



**SUDAN UNIVERSITY OF SCIENCE & TECHNOLOGY**

**Faculty of Graduate Studies**

**Synthesis and Characterization of Polyethylene /Silica  
Nano Composite**

تخليق و توصيف البولي ايثلين المدعم بدقائق السليكا

*A Thesis Submitted in Partial Fulfillment for the Requirement of the  
Degree of M.Sc in Chemistry*

*By:*

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## إِسْتِفْتَا ح

بِسْمِ اللّٰهِ الرَّحْمٰنِ الرَّحِیْمِ

قال الله تعالى:

نَرْفَعُ دَرَجَاتٍ مِّنْ نَّشَأٍ وَفَوْقَ كُلِّ ذِي عِلْمٍ عَظِيمٌ

صدق الله العظيم

سورة يوسف – الآية 76

# **Dedication**

**TO**

**My parents and brothers**

**And**

**Every one wishes me the best**

## **Acknowledgment**

I would like to thank Allah the most Gracious, the most Merciful, for giving me strength to do this work.

I am mostly indebted to my supervisor Dr. Mohamed Suliman Ali for guidance and advice

Also I would like to thank Dr. Abdalsaki Suleim ( ALnileen Universtey) who helped me in physical tests.

Also I extend my thanks to everyone who helped me in completing this project.

## **Abstract**

Polyethylene/silica Nano composite was synthesized in different concentrations (2%, 3%, 4%, 10%, 20%, 30%, 40%, and 50%)

The samples were subjected to physical evaluation; the result showed that the amount of silica is changed the optical properties (the maximum absorbance was 284 nm) and the composite had moderate refractive index in infra red region but it is de- shielding in part of ultra violet region.

Mechanical properties was enhanced .the highest load was 5.4kg to sample that contain 4% weigh of silica.

## المستخلص

تم تحضير مركب البولي ايثيلين المدعم بالسليكا بنسب مختلفة (2% ، 3% ، 4% ، 10% ، 20% ، 30% ، 40% ، 50%) واجريت عليه بعض الاختبارات الفيزيائية و وجد ان زيادة نسبة السليكا غيرت الخواص الضوئية حيث كان أعلي طول موجي لطيف الامتصاص عند 284 و كذلك تحسنت الخواص الميكانيكية والفيزيائية وكان أعلى حمل يمكن ان تتحمله العينة التي تحتوي علي 4% بالوزن من السليكا هو 5.4 كجم .

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# **CHAPTER ONE**

## **Introduction and Literature review**

# Chapter One

## Introduction and Literature Review

### 1.1 Introduction

Nano scale materials are defined as a set of substances where at least one dimension is less than an approximately 100 Nano meters.

Nano materials are of interest because at this scale unique optical, magnetic, electrical and other properties emerge, these emergent properties have the potential for great impacts in electronics, medicine and other fields.

Two approaches have been known in the preparation of ultra fine particles from ancient times.

One is more expensive “top down” approach based on lithography<sup>(1)</sup>. By which an external force is applied to a solid that leads to its break-up into smaller particles.

The second is the build-up (bottom-up) method that produces Nano particles starting from atoms of gas or liquids based on atomic transformations or molecular condensations<sup>(2)</sup>.

Nano materials are already in commercial use , with some having been available for several years or decades.

The range of commercial products available today is very broad, including stain –resistant and wrinkle free textiles, cosmetics, sun screens, electronics, paints and varnishes.

Nano coatings and Nano composites are finding uses in diverse consumer products, such as windows, sports equipment, bicycles and automobiles. Nano scale silica is being used as filler in range of products, including cosmetics and dental fillings<sup>(2)</sup> .

**Table 1-1: Classification of Nano Materials**

MOLECULES		
	Size(approx)	Materials
Nano crystals and clusters(quantum dots)	1-10 nm(diam)	Metal, semiconductors, magnetic material
Other Nano particles	1-100nm (diam)	Ceramic oxides
Nano weirs	1-100 nm (diam)	Metal, semiconductors, oxide ,sulfides, nitrides
Nano tubes	1-100 nm (diam)	Carbon, layered metal chalcogenides
Nano porous solids	0.5-10 nm(pore diam)	Zeolites , phosphates ,etc
2-Darrays (of Nano particle)	Several nm <sup>2</sup> - $\mu m^2$	Metals, semiconductors ,magnetic mater
Surfaces and thin films	1-100 nm (thickness)	A variety of materials
3-D structures(super lattices)	Several nm in three dimensions	Metals , semiconductors, ,magnetic materials
BULK MATERIALS		

## **1.2 Properties of Inorganic Nano Materials:**

Nano materials have the structural features in between of those of atoms and the bulk materials. The energy band structure and charge carrier density in material can be modified quite differently from their bulk and in turn will modify the electronic and optical properties of material. Filling polymers with Nano particles lead to significant improvement in their mechanical properties'. Filled polymer based Nano composites exhibit broad range of failure strengths and strains. This depends on the shape of filler, particles. In this class of materials, polymers filled with silicate platelets exhibits the best mechanical properties and are of the greatest economic relevance.

A very important parameter for characterizing the effectiveness of reinforcement is the ratio of surface area (A) of reinforcement to volume of reinforcement (V)<sup>(3)</sup>.

The earliest motivation for the use of Nano particles seems to have been stimulated by the Toyota research group, where the first practical application of nylon-6–montmorillonite (MMT) Nano composite was commercialized. With only a small MMT loading(4.2 wt%), the modulus doubled, the tensile strength increased more than 50%, the heat distortion temperature increased by 100°C, and combustion heat release rate decreased by up to 63% <sup>(4)</sup>.

## **1.3 Polymer Composite**

The composite material is usually composed of two components, i.e. matrix and filler called also reinforcement or more broadly dispersed phase; sometimes also additional Compounds are used, mostly compatibilizers<sup>(5)</sup> . Compatibilizers are used to provide compatibility between otherwise immiscible polymers through reduction of the interfacial tension <sup>(6)</sup>.The matrix, known also as continuous phase, integrates filler particles and allows also to shape products appropriately and determines most of physical and chemical properties of material. The dispersed phase is responsible for additional enhancement of selected material properties. While, the compatibilizer is added to increase interactions between matrix and filler what has significant impact on material cohesion and homogeneity, and as a result on its processing properties and strength <sup>(4)</sup>.

#### **1.4 Nano Composite:**

Nano composite is a multi-phase material which has Nano particles in its composition within its structure, the size will be less than 100 nm <sup>(7)</sup>.

Nano composites differ from micro composites in three aspects - they contain small amounts of fillers, the filler particles have sizes in the range of Nanometers, and the filler-polymer interfacial area is large<sup>(8)</sup>.

As in the case of micro composites, Nano composite materials can be classified, according to their matrix materials, in three different categories: Ceramic Matrix Nano composites (CMNC), Metal Matrix Nano composites (MMNC) and Polymer Matrix Nano composites (PMNC) <sup>(9)</sup>.

The choice of the polymers is usually guided mainly by their mechanical, thermal, electrical, optical and magnetic behaviors. However, other properties such as hydrophobic/hydrophilic balance, chemical stability, bio-compatibility, opto-electronic properties and chemical functionalities (i.e., salivation, wet ability, tinplating effect, etc.) have to be considered in the choice of the polymers. The polymers in many cases can also allow easier Shaping and better processing of the composite materials.

The general idea behind the addition of the Nano scale second phase is to create a synergy between the various constituents, such that novel properties can be achieved <sup>(10)</sup>.

#### **1.5 Polymer Nano Composite:**

Polymer –matrix Nano composites consist of a matrix made from a polymeric material.

The second phase (usually a few percent by Weight, wt %) which is dispersed within matrix, has Nano scale dimensions. Combining the advantages of the inorganic Nanofillers (e.g., rigidity, thermal stability) and the organic polymers (e.g., flexibility, dielectric, ductility, and processability<sup>(11)</sup>). The production methods can be categorized into two major groups: ex situ and in situ. The first synthesis route consists of adding Nano-reinforcements to the liquid or powdered metal, while in situ processes refer to those methods leading to the generation of ceramic Nano-compounds by reaction during processing, for example by using reactive

gases. Several methods have been developed for ex situ synthesis of MMnCs. In particular, different powder metallurgy techniques were successfully employed <sup>(12)</sup>.

Noora Ristolainen –Virtanen was prepared polymer Nano composite by two methods:

- By melt blending poly propylene and layered clay in the presence of compatibilizer.
- By electro spinning poly (vinyl alcohol) / Nano clay, poly (vinyl alcohol) / Nano titanium dioxide and poly amide / Nano clay dispersions. And obtained addition of fire retardant particles to the melt blend improved the degree of clay exfoliation, presumably due to increased shear stress and grinding the Nano composites showed improved stiffness and reduced heat release rates with weakened toughness and increased moisture absorption to unfilled PP or PP / clay composites <sup>(13)</sup>.

The challenge of green composite involves basically the challenge of obtaining green 'polymers that are used as matrix for the production of the composites. Polymer is said to be green when it possesses environmentally favourable properties such as renewability and degradability<sup>(14)</sup>. Polymer matrix system can be a thermoplastic, thermo set and elastomer. A thermoplastic polymer will soften when heated above the glass transition temperature (tg) and thus can be moulded into particular shape upon cooling. This process is repeatable, which makes thermoplastic materials reprocess able and recyclable.

Thermo sets they are formed into a permanent shape and cured or 'set' by chemical reactions such as extensive Cross-linking. They cannot be re-melted or reformed into another shape but decompose upon being heated to too high a temperature. Thus thermosets cannot be recycled, whereas thermo plastics can be recycled <sup>(15)</sup>. Elastomers are of soft elasticity and usually cannot be melted <sup>(16)</sup>. Rubber based Nano composites are attracting considerable interest in polymer science research. In the fact it has been widely proven that the addition of small amounts of Nanofillers such as silica, titania and carbon Nano tube to polymers can improve their mechanical properties (such as stiffness) <sup>(17)</sup> thermal, dynamic mechanical, and barrier properties along with noticeable improvements in adhesion, rheological and processing behavior. <sup>(18)</sup>. Nowadays, Nanocomposites offer new technology and business opportunities for all sectors of industry, in addition to being environmental- friendly <sup>(19)</sup>.



## 1.6 Applications of Polymer Nano Composites

The improvements in mechanical properties of Nano composites have resulted in major interest in numerous automotive and general/industrial applications. It includes potential for utilization as mirror housing on various types of vehicles, door handles, engine covers, and belt covers. More general applications include: packaging, fuel cell, solar cell, fuel tank, plastic containers, impellers and blades for vacuum cleaners, power tool housing, cover for portable electronic equipment such as mobile phones and pagers <sup>(20)</sup> and UV protection gel <sup>(6)</sup>. The use of such polymeric composite as cover materials for greenhouse or agricultural films, is growing globally because it can improve product quality and yield by protecting plants from extreme weather changes<sup>(21)</sup>.

## 1.7 Polyethylene:



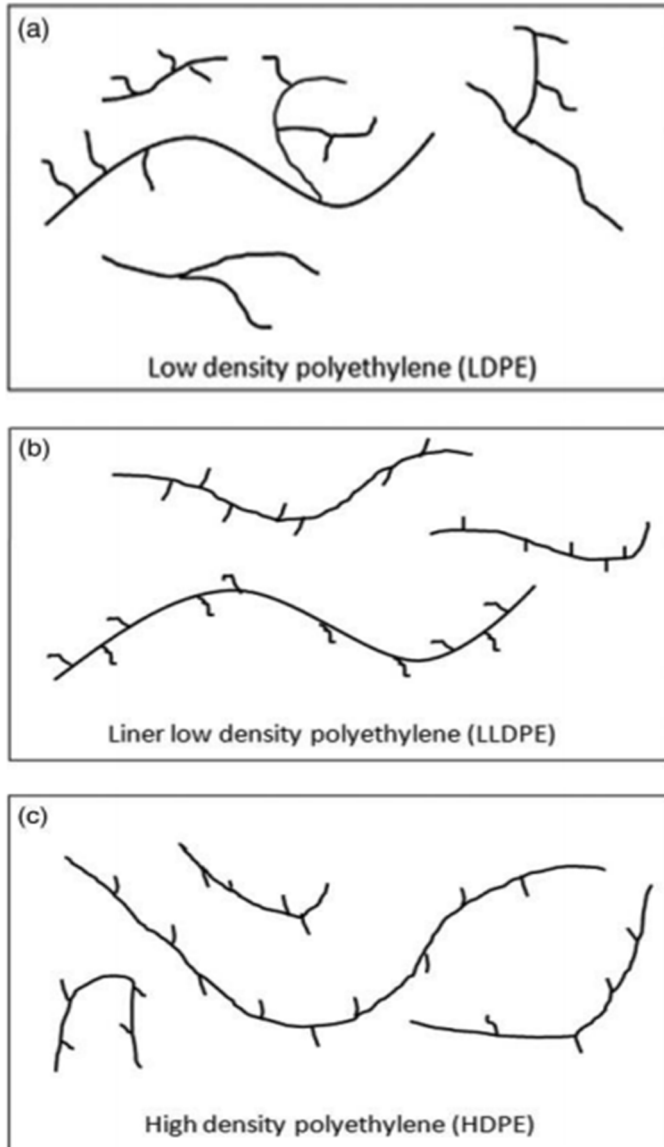
**Figure 1.1: Polyethylene**

Polyethylene is one of thermoplastic polymer, it has wide range of uses and many different manufacturing processes. Polyethylene can be classified into several different categories but mostly do not depend on its density and branching. The main forms of PE are **High-density polyethylene** (HDPE), High molecular weight HDPE (HMWHDPE), ultra high molecular weight density polyethylene (UHMW-HDPE), **linear low-density** polyethylene (LLDPE),

and very low-density polyethylene (VLDPE). These are divided based on density and branching. Generally, the most used PE grades are HDPE, low-density polyethylene (LDPE) and medium-density polyethylene (MDPE). Properties of PE composites depend on the molecular weight of PE, experimental conditions and reinforcement types and amounts.

It is important to know the structure and properties of PE composites to control and modify the needed properties of each application.

**Low-density polyethylene** is a branched thermoplastic, have many relatively long braches of the main molecular chain in This prevents the molecules form packing closely together, irregular packing cause low crystallinity content. Low-density polyethylene is flexible and has low tensile and compressive strength compared to HDPE because of irregular packing of polymer chains. Generally, LDPE is used in food packaging materials, rigid containers and plastic film applications such as plastic bags and film wraps. **Medium-density polyethylene** (MDPE) has mixed properties of LDPE and HDPE properties. Medium-density polyethylene has good impact and drop resistance, less notch sensitivity and has a better cracking resistance than HDPE, but it has lower hardness and rigidity than HDPE. It is softer than HDPE and never sleek as LDPE. Medium-density polyethylene has less branching than LDPE and more branches than HDPE. Medium-density polyethylene is typically used in gas pipes and fittings, sacks, shrink film, packaging film, carrier bags and screw closures. High density polyethylene consist of long chains, without major branching, less than 1 side chain per 200 per carbon atoms in the main chain. Long linear chains result in regular packing and high crystallinity because of stereo regularity of the PE molecules. **High-density polyethylene** is more rigid than LDPE because of the higher packaging such as milk jugs, detergent bottles, margarine tubs, garbage containers and water pipes. crystallinity content. High density polyethylene is used in many products and in packaging such as milk jugs, detergent bottles, margarine tubs, garbage containers and water pipes.



Figures 1.2: Types of polyethylene

### 1.7.1 Properties of Polyethylene:

Polyethylene does not dissolve in any solvent at room temperature, but dissolves in aromatic hydrocarbons above its melting point (90°C). On cooling, the solutions tend to form gels which are difficult to filter.

*Chemical formula: (C<sub>2</sub>H<sub>4</sub>)<sub>n</sub>*

### **1.7.2 Mechanical Properties:**

Polyethylene is of low strength, hardness and rigidity, but has a high ductility and impact strength as well as low friction, it shows strong creep under persistent force, which can be reduced by addition of short fibers. It feels waxy when touched <sup>(22)</sup>.

### **1.7.3 Chemical Properties:**

Polyethylene consists of non polar, saturated and high molecular weight hydrocarbons. The individual macro moles are not covalently linked; because of their symmetric molecular structure, they tend to crystallize, over all polyethylene is partially crystalline.

Higher crystallinity increase density, mechanical and chemical stability.

Most LDPE have excellent chemical resistance they are not dissolving in strong acids or strong bases but usually can be dissolved at elevated temperatures in aromatic hydrocarbons such as toluene or xylene or in chlorinated solvents such as tri Chloro ethane or tri chloro benzene <sup>(23)</sup>.

### **1.7.4 Electrical Properties:**

Polyethylene is a good electrical insulator.it offers good traching resistance, however it becomes easily electro statically charged (which can be reduced by additions of graphite, carbon black or antistatic agents).

### **1.7.5 Optical Properties:**

Depending on thermal history PE can vary between almost clear (transparent) and milky-opaque (translucent) or opaque.

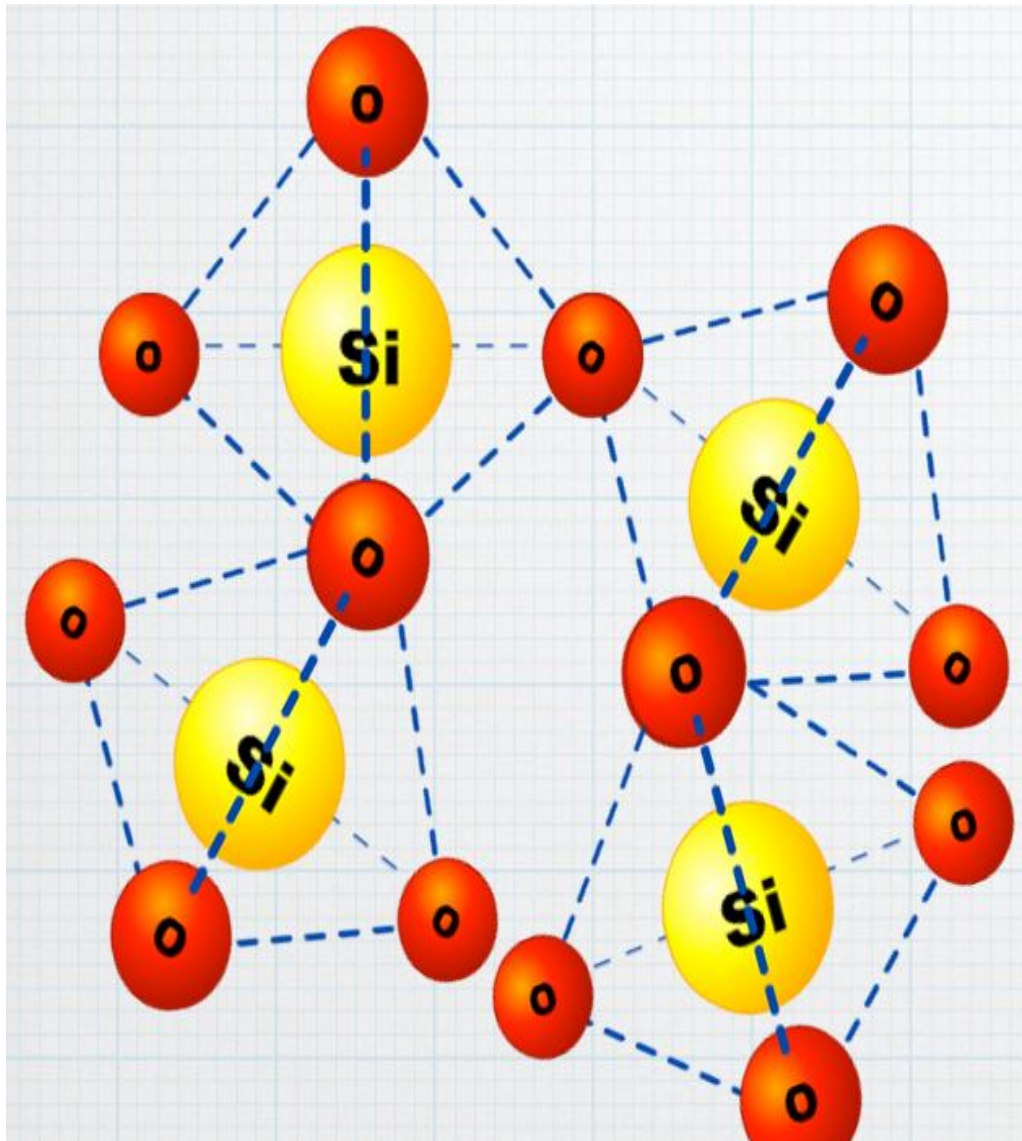
Transparency is reduced by crystallites, if they are larger than the wave length of light <sup>(24)</sup>.

PE is used as an electrical insulating material for wire and cable applications because of it's high dielectric strength and very low electrical conductivity.

## 1.8 Silicon Dioxide:

Silicon dioxide is popularly distributed on the earth. The crystalline and non-crystalline forms of silicon dioxides are well known to be named as quartz and fused silica, respectively. The interface of amorphous silica had been extensively investigated since silica surfaces play important roles in catalysis, chemical reactions, and microelectronic fabrications <sup>(25)</sup>.

### 1.8.1 Structure:



Figures 1.3: Structure of silicon dioxide

Tetrahedral arrangement with one silicon bonded to four oxygen atoms, so that two tetrahedra are joined at a corner (bridging atoms).

The orientation can be random, leading to amorphous structure. Some oxygen atoms will be bonded to only one silicon atom (non-bridging atoms). The relative amounts of bridging to non-bridging determines the "quality" of the oxide. If all oxygen atoms are bridging, then a regular crystal structure results-quartz.

### 1.8.2 SiO<sub>2</sub> Properties

We use thin layers of pure SiO<sub>2</sub> in microelectronics, the layers are amorphous (fused silica)

- Refractive index at optical wave lengths:  $n=1.5$
- The interface with silicon always results in electronic trap levels and some negative interface charge. typical interface defect density =  $10^{11}/\text{cm}^2$  this is not a high density of defects at an interface. It can be made even lower by Annealing in hydrogen.

The combination of relatively good electrical properties of silicon, the excellent insulating properties of SiO<sub>2</sub>, and the low defect interface between them is the key ingredient of modern integrated circuit

- Young modulus  $6.6 \times 10^{10} \text{ N/m}^2$
- Energy band gap  $8.9 \text{ eV}$
- Description transparent crystals

### 1.8.3 Uses of Silica

- Main component in glass

Mixed with sodium carbonate and calcium oxide (lime) to make soda-lime glass for window panes, bottles, drinking glass and etc...

- Main component in optical fibers
- Fancy drink ware and art work
- Crystal oscillators using the piezoelectricity
- Laboratory equipment
- Food additive

- Micro electronics
- Thin electrical insulator(MOSFET gate)
- Diffusion barrier
- Silica is the most extensively used as support; it has several properties that make it attractive as catalyst support: it is relatively chemically inert, stable at high temperatures, and can be synthesized with several pore size, volumes and surface areas. In addition, silica is relatively inexpensive support, ideal for the production of commodity polymers such as polyolefin's.

### 1.9 PE/SiO<sub>2</sub> Nano Composite

It is hybrid inorganic materials and the interactions between silica and polyethylene matrix are mainly physical action, the interface bonded strength is weak <sup>(26)</sup>.The poor physical interaction between the organic and the inorganic components leads to poor mechanical and thermal properties. In contrast, strong interactions between the polymer and the layered silicate Nano composites lead to the organic and inorganic phases being dispersed at the Nanometer level. As a result, Nano composites exhibit unique higher properties than conventional composites. Wenxi Cheng, Wei Miao, Linqi Zhang and Jin Peng were prepared series of PE/ SiO<sub>2</sub> Nano composites and obtained covalent bonds between SiO<sub>2</sub> and PE and Tensile strength, modulus and elongation at break of PE/ SiO<sub>2</sub> was large compared to pure Pe<sup>(26)</sup>.High-density polyethylene (HDPE) is a widely applied thermoplastic polymer, characterized by good tensile properties, flexibility, low cost and chemical resistance. <sup>(24)</sup> , Saad Mohmed hamza found electrical conductivity of low density polyethylene resin reinforced by variety weight fracture (1% , 2% , 3% , 4% , 5%) was decreased from  $5 \times 10^{-14}$  before adding silica to  $8.7 \times 10^{-17}$  (ohm.cm) <sup>-1</sup> after addition (5%) from silica at (40°C) <sup>(27)</sup>.Some authors have concluded that the appropriate percentage of NS must be small (1-5 wt%) to avoid agglomeration of particles during mixing, while others have indicated that properties can Also be improved with higher dosages up to approximately 10 wt% if these Nano particles are successfully dispersed in the initial cementious mixture<sup>(28)</sup> .

Composite materials can be classified in different ways. Broadly, polymer composites can be classified into two groups on the basis of reinforcing material.

They are fiber-reinforced polymer (FRP) and particle-reinforced polymer (PRP) composites. Fiber-reinforced polymer materials consist of fibers, which have high strength and modulus. Fibers can be bonded to the matrix, the interface that is boundary between the fiber and the matrix, which has different physical and chemical identities. Particle-reinforced polymer composites used for reinforcing include ceramics, small mineral particles, metal powders such as aluminum and amorphous materials including polymers and carbon black. Particles are used to increase the modulus and to decrease the ductility of the matrix. They are also used to reduce the cost of the composites. In the last decade, thermoplastic composite industry has shifted from the use of high performance advanced composites to cost-effective engineering composites by using different fibers <sup>(29)</sup>.

And yet the intimate blending of silica and PE remained a challenge because of the very different nature of these polymers and because of the general difficulty in handling PE, which is devoid of any functional group <sup>(30)</sup>.

## **1.10 Processing**

The first step in preparing the PE composite is processing. Processing can be defined as the technology of converting raw polymer to materials in a desired shape. Polyethylene composites are processed by many techniques such as:

### **1.10.1 Extruder:**

Is a versatile machine, which forms thermoplastic items with a uniform cross-section such as pipe, hose, wire and cable. Extruder screws are designed for the polymers that being extruded. Melting, compression and metering sections are basic sections of a screw. In melting part, the solid pellets are conveyed from the hopper and converted into molten polymer. In compression section, the molten polymer is compacted and mixed with the additive (if required). The metering section is needed to produce the desired product cross-section. Twin-screw extruder and single screw extruder are basic types of extruders. Extrusion process can be used for the compounding of the PE composites. Polyethylene granules or powder with fiber/filler are fed from the hopper to the screw and are then pushed along the barrel chamber to be heated. The processing temperature can be in the range of 190-230°C. The mixtures are fed into the hopper of the extruder, compounded, cooled and



granulated. The compounded samples are prepared as test specimens by injection molding machine or hot press molding machine <sup>(31)</sup>.

### **1.10.2 Injection-moulding**

The injection-moulding compounding process combines two processing steps: the material compounding, which normally takes place at the raw material manufacturer and the injection-moulding process which usually is done at the injection moulder. The final part is processed directly with only one plasticizing process, and the material used does not have to be granulated and plasticized again after the compounding step in the plasticizing unit of an injection-moulding machine. The molten material exits the extruder and is directly fed into a melt accumulator and further into the injection unit. After the specimen volume is reached, a conventional injection-moulding process starts <sup>(32)</sup>.

### **1.10.3 Rotational molding**

The principle of rotational molding of plastics is simple. Basically the process consists of introducing a known amount of plastic in powder, granular, or Viscous liquid form into a hollow, shell-like mold. The mold is rotated and/or rocked about two principal axes at relatively low speeds as it is heated so that the plastic enclosed in the mold adheres to, and forms a mono lithic layer against, the mold surface. The mold rotation continues during the cooling phase so that the plastic retains its desired shape as it solidifies. When the plastic is sufficiently rigid, the cooling and mold rotation is stopped to allow the removal of the plastic product from the mold. At this stage, the cyclic process may be repeated. The basic steps of (a) mold charging (b) mold heating, (c) mold cooling, and (d) part ejection <sup>(33)</sup>.

### **1.10.4 Compression moulding:**

Compression moulding can be in comparison with injection and structural foam molded parts much cheaper (about 25 % of injection moulding tooling cost) and flexible (rapid prototypes) thermoforming process. Compression moulding is ideal for large parts production such as lift trucks, car/bus interior trim parts but also smaller parts for packaging, electronics, sports and automotive products. Compression moulding is processed composed of the following steps: heating of polymer and forming of plastic sheet; transporting of hot sheet to a molding area and forming it over a two parts of mold halves cooling and

finishing of parts e.g. Trimming out. As the most used polymers for compression moulding are can be named acrylonitrile-butadiene-styrene (ABS), polypropylene (PP), polystyrene (PS), high density polyethylene (HDPE), low density polyethylene (LDPE), cellulose acetate, poly methyl methacrylate (PMMA), and polyvinyl chloride (PVC) <sup>(30)</sup>.

#### **1.10.5 Casting**

In this method, PE is dissolved in suitable solvents and mixed with filler by stirring. After the stirring, a continuous sheet of the polymer solution is formed and this liquid material is poured into the mold. A thin film of the polymer is formed on the surface of the mold, which is easily removed by stripping. After processing, specimens can be cut into the desired size and shape before starting the characterization, i.e. testing the samples <sup>(31)</sup>.

#### **1.10.6 Blending**

Melt blending is the most commonly used method in composite preparation due to its efficiency and operability. In the process, the polymer and the inorganic filler (I. e., silica) are sheared in the melt at a temperature equal or greater than the melting point of the polymer.

Under suitable conditions the material exfoliates and disperses to the desired extent. This technology is very versatile and can be applied to various polymers. It is also possible to add swelling and compatibilizing agents in order to improve the exfoliation and reach a better adhesion between the two major components. Solution blending, on the other hand, is a liquid-state powder-processing method that allows a good molecular level of mixing. Solution blending can be achieved by either dissolving only the polymer matrix or dissolving both the matrix and the Nano particles <sup>(31)</sup>.

#### **1.10.7 in Situ Polymerization**

The in situ polymerization method has many advantages, such as ease of handling and better performance of the final products. Generally, this method involves the dispersion of Nano fillers in monomer(s), and then bulk or solution polymerization. The Nano fillers are always modified by functional groups to increase the interaction between the polymers and the Nano fillers.

The advantage of this route is that it prevents particle agglomeration while maintaining a good spatial distribution in the polymer matrix.

The drawback of this method is that the un reacted educts of the in situ reaction might influence the properties of the final material Melt intercalation method <sup>(34)</sup>.

### **1.10.8 Surface-Initiated Polymerization**

The grafting strategies to construct the polymer/mesoporous silica composite are of great interesting. Generally, two routes are used to graft polymer chains on the surface of the mesoporous silica, e.g., “grafting-to” and “grafting-from” technique. The “grafting to” method refers to the grafting of polymers onto inorganic particles. This method usually generates non grafted chains. Additionally, the grafted polymer chains prevent attachment of the next ones and then limit the graft density. The “grafting-from” technique refers to polymer chains growth from the surface of the inorganic supports. This method is feasible to design polymer/mesoporous silica composite with covalent interaction between polymer and inorganic fillers <sup>(35)</sup>.

### **1.11 Objectives of this study:**

This study aims to:

- Synthesis of Nano silicon dioxide
- Support of polyethylene by silicon dioxide (PE/SiO<sub>2</sub>)
- Characterize of PE/SiO<sub>2</sub>
- Study of mechanical and optical properties of the obtained product

# **Chapter Two**

## **Experimental**

# Chapter Two

## Experimental

### 2.1 Devices and equipment

- Heating mantle swastika scientific instrument, thane, Mumbai ,India
- Glass rod
- Beakers
- Volumetric flask
- Ultra violet spectrophotometer
- Fourier transform infra red spectrophotometer

### 2.2 Chemicals

- Polyethylene ( $C_2H_4$ )<sub>n</sub>
- Toluene ( $C_6H_5CH_3$ )
- Silicon dioxide ( $SiO_2$ )
- Hydrochloric acid (HCl)
- Sodium silicates( $Na_2 SiO_3$ )
- Sodium bisulphate ( $NaHSO_3$ )

All chemicals used in this research of analytical grade type

### 2.3 Methods:

#### 2.3.1 Preparation methods:

##### 1. Preparation of Ultra Pure Silicon Dioxide:

30 g of sodium silicates were weighted and pour into a beaker (250 ml), then were dissolved in 50 ml of hydrochloric acid, 50 ml of distilled water was added then shaken until the solution was completely dissolved, 35 g of sodium bisulphate was dissolved in 100ml of water; the solution was stirred vigorously with glass rode until it's completely dissolved. The contents of the first beaker was poured into the second beaker and mixed thoroughly a thick

jelly-like precipitate was formed. The precipitate was poured into a porcelain crucible and heated, then it was dried and weighted

## **2. Preparation of Polyethylene/Silica Nano Composite (as tablet)**

0.9 g of polyethylene (PE) was weighed in conical flask and, warmed on the heating mantle to 80°C, 0.1g of silicon dioxide was added to viscous polymer solution with good mixing until the solvent was evaporated and sample was glued on glass road.

The steps was repeated for four times by used :( 0.2g of SiO<sub>2</sub> and 0.8g of PE), (0.3g of SiO<sub>2</sub> and 0.7 g of PE),(0.4g of SiO<sub>2</sub>and 0.6g of PE)and (0.5 of SiO<sub>2</sub>and 0.5 of PE) .Samples were formed as tablet to use in IR ,UV spectroscopy

## **3. Preparation of Polyethylene/Silica Nano Composite (thin film)**

A 4.95g of PE were weighed into beaker and 20 ml of toluene was added , the mixture was heated on heating mantle to 80°C .0.05g of SiO<sub>2</sub> was added to viscous polymer with strong mixing ,the blend was decanted in petry dish. The steps was repeated two times with (0.03g of SiO<sub>2</sub> and 4.97g of PE) and (0.01g of SiO<sub>2</sub> and 4.99g of PE).Samples were used in tensile test

### **2.3.2 Characterization methods:**

#### **1. Method of preparation Samples for Infra Red Spectroscopy:**

Each sample was dissolved partially in 10 ml of toluene. Small of solution was placed on glass slide.

#### **2. Method of preparation Samples for Ultra Violet Spectroscopy:**

Each sample was dissolved partially in 10 ml of toluene and the cell was filled from solvent.

#### **3. Method of tensile test:**

The thin film samples were cuted by use of dong done cutter.

# **Chapter Three**

## **Results and Discussion**



# Chapter Three

## Results and Discussion

### 3.1 Results:

#### 3.1.1 Characterization of polyethylene/silica composite:

##### 1. Fourier transform-infra red spectroscopy:

It is clear from figure 3.1 there is a strong C-H stretching modes at 2851 and 2917  $\text{cm}^{-1}$  corresponding to polyethylene-methylene bending these signals were identical with the characteristic features of bulk PE.

- The samples were inflexible and hard to cut.

With addition of Nano silica, the IR spectra exhibit an absorption behavior for mid IR in the wave range of 700-1000  $\text{cm}^{-1}$

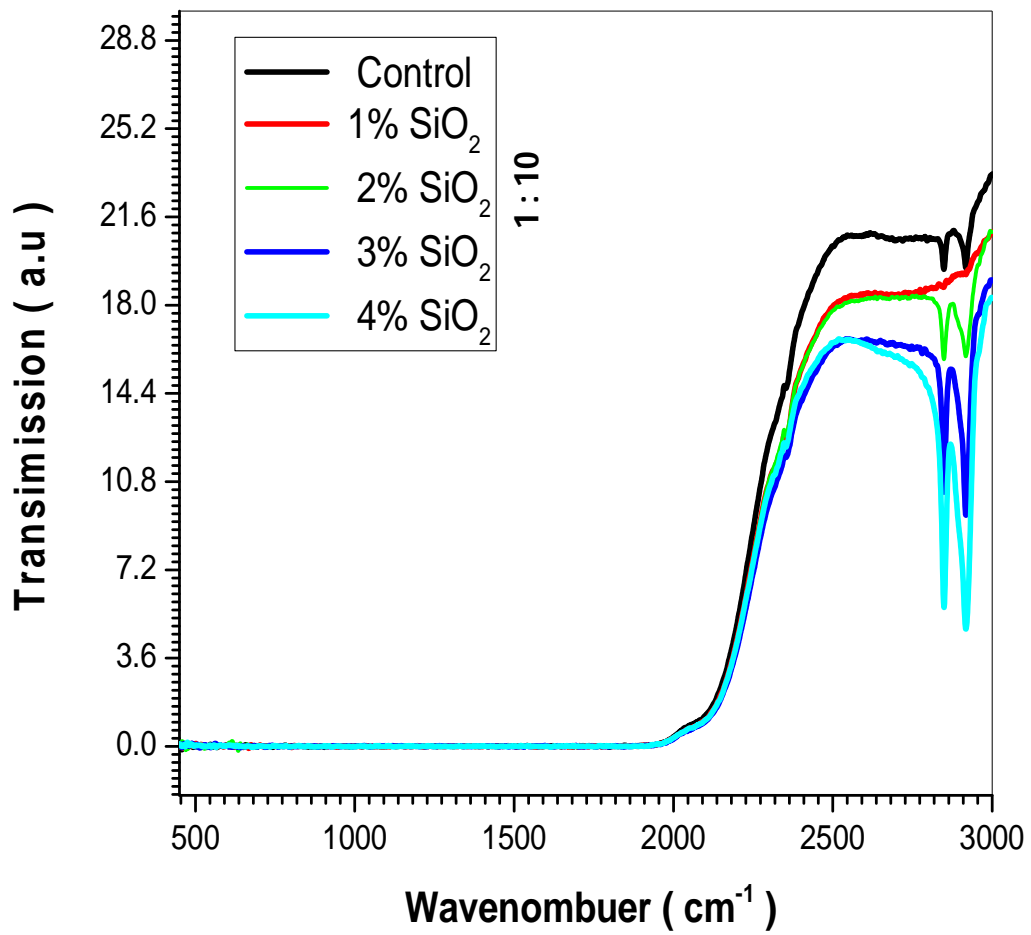


Figure 3.1: FTIR spectrum of polyethylene/silica composite

## 2. Focus FTIR spectrum:

From the focus FT-IR could say that the peaks at 400-500 corresponded to silica; The IR absorption capacity of composite is a function of the silica content .The higher silica content, the higher the IR absorbance

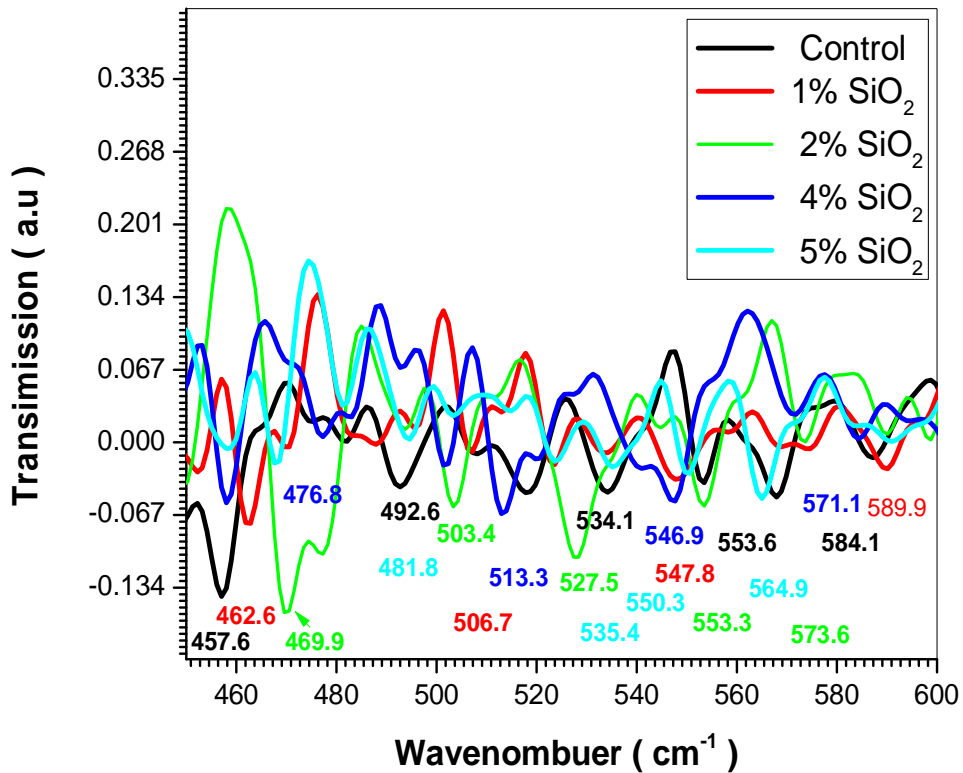


Figure 3.2: focus FTIR Spectrum of polyethylene/silica composite

### 3.1.2 Ultra violet spectroscopy:

As show in figure (3.3) all samples have absorbance, as amount of silica increase the absorbance increase and the lamda max of all samples is 284 which is characteristic of silica composite.

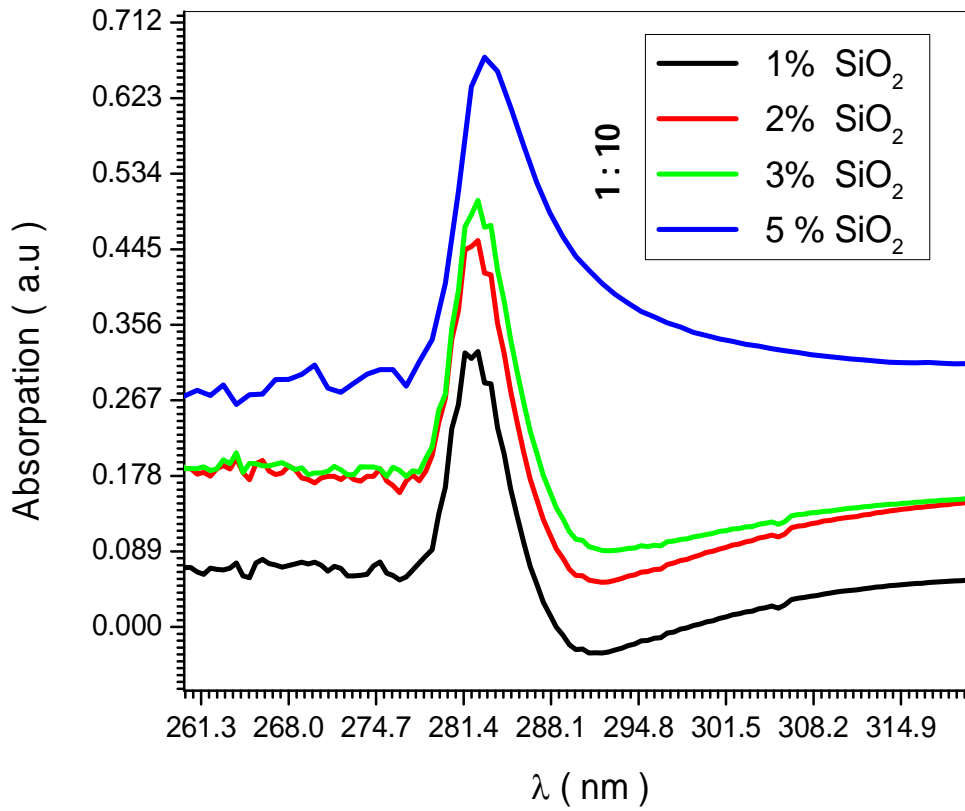


Figure 3.3 absorption spectrum of polyethylene/silica composite

### 3.1.3 Ultra violet transmission:

The results of different silica/polyethylene concentrations shown in figure 3.4 . And from this result, it could be conclude that all samples have transmission.

PE/SiO<sub>2</sub> composite would be capability of IR irradiative absorption, in turn resulting in a remarkable decrease in thermal energy loss to the surrounding.

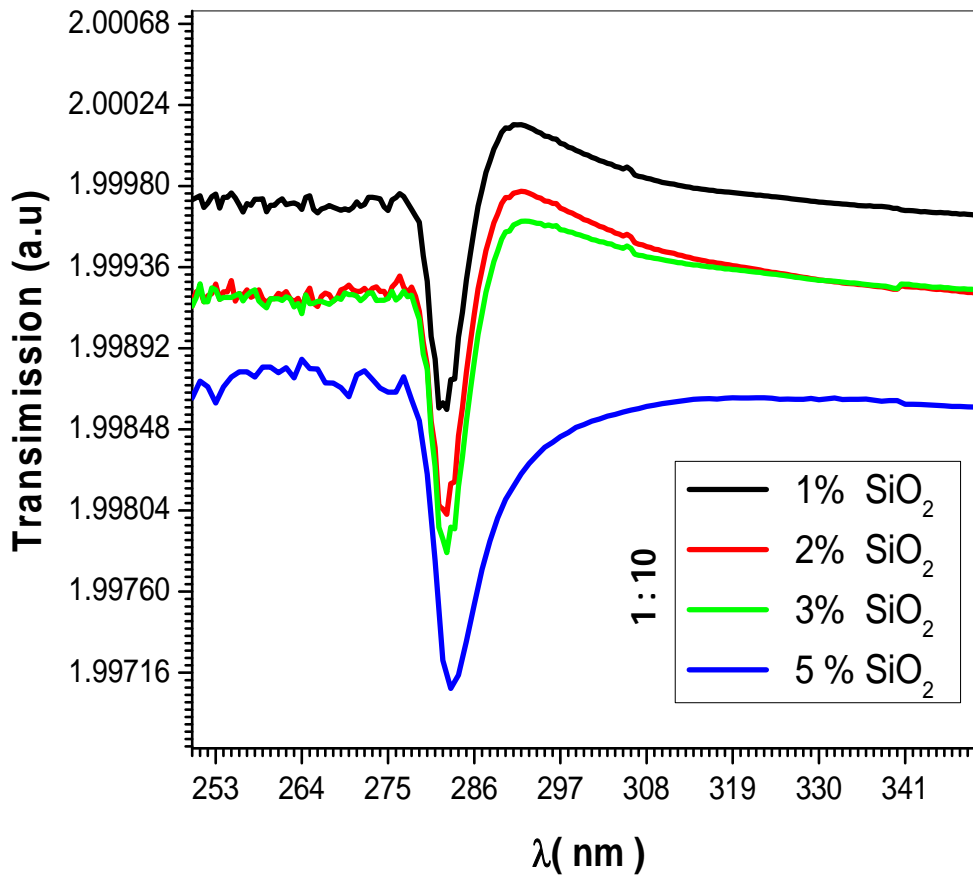
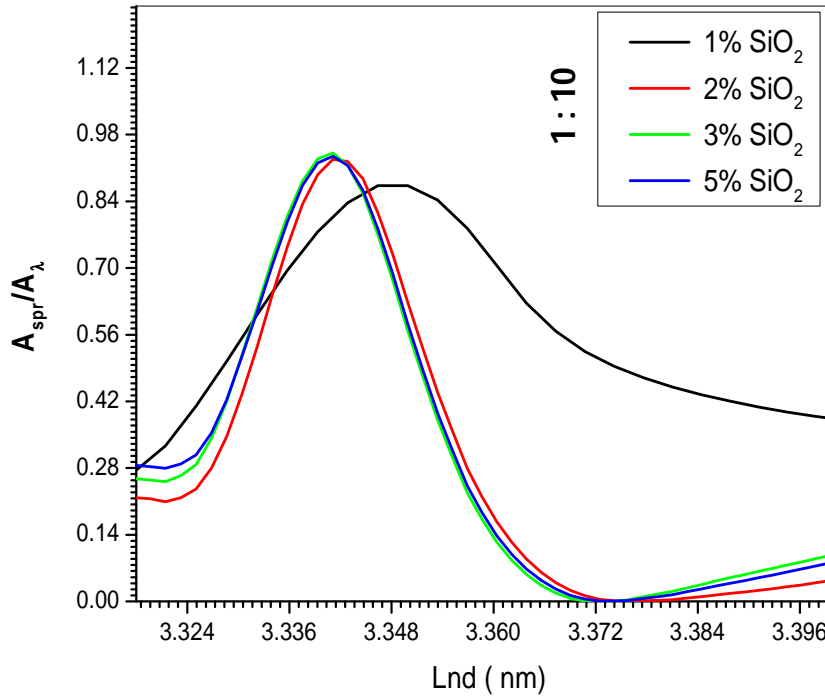


Figure 3.4: transmission spectrum of polyethylene/silica composite

### 3.1.4 Surface Plasma Resonance spectrum



**Figure 3.5: Calculated ratios of absorbance values of PE/SiO<sub>2</sub> in dependence of their diameter**

Particle size was calculated from below equation

$$D = \exp \left( B_1 \frac{A_{spa}}{A_\lambda} - B_2 \right)$$

$B_1$ : Inverse of slope of linear fut. of figure

$B_2$ : ( $B_0/m$ ): intercept of figure

$A_{SPa}$ : Absorbance at surface plasma resonance

$A_\lambda$ : Independence of the logarithm of the particle diameter

### 3.1.5 Energy band gap:

Insulator materials have large energy band gap and semi conductor particle (silica) have narrow band gap and weak electron bonded when electron is added (removed) to the bottom of the conduction band (from the top of the valence band) of a conjugated polymer, the conduction (valence) band ends up being partially filled and a radical anion(cation), commonly termed as a polarons, the formation of polarons causes the injection of states from the bottom of the conduction band and top of the valence band into band gap. So that silica is decrease resistance and energy band gap.

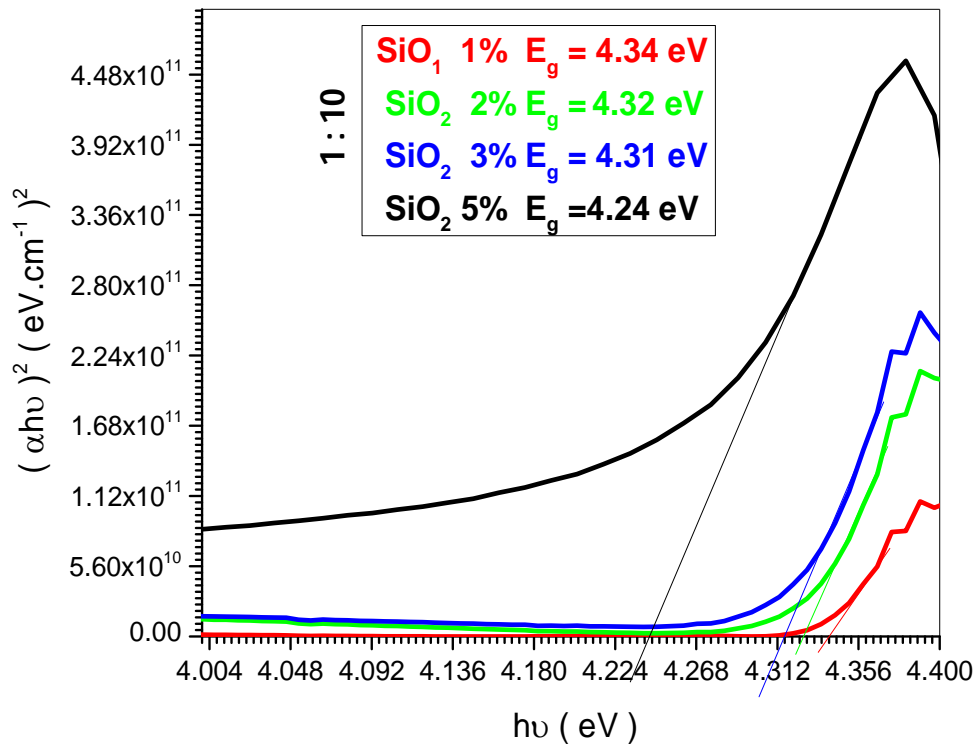


Figure 3.6: Energy band gap

### 3.1.6 Refractive index:

Polyethylene has high refractive index arrive to 1500 nm so from figure 3.7, it observed that silica was decreased the refractive index of composite until it arrived to lowest value 1.5 nm which is close to refractive index of pure silica (1.58) whereas highest value was in UV region. It concluded that this composite is shielding ultra violet radiation, as amount of silica increase the composite become transparent.

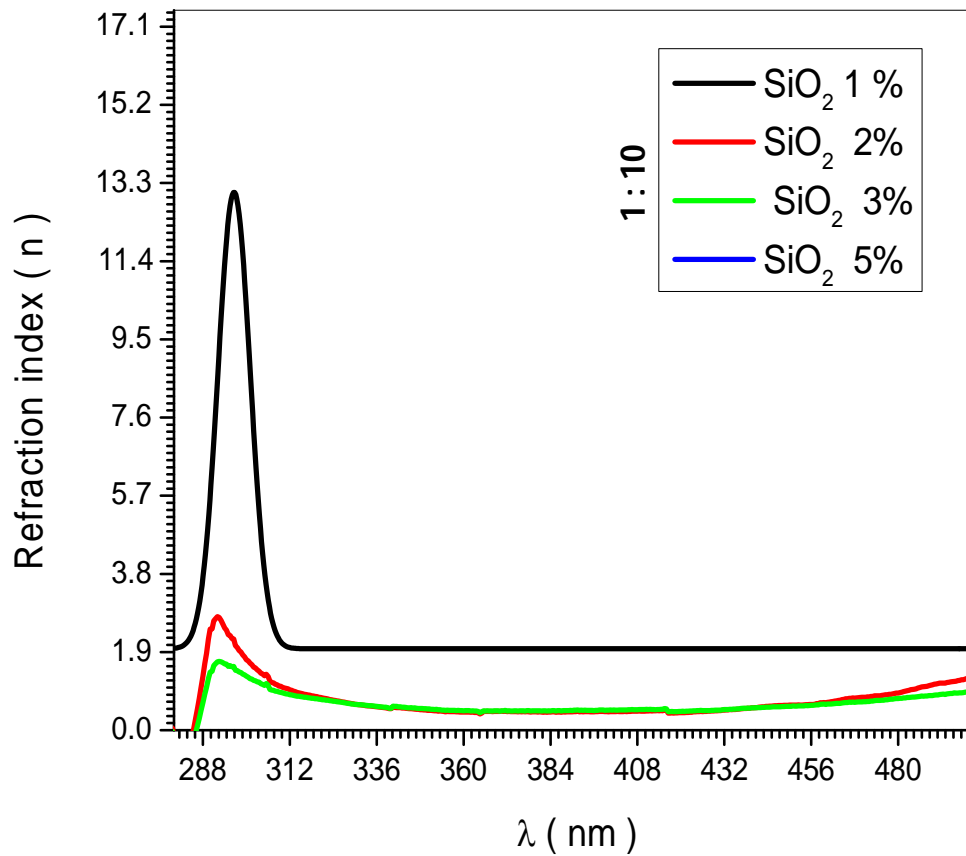


Figure 3.7: Refractive index



### 3.1.7 Particle size of Polyethylene /Silica Nano composite:

Particles size for composites was calculated mathematically from UV spectrum by Surface Plasma Resonance.

Table 3.2: Particle size of Polyethylene/silica Nano composite

Sample	Particle size
10%	13.6 nm
20%	23.26 nm
40%	35.8 nm
50%	41.99 nm

All size was between 13.6-41.99 nm indicating that the samples are Nano composites.

### 3.1.8 Tensile Test:

The thin film sample was cut by use dog bone cutter and the results as follow:

Table 3.4: Tensile Test

Sample	Thickness	Load
0.01 g of silica	0.5-0.7	4.9 kg
0.03 g of silica	0.15-0.19	5.01 kg
0.05 g of silica	0.17-0.16	5.4 kg

The samples are white milky, from the results it can be observed that samples are able to tensile by high load and as amount of silica increase the capable of sample to endurance of load is increase that mean silica is enhance the mechanical properties which widens the application of this filler.

### **3.2 Conclusion:**

The properties of polyethylene are changes after addition of silica particles:

- Addition of Nano silica particles could enhance the IR absorption performance of the composite.
- The composite is transparent in infra red region and opaque in some region of ultra violet.
- Introduction of small amount of silica in polyethylene matrix lead to substantial improvements of mechanical per forces of the resulting sample.
- The electrical properties are Near to conductor than insulator.
- Silica and polyethylene have identical transparencies.

### **3.4 Recommendation:**

We recommend for expands studies in optical properties of polyethylene /silica composite to use in protect from ultra violet because it has high refractive index in UV region.

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