

GAS SENSOR FOR TDI (TOLUENE DIISOCYANATE) USING POLYMER THIN FILMS

Submitted in partial fulfillment of the requirements for the award of
Bachelor of Technology degree in
Chemical Engineering

By

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DEPARTMENT OF CHEMICAL ENGINEERING

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SATHYABAMA

INSTITUTE OF SCIENCE AND TECHNOLOGY

(DEEMED TO BE UNIVERSITY)

Accredited with Grade "A" by NAAC

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MAY 2022



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DEPARTMENT OF CHEMICAL ENGINEERING

BONAFIDE CERTIFICATE

This is to certify that this Project Report is the Bonafide work of **NAKKEERAN M(38190008)**, **POOVARASAN S R (38190009)**, **RUBESH R (38190011)**, who have done the project as a team, who carried out the project entitled "**GAS SENSOR FOR TDI (TOLUENE DIISOCYANATE) USING POLYMER THIN FILMS**" under my supervision from September 2021 to April 2022.

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Internal guide

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ACKNOWLEDGEMENT

We are pleased to acknowledge our sincere thanks to the Board of Management of **SATHYABAMA** for their kind encouragement in doing this project and for completing it successfully. We are grateful to them.

We convey our sincere thanks to **Dr. S. SATHISH, Ph.D.**, Head of the Department, Dept. of Chemical Engineering for providing us necessary support and details at the right time during the progressive reviews.

We would like to express our sincere and deep sense of gratitude to our internal Project Guide **Dr.A. Annam Renita M.Tech., Ph.D.** for their valuable guidance, suggestions and constant encouragement paved way for the successful completion of our project work.

We also express our thanks to all Teaching and Non-teaching staff members of the Department of Chemical Engineering who were helpful in many ways for the completion of the project.

ABSTRACT

Isocyanate are used as therapeutic agents in the final mixing of solid propellants. Toxic isocyanate has a high reactive property, and exposure to these compounds can cause serious health problems. Polymers such as Polycarbazole, Polyaniline, and Polythiophene can be used in sensors to detect TDI gas traces in the workplace for worker safety. The spin coating and drop casting processes were used to create and optimize thin films of Polycarbazole and Polyaniline polymers. SEM and Raman spectroscopy were used to characterize the samples before and after they were exposed to TDI. Electrical Impedance courses and studies were conducted on the thin films. The prototype is also designed for gas phase detection

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CHAPTER 1

INTRODUCTION

1.1 POLLUTION

Pollution is defined as the addition of pollutants into the natural environment that cause negative change. Pollution can take the form of chemicals or energy in the form of noise, heat, or light. Pollutants, also known as contaminants, are all either foreign materials or contaminants that occur naturally. Pollution is frequently divided into two types: point source pollution and nonpoint source pollution. In 2015, pollution killed 9 million people worldwide. (Beil & Carrington, 2017).

Major types of pollution include air pollution, light pollution, litter, noise pollution, plastic pollution, soil contamination, radioactive contamination, thermal pollution, visual pollution, and water pollution. Air pollution has always accompanied civilizations. Pollution initially appeared in primordial times, when man kindled the first fires.

According to a 1983 Science article, "soot" found on prehistoric cave ceilings "provides ample proof of the high levels of pollution associated with inadequate ventilation of open fires" (Spengler,1983). Metal forging appears to represent a watershed moment in the production of considerable quantities of air pollution outside the home. Pollution levels in Greenland glacier core samples have increased as a result of Greek, Roman, and Chinese metal manufacture (Hong,1996).

1.2 SOURCES AND CAUSES

- Air pollution generated by both natural and anthropogenic (man-made) sources. Human-made pollutants from combustion, construction, mining, agriculture, and warfare, on the other hand, are playing a growing role in the global air pollution equation.

- Motor vehicle exhaust is one of the most significant sources of air pollution. China, the United States, Russia, and India are the four most powerful countries in the world. Mexico and Japan lead the world in terms of air pollution emissions. The main stationary pollution sources are chemical plants, coal-fired power plants, oil refineries, petrochemical plants, nuclear waste disposal activity, incinerators, large livestock farms (dairy cows, pigs, poultry, etc.), PVC factories, metals production factories, plastics factories, and other heavy industry. Modern agricultural methods such as clear felling and burning of natural flora, as well as pesticide and herbicide application, contribute to agricultural air pollution.
- Over 400 million metric tonnes of hazardous waste are created each year. In the United States alone, around 250 million metric tonnes are produced. Despite accounting for fewer than 5% of the global population, Americans produce approximately 25% of CO₂ and generate roughly 30% of the world's waste. China surpassed the United States as the world's greatest CO₂ emitter in 2007, yet it still lags far behind in terms of per capita pollution (ranked 78th among all nations).
- However, according to the Intergovernmental Panel on Climate Modify's final report this year, a shift away from fossil fuels like coal and oil must occur within decades in order to change the climate (IPCC).
- The automobile is the most common cause of noise pollution, accounting for more than 90% of all undesirable noise worldwide.

1.3 Chemical Toxicity

Isocyanate can cause respiratory issues as particles, vapors, or aerosols. Because they are routinely exposed when spray painting automobiles (Reeb-Whitaker, 2012) and can also be exposed when installing truck bed liners, autobody shop

staff are a common target for isocyanate testing (Bogaert,2009). Hypersensitivity pneumonitis is characterized by chronic inflammation apparent on lung imaging and has a later onset. Occupational asthma is a potentially fatal side effect of isocyanate sensitization (Kimber,2014). Occupational asthma is diagnosed by pulmonary function testing (PFT) by pulmonologists or occupational medicine specialists (OSHA). Shortness of breath and wheezing are common symptoms of occupational asthma, which is comparable to asthma. Depending on the dose and duration of isocyanate exposure, respiratory sensitization may occur (Daniels,2018).

Isocyanate exposure through the skin can expose a person to respiratory disease. Dermal exposure can occur when coatings are mixed, sprayed, or applied and distributed manually. Isocyanate exposure through the skin has been associated to respiratory sensitization. (Bello,2006) Exposure to body regions that are not completely covered can occur even when wearing the necessary personal protective equipment (PPE). (Ceballos,2011) Isocyanate can also permeate inadequate PPE, necessitating the frequent replacement of disposable gloves and jackets if they become overexposed.

1.4 ISOCYANATE AND ITS DERIVATIVES

In industrial, isocyanates are extensively used. Paints, glues, and resins include isocyanate, which is employed in a variety of industrial products. They are responsible for respiratory and cutaneous sensitivities, as well as asthma and allergic contact dermatitis. Exposure to isocyanates has also been related to a range of harmful health effects, including cancer. It is critical to restrict worker exposure when isocyanate is utilised or unintentionally created, including when polyurethanes are heated. There are several ways to accomplish this, and the method through which the isocyanate is utilised or made frequently influences which management strategy is required. To remain successful, all exposure controls must be maintained, and this article describes how to do this for isocyanate.

1.5 ISOCYANATE DERIVATIVES

Isocyanates are chemical compounds with one or more $\text{N}=\text{C}=\text{O}$ functional groups connected to them. Diisocyanate, which is based on molecules with two such functional groups, is the most common isocyanate encountered in industrial settings. These are some examples:

- i. Toluene diisocyanate (TDI)
- ii. Methylene bis (phenyl isocyanate) (MDI) or methylene diphenyl diisocyanate
- iii. Naphthalene diisocyanate (NDI)
- iv. Hexamethylene diisocyanate (HDI)
- v. Iso phorone diisocyanate (IPDI)

TDI, MDI, and IPDI exist as a combination of isomers. In their most basic form, these chemicals are monomers. In contrast, many industrial isocyanate preparations have molecular structures based on the chemical bonding of two or more monomer molecules. These molecules are referred to as pre-polymers and oligomers. Because they still have the $\text{N}=\text{C}=\text{O}$ functional group, these molecules carry the same health risks as isocyanate.

Pre-polymers are less likely to get airborne as a vapour because they are less volatile than the monomer with which they are linked. However, when these substances are sprayed, large inhalation exposures can occur, and the health risks associated with skin exposure persist.

Isocyanate in more complex forms, comprising various functional groups that may lessen the potential for isocyanate exposure, are also available. Isocyanate that has been blocked or stoved are commonly referred to as blocked or stoved isocyanate. The isocyanate must be free to react for the $\text{N}=\text{C}=\text{O}$ functional group to participate in the polymerisation reaction and for the paint, glue, and other materials to cure, therefore there is still isocyanate exposure potential associated with these materials at some point in the process.

Isocyanate preparations that are commercially accessible are either solids or viscous liquids. TDI and MDI, both aromatic isocyanates are the two most frequent types. MDI is used to manufacture flexible or rigid polyurethane foam, elastomers,

coatings, sealants, and adhesives, while TDI is used to make flexible or rigid polyurethane foam.

MDI is available in both pure and polymeric forms (PMDI). Isocyanate exposure can be dangerous for workers. When these substances are produced or used, TDI and MDI detection capabilities should be in place.

1.5.1 MDPI

MDI is frequently utilised in the production of rigid foams and surface coatings. Polyurethane foam boards are used in construction as insulation. When flexible foams are employed, TDI is frequently used in furniture and bedding applications. MDI and TDI are both used in the production of adhesives and sealants due to their weather-resistant properties. Isocyanate such as MDI and TDI, are often used in insulation spraying applications due to their speed and adaptability. Depending on the application, foams can be sprayed onto buildings and either harden or remain flexible. HDI is a common ingredient in high-performance surface coatings such as car paints.

1.6 ISOCYANATE EXPOSURE

Most isocyanate exposure occurs through inhalation and/or skin absorption. Depending upon that isocyanate type and mode of administration, either or both of these routes may pose significant exposure risk, which should be factored into the risk management strategy.

When isocyanates are present in the workplace air, either as a vapour or as an aerosol, they might cause inhalation exposure. In some cases, isocyanate in the air might exist in both forms at the same time.

Vapours can be formed by passive processes like evaporation, and the amount of airborne vapour produced is determined by the isocyanate's volatility (aka vapour pressure)..

Aerosols can be created on purpose, such as when spraying, or by accident, such as when isocyanates are mechanically agitated or violently disturbed. When liquids are sprayed with a brushes or poured from one vessel to another, fine aerosol particles form. However, the volume of aerosol produced in this way is typically much lower than that produced by spraying processes. When handling solid isocyanate, the danger of airborne dust is present.

Dermal (skin) exposure can occur anywhere workers' skin may come into touch with isocyanate. The main mechanisms by which dermal exposure to isocyanate occur are:

- Direct touch with the skin of the workers.
- Deposition of aerosol from the air onto the skin of workers.
- Splashing, for example, when pouring or mixing activities.
- Handling contaminated goods such as tools or used personal protective equipment (PPE)
- During maintenance, for example, contact with contaminated surfaces such as control panels or process plant.

Occupational asthma, skin, eye, nose, and throat irritation, hypersensitivity pneumonitis, chest tightness, and cancer can all be caused by isocyanate. High doses of isocyanate have resulted in deaths. While inhalation is the most common way to be exposed to isocyanates, skin contact should be avoided as well. All facilities that employ isocyanate should implement an isocyanate safety programme that includes sufficient engineering processes, protective equipment, and isocyanate monitoring, given the possible health concerns.

1.7 OSHA AND INDUSTRY STANDARDS

In the United States, the Occupational Safety and Health Administration (OSHA) has implemented a National Emphasis Program to protect workers from the serious health effects of occupational exposure to isocyanate such as TDI and

MDI. OSHA conducts national emphasis programmes to focus communication and inspection efforts on certain industrial hazards.

The chemical industry is actively advocating isocyanate use that is safe. Many chemical businesses have product stewardship initiatives to assist their customers in providing a safe workplace for their employees. The American Chemistry Council (ACC) offers information on isocyanate safety in the workplace, including isocyanate air monitoring. Isocyanate manufacturers are frequently members of the International Isocyanate Institute (III), whose mission is to promote safe MDI and TDI management in the workplace, community, and environment.

1.8 APPLICATIONS

Some common industrial uses of isocyanate are listed below :

Isocyanate is used as a hardener in several industrial paints. These are usually '2-pack' items, in which two components are combined together right before use. The isocyanate is present in the hardener component of the paint in these circumstances. Some 'one-pack' paints do include isocyanate and do not require mixing, removing one duty with the risk of exposure. The safety data sheet that comes with the paint will tell you if there are any isocyanates present. Motor vehicle repair (MVR) and the painting of large commercial vehicles and structural steelwork are common uses for these paints. They can be applied with a spray, a brush, or a roller. The spray application has the greatest potential for exposure. Brush or roller application would result in substantially lower inhalation doses. Workers in the MVR sector who use these paints have a high rate of occupational asthma. The isocyanate is included in the hardener component of the combination, and the paints are often based on pre-polymeric forms of HDI. Airborne isocyanate is not liberated by sanding and polishing fully cured isocyanate-based paints. Cure paints, on the other hand, have been proven to liberate airborne isocyanate when exposed to greater temperatures, such as those generated by grinding and welding.

Polyurethane rubbers and thermoplastic elastomers are manufactured. An aromatic isocyanate, most often MDI or TDI, is reacted with a polyfunctional alcohol (polyol) or other organic substance to produce these. Isocyanate is frequently prepared and poured by hand. In this industry area, there are usually no processes that involve spraying isocyanate. In this industry, exposure controls are provided in a variety of ways.

Soft polyurethane foam production. Other additives are used to modify the qualities of the end product, which are made from TDI and a polyol. The isocyanate is normally blended using an automated technique and cured first in an extracted cage. Buildings, residential appliances, and refrigerated transportation all benefit from thermal insulation.

Flooring for the industrial sector. MDI is a component used in the creation of high-quality industrial resin flooring with minimal porosity. This type of flooring is typically seen in food processing plants and other places where hygienic, readily cleaned flooring is necessary. In most cases, the resin is mixed in an open system, and the flooring is laid by hand with hand tools. In a single session, large expanses of up to several hundred square metres can be laid.

Binders for foundries. In foundries, MDI-containing urethane binder solutions are routinely utilised to produce moulds and cores from sand. When making the moulds and cores, as well as when pouring the hot metal into the moulds, there is a risk of exposure to thermal degradation products.

1.9 EXPOSURE MONITORING

Exposure monitoring can be an important aspect of an isocyanate risk management strategy. Air sampling and biological monitoring can be divided into two categories.

1.9.1 Air sampling

Personal monitoring is the most common and useful kind of air sampling from the standpoint of occupational hygiene. This enables for the most accurate calculation of worker exposure and can be an important factor in determining the

effectiveness of control and guiding RPE selection. The measurement of airborne isocyanate is difficult and necessitates specialised knowledge. Certain isocyanate species, most often monomers, are only quantified by some measuring methods. Industrial isocyanate preparations usually contain a combination of pre-polymers, all of which are toxic to humans. Other approaches are only relevant to airborne isocyanate in the vapour or particle phases. The measurement method must identify and quantify all isocyanate in monomeric and polymeric forms, whether in the vapour phase or present as airborne particulate, in order to be useful in the risk assessment process. When dangerous levels of airborne isocyanate are present, approaches that simply assess monomeric isocyanate can severely underestimate exposure and give the impression that risk is low. When possible, use measurement methodology that has been accredited by a credible organisation. ISO certification has been granted to a number of isocyanate measuring methods.

Continuous fixed point gas monitors and alarms are ideal where substantial volumes of isocyanate are handled under containment. These are usually only applicable to monomeric isocyanates in the vapour phase.

1.9.2 Biological Monitoring

Biological monitoring can provide a reliable indication of recent occupational exposure and is a good way to exposure assessment[24]. Biological monitoring is less expensive and easier to implement than air sampling, and it can provide data on total exposure from all routes as well as the effectiveness of PPE in limiting exposure. Certain amines used in industrial operations using isocyanate can interfere with the biological monitoring approach.

1.9.3 Health surveillance

Health surveillance is an important aspect of the isocyanate risk management strategy. Regular, focused surveillance by a competent expert can detect skin and respiratory disease in its early stages, allowing for individual and company-wide interventions.

1.10 POLYCARBAZOLE

A carbazole derivative is polycarbazole. Carbazole polymerization produces polycarbazole, an electrically conducting polymer. Two six-membered benzene rings are joined on either side of a five-membered nitrogen-containing ring in this tricyclic structure

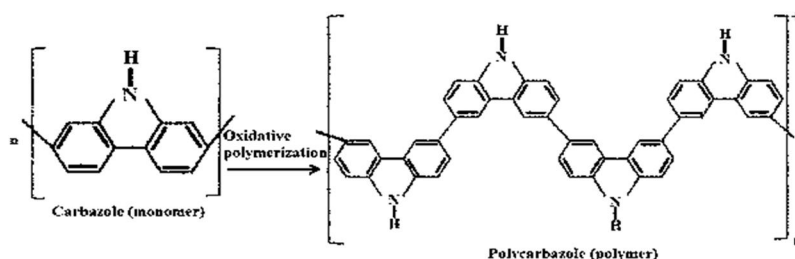


Fig1.1: Structure of Polycarbazole

1.11 POLYANILINE

Polyaniline () was the first conducting polymer to be utilised in practise as an antistatic coating and corrosion inhibitor due to its excellent chemical stability, nontoxicity, good processability, and steady intrinsic redox state obtained from the imine groups of the chain. Due to its simplicity of synthesis and ability to detect a wide spectrum of gases, , a well-known conducting polymer, plays an essential role in gas sensing applications. can be divided into two types of emeraldine compounds. Polyaniline () is a conducting semi-flexible rod polymer. Because of its ease of synthesis, environmental stability, and simple doping/dedoping chemistry, polyaniline stands out within the conducting polymer family. Despite the fact that the synthetic methods for creating polyaniline are straightforward, the mechanism of polymerization and the precise nature of its oxidation chemistry are both highly complicated.

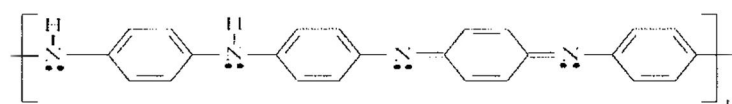


Fig 1.2 : Structure of Polyaniline

1.12 SUBSTRATE

The substrate is the parent or foundation material to which a coating is applied or the substance on which a process is carried out. Metals, polymers, and ceramics are just a few examples of substrate materials. Steel, aluminium, copper, zinc alloys, and galvanised steel are some of the most popular metals used as coating substrates.

1.12.1 ITO COATED GLASS SUBSTRATE

The ITO coated glass substrate is a single-sided Indium Tin oxide coated soda lime glass. The resistivity of the coating ranges from 4 ohms/cm square to 150 ohms/cm square. It is a TOC with only one coated side. The thickness of the conductive layer ranges from 10 nm to 300 nm. The level of haze is less than one. The thickness of the glass substrate ranges between 0.7mm and 1.1mm. It is a glass with a single-sided coating that is conductive. Touch screens, solar cells, EMI shielding, solar panels, and other applications make extensive use of it. ITO coated conductive glass is also known as conductive glass substrate.

1.13 COATING

A coating is a material layer that is applied to a substrate's surface. When it comes to corrosion prevention, the coating is used to protect the substrate while also being decorative.

1.13.1 TECHNIQUES FOR COATING

- SPIN COATING
- DIP COATING
- DROP CASTING

1.13.1.1 SPINCOATING

Spin-coating has been the most basic method of creating a film on a substrate. This technique is used to coat thin-resist layers for photolithography. The spin-coating process begins with the material to be deposited being diluted in a solvent. The solution is then sprayed onto the substrate's surface. After that, the wafer is spun at a high speed.

The spinning speed, surface tension, and viscosity of the solution all influence the thickness of the film. The solvent is removed partially during the spinning process through evaporation and partially through subsequent baking at high temperatures.

1.13.1.2 DIPCOATING

Dip coating is a highly effective process in which the substrate is immersed in a liquid and lifted out at a predetermined speed governed by a continuous motor. For effective material formation, the solution substrate is immersed in the

solution. Once the material has been deposited, the substrate can be removed by vaporization, resulting in a layer with a unique thickness.

The forces of inertia, viscous drag, gravitational force, and surface tension are all used in the dip coating process. Dip coating has the advantages of being inexpensive and having the ability to modify layer thickness simply.

1.13.1.3 DROPCASTING

Drop-casting is a simple and tunable deposition process for small substrates (less than 1 cm²) that spreads a nanoparticle dispersion over a substrate and allows it to dry under regulated pressure and temperature conditions.

The quantity of dispersion utilised and the particle concentration, both of which are entirely configurable, define the film thickness in theory. Other parameters that affect film structure include how well the solvent wets the substrate, evaporation rate, drying capillary forces, and so on. Volatile solvents that moisten the substrate and are resistant to thin film instabilities are preferred in general (de-wetting).

1.14 PREVENTIVE MEASURES

When coating a substrate, one should ensure that:

1. The surface of the substrate must be clean and clear of dirt and oil.
2. If the substrate already has a coating on it, it should be devoid of surface cuts and bruises, coating chatter, and coating defects. These flaws can result in poor coating.
3. To ensure cleanliness, the substrate is thoroughly cleaned with an ethanol solution and wiped with a tissue.

1.15 TYPES OF SENSORS TO DETECT ISOCYANATE

1.15.1 Transistor and diode sensors

Organic thin-film transistors have been used in the sensing sector since they were originally invented. There are some reviews on OTFTs and their use in sensors. A TFT is composed of a semiconductor active layer in contact with two electrodes ("source" and "drain"), as well as a third electrode ("gate") separated from the active layer by an insulating film. A source-drain voltage was applied and a source-drain current was monitored to see if it worked. A gate potential is used to modify the current via the gate. When sensing film interacts with analyte, the source-drain current changes. The structure of a thin film transistor, which was used to detect gases, exhibits two types of conducting polymer transistors, defined by whether current flowed through the polymer. Its active layer is constructed of conducting polymer, and it resembles the structure of an insulated gate field effect transistor, in which the gate electrode is made of conducting polymer and current passes through the other semiconducting layer, such as silicon.

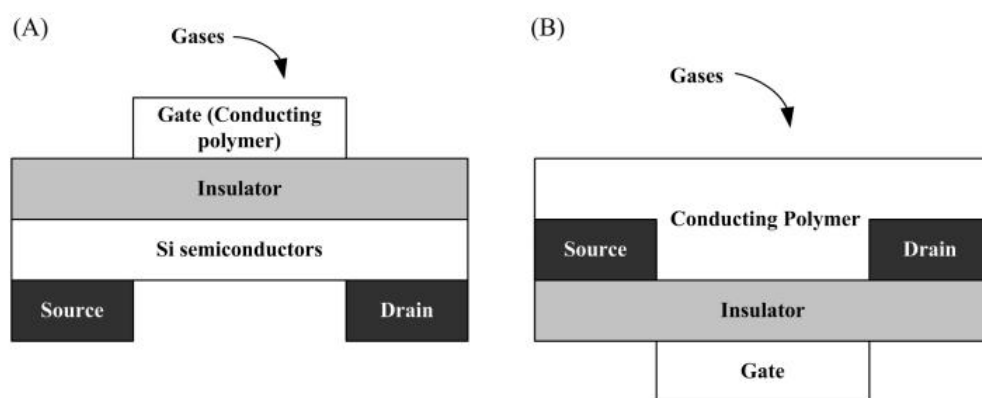


Figure 1.3: Configuration of TFT (A) and IGFET (B).

The modulation of source-drain current is interpreted as an appropriate gate potential enriching charge carrier in the semiconducting layer close to the gate electrode, resulting in the formation of a current channel. The gate capacitor is the heart of a TFT, with silicon forming one plate and a conducting polymer film

forming the other. An electric field is formed at the interface of the two chemically dissimilar plates when they are electronically coupled. This field is proportional to the difference in the work functions of the two plate materials, and it governs both the source-drain current and the turn-on voltage.

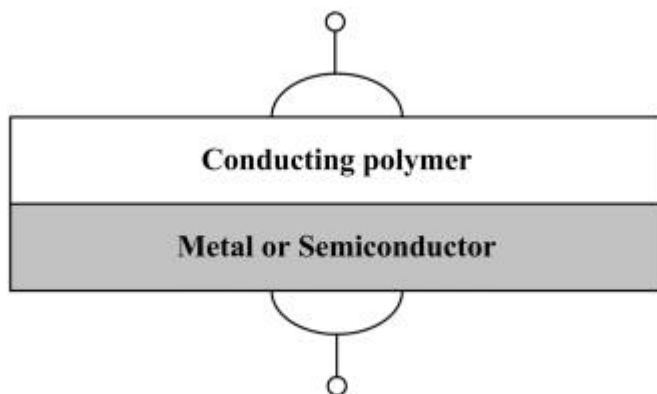


Figure 1.4: Configuration of diode device

Transistors and diodes provide more measurement parameters, which may yield more specific information about the semiconductor natures of conducting polymer sensing films. Furthermore, signal amplification in transistor devices improves the detection limit and sensitivity of transistor-based sensors. Furthermore, the ease with which conducting polymer topologies can be adjusted allows for a straightforward approach to sensing materials with varied work functions and analyte selectivity, guaranteeing that transistor-configured sensors perform well. The disadvantages of these devices are that their preparation, like that of other semiconductor devices, is slightly more difficult, and transistor characterization is more challenging.

1.15.2 Optic devices

Conducting polymers' electron configurations can be seen in UV-vis and NIR spectra. During the doping process, the spectral absorbance of a conducting polymer film changes, and new bands form due to the formation of polarons and bipolarons; nevertheless, the spectrum can return to its original shape after de doping (Brédas, 1984). Analyte gas interacting conducting polymer sheet can be identified by collecting UV-vis or NIR spectral shifts. An ultra-thin film is ideal

for producing an optic sensor since its spectrum can be easily captured using commercial spectrometers. In fact, the most basic sensor is just a piece of glass with a very thin conducting polymer sheet on top of it. Use a commercial UV-vis or NIR spectrometer to measure the spectral change online. A unique vessel is required. The sensors' reactions are usually variations in the sensing films' transmittance or absorbance. (Ewbank et al., 2004).

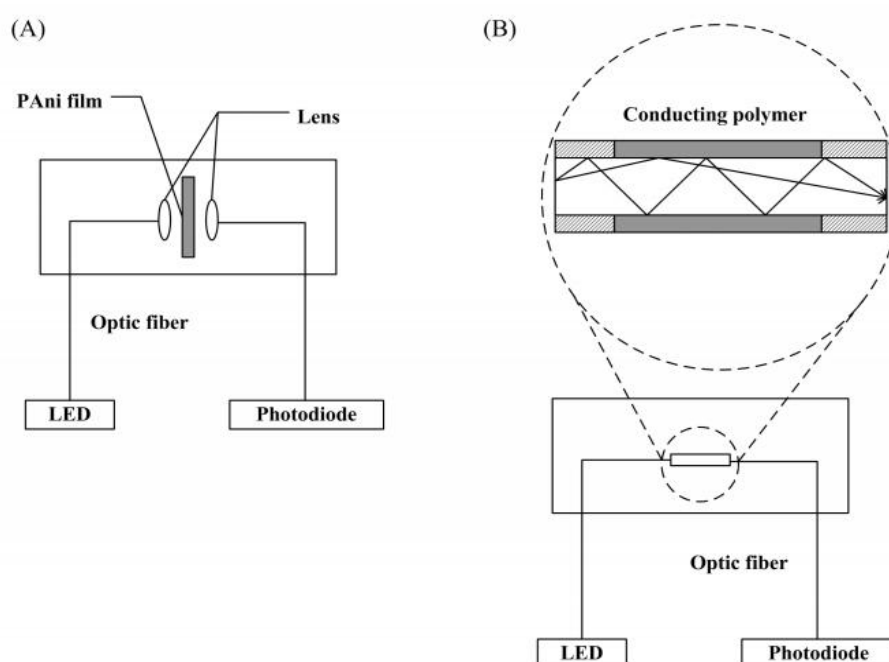


Figure 1.5: Configuration of two typical optical sensors using optical fibres.

Long-distance detection can be performed by using an optical fibre to measure the absorbance of the polymer layer. Two simple optical device architectures are shown in Figure . As shown in Figure, one way is to apply the sensing film to the cross-section of the fibre . The mechanism of this gadget is identical to that of direct measuring techniques..

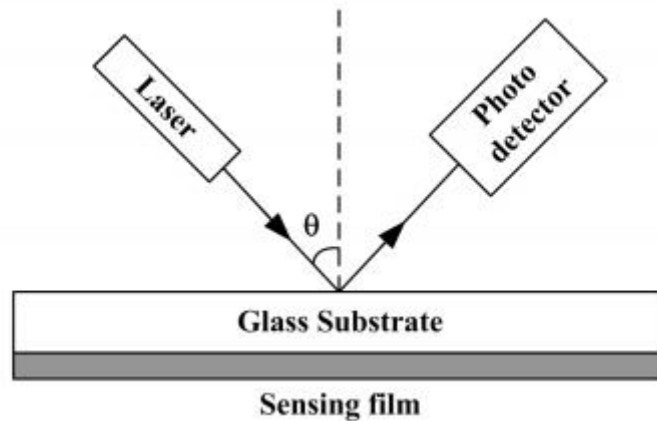


Figure 1.6: Kretschmann-type configuration of surface-plasmon resonance sensor device.

Another light-based vapour detection technology is surface-plasmon resonance (SPR). Surface plasma waves are collective oscillations of free electrons at the metal-dielectric material interface; surface plasmons are their quanta. The excitation of plasmons is affected by changes in the characteristics of the dielectric layer at the contact. Small changes in the circumstances (incidence angle) near the resonance angle might cause the reflected intensity to alter abruptly. This shows a typical SPR sensor arrangement (Kretschmann-type configuration). When exposed to analytes, the reflectance curve's minimum shifts, indicating the presence of the analytes. This sort of sensor has a great sensitivity, however the detection techniques are complicated.

1.15.3 Piezoelectric crystal sensors

Quartz crystal microbalance (QCM) and surface acoustic wave (SAW) sensors are two types of sensors that fit within this category. Chang et al. provide an excellent overview of the idea and uses of piezoelectric crystal sensors. (Chang, 2000).

Figure depicts a standard design for a SAW device (Chang, 2000). On a piezoelectric crystal, a transmitter interdigital electrode (interdigital transducers, IDTs) and a receiver interdigital electrode are linked. The gap between these two electrodes is covered with a polymer layer

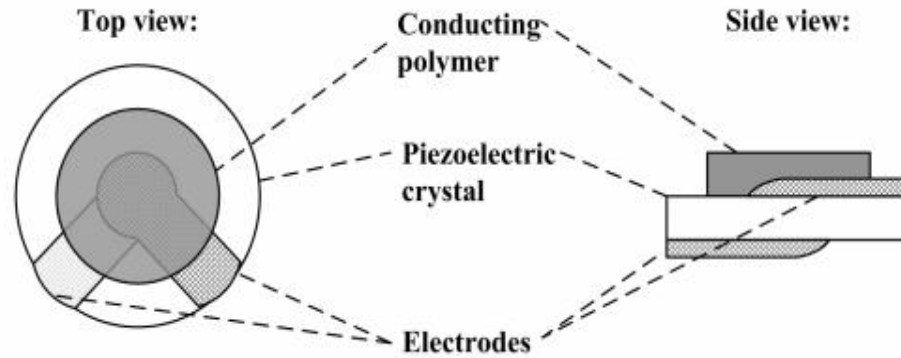


Figure 1.7 (A) : Configuration of quartz crystal microbalance sensor device.

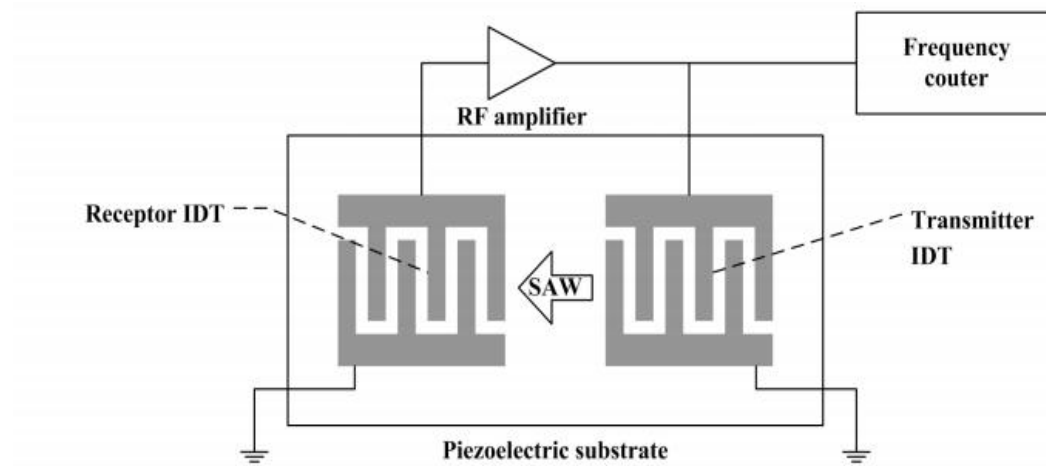


Figure 1.7(B) : Configuration of surface acoustic wave sensor device.

The transmitter IDTs are subjected to an input radio frequency voltage, which causes deformations in the piezoelectric substrate. These deformations produce an auditory wave that travels between two IDTs. The mechanical energy was converted back to radiofrequency voltage when it reached the receptor IDTs. The wave propagation characteristics will be modulated by the adsorption and desorption of gas on the polymer coating on the gap. Between the input and output voltages, a phase or frequency change will be recorded. (Milella, 1998).

The aforementioned two types of devices have very low detect limits (less than 1 ppm). Adsorption of a very small amount of analyte can be detected through frequency change since the piezoelectric crystal is sensitive to mass uptake. Piezoelectric crystal devices have low selectivity for the same reason. Conducting polymers solely serve as active layers in this system, tuning the surface property of the crystal to improve the sensors' detect limit (by adsorbing more analyte molecules) and selectivity (by establishing particular interactions with analytes). Other polymers can, in fact, fill this job.

1.15.4 Amperometric sensors

The amperometric approach has also been used to detect gases. This sensor typically has a divided cell with a working electrode made of conducting polymer, metal, or Nafion. In Nafion films, the supporting electrolyte is commonly an inorganic acid that provides H^+ ions for ionic conductivity..

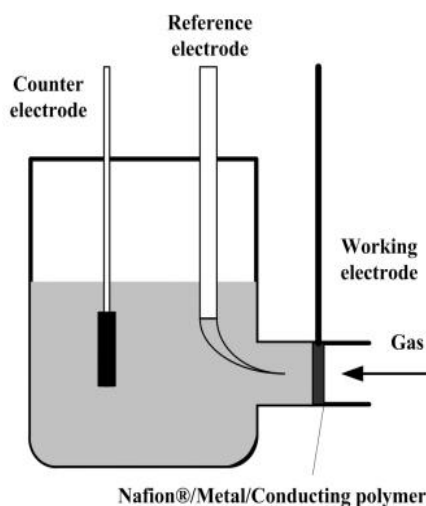


Figure 1.8: Configuration of a type of electrolytic cell for gas sensing.

The sensing mechanism is the same as that of other amperometric solutions sensors. The analyte molecules are anodic oxidised or cathodic reduced when a suitable voltage is given to the electrode, resulting in a current change.

1.16 SAMPLING TECHNIQUES FOR AIRBORNE ISOCYANATE

Because the compounds occur as a range of chemical species in workplace atmospheres, such as monomers, oligomers, or polymers, sampling and analysis of airborne isocyanate, as well as determining exposure, are difficult tasks. They can also exist as vapours, aerosols, or as particulate matter adsorbed on them (Streicher, 2000). Other than isocyanate, workplace air is usually a complex matrix containing a wide range of compounds such as alcohols, amines, oxidizers, dust particles, and water. All of these things can obstruct isocyanate sampling and analysis.

Isocyanates exist as a vapour or aerosol with a wide range of particle sizes due to their chemical and physical characteristics. Furthermore, the reaction between MDI and a polyol is exothermic, supplying the heat required for volatilization . As a result, end users who spray MDI-based devices may be exposed to aerosols from the material's mechanical atomization as well as vapour exposures during exothermic reactions.

The half-life, or cure rate, and particle size must also be taken into account when sampling isocyanate. In addition, multiple chemical isocyanate species monomeric, oligomeric, prepolymer, and polyisocyanate forms may be present in a single sample. Cure speeds can range from seconds to hours, depending on the type of isocyanate and the physicochemical qualities of the co-reactant (e.g., catalysis). Two-component STBL systems are thought to cure quickly once sprayed ,less than a few minutes. These qualities led to the creation of a collection of sample methods for MDI based on distinct derivatizing agents and desorption time.

When sample periods are not adjusted to the product half-life, NIOSH recommends using an impinger approach for airborne sampling during work operations that spray fast-curing isocyanate . As a result, during collection and post-collection sample preparation, isocyanate can be lost due to curing

processes. To avoid an underestimating of isocyanate, the impinger approach uses a solvent solution to catch, dissolve, and derivatize the isocyanate aerosols. In addition, impingers are inherently hazardous, potentially exposing workers to solvents such as toluene and dimethyl sulfoxide. Furthermore, impinger solvents are potentially flammable.

Isocyanate personal samples are often collected on filters by drawing a specified volume of air through a derivatizing agent-coated glass fibre filter (GFF). The derivatizing agent serves two purposes: it produces a stable urea derivative when it reacts with isocyanate, and it improves analytical detection of the isocyanate by increasing sensitivity by increasing molar absorptivity.

Isocyanate groups may be physically prevented from interacting with the derivatizing agent on the filter media by airborne dust or particulate debris. MDI, for example, might be utilised as a binder in the production of engineered wood.

The FIN-MP approach (Henriks-Eckerman et al., 2000; Kaaria et al., 2001; Sennbro et al., 2004, Mattsson et al., 2008) employs a GF/B filter (roughly double-thickness filter) spiked with twice the quantity of MP used to prepare MP-spiked GF/A described in MDHS 25/3. (400 l of 10 mg ml⁻¹ MP solution in toluene). The filter is inserted into an IOM head and pumped at a rate of 2 litres per minute. After sampling, 2 ml of the MP in-toluene solution (10 mg ml⁻¹ MP solution in toluene) used to create the MP-coated filters (10 mg ml⁻¹ MP solution in toluene) was added to imitate field desorption in these studies. The toluene solution is evaporated to dryness under N₂ after being allowed to stand for 2 hours, and the filter is then extracted with 5ml of acetonitrile.

The Rudzinski sampler is a PUF sampler that has been spiked with 3 ml of MP reagent solution (10 mg ml⁻¹MP solution in toluene), dried, and then placed in an IOM head with a backup MP-impregnated GF/A produced as described for MDHS 25/3. This sampler has a sampling rate of 2 l min⁻¹. To imitate field desorption in these studies, 2 ml of the MP-in-toluene solution used to create the MPcoated filters (10 mg ml⁻¹ MP solution in toluene) was added after sampling.

The toluene solution was evaporated to dryness under N₂ after being allowed to stand for 2 hours, and the PUF sampler and backupfilter were then removed with 10 ml of acetonitrile. Before analysis, the extract is dried under N₂ and the sample is treated as needed before being desorbed into 2 ml of acetonitrile.

Active and passive air-sampling methods can be divided into two categories. Pumps give the air sample to the collection device in active systems (McClenny, 2006), and the volume sampled is determined by flow rate and sampling duration. Passive sampling relies on diffusion and does not require the use of a pump (Deutsche, 2006).

1.17 PROPERTIES AND PHYSICAL CHARACTERIZATION

Table1.1: PROPERTIES

PROPERTIES	CHARACTERISTICS
Group/family of Chemical compounds	Isocyanides
Form	When exposed to air, a colourless liquid or crystal with a pungent odour turns pale yellow.
Physical Status	At room temperature, it can be found as a liquid or as crystals.
Colour	Colourless to pale yellow
Odour	Distinctpungent,sweet,fruity,odour detectablearound0.7 mg/m3
Solubility	Very soluble in acetone and benzene. Sparingly soluble in water, rapidly hydrolyzes in water
Temperature of Autoignition:	620C
Explosion Limits	For2,4-TDI Concentration (%v/v) Lower 0.9% Upper 9.5%

Boiling Point	At 760mmHg 2510 C At 10mmHg 1200 C for 2,4-TDI 1210 C for commercial mixture
Density(g/cm ³)	2,4-TDI 1.22g/m
Vapour Pressure Pa at 200 C	1.3
Relative vapour density	6.0
FlashPoint	Open cup 135 (2,4-TDI) Closed cup 127
Reference Exposure Level (0.3 ppb)	2 µg/m ³
Critical effect	Asthmatic response in non-sensitized humans with asthma
Molecular formula	C ₉ H ₆ N ₂ O ₂

CHAPTER - 2

LITERATURE SURVEY

Isocyanates and amines were analysed in the workplace atmosphere during the production of polyurethane-coated wire (Christina Rosenberg, 1984). The development and characterization of polymeric based sensing devices, mainly focused on developing novel smart textiles based on conducting polymer coatings deposited on foam substrate (Brady, Kate Lau, 2005).

Experimental characterization of electrochemically polymerized polycarbazole film and study of its behavior with different metals contacts was reported. (Aditi Srivastava, P. Chakrabarti, November 2017). Trace analysis of isocyanate gas in industrial atmospheres was done using gas chromatography and electron capture detection. A gas chromatographic method for the trace analysis of isocyanates in industrial atmospheres had been developed (G. Skarping, C. Sango, 1980). A fluorescence sensory polymer containing the pentyptcene and tetraphenyl ethylene units linked by acetylene was synthesized for direct detection of isocyanates in air (Khama Rani Ghosh, 2014). Evaluation of Total Isocyanate-in-Air Method Using I-(2Methoxyphenyl) piperazine and HPLC was reported to have significant success. (David A Bagon, Charles J Warwick, 2013). A routine method using micro-LC for the determination of toluene diisocyanate (TDI) in air was reported (Michael Boutin, Andre Dufresne, September 2005). Occupational exposure to 2,4- and 2,6-toluene diisocyanate (2,4- and 2,6-TDI) was measured during the production of flexible foam. (Ari Hirvonen, Hannu Norppa, 2001; M. Dalene, 1985). A new sampling technique was proposed by Keller and Sandridge employing PNBPA derivatives, in which sampling time was reduced to two minutes or less. (Jeffrey D. Graham, 1980). The chromatographic problems associated with excess derivatizing agent, in the commonly used HPLC method for determination of isocyanates had been eliminated. (Daniel. C. Hakes, Glenn. D. Johnson, 1986). Ion mobility spectrometer with a nonradioactive ionization source that can be operated in pulsed mode, which offers the advantage of introducing delay times after the ionization was reported. (Wolfgang Baether, Stefan Zimmermann,

2012). Sampling of Isocyanates in air in industrial hygiene and medical studies involving the measurement of isocyanates in air, a need exists to determine concentrations over varying periods of time at levels down to low ppb ranges. (R. L. Sandridge, Jiirgen Keller, 1979). Literature has been reported principally for the determination of isocyanates in relatively concentrated solutions (Kalman Marcali, 1956). Polythiophene (PT) Nanoparticles have been synthesized by oxidative emulsion polymerization of Thiophene monomer in the presence of copper nitrate catalyst (Dr.S. Sakthivel, A. Boopathi, 2014). Combined use of miniaturized non-conventional aspiration-type ion mobility spectrometer (IMS; referred as ion mobility cell, IMCell) and metal oxide semiconductor (MOS) gas sensor for detecting toxic chemical vapours in a continuous 1–2 l/min flow-through system was investigated. (MikkoUtriainen, 2003). Application of Tryptamine as a Derivatizing Agent for Airborne Isocyanate Determination. Evaluation of Total Isocyanates Analysis by High-performance Liquid Chromatography with Fluorescence and Amperometric Detection was investigated. (Weh S. Wu, Robert E. Stoyanoff, 1990). Quartz-enhanced photoacoustic spectroscopy (QEPAS) sensor had been developed for the sensitive detection of ethyleneat 10.5 μm using a continuous-wave distributed-feedback quantum cascade laser. (Zhen Wang, Zhili Li, 2016). Highly Sensitive and Selective Chemiresistor Gas/Vapor Sensors based on Polyaniline Nanocomposite was investigated (Sadananda Pandey). A gas sensor based on the incorporation of electrochromic polymers into an optic device was reported (B. Kondratowicz, R. Narayanaswamy, 2001). Regio regular polythiophene field-effect transistors was employed as chemical sensors. Soluble alkyl- and alkoxy-substituted regiochemically defined polyterthiophenes were used as active layers in sensing organic thin films transistors (OTFTs)(L. Torsia, A. Tafuria, 2003).

CHAPTER 3

AIM AND SCOPE

3.1 AIM

The aim of the research work is to fabricate a chemiresistor which will sense toxic isocyanate gas

3.2 OBJECTIVES

- Preperation of films of three conducting polymers
- Modifying the concentration of the polymer solution to be coated to optimize film thickness
- Coating of polymer on an ITO-coated glass substrate.
- A chemical resistor fabrication and respond studies
- The polymer coated substrates are set in contact with the TDI gas by passing the gas onto the substrates and testing the substrates for changes after certain interval
- Development of Prototype for enabling a complete setup to analyse the detection properties of polymers coated on substrates.

3.3 SCOPE

- Toluene di-isocyanate is a strong irritant to the eyes, skin, gastrointestinal tract, and respiratory system
- It can cause euphoria ataxia and mental aberrations. Signs and symptoms of acute exposure are nonspecific and include irritation of the nose and throat, shortness of breath, vomiting, and abdominal pain.
- NIOSH (National Institute for Occupational Safety and Health) limit is 5 ppb and MSDS limit is 10 ppb for time weighted average of isocyanate concentration during 8hrs work shift.
- The model at present being used at ISRO space station is a paper-tape which proved to be a failure.
- Hence this chemiresistor for workers in propellent plant

CHAPTER4

MATERIALS AND METHODOLOGY

4.1 MATERIAL REQUIRED

- Silane
- Silicone
- N, N-Dimethyl-Formamide (99%)
- Acetonitrile (99%)
- Distilled Aniline
- Concentrated Sulfuricacid
- De-mineralized water
- Potassium Dichromate
- Methanol
- Carbazole
- Thiophene
- Ammonium Persulphate
- Dimethyl Sulphoxide (99.5%)
- Methylene Chloride(99%)
- Tetrahydrofuran
- Sodium Dodecylsulphate
- Sodium Hydroxide
- Chloroform

4.2 METHODOLOGY

4.2.1 POLYTHIOPHENE SYNTHESIS

Materials Required: Chloroform, SDS, Ferric chloride (FeCl_3), Thiophene

1. Add Chloroform 40ml and SDS 0.4g in a beaker and mix it well.
2. Again in another beaker add ferric chloride 2.8g and chloroform 90ml and mix it well.
3. Add both the prepared solution and stir for 30 min.
4. In the mixed solution add 30 ml of thiophene in a slow process and stir it for 6 hrs .
5. Now filter the solution using what-man filter paper.
6. Again filter the obtained product .



Fig: 4.1: Preparation of Polythiophene



Fig 4.2: Filtration of Polythiophene

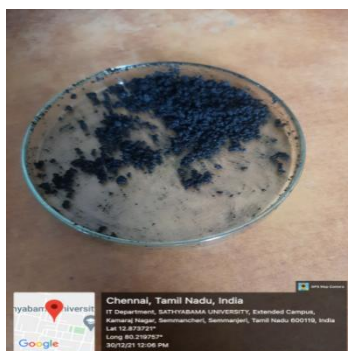


Fig: 4.3: Polythiophene Powder

4.2.2 POLYCARBAZOLE SYNTHESIS

Materials Required: Carbazole, CH_3CN (Acetonitrile), Ammonium persulphate

1. Add 0.5g of carbazole and add 50ml of CH_3CN (Acetonitrile) in a beaker
2. Place the beaker and mix it using a magnetic stirrer for 15 minutes.
3. Add 0.8g of ammonium persulphate and add 8 ml of Acetonitrile in the beaker
4. Place the Beaker and mix it using a magnetic stirrer for 15 minutes
5. Now add the Beaker II to Beaker I dropwise and let it stir for 3 hours
6. The obtained solution is black in colour
7. Add methanol and filter using whatt-man filter paper
8. The precipitate from the filter paper is collected in powder form

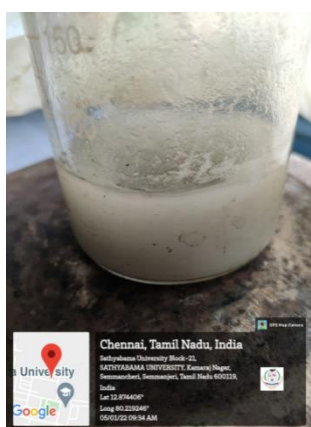


Fig 4.4: Preparation of Polycarbazole

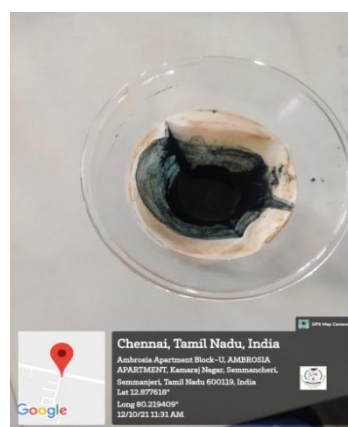


Fig 4.5: Filtration of Polycarbazole

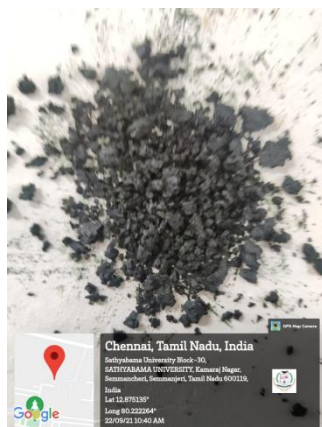


Fig 4.6: Polycarbazole Powder

4.2.3 POLYANILINE SYNTHESIS

Materials Required: Aniline, Cons H_2SO_4 , Potassium-Dichromate

1. Add aniline 20ml with 15ml of Cons H_2SO_4 in drop-wise manner .
2. Prepare a potassium dichromate solution by mixing 1g of potassium-dichromate powder and 25 ml of distilled water.
3. Add potassium-dichromate solution into previous solution using drop-wise manner.
4. Mix solution for 3.5 hrs
5. Filter the solution using what-man filter paper
6. Using doping method again filter for obtaining powder form.

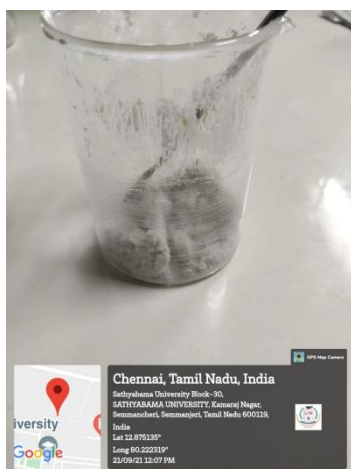


Fig 4.7: Preparation of Polyaniline



4.8: Filtration of Polyaniline

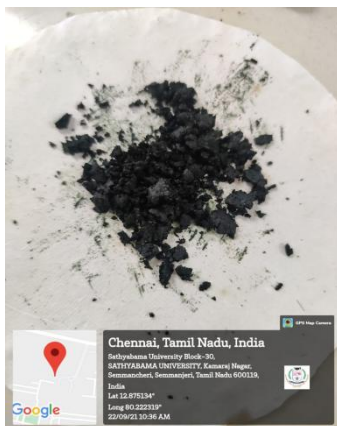


Fig: 4.9: Polyaniline Powder

4.3 PREPARATION OF POLYMER SOLUTION FOR COATING

1. The electro chemical conducting films were synthesized by dissolving the polymers into DMSO (**Dimethyl sulfoxide**) $(CH_3)_2SO$ and N,N-Dimethyl-Formamide $(CH_3)_2NCH$
2. These were taken into different composition
3. DMSO and N,N-Dimethyl-Formamide are convenient solvents which are a perfect solvent for the polymers to dissolve
4. The polymer are taken in different beaker and added each a different concentration of DMSO is added and stirred well.
5. Then the solution is transferred into a closed container and put in ultrasonic bath for 1-1.5 hrs , it is used for the dissolving the nano particles.
6. Then they were evaluated by spin coating and drop casting techniques to coat on ITO substrate , the solvent was evaporated for 10-12 hrs in dry vacuum



Fig 4.10 : Preparation Of Polymer solution



Fig 4.11 : Ultrasonication Bath



Fig 4.12 : Polymer solution

4.4 COATING AND SENSING EXPERIMENTS

The polymers was made after that, it was kept for drying purpose and followed by making thin films by dip coating, drop casting and spin coating using suitable solvents to dissolve and made coatings. The resistance values were calculated from the detection experiment made by using TDI gas passed into the thin film which we made.



Fig 4.13 : Thin Film Of Polycarbazole (Spin coating)

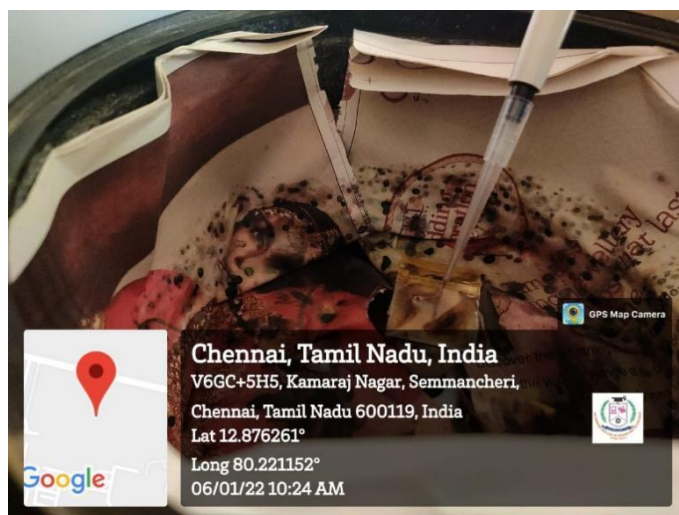


Fig 4.14 : Spin Coater

4.4.1 Spin Coating

The spin coating unit was used for making the thin films. This spin coating unit has many advantages like can change the RPM of the rotation. We have changed the RPM and made some films in which some of the films only comes good with RPM.

Steps involved in spin coating:

1. Place the substrate on the programmable spin coater
2. Drop the polymer solution on the substrate
3. Give the data set for spin coating
4. Run the program

Table: 4.1 : Spin Coating Data

Quantity(ul)	rpm	Time (sec)	substrate	sample
100	1500	55	ITO(Glass)	Polycarbazole
100	1500	55	ITO(Glass)	Polycarbazole
200	1000	50	ITO(Glass)	Polycarbazole
200	1000	50	ITO(Glass)	Polycarbazole

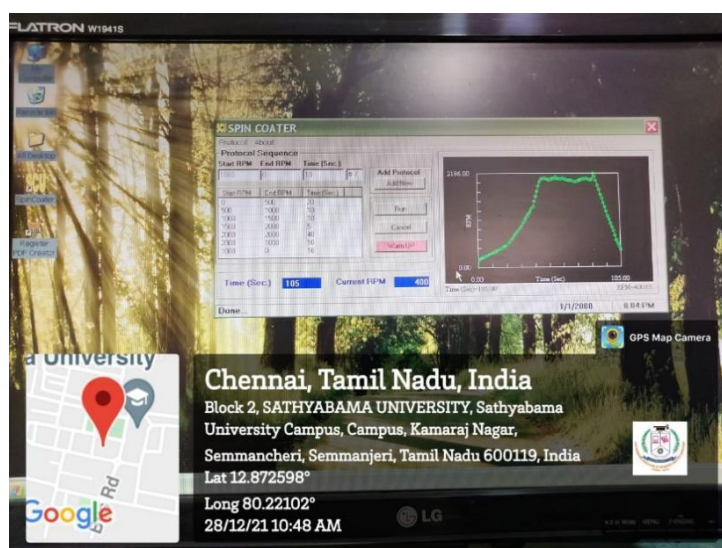


Fig 4.15 : Data For Spin Coating

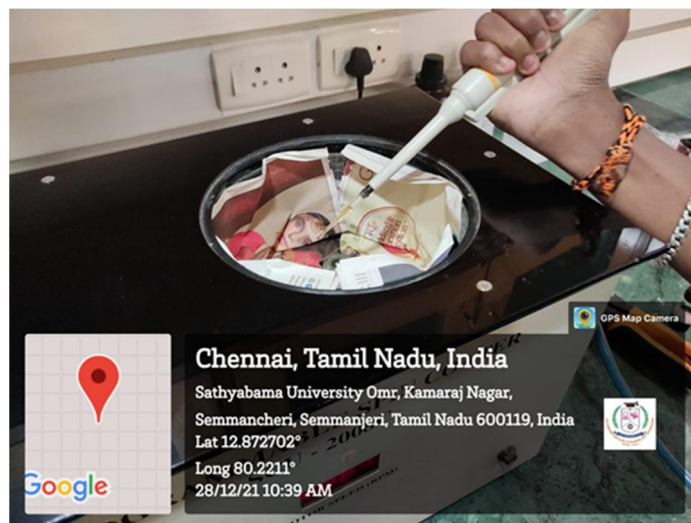


Fig 4.16 Process Of Spin Coating

4.4.2 Drop Casting Technique and Dip Coating Technique

- The coat solution is dropped on the substrate to be coated and heat is applied to the substrate to be coated in this procedure.
- The heat used causes the solvent to evaporate spontaneously, and the substrate is allowed to cool after the coat has been dropped and settled.
- The polymer coat completely settles down of appropriate thickness is formed.
- Film thickness is determined in principle by the volume of dispersion used and the particle concentration, both of which are easily adjustable. Other factors that influence the film structure include how well the solvent wets the substrate, evaporation rate, and drying capillary forces, among others.
- In terms of usage, the drop casting technique is very simple, and material waste is minimal.
- In terms of usage, the dip coating technique is very simple, and material is dipped in the solution and left for drying.
- Other factors that affect the film substrate include how well the solvent wets the substrate, evaporation rate, drying capillary forces, and so on.
- In general, volatile solvents that wet the substrate and are not susceptible

to thin film instabilities are preferred (de-wetting).

- Water is a poor solvent for drop casting because of its low vapour pressure and high surface tension. Alcohol can be substituted for water in some cases, and organic solvents such as hexane, toluene, or halogenated solvents are frequently excellent choices for coat preparation.
- In our experiment DMSO and N, N-Dimethyl-Formamide were used as a solvent for preparing the polymer mixture.

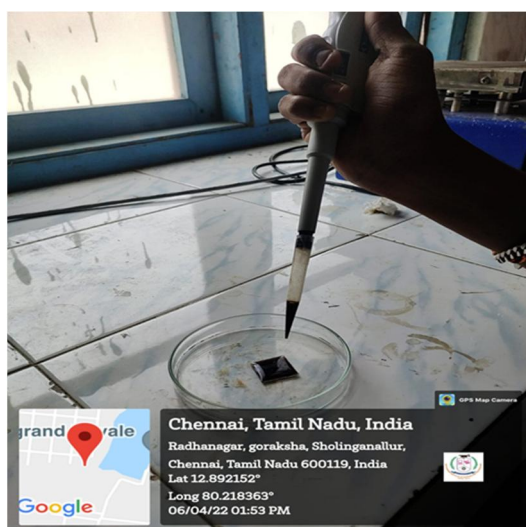


Fig 4.17 : Drop Casting Technique



Fig 4.18 : Dip Coating Technique

4.4.3 TDI Sensing Experiment

The variation of TDI to the thin film container shows the difference in the resistance and it is proof for sensing the polymers with presence of TDI content.

The TDI detection was carried out with following detailed procedure.

- Initially, the vessels and glass-wares and apparatus were taken and kept as per our requirement.
- The connections are made perfectly for detection of TDI with different concentrations.
- The setup was heated 50 degrees with 1 drop of TDI, evaporates and making the entire vessel full of TDI mixed with air.
- Then the total vessel was sucked and made the total vessel and the sensor vial is completely free of air and other gases.
- Then the TDI were added into the vessel drops of 0.5, 1, 1.5 and 2 ml of TDI were added and tested.
- The addition of TDI in different concentrations and the sensors are connected with KIT made by us and it is used for sensing the difference in the thin film when after allowed the TDI inside the vessels.
- The readings which recorded from the KIT calculated resistance from the recorded value



Fig 4.19: Gas Sensing Setup

The setup with all the required items in a single picture. Thermometer is used to measure the temperature of the vessel where the TDI was heated and evaporated.

The images of vessels and sensor KIT used for the TDI detection.

The pipeline making images in which the pipeline was shorted its length due to wastage and not a proper sensing mechanism in the total setup.

The image of total sensor setup and the image of the person who works with proper safety like mask and gloves. Electrochemical workstation for Impedance measurements to record the resistance. The electrochemical workstation is used for measuring the impedance values with and without of TDI.

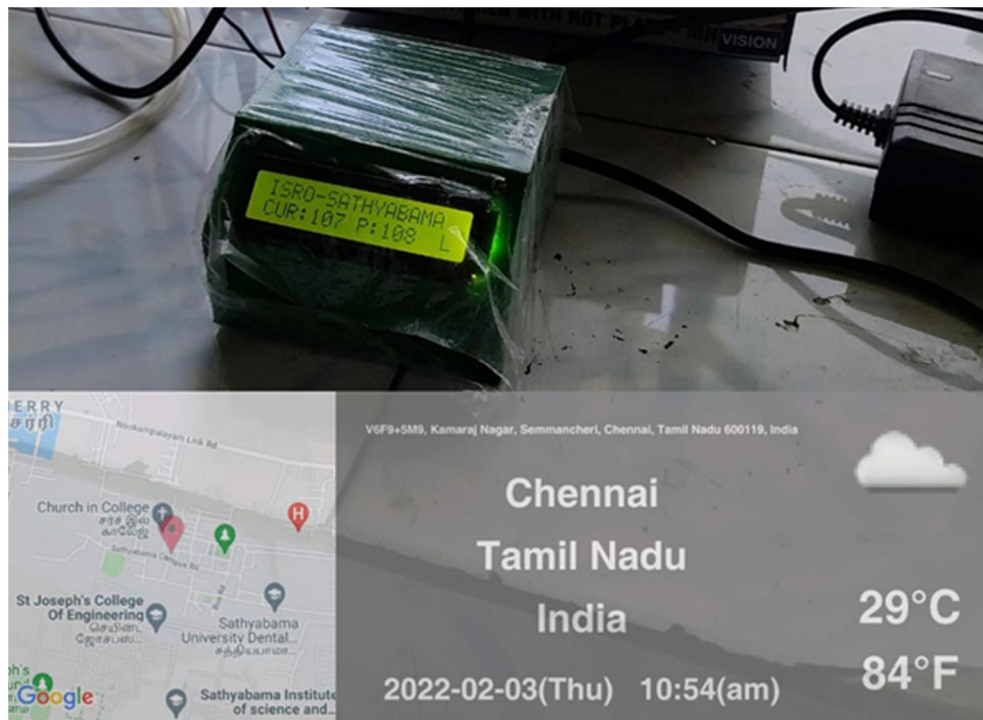


Fig 4.20 : Sensor Kit

4.5 THICKNESS OF FILM

Stylus profilometers detect the surface with a probe that is physically moved along the surface to obtain the surface height. This is accomplished mechanically by a feedback loop that measures the force exerted by the sample against the probe as it scans across the surface.

While stylus profilometry is extremely sensitive and gives high Z resolution, it is sensitive to soft surfaces and the probe can become contaminated by the surface. Some surfaces may be damaged by this procedure.

A stylus profilometer is slower than non-contact approaches because it requires physical motions in X, Y, and Z while keeping contact with the surface. The size and form of the stylus tip might affect measurements and limit lateral resolution.

The thickness of the films of polycarbazole were obtained are

Table: 4.2: Thickness Of Film

Film	Method used	Thickness (nanometer nm)
Polycarbazole	Spin coating - 5 layers	500
Polycarbazole	Spin coating - 10 layers	1100

CHAPTER 5

RESULTS AND DISCUSSIONS

5.1 POLYANILINE

5.1.1 SEM

The above figure shows FESEM image of catalyst prepared by modified Hummer's method. FESEM was performed in order to investigate surface morphology of the polymer. is a conducting polymer and is sensitive for temperature during the SEM analysis. When the sample is interacts with electron it will generate a few amount of heat which leads to cracks in the samples. It can be seen in the SEM image that the particles are well defined and also observed that are highly dispersed with agglomeration. The aggregation of these particles is due to the effect of heating. All the particles are spherical in shape with slightly agglomerated.

EDAX was done to reveal the chemical composition of the prepared catalyst and the weight percentages are given in the below table.

Table: 5.1 : Polyaniline Composition

S.No	Element	Weight%	Atomic%
1.	C	39.29	49.16
2.	N	18.81	20.18
3.	O	23.82	22.37
4.	S	17.11	8.02
5.	Cr	0.43	0.13
6.	Fe	0.55	0.15

Base(12)

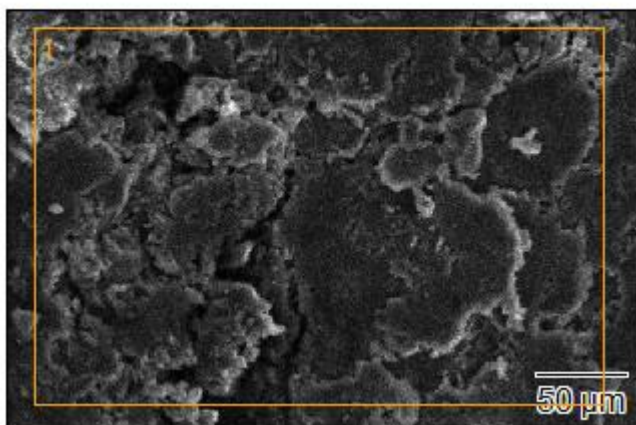


Image Name:	Base(12)
Image Resolution:	512 by 340
Image Pixel Size:	0.68 μm
Acc. Voltage:	20.0 kV
Magnification:	1200

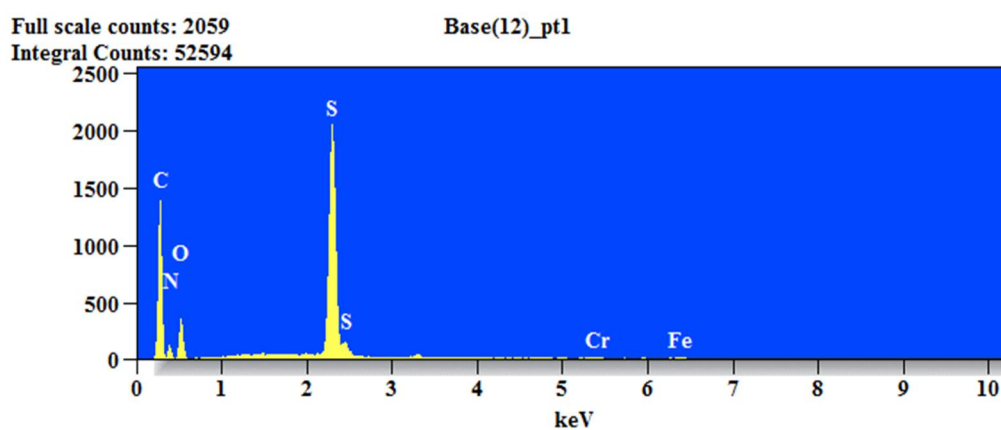


Fig 5.1 : EDAX Of Polyaniline

5.1.2 RAMAN GRAPH

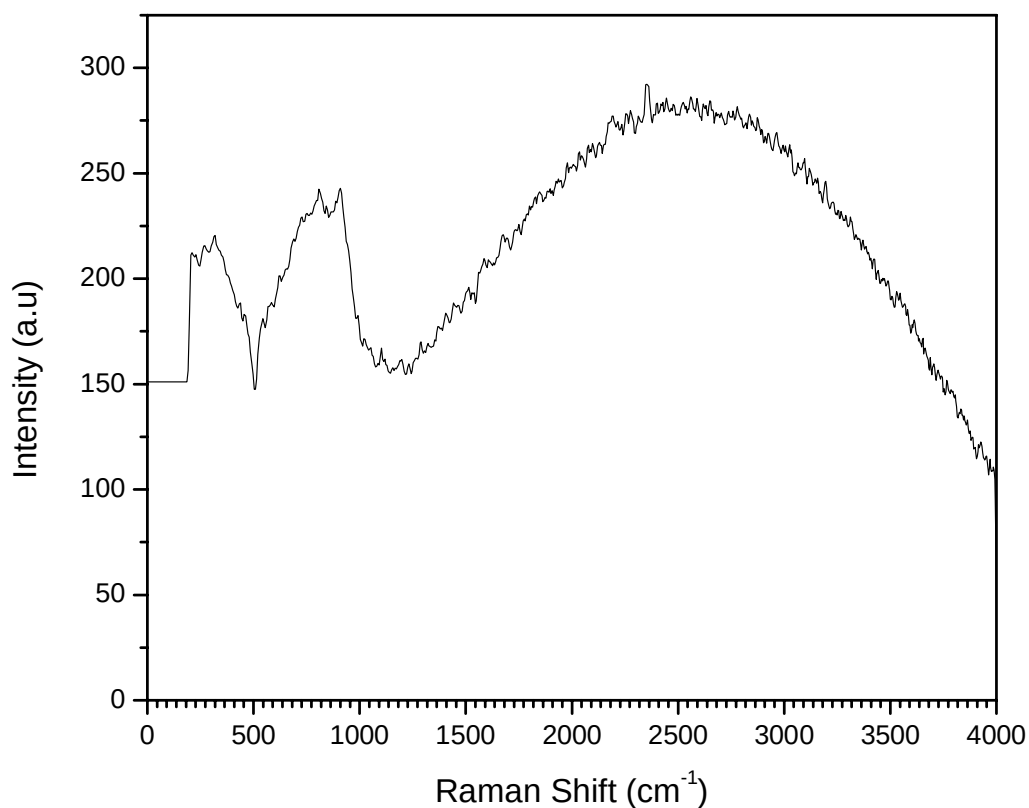


Fig 5.2 : RAMAN Of Polyaniline

Raman spectroscopy has demonstrated to be a useful analytical tool to investigate conducting polymers. Raman spectra of as shown in the above figure presented characteristic bands at 1170 (C-H bending); 1206 (C-N stretching); 1502 (C=N stretching); 1560 (N-H bending) and 1598 cm⁻¹ (C=C stretching) [1]. The conductive nature of can be associated to the band located at 890 cm⁻¹ assigned to deformation C-N of secondary amine next to aromatic ring in the polaronic form C-N⁺-C, and to the band at 1343 cm⁻¹ that is assigned to vibration of a delocalized polaron structure.

5.1.3 XRD GRAPH AND DETAILS

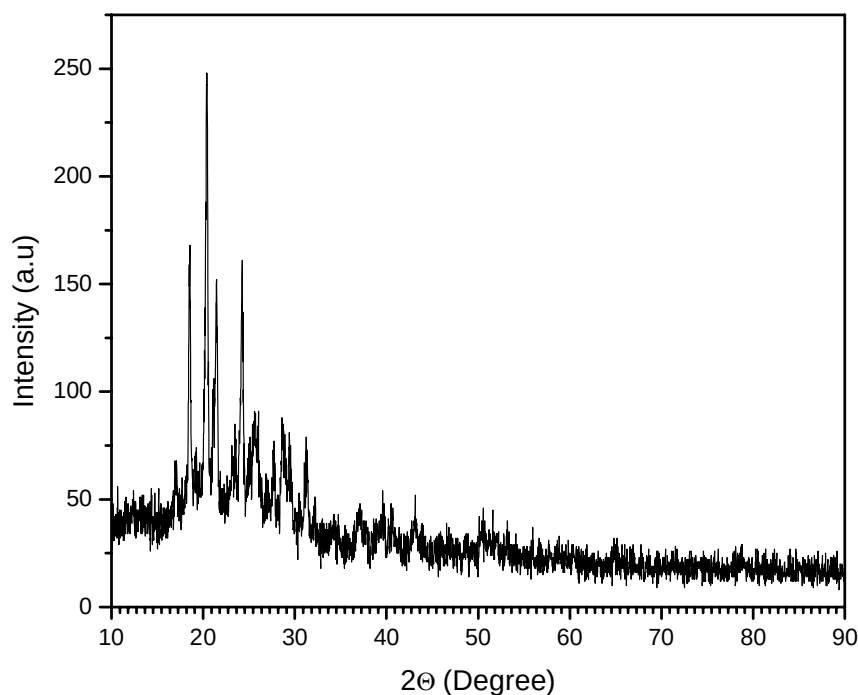


Fig 5.3 : XRD Of Polyaniline

This is the simple example template containing only headers for each report item and the bookmarks. The invisible bookmarks are indicated by text between brackets.

Modify it according to your own needs and standards.

The crystallinity degree of polymeric compounds is determined using XRD. The crystalline orientation of a conducting polymer is fascinating because a more highly-ordered system could exhibit a metallic property like conductive state. The crystalline phase may be identified in XRD spectra at $2\theta = 18^\circ, 20^\circ, 21^\circ$, and 24° , which is a sign of a more organised structure, as shown in the above picture.

Measurement Conditions Of Polyaniline :

Raw Data Origin	XRD measurement (*.XRDML)
Scan Axis	Gonio
Start Position [°2Th.]	10.0000
End Position [°2Th.]	90.0000
Step Size [°2Th.]	0.0200
Scan Step Time [s]	0.9765
Scan Type	Continuous
Offset [°2Th.]	0.0000
Divergence Slit Type	Fixed
Divergence Slit Size [°]	1.0000
Specimen Length [mm]	10.00
Receiving Slit Size [mm]	0.1000
Measurement Temperature [°C]	25.00
Anode Material	Cu
K-Alpha1 [Å]	1.54060
K-Alpha2 [Å]	1.54443
K-Beta [Å]	1.39225
K-A2 / K-A1 Ratio	0.50000
Generator Settings	0 mA, 0 kV
Diffraction Number	0
Goniometer Radius [mm]	240.00
Dist. Focus-Diverg. Slit [mm]	91.00
Incident Beam Monochromator	No
Spinning	No

Main Graphics, Analyze View

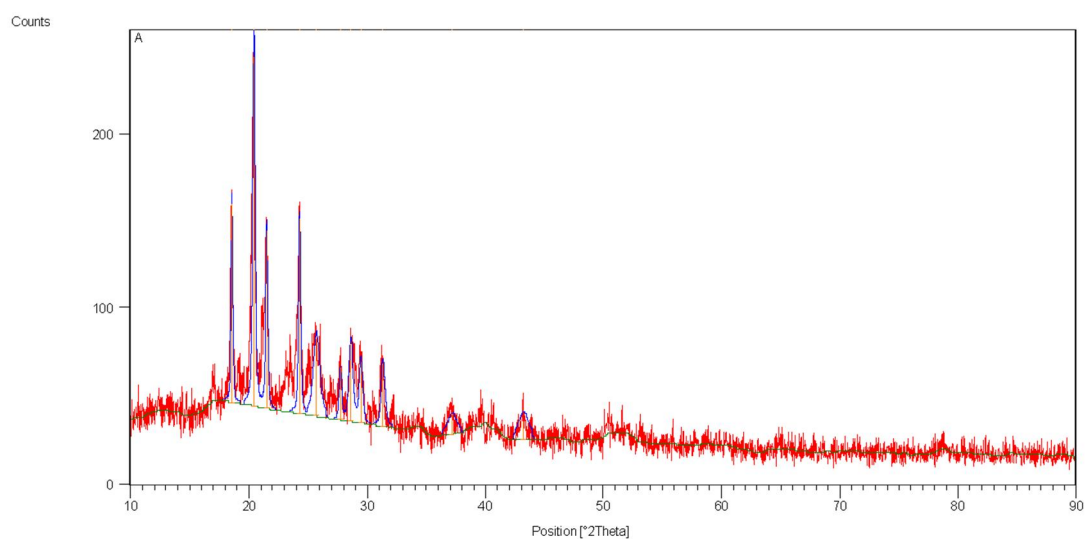


Fig 5.4 : XRD Main Graph Of Polyaniline

Table 5.2 :Peak List Polyaniline

Pos. [°2Th.]	Height [cts]	FWHM [°2Th.]	d-spacing [Å]	Rel. Int. [%]
18.5287	113.91	0.1574	4.78872	56.93
20.4215	200.07	0.2362	4.34896	100.00
21.4779	101.81	0.1968	4.13739	50.89
24.2558	111.27	0.1968	3.66948	55.61
25.7293	42.97	0.6298	3.46257	21.48
27.7009	28.61	0.2362	3.22044	14.30
28.6238	43.25	0.3936	3.11867	21.61
29.4616	34.14	0.3149	3.03187	17.06
31.3376	35.42	0.3936	2.85452	17.70
37.1465	11.07	0.9446	2.42040	5.54
43.1869	10.67	1.1520	2.09310	5.33

5.1.4 FT-IR

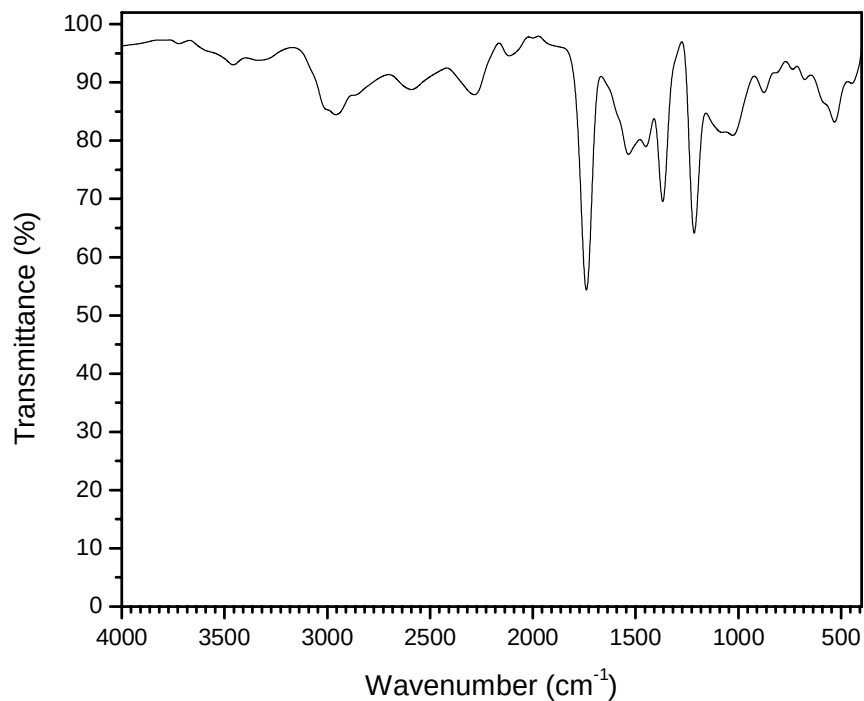


Fig 5.5 : FT-IR Of Polyaniline

Figure depicts the results of synthesised FT-IR measurements. The stretching modes of (C=C) on the quinonoid ring and (C=C) on the benzenoid ring are represented by the bands at 1562 and 1479 cm^{-1} , respectively. The 1479 cm^{-1} peak, which is lower than the 1560 cm^{-1} peak, can be seen. This demonstrates that the benzenoid rings in the synthesised polyaniline are fewer than the quinoid rings. Furthermore, the peaks at 1302 and 1246 cm^{-1} were attributed to secondary aromatic amine (C-N) stretching and polarone lattice (C-N+ •) stretching, respectively.

Table: 5.3 : Bonding Of Polyaniline

Wave Number	Bond
2924	C-H
1302	C-N
1479	C=C
3422	NH-H Stretching

The synthesis conditions determine the creation of morphology. Polyaniline powders with a granular morphology are most commonly made by precipitation polymerization with strong oxidants and high aniline concentrations under very acidic conditions, such as pH 2.5. The FESEM picture of POLYANILINE catalyst made using a modified Hummer's technique is shown above. The surface morphology of the polymer was investigated using FESEM. POLYANILINE is a conducting polymer that is temperature sensitive during SEM investigation. When a sample meets with an electron, it produces a little quantity of heat, which causes the sample to crack. The particles are well defined in the SEM picture, and they are also observed to be significantly scattered with aggregation. The effect of heating causes these particles to clump together. All of the particles are somewhat agglomerated and spherical in form. This process produces polyaniline that is strongly aggregated, and fast sedimentation from solution is common

5.1.5 SEM IMAGES

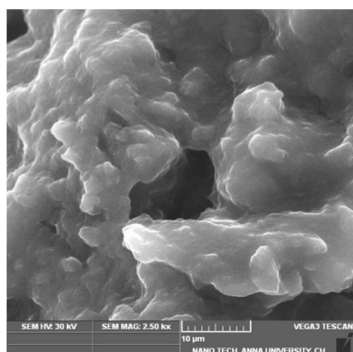


Fig 5.6 A : SEM Of Polyaniline

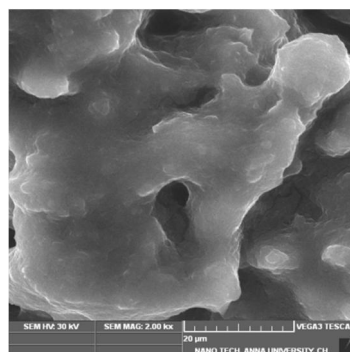


Fig 5.6 B : SEM Of Polyaniline

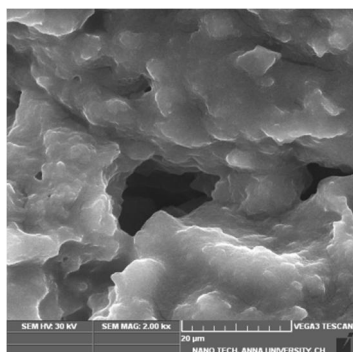


Fig 5.6 C : SEM Of Polyaniline

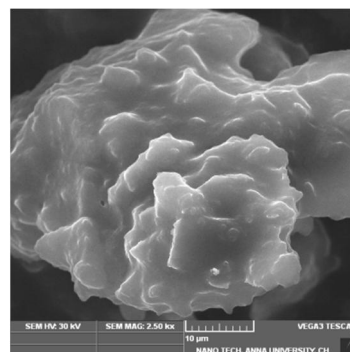


Fig 5.6 D: SEM Of Polyaniline

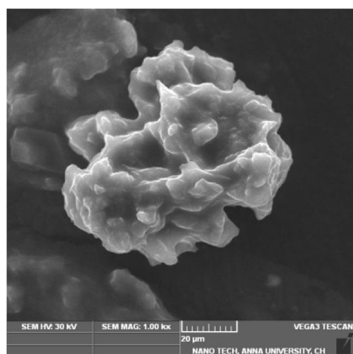


Fig 5.6 E : SEM Of Polyaniline

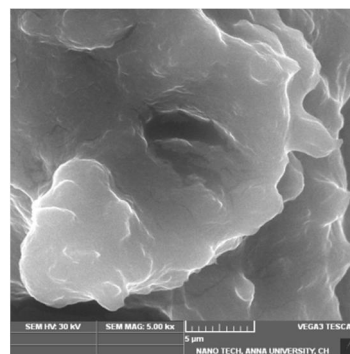


Fig 5.6 F : SEM Of Polyaniline

5.2 POLYCARBAZOLE

5.2.1 SEM

The reported SEM images revealed the polycarbazole morphologies depending on the preparation procedure. The typical SEM image of polycarbazole indicates that the polymer has irregular shape with sizes of about several micrometers. As it could be observed from the SEM image has small spheres and shows good conductivity in TDI detection.

EDAX was done to reveal the chemical composition of the prepared polycarbazole catalyst and the weight percentages are given in the below table.

Table:5.4 : Polycarbazole Composition

S.No	Element	Weight%	Atomic%
1.	C	28.86	38.15
2.	N	19.47	22.08
3.	O	28.53	28.32
4.	S	23.14	11.46

Base(13)

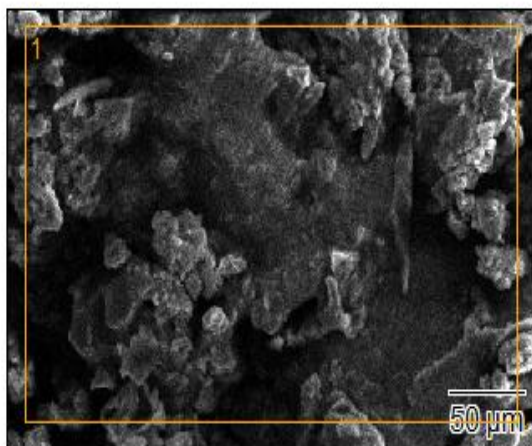


Image Name:	Base(13)
Image Resolution:	512 by 340
Image Pixel Size:	0.68 μm
Acc. Voltage:	20.0 kV
Magnification:	1200

Full scale counts: 4229
Integral Counts: 85668

Base(13)_pt1

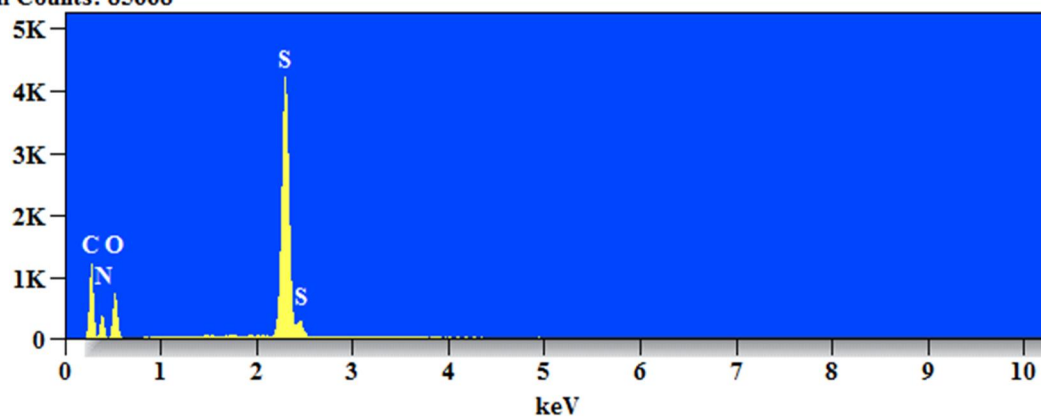


Fig 5.7 : EDAX Of Polycarbazole

5.2.2 RAMAN GRAPH

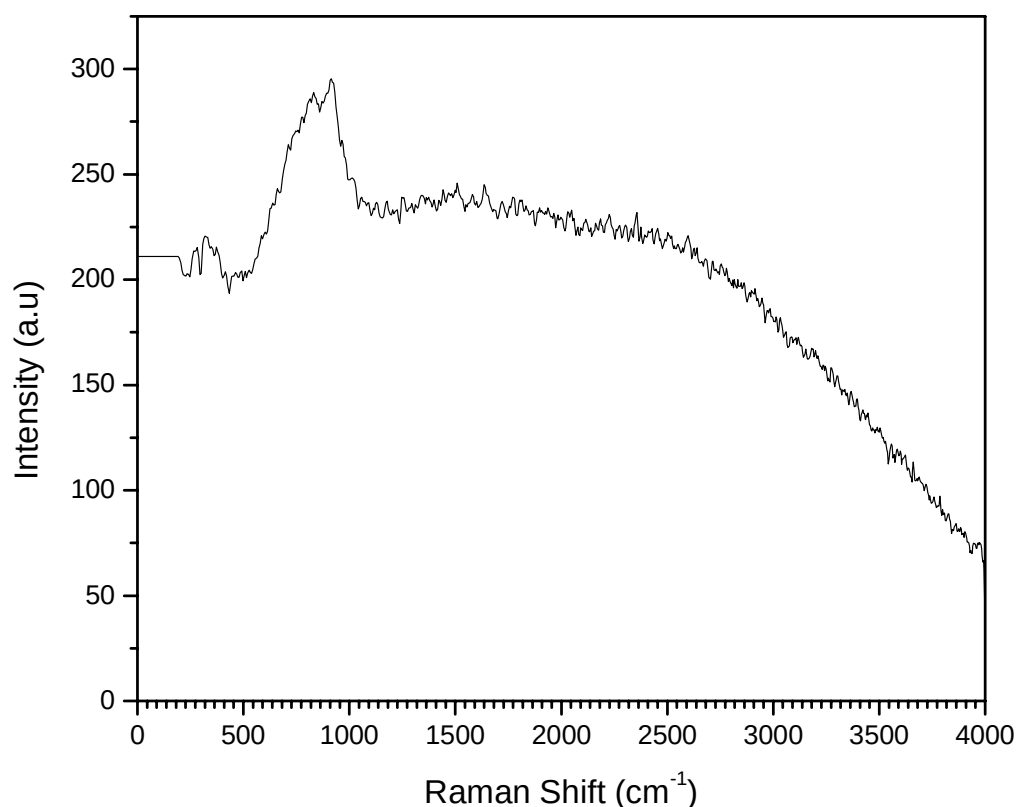


Fig 5.8 : RAMAN Of Polycarbazole

The Raman spectra of PC are shown in the diagram above. The PC polymer has a C-O stretching absorption band at 1016 cm⁻¹ and an aromatic absorption band at 1378 cm⁻¹. Bending of the C-H axis. C=C stretching causes the band at 1520 cm⁻¹, while C=O stretching causes the band at 1605 cm⁻¹. Excitation with wavelengths closer to the electronic peak of the substance, as well as any photochemical reactions that may occur, dramatically increases Raman line intensities. The intensity of Raman peaks is determined by the source's intensity, active groups, and polarizability.

5.2.3 XRD GRAPH AND DETAILS

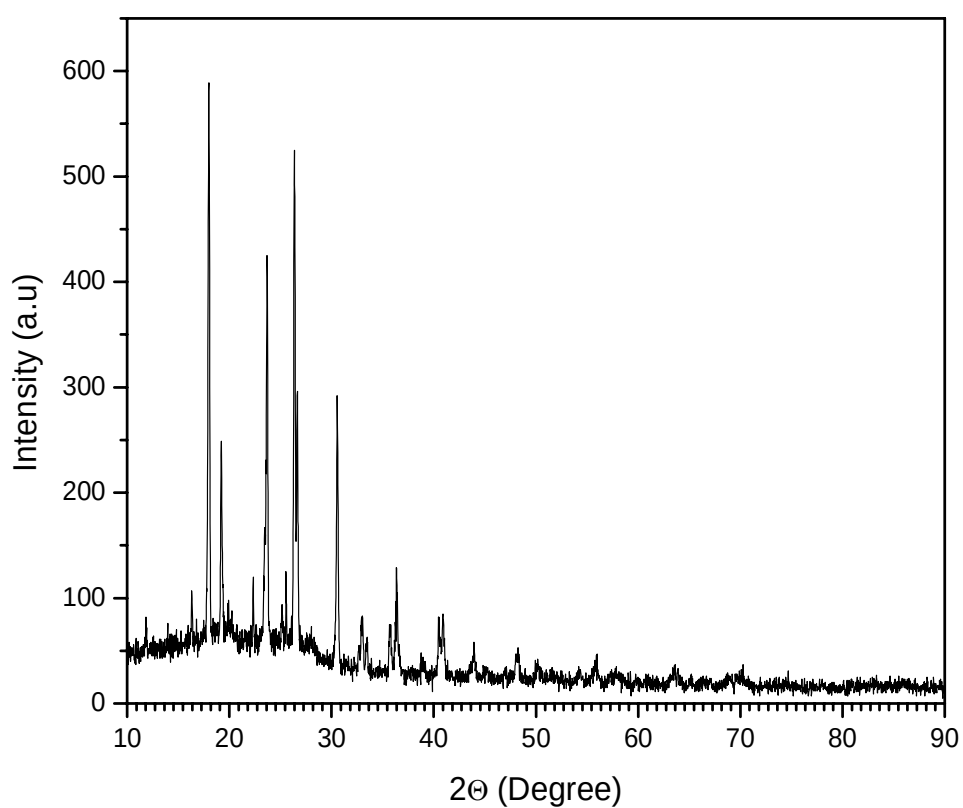


Fig 5.9 : XRD Of Polycarbazole

Measurement Conditions:

Raw Data Origin	XRD measurement (*.XRDML)
Scan Axis	Gonio
Start Position [°2Th.]	10.0000
End Position [°2Th.]	90.0000
Step Size [°2Th.]	0.0200
Scan Step Time [s]	0.9765

Scan Type	Continuous
Offset [°2Th.]	0.0000
Divergence Slit Type	Fixed
Divergence Slit Size [°]	1.0000
Specimen Length [mm]	10.00
Receiving Slit Size [mm]	0.1000
Measurement Temperature [°C]	25.00
Anode Material	Cu
K-Alpha1 [Å]	1.54060
K-Alpha2 [Å]	1.54443
K-Beta [Å]	1.39225
K-A2 / K-A1 Ratio	0.50000
Generator Settings	0 mA, 0 kV
Diffractionmeter Number	0
Goniometer Radius [mm]	240.00
Dist. Focus-Diverg. Slit [mm]	91.00
Incident Beam Monochromator	No
Spinning	No

Main Graphics, Analyze View :

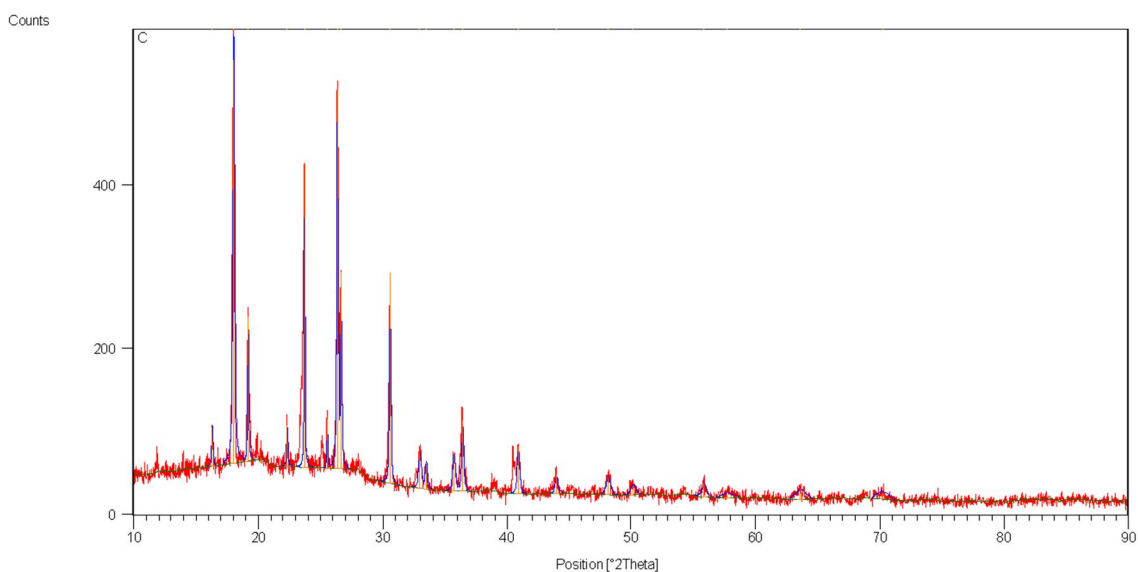


Fig 5.10 : XRD Main Graph Of Polycarbazole

Table 5.5 : Peak List Polycarbazole

Pos. [°2Th.]	Height [cts]	FWHM [°2Th.]	d-spacing [Å]	Rel. Int. [%]
16.3262	46.11	0.1181	5.42946	9.43
18.0145	488.90	0.1771	4.92425	100.00
19.2040	174.67	0.0984	4.62183	35.73
22.3394	49.17	0.1181	3.97973	10.06
23.7061	370.32	0.0787	3.75331	75.75
25.5607	59.53	0.0787	3.48503	12.18
26.3507	458.32	0.1181	3.38231	93.74
26.6449	239.38	0.0984	3.34563	48.96
30.5585	254.59	0.1181	2.92549	52.07
32.9710	41.93	0.2362	2.71674	8.58
33.4677	31.19	0.1968	2.67755	6.38
35.6961	42.51	0.2362	2.51534	8.69
36.3952	85.21	0.1574	2.46861	17.43
40.9003	56.11	0.1968	2.20651	11.48
43.9697	21.77	0.2362	2.05934	4.45

48.1611	20.63	0.3936	1.88946	4.22
50.1682	12.94	0.4723	1.81847	2.65
55.8516	16.28	0.4723	1.64615	3.33
57.7350	6.16	0.9446	1.59685	1.26
63.5831	11.29	0.9446	1.46335	2.31
70.2012	6.56	1.1520	1.33962	1.34

The PCz XRD pattern is depicted in the diagram above, and it comprises of three primary peaks at 218o, 23o, and 26o, as well as three smaller peaks at 50, 57, and 70o. Sharp diffraction peaks at 18, 23, and 26 degrees are attributed to periodicity parallel to the polymer chain, but weak peaks at high angles are attributed to periodicity perpendicular to the polymer chain .

5.2.4 FT-IR

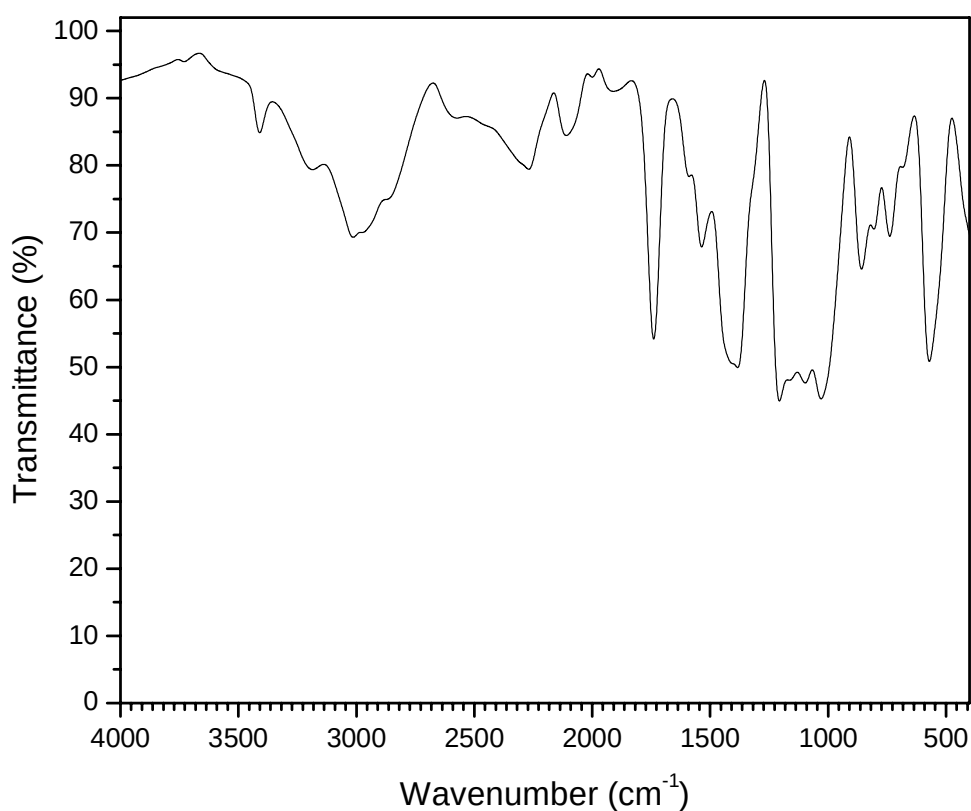


Fig 5.11 : FT-IR Of Polycarbazole

The FTIR spectra of polycarbazole are shown in the diagram above. The O-H group is ascribed to the strong band in polymer at 3401cm^{-1} . The absorption was powerful and widespread. After electrochemical oxidation, all of the peaks become broader, as seen for the N-H group, which was displaced to 3547cm^{-1} . The nitrile group is responsible for the IR spectra of PC at 2243cm^{-1} . The C-H stretching vibration mode of PC is responsible for the bands at 2956cm^{-1} and 2869cm^{-1} . Aromatic ring is represented as a band in the spectral range of $1400\text{-}1600\text{cm}^{-1}$. The CH₂ group is responsible for the band at 1325cm^{-1} . C-N and C-C groups are assigned to the bands at 1191cm^{-1} and 1325cm^{-1} , respectively [1]. The band at 1620cm^{-1} may be attributed to C=O group and the band at 1215cm^{-1} attributed due to C-O group.

5.2.5 SEM IMAGES

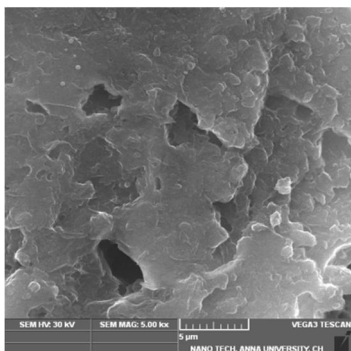


Fig 5.12 A : SEM Of Polycarbazole

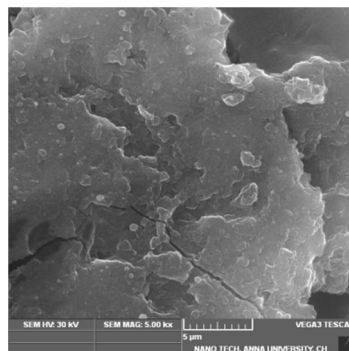


Fig 5.12 B : SEM Of Polycarbazole

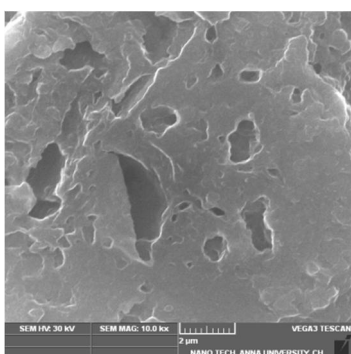


Fig 5.12 C : SEM Of Polycarbazole

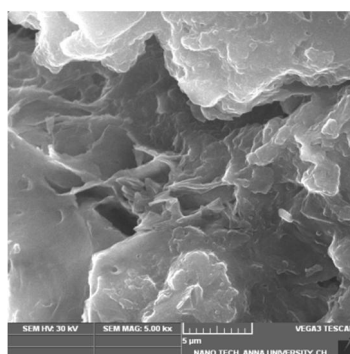


Fig 5.12 D : SEM Of Polycarbazole

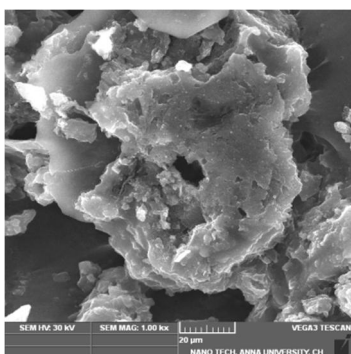


Fig 5.12 E : SEM Of Polycarbazole

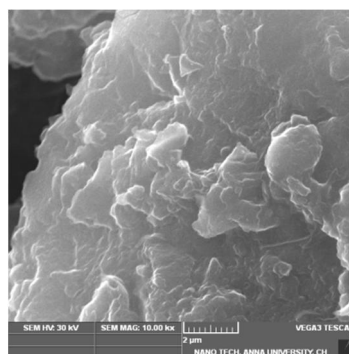


Fig 5.12 F: SEM Of Polycarbazol

CHAPTER 6

CONCLUSION

Sensor prototype for detecting isocyanates is proposed in the research work and films of conducting polymers were made for the detection of isocyanate gas. The polymers were selected based on the literature survey and only three polymers showed response to isocyanate gas in electrochemical workstation. Hence further work was carried out to prepare polyaniline, polythiophene, polycarbazole and blended polymers such as polyaniline-polythiophene, polyaniline-polycarbazole and polycarbazole-polythiophene. The polymers were coated on indium tin oxide films by three coating techniques: Dip Coating, Drop coating and Spin coating. Thickness of the spin coated films were found by Stylus profilometer. The polymers were characterised by XRD, SEM, FTIR and Raman spectra. All the polymer samples were characterised at the stage of powder form and also at the stage of thin film and their presence were confirmed. A prototype to electronically sense the isocyanate was fabricated using Arduino software. The detailed studies were carried out to check the complete electrical property and detection of isocyanate with various concentration of isocyanates. Since Polythiophene did not show any response to isocyanate gas, further trials were carried out using poly aniline and poly thiophene. Poly Aniline showed a declining and erratic response to isocyanate gas, whereas polycarbazole showed a robust response to isocyanate exposure. Repeatability studies were carried out with polycarbazole with a variance of $\pm 0.1-0.5$. Hence it can be concluded that Polycarbazole has shown better isocyanate detection in closed container with help of electronic prototype kit.

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