Sudan University of science and technology

Collage of graduated studies

Department of plastic engineering

Study of the effect of graphite on electrical properties of High Density Polyethylene

دراسة تأثير الجرافيت على الخواص الكهربائية للبولي إثيلين عالي الكثافة

A thesis submitted in partial fulfillment of the degree of M.S.c in plastic engineering

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الآيـــة

﴿وَقُلْ رَبّ أَدْخِلْنِي مُدْخَل صِدْق وَأَخْرِجْنِي مُخْرَج صِدْق
وَاجْعَلْ لِي مِنْ لَدُنْكَ سُلْطَاناً نَصْيراً ﴾

صدق الله العظيم ..

DEDICATION

TO

MY

FAMILY ..

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PREFACE

Conducting polymer, because of their unusual properties, have attracted great interest in recent years. Despite the short history, they have found a place in various application .this research is about a study on conducting polymer s and conductive thermoplastic composite.

This research is divided into five chapters as follows:

Chapter 1 Present an overview introduction about conducting polymers.

Chapter 2 Contains conducting polymer materials including their conductivity Mechanism , synthesis, characterization and applications.

Chapter 3 Deals with the materials used and the experimental procedures adopted for the research.

Chapter4 shows the calculation, results and discussions of the experiment.

Finally, summary and conclusions of the presents study is described in chapter 5.

At the end of chapters a list of references has been given .at list of abbreviations used in this research id also cited.

ABSTRACT

A sample of high density polyethylene and graphite powder was made to study the effect of graphite power content on the electrical properties of high density polyethylene, graphite offers the benefit of low density and cost when compared to metallic substances used for the same function , the sample was tested with different concentrations of graphite powder (30,40,50)% and in different temperatures, the study reached to the following results: The conductivity of the HDPE was increased according to the increase of temperature, the conductivity of the HDPE was increased according to the increase of graphite concentration, recommend to open the door to study this new exciting type of polymer that can help in application would be impossible using metal.

المستخلص

تم عمل عينة مكـ نة مـ ما لبـ لي يثلي عالي لكثافة لجـ في لـ سة تأثي محتـ لجـ في على لخـ لكهـ بية للبـ لي ثيلي عالي لكثافة، يقـ فائـ كثافة منخفضة تكلفة عنـ مقا نتها بالمـ لمعـ نية لمستخـ مة لنفـ لـ يفة تـ ختبا لعينة بتـ كيـ مختلفة مـ لجـ في (30،40،50)% في جا حـ مختلفة، تـ صلـ لـ سة لى لنتائج لتالية: تـ مـ صلية لبـ لي يثلي عالي لكثافة تبعا لـ يا جة لحـ ، تـ مـ صلية لبـ لي يثلي عالي الكثافة تبعاً لزيادة تركيز الجرافيت ، يوصي لفتح الباب لدراسة هذا النوع الجديد من البوليمر أن يمكن أن تساعد في تطبيق سيكون من المستحيل باستخدام المعادن .

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Chapter four: Results

Chapter Five: Conclusion and recommendations

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List of Abbreviations &Symbols

ASF6	Hexafluoroarsir
HCLO4	Perchloric acid
BCL3	Boron trichloride
PF6	Hexafluorphosphate
CH3 F	Fluoromethane
NO2 F	Nitryl fluoride
LiCLO4	Lithium perchlorate
(CHBr)x	Bromo methyl
(NH_4)2 S2 O8	Ammonium peroxydisulfate
CB	Conduction band
VB	Valence band
EB	Emeraldine base
ES	Emeraldine salt
Eg	Energy gap
(W/ m.k)	Watt per meter Kelvin
(S/ cm)	Siemens (1/ Ω) per centimeter
U. V	Ultraviolet
MFI	Melt flow index

Chapter One

Introduction

1.1 Preface

Polymer (or plastics) are Known to have good insulation properties, but recently new plastic have been discovered that can conduct electricity which Known as conducting polymers, Electrically conducting polymer composed of macromolecules having fully conjugated sequences of double bonds along the chains.

1. The Electrical Conductivity :

Conductivity as general is ability of material to conduct electricity current.

Conductivity can be defined by Ohms law

$$V= I R$$

Where:

R= Resistance.

I= Current.

V= Voltage .

2. The Electric Current

Is the movement of free electrons that migrate from atom to atom inside the conductor.

3. The reason why polymer are insulators:

Insulators however have tightly bound electrons so that nearly no electron flow occurs so they offer high resistance to charge or current flow.

4. How can polymer become conductive :

Electric current move easily through some materials but with great difficultly through others, Substances that permit the movement of a large number of free electrons are called conductors.

In becoming electrically conductive, a polymer has to imitate a metal, that it's electrons need to be free to move from atom to atom and not bound the atoms.

5. Definition of conductive polymers

Conductive polymer are a sub- group of a larger , older group of organic and inorganic electrical conductors.

That conduct electricity such compounds may have metallic conductivity or can be semiconductors the biggest advantage of conductive polymers is their process ability, mainly by dispersion conductive polymers are generally not thermoplastics they are not thermo formable. But, like insulating polymer, they are organic materials. They can offer high electrical conductivity but do not show similar mechanical properties to other commercially available polymer.

The filed of nanoscience has blossomed over last two decades and the importance of nanotechnology increase in areas such as computing, sensors, biomedical and many other application .in this regard the discovery of graphene and graphene- based polymer nanocomposites is an important addition in the filed of nanoscience . graphene, a single – layer carbon sheet with a hexagonal

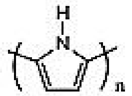
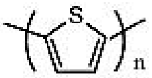
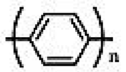
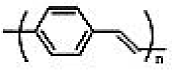
Packed lattice structure , has shown many unique properties such as the quantum hall effect (QHE), high carrier mobility at room temperature (10,000 cm2/ (v.s), large theoretical specific surface area (2630m2/g), good optical transparency (97.7%) , high young's modulus (1TPa) and excellent conductivity (3000-5000 Wmk). The superior properties of graphene compared to polymers are reflected in graphene- based polymer composites. Graphene- based polymer composites show superior mechanical , thermal , gas barrier , electrical and flame retardant properties.

6. Classification of conducting polymers

I .Intrinsically conducting polymers (ICP):

This type of polymer can conduct electricity of their of own because of their structural features, these are linear and have high planarity in structure and conjugation in the polymer chain.

Table 1.1 Intrinsically conducting polymers

Polymer (date conductivity discovered)	Structure	π-π^* gap (eV)	Conductivity[#] (S/cm)
I. Polyacetylene and analogues			
Polyacetylene (1977)		1.5	$10^3 - 1.7\times10^5$
Polypyrrole (1979)		3.1	$10^2 - 7.5\times10^3$
Polythiophene (1981)		2.0	$10 - 10^3$
II. Polyphenylene and analogues			
Poly(paraphenylene) (1979)		3.0	$10^2 - 10^3$
Poly(p-phenylene vinylene) (1979)		2.5	$3 - 5\times10^3$
Polyaniline (1980)		3.2	$30 - 200$

II. Doped conducting polymer :

ICP posses low conductivity, but their conductivity can be improved by creating positive or negative charges on the polymer chain by oxidation or reduction, This technique is called as Doping.

III. Extrinsically conducting polymers:

These are conducting polymer whose conductivity is achieved by adding external ingredients to them.

a. Conducting element filled polymer:

Metallic fibres, metal oxides, or carbon black can be mixed in the polymer during moldingprocess .

b. Blended conducting polymer :

it is obtained by blending conducting polymer with conventional polymer , physically or chemically.

IV. Coordination conducting polymer :

It is a charge transfer complex containing polymer, obtained by combining ametal atom with Polydentateligand, So there is a formation of coordination bond between the polymer and metal which allow the transfer of electrons easily. This conduction takes place as energy level decreases.

7. Previous studies :

Polymers have long been used as insulating materials, that is plastics being somehow the opposite of metals. They insulate, they do not conduct electricity. Electric wires are coated with polymer to protect them and us from short circuits.

Yet Alan J.Heeger, Alan G.MacDiarmid and Hideki Shirakawa have changed this view with their discovery that a polymer, polyacetylene can be made conductive almost like a metal. Polyacetylene was already Known as black powder when in 1974 it was prepared as a silvery film by Shirakawa and co-workers from acetylene, using a Ziegler – Natta catalyst (K. Ziegler and G Natta , Nobel prize in chemistry 1966).

But despite its metallic appearance it was not a conductor. In 1977, however Shirakawa, MacDiarmid and Heeger discovered that oxidation with chlorine, bromine or iodine vapor made polacetylene films 109 times more conductive that they were originally. Treatment with halogen was called "doping" by analogy with the doping of semi- conductors.

The "doped" form of polyacetylene had a conductivity of 105 Siemens per meter, which was higher than that of any previously Known polymer.

As a comparison, Teflon has a conductivity of 10^{-6} $Sm^{-1}$and silver and copper 108 S $m^{-1.}$

Iodine has a great yearning for electrons and it grabbed electrons from the bonds in the polymer backbone in the process, the polymer backbone acquired positive charge or holes, as they are called. the positive holes can travel very easily and provide a method of transfer of electric charge through the polymer .

Addition of an electron acceptor like iodine is called doping , the dopants could be electron donors also , in which case extra electrons added to the polymer impart a negative charge .

The polymer chain again become electrically unstable and applying avoltage makes the electrons run from one end to the other.

1.2 Objective of the research:

1.2.1 Specific objectives:

The main objective of this work is to study the electrical conductivity of thermoplastic material (HDPE) and enhance it by addition of graphite and temperatures.

1.2.2 General objectives:

- To overview thetheory, types synthesis and application of conductive polymers.
- To study the effect of graphite on HDPE with ration (30, 40 ,50 %) at different temperatures at (450 ,600,1000C$^{\circ}$)
- To compare the results.

.

Chapter Two

Literature Review

2.1 Introduction

Conducting polymer is an organic based polymer that can act as a semiconductor or a conductor . the most widely studied organic polymer are polyaniline (PANI), polypyrroles, polythiophenes, and polyphenylenevinylenes as given in table (1.1) The are conjugate π electron delocalization along their polymer backbone , hence giving them unique optical and electrical properties .

The conductivity (σ), of any conducting material is proportional to the product of the free- carrier concentration (n) an the carrier mobility (μ) where (e) is the unit electronic charge

$$\boldsymbol{\sigma = n\ \mu\ e} \rightarrow (1)$$

2.2Conductivity Mechanism:

The excitation and (or removal) insertion of electrons in conjugated polymers as a result of doping processes necessitate discussion of band theory. in its most simple form for conjugated polymer , the high extent of conjugation gives rise to two discrete energybands , the lowest energy containing the highest occupied molecular orbital (HOMO), also known as the valence band (VB) and that containing the lowest unoccupied molecular orbital (LUMO) , known as the conduction band (CB).The energy distance between these two bands is defined as the band gap(Eg), and in neutral conjugated polymers refers to the onset energy of the π-π* transition , the Eg of conjugated polymer.

Can be approximated from the onset of the π-π* transition in the UV-V is spectrum. in their neutral form, conjugated polymer are semiconducting, but upon oxidation (p-doping)or reduction (n-doping) inter band transition from between the VB and CB, lowering the effective band gap, resulting in the formation of charge carriers along the polymer backbone the band structure of a conjugatedpolymer originates from the interaction of the orbitals of the repeating units throughout the chain.

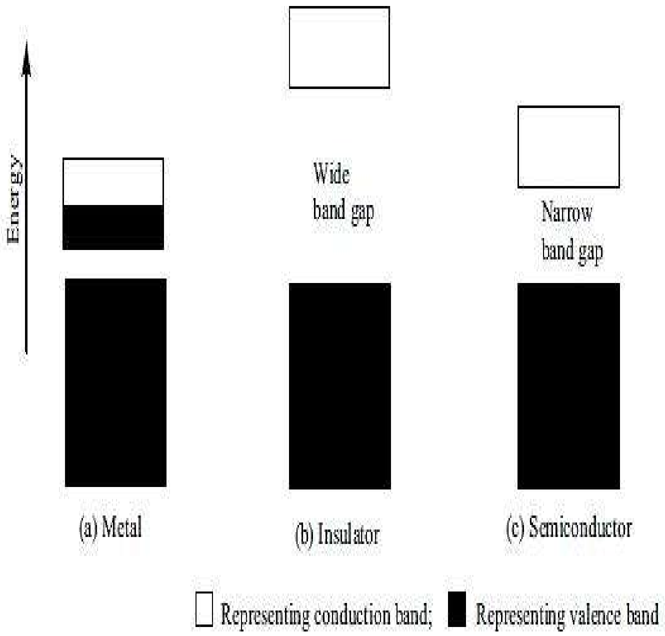


Fig . 2.1 A schematic representation of energy gaps in

(a) Metal (b) Insulator (c) Semiconductor

When an electron is added to the bottom of the conduction band from the top of the valence band of a conjugated polymer (fig.2.2(a)), the conduction band ends up being partially filled and a radical anion , commonly termed as a polaron , is created (fig2.2(b)). The formation of polaronscauses the injection of states from the bottom of the conduction band and top of the valence band into the band gap. A polaron carries both spin and charge .

Addition of a second electron on a chain already having a negative polaron results in the formation of a bipolaron through dimerization of two polarons, which can lower the total energy (fig.2.2(c)).

In conjugated polymer with a degenerate ground state (i.e two equivalent resonance forms), like trans- polyacetylene, the bipolarons can further lower their energy by dissociating into two spinlesssolitons at one – half of the gap energy (fig.2.2(d)). Solitons do not form in conjugated polymer with non degenerate ground states, such as in polypyrrole, polythiophene and polyaniline. The population of polarons, bipolarons, and /or solitons increases with the doping level . At high levels, the localized polarons ,bipolarons or solitons near to individual dopantions could overlap, leading to new energy bands between and even overlapping the valence and conduction bands, through which electrons can flow.

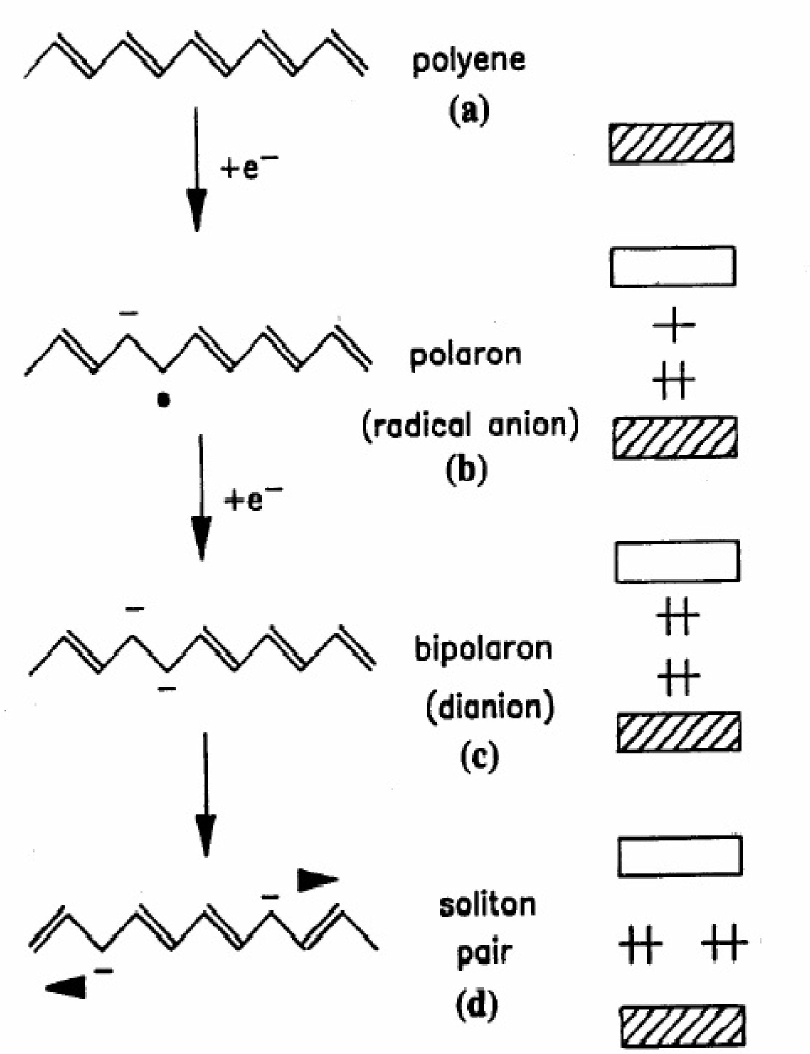


Fig 2.2 A schematic description of the formation of polaron, bipolaron , and soliton pair on a trans- polyacetylene chain by doping

In metals there is no range of energies which is deemed unavailable to electrons, which simply means that forbidden gap or band gap in metals is Eg = 0 Ev.

Hence metals always have a partially filled free- electron band, because the conduction and valence bands overlap . Hence the electron can readily occupy the conduction band Insulators have a bond gap which is large, hence the electron is not able to make that jump to detach from its atom , in order to be promoted to the valance band, Consequently they are poor electrical conductors at ambient temperatures.

Insulators can be defined as materials in which the valence bands are filled and the forbidden energy gap between valence bands and conduction band is too great for the valence electrons to jump at normal temperatures from VB to the CB.

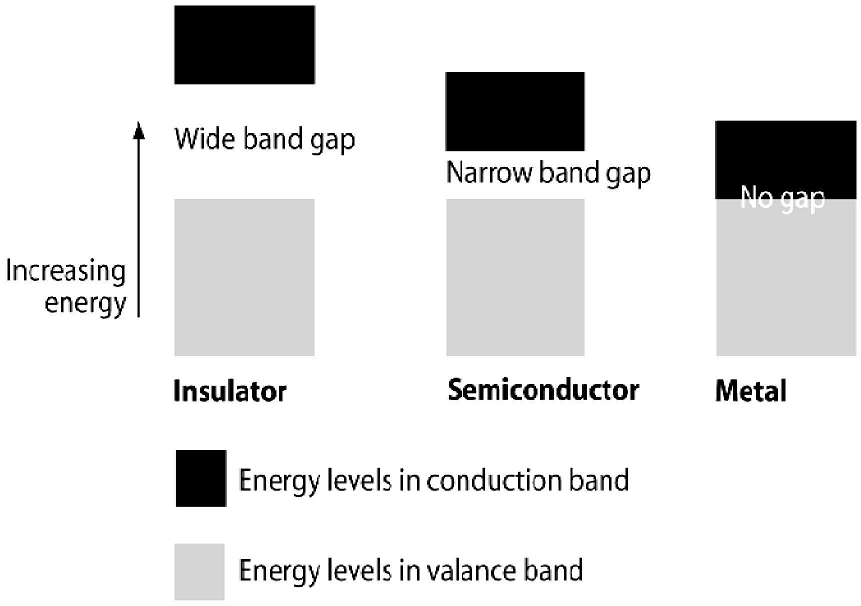


Fig 2.3 energy band diagram demonstrating band gaps

Organic chemistry shows that conjugated double bounds behave quite differently from isolated double bonds.

As the word indicates, conjugated double bonds act collectively, knowing that the next-nearest bond is also double. Huckel's theory and other simple theories predict that п electrons are delocalized over the entire chain and that the band gap becomes vanishingly small for along enough chain .One reason for this prediction is the character of a π molecular orbital, including the p orbitals of all carbon atoms along the chain of conjugated double bonds. When looking at the distribution of electron density, to which all filled molecular orbitals contribute, the electrons are predicted to be spaced out rather evenly along the entire chain .in other words, all bonds are predicted to be equal .

One reason why polyactylene is a semiconductor and not a conductor is due to that the bonds are not equal , there is a distinct alternation , every second bond having some double – bond character .

2.3Doping process:

Doping is a process in which a virgin polymer is treated with a strong oxidizing or reducing agent that either abstracts electrons from the polymer or donates electrons to it through the formation of a charge carrier into the polymer for the enhancement of itsconductivity.

$$\text{Polymer} + \text{acceptor dopant} \xrightarrow{\text{(oxidation)}} (\text{polymer}^{+}\,\text{dopant}^{-})$$

$$\text{Polymer} + \text{donor dopant} \xrightarrow{\text{(reduction)}} (\text{polymer}^{-}\,\text{dopant}^{+})$$

The doping of conjugated polymer increases the carrier concentration.

2.4Nature of Dopant:

Doping agents or dopants are either strong reducing agents or strong oxidizing agents. Salts which can easily form ions, organic and polymeric dopants . the nature of dopants play an important role in the stability of conductive polymers.

For example, perchloric acid doped polyacetylene is not sensitive to water and oxygen .Similarly, electrochemical doping of polyacetylene with sodium fluoride makes it more resistant to oxygen .

Oxidative dopants are usually electron- attracting substances, the common p-type dopants are Br_2 ,$A sF_6$, $H_2 SO_4$, $HCIO_4$,BCL_3, PF_6, CH_3F, NO_2,$FeCI_3$.

n- type dopants are electron donating substances like sodium naphthalideNalk alloy , molten potassium.

2.5 Doping Methods:

There are number of ways by which doping can be carried out, thesedifferent methods can be broadly summarized as being:

1. Chemical doping .
2. Electrochemical doping.
3. Photo chemically initiated Doping.

2.5.1 Chemical doping

Almost all conjugated polymers, including those listed on Table (1.1), can be either partially oxidized (p-type redox doping) or partially reduced (n-type redox doping) by electron acceptors or electron donors. For example , the treatment of trans- polyacetylene with an oxidizing agent such as iodine leads to the doping reaction [Equation (2.1) and a concomitant increase in conductivity of about10^{-5} to 10^2 S/cm .

$$trans\text{-}(CH)_x + 3/2xyI_2 \rightarrow [CH^{+y}(I_3)_y^{-}]_x \tag{2.1}$$

Similarly, most conjugated polymer like trans – polyacetylene can be doped with electron donors (n –doping) to gain high conductivities.

$$trans\text{-}(CH)_x + [Na^{+}(C_{10}H_8)^{-\bullet}] \rightarrow [(Na^{+})_y(CH)^{-y}]_x + C_{10}H_8 \tag{2.2}$$

More interestingly, it was found that the n- and – type dopants could compensate each other. This compensation process is by the undoping of an Na-doped polyacetylene film by I_2 . As can be seen in Figure 2.5, the electrical conductivity of the Na- doped sample gradually decreases upon I_2 doping and increases, after reaching a minimum, with further p-doping.

The relative low conductivities attainable by the I_{2-} doping can be attributed to Na^+ ions remaining in the initially n- doped polyacetylene film in the form of Nal (o.5 Nal / CH unit). Although the minimum conductivity for the fully compensated sample is still higher than that of the pristine polyacetylenefilm prior to Na- doping , the observed compensation process clearly demonstrates the feasibility to reversibly change the electrical properties of conjugated polymers in a controllable fashion .

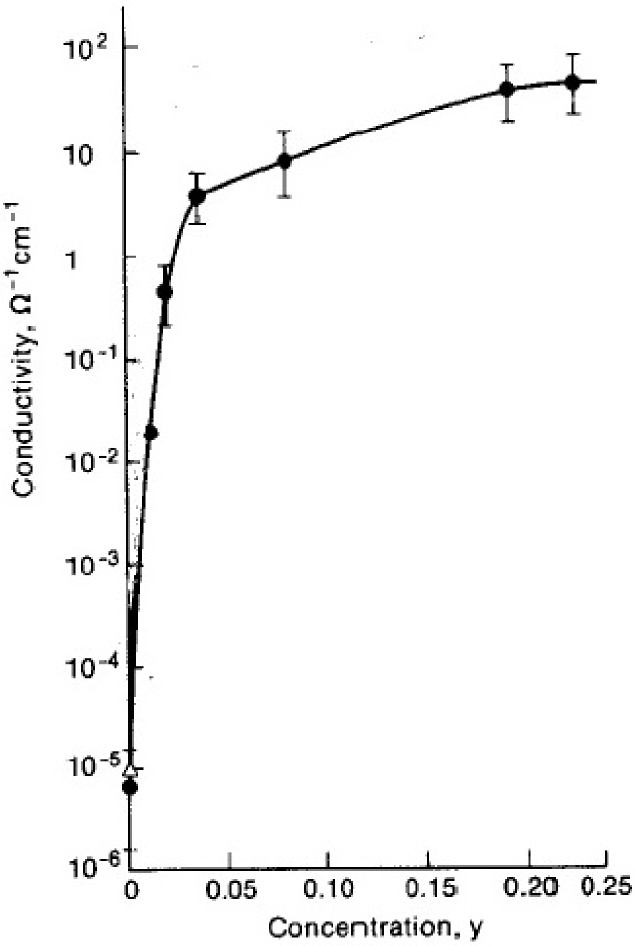


Fig2.4 electrical conductivity of I_2- doped trans- polyacetylene as a function of iodine concentration .

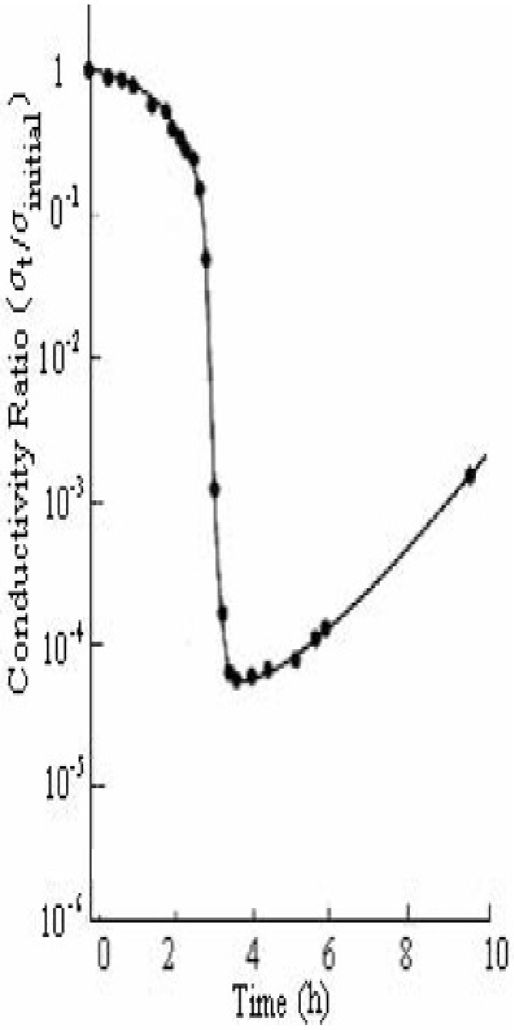


Fig 2.5 electrical conductivity ratio of an Na- doped polyacetylene as a function of time of exposure to iodine

2.5.2 Electrochemical Doping:

Owing to the extensive conjugation of π- electrons, conjugated polymers can also be easily oxidized (p-doping) or reduced (n- doping) electrochemically with the conjugated polymer acting as either an electron source or an electron sink.

Applying a DC power source between a trans- polyacetylene coated positive electrode and a negative electrode . Both of them are immersed in a solution of LiCLO4 in propylene Carbonate.

$$\textit{trans}\text{-}(CH)_x + (xy)(ClO_4)^- \rightarrow [CH^{+y}(ClO_4)_y^-]_x + (xy)e^- \quad (y \bullet \bullet 0.1)$$

Compared with chemical doping electro chemical doping has several distinct advantages **Firstly,** a precise controlof the current passed.

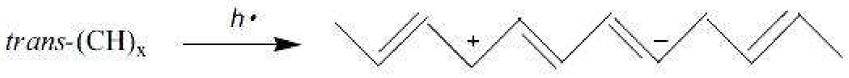
Secondly ,doping – undoing is highly reverible with no chemical products requiring removal . **Finally** , both p- or n –type doping can be achieved even with dopant species that cannot be introduced by conventional chemical means in both cases.

However, counter “doping “ ions may cause an undesirable structural distortion and a deteriorated effect on conductivity, they facilitate conjugated conducting polymers for actuation applications.

In order to eliminate the incorporation of counter ions, “ photo- doping’’ and “ charge – injection doping “ method have been exploited to achieve the redox doping effects . besides, some conjugated polymers, such as polyaniline and poly(heteroaromaticvinylenes), can also acquire high conductivities through the protonation of imine nitrogen atoms without any electron transfer between the polymer and “ dopants” occurring - i-e. “non redox” doping .

2.5.3 Photo- doping :

The irradiation of a conjugated polymer (e.g. trans- polyacetylene) macromolecule with a light beam of energy greater than its band gap could promote electrons from the valence band into the conduction band, Although the photo generated charge carriers may disappear once the irradiation ceases, the application of an appropriate potential during irradiation could separate electrons from holes, leading to photoconductivity.



2.5.4 Charge – injection Doping:

Using a field – effect transistor (FET) geometry , charge carriers can be injected into the band gap of conjugated polymer by applying an appropriate potential on the metal/ insulator / polymer multilayer structure just like photo- doping the charge – injection doping does not generate counter ions, allowing a doping the charge – injection doping does not generate counter ions, allowing a systematic study of the electrical properties as a function of the charge carrier density with a minimized distortion of the material structure . Using the charge- injection doping method ,schon have recently demonstrated that a thin P3HT self – assembled film exhibits a metal – insulator transition with a metallic- like temperature dependence. At temperatures below 2.35 K, these authors observed superconductivity when the charge density exceeds $2.5\times10^{-14}cm^{-2}$. This observation of superconductivity appears to be closely related to two – dimensional charge transport in the self – assembled polymer film.

Although much of Schon's work is currently in question and the detailed superconducting mechanism remains to be found the above observation may suggest that the conductivity of conjugated polymer could be tuned over the largest possible range from insulating to superconducting .

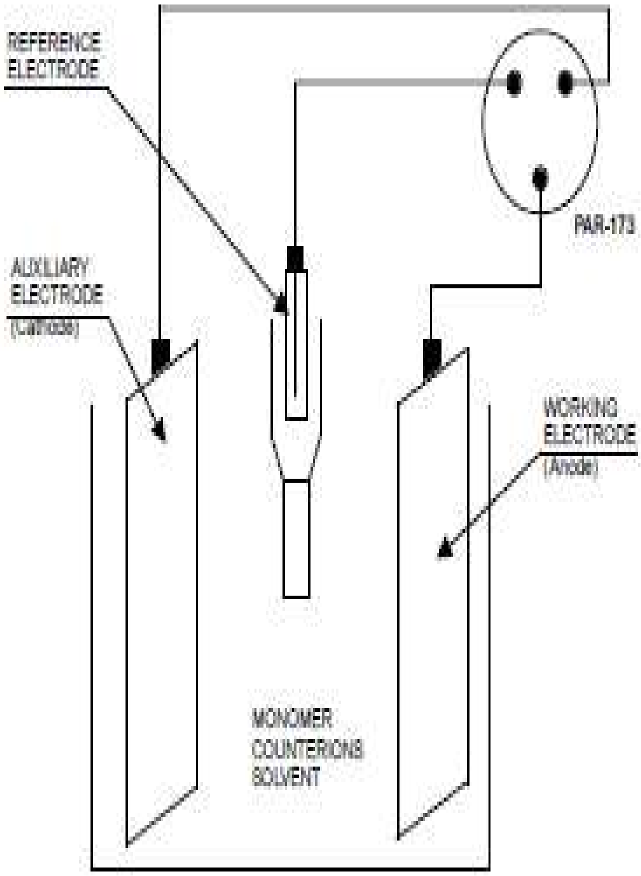


Fig 2.6 the electrochemical polymerization cell

2.6 Conductivity measurement

Conductivity measurements can be performed by four probe and two probes techniques. Among available conductivity techniques, four probe method has several advantages for measuring electrical properties of conducting polymers. First, four probe techniques eliminate errors caused by contact resistance, since the contacts applying the current across the sample. Second, this technique allows for conductivity measurements over a broad range of applied currents, usually varying between 1 μ A and 1 m A for conducting polymers.

In four equally spaced osmium tips were placed into a head is lowered to the sample until the four probe touch the outermost probes and voltage drop across the inner two was measured (fig.2.7), conductivity was given by the equation:

$$\boldsymbol{\sigma = \mathrm{In}2 / (\pi d \times i / V) \rightarrow (2)}$$

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

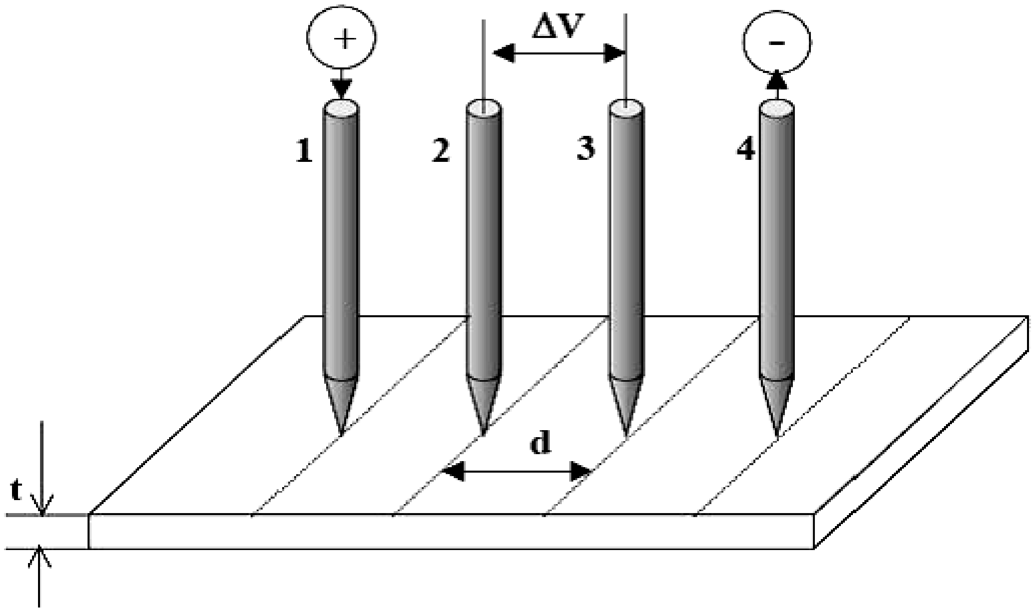


Fig . 2.7 Schematic diagram of four probe technique

2.7 General properties of intrinsically conducting polymer:

Conducting polymers have all the desirable properties:

- They are readily engineered at the molecular level to recognize specific stimuli .
- Because they are conductive, they facilitate transport of electrical information.
- They are capable of localized processing as well as actuation of response mechanisms.

2.8Polyacetylene(PAC)

Polyactyleneis the simplest conjugated polymer. In its linear form it precipitates as a black, air sensitive, infusible and intractable powder out of solution and cannot be processed.

Table . 2.1 Properties ofPolyacetylene

Chemical formula	$[C_2H_2]_n$
Density (g/cm^3)	1-1.15
Melting point(C^o)	120
Molecular weight	200-500

2.8.1Synthesis and processingof PAC:

There is often a big step between the first chemical synthesis of a molecular substance and the development of processing methods for practical application.

The first polyacetylenes were obtained from actetylene which polymerized in the presence of a catalyst. Of the two polyacetyleneconformation ,cis and trans, the trans from is thermodynamically more stable Shirakawa's

Polyacetylene had mainly the cis from and was a copper – coloured flexible film which could be converted to the silvery trans from by heating above 150^{o}C.

2.8.2Application of polyactylene:

Power cable sheathing, prime conductor, energy load leveling systems, batteries, and signal processing devices.

2.9 Polypyrrole(PPY)

(PPY) was obtained in 1979, it is formed by the oxidation of pyrrole or substituted pyrrole monomers, it has the following properties shown below in (table.2.2).

Table 2.2Properties of Polypyrrole

Chemical formula	C_4H_5N
Density (g/m^3)	1.05
Melting point (C^o)	300
Molecular weight	1500-100,000

The mechanical properties of ppy vary widely from strong, tenacious materials to extremely brittle ones. As a consequence, it is necessary to understand how the mechanical properties are affected by the chemical structure, the processing conditions and the conditions of use (service environment).

The conductivity of polypyrrole increases as the synthesis temperature is reduced. This is thought to be due to a reduction in the number of side reactions. Polypyrrole,s conductivity as a function of temperature is studied as well as reflectivity as a function of temperature is studied as well as reflectivity, and classified into metallic, critical and insulating regions.

The solubility of polypyrrole is limited due to its rigid structure and cross-linking. At room temperature chemically formed polypyrrole is less stable than that formed by electrochemical methods due to a larger surface area.

2.9.1Synthesis of polypyrrole:

It can be synthesized by

1. Electron polymerization at a conductive substrate (electrode) through the application of an external potential.
2. Chemical polymerization in solution by the use of a chemical oxidant .

I. Chemical synthesis:

Oxidative polymerization in either solution or vapor phase polymerization on colloidal cerium oxide particles in the presence of ammonium persulfate (oxidant) and dodecylbenzene sulfonic acid (dopant).

II. Electrochemical synthesis electrodes:

Anode :

(platinum , n-type silicon, conducting glass, stainless steel, gold /

Electrolytes :

Copper sulfate, acetonitril, p- toluenesulfonocacid (HTSO), lithium perchlorate, sodium perchlorate, sulfuric acid.

2.10 Polyaniline (PANI):

Polyaniline was initially discovered in 1834 by Runge, and it was referred to as aniline black, Following this, Letheby carried out research to analyze this material in 1862 PANI is know as a mixed oxidation state polymer composed of reduced benzoid unite and oxidation state polymer composed composed of reduced benzoid units and oxidation quinoid units, Green and Woodhead (1912) discovered this interesting characteristic of polyaniline, it has the following properties shown below in (table. 2.3)

Table .2.3 Properties of Polyaniline

Chemical formula	$(C_6H_4N)_n$
Density (g/cm^3)	1.4
Melting point (C^o)	300
Molecular weight	5300

Polyaniline has good conductivity, environmental stability, ease of synthesis and has low synthetic cost, it offers transparency, different dyes and can be both melt and solution processable which means that it can easily be mixed with conventional polymers and get products in wanted shapes and it is easy to synthesis chemically or electrochemically by oxidative polymerization.

The conductivity of PANI (emeraldine salts)is dependent on the temperature as well as humidity. The emeraldine base which is a less ionic state of PANI, is soluble in a number of organic solvents such as , dimethyl sulfoxide, chloroform, tetrahydrofuran, dimethyl formamide, and methyl pyrrolidinone.

The conductivity of PANI is affected by the water content, completely dry samples are five times less conductive of PANI is affected by the molecular weight, the conductivity increases when the MW increases.

Furthermore, it was discovered that PANI had characteristics of switching between a conductor and an insulator under certain experimental conditions. Since then, the material has become a subject of great interest in research and polymerized from the monomer aniline and exists in three stable oxidation states which are :

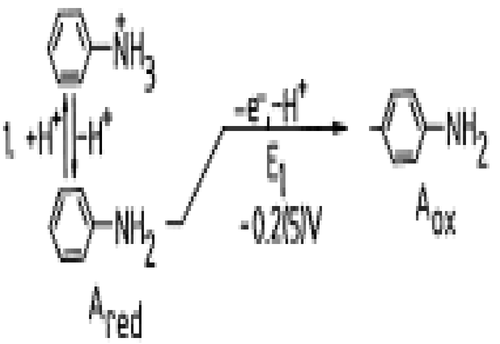
Leucoemeraldine: white / clear poor conductivity.

Emeraldine : green or blue good conductive if doped.

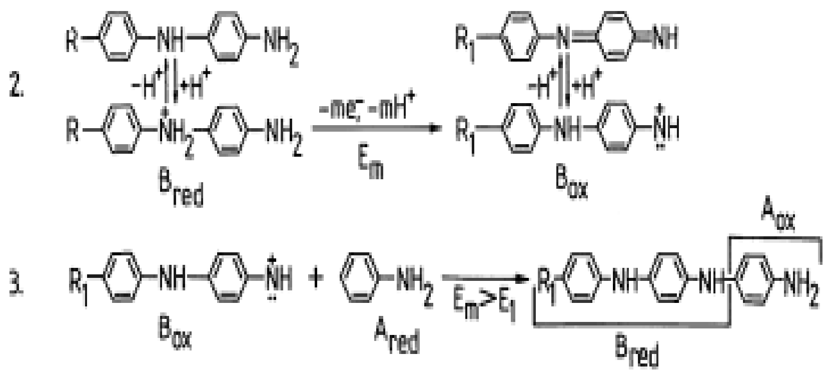
Pernigraniline:blue / violet poor conductivity .

The one that can be doped to highly conducting state is called “emeraldine” it consists of amine (- NH-) and imine(=N-) sites in equal proportion .the state of polyaniline which mentioned previously can be described by the following steps:

Propagation of chain



Reduction of pernigraniline Salt to emeraldine salt:



The leucoemeraldine state is fully reduced when the pernigraniline state is fully oxidized and in the emeraldine state there is an equal amount of reduced and oxidized repeating unite.

The emeraldine state that is also called as the emeraldine base (EB) is the most useful state of these three, because of its stability at room temperature and conductivity. EB can be either neutral or doped with to achieve conductivity. Doping EB can be either neutral or doped with to achieve conductivity. Doping EB with an acid (dopant) results in an emeraldine salt (ES) that is electrically conductive (Fig.2.8). Theleucoemealdine and pernigraniline states are poor conducting PANI have ordered structure, they contain regularly alternating phenyl rings and nitrogen – containing groups. This structure provides for polyconjugation: polymer chain forms a zigzag lying in one plane, and π- electron clouds overlap above and below this plane.

2.10.1 Applications of polyaniline:

Polyaniline is finding widespread use in novel organic electronic applications such as:

Light emitting diodes (LED) , electroluminescense , metallic corrosion resistance, organic rechargeable batteries, biological and environmental sensors, composite structures, textile structures for specialized application or static dissipation, membrane gas- phase separation , actuators, EMI shielding, organic semiconductor devices for circuit application , blends with isolative host polymer to impart a slight electrical conductivity, bioelectronicmedical devices, and a variety of other application where tunable conductivity in organic polymer is desirable .

Fig. 2.8 PANI for printed electronic applications

2.10.2Processing techniques of PANI :

Polyanilinecan be processed by following methods:

1. Injection moulding coating (films).
2. Extrusion and co- extrusion spraying.
3. Blow moulding .
4. Calandering casting (films).
5. Fiber spinning spin coating (this films).
6. Compression mouldinggels (high strength fibers and films).

2.11 Polyphenylenevinylene (PPV):

PPV was first reported in 1990 and was used as the single semiconductor layer. It process a chemical structure which is intermediate between that of (polyacetlene)and (polyvenylene), PPV is highly crystalline,environmentally stable, mechanically strong , it has the following properties shown below in (table.2.4)

Table 2.4 properties of Polyphenylenevinylene

Chemical formula	$(C_8H_6)_n$
Density (g/cm^3)	1.24
Melting point (C^o)	400
Molecular weight	3,000-10,000

2.12 Polythiophene(PTH) :

Polythiophenewas first chemically prepared in the early 1980s, it can be synthesized either electrochemically or chemically and it has the following properties shown below in (table. 2.5)

Table 2.5 Properties of Polythiophene

Chemical formula	$(C_4H_5S)_n$
Density (g/cm^3)	1.4 – 1.6
Melting point (C^o)	350
Molecular weight	13956

PTs show variation in their magnetic properties. In the doped state they undergo transition from a paramagnetic state at high temperature to an ordered phase at low temperatures.

PT by itself is insoluble and infusible. Substitution of alkyl unitsin the 3-position and copolymers of PT increase thesolubility andease of processability , the penalty being some decrease in its conductivity.

2.12.1 Synthesis of polythiophene:

I. Chemical synthesis

- Polycondensation reaction of di- function thiophene in presence of Ni catalysts.
- Oxidative coupling reaction of bi- thiophene in presence of ferric chloride using $AICI_3$ $CuCI_3$ and organic solvents.
- Plasma polymerization from 3-methyl thiophene or thiophene.

II. Electrochemical synthesis

- Electrodes (platinum , gold , and Au coated Ni).
- Electrolytes (acetonitrilein tetra- alkylammonium, iodide salts).

2.12.2 Applications of polythiophene:

Polythiophenes and the substituted polythiophenes are utilized in a variety of application where their conducting properties pose an advantage. They are presently used as antistatic coatings and films. Research is being done to explore their use in electrochromic and electroluminescent devices. They have also shown some promise as material for biosensors and storage batteries. Used in making Schottky barrier diodes and field effect transistors.

2.13 Application of conducting polymers :

1. Rechargeable light weight batteries .
2. Electronic devices such as transistors, photodiodes & light emitting diodes (LED).
3. Optical display devices.
4. Antistatic coating for clothing .
5. Solar cells.
6. Drug delivery system for human body .
7. Molecular wires & molecular switches .

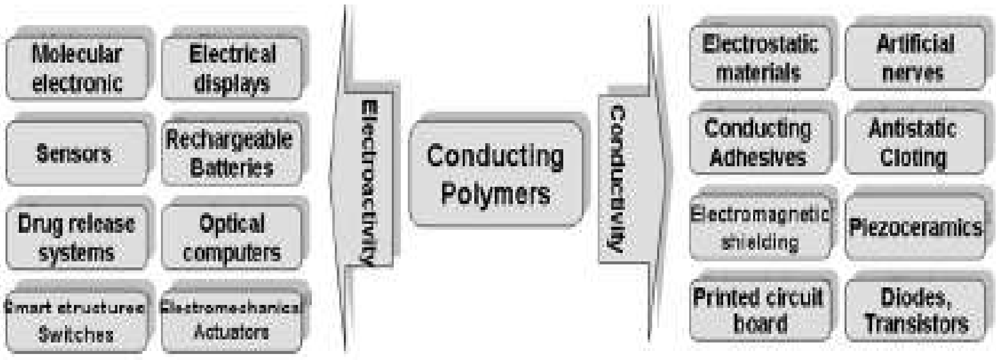


Fig 2.9 Applications of conducting polymers

2.14 Advantages of conducting polymers :

1. Process ableinto powders, films, and fibers from a wide variety of solvents, and also air stable.
2. Reasonably good conductivity , stability .
3. Ease of preparation .
4. Affordability and redox properties compared to other organic compounds.

2.15 Disadvantages of conducting polymers:

1 . High Cost.
2 . Difficult In Processing.
3 . Lack of Mechanical Stability after Doping.
4 . Difficult to fabricate.

2.16 Conductive fillers:

Conductive fillers including copper powder, graphite powder and the resulting composite materials exhibit a wide spectrum of conductivity and it and it can offer a combination of inexpensive material and economical processing , the conductivity is very close to the of the pure polymer matrix, at some critical loadings (percolation threshold) the conductivity increases several orders of magnitude due to the particles come in contact with each other and a continuous conductive network through the composite begins to form .

Conducting polymer composites based on a polymer matrix and dispersed conducting particles are an interesting class of materials used in a wide variety of industrial application such as antistatic media , electromagnetic shielding of computers and electronic equipments, switching devices, static charge dissipating materials , devices for surge protection, corrosion resistant materials and bipolar plates for fuel cell.

2.17 Mechanism of electric conductivity by particles of filler:

Filler in a polymer matrix form current- conductive structure. Naturally, such structures should be characterized by direct contacts between metal particles, or by their approach, at least to within a distance at which transfer of current carriers from one particle to another is possible.

Study the ability of fabricating high quality graphene and using it as alternative filler based on polymers to make a new class of polymer nano-composites materials

Graphite can enhance the conductivity according to it's classification as semiconducting material , However it is not necessarily an easy task to significantly increase the conductivity of plastic by a simple addition of graphite & and nano graphite . The problem becomes one of " dispersed through a non- conductive medium one possible configuration is a composite of conductive particles wrapped in an insulative polymer . this configuration would result in an article that is no more conductive polymer is development of a continuous pathway of interconnected conductive particles through the polymer.

Conductive continuity can be improved by reducing the particle size of the graphite and the homogenization of the mixture.

Chapter Three
Materials and Methods

3.1 Materials

The materials used were High Density Polyethylene as matrix and Graphite powder as a filler.

3.1.1 Graphite

Is one of four forms of crystalline carbon, the others occurs naturally in metamorphic rocks, such as gneiss, marble and schist, it has the following properties shown in table (3.1)

Table 3.1 properties of graphite

Chemical formula	C
Color	Iron- black to steel-gray
State	Solid/ powder
Density (g/cm^3)	2.09- 2.23
Melting point (C^o)	3,937
Thermal conductivity (w/m.k)	25- 470
Electrical conductivity (S/cm)	2-3×10^5
Electrical resistivity (Ω.m)	5×10^{-6}-30×10^{-6}

3.1.2 High Density polyethylene (HDPE)

Is a polyethylene thermoplastic polymer it has high molecular weight, High strength and stiffness among polyethylene grades.

Table 3.2 properties of HDPE

Chemical formula	$(C_2H_4)_n$
Color	White
State	Solid/ powder
Density (g/cm^3)	0.93- 0.97
Melting point (C^o)	120-180
Thermal conductivity (W/m.k)	0.46-0.52
Electrical conductivity (S/cm)	Insulator
Electrical Resistivity (Ω.m)	10^{13}-10^{16}

3.2 Equipment

Melt flow index device for measuring the viscosity exists in (center of Researches and industrial consultant)

Fig 3.1 Melt flow index device

Digital Multimeter 6.$\frac{1}{2}$for measuring the resistance of sample exists in Nano center for Measurement and calibration – Alzarqaa for electronics

Fig. 3.2 Digital Multimeter 6.$\frac{1}{2}$

Electronic Vernier for measuring the thickness of sample ,exists in Al-Neelen university

Fig3.3 Electronic Vernier

Fig.3.4 : Graphite powder at different temperature

Nano device to crush the graphite , exists in Al- Neelen university

Fig3.5 Nano device

UV system for measuring the permeability of light through the sample

Fig3.6 UV system , exists in Khartoum university

Thermal furnace for heating the sample , exists in Sudan University of science and technology

Fig3.7 Thermal furnace

Infrared spectroscopyfor measuring the frequency of sample , exists in Al –Neelen University

Fig3.8 Infrared spectroscopy device

3.3 General methods

First step

The graphite was heated above the coking temperature 450 °C to 600 °C to remove some hydrogen and light oils.

It is then heated above 1000 °C to remove :

1. Hydrogen
2. Oxygen
3. Sulphur
4. Nitrogen

To purify graphite of dirt and other impurities Situation the sample graphite of nana system Functioning vestibular situation the sample into the device period of time 30 min in order to separate the particle size .

Notes:

- Increase sample size
- Improve electrical properties
- Disposal of impurities
- Change in properties

Second step

Graphite powder was dispersed in high density polyethylene powder with continuous stirring using stirrer so that graphite powder and polymers powder, the weight percentages of graphite were (30,40,50) % and the total weight required to form the composite was 14 gram the mixture was added to (MFI) for 14 minutes and melted in temperature 190 C^o then cooled to room temperature . The samples were of a cylindrical shape of diameter 10 mm. An electronic vernier has been used to measure the diameter of the samples.

3.4 Testing Method :

3.4.1 Electrical test:

I. Samples preparation

Twelfth different samples were prepared _ according to graphite percentages and matrixes used _ by reducing their length to 10 cm.

Because of surface irregularity of sample produced , a thin wire of silicon metal have a small resistance value was joined to both ends of sample as to accuracy measurement , the resistance was measured over range of temperature (23±0.5) C using (digital Multimeter $6.\frac{1}{2}$ (34401A).

See figure (3.9), (3.10), and

II. UV Testing

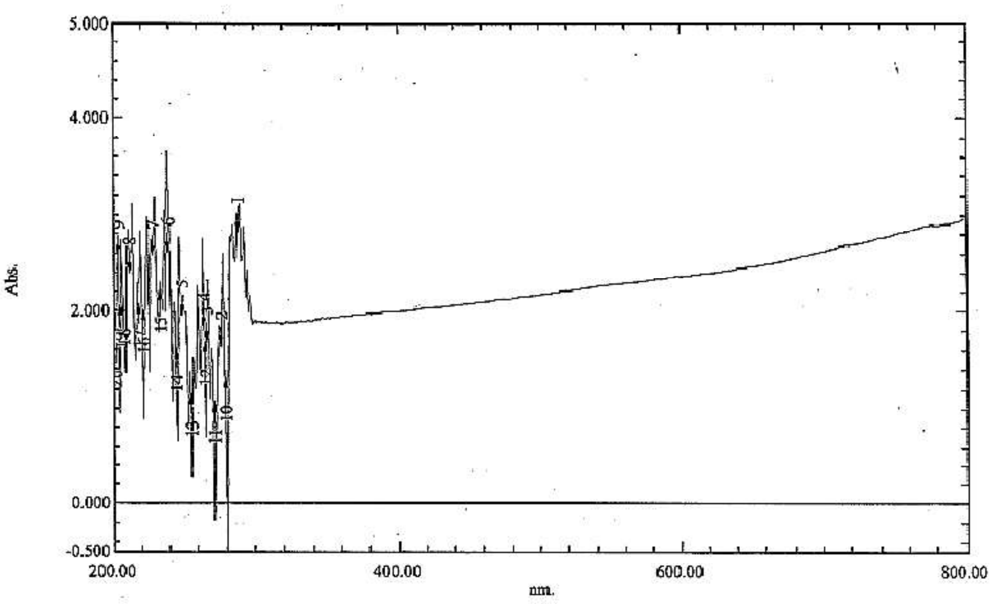


Fig 3.9Pure graphite at normal case

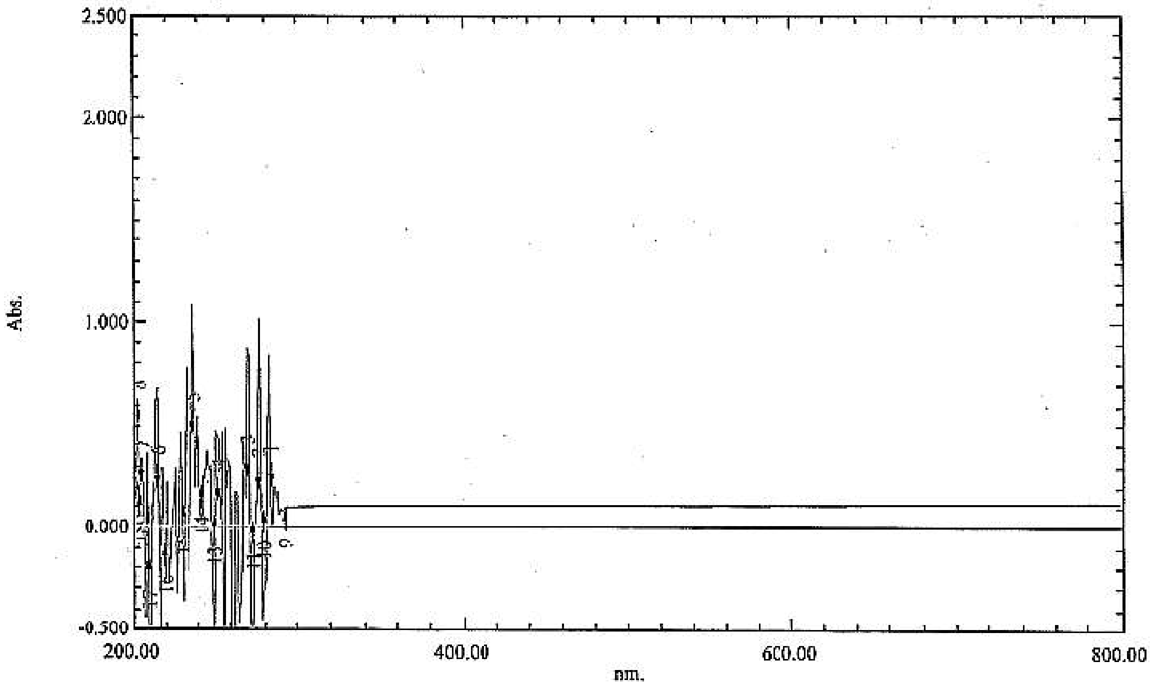


Fig 3.10 graphite after heating at 450 ℃

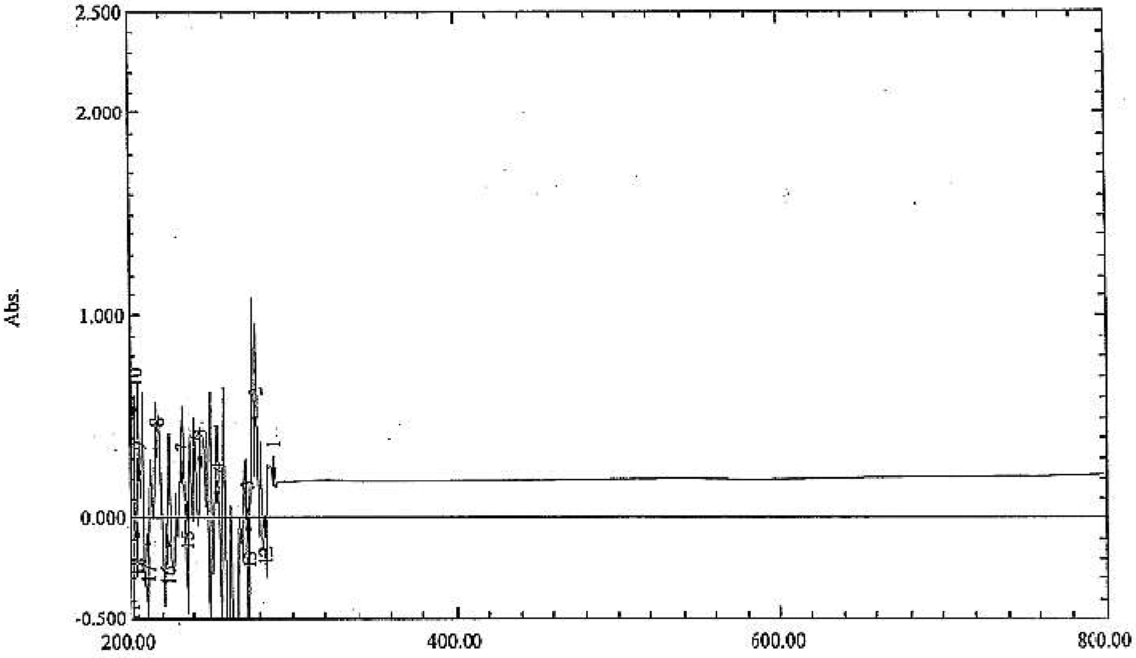


Fig 3.11 graphite after heating at 600 ℃

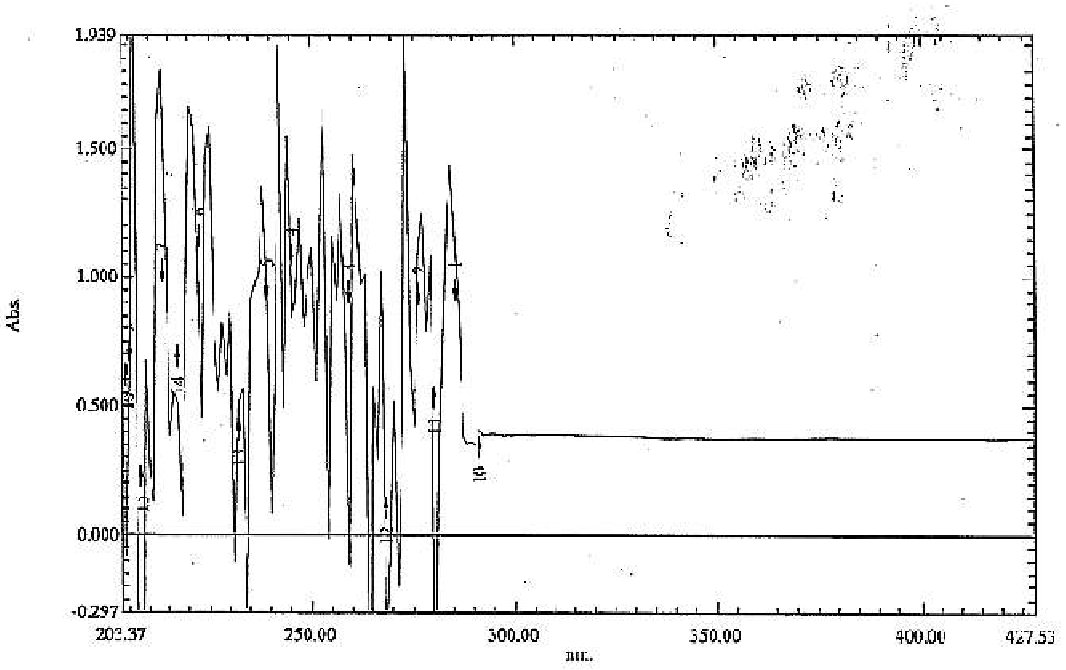


Fig 3.12 graphite after heating at 600 ℃

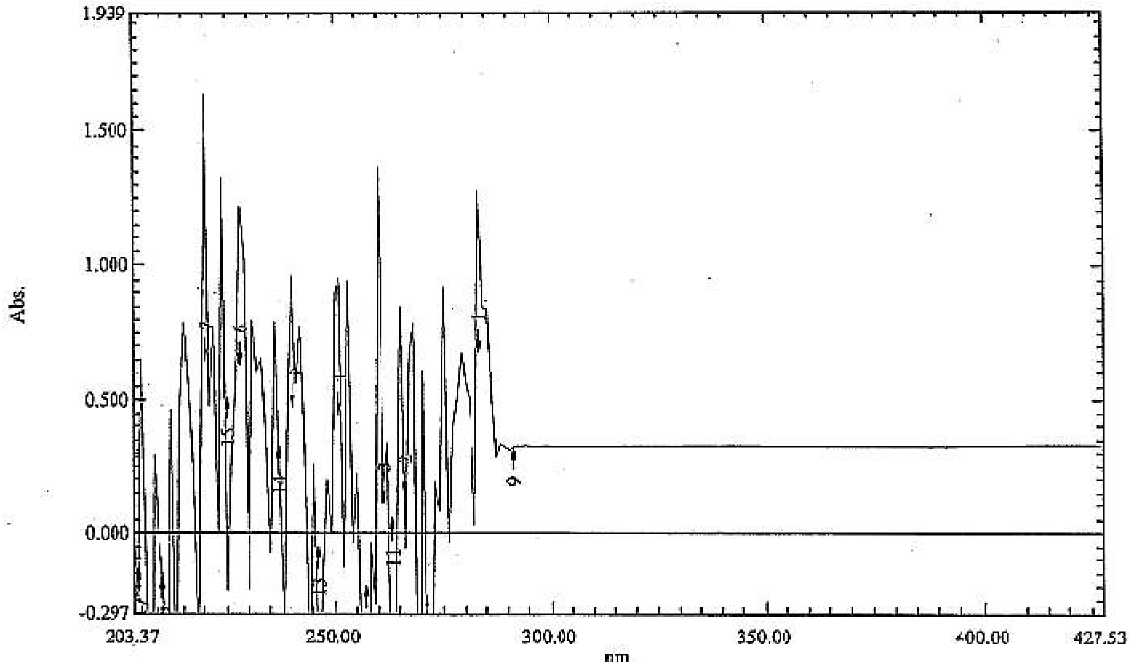


Fig 3.13 Nano graphite

III. IR testing

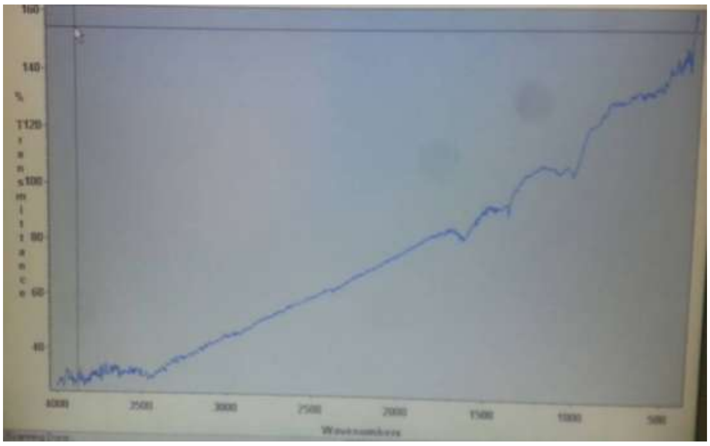


Fig 3.14IR for graphite at 450 ℃

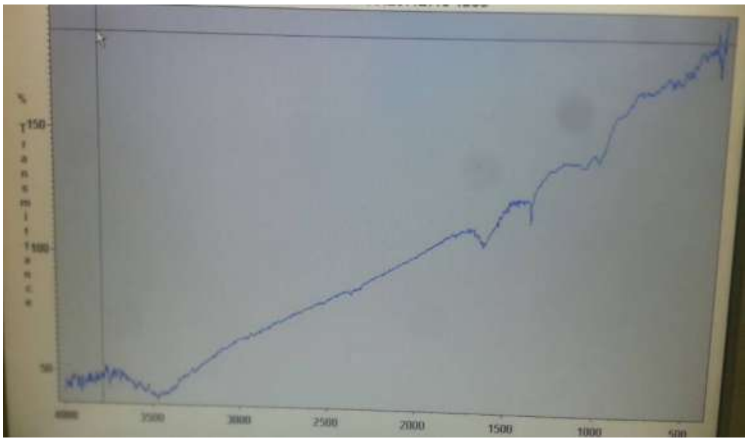


Fig 3.15 IR for graphite at 600℃

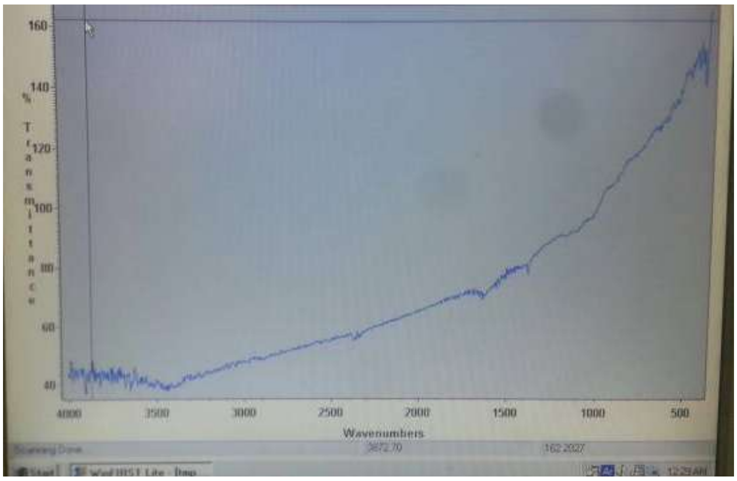


Fig 3.16 IR for graphite at 1000℃

Chapter four
Results and discussion

4.1 Result of HDPE /Graphite composite:

The conductivity can be estimated by the following equations:

$$\boldsymbol{\sigma = \frac{1}{p}} \qquad [1]$$

$$\boldsymbol{\rho = \frac{R\,A}{L}} \qquad [2]$$

While:

P ≡ Resistivity (Ω.m) .

R ≡ Resistance (Ω).

L ≡ Length (m).

A≡ Cross sectional area (m^2), (A= 2πrL +2πr^2).

1. At 450 C^o

The resistance values of (HDPE/ Graphite) samples have been measured and recorded to the following tables :

Table 4.1 Resistance of graphite (concentration (30%) L =8.5cm)

Number	Resistance KΩ
1	6.91
2	6.88
3	6.82
4	6.76
5	6.71
Average	6.816

Table 4.2 Resistance ofgraphite (concentration (40%),L =8.5cm)

Number	Resistance KΩ
1	2.81
2	2.79
3	2.68
4	2.61
5	2.60
Average	2.698

Table 4.3 Resistance of graphite (concentration (50%), L=8.5)

Number	Resistance KΩ
1	3.2
2	2.8
3	2.6
4	2.31
5	2.30
Average	2.642

2. At 600 C^o

Table 4.4 Resistance of graphite (concentration (30%), L = 8.5)

Number	Resistance KΩ
1	1.98
2	1.97
3	1.96
4	1.95
5	1.90
Average	1.952

Table 4.5Resistance of graphite (concentration (40%), L = 8.5)

Number	Resistance KΩ
1	76.9
2	76.8
3	73.05
4	71.5
5	69.4
Average	73.53

Table 4.6Resistance of graphite (concentration (50%), L= 8.5cm)

Number	Resistance KΩ
1	1.84
2	1.82
3	1.79
4	1.78
5	1.76
Average	1.798

3. At 1000 C^o

Table 4.7Resistance of graphite (concentrations (30%), L= 10 cm)

Number	Resistance KΩ
1	3.9
2	3.8
3	3.06
4	2.9
5	2.7
Average	3.275

Table 4.8Resistance of graphite (concentrations (40%), L= 10 cm)

Number	Resistance KΩ
1	2.95
2	2.85
3	2.75
4	2.59
5	2.46
Average	2.75

Table 4.9Resistance of graphite (concentrations (50%), L= 10 cm)

Number	Resistance KΩ
1	77.64
2	76.09
3	75.06
4	74.01
5	73.25
Average	75.21

4. At Nano graphite

Table 4.10 Resistance ofNano graphite (concentration (30%), L=10cm)

Number	Resistance KΩ
1	0.497
2	0.499
3	0.500
4	0.503
5	0.551
Average	0.5154

Table 4.11Resistance ofNano graphite (concentration (40%), L=10cm)

Number	Resistance KΩ
1	149.75
2	152.85
3	153
4	153.5
5	154
Average	153.22

Table 4.12Resistance ofNano graphite (concentration (50%), L=10cm)

Number	Resistance
1	81.1
2	82.6
3	82.9
4	83.31
5	83.4
Average	82.66

4.2 Calculations of results:

The shape of sample was considered as a cylinder with a diameter of1mm and length of 100mm so :

$$A= 2\pi rL +2\pi r^2$$

$$A= 471\times10^{-6}\ m^2$$

Equation [1] , [2] have been used to determine the conductivity and resistivity values :the data in tables (4.1,4.2, 4.3,4.4,4.5,4.6,4.7,4.8,4.9,4.10,4.11,4.12)

At graphite (30%) at 450 C^o

Average resistance=6. 816 KΩ

ρ= 366.73Ω.m

$\sigma = 29.4\times10^3$ S/cm

At graphite (40%) at 450 C^o

Average Resistance = 2.698×10^3

ρ = 13.458Ω.m.

$\sigma =74.3\times10^3$ S/cm.

At graphite (50%) at 450 C^o

Average resistance= 2.642 KΩ

ρ = 12.443 Ω.m.

$\sigma =80.36\times10^3$ S/cm.

At graphite (30%) at 600 C^{o}

Average resistance= 1.952 KΩ

ρ =366.735 Ω.m.

σ =2.726×10^{3} S/cm.

At graphite (40%) at 600 C^{o}

Average resistance= 73.53 KΩ

ρ =9.727 Ω.m.

σ =10.28×10^{2} S/cm.

At graphite (50%) at 600 C^{o}

Average resistance= 1.798 KΩ

ρ =8.968 Ω.m.

σ =11.150×10^{3} S/cm

At graphite (30%) at 1000 C^{o}

Average resistance= 3.2756.816 KΩ

ρ =354.239 Ω.m.

σ =2.822×10^{3} S/cm.

At graphite (40%) at 1000 C^o

Average resistance= 2.75 KΩ

ρ =15.425 Ω.m.

σ =64.82×10^3 S/cm.

At graphite (50%) at 1000 C^o

Average resistance75.21 KΩ

ρ =12.95 Ω.m.

σ =77.22×10^3S/cm

At Nano graphite (30%)

Average resistance= 0.5154 KΩ

ρ =721.666 Ω.m.

σ =1.385×10^{-3} S/cm.

At Nano graphite (40%)

Average resistance= 153.22 KΩ

ρ =389.32 Ω.m.

σ =2.568×10^{-3} S/cm.

At Nano graphite (50%)

Average resistance82.66 KΩ

ρ =2.4256 Ω.m.

σ =4.122×10^1S/cm

Table 4.13Resistivity and conductivity values with variation of graphite concentration At 450C°

Graphite content	Resistivity (Ω.m)	Conductivity (S/cm)
30%	366.73	29.4×10^{3}
40%	13.458	74.3×10^{3}
50%	12.443	80.36×10^{3}

Table 4.14Resistivity and conductivity values with variation of graphite concentration At600C°

Graphite content	Resistivity (Ω.m)	Conductivity (S/cm)
30%	366.735	2.726×10^{-3}
40%	9.727	10.28×10^{2}
50%	8.968	111.50×10^{3}

Table 4.15Resistivity and conductivity values with variation of graphite concentration At 1000C°

Graphite content	Resistivity (Ω.m)	Conductivity (S/cm)
30%	354.239	2.822×10^{-3}
40%	15.425	64.82×10^{3}
50%	12.95	77.22×10^{3}

Table 4.16 resistivity and conductivity values with variation of graphite concentrationAt Nano graphite

Graphite content	Resistivity (Ω.m)	Conductivity (S/cm)
30%	721.666	1.385×10^{-3}
40%	389.32	2.568×10^{-3}
50%	2.4256	4.122×10^{1}

4.3 Discussion

The conductivity increases due to the filler content, figure (4.1) shows the electrical conductivity enhancement of the composite by increasing the concentration of the graphite filler , at lower concentration (30%) of the filler, the electrical conductivity of composite increases sharply, while

4.4 Comparison between (HDPE/graphite) composite at different temperature

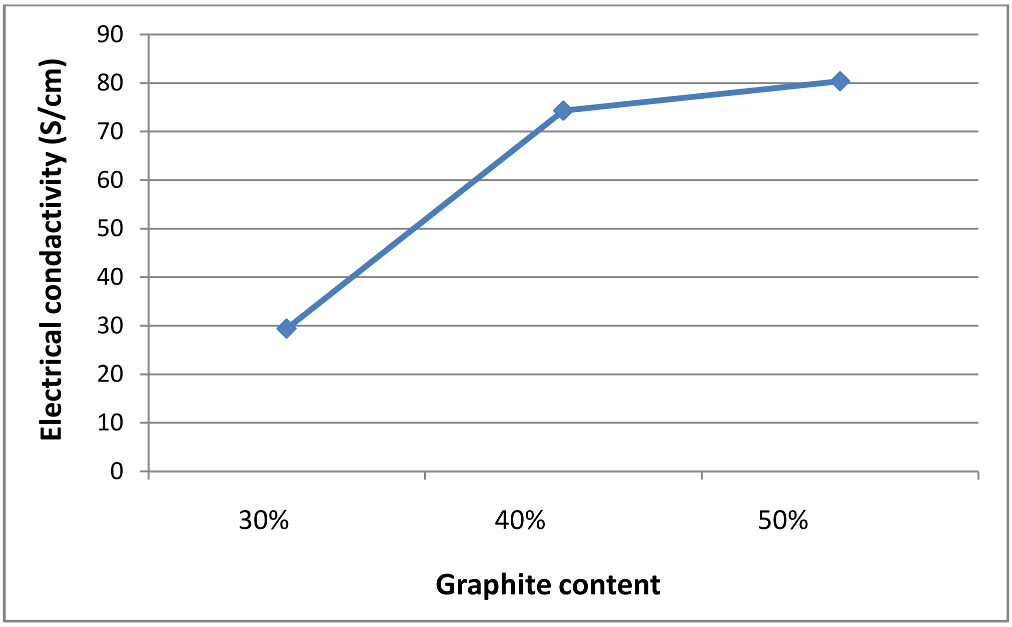


Fig 4.1 Electrical conductivity of graphite at 450 ℃

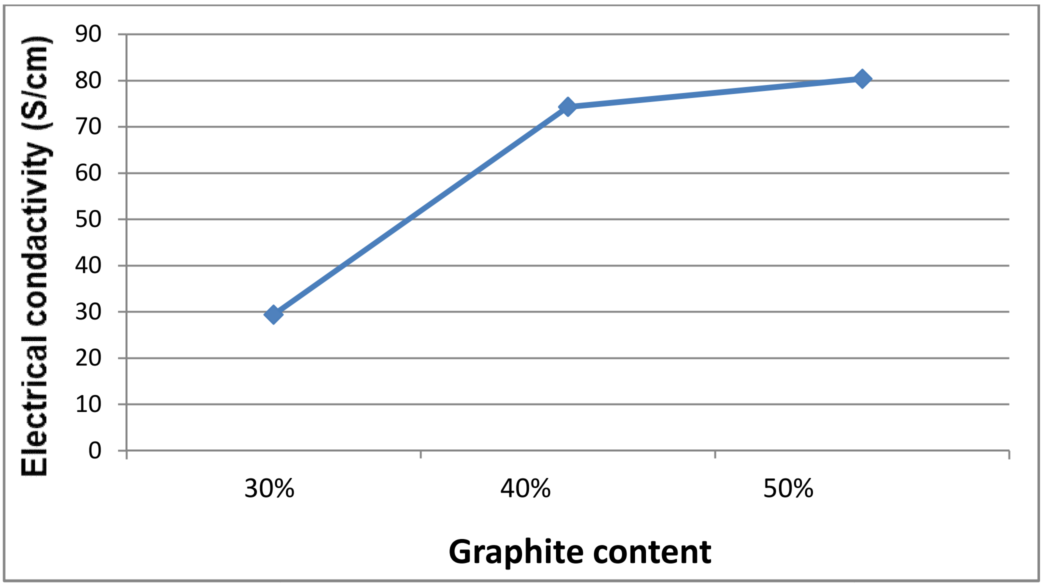


Fig 4.2 Electrical conductivity of graphite at 600 ℃

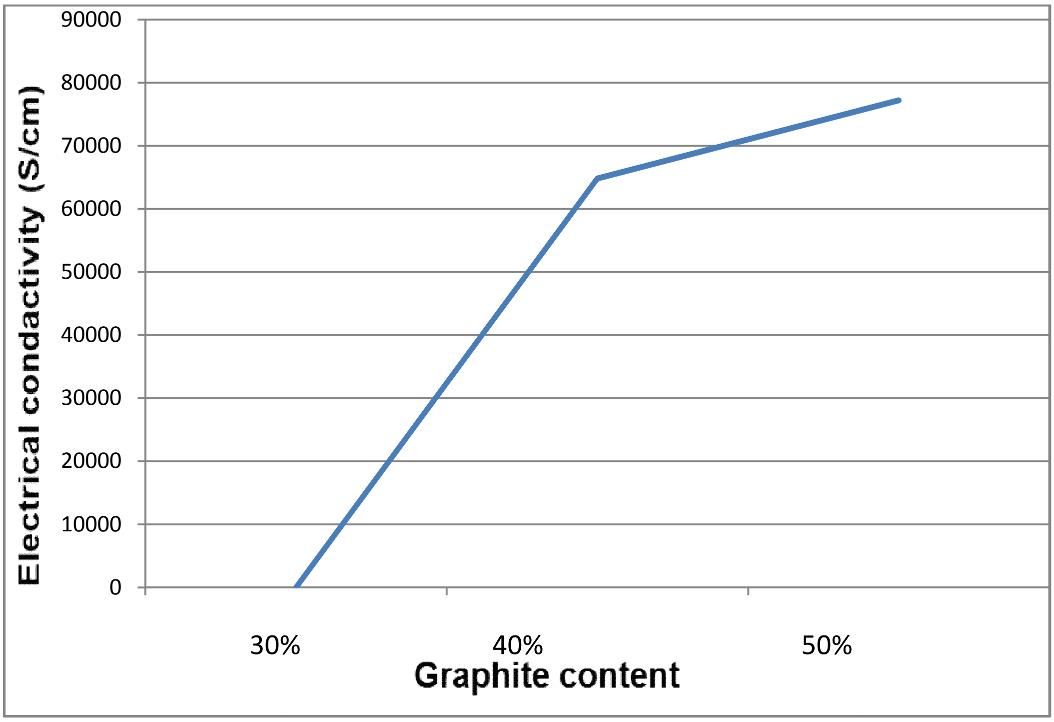


Fig 4.3 Electrical conductivity of graphite at 1000 ℃

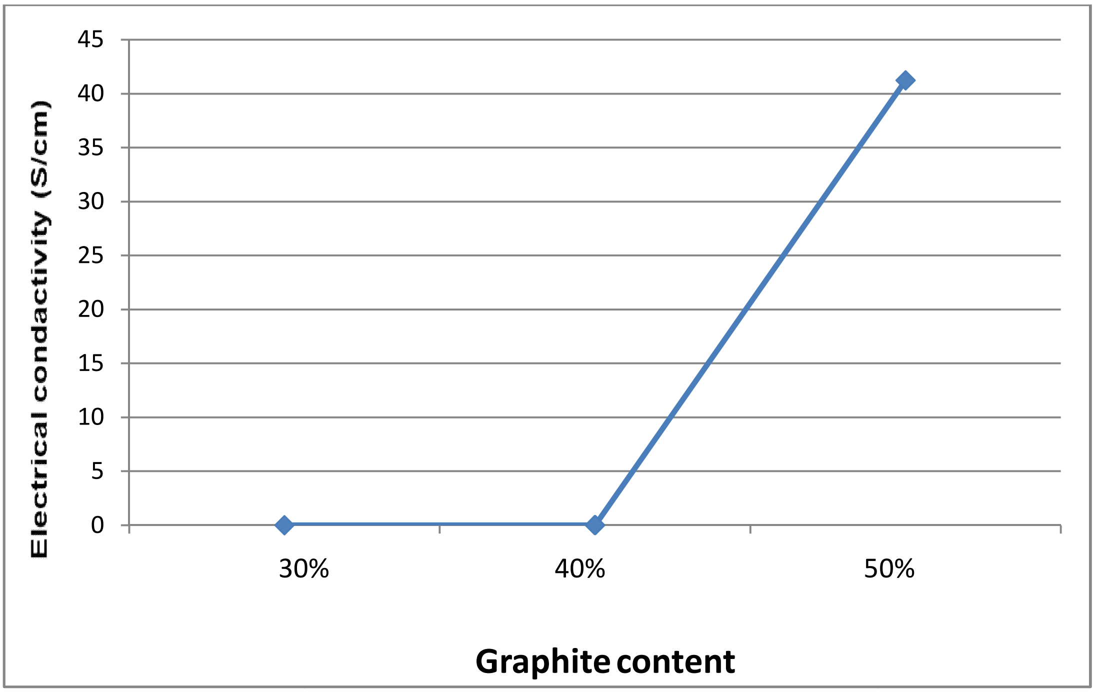


Fig 4.4 Electrical conductivity of Nano graphite

4.5 Further discussion of sample:

4.5.1 Viscosity Effect:

As with most other additives the particle size of graphite is inversely proportional to surface area, therefore if particles of a smaller size are added to a polymer system there will be a corresponding increase in viscosity.

4.5.2 Mechanical properties Effect:

The mechanical properties of polymer are typically not improved by the addition of graphite particles so the properties which are enhanced by it,s addition i.e.conductivity , thermal – tensile strength , elongation, creep, etc.

4.5.3 Friction and wear Effect:

Addition of graphite material to polymers for electrical property enhancement may also simultaneously enhance the friction and wear properties of the system, the addition of graphite to polymers can improve the friction characteristics in both processing and application .

Due to the low coefficient of friction inherent to graphite, its addition to a polymer can significantly reduce the shear forces required in vigorous blending operation.

4.6 Advantages of the experiment :

Polymer – based electrically conducting materials have sevral advantages over their pure metal counterparts, which include cost, flexibility , reduced weight , Combination of the elastic properties in plastic and conductivity properties in metal , ability to absorb mechanical shock, corrosion resistance, ability to form complex parts, availability in controlled particle size, and conductivity control.

Chapter Five

Conclusion and recommendations

5.1Conclusions

1. Intrinsically conducting polymer are naturally classified as semiconductors and can increase its electrical conductivity through doping process.
2. The effect of filler content on the electrical properties of High Density polyethylene filled with graphite powder has been investigated.
3. Graphite offers the benefit of low density and cost when compared to metallic substances used for the same function
4. Addition of graphite to polymer matrix can effect on the polymer
5. The electrical conductivity of High Density polyethylene increased with increasing the graphite concentrations.
6. The D.C conductivity of such composites increase suddenly by several order of magnitude at a critical weight concentration.
7. There is relationship between the increase the temperature and the improvement of properties of the material .

5.2 Recommendations

I highly recommend to open the door to study this new exciting type of polymer that can help in applications would be impossible using metal.

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