İZMIR KATIP CELEBI UNIVERSITY

GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES

INVESTIGATIONS OF MECHANICAL AND FLAMMABILITY PROPERTIES OF HDPE REINFORCED FLAME RETARDANT ADDITIVES INCLUDING ANTIMONY TRIOXIDE

M.Sc. THESIS

Berk ENGİN

Department of Materials Science and Engineering

Thesis Advisor: Assoc. Prof. Dr. Hüsnügül YILMAZ ATAY

DECEMBER 2020

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İZMİR KATİP CELEBİ ÜNİVERSİTESİ
FEN BİLİMLERİ ENSTİTÜSÜ

ANTIMON TRIOKSİT İÇEREN ALEV GECİKTİRİCİ KATKILI YÜKSEK YOĞUNLUKLU POLİETİLEN'İN MEKANİK ve ALEV GECİKTİRİCİLİK ÖZELLİKLERİNİN İNCELENMESİ

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ARALIK 2020

…Berk ENGİN…. , a **M.Sc.** student of **IKCU Graduate School of Natural And Applied Sciences**, successfully defended the thesis entitled "…**INVESTIGATIONS OF MECHANICAL AND FLAMMABILITY PROPERTIES OF HDPE REINFORCED FLAME RETARDANT ADDIVITES INCLUDING ANTIMONY TRIOXIDE…**", which he/she prepared after fulfilling the requirements specified in the associated legislations, before the jury whose signatures are below.

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Date of Defence : 25.12.2020

To my family

FOREWORD

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Berk ENGİN

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

ABBREVATIONS

HDPE: High Density Polyethylene

FR: Flame Retardant

Sb_2O_3: Antimony Trioxide

FTIR: Fourier Transform Infrared Radiation

SEM: Scanning Electron Microscope

EDX: Energy Dispersive X-ray

TGA: Thermal Gravity Analysis

PVC: Polyvinyl Chloride

ABS: Acrylonitrile-Butadiene-Styrene

PE: Polyethylene

MDPE: Middle Density Polyethylene

LLDPE: Linear Low Density Polyethylene

LDPE: Low Density Polyethylene

UHMWPE: Ultra-High Molecular Weight Polyethylene

VLDPE: Very Low Density Polyethylene

PB: Polybutylene

PP: Polypropylene

PEX: Cross-Linked Polyethylene

$SBCI_3$: Antimony Trichloride

PIB: Polyisobutylene

L/D: Length / Diameter

ISO: International Organization for Standardization

ASTM: American Society Testing and Materials

CRF: Cold Ring Fraction

UL-94: Underwriters Laboratories-94

MFR: Melt Flow Rate

MFI: Melt Flow Index

INVESTIGATIONS OF MECHANICAL AND FLAMMABILITY PROPERTIES OF HDPE REINFORCED FLAME RETARDANT ADDIVITES INCLUDING ANTIMONY TRIOXIDE

ABSTRACT

In this day and age, High density polyethylene (HDPE) has an extensive usage area in terms of lightweight, chemical resistance, easy production, thermally and electrically insulating, high strength-to-density ratio. However; HDPE is extremely flammable because of its chemical structure, which consists of carbon and hydrogen. There is some flame retardant reinforcement process which may be applied to improve the flammability property of HDPE. In this study; two different types of a commercial flame retardant masterbatch which consist of Antimony trioxide (Sb_2O_3) was loaded into the HDPE matrix; in this way the HDPE matrix specimen will be gain flame retardant property to be used in cable covering systems. This study will be performed in order to be a beneficial source for industrial organizations, plastic pipe producers in particular. During the experimental phase of the current study, production was carried out with a relatively small amount of raw materials and laboratory equipment. Therefore; the followed efficient energy-cost method during the production part of the study was expected to serve as a guideline for the production process of the factory. In the production phase, compounding process was performed in the first place by the twin-screw extruder, and then paste, which is a hot mixture of ingredients, was pressed to obtain plates at available pressure and temperature. Specimens were taken from each plate at the end of the production process to perform characterization. Later on, specimens were characterized by using the following methods; Fourier transform infrared radiation (FTIR) spectroscopy was implemented to detect functional groups and characterizing. Scanning electron microscopy- Energy Dispersive X-Ray Spectroscopy (SEM-EDS) were used to investigate elemental analysis and

morphology. Density and Melt flow index (MFI) measurements were carried out to define the viscosity of plastic samples. Moreover, the UL-94 vertical test was carried out to observe the flammability properties of samples. Tensile test was applied to each specimen to determine the mechanical properties.

ANTİMON TRİOKSİT İÇEREN ALEV GECİKTİRİCİ KATKILI YÜKSEK YOĞUNLUKLU POLİETİLEN'İN MEKANİK VE ALEV GECİKTİRİCİLİK ÖZELLİKLERİNİN İNCELENMESİ

ÖZET

Günümüzde, Yüksek Yoğunluklu Polietilen (HDPE)'nin, kimyasal direnç, kolay üretim tekniği, termal ve elektriksel yalıtımı, yüksek mukavemet/yoğunluk oranı gibi özelliklere sahip olmasından olayı yaygın bir kullanım alanı mevcuttur. Ancak; HDPE, içerdiği karbon ve hidrojenden dolayı son derece yanıcıdır, HDPE'nin yangına karşı dayanıklılığını geliştirmek için uygulanabilecek bazı Alev Geciktirici takviye işlemleri vardır. Bu çalışmada; Antimon Trioksit (Sb_2O_3) içeren iki farklı tipte ticari Alev Geciktirici masterbatch; belli oranlarda HDPE matrise takviye edilmiştir. Bu şekilde HDPE matris örneği kablo kaplama sistemlerinde kullanılacak alev geciktirici özellik kazanacaktır. Bu çalışma, plastik boru üreticisi olan bir firmanın ihtiyaçlarını karşılama üzerine yapılmıştır. Bu çalışmanın deneysel basamağında, laboratuvar ekipmanları ile nispeten az miktarda hammadde üretimi gerçekleştirilmiştir. Bu sayede; maliyet ve enerji tasarruf edilmiştir. Ayrıca bu çalışma; fabrikanın alev geciktirici boru üretiminde yol gösterici bir formülasyon sağlayacaktır. Üretim aşamasında; ilk olarak bileşimlerin hazırlanması işlemi çift vidalı ekstrüder ile gerçekleştirildi ve daha sonra bileşenlerin sıcak bir şekilde karıştırıldığı macun, mevcut basınç ve sıcaklıkta plakalar elde etmek üzere preslendi. Malzeme karakterizasyonun gerçekleştirilmesi için üretim işleminin sonunda, her plakadan örnekler alınmıştır. Numunelerin içerdiği fonksiyonel grupların taranması için Fourier Tranform Kızılötesi Radyasyon (FTIR) spektroskopisi uygulandı.

Elemental analiz ve morfolojinin araştırılmasında Fourier Tranform Kızılötesi Radyasyon (FTIR) spektroskopisi ve Taramalı Elektron Mikroskopisi- Enerji Dağıtıcı X-Işını Spektroskopisi (SEM-EDS) kullanılmıştır. Plastik numunelerin viskozitesini tanımlamak için Yoğunluk ve Erime Akış İndeksi (MFI) ölçümleri yapıldı. Ayrıca

numunelerin yanıcılık özelliklerini gözlemlemek için UL-94 Dikey testi yapılmıştır. Mekanik özelliklerin belirlenmesi için her bir numuneye çekme deneyi uygulanmıştır

Anahtar Kelimeler: Yüksek Yoğunluklu Polietilen, Mekanik Özellikler, Mukavemet, Alev Geciktirici

1. INTRODUCTION

1.1 History of HDPE

The accidental discovery of the polymerization reaction of ethylene occurred in 1930 by the British chemical products company named Imperial Chemical Industries. Yet, it took years to make the technology of this reaction easily applicable, which was carried out under extremely high pressures of 2000 bars. In a short period of time, polyethylene, of which mechanical and electrical properties were realized, began to be utilized in many different applications. In the 1950s, chemist K. Ziegler developed a technique for the polymerization reaction under low pressure. This method was extended to all types of polyethylene in the 1970s; consequently, polyethylene has become the most applicable plastic material throughout the world. It has been used in a wide variety of fields, ranging from garbage bags to electrical insulation. There are many different types of polyethylene; first, low density polyethylene are the oldest ones of the thermoplastic family. Recently three new polyethylene types are discovered and joined to the family: high density polyethylene, linear polyethylene and medium density polyethylene. These four types of widely used polyethylene are the fundamental polymeric materials of the industry and have a broad area of application. Along with the addition of the new types, namely the improvement of polyethylene, it is used in many areas from toys to household goods, to drums and bags. The reason of the extensive use of polyethylene originates from its superiority, durability, easy processing and dielectric properties [1]. Figure 1.1 Demonstration of HDPE in granules form.

Figure 1.1 HDPE in granule form.

Polyethylene is generally classified into three subgroups in terms of its density. Low density polyethylene (LDPE) (0.910 g/cm^3 <density <0.925 g/cm^3), medium density polyethylene (MDPE) (0.926 g/cm^3 to 0.940 g/cm^3) and high-density polyethylene (HDPE) (0.94 g/cm^3 to 0.96 g/cm^3). Linear low -density polyethylene (LLDPE) is a type of combination of HDPE and LDPE, which holds a high proportion of the strength of HDPE and the flexibility of LDPE. Other PE types with lesser use in the industry are the ultra-high molecular weight polyethylene shortly named UHMWPE, (density>0.965 g/cm^3) and very low-density polyethylene (VLDPE) (density <0.910 g/cm^3) [2].

Polymers are divided into three subgroups as linear, branched, and cross-linked based on the structural shape of their molecules. Structural shapes can be seen in Figure 1.2. Linear polymers consist of repeating units that are continuously connected to each other. Van der Waals and hydrogen bonds provide the connection of linear polymer chains between each other. These types of polymers are referred to as branched polymers when side branches appear at irregular intervals on the main polymer chain. The branches can be long or short to form a whole structure or split to form a dendritic structure. Aforementioned side branches cause the decrease of the chain density, which generates the polymer density to reduce.
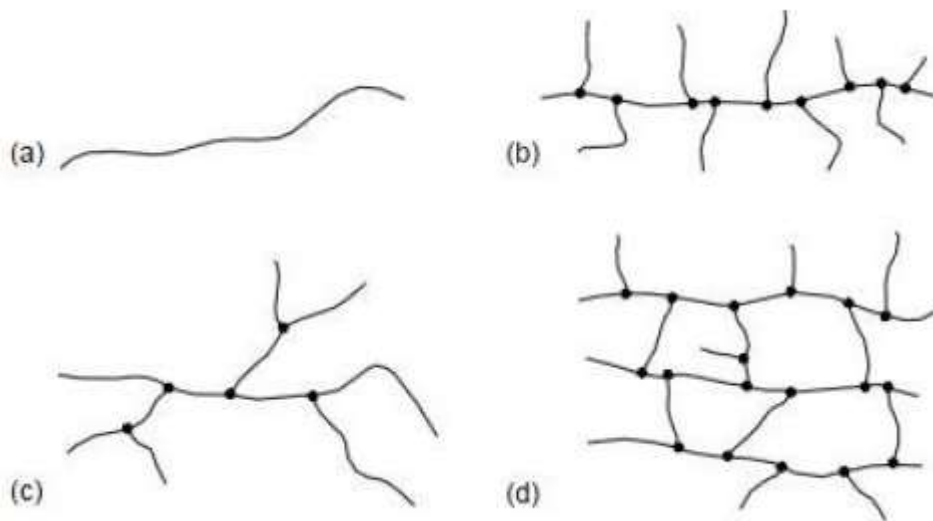
Figure 1.2 a) Linear b-c) branching d) cross-linking [3].

1.2 Crystallization of HDPE

Morphology determining the macro structure is essential as well in addition to the chemical formula that determines the local structure of polymers. In regard to morphology, the presence of crystalline or amorphous regions in the structure of the polymer in the solid state comes to mind, their size, shape, settlement order, and distribution in the structure. There are two basic intermolecular distributions in solid polymers called amorphous and crystalline structures [4].

A spaghetti bundle or a group of living worms can be held up as an example for amorphous polymers. A group of worms establishes a better analogy because of the constant motion of the polymer molecules. Continuous motion in space is not the movement of all worms together, rather the movement of every single one individually. Chains make random twisting and twisting movements from one conformation to another [4].

In crystalline polymers, atoms are placed at certain points and entered into an immobile order. Depending on the crystallinity of the polymers, these unit elements come together to form structural shapes in larger, various shapes and ultimately determine the morphology of the polymer [4].

When polymers are solid, they generally show a mixture of amorphous and crystalline structures instead of 100% crystalline structure, which are called semi-crystalline polymers.

There are two different phases in the structure of HDPE, crystalline and amorphous. The regular phase of semi-crystalline polyethylene consists of crystals in which the chain segments are arranged in regular order. While the crystalline thickness of the molded HDPE sample is generally between 80-200 Å, its lateral dimension is up to a few micrometers. The non-crystalline region separate from the crystalline region varies approximately in the range of 50-300 Å. A typical polyethylene molecule can have an unfolded length of 10000 Å or more, which is many times the thickness of the crystal. In this case, any molecule segment passes through its multiple times along the thickness of one or more regular and irregular regions [5]. Both phase regions play a major role in determining the macroscopic behavior of the material. The amorphous element allows the crystalline region to move and change its structure without losing its shape and is generally rubbery at room temperature. This type of deformation is often described as plastic. Molecular chains are unbreakable and deformation is often recoverable. This type of deformation provides high toughness in semi-crystalline polymers [6].

There is a third phase consisting of a chain segment at the boundary between the irregular/amorphous region and the crystalline surfaces called the interface or partially regular zone. In Figure 1.3, the interconnected crystalline, amorphous, and interfacial regions are demonstrated. The character of the interface region is particularly important as it creates a connection between the two main phases. In the case of the absence of the interface layer connecting the irregular and crystalline region, polyethylene would be a weak material. The characterization of the interface region is complicated because of its chain segments with different conformation. These chain segments adjacent to the crystalline surface are a much more ordered region than the irregular region. The boundary between the irregular and this partially regular region is indistinct and is not separated by a clear dividing line [5].
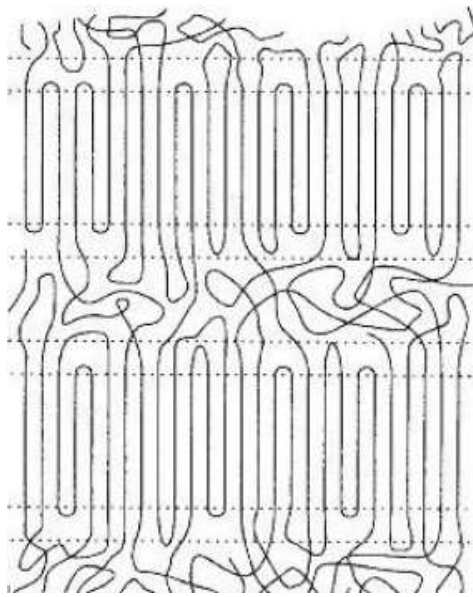
Figure 1.3 Morphology of triple phase in PE [7].

Polyethylene is a material consisting of a combination of crystalline and non-crystalline regions. A polyethylene consisting of just a crystalline matrix would be a brittle material, and if it were a completely amorphous material it would be a highly viscous fluid material. In practice, polyethylene is a tough and elastic material. The arrangement, ratio and degree of connection of these three phases to each other determine the properties of a polyethylene material. Neither completely pure crystalline nor completely pure amorphous polyethylene material exists [5].

Polyethylene generally becomes crystalline from molten state. Polyethylene crystallized from molten state has a spherical crystalline morphology. Here the lamellae forming the spherical crystal are embedded in an amorphous matrix and radiate out from the central core. Spherical crystals consist of thin flat lamellae as shown in Figure 1.4. The structure of the lamellae generally consists of a regularly folded chain arrangement. Expansion of regularly folded chains of a lamella; Its size in the lateral direction (1-50 μm) results in a crystal that is much larger than its thickness (2-25nm). In addition to the folded chain model, there are also lamella structures arranged in the form of irregularly folded (non-regularly folded), hair-pin and electrical panel (switch board). Studies have shown that both regular and irregular type crystal structure is present in melt crystallized polyethylene. In studies with

polyethylene, the regular folded chain model is used less than the irregularly folded chain model [8].
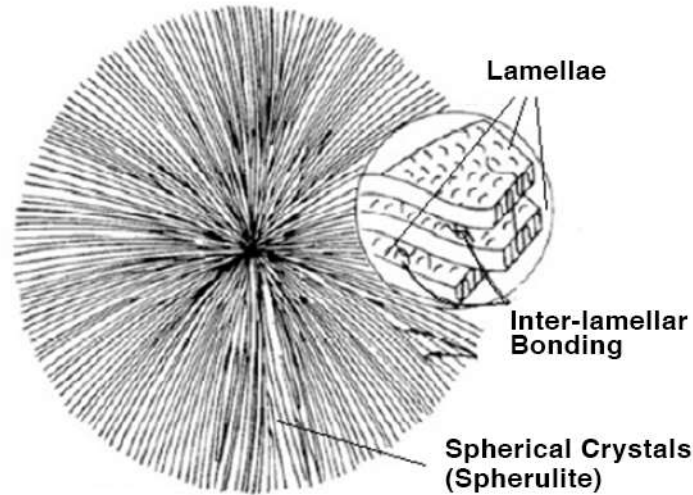
Figure 1.4 Schematic representation of the spherical crystal structure [8].

Spherical crystal formation occurs with growth by spreading in the form of circular areas from the center of the nucleus, and this growth stops when the advancing surfaces meet each other and primary crystallization is terminated [4]. Figure 1.5 shows that a spherical crystal and spherical crystals expanding from the nucleus meet each other as a result of the expansion.
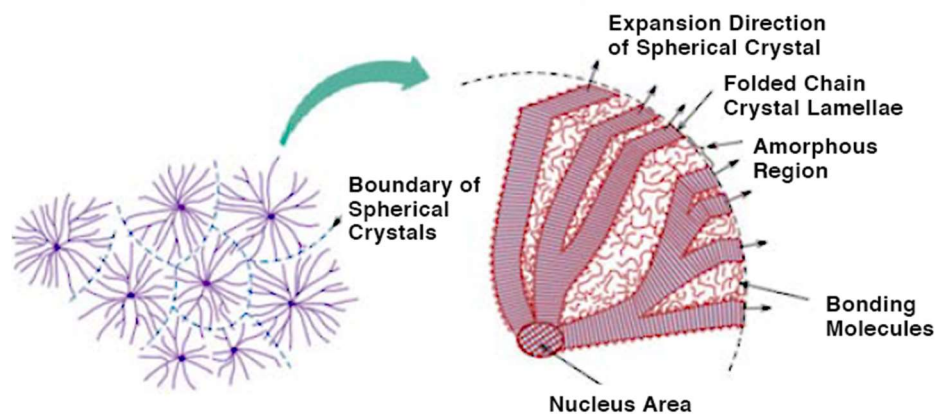
Figure 1.5 Spherical crystal expansion and the boundary they form with each other [9].

Crystallization of polyethylene is not always complete, even when the resulting sample is heated to room temperature. Secondary crystallization can continue at room temperature, albeit at a low rate. Different samples undergo physical changes in ambient temperature, ranging from a few hours to several weeks after molding. Changes in physical properties reflect a gradual increase in crystallinity. This effect is much more noticeable in a part with a medium initial crystallinity. A slow increase in density is observed when UHMWPE is rapidly cooled from molten to room temperature. The increase in density can be explained in two ways. (1) increase in percentage of crystal or (2) increase in density of this region as a result of recovery in the non-crystalline region [5].

During the solidification of the molten polyethylene, the liquid molecules in an irregular state turn into a regular crystalline state as the temperature drops below the melting point. The crystallization process varies depending on the cooling rate. The wide temperature gradient that occurs in the polymer production process causes different crystallinity in different parts of the product. This leads to a density difference in the product. By controlling the crystallization, the morphology of the material and the properties of the material can be controlled. Morphological properties of semi-crystalline polymeric material like HDPE also change according to cooling conditions. HDPE, which is cooled slowly while in the molten state, has a higher rate of crystallinity compared to fast cooling [6].

1.3 Mechanical Approach to HDPE

Polyethylene which is used in pipe industry may be investigated as its density difference. *High-density polyethylene (HDPE)* is a type of thermoplastic material composed of carbon and hydrogen atoms combined together forming high molecular weight products. Firstly; methane gas is converted to ethylene after that, applying of required heat and pressure, into polyethylene. Chain of polymer can be 500,000 to 1,000,000 carbon units long and size of chain molecules determines to mechanical property of HDPE. The longer chain means that has the greater the number of atoms, and so that, the higher the molecular weight. Additionally, greater molecular weight, and the amount of branching directly effect to mechanical and chemical property to end- product [2].

HDPE may be a non-linear viscoelastic fabric with time-dependent properties. A thermoplastic pipe, serving as it were one component of a pipe/soil composite structure, benefits by its property of stretch unwinding wherein stresses (strengths) are shed and exchanged to the soil.

Cell classification according to ASTM D 3350 is given in Table 1.1, briefly.

Table 1.1 Cell classifications for density and molecular weight [2].

CELL CLASSIFCATIONS (ACCORDING TO ASTM D 3350)			
Property	**ASTM Specification**	**Classification**	**Classification Requirement**
Density	**ASTM D 1505 –** Test Method for Density of Plastics by the Density-Gradient Technique	3	$0.941 - 0.955$ gr /cm^3
Melt index (MI)	**ASTM D 1238 –** Test Method for Flow Rates of Thermoplastics by Extrusion Elastomers	3	$0.4 >$ MI ≥ 0.15
Flexural modulus (E$_f$)	**ASTM D 790 –** Test Method for Flexural Properties of Unreinforced and Reinforced Plastics and Electrical Insulating Materials	5	$758 \leq E_f \leq 1103$ MPa $110{,}000 \leq E_f \leq 160{,}000$ psi
Tensile strength F$_t$	**ASTM D 638 –** Test Method for Tensile Properties of Plastics	4	$21 <$ ft < 24 MPa $3000 \leq$ ft ≤ 3500 psi
Slow crack growth resistance – Environmental stress crack resistance (ESCR)	**ASTM D 1693 –** Test Method for Environmental Stress-Cracking of Ethylene Plastics	2	Test condition B, 24 hr duration 50 % failure (max)
Hydrostatic Strength Classification – Hydrostatic Design Basis (HDB)	**ASTM D 2837 –** Obtaining Hydrostatic Design Basis for Thermoplastic Pipe Materials	0	(not pressure rated)
Color (C)	(not specified by ASTM)	C	$2\% \leq C \leq 5\%$

Consistency of execution of a pipe in benefit (stretch, strain and distortion reactions, steadiness) requires information of the mechanical properties of the HDPE tar and information of the geometry. ASTM D 3350 tar cell classifications give the implies for recognizable proof, near characterization and determination of fabric properties for polyethylene. Producers of HDPE waste channels may select higher cell classifications than the minimums required by these determinations in order to optimize competing financial and execution limitations of generation, dealing with and benefit.

1.3.1 Density effect on mechanical properties

Polyethylene density is a metric of the proportion of crystals within its mass. Crystals are denser than the twisted, disordered arrangement of molecules in the amorphous regions as a result of the layering and tight packing of polyethylene molecules. In order to establish and regulate the formation of side branches, copolymers are also used. Homo-polymers are formed without copolymers and undergo very little branching, with densities of 0.960 and above. Butane, hexane or octane are added to create a copolymer in order to decrease the density. Two carbon units long; hexane, four carbon units long; and octane, six carbon units long, would add branches of Butane. The longer the length of the carbon chains that are branched, the lower the final density.

1.3.2 Effect of molecular weight distribution on mechanical properties

If a polymeric structure consists of polymer chains of the same size, this is monodispersed. However, many polymeric structures have quite different lengths of polymer; these types of polymers are called, poly-disperse systems. Therefore, polymers are they do not have molecular weight. It's not just molecular weight, it's the polymer heterogeneous structure, i.e. molecular weight distribution, all properties of the final product dramatically change.

Short chains act as lubricants (inner slider) during the process and facilitate flow, while long chains determine the strength. The fact that the small chains are relatively more causes the material to be relatively harder because of the more chains that can easily crystallize. The fact that the chain lengths are very different from each other leads to the formation of crystal structures of different sizes and structures; small chains act as a weak point, causing a decrease in impact strength. In this case, they cannot be strong enough when they are loaded.

1.3.3 Effect of melt index on mechanical properties

Melt flow Index is a basic method to investigation of the viscosity of the molten plastic resin. It is a parameter related to the average molecular weight of polymer resin chains extruded from a standard size hole under a specified pressure and temperature conditions over a ten-minute period. The larger the lengths of the molecules, the greater the molecular weight and the greater the difficulty in extruding the resin through the standard hole. The result: resins with higher viscosity as measured with lower melt flow rate. According to TS EN 1133; test is performed at standard weight as 5 kg and 190 °C. The higher the viscosity is referred the lower the melt index value.

A lower Melt Flow Index in polymers means higher average molecular weight which has is higher tensile strength, toughness, and higher stress crack resistance. However, the lower the Melt Flow Index the required greater energy to production process of extrusion. The effects of density, molecular weight and molecular weight distribution on physical properties of HDPE is given Table 1.2.

Table 1.2 The effects of density, molecular weight and molecular weight distribution on physical properties [2].

EFFECTS OF CHANGES IN DENSITY, MELT INDEX AND MOLECULAR WEIGHT DISTRIBUTION			
Property	As Density Increases, Property:	As Melt Index Increases, Property:	As Molecular Weight Distribution Broadens, Property:
Tensile Strength (At Yield)	Increases	Decreases	
Stiffness	Increases	Decreases, Slightly	Decreases, Slightly
Impact Strength	Decreases	Decreases	Decreases
Low Temperature Brittleness	Increases	Increases	Decreases
Abrasion Resistance	Increases	Decreases	
Hardness	Increases	Decreases, Slightly	
Softening Point	Increases		Increases
Stress Crack Resistance	Decreases	Decreases	Increases
Permeability	Decreases	Increases Slightly	
Chemical Resistance	Increases	Decreases	
Melt Strength		Decreases	Increases
Gloss	Increases	Increases	Decreases
Haze	Decreases	Decreases	
Shrinkage	Decreases	Decreases	Increases

Average molecular weight measured by MI provide identification of molecular weight distribution instead of range of chain lengths within molecules; Polyethylene groups of the same MI and same density may have very different properties if their molecular weight distribution (MWD) are different. A polymer with a narrow MWD crystallizes faster and with greater uniformity, providing less distortion and greater fidelity to the intended geometry. A polymer with a large MWD can have better stress crack resistance, impact resistance, and ease of processing.

The property of polyethylene related to the arrangement of the molecular chains. The molecular chains, has three-dimensional, lay down in wavy planes. Branching on the main chains, are side chains of varying lengths. The number, size and type of these side chains determine, the properties of mechanical properties such as, elongation, stiffness, tensile strength, flexibility, hardness, brittleness, creep characteristics and melt viscosity which directly affect the results of the manufacturing parameters and service performance of polyethylene pipe [2].

Polyethylene can be defined as a semi-crystalline polymer, consist of crystalline regions and also amorphous regions. Crystalline regions shortly explain as perfect structure which are highly ordered, neatly folded, layered, and high dense packed molecular chains [2]. Branching in polyethylene directly affect the density, melt point and also crystallinity. Diagrams in Figure 1.6 show differences in branching affect to melt points and density. Crystal structure of PE is shown in Figure 1.7. While shaded rectangles indicates that highly ordered areas in crystalline region; high degree of branching in PE reduces the size of the crystalline regions.
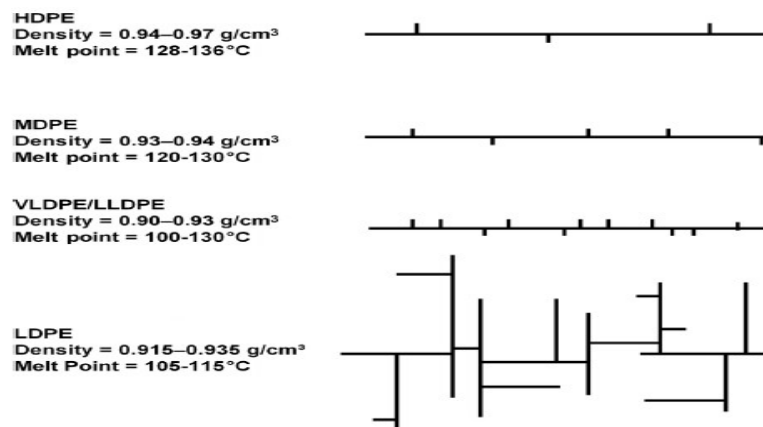
Figure 1.6 Graphical description of polyethylene types [7].
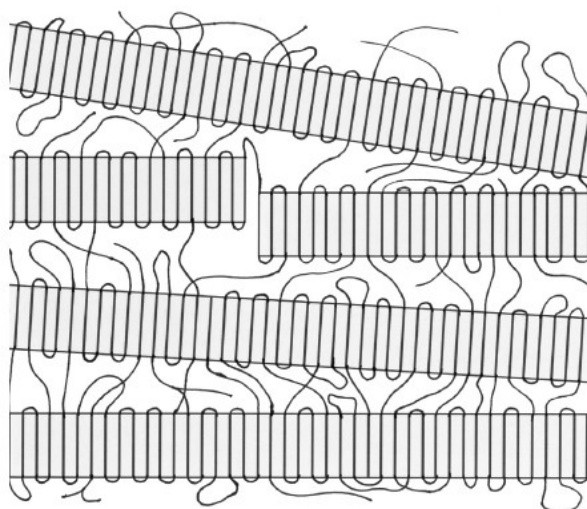
Figure 1.7 Schematic of polyethylene crystal structure [7].

HDPE is defined as a member of thermoplastics which can be reshaped or moldable at elevated temperature. However; with some reinforcing, HDPE can be converted to thermosetting polymers. In this way; HDPE exhibit higher strength, impact resistance, thermal resistance. Converting to thermosetting can be explained by crosslinking methods. Crosslink may be defined as process that; covalent or ionic bonds to join two polymers chain. Curing process related to crosslinking of thermosetting polymers.

After the discovery of HDPE; introduction of cross-linked polyethylene shortly called is PEX in the 1970's was another innovation for plastic industry. Since 1970; PEX has highly preferred by the market because of its excellent properties when compared to other commercial polymers. Crosslinking process can be performed by mainly chemically process, which based on the induce of linking to polymer chain which needs chemical initiator such as peroxide or silane [10].

Crosslinking reaction by peroxide takes place in three steps:

Step I:

This step based on homolysis process which is performed oxygen bond break and then unpaired electron stays in each oxygen atoms and promotes the formation of peroxide radicals. All of this process; happens by the peroxide thermal decomposition because of addition heat.

Step II:

Each peroxide radical reacts with the PE molecule, i.e., abstracts a hydrogen atom from the polymer chain, becoming a stable ROH species. The abstraction of hydrogen causes the formation of polymer radicals.

Step III:

Two polymer radicals react with each other forming stable PEX.

Today; peroxides process is commonly used for the production of HDPE pipes in terms of improving mechanical properties. The peroxide which has liquid or molten phase, is sprayed on PE granules, they are mixed properly. Second one is extrusion manufacturing process; The compound which can be also soaked granules plus eventual additives is poured into the hopper of extruder where it is shaped and melted for available temperature. The cross-linking reaction starts with the temperature of head of extruder. When the melted polymer granules meet to high pressure which is performed by screw, curing process is started; The extruded product are cross-linked optimum under temperature and pressure [10]. Schematic for Cross-linked- HDPE is shown in Figure 1.8.

Figure 1.8 Schematic for cross-linked- HDPE [10].

Cross-linked polyethylene is commonly applied in packaging industry, electric-electronic fields, medicine, and civil engineering. In this study; importance of cross-linked were observed in terms of application in pipes.

PE-X is preferred Cross-Linked polyethylene. "PE" represents the polyethylene raw material and "X" represents the crosslink.

Polyethylene (PE-X) pipes are used in plumbing, heating installation, gas installation and compressed air installation. Example of usage area of HDPE is given Figure 1.9 Pipes are available in very large lengths in coils. Thus, fewer fittings need to be used. It is not fragile, it can burn. It can be delivered in soft and hard PE. Polyethylene pipe can be made resistant to pressure by creating intermolecular cross-links with special processes.
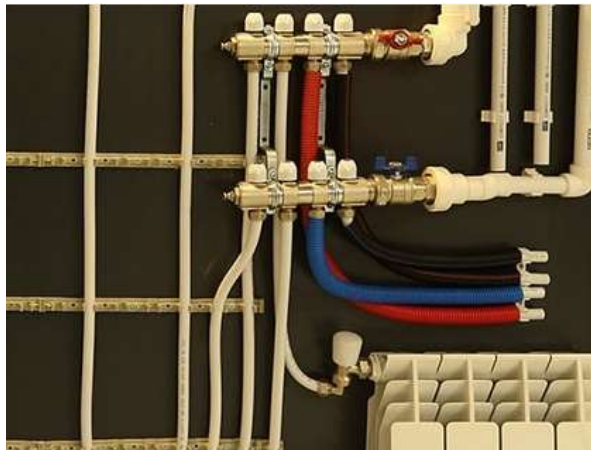
Figure 1.9: Electrical cables produced by cross-linked PE [11].

These pipes can be used in hot water installations, especially in floor heating applications. PE-X pipes are non-corrosive, practical and easy to cut, their diameter does not shrink, rot or calcify. PE-X pipes maintain their strength properties between -100 °C and +110 °C. Polyethylene raw material is a material with high density. As a result of some processes performed on this material, its resistance to temperature and pressure is increased. PE-X pipes can be manufactured in two different ways, with or without an oxygen barrier. The oxygen barrier is provided by coating the outer surface of the pipe with a special material during manufacturing. The barrier protects the metal parts of your installation from the corrosive effect of the oxygen passing through the pipe surface to the heating fluid.

It is the most used pipe type in underfloor heating installation. PEX pipes are produced as coils. PEX pipes are laid in a protective cover in underfloor heating installation. The main function of the protective cover is to prevent impacts on the PEX pipe, to prevent the PEX pipe from wearing out and to allow the pipe to be changed easily in case of any damage. One of its important tasks is that the flexes that may occur in the pipe during the PEX pipe heating can damage the screed floor. In order to prevent such negativities, PEX pipes are laid in a protective cover. Summarize, superior features of PEX pipes are given in below respectively;

- Thanks to their flexible structure, they are suitable for shaping and can be easily applied to the floor.

- It does not lime, rust or corrode.

- It is light, easy to carry and install.

- It has a low friction coefficient.

- As it is produced as coils, it is laid without wastage.

- It is resistant to chemical substances.

- It does not transfer the oxygen in the air into the pipe.

- Long service life (50 years)

In 2019; Global High Density Polyethylene Market was valued US$ 66.24 and is expected to increased US$ 87.5 Bn by 2026 at CAGR of about 4.32 % during forecast period [12]. Global Market Value HDPE is shown in Figure 1.10
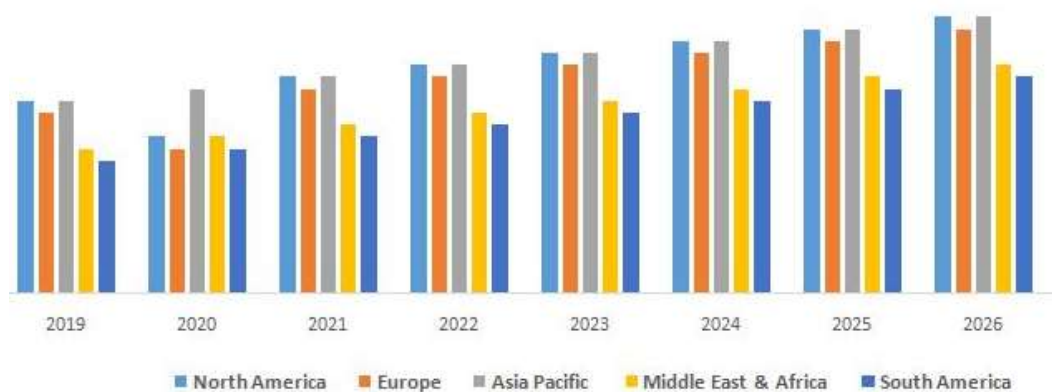
Figure 1.10 Global market value HDPE [12].

In 2017, with the packaging industry, Asia Pacific was the largest market for HDPE in. It is expected that; boost of using in countries like China and India which are increasing government spending on infrastructure development [12]. Scope of global HDPE market is shown in Table 1.3.

Table 1.3 Scope of global HDPE market [12].

Global HDPE Market, by End User	Global HDPE Market, by Application	Global HDPE Market by Region	Key Players in Global HDPE Market
- Packaging - Transportation - Electrical and Electronics - Building and Construction - Agriculture - Industry and Machinery	- Film and Sheet - Blow molding - Injection molding - Pipes and Tubes	- North America - South America - Middle East Africa - Europe - North Africa	- SABIC - Dow Chemical Corporation. - Exxon Mobil Corporation. - INEOS - Lyondell Basell Industry - Formosa Plastics Corporation - Chevron Phillips Corporation - Braskem S.A

1.2 Review of Fire

Fires can lead to the death of people, material losses, and the loss of unique historical artifacts. As a result of rapid population growth, distorted urbanization and rapid industrialization all over the world, the number of fires that occur each year and the amount of damage caused by fires are increasing.

Approximately 12 fire victims and 120 people were seriously injured per diem in Europe and the World Health Organization noted that there were approximately 300,000 deaths per year from fire-related burns. In 2009 more than 1,300 fires in the United States were carried out by the local fire brigade, resulting in 3,010 civilian casualties and 17,050 civilian casualties. According to joint indicators of fire statistics in world countries in 2003, there are about 505 deaths in Turkey [13]. Unfortunately,

it is not possible to reduce the risk of fires occurring. For this reason, products that have to be protected against fire must be designed. At this point, fireproof products come to the fore. These can be defined as substances that do not ignite at all or stop the progression of the flame after ignition and end the burning event. Fireproof materials can be produced thanks to auxiliary flame retardant additives that are included in combustible products. These substances can be used directly in the production of the materials we use or they can be added to the combustible materials in certain ratios to make the final product flame-retardant. For example, plastics, textiles, furniture, electrical goods.

Flame retardant materials, which have gained importance in recent years with their features such as reliability, fire resistance and delaying the spread of fire, appear in various types. Considering the market and consumption situation, it is estimated that the flame retardant and smoke suppressor consumption was around 1 million tons in 2016. This corresponds to a market of $ 2 billion annually. Different flame retardant materials can be added to different polymer systems. Since polymers are organic substances, they are easily affected by fire / flame. Flame retardant additions are a measure of the resistance to fire. After all; polymers burn. However, the importance of flame retardants is due to delaying catastrophic burning or minimizing fire damage.

Flame-retardant substances prevent the flames from spreading even if the fire has started, helping to extinguish the fire in the early stages. It saves time for those in the area to escape. As; it will be increased to using fireproof materials, the time gained for security will increased that much.

1.3 Flame Retardant Mechanism

Flame retardant term is a chemical reinforced to flammable materials such as plastics, textiles to give them more resistant ignition. Flame retardant are intended to prevent or slow the further development of ignition; therefore, it minimizes the risk of fire starting and increases the safety of lives and property.

It is desirable that the flame retardant substances generally have flame retardant effect and that they do not harm the processing properties of the main material into which they are incorporated. Flame retardant additives added in certain proportions both

dilute the flammable base material and reduce the oxygen index of the parent substance. The mechanism of flame retardant is quite complex and suddenly comes into being when several different mechanisms are intertwined. There are three mechanisms that determine to the material's incombustibility.

First flame retardant mechanism is vapor phase inhibition. Free radical groups known HC are created by vapor phase which improves combustion process when the polymer burns. Additives as alone or combination with other materials, provide flame retardation by inhibiting the creation of radicals released from the bottom layers by chain reactions. This is the working principle for Brominated and Chlorinated flame retardants. If Sb_2O_3 is present in the environment; the effects combined. The reaction between halogenated materials and Sb_2O_3 forms volatile $SbCI_3$ therefore free radicals are created as a result of thermal decomposition. For this reason; the brominated and chlorinated materials are used in combination with Sb_2O_3. $SbCI_3$ may use flame retardant as alone. Sb_2O_3 is used PVC and in this case the polymer itself serves as a halogen source. Steps of thermal decomposition of Sb_2O_3 is shown in Figure 1.11 and all of the reactions of decomposition of Sb_2O_3 are given in following equations (1.3.1) through (1.3.6).
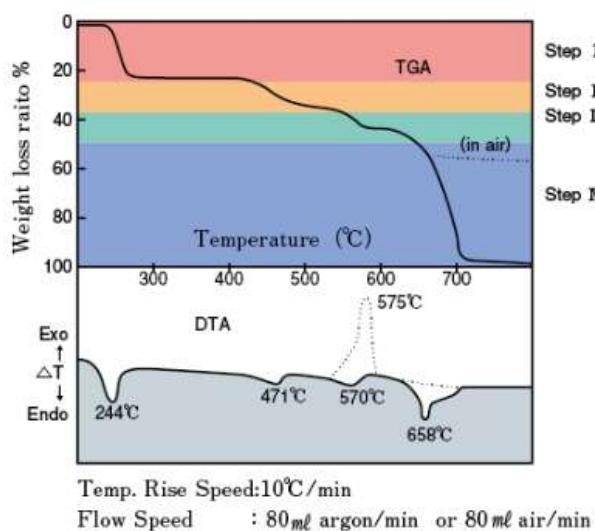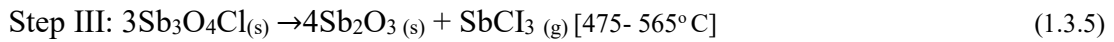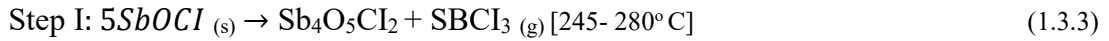

Figure 1.11 Thermal decomposition of Sb_2O_3 [14].

$R \cdot HCI \rightarrow R + HCI$ [250° C]   (1.3.1)

$2HCI + Sb_2O_3 \rightarrow 2SbOCI + H_2O$ [250° C]   (1.3.2)

Step I: $5SbOCI_{(s)} \rightarrow Sb_4O_5CI_2 + SBCI_{3\ (g)}$ [245- 280°C] $\hspace{2cm}$ (1.3.3)

Step II: $4Sb_4O_5CI_{2\ (s)} \rightarrow 5Sb_3O_4CI_{(s)} + SbCI_{3\ (g)}$ [410- 475°C] $\hspace{1.5cm}$ (1.3.4)

Step III: $3Sb_3O_4Cl_{(s)} \rightarrow 4Sb_2O_{3\ (s)} + SbCI_{3\ (g)}$ [475- 565°C] $\hspace{1.5cm}$ (1.3.5)

Step IV: $Sb_2O_{3\ (s)} \rightarrow Sb_2O_3$ ($\rightarrow$ Step I) [658°C] $\hspace{2.5cm}$ (1.3.6)

The second mechanism is endothermic reaction. Materials decomposition with heat act as flame retardants with a combination of various effects. The decomposition reaction is strong endothermic so that the heat escapes from the combustion surfaces, the burning lower layer cools down and eventually the flames spread and smoke formation is limited. If the gaseous by products are released as a result of decomposition reaction, it causes the heat load to spread further in the immediate vicinity of fire. Gas products also reduce the oxygen concentration in the combustion zone, thus reducing flame spread.

The last mechanism is the intumescent motion; in the pre-combustion phase it is called to form a stable volumetric core (char) on the plastic surface which ensures that the combustible polymer is isolated from the continuing combustion. Components of the swelling formation include: Oxalic acid, such as strong phosphoric acid by heating, forms a protected polyalcohol type compound and creates a gas source for the formed protection foaming. Typical systems are organophosphates or inorganic phosphates (ammonium phosphate) oxyacid source; pentaerythritol is a multifunctional alcohol molecule and melamine is found as a nitrogen gas generator.

1.4 Combustion of Polymers

Polymers are extremely flammable because of their chemical structure, consist of carbon and hydrogen [15]. Amount of heat released directly effect to the service time of the combustion, the during the burning of the fuel. Combustion process depending on changing of lots of decomposition reactions. New decomposition reactions start with releasing of required heat reaches to critical level. In this way; intensity of combustibles is increased. Cycle of combustion is keep going in that way and called a fire triangle as presented in Figure 1.12 [16].
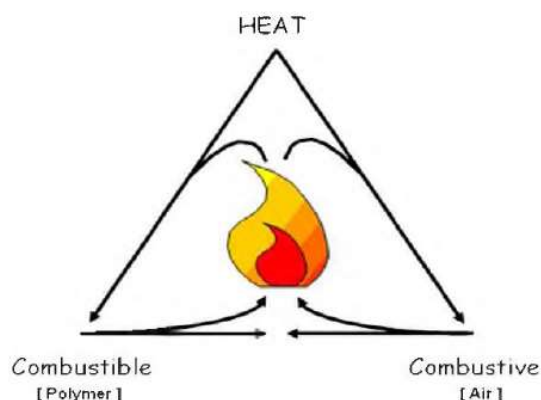
Figure 1.12 Fire Triangle [16].

First of all; heat source contacts with highly flammable polymer materials. During this event; simultaneously oxygen from air reacts with degradation products in polymer to produce a flame. Some polymers have low ignition temperature so it makes them resistant to fire. Safety factor is related to; ignition temperature of polymers is being higher [17].

Dissociation of covalent bond is needed to happening of thermal decomposition of a polymer. Therefore, energy must be entered to system. This concept shortly as endothermic reaction. The energy which is entered to system should be much more than binding energy between atoms which covalently bonding. (200-400 kJ/mole for most C-C polymers). Furthermore; thermal decomposition can be taken place with existing weak bonds and absence or presence of oxygen in any phase. Mostly, thermal decomposition of polymer is concept which is combination of the effects of oxygen and heat simultaneously [15].

Extinguishing a flame of polymer depends on the mechanism of thermal decomposition of the polymer. Polymers of thermal decomposition can be based on four general mechanisms. First one is *separation of random chain* in which the backbone of polymer is randomly break into small pieces. Secondly; *chain-end scission*, which is about polymer depolymerizes from the chain ends. Third one is elimination of pendant groups (chain stripping) without breaking of the backbone (cleaved off); and Fourth one is cross-linking which is bonds created between the polymer chain. There are only a few polymers decompose thermally by one certain

mechanism; generally, two or more mechanisms are needed to effect of decomposition [31]. In Table 1.4; some polymers degradation mechanisms are shown.

Table 1.4 Thermal decomposition of some polymer [17].

Mechanism	Examples of Polymer	Typical Products
Random chain scission	Polyethylene Polypropylene Polystyrene More Generally	Alkanes, alkenes very little monomer, Styrene monomer, dimer and trimer, Monomers and oligomer
End- chain scission	PMMA PTFE More generally	90%- 100% monomer 90%- 100% monomer Monomer
Chain stripping	Poly (vinyl chloride) Polyvinyl alcohol General	Hydrogen chloride aromatic hydrocarbons and char Water and char Small molecules and char
Cross-linking	Polyacrylonitrile, poly(oxy-m-xylene) General	Char (and HCN), char Much Char, few volatile products

Flammability concept in polymers can be correlated strengthens or chemical structure like straight chain or branched chain. Thermal half time of polymers and effect of chemical structure on combustion process of polymer is presented as Table 1.5 and Table 1.6. Cross-linking or removing pendant group make gain strength to polymer structure. Cross-linking provides to precursors of char and finally polymer resists to flammability [17]. Thermosets which do not melt and decompose yielding char and evolving volatiles however; thermoplastics softens and melt before decomposing. In the other words; pure polymers degraded by kinetic process. Half-life of polymers equaled 30 min called as T_h. Madorsky method was found that a polymer has lost half of its initial weight in 30 min. However, T_h only related to assumption of first order decomposition process so fundamental decomposition process should not be resulted from value of T_h.

Table 1.5 Thermal half-life of polymers [17].

Polymer	T_h (ºC)
Polymethlmethacrylate A (molecular wt. 1.5 x10^5)	283
Polymethlmethacrylate B (molecular wt. 1.5 x10^5)	327
Poly a-styrene	287
Polyisoperene	323
Polymethylacrylate	328
Polyethylene oxide	345
Polyisbutylene	348
Polystyrene	364
Polypropylene	387
Polydivinyl benzene	399
Polyethylene	406
Polymethylene	415
Polytetrafluoroethylene	509

Table 1.6 Thermal stability of some polymers [17].

Polymer	Effect on Thermal Stability	Examples	T_h ºC
Chain branching	Weakens	Polymethylene	415
		Polyethylene	406
		Polypropylene	387
		Polyisopropylene	348
Double bonds in polymer backbone	Weakens	Polypropylene	387
Aromatic ring in polymer backbone	Strengthens	Polyisoprene	323
		Polybenzyl	430
High molecular weight	Strengthens	Polystyrene	364
		PMMA B	327
		PMMA A	283
Cross linking	Strengthens	Polydivinyl benzene	399
		Polystyrene	364
Oxygen in the polymer backbone	Weakens	Polymethylene	415
		Polyethylene oxide	345
		Polyoxymethylene	<200

Schematic of polymer fire is given in Figure 1.13. The flame is feed by combustible by product of pyrolysis escaping from the polymer surface owing to heat being conducted from the flame in contact with the polymer surface and also that radiated from the flame [18].
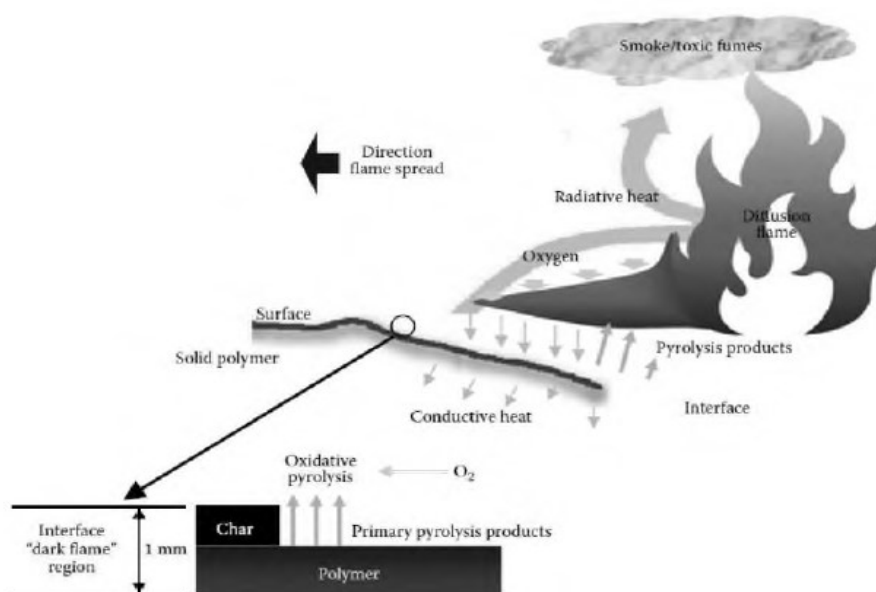
Figure 1.13 Schematic representation of a burning polymer [18].

1.5 Thermal Degradation of Polyethylene

PE thermally degrades by random scissions of the chains, the products being dependent on the reactivity and possible reactions of the various radicals produced. The predominant products appear as a cold ring fraction (CRF). When each of these polymers is degraded to beyond 800/0 weight loss, the percentage by weight of CRF for PE, to> 90%. The volatile products when produced by degradation of PE were occurred from de-polymerization or intramolecular transfer [19].

PE shows a decrease in molecular weight due to scission at these structures, which provide weak links [19]. Figure 1.14 depicts thermal degradation of PE.

Figure 1.14 Steps of thermal degradation of PE [19].

Considering the studies in the literature, Jian-dong et al (2008) enhanced flammability properties of ABS by using decabromodiphenylethane (DBDPE) and antimony trioxide (Sb_2O_3). Sb_2O_3 supplied as powder form. As production process; DBDPE and Sb_2O_3 were blended with ABS, High Impact Polystyrene (HIPS) and PP at a certain proportion to granulate in a two-screw extruder. Thermal characterization of composites was studied by cone calorimeter and termogravimetry (TG). Results shown that, Increasing the content of Sb_2O_3 in ABS matrix makes flammability and thermal stability of fire retarded are greatly improved. It may be concluded that, S_2O_3 has good synergistic effect with DBDPE.

Ran et.al (2014), to improve thermal stability and flame retardancy of high-density polyethylene, produce composite consist of Graphene Nano platelets (GNPs), with brominated polystyrene (BPS) and antimony trioxide (Sb_2O_3). Production process performed by thermomixer and traditional press method after HDPE reached melt compounded. The combination of the BPS–Sb and GNPs in the HDPE matrix has UL-

94 V2 level. When compared sample of the BPS–Sb in HDPE matrix; adding GNPs provides flame retardancy property to HDPE matrix

Altunbaş et al (2017), compared the effects of boron based fire retardants in matrix of medium-density fiberboard waste (MDFw) filled high-density polyethylene (HDPE). To investigation difference in flame retardancy, synergistic influential compounds which are, Antimony trioxide (Sb_2O_3), ammonium phosphate ($NH4)_3PO_4$), and magnesium hydroxide (Mg $(OH)_2$) were used. A twin-screw extruder was used to obtain composite pellets and then all pellets were pressed to take composite board. Results showed that, samples of H-CB (47 % MDF, 40% HDPE, 12% Zinc Borate, 1% PE wax) has lower burning rate as 7.33 mm/min and higher tensile strength with 13.1 MPa than samples of H-ACB (consist of 47% MDF, 40% HDPE, 6% Zinc Borate, 6% Sb_2O_3, 1 PE wax) which has burning rate of 10.25 mm /min and 12.9 MPa.

Zhang et al. (2010), the influences of expanded graphite (EG) on the thermal properties of chlorinated paraffin (CP) and antimony trioxide (Sb_2O_3) on phase change material which bases on paraffin/high density polyethylene (HDPE) are studied. The microscale combustion colorimeter (MCC) results indicated that the more mass fraction EG in the PCM (phase change materials) showed lower value of heat release capacity (HRC) and total (heat release) HR. The cone calorimeter experiment approved that the addition of EG in Paraffin/HDPE matrix, provide, reducing in the peak heat release rate (pHRR) of the PCM. Sample of PCM4 consist of Paraffin 50 % + HDPE 15% + (CP + AT)30 % + 5 % EG which has better flame retadancy properties than other samples.

Niu et al. (2018) applied nano-Sb_2O_3 and brominated epoxy resin (BEO) in matrix of poly(butylene terephthalate) (PBT) to investigate flame retardancy and mechanical properties of PBT. As production process, nanocomposites specimens prepared by traditional melt blending method. While neat/PBT has 28 % LOI - not rated of UL-94 tests, sample of PBT/BEO/nano-Sb_2O_3 1% has 24.6 % LOI and V1 level of UL-94 test. Moreover, sample of PBT/BEO/nano-Sb_2O_3 5% has 28.7% LOI and V0 level of UL-94 test. Another remarkable point in study, tensile strength improved until 3% reinforced Sb_2O_3. However tensile strength decreased nano-Sb_2O_3 content reached 5 wt %. The decrease of the tensile strength was due to the poor dispersion of the nano-

Sb_2O_3 particles in the PBT matrix and the low level of interfacial adhesion between the two components.

Aim of this study was to manufacture fire resistive HDPE composites by using two different types of commercial flame retardant masterbatches including Sb2O3. The samples obtained after the production of composites were examined structurally, their mechanical and non-flammability properties were determined and their suitability for industrial use was investigated. This study was performed to be beneficial for industrial organizations especially the pipe manufacturers based on HDPE. In this way, the cost and energy will be saved and guiding the formulation of the factory for its production process.

As production process, first of all, compounding process was performed by twin-screw extruder, all of ingredient mixed in proper ratio and head of extruder disassembled before pelletizing process. In this way; melted paste obtained to pressed. At the end of the pressing process, specimens were ready to testing. As mechanical investigation of specimens; tensile test; as characterization of specimen; FTIR, TGA, SEM/EDX analyses taken placed. In addition; to examination of flame retardancy properties of plastics specimens; UL-94 vertical test performed each samples as a main objective of this study.

The following considerations contain the targeted originality of this study; the above literature results show that Sb_2O_3 is generally used together with one or more additives to provide synergetic effect such as flame retardant properties for the plastic matrices. In this study, specifically, we aim to contribute the flame retardancy while saving direct mechanical conditions of microduct pipe based on HDPE by using commercial flame retardant masterbatch. By considering of related literatures, we have accomplished flame retardant property for HDPE matrix by lower percentage of commercial masterbatch.

2. EXPERIMENTAL PROCEDURE

2. 1 Materials

2.1.1 Matrix material

PETILEN YY B00552 is a high density polyethylene copolymer resin developed for high pressure pipe extrusion. The structure of the material is bimodal and it has broad molecular weight distribution. The product's excellent ESCR and long term hydrostatic strength proves an advantage especially in underground applications. Table 2.1 demonstrates the properties of HDPE matrix.

Table 2.1 Properties of HDPE matrix.

Properties	Typical values	Units	Test Methods
Resin Properties			
Melt Flow Rate (190°C/2.16 kg)	0.05	g/10 min	ASTM D1238
Melt Flow Rate (190°C/5 kg)	0.25	g/10 min	ASTM D1238
Density, 23°C	0.950	g/cm³	ASTM D1505
Melting Point (DSC, 2nd heating)	131	°C	ASTM D3418
Oxygen Induction Time	> 20	min	TS EN 728
Volatiles	<350	mg/kg	TS EN 12099
Moisture Content	<300	mg/kg	TS EN 12118
Mechanical Properties			
Tensile Strength at Yield	24	MPa	ASTM D638
Tensile Strength at Break	31	MPa	ASTM D638
Elongation at Break	875	%	ASTM D638
Flexural Modulus,	950	MPa	TS EN ISO 178
Izod Impact Strength, 23°C (notched)	380	J/m	ASTM D256
Hardness (Shore D)	63	-	ASTM D2240
Environmental Stress Cracking Resistance (10% Igepal, F50)	>3000	h	ASTM D1525

2.1.2 Reinforcing materials

2.1.2.1 Fr-kk additive

FR-KK masterbatches inhibit or prevent the combustion process. Material is in pellet form. It is convenient for processing temperature higher than 260°C. It includes

intensely, Sb_2O_3 and also halogen elements such as Br and CI to provide synergistic effect to extinguish. Table 2.2 is represented of commercial flame retardant additives.

Table 2.2 Properties of commercial flame retardant additives.

Physical Property	Test Method	Unit	Value
Carrier resin	-	-	LLDPE
MFR (150ºC -21,6 kg)	ASTM-D 1238-10	gr/10min	23±5
Density	ASTM D 792	g/cm^3	2,64± 0,03

2.1.2.2 Fr-m additive

Another Flame Retardant called as FR-M which has close properties with FR-KK, density of 2.10 gr/cm^3 MFI of 3g/10 min at 2.16kg/190ºC, appears White color and also includes Sb_2O_3 and halogen elements.

HDPE matrix-flame retardant additives samples can be 2 different categories according to their material to content. First group is reinforced FR-KK; second one is reinforced FR-M. Each groups includes different ratio of HDPE and also compare to reinforced specimen; Neat/HDPE specimen was produced. Weight percent of all samples are shown Table 2.3. Each samples were produced over 500 g.

Table 2.3 Formulations of flame retardant reinforced HDPE specimens.

	Petkim 552 %	FR –KK %	FR-M %
Neat HDPE	100	-	-
KK1	82	18	
KK2	79	21	
KK3	76	24	
KK4	73	27	
M1	95		5
M2	92		8
M3	89		11
M4	86		14

2.2 Production Process

2.2.1 Compounding process by extruder

Paste of composites were obtained by twin-screw extruder branded Labtech in Budin-Akarca Industry and Trade Limited Company. Initially; All of flame retardant additives and HDPE were blended. This new mixing was 500 g and after that; prepared mixing was placed to feeder of extruder and feed with 20 rpm. Screws are provided to moving of mixing to openings. Zone temperatures of extruder were set between 185°C and 240 °C. L/D ratio of the extruder was selected as 44:1 and screw speed was adjusted 190 rpm. Head of extruder was disassembled and paste of hot plasticized was obtained to pressing into plastic plate. Figure 2.1 shows the pressing process.
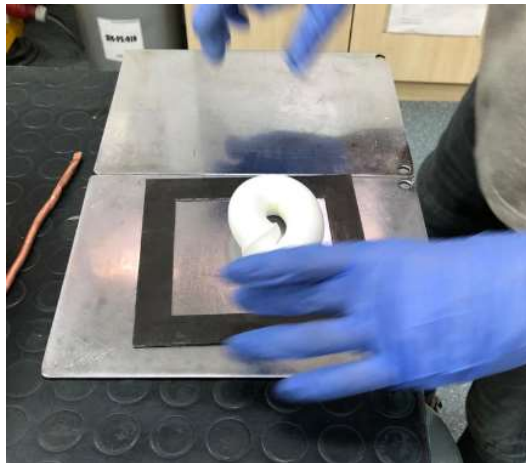

Figure 2.1 Pressing process of specimen.

2.2.2 Hydraulic presses machine

Pressing process was performed by machine branded of M Scientific/Labtech. First of all; hot pastes were placed into mold cavity between two Teflon plates. Pressing process applied by two identical moving platens. Process is performed by two different temperatures. Hot press was performed at 220° C for 20 seconds at 39 bar. After that; cold press was performed for 180 seconds about 25°C. At the end of the pressing process; Plastic plates was ready to take out of specimen to testing. Figure 2.2 is represented as specimens shaped in plastic plates.

Figure 2.2 Specimens shaped in plastic plates.

2.3 Testing Methods

2.3.1 Mechanical test

Tensile testing one of the most popular method for investigation of mechanical properties of any materials. Some concepts about test should be known, before application.

The force or load applied on a specimen creates a stress and elongation on the part. Stress; It indicates the strength of the force at any point on the part and is measured by the force acting per unit area. The dimensional difference that this stress makes on the part is called deformation.

When the applied force is outward from the part, this pulling force creates a tensile stress:

$$\sigma = \frac{F}{A}$$
(2.4.1)

If the original, un-deformed, cross-sectional area is used as the cross-sectional area, the resulting stress is the engineering stress. Tensile stress-strain values are obtained from the following equation 2.4.1 and 2.4.2

$$\varepsilon = \frac{\Delta l}{l_0} = \frac{(l - l_0)}{l_0}$$

(2.4.2)

ISO 6259 specifies a method of determining the tensile properties of polyolefin (polyethylene, cross-linked polyethylene, polypropylene and polybutane) pipes, and in particular the following properties: elongation at break and tensile strength

Specimens were cut to according to ISO 6259; section of Type-2 shown in Figure 2.3 with using a steel mold [20].
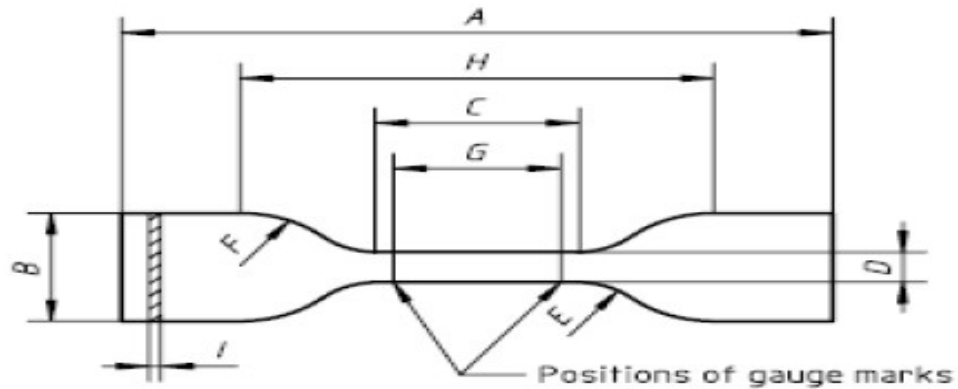

Figure 2.3 Schematic of tensile section according to ISO 6259-Type 2 [20].

Test pieces shall be either of type 2, the shape and dimensions of which are given in Table 2.4.

Table 2.4 Dimensions of tensile section [20].

Symbol	Description	Dimensions (mm)
A	Overall length (min.)	115
B	Width of ends	25±1
C	Length of narrow, parallel –sided portion	33±2
D	Width of narrow, parallel-sided portion	6±0.4
E	Small radius	14±1
F	Large radius	25±2
G	Gauge length	25±1
H	Initial distance between grips	80±5
I	Thickness	That of the pipe

The test speed, the speed of separation of the grips in tensile testing device directly depend on the thickness of the pipes, which are seen in Table 2.5.

Table 2.5 Requirement test parameters depending on thickness of pipe [20].

Nominal Wall thickness of pipe e_n mm	Method of preparation of test piece	Type of test piece	Test speed mm /min
$e_n < 5$	Die cutting or machining	Type 2	100
$5 < e_n < 12$	Die cutting or machining	Type 1	50
$e_n \geq 12$	Machining	Type 1	25
$e_n \geq 12$	Machining	Type 3	10

SHIMADZU AGS-X 5kN tensile machine was used for polymeric composites at room temperature with a crosshead speed of 100 mm/min. According to standards to obtain average value for each specimens; 5 section were taken each samples, it means that; 5 tensile testing is performed for one sample. Tensile test gives two crucial value about the mechanical properties o sample which are Elastic Modulus; conclude of slope of stress-strain curve and tensile strength which is the capacity of a sample to withstand loads tending to elongate. Figure 2.4 is represented as device of tensile testing.

Figure 2.4 Device of tensile testing.

2.3.2 Scanning electron microscopy analysis

Scanning electron microscope, shortly is called SEM, is a type of electron microscope that obtains images by scanning the sample surface with a focused electron beam. Electrons interact with atoms in the sample, producing different signals that contain information about the topography and composition of the sample surface. In SEM,

secondary electrons emitted by sample atoms excited by the electron beam are mostly used to create image [21].

Scanning electron microscopy, shortly SEM was carried out to investigation of morphology of polymeric composites by Zeiss/Gemini Sigma 300 Vp machine. Before the SEM; all samples were coated with gold to electron conductivity by Quorum/ Q 150R ES machine. Analysis was performed by secondary electron detectors at 5.00kV and images were taken as 500, 1000x, 2000x, 5000x magnifications. Figure 2.5 is represented as samples coating machine before SEM analyzing.

Figure 2.5 Samples coating machine.

2.3.3 Energy dispersive x-ray spectroscopy analysis

Energy Dispersive X-Ray Spectroscopy Analysis, briefly EDX was performed after SEM simultaneously. It is a kind of elemental analysis of samples and test was made by point and area scanning. Figure 2.6 is represented as SEM and EDX device.
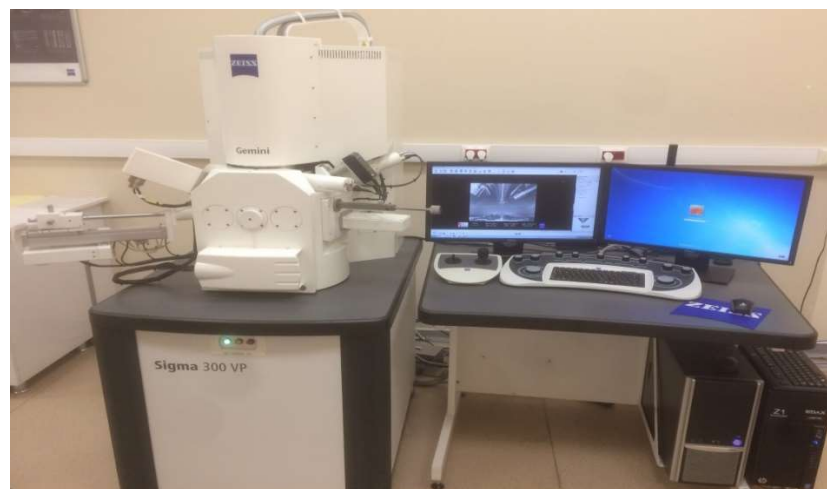

Figure 2.6 SEM equipment.

2.3.4 Analysis of fourier transform infrared radiation

Fourier Transform Infrared Radiation or FTIR is a technique used to obtain an infrared spectrum of absorption or emission of sample. This analysis is performed between 5000-400 cm^{-1} by Thermo Scientific/ Nicolet i S5 device. Peaks that coming from 4 elements in samples were taken and evaluated. Figure 2.7 is represented as Fourier Transform Infrared Radiation device.

Figure 2.7 Fourier transform infrared radiation device

2.3.5 Flammability test

Vertical burning test was performed according to ASTM D 3801 standard and tested at ZLT–ZY2 needle flame tester machine. The rate of burn test is set up to determine the burning time and extent of burning for plastics materials in the vertical position. The standard specimen geometry shall be 13.0±0.5 by 125±5 mm in the thickness.

This test is also described in ASTM D3801-10, which is used to measure and explain the response of materials, products, or assemblies to heat and flame under controlled conditions but does not contain all the necessary factors for fire hazard or fire risk assessment on its own [22]. Figure 2.8 is represented as UL-94 vertical testing.

Figure 2.8 UL-94 vertical testing.

The burner can provide flame which has energy of 50 W and 20 mm high central cone. The flame is applied to the bottom side of the specimen which has distance 125 x 13 x 3 mm and the top of the burner has to be positioned at 10 mm from the bottom edge of the specimen. Firstly, the flame is applied for 10 s and removed. The flame time is called t1 which is noted. After extinction, the flame is applied for another 10 s. The after flame time which is called t2 is noted, together with the afterglow time t3 (the time required for the fire glow to disappear). During the application of the flame, the distance between burner and sample should keep stable. If presence of burning drops is seen, this issue must be noted. According to standard, five specimens must be tested. Figure 2.9 is represented as set of UL 94 testing in a vertical configuration.
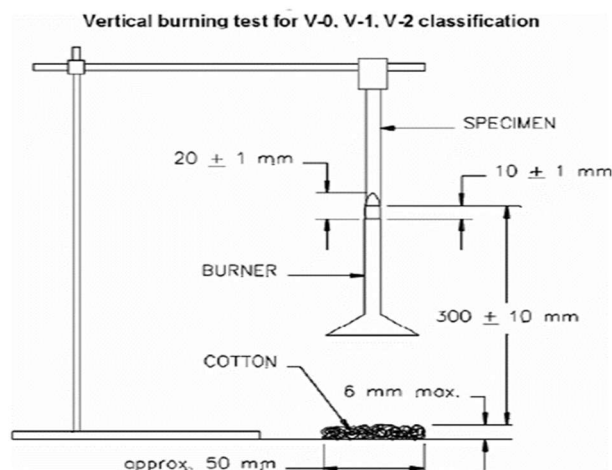

Figure 2.9 Set of UL 94 test in a vertical configuration [23].

Criteria of flammability level of specimens calculate by considering of the burning and afterglow times and dripping of the burning test specimen [23]. Table 2.6 shows the criteria of flammability level of specimens.

Table 2.6 Criteria of flammability level [23].

Criteria Conditions	V-0	V-1	V-2
Total flaming combustion for each specimen	≤10 s	≤30 s	≤30 s
Total flaming combustion for each specimen of any set	≤50 s	≤250 s	≤250 s
Flaming and glowing combustion for each specimen after second burner flame application	≤30 s	≤60 s	≤60 s
Cotton ignited by flaming drips from any specimen	NO	NO	YES
Glowing or flaming combustion of any specimen to holding clamp	NO	NO	NO

2.3.6 Melt flow index – density measurement

Melt Flow Index shortly MFI is basically measure of viscosity of any polymer. According to TS EN 1133; test is performed in 190^0C, using by 5 kg. Resin of polymer is cut in period of 60 seconds. As the MFI value increases; viscosity of polymer decreases which means lesser tensile strength, toughness and less stress crack resistance. In terms of greater mechanical properties; MFI value of polymer is expected lower. However, the lower value in MFI totally influence production process. Greater the energy is needed to extrude polyethylene resin when applying lower MFI of polymer. In equation 2.4.6.1; measurement of MFI value of polymer is shown. Measurement of MFI, which is T: Time of extruded in seconds and Unit- g/10 min [24].

$$MFI = \frac{600\ sec}{t} \times Weight\ of\ Extrudate \qquad (2.4.6.1)$$

The device essentially contains an extrusion plastometer operating at constant temperature. General design of the device is given in Figure 2.10. Thermoplastic

material placed in a cylinder in a vertical position, it is extruded in a die with the help of a moving piston applied [24].
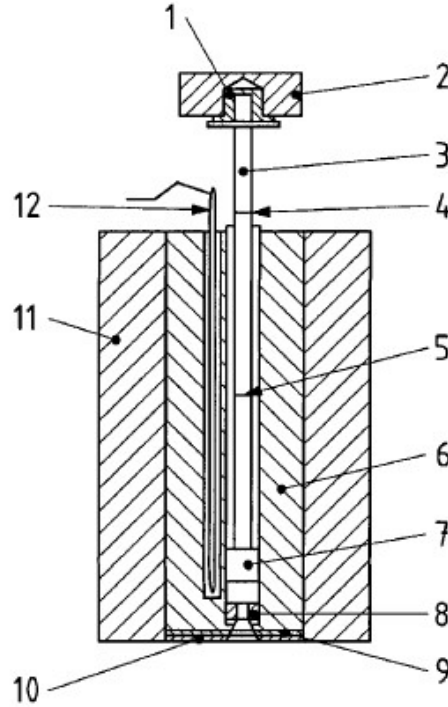

Figure 2.10: Schematic of MFI device; 1: Insulation, 2: Switchable Load, 3: Piston, 4: Upper Mark Line, 5: Lower Mark Line, 6: Cylinder, 7: Head of Piston, 8: Mold, 9: Mold Retainer Plate, 10: Insulation Plate, 11: Insulation, 12: Temperature Sensor [24].

Density measurements were performed by cut pieces formed as result of MFI analysis. According to TS-EN ISO 1183-1; Archimedean immersion method was used to determination of density of specimens [25]. Formula is used for density measurement is given in equation 2.4.6.2

$$\rho_{solid} = \rho_{liquid}\left(\frac{m_1}{m_1 - m_2}\right)$$

(2.4.6.2)

3. RESULTS AND DISCUSSION

3.1 FT-IR Analysis

FT-IR analysis was performed in brand range of 400 cm^{-1} and 4000cm^{-1}. In this section; to compare the analysis of HDPE with KK4 and M4 which have highest reinforced specimen are selected. Figure 3.1 represents FT-IR Analysis of HDPE. All of peaks in spectrum of HDPE were interpreted depending on literature. Peaks at 2914 cm^{-1} and 2847 cm^{-1} may be occurred due to C-H stretching asymmetric and symmetric. Peaks at 1472 cm^{-1} and 1462 cm^{-1} can be based on CH_2 bending (scissoring) and CH_3 bending (asymmetric) [26]. Peaks at 730 cm^{-1} and 718 cm^{-1} can be caused by CH-CH bending and C-C bending [27]. All peaks in graphs are based on existing alkynes group.
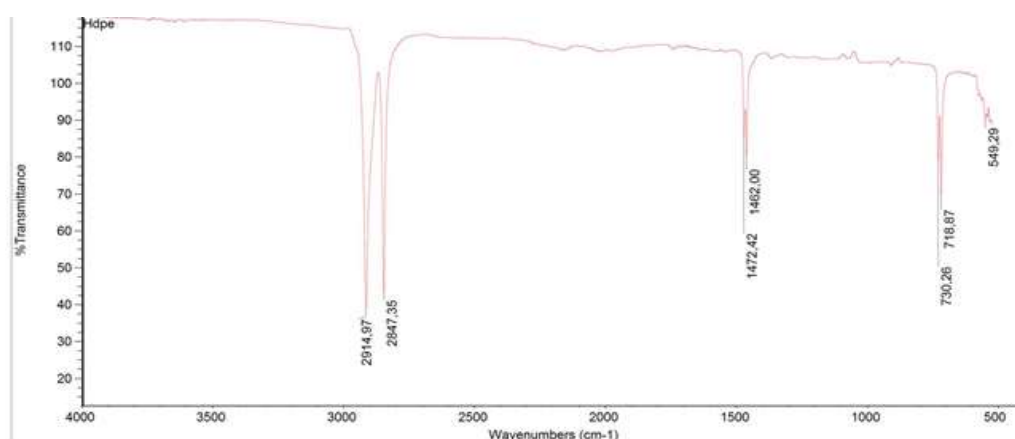

Figure 3.1 FT-IR analysis of HDPE.

Figure 3.2 and 3.3 are represented as results of FT-IR Analysis of KK4 and M4. There are remarkable things between FT-IR analysis of HDPE and other specimens analyzes; that peaks are similar. Characteristic peaks form Antimony Tri-Oxide, and other reinforced elements which provide flame retardant mechanisms in end-product not seen as a peak. Interaction does not exist between elements which make up flame retardant and HDPE. Since the additives elements may not contain organic bonds; this state may not has appeared as a peak as a result; Flame Retardant reinforcements does not react with HDPE matrix, because of this reason; intensity of band peaks do not change specifically.
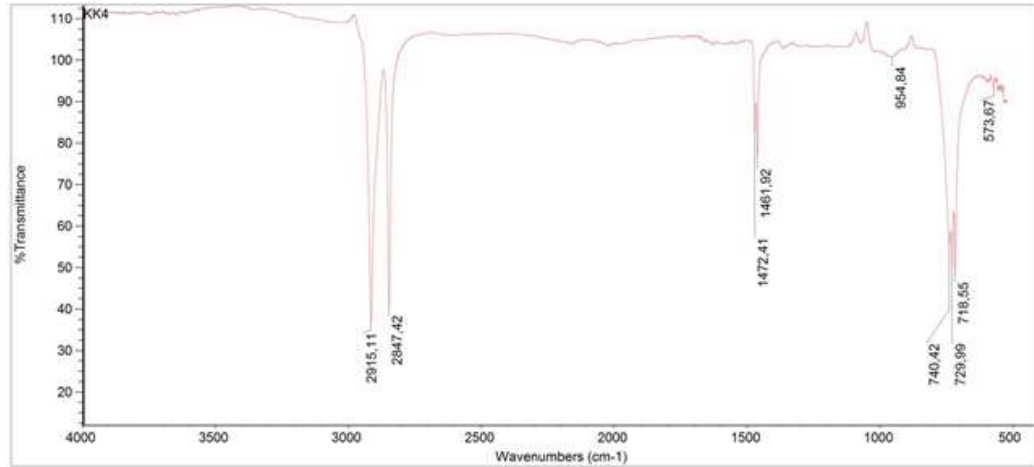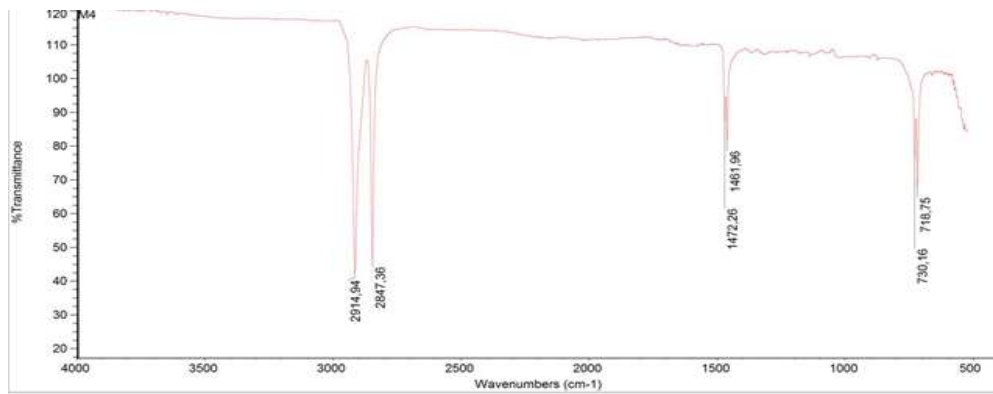
Figure 3.2 FT-IR analysis of KK4.

Figure 3.3 FT-IR analysis of M4.

Amount of crystallinity of specimens can be examined by equation [28] which is given in equation 3.1.

$$X = \frac{\dfrac{1 - I_a / I_b}{1.233}}{1 + \dfrac{I_a}{I_b}} \cdot 100$$

(3.1)

In the equation; X indicates the percentage of the amorphous content in the semi crystalline HDPE, Ia and Ib are called the intensities of absorption in the bands. Constant with 1.233 corresponds to the relations of intensity bands of fully crystalline of HDPE. At the literature; part of crystalline regions being around 1423 cm⁻¹ – 1473

cm^{-1} while peaks in amorphous regions at 730-710 cm^{-1}. In this study; intensities of absorption in the above mentioned bands were formulized according to equation in 3.1. Amorphous contents of 718 cm^{-1} and 730 cm^{-1} are same value as 3.96 % while; peaks of 1462 cm^{-1} -1472 cm^{-1} is 2.37% [29].

3.2 SEM-EDX Analysis

Elemental analysis was carried out by EDX instrument and the results of M series are shown in Figure 3.4 and 3.5. Element of Sb and O were detected which belong Antimony (III) oxide in series each specimen. It was expected that; halogenated elements which provides synergetic effect for flame retardant mechanism was detected as element of Br. Moreover, existence of C and H elements are proof of including ethylene group in specimens.
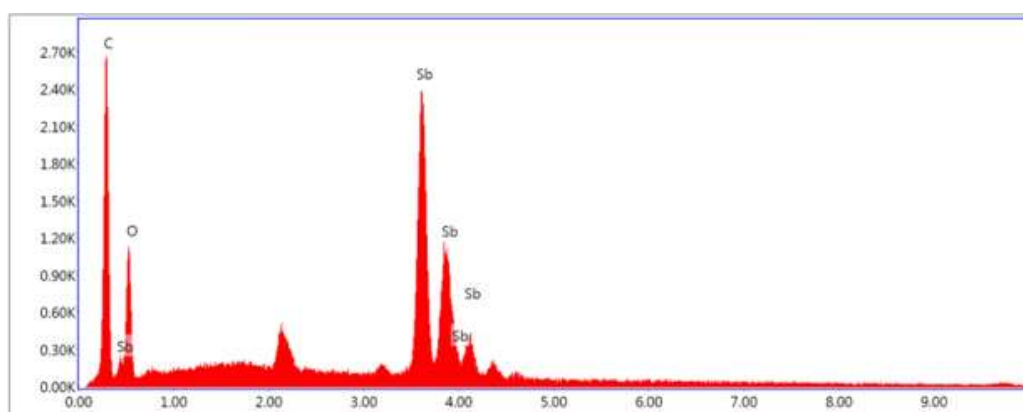

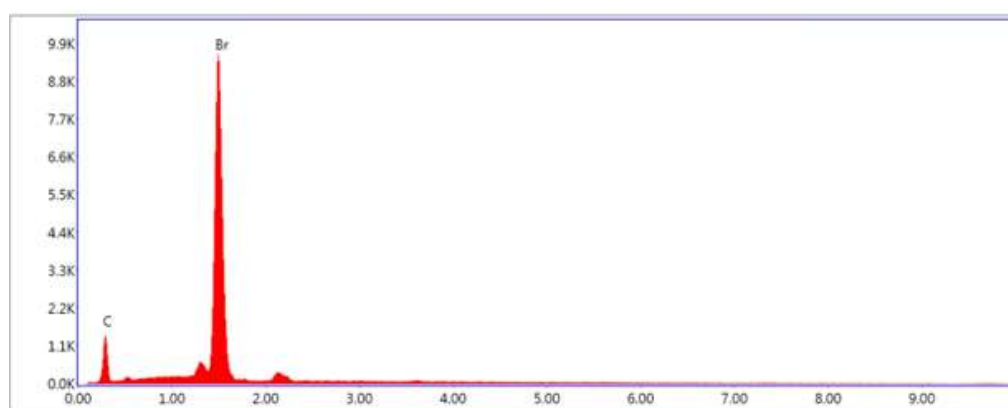**Figure 3.4** EDS result of FR-M4 series specimens.

Figure 3.5 EDS result of FR-M4 series specimens.

SEM images of each group of specimens are presented in figure 3.6-a-b-c-d-e-f. "Cup Cone" pattern was observed for SEM image of HDPE, not surprisingly, it is caused by ductile fracture mechanism.
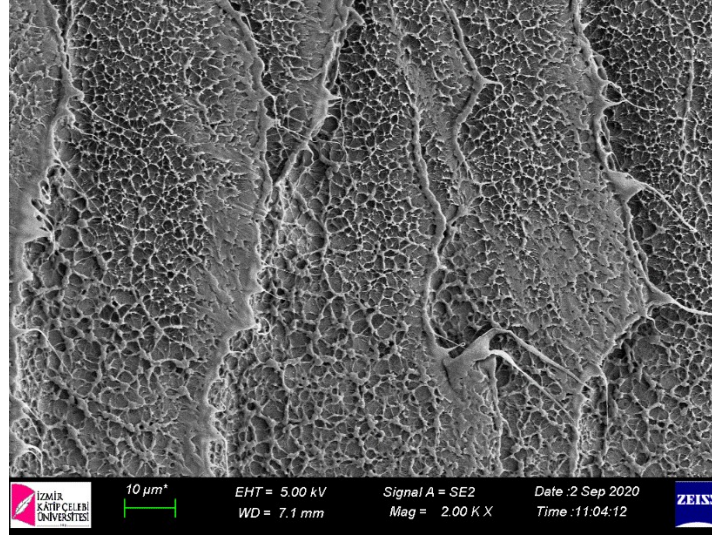

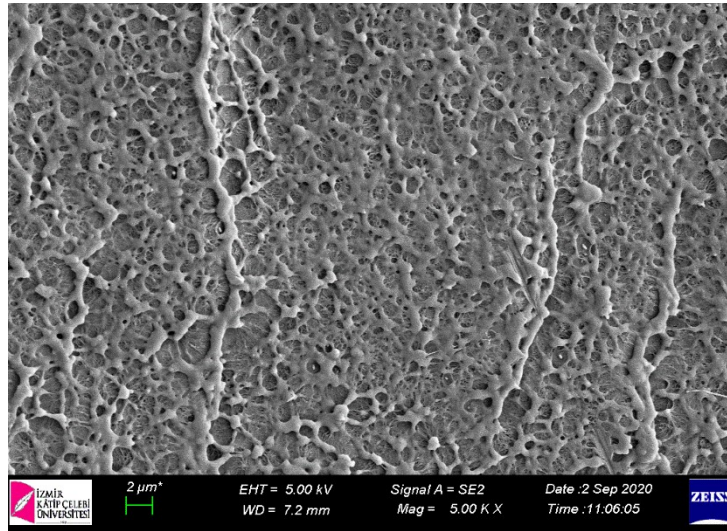**Figure 3.6-a** SEM image of HDPE.

Figure 3.6-b SEM image of HDPE.

SEM outputs of samples about reinforced flame retardant additives are quite similar. Each groups samples have weak interface which small space between matrix and additive was examined. This is the proof that the mechanical test results are close to each other for both groups. All of them has similar tensile strength with neat HDPE.
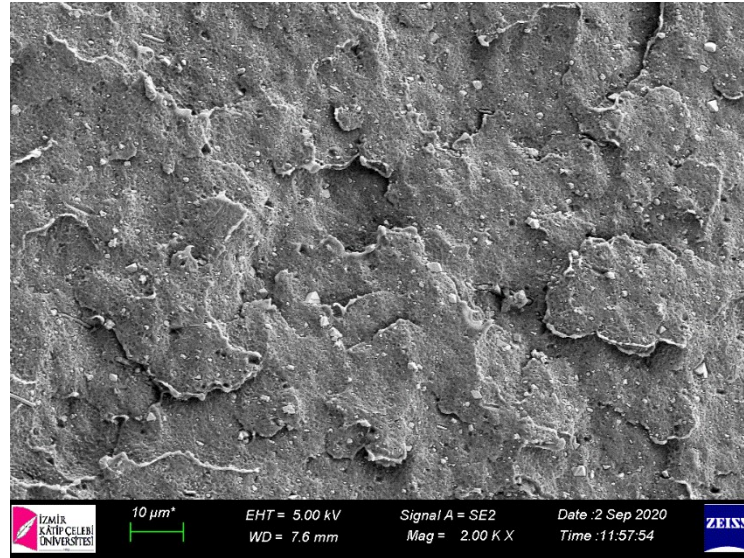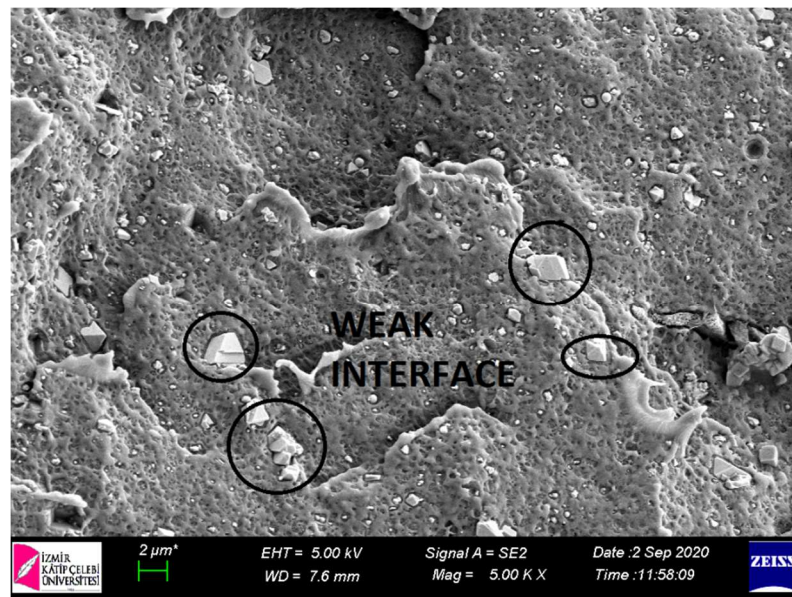
Figure 3.6-c SEM image of KK4.

3.6-d SEM image of KK3.
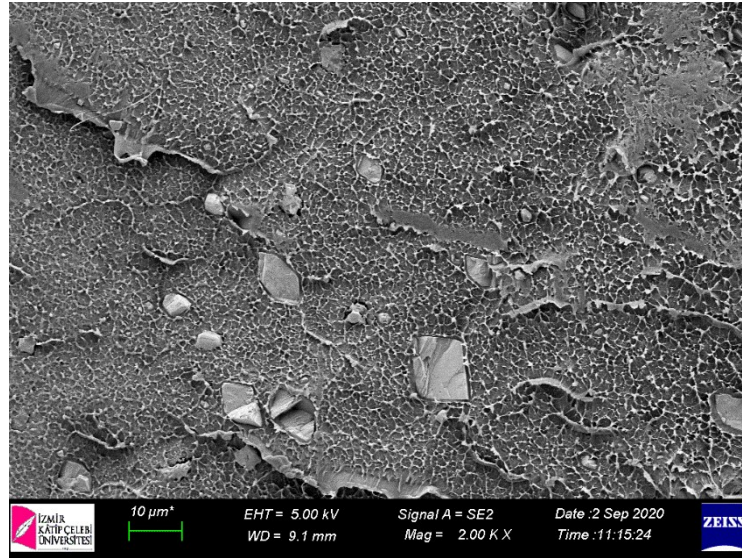
Figure 3.6-e SEM image of M4.
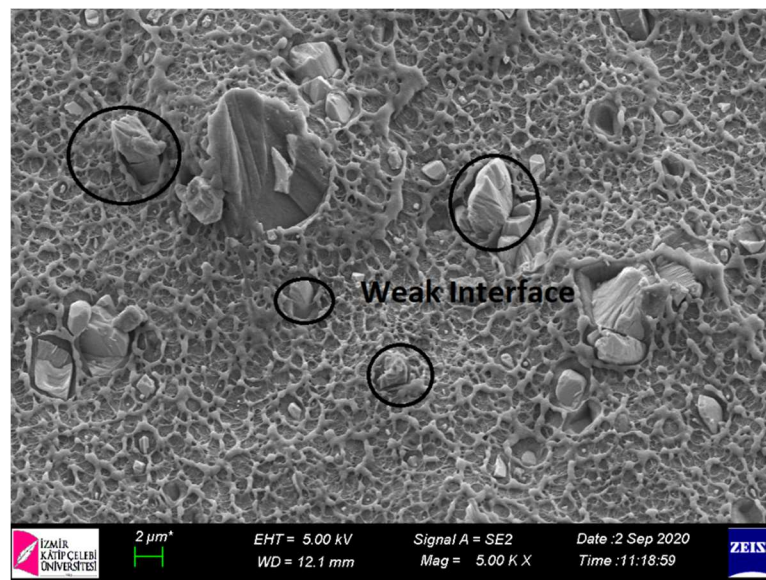
Figure 3.6-f SEM image of M3.

3.3 Results of Flame Retardant Properties

UL-94 vertical test was performed each specimen; result is shown in table 3.1. It is expected that; Neat-HDPE specimens was excluded test criteria. All specimens were ignited at first giving flame process. Specimens of M-series after take out; flame extinguished in 10 seconds. However; dripping of burning specimens was occurred thus M-series can be called V2 level flame retardant. Interesting things about M series

that; level of flammability did not alter with content of flame retardant increased. In such studies it can be assumed that there is a specific additive ratio for the level to change.

Table 3.1 Result of UL-94 testing of each specimen.

Sample Code	Burning Time(s)	Melt Dripping	Extinguish Time (s)	Level
M1	≤30	no	10	V2
M2	≤30	no	10	V2
M3	≤30	no	10	V2
M4	≤30	no	10	V2
Neat HDPE	≥30	yes	Not	N/A
KK1	≥30	yes	Not	N/A
KK2	≥30	yes	Not	N/A
KK3	≥30	yes	Not	N/A
KK4	≥30	yes	Not	N/A

Another remarkable point is nonconformity of series of KK Flame retardant additives. It has even 27% reinforced of samples; Flame did not burn out in 30 seconds and also ignition of cotton batting was observed. This result may be lack of halogenated elements in commercial flame retardant.

3.4 Result of Melt Flow Index and Density Measurements

MFI results of reinforced M-series and KK-series of polymeric composites are given in figure 3.7 and 3.8. Striking point is averagely difference of MFI between neat HDPE and reinforced polymers is 50%. It can be concluded; flame retardants provide followability to HDPE. In some cases; this state may not be conformity with customer requirements which is complying 20% difference with neat HDPE and also this can be explained by reinforcement contains as LLDPE carrier resin.
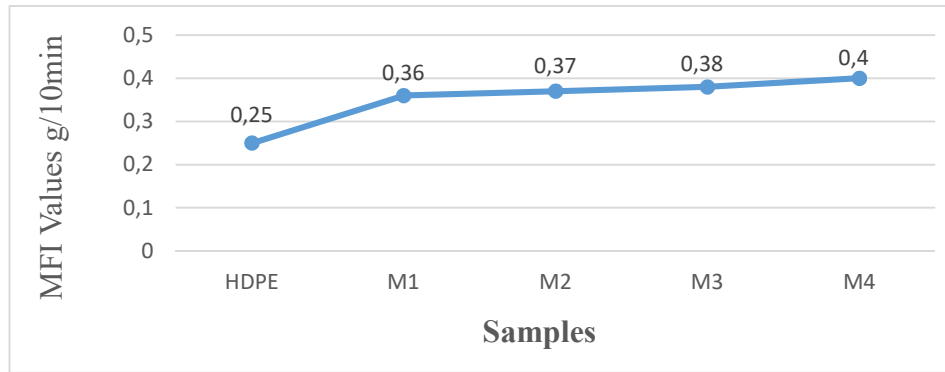
Figure 3.7 Reinforced M-series of polymers MFI result.

Figure 3.8 Reinforced KK-series polymers of MFI result.

Density results of reinforced M-series and KK-series of polymers composites are given in figure 3.9 and 3.10. It is expected that; density values increased with addition ratio respectively. The reason for that; totally depending on high density content of additions that such as existence of Sb_2O_3 and Br.
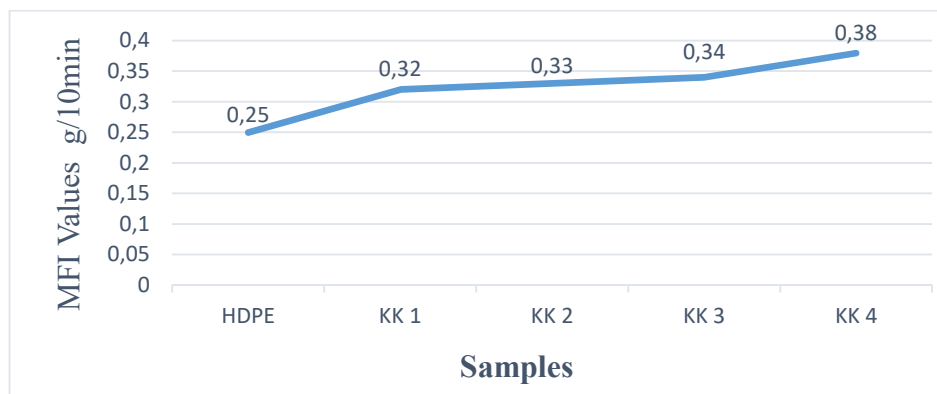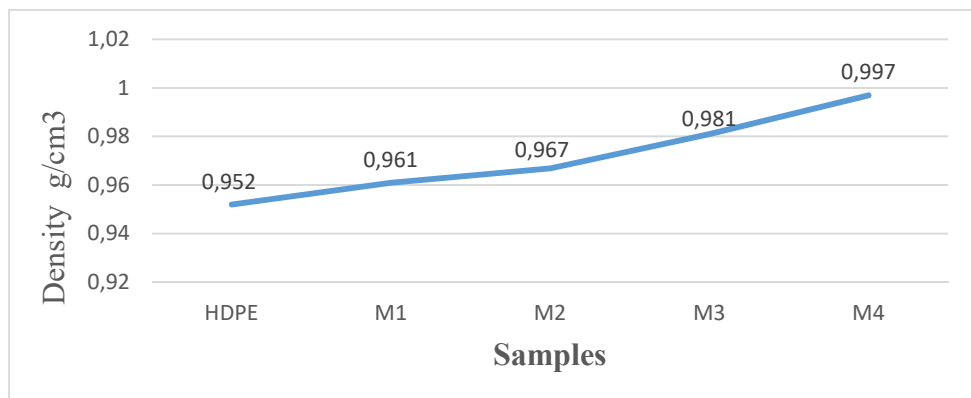

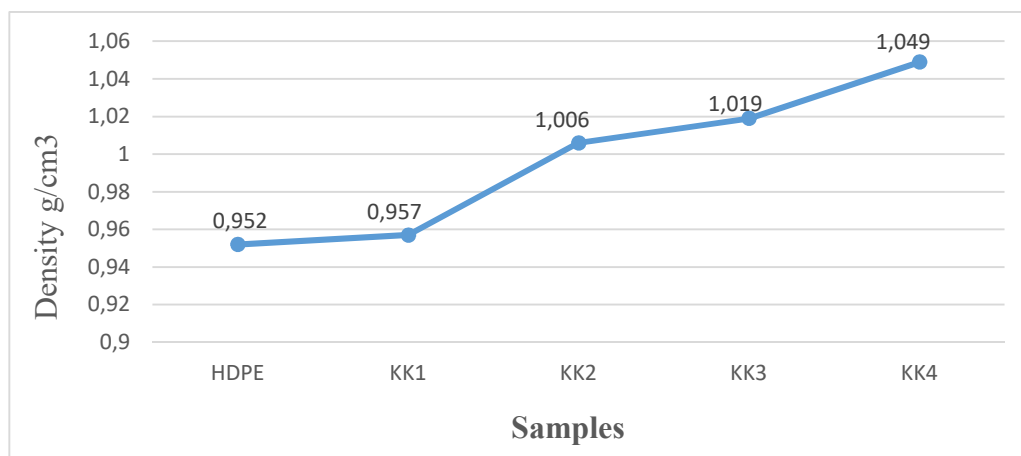**Figure 3.9 Reinforced** M-series of polymers density result.

Figure 3.10 Reinforced KK-series of polymers density result.

3.5 Tensile Testing Results

Tensile Strength values of both neat HDPE, M-series/ HDPE and KK series/HDPE composites at different filler loading are shown in Figure 3.11 and 3.12. Tensile strength values of neat HDPE, M1, M2, M3, M4 samples were obtained to be about 23,1- 21- 22- 25-18,2 MPa respectively. There can be mentioned similarity with KK and M series in case of tensile strength. Tensile strength values of KK1, KK2, KK3, KK4 samples are 21- 21.5- 22-20 MPa respectively. It is clearly seen that; for M series; 11% reinforced M filler FR/ HDPE composite showed best improvement in Tensile and also for the KK series; 24% reinforced KK series FR/ HDPE composite has highest tensile strength. When compared to M3 and KK3, decreasing was seen in tensile strength for 14 wt. % M filler loading (M4) and 27 wt. % KK filler loading(KK4). This state may be explained as Antimony trioxide content reinforced flame retardant may has a tendency to poor compatibility with HDPE. Incorporation of Sb_2O_3 deteriorates the mechanical properties of HDPE matrix owing to the poor compatibility between PP and Sb_2O_3 [30].
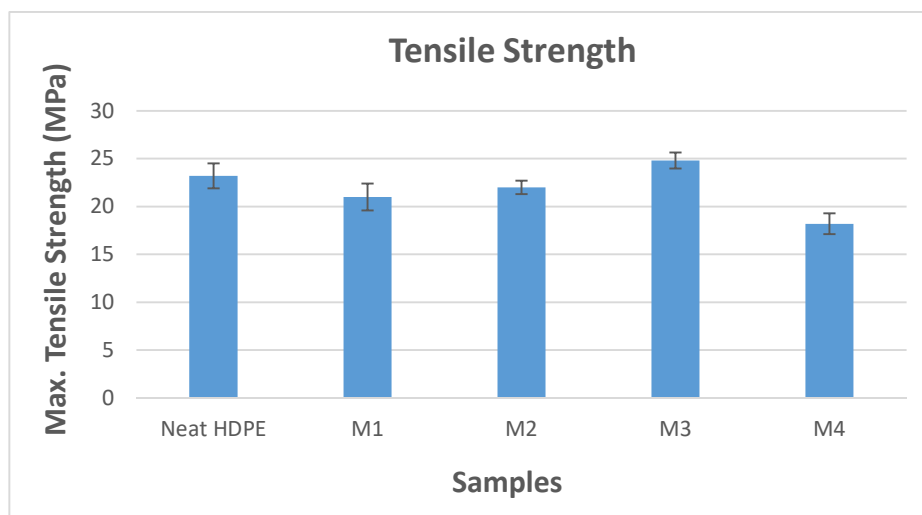
Figure 3.11 Tensile strength of reinforced M-series of polymers.
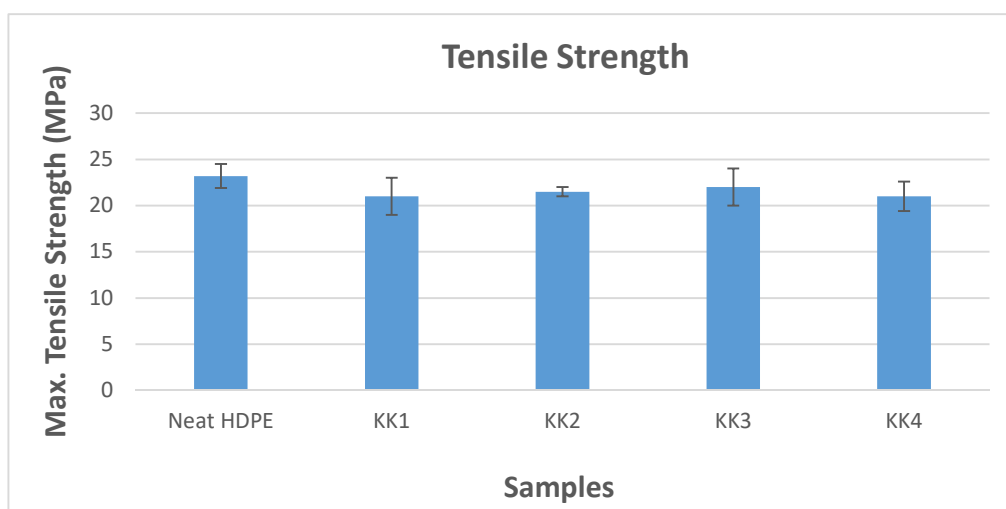
Figure 3.12 Tensile strength of reinforced KK-series of polymers.

Considering the results described above and what has been obtained in the literature, it can be said that some parallel and some different results have been obtained. For example, in study of Jian-dong et al. (2008) Decabromodiphenyl Oxide(DBDPO) and decabromodiphenylethane (DBDPE) was used with Sb_2O_3 in ABS, PP and PS matrices. After cone calorimetric technique for fire test and researching, with sample which is called ABS-3 consist of 80% wt of ABS, 15% wt of DBDPE, 7.5% wt of Sb_2O_3; they have found LOI higher level with 28. However, sample of ABS-1 consists of 80% wt of ABS, 15% wt of DBDPE, 5 % wt of Sb_2O_3 has LOI level of 18 [32]. At another important study (Ran et al. 2014), to improve thermal stability of HDPE;

Sb_2O_3, Graphene nanoplates (GNP) and Brominated Polystyrene (BPS) were used as additives of FR. Sample with weight fraction of 92-HDPE, 6-BPS, 2-Sb_2O_3, 1-GNP has V2 level of UL-94 grade however sample of 92-HDPE, 6-BPS, 2-Sb_2O_3 has not grading of UL-94 test [50]. Study of Zhang et al. (2010) was about the influences of expanded graphite (EG) on the thermal properties of chlorinated paraffin (CP) and antimony trioxide (Sb_2O_3) on phase change material which bases on paraffin/high density polyethylene (HDPE). Specimens consist of 50% Paraffin, 15% HDPE, (CP+Sb_2O_3)30% and 5% EG which has higher thermal stability than that of other specimens [33]. Studies in literature show that thermal stability could be improved when more than one flame retardants as nano-level are used together as additives in the polymer matrix. At our study, compounding and pressing processes, which are the same production techniques as the studies mentioned in the literature, were used. However, in our study using different types of commercial additives did not reach V0 and V1 level of UL94 standard. This can be interpreted as the components constituting the additives do not perform a perfect synergistic effect depending on thermal and flammability properties of additives.

Niu et al. (2018) applied nano-Sb_2O_3 and brominated epoxy resin (BEO) in matrix of poly (butylene terephthalate) (PBT) to investigate flame retardancy and mechanical properties of PBT. They used to follow tensile strength of samples; Neat-PBT with 54,6 MPa, sample PBT/BEO/nano-Sb_2O_3 3% with 61,7 MPa and sample of PBT/BEO/nano-Sb_2O_3 5% with 58.5 MPa [34]. At the another study (Jianlin et al. 2020), Sb_2O_3 nanoparticles (nano-Sb_2O_3) modified by silane coupling agent of KH550 were dispersed into brominated polystyrene (BPS)-PP matrix to improve mechanical properties of matrix. When the mass fraction of nano-Sb_2O_3 particles is more than 3 wt%, the tensile strength and static fracture toughness of nano-Sb_2O_3/BPS -PP composites decrease [35]. Tensile strength results of studies of Niu et al. (2018) and Jianlin et al (2020) similar with our study. Although the tensile strength of HDPE matrix composites reinforced with M and KK flame retardant additives increased up to a certain point; then a gradual decreasing in tensile strength was observed. The decrease of the tensile strength was due to the low level of interfacial adhesion between Sb_2O_3 particles and the polymer matrix. On the other hand, less Sb_2O_3 additives could act as lower stress concentrators in the polymer matrix composites, which could absorb

more energy to improve the tensile strength, consistently with the tensile test results [34,36].

4. CONCLUSIONS

The purpose of the current study was to determine the best formulation to reduce the flammability of the microduct pipes consists of HDPE. Two different types of flame retardant additives with extinguishing properties containing an intense amount of Sb_2O_3, Br, CI were selected for the HDPE matrix. The production process of the samples consisted of two traditional methods; extrusion and pressing. This study has gone some way towards enhancing our understanding of cost and energy efficiency within the pipe industry. The key finding in this research was the emerged empirical evidence regarding the role of using lab-type extrusion for the purpose of saving cost and energy. Results indicate that only 5-6 kg of raw materials were used at the end of the production process for the reproduction of samples, on the other hand, approximately 300-400 kg of raw materials would be consumed to get the desired formulation of samples in case the use of industrial equipment.

Regarding the results of FTIR; the amount of semi-crystalline in samples reveals that the matrix material contains high purity. Considering flame retardant additives do not own any organic bonds; only C-H interactions were observed.

In the tensile testing results, all of the outputs were similar. When considering customer requirements an interval of 23 MPa – 27MPa in tensile strength is reasonable, however, increasing the amount of the additives after a certain point induces an extreme decrease in tensile strength. SEM images have allegedly explained this problem, showing poor compatibility between matrix and additive. It was clearly seen that the interface was not observed whatsoever.

UL-94 test results of KK series were disappointed. There was no improvement, even in the highest reinforced matrix. For M-series; V2 level has reached all of samples. Although the additive density increases; any improvement in flame retardancy properties was observed.

Since both additives contain LLDPE resin; The increase in MFI values was observed. HDPE's MFI result with reinforced flame retardant was increased by 25% compared to neat HDPE. In addition, the effect of Br, CI elements on density analysis results is

incontestable. This would not comply with the standards that include the MFI value below 20%.

If all these results are considered, using a low amount of M series additive in production process of microduct pipes; it will be an advantageous choice because it provides mechanical and flame retardancy to HDPE.

4.1 Future Plans

In future, to get better results, Nano Sb_2O_3 can be used as flame retardant additive in HDPE matrix. To obtain good interfacial bonding between additives and matrix, proper coupling agent may be searched. To enhanced flame retardancy of HDPE; nano-level additives such as carbon nanotubes, expanded graphite may be used. To get more comprehensive results about study, LOI test, TGA - DSC analysis and combustion calorimetry under a forced combustion can be performed.

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CURRICULUM VITAE

Education

Bachelor of Science in Materials Scince and Engineering (100% English) Izmir Katip Celebi University   2.84/4.00

Master of Science in Materials Science and Engineering (100% English) Izmir Katip Celebi University

List of Publications

Yılmaz Atay Hüsnügül, ENGİN BERK, Use of Glass Fibers and Glass Spheres to Improve Mechanical Properties of Huntite and Hydromagnesite Reinforced Flame Retardant Composites, Romanian Journal of Materials, 2019, 49, 468 474

Conference Papers

Yılmaz Atay Hüsnügül, ENGİN BERK, Improvement of Mechanical Properties of Huntite and Hydromagnesite Reinforced Flame Retardant Composites by Using Glass Fibers, IMSMATEC'18, The Internatinonal Conference on Materials Science Mechanical and Automotive Engineerings and Technology in Ceşme/ Izmir, 10.04.2018 12.04.2018

Yılmaz Atay Hüsnügül, ENGİN BERK, Investigation of Mechanical and Flammability Properties of Hdpe Reinforced flame Retardant Addıvites Including Antimony Trioxide, 16/10/2020 – IMSTEC 2020 (International Conference, 5. Materials Science and Technology in Cappodocia)

Projects

Graduation Thesis supported industry which is called "Improvement of Mechanical Properties of Huntite and Hydromagnesite Reinforced Flame Retardant Composites by Using Glass Fibers" with The Scientific and Technological Research Council of Turkey (TUBITAK- BIDEB 2209)

Experience

05.2020- Currently; Supply Chain and Import Supervisor / Chil Tıbbi Malzemeler Izmir-Turkey

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