164.08	33.5 %
	33	56.877	110.52	27.736	125.13	13.16	163.5	24.1 %

Table 2 DSC Crystallization



Sample	Age	Onset T (°C)	10% wl	90% wl
Reference	0	447.6	444.28	482.28
	15	447.37	445.22	482.00
	33	428.13	369.64	477.24
Irganox B 215 0.2 %	0	449.98	445.44	481.49
	15	448.48	445.78	483.72
	33	445.81	403.80	484.13
Irganox B 215 0.4 %	0	456.17	445.96	482.74
	15	456.32	445.81	483.69
	33	448.88	445.59	483.35
Songnox 11B 0.2%	0	450.56	447.40	483.17
	15	449.28	444.95	481.54
	33	447.13	440.10	480.98
Songnox 11B 0.4%	0	457.80	445.20	493.41
	15	455.22	444.37	482.86
	33	453.24	446.22	483.00
Songnox 2124 + 168	0	455.64	446.62	484.87
	15	452.82	444.10	481.71
	33	450.17	446.08	484.68
IrgaStab	0	453.86	448.28	494.19
	15	448.25	444.43	482.72
	33	443.52	420.13	486.80
Lowinox	0	449.86	445.81	481.91
	15	448.23	446.07	482.25
	33	406.59	349.96	480.29

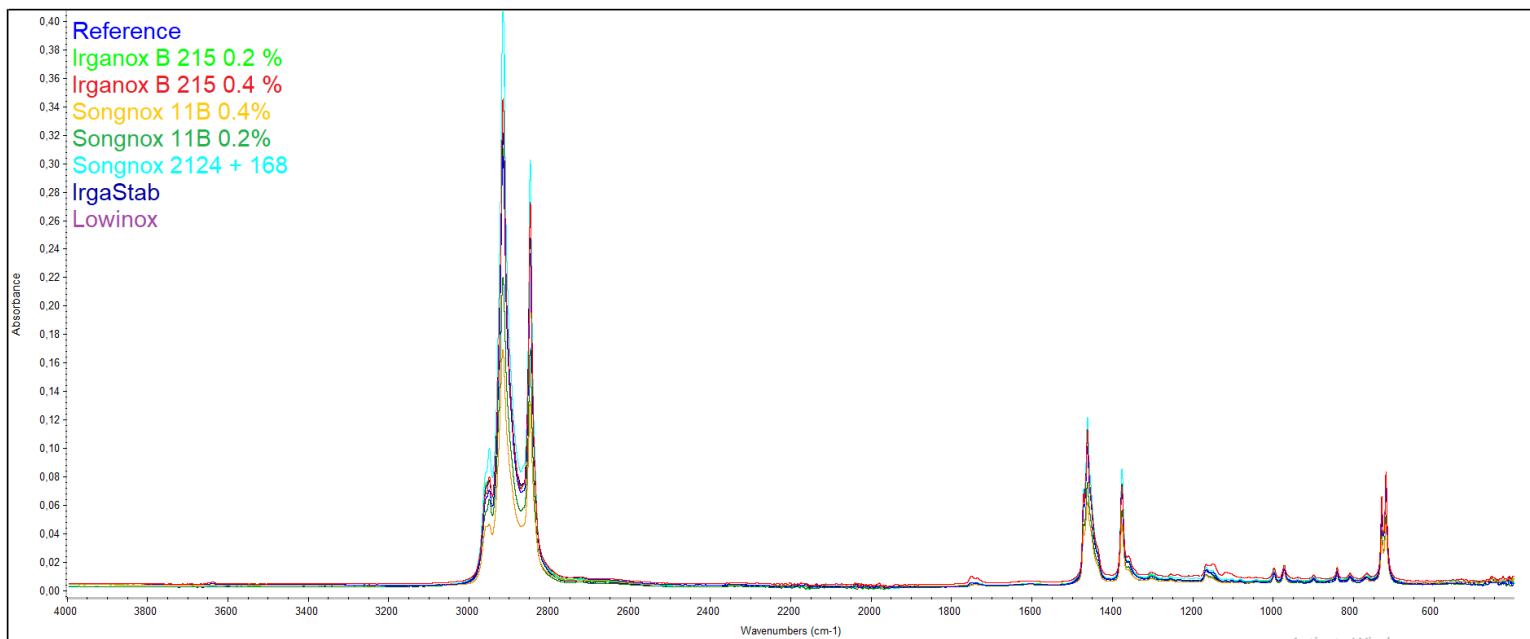
Table 3 TGA onset and weight loss percentage

OIT (min)	Songnox 11B 0.4%	Songnox 2124 + 168	IrgaStab	Lowinox
no Age	98.24	147.86	26.97	24
Age 3	49.32	128.41	12.34	8.39
Age 6	37.89	41.86	8.66	7.47
Age 9	25.16	43.34	7.96	7.22
Age 12	18.81	55.86	6.22	4.46
Age 15	14.79	44.95	6.26	5.15
Age 21	12.22	51.62	5.22	3.09
Age 27	8.69	46.63	5.14	0.87
Age 33	7.97	16.17	3.7	0.16

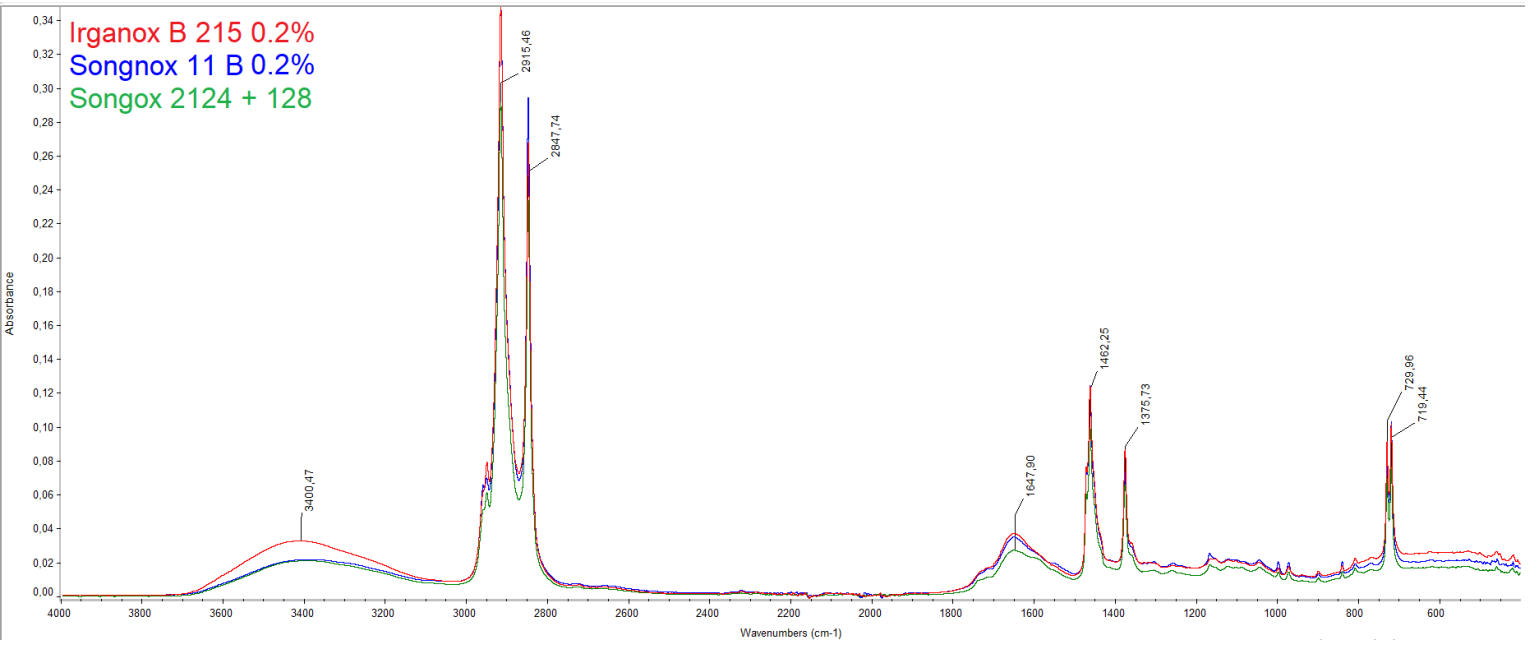
Table 4 Oxidative induction time

OIT (min)	Reference	Irganox B215 0.2%	Irganox B215 0.4%	Songnox 11B 0.2%
no Age	18.31	44.49	66.3	65.23
Age 3	8.15	34.49	46.52	25.44
Age 6	4.88	26.47	40.7	15.74
Age 9	2.82	15.98	35.82	13.66
Age 12	4.17	15.9	26.51	9.28
Age 15	3.73	10.18	17.05	8.62
Age 21	0.4	4.59	9.2	6.98
Age 27	0.47	4.77	6.12	5.74
Age 33	0.47	0.15	4.11	3.68

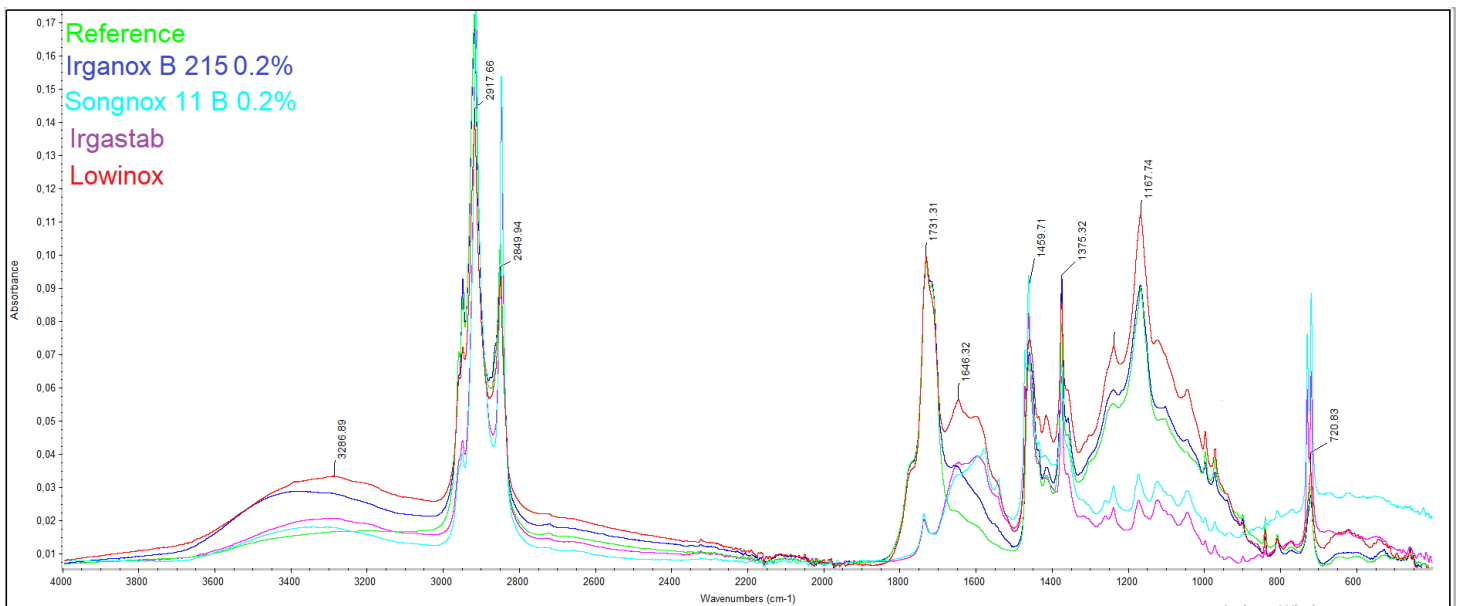
Table 5 Oxidative induction time



Graph 1 No aging



Graph 2 Age 33, good performance



Graph 3 Age 33, bad performance