ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE ENGINEERING AND TECHNOLOGY

RECOVERY OF CROSSLINKABLE POLYETHYLENE

M.Sc. THESIS

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Department of Polymer Science and Technology

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İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

ÇAPRAZ BAĞLANABİLEN POLİETİLENİN GERİ KAZANILMASI

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ARALIK 2015

Alaettin ŞENKAYA, a M.Sc. student of ITU Graduate School of Science Engineering and Technology student ID 515121001, successfully defended the thesis entitled "RECOVERY OF CROSSLINKABLE POLYETHYLENE", which he prepared after fulfilling the requirements specified in the associated legislations, before the jury whose signatures are below.

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To my beautiful wife,

FOREWORD

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December 2015

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ABBREVIATIONS

PE : Polyethylene
XLPE : Crosslinked Polyethylene
PEX : Crosslinked Polyethylene
CPEC : Crosslinkable Polyethylene Compound
AO : Antioxidant
RPA : Rubber Process Analyser
DSC : Differential Scanning Calorimeter
MFR : Melt Flow Rate
MFI : Melt Flow Index
UV : Ultraviolet
LDPE : Low Density Polyethylene
VLDPE : Very Low Density Polyethylene
MDPE : Medium Density Polyethylene
HDPE : High Density Polyethylene Coefficient of friction
HMWPE : High Molecular Weight Polyethylene
UHMWPE : Ultra High Molecular Weight Polyethylene
HDXLPE : High Density Crosslinked Polyethylene
CB-D : Chain Braking Donor
CB-A : Chain Braking Acceptor
HD : Hydroperoxide Decomposer

LIST OF SYMBOLS

T_m	: Melting Temperature
M_H	: Maximum Torque
M_L	: Minimum Torque
ts_2	: Scorch time
t_{90}	: Time to Reach 90% of Maximum Torque
ΔHm	: Fusion Enthalpy

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RECOVERY OF CROSSLINKABLE POLYETHYLENE

SUMMARY

Polyethylene (PE) has excellent electrical insulating properties, stable mechanical properties, good fatigue resistance and resistance to chemical attacks. Because of these properties, polyethylene is one of effective and important insulating material in the cable production. PE is suitable till 75°C working temperature. Moreover, many power cables require 90°C for working temperature. Therefore, thermoplastic PE is not suitable for this kind of cables, which require 90°C working temperature.

PE has molecular structure, which has linear chains of independent polyethylene molecules loosely held together by weak molecular bonds. This molecular structure of PE can be converted in to more thermal stable thermosetting compound by the process of crosslinking. Perpendicular chemical bonds are formed between parallel chains of the polyethylene molecules by crosslinking process. The parallel loose two-dimensional molecular structure is converted into a cellular three-dimensional polymeric structure. Crosslinked polyethylene (XLPE) shows superior insulation properties and high thermal stability over conventional thermoplastic insulating materials.

Crosslinking reaction can be ontained by three different methods which crosslinking with organic peroxides, silane curing and electron beam crosslinking. In crosslinking with organic peroxides method, peroxide based chemicals such as dicumyl peroxide are used and thus create carbon-carbon links to form the network in polyethylene by the elimination of hydrogen atoms. Peroxide decomposes to free radicals at high temperatures. The obtained radicals on carbon atoms along the chains react each other and create carbon-carbon bonds between polyethylene chains.

Silane coupling agents are silicon-based organic chemicals. Their general formula is $(X)_3Si\text{-}Y$, where X represents a hydrolyzable group such as ethoxy or methoxy, Y is a functional organic group (amino, methoxy, acetoxy, epoxy, etc.) that reacts with water to form silanol (Si-OH). The mostly used silane-coupling agents are vinyl alkoxy silanes such as vinylmethyldimethoxysilane, vinyltriethoxysilane, vinyltrimethoxysilane. The silane curing method consists of at least two stages. Proper silane is grafted via its vinyl groups on polyethylene through a peroxide initiated free radical reaction in the first stage. New polyethylene radicals are formed. In the second stage, the polyethylene is cross-linked via the exposure to hot water or steam which leads to hydrolysis of alkoxy groups of silane with the help of a catalyst. Based upon the possibility of performing the two stages in silane crosslinking either together or separately, two processes have been introduced, namely Sioplas® and Monosil®.

For the electron beam crosslinking, the highly energetic electrons hit the PE chains, and they break some carbon-hydrogen or carbon-carbon bonds, what leads to the formation of radicals in electron beam (e-beam) method. These radicals usually react with another radical in its vicinity, creating locally bonds between the main chains.

The desirable properties of polymers are achieved through proper molecular weigth and molecular weigth distribution. Any change to the original molecular structure will change these properties and usually is considered degradation. Antioxidants are very important additives whose role it is to maintain the chemical and physical properties of polymer during transportation, storage, processing, and serving conditions.

Antioxidants are chemical substances, which are added to polymers in small amounts with generally 1-2% and are capable in the course of autoxidation of trapping emerging free radicals or unstable intermediate products such as hydroperoxides and to transform them into stable end products.

Primary antioxidants act by trapping or deactivating radicals after they are formed. Secondary antioxidants prevent the formation of free radicals through non-radical decomposition of hydroperoxides. In general, primary antioxidants can be used alone more or less successfully, whereas secondary are used to enhance the performance of the primary antioxidant and are not used alone.

Molecular network of XLPE gives high thermal stability but makes recycling nearly impossible. Thus, the waste of XLPE is mainly burnt as a fuel or disposed in landfills. Some recycling attempts are also known, such as grinding in small particuls and put into road fillers. Some works are known in which the XLPE is tried to plasticize by various techniques. One of them applies alcoholysis of the silane crosslinked polymer in supercritical reactor. The others apply suitable heating and shearing process for partially decomposition of polymers.

Commercially crosslinkable polyethylene compounds (CPEC) which contains crosslinking agent inside are ready to crosslinking. They can crosslinked easily when they faced proper condition such as high temperature. One of the main applications of CPEC is cable insulation. Some amount of CPEC needs to be bleeded from the dies of the extruders due to the providing of required process condition before starting the process. Bleeded material becomes scrap because of presence of crosslinking agent inside which limits reuse of material. Terminate crosslinkability of bleeded material will be it is reusable and prevents it to be a scrap.

In this study, for recovery of commercial crosslinkable polyethylene compound (CPEC) was studied. CPEC has crosslinking agent inside and is ready to crosslinking when appling to appropriate conditions such as high temperature. Phenolic antioxidant (AO1), blend type of antioxidant (AO2), which has primary hindered phenolic and secondary phosphite, and amine class antioxidant (AO3) be on the point of being three different types of commercial antioxidants were used. Each type of antioxidant was added 1%, 3% and 5% into CPEC of separately. Another sample was prepared without adding any antioxidant into CPEC as blank sample. The samples with 1.5% AO1 + 1.5% AO2 and 2.5% AO1 + 2.5% AO2 were prepared to check the synergetic effects of AO1 and AO2. Laboratory plasticorder was used for mixing. All samples were mixed at 110°C with 50 rpm. The effect of antioxidants on crosslinking characteristics of samples were investigated structurally, mechanically, and thermally.

Crosslinking characteristics minimum torque (ML), maximum torque (MH) of the compounds were obtained by using rubber process analyser (RPA) at 185 °C. While MH values decreasing, while the ML values were about stable when the types and the amounts of antioxidants were changed. The difference between MH and ML (MH-ML) can be expressed cure extend which gives information about degree of crosslinking of the compounds due to torque values are close to each other. The smallest crosslinking degrees, which was 0.36 and 0.37, obtained when CPEC mixed with 5% AO1 and 2.5% AO1 + 2.5% AO2 respectively.

Mechanical property analysis of the samples showed that amount of antioxidants had a pronounced effect on the tensile properties of samples. The maximum tensile strengths decreased approximately 30% when all type antioxidants were used with 5%. Maximum decrease in elongation at break was observed when 5% of blend type of

antioxidant AO2. Minimum change at tensile strength and elongation break values observed, when phenolic antioxidant used as 1%.

Differential thermal calorimetry was used to measure the melting temperatures and enthalpy of fusion of the samples. There were not significant changes in melting temperatures (Tm), when any type and amount of antioxidants were added. Results of Tm values of all samples were obtained between 107 °C to 109°C. Although addition of AO1 and AO2 increased enthalpy of fusion of the samples, while those of AO3 decreased. The highest value was 117.7 J/g when 1% of AO2 was added into CPEC. On the other hand, the lowest value of enthalpy was 79.7 J/g with 1% of AO3.

Hot-set test is special test for cable sector that represents mechanical resistance of XLPE by controlling its crosslinking degree. Positive result in hot-set test means polyethylene chains crosslinked each other under specified conditions. On the other hand, crosslinking is not satisfactory when negative results are obtained. Hot-set test was performed to check that CPEC can crosslinkable after antioxidant addition. According to hot-set results CPEC, CPEC with 1% blend antioxidant (AO2) and CPEC with 1% amine class (AO3) antioxidant passed the test. The other combinations failed in hot-set test. It means that, the addition of antioxidants to CPEC prevented the crosslinkability of the other samples.

Melt flow rate (MFR) analysis were carried out for CPEC and CPEC with antioxidants samples. Increased antioxidant content of the sample resulted in increased MFR. Highest MFI values were obtained as 46.34%, 40.24% and 30.89% when %5 of phenolic (AO1), blend type (AO2) and amine class (AO3) antioxidants respectively.

ÇAPRAZ BAĞLANABİLEN POLİETİLENİN GERİ KAZANILMASI

ÖZET

Polietilen (PE), kimyasallara karşı dirençli, iyi mekanik özellikler sahip, yorulma dayanımı yüksek ve elektriksel dayanımı mükemmel bir polimerdir. Sahip olduğu bu özelliklerden dolayı polietilen kablo üretiminde kullanılan önemli ve etkin bir izolasyon malzemesidir. Maksimum çalışma sıcaklığı 75°C olan kabloların izolasyonunda polietilen problemsiz olarak kullanılır. Diğer taraftan bir çok enerji kablosu için 90°C çalışma sıcaklığı istenmektedir. Bu nedenle termoplastik yapıda olan PE bu tip yüksek çalışma sıcaklığı gereken kablolar için uygun bir izolasyon malzemesi değildir.

PE, birbirinden bağımsız düz zincirli bir yapıya sahiptir. Bu düz zincirler birbirlerine zayıf moleküler bağlar ile bağlıdır. PE nin bu zayıf yapısı, çapraz bağlanma prosesi termal dayanımı daha yüksek bir yapıya dönüştürülür. Çapraz bağlanma prosesi esnasında birbirine parallel zincirler arasında kuvvetli bağlar oluşur. Paralel ve gevşek 2 boyutlu bir yapı, 3 boyutlu çapraz bağlı bir yapıya dönüşür. Oluşan çapraz bağlı polietilen (XLPE) mükemmel elektriksel özelliklerin yanısıra daha yüksek termal dayanıklılığa sahiptir.

Polietileni çapraz bağlayabilmek için organik peroksit, silan ve electron demeti olmak üzere 3 farklı metod mevcuttur. Organik peroksit ile çapraz bağlanma da dikumil peroksit gibi peroksitler başlatıcı olarak kullanılmaktadır. Başlatıcının ısıtıldığında parçalanması ile oluşan radikaller PE zincirinden H atomu kopartarak, PE zincirileri arasında C-C bağları kurularak çapraz bağlanma gerçekleşir.

İkinci metod silan ile çapraz bağlama metotudur. Bu metodta fonksiyonel silan grubu polietilen zincirine aşılanır. İkinci aşamada, katalizör ve su varlığında fonksiyonel silan gruplar vasıtasıyla polietilen zincirleri birbirlerine bağlanarak çapraz bağlanma gerçekleşir. Sioplas® and Monosil® olmak üzere iki farklı proses şekli vardır. Sioplas® prosesinde, silan ve peroksit karışımı eriyik polietilene ilave edilir. Peroksit vasıtasıyla silan polietilene aşılanır. Aşılama ekstruder de reaktif ekstruzyon ile yapılır. Silan aşılanmış polietilen granül hale getirilerek kuru ve serin ortamda depolanır. Diğer taraftan, içerisinde polietilen, katalizör, antioksidan ve kaydırıcı bulunan katalizör karışımı hazırlanır. Son ürünün üretileceği esnada silan aşılanmış polietilen ile katalizörlü karışım belirli oranlarda (genellikle 95:5) karıştırılarak üretim gerçekleştirilir. Üretilen ürünün çapraz bağlanması belirli sıcaklık ve nem koşullarının altında tamamlanır. Monosil® prosesinde ise Sioplas® prosesinden farklı olarak polietilen, başlatıcı, silan, antioksidan, katalizör ve diğer katkı malzemeleri son ürünün ekstrüzyonu esnasında ekstrudere beslenir. Yine üretilen ürünün çapraz bağlanması belirli sıcaklık ve nem koşullarının altında tamamlanır.

Elekton demeti altında çapraz bağlanma üçüncü yöntemdir. Polietilen zincirleri üzerine gönderilen yüksek enerjili elektron demeti C-H veya C-C bağlarını kırar. Bunun sonucunda radikaller oluşur. Bu radikaller en yakındaki polietilen zinciri ile reaksiyona girerek çapraz bağlı yapıyı oluşturur.

Antioksidanlar, polimerlerin işleme, taşıma, depolama ve kullanma koşullarında kimyasal, fiziksel ve diğer özelliklerini korumaları için kullanılan katkı malzemeleridir. Polimer içerisine genellikle %1-2 oranında katılırlar ve otoksidasyon esnasında oluşan radikallerin ve reaktif hidroperoksitlerin polimere saldırıp polimer

yapısının bozulmasına engel olurlar. Birincil antioksidanlar, reaktif radikallare aktif H atomu vererek veya radikallere bağlanarak istenmeyen reaksiyonların oluşmasını engeller. İkincil antioksidanlar ise hidroperoksitlerin bozulup serbest radikallerin oluşmasını engeller. Birincil antioksidanlar tek başlarına kullanılabilinirken, ikincil antioksidanlar birincil antioksidanlarla beraber kullanılarak sinerjetik etki yaparlar.

Termal dayanıklılık veren moleküler network yapı, XLPE'nin yeniden işlenmesini neredeyse imkansız kılar. Bu nedenle XLPE çöpleri genellikle yakıt olarak yakılır veya dolgu olarak kullanılmaktadır. XLPE nin geri kazanımı hakkında bazı çalışmalar yapıldığı bilinilmektedir. Örnek olarak, XLPE küçük parçalara öğütülmekte ve zemin döşeme kalıplarının içine belirli oranda beslenmesi üzerine çalışma yapılmıştır. Diğer çalışmalar, XLPE'nin çeşitli teknikler ile plastikleştirilmesi üzerinedir. Bu çalışmalardan bir tanesi bir reaktör kullanarak, XLPE'nin super kritik bir sıvı içerisinde dekompozisyonuna dayanır, bir diğeri de uygun ısıtma ve mekanik kırma yöntemi ile XLPE'nin daha düşük dayanımlı PE olarak yeniden kazanımını üzerine yapılmıştır.

Ticari çapraz bağlanabilen polietilen kompoundlar (CPEC) çapraz bağlayıcı katkı malzemesi içerirler ve çapraz bağlanmaya hazırdırlar. Yüksek sıcaklık gibi uygun koşullar oluştuğunda kolayca çapraz bağ oluştururlar. En önemli CPEC kullanım alanlarından bir tanesi kablo izolasyonudur. Bir miktar CPEC, uygun proses koşullarını elde etmek için izolasyon üretimine başlamadan ekstruderin kafasından akıtılmalıdır. Akıtılan CPEC içerisinde çapraz bağlayıcı olduğu için yeniden kullanılamamakta ve hurda olarak atılmaktadır. Akıtılan malzemenin çapraz bağlanma kabiliyetinin azaltılması, malzemenin yeniden kullanılabilmesini ve hurda olmamasını sağlayacaktır.

Bu çalışma, ticari ve çapraz bağlanma özelliği olan polietilen kompound (CPEC) üzerine yapılmıştır. CPEC, içerisinde çapraz bağlayıcı katkı içeren ve yüksek sıcaklık gibi uygun koşulları bulduğu zaman çapraz bağlanan bir kompondtur. Fenolik (AO1), fenolik ve fosfit antioksidanların belirli bir oranda bulunan karışım (AO2) ve amin sınıfı (AO3) olmak üzere 3 farklı tipte antioksidan kullanılmıştır. Her antioksidan ayrı ayrı %1, %3 ve %5 olmak suretiyle CPEC içine katılarak 9 tane karışım ile içerisine herhangi bir antioksidan katılmamış CPEC numunesi de kontrol amaçlı hazırlanmıştır. Bunlara ilave olarak sinerjitik etkiyi görmek için 1.5% AO1 + 1.5% AO2 ve 2.5% AO1 + 2.5% AO2 içeren antioksidan karışımları CPEC içine katılarak 2 ayrı numune daha hazırlanmıştır. Bütün karışımlar laboratuvar mikserinde 50 rpm devir 110°C'de karıştırılmıştır. Kullanılan antioksidanların, CPEC'nin çapraz bağlanma karakteristikleri, yapısal, mekaniksel ve termal özelliklerine etkisi araştırılmıştır.

Kauçuk proses analiz cihazı (RPA) kullanarak, hazırlanan karışımların çapraz bağlanma karakteristikleri olan maksimum tork (MH) ve minimum tork (ML) değerleri RPA'da 185 °C'de ölçülmüştür. Eklenen antioksidan çeşidi ve miktarı değiştirildiğinde, minimum tork değeri olan ML çok fazla değişmezken, maximum tork değerinde değişimler gözlenmiştir. MH ile ML arasındaki fark (MH-ML) çapraz bağlanma derecesi olarak değerlendirilebilir En küçük çapraz bağlanma dereceleri 0,36 ve 0,37 ile sırasıyla AO1'in %5 ve 2.5% AO1 + 2.5% AO2 karışımının kullanıldığı numunelerde elde edilmiştir.

Örneklerin mekanik karakterizasyonunda, antioksidan miktarının, ürünlerin kopma-çekme özelliklerini belirgin bir biçimde etkilediğini ortaya koymuştur. Tüm antioksidanların %5 kullanılmında başlangıçtaki çekme sağlamlığı değerinde yaklaşık %30 azalma gözlemlenmiştir. Kopma uzamasındaki en büyük düşüş, karışım tipi

antioksidanın %5 kullanıldığı numunede elde edilmiştir. Çekme sağlamlığı ve kopma sağlamlığındaki en küçük değişim fenolik antioksidanın %1 kullanıldığı durumda gerçekleşmiştir.

Tüm karışımların ısıl özellikleri DSC analizi ile incelenmiştir. Ergime sıcaklıklarında kayda değer bir değişiklik olmamıştır. Tüm değerler 107 °C to 109°C arasında ölçülmüştür. Fenolik (AO1) ve karışım tipi (AO2) antioksidan eklendiği durumda ergime entalpi değeri yükselirken, amin tipi (AO3) antioksidan eklendiğin ergime entalpi değeri azalmıştır. En yüksek entalpi değeri 117.7 J/g olarak karışım tipi (AO2) antioksidan %1 eklendiği durumda; en düşük entalpi değer ise amin tipi (AO3) antioksidanın %1 eklendiğinde 79.7 J/g olarak gerçekleşmiştir.

Hot-set testi kablo sektöründe uygulanan polietilenin çapraz bağlanması ile ilgili özel bir testtir. Bu testin başarılı olması belirli koşullar altında polietilenin çapraz bağlandığı anlamına gelir. Diğer taraftan, teste başarısız olunması çapraz bağlanmanın gerçekleşmediği veya yeterli olmadığı anlamına gelmektedir. Bu çalışmada hot-set testi, CPEC içine antioksidan eklendikten sonra çapraz bağlanma özelliğini koruyup koruyamadığını anlamak için yapılmıştır. Sonuçlara göre, saf CPEC, %1 karışım (AO2) ve %1 amin tipi (AO3) antioksidanlarının eklendiği numuneler hot-set testleri olumludur. Diğer numunelerin sonuçları olumsuzdur. Bu numunelerde plaka presleme koşularında çapraz bağlanma gerçekleşmemiştir. Yani diğer örneklerde, antioksidanların eklenmesi ile çapraz bağlanma engellenmiştir.

Tüm numuneler için eriyik akış indeksi (MFI) testi yapılmıştır. Artan antioksidan miktarı eriyik akış indeksi değerini arttırmıştır. En yüksek indeks değerleri olarak %46,34, %40,24 and %30,89, sırasıyla fenolik (AO1), karışım tipi (AO2) ve amin tipi (AO3) antioksidanların %5'lik kullanımlarında elde edilmiştir.

1. INTRODUCTION

Polymers have become one of the most important materials in our daily life. Increasing demand for using them forced the scientists to improve their properties. For enhancement of properties of polymer; they can be blended with other polymers, preparing polymeric composites and nanocomposites are the most common methods, lastly. On the other hand, in the last decade, "crosslinking" can be used for improving the mechanical properties of polyolefins at high temperatures, especially.

Polyethylene (PE) has excellent electrical insulating properties, good stable mechanical properties and resistance to chemical attacks. All these properties give polyethylene to be an effective and important insulating material in the cable production. Polyethylene is however not suitable for use under high temperature. This is mainly due to the molecular structure of the polyethylene polymer, which is made up of linear chains of independent polyethylene molecules loosely held together by weak molecular bonds. These weak molecular bonds break when subjected to the temperature above 70° C, causing the individual molecules to slide over one another. The resultant polyethylene starts to change its shape and consistency and becomes soft plastic-like in nature. This nature of polyethylene can be converted in toa thermal stable thermosetting compound by the process of crosslinking. In the process of crosslinking, perpendicular chemical bonds are formed between parallel chains of the polyethylene molecules. The parallel loose two-dimensional molecular structure is converted into a cellular three-dimensional polymeric structure. Crosslinked polyethylene (XLPE) exhibits all the superior insulation properties of PE but not its inferior properties. XLPE compound is a durable and excellent insulating material which exhibits some advantages over conventional thermoplastic insulating material (Url-1,2015). The main characteristics of XLPE and thermoplastic PE are given at Table 1.1.

Table 1.1: Main characteristics of PE and XLPE (Url-2,2015).

Characteristics	**PE**	**XLPE**
Density (g/cm^3)	0.935	0.935
Stress strength (kg/cm^2)	1.2 – 1.5	1.5 – 2.3
Operational temperature (°C)	70	90
Overload temperature (°C)	90	130
Minimum temperature permitted (°C)	-60	-60
Short-circuit temperature (°C)	130	250
Dielectric rigidity (kV/mm)	35 - 50	35 – 50
Volumetric electrical resistivity (Ω.cm)	10^{18}	10^{18}
Dielectric constant	2.3	2.3

XLPE is far tougher and has much better thermal deformation resistance than plain polyethylene. Unfortunately, the same properties that are advantageous for insulation are disadvantageous for recycling. Because of the bridges, crosslinked polyethylene does not readily melt with the application of heat, and therefore cannot be heat formed into material recycle products (Hashmi et al,2011).

In this study, for recovery of commercial crosslinkable polyethylene compound (CPEC) was studied. CPEC has crosslinking agent inside and is ready to crosslinking when appling to appropriate conditions such as high temperature. Three different commercial antioxidants with three different ratios were added into CPEC by using laboratory mixer to obtain PE compound from CPEC. The effect of antioxidants on crosslinking, mechanical and thermal properties of samples were investigated.

Curing parameters were measured by Rubber Process Analyser (RPA). Mechanical properties were characterized by tensile tester. Thermal properties of blends were characterized by DSC analysis and hot-set test which is a special test for cable sector. MFI characterizations were also made by using MFR device.

2. THEORETICAL PART

Polymeric insulating materials are increasingly employed in power and comunicaiton cables for power and data supply. The major alternative type of polymers used as an insulation material in this area is especially crosslinked polyethylene (XLPE). It needs to increase the long term performance and properties of the PE under thermal and UV ageing conditions. First of all the properties of PE and XLPE will be investigated in this part.

2.1 Polyethylenes

Polyethylene is classified into several different categories based mostly on its density and branching (Figure 2.1). The mechanical properties of PE depend significantly on variables such as the extent and the type of branching, the percent crystalinity, and the molecular weight. The types of polyethylene mostly consumed are LDPE (low density PE), LLDPE (linear low density polyethylene), VLDPE (very low density PE), MDPE (medium density polyethylene), HDPE (high density PE), HMWPE (high molecular weight polyethylene), UHMWPE (ultra high molecular weight polyethylene), XLPE (crosslinked polyethylene) and HDXLPE (high density crosslinked polyethylene).

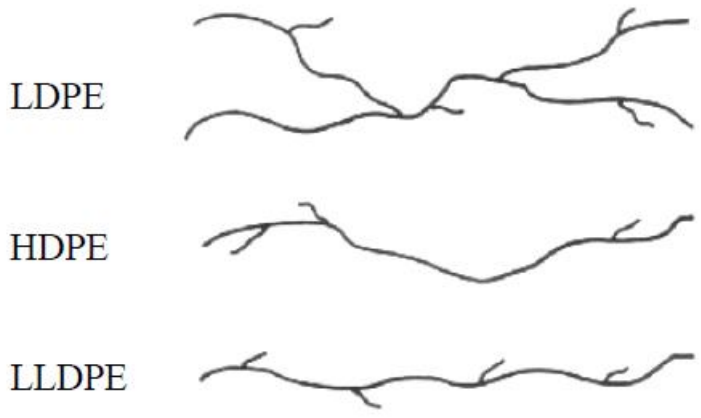


Figure 2.1 : Molecules of LDPE, LLDPE and HDPE.

Polyethylene and its copolymers find applications in major industries such as packaging, housewares, appliances, transportation, communications, electric power, agriculture, and construction. The majority of LDPE is used as thin film for packaging. Other uses of PE can be seen in Table 2.1 including wire and cable insulation, coatings, and injection-molded products.

Table 2.1: Applications of PE (Ebewele, 2000).

Product Type	Typical Applicaitons
Film Extrusion	LDPE films used in packaging (bags and wrappings for frozen and perishable foods, produce and textile products); construction cover (moisture barriers and utility covering material); agriculture (greenhouse; ground cover; tank, pond, and canal liners); garment and stripping bags. HDPE film used for floral wrapping, grocery bags, snack and food packaging; EVA film used as produce bags, heavy-duty shipping bags, disposable protective gloves.
Extrusion coating	Laminates of foil, paper and used in milk-type cartons (LDPE) for a variety of foods and drinks. Some HDPE used in extrusion coatings over flexible foil packages either as a glue layer between paper on plastics film and aluminium foil or as a heat-seal layer.
Wire and cable insulation	LDPE used as insulation of high-frequency electrical cables, insulation materials for television, radar, and multicircuit long-distance telephones.
Blow molding	Squeeze bottles, toys, housewares, lids, containers made from LDPE. Blow-molded HDPE used as containers for belaches, liquid detergents, milk and other beverages, automobile and truck gas tanks, crates and pails.
Injection molding	Packaging containers, pails and lids, houseware dishpans, and waste baskets, molded furniture seats, med,cal labware. HDPE is used in molded structural foam pallets, and crates, underground conduits and housings.

2.1.1 Low density polyethylene (LDPE)

LDPE is defined by a density range of 0.910 - 0.940 g/cm^3. LDPE has a high degree of short and long chain branching, which means that the chains do not pack into the crystal structure as well. This results in a lower tensile strength and increased ductility. LDPE is created by free radical polymerization. The high degree of branches with long chains gives molten LDPE unique and desirable flow properties. LDPE is used for both rigid containers and plastic film applications such as plastic bags and film wrap (DuBois and John,1981). LDPE is produced by a free-radical initiated reaction using oxygen or other free radical initiators such as organic peroxides or azo compounds. Synthesis conditions are usually 250–300 °C outlet temperature, 3000 atm. pressure. Nominal reactor residence times are about 10–50 seconds (Fenner, 1979).

Heat of polymerization is about 800 KCal/gm, which must be removed during the short residence time available. Only a small part of this heat can be removed through the

reactor walls because of their comparatively limited area and necessary thickness. In addition, the polymer tends to deposit on cool surfaces. In practice, heat is removed by recirculating excess cool monomer and the system operates essentially adiabatically. Therefore, production rates vary directly with the ethylene recirculation rate and the allowable temperature rises through the reactor. Heat balance limits conversion to 15–20% on each pass. Reactors are of two general types, autoclaves and high pressure tubes. Each of these types produces slightly different polymers, primarily because of differing temperature profiles through the reactors (USI, 1986).

2.1.2 Linear low density polyethylene (LLDPE)

LLDPE is defined by a density range of 0.915 - 0.925 g/cm^3 is a substantially linear polymer, with 4-6 carbon containing short branches (short-chain alpha-olefins) with approximately, every 100 carbons on the main chain. LLDPE has higher tensile strength, higher impact and puncture resistance than LDPE. Lower thickness films can be blown compared to LDPE, with better environmental stress cracking resistance compared to LDPE but is not easy to process in packaging. Cable covering, toys, lids, buckets and containers, pipe are some of the products can be made by LDPE. While other applications are available, LLDPE is used redominantly in film applications due to its toughness, flexibility, and relative transparency (Kahovec et al, 2002).

2.1.3 High Density Polyethylene (HDPE)

HDPE produced using organometallic catalysts such as the ZNC or Phillips catalysts have less than 15 (normally within the range of 1–6) short alkyl branches (essentially no long branches) for 1000 ethylene units. Because of the regular structure of the ethylene units themselves and the low extent of branching, HDPE chains can pack more efficiently resulting in a material with greater crystallinity (generally up to 90%), higher density (0.96), with increased chemical resistance, hardness, stiffness, barrier properties, melting point (about 1308 °C), and tensile strength. Low-molecular weight (chain lengths in hundreds) HDPE is a ‘‘wax,’’ while ‘‘typical’’ HDPE is a tough plastic (Charles and Carraher, 2007).

2.2 Crosslinked Polyethylene (XLPE)

Crosslinked polyethylene, commonly abbreviated PEX or XLPE, is a low density polyethylene (LDPE) or high density polyethylene (HDPE). XLPE is a thermoset material produced by the compounding of polyethylene with a crosslinking agent such as dicumyl peroxide. Al Gilbert and Frank Precopio invented XLPE in March 1963 in the GE Research Laboratory located in Niskayuna, New York (Precopio, 1999). In this process, the long chain PE molecules crosslink during a curing process to form XLPE shown at Figure 2.2. XLPE has electrical characteristics that are similar to thermoplastic PE, but with better mechanical properties, particularly at high temperature.

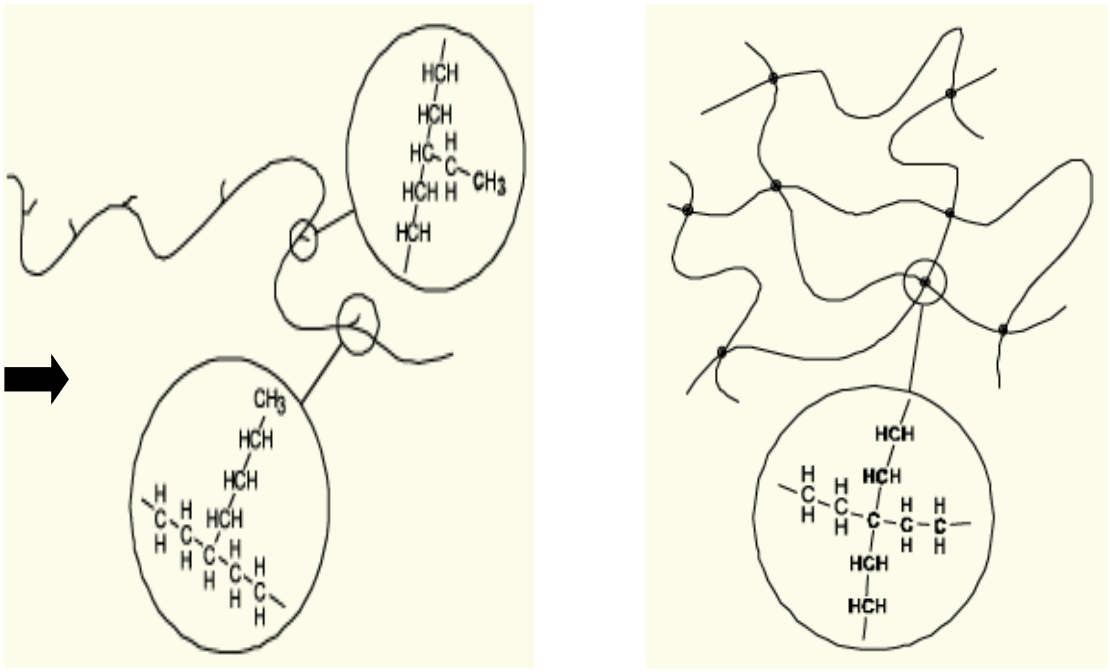


Figure 2.2 : XLPE vs PE structures.

During the crosslinking process, the polyethylene macromolecules are chemically linked to form a three-dimensional network. This reaction can be achieved by various processes (Url-3,2015);

- Organic peroxide curing: C-C crosslinks are formed by means of a radical mechanism; the process is a one-step-cure-process (PEX-a)
- Silane cure technology: funcioanl silane groups are grafted onto the polyethylene backbone. In a second step, these reactive groups can be further

react under influence of a catalyst and water to form crosslinks having a C-Si-O-Si-C structure. (PEX-b)

- Electron beam crosslinking, also called radiation cure: C-C crosslinks are formed by applying a seperate electron beam process. (PEX-c)

2.2.1 Peroxide Crosslinking

Peroxide crosslinking of polyethylene at high temperatures was the very first commercial method, similar to rubber vulcanization. In this method, peroxide based chemicals (dicumyl peroxide as the most common initiator) are used and thus create carbon-carbon links to form the network in polyethylene by the elimination of hydrogen atoms (Kang and Ha, 2000).

Polyethylene is crosslinked by using peroxides "Engel method", which initiate the formation of radicals on carbon atoms along the chains and the consecutive creation of carbon-carbon bonds by recombination (Figure 2.3). This can be performed thanks to a high temperature (above the melting temperature) and high pressure extrusion, with a very good control of the heating (rather tight operating window). The crosslinking obtained is usually very constant and uniform, adapted to LDPE and HDPE (Gouttefarde, 2009).

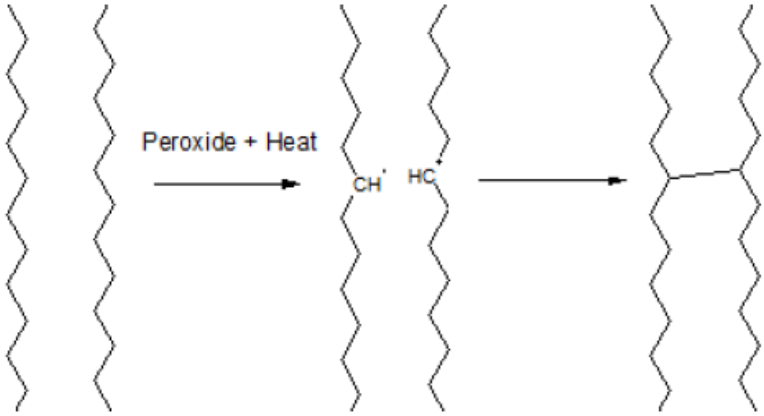
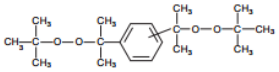
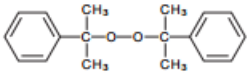
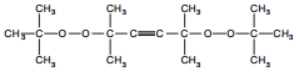
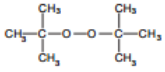
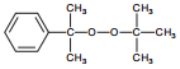
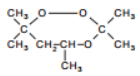


Figure 2.3 : Schematic representation of the peroxide crosslinking.

Organic peroxides can be used for the crosslinking of thermoplastics to produce PEX-a or XLPE. The major criterias for selection of suitable crosslinking peroxide are below;

- Physical form of the peroxide
- Thermal stability of the peroxide
- Crosslinking ability of the radicals formed
- Environmentali health and safety aspects
- Efficiency

Table 2.2: Comercial crosslinking peroxides for PE, (Url-4, 2015).

Product Name	Chemical Description	CAS No.	Structure	Typical Crosslink Temperature (°C)	Safe Processing Temperature (°C)
PERKADOX 14S	Di(tert-butylperoxyisopropyl)benzene	2212-81-9; 25155-25-3		175	135
PERKADOX BC-FF	Dicumyl peroxide	80-43-3		170	130
TRIGONOX 145-E85	2,5-Dimethyl-2,5-di(tert-butylperoxy)hexyne-3, 85% solution in mineral oil	1068-27-5		185	145
TRIGONOX B	Di-tert-butyl peroxide	110-05-4		180	145
TRIGONOX T	tert-Butyl cumyl peroxide	3457-61-2		175	135
TRIGONOX 311	3,3,5,7,7-Pentamethyl-1,2,4-trioxepane	215877-64-8		205	170

2.2.2 Silane Crosslinking

Silane coupling agents are silicon-based organic chemicals that contain two types of substituent (inorganic and organic) in the same molecule. Their typical general formula is $(X)_3Si\text{-}Y$, where X represents a hydrolyzable group such as ethoxy or methoxy, Y is a functional organic group (amino, methoxy, acetoxy, epoxy, etc.) that reacts with water to form silanol (Si-OH). They include more than 90 percent of the plastic coupling agents market and are also used in crosslinking of polyolefins and some other polymers (Cartasegna, 1986). Since the silane groups are polar, they provide compatibility in polyethylene based blends, where the polyethylene is non-polar in nature (Gale, 1988). Vinyl alkoxy silanes (e.g., vinylmethyldimethoxysilane, vinyltriethoxysilane, vinyltrimethoxysilane) are suitable compounds for these kinds of reactions due to their double bonds and ability to rapid cross-linking. Vinyltrimethoxysilane (Figure 2.4.). is the most common silane used in the manufacturing of silane cross-linkable polyethylene (Smedberg et al, 1997).

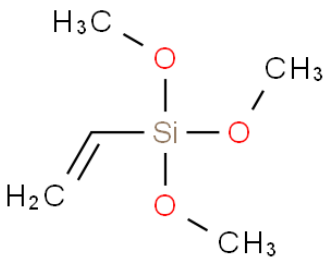


Figure 2.4 : Structure of Vinyltrimethoxysilane.

The silane grafting by water-cross-linking method consists of at least two stages that would also proceed consecutively. In the first stage, a proper silane (vinylalkoxysilane) is grafted via its vinyl groups on polyethylene through a peroxide initiated free radical reaction; it should be noted that during the grafting reactions, new polyethylene radicals are formed and the required amount of peroxide is relatively low. In the second stage, the resultant copolymer is crosslinked via the exposure to hot water or steam with the aid of a catalyst. Moisture leads to hydrolysis of alkoxy groups of silane and thereafter, these hydroxyl groups condense to form stable siloxane linkages (the cross-links). Figure 2.5. illustrates the reaction mechanism during peroxide induced melt grafting of vinyl silane onto polyethylene, followed by the hydrolysis and condensation step during the silane cross-linking reaction (Yussuf et al, 2007).

The grafting step may be performed while the polymer is in molten state and the cross-linking step is normally carried out after the grafted polymer has been shaped into the final product and is below its melting temperature. Easy processing, low capital investments, and favourable properties of processed materials are the advantages of silane method.

The term "silane cross-linkable polymer" refers to a silane grafted polymer which is intended for curing but has not yet been cured, and the term "silane crosslinked (cured) polymer" refers to a product which has already been subjected to a moisture curing step and is the finally cured product which is intended for end use (Giacobbi and Miglioli, 2005). Based upon the possibility of performing the two stages in silane cross-linking either together or separately, two processes have been introduced, namely Sioplas® and Monosil®.

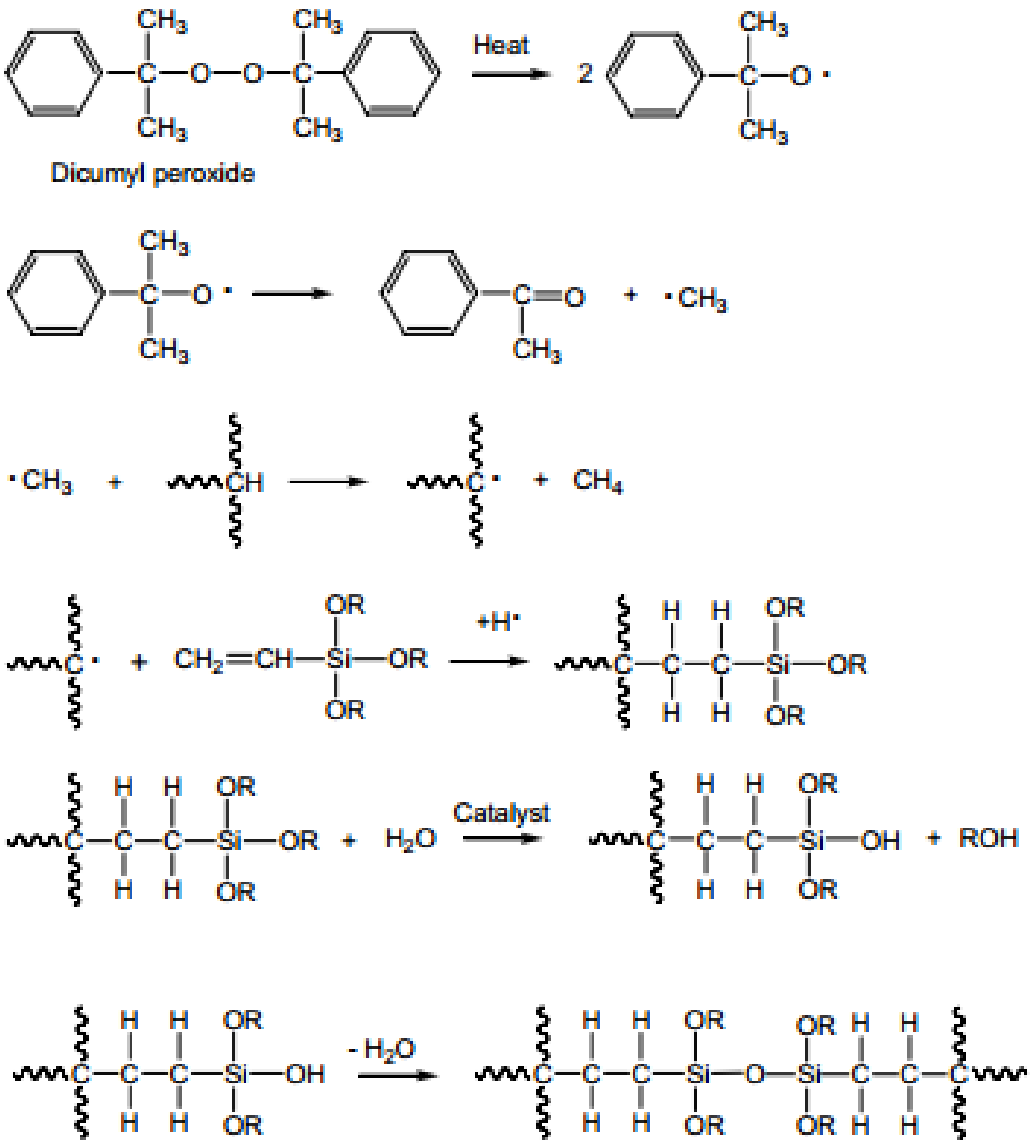


Figure 2.5 : Reactions of silane cross-linking of polyethylene.

Midland Silicones Co. (Dow Corning Co.) developed Sioplas® process in 1968 (Scott, 1972). In this method, a mixture of silane and peroxide is added to molten polyethylene, leading to silane grafting reaction, which is a classical free radical chain reaction involving a catalyst. The silane grafting reaction is usually performed in molten polyethylene by means of reactive extrusion, where an extruder is used as a reactor of continuous action.

Feeding may be done by discontinuous or continuous metering and mixing of ingredients into the extruder hopper or direct injection of the silane and peroxide solution into the melted polymer. Thereafter, the grafted polymer is pelletized and is capable of being stored in a dry place. When it is intended to produce the final product, a catalyst masterbatch (consists of polyethylene, a catalyst, an antioxidant, a proper stabilizer, and an internal lubricant) is mixed with the above mentioned pellets in a typical weight ratio of 5:95 (Morshedian and Hoseinpour, 2009).

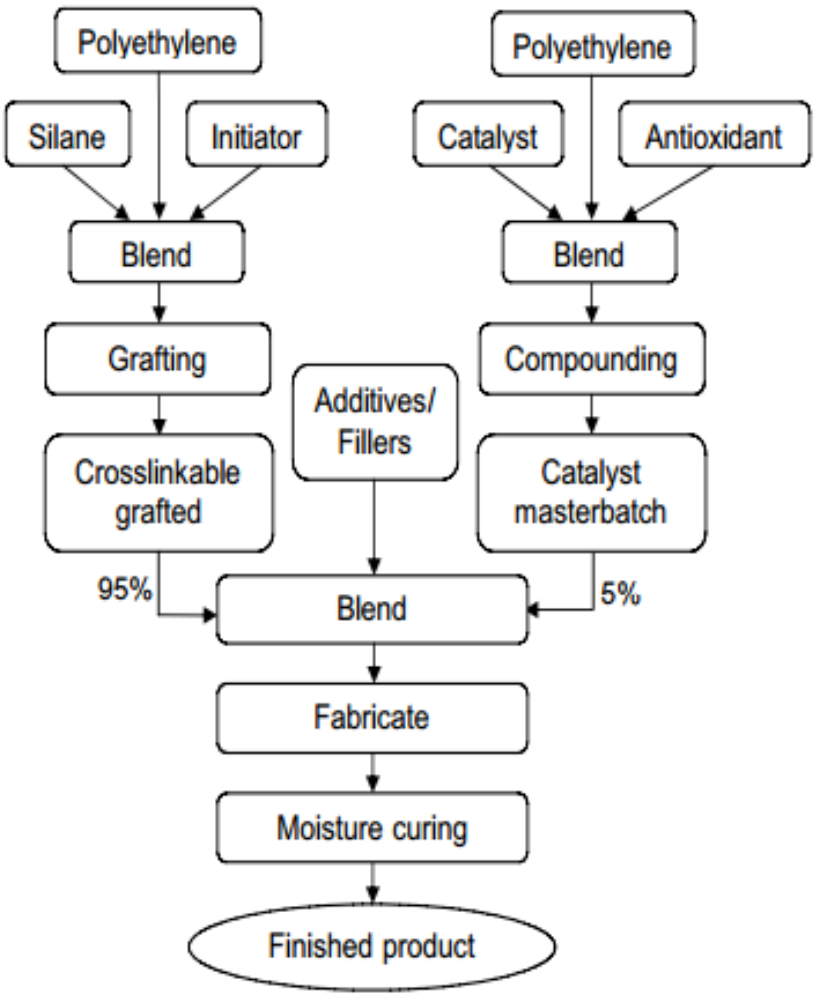


Figure 2.6 : Procedures of Sioplas® process.

The final mixture is melted, followed by extruding into the product (Figure 2.6). Cross-links are created through exposing the product to water or steam at temperatures of 70 to 90ºC.

Monosil® process, announced by BICC Limited and Establishments Maillefer SA in 1974 is a onestep process by using a specially designed extruder with a high L:D ratio, silane is grafted onto polyethylene and the product is cross-linked in presence of moisture (Swabrick and Green, 1978). Initially all the equipment for this type of process bore the name Monosil. In this process, all the ingredients are fed directly into the extruder (Figure 2.7).

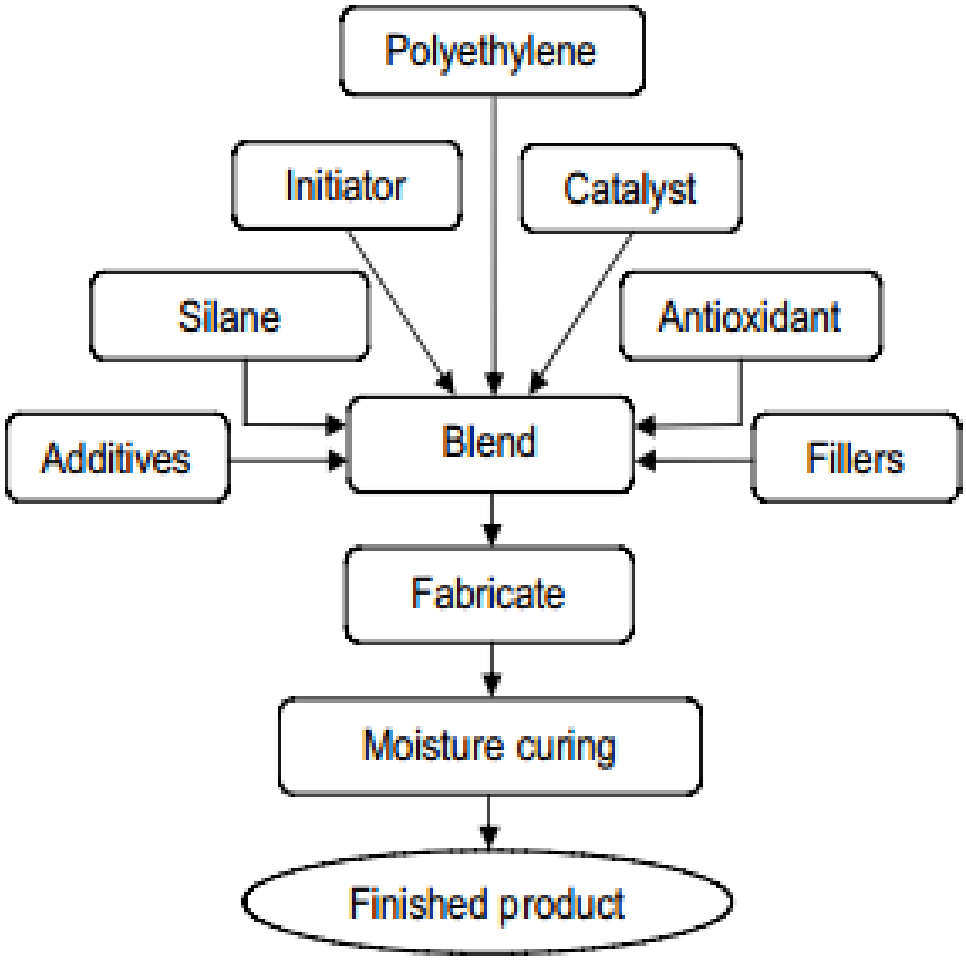


Figure 2.7 : Procedures of Monosil® process.

2.2.3 Crosslinking by electron irradiation

Crosslinked polyethylene is manufactured through an electron irradiation: when the highly energetic electrons hit the PE chains, they break some carbon-hydrogen or carbon-carbon bonds, what leads to the formation of radicals. These radicals usually react with another radical in its vicinity, creating locally bonds between the main chains. The beaming is usually performed on highly amorphous LDPE materials, as

the irradiation is less effective on rigid crystalline regions (hard to penetrate). The process requires costly tools and machines and the crosslinking is less uniform than peroxide crosslinking, but it is the most environmentally friendly method (no chemicals or solvents). The representative mechanism is given in Figure 2.8 (Gouttefarde, 2009).

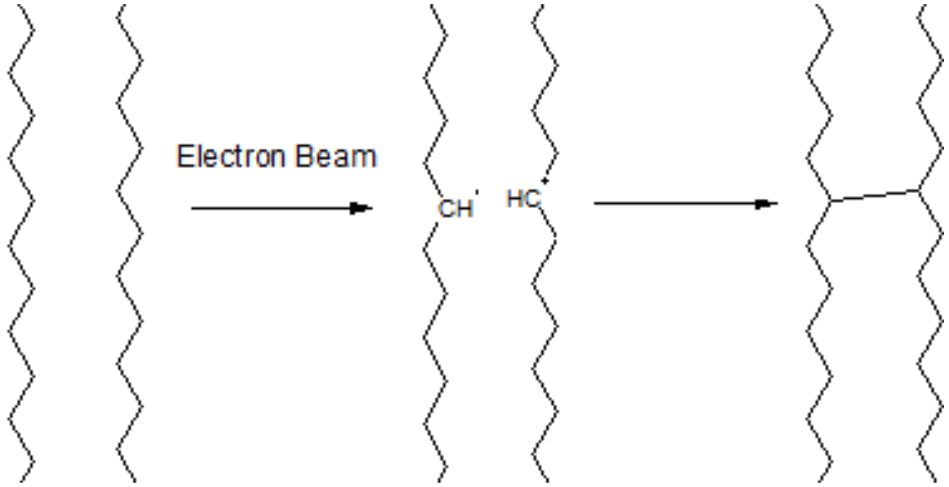


Figure 2.8 : Schematic representation of the radiation cross-linking.

2.2.4 Crosslinked polyethylene properties

At a significant degree of cross-linking, the XLPE turns into a thermoset, consequently displaying, in comparison with a non crosslinked material, a better dimensional stability and better mechanical properties. Indeed, it is usually stronger and tougher, with an improved Environmental Stress Crack resistance. Its chemical, electric and thermal resistances are also higher, and it withstands more easily corrosion and abrasion. However, the most interesting improvement is its increased high temperature resistance, which allows higher service temperatures.

2.2.5 Crosslinked polyethylene applications

2.2.5.1 Crosslinked polyethylene pipes

One of main applications for crosslinked polyethylene hot water pipes for under floor or central heating and domestic or portable water piping system. The benefits of crosslinking become obvious above ambient temperatures where a reduction in the rate of creep for the corresponding hoop stress is observed (Gale, 1988).

2.2.5.2 Injection and blow moulded articles

Specially moulded articles such as containers with significant improvement in ESCR and chemical resistance characteristics can be made using crosslinked polyethylene. Increasing the molecular weight by crosslinking increases its solvent and creep resistance. The increased dimensional stability at evaluated temperatures allows the article to come in contact with heated fluids (Lazar et al, 1990).

2.2.5.3 Crosslinked film

Crosslinked polyethylene in packaging applications is confined to multi-layer film constructions, in which the cross linked layer provides a number of specific effects including: increased temperature resistance especially for hot filled or heat sterilization applications; increased heat seal strength where a thermoplastic seal is subsequently crosslinked; increased impact, tear and abuse resistance capability especially for packing irregular shaped items to impart heat shrinking properties to the film (Khonakdar et al, 2003).

2.2.5.4 Crosslinked polyethylene foam

Crosslinked polyethylene (XLPE) foams have various kinds of applications, such as thermal insulation, floatation, automotive trim, and sports goods. The advantages of crosslinking, prior to foaming are that high quality closed cell structure can be achieved which gives the following benefits increased mechanical properties, increased resistance and recovery from deformation, increased thermal resistivity, reduced vapour and liquid transport, to improve elevated temperature and load bearing characteristics of the foam, to permit secondary moulding and foaming without collapse of the cell structure (Cardoso, 1998).

2.2.5.5 Cable insulation

The most advanced area of application for crosslinked polyethylene is in the electrical cable industry. Crosslinking, while not interfering with the dielectric properties of polyethylene, introduces resistance to flow and permanent deformation above the softening point. This permits higher conductor operating temperature and reduces the level of short circuit and overload protection required.

LDPE was first developed in 1930's and started to used in cables after 1940's. It became very popular, compared to paper insulation, because of its low cost, electrical properties, processability, moisture and chemical resistance and low-temperaure flexibility. Nevertheless, the maximum operating temperature of PE is 75°C. It could not match the operation temperature in the range of 80-90°C. This problem was solved with the advent of XLPE that had the ability to match. In the 21st century, XLPE has become a common alternative for cable insulation.

Layer	Explanation
1	Conductor
2	Semicon WaterProof Tape
3	Conductor Screen
4	Insulation
5	Insulation Screen
6	Semicon WaterProof Tape
7	Metallic Screen
8	Barrier Blocking Tape
9	Aluminium Tape
10	Outher Sheath

Figure 2.9 : XLPE insulated cable and its layers.

XLPE insulated cables have a rated maximum conductor temperarure of 90 °C and an emergency rating of up to 140 °C, depending on the standard used to rate XLPE insulated cables. Cables insulated with XLPE also have a conductor short-circuit rating of 250 °C. XLPE has excellent dielectric properties making it useful for a large range of voltage applications 600V to 500kV (Hartlein and Orton, 2006).

The Catenary Continous Vulcanization Line shown in Figure 2.10. is used for XLPE insulation production of medium voltage (MV) and high voltage (HV) cables (Url-5, 2015).

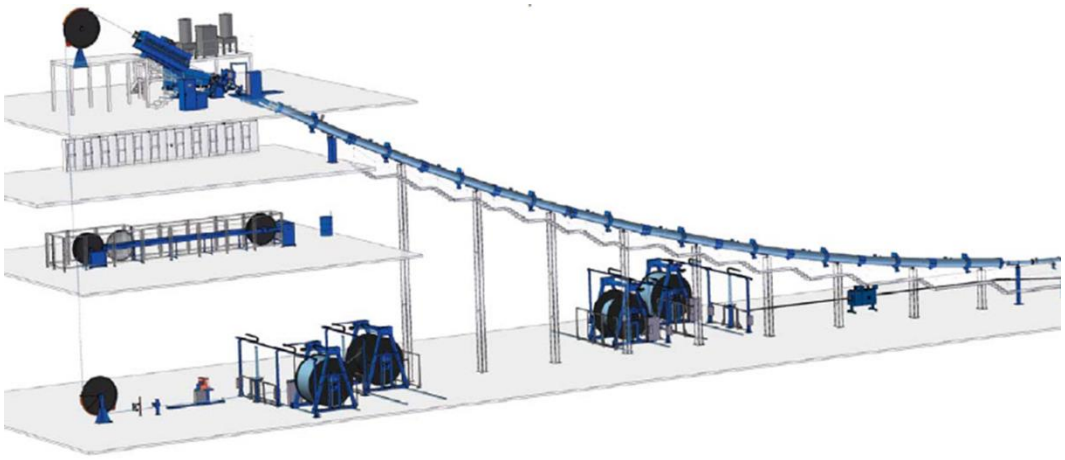


Figure 2.10 : Catenary Continous Vulcanization Line.

The MV or HV cable insulation consists 3 layers (Figure 2.11) which are inner semiconducting screen (ISS), XLPE insulation and outer semiconducting screen (OSS) . ISS is extruded over the conductor to smooth out the discontinuities of conductor. It gives a smooth interface to the electric field in the insulation. OSS is extruded over the insulation to contain the electrical field within the insulation to maintain uniform electrical field. ISS and OSS are polymer contains conducting carbom black, so they are neither an insulator nor a conductor.

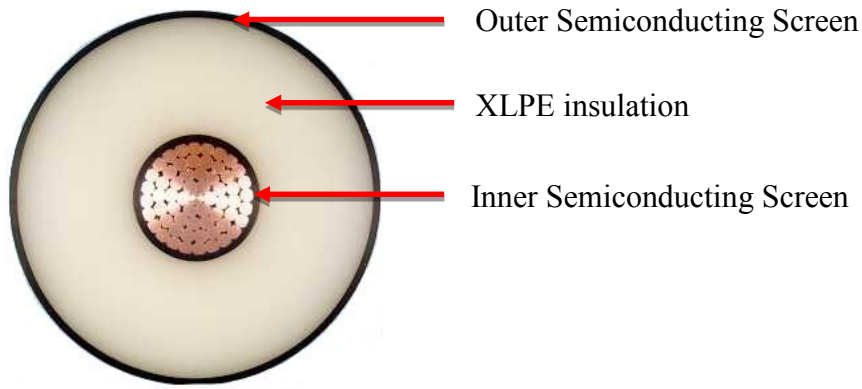


Figure 2.11 : MV or HV cable insulation layer.

Three extruders (Figure 2.12) and a triple extrusion crosshead (Figure 2.13) are used to insulate the conductor. Triple extrusion means all three layers of insulation are added in one pass through a group of extruders. The three layers are extruded within a single head. This approach limits the chance of contamination and improves interfacial properties.

Figure 2.12 : Three extruders for each layers.

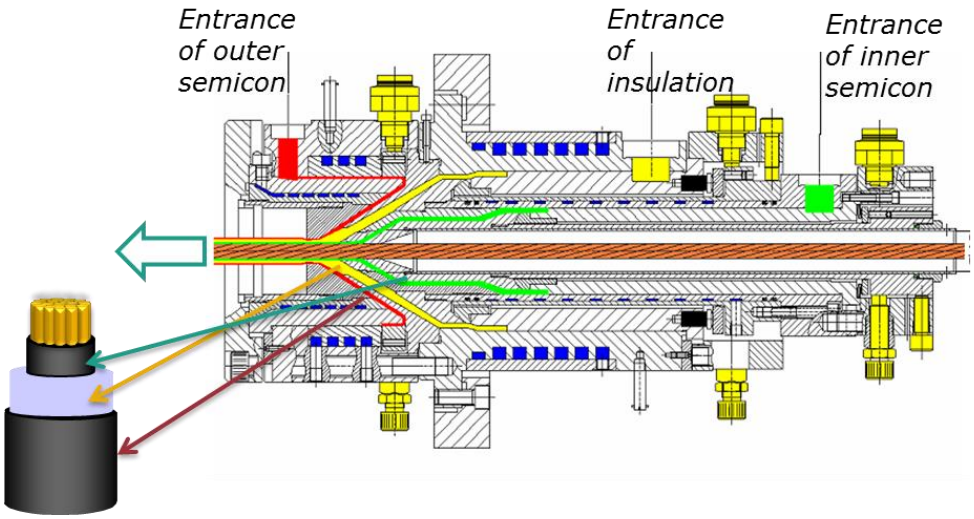


Figure 2.13 : Triple extrusion crosshead.

After extrusion, the insulated conductor is cured in an inert such as nitrogen atmosphere by heating to the crosslinking temperature. The maximum curing speed is achieved by computing the temperature profile of continuous vulcanization tube so that the cable surface is kept at its maximum stable temperature. The insulation is cool down after curing section and wrap on the drum for next production sections.

2.3 Antioxidants

The desirable properties of polymers are achieved through proper molecular weigth and molecular weigth distribution. Any change to the original molecular structure will change to the original molecular structure will change these properties and usually is considered degradation. Polymer, especially polyolefins, undergo a wide variety of oxidative reactions that either cause chain scission (decreased molecular weight) or molecular enlargement (increase molecular weigth and broder molecular weight distribution).

2.3.1 Autoxidation

Polymers undergo degradation reactions in the presence of oxygen. Peroxides, alcahols, ketones, aldehydes, acids, peracids and peresters are formed as products a result of oxidation. Elevated temperatures, heat, metals and metal ions which act as catalyst assist oxidation.

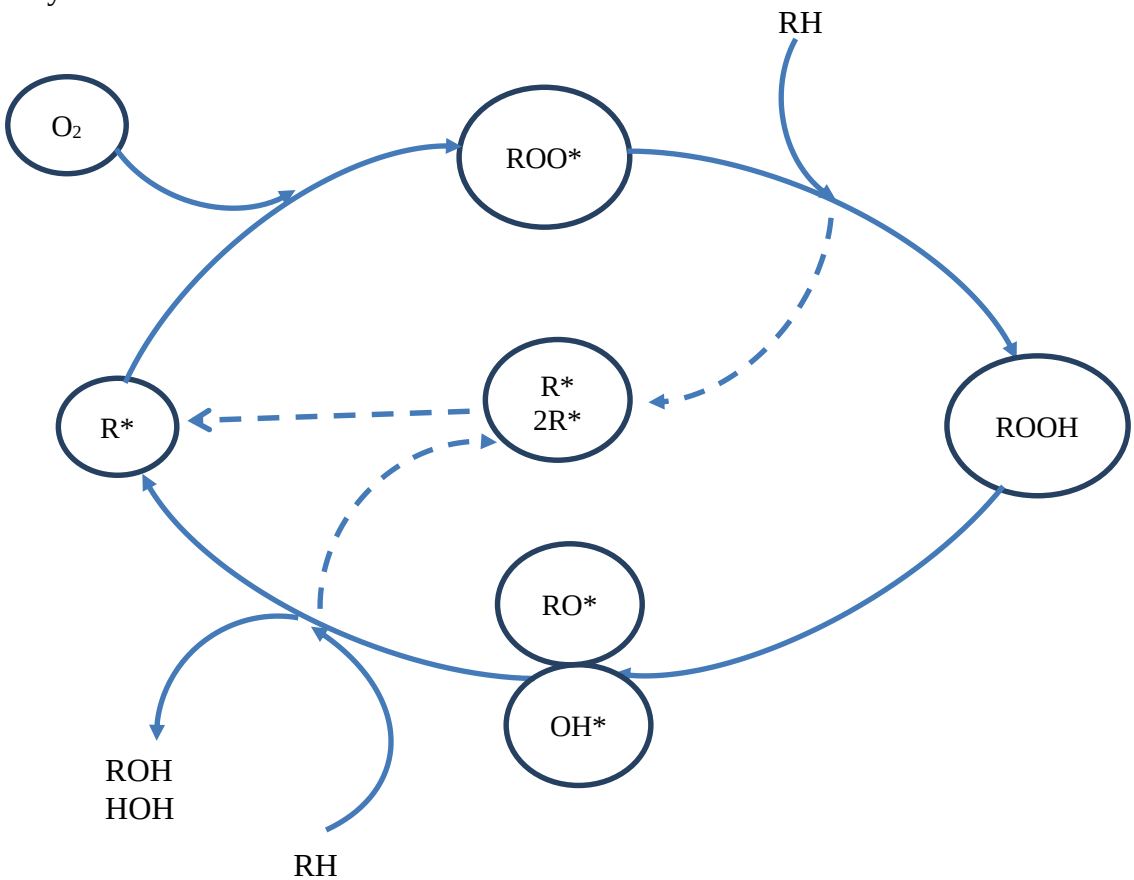


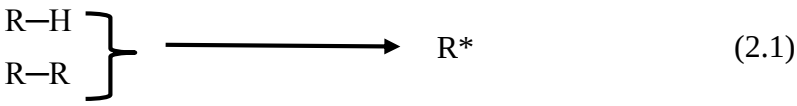
Figure 2.14 : The Cycle of Autoxidation.

Polymer oxidation was investigated very early on in connection with the ageing of natural rubber. The ageing and the absorbtion of oxygen are connected eachother.

Hydrocarbon compounds react with molecular oxygen forming oxidation products, the scheme of autoxidtion was developed showing as free radical-initiated chain reaction. The oxidation of hydrocarbons proceeds autocatalytically (Zweifel, 1998). The autoxidation is shown schematically in Figure 2.14.

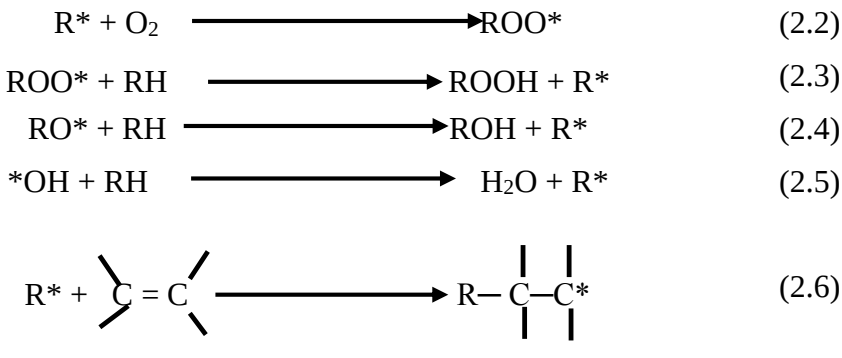
The reaction is slow at the start, generally associated with a short induction period and accelerates with the concentration of the resulting hydroperoxides. As other radical reactions, the free radical initiated chain reaction of autoxidation can be regarded as proceeding in three distinct steps: chain initiation, chain propagation, and chain termination (Eq. 2.1-2.14) (Charles and Carraher, 2007).

Chain Initiaion:



(2.1)

Chain propagation



(2.2)
(2.3)
(2.4)
(2.5)
(2.6)
(2.7)
(2.8)

Chain branching

$$ROOH \longrightarrow RO^* + OH^* \quad (2.9)$$

$$2ROOH \longrightarrow RO^* + ROO^* + H_2O \quad (2.10)$$

Chain termination

$$R^* + ROO^* \longrightarrow ROOR \quad (2.11)$$

$$R^* + R^* \longrightarrow R-R \quad (2.12)$$

$$R^* + RO^* \longrightarrow R-O-R \quad (2.13)$$

$$2R^* \longrightarrow RH + Olefin \quad (2.14)$$

The origin of the primary alkyl radical R* (Eq. 2.1) as initiating species for the chain reaction is still controversial. Direct reaction of hydrocarbons with molecular oxygen in a bimolecular reaction is not favoured because of thermodynamic and kinetic considerations. One explanation is that in the course of polymerization, adventitious catalyst such as transition metals, radical initiators, impurities in the monomers, and trace amount of oxygen react and form peroxy radicals ROO* (Eq. 2.2) which abstract hydrogen from the polymer and form an alkyl radical (Eq. 2.3). The technical preparation of "purest" polymer is simply no possible. Structural defects and impurities can not be excluded. Furthermore, during the first processing step of the melt, e.g. extrusion, blow molding, or injection molding, additional peroxide radicals are formed by the reaction with molecular oxygen under the effect of heat and mechanical shear. Subsequently, they form hydroperoxides upon abstraction of hydrogen (Eq. 2.3). The rate of decomposition of hydroperoxides (Eq. 2.9) to alkoxy and hydroxyl radicals increases with rising temperature. It can proceed, however, under the influence of light or metal ions from eqs. 2.15 and 2.16 (Zweifel, 1998).

$$M^{n+} + ROOH \longrightarrow M^{(n+1)} + RO^* + HO^- \quad (2.15)$$

$$M^{(n+1)} + ROOH \longrightarrow M^{n+} + ROO^* + H^+ \quad (2.16)$$

The rate constant for the reaction of most alkyl radicals with oxygen is of the order of 10^7- 10^9 $mol^{-1}s\text{-}^{1}$. The abstraction of a hydrogen, H, by a peroxy radical ROO* (Eq. 2.3) requires the breaking of a C-H bond. This reaction (Eq. 2.3) requires corresponding activation energy and is, therefore, the rate-determining step in autoxidation. The rate of the abstraction reaction decreases in the following order:

hydrogen in a-position to a C=C double bond (“allyl”) > benzyl hydrogen and tertiary hydrogen > secondary hydrogen > primary hydrogen (Denisov, 1995).

Primary and secondary peroxy radicals are more reactive than the analogous tertiary radicals with regard to hydrogen abstraction. The most reactive are acylperoxy radical.

If sufficient oxygen is avaible and the formation of peroxy radicals does not occur at too high a temperature, then chain termation mainly proceeds by recombination of peroxy radicals. Under oxygen deficient conditions, for example if the concentration of [R*] is much higher than that of [ROO*], chain termination is caused by recombination with other available radical species according to Eqs. 2.11 and 2.12. An important termination reaction is disproportionation of alkyl radicals according to Eq. 2.14 (Zweifel, 1998).

2.3.2 Inhibitation of autoxidation

Antioxidants are very important additives whose role it is to maintain the chemical and physical properties of different materials such as plastics, elastomers, processed food, lubricants, etc., during transportation, storage, processing, and serving conditions.

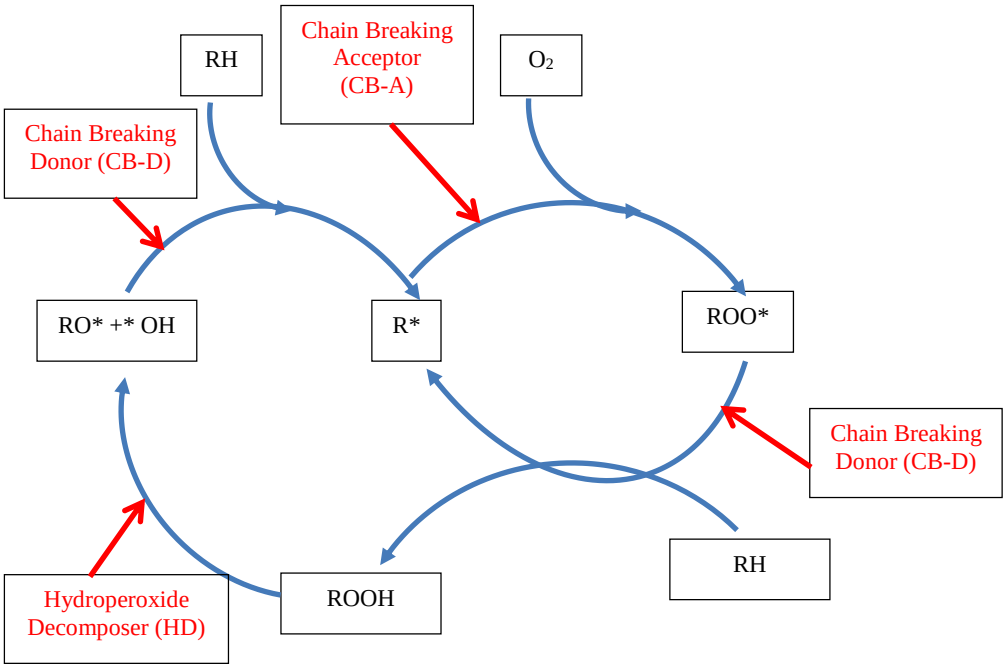


Figure 2.15 : Inhibition of thermooxidaitve degradation.

Antioxidants are chemical substances, which are added to polymers in small amounts with generally 1-2% and are capable in the course of autoxidation of trapping emerging

free radicals or unstable intermediate products such as hydroperoxides and to transform them into stable end products (Cirilo and Iemma, 2012). General scheme of inhibition is given at Figure 2.15.

In princible, scavenging of the primary macroalkyl radicals, R*, would immediately stop autoxidation. However, the rate of reaction of molecular oxygen k_2 (Eq. 2.17.) is so high (10^7-10^9 $mol^{-1}s$-^{1}) that this reaction can hardly be avoided.

Under oxygen-deficient conditions, the use of alkyl radical scavengers can contribute significantly to the stabilization of the polymer. Such stabilizers are referred to as chain breaking acceptors (CB-A).

The rate-determining step in the course of autoxidation is the abstraction of a hydrogen from the polymer backbone (Eq 2.18). The peroxy radical (ROO*) forms hydroperoxide (ROOH). If the peroxy radical is offered a substantially more easily abstractable hydrogen by a suitable hydrogen donor, ln H, then the reaction meets competition according to Eq. 2.19, i.e. $k_a[lnH] > k_3[RH]$.

H donors (designated as lnH) are known as chain breaking donors (CB-D). Suitable H-donors are characterized by the fact that they de not react further by abstraction of hydrogen from the polymer backbone, according to Eq. 2.20. , i.e. k_{ct} is small.

$$R^* + O_2 \xrightarrow{k_2} R-R \qquad (2.17)$$

$$ROO^* + RH \xrightarrow{k_3} ROOH + R^* \qquad (2.18)$$

$$ROO^* + lnH \xrightarrow{k_a} ROOH + ln^* \qquad (2.19)$$

$$ln^* + RH \xrightarrow{k_{ct}} lnH + R^* \qquad (2.20)$$

Scavenging of the RO* and HO* radicals, which are far more reactive than the peroxy radicals, ROO*, is not possible practical by using radical scavengers. For this reason, to avoid chain branching during autoxidation according to E.q. 2.9. Hydroperoxide decomposers are used as co-stabilizers. They decompose hydroperoxides forming "inert" reaction products (Zweifel, 1998). Stabilizers of the type of CB-D and CB-A are also referred as primary antioxidants. Hydroperoxides decomposers (HD) are classified as secondary antioxidants.

2.3.3 Antioxidant Types

Antioxidants retard oxidative degradation. Heat, mechanical shear, and UV radiation can be responsible for the formation of free radicals, which, in turn, can act to shorten polymer chains and increase crosslinking, both leading to deterioration in material properties. Free radical production often begins a chain reaction. Primary antioxidants donate active hydrogen atoms to free radical sites thereby quenching or stopping the chain reaction. Secondary antioxidants or synergists act to decompose free radicals to more stable products.

The first synthetic antioxidants were synthesized independently by Caldwell and by Winkelman and Gray by the condensation of aromatic amines with aliphatic aldehydes. Many naturally occurring antioxidants are derivatives of phenol and hindered phenols, such as di-tert-butyl paracresol. It has the ability to act as a chain transfer agent forming a stable free radical that does not initiate chain radical degradation. However, the phenoxy free radical may react with other free radicals producing quinone derivatives (Charles and Carraher, 2007).

Primary antioxidants act by trapping or deactivating radicals after they are formed. Secondary antioxidants prevent the formation of free radicals through non-radical decomposition of hydroperoxides. In general, primary antioxidants can be used alone more or less successfully, whereas secondary are used to enhance the performance of the primary antioxidant and are therefore employed alone.

2.3.3.1 Primary Antioxidants

Hindered phenols are the mostly used as primary antioxidants for polyolefins. They function in a sacrificial role as peroxy radical traps and are used to impart both processing and long term stability. Hindered phenols donate a H* radical to deactivate peroxy-free radicals, thereby breaking the propagation step of the oxidative reaction. Ideally, the antioxidant radical, A*, is resonance stabilized and does not react with the polymer to initiate new radicals. It can, however, react with one additional polymer peroxy-radical (Eq.2.21 and Figure 2.16). Generally each phenolic group present in the molecule reacts with two peroxy radicals (Klemchuck and Horng, 1991).

$$ROO^* + AH \longrightarrow ROOH + A^* \qquad (2.21)$$

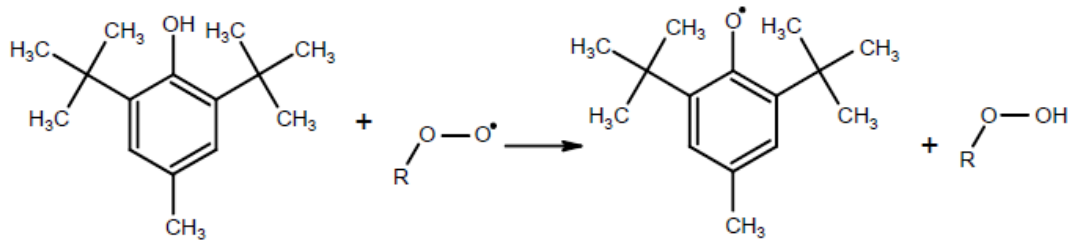


Figure 2.16 : Princible reactions of hindered phenols.

Some of the hindered phenols widely used as primary antioxidants and their application substrates are listed in Table 2.3 (Edenbaum, 1992).**Table 2.3 :** Primary antioxidants (Hindered Phenols).

Table 2.3 : Primary antioxidants (Hindered Phenols).

Trade name	Cas No.	Producer	Application Substrates
Cyanox 1790	4061-76-1	Cyanamid	1,2,3,5,6,9,10
Cyanox 2246	119-47-1	Cyanamid	5,9,10
Cyanox 425	88-24-4	Cyanamid	1,4,9,10
Ethanox 330	1709-70-2	Ethyl	
Irganox 1330		Ciba-Geigy	1,4,6
Irganox 245	36443-68-2	Ciba-Geigy	5,8,9,10
Irganox 259	35074-77-2	Ciba-Geigy	1,2,10
Irganox 1010	6683-19-8	Ciba-Geigy	1,2,3,4
Irganox 1035	41484-35-9	Ciba-Geigy	5
Irganox 1076	2082-79-3	Ciba-Geigy	1,2,3,5
Irganox 1098	23218-74-7	Ciba-Geigy	6,7,8
Irganox 1425	65140-91-2	Ciba-Geigy	1
Irganox 3114	27676-91-2	Ciba-Geigy	1,2,3
Topanol CA	1843-03-4	ICI	1,5

1= Polypropylene, 2= Linear low density polyethylene, 3= Polystyrene, 4=EPDM, 5=ABS, 6= High density polyethylene, 7= Adhesives, 8= Polyamides, 9= SBR, 10= Engineering plastics.

2.3.3.2 Secondary Antioxidants

Phosphorous or sulfur cantaining compounds are commonly used as secondary antioxidants that decompose hydroperoxides formed during oxidative degradation.

Phosphites do not contribute directly to long-term stability of polyolefins. They stabilize indirectly, by minimizing polymer degradation and by reducing the consumption of hindered phenol. In this manner, improved resistance to aging is found when the proper concentrations and ratios of phosphite and hindered phenol are used (Zweifel and Moss, 1989).

Phosphites function by reduction hydroperoxides to alcohols, with subsequent formation o the corresponding phosphate.

$$\sim COOH + P(OR)_3 \longrightarrow \sim COH + O{=}P(OR)_3 \qquad (2.22)$$

The widely used secondary antioxidants and their proposed application areas are listed in Table 2.4 (Edenbaum, 1992).

Table 2.4 : Secondary antioxidants and application substrates.

Trade name	Cas No.	Producer	Application Substrates
Dilaurylthiodipropionate	123-28-4	Several	1,2,3,5,6,9,10
Distearylthiodipropionate	693-36-7	Several	1,2,3,5,6,9,10
Ethanox 398	18337-09-0	Ethyl	1,4,9,10
Irgafos 168	31570-04-4	Ciba-Geigy	1,2,3,4,6
Sandostab P-EPQ	38613-77-3	Sandoz	1,2,3,4,5,6,8,9
Irgafos PEPQ			10
Ultranox 618	3806-34-6	GE	1,2,10
Ultranox 626	26741-53-7	GE	1,2,3,4
Ultranox TNPP	26544-23-0	GE	1,2,3,4,5

1= Polypropylene, 2= Linear low density polyethylene, 3= Polystyrene, 4=EPDM, 5=ABS, 6= High density polyethylene, 7= Adhesives, 8= Polyamides, 9= SBR, 10= Engineering plastics.

It is customary to add small amounts of other antioxidants to enhance the stabilization by a ‘‘synergistic effect’’ whereby many antioxidant combinations are more stable than using only one antioxidant.

2.4 Recent studies on degradation of XLPE

Crosslinked polyethylene (XLPE) has been widely used as an insulation material in power cables because of its excellent mechanical properties and dielectric properties. However, the three-dimensional network structure formed after crosslinking not only improves its desirable properties, but also changes polyethylene from a thermoplastic to a thermoset. Therefore, it is very difficult to recycle XLPE due to its low fluidity and poor moldability caused by crosslinking (Wu et al, 2012).

In the case of the thermoset XLPE, which is neither remeltable nor soluble because of the cross-links, some investigations for finding an economically viable recycling method have been running for more than 20 years, considering any kind of recovery.

At the beginning of the studies, a feedstock recovery was considered: by heating the XLPE to 430°C with the presence or not of a catalyst, the thermoset degrades to become light fuel oils or waxes. Particularly, a catalytic degradation (with a silicaalumina solid catalyst) turns out to give liquid olefins (mostly from n-C5 to n-C12) at a good rate. Thermal and catalytic cracking might be accompanied by a large amount of energy consumption since it is usually carried out at high temperatures was limiting the application (Uddin et al, 1997).

Some studies interested thermoset properties of XLPE (dimensional stability, chemical resistance), but reduce the length of the network by cutting it into pieces. This is practically achieved by grinding or pulverizing the scraps collected. The chips or powder obtained are put into road fillers. A more common reprocessing way is to blend the XLPE with another material, mostly HDPE. After being pulverised in granules of an average 0,6 mm size, the XLPE was successfully blended by injection moulding with HDPE. The processability was satisfying up to 40 wt-% of XLPE, and the higher the content of thermoset, the better the impact strength. It was consequently concluded that the XLPE could be a useful impact modifier of virgin resins (Myung-Kie et al,1994).

Some researchers have proposed the application of supercritical fluids such as water (Watanabe et al, 2003) and alcohols (Goto and Yazamaki, 2004) as a recycling method to achieve selective decrosslinking at crosslinking points of XLPE, which is difficult in conventional processes.

A supercritical fluid is a molecular substance at a temperature and pressure above its critical point; the conditions above which the substance has intermediate properties between gas and liquid. For this purposes, it has high diffusivity similar to a gas, and good solvency and reactivity similar to a liquid. In addition, near the critical point several properties, such as polarity and thermal conductivity, can be controlled by adjusting the temperature and pressure. With these characteristics, supercritical fluids have been studied and used to replace toxic solvents and achieve useful reactions generally impossible under conventional conditions (Arai et al, 2002).

Water and alcohols were mainly used as and supercritical fluids in depolymerization processes of plastics. In most of the case, role of supercritical fluids is both solvent as a reaction medium and reactant. In hydrolysis or alcoholysis reaction of condensation polymerization plastics, water or alcohol is evidently one of the reactants and transformed into the product molecules. In depolymerization of polyethylene, hydrogen was supplied from water, so that, the role of water is not only a solvent but also a reactant (Moriya and Enomoto, 2001).

The critical temperature of methanol is much lower than that of water (Table 2.5). Properties of water such as dielectric constant and ion product, change drastically around the critical point. Thus,catalytic effect of water can be expected. When the

depolymerized products are not enough stable in high temperature solvent and supercritical condition is required, alcohols may be better solvent than water due to lower critical temperature (Goto, 2009).

Table 2.5 : Critical points of water and alcahols.

	Critical Temperature (°C)	**Critical Pressure (Mpa)**
Water	374.1	22.1
Methanol	239.6	8.1
Ethanol	240.9	6.1
1-Propanol	263.8	5.2
Acetone	235.1	4.7
Benzyl alcohol	442.0	4.3

It was that studied a decrosslinking reaction of XLPE in supercritical alcohol using a batch reactor. Peroxide crosslinked polyethylene foam and methanol used for experiment. Decrosslinking of XLPE was carried out in a batch reactor (Figure 2.17).

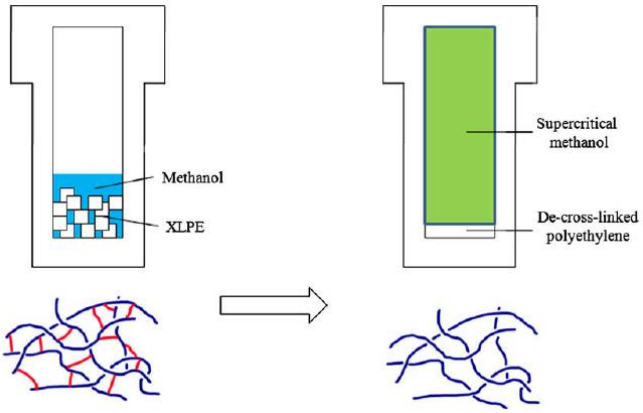


Figure 2.17 : Decrosslinking process of XLPE.

At the end of the study, it was developed a first-order kinetics based on experimental results in which the reaction rate was linearly proportional to the gel concentration and related exponentially to the temperature model (Lee et al, 2008).

A serious of studies carried out on silane crosslinked PE. Degradation of silane cross-links developed consists of a selective decomposition of the siloxane bound using supercritical alcohol. Chemical reaction in the supercritical alcohol is shown in Figure

2.18. Siloxane bond (Si-O-Si) can be decomposed to alkoxide group (-OR) or hydroxyl group (-OH) by supercritical alcohol selectively (Goto et al, 2008).

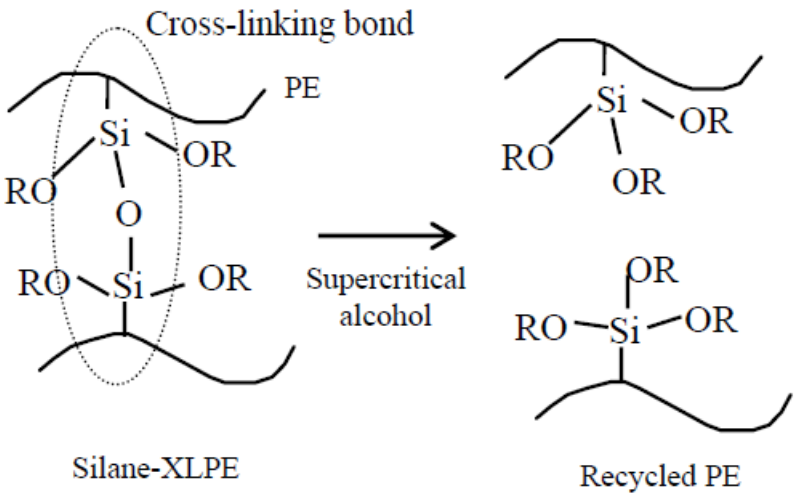


Figure 2.18 : Chemical reaction of crosslinking bond in supercritical alcohol.

The reaction with supercritical alcohol occurred in a batch reactor. First issue was the development of a method for the continuous feed of solid material into supercritical fluid. A common continous process for supercritical fluid proce produces a slurry which requires large amount of supercritical fluid (Arai, 2002). As a result, a large amount of energy is consumed. A potential solution was using extruder which could be applied as the feeder and reactor of the continous process for the reaction of silane XLPE in supercritical alcahol (Goto et al, 2005).

The continuous process (Figure 2.19) and silane crosslinked XLPE waste obtained from cable insulation was used during experiment. The main sections of continuous process were feeding, reaction, separation and condensation.

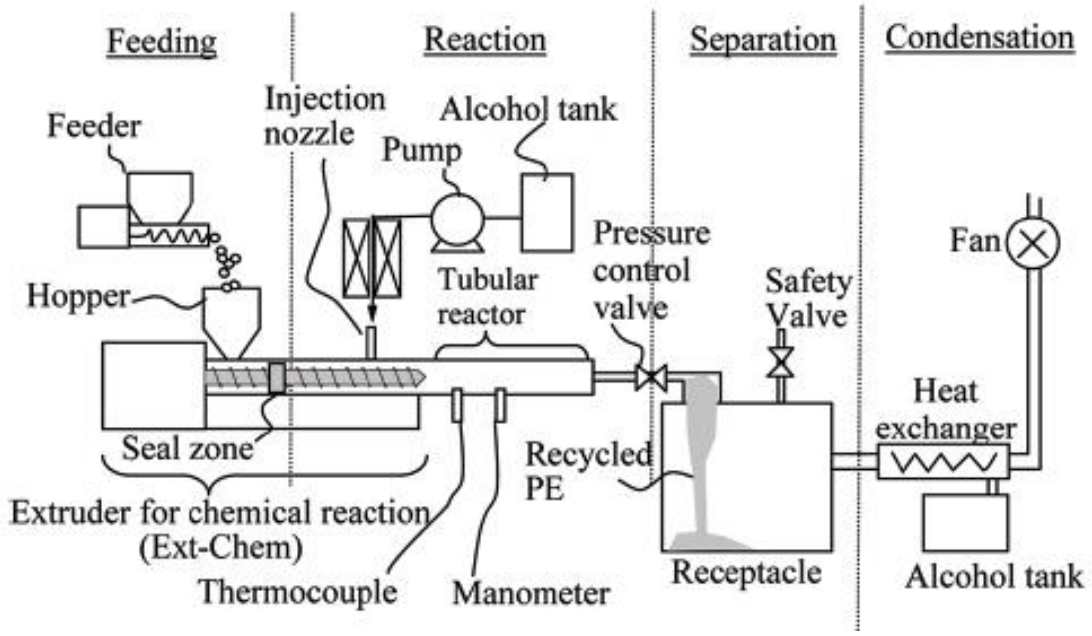


Figure 2.19 : Overview of continuous processing line.

The reactor temperature was regulated in the range of 330−335 °C, and the pressure was maintained at ~8 MPa, which was as same as the critical pressure of methanol. Recycled PE was produced at a rate of 6 g/h with 8.5 wt-% alcohol (Goto et al, 2008). As a result of the study, the scission mainly occured at the crosslinking bonds, so it appeared that the continous process with single screw extruder can be used for recycling of silane crosslinked PE.

Another study was carried out by and related to degradation of XLPE is thermoplasticizing which's goal is to get rid of the thermosetting structure by breaking the cross-links, so that the meltability of the material is improved, and the viscosity reduced. The process can be seen at Figure 2.20. The degradation of these crosslinks can be achieved mechanically, with an adapted melt and shear kneading method. In this thermoplasticizing process, first the XLPE has first been chopped in chips of 5 to 10 mm^2. Then, the XLPE chips are fed the thermoplasticizing equipment, where they converted under differing process conditions into 2-3 mm pellets of recycled material.

The results of the study show that the recycled materials made from XLPE by a process of thermoplasticizing showed differences from virgin polyethylene.

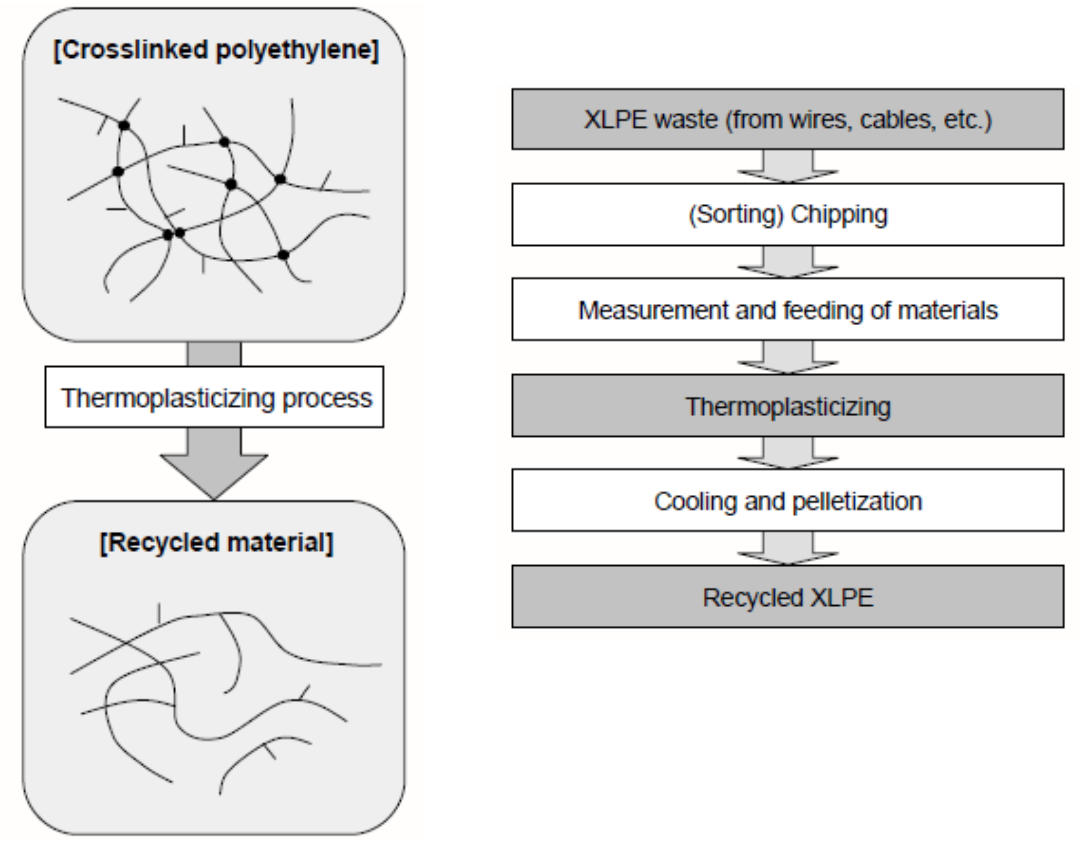


Figure 2.20 : Thermoplasticizing process.

From the chemical standpoint, however, it can still be called polyethylene. The recycled materials can be press-molded and extrusion molded without additional material. The chemical composition of the recycled materials is substantially the same as that of polyethylene, with some slight increase in double-bond component. There are also residual components with molecular weights greater than 100,000. These results confirm that thermoplasticizing recycling technology enables crosslinked polyethylene to be reused. (Tokuda et al, 2003).

An eco-friendly mechanochemical technology called “solid state mechanochemical milling” using a pan-mill equipment to recycle crosslinked polymers has been developed by Hejun et al. The pan-mill equipment was designed for solid-state mechanochemical reactions of polymers, showing multifunction, such as pulverizing, dispersion, mixing, and activation. The selective decrosslinking was successfully achieved at crosslinking elements by mechanochemical milling, and consequently led to the higher chain mobility of XLPE, which might affect its crystallization process (Wu et al, 2012).

It is known that crystallization behaviors play an important role in the physical, chemical, and mechanical properties of polymers. Moreover, from the practical view the non-isothermal crystallization is more useful than the isothermal crystallization because most processing techniques actually occur under non-isothermal conditions (Lorenzo and Silvestre, 1999). Therefore, it is important that the effect of milling process on the thermal behavior and the crystallization kinetics of XLPE, due to the fact that the resulting physical properties are strongly dependent on the morphology formed and the extent of crystallization occurring during processing (Run at al, 2005). In this study, to investigate the effect of the decrosslinking on the non-isothermal crystallization kinetics of XLPE, low-density polyethylene was crosslinked by dicumyl peroxide without further additives, and then subjected to solid state mechanochemical milling using a pan-mill equipment to obtain decrosslinked XLPE Several theoretical models were applied to describe the process of non-isothermal crystallization based on the differential scanning calorimeter data. Simultaneously, pure LDPE was analyzed in the same process for comparison.

2.5 Purpose of antioxidant usage in crosslinkable polyethylene compound

Commercially crosslinkable polyethylene compounds (CPEC) are so common for cable insulation. They are called ready XLPE which contain peroxide or silane curing systems inside. CPEC is extruded on conductor and then cured to obtain crosslinked insulation. Homogenous material flow should be taken and thickness and diameter of cable insulation need to be adjusted before start to continuous extrusion of cable insulation. Obtaining homogenous material flow and adjustment of thickness and diameter of insulation from the die of extruder, some material should be bleeded as Figure 2.21. Bleeded material becomes scrap because of it contains crosslinking agent inside which limits reuse of material. In this study, the purpose of antioxidant usage in CPEC is to terminate crosslinkability of polyethylene compound. It means that, the addition of antioxidants to CPEC preventes the crosslinkability of polyethylene no longer.

Figure 2.21 : Crosslinkable polyethylene bleeding and scrap.

3. EXPERIMENTAL

3.1 Materials

3.1.1 Commercial crosslinkable polyethylene compound (CPEC)

CPEC was the commercial Supercure™ LS4201R which is homopolimer and contains peroxide as crosslinking agent supplied from Borealis company. Physical properties declared by company datasheet are given in Table 3.1.

Table 3.1 : Physical properties of commercial CPEC.

Property	Typical Value	Test Method
Density (Base Resin)	922 kg/m^3	ISO 1872-2/ISO 1183
Melt Flow Rate (190°C/2.16 kg)	2 g/10min	ISO 1133
Tensile Strain at Break (250 mm/min)[1]	> 450%	ISO 527
Tensile Strength (250 mm/min)[1]	> 17 Mpa	ISO 527
Retention of Tensile Properties After Ageing (500h, 135 °C)[1]	< 20%	IEC 60811-1-2
Hot-set Test (200°C, 0.20Mpa)		IEC 60811-2-1
Elongation under load	75 %	
Permanent deformation	5 %	
Göttfert Elastograph	0.56-0.67	
Methanol Wash	< 1000 ppm	
Moisture	< 200 ppm	Karl Fischer-titration

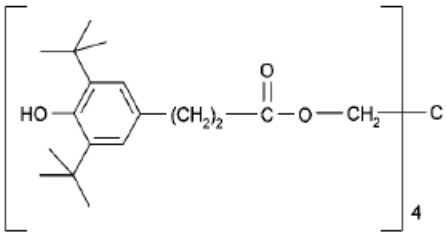
[1] Measured on crosslinked specimens

3.1.2 Antioxidant 1 (AO1)

Irganox® 1010 from Basf was used as AO1. Irganox 1010 – a sterically hindered phenolic antioxidant – is a highly effective, non discoloring stabilizer for organic substrates such as plastics, synthetic fibers, elastomers, adhesives, waxes, oils and fats. It protects these substrates against thermo-oxidative degradation. Irganox 1010 can be applied in polyolefins, such as polyethylene, polypropylene, polybutene and olefin copolymers such as ethylene-vinylacetate copolymers. In addition, its use is recommended for the processing of polymers such as polyacetals, polyamides and polyurethanes, polyesters, PVC, styrene homo- and copolymers, ABS, elastomers such as butyl rubber (IIR), SBS, SEBS, EPM and EPDM as well as other synthetic rubbers,

adhesives, natural and synthetic tackifier resins, and other organic substrates. Chemical and physical parameters declared by company datasheet are given Table 3.2.

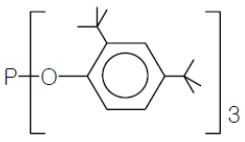
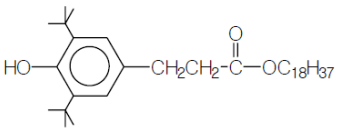
Table 3.2 : Physical properties of phenolic antioxidant AO1.

Properties	Values
Chemical name	Pentaerythritol tetrakis(3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate)
CAS number	6683-19-8
Chemical formula	
Molecular weight	1178 g/mol
Melting range	110 – 125 °C
Flashpoint	297 °C
Density (20 °C)	1.15 g/ml

3.1.3 Antioxidant 2 (AO2)

SONGNOX® 217B was from Songwon was used as AO2. SONGNOX® 217B is the physical blend of SONGNOX® 1076 (33.3%), a primary hindered phenolic antioxidant, with SONGNOX® 1680 (66.7%), a secondary phosphite antioxidant. It provides excellent melt flow and provides long term heat stability and protects physical properties during storage and in the end use application.

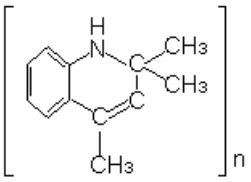
Table 3.3 : Physical properties of blend antioxidant AO2.

Properties	Songnox® 1680	Songnox® 1076
Chemical name	Tris(2,4-di-tert-butylphenyl) phosphite	Octadecyl-3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate
CAS number	31570-04-4	2082-79-3
Chemical formula		
Molecular weight	647	531
Melting range	181-187 °C	50-55 °C
Percentage	66.7 %	33.3%

3.1.4 Antioxidant 3 (AO3)

Amine class antioxidant Vulkanox HS/LG from Lanxess was used as AO3. Vulkanox HS is an antioxidant with relatively weak staining and discoloration characteristics. This antioxidant offers very good protection against oxidation and heat. Product chracteristics declared by company datasheet are in Table 3.4.

Table 3.4 : Physical properties of amine class antioxidant AO3.

Properties	**Values**
Chemical name	2,2,4-trimethyl-1,2-dihydroquinoline, polymerized (TMQ)
Form	Yellow to brownish lentil-shaped granules
Chemical formula	
Softening point	85 – 95 °C
Alkalinity index	510-570
Ash content	≤ 0.3 %
Density (20 °C)	1.1 g/cm^3
Bulk density	600 kg/m^3
Volatile matter	0.3 %

3.2 Equipments

3.2.1 Plasticorder PL2000

Plasticorder was used to mix CPEC and AO's with different ratio. Plasticorder is a torque rheometer for applicational investigations or processing tasks in laboratories and for simulation. This instrument is suited for mixers and extruders including a temperature control. General properties are as below.

Speed : 0 - 120 min^{-1}

Torque : max. 200 Nm

Temp : max. 300 °C

Volume : 55 cm^3

Figure 3.1 : Plasti-corder PL2000.

3.2.2 Rubber process analyser (RPA)

RPA 2000 from Alpha Technologies was used to measure crosslinking properties such as MH, ML, T2 and T90.

Figure 3.2 : Rubber process analyser.

3.2.2 Universal testing machine

A Zwick Z050 universal testing machine was performed for the evaluation of tensile properties of the samples. The machine had 20000 N capacities. It has two load cells with 2000N and 20000N. The load cell was capable of applying 2000 N force and testing samples up to 250 mm/min speed.

Figure 3.3 : Universal testing machine.

3.2.3 Differential scanning calorimetry

THERMAL ANALYZERS Q100 Differential Scanning Calorimetry equipment was used for thermal analysis of the samples. The analysis were done for pure CPEC and CPEC with AO samples between 30ºC and 200ºC at 10ºC/min heating rate under inert atmosphere. Melting temperatures (Tm) of the samples were obtained using a differential scanning calorimeter (DSC).

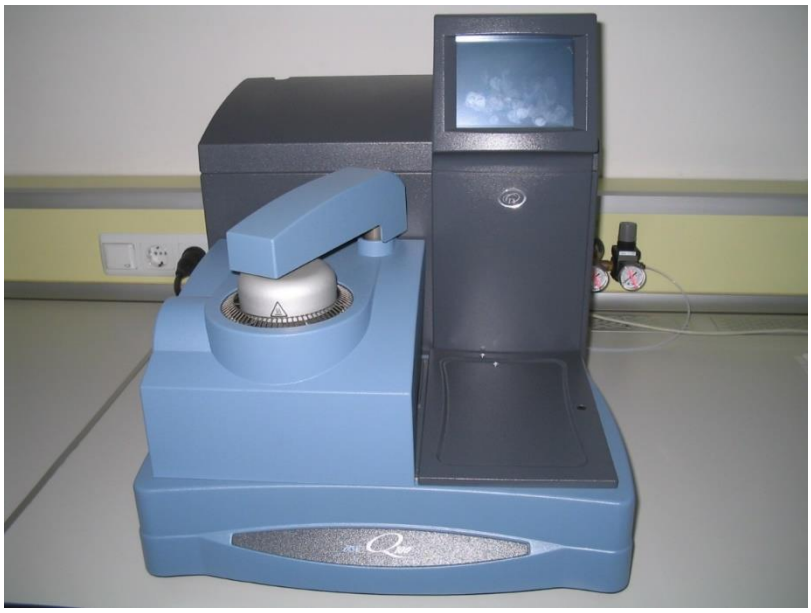


Figure 3.4 : Differential scanning calorimetry.

3.2.4 Melt flow index device

GÖTTFERT MP-D was used to measure melt flow rate (MFR) values of the samples. It is equipped with a standard 8 mm in length and 3 mm in diameter die, a standard 6.35 mm in length and 9.4772 mm in diameter piston, and a standard load to apply 2.16 kg force during the extrusion.

Figure 3.5 : Melt flow index device.

3.2.5 Hot press

SCHWABENTHAN Polystat 200S was used to prepare the plaques with 1mm thick after mixing of CPEC and CPEC with AO. The samples for tensile test and Hot-set tests were taken from these plaques.

Figure 3.6 : Hot press.

3.2.6 Hot-set test equipments

Hot-set test is performed to understand if sample crosslinked or not. 20 mm is marked on the middle of sample. The weigth (load) which is equal to (20 x crossection area) is hanged to sample. The sample with load is kept in the oven at 200°C for 15 minutes. After this period, the elongation is measured from marked length. Elongation should be in the limit of 175%. The sample without load is kept further 5 minutes in oven but permanent elongation is measured. Permanent elongation should be max 15%.

Figure 3.7 : Hot-set test device.

3.3 Experimental Procedure

3.3.1 Preparation of samples

In this study, %1, %3 and %5 weight percentages of AO1, AO2, and AO3 were used in CPEC. 12 samples were weighed according to Table 3.5. Plasticorder was used for mixing. Weighed CPEC and AOs were put in to plasticorder and mixed for 12 minutes at 110 °C with 50 rpm. Mixed sample was unloaded from plasticorder and cooled to room temperature.

Table 3.5 : Sample preparation table.

Material	Sample No											
(AO percents)	1	2 (%1)	3 (%3)	4 (%5)	5 (%1)	6 (%3)	7 (%5)	8 (%1)	9 (%3)	10 (%5)	11 (%3)	12 (%5)
CPEC (g)	50	49.5	48.5	47.5	49.5	48.5	47.5	49.5	48.5	47.5	--	--
AO1 (g)	--	0.5	1.5	2.5	--	--	--	--	--	--	0.75	1.25
AO2 (g)	--	--	--	--	0.5	1.5	2.5	--	--	--	0.75	1.25
AO3 (g)	--	--	--	--	--	--	--	0.5	1.5	2.5	--	--
Total (g)	50	50	50	50	50	50	50	50	50	50	50	50

Some portion of mixed samples was used to prepare the plaques for mechanical characterization including tensile and hot-set test. Hot press was used for plaque preparation. Mixed sample was put in to 1mm rectangular mold. The mold was put in to press for 10 minutes which first 2 minutes without pressure and the last 8 minutes under 150 bar pressure. Plaques were cooled down to room temperature. The rest of samples was used for RPA, DSC and MFR tests.

3.3.2 Crosslinking property characterization

Cure characteristics of samples were determined by RPA, which measures the flow behaviour crosslinkable compounds during crosslinking and gives the rheometer curve. It applies to crosslinkable compound an oscillation at desired temperature and pressure. As a result of the increasing of crosslinking density, torque force increases

which are effective on the rotation center of equipment. RPA gives this increment as a function of time, which can be seen from Figure 3.8.

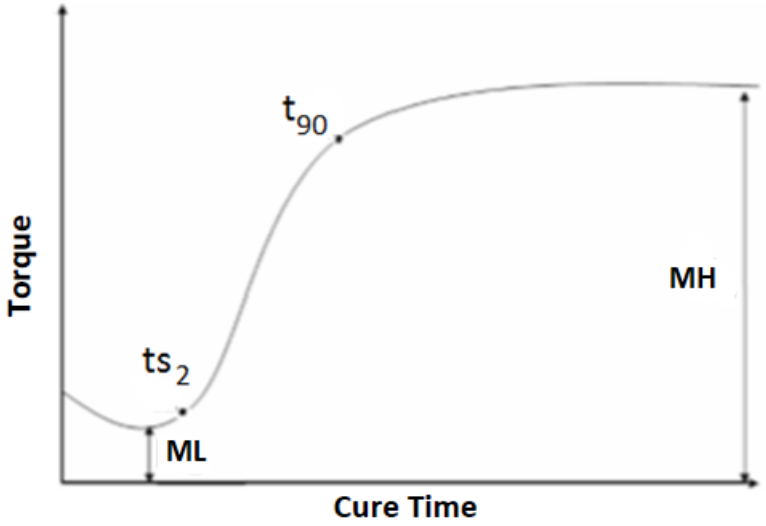


Figure 3.8 : Typical rheometer curve.

In a crosslinking isotherm for elastic response ML is the minimum torque value and gives the minimum viscosity of crosslinkable compound. MH, is the final rheometer indication constant in time, on completion of crosslinking reaction and give the maximum torque of compound. ts_2 (scorch time) is the time after two torque units above ML is reached in an elastic torque curve. Scorch time is essential to the safe processing of a crosslinkable compound, on machinery that further shapes the compound while heating it up. t_{90} is the time required for elastic torque curve to reach 90% of maximum torque time (Çavdar, S., 2007).

3.3.3 Mechanical property characterization

Specimens were prepared as dumb-bell form. After the measurements of dimensions, which are width and thickness, the specimens of the samples were placed between gauge. The tensile tests were carried out at 250 mm/min rate according to IEC 60811-501 (specifies a short-term tensile test method for determining the tensile properties of cable sheath and insulation) standards. From the measured stress and strain values, maximum tensile strength and elongation at break were calculated.

For the comparison of the mechanical tests results on the samples; mechanical properties of CPEC and CPEC with AO specimens were measured and calculated.

3.3.4 Hot-set test

Many required properties of polyethylene insulation of cables depend on the degree of crosslinking. Determination of crosslinking can be carried out with the help of hot set test.

The elongation of the insulation material at an elevated temperature under the load and its recovery after removal of the load are determined to evaluate the efficiency of the crosslinking. A sample is hanged from a vertical frame inside a hot air oven with a specified load hanged from its lower end. The elongation of the sample after fifteen minutes under the above conditions should be max.175% and the permenant elongation should be max.15% when its subsequent recovery after removal of the load.

3.3.5 Thermal property characterization

The thermal properties of the blends were determined by differential scanning calorimetry (DSC). The heating scans were carried out at 10ºC/min rate in the temperature range of 30ºC - 200ºC in the DSC analysis of the samples. Melting parameter were calculated from Heat Flow (W/g)) vs Temperature (T) graphs.

3.3.6 Melt flow rate determination

The melt flow rates (MFR) of samples were measured at 130ºC with 2.16 kg load according to ASTM D1238 standard.

4. RESULTS AND DISCUSSION

In this study, sample of CPEC and CPEC with antioxidants were prepared according to the procedure given in the Section 3.3.1. Pure CPEC was mixed with 1%, 3% and 5% ratios of 3 different antioxidants. Laboratory plasticorder was used for mixing of sample. The prepared 12 samples were characterized and the measurements results of the crosslinking, mechanical and thermal properties of the samples were given.

4.1 Evaluation of Crosslinking, Mechanical and Thermal Properties

4.1.1 Crosslinking properties test results

Crosslinking characteristics (ML, MH, ts_2 and t_{90}) of the compounds were obtained by using RPA at 185 °C according to ASTM D2084. Crosslinking datum and curves can be seen at Table 4.1 and Figure 4.1

Table 4.1 : Crosslinking data.

Sample	Mixture	MH (dNm)	ML (dNm)	MH-ML (dNm)	T2 (min)	T90 (min)
1	CPEC	2.9	0.19	2.71	0.66	4.48
2	CPEC + %1 AO1	1.52	0.16	1.36	0.64	4.30
3	CPEC + %3 AO1	0.90	0.17	0.73	0.60	3.95
4	CPEC + %5 AO1	0.55	0.19	0.36	0.77	4.09
5	CPEC + %1 AO2	1.90	0.27	1.63	0.62	4.19
6	CPEC + %3 AO2	1.00	0.17	0.83	0.59	3.49
7	CPEC + %5 AO2	0.65	0.14	0.51	0.54	3.45
8	CPEC + %1 AO3	2.42	0.19	2.23	0.67	4.40
9	CPEC + %3 AO3	1.70	0.20	1.50	0.61	4.43
10	CPEC + %5 AO3	0.98	0.13	0.85	0.69	4.40
11	CPEC + %1.5 AO1 + %1.5 AO2	0.78	0.14	0.64	0.66	3.95
12	CPEC + %2.5 AO1 + %2.5 AO2	0.49	0.12	0.37	0.70	4.01

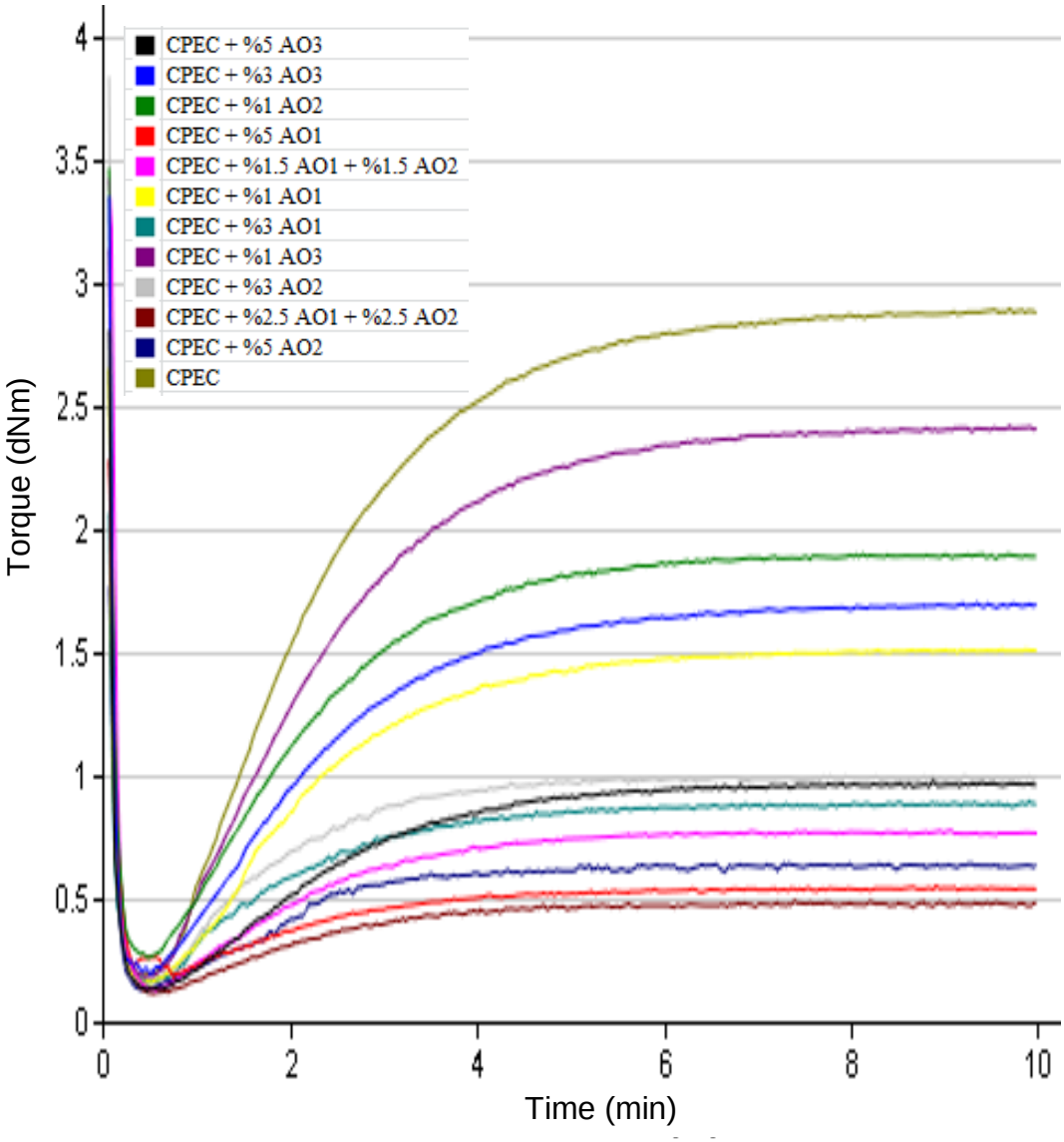


Figure 4.1 : Crosslinking curves of prepared samples.

When crosslinking data were checked, It is observed that ML values were not change so much. MH values were decreased when antioxidant percentages were increased. The smallest MH values were obtained with 5% percent of AO1 and blend of 2.5% AO1 + 2.5% AO2. The difference between MH and ML values can be used as degree of crosslinking of the compounds. The difference, which was 0.36 between MH and ML, observed when 5% of AO1 was added into CPEC. The similar value which was 0.37 was obtained with blend of 2.5% AO1 + 2.5% AO2. MH, ML and "MH-ML" (cure extent) values are given at from Figure 4.2 to 4.5.

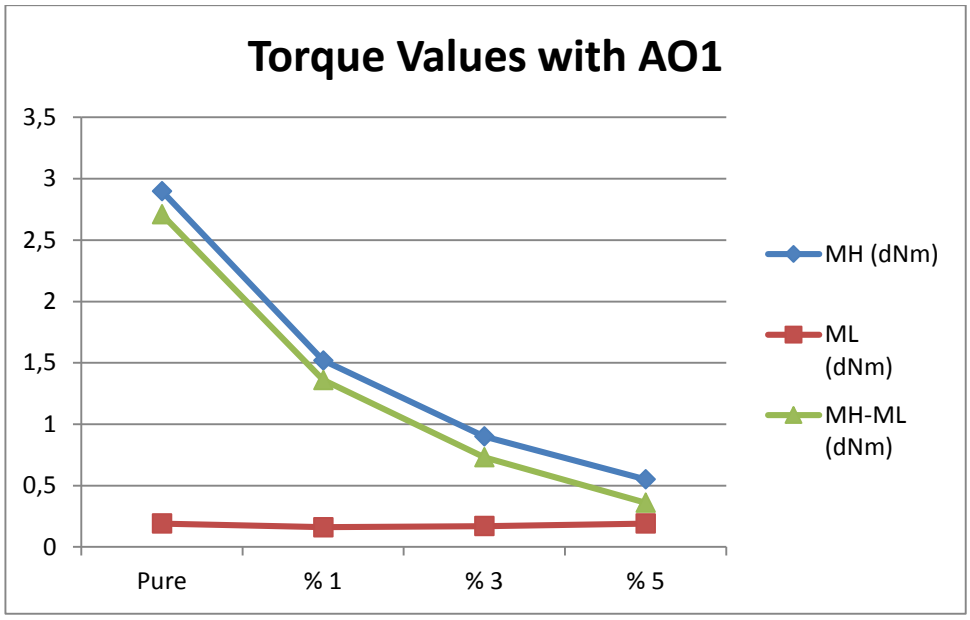


Figure 4.2 : Torque values with AO1.

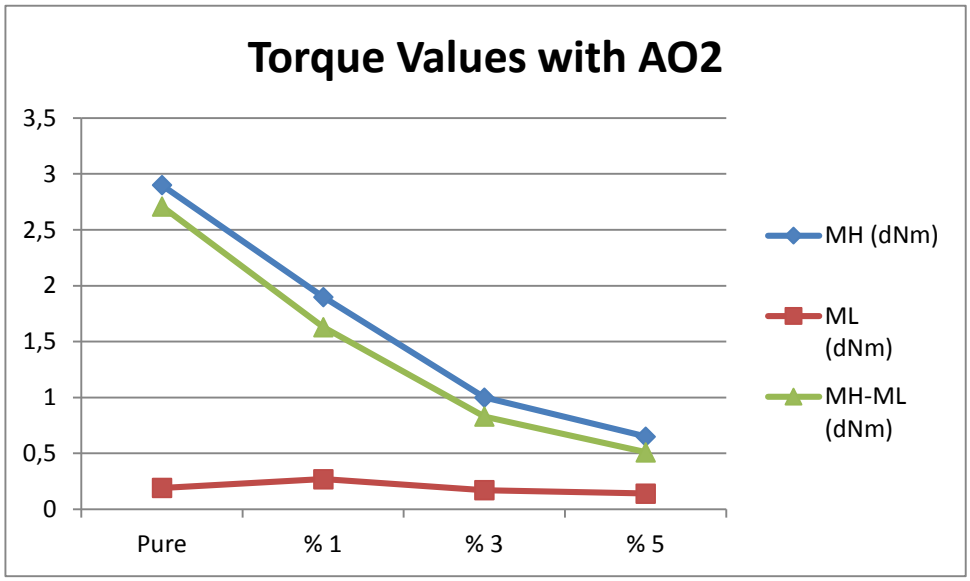


Figure 4.3 : Torque values with AO2.

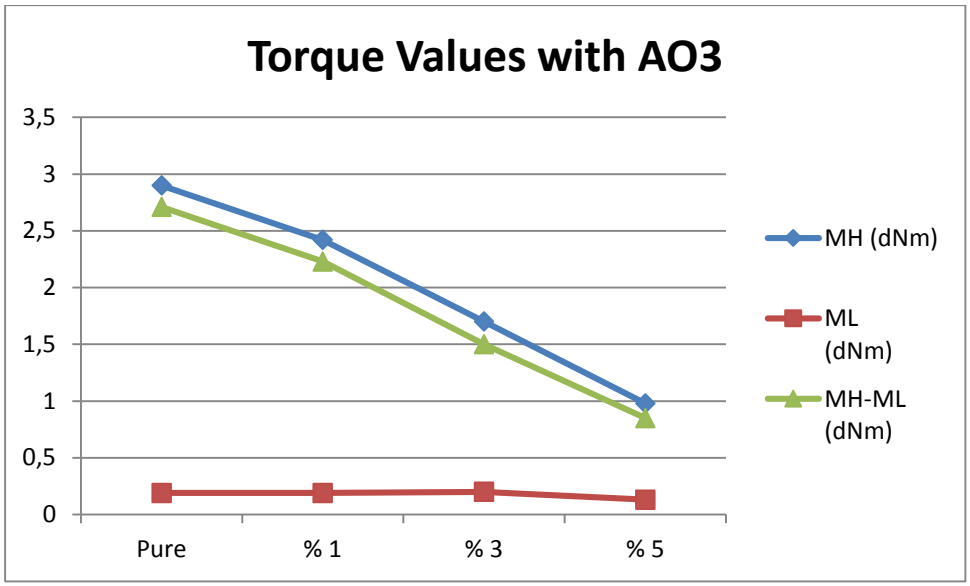


Figure 4.4 : Torque values with AO3.

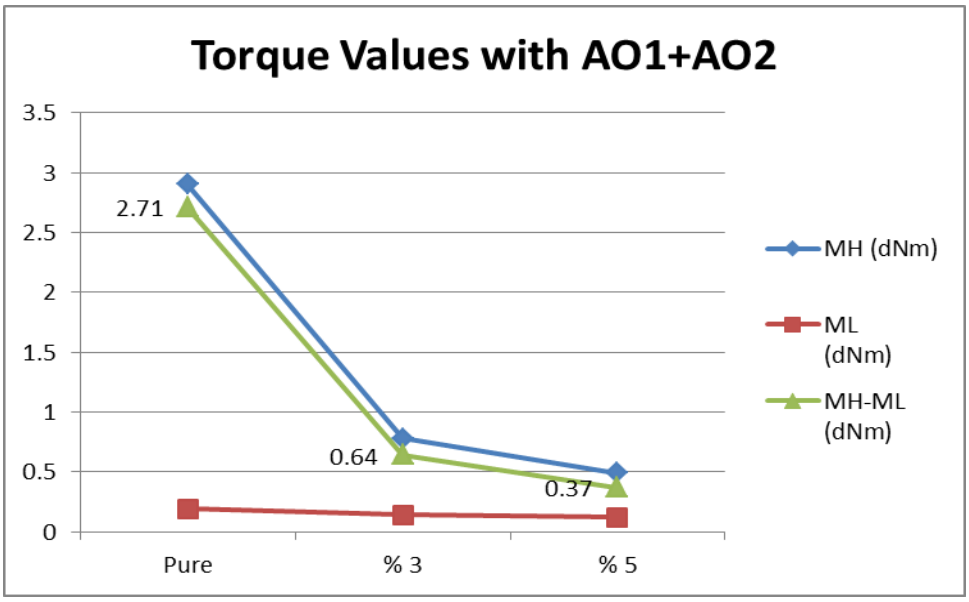


Figure 4.5 : Torque values with AO1 + AO2.

4.1.2 Tensile test result of samples

Tensile tests were performed with universal test machine at 25±2 ^{0}C. The tensile properties of the materials are shown in Table 4.1. The values of all the mechanical parameters are calculated as 3 specimens for each composition and the data of samples is plotted on Figures from 4.1 and 4.2. From these results, it is clear that addition of antioxidants has significant effect on the mechanical properties of pure CBEC.

Table 4.2 : Tensile strength and elongation break results.

Sample	Mixture	Tensile Strength N/mm^2	Elongation at Break %
1	CPEC (pure)	20.88	562
2	CPEC + %1 AO1	21.48	588
3	CPEC + %3 AO1	17.89	580
4	CPEC + %5 AO1	14.93	531
5	CPEC + %1 AO2	20.84	575
6	CPEC + %3 AO2	18.15	570
7	CPEC + %5 AO2	14.32	434
8	CPEC + %1 AO3	17.18	479
9	CPEC + %3 AO3	16.71	462
10	CPEC + %5 AO3	15.14	509
11	CPEC + %1.5 AO1 + %1.5 AO2	19.23	633
12	CPEC + %2.5 AO1 + %2.5 AO2	17.90	674

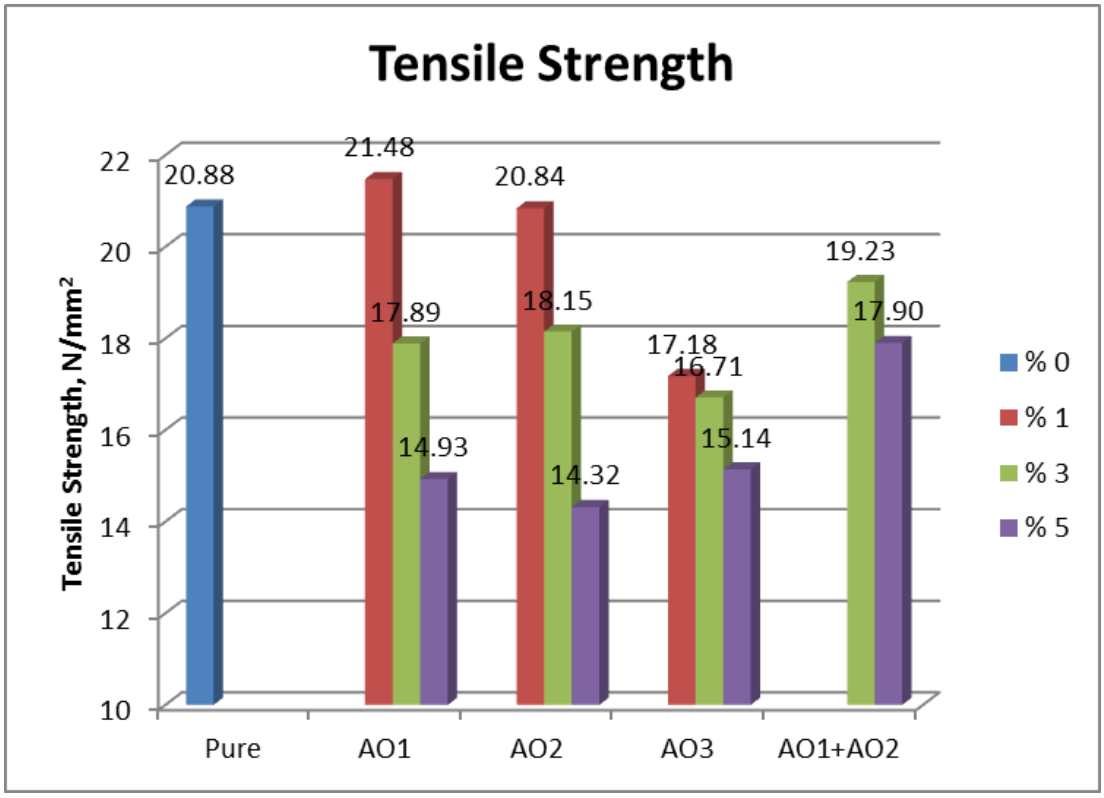


Figure 4.6 : Maximum tensile strength values of samples.

The maximum tensile strengths decrease by increasing amount of antioxidants. When %1 of AO1 was added into CPEC, change at tensile strength observed 2.87%.

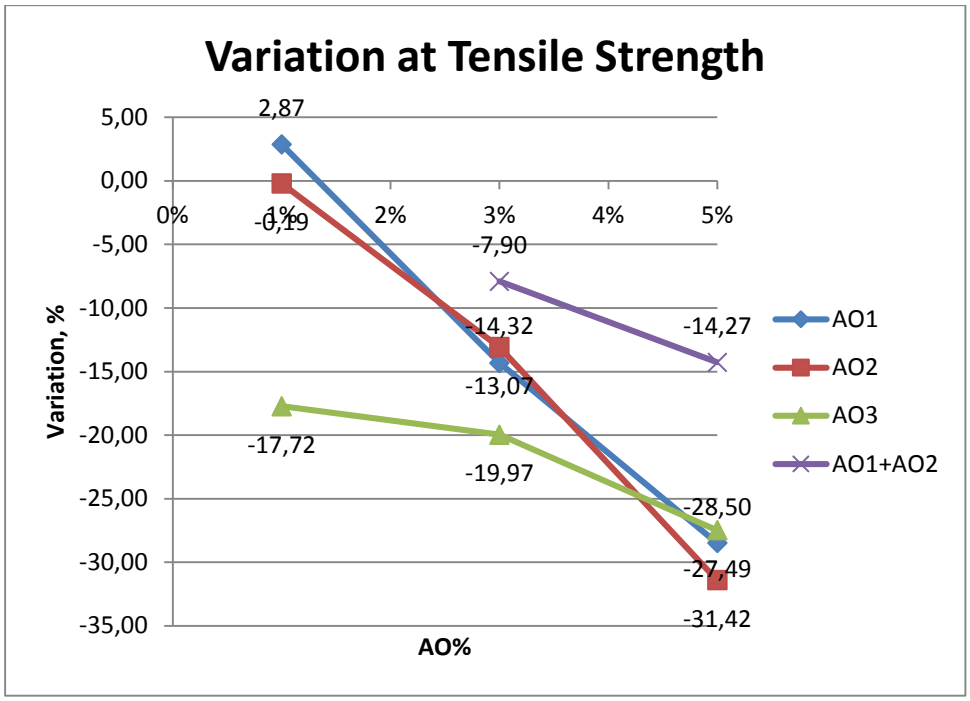


Figure 4.7 : Variation at maximum tensile strength values.

Dramaticaly decreased which was about 28.50% occurred, when 1% of AO3 was added in to CPEC. When 5% of AO1, AO2 and AO3 antioxidants were added in to CPEC, variation at tensile strength observed -28.50%, -31.42% and -27.49% respectively.The variation was -14.27% when blend of 2.5% AO1 + 2.5 AO2 was used.

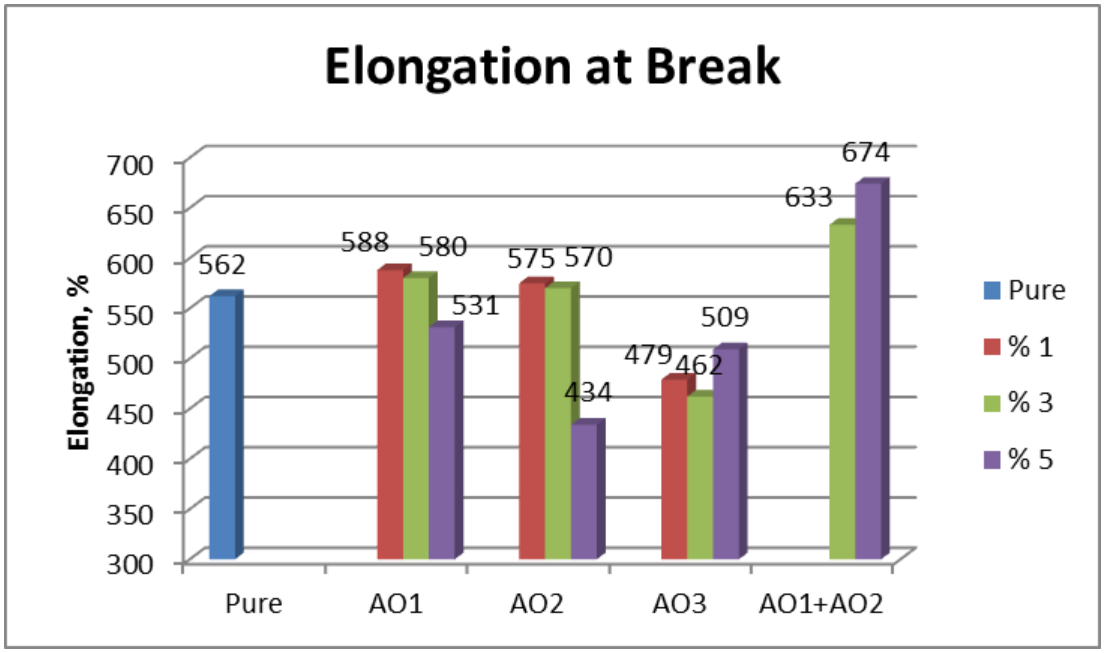


Figure 4.8 : Elongation at break values of samples.

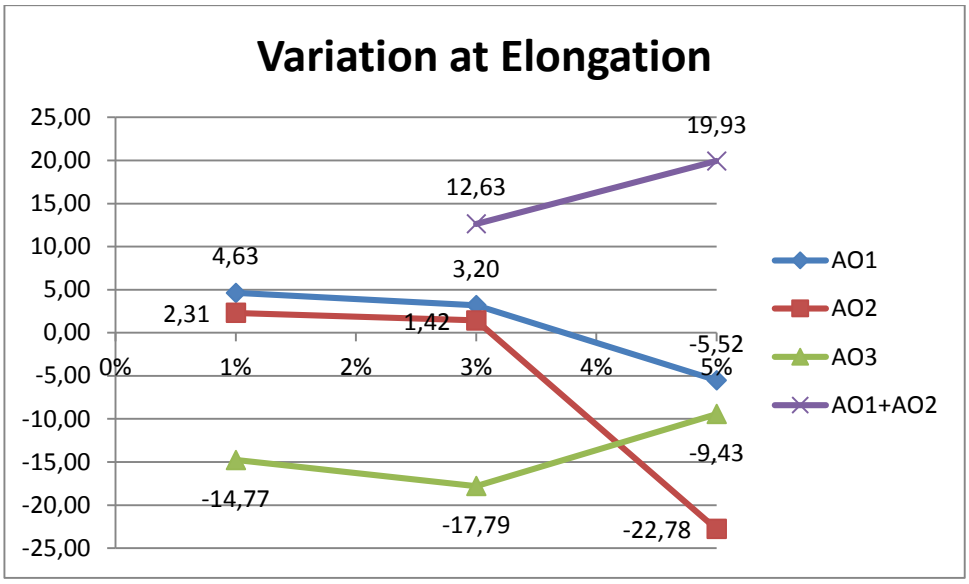


Figure 4.9 : Variation at elongation at break values.

There was not significant change at elongation at break when AO1 and AO2 were added with 1% and 3%. But AO3 was added 1% and 3% into CPEC, elongation at breaks were increased by 14.8% and 17.8 respectively. The maximum reduction was observed as 22.8%, when 3% of AO2 was used. The variation at elongation was positive when blend of AO1 and AO2 was used. Elongation increased with ~20%, when blend of 2.5% AO1 + 2.5 AO2 was added

4.1.3 Hot-set result of the samples

Hot-set test is special test for cable sector that represent mechanical resistance of crosslinking of XLPE. Positive result in hot-set test means polyethylene chains crosslinked eachother under specified conditions. On the other hand, crosslinking is not satisfactory when negative results are obtained. In this study, negative results are desired besides low MH-ML difference to obtain recovery of XLPE. Hot-set tests were performed according to item 3.2.6. Results are given at Table 4.5.

According to results pure CPEC, CPEC with 1% AO2 and CPEC with 1% AO3 passed the hot-set test. The other samples were failed because elongations under load were grather than 175%. Measurement could not performed because of elongations were too high for sample number 3, 4, 6, 7, 9 and 10. So the results were indicated as >500%.

Table 4.3 : Hot-set results.

Sample	Mixture	% Elongation under load 15 minutes at 200°C Max 175%	% Elongation without load 5 minutes at 200°C Max ±15	Hot-Set Result
1	CPEC	80	0	Passed
2	**CPEC + %1 AO1**	**230**	**---**	**Failed**
3	**CPEC + %3 AO1**	**> 500**	**---**	**Failed**
4	**CPEC + %5 AO1**	**> 500**	**---**	**Failed**
5	CPEC + %1 AO2	165	0	Passed
6	**CPEC + %3 AO2**	**> 500**	**---**	**Failed**
7	**CPEC + %5 AO2**	**> 500**	**---**	**Failed**
8	CPEC + %1 AO3	110	0	Passed
9	**CPEC + %3 AO3**	**> 500**	**---**	**Failed**
10	**CPEC + %5 AO3**	**> 500**	**---**	**Failed**
11	**CPEC + %1.5 AO1 + %1.5 AO2**	**> 500**	**---**	**Failed**
12	**CPEC + %2.5 AO1 + %2.5 AO2**	**> 500**	**---**	**Failed**

4.1.4. Thermal tests results of the samples

Thermal properties of sample of CPEC and samples CPEC with antioxidants were analyzed by differential scanning calorimetry. Samples were heated from room temperature to 200 °C at 10 °C /minute. Parameters of melting data showed in Figures from 4.9 to 4.8 gained from these runs.

Table 4.4 : DSC test results.

Sample	Mixture	ΔHm (J/g)	Melting °C
1	CPEC	100.9	108.7
2	CPEC + %1 AO1	106.2	108.5
3	CPEC + %3 AO1	103.8	108.5
4	CPEC + %5 AO1	103.1	108.5
5	CPEC + %1 AO2	118.0	109.1
6	CPEC + %3 AO2	112.7	108.7
7	CPEC + %5 AO2	106.3	108.5
8	CPEC + %1 AO3	93.6	107.9
9	CPEC + %3 AO3	92.4	107.3
10	CPEC + %5 AO3	91.8	107.3

By using the software of DSC analyzer, the first derivative of heat flow change with respect to temperature change were calculated in order to determine the start and end temperatures of the melting regions (Table 4.4).

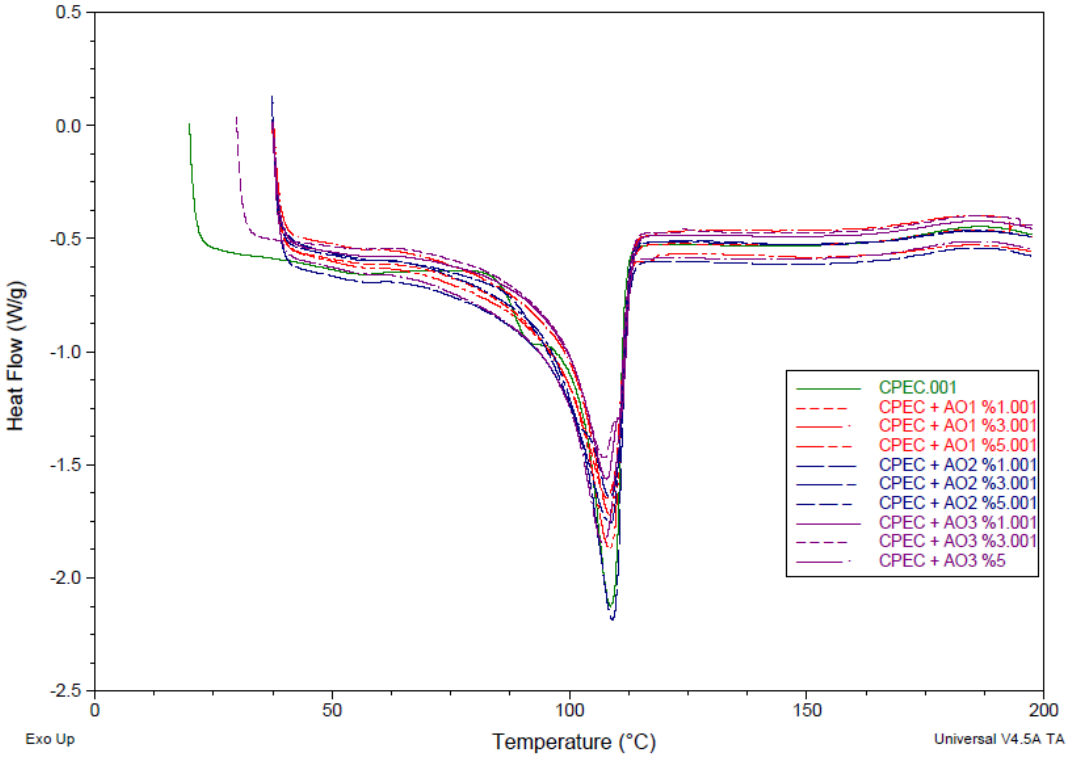


Figure 4.10 : Melting peaks of CPEC and CPEC with AO.

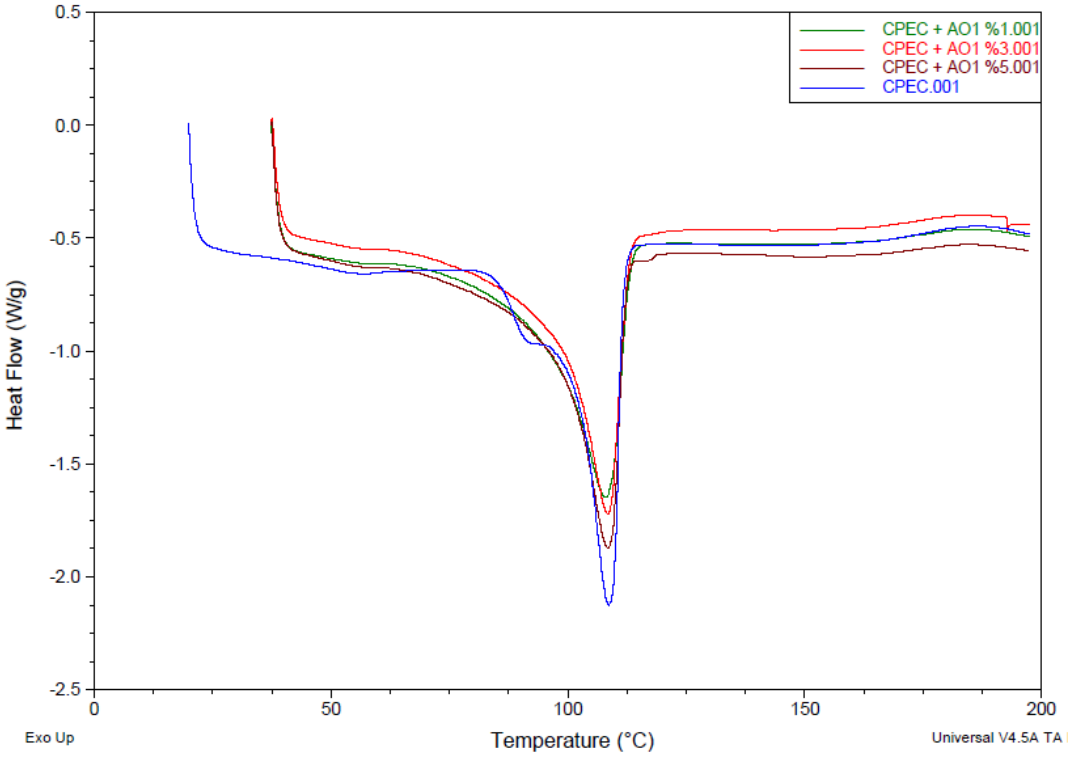


Figure 4.11 : Melting peaks of CPEC with AO1.

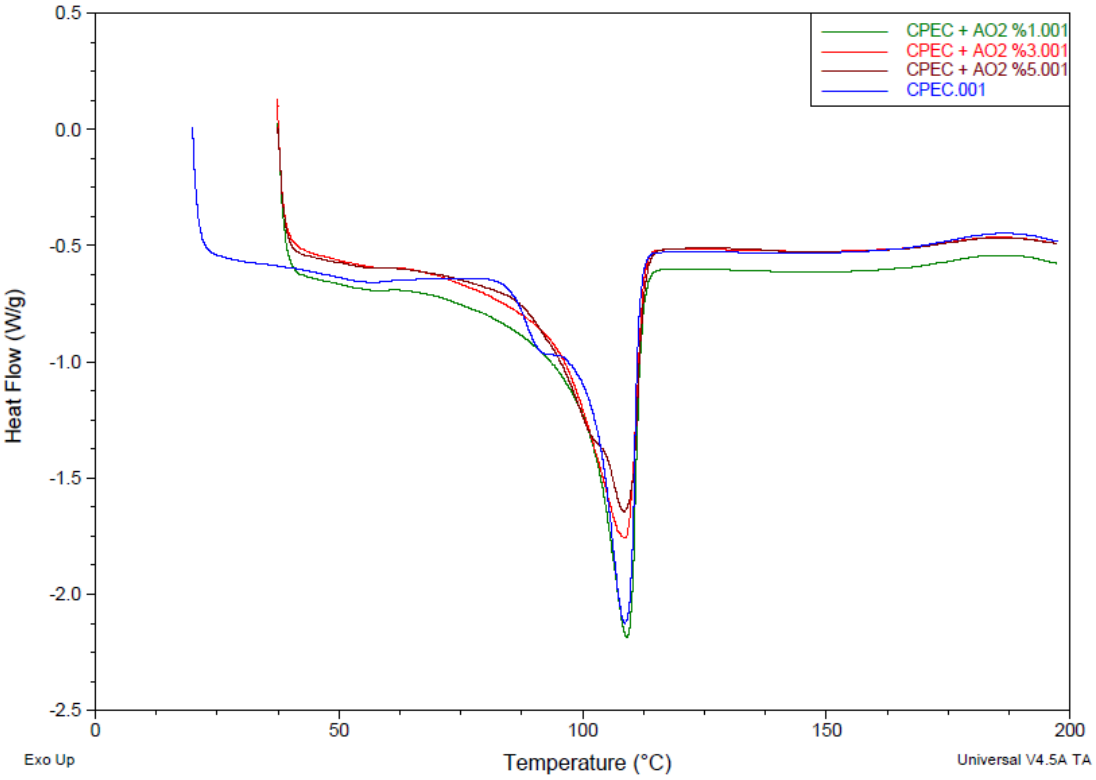


Figure 4.12 : Melting peaks of CPEC with AO2.

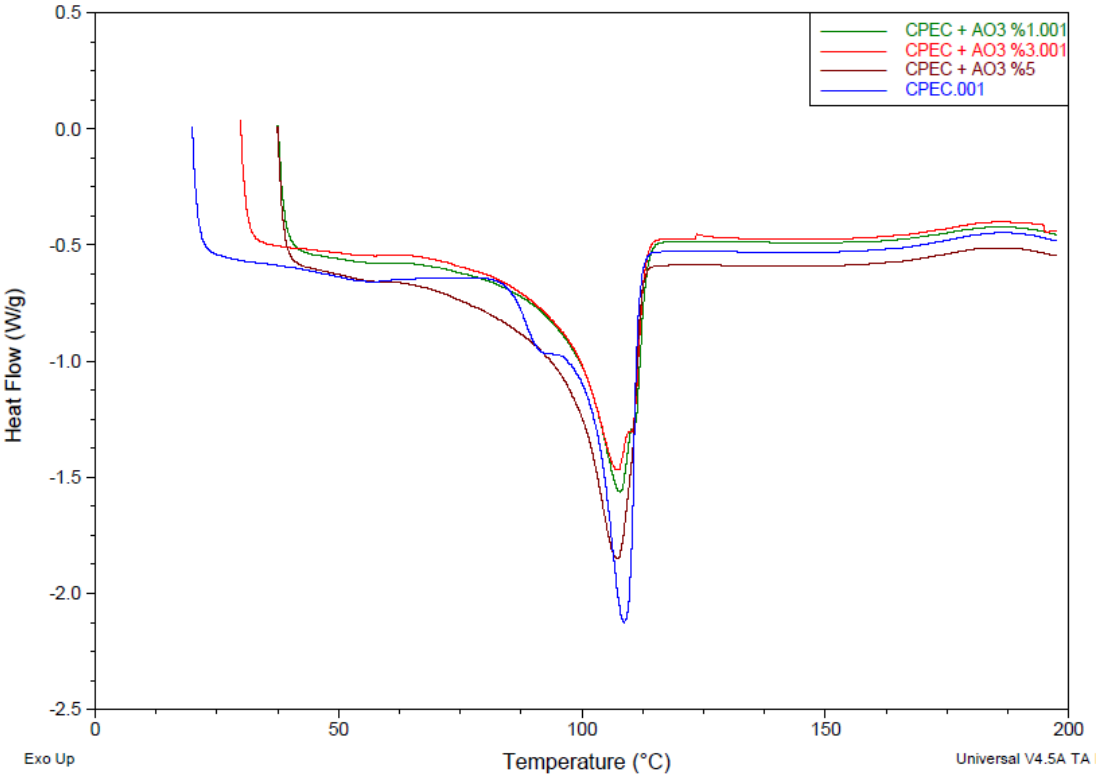


Figure 4.13 : Melting peaks of CPEC with AO3.

4.1.5 MFR result of the samples

The melt flow rates (MFR) of CPEC and CPEC with antioxidants were measured according to ASTM D1238 standard. The MFR results obtained increase when antioxidant contents in CPEC. The results are given in Table 4.5 and Figure 4.13.

Table 4.5 : MFR results of mixtures.

Sample	Mixture	MFR (gr/10 min)
1	CPEC	0.246
2	CPEC + %1 AO1	0.247
3	CPEC + %3 AO1	0.294
4	CPEC + %5 AO1	0.360
5	CPEC + %1 AO2	0.244
6	CPEC + %3 AO2	0.298
7	CPEC + %5 AO2	0.345
8	CPEC + %1 AO3	0.231
9	CPEC + %3 AO3	0.274
10	CPEC + %5 AO3	0.322

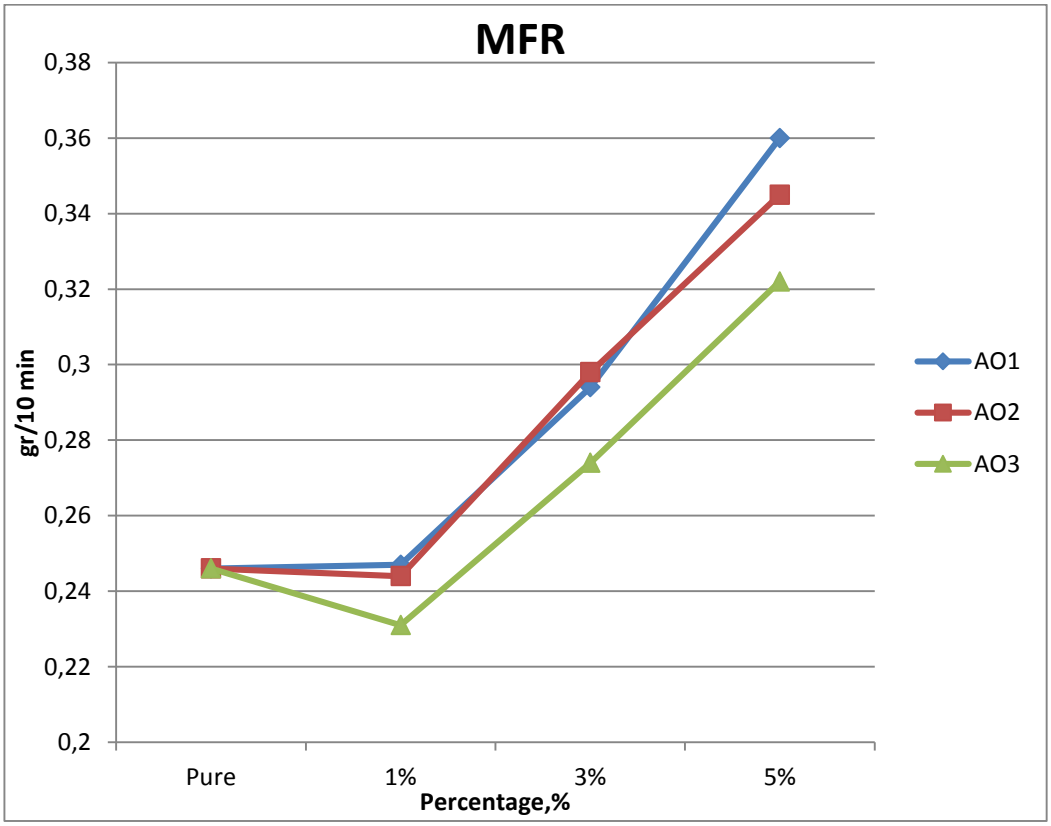


Figure 4.14 : Effect of antioxidants on the MFR of CPEC.

5. CONCLUSION

In this study, %1, %3 and %5 weight percentages of different types of antioxidants AO1, AO2, and AO3 were mixed in to CPEC. In addition a blend of 1.5% AO1 + 1.5% AO2 and a blend of 2.5% AO1 + 2.5% AO2 were added in to CPEC. The effects of antioxidants type and its usage percentage on crosslinking, mechanical and thermal properties were investigated.

Different usage ratios of antioxidants were mixed in to CPEC by using laboratory plasticorder, which was used as mixer. Samples were mixed for 12 minutes at 110 °C with 50 rpm.

Crosslinking characteristics (ML, MH) of the compounds were obtained by using RPA at 185 °C. The curing properties show that minimum torque (ML) values did not changed significantly and assumed that stable. On the other hand, the maximum torque (MH) values were decreased proportional to amount of antioxidant increase. MH values were decreased with increase of antioxidant contents. The lowest MH values were obtained on sample number 12 which has 2.5% AO1 + 2.5% AO2 where MH was 0.49. The difference between MH and ML (MH-ML) can be expressed as cure extend which gives information about degree of crosslinking of the compounds due to torque values are close to each other. The smallest cure extent value, which was 0.36, obtained from sample number 4. The similar result which was 0.37 obtained with sample number 12. It can be said that CPEC with 5% AO1 and CPEC with 2.5% AO1+ 2.5% AO2 has lowest crosslinking degree.

Some portions of samples were also used for plaque preparation. The plaques with 1 mm thickness were prepared by using hot press. Tensile strength, elongation at break and hot-set tests were performed on specimen taken from these plaques. The rest of samples were used for tests for crosslinking properties DSC and MFR.

Mechanical property analysis of the samples showed that the types and the percent of addition of antioxidants in CPEC had pronounced effect on the tensile properties of materials. Mechanical results showed that the maximum decrease in tensile strength observed on sample number 7 which was CPEC with 5% of AO2. Tensile strength

value was decreased by 31.42 %. AO1 and AO3 with 5% adding ratio caused significant reduction as well. Reductions of tensile strength were observe 28.50% and 27.49% when 5% of A01 and AO3 used respectively. The tensile strength value decreased ~14% when blend of 2.5% AO1+ 2.5% AO2 was added. However, obtained tensile strength value was almost 18 N/mm^2 which was quite satisfactory.

Another characteristic in mechanical properties was elongation at break. The smallest change was at sample number 6. The change was only 1.42% in elongation at break when 3% of AO2 was added in to CPEC. The highest decrease in elongation at break which was 22.78 %, observed when AO2 used with 5% adding ratio. The changes of elongation at break values were in the limit of ± 6% for all adding ratio of AO1. There was significant reduction when AO3 was used. Reductions were 17.77%, 17.79% and 9.43% when 1%, %3 and %5 of AO3 used respectively. On the other hand, elongation at break value was increased and obtained ~670% when blend of 2.5% AO1+ 2.5% AO2 was added into CPEC. This was the result for elongation at break test.

When curing and mechanical properties evaluated together, low cure extend value with high mechanical properties were desired in this study. If the results were evaluated in this scope, sample number 12 which CPEC has 2.5% AO1+ 2.5% AO2 was the best. Cure extend obtained 0.37 which was lowest crosslinking density. Tensile strength was ~18 N/mm^2 and elongation at break was 670%. These mechanical properties were quite satisfactory for recovered XLPE material.

Hot-set test performed on sample 1 mm material plaques obtained hot press at 200 °C. The aim of test to understand if material has been already crosslinked or not. During test, if material has already crosslinked, elongation under load should be below 175% at 200 °C. If this requirement is valid, then elongation without load should be below ± 15%. According to hot-set results CPEC, CPEC with 1% AO2 and CPEC with 1% AO3 passed the test. It means these samples crosslinked under hot press condition. The other samples failed in hot-set test. It means that addition of antioxidants, crosslinking did not occurred under hot press condition.

Thermal properties of CPEC and CPEC with antioxidants were analyzed. Addition of AO1 and AO2 increased enthalpy of fusion. The highest increase in ΔHm was observed when 1% of AO2 was added into CPEC. On the other hand, enthalpy of fusion was decreased when all ratio of AO3 were added into CPEC. The lowest value

of enthalpy was ~92 J/g with 1% of AO3. There were not significant changes in melting temperatures. Results of all samples were obtained between 107 °C to 109°C.

Melt flow rate (MFR) analysis were carried out for CPEC and CPEC with antioxidants samples. Increased antioxidant content of the sample resulted in increased MFR. Highest MFI values were obtained highest antioxidant contents. Increase at MFI values were 46.3%, 40.2% and 30. 9% when %5 of AO1, AO2 and AO3 were added respectively. Increase in MFR values can be considered that molecular weigth of CPEC decreased with addition of antioxidant.

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