SEPTEMBER 2019
M.Sc. in Mechanical Engineering
TUĞÇE GÜL POLAT

REPUBLIC OF TURKEY
GAZİANTEP UNIVERSITY
GRADUATE SCHOOL OF NATURAL & APPLIED SCIENCES

MECHANICAL PROPERTIES OF GRAPHENE NANO-PLATES REINFORCED LDPE COMPOSITES

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IN
MECHANICAL ENGINEERING

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M.Sc. Thesis
in
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Supervisor
Assoc. Prof. Dr. Ahmet ERKLİĞ

by
Tuğçe GÜL POLAT
September 2019

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Approval of the Graduate School of Natural and Applied Sciences.

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Head of Department

This is to certify that we have read this thesis and that in our consensus opinion; it is fully adequate, in scope and quality, as a thesis for the degree of Master of Science.

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Tuğçe GÜL POLAT

ABSTRACT

MECHANICAL PROPERTIES OF GRAPHENE NANO-PLATES REINFORCED LDPE COMPOSITES

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M.Sc. in Mechanical Engineering
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In this thesis, the effects of graphene on the mechanical properties of low density polyethylene (LDPE) film used in packaging industry are investigated. Graphene was added to the LDPE F2-12 raw material in 0.1%, 5% and 10% by weight. The mixture prepared by twin screw extrusion machine was filmed in blown line. Film thickness was obtained as 17, 19, 25 and 27µ due to the effect of graphene addition. Thickness, heat seal, tear, coefficient of friction (COF) and tensile strength tests of the produced films were carried out in accordance with ASTM standards. When the graphene additive test results were examined in LDPE film 58.82% increase in thickness was observed. It was observed that the mechanical properties of LDPE film which was added graphene generally decreased and the film was found to be weakened compared to the non-graphene film. When a mechanical compound is tried to be combined with a standard compound twin screw machine, no chemical bond is formed between the components, since maleic anhydride is not the binding raw material, the resulting filmed dispersion has not been dispensed and regional differences have occurred.

Key Words: Nanocomposites, LDPE, Graphene, Tensile Strength, Blown Film.

ÖZET

GRAFEN TAKVİYELİ ALÇAK YOĞUNLUKLU POLİETİLEN NANOKOMPOZİTLERİN MEKANİK ÖZELLİKLERİ

GÜL POLAT, Tuğçe
Yüksek Lisans Tezi, Makine Mühendisliği
Danışman: Doç. Dr. Ahmet ERKLİĞ
Eylül 2019
57 sayfa

Bu tez çalışmasında, grafenin ambalaj sektöründe kullanılan alçak yoğunluklu polietilen(AYPE) filmin mekanik özelliklerine etkileri araştırlmaktadır. AYPE F2-12 hammadde içerisine ağırlıkca %0.1, %5 ve %10 oranlarında grafen katılmıştır. Çift vidalı ekstrüzyon makinesi ile hazırlanan karışım blown hattında film olarak çekilmiştir. Grafen katkısının etkisinden dolayı film kalınlığı 17, 19, 25 ve 27µ olarak üretilmiştir. Üretilen filmlerin kalınlık, ısıl yapışma, yırtılma, sürtünme ve çekme testleri ASTM standartlarına uygun olarak yapılmıştır. AYPE film içerisinde grafen katkısı test sonuçları incelendiğinde kalınlıkta %58.82 artış görülmüştür. Grafen katkılı AYPE filmin mekaniksel özelliklerinin genel olarak düştüğü ve filmin grafensiz filme oranla zayıfladığı görülmüştür. Grafen standart bir compound çift vidalı makina yardımıyla mekanik olarak birleştirilmeye çalışıldığında bileşenler arası kimyasal bir bağ oluşmamıştır, bağlayıcı hammadde olarak maleic anhidrit olmadığı için oluşan filmde dispersion olmamıştır ve bölgesel farklılıklar oluşmuştur.

Anahtar Kelimeler: Nanokompozit, AYPE, Grafen, Gerilme Mukavemeti, Şişirmeli Film.

''To my family''

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I would like to thank my advisor Assoc. Prof. Dr. Ahmet ERKLİĞ for sharing his knowledge and experiences with me during this study.

To my cousin Mustafa KAPLAN, who always helped me and supported my studies during my graduate studies, where the first foundations of this study were laid.

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LIST OF SYMBOLS

μ	Mikron
β	Beta
Ω	Ohm
π	Pi

LIST OF ABBREVIATIONS

PE	Polyethylene
PP	Polipropilen
HDPE	High Density Polyethylene
MDPE	Medium Density Polyethylene
LDPE	Low Density Polyethylene
Gpa	Gigapascal
GNP	Graphene Nano Plate
TEM	Transmissin Electron Microscopy
SEM	Scanning Electron Microscopy
MFI	Melt Flow Index
COF	Coefficient Of Friction
ASTM	American Society For Testing Materials
Tm	Melting Temperature
MW	Molecular Weight
MWNT	Multi-Walled Carbon Nanotube

CHAPTER 1

GENERAL INTRODUCTION

1.1 Definitions of Graphene

Graphene attracted great attention, after Andre Geim and Konstantin Novoselov were awarded the Nobel prize (2010) in Physics because of their “groundbreaking experiments” on the “miracle material” graphene. Graphene is a two dimensional nanomaterial, which has superior properties, and a layer of covalently bound carbon atoms arranged in a perfect honeycomb (hexagonal) lattice. The carbon-carbon bond length of graphene is approximately 0.142 nm. The electrons on the structure of graphene acts as massless particles and therefore, it causes unique properties like quantum hall effect. Single layer graphene properties are given in Table1.1. Some main properties of graphene are high electron mobility, large surface area (2630 m^2g^{-1}), high thermal conductivity (5000 $Wm^{-1}K^{-1}$) and high young modulus (~1,100 GPa). Because of its superior properties, graphene found applications in many areas such as transparent conductors, clean energy devices, sensors, nanocomposites and organic photovoltaic devices [1].

Table 1.1 General properties of single layer graphene [2]

FEATURES	VALUE
Hybrid shape	Sp^2
Number of layers	Monolayer
Crystal structure	Hexagonal
Dimensions	2D
Degree of purity(%)	99
Bulk density(g/cm^3)	-0.3
True density(g/cm^3)	2.25
Thickness(nm)	-1 - 2
Surface area(m^2/g)	2600
High temperature resistance	-75 does not change properties between +200
Thermal conductivity($W\bar{K}^1/m$)	4840 - 5300
Electron mobility($cm^2/(V.s)$)	-2.5x10
Modulus of elasticity(Tpa)	-1

1.2 Structure of Graphene

Graphene has the 2-dimension nanomaterial containing a single layer of sp^2 hybridization of C atoms. Because of its two dimensions, each atom of graphene can be considered as a surface atom. The fact that 1 g of graphene and a quarter of a football field can be covered is one of the basic indicators of how unique the graphene. Carbon atoms (carbon nanotubes, fullerenes), which make the graphene more specific than the carbon atoms in honeycomb (hexagonal) structure are connected. Since the carbon sequence of the carbon atom is in the form of $1s^2 2s^2 2p^2$, the carbon bonds in the grapy sp^2 hybridize, while the pz orbitals that remain idle give unusual properties. Because of this hexagonal structure consisting of two intertwined triangular structured sub-braids, the unit cell of the graphene contains two carbon atoms and 120 an of the inverse symmetry. Each carbon atom has three p orbits. In one s and plane, the two p orbital grooves the strong covalent bond of the graphene and do not contribute to the transmission. The remaining p orbital is perpendicular to the molecular plane and hybridizes to form π (valence) and π * (conduction) bands.The ideal graphene has a high degree of impurity and does not contain any foreign atoms other than carbon. Figure 1.1 gives graphene structure. Yellow dots represent carbon atoms and blue lines represent the bond between two carbon atoms. Figure 1.2 gives monolayer graphene structure. The bond length between carbon-carbon in the graphene is approximately 0.142nm. Figure 1.3 shows graphite structure of two-dimensional carbon atoms with high resolution permeation electron microscope (TEM). It is clear that the distance from the TEM photographs to the carbon atoms is 0.14 nm [3].

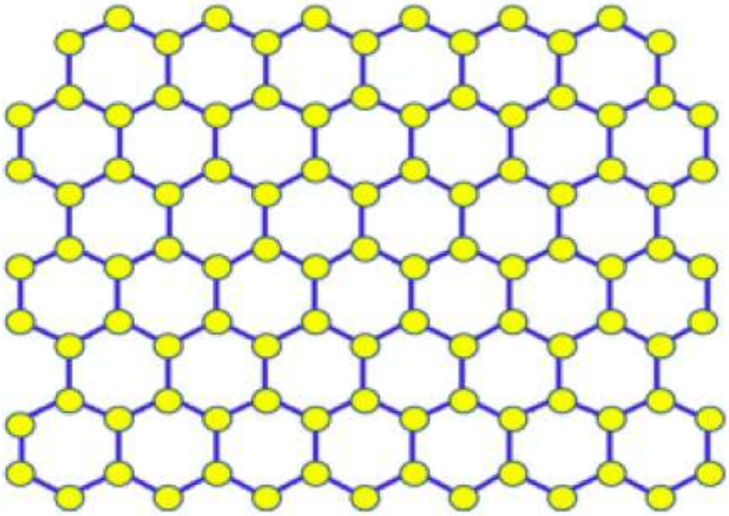

Figure 1.1 Graphene structure [3]

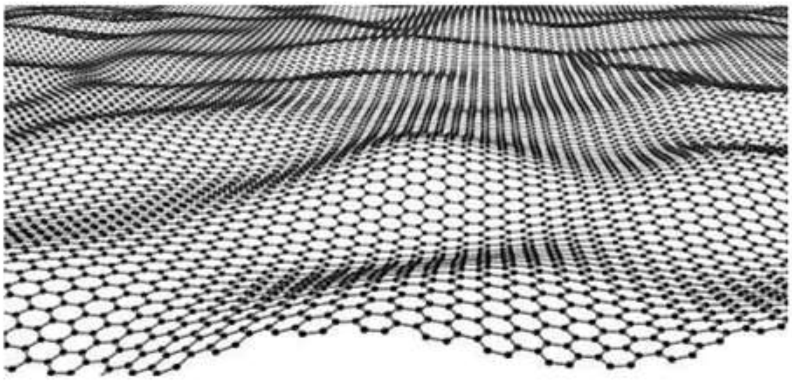

Figure 1.2 Monolayer graphene structure [4]

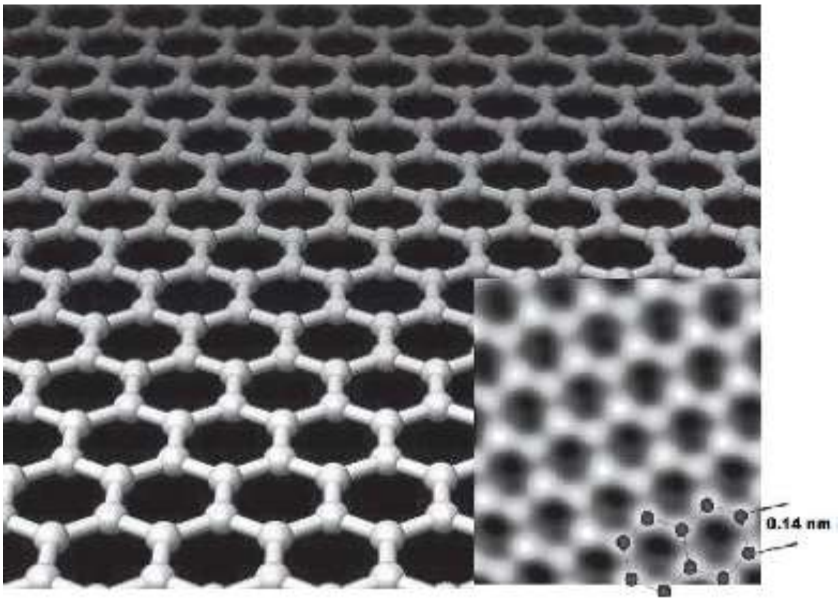

Figure 1.3 TEM image of graphene [3]

1.3 Usage Areas of Graphene

The control of the properties of graphene can greatly help to create graphene-based systems with magnetic and superconducting properties. Although it is still not fully understood, it is certain that graphene will have a more effective place with scientific and technological means in accordance with the researches. Understanding the properties of this material can provide improvement in the electronic field. The conductivity of graphene is particularly noteworthy. It is estimated that graphene transistors will be faster than silicon transistors.

Graphene can be used in the production of transparent touch screens, light panels and perhaps even solar cells as it is both transparent (almost 98%) and it can transmit electricity.

Researchers in England are trying to use graphene on touch screens. The currently produced screen is only one pixel resolution and one millionth of a meter. Researchers are trying to produce larger sizes of graphene. Now, indium tin oxide is used on the surface of the touch screens. Since indium is a rare element in the nature, the future of touch screens depends on the presence of other substances that can be used instead of this element. In addition, only 1% of the plastics structures can be made to transmit electricity by mixing graphene. Similarly, a graphene can be mixed with a thousand per thousand in the construction of plastics. This durability can also help to create new super-durable materials that are thin, elastic and lightweight. Future satellites, planes and cars can be produced from new mixed materials. The excellent structure of the graphene is also suitable for the production of ultra-sensitive sensors that can even detect very low levels of contamination. Even a single molecule attached to the graphene surface can be recognized. The fields of use described in detail above can be summarized as follows.

1. To make better lighting and energy systems with this transparent layer.
2. Forming electrodes for solar cells,
3. Use of lithium batteries as anode and electrode material,
4. Use in field effect transistor construction,
5. It is planned to be used as semiconductor.[5]

Apart from these areas of use

It has been proven by studies at the University of Texas, where ultracapacitors can store electricity with more capacity than normal batteries with a graphene base. As a result, ultracapacitors with twice the normal capacity will be very useful for the renewable energy industry, which is looking for a large amount of energy storage methods for windless or solar-free days, as well as charging battery-powered devices.

Graphene material plays a very important role in hydrogen storage. Increasing global warming and the gradual decline of fossil fuels have led researchers to seek new challenges. Intensive research is being carried out to ensure that hydrogen is stored efficiently and where electricity is needed.

The importance of graphene in spintronic technology is important. In addition to the load of electrons, this technology, which tries to use their spins, is vital in today's information storage systems. Due to the magnetic properties of graphene nanoscones, the usage areas of spintronics arise.

When the health sector is taken into consideration, the fact that graphene can remain intact in the body's ionic fluids is promising for biological applications. Bionic ears appear to be possible with the development of bionic eyes graphene technologies. Although researches for use as bioelectronics and biomaterials have not been very early, researchers are thought to be very promising for the future.

Regulatory institutions, such as the Ministry of Environment, use graphene-based phosphate sensors to continuously detect phosphate levels in many environments, such as aquatic organisms and microorganisms. In addition, graphene-based nanographene membranes are considered to be the best technology among water purification technologies with their low salt content, which allows water to pass through but not allow salt molecules to pass through, and that it will play an important role in the future. This technology is also used to purify carbon dioxide from the nitrogen mixture in the purification of water-dissolved gases. Thanks to nitrogen bonding to these bonds which are broken by breaking the carbon bonds with direct ball milling method in graphene nitrogen atmosphere, the production will be very cheap by using it in industry branches such as fertilizer, ammonia gas production and explosives.

Graphene-based sensors are noteworthy for the amount and removal of heavy metals with high environmental impact and adverse effects on human health. Also as the graphene increases the catalytic activity to Pt by localizing the electrons near the Pt, environmentally friendly renewable electricity production is among the studies carried out [6].

1.4 Obtaining Graphene

Thanks to the discovery of graphene, an unknown material group has emerged. Although 2D crystal materials have been discovered in recent years, it has begun to be analyzed by developing characterization techniques. This material, which was originally thought to be graphite, was later named as graphene.

Graphene is the constituent of all others graphite materials packaged in a two-dimensional honeycomb cage of a uniform monolayer sp^2 hybrid honeycomb. The fact that graphene is two-dimensional gives a very important feature to graphene. Graphene has very good electrical conductivity, thermal properties and optical properties.

Graphene and it is derivatives have been developed. Graphene, which enters more in our daily lives, has been researched and developed by many researchers to synthesize physical and chemical synthesis methods [7].

1.5 General Definitions of Plastics

Plastics are chemically incorporated into the group of polymers. Small molecule individuals (monomers) are obtained by adding each other. Depending on the number of individuals (mer) in the molecular structure, they are present in gas, liquid and solid form. Dyes, varnishes, adhesives, etc. in liquid form are also considered as polymers.

The word plastic refers to a material type as the name, in fact plastic means the object that can change the shape permanently.

Plastics are fluent at a certain stage of their production and can be shaped by injecting pressure into a mold.

In fact, the plastics are lightweight and easy to shape, with the least amount of information the most complex geometric shapes can be easily given. Therefore, they have a very wide application area [8].

1.6 History of Plastic

It is assumed that the plastics industry starts with commercial production of nitrocellulose (1868).

Following nitrocellulose, phenol-formaldehyde based polymers were developed in the historical process. Their production was realized approximately 40 years after this date. Polymers, which are the basic building blocks and raw materials of these and other plastic materials followed, have emerged by chance in the mid-19th century and many of them have emerged by chance.

It has been shown that plastics are composed of chain-shaped macromolecules and these molecules are composed of small units covalently connected with each other.

Plastics, which are the most important properties, were developed rapidly and in 1927 cellulose acetate and polyvinyl chloride, in 1928, olimethylmethacrylate and in 1929 urea-formaldehyde resins were obtained. These were followed by polyethylene in 1932, nylon, polyacrylonitrile, styrene-acrylonitrile and polyvinyl acetate in 1934, polyurethane in 1937, poly (tetrafluoroethylene), known in 1939 as teflon trade, followed by polyacrylonitrile fiber in 1941 known as polyethylene terephthalate and orlon.

An important step in the development of plastics is the production of 3 plastics reinforced by mixing these materials with glass, graphite and carbon fibers. The mechanical properties of these materials reach the level of metals, and in many applications, plastics are competing with metals. Sample composite materials can be given to the material which is brought to the level close to the metal [8].

1.7 Molecular Structures of Plastics

The main primary substances of plastics are hydrocarbons. Unsaturated hydrocarbons also have two or more covalent bonds between C atoms. C atoms are generally H, others have CI, F, O, N and S atoms. One of the double covalent bonds between the C atoms is usually removed by temperature, pressure or catalyst.

As shown in Figure 1.4.b, there are electrons in the two side reaction bonds and therefore the valence energy level is aborted. In this case, two neighboring ethylene monomers share one electron and form a covalent bond between them. Thus, a large number of ethylene monomers are added together to form a polyethylene polymer chain. Polymer chains can only form weak bonds with each other.

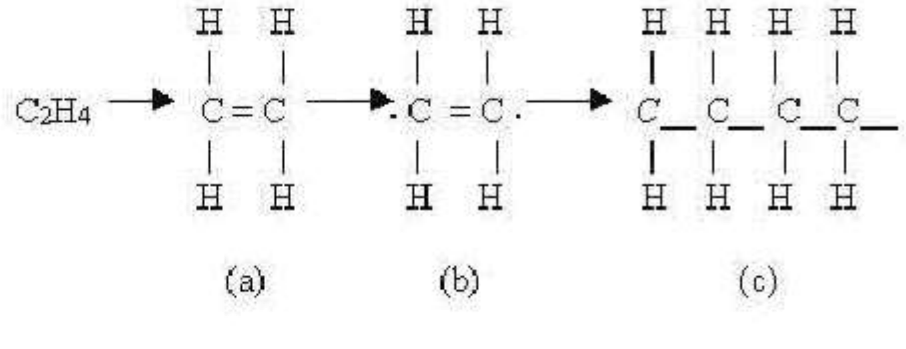

Figure 1.4 a) Ethylene Monomer **b)** Two Reaction Bound Ethylene Monomers, **c)** Ethylene Monomer [8]

The hydrocarbon chains have the general formula $C_m H_{2m+2}$**.** As the number of m in the chain increases, the size of the molecule grows, the number of weak bonds between them increases, while in the first gaseous state, the liquid then becomes solid. As can be seen in Figure 1.5 (a), while the number m is between 1-4 gas, between 5-11 liquid, between 12-20 oil, between 20 and 50 candles and the larger, solid. As the length of the molecular chain increases.

The number of bonds increases, so the strength increases naturally. This is seen in Figure 1.5.b.

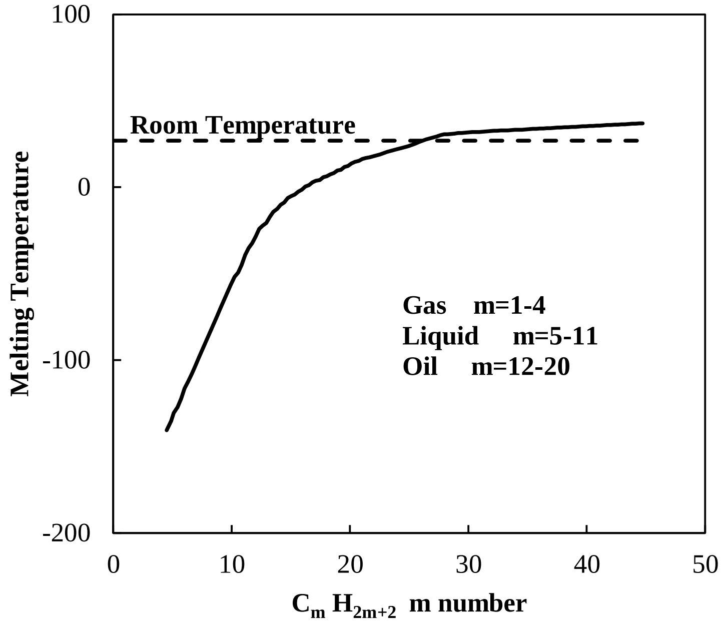

Figure 1.5 (a) The number of m in the polymer and the melting temperature change

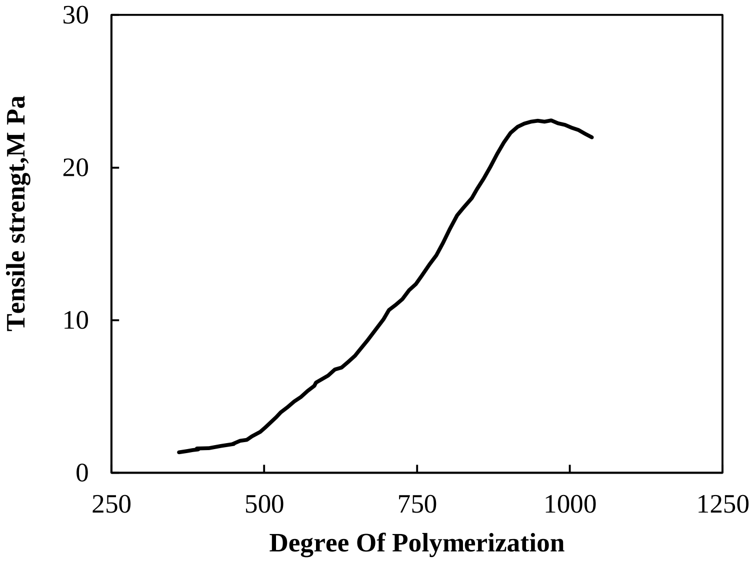

Figure 1.5 (b) The change in the number of m and the strength

1.8 Properties of Plastics

The properties and variety of plastics vary widely. The main properties of plastics can be listed as follows;

- Their shape ability is easy and simple to process. Plastics can deform under lower forces than metals. The processing temperatures are below 400°C, but this temperature range is between 120°C and 320°C. The low values of these temperatures ensure that the amount of energy required to process plastics is also low. They are suitable for the production of complex structured products without requiring time consuming and high cost finishing processes as well as the automation techniques that enable mass production, i.e. production in high production quantities.

- Their density is lower than other materials. They are lighter than metals and ceramics. Their density ranges from 0.8 g / cm^3 to 2.2 g / cm^3. While low density values are lightweight, high strength plastics have become the most preferred class of lightweight materials in systems where the weight / strength ratio is important.

-The properties of additives can be changed. These additive materials; fillers such as mineral and calcite used for economic reasons that do not change the properties of the material.

- Reinforcing material such as glass fibers and carbon fibers, which improve the mechanical properties of the material such as the modulus of elasticity and tensile strength.

- Flame retardants added to increase the flame resistance of the material and reduce flammability.

- Materials used to prevent material deterioration.

- They have variable mechanical properties. Although they have a lower tensile strength and a modulus of elasticity than metals, but these values changing within a

wide-frame. So much so; the tensile strengths of glass-fiber reinforced plastics have become competitive with aluminum, one of the lightest metals.
Nowadays, by using some filling materials, plastics having higher mechanical strength than metals can be formed.

- Plastics hardly transmit or transmit heat and electricity. Compared with metals, the relatively low conductivity of plastics has led to the use of plastics as insulation material. Low electrical conductivity has incorporated plastics into electrical insulating materials. Some plastics may be required to transmit electricity. Additives such as carbon black may also be used to deliver electricity to the electricity.

- Some plastics have a transparent appearance. This feature makes it suitable for the production of plastic glasses, cd, and optical discs. These translucent plastic materials are more easily processed than glass and have highly advanced optical and mechanical properties.

- Plastics have high resistance to chemicals. Due to the fact that the atomic structures of plastics are different from metals, they exhibit more resistance to corrosion than metals. Although there are not many chemical environments with which they are resistant, plastics have gained many applications with the help of these properties. Examples include home appliances, vehicle-resistant auto parts, plastics and acid tanks used in food and cosmetics industries for packaging purposes.

- Producing plastics as raw materials requires less energy than its predecessor (metals, ceramics and other composites). Therefore, considering the production methods used in the production of plastics, plastic production becomes an economic situation. [9]

1.9 Thermoplastics

Plastics can be classified as thermosets, elastomers and thermoplastics. In this thesis LDPE thermoplastic material will be used as thermoplastic material. For that reason only thermoplastics are examined.

In recent years, the increase in the use of thermoplastic products in various industries such as automotive, micro-electro-mechanical systems, computing, medical, and optical and telecommunication has brought with it the fast production requirement of high quality products in these industries [10].

Plastic injection is achieved by fluidizing the thermoplastic material under a certain temperature and friction, by applying pressure and shaping it in the mold.

The fact that the raw material can be molded as desired in a single operation and does not require final processing applications for the product manufactured in many cases has made this method very suitable for mass production according to other plastic material forming techniques (pressure molding, rotary molding, heat forming by pressure, blowing)[10].

Thermoplastic polymers are meltable and reshapable polymers when heated. These are long chain linear or branched molecules formed by heat and pressure above a critical temperature called glass transition temperature. London's forces, polar interactions, hydrogen bonds keep polymer chains together. There is no physical link between the molecules. There are only weak electrostatic tensile forces holding the molecules together. This is a heat-sensitive force that prevents the movement of intermolecular traction chains between each other. Thus, when a thermoplastic consisting of linear molecule chains is heated, the force between the molecules is weakened, the molecular chains are free to act as liquids relative to each other, and the material can be easily shaped in a mold. When the material is cooled, the intermolecular force grows and freezes the molecular chains in the new manner given. Once melted, they can be molded in almost any form by common techniques such as injection molding and extrusion.

Each thermoplastic polymer has a unique glass transition temperature. If it is a thermoplastic with a crystal structure, there is a wide melting temperature range (Tm) in addition to Tg. Unlike small molecules, polymers of average molecular weight (polydispers) do not melt at a single temperature[11].

1.9.1 Polyethylene

In its simplest form, the polyethylene molecule is a polymer molecule formed by the coupling of an even number of carbon atoms together with a covalent bond with a pair of hydrogen atoms terminated with a chain end methyl group. Chemically, the polyethylene plastic consists of those having the formula C2nH4n + 2. The "n" in this formula is called the degree of polymerization. Chemical structure of PE material gives Figure.1.6. Polyethylene molecules do not have a descriptive molecule as in organic compounds. Typically, the polyethylene molecule is formed by combining between 100 and 250000 monomers. Low molecular weight polyethylenes contain from 8 to 100 monomers. The structure of this type of low molecular weight polyethylene is waxy and generally does not have plastic properties [12].

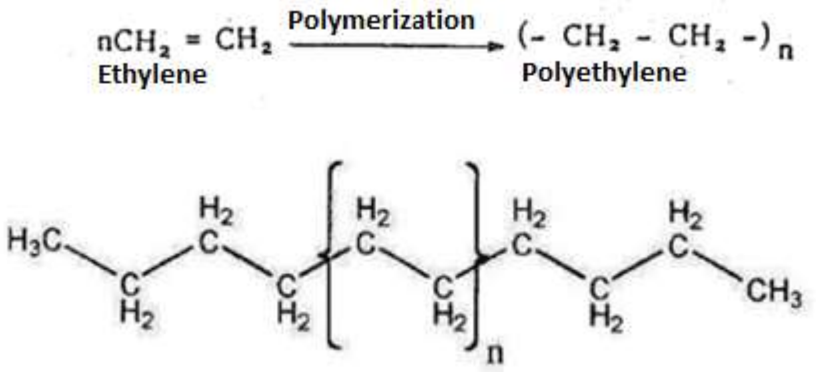

Figure 1.6 Chemical structure of PE material

It is resistant to polyethylene chemicals and abrasion. Electrical property, impact notch strength is high [15]. Polyethylene is one of the oldest polymers of the thermoplastic family and has only been developed while producing only low density and three new types of polyethylene, high density, linear and medium density, have been added to the family.

Each of the four polyethylene species is monomer ethylene and the various structures of the polymer molecule have led to the emergence of these three new species. The different branching states of the macromolecules, which form the polymer molecule, provide the diversity of polyethylene. For example, in linear low density polyethylene, the branching is almost non-existent, slightly high in high density and more in medium density polyethylene. In low-density polyethylene, branching is at the maximum level and branching is long and short, affecting polymer properties. These four types of polyethylene are the basic polymeric materials of industry and have very different fields of use. General characteristics of polyethylene are as follows:

a) Strong,
b) Resistant to acids, bases and solvents,
c) Dielectric properties are superior,
d) Resistant to environmental conditions,
e) Easy to process[12].

Branches in the polymer chain determine the degree of crystallinity. Linear and high density polyethylene branching is very small and the molecular structure is linear. A schematic representation of the polyethylene chain is given in Figure 1.7 (a) and PE branched chain is given (b). Crystallinity is generally higher in molecular structures with low branching. As the crystallinity in the polymer increases, the hardness increases, the mechanical and chemical properties are improved and the resistance to liquids and gases increases. The polymer that best describes the polymers is the average MW of that polymer. The average MW is determined by approximately the melt index. The melt index is inversely proportional to the molecular weight. Higher molecular weight PEs have higher hardness and toughness, and lower melt flow indices (MFI). Generally, the high molecular weight is equivalent to the low melt flow index (DPT 2001), according to the rule that applies to all polymers [12].

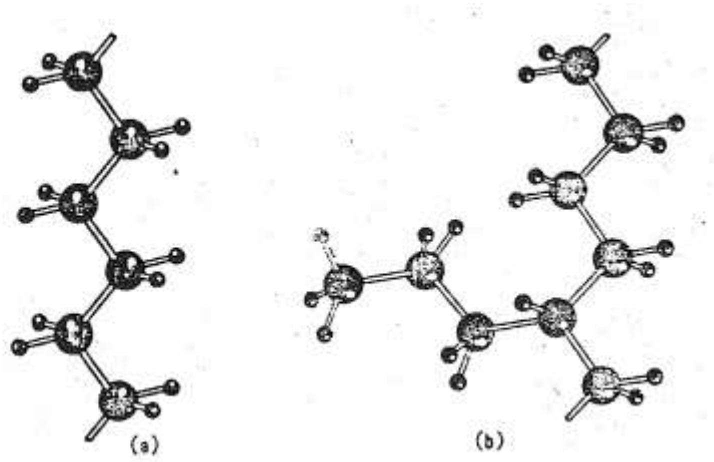

Figure 1.7 (a) Schematic representation of the polyethylene chain **(b)** Polyethylene branched chain [12]

1.9.2 Low Density Polyethylene (LDPE)

LDPE is produced from polymeric microorganisms in the temperature range of 130-350 ° C under 1200-3000 atmospheric pressure. The density of LDPE varies between 0.910-0.925 gr / cm^3. LDPE films are bright, transparent and easy to use. Food packaging, construction covers, garbage bags, garbage bags are examples of usage areas of LDPE films [13].

1.9.2.1 Mechanical Properties of LDPE

LDPE's fatigue resistance under dynamic load is good. Yield increases as the elongation increases depending on the flow temperature. LDPE surface is smooth and slippery material in terms of friction. It has a lower surface friction coefficient than many plastics and metals (e.g. aluminum) [14].

1.9.2.2 Electric Properties of LDPE

Because PE is a very good insulator, it is produced for the isolation of radar cables in World War II. Nowadays, PE is the material that is used more often in the handling of materials related to power and communication.

The dielectric coefficient increases in direct proportion to the LDPE density. The electrical properties of LDPE do not change when heated, and are not affected by temperature and frequency [10].

1.9.3 Medium Density Polyethytlene (MDPE)

MDPE density is between 0.925-0.94gr / cm³ and is obtained in high or low pressure processes. Natural gas and water lines find use in pipe manufacturing [10].

1.9.4 High Density Polyethylene (HDPE)

HDPE is obtained by polymerization of ethylene gas at low pressure and temperature in hexane medium by redox polymerization or in combination with Ziegler -Natta type coordination catalysts.

As shown in Figure 1.8 HDPE is a thermoplastic material having a crystalline phase of 90-95%. It can be used at temperatures between -80 ºC and 80 ºC. The microstructure of HDPE contains two phases, amorphous and crystal.

This is important for the macroscopic measurements of both phases to appear. The amorphous phase, such as rubber at room temperature, allows the crystal phase to move and change in certain amounts without any separation. This form of deformation is called plastic, which can be recovered in large amounts and occurs without any break in the molecular chain. This feature allows the semi-crystalline polymers to have high toughness.
During the slow cooling of the HDPE, the rate of crystallization is higher than the rapid cooling.

The cooling process causes material properties to change significantly. During the extrusion or injection molding process, the flow of the polymer melt causes different orientations and consequently the formation of anisotropic structure. This results in large differences in mechanical properties. Molecular orientation; increases the strength, toughness and crack resistance.

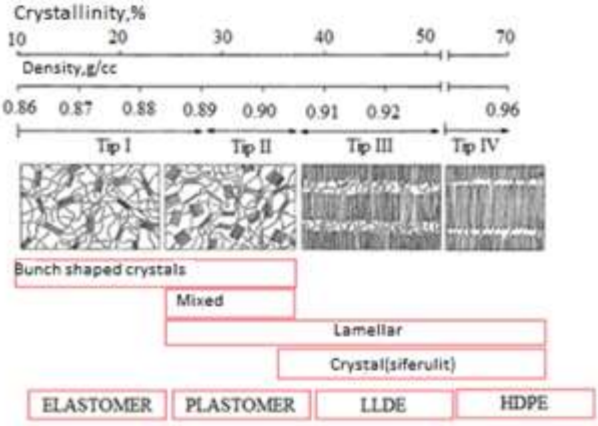

Figure 1.8 Schematic comparison of 4 polymer types in terms of HDPE density and crystal.

The microstructure of semi-crystalline polymers is quite complex. The physical properties of HDPE depend on three interrelated fundamental variables; density, MW and MW distribution. HDPE has a spherulite morphology. An increase in the crystalline phase region results in increased density. Hardness and yield stress of polyethylene material increase due to increase in density. HDPE is often used in pipe construction due to its high strength. In addition, the softening temperature and chemical resistance increase with increasing density.

Impact strength, elongation, permeability and crack resistance at low temperatures are reduced by increasing density. Most commercial HDPEs range from 50000 to 250000 (g / mol) molecular weight. By increasing molecular weight, the tensile strength (creep and rupture), elongation, toughness, tensile crack resistance, creep resistance, chemical resistance, gas barrier properties are improved. Different molecular weight distribution can also be obtained from HDPE. If this distribution is within the narrow range; low temperature effect, toughness, tensile crack resistance and softening temperature increases.

Low melt viscosity, high injection and creep resistance are obtained in wide molecular distribution. Tensile strength and elongation are not affected by the molecular weight distribution.

The properties of semi-crystalline polymers vary not only by their chemical properties but also by their morphological and they are exposed to crystallization structure according to the thermal processes. Therefore, production process conditions are highly effective on the final product properties.

The mechanical properties of the semi-crystalline polymers are achieved by the molecular bonds between the crystals. Polymer chain arrangements and bonding molecules are two major factors affecting mechanical properties. If the molecular bonds do not consist of covalent bonds, the crystals are held together with weak van der Waals or hydrogen bonds. Weak van der Waals ties easily allow for slippage and disintegration. High deformation shrinkage of semi-crystalline polymers leads to orientation of the crystalline phase in the amorphous phase in the direction of traction and results in the reorganization of the molecular structure, in other words, hardening (deformation hardening).

On the other hand, no significant change in the polymer morphology is observed at small voltage levels (below the pour point). The elastic deformation mechanism in the red crystalline polymers is related to the forced extension of the chain molecules in the stable order. The reaction of the material with the applied stress is caused by the elongation and bending of the strong covalent bonds in the chains. In addition, very weak secondary resistance or van der Waals bonds between neighboring molecules also have effects. The most important effect on elastic behavior is undoubtedly on the modulus of elasticity. Since the semi-crystalline polymers consist of two different phases, the elastic modulus can be calculated from its composition in two combinations of two phases, considering the composite material [16]. The PE classification and densities are given in the Table 1.2.

Table 1.2 Density classification of polyethylene [14]

Density(g/cm³)	General Name	Symbol
0,91 - 0,925	Low density polyethylene	LDPE
0,926 - 0,940	Medium density polyethylene	MDPE
0,941 - 0,959	High density polyethylene	HDPE
Above 0,96	Very high weight polyethylene	UHMW-PE

1.10 Importance of the Study

In recent years, researchers have focused their attention on polymers reinforced with nano-sized materials with an alternative to conventional filled polymers. The number of carbon-based nano reinforcement materials is increasing; they range from carbon nanotubes to carbon nanofibers and fullerenes to graphene. The superior properties of graphene compared to polymers are also reflected in polymer / graphene nanocomposites. Polymer / graphene nanocomposites have superior mechanical, thermal, gas barrier electrical and flame-retardant properties compared to neat polymer. It has also been reported that improved mechanical and electrical properties of graphene-based polymer nanocomposites are better than clay of other carbon filler-based polymer nanocomposites. For that reason, effects of graphene nanoplatelets on properites of PE material is investigated in this study.

1.11 Methods and Outline of the Study

In this work three different (0.1, 5 and 10 wt.%) nanographene ratios have been added to the LDPE. The nanocomposites were prepared by the double screw extrusion machine and filmed in the blown line.

- The thickness,
- heat seal,
- tear,
- coefficient of friction,
- tensile tests of the produced films were carried out in accordance with ASTM standards.

The study is divided into five sections.

1. General introduction and definitions of graphene, plastics and PE and their properties are given in the first chapter. Types of PE is also given.

2. In the second chapter, general literature survey has been carried out for nano-additives in plastics and their effects were examined.

3. In chapter 3, information about production of graphene nanoplates based PE materials, test methods and general description of blown film machine were given.

4. In chapter 4, the test results were given and discussed.

5. In chapter 5, general conclusions and future works were given.

CHAPTER 2
LITERATURE SURVEY

2.1 Introduction

In this section, literature survey has been carried out for nano particle additives in materials. Literature survey has grouped as LDPE with nano additives, LDPE based nanocomposites and PE based thermoplastic material with nanographene.

2.2 Polyethylene and Polypropylene thermoplastics with Nano Additive Nanocomposites

Atar et al. [17] examined mechanical properties of HDPE with addition of thermoplastic starch (TPN) and maleic anhydride (MAPE). The samples were produced by injection molding method. Specific gravity, tensile strength, tensile modulus, flexural strength, flexural modulus and elongation at break of the manufactured polymer composites were investigated. Thermoplastic starch amount is effecting the mechanical properties in different way. Such that when thermoplastic starch increased, elongation at break and tensile strength decreased, but flexural strength and flexural modulus increased.

Güldaş et al. [18] PP to different proportions of zinc borate was added in the study of maleic anhydride as the binding agent. According to this study, it was found that viscosity value of composite increased depending on zinc borate ratio but viscosity decreased depending on increasing temperature and pressure. It was determined that MFI values have been increased depending on increasing temperature and pressure whereas MFI values have been decreased according to increasing zinc borate rate. In addition, it has been seen that shear rate decreases depending on increasing proportion of additive but it increases with the increase of temperature and pressure.

Mirik et al. [19] studied charpy impact resistance of the high density polyethylene reinforced with multi-walled carbon nanotube material. Mechanical and impact resistance tests were examined according to ASTM standards. As a result of the researches, when; MWNT/HDPE tensile strength test, mass loss temperature and melting point temperature were observed to increase. However, it was observed that impact resistance decreased.

Lai C et al. [20] examined two types of commercial fumed nanosilica, were incorporated into mPE to improve the mechanical properties of mPE/silica nanocomposites using a melt-mixing approach. Tensile strength and young's modulus, dynamic shear storage modulus were investigated. The surface modified silica system showed slightly higher tensile strength and young’s modulus than the bare silica system an high levels of interaction between the modified silica and mPE matrix rendered limited increments in terms of the dynamic shear storage modulus at the terminal zone region. High levels of interaction between the modified silica and mPE matrix rendered limited increments in terms of the dynamic shear storage modulus at the terminal zone region. Young modulus and tensile strength increased in silica added product.

Zhao et al. [21] investigated the mechanical properties of polyethylene / clay compound by melting the polyethylene montmorillonite clay and using a different binder. Nanocomposite was added to 2 phr organoclay and the peak heat release rate of the nanocomposite was reduced. When the clay content is increased, the strength modulus increases and the notched impact strength decreases.

Liang et al. [22] mechanical properties of polyethylene, maleic anhydride grafted polyethylene, organic-montmorillonite nanocomposites were prepared to modify montmorillonite. Tensile strength increased at the beginning, but decreased when the maleic anhydride ratio was increased. When the highest tensile strength value was 23.3Mpa, the maleic concentration was 6%.When the maleic anhydride ratio was 9%, the impact strength was 122.2 J / m. The impact strength increased by 60% compared to the composite without maleic anhydride test result.

Brian et al. [23] examined to wear behavior carbon nanotube reinforced (1%, 3%, 5%) of high density polyethylene composites. The wear resistance of the molded specimens for the abrasion test was investigated by mixing the carbon nanotubes with extrusion, and they indicated that the abrasion resistance decreased when the carbon nanotube content increased.

Lotti et al. [24] studied mechanical properties by adding maleic anhydride and clay to high density polyethylene. Production by changing the screw profile from a small dispersion to a high dispersion configuration. Both films had a 95% increase in elastic modulus and a reduction of 60% and 45% and water vapor permeability rates compared to pure HDPE film, respectively.

Yetkin et al. [25] examined mechanical properties of PP raw materials added to EPDM rubber, nanoclay and adaptive substance. The PP polymer blend in the form of a granule and the PP polymer nano-composites were produced using an extrusion machine, and then the samples for tensile and impact tests were molded by an injection molding machine. The results showed that with the addition of EPDM and nanoclay filler to the PPD polymer, tensile strength and tensile modulus decreased with increasing tensile strength and tensile strength. The friction coefficient and specific wear rate of PP polymer composites increased with increasing shear rate and applied load. While tensile strength and tensile coefficient decreased, impact strength and elongation at break were increased by the addition of EPDM and nanoclay filler to the PP polymer. The friction coefficient and specific wear rate of PP polymer composites increased with increasing shear rate and applied loads. The COF and specific wear ratio of PP polymer composites increased with increasing shear rate and applied load.

2.3 LDPE Based Nanocomposites

There are a lot of studies about nano particle addition on LDPE materials. In this section only important studies will be examined.

Lee et al. [26] investigated morphology of clay dispersion on LDPE/clay nanocomposite. Nanocomposites were produced by melt blending with and without a maleated polyethylene (PE-g-MAn) as the coupling agent. As a result of their study, 0.1 wt% of clay addition gave the best performance.

Mechanical and gas barrier properties of LDPE/clay nanocomposite film were examined by Arunvisut et. al. [27] LDPE and clay nanoparticles were melt-mixed with twin screw extruder, after that material was re-extruded through blown-film die. 1, 3, 5 and 7 wt. % of nanoclay was used. Tensile modulus and tensile strength at yield of blown film LDPE/clay nanocomposites improved in both TD and MD tests when compared between 7 wt. % PE/clay nanocomposites and neat PE. Gas permeability capacity was also increased with increase of clay content. However, elongation at yield decreased when increased in clay loading. Similar study was carried out by Zhon et al. [28]. They found that mechanical properties increased up to 5 wt. % of clay nanoparticle addition.

Durmuş et al. [29] investigated thermal, mechanical and barrier properties of low molecular weight oxidized polyethylene LDPE / clay nanocomposites. The added of only oxidized polyethylene compatibilizer to LLDPE reduced permeability by 44%. The addition of 5 phr of clay resulted in a combined nanocomposite structure and reduced permeability by 11%. The physical performance of the nanocomposites was not only affected by the clay dispersion and it was found that the oxidized polyethylene compatibilizers affected both the melt viscosity and polarity.

Electrical properties of LDPE/ZnO nanocomposites were examined by Hong et al. [30][31]. Melt mixing method was used to get homogeneous dispersion of ZnO particles on PE material. They investigated the effect of particle size on dielectric properties as conventional particles (submicrons) and nanoparticles. As the decrease of particle size, dielectric properties of LDPE material were increased.

Xia et al. [32] examined the structure and thermal characteristics of copper/low-density-polyethylene (Cu/LDPE) nanocomposites produced using a melt-blending technique in a single-screw extruder. Structure and thermal characteristics of Cu/LDPE composites were characterized by XRD, SEM, EDS, DSC and TGA. The thermal stability of the Cu/LDPE nanocomposites decreased after 2 wt. % of copper nanoparticles.

Joker et al. [33] studied on melt production of low density polyethylene (LDPE)-Silver nanocomposite film. They compared mechanical properties of LDPE/silver nanocomposites with silver free LDPE films. As a result of the study there were not significantly difference between results.

Xiao et al. [34] examined the rheological and mechanical properties of LDPE composites reinforced by MWNT. Young's modulus increased by 85% and tensile strength by 46% when 10% MWNT was added to low density polyethylene.

Çakır et al. [35] investigated to the effect of poly (dimethyl siloxane) (PDMS) admixture and the composition of LDPE / mPE blends on the thermal and mechanical properties of nanocomposites containing organic modified clay (O-MMT). When PDMS is added to the nanocomposites, mechanical properties of the product change importantly. In general, the elasticity modulus of the samples decreased with increasing amount of PDMS and an increase in elongation at break was observed.

Izod impact strength and stiffness values are reduced with the addition of PDMS. The hardest samples were identified as not included PDMS nanocomposites. The varying amounts of LDPE and mPE showed the same trend in mechanical test results of pure PE blends and PDMS-containing / non-PDCs. Thermal properties of all mixtures were examined by DSC analysis. The degree of crystallization (Xc) of the samples decreases with increasing amount of PDMS. This is more pronounced in LDPE rich nanocomposites. The degree of crystallization in mPE matrix nanocomposites is higher and values decrease as the amount of LDPE in the blends increases.

Durmuş et al. [36] examined the low density polyethylene (LLDPE) / clay nanocomposites were prepared by melt blending method and the rheological properties of the products were examined by dynamic rotational rheometer. Linear viscoelastic behaviors of the prepared nanocomposite sample was tested depending on the composition. In the prepared nanocomposites, it was determined that the materials exhibited solid phase behavior in the low frequency region with the increase of clay amount and / or improvement of the clay distribution, the melt viscosities of the samples shifted towards the power-law behavior and the clay distribution caused a strong shear thinning.

Jacquelot et al. [37] examined the nanocomposites were studied in two ways, the first with pure LDPE and the second with an organo-modified montmorillonite bonded with maleic anhydride. Increased montmorillonite content caused a significant increase in barrier properties. Intermediates such as oxidized paraffin’s have been shown to be more effective in reducing gas permeability than polyethylene and the dependence of gas transport properties has been discussed not only as a function of the clay dispersion but also as a function of the clay / compatibilizer.

2.4 Graphene Addition to Thermoplastic

Sever and Tavman [38] examined mechanical and electrical properties of HDPE reinforced with two different graphite particle sizes (5-7µm and 40-55µm in diameter). Tensile strength, young's modulus and elongation at break were obtained from tensile tests and storage modulus and loss modulus were obtained from dynamic mechanical analysis. Different weight percentages of graphite particles (5%, 10%, 15%, 20% and 40%) were added matrix. As a result of experiments, tensile strength were increased up to 10 wt. % of graphite addition. 40 wt. % of graphite have the highest conductivity value.

Emek [39] studied forming of nanocomposite by adding different amounts of graphite powder to high density polyethylene. The purpose of the studies to understand the heat capacity of the added graphite powder at different rates and to compare with the theoretical model. It was observed that the heat capacity decreased by increasing the grafit ratio.

Erikli and Hasanoğlu [40] studied the effects the graphene oxide, reduced graphene oxide and aramid, reduced graphene oxide aramid material on high density PE. Air bubbles remaining in the composite have been found to adversely affect the tensile properties. However, when SEM images were examined, it was found that the distance between the reduced graphene oxide layers decreased compared to the graphene oxide.

Altay et al. [41] studied the mechanical and thermal performance of graphite reinforced UHMWPE nano-composite materials produced by distributing different quantities of graphite. In the study results, when the graphite was added to the sample, it was determined that the maximum decomposition temperature were not affected due to increase in elasticity and hardness modulus and decrease in surface roughness. The tensile strength being increased at a rate of 0.1% by weight and graphite additive ratio was found to decrease after this rate.

Subaşı et al. [42] investigated the mechanical and thermal properties of nanocomposites obtained from the incorporation of nano materials such as graphene, graphene oxide and graphite into the polyester matrix. As a result of the study was an important development in mechanical and thermal properties in polyester matrix composites using nano material such as graphene, graphene oxide and graphite in the range of 0.05% -3% by weight.

Kim et al. [43] studied the mechanical properties by adding different amounts of graphene nanocomposite to LLDPE. Tensile modulus was higher for composites with functionalized polyethylenes when solvent blending was used. However, at less than 3 wt. % of thermally reduced graphene (TRG), electrical conductivity of the unmodified LLDPE was higher than that of the functionalized ones. This may be due to phase segregation between graphene and PE, and electrical percolation within the continuous filler-rich phase.

Zheng et al. [44] investigated mechanical and electrical properties of reinforced HDPE with expanded and untreated graphite. When the graphite was added, the viscosity increased, the increase in the expanded graphite viscosity was higher than the untreated graphite viscosity. The values overall degree of crystallinity and the melting temperature of HDPE decreased with the addition of expanded and untreated graphite.

C Fim et al. [45] examined mechanical, thermal and electrical properties of PE and different proportions of graphene added to PE nanoplates. Tensile strength, gas barrier properties, electrical conductivity, thermal stability composites were investigated. Thermal stability was evaluated by thermogravimetric analysis (TGA) and showed that the addition of GNS to the polyolefin matrix increased the initial decomposition temperature by 30 ° C. A slight reduction in tensile strength was found. On the other hand, dynamic mechanical analysis showed an increase in the storage modulus of nanocomposites compared to pure PE.

Krupa et al. [46] examined the thermal diffusivity, electrical conductivity and mechanical properties of high density polyethylene, polystyrene/graphite composites. Increased electrical conductivity at a given filler concentration. Increased nonlinear thermal conductivity was observed with an increase in graphite content.

Gaska et al. [47] investigated the electrical, mechanical and thermal properties of nanocomposites based on low density polyethylene (LDPE) filled with graphene nanoplatelet (GnP). It can be observed that the maximum stress in the MD and TD direction decreases as the filler content increases and the tensile strength increases for the filler samples. Increased yield strength is observed in all samples as filler increases. Observe that 1% and 5% by weight samples show lower DC conductivity than reference LDPE. Inclusion of low concentrations of GnP in polyethylene has been found to reduce the effective conductivity of the LDPE-GnP composite.

Pang et al. [48] investigated the thermal performance of GO / ultrahigh molecular weight polyethylene (UHMWPE) composites using liquid phase ultrasonic mixing followed by hot pressing. The results show that crystallinity increases with the addition of GO. The addition of GO improved the thermal performance of the GO / UHMWPE. Not only did the impact strength increase significantly with the addition of GO, but also the micro-hardness was gradually improved and the tensile properties were improved with the addition of GO.

Lin et al. [49] tested the stress, dynamic, mechanical and thermal properties of pure HDPE and HDPE by adding graphite nanoplatelets (GNPs) and graphene oxide (GO) as reinforcing fillers. Injection molding method was used for production. The additive rates for GNP were in the range of 0.1% and 10%, and the additive rates for GO were 0.05% and 1.5%. The additives were found to improve mechanical properties, with a 56% increase in elastic modulus of the composite with 10% GNP added and a 23% increase in maximum stress on clean HDPE. A slight increase in crystallization temperature was observed for GNP composites, while a similar decrease in melting point was recorded for both systems.

Suner et al. [50] studied GO's mechanical properties by adding GO to UHMWPE. It was shown that the thermal stability, oxidative resistance, mechanical properties and wettability of UHMWPE are improved by the addition of GO. UHMWPE / GO materials prepared with GO concentrations up to 0.5% by weight showed optimum mechanical and wettability properties compared to pure UHMWPE and nano-composites with high GO content. Additionally, Ionita et al. [51] reported similar results on the effect of graphene oxide on polysulfone; compositions with a low GO content of up to 1% by weight showed increased tensile strength compared to smooth polysulfone, but due to poor dispersion, the addition of the detection of GO-induced mechanical properties was added. Tai et al. [52] found that the wear resistance of UHMWPE / GO composites decreased by up to 0.7% by weight as the GO content increased, but after that the wear rate showed little change.

2.5 Conclusion of Literature Survey

The following conclusions can be obtained from the previous literature review:

- Nanomaterials were used to improve mechanical and thermal properties of the polymers because nanomaterials have high surface area/volume ratio which causes exceptional properties. Since the aspect ratio of the nanomaterials is very high, it is sufficient to add the small weight percentages to obtain the desired properties. Thus, the properties can be increased exponentially with a negligible weight increase.
- There are a lot of nanoparticles that are used to improve mechanical and thermal properties of polymers.
- Carbon nanotubes, ZnO, TiO, nanoclay, nanosilica nanoparticles were generally used in nanocomposites.
- LDPE and HDPE thermoplastics were generally used as a matrix for nanocomposites.
- Production of thermoplastic nanocomposites were generally obtained by melt-mixing method with twin screw extruder.
- Maleic anhydride was generally used as filler and binder material. $CaCO_3$ was also used as a filler in thermoplastics.

According to known literature, there is no any study mechanical properties of LDPE/graphene nanocomposite. For that reason, the effect of graphene nano particles on the LDPE thermoplastic films is investigated in this study. The ratios of graphene nanoparticles were used as 0.1, 5 and 10 wt. %. The graphene and granular LDPE material were mixed and extruded by twin screw extruder. After that taken film nanocomposite were obtained by blow film method. Tensile strength, thickness, heat performance, tensile stress, tear, COF tests were carried out in accordance with ASTM standards.

CHAPTER 3

MATERIALS AND METHODS

3.1 Introduction

This chapter deals with explanation of materials used, production methods and test methods in the thesis. Petkim LDPE F2-12 thermoplastic material was used as a matrix and graphene nanoparticles were used as a reinforcement. To improve productivity of thermoplastic films some of the agents were used.

In this work three different (0.1, 5 and 10 wt.%) nanographene ratios have been added to the LDPE. The nanocomposites were prepared by the double screw extrusion machine and filmed in the blown line. The thickness, heat seal, tear, coefficient of friction, tensile tests of the produced films were carried out in accordance with ASTM standards.

3.2 Materials

LDPE(F2-12) material was supplied from Petkim Petrokimya Holding Co, İstanbul, Turkey and nano graphene material was supplied from Grafen Chemical Industries Co., Ankara, Turkey. LDPE F2-12 type material properties are given in Table 3.1 and nanographene material properties are given in Table 3.2.

Table 3.1 Properties of LDPE

Properties	**Typical Value**	**Unit**
Resin Properties		
Melt Flow Rate (190°C/2.16 kg)	2.5	g/10 min
Density, 23°C	0.920	g/cm^3
Melting Point (DSC)	110	°C
Film Properties		
Tensile Strength at Yield, MD	11	MPa
Tensile Strength at Yield, TD	10	MPa
Tensile Strength at Break, MD	23	MPa
Tensile Strength at Break, TD	17	MPa
Elongation at Break, MD	>200	%
Elongation at Break, TD	>500	%
Tear Strength, MD	330	cN
Tear Strength, TD	240	cN
Thermal Properties		
Vicat Softening Point, 10 N	92	°C

Table 3.2 Properties of graphene nano platelets

Density	50 kg/m^3
Fibre thickness	5-8 nm
Surface area	120-150 m^2/g
Diameter	5 µm

3.3 Production of Nanocomposite Films

LDPE-graphene nanocomposite was fabricated by melt blending method by extrusion with the use of LAB TECH twin-screw extruder as shown in Figure 3.1. The fabrication process was done in one step; different ratios of graphene nanoparticles were added (0.1, 5 and 10 wt. %) to the LDPE (F2-12) in the twin screw extruder from the feed line, and it was homogenized with heat in the head section and granulated by passing through the water.

Temperature profile of extruder was 170 ºC, 170 ºC, 165 ºC, 165 ºC, 165 ºC, 165 ºC, 160 ºC, 160 ºC, 160 ºC, 160 ºC , 160 ºC and 160 ºC, respectively, from input (feeding spot) to the output (die spot). Extruder head temperatures generally range from 150-

160 ° to 200 °. The screw speed of the extruder was 140 rpm. The attractive speed was 6m/min. The machine L/D ratio was 30.

Figure 3.1 LAB TECH twin-screw extruder

The LDPE raw material entered the main feeder point of the extruder by the volumetric feeder, and the LDPE granule melted in the extruder was manually filled into the graphene extruder from the second feeder point and the amount of each inlet was continuously controlled. The nanocomposites exiting the extrusion process were long tubular and passed through the cooling bath before exiting. At this stage, it is aimed to obtain homogeneous nanocomposite.

LDPE/nanographene nanocomposite films were produced by blown film method. The granulated LDPE (F2-12) and graphene material were added to the blown film machine, the prepared mixture was compressed by heaters and transmitted to the head region. The molten substance coming into the head was passed through three-stage cooling and its diameter was adjusted and thickness control was performed. After that finished film was wrapped in the winder and process was finished.

LDPE-graphene nanocomposite was fabricated by blown extrusion method with the use of LAB TECH extruder as shown in Figure 3.2. The fabrication process was done in one step; different ratios of graphene nanoparticles granulated were added (0.1, 5 and 10 wt. %) to the LDPE (F2-12) in the blown extruder from the feed line.

All samples are in screw speed control mode at 120 rpm extrusion was fed manually. Temperature profile of extruder was 170 ºC, 170 ºC, 170 ºC, 165 ºC, 165 ºC, 160 ºC, 160 ºC, 160 ºC, 160 ºC, 160 ºC and 160 ºC, respectively, from input (feeding spot) to the output (die spot). Extruder head temperatures generally range from 150-160 °C to 200 °C. The molten plastic from the extruder is extruded vertically. Then the spilled material is squeezed between the mold and air is blown into the mold. The screw speed of the extruder was 120 rpm. The attractive speed was 2.7m/min. The machine L/D ratio was 30. All parameters were kept constant conditions of production parameters because the mechanical properties of nanocomposite films would be significantly affected.

Figure 3.2 LAB TECH blown extruder

Three different LDPE/graphene nanocomposites were produced. Composition and names of nanocomposites are tabulated in Table 3.3 and named as F1, F2, F3 and F4.

Table 3.3 Composition and names of nanocomposites

Name	**F1**	**F2**	**F3**	**F4**
Mixing Ratios	%100 F2-12	90% F2-12 + 9.9% $CaCO_3$ + 0.1% Graphene	%95 F2-12 + %5 Graphene	%90 F2-12 + %10 Graphene

3.4 Tensile Test

Tensile tests measure the force required to break the specimen and the extent to which the specimen stretches or elongates to that breaking point. Tensile tests produce a stress-strain diagram, which is used to determine tensile modulus. The data is often used to specify a material, to design parts to withstand application force and as a quality control check of materials.

The Zwick tensile test machine (as shown in Figure 3.3) grip the start position at 65mm, speed start position at 1000mm/min, pre-load 0.2N, specimen width constant 25mm, test speed 500mm/min. The device measures the breaking, elongation and tensile forces by pulling the cut sample from the upper and lower jaw to a certain extent. Tests were carried out in accordance with ASTM D882 standard.

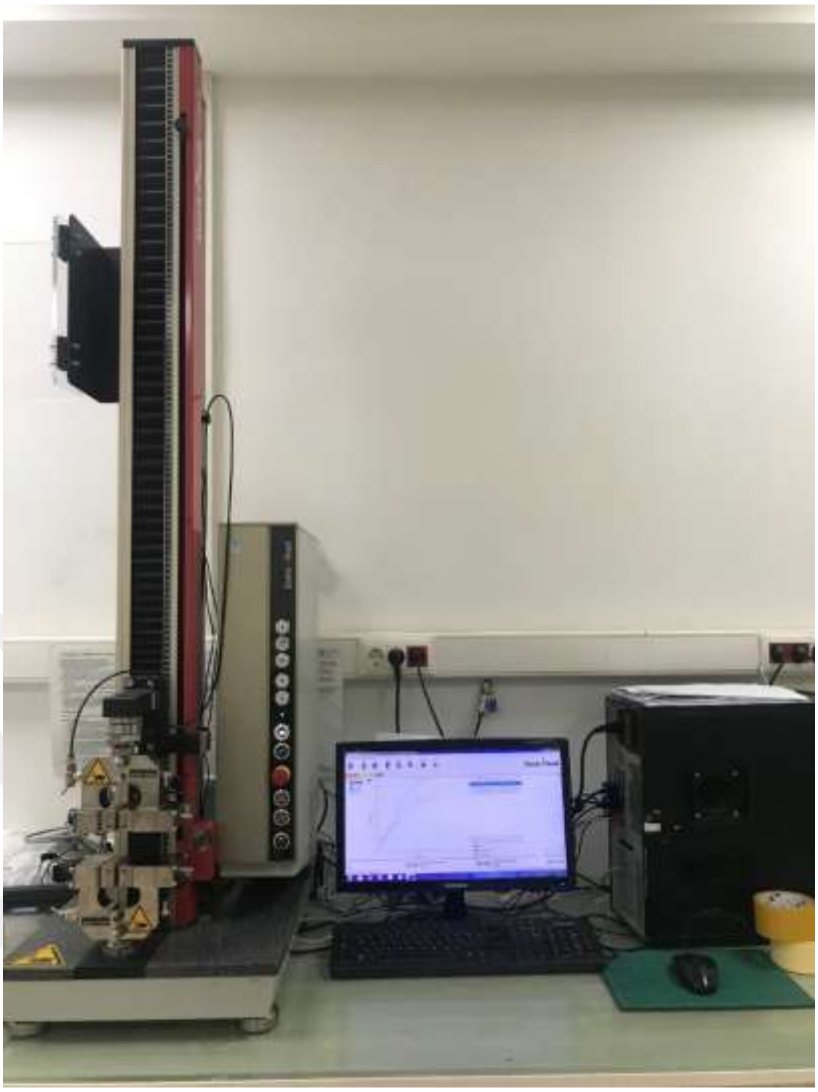

Figure 3.3 Zwick tensile test machine

3.5 Heat Seal Test

CLASSIC 513 Gradient Heat Seal Tester (as shown in Figure 3.4) is professionally designed for the determination of heat sealability of plastic films, composite films, coated paper, and other sealing films under certain sealing speed, pressure and 5 different temperatures.

Each jaw applies a pressure of 120kPa and has a 1.5cm jaw width. Tests have been carried out in accordance with ASTM F88 standard.

The heat sealability of heat sealing materials would be greatly affected by the factors of melting point, thermal stability, fluidity and thickness. The optimal heat sealability parameters can be obtained accurately and efficiently through this instrument.

Figure 3.4 Heat seal tester

In order to find suitable degree of heat seal property of the LDPE product, the film is conglutinationed in two layers with a hot jaw and then allowed to cool, the film has been cooled. The upper and lower layers are separated as gives Figure 3.5 and it is the most suitable degree when the film layers are stuck together.

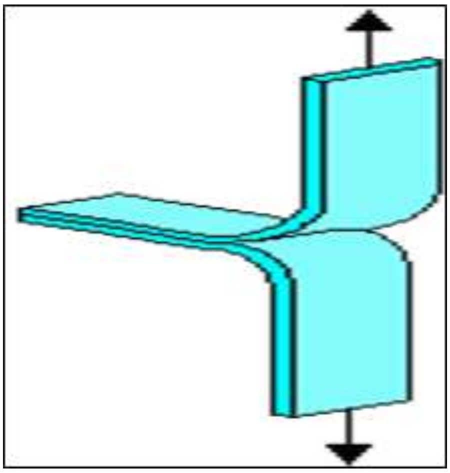

Figure 3.5 Separation of the film surfaces affixed with heat sealing device

3.6 COF Test

The LabThink COF tester (as shown in Figure 3.6) was used for measuring the lubricity of the film. It is also measuring the coefficient of friction of the film. ASTM D1894 standard was used. The film cut to a certain size (10 x 10 mm) was placed on a 200gram apparatus and the table was placed on a sliding device. The device works at a speed of 200 m/min and has a frictional force by applying force to the film in the opposite of rotation direction. As the COF value grows, the slippage of the film decreases. The film slippage increases as the COF value decreases.

Figure 3.6 LabThink COF Tester

3.7 Measurement of Thickness

The LabThink thickness tester determined min - max and average thicknesses by measuring the thickness of the film at exact intervals. When the film is placed, thickness measurement is made by applying 0.5N force at certain intervals with the upper apparatus. Usually this process is done by measuring the thickness or micrometer at the end of 5 cm. This range can be narrowed and expanded according to the width of the film. 0.5N force is generally used in the films used in the packaging sector of PE and PP.

The measurement range is important because the thickness device measures the micron distribution of the film from point regions. It also automatically calculates the standard deviation of the measurement results.

Figure 3.7 LabThink thickness tester

3.8 Tear Test

The overall goal of a tear test is to determine a materials ability to resist the growth of the initial tear or its “tear resistance”. The value of a material’s tear resistance is generally accepted to be the force required to complete the tear so that it has gone completely though the material so that it has been separated into two sections. This characteristic is particularly important to applications that use flexible materials that may suffer a partial rupture intentionally or otherwise.

A tear test is generally only performed upon flexible materials as they are more susceptible to accidental fractures and punctures as well as partial ruptures (tears and holes). The more common materials that benefit from tear testing are textiles, fabrics, elastomers, rubbers, polymers, packaging and paper products. Each of these materials can have serve in a wide range of industries such as clothing, medical, biomedical, and dental.

The LabThink tear tester (as shown in Figure 3.8) use the Elmendorf tear method, notch is cut at certain dimensions and tearing is provided from that point, depending on the pendulum angle. The apparatus is used as 800gf.

A tear test applies a force to a material that already contains a partial fracture or rupture otherwise known as a “tear” in order to bring the material to complete failure. This is done by placing the test sample into a tensile testing or universal test machine so that the section on one side of the fracture is pulled up and the section on the other side is pulled down. A steady load is then applied until the tear has propagated through the entirety of the sample and the two sections have been completely separated from one another.

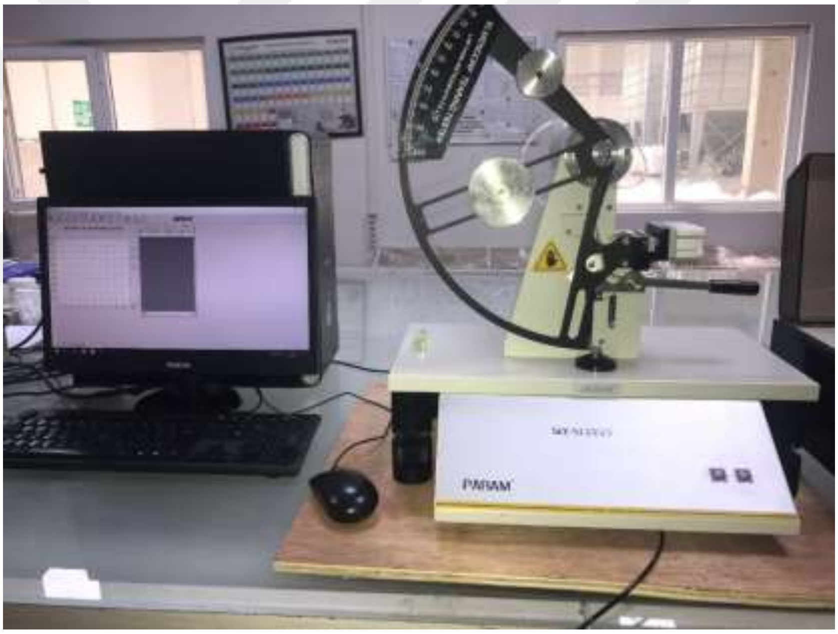

Figure 3.8 LabThink tear tester

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Introduction

In this section, experimental results are discussed to examine the effect of graphene on the mechanical properties of the LDPE.

4.2 Production of Specimens

The images of the films having 100% F2-12 and 0.1, 5 and 10 wt. % graphene ratios produced by the blown method is shown in Figures 4.1 to 4.4. When the graphene ratio increased, color of films are become darker.

Figure 4.1 100% F2-12 (Pure LDPE Film)

Figure 4.2 90% F2-12 + 9.9% $CaCO_3$ + 0.1% Graphene (LDPE/0.1 wt.% graphene)

Figure 4.3 95% F2-12 + 5% Graphene (LDPE/5 wt.% graphene)

Figure 4.4 90% F2-12 + 10% Graphene (LDPE/10 wt.% graphene)

4.3 Thickness Results

Pure LDPE and LDPE added in different proportions of graphene thickness test results given the Table 4.1.

Table 4.1 Thickness Values of Produced Samples

Name	**F1**	**F2**	**F3**	**F4**
Mixing Ratios	%100 F2-12	90% F2-12 + 9.9% $CaCO_3$ + 0.1% Graphene	%95 F2-12 + %5 Graphene	%90 F2-12 + %10 Graphene
Thickness (μm)	17	19	25	27

The thickness results of the 17, 19, 25 and 27 micron. According to the test results an increase of 12%, 47% and 59% in thickness is observed for F2, F3 and F4 specimens, respectively. According to the thickness results, when the graphene ratio increased, the film hardened and tried to be formed under higher temperature. Therefore, the thickness increases as the graphene ratio increases due to drafting difficulty.

4.4 Tensile Results

Tensile test results of LDPE and LDPE with different graphene ratio are given in the Table 4.1 as results in machine direction (MD) and transverse direction (TD). Figures 4.6-8-10-12 give deformed specimens and Figures 4.5-7-9-11 give force elongation diagram of the samples. All tensile results were compared with pure LPDE film results.

Table 4.2 Tensile Values of Produced Samples

Name		**F1**	**F2**	**F3**	**F4**
Mixing Ratios		%100 F2-12	%90 F2-12 + %9,9 $CaCO_3$ + %0,1 Graphene	%95 F2-12 + %5 Graphene	%90 F2-12+ %10graphene
Thickness (µm)		17	19	25	27
Tensile Strength (N/25mm)	**MD**	12,55	12,15	12,52	14,22
	TD	7,22	6,35	4,65	5,7
Tensile Strength (MPa)	**MD**	28,92	24,75	21,12	19,75
	TD	16,72	12,87	7,35	6,72
Break Elongation (%)	**MD**	251	219	180	172
	TD	569	504	313	178

The tensile strength in the machine direction of the specimens are 28.92, 24.75, 21.12 and 19.75 MPa. Tensile strength in machine direction of LDPE/graphene films were decreased with 14.41%, 26.97% and, 31.7%, for F2, F3 and F4 specimens, respectively.

The tensile strength in the transverse direction of the specimens are 16.72, 12.87, 7.35 and 6.72 MPa. Tensile strength in transverse direction of LDPE/graphene films were decreased with 23.02%, 56.04% and, 59.8%, for F2, F3 and F4 specimens, respectively.

The percent elongation in the machine direction of the specimens are 251, 219, 180 and 172. A decrease of 12.74%, 28.28% and 31.47% in percent elongation is observed in machine direction for F2, F3 and F4 specimens compared with pure LDPE film.

The percent elongation in the transverse direction of the specimens are 569, 504, 313 and 178. A decrease of 14.42%, 44.99% and 68.71% in percent elongation is observed in transverse direction for F2, F3 and F4 specimens compared with pure LDPE film.

The low tensile test results in LDPE/graphene nanocomposites are thought to be due to the low graphene content or due to agglomeration of the polymer in the matrix or due to poor bonding of the polymer matrix to the graphene particles. According to breaking samples, when the graphene ratio increased, sample elongations decreased and also contraction in transverse direction of broken points decreased due to increase of hardness and thickness of films.

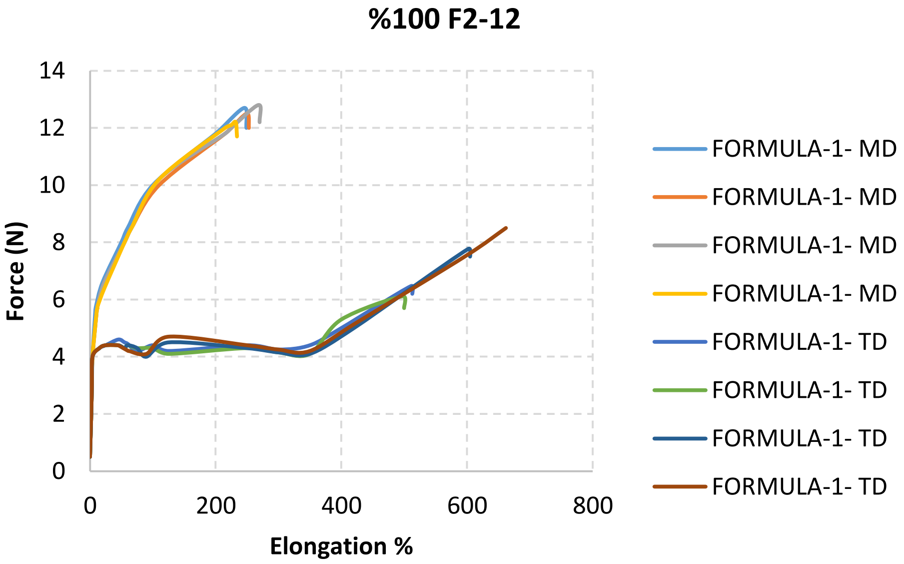

Figure 4.5 %100 F2-12 (pure LDPE film) Force-Elongation Diagram

Figure 4.6 %100 F2-12 (pure LDPE film) **(a)** Machine Direction Break Form **(b)**Transverse Direction Break Form

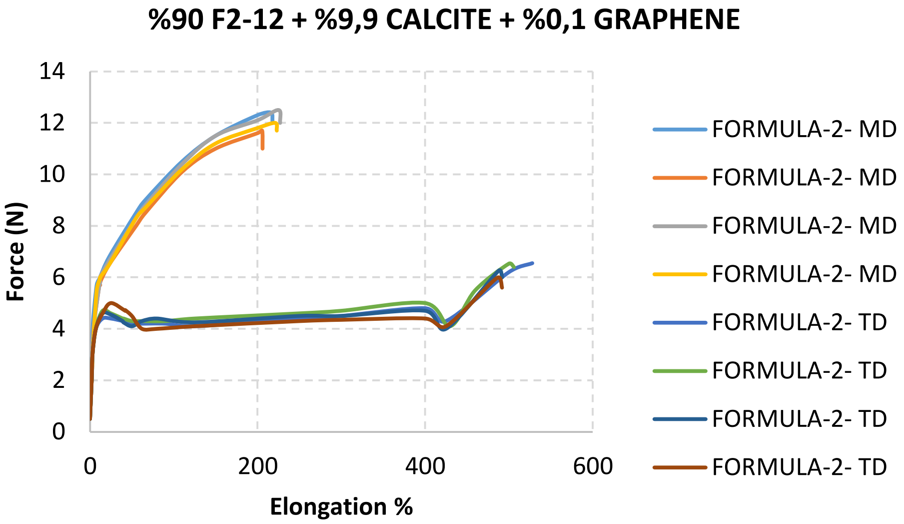

Figure 4.7 %90 F2-12 + %9.9 CALCITE + %0.1 Graphene (LDPE/0.1 wt.% graphene) Force-Elongation Diagram

Figure 4.8 %90 F2-12 + %9.9 Calcite + %0.1 Graphene (LDPE/0.1 wt.% graphene) **(a)** Machine Direction Break Form **(b)** Transverse Direction Break Form

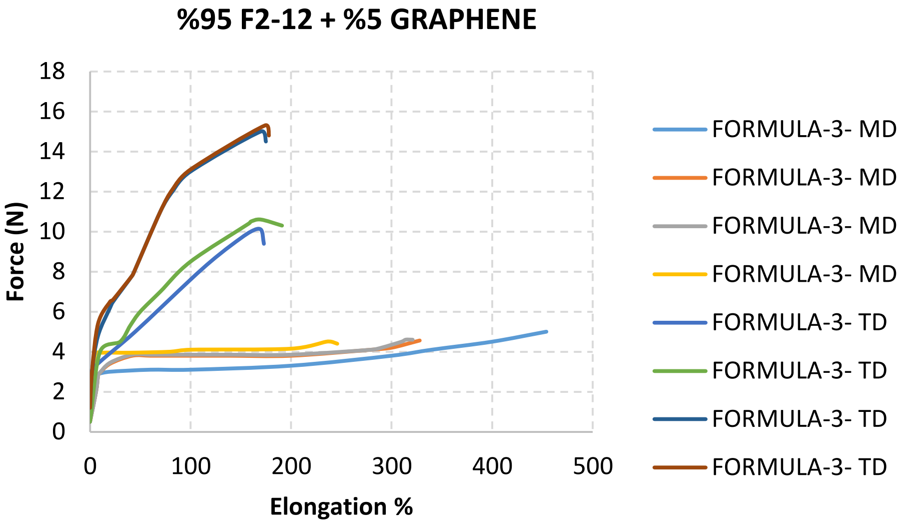

Figure 4.9 %95 F2-12 + %5 Graphene (LDPE/5 wt.% graphene) Force-Elongation Diagram

Figure 4.10 %95 F2-12 + %5 (LDPE/5 wt.% graphene) **(a)** Machine Direction Break Form **(b)**Transverse Direction Break Form Diagram

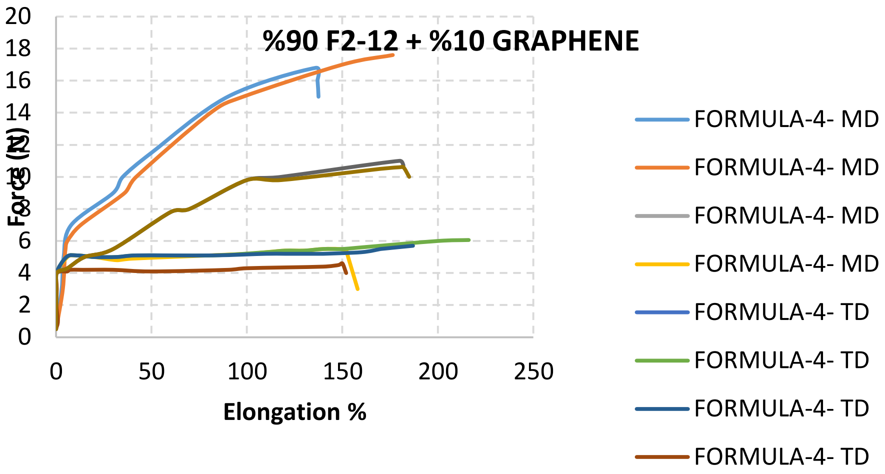

Figure 4.11 %90 F2-12 + %10 (LDPE/10 wt.% graphene) - Graphene Force-Elongation Diagram

Figure 4.12 %90 F2-12 + %10 (LDPE/10 wt.% graphene) **(a)** Machine Direction Break Form **(b)**Transverse Direction Break Form

4.5 Heat Seal Results

LDPE and LDPE in different proportions of graphene heat seal test results are given the Table 4.3. Heat seal test were carried out based on KTL-022 ASTM F88 standard. Although the micron and graphene ratio changed, the heat seal test results did not change. Because graphene did not make chemical bond with LDPE that could change the heat adhesion properties.

Table 4.3 Heat Seal Values of Produced Samples

Name		**F1**	**F2**	**F3**	**F4**
Mixing Ratios		%100 F2-12	%90 F2-12 + %9,9 $CaCO_3$ + %0,1 GRAPHENE	%95 F2-12 + %5 GRAPHENE	%90 F2-12 + %10 GRAPHENE
Thickness (µm)		17	19	25	27
Heat Seal Temperature (°C) (120 KPa - 1 Sec.)	**A/B**	-	-	-	-
	B/B	108 - 109	108 - 109	109	109

4.6 COF Results

LDPE and LDPE in different proportions of graphene COF test results are given the Table 4.4. COF test were carried out based on KTL-023 ASTM D 1894 standard. Friction force is not changed in specimen F3 and F4, because there is no binding between maleic anhydride and graphene nano particles. COF value for F2 specimen is lower than pure specimen because there was a $CaCO_3$ in the formulation as a binder for LDPE and graphene.

Table 4.4 COF Values of Produced Samples

Names		**F1**	**F2**	**F3**	**F4**
Mixing Ratios		%100 F2-12	%90 F2-12 + %9,9 $CaCO_3$ + %0,1 GRAPHENE	%95 F2-12 + %5 GRAPHENE	%90 F2-12 + %10GRAPHENE
Thickness(µm)		17	19	25	27
Coefficient Of Friction (Film/Metal)	**B/M**	0,20	0,11	0,16	0,16
	B/M	0,19	0,12	0,19	0,15

4.7 Tear Test Results

LDPE and LDPE in different proportions of graphene tear test results is given the Table 4.5. According to the machine direction tear results, there was a 15.82% increase in F2 specimen, 44.1% and 97.16% decrease in F3 and F4 specimens. For the transverse direction there was a 15.82%, 35.25% decrease in F2 and F3 specimens and 7.91% increase in F4 specimens.

As the thickness and graphene ratio increased, the tear test values decreased. This indicating that the nanoparticles did not distribute well in the matrix.

Table 4.5 Tear Values of Produced Samples

Names		**F1**	**F2**	**F3**	**F4**
Mixing Rations		%100 F2-12	%90 F2-12 + %9,9 $CaCO_3$ + %0,1 GRAPHENE	%95 F2-12 + %5 GRAPHENE	%90 F2-12 + %10 GRAPHENE
Thickness (μm)		17	19	25	27
Tearing Test (800 gf)	**MD**	214 - 244	217 - 311	70 - 186	0 - 13
	TD	126 - 152	159 - 163	60 - 120	107 - 194

4.8 Microscope Image (50X)

The microscope images of the films having is shown in Figures 4.13-16. According to images, when graphene content increases, agglomeration in graphene particles increases. Due to increase of thickness and need more heat to get a film, there was scratches on the surface of the films especially on F2 specimen. Also, it’s seen that, when the ratio of graphene particles increased, there were not homogeneously distributed inside the matrix.

Figure 4.13 F1 (%100 LDPE)

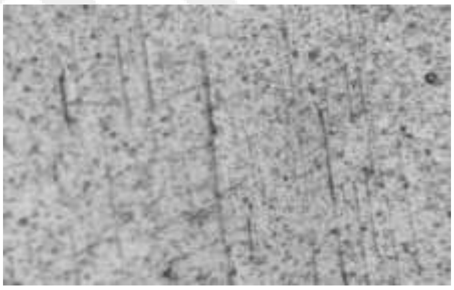

Figure 4.14 F2 (LDPE/0.1 wt.% graphene)

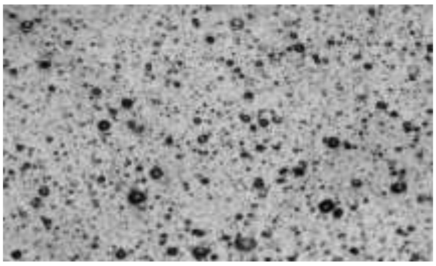

Figure 4.15 F3 (LDPE/5 wt.% graphene)

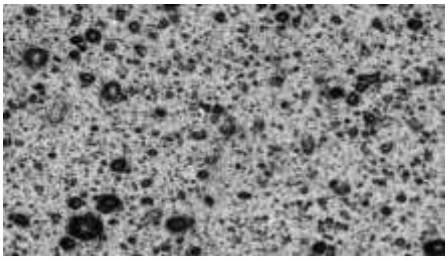

Figure 4.16 F4 (LDPE/10 wt.% graphene)

CHAPTER 5

GENERAL CONCLUSIONS AND FUTURE WORKS

Thickness, heat seal, COF, tear, tensile behavior of LDPE/graphene nanocomposites were investigated under the effects of nano particle addition. LDPE/graphene films were fabricated using twin screw extruder, blown film machine by adding various weight content of graphene nano particles. Tests were carried out according to ASTM standards. Based on the experimental results following conclusions can be summarized:

Thickness of samples were increased with increase of graphene nanoparticles. Thickness of LDPE/graphene films were increased with an amount of 12%, 47% and 59% compared with pure LDPE film for F2, F3 and F4 specimens, respectively.

Tensile strength and elongation decreased with the addition of graphene nanoparticles.

Tensile strength in machine direction of LDPE/graphene films were decreased with 14.41%, 26.97% and, 31.7%, for F2, F3 and F4 specimens, respectively.

Tensile strength in transverse direction of LDPE/graphene films were decreased with %23.02, 56.04% and, 59.8%, for F2, F3 and F4 specimens, respectively.

The percent elongation in the machine direction of the specimens are 251, 219, 180 and 172. A decrease of 12.74%, 28.28% and 31.47% in percent elongation is observed in machine direction for F2, F3 and F4 specimens compared with pure LDPE film.

The percent elongation in the transverse direction of the specimens are 569, 504, 313 and 178. A decrease of 14.42%, 44.99% and 68.71% in percent elongation is observed in transverse direction for F2, F3 and F4 specimens compared with pure LDPE film.

The increase in graphene contribution did not affect the heat seal results.

The increase in graphene contribution did not affect the COF results.

According to the machine direction tear results, there is a 15.28% increase in F2 specimen, 44.1% and 97.16% decrease in F3 and F4 specimens. For the transverse direction there is 15.82%, 35.25% decrease in F2 and F3 specimens and 7.91% increase in F4 specimens.

5.1 Future Works

It can be extended in the following aspects:

- Investigation of mechanical properties by adding graphene to GNP

- The impact resistance test method can be viewed by pulling GNP in larger widths

- Graphene can be used as an additive to polypropylene and its properties can be examined

to provide GNP electrical conductivity gain.

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