INVESTIGATION OF DIFFERENT UV STABILIZER EFFECTS ON HDPE GRADES

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ABSTRACT

INVESTIGATION OF DIFFERENT UV STABILIZER EFFECTS ON HDPE GRADES

In this study, a performance Hindered Amin Light Stabilizer (HALS), used to prevent the structure of polymeric materials from UV and thermal degradation, was investigated using High Density Polyethylene (HDPE) injection grade. The primary goal of this study is to understand the effects of different HALS types, that consist of low molecular mass and high molecular mass, on mechanical and physical properties of HDPE using a design of experiment method. In addition, Minitab program was used to analyze the data, obtained with the experimental design, with ANOVA analyses to estimate the OIT and Loss Elongation% responses of the samples made with varying HALS amounts and types.

Briefly, Elongation Lost% which is the ratio of Elongation% Before Aging to Elongation % After Aging and OIT(Oxidative Induction Time) were studied in different recipes of HDPE Injection Molding Plaque specimens in order to measure the effect of HALS1 (Tin770), HALS2(Tin622) and HALS3(Chim944) on aging. One-year of aging was simulated using a standard aging chamber.

It was observed that synergetic effect of HALS1 with HALS3 was much more effective than thatof HALS2 with HALS3. Moreover, it was determined that the samples containing antioxidant which did not contain any HALS additive were completely degraded at the end of the same aging process. This study showed that OIT results of samples were affected directly by the amount of HALS3 which protected the polymer against long-term exposure to UV radiation and high temperature whereas neither HALS1 nor HALS2 showed the same protection.

ÖZET

YYPE TÜRLERİNDE FARKLI UV STABİLİZER KATKILARIN ETKİLERİNİN İNCELENMESİ

Bu çalışmada, polimerik malzemeleri, UV bozunma ve termal bozunmadan koruyan Hindered Amin Işık Stabilzanlarının (HALS), YYPE (Yüksek Yoğunluk Polietilen) enjeksiyonluk türündeki performansı incelenmiştir. Çalışmanın ana amacı, düşük ve yüksek molekül ağırlığına sahip HALS türlerinin, YYPE'nin fiziksel ve mekanik özelliklerine etkisidir. Ayrıca, Minitab programı yardımıyla, istatistiksel yöntemlerden faydananılarak, farklı HALS reçeteleriyle (bağımsız değişkenler), OIT(Oksijenle Indüklenme Süresi) ve Uzama Kaybı%'ni tahmin etmek için regresyon denklemleri üretilmiştir.

HALS1 (Tin770), HALS2(Tin622) and HALS3(Chim944)'ün, değişik reçetelerde hazırlanmış YYPE Enjeksiyonla kalıplanmış plaka numunelerine etkisi Yaşlandırma Sonrası Uzama%'nın Yaşlandırma Öncesi Uzama %'ya oranı olan Uzama Kaybı% ve OIT analizleriyle çalışılmıştır. Bir yıllık yaşlandırma simule edilmiştir.

HALS1'in HALS3 ile sinerjetik etkisinin, HALS2'nin HALS3 ile sinerjetik etkisinden çok daha güçlü olduğu görülmüştür. Ayrıca, herhangi bir HALS katkı maddesi içermeyen ancak antioksidan içeren numunelerin yaşlandırmanın sonunda tamamen bozulduğu tespit edilmiştir. Bu çalışma, HALS1 ve HALS2 katkılarından ziyade, polimeri uzun vadeli şiddetli koşullara (UV radyasyonu, yüksek sıcaklık) koruyan HALS3 miktarının, numunelerin OIT sonuçları üzerinde direk etkili olduğunu göstermiştir.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

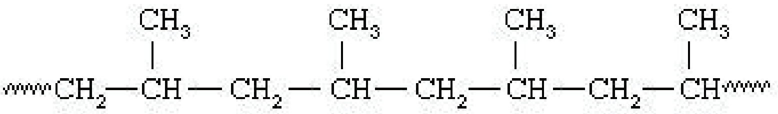
CHAPTER 1

INTRODUCTION

Plastics have been used in the manufacture of many domestic and industrial articles, such as kitchenware and pipes, for decades and offered many advantages as compared to the articles made with traditional materials, such as woods and glasses. Among industrial articles, pipes, used in plumping for water, gas, or sewage system, are the key in the development of modern cities with populations exceeding million people. Unfortunately, old pipes were made with lead or steel or copper metals; thus, giving rise to health problems and high maintance costs. Thus, plastics are preferred more than the traditional raw materials for piping like cast and ductile iron, steel and concrete due to substantial benefits. One of the reasons of why the demand on plastics is increasing, is longer service life with excellent durability, integrity of joints, resistance to corrosion and chemicals more than pipe made of other materials. Demand on plastic pipe has been forcasted to increase as 2.5% per year in accordance with 2007 plastic industry growth in the United States. Besides, low density polyethylene (LDPE) has been used in pipe applications for more than 40 years (www.4spe.org).

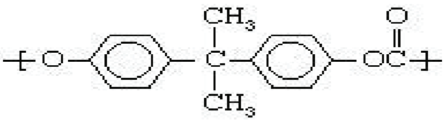
General plastic articles used in daily activities made with polymers could be molded or shaped usually with heating and pressurization by using industrial injection and blow molding machines. During processing of plastic products, some additives that ensure low density, low electrical conductivity, transparency, and toughness, are added into plastic raw materials in order to prevent them from environmental factors, such as day light (UV beams) and oxygen,. and improve their physical properties.

Chemical compositions of plastics consist of aliphatic (linear) carbon atoms in their backbone chains and also heterogeneous polymers. Polymers with aliphatic (linear) carbon atom structure generate High Density Polyethylene and also Linear Low Density Polyethylene or Polypropylene., are known as thermoplastics. Most of commercial products, such as beverage and trash containers, are produced from these. To illustrates, pendant methyl group (CH_3) attach to every carbon atom in order to compose the structure of polypropylene can be seen below :



$$\sim CH_2-\overset{\overset{CH_3}{|}}{CH}-CH_2-\overset{\overset{CH_3}{|}}{CH}-CH_2-\overset{\overset{CH_3}{|}}{CH}-CH_2-\overset{\overset{CH_3}{|}}{CH}\sim$$

Heterochain polymers can be investigated as other polymers in terms of chemical composition. For instance, oxygen, nitrogen, or sulfur in their backbone chains combine with carbon atoms during heterochain polymer compounds. As can be seen in below, polycarbonate includes molecules of two aromatic (benzene) rings:



In Table 1.1, the most important chain-chain and heterochain plastics are listed in accordance with chemical and physical properties. Density, transition glass temperature, crystal melting temperature, and degree of crystallinity define their usage area in industry.

The progress of global plastic production, measured in tonnes per year, can be seen annually in Figure 1.1 for the years from 1950 to 2015.

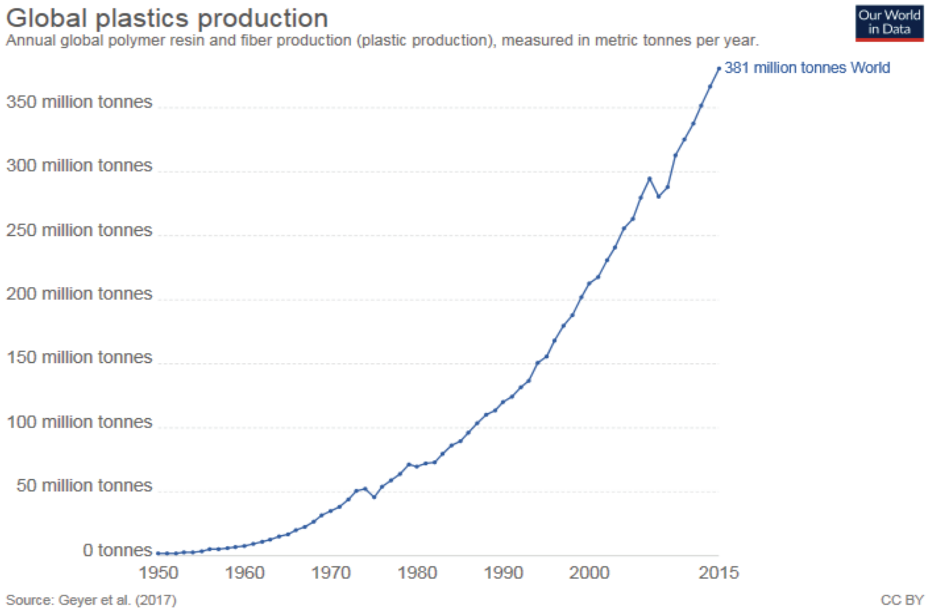
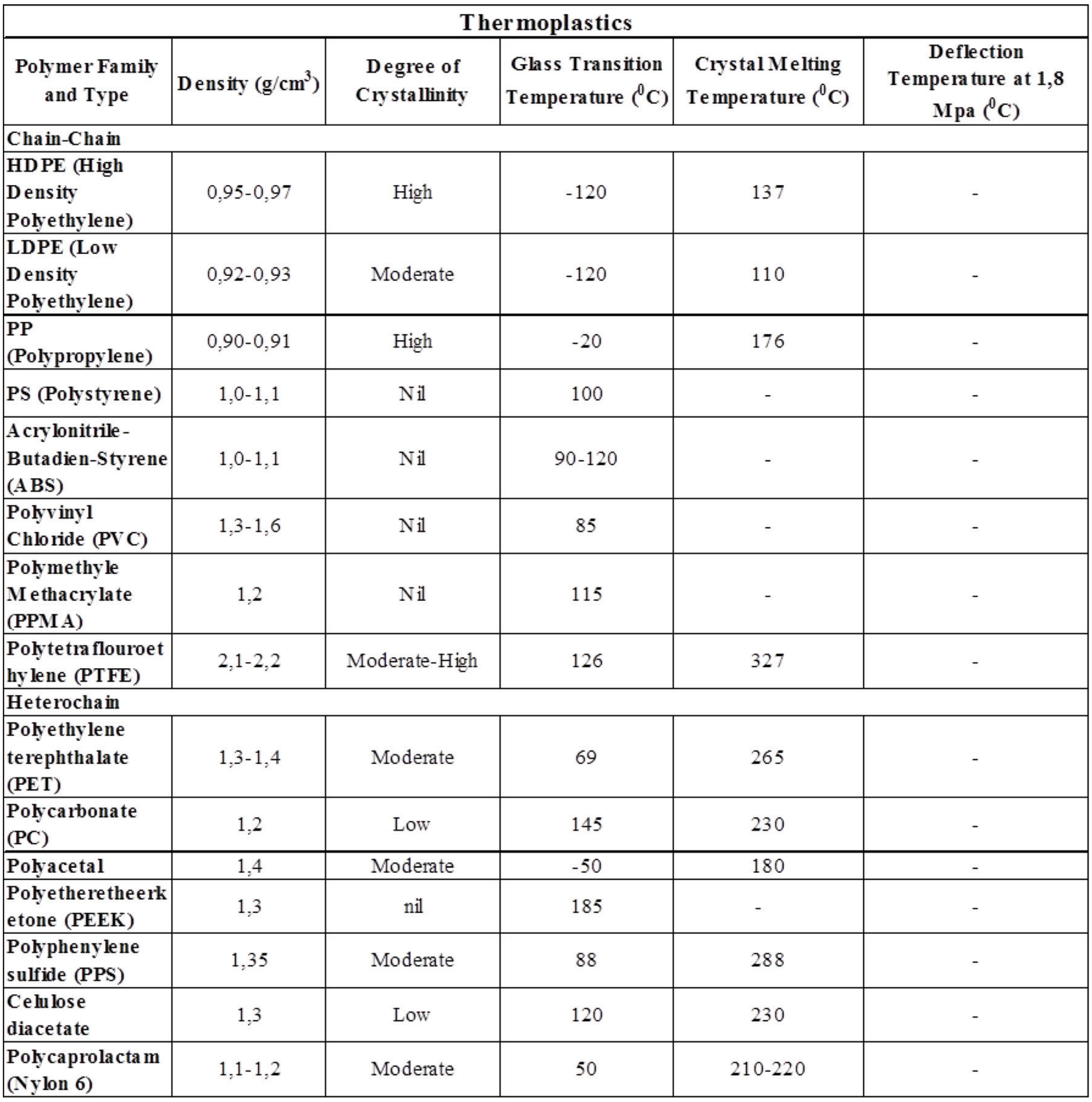


Figure 1.1 Annual Global Plastics Production
(Source: Ourworldindata, 2017)

Table 1.1 Chemical and Physical Properties of Significant Thermoplastics
(Source : Britannica)

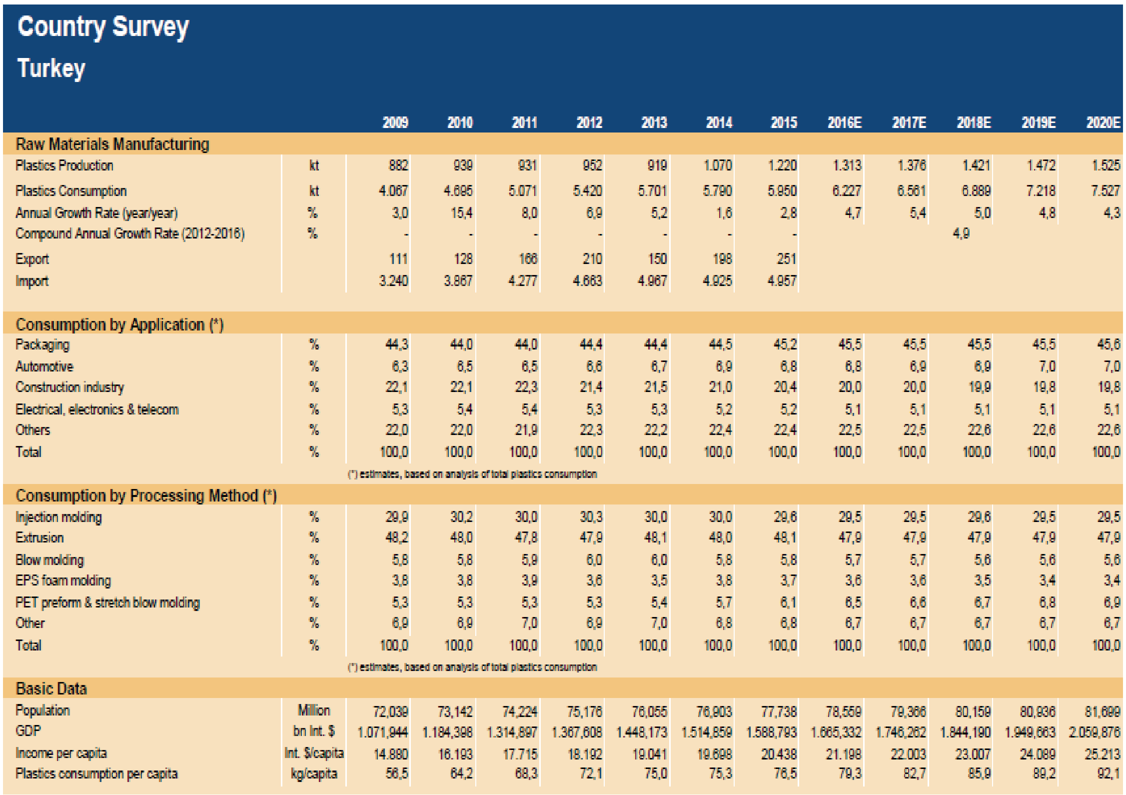


Thermoplastics					
Polymer Family and Type	**Density (g/cm^3)**	**Degree of Crystallinity**	**Glass Transition Temperature (^{0}C)**	**Crystal Melting Temperature (^{0}C)**	**Deflection Temperature at 1,8 Mpa (^{0}C)**
Chain-Chain					
HDPE (High Density Polyethylene)	0,95-0,97	High	-120	137	-
LDPE (Low Density Polyethylene)	0,92-0,93	Moderate	-120	110	-
PP (Polypropylene)	0,90-0,91	High	-20	176	-
PS (Polystyrene)	1,0-1,1	Nil	100	-	-
Acrylonitrile-Butadien-Styrene (ABS)	1,0-1,1	Nil	90-120	-	-
Polyvinyl Chloride (PVC)	1,3-1,6	Nil	85	-	-
Polymethyle Methacrylate (PPMA)	1,2	Nil	115	-	-
Polytetraflouroethylene (PTFE)	2,1-2,2	Moderate-High	126	327	-
Heterochain					
Polyethylene terephthalate (PET)	1,3-1,4	Moderate	69	265	-
Polycarbonate (PC)	1,2	Low	145	230	-
Polyacetal	1,4	Moderate	-50	180	-
Polyetheretheerketone (PEEK)	1,3	nil	185	-	-
Polyphenylene sulfide (PPS)	1,35	Moderate	88	288	-
Celulose diacetate	1,3	Low	120	230	-
Polycaprolactam (Nylon 6)	1,1-1,2	Moderate	50	210-220	-

In 1950, 2 million tonnes per year of plastics were produced worldwide but the annual production increased nearly 200 fold; hence, reaching 381 million tonnes in 2015. Similarly, 1.4 times increase in the production of plastics was observed in Turkey, as seen in Table 1.2.

Polyolefins, because of their widespread availability and low price and the availability of various matured processing technologies, are especially preferred in the whole synthetic polymers. The well known polyolefins are polyethylene and polypropylene and polybut-1-ene, polyisobutylene and poly-(4-methylpent-1-ene).

Table 1.2 Plastics Resin Production and Consumption in Turkey
(Source : Pagder, 2016)



Country Survey

Turkey

		2009	2010	2011	2012	2013	2014	2015	2016E	2017E	2018E	2019E	2020E
Raw Materials Manufacturing													
Plastics Production	kt	882	939	931	952	919	1.070	1.220	1.313	1.376	1.421	1.472	1.525
Plastics Consumption	kt	4.067	4.695	5.071	5.420	5.701	5.790	5.950	6.227	6.561	6.889	7.218	7.527
Annual Growth Rate (year/year)	%	3,0	15,4	8,0	6,9	5,2	1,6	2,8	4,7	5,4	5,0	4,8	4,3
Compound Annual Growth Rate (2012-2016)	%	-	-	-	-	-	-	-			4,9		
Export		111	128	166	210	150	198	251					
Import		3.240	3.867	4.277	4.663	4.967	4.925	4.957					
Consumption by Application (*)													
Packaging	%	44,3	44,0	44,0	44,4	44,4	44,5	45,2	45,5	45,5	45,5	45,5	45,6
Automotive	%	6,3	6,5	6,5	6,6	6,7	6,9	6,8	6,8	6,9	6,9	7,0	7,0
Construction industry	%	22,1	22,1	22,3	21,4	21,5	21,0	20,4	20,0	20,0	19,9	19,8	19,8
Electrical, electronics & telecom	%	5,3	5,4	5,4	5,3	5,3	5,2	5,2	5,1	5,1	5,1	5,1	5,1
Others	%	22,0	22,0	21,9	22,3	22,2	22,4	22,4	22,5	22,5	22,6	22,6	22,6
Total	%	100,0	100,0	100,0	100,0	100,0	100,0	100,0	100,0	100,0	100,0	100,0	100,0
		(*) estimates, based on analysis of total plastics consumption											
Consumption by Processing Method (*)													
Injection molding	%	29,9	30,2	30,0	30,3	30,0	30,0	29,6	29,5	29,5	29,6	29,5	29,5
Extrusion	%	48,2	48,0	47,8	47,9	48,1	48,0	48,1	47,9	47,9	47,9	47,9	47,9
Blow molding	%	5,8	5,8	5,9	6,0	6,0	5,8	5,8	5,7	5,7	5,6	5,6	5,6
EPS foam molding	%	3,8	3,8	3,9	3,6	3,5	3,8	3,7	3,6	3,6	3,5	3,4	3,4
PET preform & stretch blow molding	%	5,3	5,3	5,3	5,3	5,4	5,7	6,1	6,5	6,6	6,7	6,8	6,9
Other	%	6,9	6,9	7,0	6,9	7,0	6,8	6,8	6,7	6,7	6,7	6,7	6,7
Total	%	100,0	100,0	100,0	100,0	100,0	100,0	100,0	100,0	100,0	100,0	100,0	100,0
		(*) estimates, based on analysis of total plastics consumption											
Basic Data													
Population	Million	72,039	73,142	74,224	75,176	76,055	76,903	77,738	78,559	79,366	80,159	80,936	81,699
GDP	bn Int. $	1.071,944	1.184,398	1.314,897	1.367,608	1.448,173	1.514,859	1.588,793	1.665,332	1.746,262	1.844,190	1.949,663	2.059,876
Income per capita	Int. $/capita	14.880	16.193	17.715	18.192	19.041	19.698	20.438	21.198	22.003	23.007	24.089	25.213
Plastics consumption per capita	kg/capita	56,5	64,2	68,3	72,1	75,0	75,3	76,5	79,3	82,7	85,9	89,2	92,1

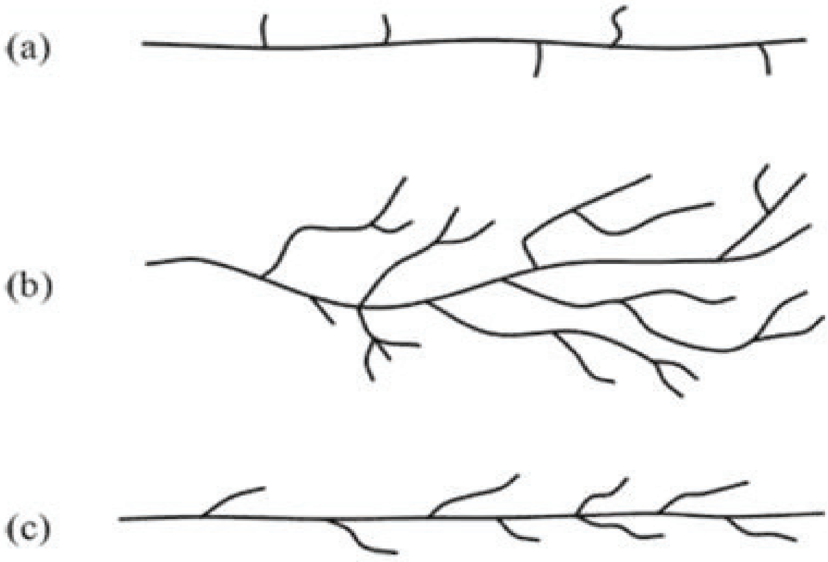


Figure 1.2 Structure of Different Types of Polyethylene a) HDPE   b)LDPE   c)LLDPE

Polyethylene (PE) are Produced as Linear low-density polyethylene (LLDPE), branched low-density polyethylene (LDPE) and Linear high-density polyethylene and their structures are shown in Figure 1.2 (Kutz, 2002).

Polyethylene among other polymer types, has the simplest structure. Every molecule of polyethylene is formed with long chain of carbon atoms, with two hydrogen atoms combined to each carbon. General polymerization reaction can represented as seen in Fig. 1.3.

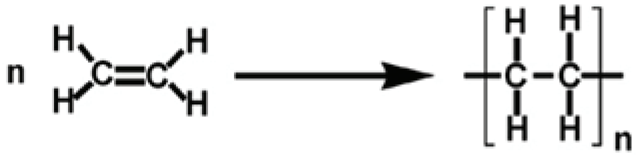


Figure 1.3 General Polymerization Reaction of Ethylene

PE is a type of thermoplastic that has melting point ranging from 80 to 130 ^{o}C and it has less density than water. Most common properties of PE are listed as: Excellent chemical resistance, Near-zero moisture absorption, Excellent electrical insulating and also Easy processing. Thus, commercially PE is preferred synthetic polymers.

PE is available as opaque in the bulk form with respect to crystal structure whereas it can be transparent in thin film form (Brydson, 1999). The molecular weight and the degree of polymer branching are the most factor affecting mechanical properties of PE but the rate of testing and the temperature of test could affect the mechanical properties, too.

Table 1.3. exhibits the effects of molecular weight and branching (density) on some polymer properties, such as tensile strength, elongation at break, crystalline melting point.

The chemical structure of polyolefins is relatively vulnerable to the oxidation. Oxidation rate is increased by the traces of highly efficient catalysts, such as chromium, Ziegler-Natta, metallocene remaining in ppm levels in the polymer matrix after polymerization (Schiers et. Al.)(Gächter et. Al.). Moreover, most of polyolefins leave the reactor in the form of a coarse fluff, with a relatively high specific surface allowing a easy access to atmospheric gases, especially oxygen.

Table 1.3 Molecular Weight and Density (branching) Effect on Some Mechanical and Thermal Properties of PE (Source: Brydson, J., 1999)

Property	Test	Density = 0.92 g/cm3 high pressure polymers					Density = 0.94 g/cm3 high pressure polymers	Density = 0.95 g/cm3 Ziegler-type polymers			Density = 0.96 g/cm3 Phillips-type polymers	Density = 0.98 g/cm3 polymethylene
Melt flow index (g/10 min)	BS2782	0.3	2	7	20	70	0.7	0.02	0.2	1.5	~	~
Tensile strength (MPa)	BS903	15.3	12.5	10.2	8.9	~	20.7	22.0	23.0	23.0	27.5	34.5
Elongation at break (%)	BS903	620	600	500	300	150	~	>800	380	20	500	500
Izod impact strength (J)	BS2782	13.5	13.5	13.5	13.5	13.5	~	4.3	2.7	2.0	6.8	~
Vicat softening point (℃)	BS2782	98	90	85	81	77	116	124	122	121	~	~
Softening temperature (℃)	BS1493	~	~	~	~	~	~	110	19.4	15.4	122	~
Crystalline melting point (℃)	~	108	108	108	108	108	125	130	130	130	133	136
Number average molecular weight	~	48000	32000	28000	24000	20000	~	~	~	~	~	~
CH_3 groups per 1000 C atoms	~	20	23	28	31	33	~	5-7	5-7	5-7	<1.5	unbranch.

Artificially accelerated weathering and outdoor natural weathering are applied to estimate the endurance of polyolefins extensively. Under standard conditions, exposition of UV radiation was performed on different types of plastics in the BASF performed experiments. As a result of these, plastics appearance and mechanical properties was found to change by UV radiation exposure and also required time to change the observing appearance and mechanical properties of plastics was varied from a few hours to a few thousand hours with respect to the type of polymer.

In Figure 1.4, increasing UV radiaiton time under the constant UV radiation, was reported to inversely influence the mechanical characteristics of different types of polymers. Performance characteristics of plastics reduced directly proportional to decreasing amount of protection againist photoinduced aging additives.

According to Figure 1.4, Film (200 µm thick) samples; 1, 3 and 5 shows the passing time of occurring embrittlement under the constant UV radiation and also, the compression moulded sheet (1 mm thick) samples; 2, 4 and 6 shows the passing time of observing the residual strain at break drops to ≤50% of the initial value. Finally, polyamide injection moulding (2 mm thick) sample (7) shows the passing time until observing cracks on the sample surface.

The main limitation of synthetic polymers active life depends on generation of oxidative degradation reactions. Exposure time of UV radiation accelerates mechanical degradation. As the polymer technology develops, oxidative degradation mechanisms has been well known using artificial aging devices.

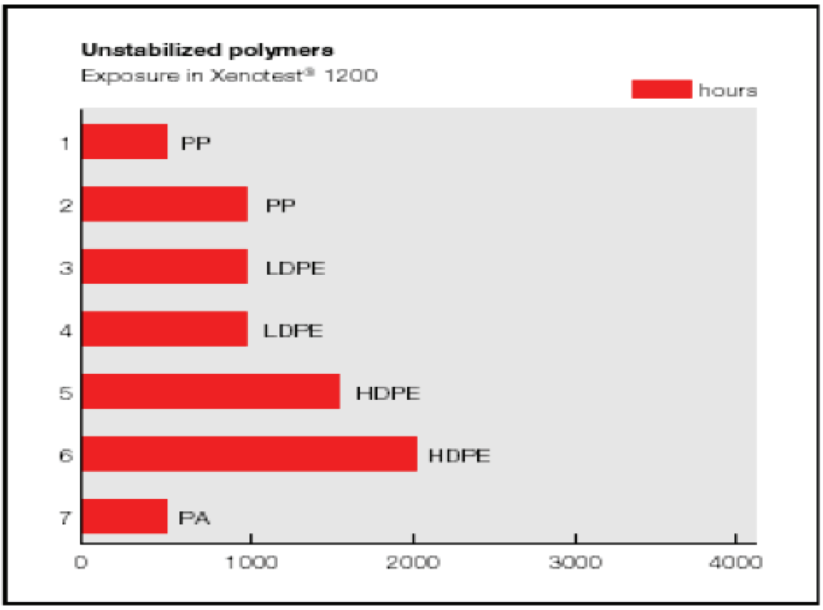


Figure 1.4 UV Radiation Exposure Time Effects on Unstabilized Polymers

It is well known that natural light has 300 nm to 1000 nm wavelength spectrum; however, 300-400 nm which has the most adverse effects on polymers reaches the surface of earth. Degradation reactions and breaking chemical bonds, happened by exposure to natural UV light excessively, occur in polymers. For example, the energy for a 300 nm wavelength is 400 kJ/mol, which is enough to break carbon-carbon (C-C) bonds (Al-Madfa *et al.,* 1998). After breaking carbon-carbon bonds, the production of photo-products occurs and it is known that the quantum yield of hydroperoxide decompositon is high by under UV radiation exposure. In fact, photo-products, such as alcohol, carboxylic acid, ester, ketone, are generated by hydroperoxide decomposition as seen in Figure 1.5.

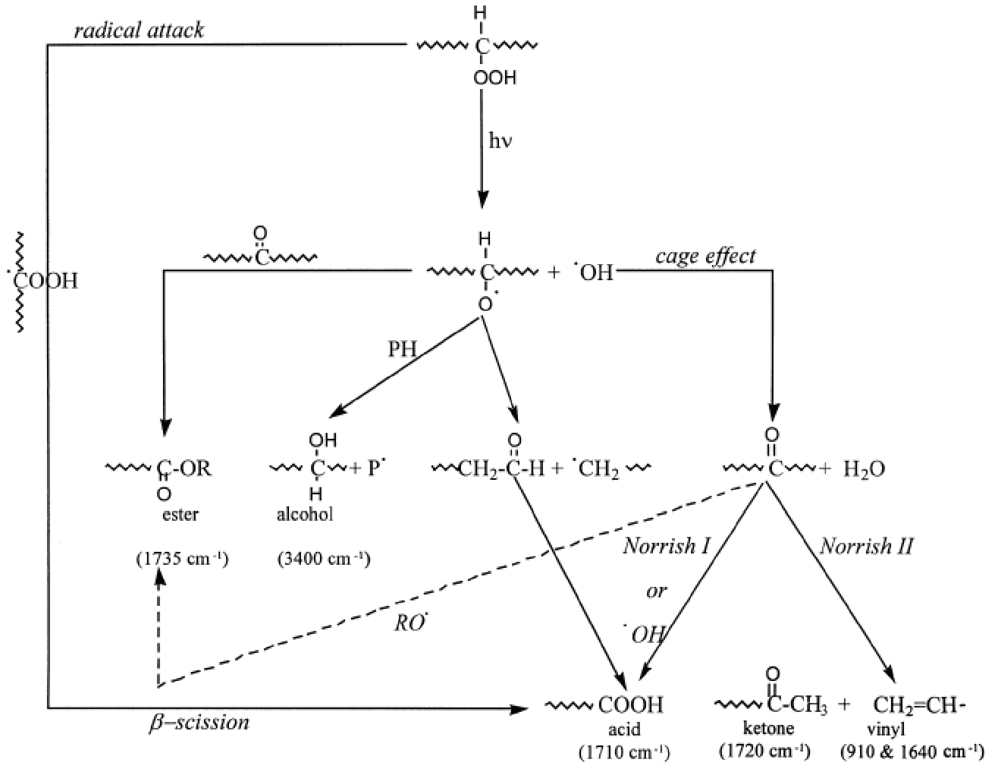


Figure 1.5 Photo-Products of LLDPE Decompositon by Radiation
(Source : Tidjani, 2000)

All these adverse effects requires that most of polyolefinic grade polymers must be modified with efficient stabilizer systems to eliminate all the effects mentioned above. In most of the technologies, stabilizers and other additives are dry blended with fluffy polymer and then converted into pellets. The presence of stabilizer system helps to prevent the loss of the original physico-chemical properties during processing and subsequent applications.

Stabilizers, applied in synthetic polymers, have a variety of chemical structures depending on the mechanism of action and site, where they enter and compete with the deteriorative processes. The following structure types are used (Tidjani, 2000) (Hawkins, 1972)

a) Hindered phenolics (primary antioxidants)

b) Organic phosphites (secondary antioxidants)

c) Thiostabilizers (secondary antioxidants)

d) UV absorbers (light stabilizers)

e) HALS (Hindered Amine Light Stabilizers)

Stabilizers may also be considered as processing and long-term acting stabilizers, depending on the type of application. The role of processing stabilizers is the protection of polymer during melting processing, such as extrusion, which is characterized by high temperatures (200 - 320 °C), increased mechanical stress and short exposure times. On the other hand, long-term acting stabilizers perform in the solid matrix under the conditions of lower temperatures (up to 100 °C) and long-term periods of exposure (months to years)

Oxidative degradation can be slowdowned by adding common antioxidants to polyethylene grades. Chemical and physical properties of polyethylene depend on efficacy of the antioxidants. Hence, the major characteristic of an antioxidant must have effectiveness of chemical behavior to slowdown the oxidative degradation of the polymers. In addition to this, adequate concentration of added antioxidant must provide strong physical properties, such as sustained resistance againist to environmental effects.

Some of the most effective parameters are the rate of volatilization of the antioxidant from the polymer surface, the equilibrium solubility of the antioxidant in the polymer and the rate of diffusion of the antioxidant in order to increase the effectiveness of antioxidant remaining in the polymer bulk.

UV absorbers and Hindered Amine Light Stabilizers are added to polyethylene to prevent them from UV light induced chemical bonds breaking in polymers and also from producing degradation reactions. Some of the PE applied in outdoor weathering is HDPE and LDPE. Sufficient additives must be added into polymer bulk,that will be used in polyethylene articles, to extend the period of durability of polyethylene against UV radiation and heat. Environmental conditions and stabilizers used during processing influenced the period of stabilization of polyethylene types.

Low molecular weight HALS was only available during the early introduction of the polymers in the production of the plastics. Although low molecular weight HALS had several advantages, many disadvantages, such as moderate resistance to extraction and high migration rate, were reported. To avoid these disadvantages of low molecular weight HALS, polymeric HALS were developed. Sustained thermal stability of polyolefins was increased with developing high molecular weight HALS in recent years. The effect of HALS on polymer oxidation can be explained as primary initiation reaction on photo-oxidation of polyethylene as seen in Figure 1.6.

$$
\begin{aligned}
O + PH &\longrightarrow {}^{\bullet}OH + P^{\bullet} \\
{}^{\bullet}OH + PH &\longrightarrow H_2O + P^{\bullet} \\
P^{\bullet} + O_2 &\longrightarrow POO^{\bullet} \\
POO^{\bullet} + PH &\longrightarrow POOH + P^{\bullet} \\
POO^{\bullet} + POO^{\bullet} &\longrightarrow \text{products}
\end{aligned}
$$

Figure 1.6 Initiation of Polymer Oxidation

Figure 1.7 shows the probable influence of some HALS on primary initiation by oxygen. The possibility of the reaction 1 is so weak that the major stabilizing process reaction is called as attachment formation. The HALS can catch free radicals as soon as they occurred. Thus, a complex is formed by a HALS molecule and a peroxy radical. The reaction of this complex with a second peroxy radical leads to the termination between the two peroxy radicals and also the liberation of the HALS molecule. This is seen as one of the major stabilization reactions involving peroxy radicals (Gugumus and Lelli, 2001).

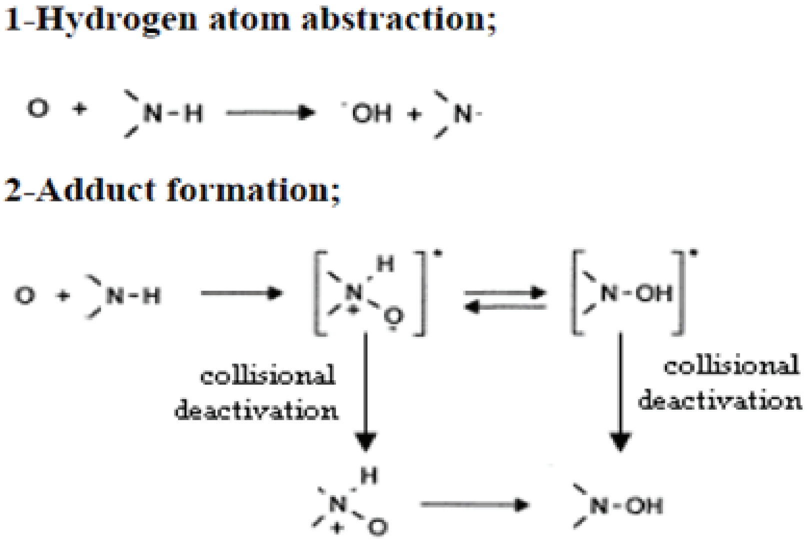


Figure 1.7 Some HALS Influence on Primary Oxidative Initiation

A sufficent amount of UV stabilizer in HDPE must be used to provide both photo-degradation resistance and thermal degradation resistance and also to extend HDPE stabilization time.

At the beginning of UV absorbers usage, two types of absorbers, such as benzotriazole and benzophenone, were generally used to prolong the HDPE lifetime. A development for UV stabilization of HDPE was found when 0.2 -0.3% concentrations was used in thick sections. Following the improvement of Ni-quenchers, UV absorbers was also effective on thin section stabilization. As a result of studies of CIBA-GEIGY Ltd. and Sankyo Co. Ltd., UV stabilization of HDPE was developed with Hindered Amine Light Stabilizers (HALS).

In this study, Tinuvin 770 and Tinuvin 622, known as HALS, were used based on molecular weight differences to compare mechanical and physical effects on HDPE injection grade samples. One of the low molecular weight Hindered Amin Light Stabilizer, Tinuvin 770, is generally used for the prevention of the UV degredation for thick sections and films. The efficiency of HALS, such as Tinuvin 770, does not depend on sample thickness unlike UV absorbers. Hence, many studies stated that Tinuvin 770 leads to an excellent light stability for films and tapes. In spite of its efficiency, it has some shortcomings like the relative volatility and limited resistance to extraction and especially migration caused due to its low molecular weight structure.

Another light stabilizer, e.g. Tinuvin 622, has oligomeric structure and high molecular weight that cause minimum migration and low volatility. In addition to this, Tinuvin 622 shows antioxidant strong effect and provides considerably sustained heat stability for all polyolefins. As seen in Figure 1.8, the concentrations of the additives are stated in % w/w commercially.

Some of the most important parameters in the polymer product development and its production process are the test of their physical and mechanical properties. These tests indicate their compatibility with respect to related specific industry application.

These tests basicly consist of elongation at break, elasticity, strength at break, strength at yield, elongation at yield, and oxygen induction test. Unfortunately, under natural conditons, the service life of plastics cannot accurately be estimated by using these laboratory tests. Spending many times and including several environmental parameters, e.g. atmospheric pollutants, temperature, humidity, sunlight, are applied in order to achieve accurate results for natural weathering performance on plastics (Tidjani, 2000).

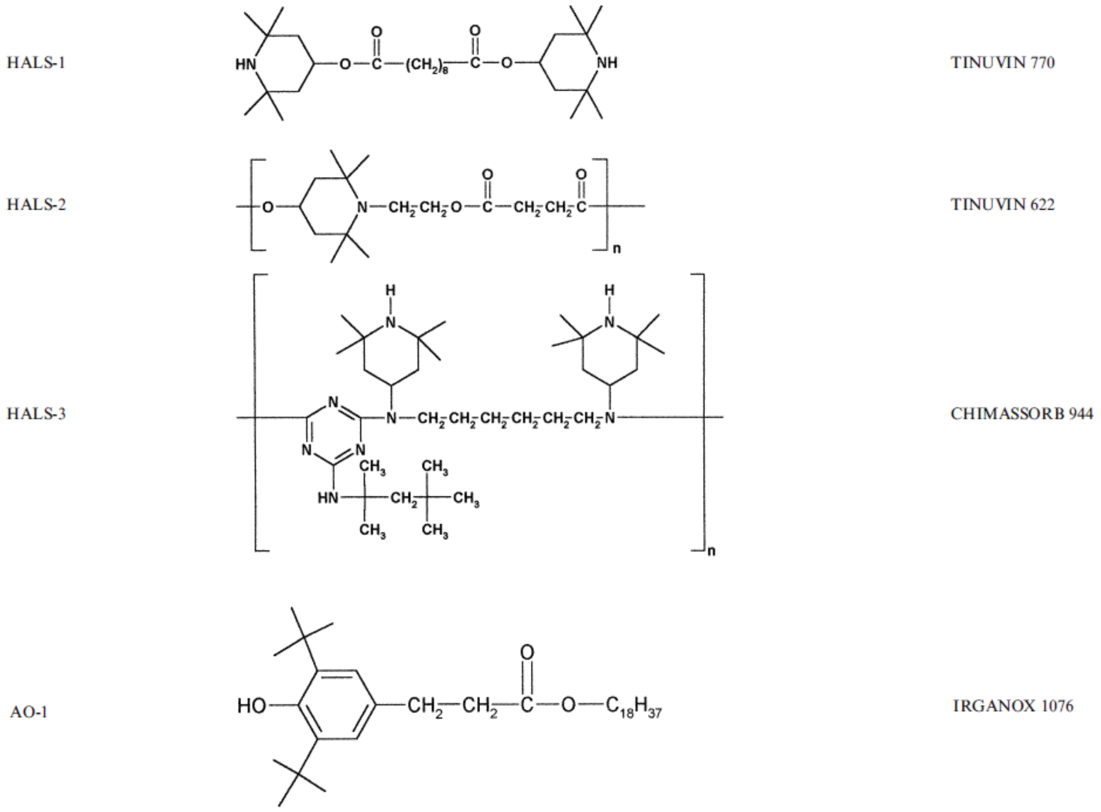


Figure 1.8 Commercial Light Stabilizers and Antioxidants
(Source : BASF-Product Technical Data Sheets)

The main objective of this study is to investigate how the usage of different HALS types with varying ratios in HDPE production affects its mechanical properties. For this purpose, three different types of HALS stabilizers, HALS1 (commercial name: Tinuvin 770), HALS2(commercial name: Tinuvin 622) and HALS3(commercial name: Chimmasorb 944) will be used to investigate their effects on Elongation Lost (%) of the HDPE before and after aging under UV radiation and also, on Oxidative Induction Time (OIT) of HDPE.

This thesis consists of five chapters. In the first chapter, general information about plastics, their advantages and its consumption in the world are given. Besides, types of polyolefins, general physical properties of polyethylene, weathering and its effects on polyethylene and the use of stabilizers to prevent from weathering are mentioned in this chapter. In the second chapter, the studies on the usage of HALS in the polymers for weathering purposes in the literature are discussed.

In the third chapter, polymers and HALS used in this thesis and also the mechanical testing procedures together with an experimental design are given. In chapter four, the results are given and discussed. Finally, the conclusions are listed in chapterfive.

CHAPTER 2

LITERATURE SURVEY

2.1 UV Stabilization of HDPE with HALS

Some UV stability experiments with various stabilizer were carried out and examined to see deceleration of Carbonyl generation on compression molded 0.1 HDPE films under Xenotest 1200 UV radiation exposure as seen in Figure 2.1.

Twice UV stability was observed when UVA-l, the benzophenone type UV absorber and Ni-l, the Ni-quencher, were added as 0.2% together into the HDPE film sample with small amount of a phenolic antioxidant in order to control.

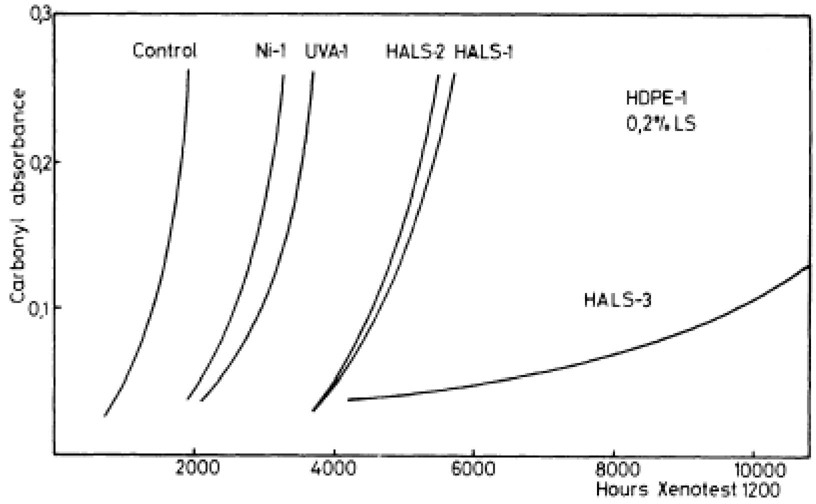


Figure 2.1 Carbonyl Absorbance vs. UV Radiation Time (Hours) for 0.1 mm HDPE (Ziegler) Films (Source: Gugumus and Lelli, 2001)

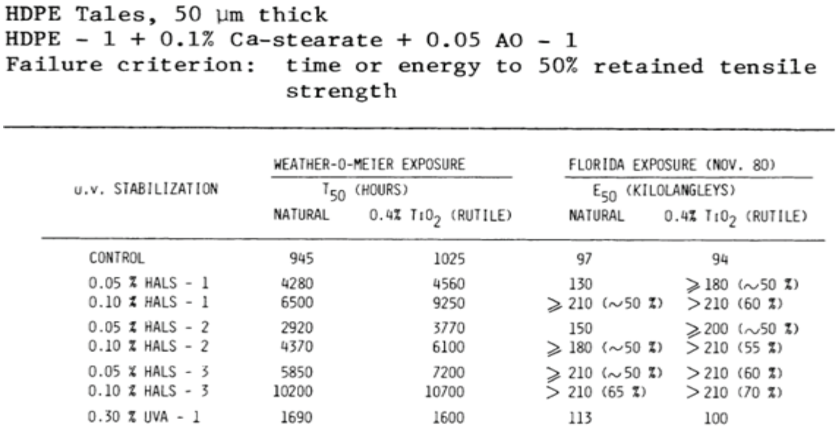
In accordance with Figure 2.1., HALS1 that is low molecular weight HALS type gave more progress, such as a factor of about 3 in this test. Despite its performance with polypropylene samples, HALS1 exhibits some deficiencies in exclusive cases where limited resistence to extraction, migration rate and relative volatility due to its low molecular weight issues such as in fine fibers. To pass over such problems, HALS2 and HALS3, that are type of polymeric HALS, can be used instead of HALS1.

It was reported that HALS1, low molecular weight HALS, showed the same performance with HALS2 as seen Figure 2.3. HALS3, the other polymeric HALS, showed twice effective performance than HALS1 and HALS2 influences due to its molecular weight difference startlingly.

The amount of additives related almost directly proportional to controlling of the development. Consequently, HALS1 effect on polypropylene was identical with HALS3 effects on HDPE in terms of UV stability improvement.

In Figure 2.2, even for 0.05 mm thick HDPE stretched tapes results indicate approximately the same values with carbonyl improvement in 0.1 mm HDPE films results. Also, tape samples including HALS showed outstanding effectiveness over the UV absorber for much lower concentrations of HALS particularly.

The superiority of 50% HALS1 over the HALS2 with polymeric structure was pronounced in unpigmented tapes from results obtained on Weather-a-Meter exposure. However, both HALS2 and HALS1 HDPE samples stated twice inferior effect comparing with HDPE films including HALS3. Also, the same effect was observed by Weather-O-Meter exposure of included 0.4% TiO_2 (rutile crystalline phase) white pigmented tapes. UV stability of HDPE with pigment added and no pigment added tapes that were consist of 0.5% the polymeric HALS-3 improved with increasing HALS3 concentration. Also another considerable improvement on HALS3 in HDPE tapes was understood when comparing 3 times big amount of UVA1 in HDPE tapes.



HDPE Tales, 50 µm thick
HDPE - 1 + 0.1% Ca-stearate + 0.05 AO - 1
Failure criterion: time or energy to 50% retained tensile strength

u.v. STABILIZATION	WEATHER-O-METER EXPOSURE T_{50} (HOURS) NATURAL	WEATHER-O-METER EXPOSURE T_{50} (HOURS) 0.4% TiO_2 (RUTILE)	FLORIDA EXPOSURE (NOV. 80) E_{50} (KILOLANGLEYS) NATURAL	FLORIDA EXPOSURE (NOV. 80) E_{50} (KILOLANGLEYS) 0.4% TiO_2 (RUTILE)
CONTROL	945	1025	97	94
0.05 % HALS - 1	4280	4560	130	⩾ 180 (~50 %)
0.10 % HALS - 1	6500	9250	⩾ 210 (~50 %)	> 210 (60 %)
0.05 % HALS - 2	2920	3770	150	⩾ 200 (~50 %)
0.10 % HALS - 2	4370	6100	⩾ 180 (~50 %)	> 210 (55 %)
0.05 % HALS - 3	5850	7200	⩾ 210 (~50 %)	> 210 (60 %)
0.10 % HALS - 3	10200	10700	> 210 (65 %)	> 210 (70 %)
0.30 % UVA - 1	1690	1600	113	100

Figure 2.2 UV Stabilization of HDPE (Ziegler) Thin Section

In another the study of Gugumus and Lelli (2001), the effectiveness of HALS and HALS systems was found as so high in the conventional polyolefin sorts that were used with metallocene polymers (m-PE). They achieved a synergism of HALS-6 with the coalescence of HALS-2 and HALS-3, polymeric HALS. It can be seen that the synergetic effect of HALS-6 with HALS-1 and HALS-2 in m-PE in Figure 2.2. For this experiment, HALS-6 involved 1:1 weight ratio combination of HALS-2 and also HALS-2 (Tinuvin 622) and HALS-3 (Chimmasorb 944) were procured from CIBA.

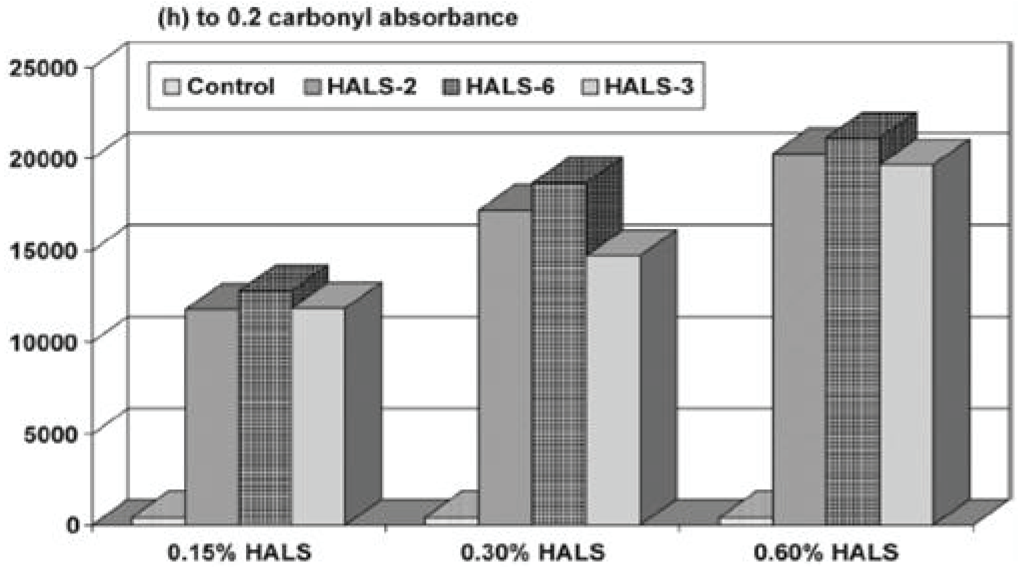


Figure 2.3 The Effect of Polymeric HALS amount in m-PE films by using weatherometer Ci 65 exposure (Source : Gugumus and Lelli, 2001)

2.2 Influence of Aging Degradation on Mechanical Properties of PE

Previous studies indicated that UV radiation exposure caused to change both the chemical and the mechanical proterties of the polymers. It was observed that the elongation at break showed a dual behavior. The optimum elongation at break consequence of polymer was observed at approximately 1715 cm^{-1} absorbance of 0.075 during UV exposure accelerates continuously. After that, the elongation at break of the same polymer gave the lowest value. However, this degradation of elongation occurred almost in the beginning of the experiment (Tidjani, 2000).

The mechanical properties of polymers were influenced adversely by the photo-oxidation. Gijsman and Sampers (1997) determined that the characterization of chemical structure modification of PE by the UV radiation degradation was directly depenedent on increasing oxygen concentration, the formation of CO and CO_2, of test environment as seen inthe FTIR spectra. In addition, they stated that reduction of elongation at break was affected by both oxygen raising and also oxygen pressure uptake. Consequences of their study, in the daylight UV exposure test with a few amount of oxygen, defined that the elongation at break decreased with increasing oxygen pressure (Gijman and Sampers, 1997).

Another point of view for UV degradation effect on PE was investigated on different UV sources by Liu and Horrocks (2002). Consequences of the pure LLDPE film UV degradation tests showed that elongation at break depended on both UV degradation exposure time and also various UV types; for instance, xenon<UVA<UVB<UVB(C). The UVB(C) light radiation exposure showed more effective UV degradation on LLPE films. It may be caused by a final reaction that occurs in a dark environment with the relative humidity during condensation cycle that increases the influence of following UVB degredation. In addition to moisture effect, when comparing wavelength radiation damage on unfilled LLDPE films, the shorter wavelength UV radiation, UVB (280 – 315 nm), inflict more damage than other wavelength radiation, UVA (315 – 400 nm), in terms of the same exposure time (Liu and Horrocks, 2002).

In another study, F. Carrasco et al. (2000) investigated artificial aging of HDPE exposed to UV irradiation. During injection process, HDPE test samples were generated as dog bone form, also called as specimen, with respect to ASTM D-638 standard conveniently. HDPE specimens artificial aging was performed in an accelerated aging chamber. In the presence of oxygen and controlled relative humidity with temperature, HDPE samples were exposed to UV irradiation. Visible chemical and structural changing occurred with the aging exposure and mechanical properties also changed. On the other hand, degree of crystallinity sowed minimal random variations.

Finally, it was seen that increase of Young's Modulus with the irradiation time was observed. This result showed that the hardness of HDPE increased with UV aging substantially. On contrary, it was reported that depending on the irradiation time, the elongation at break decreased dramatically. This decrease was noticed easily at the end of 60 days.

Even though a dramatic decrease in the tensile strength was seen between 60 days and 120 days, a slow increase was also observed until the end of 60th day. Although the chemical changes were more effective during irradiation time over 60 days, the results confirmed that molecular and structural changes was influenced by the part of irradiation.

Consequently, degredation mechanisms can be explained as ;

- Homolytic and heterolytic decomposition leads to chain breaking.
- Radicalary addition brang about cross-linking and branching
- Photo-oxidation or self oxidation leads to these all changes.

A conclusion coud be drawn in such a way that the hardness of samples increases with irradiation time in regarding mechanical properties. While Young's Modulus decreases, all of other physical propertiesincrease. As a result, UV radiation, led to significant chemical changes on PE like loss of elasticity and capacity of deformation, appeared in the carbonyl groups existed in the polymeric structure.

2.3 Influence of Degradation on Melt Flow Rate of PE

In PE and polypropylene (PP) significant degradation occurs in the presence of oxygen when these materials are exposed to heat or UV radiation (Moore and Kline, 1984). The susceptible sites are the tertiary hydrogens that are on the branches of PE molecule or adjacent to the methyl groups on PP.

Şenol et al. (2003) investigated the degradation of PP packaging bags kept in transparent (without color additives) and white (with TiO_2 additives) LDPE bags and also the degree of influence of natural degradation on various properties of PP was investigated. The PP chain ceasing occurs due to the sensitivity of PP to heat and UV beams, and thus causes decreasing of its average molecular weight. In order to observe this change they measured the melt flow rate (MFR) of PP pellets periodically. They found that the MFR which is also defined as melt flow index (MFI) of PP pellets from transparent bags was rapidly increasing, while that of the pellets in the white bags was quite constant under the same conditions. After 84 days, increment of MFR of PP in the transparent bag was by 72 % while the ones in white bag was by 12 %.

Along with extrusions, HDPE/PP mixture that collected from environment waste plastics was investigated in order to estimate degree of degradation and stabilization by using MFI results (Santos et al., 2002). Consequences of few using additives e.g. under 0.1 wt%, showed inadequate results for stabilizing of HDPE/PP blend. If MFI results of first recycle polymeric process was compared to second recycle results of samples included 0.1, 0.2 and 0.4 wt% of antioxidant, it was noticed that a slight decrease, a constant value and a little increasing respectively. It noticed that at the third cycle, included 0.4 wt% antioxidant sample showed increment disposition for MFI value. Also this increment was changed with both existence of antioxidant in the HDPE samples and magnitude of oxygen concentration in the environment.

2.4 The Effect of Molecular Mass on HALS Performance in PE

Another study that is related to performance of molecular mass of HALS in HDPE was carried out by Gugumus (2000). Firstly, the performance of low molecular weight HALS was associated with the performance of medium and high molecular mass HALS. Secondly, the activity of increment number average molecular mass of polyacrylate HALS in polyethylene was investigated.

HDPE plaques that, generated with injection molded as 2-mm thickness, exposure to artificial aging. Previously generating HDPE plaques, the HALS types whose of them are polymeric ester HALS7, HALS1 (low molecular mass HALS esters) and HALS6 (medium molecular mass ester) are added to samples. According to the result, increasing HALS concentration influence negatively performance of HALS effectiveness. Furthermore, increment of molecular mass of HALS led to reducing performance of HALS.

Many experiment results for HDPE indicated the inferiority of the polymeric triazine-type HALS-3 compared with the low molecular mass HALS-1. However, the exact opposite situation was also reported. It can be possible that HDPE thick cross-section samples included various type of HALS resulted different because the consequences of the experiment also depended extremely on HDPE type. In addition to this situation, another contrast were between HALS-1 and HALS-3 with respect to performance of HALS in HDPE that there was a significant difference on the molecular mass and also the chemical structure of HALS in HDPE thick cross-sections.

In second part of the study, various amount of the triazine type HALS in HDPE films and tapes were analyzed to observe the performance of HALS molecular mass; changed low, medium and high.

The results showed that, the HALS with triazine gave perfect effectiveness and more effective results than HALS1 during tests. As well as, various triazine HALS did not differ considerably from polymeric compound HALS3 that equaled to low molecular mass stabilizers This consequence seems to show deterioration process on specific surface area with the HDPE film samples. It can explain that these type of processes supports the diffusing of HALS with low molecular mass. Moreover, the supremacy of the HALS with polymeric structure comparing low molecular mass HALS can show latter loss due to vaporization from the surface.

Polyacrylate HALS (HALS11) was also used with PE to search performance of a polymeric HALS in HDPE films.

The molecular masses of HALS almost arranged from 2700 to 23000. The consequences pointed out that decreasing of the light stabilizing activity occurs when the molecular mass of stabilizer increase from 2720 to 6800. Nevertheless, the activity keeps constant, when molecular mass of stabilizer increased from 6800 to 23000.

Gugumus, 2000 study resulted that the surface preserving of PE for instance particularly HDPE provided whole UV stabilization of HDPE. Consequences of the HDPE thin or thick cross-sections that were exposure drawn or undrawn and also various sort of artificial and daylight aging, referred to significant performance of either low or high molecular mass HALS. Also, higher performance was observed on thick HDPE sections with low molecular mass HALS than thin HDPE sections. This situation can be changed in thin sections vice versa.

CHAPTER 3

MATERIALS AND METHODS

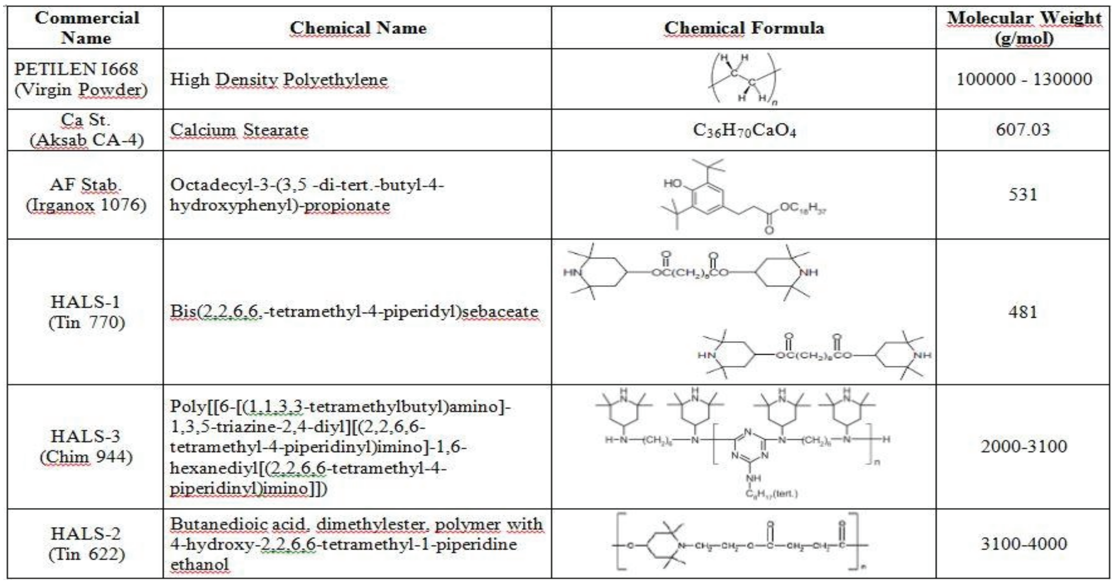
3.1. Materials

High density polyethylene (HDPE) grade I 668 (UV) (MFR = 4.5 - 6 g/10 min; density = 0.963 – 0.967 g/cm^3) was produced by HDPE plant of Petkim Petrokimya Holding Company, Aliağa/Izmir complex whose licensor firm is Mitsui Chemicals Incorporation.

Aksab CA-4 (Calcium stearate), Irganox 1076 (Octadecyl-3-(3,5-di-tert.-butyl-4-hydroxyphenyl)-propionate), HALS-1 (Tin 770) (Bis(2,2,6,6,-tetramethyl-4-piperidyl)sebaceate), HALS-3 (Chim 944) (Poly[[6-[(1,1,3,3-tetramethylbutyl)amino]-1,3,5-triazine-2,4-diyl][(2,2,6,6-tetramethyl-4-piperidinyl)imino]-1,6-hexanediyl[(2,2,6,6-tetramethyl-4 piperidinyl) imino]])) and HALS-2 (Tin 622) (Butanedioic acid, dimethylester, polymer with 4-hydroxy-2,2,6,6-tetramethyl-1-piperidine ethanol) chemicals were used in this study. Mass percentage of HALS-1 (Tin 770) or HALS-2 (Tin 622) associated with HALS-3 (Chim 944) were changed in the additive blend and wt. % quantity of Aksab CA-4 and Irganox 1076 were kept constant. Chemicals used in this synthesis are listed in Table 3.1.

Firstly, all additives premixed before blending with virgin HDPE samples in accordance with commercial stabilizer recipe of HDPE injection grade. Secondly, virgin HDPE powder blended with additive mixture and this homogen powder blending samples were fed to the extruder to obtain HDPE pellet semi-products. Finally, these semi-products were fed to injection machine to get test specimens for every recipes. Each HDPE test specimens containing 0.01 wt. % of a processing stabilizer based on an additive blend were prepared in this study.

Table 3.1. Properties of chemicals used in the additive blends



Commercial Name	Chemical Name	Chemical Formula	Molecular Weight (g/mol)
PETILEN I668 (Virgin Powder)	High Density Polyethylene		100000 - 130000
Ca St. (Aksab CA-4)	Calcium Stearate	$C_{36}H_{70}CaO_4$	607.03
AF Stab. (Irganox 1076)	Octadecyl-3-(3,5 -di-tert.-butyl-4-hydroxyphenyl)-propionate		531
HALS-1 (Tin 770)	Bis(2,2,6,6,-tetramethyl-4-piperidyl)sebaceate		481
HALS-3 (Chim 944)	Poly[[6-[(1,1,3,3-tetramethylbutyl)amino]-1,3,5-triazine-2,4-diyl][(2,2,6,6-tetramethyl-4-piperidinyl)imino]-1,6-hexanediyl[(2,2,6,6-tetramethyl-4-piperidinyl)imino]])		2000-3100
HALS-2 (Tin 622)	Butanedioic acid, dimethylester, polymer with 4-hydroxy-2,2,6,6-tetramethyl-1-piperidine ethanol		3100-4000

3.2. Methods

In this study, all the works can be categorized into two parts;

- Production of HDPE test specimens
- Mechanical characterization of HDPE specimens

3.2.1. Production of HDPE Test Specimens

Since HDPE samples that have different mass fraction of HALS-1 and HALS-3 are known to affect mechanical properties of HDPE samples, 2 kilograms stabilizer blends were prepared to achieve high density polyethylene pellets involving Calcium Stearate(CaSt), AF, HALS-1 and HALS-3 additives in different rates. To illustrate; each of 2 kilograms blend samples involved 300 grams CaSt to gain 50 ppm HALS-1 or HALS-3 additive that was present at 10 grams blend. This mixture was fed to the extruder at 100 grams/hour as 9.9 kilograms high density polyethylene was fed to the extruder from a different feeder. Thus, the quantity of CaSt in the mixture was reduced to 0.15 wt. % and also 10 grams of additive in 2 kg of concentrated blend was diluted with powder polymer; thus, resulted in 50 ppm HALS-1 or HALS-3 additive in the final product.

Figure 3.1 Sample blends were processed in the double screw Coperion ZSK-18 brand extruder.

Table 3.2 Mixing ratio of additives in the sample blends

Sample #	**CaSt (gr)**	**Antioxidant AF St. (gr)**	**Tin770 HALS1(gr)**	**Chim944 HALS3 (gr)**	**HDPE (Powder)(gr)**
S-1	300	60	0	0	1640
S-2	300	60	10	10	1620
S-3	300	60	20	20	1600
S-4	300	60	30	30	1580
S-5	300	60	10	30	1600
S-6	300	60	20	30	1590
S-7	300	60	30	10	1600
S-8	300	60	30	20	1590
S-9	300	60	10	0	1630
S-10	300	60	20	0	1620
S-11	300	60	30	0	1610
S-12	300	60	0	10	1630
S-13	300	60	0	20	1620
S-14	300	60	0	30	1610

(Cont. on next page)

Table 3.2 (Cont.)

Sample #	**Calcium St. (gr)**	**Antioxidant AF St. (gr)**	**Tin770 HALS1(gr)**	**Chim944 HALS3 (gr)**	**HDPE (Powder)(gr)**
S-15	300	60	10	10	1620
S-16	300	60	20	20	1600
S-17	300	60	30	30	1580
S-18	300	60	10	30	1600
S-19	300	60	20	30	1590
S-20	300	60	30	10	1600
S-21	300	60	30	20	1590
S-22	300	60	10	0	1630
S-23	300	60	20	0	1620
S-24	300	60	30	0	1610

In this thesis, tension test were used to determine the mechanical properties of a HDPE samples including HALS-1 and/or HALS-3 additives in different amounts. To understand stress-strain diagram and also strength and specification of HDPE samples, the major parameters; modulus of elasticity (E), strength at yield, strength at break, elongation at yield and elongation at break were determined by the use of ISO 527 testing technique; hence, obtaining the mechanical behavior and the engineering performance of the HDPE test specimens. Firstly, in this test, rectangular test specimens with the same characteristics were prepared at injection machine as $L_{tot} \geq 150$ mm, L = 115 ± 1 mm, $L_1 = 60 \pm 0.5$ mm, D = 4 mm and W = 20 ± 0,2 mm. Also, during injection process, the parameters of injection machine, Engel Victory 80, were kept constant at injection pressure of 20 bar, injection screw press speed of 20 mm/s, model cooling time of 30 s, cooling water temperature of 15 ^{o}C and also screw temperature profile ranged from 190 to 205 ^{o}C.

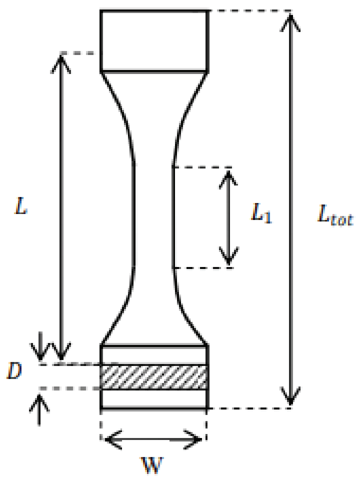
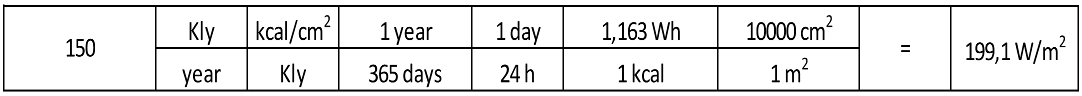


Figure 3.2 Model of pressed rectangular test specimens for tension tests.

Figure 3.3 Rectangular test specimens were constituted in Engel Victory 80 brand injection machine.

3.2.2. Mechanical Characterization of HDPE Specimens

After having prepared the rectangular test specimens, some of them were treated with Xenon-Arc using ASTM D2565 standard procedure (Standard Practice for Xenon-Arc Exposure of Plastics Intended for Outdoor Applications). Before the ASTM D2565 test method, the calculation of ultraviolet (UV) irradiation was determined in terms of region and climate because UV intensity varies with the region, and depends strongly on geography. The intensity of UV radiation is measured in kLy (kilo-Langley); defined as how much UV radiation energy falls on a cm^2 per year. To define standby time of HDPE test specimens in the artificial aging chamber, calculation of UV irradiation was determined for Izmir and Aegean region as 150 kLy. This indicated that a sample could expose to 199.1 W/m^2 of UV irradiation a year.



150	Kly	$kcal/cm^2$	1 year	1 day	1,163 Wh	$10000\ cm^2$	=	$199{,}1\ W/m^2$
	year	Kly	365 days	24 h	1 kcal	$1\ m^2$		

Figure 3.4 UV irradiation calculation of HDPE test specimens for 1 year

At ASTM D2565 (Standard Practice for Xenon-Arc Exposure of Plastics Intended for Outdoor Applications) test method, the samples were exposed to only light for 102 minutes and the following of this application, test specimens were exposed to 18 minutes of light under water spray. This process was repeated for 9 times. After that, test specimens were exposed to dark for 6 hours at 95 ±4 % RH without water spray. Thus, whole process accounts for 24 hours of UV exposure. To reach 1 year of aging under UV irradiation, whole procedure was repeated for 30 days.

Table 3.3. Standard Practice for Xenon-Arc Exposure of Plastics Intended for Outdoor Applications for General Plastics. (Source : ASTM D2565)

Cycle Description		**BPT (^oC)**	**Irradiance**
General Plastics	18-h, alternating intervals of 102/18cycle 6h dark, at 95 ±4 % RH with no water spray	63±2 38±2	0,35 ±0,02 W/m^2 at 340 nm -

Organic polymers are subject to degradation by atmospheric oxygen even at ambient conditions. After polymer oxidation, mechanical strength and electrical property was affected adversely. Differential Scanning Calorimetry (DSC) method was used in this thesis to evaluate oxidative stability; oxidative induction time (OIT) of HDPE pellet samples. Firstly, each pellet sample was 10 grams in weight and then, inserted to the open-top part of the DSC crucible. Open-top DSC crucibles was inserted into the sample cells and these crucibles were processed briefly;

1. Samples were heated under N_2 atmosphere that was kept constant at specified temperature.
2. N_2 atmosphere was changed to oxygen (O_2)
3. After atmosphere changed to oxygen, observed exothermic peak was measured. (OIT measurements by DSC)

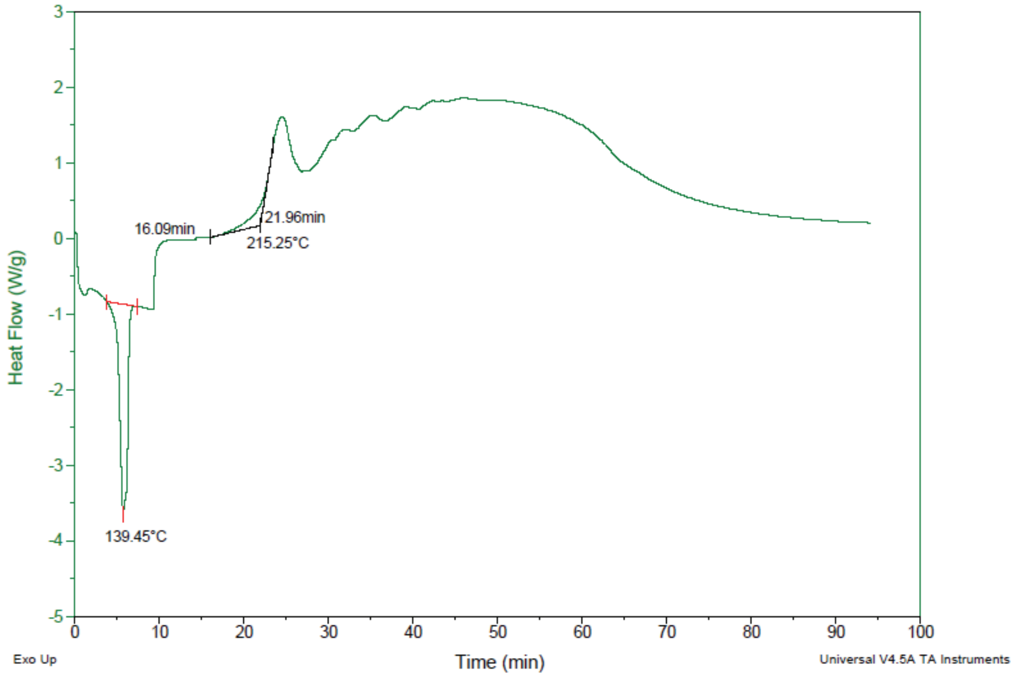


Figure 3.5 OIT Thermogram of S-4 DSC Sample.

As seen in Figure 3.5, Oxidative Induction Time (OIT) time was set at 21.96 minutes at 215 °C for S-4 sample.

Besides, Melt Flow Rates (MFR) of Thermoplastics test method is commercially the most significant and also especially useful for quality control tests on thermoplastics. The uniformity of the flow rate of the polymer, that was gained by different production process methods, such as gas phase, bulk phase, slurry phase, was determined by this method. In this thesis, MFR test method was applied to the HDPE pellet samples. MFR test method was run at 190 °C temperature and 2.16 kg of a total load including piston in accordance with D1238 standard (Standard Test Method for Melt Flow Rates of Thermoplastics by Extrusion Plastometer).

CHAPTER 4

RESULTS AND DISCUSSION

Elongation Lost (%) which is the ratio of Elongation (%) before aging to Elongation (%) after aging and Oxidative Induction Time (OIT) were studied in different recipes of HDPE Injection Molding Plaque specimens in order to measure the effect of HALS1 (Tin770), HALS2(Tin622) and HALS3(Chim944) on aging. Minitab programme was used to analyse the experimental results through statistical methods.

Carrasco F. (2000) investigated variation of mechanical properties as a function of UV exposure time by using artifical accelerated aging method. According to results of Carrasco, Young's Modulus increases with the irradiation time. That means Elongation at Break decreases strongly with time. In addition to that the strain is also decreased and UV aging greatly increases the HDPE stiffness.

In this study, one year aging of UV radiation process was simulated for one month and after that Elongation lost % were determined in 5 replicates for each sample according to ISO 527. Additionaly, oxidative degradations are considered to be the most harmful to HDPE when exposed to thermal or radioactive energy. It creates major changes in the molecular structure and morphology due to chemical reactions between polymer chains and oxygen. In this study, whole samples contain same amount of phosphite antioxidant (Irganox 1076), halogen absorber (Calcium Stearate) and different types and amounts of HALS. Phosphite antioxidants are efferctive at ambient temperatures, even though HALS3 is effective at elevated temperatures (Inamuddin et al, 2016) . OIT experiments were carried out in order to measure antioxidant depletion time and HALS3 performance.

Avg.Elongation Lost% calculated for 5 replicates of each sample and OIT results of all HDPE samples, each of them having different mass fraction (wppm) of HALS1, HALS2 and HALS3, are listed Table 4.1.

Table 4.1 Results of Average Elongation at Break and OIT for 5 Replicate of HDPE Samples

SAMPLE CONC. (weight-ppm)	**AVG. ELONG. AT BREAK BEFORE AGING (%)**	**AVG. ELONG. AT BREAK AFTER AGING (%)**	**% ELONG. LOST**	**OXIDATIVE INDUC. TIME (OIT) (min.)**
SAMPLE-1	838.5	2.08	99.8	15.88
SAMPLE-2 (HALS1 50+HALS3 50)	955.96	734.6	23.2	18.77
SAMPLE-3 (HALS1 100+HALS3 100)	918.78	803.8	12.5	20.16
SAMPLE-4 (HALS1 150+HALS3 150)	919.02	851.4	7.4	21.97
SAMPLE-5 (HALS1 50+HALS3 150)	963.58	793.8	17.6	22
SAMPLE-6 (HALS1 100+HALS3 150)	951.26	822.18	13.6	20.44
SAMPLE-7 (HALS1 150+HALS3 50)	925.84	769.88	16.8	17.95
SAMPLE-8 (HALS1 150+HALS3 100)	910.64	805.78	11.5	18.58
SAMPLE-9 (HALS1 50+HALS3 0)	915.28	467.46	48.9	17.36
SAMPLE-10 (HALS1 100+HALS3 0)	882.72	550.1	37.7	17.78
SAMPLE-11 (HALS1 150+HALS3 0)	848.36	689.12	18.8	17.37
SAMPLE-12 (HALS3 50)	926.58	546	41.1	18.27
SAMPLE-13 (HALS3 100)	921.36	636.06	31.0	17.69
SAMPLE-14 (HALS3 150)	860.7	634.48	26.3	22.23
SAMPLE-15 (HALS2 50+HALS3 50)	923.84	621.76	32.7	17.17
SAMPLE-16 (HALS2100+HALS3 100)	933.96	784.2	16.0	18.37
SAMPLE-17 (HALS2 150+HALS3 150)	936.64	826.6	11.7	20.79

(Cont. on next page)

Table 4.1 (Cont.)

SAMPLE CONC. (weight-ppm)	**AVG. ELONG. AT BREAK BEFORE AGING (%)**	**AVG. ELONG. AT BREAK AFTER AGING (%)**	**% ELONG. LOST**	**OXIDATIVE INDUC. TIME (OIT) (min.)**
SAMPLE-18 (HALS2 50+HALS3 150)	917.24	747.32	18.5	19.63
SAMPLE-19 (HALS2 100+HALS3 150)	866.34	754.4	12.9	19.05
SAMPLE-20 (HALS2 150+HALS3 50)	947.04	689.98	27.1	18.87
SAMPLE-21 (HALS2 150+HALS3 100)	954.56	725	24.0	18.19
SAMPLE-22 (HALS2 50+HALS3 0)	856.22	375	56.2	17.24
SAMPLE-23 (HALS2 100+HALS3 0)	898.18	565.4	37.1	16.49
SAMPLE-24 (HALS2 150+HALS3 0)	962.18	807.6	16.1	16.44

Although S-14 sample which had 150 wppm HALS3 content, gave the best OIT result, S-4 sample having 150 wppm HALS1 and HALS3, showed the best Avg.Elongation Lost% value and also close to OIT result of S-14 sample. Hence, it can be accepted that S-4 sample provides the best results, considering Avg.Elongation Lost% and OIT. In Table 4.1, when only HALS1 added samples (S-9, S-10 and S-11) are examined, Avg.Elongation Lost% decreased clearly; however OIT results were not affected with increasing concentration of HALS1. In the same way, it was observed that Avg.Elongation Lost% was affected positively apart from that OIT results were kept constant for only HALS2 added samples (S-22, S-23 and S-24). Besides, only HALS3 added samples (S-12, S-13 and S-14) results showed that increasing concentration of HALS3 influenced positively on %Avg.Elongation Lost, furthermore, OIT was increased with increasing its concentration. At the end of test results, it was observed that HALS3 influenced OIT more than Avg.Elongation Lost%.

In addition to individual results of HALS additives, synergetic effect of HALS1 and HALS3, HALS2 and HALS3 were analyzed in this study, as well. HALS2 and HALS3 synergetic effect on Avg.Elongation Lost% of HDPE samples and OIT results was seen with S-17, S-18 and S-19 samples. It can be mentioned on the same effect for

HALS1 to HALS3 synergy as seen in S-4, S-5 and S-6. These results showed that this synergetic effect was much more efficient than others individual effects on Avg.Elongation Lost% and OIT tests, such as the results of S-4 and S-14 samples. It can be seen clearly that, HALS1 to HALS3 blend synergetic effect had much more influence than HALS2 to HALS3 blend synergetic effect on Avg.Elongation Lost% and OIT result. For instance, this can clearly be noticed with S-4 and S-17.

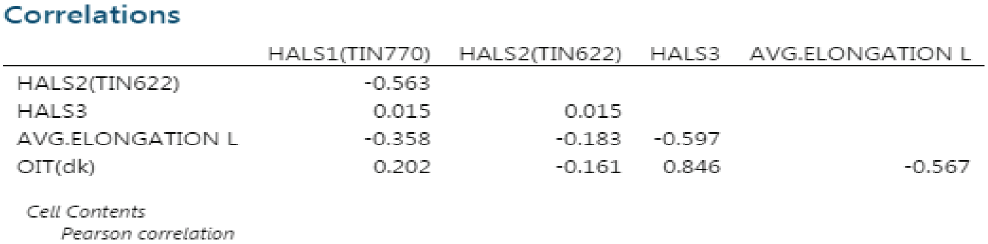
Hence, it can be said that HALS1 synergetic effect is higher than HALS2 synergetic effect with HALS3. The main reason of that HALS1 has low molecular weight than HALS2 and hence HALS1 can effectively diffuse inside the polimeric carbon chain structure. Gugumus 2000, also explained that the performance of Elongation durability of HDPE samples are increasing with decreasing molecular mass of the HALS.

In addition, as it was specified before, HALS3 has much more effect on Av. Elongation Lost % and OIT strongly as seen with individual influence of HALS1 and HALS2. Literature Survey also confirmed that polymeric HALS, especially HALS3 and other HALS types that had high molecular weight gave better result in accordance with HALS that has low molecular weight. Hence, HALS1/HALS2 blends or HALS1/HALS2/HALS3 blends haven’t been tried in this study. All results confirmed the correctness of this assumption in this study.

Whole results of 5 replicates of each sample were analyzed in Minitab in order to estimate Pearson correlation and linear regression between HALS concentations and OIT. Additionally, it is estimated a nonlinear regression model between HALS concentration and Elongation Lost %. So, the regression models enhanced to predict the amount of HALS additives in product recipe.

Pearson Correlation relationships are studied before non-linear regression analysis which is given in Figure 4.1. Correlation coefficient is a valuable numerical measure of association between two variables which is a value between -1 and 1 indicating the strength of the association of the observed data for the two variables. Correlation between Elongation Lost% and HALS3 is about -0.597, which indicates that as HALS3 amount in polymer increases, Elongation Lost% decreases. The Pearson correlation between OIT and HALS3 is about 0.846, which indicates that there is strong positive relationship between the variables. Correlation between Elongation% and OIT results is determined to be -0.567, which indicates moderately negative relationship.

Low Pearson correlation coefficient does not mean that no relationship exists between the variables. The variables may have a nonlinear relationship.



Correlations

	HALS1(TIN770)	HALS2(TIN622)	HALS3	AVG.ELONGATION L
HALS2(TIN622)	-0.563			
HALS3	0.015	0.015		
AVG.ELONGATION L	-0.358	-0.183	-0.597	
OIT(dk)	0.202	-0.161	0.846	-0.567

Cell Contents
Pearson correlation

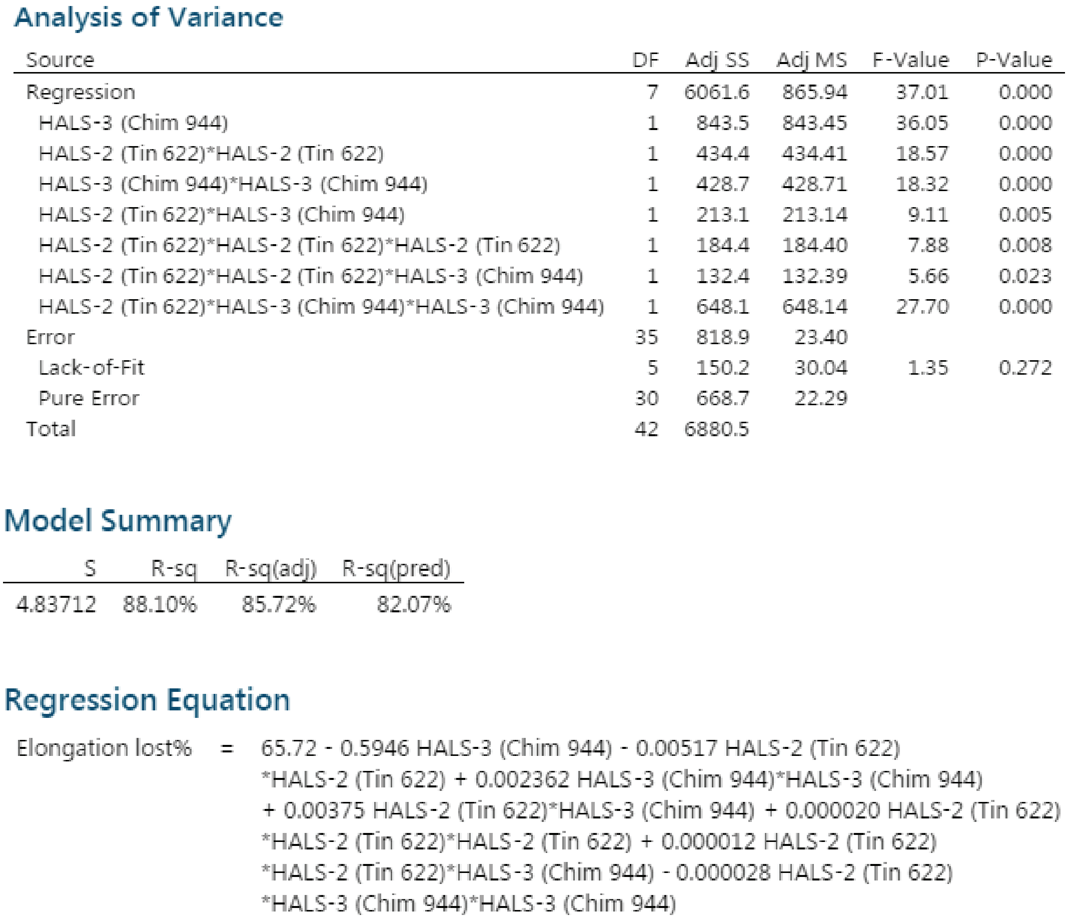
Figure 4.1 Correlation Relationships between HALS1(TIN770), HALS2(TIN622) and HALS3 Concentration and OIT & Avg. Elongation

After correlations, regression models were investigated to enhance amount of HALS additives comparatively in product recipe. Firstly, linear models were studied and then nonlinear models were studied. Finally, Nonlinear models for HALS concentration and Elongation Lost% are used instead of linear models since Rsq value of linear model is below 80%.

4.1 Investigation of Relationship Between HALS2 to HALS3

4.1.1 Regression Analysis of HALS2 & HALS3 Blends on % Elongation Lost

After Correlations, Nonlinear Regression Models are estimated for Elongation Lost %. Nonlinear regression attempts to model the relationship between two variables by fitting a nonlinear equation to observed data. As seen in Figure 4.2, regression analysis of Elongation Lost % vs. HALS2 (TIN622) and HALS3 was studied firstly and a regression equation was obtained. Amount of sample is sixty five, which are enough for analysis, in order to fit accurately. In the Analysis of Variance (ANOVA) table, the p-values for all of the terms are less than the significance level of 0.05, therefore HALS2(TIN622) and HALS3 effects on Elongation Lost % are statistically significant. R-sq is a statistical measure of how close the data are to the fitted regression line. R-sq was calculated 85% approximately which is enough to say this nonlinear model fit well for the data obtained in this study.



Analysis of Variance

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Regression	7	6061.6	865.94	37.01	0.000
HALS-3 (Chim 944)	1	843.5	843.45	36.05	0.000
HALS-2 (Tin 622)*HALS-2 (Tin 622)	1	434.4	434.41	18.57	0.000
HALS-3 (Chim 944)*HALS-3 (Chim 944)	1	428.7	428.71	18.32	0.000
HALS-2 (Tin 622)*HALS-3 (Chim 944)	1	213.1	213.14	9.11	0.005
HALS-2 (Tin 622)*HALS-2 (Tin 622)*HALS-2 (Tin 622)	1	184.4	184.40	7.88	0.008
HALS-2 (Tin 622)*HALS-2 (Tin 622)*HALS-3 (Chim 944)	1	132.4	132.39	5.66	0.023
HALS-2 (Tin 622)*HALS-3 (Chim 944)*HALS-3 (Chim 944)	1	648.1	648.14	27.70	0.000
Error	35	818.9	23.40		
Lack-of-Fit	5	150.2	30.04	1.35	0.272
Pure Error	30	668.7	22.29		
Total	42	6880.5			

Model Summary

S	R-sq	R-sq(adj)	R-sq(pred)
4.83712	88.10%	85.72%	82.07%

Regression Equation

Elongation lost% = 65.72 - 0.5946 HALS-3 (Chim 944) - 0.00517 HALS-2 (Tin 622)
*HALS-2 (Tin 622) + 0.002362 HALS-3 (Chim 944)*HALS-3 (Chim 944)
+ 0.00375 HALS-2 (Tin 622)*HALS-3 (Chim 944) + 0.000020 HALS-2 (Tin 622)
*HALS-2 (Tin 622)*HALS-2 (Tin 622) + 0.000012 HALS-2 (Tin 622)
*HALS-2 (Tin 622)*HALS-3 (Chim 944) - 0.000028 HALS-2 (Tin 622)
*HALS-3 (Chim 944)*HALS-3 (Chim 944)

Figure 4.2 Analysis of Variance and Regression Model for Elongation Lost % vs. HALS2(TIN622) and HALS3

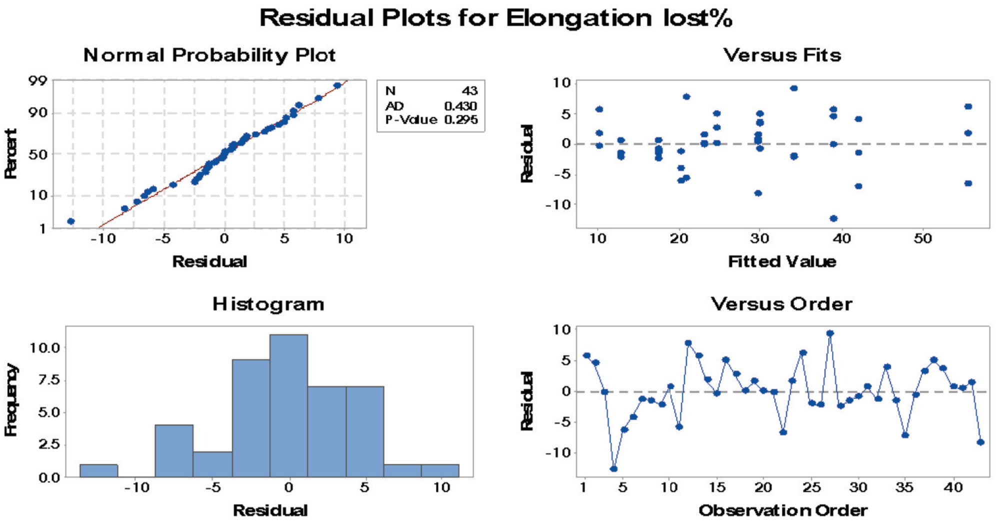


Figure 4.3 Residual Plots for Elongation Lost % for HALS2 & HALS3 Blends

Residual versus fitted value graph is given in Figure 4.3 that shows the residuals on the vertical axis and the independent variable (Fitted value) on the horizontal axis. If the points in a residual plot are randomly dispersed around the horizontal axis, regression model is appropriate for the data. In this model, residuals show a random pattern, indicating a good fit (i.e. unbiased) for this model. Furthermore, normal probability plot of Residuals are also given in Figure 4.3 for comparing a data set with the normal distribution. It can be said that residuals shows normal distribution because p-value was approximately calculated %30.

4.1.2 Relationship Between Elongation Lost with HALS2 & HALS3 Blends

As seen in Figure 4.4, multi vari-chart indicates possible interaction between HALS2 and HALS3. HALS2 and HALS3 blend sample; S-17, which contained 150 wt-ppm HALS2 and 150 wt.-ppm HALS3 gave the smallest Elongation Lost % result among all HALS2 & HALS3 blends. On contrary, S-22 gave the highest Elongation Lost % among them. Besides, S-19 sample that consists of 100 wt-ppm HALS2 and 150 wt.-ppm HALS3 showed no difference on Elongation Lost% value comparing with S-19 test result. Similarly, Figure 4.5. confirmed this situation with interaction between HALS2 to HALS3.

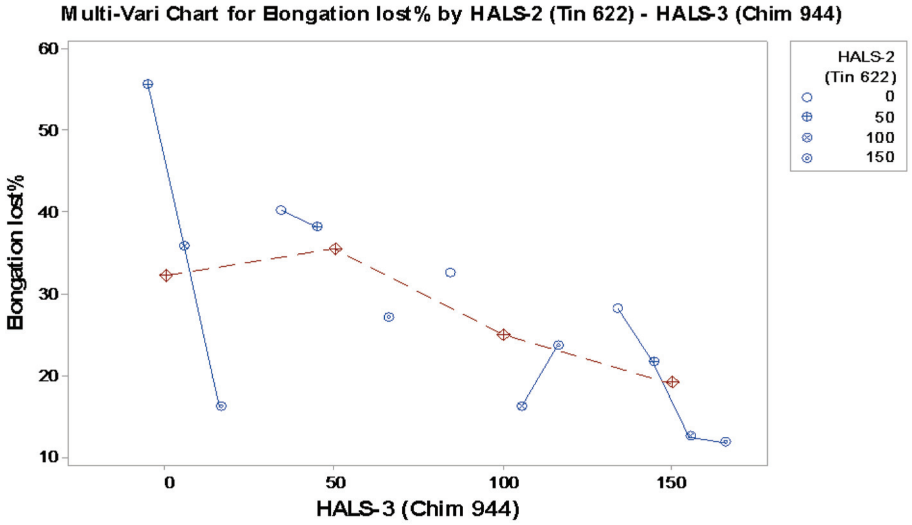


Figure 4.4 Multi-Vari Chart for Elongation Lost % by HALS2 & HALS3 Blends

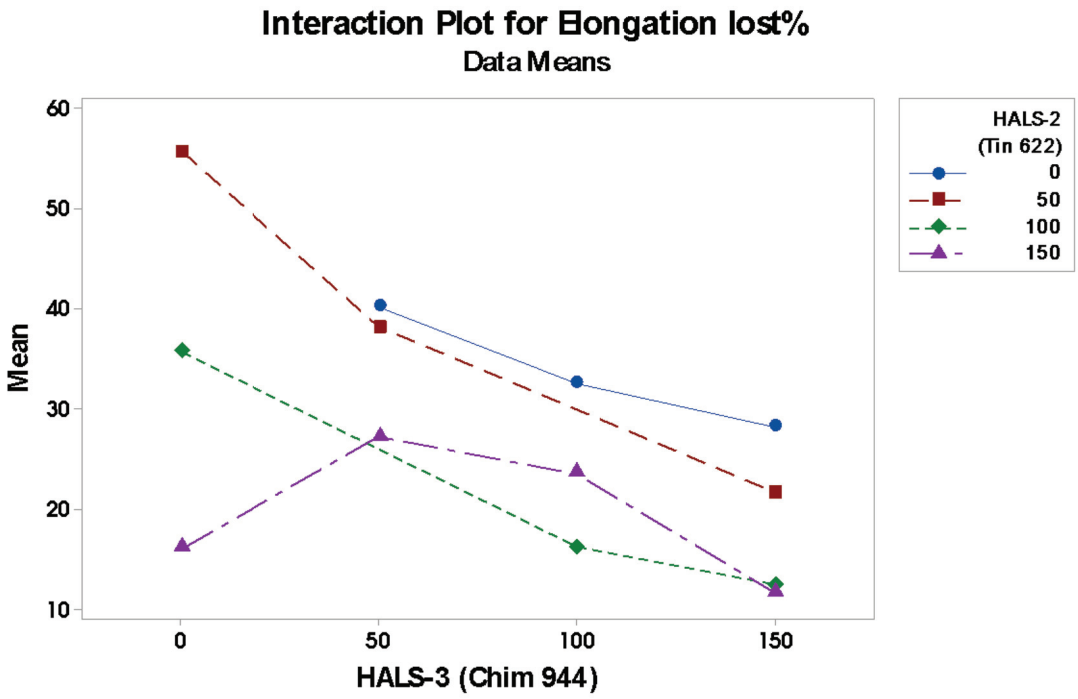


Figure 4.5 Interaction Plot of HALS2 & HALS3 Blends for Elongation Lost %

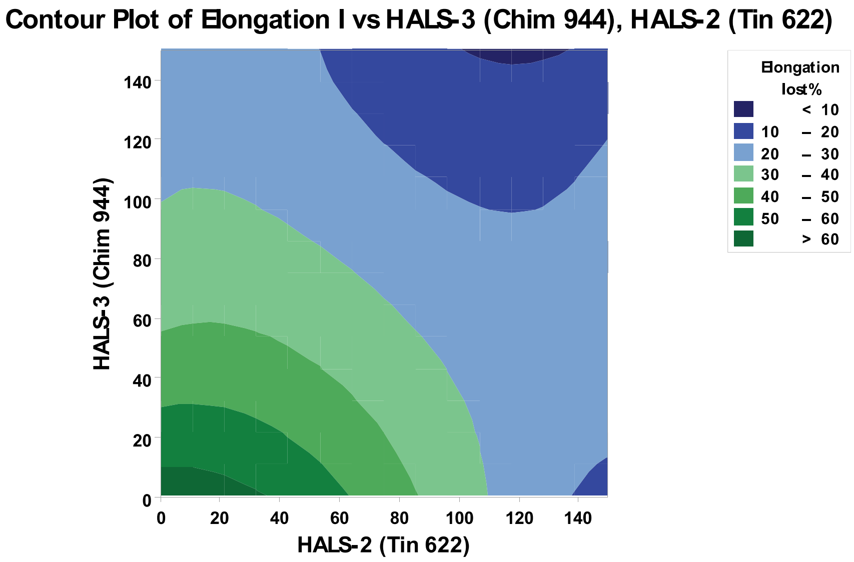


Figure 4.6 Contour Plot of Elongation Lost % for HALS2 to HALS3 Interaction

In Figure 4.6, blue and dark blue regions shows degradation of polymeric chain structure. If it is aimed to reach maximum <10% Elongation Lost, minimum 120 wt-ppm HALS2 and 150 wt-ppm HALS3 have to be added.

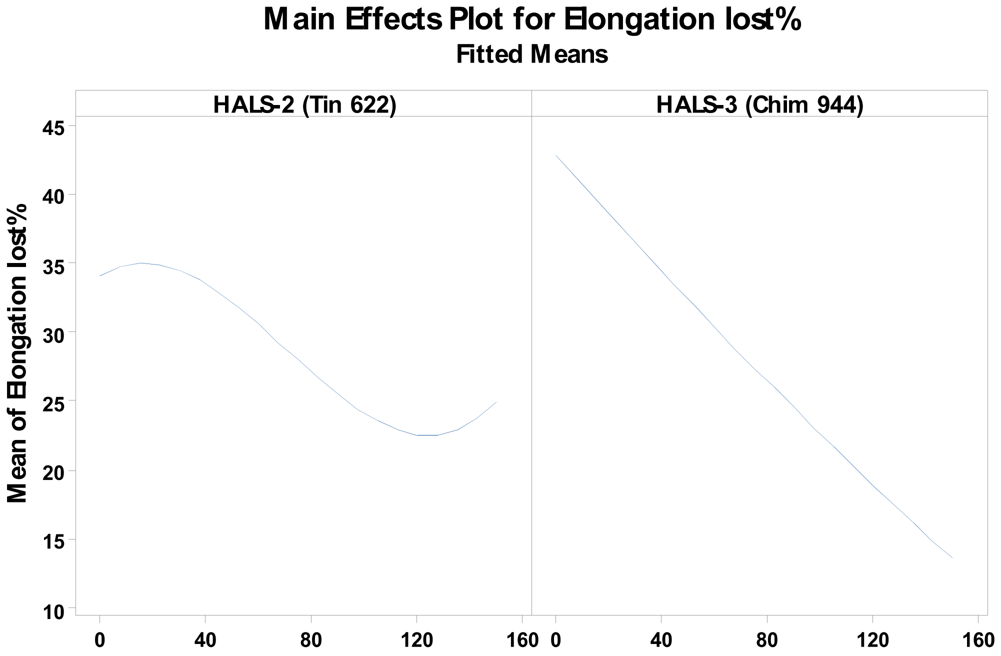


Figure 4.7 Main Effects Plot for Elongation Lost % for HALS2 and HALS3

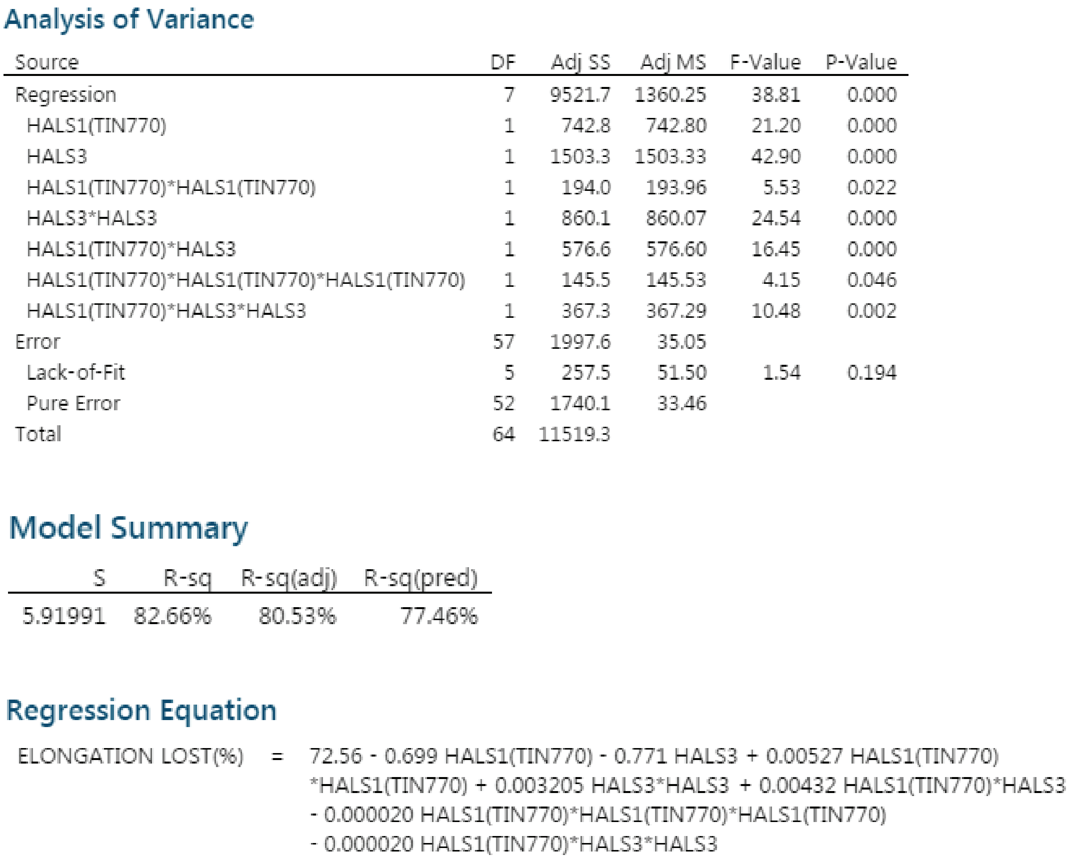
Main Effects Plot for Elongation Lost % for HALS2 and HALS3 which is a graphs the response mean for each factor level connected by a line is shown in Figure 4.7. Main effects plots will not show interactions. To view interactions between factors, it is used interaction plot which is given in Figure 4.5 for HALS2 and HALS3. For main effects plots, when the line is not horizontal, then there is a main effect. Different levels of the factor affect the response differently. The steeper slope of the line has greater effect. In Figure 4.7, it can be seen clearly HALS3 is much more effective than HALS2 because of the steeper the slope of the line.

4.2. Investigation of Relationship Between HALS1 to HALS3

Regression analysis were also studied for HALS1 and HALS3 blends to compare HALS1 and HALS2 synergetic performance with HALS3.

4.2.1. Regression Analysis of HALS1 & HALS3 Blends

First of all model summary of HALS1 & HALS3 blends were composed in order to obtain regression analysis of Elongation Lost% vs. HALS1 (Tin770) & HALS3 and a regression equation as seen in Figure 4.8. In this study, sixty five samples were used alike HALS2 & HALS3 mathematical model. HALS1 (Tin770) and HALS3 effects on Elongation Lost % were meaningful because, analysed the p-values for all of the variations are less than the significance level <0.05. Also, the model of HALS1 and HALS3 blend was suitable due to approximately 81% R-sq value.



```
Analysis of Variance

Source                                  DF   Adj SS   Adj MS  F-Value  P-Value
Regression                               7   9521.7  1360.25    38.81    0.000
  HALS1(TIN770)                          1    742.8   742.80    21.20    0.000
  HALS3                                  1   1503.3  1503.33    42.90    0.000
  HALS1(TIN770)*HALS1(TIN770)            1    194.0   193.96     5.53    0.022
  HALS3*HALS3                            1    860.1   860.07    24.54    0.000
  HALS1(TIN770)*HALS3                    1    576.6   576.60    16.45    0.000
  HALS1(TIN770)*HALS1(TIN770)*HALS1(TIN770)  1    145.5   145.53     4.15    0.046
  HALS1(TIN770)*HALS3*HALS3              1    367.3   367.29    10.48    0.002
Error                                   57   1997.6    35.05
  Lack-of-Fit                            5    257.5    51.50     1.54    0.194
  Pure Error                            52   1740.1    33.46
Total                                   64  11519.3

Model Summary

      S    R-sq  R-sq(adj)  R-sq(pred)
5.91991  82.66%     80.53%      77.46%

Regression Equation

ELONGATION LOST(%)  =  72.56 - 0.699 HALS1(TIN770) - 0.771 HALS3 + 0.00527 HALS1(TIN770)
                       *HALS1(TIN770) + 0.003205 HALS3*HALS3 + 0.00432 HALS1(TIN770)*HALS3
                       - 0.000020 HALS1(TIN770)*HALS1(TIN770)*HALS1(TIN770)
                       - 0.000020 HALS1(TIN770)*HALS3*HALS3
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Figure 4.8 Analysis of Variance and Regression Model for Elongation Lost% vs. HALS1(TIN770) and HALS3

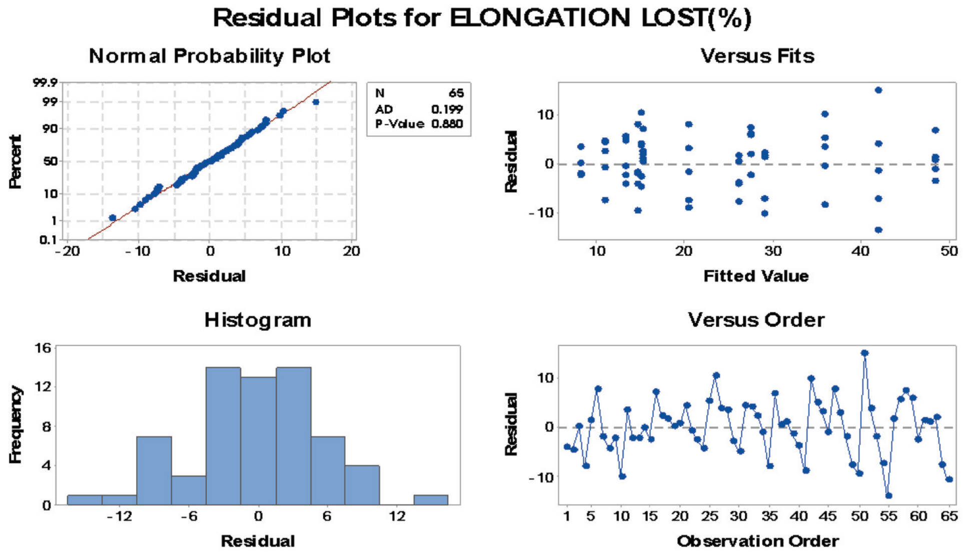

Figure 4.9 Residual Plots for Elongation Lost % for HALS1 & HALS3 Blends

Residual versus fitted value graph is given In Figure 4.9. In this nonlinear model, residuals shows a random pattern. Moreover, normal probability plot of Residuals are given in the same Figure. According to normal probablity plot, if the data is not distributed normally, the risk is 88%. So, it can be said that data is certainly distributed normally.

4.2.2 Relationship Between Elongation Lost with HALS1 & HALS3 Blends

Probable interaction between HALS1 and HALS3 can be seen in Multi-Vari Chart or Elongation Lost % in Figure 4.10. Contained 150 wt-ppm HALS1 and 150 wt.-ppm HALS3 blend sample (S-4) has the smallest Elongation Lost % result when evaluated all HALS1 & HALS3 blends. In the meantime, it can be said S-4 gave the best result for Elongation Lost % among all samples. Contrarily, the biggest Elongation Lost % value was observed at S-9 sample among HALS1 and HALS3 blends. The same effect of HALS1 and HALS3 blends on Elongation Lost % was confirmed by Figure 4.9.

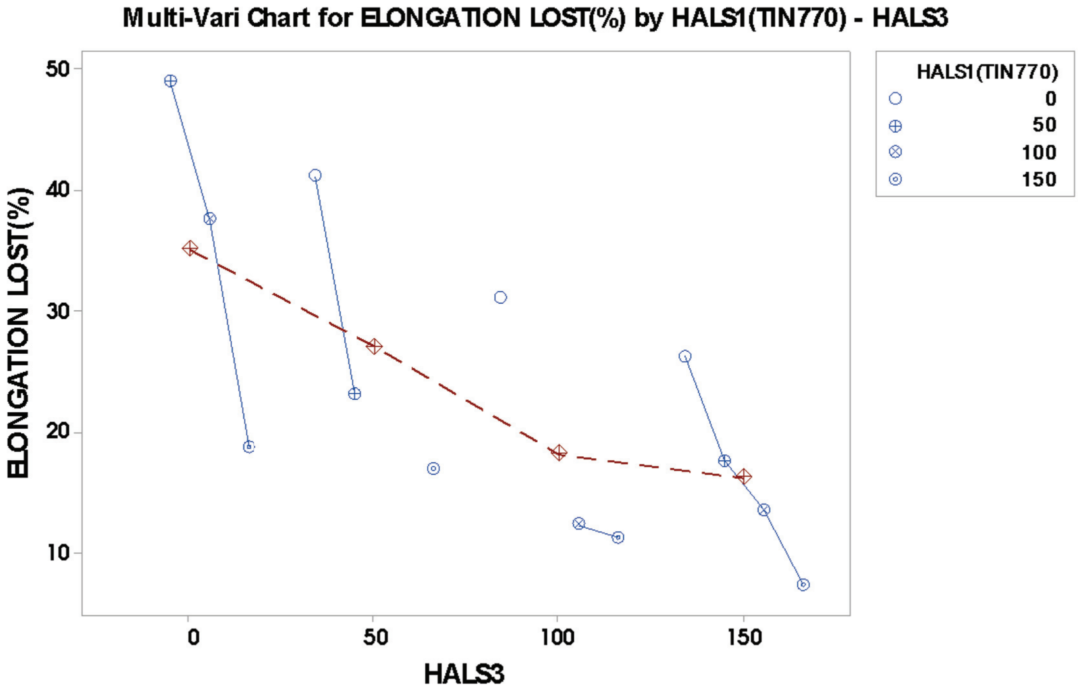

Figure 4.10 Multi-Vari Chart for Elongation Lost % by HALS1 & HALS3 Blends

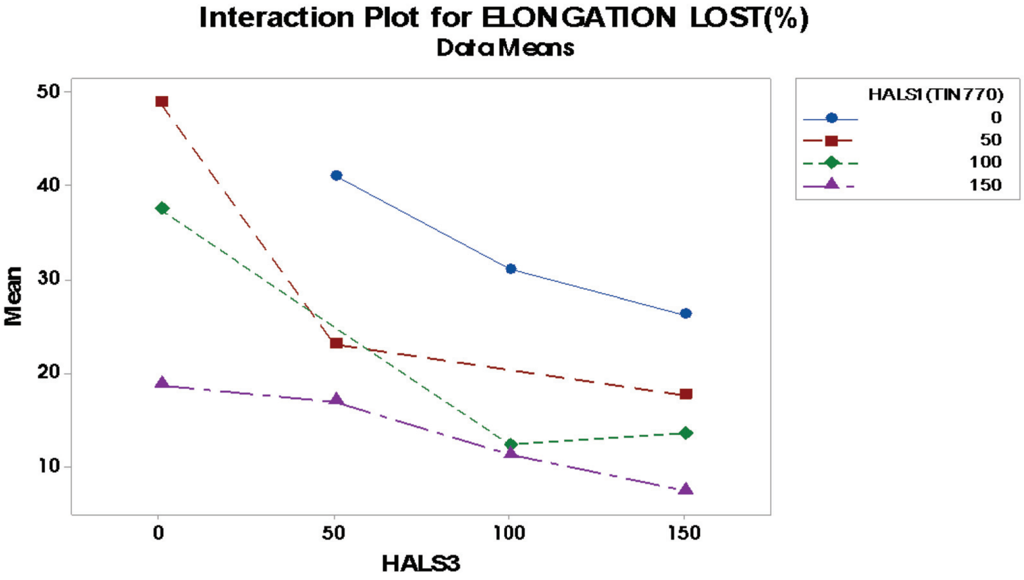

Figure 4.11 Interaction Plot of HALS1 & HALS3 Blends for Elongation Lost %

Blue and dark blue areas of Elongation Lost % Contour Plot define the least degradation of HDPE polymeric structures unlike green areas. As a result of this diagram, in order to achieve <10% Elongation Lost, 150 wt-ppm HALS1 and 150 wt-ppm HALS3 have to be used in HDPE sample blends as seen in Figure 4.12. Moreover, blue areas cover much more in Figure 4.82. It can be said that HALS1 and HALS3 blends protect HDPE polymeric samples more than HALS2 and HALS3 blends.

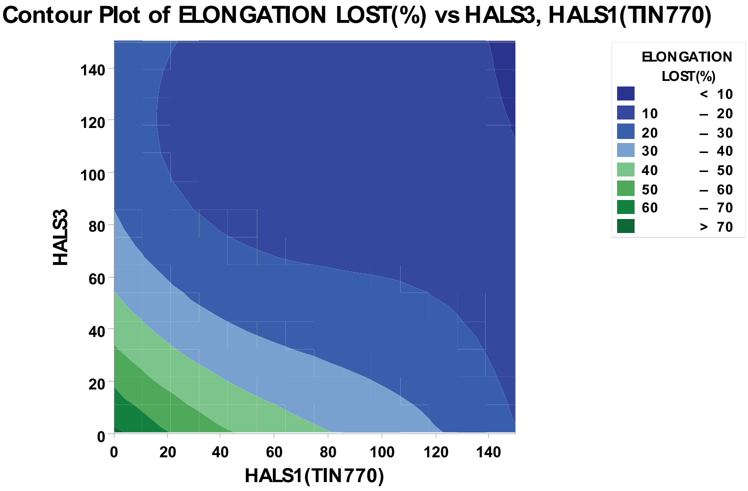

Figure 4.12 Contour Plot of Elongation Lost % for HALS1 to HALS3 Interaction

In Figure 4.13, Main Effects Plot for Elongation Lost % for HALS1 and HALS3 is shown. In this figure, HALS3 should be used at a minimum 120 wt-ppm and HALS1 should be used at a amount greater than 120 wt-ppm to obtain %15 Elongation Lost in HDPE samples. It can be certainly seen that HALS3 is more effective than HALS1 because if it is not feed, %Elongation Lost is much more greater than if HALS2 is not fed.

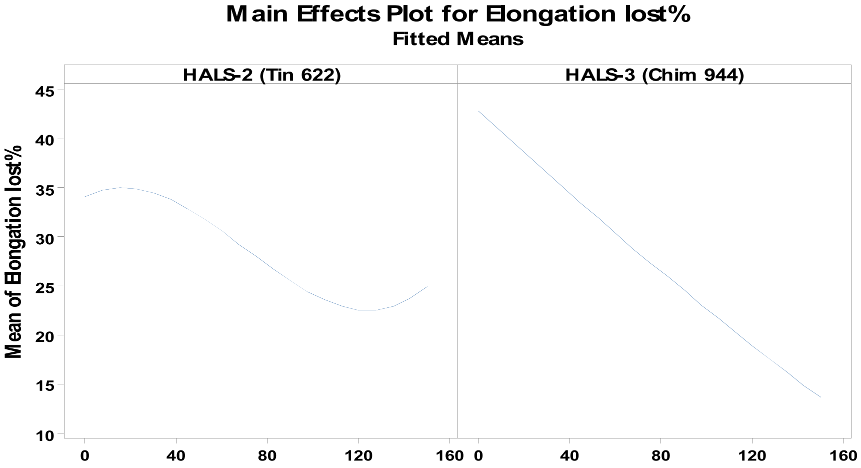

Figure 4.13 Main Effects Plot for Elongation Lost % for HALS1 and HALS3

Main Effects Plot for Elongation Lost % for HALS1 and is shown in Figure 4.13. Different levels of the HALS3 affect the Elongation Lost% greater magnitude than HALS1. If it compare with HALS2 and HALS3 Main Effects Plot (Figure 4.6), HALS1 level in the sample is effects more than HALS2 on %Elongation Lost.

4.3. Different Types of HALS Blends Effect on Oxidative Induction Time

25 experiments have done for OIT. Hence, correlation results were prefered instead of regression. It has indicated that HALS1-HALS3 and HALS2-HALS3 correlations were defined as 0.2 and -0.2 coefficients respectively. So, it can be said that HALS3 is the only parameter that has an effect on OIT according to correlations. For this reason, HALS2 and HALS1 were neglected due to that there was no effect on OIT. As seen in Figure 4.14, OIT Fitted Line Plot was carried out for twenty eight samples to determine HALS3 effect. It is able to consider that when HALS3 amount increases, OIT increases linearly.

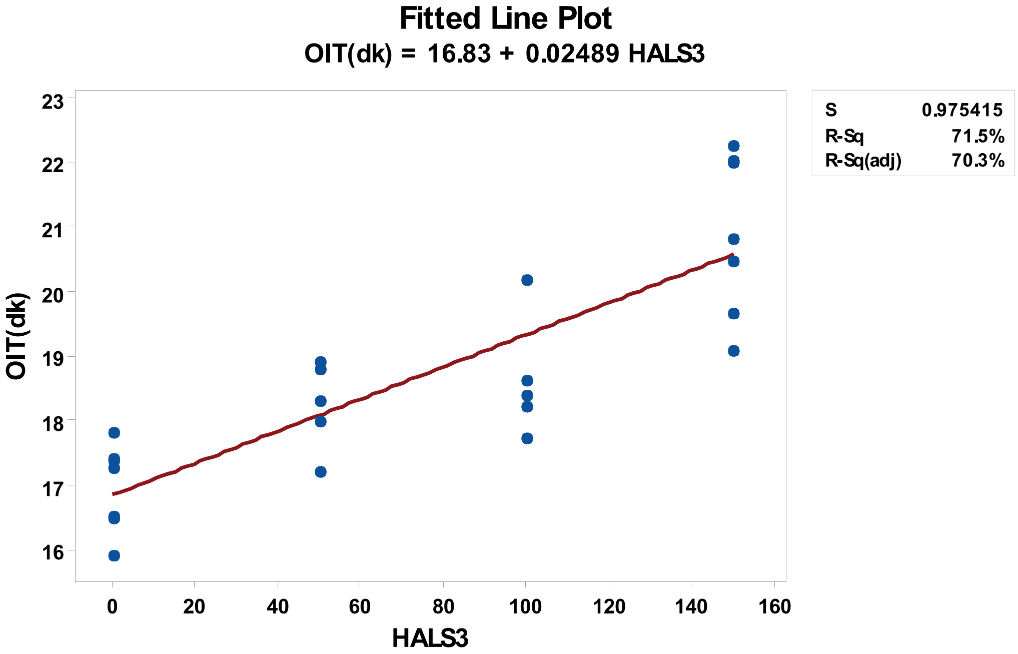

Figure 4.14 Fitted Line Plot of OIT for HALS3

CHAPTER 5

CONCLUSIONS

In this study, the effect of single HALS1, HALS2 and HALS3 and also in different mass ratios HALS2-HALS3 and HALS1-HALS3 blends in High Density Polyethylene were studied on Avg.Elongation Lost%, Elongation Lost% and Oxidative Induction Time.

Physical and mechanical tests analyzed for single HALS type and HALS blended samples in different mass ratios before artificial aging and after.

When comparing this study to the reported literature studies, effect of different types of HALS and special HALS blends used in commercial HDPE process were defined with result of Avg.Elongation Lost%, Elongation Lost% and Oxidative Induction Time. The compose of HALS blends were varied 0 to 150 wppm for each HALS type in accordance with commercial HDPE process injection grade production recipe.

To conclude this study; single HALS3 samples could not indicate minimum Elongation Lost% result even though maximum Elongation Lost% was observed at samples without HALS3. Further, HALS1-HALS3 blends indicated more effective results than result of HALS2-HALS3 blends on Elongation Lost% tests, so it was clear that synergetic effect of HALS1 with HALS3 was much more effective than synergetic influence of HALS2 with HALS3. Besides, increased mass concentration of HALS2 and HALS3 in blends enhanced synergetic effect of HALS2 and HALS3 on Elongation Lost% Similarly the same effect was observed for HALS1 and HALS3 synergetic effect on Elongation Lost%. OIT results indicated that only effective additive was HALS3 and neither single HALS1 nor HALS2 or blending of them with HALS3 had any effect on xidative Induction Time.

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