ELECTRICAL AND MECHANICAL PROPERTIES OF CARBON BLACK REINFORCED HIGH DENSITY POLYETHYLENE/LOW DENSITY POLYETHYLENE COMPOSITES

A THESIS SUBMITTED TO
THE GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES OF
THE MIDDLE EAST TECHNICAL UNIVERSITY

BY
BEKIR ALTINTAS

IN PARTIAL FULLFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF
MASTER OF SCIENCE
IN

THE DEPARTMENT OF POLYMER SCIENCE AND TECHNOLOGY

MAY 2004

Approval of the graduate school of the Natural and Applied Sciences.

Prof. Dr. Canan Özgen
Director

I certify that thesis satisfies all the requirements as a thesis for the degree of Master of Sciences.

Prof. Dr. Ali Usanmaz
Head of the Department

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

Prof. Dr. Zuhal Küçükyavuz
Supervisor

Examining Committee Members

Prof. Dr. Ali USANMAZ (Chair Person) ________________________

Prof. Dr. Zuhal KÜÇÜKYAVUZ ________________________

Prof. Dr. Erdal BAYRAMLI ________________________

Prof. Dr. Olgun GÜVEN ________________________

Prof. Dr. Teoman TINÇER ________________________

I hereby declare that all information in this document has been obtained and presented in accordance with academic rules and ethical conduct. I also declare that, as required by these rules and conduct, I have fully cited and referenced all material and results that are not original to this work.

Bekir ALTINTAS

ABSTRACT

ELECTRICAL AND MECHANICAL PROPERTIES OF CARBON BLACK REINFORCED HIGH DENSITY POLYETHYLENE/LOW DENSITY POLYETHYLENE COMPOSITES

Altintas, Bekir

M.S., Department of Polymer Science and Technology
Supervisor: Prof.Dr. Zuhal Küçükyavuz

May 2004, 73 pages

In this study, the High Density Polyethylene (HDPE) and Low Density Polyethylene (LDPE) blends prepared by Plasticorder Brabender were strengthened by adding Carbon Black (CB).

Blends were prepared at 190 °C. Amounts of LDPE were changed to 30, 40, 50 and 60 percent by the volume and the percent amounts of CB were changed to 5, 10, 15, 20 and 30 according to the total volume. Thermal and morphological properties were investigated by using Differential Scanning Calorimeter (DSC), Scanning Electron Microscope (SEM). Mechanical properties were investigated by tensile test and hardness measurements. Melt flow properties were studied by Melt Flow Index (MFI) measurements. Electrical conductivities were measured by four probe and two probe techniques. Temperature dependence of electrical conductivity was also studied.

In general, it is observed that stress at break and MFI values decrease by the addition of CB; however, modulus and hardness increase. DSC results indicated that the crystallization of the polymer blend was decreased by the addition of CB. SEM results showed that the components were mixed homogenously. Increasing CB content increased electrical conductivity. Furthermore, by increasing the temperature, positive temperature coefficient behavior was observed which increases when CB content decreased.

Keywords: HDPE-LDPE Blend, Carbon Black, Mechanical, Morphological, Thermal, Melt Flow and Electrical Properties.

ÖZ

KARBON SIYAHI ILE GÜÇLENDIRILMIS YÜKSEK YOGUNLUKLU POLIETILEN/ALÇAK YOGUNLUKLU POLIETILEN KOMPOZITLERININ ELEKTRIKSEL VE MEKANIK ÖZELLIKLERININ INCELENMESI

Altintas, Bekir

Yüksek Lisans, Polimer Bilimi ve Teknolojisi Bölümü,
Tez Yöneticisi: Prof.Dr. Zuhal Küçükyavuz

Mayis 2004, 73 sayfa

Bu çalismada Plasticorder Brabender ile hazirlanan Yüksek Yogunluklu Polietilen (YYPE) ve Alçak Yogunluklu Polietilen (AYPE) karisimlari çesitli oranlarda karbon siyahi (KS) ilavesi ile güçlendirildi.

Karisimlar 190 °C de hazirlandi. Karisimlarda AYPE yüzdeleri hacimce 30, 40, 50 ve 60, KS yüzdeleri toplam hacme göre 5,10,15,20 ve 30 olarak degistirilmistir. Termal özellikleri Diferansiyel Taramali Kalorimetre, morfolojik yapilar Taramali Elektron Mikroskobu, mekanik özellikleri ise gerilme testi ve sertlik testi ile incelendi. Erime akis özellikleri ise Erime Akisi Indeksi ile çalisildi. Örneklerin elektriksel iletkenlikleri dört nokta ve iki nokta teknikleri kullanilarak ölçüldü. Elektriksel iletkenligin sicakliga bagliligi incelendi.

Yapilan ölçümler sonucunda genel olarak kopmadaki mukavemeti ve eriyik indeksi degerleri karbon siyahi ilavesi ile azaldigi; elastisite modülü ve sertligin arttigi gözlenmistir. Taramali Elektron Mikroskobu sonuçlarindan malzemelerin birbiri ile tamamen karistigi gözlemlenmistir. Diferansiyel Taramali Kalorimetre sonuçlari polimer karisimlarinin kristalinitesinin karbon siyahi ilavesi ile azaldigini göstermistir. Karbon siyahi miktarinin artmasi iletkenligi arttirmistir. Diger yandan sicakligin artmasi ve karbon siyahi miktarinin azalmasi ile artan pozitif sicaklik katsayisi davranisi gözlemlenmistir.

Anahtar Kelimeler: YYPE-AYPE Karisimi, Karbon Siyahi, Mekanik, Morfolojik, Isisal, Eriyik Akiskanligi ve Elektriksel Özellikler.

To My Family

ACKNOWLEDGEMENTS

I would like to express my sincere gratitude to my supervisor Prof. Dr. Zuhal Küçükyavuz for her guidance, patience, advice and encouragement throughout this work.

I would like to thank to my forever love and fiancée Sena Yesir for her support during my studies.

I wish to express my special thanks to Hasan and Güliz Çakmak for their endless helps, unceasing encouragements, technical and moral support throughout this study.

I also wish to thank to my friends M.Fatih Sözbir, Taner Atalar, Cemil Alkan, Yasin Kambur, Tugba Öztürk, Seniz Beyaz Yildirim, Güralp Özkoç, Serkan Ekenel and Semra Can for their technical help and friendships.

I would like to thank to my family for their great sacrifice, unshakeable faith and moral support during my education.

TABLE OF CONTENTS

CHAPTER

LIST OF TABLES

TABLES

LIST OF FIGURES

FIGURE

ABBREVIATIONS

HDPE	High Density Polyethylene
LDPE	Low Density Polyethylene
CB	Carbon black
ASTM	American Society for Testing and Materials
EPDM	Ethylene-Propylene-Diene Terpolymer
PTC	Positive Temperature Coefficient
NTC	Negative Temperature Coefficient
MFI	Melt Flow Index
DSC	Differential Scanning Calorimeter
SEM	Scanning Electron Microscope
PP	Polypropylene
PVC	Poly (Vinyl Chloride)
PS	Polystyrene
DBP	Di-Butyl-Phthalate

CHAPTER I

INTRODUCTION

1.1 Plastics

1.1.1 The Production and Consumption of Plastics

It has been assumed that plastic industry has started with the production of nitrocellulose in commercial scale in 1888. Since phenol formaldehyde polymers were marketed 40 years later as a second commercial polymeric material, it seems that plastics industry did not have a fast start. These two pioneering plastics could be made available depending on the studies in chemistry. On those days, no one was talking about such concepts as molecular structure, high molecular weight-chain like polymer molecules, morphology etc. Due to studies of Staudinger on polystyrene, polyoxymethylene and rubbers in early nineteen twenties, structure of polymeric materials, as well as their chemistry could be understood better and thus their usage as materials could take of considerably. Between 1925-1950, due to good and useful properties, production of many polymeric materials in commercial scale were realized. Some of these polymers were produced from known monomers such as ethylene and styrene while production of others such as polyamides and polyesters could be achieved due to newly developed monomers in this period. (1)

In today's world, in line with the vast amount of knowledge accumulated concerning property-structure relations of polymers and the new monomers developed since the fifties, numbers of polymers which are commercially produced have considerably been increased. Incorporating the desired properties to polymers has also become possible thus; polymer chemists could practically “tailor make” polymers. In addition, in line with the developments in chemical process engineering, many polymers could be produced in low, competitive prices and in big quantities. Therefore, production units with 200-300.000 tons/annual capacities have become average size accustomed plants. (1)

As can be understood from tailor making polymers, the properties and areas of usages of polymers have also become much diversified. Polymeric materials are now produced to be used rigid or flexible plastics, fibers, foams, films, coatings, adhesives etc. As materials, polymers are considered in three large categories as plastics, fibers and rubbers. Plastics have been the polymers whose production and thus consumption rates have been the fastest since the commercialization of polymers. (1)

When examining resource use, it is vital to consider all stages of the life cycle – from extraction and manufacture through the use phase, to end-of-life. Throughout this life cycle, plastics are unique in their ability to save resources. In fact, it is estimated that the use of plastics actually saves more oil than is used for their manufacture. For this reason they should be viewed as ‘champions’ of prevention or resource efficiency –key goals for resource and waste management. Constant research and technological advances mean that plastics are one of the most versatile, lightweight, resource-efficient materials available to society. Improved manufacturing processes, giving plastic materials improved processing and physical properties, have had a huge impact on the resource efficiency of plastics. So, too, having advances in recovery options at end-of-life, including the refinement of recycling options, the increase in energy recovery options from municipal solid waste (MSW) incineration and the producers, development of high calorific alternative fuels. However, it is during the use phase that plastics products can be seen to have their greatest impact on resource efficiency. In Figure 1.1, it’s seen easily that production of plastics increases year to year and higher than other materials like aluminum and steel (2).Demand for plastics remained strong across all industry sectors in 2002, continuing the growth trend and with no particular changes in relative consumption patterns. Fields of application for polymers are shown in Figure 1.2. The packaging sector continues to be the major consumer of plastics. (2)

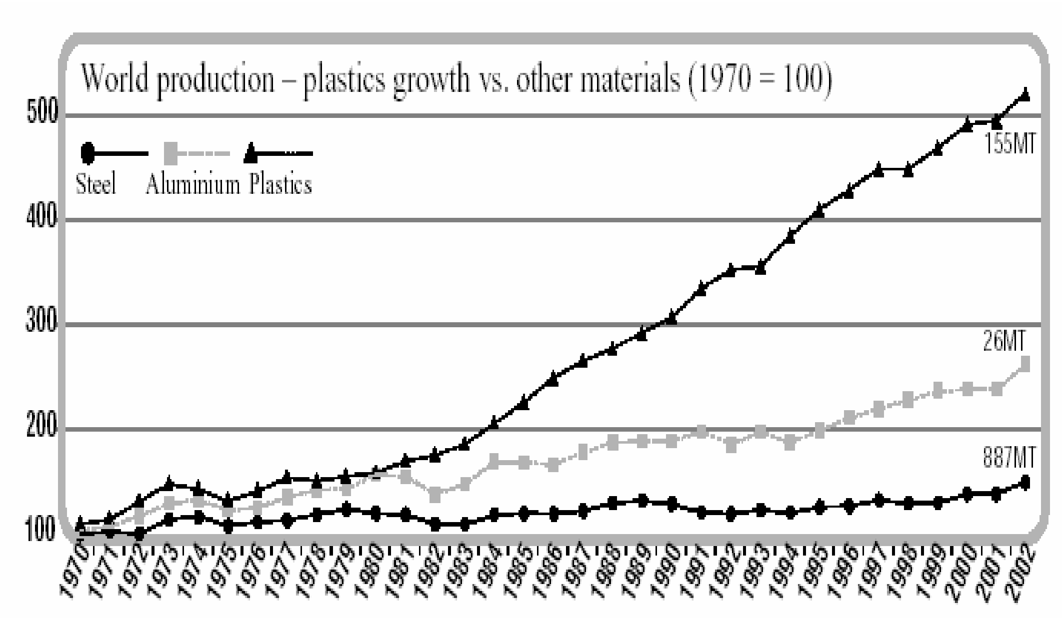


Figure.1.1: World Production – Plastic growth vs. other materials (2).

Dating back only to sixties the Turkish plastic industry is relatively young and one of the fastest growing in the world. The average annual growth rate during the last ten years of the consumption has been in excess of 10% and outperformed the GDP growth of the nation. Applying modern processing technologies results in products, which are not only consumed nationwide but also exported in significant quantities both directly and indirectly.

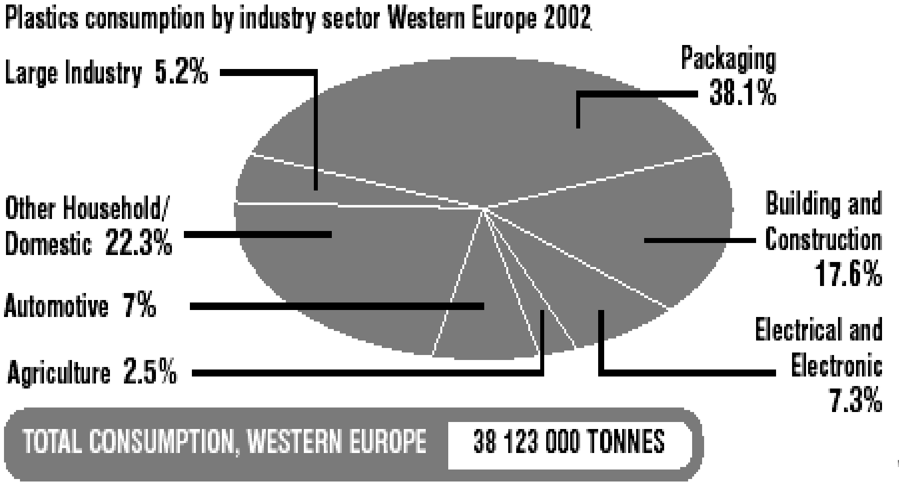


Figure 1.2: Total Consumption of Plastics in Western Europe (2).

The Turkish plastics industry does not only export finished goods. Plastic compounds and additives as well as state of the art processing plants and technologies are produced in Turkey and exported abroad. Currently, Turkish annual polymer consumption of 2.2 million tones ranks number 6 in Europe just behind Spain (Figure 1.3). However, the per capita consumption of 35 kg being far from saturation (though it is higher than the world average) is a clear indication of the future growth. When the consumption reaches 75 - 100 kg, the level of developed countries; Turkey will become a significant player in the world plastic industry with its 65 million populations (3).

The industry houses more than 5000 small to medium scale companies that employ about 120000 people. The major subsegments are packaging and construction materials. The increased exports and changes in the consumption behavior of the population resulted in a rapid growth of the packaging industry in Turkey.

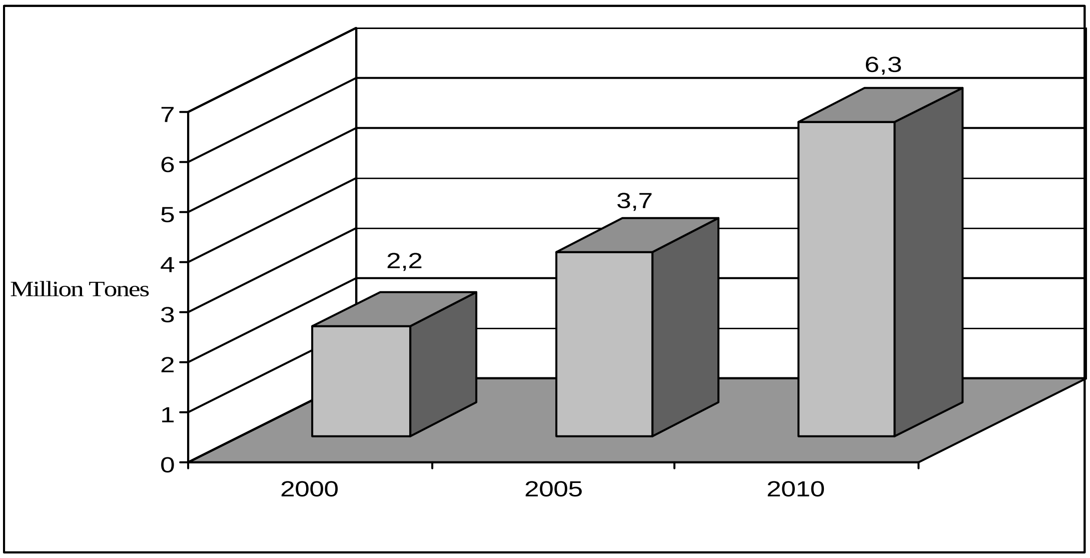


Figure 1.3: Domestic Polymer Consumption in Turkey (3).

On the other hand, automotive and appliance industries - major users of plastic components - are rapidly expanding and new investments are realized in these sectors. Turkey ranks second in synthetic fibers and third in PVC profiles production capacities in Europe. The commodity polymers (PE, PP, PVC, PS) constitute the majority of the consumption (Figure 1.4). PE is used for packaging films, greenhouse films, irrigation pipes, canisters, containers and household items. PP finds its uses in big bags, woven sacks, oriented films, sanitary piping and household items. PVC is used for profiles, claddings, pipes, packaging films, and artificial leather. PS is preferred for packaging cups and appliances. There is a double-digit growth both for PET in bottles and for engineering plastics in electrical and automotive applications (3).

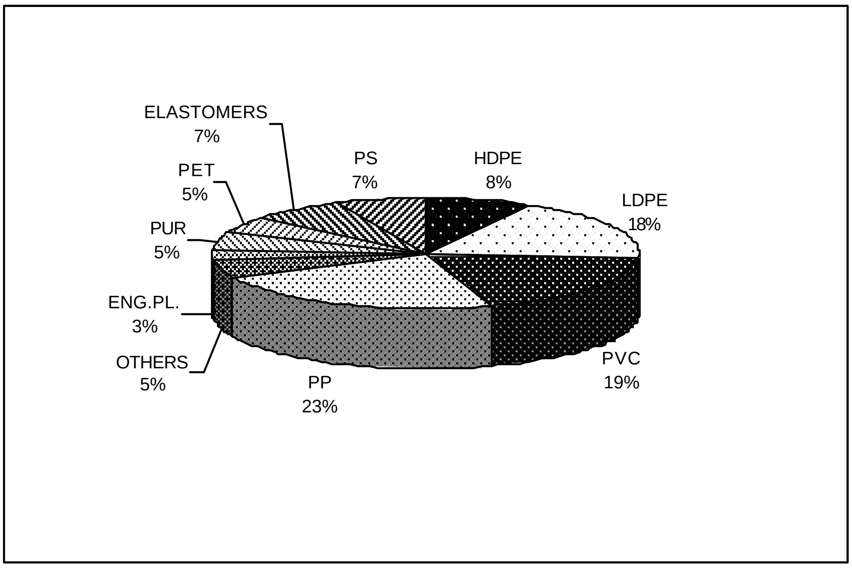


Figure 1.4: Consumption by polymer type in Turkey in 2000 (3).

1.2 Polymer Composites:

A composite material is made by combining two or more materials to give a unique combination of properties. The above definition is more general and can include metals alloys, plastic co-polymers, minerals, and wood.

Without engaging in a through description of what polymer composites are molecularly and chemically, the basic premises for a composite is two or more components comprised together on some level of order of mixing. The general purpose for having multiple components is to either soften or toughen a hard material or harden or strengthen a soft material. Below are 4 general classifications of composites (4):

1. IPN's (Inter-Penetrating Networks)
2. Fiber Composites
3. Nanocomposites
4. Polymer Blends

1.2.1 IPN ' s (Inter-Penetrating Networks)

Inter-penetrating networks is an area of composites which can produce synergistic properties (the material produced has better characteristics than the separate components combined). Most composites do not display properties that exceed the additive properties of the components. A tradition definition of an IPN conveys a co-continuous phase morphology. Recently, however, several amendments have been added to the original definition. (4)

1.2.2 Fiber Composites

Composites, which contain fibers in the matrix material, are used for many applications. A common fiber-containing composite is fiberglass, which has an epoxy resin (polyester polymer) matrix and glass fiber fillers for reinforcement. The glass fibers strengthen the resin and make it more impact resistant. Many boat hulls are made of fiberglass and must with stand the constant beating of waves and other hard objects in water such as wood and rock. (4)

1.2.3 Nanocomposites

Composites in which the fiber reinforcement is on the extremely small "nano scale" (10^{-9} meters) are known as nanocomposites. A clay particle is a common nano-component in composites and it offers a selection of applications not seen in other "large" fiber composites. (4)

1.2.4 Polymer Blends

As one would expect, a blend is a mixture of two or more substances. These materials can be polymers, metals, or other components. Typically, there is no chemical bonding between the two components, but intermolecular forces do occur. The blends can be homogenous (mixed to the extent in which the original components can not be distinguished from one other) in different dimensions of the mixture. Some blends are mixed on the order of one millionth of a meter (molecular) while some are just homogenous to the naked eye. When adequate blending occurs, the properties of the individual components can be seen on the whole much like the marriage of two opposite people, both offer the other various traits Historically, the oldest and simplest method involves mechanical blending, a plastic and a noncrosslinked elastomer are blended either open rolls or through extruders. Materials prepared in this manner usually contain several percent of elastomer dispersed in a plastic matrix.

In simple mechanical blends, the plastic component usually predominates, with the dispersed elastomer having dimensions of the order of several micrometers. The free radicals thus increased by mechanochemical action subsequently react to form a small number of true chemical grafts between the two components. The quantity and importance of such grafted material obviously depend on the exact mode of blending. Significant improvements in impact resistance and toughness are usually noted for such blends over the plain parent plastic, even in cases where no particular amount of grafting is noted (5).

Mixing of two or more polymers of different chemical composition offers a powerful way of tailoring performance and economic relationships using existing materials. As a result, the area of polymer blends has become an important for both scientific investigation and commercial product development. Fundamental issues that affect the properties of blends include equilibrium phase and interfacial behavior, physical and chemical interactions between the components, phase morphology, and rheology, all of which relate to pragmatic issues of compatibility. One of the most important examples of polymer blends is the judicious incorporation of an elastomeric phase in a rigid matrix to enhance mechanical toughness (6).

As plastics technology has progressed, polymer blends have become increasingly important material subgroups because they offer unique combinations of properties of each of their parent polymers. Polymer blends fall into three main categories: miscible, immiscible and partially miscible. The pinhole small-angle neutron scattering (SANS) experiments, which probe the melt directly, indicate that HDPE/LDPE blends are homogenous (7). In addition to this, HDPE-LDPE mixtures are one-phase mixtures in the melt (8). Miscible blends consist of a single polymer phase – two or more polymers that are completely soluble in each other. A simple and usually reliable approach for determining whether a blend system is miscible or not is to examine its glass-transition behavior using thermal, mechanical, or dielectric techniques. Miscible blends show a single, composition-dependent glass transition temperature T_g. This method is of limited usefulness when the glass transitions of the two polymers are very close together and cannot be adequately resolved. Similarly, crystallinity may render the Tg hard to detect by thermal analysis. When two glass transitions are observed, they may not be identical to those of the pure polymers if there is partial miscibility of the components in the phases. The use of glass transition temperature in the determination of polymer/polymer miscibility is based on the fact that a single glass transition temperature indicates that the size of the domains is below

15 nm. A review on the relation between glass transition temperature and the structure in blends has been given by Cowie (9). Equilibrium – phase behaviour of mixtures is governed by the free energy of mixing and how this quantity, consisting of enthalpic (ΔH) and entropic (ΔS) parts, is affected by concentration, temperature T, and pressure P, or volume V (10).

To have miscibility ΔG_{mix} must be negative (11). ΔH_{mix} does not depend on polymer molecular weight, whereas ΔS_{mix} does.

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$$

The combinatorial entropy of mixing becomes progressively smaller as the molecular weights of the components increase and become zero as they approach infinity. Endothermic mixing does not favor miscibility. Thus, forming a homogenous mixture requires that molecular weights must be low enough that the favorable entropic contribution offsets the unfavorable enthalpic effect. For exothermic mixing, the conditions for miscibility will be satisfied no matter how large the molecular weights are. Thus, miscibility of high molecular weight polymers is only assured when mixing is exothermic (6).

The phase structure, the morphology, and the crystallization behavior of a crystallizable blend depend mainly on the mutual miscibility of the two components in the melt and in the amorphous state. In crystallizable polymer blends, the investigation of the miscibility must be focused only on the amorphous phase of the material. Below the melting temperature, a separate crystalline phase can be formed, and the miscibility degree concerns only the remaining amorphous phase. Only above the melting point of the crystallizable component can a complete homogenous mixture be presented for components miscible in the melt (10).

The term of compatibility is often assumed to mean the miscibility of polymers with other polymers, plasticizers, or diluents. Incompatible blends often have little commercial value because of the deficiencies in ductility-related properties such as impact resistance, elongation at break. This overall response is usually related to the lack of interfacial adhesion between the phases in immiscible systems and to poor control of morphology. Two general methods are used to remedy these problems: copolymer addition and reactive compatibilization. Addition of block or graft copolymers to improve the mechanical properties of immiscible polymer blends has been used since the mid 1970s with varying degrees of success. Studies have shown that interfacial adhesion and mechanical compatibility can be improved by the addition of appropriate block and graft copolymers. In their simplest forms the copolymers have block or graft segments that are chemically identical to those in the respective phases, although nonidentical segments, which are miscible or partially miscible in the respective phases, are also effective. (6)

1.3 Carbon Black:

Carbon black is a generic term for an important family of products used principally for the reinforcement and electrically conductive properties. It is a fluffy powder of extreme fineness and high surface area, composed essentially of elemental carbon. Plants for the manufacture of carbon black are strategically located worldwide in order to supply the rubber tire industry, which consumes 70% of production. About 20% is used for the other rubber products and 10% is used for nonrubber applications.

Carbon black differs from other forms of bulk carbon such as diamond, graphite, cokes, and charcoal in that they are particulate, composed of aggregates having complex configurations, quasigraphitic in structure, and of colloidal dimensions. (Figure 1.5)

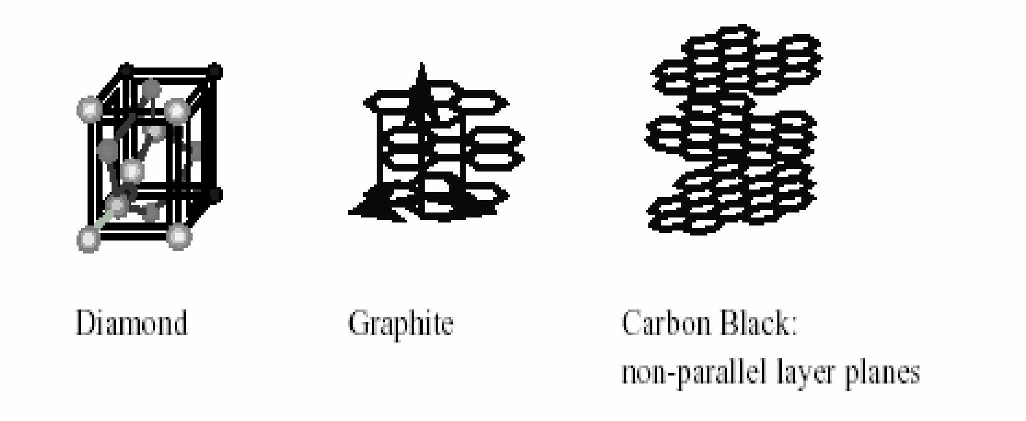


Figure 1.5: Carbon black “quasi-graphitic” microstructure compared to the two regular crystalline forms of carbon (diamond and graphite) (10).

Carbon black is a product of a process incorporating the latest engineering technology and process controls. Its purity differentiates it from soots that are impure by-products from the combustion of coal and oils and from the use of diesel fuels. Carbon blacks are essentially free of the inorganic contaminants and extractable organic residues characteristics of most forms of soot. (10).

A number of processes have been used to produce carbon black including the oil furnace, impingement (channel), lampblack, and the thermal decomposition of natural gas and acetylene. These processes produce different grades of carbon and are referred to by the process by which they are made, eg, oil-furnace black, lampblack, thermal black, acetylene black, and channel-type impingement black. A small amount of by-product carbon from the manufacture of synthesis gas from liquid hydrocarbons has found applications in electrically conductive compositions. The different grades from the various processes have certain unique characteristics, but it is now possible to produce reasonable approximations of most of these grades by the oil-furnace process (6). Since over 95% of the total output of carbon black is produced by the oil-furnace process; a highly aromatic feedstock is partially burned by atomization into a hot flame made of natural gas and preheated air, the reactor temperature reaching more than 1500°C. At the process end, powder ("fluffy") or pelletized carbon black is collected. The oil furnace process permits efficient control of end product physical and chemical properties (12).

$$C_xH_y + O_2 \longrightarrow C + CH_4 + CO + H_2 + CO_2 + H_2O$$

The first commercial oil-furnace process was put into operation in 1943 by the Philips petroleum Co. in Borger, Texas. The oil-furnace blacks rapidly displaced all other types used for the reinforcement of rubber and today account for practically all carbon black production. In the oil-furnace heavy aromatic residuals oils are atomized into a primary combustion flame where the excess oxygen in the primary zone burns a portion of the residual oil to maintain flame temperatures, and the remaining oil is thermally decomposed into carbon and hydrogen. Yields in this process are in the range of 35 to 50% based on the total carbon input. A broad range of product qualities can be produced. Before World War I carbon black was almost exclusively used as a black pigment for printing inks, paints, and enamels. The singular event that changed the industry from a small specialty product manufacturer to large volume producer of vital raw material was the discovery of rubber reinforcement in 1904. The automobile and the tire industries were expanding rapidly, and there was a demand for longer wearing automobile tires. The use of carbon black as a filler for rubber fulfilled this need providing longer wearing and more durable pneumatic tires. The use of carbon black in tires remains its most important application, coupling the fortunes of the carbon black industry to that of the automotive industry (6).

The primary units of carbon black are aggregates, which are formed when particles collide and fuse together in the combustion zone of the reactor. Several of those aggregates may be held together by weak forces to form agglomerates. These agglomerates will break down during mixing into rubber, so the aggregates are the smallest ultimate dispersible unit of carbon black. The difference between primary particle, aggregate and agglomerate is presented in Figure 1.6 (6).

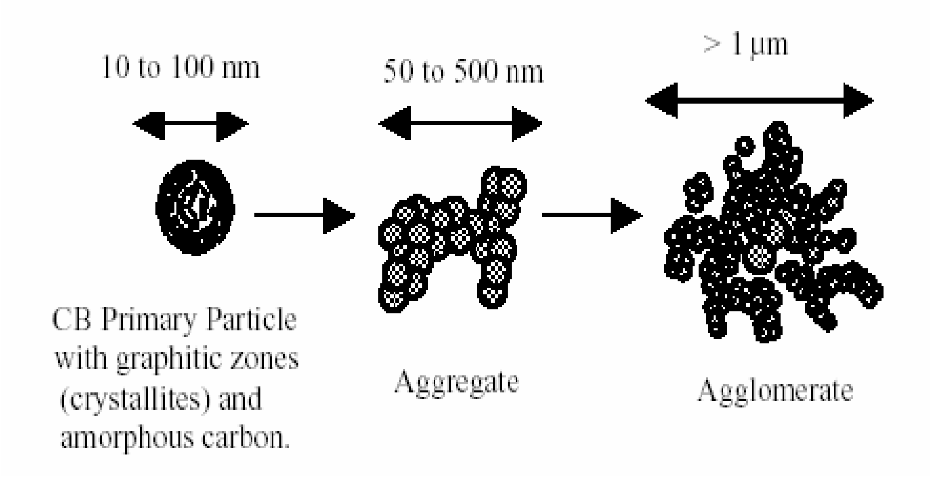


Figure 1.6: CB primary particles fuse together in the reactor and form aggregates and agglomerates (6).

Carbon black is a particulate form of industrial carbon, which exhibits a “quasi-graphitic” microstructure (Figure 1.5). The manufacturing process leaves various forms of oxygenated groups on carbon black layer planes: mainly phenolic, quinolic and carboxyl chemisorbed complexes (13). During the nucleation processes (Figure 1.6), three to four layers form crystallites, which combine to form primary particles which continue to grow into aggregates.

Agglomerates are a dense collection of aggregates formed due to the small distances between them and the strong Van der Walls forces present. CB dispersion into a polymer matrix will require the breaking of these links. An aggregate is indivisible and represents the carbon black "base unit", although a carbon black is often characterized by its primary particle size (6).

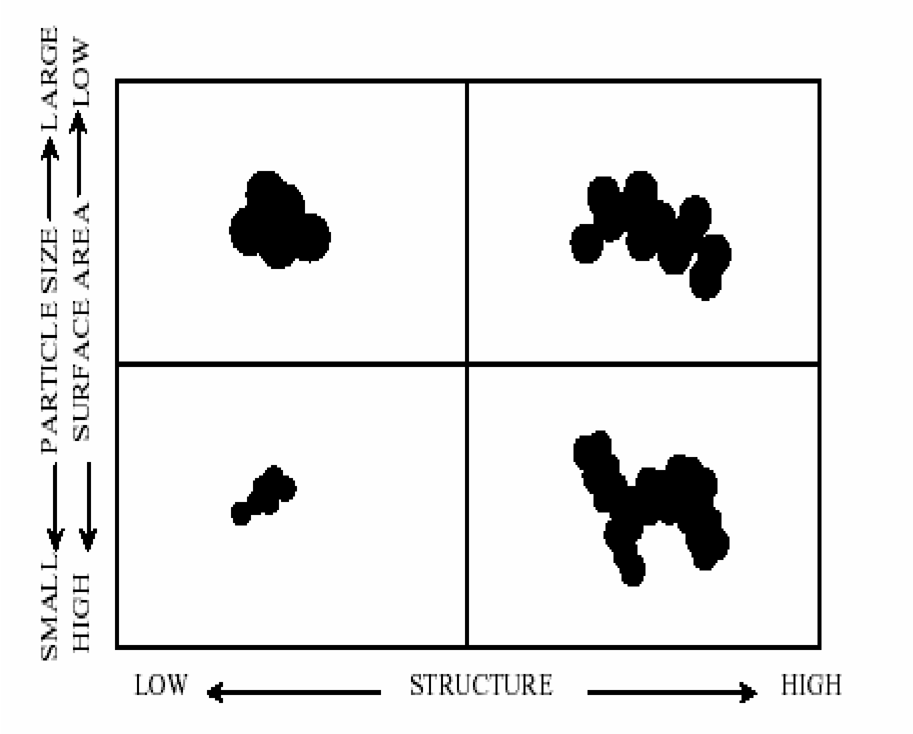


Figure 1.7: Visualization of carbon black particle size / surface area and structure (6).

Some carbon black fundamental characteristics (Figure 1.7) are;

- Particle size (nm): arithmetic mean of diameters of a sufficient number of primary particles of a carbon black grade. Diameters are determined by TEM (Transmission Electron Microscopy) measurements using ASTM D-3849.

- Surface area (m^2/g): specific surface area is determined by nitrogen adsorption capacity using the BET (Brunauer-Emmet-Teller) procedure. Small particles will confer a large surface area per unit weight.

- Structure or DBP (Di-Butyl-Phthalate) oil absorption (ml/100 g): the amount of DBP absorbed by 100g of carbon black at a fixed torque value, according to ASTM D-2414. Structure or the DBP adsorbed is function of the aggregates void volumes and describes the degree to which the CB particles have fused together to form aggregates: a low structure black (low DBP) is made of few primary particles compactly fused together while a high structure black (high DBP) is made of many primary particles with considerable branching and chaining (6).

1.4 Crystallinity

HDPE and LDPE are found to be partly crystalline and partly amorphous, termed semi-crystalline. When molten the molecular chains are in a random writhing mass and there is a great deal of free volume between the chains. During cooling and solidification, the chains can become locally aligned and can pack into regular crystalline arrays. These crystalline regions are termed crystallites and are separated from each other by amorphous regions. The simplest model, which describes this, is the fringed-micelle model (Figure 1.8). It proposes that the lengths of the crystals are less than the lengths of the molecules. Hence a molecule may meander from one crystal to another through the intervening amorphous region. All adjacent crystals are consequently woven together by thread-like macromolecules. Optical microscopy and X-ray diffraction studies have proved this model to be not entirely correct. A more recent model for the observed mixed crystalline/amorphous structure of some polymers is termed the folded chain model (Figure 1.9). This shows that the crystalline regions take the form of thin platelets (crystallites) in which the chains are aligned perpendicular to the flat faces of the platelets and folded repeatedly. The crystallites are around 10 nm thick but the lateral dimensions are up to 0.01 mm. It has been observed during solidification that many platelets grow out from a central nucleus into larger structures called spherulites (Figure 1.10), which can range from a few microns to several millimetres in diameter. Between each flat crystallite is a flat amorphous region. Each spherulite consists of many smaller crystallites separated by thin amorphous regions. It is therefore probable that individual macromolecules bridge the amorphous and crystalline regions as suggested by the fringed micelle model (14).

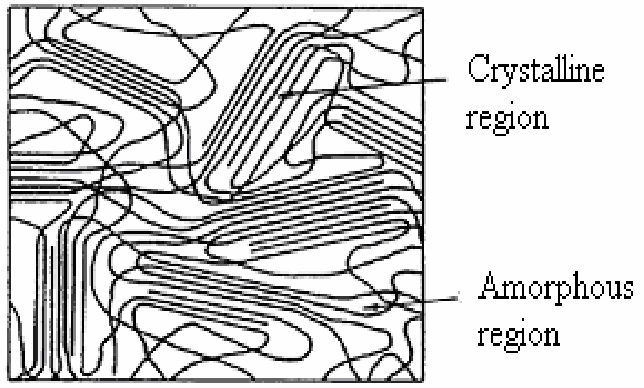


Figure1.8: Fringed micelle model (14).

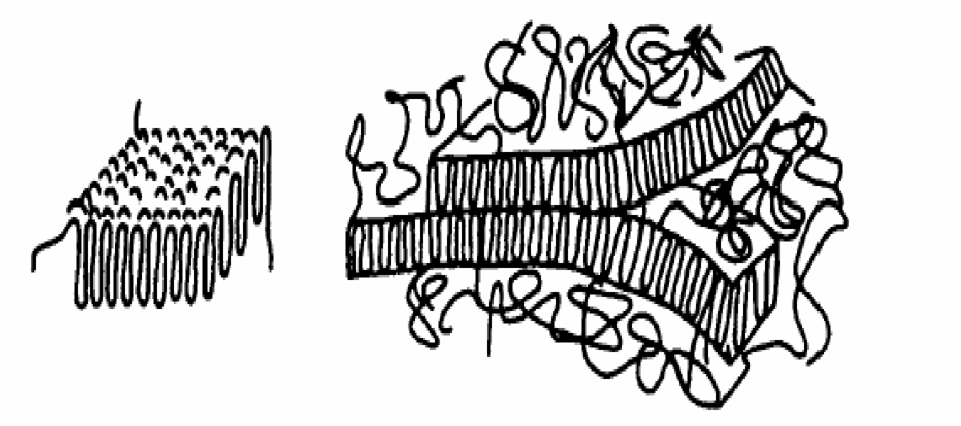


Figure 1.9: Folded chain model (14).

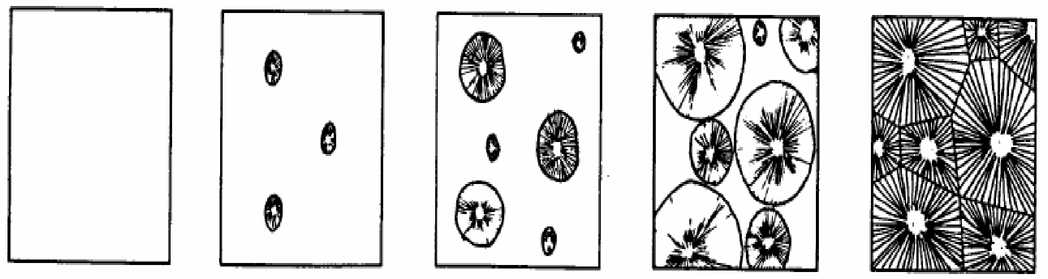


Figure 1.10: Nucleation and growth of spherulites during the cooling of a molten polymer (14).

1.5 Conduction Mechanisms

The electronic conductivity of a material is determined by the properties of its constituent atoms or molecules, and by the manner in which they are arranged in the lattice (15). Conductivity can be described in terms of a solid-state model that relates electronic processes to valance and conduction energy bands. The valance band consists of electrons that, because they have relatively low energy, are associated with individual atoms or molecules: the conduction band contains more energetic electrons that are free to move throughout the material in response to applied electromagnetic energy.

The number and mobility of conduction electrons determine the electronic conductivity of a material. If the valance and conduction bands are separated by a small gap, then, at typical temperatures, thermal activity will deplete the valance band and populate the conduction band; such a material is a conductor. If the bands are widely separated in energy, the conduction band will be vacant and the material will be an insulator. A semiconductor is a material whose band structure falls between that of a conductor and an insulator-it can be an insulator at one temperature and a conductor at a higher temperature. Semiconductors can contain impurity atoms whose energy states lie within the gap between the valance and conduction bands; such impurities strongly affect conductivity by donating or accepting electrons (16).

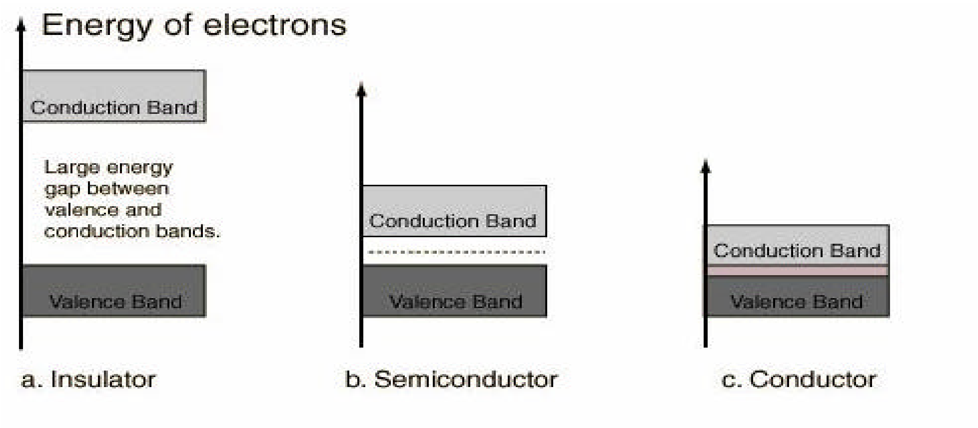


Figure 1.11: Band representation of insulator, semiconductor and conductor materials (17).

A useful way to visualize the difference between conductors, insulators and semiconductors is to plot the available energies for electrons in the materials (Figure 1.11). Instead of having discrete energy as in the case of free atoms, the available energy states form bands. Crucial to the conduction process is whether or not there are electrons in the conduction band. In insulators the electrons in the valence band are separated by a large gap from the conduction band, in conductors like metals the valence band overlaps the conduction band, and in semiconductors there is a small enough gap between the valence and conduction bands that thermal or other excitations can bridge the gap. With such a small gap, the presence of a small percentage of a doping material can increase conductivity dramatically (17).

The application of band theory to n-type and p-type semiconductors shows that extra levels have been added by the impurities (Figure 1.12). In n-type material there are electron energy levels near the top of the band gap so that they can be easily excited into the conduction band. In p-type material, extra holes in the band gap allow excitation of valence band electrons, leaving mobile holes in the valence band (17).

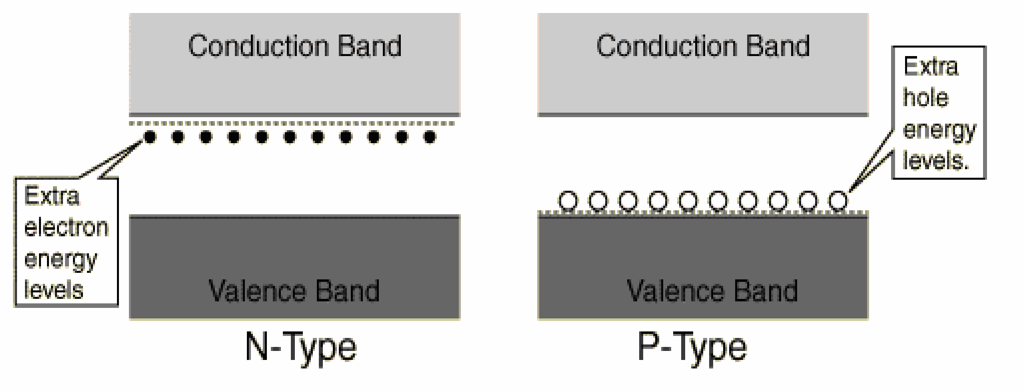


Figure 1.12: N-Type Band Structure: The addition of donor impurities contributes electron energy levels high in the semiconductor band gap so that electrons can be easily excited into the conduction band. P-Type Band Structure: The addition of acceptor impurities contributes hole levels low in the semiconductor band gap so that electrons can be easily excited from the valence band into these levels, leaving mobile holes in the valence band (17).

1.6 Studies on HDPE/LDPE blends and Carbon Black

Nugay and Tinçer (18) studied the effect of mixing time on mechanical, thermal properties and oxidative degradation on low density and high density polyethylenes. They did the experiments at four different mixing times and evaluated the results according to the blend composition and the time of mixing. The tensile strength was found to be affected mostly by mixing time as compared with the elongation at break while the modulus remained unchanged with time of mixing. Longer mixing time appeared to enhance the ultimate strength properties in the region with high LDPE content with the maxima at 70% LDPE. The longer mixing time of blending after a certain period (i.e.> 20 min) did not changed the measured properties to a greater extent except the increase in oxidative degradation. The compositions, which show minimum, represent the highest tensile strength at the same time in particular for longer mixing times. The Young’s Modulus is not affected by mixing time.

Feng Zhang and Su Yi (19) studied the dynamic rheological behavior of High Density Polyethylene filled with carbon black by controlling periodic small shear strains at constant temperatures. At sufficiently high filler concentration a structural skeleton seemed to appear, which significantly raised the modulus at the low frequency region. High structure, finer acetylene black raised the modulus significantly more than does the low structure and larger size one. Oxidized CB increased the modulus in the whole frequency region for the enhanced interaction between polymer matrix and CBs.

Malette, Quel, Marquez and Manero (20) studied on carbon black filled PET/HDPE blends. Four types of CB samples were used; BP2000, Ketjenblack, Printex and Vulcan. Printex CB presented a structure formed by long branches of particles with a low apparent density and high porosity. BP-2000 CB possesed short branches with agglomerates and Ketjenblack CB presented larger branches with bigger agglomerates and with bigger agglomerates than that of BP-2000 CB. In general, viscosity increased in the more structured samples, that is, those with high porosity and high surface area. The torque values obtained after CB addition clearly reflect high viscosity in the Printex sample and low viscosity in the Vulcan system. CB was preferentially located in HDPE phase, which presented a higher viscosity than that of the PET phase, due to lower interfacial tension between them. High conductivities were reached when this polymer phase was dispersed in the PET matrix since its relative CB concentration is higher.

Ezquerra, Bayer and Calleja (21) studied the distribution of electrical conductivity in elongational-flow injection moulded HDPE materials containing carbon black. Radial and axial conductivity profiles were discussed in terms of molecular orientation variations across the bars. It was shown that for low and intermediate molecular weight matrices the conductivity decreased after material orientation through injection moulding. For high molecular weight polyethylene, conductivity increased with orientation.

Malik, Carreau, Garmela and Dufresne (22) studied the mechanical and rheological properties of CB filled polyethylene. Two sources of CB (one commercial and other obtained from a pyrolysis process) and various treatments have been studied. Comparison of carbon black from two sources showed that the carbon from the pyrolysis process has a good potential as a reinforcing agent. It had good mechanical and rheological properties as compared with other. The pyrolysis processed CB showed better dispersion in PE matrix, showed also overall better mechanical and rheological properties, and was more responsive towards the particle surface treatment. Surface treatment of CB particles by the coupling agents did not have significant effects on mechanical properties.

Laguna, Collar and Taranco (23) studied on HDPE and LDPE homopolymers and their blends as virgin materials. The micrographs from the HDPE/LDPE system, obtained by SEM, showed a network or entanglement microstructure which broke in a brittle way. The rather rounder features forming the knots were smaller when the LDPE content was lower. These knots were not distinguished when LDPE content reached 85% or more. In the DSC studies, they observed that in blends of HDPE/LDPE separate crystals were formed and this fact might be attributed to differences in chain linearity since LDPE was of branched type while HDPE was essentially linear. The melting temperatures of the HDPE decreased with the addition of LDPE content.

Yang, Brady and Thomas (24) studied the microstructure of highly oriented single-phase blend films of high and low density polyethylene by transmission electron microscopy, electron diffraction, X-ray diffraction, and DSC. The average crystal size, as well as long period, crystalline content, and melting endotherm peak, decreased as LDPE was added to the blend. When the LDPE content exceeded 50% the film texture changed from a single crystal texture to fibre symmetry. Segregation of the two polyethylenes was not detected at low LDPE contents and a low temperature tail began to appear on the endothermic melting peaks at LDPE contents >70%, indicating the onset of segregation. In the melting of crystallized films, however, two distinct melting endothermic peaks were visible for LDPE contents > 50%. They observed that the crystals present in HDPE/LDPE blends were thermodynamically equivalent to the HDPE crystals of equal size, implying that branches were excluded from the crystalline phase.

Fu, Men and Strobl (25) studied the mechanism of tensile deformation in HDPE/LDPE blends by video-controlled tensile set up, combined with dynamic mechanical analysis and small angle X-ray scattering. When quenching from the melt to room temperature, HDPE formed well-organized spherulites with high crystallinity and rigid amorphous layers between lamellae, and LDPE formed irregular aggregated with low crystallinity and mobile amorphous layers between lamellae. A separate lamellar stack-like structure was formed in HDPE/LDPE blends during the quenching. The deformation was affected by both the crystal structure and the phase morphology. HDPE had a smaller critical strain (0.4) due to its rigid amorphous, compared with that of LDPE (0.6).

The melt miscibility of LDPE/HDPE blends was determined by calculating their corresponding Florry-Huggins interaction parameters based upon the computed solubility parameters by Fan, Williams and Choi (26). Phase separation in

LDPE/HDPE blends in the melt was predicted for high branch contents at high temperatures in their simulations. The results imply that the long branches may significantly influence the miscibility of polyethylene blends.

Tang, Chen and Luo (27) studied the positive temperature coefficient (PTC) and negative temperature coefficient (NTC) effect of carbon black (CB) filled low density polyethylene (LDPE) composites using electrical X-Ray scattering (SAXS) techniques. The three LDPEs used had a similar crystallinity and different melting index. The experimental results indicated that the CB had no significant effect on the crystallinity and the long spacing of crystalline domains of LDPE. The PTC effect was related to the thermal expansion of the polymer matrix, and the NTC effect was caused by a decrease of the elastic modulus of the polymer at high temperatures. Enhancing either the elastic modulus or the interaction between carbon black and matrix could reduce the NTC effect.

Jia and Chen (28) studied the dependence of electrical resistivities on the temperature of different polymer systems (including the rubbers and plastics/rubber blends) loaded with carbon blacks (including oxidized and normal carbon blacks). They found that polymer-carbon black interactions could greatly influence the electrical resistivity and temperature relations of the polymer composites. The polymer blends filled with oxidized carbon black, or the elastomer, which had polar functional groups, filled with carbon black, and had a very weak NTC effect, which was due to the strong polymer-filler interactions.

Conductive polymer composites used as candidates for PTC materials were faced with performance decay characterized by gradually increased room-temperature resistivity and decreased PTC intensity studied by Hou and Zhang (29). Considering that deterioration of the properties was mainly related to the capability of conductive networks established by conductive fillers to recover from the effect of repeated expansion/contraction in a timely manner, this work introduced chemical bonding into the filler/matrix interphase. The experimental results indicated that in the composites consisting of conductive CB, LDPE, and ethylene–vinyl acetate copolymer, CB particles could be covalently connected with LDPE through melt grafting of acrylic acid. As a result, the composites were provided with reduced room temperature resistivity and significantly increased PTC intensity. Compared with the composites filled with untreated CB, the present composited possessed reproducible PTC behavior and demonstrate stable electrothermal output in association with negligible contact resistance at the composites/metallic electrodes contacts.

Hou, Zhang and Rong (30) studied the carbon black filled polyolefins as positive temperature coefficient materials; the effects of in situ grafting during melt compounding. For the production of polymer-based conducting composites serving as PTC materials with lower room temperature resistivity and sufficiently high PTC intensity, carbon black had been pretreated with acrylic acid and some initiator and then melt-mixed with low-density polyethylene. Because of the in situ formation of covalent bonding at the filler/matrix interface, the distribution status and thermally induced displacement habit of the conductive fillers had changed accordingly. As a result, the electrical performance of the composites could be tailored as desired. The amount of acrylic acid and the treatment sequence of carbon black exerted an important influence on the effectiveness of the modification.

Agamalian, Alamo, Londono, Mandelkern and Wignall studied the phase behaviour of blends of linear and branched polyethylenes on micron length scales via ultra-small-angle neutron scattering (8). Small angle neutron scattering (SANS) experiments had indicated that mixtures of linear (high density) and long chain branched (low density) polyethylenes (HDPE/LDPE) form a one-phase mixture in the melt.

1. 7 Aim of the Study

Conducting polymers have been one of the main research areas owing to their potential applications in various fields. However better mechanical and thermal properties and processibility are desired for new developments. In the present studies conductive filler (C-black) is added to an insulating matrix to obtain conducting composites having good mechanical and thermal properties.

CHAPTER II

EXPERIMENTAL

2.1 Materials

2.1.1 High Density Polyethylene (HDPE)

In this study, HDPE (S 064), which is produced by PETKIM, was used in white granular form. Melt Flow Index (MFI) value is 0.35 g/10min (at 190 ^{o}C and under 2.160 kg load) and density value is 0.964 g/cm^3. The technical data of this product is given in Table A.1 in Appendix A.

2.1.2 Low Density Polyethylene (LDPE)

LDPE (F 212), which is produced by PETKIM, was used. Melt flow index value is 2.75 g/10 min (at 190 ^{o}C and under 2.160 kg load). Density value is 0.920 g/cm^3. Technical data of this product is given in Table A.1 in Appendix A.

2.1.3 Carbon Black

Vulcan XC-72 type carbon black produced by oil furnace process was obtained from Cabot Corporation. The technical data of this product is given in Table A.2 in Appendix A.

2.2 Sample Preparation

2.2.1 Pre-Blend preparation

By keeping volume percent of LDPE from 20 to 60, LDPE and HDPE granules were mixed. After that, 5, 10, 15, 20 and 30 percentage of CB, with respect to total volume was added to these blends.

2.3 Blend preparation

2.3.1 Preparation of mixed and moulded blends

LDPE/HDPE/CB blends were prepared by using Brabender Plastic Coder, PLV-151. Experiment was done at 190 ^{o}C and 30 rpm by mixing the materials 10 minutes. Obtained blends were compressed in a mould for 5 minutes at 190 ^{o}C and than these moulds were fast cooled.

In table 2.1, the compositions of the blends used in this study were tabulated.

2.4. Melt Flow Properties of Blends

The measurements were done by Coesfield Material Test, Meltfixer LT. The instrument is pre-heated to 190 ^{o}C. The particles were filled into the orifice and they were kept for 5 minutes in the orifice in order to allow the material to melt. Throughout this process, the hole is closed with a piston to compress the material and remove air bubble. After this period, standard weight was placed on the piston to compress the test sample through an orifice. The amounts of flow of sample through an orifice during 10 minutes were reported.

Table 2.1 Volume fraction of LDPE, HDPE and CB

% LDPE: % HDPE: %CB by volume	
30 : 70 : 0	50 : 50 : 0
30 : 65 : 5	50 : 45 : 5
30 : 60 : 10	50 : 40 : 10
30 : 55 : 15	50 : 35 : 15
30 : 50 : 20	50 : 30 : 20
30 : 50 : 30	50 : 20 : 30
40 : 60 : 0	60 : 40 : 0
40 : 57 : 5	60 : 35 : 5
40 : 54 : 10	60 : 30 : 10
40 : 51 : 15	60 : 25 : 15
40 : 48 : 20	60 : 20 : 20
40 : 40 : 30	60 : 10 : 30

2.5 Analyzing of Mechanical Properties of Blends

2.5.1 Tensile Tests

Tensile tests were done by Lloyd LS computer controlled tensile machine on dog bone shaped moulded samples at room temperature. The results were reported as the average of 6 samples.

Crosshead speed and gauge lengths used in measurements were 5.0 cm/min and

7 cm, respectively 5 kN load cell was used for testing.

2.5.2 Hardness Tests

Hardness measurement was done according to ASTM D 2240 by using Durometer in shore D scale.

2.5.3 Impact Tests

Charpy impact test (unnotched) was applied by using Pendulum Impact Tester of Coesfield Material Test machine. The test specimens were prepared by compressing in a mould with a bar-shaped mould having size of 69x10.5x5 mm. The 11, 59 kJ / m^2 energy was applied but the test specimens were not broken.

2.6 Thermal Properties of Blends

2.6.1 Differential Scanning Calorimeter (DSC)

Dupont thermal Analyst 2000 DSC 910S was used for studying thermal properties of blends in this part. The measurements were done under N_2 atmosphere. The range of applied temperature was 50-150 ^{o}C at 2 ^{o}C/min heating rate but, for some samples, the 25-300 ^{o}C temperature range with 10 ^{o}C /min heating rate were applied.

2.7 Morphological Properties of Blends

2.7.1 Scanning Electron Microscope (SEM)

JEOL, JSM 6400 SEM was used to investigate morphological properties. The samples were cut in rectangular shape than were put into liquid $N_{2.}$ After that they were fractured and the fracture surfaces were analyzed.

2.8 Conductivity Measurement

Two probe and four probe techniques were used to measure conductivity. The procedure consists of a voltage –current and sample thickness measurement. Four probe technique gives more rapid and reliable results than two-probe technique.

In four probe technique, four equal tips were placed on a head. The head was lowered to the sample until the four probes touch the sample. A direct current is passed through the specimen between the outer probes and resulting potential difference is measured between the inner probes (Figure 2.1).

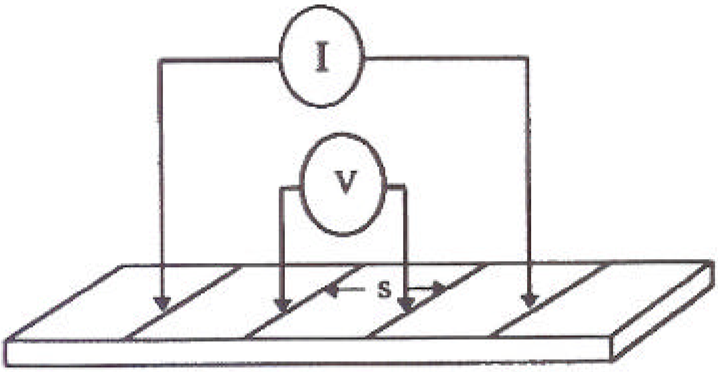


Figure 2.1: Four Probe Technique

The conductivities were calculated by the following equation:

$$s = (\ln 2 / ? d)(I / V)$$

Where s is the conductivity, I is the current applied through the outer probes, V is the voltage drop measured across the inner probes and d is the sample thickness.

In determining sample conductivities by four probe technique, current-voltage measurements are done by using Keithley 617 Electrometer.

CHAPTER III

RESULTS AND DISCUSSION

3.1 Melt Flow Properties of HDPE/LDPE/CB Blends

Many important flow characteristics of the polymer can be found by using a simple test called the Melt Flow Index (MFI). The melt index is one of the most common parameters specified when describing a polymer. The weight of the material extruded during the specified time is the melt index expressed in grams per 10 minutes.

Melt Flow Index were measured according to ASTM D 1238. The barrel temperature was 190 ° C and the load was 2.16 kg. In general, MFI values increased with increasing LDPE content of blends because pure LDPE has higher MFI value, 2.75-g/10 min, than pure HDPE, 0.35 g/min (Appendix A). MFI values of all blends are shown in Figure 3.1. Addition of CB into different compositions of HDPE-LDPE blends decreased the MFI values. It is because of the fact that CB adsorbs the polymer chains and so the blend resists melting flow. This phenomenon is called bound polymer formation. Increasing CB content increases bound polymer formation because of the fact that bound polymer formation causes more entangled chain structure so the blend resists flowing.

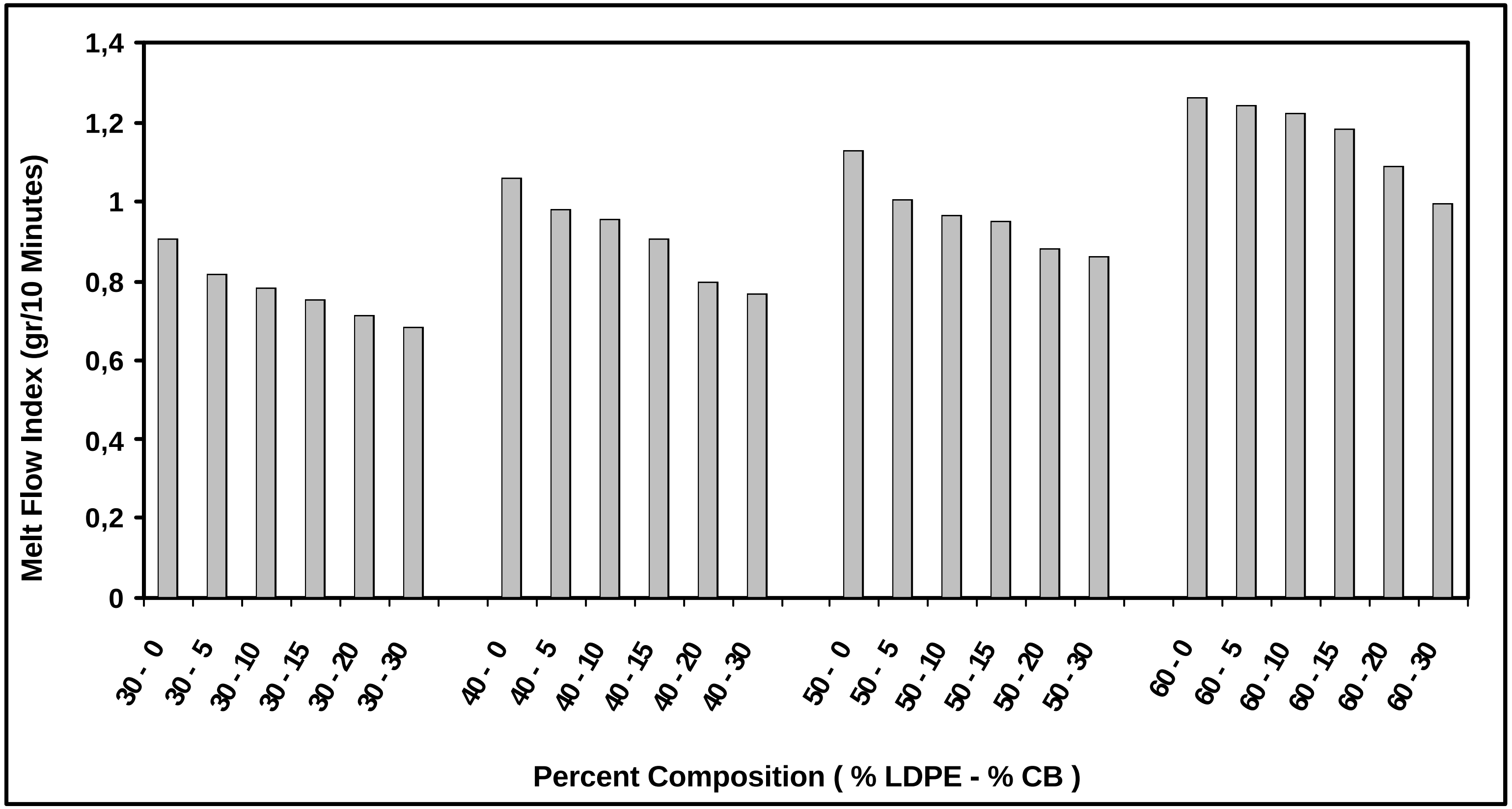


Figure 3.1: Melt Flow Index values versus percent compositions of blends.

3.2 Tensile Properties of HDPE/LDPE/CB Blends

It is difficult to obtain 100% crystallinity in polymers. Generally, semicrystalline polymers present depending on the percent crystalline phase of structure. At first all changes in structure in semicrystalline polymers occur in amorphous part and activity is not observed in crystalline part (Figure3.2.a). By increasing the tensile force, the moving in crystalline region starts. Amorphous phases give permission to this movement and crystalline region is oriented to the direction of applied force without changing the structure. (Figure 3.2.b) (31).

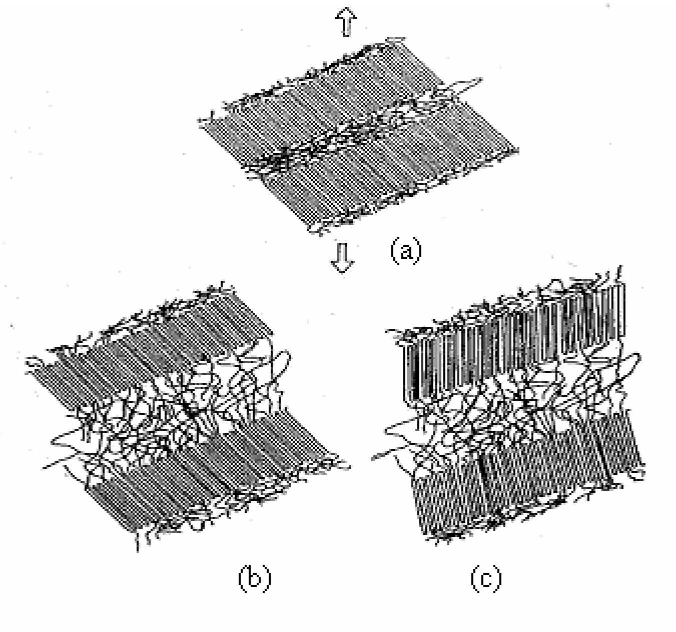


Figure 3.2.a: Deformation mechanism of semicrystalline plastics (31).

Tensile tests were done for blends according to ASTM D638-776. The stress-strain graphs are given in Appendix B. Percent strain at break values are given in Figure 3.3. An increase in percent strain was observed by increasing HDPE. It is because of the fact that firstly the elongation occurs by amorphous parts, then the folded chains of crystalline HDPE opens so elongation increases.

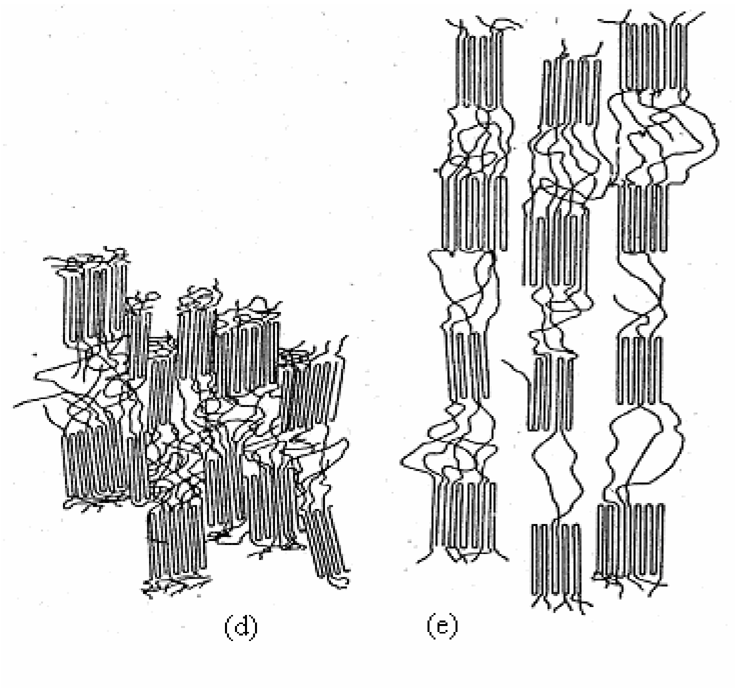


Figure 3.2.b: Deformation mechanism of semicrystalline plastics-2 (31).

This mechanism is illustrated in Figure 3.2. Highest percent strain was observed from 30% LDPE with 5% CB as 625. In general, increasing CB content decreased the elongation because higher CB content encourages the bound polymer formation. However, adding low concentration CB content increased percent elongation. It is because of the fact that CB particles fill the blanks in the tie molecules so elongation becomes easier.

Tensile stresses at break values of blends according to different compositions are given in Figure 3.4. Increasing percentage concentration of LDPE tends to decrease in stress values. Moreover addition of CB enhanced the stress at break values in all compositions because; polymer interacts with CB strongly by forming bound polymer so this situation increased the mechanical strength. However, adding high concentration CB content decreased stress at break values due to the strain stress.

In Figure 3.5, variations of Young's modulus with respect to blend compositions are given. It is observed that increasing CB content generally has an increasing effect on Young's modulus. The principal function of reinforcing fillers is to increase the modulus of the composite. Addition of CB reinforces the blends. Increasing HDPE content increases Young's modulus because of the fact that the stiffness of HDPE enhances modulus. Highest modulus was observed from 50% HDPE with 20% CB as 845 Mpa.

3.3 Hardness Measurements of HDPE/LDPE/CB Blends

Hardness is defined as a material's resistance to indentation when a static load is applied. Several hardness tests are designed for materials of widely differing hardness. The most common instrument for measurement of hardness is called the Shore Durometer. This instrument measures the depth of penetration from zero to 0.100 inches. A zero reading on the scale means the indenter penetrated with maximum depth. Likewise, a reading of 100 indicates no penetration of the indenter. Shore A and Shore D hardness scales are used to determine hardness numbers. Shore A scale is used for softer materials. On the other hand, Shore D scale is used for harder materials.

.

Hardness test were done according to ASTM D 2240 by using a Durometer in Shore D scale. The results are given in Figure 3.6. Increasing the percent amount of HDPE tends to increase in hardness values. This result is because of the stiffness of HDPE. Moreover, an increase in hardness was observed by the addition of CB because the bound polymer formation causes stronger surface interaction.

3.4 Thermal Properties of HDPE/LDPE/CB Blends

Thermal properties are related with the structure and thermal history of samples. In differential scanning calorimetry (DSC), the thermal properties of a sample are studied. When the sample is under the thermal transition, the heat absorbed by the sample is measured. The DSC gives the data of the absorption of heat by a plot of heat versus temperature graphic. By this method, degree of crystallinity is determined according to heat needed to melt the sample. The percent crystallinity is determined by the ratio of measured heat-to-heat required obtaining a hundred percent crystalline of pure substance. The glass transition temperature can also be measured by using DSC.

The samples were analyzed by DSC to obtain the heat of fusion. Then percent crystallinity of HDPE in HDPE/LDPE blends can be calculated from;

$?H_{exp}$ = (Heat of crystallinity of HDPE) x (g of sample)$^{-1}$ x 100
Percent Crystallinity = ($?H_{exp}$/ $?H_f$) x 100

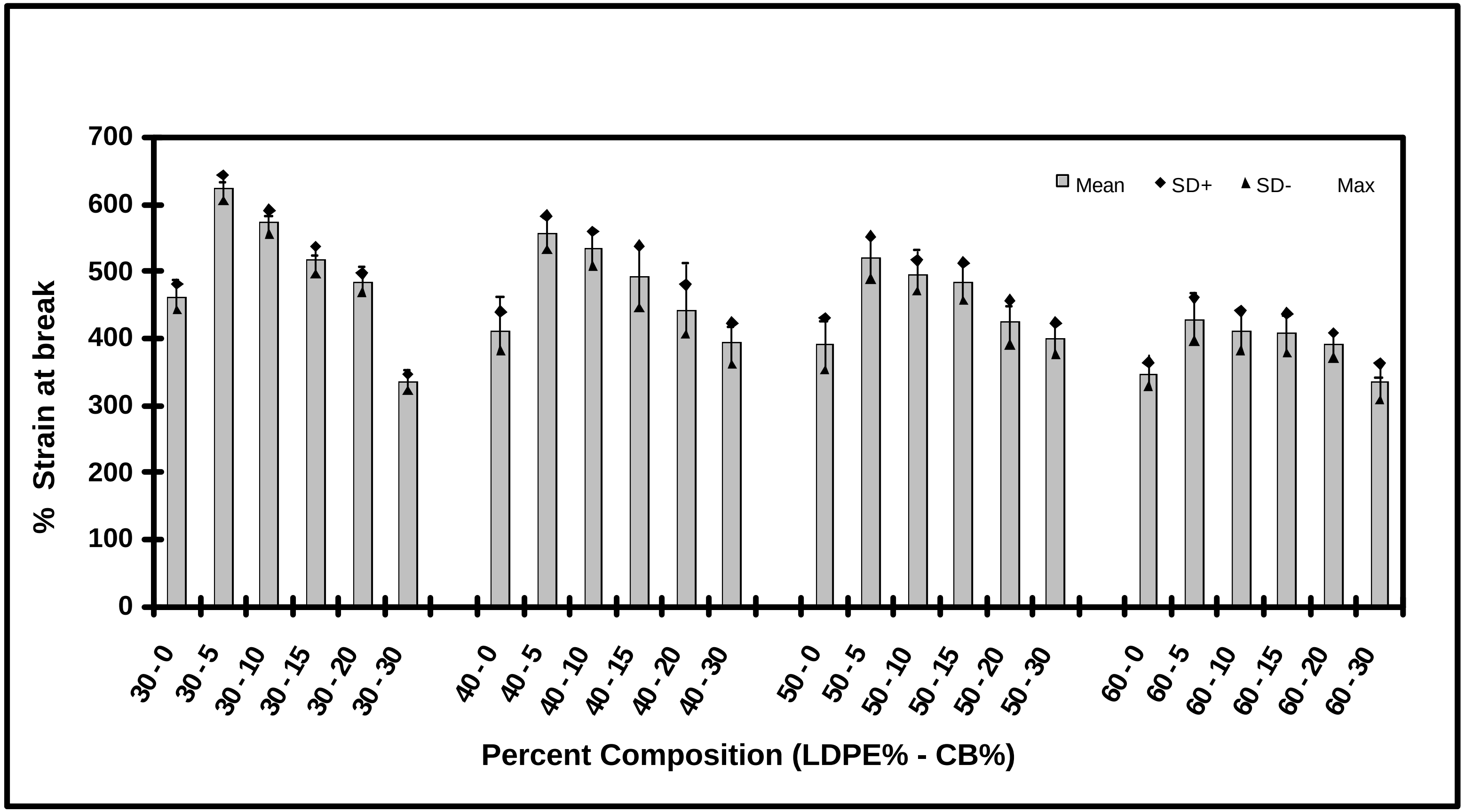


Figure 3.3: Strain at break values versus percent compositions of blends.

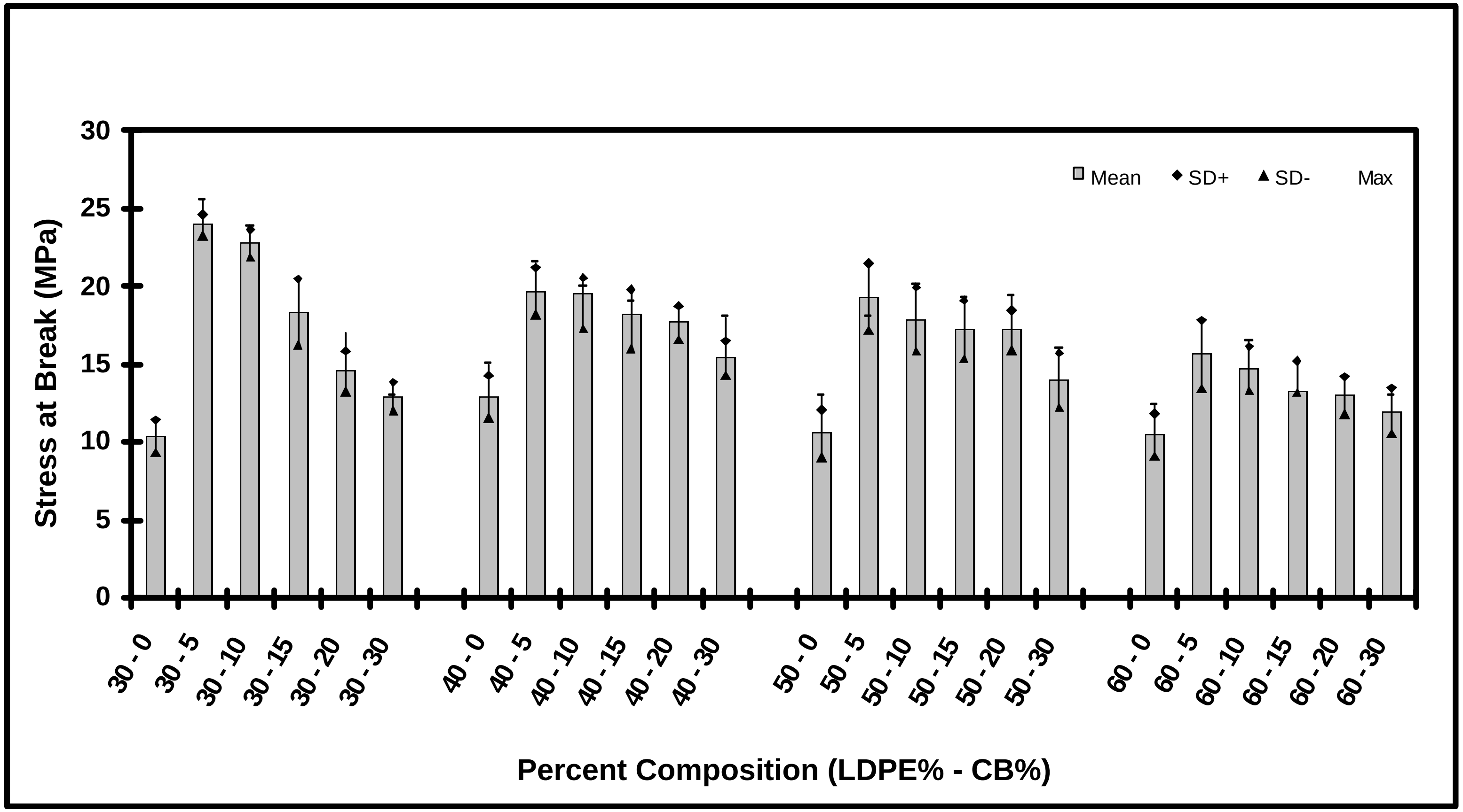


Figure 3.4: Stress at break values versus percent compositions of blends.

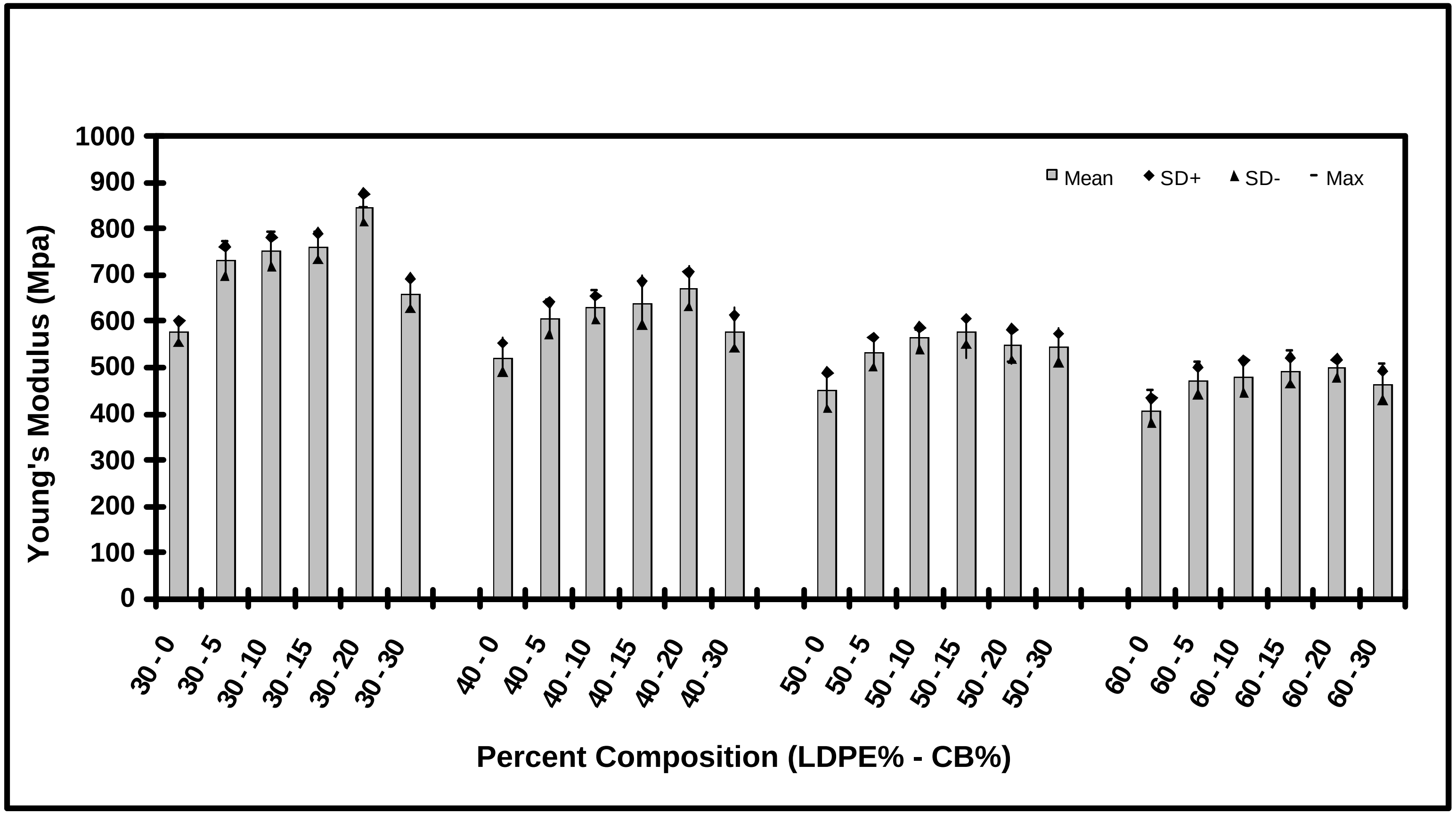


Figure 3.5: Young Modulus values versus percent compositions of blends.

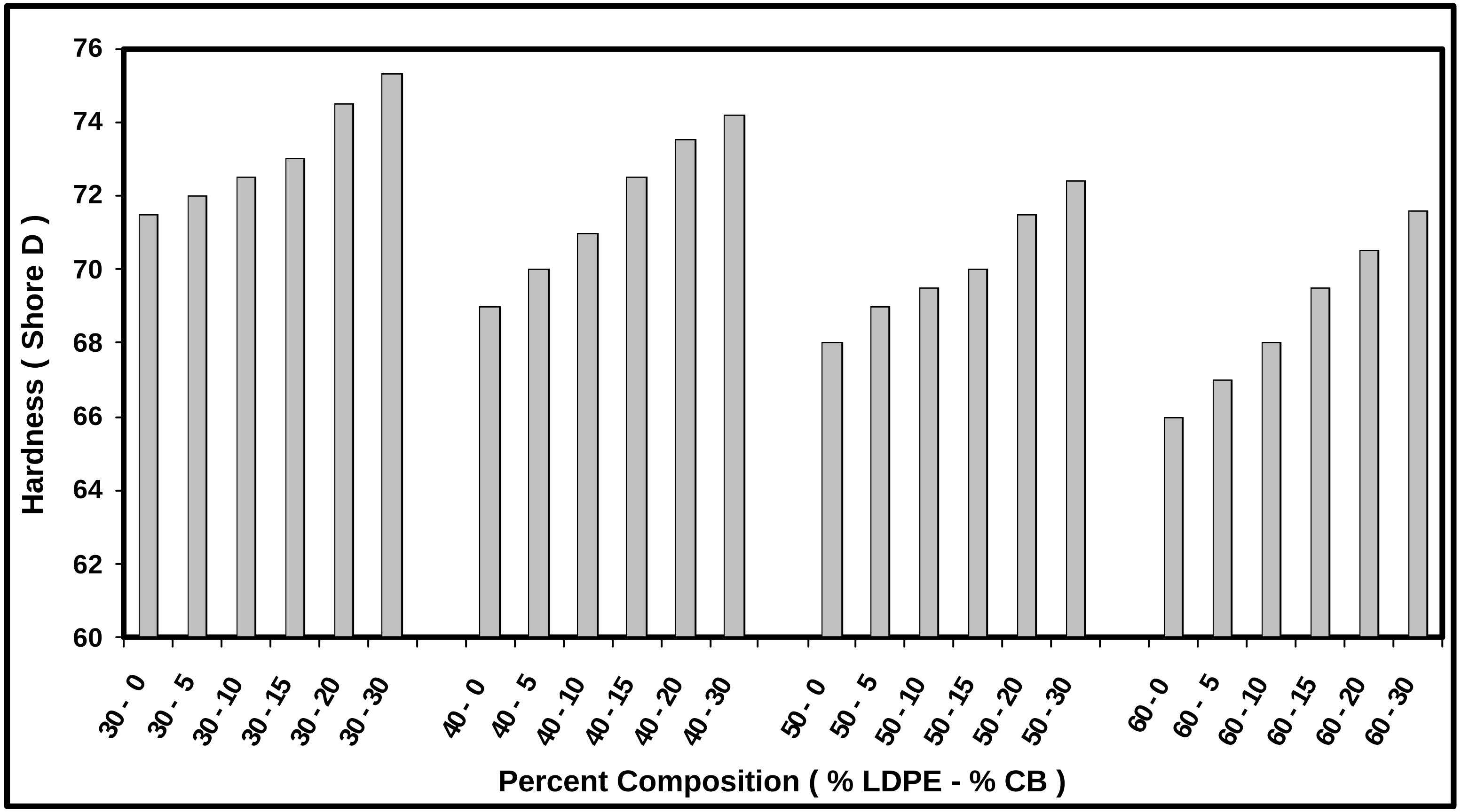


Figure 3.6: Durometer Hardness in Shore D scale versus percent LDPE composition graph.

? H_f is taken as 293 J/g (22) based upon a perfect crystal.

The DSC thermograms for the melting peak of HDPE are given in Appendix C. The DSC diagrams of blends had T_m peaks of HDPE between 128-131 °C. The change in crystallinity of HDPE was studied, on the other hand the LDPE crystallity was not studied because of the fact that LDPE peaks were not observed clearly up to 60% so the LDPE peak in the blends is negligible compared with that of the HDPE. This is because the LDPE cannot readily crystallize as HDPE does when quenched from the melt to room temperature. Figure 3.7 shows the percent crystallinity of HDPE/LDPE blends containing 10-70 % HDPE including 5-10-15-20-30% CB.

Because of the dispersion of carbon black in the molten crystal part, the crystallization of the polymer matrix was decreased by the presence of CB. This result can be seen in Figure 3.7. The typical DSC thermograms of composites and DSC thermogram of pure HDPE were given in Appendix C.

3.5 Morphological Properties of HDPE/LDPE/CB Blends

Morphological properties of blends were studied by SEM. SEM microphotographs are given in Figures 3.8 - 3.15. Some parts of the blends were broken so as to be able to observe fracture surface and the interactions between HDPE, LDPE and CB.

There is no difference in SEM microphotographs of samples as can bee seen in Figures. These results indicate that homogenous distribution of CB particles exists thought the matrix.

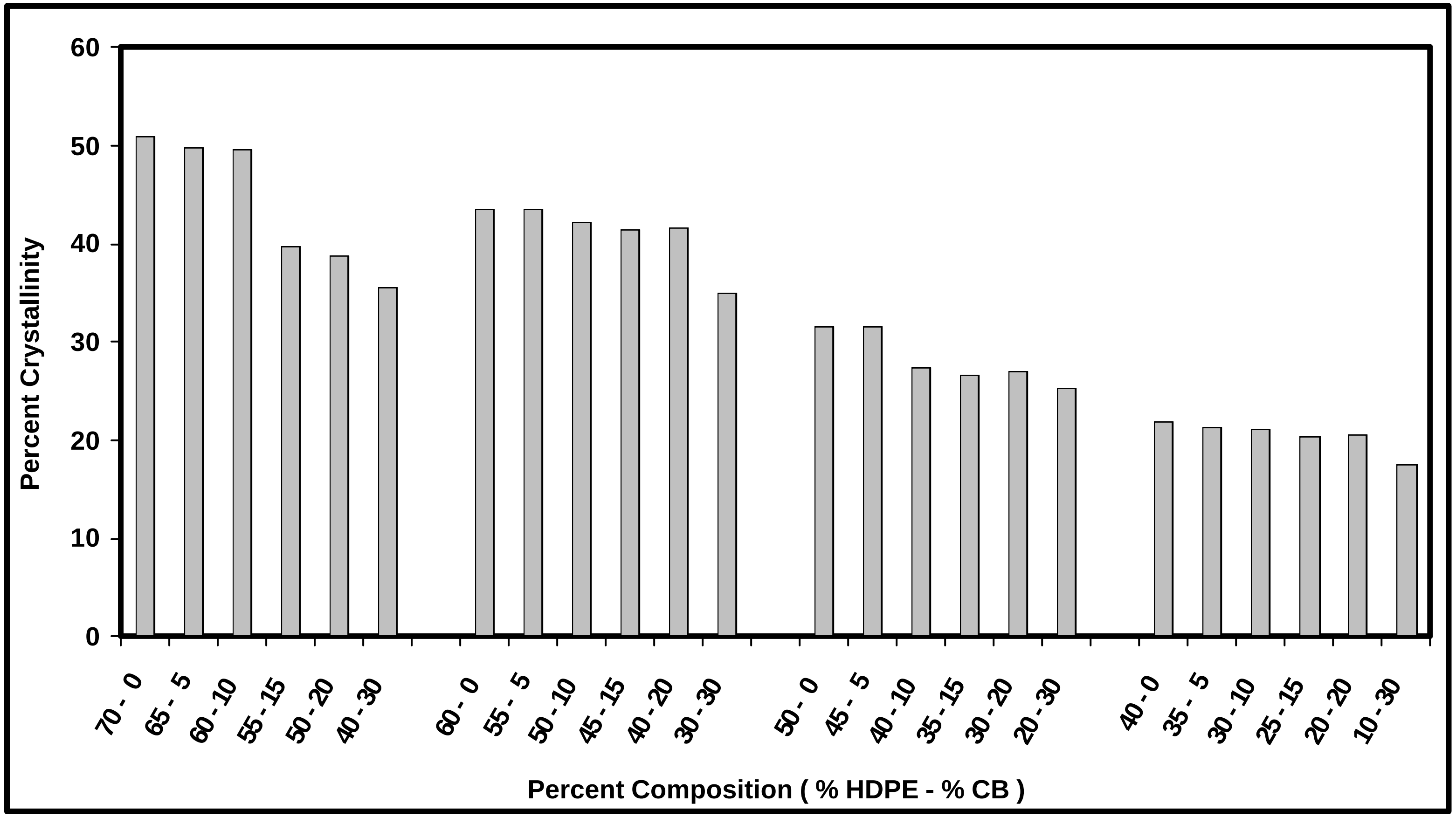


Figure 3.7 Percent Crystalinity of HDPE versus percent composition graph.

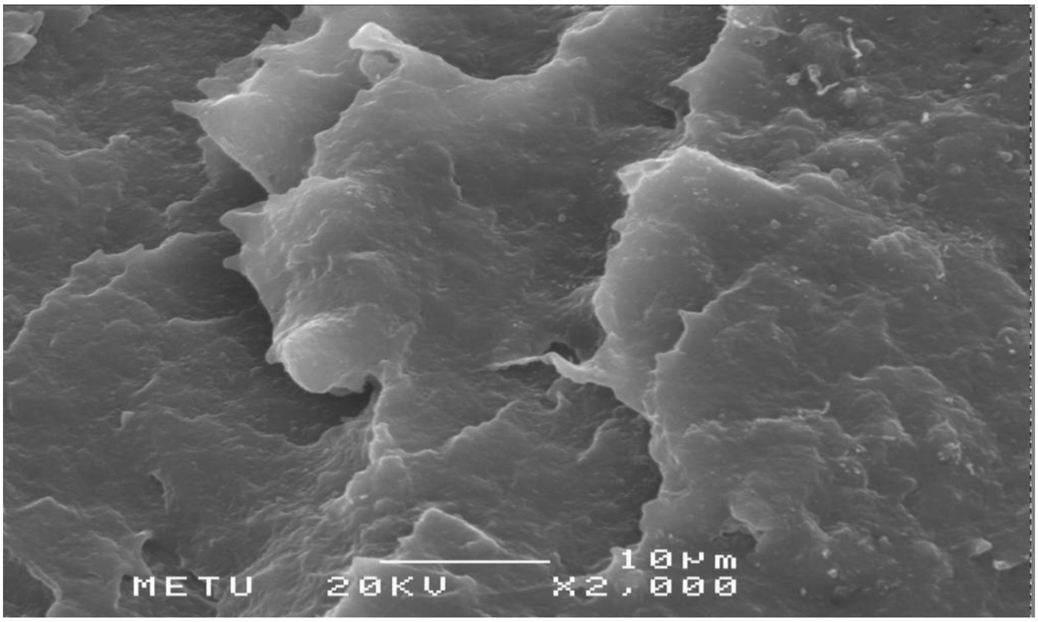


Figure 3.8 Fracture surface of blend containing 30% LDPE with 0% CB.

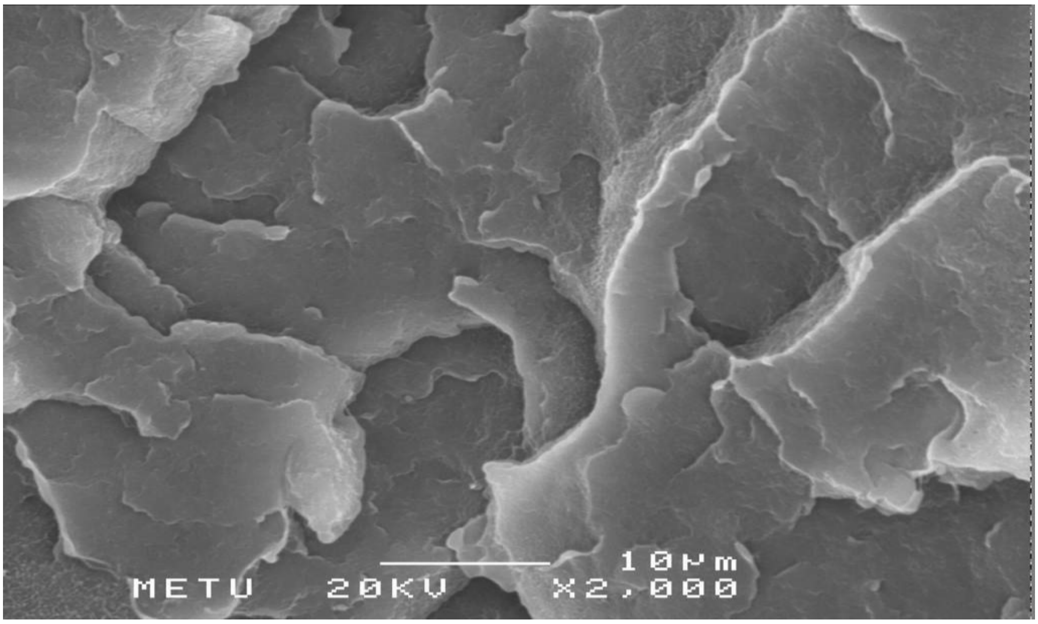


Figure 3.9: Fracture surface of blend containing 40% LDPE with 0% CB.

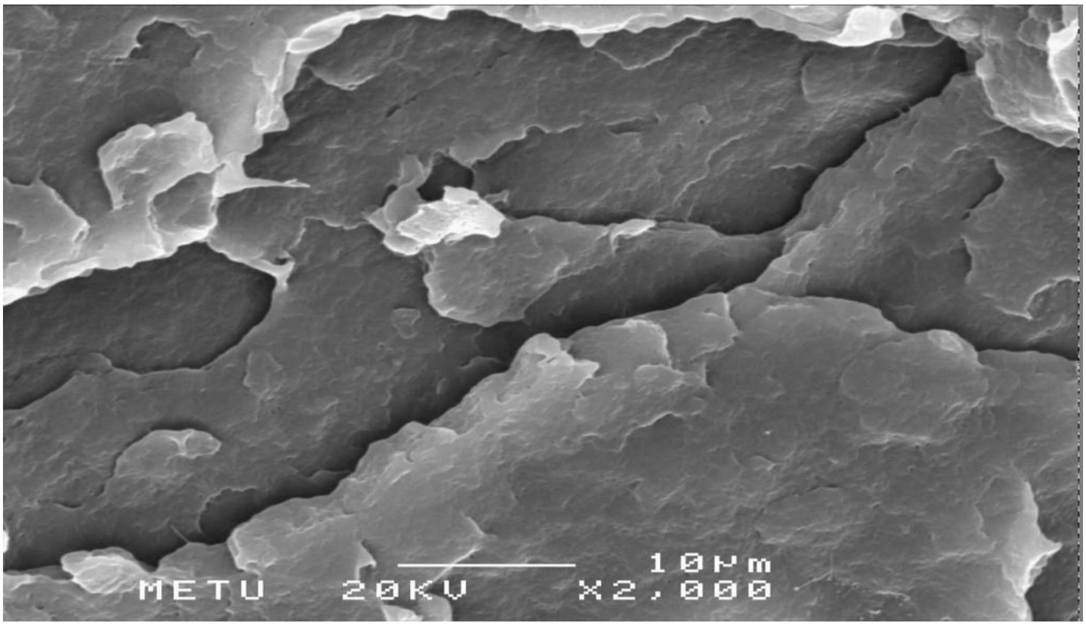


Figure 3.10: Fracture surface of blend containing 50% LDPE with 0% CB.

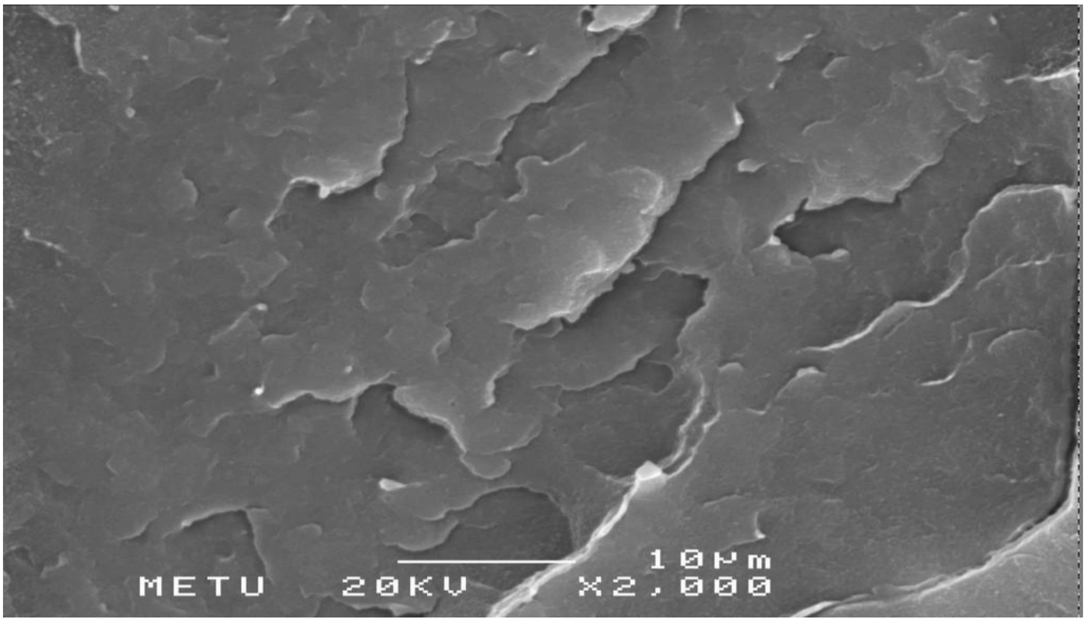


Figure 3.11: Fracture surface of blend containing 60% LDPE with 0% CB.

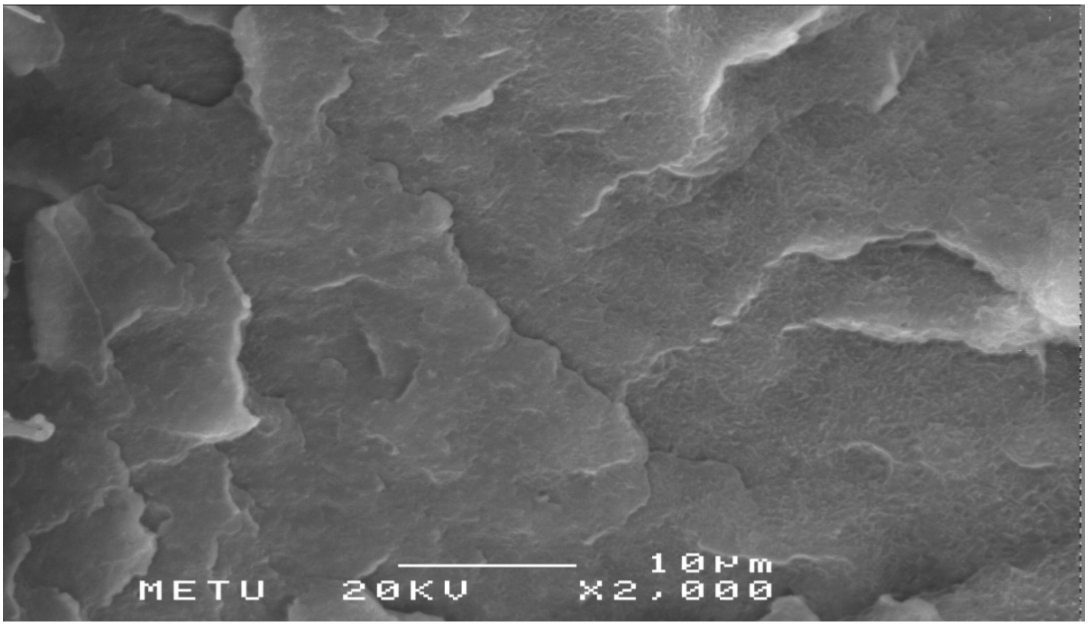


Figure 3.12: Fracture surface of blend containing 30% LDPE with 15% CB.

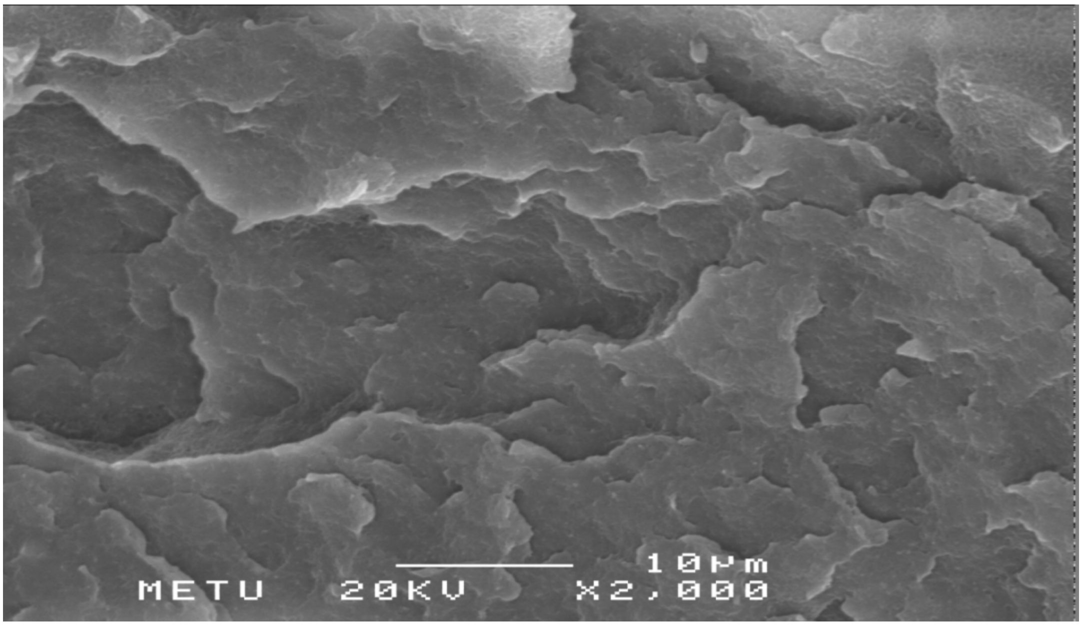


Figure 3.13: Fracture surface of blend containing 40% LDPE with 15% CB.

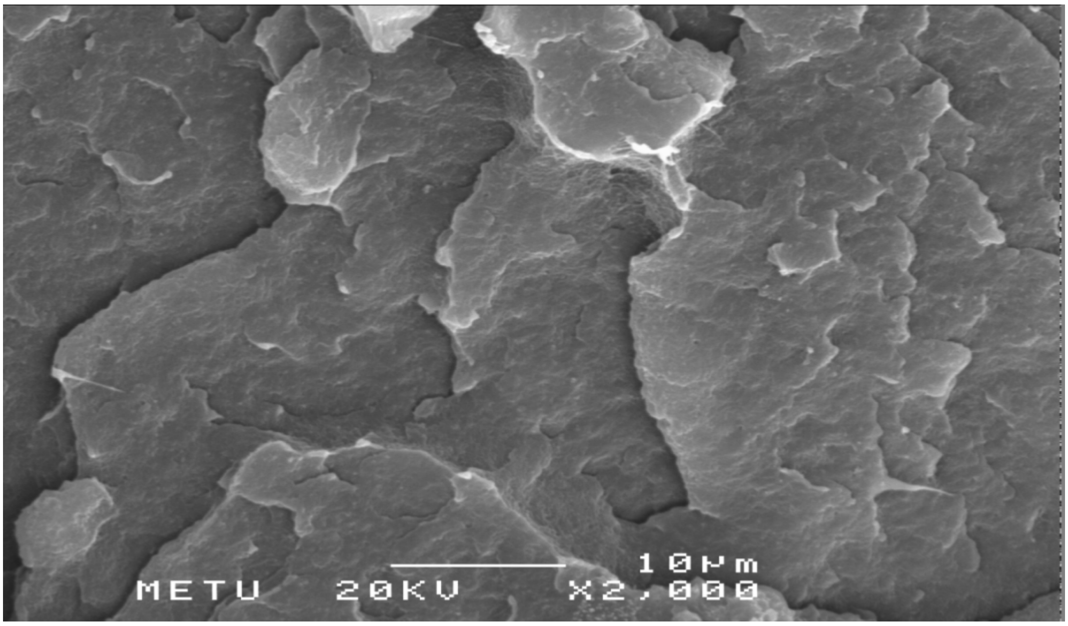


Figure 3.14: Fracture surface of blend containing 50% LDPE with 15% CB.

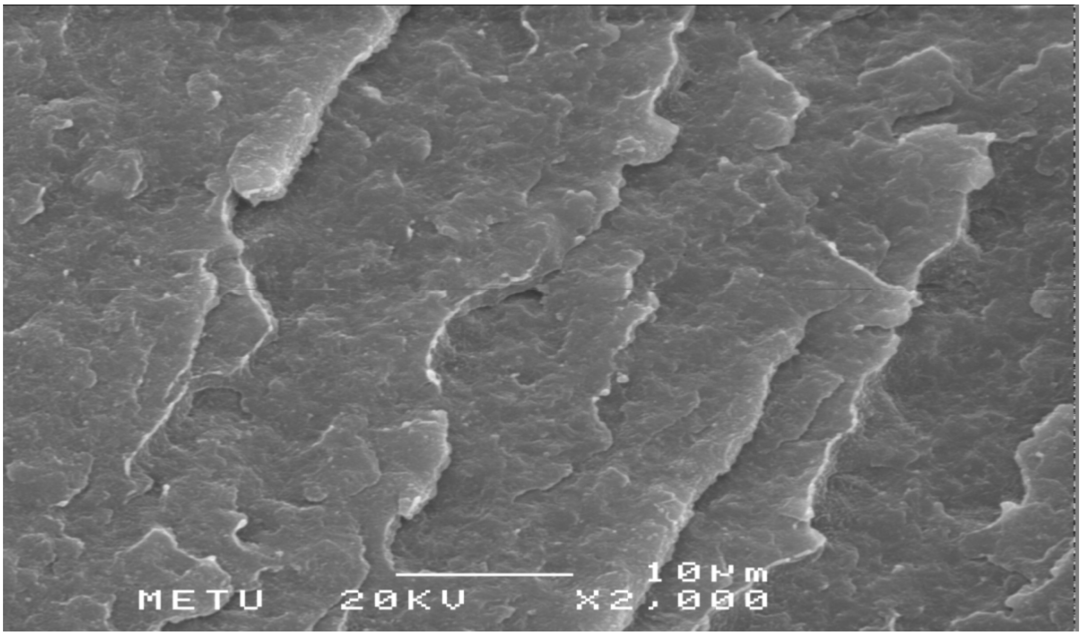


Figure 3.15: Fracture surface of blend containing 60% LDPE with 15% CB.

3.6 Conductivity Measurement

At room temperature conductivities of composites are measured using four point probe technique. As expected increasing CB content increased conductivity. The conductivity values are in the range of 0-5.10^{-3} S/cm. It is because of the fact that HDPE and LDPE are insulating polymers. In Figure 3.16 it can be seen clearly that there is an abrupt increase in conductivity when CB content exceeds 30%.

Temperature dependence of conductivity of the samples was studied in the 20-160 °C. Resistivities were measured at 10 °C intervals. A sudden increase in resistivity with increasing temperature near the melting point of HDPE was observed (Figure 3.17). In literature this effect is called as Positive Temperature Coefficient (PTC) behavior (27-30). Beyond the melting point of matrix resistivity decreases which is called as Negative Temperature Coefficient (NTC) behavior.

The electrical resistivity of PTC materials changes abruptly near the melting point of the polymer matrix also has its largest thermal expansion coefficient. Therefore, it was assumed that the PTC effect is due to the difference of the thermal expansion coefficient (27). Moreover, we observed that increasing the content of CB decreases resistance. There is no NTC effect in higher content CB sample. In contrast this situation; lower content CB sample has NTC effect. The NTC transitions immediately follow the PTC transition. The NTC effect is presumably due to reaggregating of CB particles in the polymer melt and repairing of the disconnected conducting pathways (32).

In the case of high filler concentration, CB particles form structures, which are in contact throughout the sample resulting in a low electrical resistivity. However, with increasing temperature, the molecular chain movement will make the conduction network break down. This results in an increase of the electrical resistivity, especially near the melting point of the polymer matrix. At this temperature the expansion coefficient is large. We assume that electrical resistivity increase results from the movement of the molecular chain of the polymer matrix. As a result, the electrical resistivity changes abruptly due to the breakdown of conducting networks and the enlargement of an insulating layer around the particles. This movement is strong near the melting point of crystalline polymers, so the PTC intensity is large for CB filled crystalline polymer compounds. It can be seen clearly in Figure 3.18. The DSC thermogram of pure HDPE is given in Appendix C.

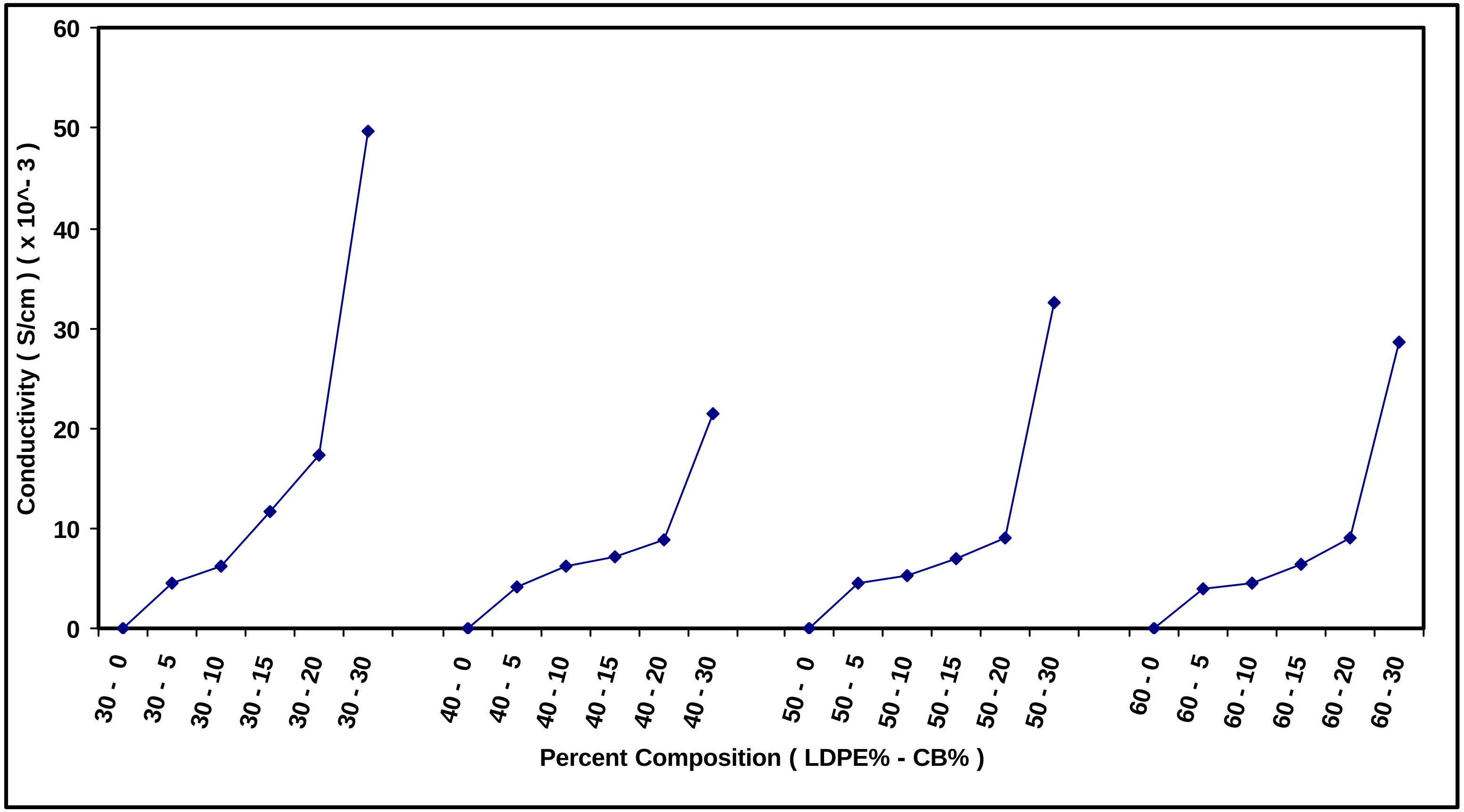


Figure 3.16: Conductivity vs. Percent Composition Graphic.

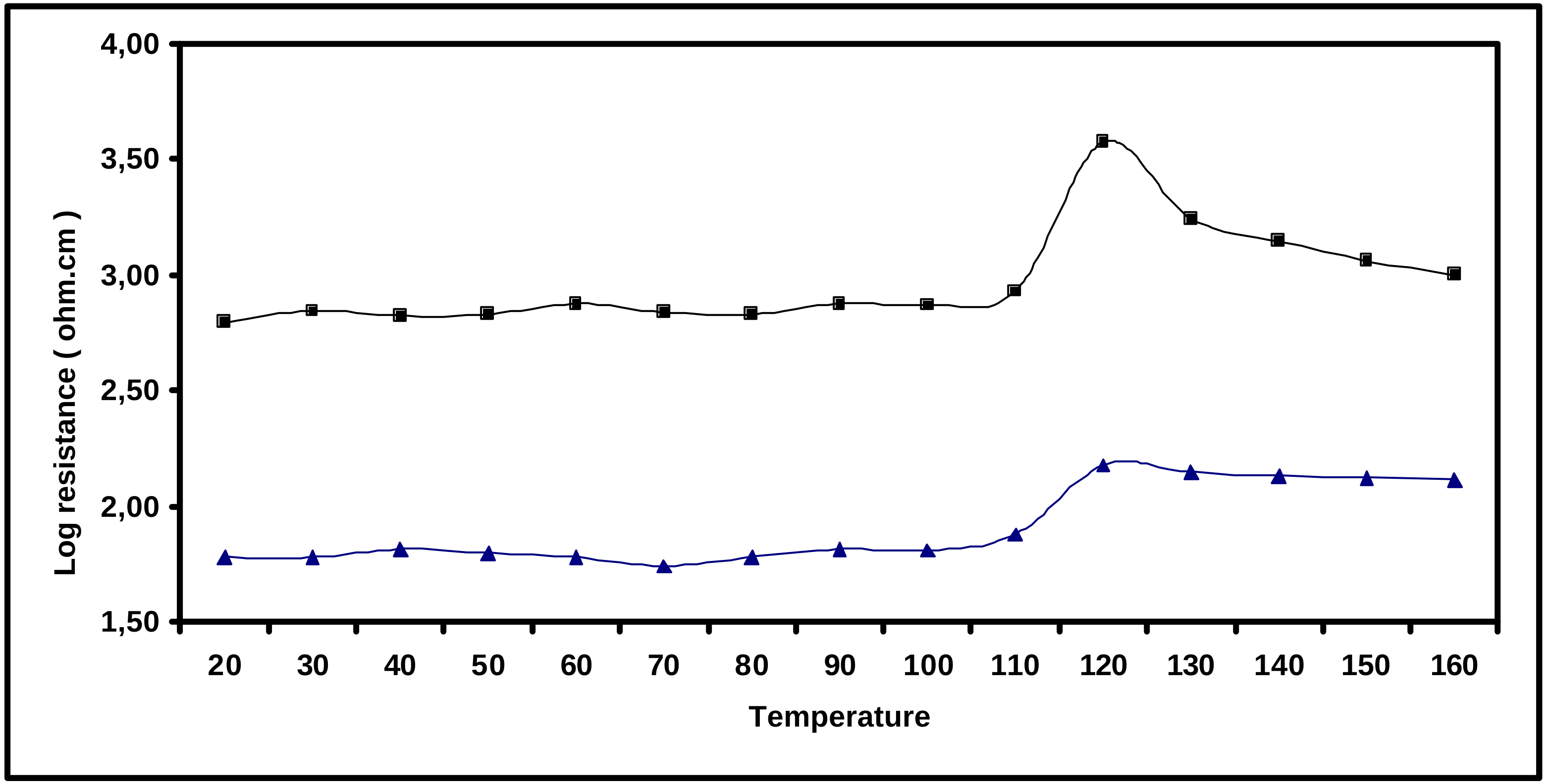


Figure 3.17: Log resistance vs. Temperature Graphic.

(¦) Percent Composition (67-5 HDPE-CB) (?) Percent Composition (50-30 HDPE-CB)

CHAPTER IV

CONCLUSION

In plastic industry HDPE and LDPE are used commonly. These are very important polymers in industry. Many studies were done by using these polymers. Some of the studies showed that HDPE and LDPE blends are miscible. There are studies on the mechanical properties of HDPE-LDPE blends but mechanic, thermal, morphological and electrical properties of HDPE-LDPE blends have not been studied yet.

In general, MFI values increased with increasing LDPE content of blends. Because pure LDPE has higher MFI value than pure HDPE. Addition of CB into different compositions of HDPE-LDPE blends decreased the MFI values. It is because of the fact that CB adsorbs the polymer chains and so the blend resists to melt flow.

It can be seen easily that CB generally improves mechanical properties of blends. Increasing CB content has an increasing effect on Young's modulus. The principal function of reinforcing fillers is to increase the modulus of the composite. CB reinforces blends. In our system, CB has a reinforcing effect on blends as filler. An increase in percent strain was observed by increasing HDPE. It is because of the fact that firstly the elongation occurs by amorphous parts, then the folded chains of crystalline HDPE opens so elongation increases. In general, increasing CB content decreased the elongation because higher CB content encourages the agglomeration. Addition of CB into enhanced the stress at break values in all compositions because polymer interacts with CB strongly by forming bound polymer

The change in crystallinity of HDPE was studied because of the fact that T_m value of LDPE peaks was not observed in DSC clearly up to 60% LDPE. The crystallization of the polymer matrix was decreased by the presence of CB because of the dispersion of carbon black in the molten crystal part.

SEM studies showed that, in general, homogenous distribution was obtained in blends. The changing in LDPE, HDPE and CB contents had no effect on morphology. No phase separation is observed.

In the case of high filler concentration, CB particles form structures, which are in contact throughout the sample resulting in a low electrical resistivity. However, with increasing temperature, the molecular chain movement will make the conduction network break down. This result an increase of the electrical resistivity, especially near the melting point of the polymer matrix.

REFERENCES

(1) Savasçi, Ö. Tunç, *A Perspective of Turkish Plastics Industry Present&Future,* PPS-**2001** Antalya-Türkiye,October, pp: 22-24.

(2) The association of Plastics Manufacturers in Europe (APME) Annual Report, **2002,** pp: 1-2.

(3) Committee Report of VIII. Development Plan in Petrochemical Industry, **2001**, pp: 80-92.

(4) David A. Reuschle (Dr.), The University of Southern Mississippi, Department of Polymer Science.
www.psrc.usm.edu/macrog/mpm/index.htm

(5) Manson John A. and Leslie H. Sperling, *Polymer Blends and Composites*, New York: Plenum Press, **1976,** pp: 25.

(6) Jacqueline I. Kroschwitz, Mary Howe-Grant, *Encyclopedia of Chemical Technology*, Fourth edition, Volume 19, 837-854, 1037-1038.

(7) Alamo R.G., J.D. Londono, L. Mandelkern, F.C. Stehling and G.D. Wignall, *The Phase Behavior of Blends of Linear and Branched Polyethylenes in the Molten and Solid States by Small-Angle Neutron Scattering*. Macromolecules, Vol.27, **1994** pp: 411.

(8) Agamalian, M., Alamo, R.G., Londono, J.D., Mandelkern, L., and Wignall, G.D., *The phase behaviour of blends of linear and branched polyethylenes on micron length*

scales via ultra-small-angle neutron scattering, Macromolecules, Vol.32, **1999**, pp: 3093.

(9) Cowie J. M. G., *Relaxation processes in the glassy state: molecular aspects*, Journal of Macromolecular Science, Phy. Ed., B18, **1980**, pp: 569.

(10) Silvestre Clara, Cimmino Sossio, and Di Pace Emilia, *Crystallizable Polymer Blends, Concise Encyclopedia of Polymeric Materials Encyclopedia* / Editor in Chief Salamone Joseph C., **1990**, Vol. 2-C, pp: 1595-1607.

(11) Olasibi O.; Robeson, L. M.; Shaw M. T., *Polymer-Polymer Miscibility*; Academic: New York, **1979**, pp: 46.

(12) Accorsi John V., Cabot Corporation, *The Impact of Carbon Black Morphology and Dispersion on The Weatherability of Polyethylene*, International Wire & Cable Symposium, Atlantic City, November 18, **1999**.

(13) Rivin D., *Surface Properties of Carbon*, Rub. Chem. Tech., Vol.44, **1971**, pp: 307-343.

(14) Long A.C., (Professor), University of Nottingham; School of Mechanical, Materials, Manufacturing Engineering & Management, **http://www.nottingham.ac.uk/~eazacl/H3CPOE/Polymer%20Structure.pdf**

(15) Kittel C., *Introduction to solid-state physics*, Wiley: New York, **1971**, pp: 48-49

(16) Andrew A. M., Louisiana State University Health Sciences Center Department of Orthopaedic Surgery Department of Cellular Biology and Anatomyarino, Ph.D., J.D,

http://www.ortho.lsumc.edu/Faculty/Marino/EL/EL4/Energy.html

(17) Carl R. (Rod) Nave (Dr.), Georgia State University, Department of Physics and Astronomy,
http://hyperphysics.phy-astr.gsu.edu/hbase/hframe.html

(18) Nugay N., Tinçer T., *A Study On Blends of Low and High Density Polyethylenes: Effect of Mixing Time on Mechanical, Thermal Properties and Oxidative Degradation*, Europan Polymer, Vol. 30, **1994**, pp: 473-477.

(19) Zhang Jian-Feng, Yi Xiao-Su, *Dynamic Rheological Behavior of High Density Polyethylene Filled with Carbon Black*, Lornal of Applied Polymer Science, Vol.86 , **2002**, pp: 3527-3531.

(20) Mallette Lavier G, Quel Luis M., Marquez Alfredo, Manero Octavo, *Carbon black-filled PET/HDPE blends: Effect of the CB structure on rheological and electric properties*, Journal of Applied Polymer Science, Vol.81, **2001**, pp: 562-569

(21) Ezquerra T. A., Bayer R. K., Calleja Balta F.J., *Conductive polyethylene-carbon black composites by elongational flow injection molding. Part 2. Variation of the molecular weight of the matrix,* Journal of Material Science, Vol.23, **1988**, pp: 4121-4126.

(22) Malik Tariq M., Carreau Pierre J., Germela Miroslav and Dufresne Alain, *Mechanical and rheological properties of carbon black-filled polyethylene*, Polymer Composites, Vol.9, **1988**, pp: 412-418.

(23) Laguna O., Collar E. P. and Taranco J., *Reuse of plastics recovered from solid wastes*, Journal of Applied Polymer Science, Vol. 38, **1989**, pp: 667-685.

(24) Yang Decai C., Brady Jean M., Thomas Edwin L., *Highly oriented single-phase blend films of high- and low-density polyethylene*, Journal of Material Science, Vol.23, **1988**, pp: 2546-2552.

(25) Fu Q., Men Y., Strobl G., *Understanding of the tensile deformation in HDPE/LDPE blends based on their crystal structure and phase morphology* Polymer, Vol.44, **2003**, pp: 1927-1933.

(26) Fan Z. J., Williams M. C. and Choi P., *A Molecular Dynamics Study of the Branching Characteristics of LDPE on its Miscibility with HDPE*, Polymer, Vol. 43, **2002**, pp: 1497 – 1502.

(27) Tang Hao, Chen Xingang and Luo Yunxia, *The PTC and NTC effect of CB filled LDPE composites*, Europan Polymer Journal, Vol.33, **1997**, pp: 1383—1386.

(28) Jia Wento, Chen Xinfang, *The Dependence of Electrical Resistivities on the Temperature of Different Polymer Systems*, Journal of Applied Polymer Science, Vol. 66, **1997**, pp: 1885-1890.

(29) Hou Yan Hui, Zhang Rong, *Performance stabilization of conductive polymer composites*, Journal of Applied Polymer Science, Vol.89, **2003**, pp: 2438-2445.

(30) Yan Hui Hou, Rong Zhang, *Carbon black-filled polyolefins as positive temperature coefficient materials: The effect of in situ grafting during melt*

compounding, Journal of Polymer Science, Part B: Polymer Physics, Vol.41, **2003**, pp: 127-134.

(31) Peterlin A, "*Morphology and Fracture of Drawn Semicrystalline Polymers*," Journal of Macromolecular Science Phys., B: 8, **1973,** pp: 83-89.

(32) Xiao-Su Yi, Guozhang Wu, Dongling Ma, *Property balancing for polyethylene-based carbon black-filled conductive composites***,** Journal of Applied Polymer Science, Vol. 67, **1998**, pp: 131-138.

APPENDIX A

Table A.1: Properties of pure HDPE and LDPE

	Tensile Strength (MPa)	Tensile Modulus (Gpa)	Elongation at Break (%)	Hardness Shore D	Melt Flow Index (g/10 min)	Density (g/cm³)
HDPE	30	0,86	840	62	0,35	0,964
LDPE	13	0,25	600	48	2,75	0,920

Table A.2: Properties of Vucan XC-72 Carbon Black

Description	Value
Surface Area, m^2/gm	254
Particle Size, nm	30
Tint Strength, % ITRB	87
Iodine Number, mg/g	253
DBP Absorption, cc/100g	174

APPENDIX B

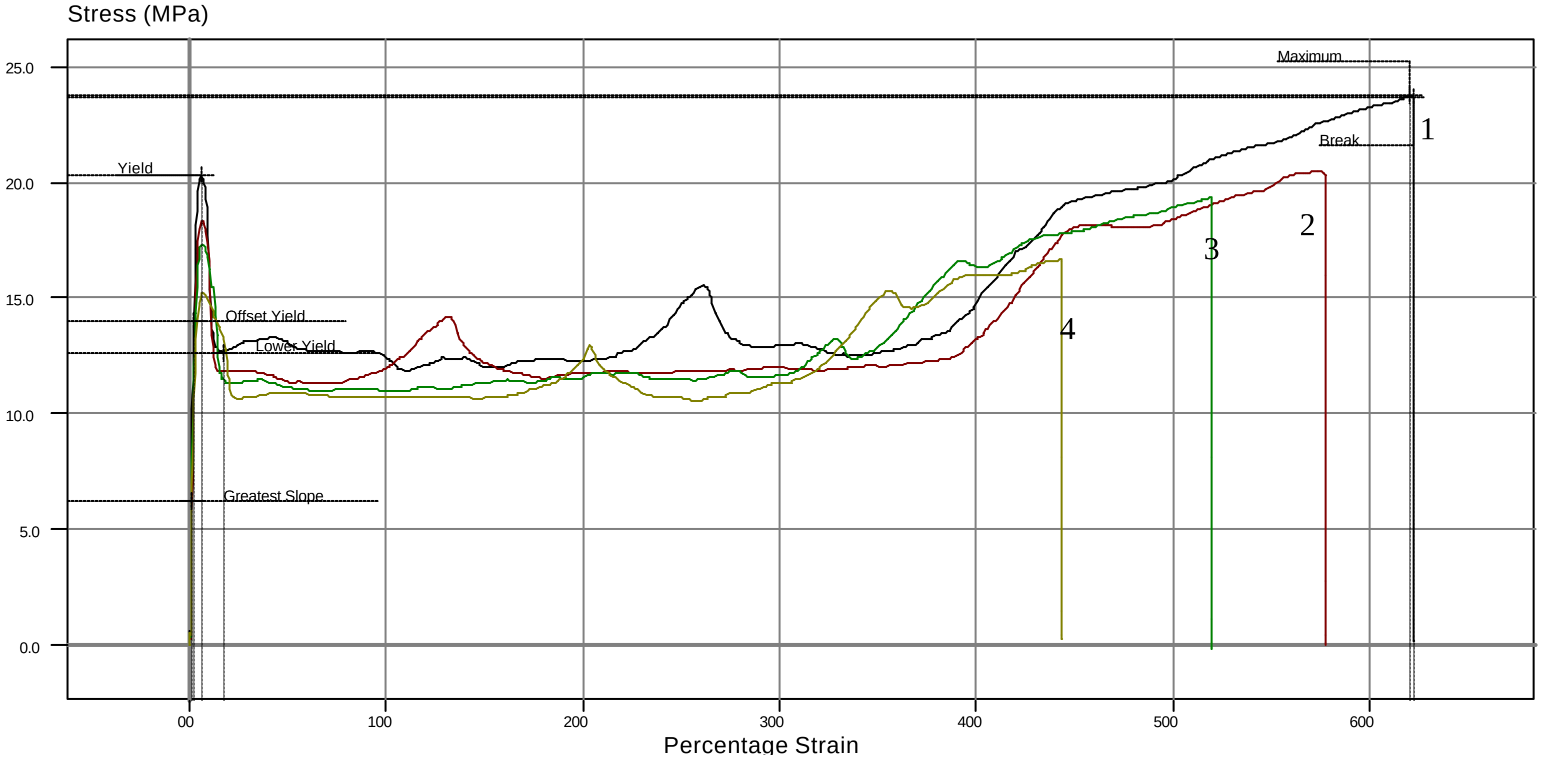


Figure B1: Stress strain curves for blends containing 5% CB

1) 65% HDPE-30%LDPE 2) 55% HDPE-40%LDPE 3) 45%HDPE-50%LDPE 4) 35%HDPE-60%LDPE

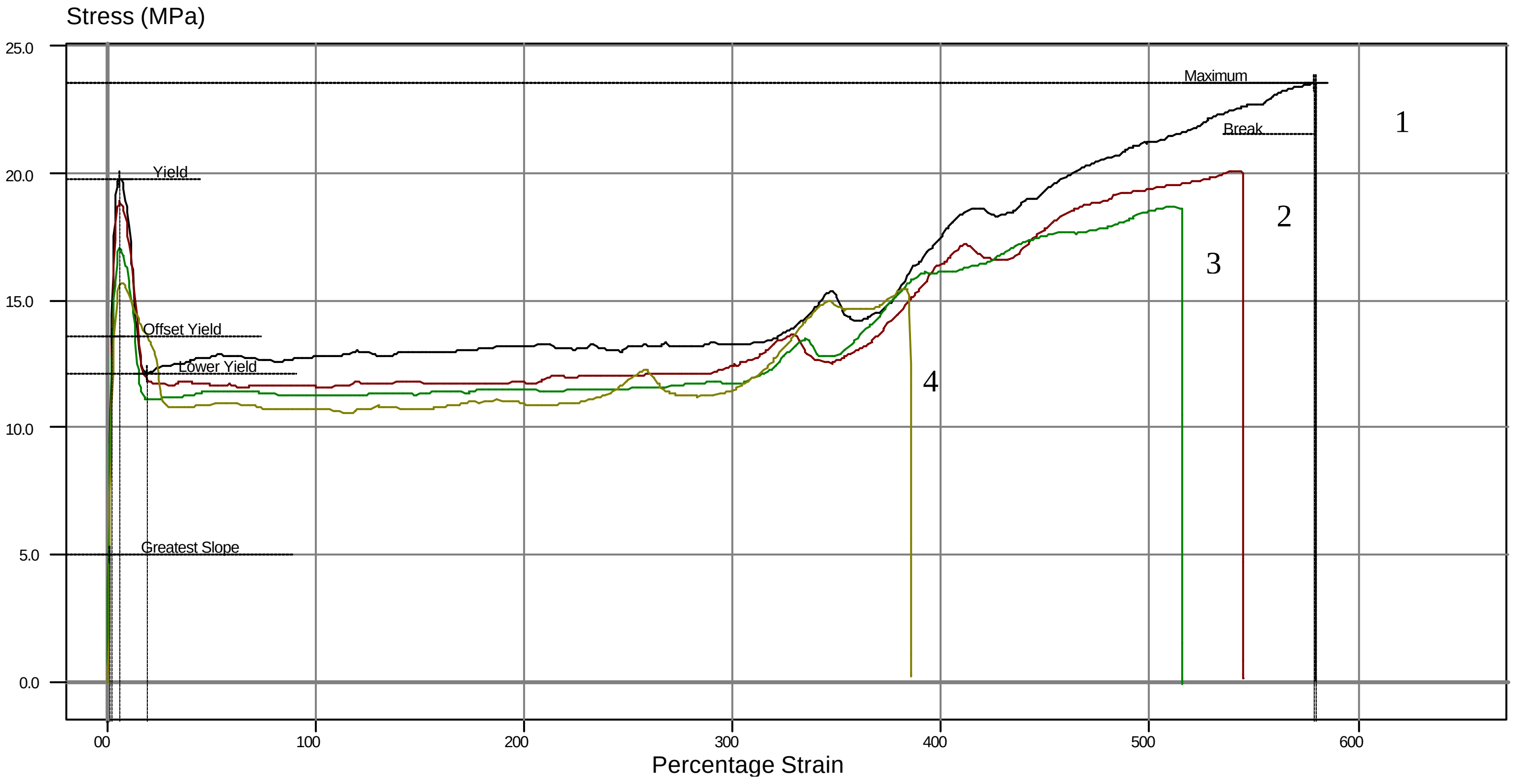


Figure B2: Stress strain curves for blends containing 10% CB

1) 60% HDPE-30%LDPE 2)50% HDPE-40%LDPE 3)40%HDPE-50%LDPE 4)30%HDPE-60%LDPE

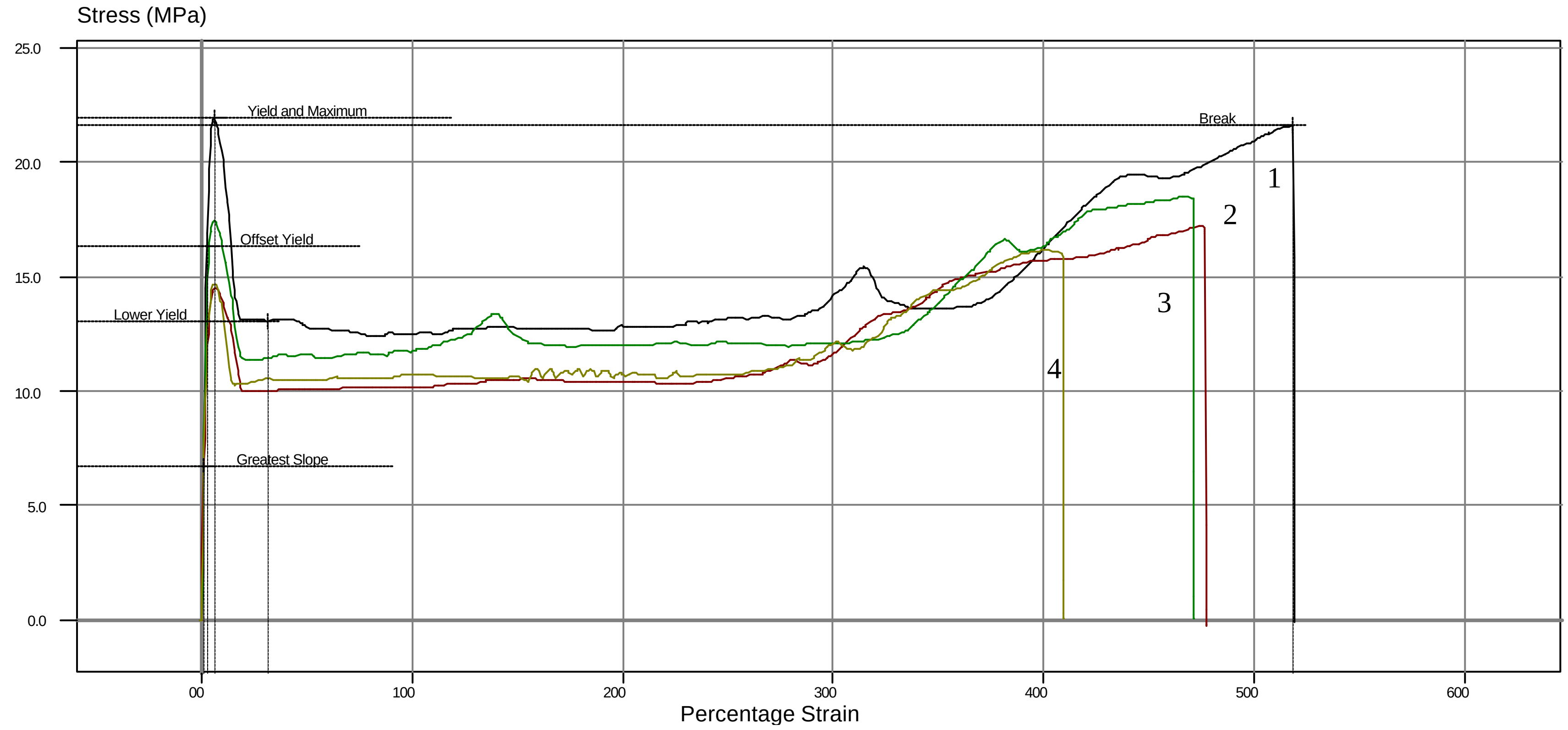


Figure B3: Stress strain curves for blends containing 15% CB

1) 55% HDPE-30%LDPE 2) 45% HDPE-40%LDPE 3)35%HDPE-50%LDPE 4)25%HDPE-60%LDPE

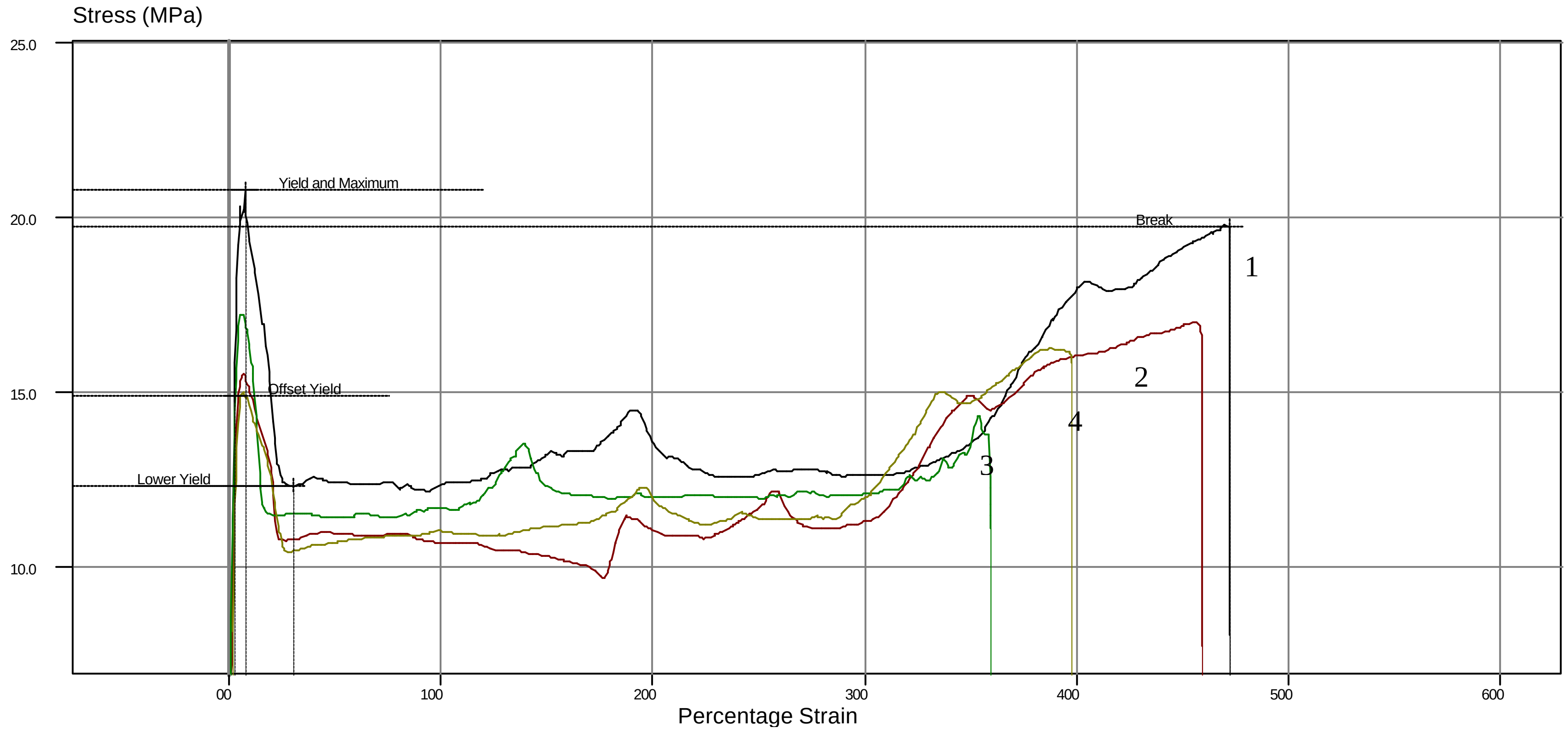


Figure B4: Stress strain curves for blends containing 20% CB

1) 50% HDPE-30%LDPE 2) 40% HDPE-40%LDPE 3) 30%HDPE-50%LDPE 4) 20%HDPE-60%LDPE

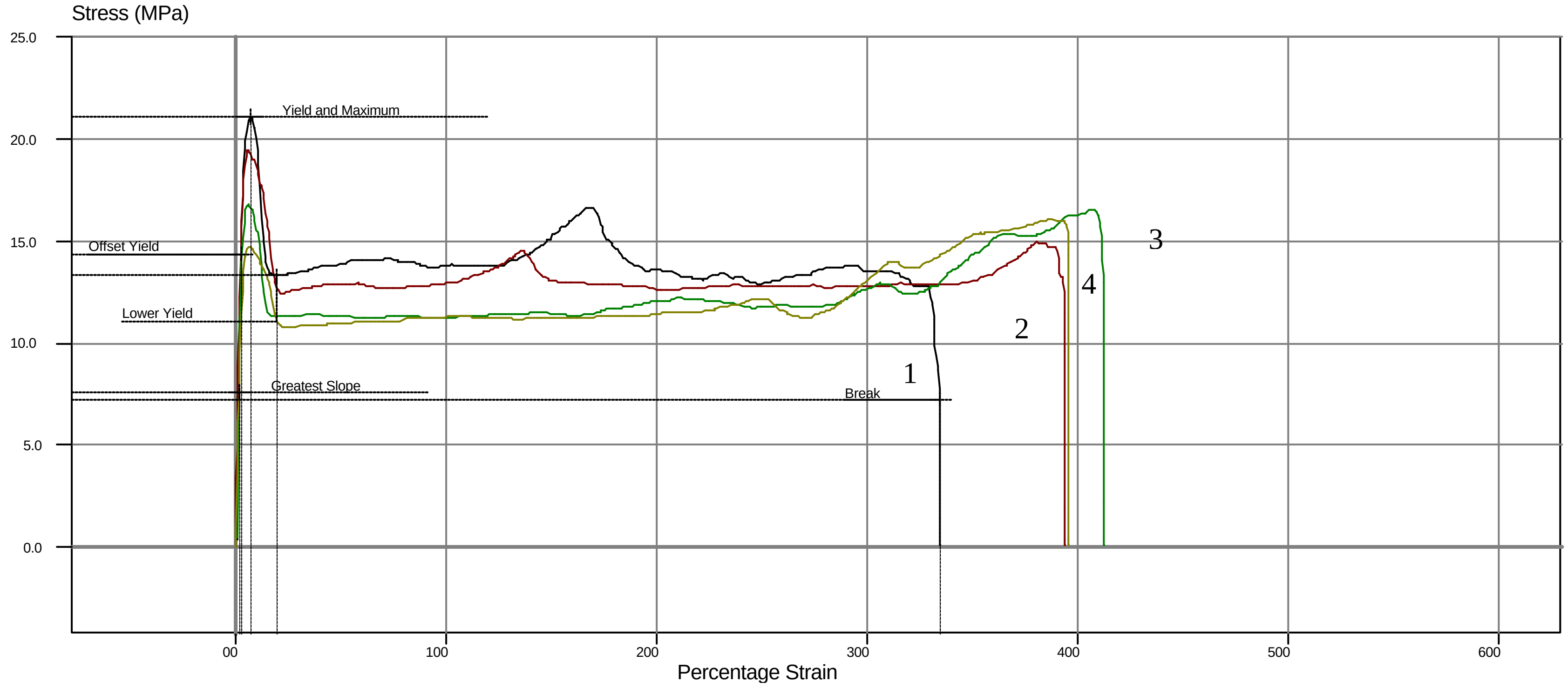


Figure B5: Stress strain curves for blends containing 30% CB

1) 40% HDPE-30%LDPE 2) 30% HDPE-40%LDPE 3) 20%HDPE-50%LDPE 4) 10%HDPE-60%LDPE

APPENDIX C

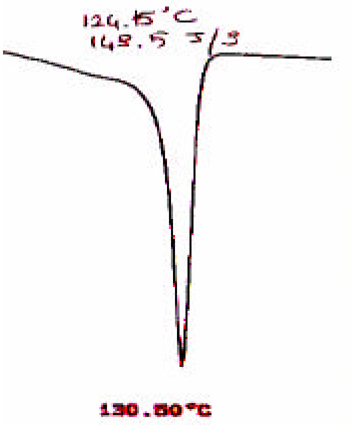
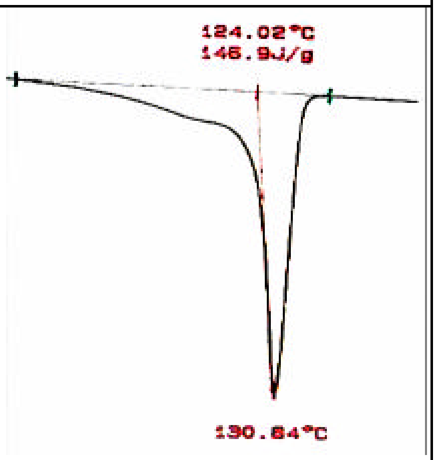
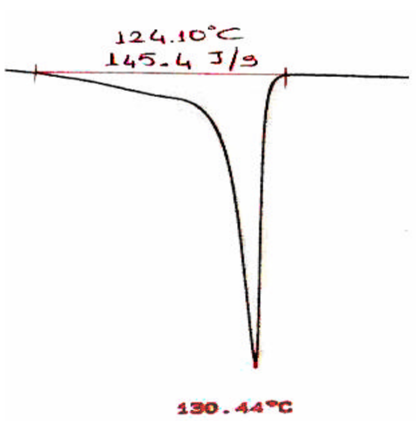
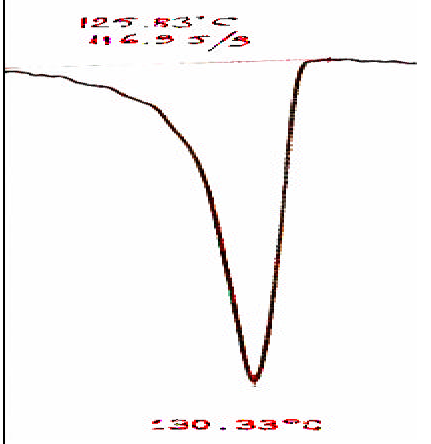
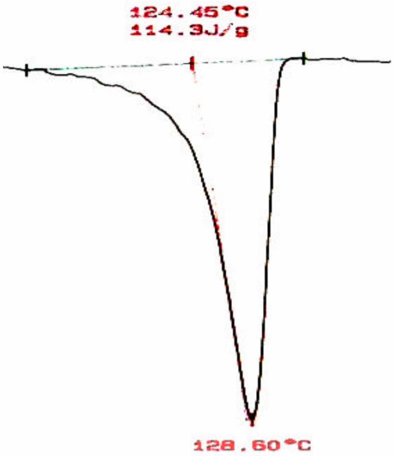
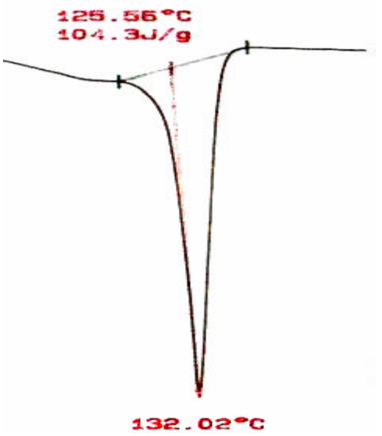
	0% CB	5% CB
70% HDPE 30% LDPE 65% HDPE 30% LDPE		
	10%CB	15% CB
60% HDPE 30% LDPE 55% HDPE 30% LDPE		
	20% CB	30% CB
50% HDPE 30% LDPE 40% HDPE 30% LDPE		

Figure C1: DSC thermograms for the melting peak of HDPE (40%-70%).

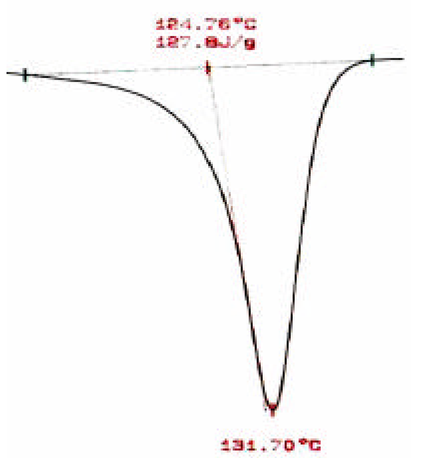
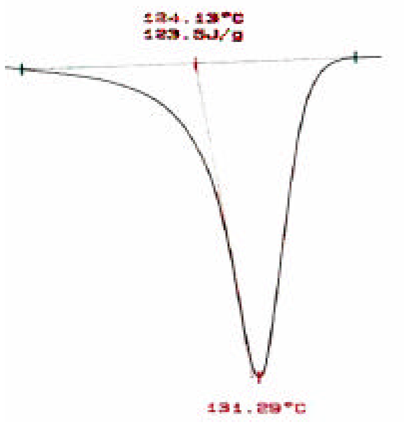
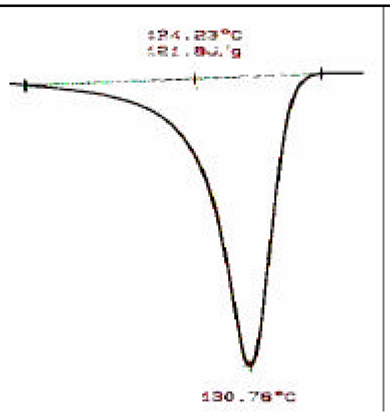
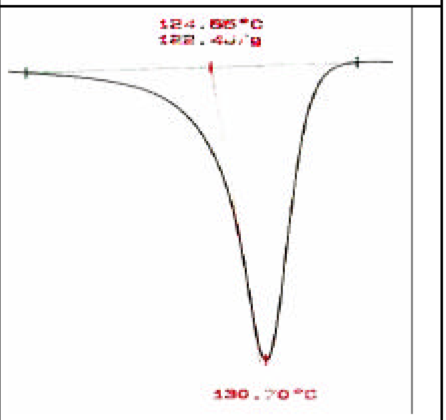
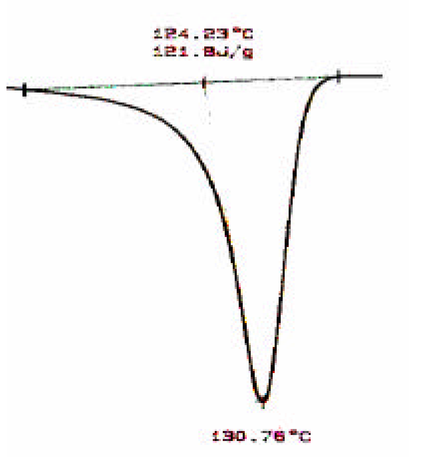
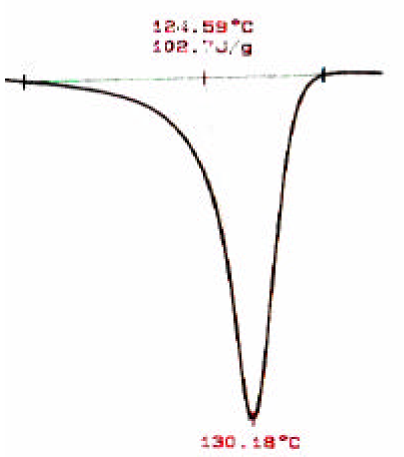
<table>
<tr><td></td><td>0% CB</td><td>5% CB</td></tr>
<tr><td>60% HDPE
40% LDPE
55% HDPE
40% LDPE</td><td>
</td><td>
</td></tr>
<tr><td></td><td>10%CB</td><td>15% CB</td></tr>
<tr><td>50% HDPE
40% LDPE
45% HDPE
40% LDPE</td><td>
</td><td>
</td></tr>
<tr><td></td><td>20% CB</td><td>30% CB</td></tr>
<tr><td>40% HDPE
40% LDPE
30% HDPE
40% LDPE</td><td>
</td><td>
</td></tr>
</table>

Figure C2: DSC thermograms for the melting peak of HDPE (30%-60%).

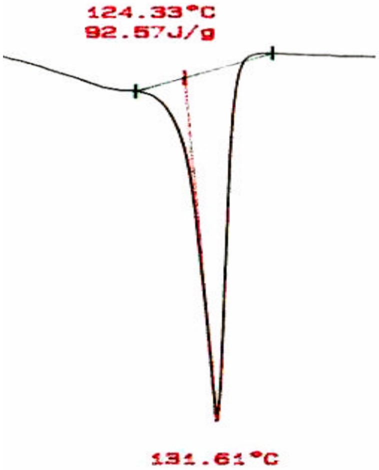
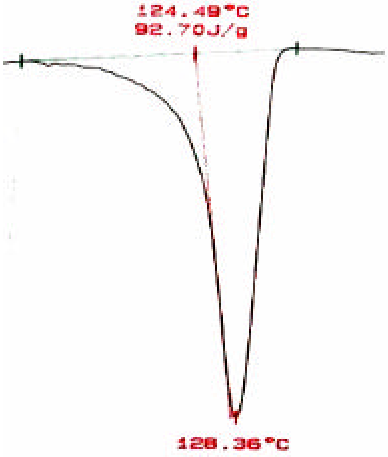
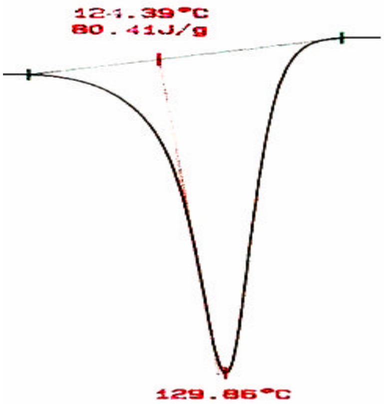
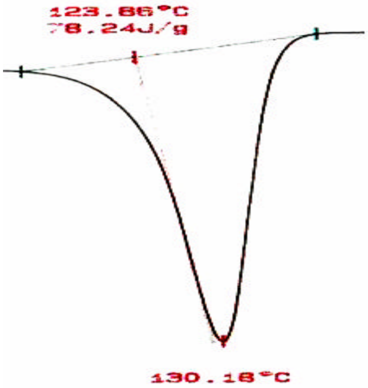
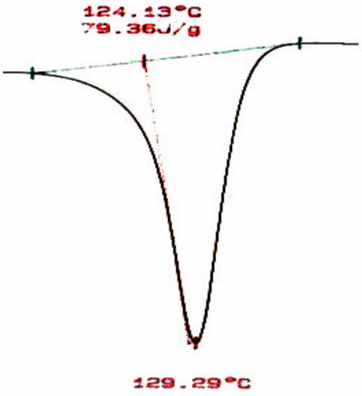
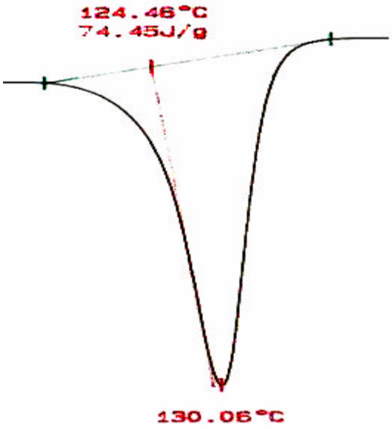
	0% CB	5% CB
50% HDPE 50% LDPE 45% HDPE 50% LDPE		
	10%CB	15% CB
40% HDPE 50% LDPE 35% HDPE 50% LDPE		
	20% CB	30% CB
30% HDPE 50% LDPE 20% HDPE 50% LDPE		

Figure C3: DSC thermograms for the melting peak of HDPE in (20%-50%).

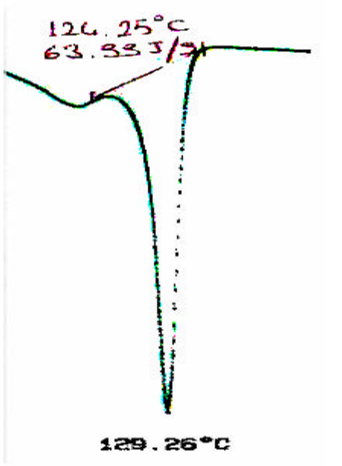
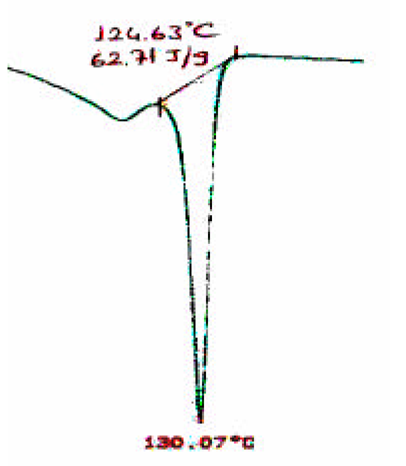
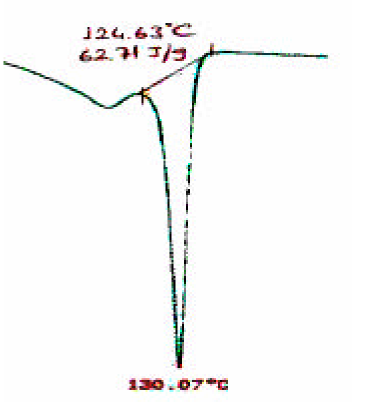
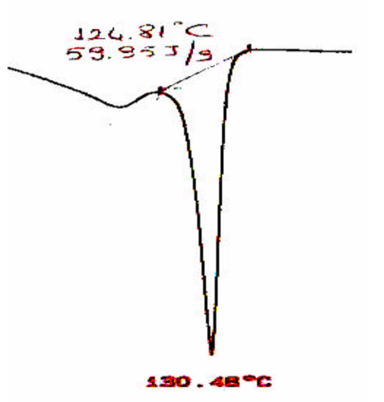
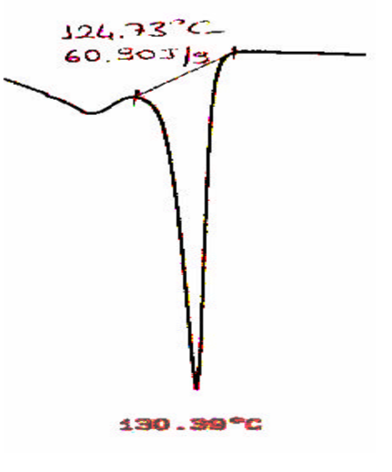
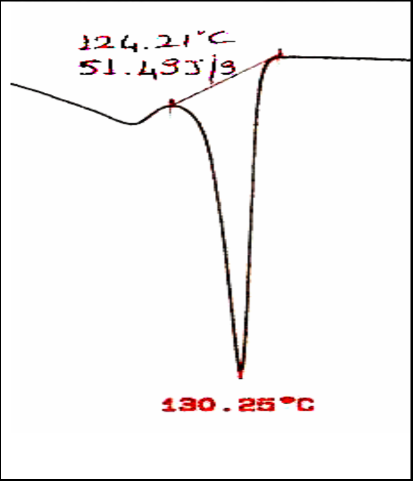
	0% CB	5% CB
40% HDPE 60% LDPE 35% HDPE 60% LDPE		
	10%CB	15% CB
30% HDPE 60% LDPE 25% HDPE 60% LDPE		
	20% CB	30% CB
20% HDPE 60% LDPE 10% HDPE 60% LDPE		

Figure C4: DSC thermograms for the melting peak of HDPE (10%-40%).

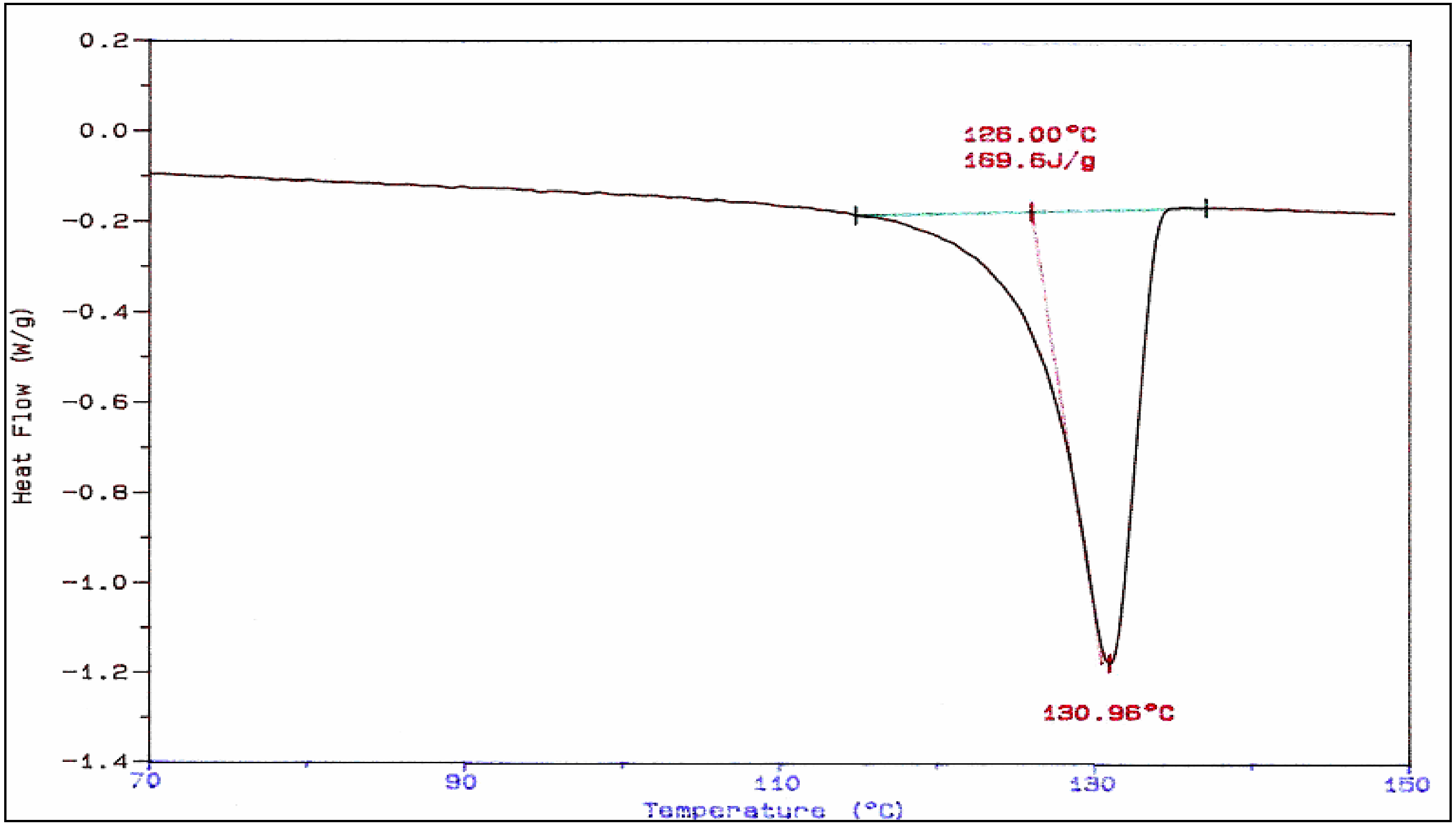


Figure C5: DSC thermogram of pure HDPE.

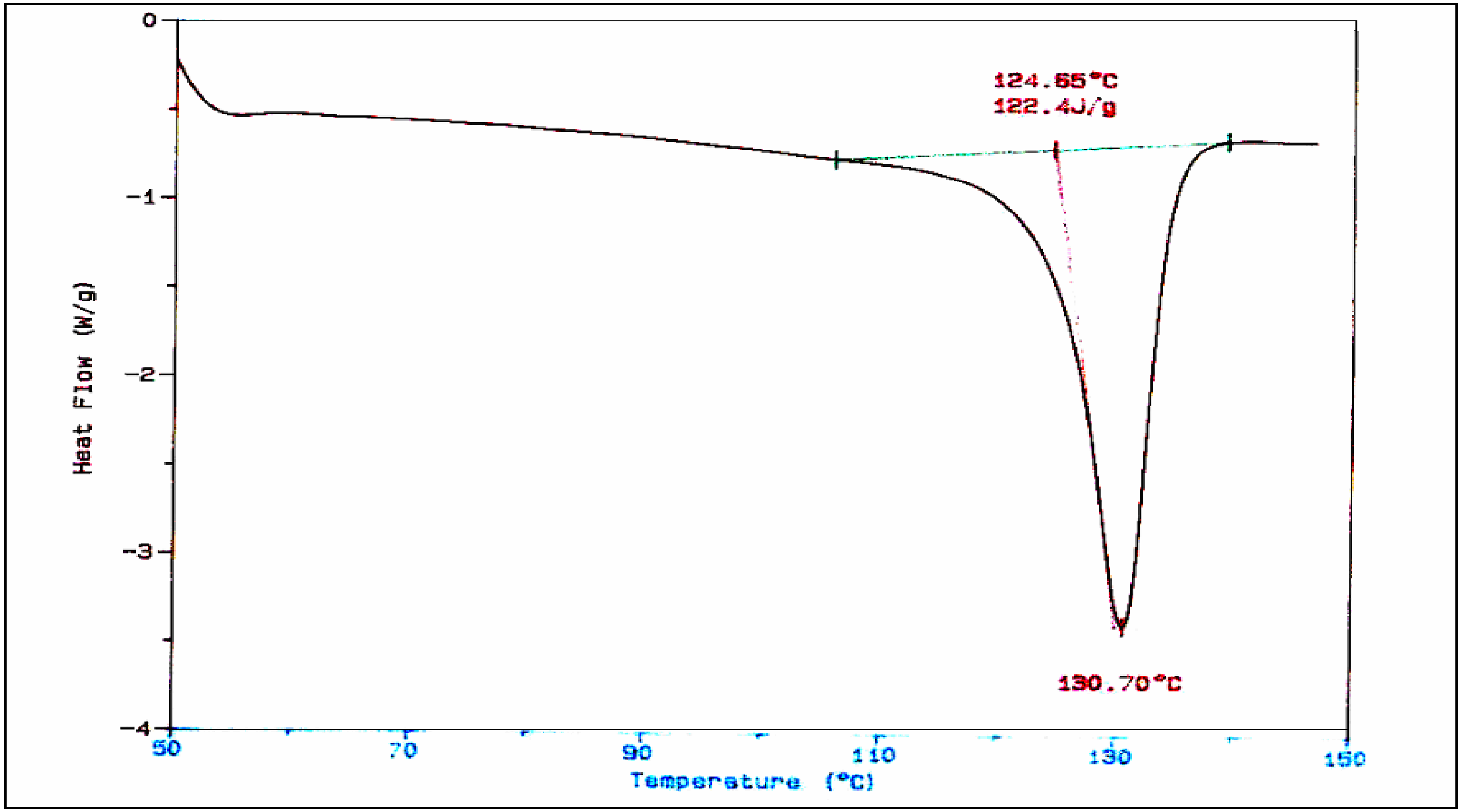


Figure C6: DSC thermogram of HDPE-CB (45% - 15%).

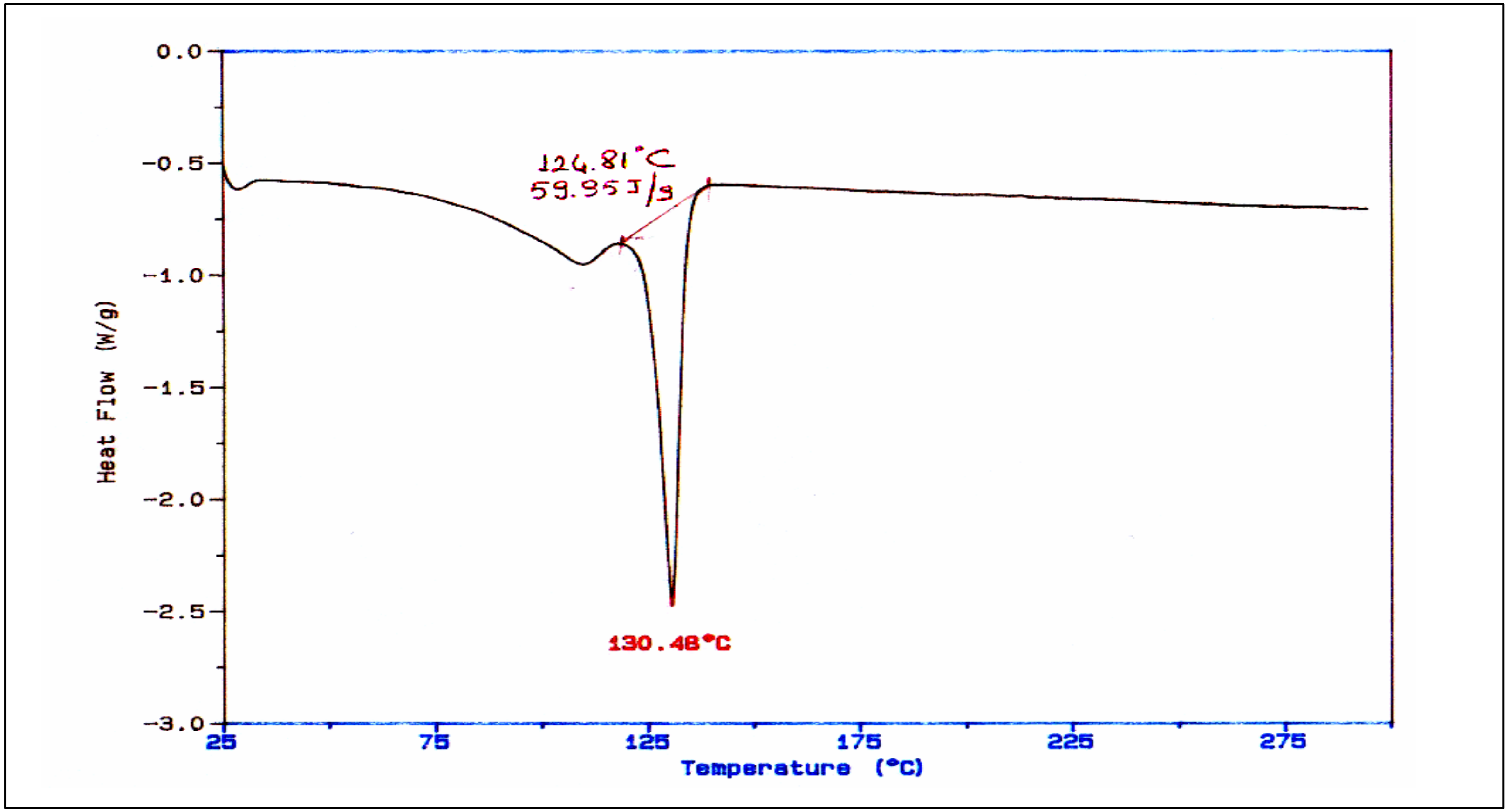


Figure C7: DSC thermogram of LDPE-CB (60% - 15%).