SYNTHESIS & CHARACTERIZATION OF SENSING MATERIAL FOR REAL TIME MONITORING OF PROTIEN RICH FOOD

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CERTIFICATE

This is to certify that work in this thesis has been completed by Ms. Nimra Amanullah, Mr. Rehan Ali, Mr. Shawaiz Ali Sabir and Mr. Shahzad under the supervision of Dr. Iftikhar Hussain Gul and Dr. Uman Liaqat at the school of Chemical and Materials Engineering (SCME), National University of Science and Technology, H-12, Islamabad, Pakistan.

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DEDICATION

With profound reverence,

We dedicate this project to our **beloved parents**, **respected teachers**, and **lab engineers** whose guidance and unflinching support helped us throughout the process.

DECLARATION

We, **Nimra Amanullah**, **Rehan Ali**, **Shawaiz Ali Sabir**, and **Shahzad** declare that this thesis titled " **SYNTHESIS & CHARACTERIZATION OF SENSING MATERIAL FOR REAL TIME MONITORING OF PROTIEN RICH FOOD**" is our original work completed as a prerequisite for the fulfilments of our bachelor's degree in Metallurgy and Materials Engineering. Under the supervision of Dr. Iftikhar Hussain Gul and co-supervision of Dr. Usman Liaqat, we conducted the research, analyzed the data, and formulated the conclusions with no plagiarism. All sources used have been appropriately cited, and ethical guidelines have been followed. This work is submitted to the Department of Materials Engineering SCME as a requirement for the completion of our bachelor’s degree program.

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ABSTRACT

Real time monitoring of food is essential to ensure the safety and quality of food with the growing demand for food around the globe. However, means to monitor food are becoming more and more abundant, as the economy develops, and the pursuit of good quality food becomes stronger. Traditional methods of spoilage monitoring of food are either time consuming, lab extensive, need expertise and cause significant damage to food, so such methods are required that are less time consuming, non-destructive, fast and does not need any expertise for the spoilage monitoring of food. This project aims to synthesize sensing material for real time food monitoring. PSMA (poly styrene co maleic anhydride) will be used for real time spoilage monitoring of food by measuring volatile biogenic amines. PSMA is a biomarker of biogenic amines released when food starts to degrade. PSMA is used for real time monitoring of key food spoilage marker gas (e.g. Ammonia) and gives LOD value of 55ppm by maintaining excellent stability under various storage conditions. This material can be the life safer for food authorities that use conventional, expensive and laboratory dependent methods. The material synthesis is addressing industrial and societal problems related to food spoilage, such as reducing food waste, ensuring food safety, and promoting responsible consumption and production. PSMA will be synthesized using Styrene and Maleic Anhydride units and several characterization steps such as Fourier Transform Infrared Spectroscopy (FTIR), X-ray diffraction (XRD), and Impedance analyzer will be used to ensure sensitivity of material. For on demand spoilage monitoring via mobile phones, this sensing material will further be integrated into a capacitive sensor.

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CHAPTER NO 1

INTRODUCTION

Since the start of mankind, food has been the priority of humans to survive. As stated by the World Food Program, the food assistance branch of Unted Nations, "One in nine people in the world still go to bed hungry each night, while one-third of all food produced is wasted." This statement illustrates the importance of food and the need for a food management system.

Billions of tons of food is wasted every year around the globe due to poor management of food resources. The majority of our diet, such as meat products, are made up of protein-rich foods, that are thrown away because of spoilage and poor food management. When protein decarboxylation occurs, meat or other protein-rich foods spoil. During protein degradation, various volatile molecules are released. Biogenic Amines (BAs) are essential biomarkers of food spoilage. These molecules are responsible for the smell of spoiled food, which can be a warning sign to consumers.

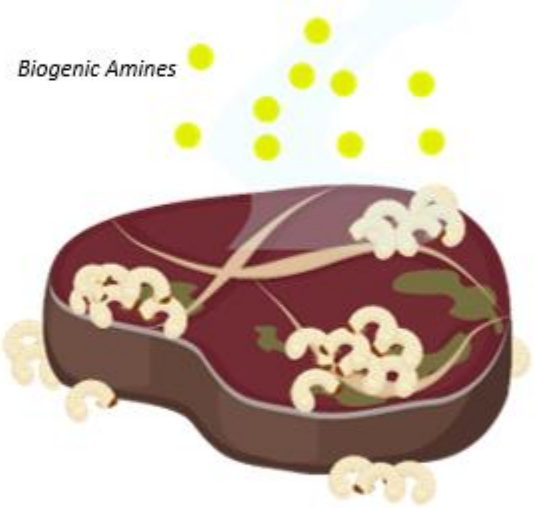


Fig.1 Biogenic Amines releasing from

Currently, BAs are detected using chromatographic instruments. However, these instruments are costly, destructive, need expertise, and can only be used in a lab setting. For sustainable production fast, non-destructive, portable, easy to use and low-cost monitoring sensors are needed to analyze on demand spoilage promptly. For this type of sensor Polystyrene co-maleic anhydride (PSMA) is a sensing material. When biogenic amines interact with this sensing material PSMA, it results in the formation of new bonds as shown below in the given reaction. Dielectric properties are structural dependent properties So, the formation of new bonds ends up in changing the dielectric values of the sensing material of the sensor.

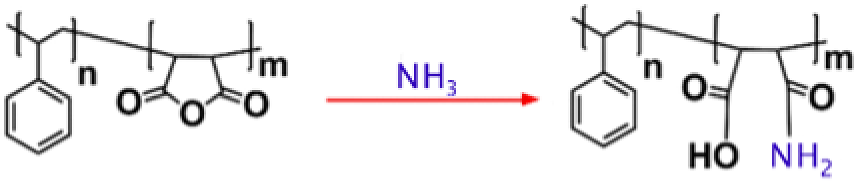


Fig.2. Chemical changes occurring in polystyrene co maleic anhydride.

The change in chemical structure and the dielectric value of the polymer indicate the level of spoilage that has occurred. Several factors influence spoilage. The spoilage rate of meat is directly proportional to its temperature and time. Formation of new bonds occurs in the polymeric layer of PSMA due to the presence of biogenic amine content in meat which increases over time. This, in turn, leads to a greater deviation of its dielectric value. Similarly, the same effect can be seen if the meat is exposed to higher temperatures because the rate of spoilage also increases due to the decarboxylation of protein. In summary, factors such as time and temperature of meat significantly influence spoilage, largely by influencing the formation of biogenic amines and decarboxylation of protein.

1.1. Food borne diseases and Food Spoilage

Food spoilage results in significant health risks, primarily due to the proliferation of harmful microorganisms that can cause food-borne diseases. Some of the diseases infections caused by pathogens such as Salmonella, Escherichia coli, and Listeria, which can lead to severe gastrointestinal issues, including diarrhea, vomiting, and abdominal pain. In the worst cases, food-borne diseases can lead to long-term health complications or mortality.

Food spoilage, especially in protein-rich foods such as meat, poultry, and fish, poses substantial health and economic issues worldwide. Consuming spoiled food can have serious effects, including a variety of foodborne infections. In addition to health problems, food rotting adds significantly to food waste, with nearly 240 million tons of protein-rich foods discarded each year worldwide.

1.1.1 Economic and Environmental Impact

Spoilage is a major contributor to the world's food waste problem, with negative effects on the environment and economy. Each year, around 1.3 billion metric tons of edible food is being wasted, accounting for 30% of agricultural land use, 20% of freshwater usage, 8% of global greenhouse gas emissions. The annual financial cost of food waste is projected to be 143 billion euros in the European Union alone.

1.1.2 Limitations of Current Technologies

Although chromatographic instrumentation is one of the most effective methods now available for detecting food spoilage, it has considerable limitations. These techniques are too costly, non-portable, and labor-intensive to use on a regular basis by customers or supply chain employees. Their relevance for on-site, real-time testing is further limited by the requirement for laboratory environments.

1.1.3 Gaps in Rapid, On-Demand Testing

The current solutions are not able to test for food testing quickly or on demand. Colorimetric sensors can be straightforward and inexpensive, but they frequently produce inaccurate findings at low analyte concentrations. Colorimetric sensors use dyes or nanomaterials to detect volatile biogenic amines (VBAs). Additionally, these sensors need high-resolution cameras and ideal lighting, which are not always feasible for daily use. Another possibility is resistive sensors, but their general use is further required by their specific equipment needs and motion artifact susceptibility.

1.2 Importance of Sensing Materials

Sensing material is the key element for all types of sensors as change occurs in it. Sensing material is necessary while establishing the effectiveness and sensitivity of capacitivity of sensor. Therefore, material selection is vital in determining the change in the capacitance of the material, a sign of spoilage caused by VBAs.

1.3 Poly Styrene Co Maleic Anhydride (PSMA)

The research papers focus on the PSMA as a sensing material for the capacitive sensor that has been developed. The sensitivity of the PSMA to polymers impacts the capacitance of the sensor to also undergo chemical modifications. This level of sensitivity is such that foods high in protein are able to be accurately detected when they are spoiled. Moreover, PSMA can be harnessed with low-cost batch fabrication methods, so it is a suitable material to generate scalable and low-cost sensors.

1.4 Problem Statement

The economic, environmental and adverse consequences of these have been the significance of threats to the environment and human health as they result in food spoilage and many other losses including the loss of various animal protein sources of meat, poultry, and fish. The traditional methods for detecting spoilage using chromatographic equipment are efficient but at the same they have some disadvantages as being costly, cumbersome and demanding highly skilled personnel. These limitations make its general use for in-situ and ratio metric detection of food products in real-time impossible. Furthermore, high protein foods degrade and have the potential of generating volatile biogenic amines (VBAs), that when ingested could cause food borne illnesses. It dramatically increases food waste, while also being a public health and environmental hazard — in addition to the associated financial losses. This naturally demands a reliable, low-cost, yet simple food spoilage monitoring real-time system. These technologies could be used to create technology that promotes sustainable food management and reduces food losses, while also helping to prevent foodborne disease.

1.5 Objectives

1. **Providing Easy, Fast, and Non-Destructive Testing**

The main goal of our project is the development of a simple, easy to use and non-destructive sensor. This develops a mechanism that supply chain, and consumers can use to instantly check the health of protein rich food without any expertise.

2. **Enhancing Food Safety and Reducing Waste**

The sensor aims to enhance food safety by reducing the frequency of food -borne diseases, by real time spoilage monitoring of food. Early-stage food spoilage detection reduces food wastage and sustainable food management techniques.

3. **Integration with Mobile Technology**

The integration of sensor with phone is another important goal, as it will enable easy access. This property guarantees spoilage detection accessibility to a wider audience; hence it is increasing its application in routine life.

CHAPTER NO 2

LITERATURE REVIEW

The literature review will cover the following topics, emphasizing their relevance to the research:

- The environmental footprint of food wastage
- Essential Spoilage Markers
- Reported detection/Measurement Methods
- Suitable Sensing Material
- Road map following Literature Review
- Type of sensors
- Advances in sensing materials and their application in capacitive sensors.
- Fabrication techniques for sensors, including photolithography and etching.

2.1 Overview

According to the estimations, approximately one-third of the consumable food production globally for human's consumption is either lost or wasted. This is a manner in which the food being produced goes to waste and a good opportunity is lost especially in the conservation of scarce resources and protection of the environment whilst at the same time enhancing food security to feed the world's growing population. Thus, to ensure food safety and quality of protein rich foods, real time spoiling detection, with minimal chances of error must be executed rigorously. A good amount of attention has been given on the development of novel signalling materials which have been tailored for this purpose in the past few years. These substances perform the roles of part of the sensor devices and allow them to detect and measure spoiling markers on time. They help organizations save on costs due to food wastage and also help to eliminate any possible health risks associated with the intake of contaminated food by removing any barrier to taking preventive measures. The aim of the current literature review is to assess the methodologies of preparation of sensing materials with the purpose of protein-rich food spoilage detection. The goal of the review is to present some relevant information regarding the updated advancements, core issues, as well as possible future trends in investigations.

2.2 The environmental footprint of food wastage

Food waste has a profound environmental impact on the survival of ecosystems, which is not limited to several links in the food chain. Through the direct consumption of land space, water, and energy during the production of crops and rearing of livestock, the following becomes true; The ecosystems are reduced, forests cut down and the sources of fresh water depleted. However, consequences including air pollution and climate change are amplified because greenhouse gases like nitrous oxide from fertilizers and gas from cattle are released during agriculture. Another disadvantage in delivery and storage is the energy consumed, which contributes to the emission of greenhouse gases. When consumers throw food, organic matter is directly fed to landfill whereby it decomposes under conditions of little oxygen and results to methane, which is a powerful gas on emission of greenhouse effect than CO_2. Furthermore, the effects of food waste on other species by contributing to loss of habitats through changes in land use and degradation of ecosystems also has a broad ecological implication. Hence, mitigating the environmental impacts of food waste require the use of efficient resources in production, invention of efficient channels for food distribution, use of other strategies in educating the consumers, and eradicating food waste to reduce its impact on the environment and to improve the food chain in the society.

About 1.3 billion tons of food is being wasted every year across the globe. This means massive resources used for production of food and the greenhouse gas emissions being wasted or lost are all in vain. Increase in the production of food is required with the increasing population worldwide. The study shows, the first step to reduce tension and fighting the imbalance of food resources is sustainable consumption of food, which significantly increases the efficiency of entire food chain. Decreasing food losses and the need to find cost effective methods for food spoilage detection should not be overlooked in a world with limited natural resources such as land, water, energy and fertilizers.

Around 88 million tons of food is being wasted by the European Union alone annually, it impacts the environment significantly. The European food waste management report shows that 186 Mt CO_2-eq, 1.7 Mt SO_2-eq., and 0.7 Mt PO_4-eq contribute to food wastage, accounting for 15-16% of total impact on food supply chain of Europe. Study demonstrated the environmental impact of primary steps of food production, where protein rich foods showed the most significant impact out of all other types of food. Greenhouse gas emissions from food production, distribution, consumption and disposal impacts where greenhouse gas emission during production steps contributes to three quarters of all food wastage related impact on Global warmings [1].

2.3 Essential Spoilage Markers

The development of biogenic amines in food items is a reliable indicator of the quality of food and preservation level [2]. Biogenic amines are naturally occurring metabolic chemicals found in many dietary products, usually in low amounts. These substances are created either by microbial decarboxylation of amino acids during storage or by enzymatic activity in raw meats. The most important biogenic amines that can be detected in food and drinks are Histamine, putrescine, cadaverine, spermidine , and spermine [3]. Because biogenic amines can act as fake neurotransmitters, they can produce diarrhea, vomiting, respiratory problems, and even neurotransmission issues when ingested in high concentrations [4, 5].

A small number of biogenic amines are required for normal physiological and metabolic activities in microbes, plants and animals. BAs are commonly formed by microbial decarboxylation of amino acids. The most common biogenic amines in food are Histamine, putrescine, cadaverine, tyramine, tryptamine, 2-phenylethylamine, spermine, and spermidine. Factors affecting the production of BA in food are availability of free amino acid, presence of decarboxylase-positive microorganisms, quality of raw material, manufacturing processes, distribution and storage conditions, and physiochemical parameters of food such as PH, NaCl, ripening temperature [6]. However, consumption of drinks and food containing such type of substances has ill effects such as heart palpitations, headache, diarrhea, nausea, localized inflammation, flushing, and hypertension, it may become fatal in extreme cases [5].

Some of the major factors that affect microbial activities in food are PH, salt concentration and temperature. Formation of BAs is affected in two ways by these factors. First, they are responsible for all the metabolism of decarboxylation of cells, where the activity of decarboxylase is influenced by the same factors. The final values of BAs are the result of the double influence of these two activities as the optimal values of environmental factors of these two different aspects can be different [7].

2.4 Reported detection/Measurement Methods

Protein-rich foods, like meat, poultry, fish, eggs, and dairy, are prime targets for spoilage due to their abundance of nutrients that microorganisms find readily available. Ensuring their safety for consumption necessitates reliable testing methods. This essay explores various techniques used to detect spoilage in protein-rich foods, along with their limitations, while referencing relevant scientific publications.

One common approach is **sensory evaluation**. Trained inspectors rely on sight, smell, and touch to identify spoilage indicators like discoloration, off-odors, and slimy texture [1]. While rapid and inexpensive, this method is subjective and prone to human error. Additionally, it cannot detect early spoilage or spoilage caused by pathogens that do not affect sensory characteristics [2].

As people's standard of living continues to improve, there is an exponential increase in the demand from consumers for safe and high-quality foods. It lead to a constant concern around the world of monitoring of food quality and safety [8]. Modern, innovative techniques for determining the durability, quality, and safety of food and agricultural products are gaining more and more attention from chemists. To monitor food safety, several conventional and innovative analytical technologies and procedures have been created [9]. The instrument-based analytical methods include fluorescence spectroscopy [10], Fourier transform infrared (FTIR) spectroscopy [11], high-performance liquid chromatography [12], Raman spectroscopy [13], and gas chromatography [14] These methods do have some drawbacks thus making their applications a concern in real-life scenarios.

To be more specific, all the previously mentioned detection techniques have excellent accuracy, sensitivity, and specificity for identifying common chemical compound categories that are released during food spoilage, such as volatile organic compounds (VOCs) and total volatile basic nitrogen (TVB-N). However, their use is further limited outside of research laboratories due to their high cost of purchase and complex analytical setups [15]. In addition, these labour-intensive methods of gathering and analysing information cannot be utilized to build small, portable systems that can quickly identify food spoiling due to the relatively large size of the devices. In addition, each approach takes a lot of time and requires specialists to do its operations. The food industry frequently searches for production line techniques that are easy, rapid, affordable, and effective. Chemosensors are thus great options for food deterioration monitoring, provided that spoilage is simply indicated. Chemosensors have limited use in situations where legal and accurate values are needed since they lack the level of selectivity and accuracy that analytical instruments can provide for detecting analytes [16]. Chemosensors are small, lightweight monitoring devices used for food standards analysis that can analyse volatile bacterial indicators released during food deterioration in real time. Chemosensors can be classified as colorimetric, optical, electrochemical, or piezoelectric sensors, depending on the type of transducer they contain [17].

Previously published VBA sensors use colorimetric techniques based on color-changing dyes [18-28], inks [29, 30] or nanomaterials [31-34]. Colorimetric methods provide an easy to use and cost-effective approach to monitor quality of food using digital cameras or the naked eye. However, there are still hurdles in designing colorimetric sensors for providing a meaningful color response, particularly at low analyte concentrations [35]. To build a color difference map from such tiny concentrations, a high-resolution optical camera with adequate lighting conditions is required, limiting its practical application. A resistive sensor was coupled to an inductor to develop passive wireless VBA sensors [36-39]. However, such methods are prone to motion artefacts since the signal amplitude is also affected by the space between the reader and the sensor. Furthermore, such non-standardized antennas need separate electrical equipment for measurement and are incompatible with cell phones. In this context, capacitive sensing is promising for wireless sensors since it provides frequency-specific information that is unaffected by motion artefacts. Mobile phones may wirelessly read sensor data by combining capacitive sensors with millimeter-sized integrated circuits that cost less than \$1. Furthermore, materials that are processable, inexpensive to synthesize and sensitive to VBAs are being investigated for the development of low-cost food sensors. Recently, Andre et al [40] A chemiresistor sensor was developed using inorganic nanofibers of SiO2:ZnO (an n-type material) and functionalized nanotubes. Multiple steps are required for the synthesis of the chemiresistor sensor. It increases the cost of the device production and restricts the batch fabrication of the device.

2.5 Methods for testing of food Spoilage

2.5.1. **Chemical testing**

It offers a more objective approach. Techniques like measuring volatile amines, a byproduct of protein breakdown, or quantifying pH changes can indicate spoilage [3]. However, these methods require specialized equipment and expertise, limiting their widespread use [1]. Furthermore, some spoilage organisms might not produce readily detectable chemical changes [4].

2.5.2. **Microbiological testing**

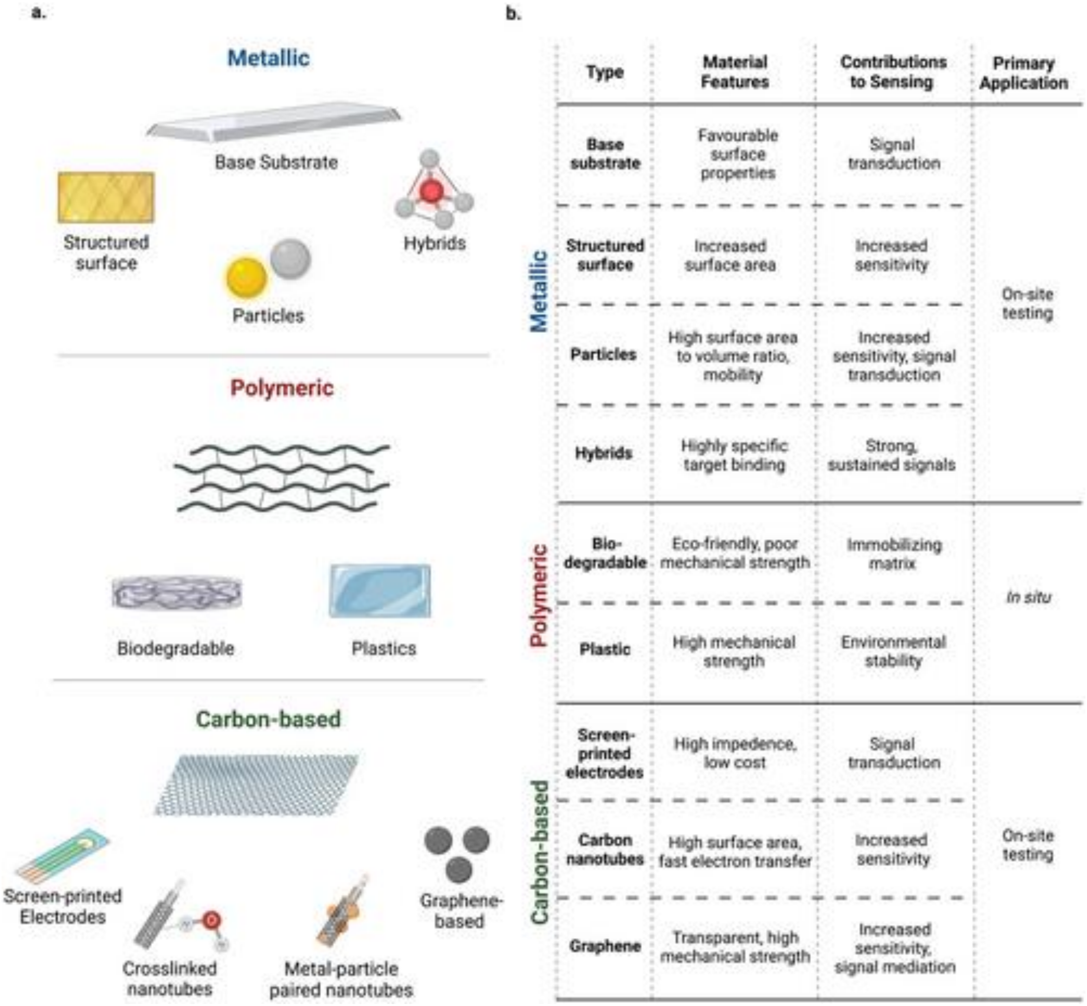
It involves culturing and identifying spoilage microorganisms. This method provides valuable information about the type and level of contamination [5]. However, it can be time-consuming (taking days to yield results) and requires a controlled laboratory environment [6]. Additionally, some pathogens might not be easily culturable using standard methods [7].

2.5.3. **Rapid methods**

These methods have emerged to address the limitations of traditional techniques. These include biosensors, immunoassays, and electronic nose technology. Biosensors detect specific spoilage markers, offering faster results than traditional microbiological methods [8]. Immunoassays use antibodies to target specific pathogens, providing a highly specific detection method. Electronic noses mimic human olfaction, electronically detecting volatile compounds indicative of spoilage in a rapid manner. While promising, these methods are often expensive, require validation for specific food types, and might not be readily available in all settings.

2.6. Suitable Sensing Material

Materials used for smart sensing of food spoilage can be categorized based on their different characteristics, and uses into polymers, metals, and carbon-based (Figure 4).



	Type	Material Features	Contributions to Sensing	Primary Application
Metallic	Base substrate	Favourable surface properties	Signal transduction	On-site testing
	Structured surface	Increased surface area	Increased sensitivity	
	Particles	High surface area to volume ratio, mobility	Increased sensitivity, signal transduction	
	Hybrids	Highly specific target binding	Strong, sustained signals	
Polymeric	Bio-degradable	Eco-friendly, poor mechanical strength	Immobilizing matrix	*In situ*
	Plastic	High mechanical strength	Environmental stability	
Carbon-based	Screen-printed electrodes	High impedence, low cost	Signal transduction	On-site testing
	Carbon nanotubes	High surface area, fast electron transfer	Increased sensitivity	
	Graphene	Transparent, high mechanical strength	Increased sensitivity, signal mediation	

Fig.3. Some common substrate materials for the monitoring of food spoilage. a) Substrate materials used within food sensors. b) Substrate material properties and uses summary.

Although prime application should not be considered as comprehensive, it refers to situations in which the item is most used.

Food sensing often employs metallic substrates like gold (Au) and silver (Ag) because of their excellent sensitivity, stability, and selectivity. Thiol-modified agents can readily functionalize Au substrates, facilitating the arrangement of self-assembled sensing agent monolayers on the substrate [41]. The capacity of Au nanoparticles (AuNPs) to reduce or boost the signal of fluorescent molecules is widely recognized. Au and Ag nanoparticles are employed in plasmonic sensors, and hybrid platforms have been developed that use metallic agents as sensing substrates. Metal-organic frameworks (MOFs) have also been explored for food biosensing due to their fine-tunable and modifiable structure[41].

Polymeric substrates dominate the food sensing area, because of their low cost and excellent tunability. [42]. These substrates are commonly utilized for both on-site sensors and in situ package sensors. Polymeric substrates, such as biodegradable polymers and plastics, are employed for on-site and in-place package sensors. Biodegradable polymers are driven by environmental concerns and have a high biocompatibility. However, they have typically provided poor stability in food-related environments. Recent advancements have tried to strike a balance between environmental durability and sensing capability, with cellulose paper-based substrates being widely used for on-site detection systems.

Carbon-based substrates are widely used as substrate material in electrochemical biosensors due to their good surface impedance and low price. Carbon nanotubes and nano horns improve detection sensitivity. Graphene-based substrates are keystones due to their surface properties, high mechanical strength, and electron transfer capabilities. Laser-induced graphene and graphene quantum dots are also popular for optical transduction[43].

So far, no material has achieved commercial acceptance despite the material driven development of food spoilage detection and contamination detecting sensing system, with their distinct pros and cons. Some major issues such as insufficient material, poor in situ compatibility, lack of specificity and cost are continuously hindering the real-world viability of an individual platform.

Polystyrene co-maleic anhydride (PSMA) stands out as a versatile, amphiphilic, and biocompatible polymer that can be suited for sensor applications. Its exceptional utility lies in its capacity to chemically interact with volatile biogenic amines found in protein-rich food spoilage. This interaction induces measurable changes in PSMA's properties, enabling precise monitoring of food freshness and spoilage. We can achieve our objectives by synthesizing, characterizing, and strategically optimizing PSMA, it can advance food safety and quality control in protein-rich foods.

2.7. Road map following Literature Review

This project aims to synthesize material for real-time food monitoring. PSMA will be utilized for real-time monitoring of food by measuring volatile biogenic amines. PSMA is a biomarker of biogenic amines released when food starts to degrade. The primary food spoilage indicators gas, such as ammonia, will be monitored in real-time by PSMA while maintaining outstanding stability under various storage conditions and giving an LOD value of 55ppm. This material can be life safer for food authorities that use conventional, expensive and laboratory-dependent methods. The material synthesis is addressing industrial and societal problems related to food spoilage, such as reducing food waste, ensuring food safety, and promoting responsible consumption and production. PSMA will be synthesized using styrene and MA units and several characterization steps such as back titration, gel permeation chromatography and FTIR will be done to ensure the sensitivity of the material. However, some limitations of the presented project include careful ammonia handling, lengthy characterization tests, and lab protocols. This PSMA material can further be integrated into a miniature sensor for on-demand spoilage detection and analysis via mobile phones. We anticipate the material to show exceptional sensitivity under various conditions such as at low, high and room temperature condition.

2.8. Type of Sensors

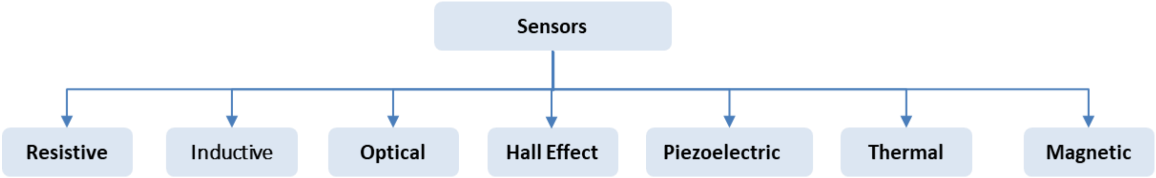


Fig.4. Types of sensors.

1. Resistive Sensors

These sensors react to physical stimuli like strain, pressure, or force by altering their resistance. Force-sensitive resistors (FSRs), pressure-sensitive resistors (PSRs), and strain gauges are a few examples.

2. Inductive Sensors

By producing electromagnetic fields, inductive sensors identify metallic items. A conductive material that enters the field causes eddy currents, which alter susceptibility and are subsequently picked up by the sensor. Applications involving proximity sensing frequently take advantage of them.

3. Optical Sensors

Optical sensors detect changes in their environment by use of light. Phototransistors, photodiodes, and optical encoders are a few examples. They are employed in many different applications, including position sensing, object counting, and presence detection.

4. Hall Effect Sensors

These sensors identify magnetic fields when they are present. The voltage produced by the magnetic field applied perpendicular to the sensor is proportional to magnetic field's strength. These sensors are commonly utilized in current sensing applications as well as those involving location and speed sensing.

5. Piezoelectric Sensors

Piezoelectric sensors produce electric charge because of applied mechanical stress and pressure. They are frequently employed in acoustic, force, and vibration sensing applications.

6. Thermal sensors

Thermal sensors measure various thermal signals i.e. temperature, acceleration, angular velocity and flow. Some of the examples of thermal sensors for monitoring temperature changes are thermocouples, thermistors, and resistance temperature detectors (RTDs). These sensors are used in industrial operations, HVAC systems, and temperature monitoring.

7. Magnetic Sensors

There are different types of magnetic sensors such as resistive, magneto, and hall effect sensors. They are used in navigation systems, compass and magnetic encoders to detect change in magnetic field.

8. Capacitive Sensors

The ability of a system to store electric charge is called capacitance. Variation in capacitance is used to identify changes in an object or its surroundings. Capacitance changes as a material approaches the sensor, the change in capacitance is converted into an electrical signal, which ultimately defines the properties of the material.

Capacitive sensors sense a wide range of materials including solids and liquids, as they work through non-conductive materials. Capacitive sensors are frequently found in industrial applications such as in manufacturing, automation, proximity sensors, level sensors, and touchscreens. They provide minimum response time, challenging conditions depending on dependability and high sensitivity.

2.9. Sensing Materials in Capacitive Sensors

For all types of sensors, sensing material is the key element. When it comes to establishing the sensitivity and effectiveness of capacitive sensors used to detect food deterioration, sensing materials are essential. The material selection influences the sensor's capacity to recognize variations in capacitance, a sign of spoilage brought on by VBAs. For instance, the use of PSMA in the development of capacitive sensors allows for efficient detection of biogenic amines produced during spoilage, making it an excellent candidate for such applications.

2.10. Fabrication Methods for Capacitive Sensors

Photolithography and etching are standard techniques for fabricating interdigitated electrode (IDE) patterns in capacitive sensors. These methods allow precise patterning and integration of sensor components, ensuring high performance and reliability. The development of cost-effective and scalable fabrication processes remains a key focus in this field.

2.11. Challenges in Fabrication and Application

Scalability, cost, and material stability are significant challenges in the fabrication and application of capacitive sensors. Sensing consistent performance across large-scale production and maintaining sensor stability under various environmental conditions are critical issues that need addressing to make these sensors viable for widespread use.

2.12. Recent Research and Developments

Current research is mainly concerned with the development of new materials for capacitive sensors, realizing a comparable low-cost material with a high sensitivity and the investigation of new fabrication methods to improve the capacitive sensor. Innovations in the field that promise to enable the kind of fusion protection desired are related to breakthroughs composed of advanced nanomaterials and composite structures developing that blend greater sensitivity with higher durability. Breaking new ground in sensor wire technology has also contributed to a new response time, essentially enabling the use of these sensors to be viable in daily life, as well as improvements in wireless technology integration, thereby allowing real-time monitoring capabilities.

CHAPTER NO 3

POLYMER

The word polymer comes from the Greek word that means “many parts.” A polymer is known as a macromolecule, that is formed by linking together many smaller repeating units known as monomers. Monomers chemically react together to form polymers, through the process of polymerization.

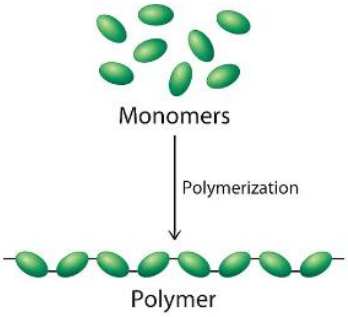


Fig.5. Polymerization of polymers.

3.1 Properties of Polymers

Physical, chemical and optical properties of polymers are discussed below:

3.1.1 Physical Properties

- good tensile strength due to long chains and cross-linking.
- Polymers are either semi-crystalline or amorphous.
- Polymers have good hardness resistance properties as they are resistant to being penetrated by hard material.
- They exhibit high melting and boiling points.

3.1.2 Chemical Properties

- The cross-linking strength of polymers is enhanced by hydrogen and ionic bonding.
- Good flexibility in polymers is a result of dipole-dipole bonding side chains.
- Polymers have a low melting point due to weak Van der Waal forces.

- Synthetic polymers are non-degradable while natural polymers are degradable.

3.1.3 Optical Properties

- Polymers such as PMMA and HEMA, MMA are commonly employed in lasers for spectroscopic and analytical applications due to their temperature-dependent refractive index.

3.2 Classification of Polymers

Polymers are classified based on sources, structures, reactions, and molecular forces due to their complex structures, diverse behaviors, and various applications. Thus, their classification is shown in figure 6.

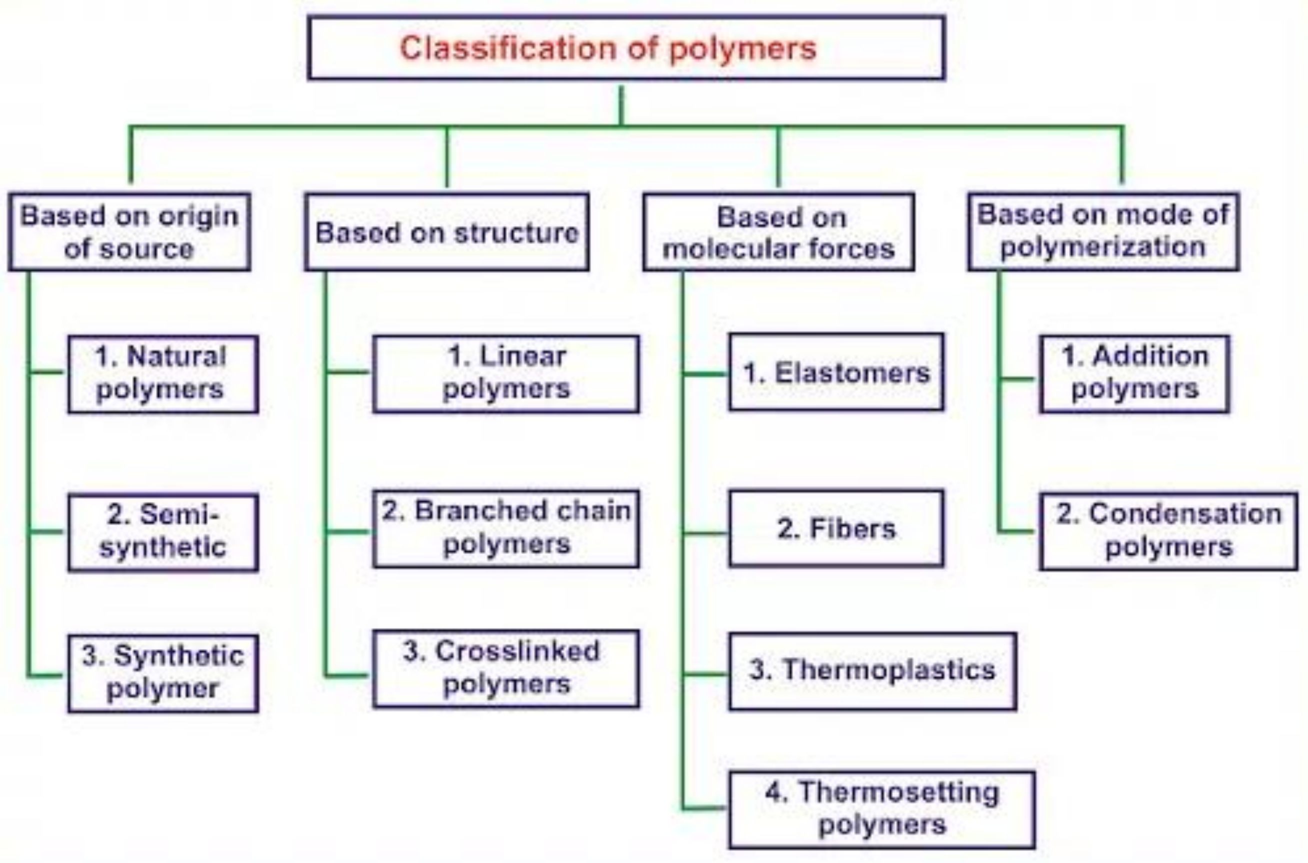


Fig.6. Classification of polymers.

3.2.1 Based on the Source of Availability

Polymers are classified into three types based on availability of source such as natural, synthetic, and semi-synthetic polymers.

1. **Natural Polymers**

Polymers that exist naturally in plants and animals are called natural polymers. For example, starch, rubber, proteins, and cellulose. Furthermore, biodegradable polymers are known as biopolymers.

2. **Semi-synthetic Polymers**

Polymers produced by chemical modification of natural polymers are called semi-synthetic polymers. For example, cellulose acetate and cellulose nitrate.

3. **Synthetic Polymers**

Polymers synthesized in labs by humans are called synthetic polymers. One of the most widely used synthetic polymers is plastic. Some other examples of synthetic polymers include nylon-6, polyether, etc.

3.2.2 Based on the Structure of the Monomer Chain

Polymers based on the structure of monomer chain is further categorized into the following types: This category has the following classifications:

1. **Linear Polymers**

Linear polymers possess long, and straight chains. Physical attractions keep the polymeric chains together. The polymeric chains are kept together through physical attractions. Extensive Vander Waals forces keep the chains together. Linera polymers are generally more rigid as they are made up of monomers with single-end groups. For example, polyvinyl chloride (PVC), a linear polymer is commonly used to make pipes, and an electric cable.

2. Branched chain Polymers

Linear polymer chains produce branches from side reactions during polymerization, the polymers are referred to as branched chain polymers. Monomers constituting two or more end groups are likely to support branching. Polymers should comprise a minimum of one complete monomer unit. For example, low-density polythene.

3. linked Polymers

Linked polymers are connected in a three-dimensional network structure. The connections are also known as crosslinks. Crosslinks are the consequence of covalent bonding between the chains or branches with a stronger covalent bond. Examples of cross-linked polymers include materials like Bakelite and melamine.

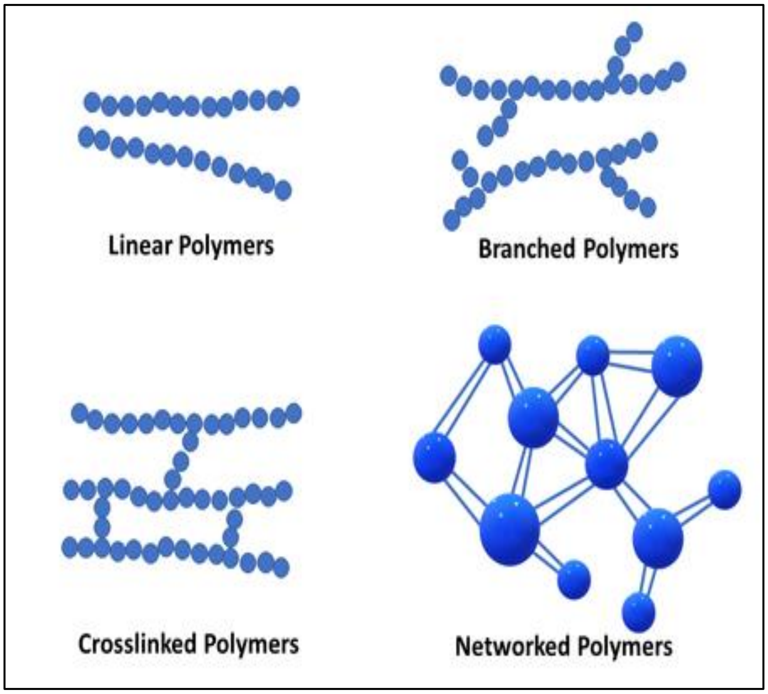


Fig.7. types of polymers based on the structure of monomer chains.

3.2.3 Classification Based on Monomers

Hetero and homo copolymers are explained below:

1. Homomer or homopolymers

Homomers contain only one type of monomer unit. For example, polyethylene.

2. Heteropolymer or co-polymer

Heteropolymer, also known as co-polymer, is made up of different types of monomer units. For example, nylon-6,6, PSMA (polystyrene-co-maleic anhydride).

Chain polymerizations can be carried out with mixtures of two monomers to form polymeric products with two different structures in the polymer chain (not as condensation polymerization). This type of chain polymerization process in which two monomers are simultaneously polymerized is termed a copolymerization and the product is a copolymer.

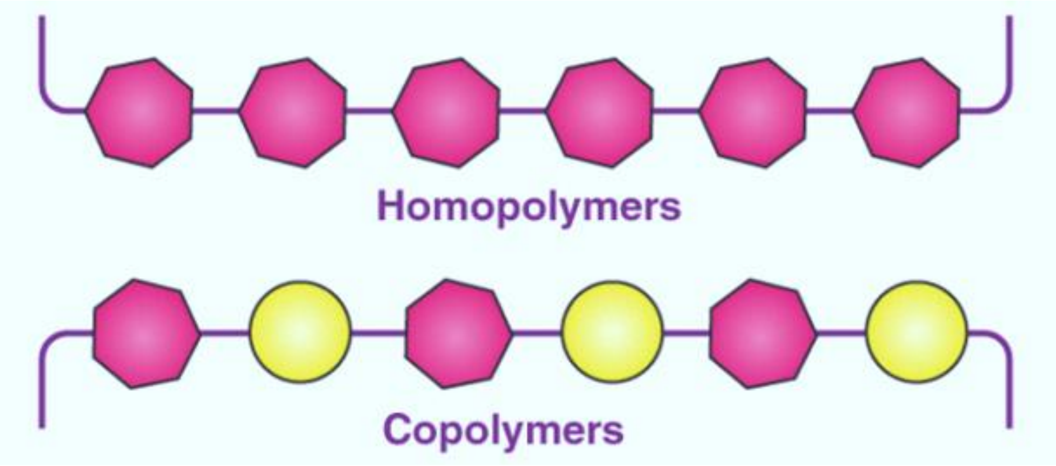


Fig.8. Structure of homopolymers and copolymers.

3.3. Properties of Copolymer

The molecular weight, chemical makeup, and morphology of copolymers all affect a variety of their physical and mechanical characteristics.

- Copolymers with shorter chains are more likely to be brittle, those with longer chains are often more ductile and flexible.
- The mechanical characteristics of copolymers can also be influenced by branching and cross-linking, with heavily branched copolymers frequently exhibiting lower stiffness and higher toughness.

- The degree of crystallinity in a copolymer influences its mechanical characteristics, with highly crystalline copolymers often exhibiting greater stiffness and strength than amorphous copolymers.

3.3.1 Types of Copolymers

If monomer (A) is reacted with monomer (B) by chain growth polymerization, the structure of the polymer formed will be:

1. Random Copolymers

In random copolymers the two monomers are randomly distributed along the polymer chain. This type of copolymer has a wide range of properties, making it suitable for a variety of applications. For example, random copolymers are often used in adhesives, sealants, and coatings.

Fig.9. Random copolymer.

2. Alternating Copolymers

Alternating copolymers have alternating, regular and repetitive arrangement of two monomer species. For example: Nylon 6,6. The general formula for the monomers A and B is be given in fig.10.

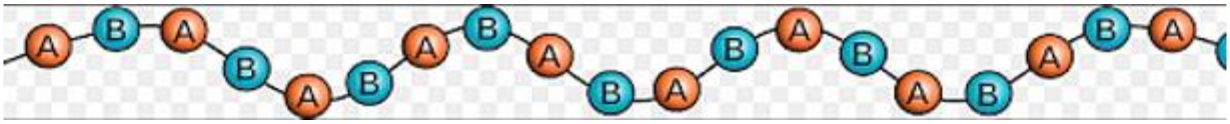


Fig.10. Alternating copolymer chains.

3. Block Copolymers

Block copolymers are made up of homopolymer chains joined by covalent bonding. The joining point, or intermediate unit is called junction block. They can be di or tri block copolymers.

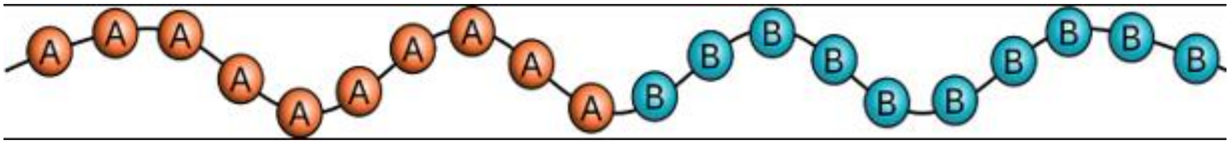


Fig.11. Structure of block copolymers.

4. Grafted Copolymers

In graft copolymer one type of monomer is "grafted" onto another type of monomer. This type of copolymer has unique properties, making it ideal for applications where the monomers need to be strongly bonded together. For example, graft copolymer is often used in rubber products and plastic products.

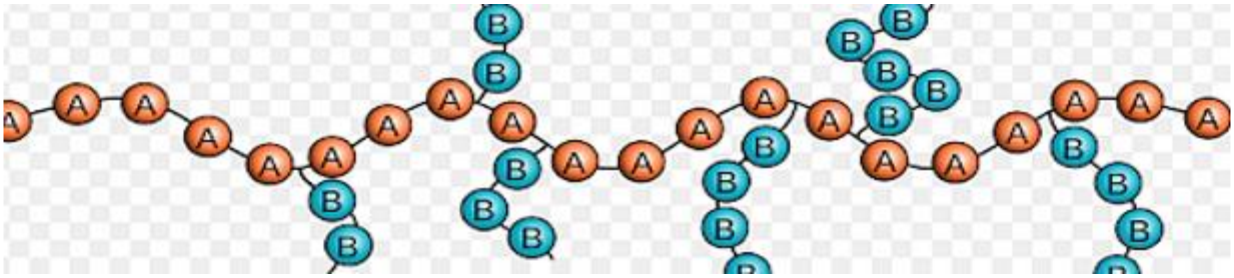


Fig.12. Grafted copolymer chains structure.

CHAPTER NO 4

POLYMERIZATION METHODS

Polymerization processes are defined as homogeneous and heterogeneous. In homogeneous polymerization all reactants, including monomers, initiators, and solvents, are mutually soluble and compatible with the resultant polymer. In heterogeneous polymerization, the catalyst, monomer, and polymer product all are insoluble.

Table.1. Types of polymerization methods.

Sr. No	**Method**	**Initiator**	**Stabilizer/ Surfactant**	**Temp ^oC**
1	Solution Polymerization	BPO	-	130
2	Emulsion Polymerization	KPS	SDS (surfactant)	70
3	Suspension Polymerization	APS	PVA (stabilizer)	80

4.1 Suspension Polymerization

Suspension polymerization is a technique for radical polymerization that uses monomers with vinyl groups. This process uses strong continuous agitation to break down an insoluble monomer and suspend it in a liquid, typically water. This agitation produces monomer droplets ranging in size from 0.01 to 1 millimeter. A soluble initiator, such as benzoyl peroxide or azobisisobutyronitrile, is then introduced into the monomer. Suspension polymerization can also be used in polyaddition reactions, such as the formation of polyurethane.

The polymerization reaction occurs within the monomer droplets, producing polymer particles. Spherical particles can be produced using suspension polymerization with monomers such as styrene, vinyl acetate, or methyl methacrylate. Pearl polymerization refers to a specific type of suspension polymerization.

A major challenge in suspension polymerization is that as the reaction progresses, the monomer droplets transform into concentrated polymer solutions, with the monomer acting as a solvent. This may cause the droplets to stick together. To prevent this, constant vigorous agitation is required. Water-soluble polymers such as gelatin, starch, polyvinyl alcohol, and carboxymethylcellulose, as well as insoluble powders like calcium carbonate and magnesium carbonate, are used to stabilize the droplets. The speed of agitation can affect the size of the final polymer particles. Another advantage of suspension polymerization is that the surrounding solvent absorbs the heat produced during the polymerization process, preventing specific overheating and facilitating temperature control.

A common industrial manufacturing technique for creating polymers used in products like forming materials is suspension polymerization. This is because it facilitates the synthesis of polymers with high polymerization levels and eases the process of isolating the end polymer.

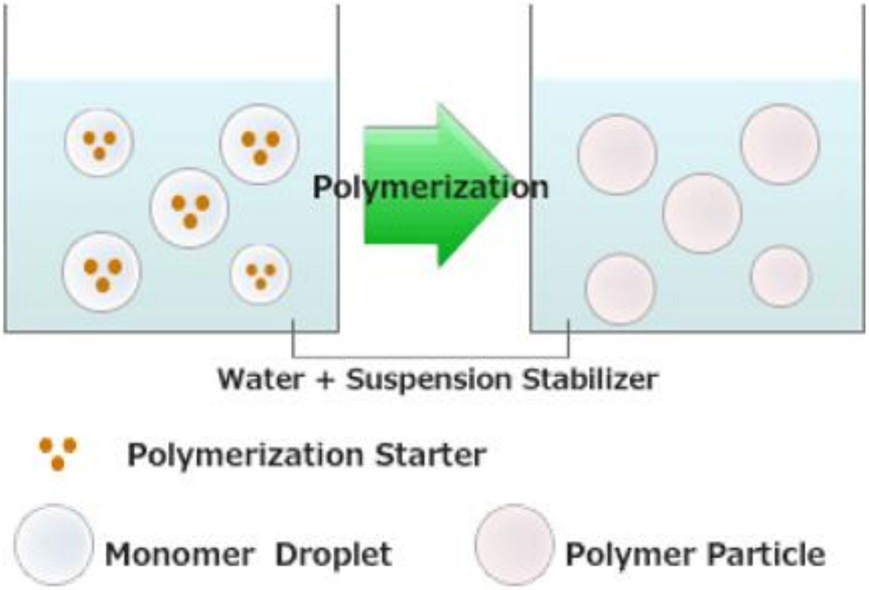


Fig.13. Schematic of suspension polymerization.

4.2 Emulsion Polymerization

Unlike bulk and suspension polymerization, emulsion polymerization is a radical vinyl group monomer polymerization technique. Using this technique, an emulsion or surfactant is dissolved in water, and a poorly soluble or water-insoluble monomer is then added. The polymerization process is then initiated with a soluble initiator, such as azobisisobutyronitrile or benzoyl peroxide, which are similar to those used in suspension polymerization. Surfactant molecules self-assemble in water solutions above a certain concentration, forming micelles. These micelles have a distinguishing feature: they contain both hydrophobic (water-hating) and hydrophilic (water-loving) regions. The hydrophilic regions face outward, surrounding the micelle in water, whereas the hydrophobic regions cluster in the center. When the monomer is added to the aqueous solution containing micelles, its water-insoluble nature causes it to partition into the micelles, effectively trapping it within their hydrophobic core. The initiator used in emulsion polymerization is water soluble and produces radicals in the water phase. These radicals can then migrate to the micelles and react with the trapped monomers, resulting in polymerization within the micelle.

Another benefit of emulsion polymerization is effective temperature control. The heat produced during polymerization is absorbed by the surrounding water, similar to what happens in suspension polymerization, which helps to simplify temperature control and prevent localized overheating. Without additional processing, the final polymer product of emulsion polymerization finds application in paints, textile treatment agents, and adhesives, among other industries.

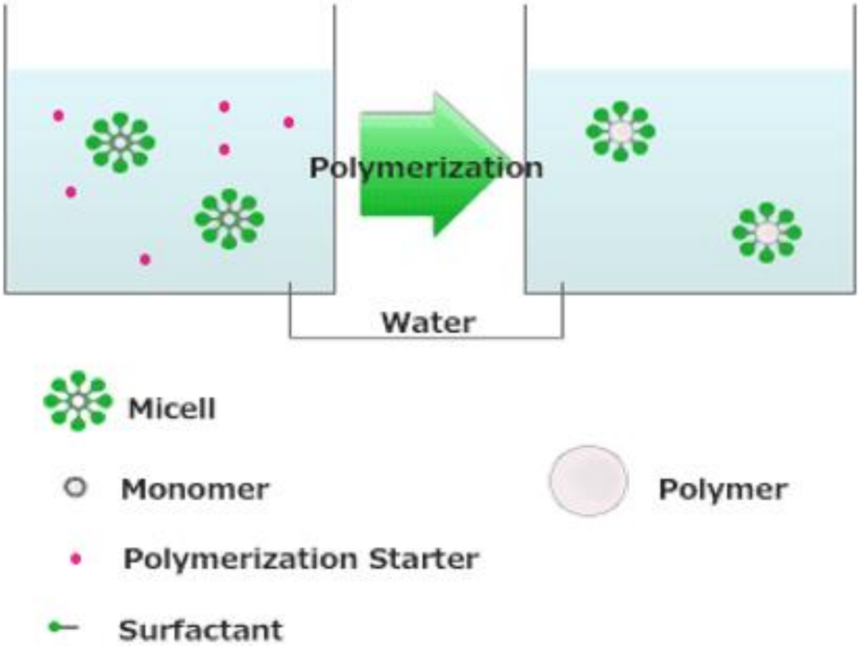


Fig.14. Schematic of emulsion polymerization.

4.3 Solution Polymerization

Solution polymerization is a process in which monomers are dissolved in a solvent. In this method, the monomer, solvent, and initiator are all dissolved in the same phase. The solvent plays an important role because it helps maintain the temperature stable by dispersing heat produced during the exothermic polymerization reaction. Furthermore, the solvent can affect the characteristics and molecular weight of the polymer by varying the pace of reaction and chain transfer activities. The monomers undergo an artificial chemical process to produce long polymer chains while the solvent preserves the other composite's uniformity so that it doesn't form gels or very viscous mixtures. Once a required level of polymerization has been reached, the polymer can be compounded by extracting it through precipitation solution or evaporating through solvent. One of the major advantages of solution polymerization is that it yields polymers of high purity and well-defined molecular weight and composition that satisfies the requirements of applications where utmost clarity of material is needed. PVDF as fluid is indeed advantageous when used through solution polymerization but it becomes a problem because a solvent would have to be removed and polymer is collected before it is formed into a solid mass. They provide output that is purer and more accurate than the other two and it also saves time.

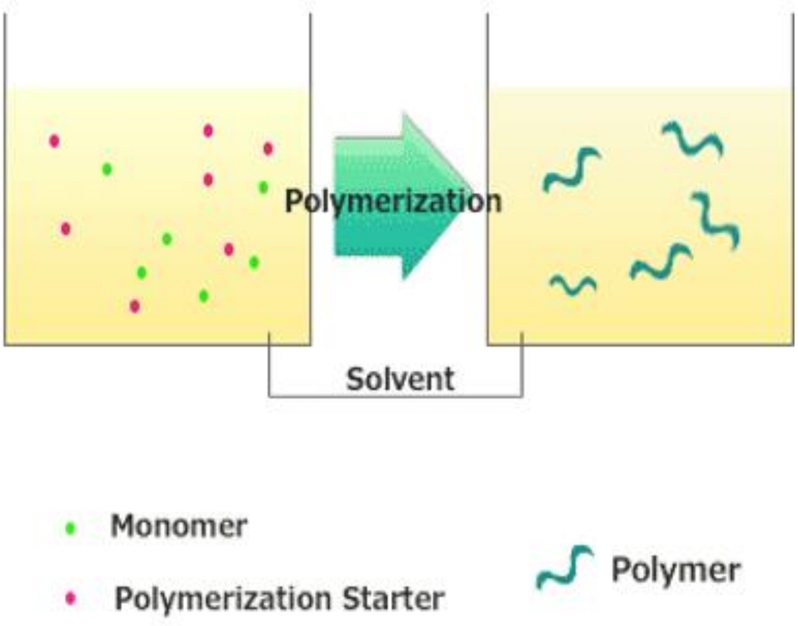


Fig.15. Schematic of solution polymerization.

CHAPTER NO 5

SYNTHESIS OF PSMA

Polystyrene-co-maleic anhydride is a random copolymer. The synthesis of Polystyrene-co-maleic anhydride (PSMA) was carried out using the process of solution polymerization. The apparatus, chemicals, and process being used have been discussed in this section.

5.1 Chemicals and materials

- Styrene
- Maleic Anhydride
- Benzoyl peroxide (BPO)
- Toluene
- Methanol
- Ethanol
- N-hexane
- Deionized water (DI water)
- Nitrogen Gas
- Silicon oil bath
- Grease

Styrene and Maleic Anhydride were the monomers used in the polymerization process whereas the BPO was used as the initiator and the Toluene was used as the solvent.

5.2 Apparatus

The following apparatus was used to carry out the synthesis:

- 3 necks round bottom flash
- Hot plate
- Aluminum foil
- Nitrogen Cylinder
- 200 ml Beakers
- Magnetic stirrer
- Spatula
- Clamp stand
- Filter papers
- Condenser

- Weighing balance
- Petry dishes
- Vacuum pump

5.3 Procedure

1. Initially the oil bath was placed over the hotplate and the temperature was set to 130°C. While the temperature was rising to the set point, we simultaneously weighed and measured the chemicals to be added to the ratios.
   S: MA: BPO: 215: 225: 1
    a. 7406.0 g of Styrene is measured using a weighing balance
    b. 7289.4g of Maleic anhydride
    c. 80g of BPO
    d. 250 ml of Toluene
2. Now all the components are transferred to the 3-neck round bottom flask and to mix well magnetic stirrer is inserted into the flask and the stirring is turned on.
3. As the temperature of 100°c is reached, the 3-neck round bottom flask held by the clamp stand is placed in the hot oil bath and magnetic stirring is turned on again.
4. Purging of nitrogen gas is also carried out through one of the flask's necks to create an inert atmosphere.
5. And one of the 3 necks round bottom flask is connected to the condenser's arm to exhaust vapors efficiently.
6. The reaction is carried out for the continuous 4 fours; after completing the reaction, the next step is to filter the yield so that unreacted monomers can be filtered out.
7. Filtration is carried out using PTFE (Polytetrafluoroethylene) paper in vacuum pump filtration.
8. After filtration, the process of washing is performed, firstly by using methanol and then by using n-hexane.
9. Once the filtration and washing are completed, the sample yield is placed in a vacuum drying oven for 24 hours to evaporate the leftover solvent.
10. As this step is completed, we get the PSMA (polystyrene-co-maleic anhydride) with more than enough purity.

The sample was then characterized using different techniques.

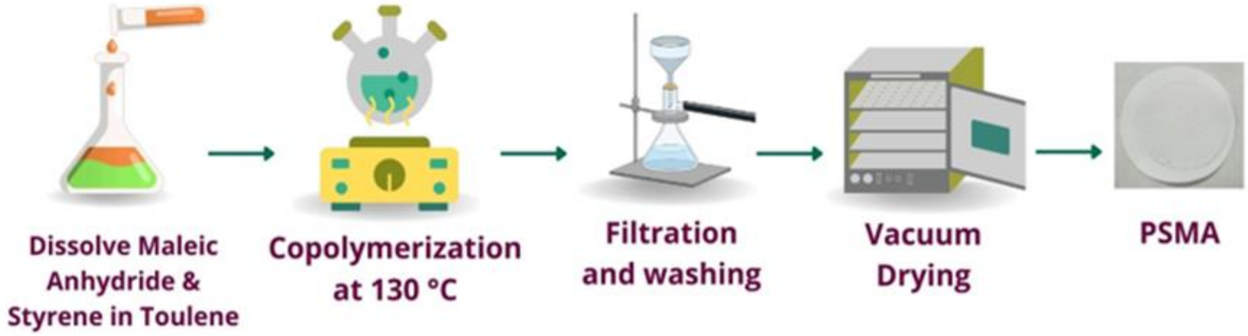


Fig.16. Solution polymerization of poly styrene co maleic anhydride

CHAPTER NO 6

MANUFACTURING OF INTERDIGITATED ELECTRODES (IDES)

The proposed design of IDEs (Interdigitated Electrodes) involves the use of commercial 35-mm thick copper-coated, double-sided PCBs whose patterns were cut using an ultraviolet laser cutter to produce the IDEs with a gap of 150 μm [44] On the front side of the PCB layer, the design requirements for the antenna for the integration of the NFC chip were engraved. This antenna has a rectangular shape and has nine turns with a line width and an interval of 100 μm between each turn. To comply with the NFC technology standard, the antenna's frequency resonance was adjusted to approximately 13.56 MHz To change the capacitance of the sensor according to the volatile biogenic amines (VBAs) at which it was exposed, PSMA sensitive dielectric layers were laminated over the IDEs. On exposure to the VBAs, the PSMA layers became polarized, allowing the capacitance of the sensor to change accordingly.

6.1. Design of IDES

Adobe Photoshop was employed to design interdigitated electrodes (IDEs). The size of each IDE was 1 × 1 inches, and their electrodes were 0.3 mm apart. Shown in Figure 1 is the layout of IDEs which were then subject to downstream processing steps.

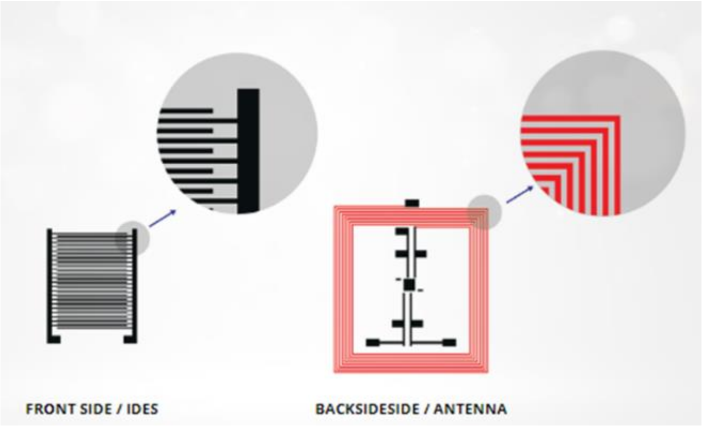


Fig.17. Design of IDES front and backside.

6.2 Masking of IDEs

The design created in Photoshop was transferred to a copper-coated printed circuit board (PCB). This process involved several meticulous steps:

1. **Printing the Design**

   IDE pattern onto toner transfer paper with a laser printer. This paper is made for the purpose of enabling transfer of designs onto other surfaces using toner.

2. **Preparing the PCB**

   Print the IDE pattern onto toner-transfer paper using a laser printer. This paper will transfer toner designs to other surfaces due to its design.

Fig.18. Copper coated PCB board.

3. **Transferring the Design**

   The PCB with a copper film was surface prepared for cleaning with more than one cleaning (so that there would be no oxidation) in order to good transfer blog on copper.

4. **Heat Transfer Process**

   The constant source of heat came from an iron for 5 minutes with continuous pressure. This process moved the toner from the paper to the copper surface of the PCB. The toner, drawn to the copper surfaces by the heat, bonded to the copper during the ironing stage, and became a resist mask for those areas of copper that we wanted to etch.

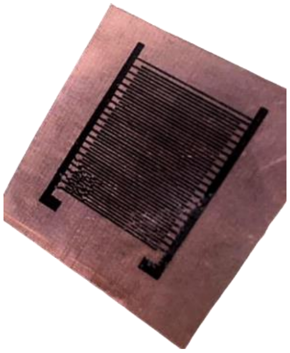


Fig.19. IDE printed PCB board.

6.3 Etching of the PCB Board

To etch the PCB and remove the exposed copper, a ferric chloride solution was prepared and used as follows:

1. **Preparation of the Etching Solution**

Hot Boiling water containing 10 grams of ferric chloride was used to make a solution. It is possible to get good copper etching action from this solution, without producing very toxic and corrosive fumes.

Fig.20. Ferric Chloride being dissolved in water.

2. Etching Process

PCB with toner pattern was dipped in the Ferric Chloride solution. The board was carefully shaken for 15-20 seconds to allow the solution to etch the copper areas that were in contact with the light.

Fig.21. IDE printed PCB board immersed in Ferric Chloride solution.

3. Completion of Etching

The reaction of the ferric chloride with the copper exposed caused the dissolution of the copper and the rest of the copper, which was protected with the toner forming the IDE pattern. We then carefully retrieved the PCB from the etching solution.

Fig.22. PCB board removed after etching.

6.4 Chemistry of Copper Etching

The etching process relies on the chemical properties of ferric chloride and its reaction with copper. Here’s a detailed explanation of the chemistry involved:

1. **Ionization of Ferric Chloride**

   $FeCl_3 \rightleftharpoons Fe^{3+} + 3Cl^-$

   When ferric chloride is dissolved in water, it ionizes into ferric (Fe^{3+}) and chloride (Cl^-) ions.

2. **Ionization of Water**

   $H_2O \rightleftharpoons H^+ + OH^-$

   Water naturally ionizes into hydrogen (H^+) and hydroxyl (OH^-) ions.

3. **Formation of Ferric Hydroxide**

   $Fe^{3+} + 3OH^- \rightarrow Fe(OH)_3$

   A compound precipitates out of the solution as a brown solid when Ferric ions react with hydroxyl ions to form ferric hydroxide, removing hydroxyl ions and increasing the acidity of the solution.

4. **Reaction with Copper**

   $2Fe^{3+} + Cu\ (solid) \rightarrow 2Fe^{2+} + Cu^{2+}$

Copper, due to its electro-negativity, displaces iron in the solution, effectively dissolving without producing any gas. This reaction facilitates the etching of copper from the PCB.

6.5 Post-Etching Treatment

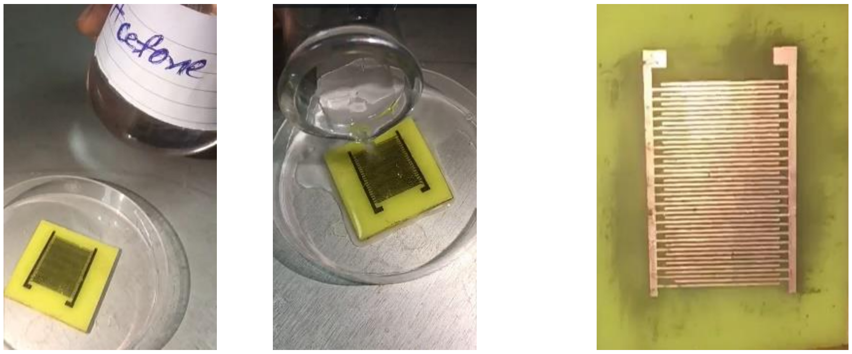
Following the etching process, several steps were undertaken to finalize the preparation of the IDEs:

1. **Rinsing**

   The etched PCB was thoroughly rinsed under running water to remove any remaining ferric chloride solution, preventing further unwanted etching.

2. **Cleaning**

   Acetone was applied to the PCB to dissolve and remove the toner ink used for masking, along with any residual debris. This revealed the copper-based IDE pattern clearly, as shown in Figure.



(a) (b)

Fig.23. (a) Ink pattern removed using acetne (b) IDE design after removing ink.

3. **Soldering**

   Connections were made by soldering lead-tin solder wire to the appropriate points on the IDEs, ensuring reliable electrical connections, as depicted in Figure.

Fig.24. Soldering two wire connection on IDES.

4. Polymer Coating

A polymer solution dissolved in toluene was prepared and applied to the IDEs using a spin coating technique. This involved placing the PCB on a spinning platform and applying the polymer solution, which spread evenly across the surface. The coated PCB was then dried to solidify the polymer layer.

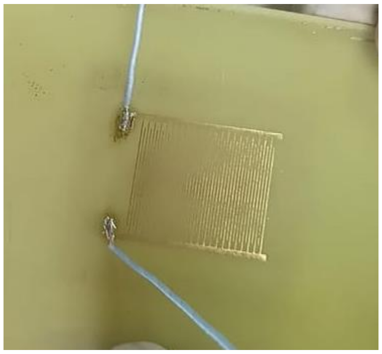


Fig.25. Polymer Coated IDES.

This detailed process ensured the precise fabrication of the capacitive sensor for spoilage monitoring of protein rich foods.

CHAPTER NO 7

CHARACTERIZATION TECHNIQUES

The material PSMA underwent various characterization techniques to ensure optimal performance. FTIR identified any structural changes in the polymer, while Impedance Analysis observed how the material interacts with volatile biogenic amines through capacitance changes. Both FTIR and Impedance Analysis are done before and after exposing the polymer with VBAs. Finally, XRD confirmed the all-important amorphous structure of PSMA, crucial for maximizing its reactivity with these volatile amines.

7.1 FTIR

Among the most used techniques to identify materials we can distinguish the Fourier Transform Infrared Spectroscopy, more commonly referred to as FTIR. With this non-destructive analytical technique, symbols and characteristics of different functional groups contained in a molecule could be defined and easily identified. FTIR relies on the principle of differentiation between the vibrational characteristics of atoms within molecules and the coolant for infra-red (IR) radiation. This paper reveals and describes in detail how some functional groups are characterized in the infra-red region of the electromagnetic spectrum. Fourier Transform Infrared Spectroscopy (FTIR) is an analysis method which provides information about materials without the need for sample destruction. It studies how the material absorbs IR light (figure 26) and yields a selective chemical structure code based on discrete absorption bands of certain functional groups. This fingerprint helps in identification of the material under test and in identification of chemical nature of the material in testing process.

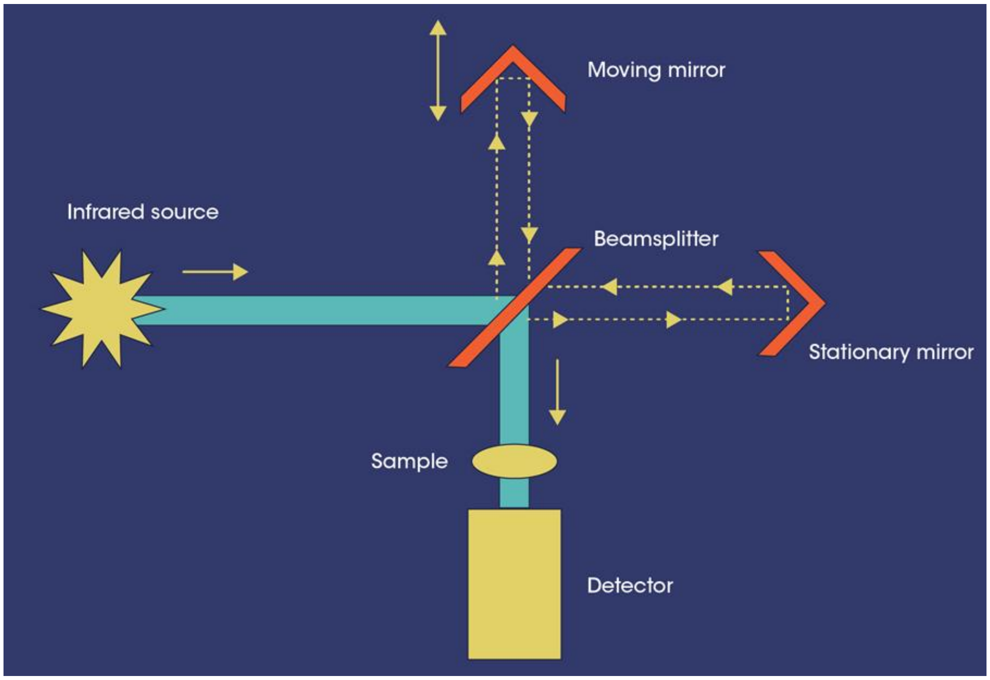


Fig.26. demonstration of mechanism of FTIR.

In an FTIR spectrometer some of the essential features include interferometer, detector, sample holder and light source particularly in the range of infrared light. For instance, in the case of the sample used in this experiment, the sample is exposed to a number of radiations from the I.R light source. These frequencies are transformed as specific characteristics of molecular motions or vibrations are being absorbed. Concerning these specific frequencies, these molecular functional groups are in turn defined in terms of the masses of their constituent atoms, bond strength, and position. It is crucial here that the beam of infrared light is modulated by the interferometer, which is crucial in creating the detailed interference pattern. When the algorithm of the Fourier transform mathematical operation is performed over this pattern, a spectrum indicating the degree of light that has been absorbed at the frequencies is generated. In the context of spectroscopy, an FTIR spectrum refers to the final spectrum that indicates the unique molecular signature of the substance under analysis.

7.2 XRD

XRD has been considered an effective tool for analyzing materials; indeed, XRD provides reliable and no destructive means to analyze the crystal structure of a material. This technique is based on the physical phenomenon that when a solid is exposed to an X-ray beam, the scattered X-ray intensity depends on the distance between atoms in the substance. X-rays tend to scatter when a beam of them passes through a crystalline material; this is because they are scattered by the electron orbiting around the nucleus of each atom of the crystalline material. But in a crystalline material, the scattered X-rays are faced with something that the light waves are not –the regularly ordered atomic planes in the crystal lattice as depicted by the finger below. This specific arrangement leads to a phenomenon known as diffraction whereby the x-rays strike the target in certain directions with resultant constructive and destructive interferences.

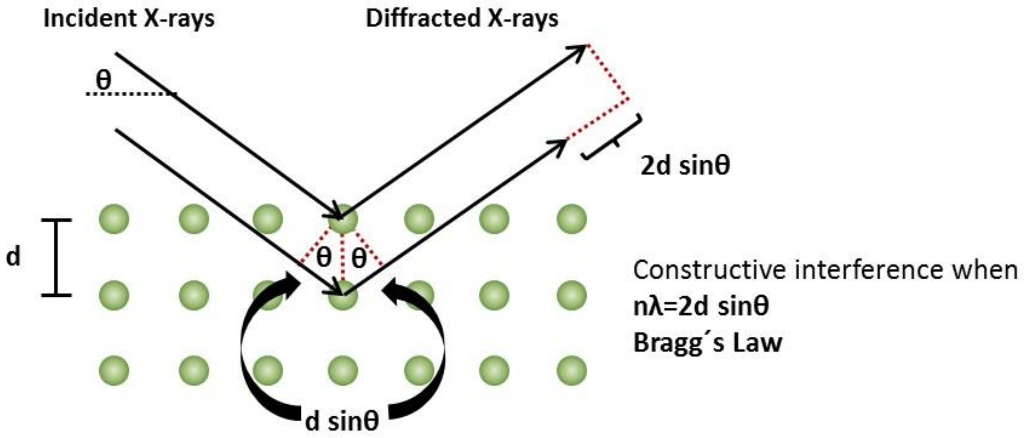


Fig.27. working of XRD

Through the measurement of diffracted X-ray intensity by the detector at different angles, a distinct pattern is revealed. The interaction of the scattered X-rays' constructive and destructive interference is reflected in this pattern. The interatomic distances and angles within the crystal lattice can be learned a great deal about by examining the peak positions and intensities within this pattern. The crystal system, unit cell parameters, and possibly even the material's particular crystalline phase can all be determined using this information.

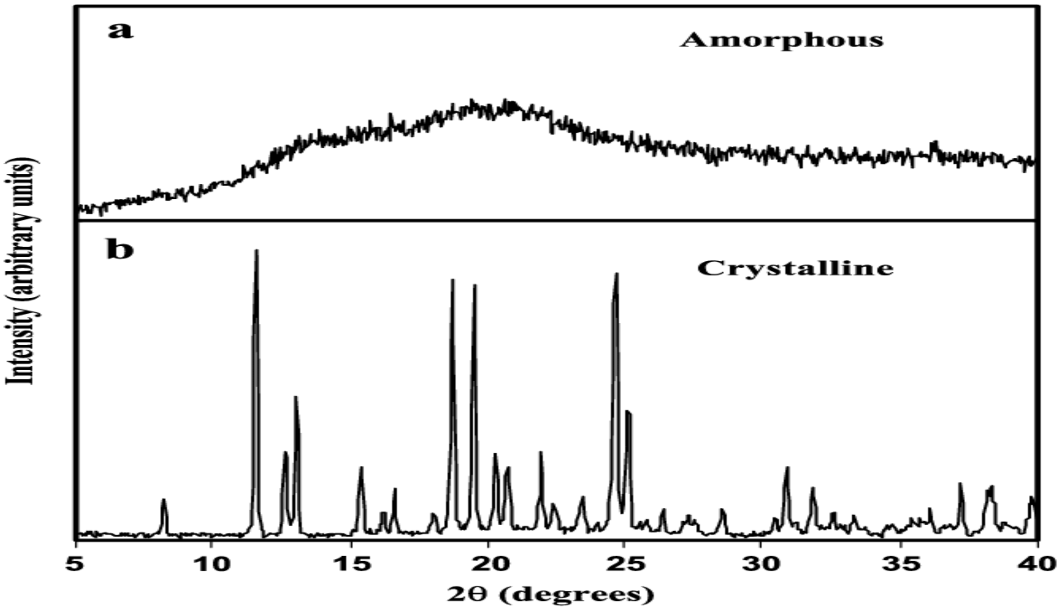


Fig.28. XRD of amorphous and crystalline structure.

The versatility of XRD extends beyond simply identifying crystal structures. By comparing the obtained diffraction pattern with established databases, we can identify unknown crystalline materials. Additionally, XRD offers the ability to quantify the degree of crystallinity within a material. On the other hand, amorphous materials show no peaks. Crystalline materials exhibit distinct, well-defined peaks in the diffraction pattern (Fig 28, b), whereas amorphous materials, lacking a long-range order, produce broader and less distinct peaks (Fig28, a). This information proves invaluable in material science applications, where the degree of crystallinity can significantly influence a material's properties. In essence, XRD serves as a powerful tool for deciphering the secrets of a material's atomic structure, providing crucial insights for material characterization and development.

7.3 Impedance Analyzer

The limits of straightforward resistance measurements are overcome using impedance analysis. It provides a thorough understanding of how an electrical current interacts with a substance. Using a more in-depth approach, this method sheds light on the intricate interactions that exist between a material's intrinsic characteristics and how it reacts to an AC field.

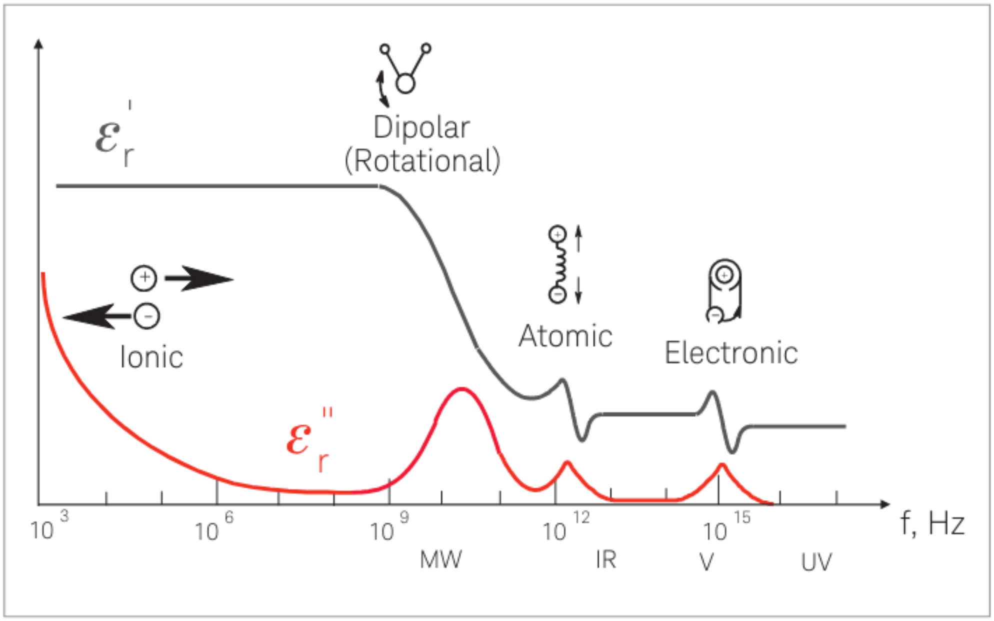


Fig.29. Working of Impedance analyzer.

Consider a substance that facilitates the passage of electricity. Metals have high conductivity, which makes it easy for electricity to flow through due to their well-organized atomic structure. On the other hand, insulators (poor conductivity) greatly impede the flow of electricity and are similar to uneven, single-lane roads due to their more chaotic structure. For impedance analysis, an innovative tool works by measuring the dynamic AC current movement which any substance let provide. This opposition, called impedance (Z), includes not only the direct resistance, but also any reactive components — capacitance (C) and inductance (L) — which can impact the behavior of the current flow.

Applying an AC voltage across the material and monitoring the resulting current forms is the basis of the impedance analysis theory. With this method, the impedance at different frequencies is calculated by carefully examining the voltage-current relationship. The speed of the electrical current might be compared to frequency in this context. The study basically looks into how the material responds to quicker electrical fluctuations as the frequency rises.

Certain materials display different electrical behaviors based on the applied current frequency, so knowing this information is essential.

Impedance analysis provides useful information about a material's capacity to store electrical energy in addition to resistance. Dielectricity (ε') is the name given to this characteristic. High dielectric materials have the capacity to store more electrical energy like capacitors; this is comparable to a broader highway shoulder that can accommodate more parked cars (stored energy). We can determine a material's dielectric by examining the impedance data collected at different frequencies. From creating effective capacitors to comprehending how materials interact with electromagnetic waves, this information is extremely useful in a wide range of applications. Basically, impedance analysis is a flexible method that scientists can use to investigate the electrical characteristics of materials, giving important information about the materials' conductivity, capacitance, and general dielectric behavior.

7.4 Digital Multimeter (DMM)

A digital multimeter (DMM) measures capacitance by charging and discharging the capacitor and monitoring the voltage change. Here's a detailed explanation of the principle behind it:

7.4.1 Principle of Measuring Capacitance with a Digital Multimeter

1. Charging the Capacitor

When the digital multimeter is set to the capacitance measurement mode and connected to the capacitor, it applies a known constant current to the capacitor.
As the capacitor charges, the voltage across its plates increases over time according to the relationship:

$V(t)=I/Ct$

where $V(t)$ is the voltage across the capacitor with constant current I, C is the capacitance, at time t.

2. Voltage Measurement

The DMM measures the time t it takes for the voltage to reach a specific threshold value. Since the current I and the voltage threshold are known, the capacitance C can be calculated using the formula:

$C = I \cdot t / V$

3. Discharging the Capacitor

The DMM may also discharge the capacitor to ensure it is fully discharged before taking a new measurement to avoid errors caused by any residual charge.

4. Displaying the Result

After calculating the capacitance based on the charging time, the DMM converts the result into a readable digital value and displays it on the screen.

7.4.2 Steps for Measuring Capacitance with a Digital Multimeter

1. Preparation

Ensure the capacitor is fully discharged before measuring. This can be done by shorting the capacitor's leads together briefly.

Set the multimeter to the capacitance measurement mode, it is commonly indicated by a symbol similar to ||.

2. Connecting the Capacitor

Connect the multimeter probes to the capacitor terminals. Polarity is generally not a concern for capacitance measurement, except for polarized capacitors (electrolytic capacitors), which should relate to correct polarity.

3. Reading the Measurement

The multimeter will automatically perform the charging and measuring process.

The capacitance value will be displayed on the multimeter screen, typically in units of picofarads (pF), nano farads (nF), or microfarads (μF), depending on the capacitance range.

7.4.3 Key Factors Affecting Capacitance Measurement

1. **Residual Charge**

Ensure the capacitor is fully discharged before measurement to avoid inaccurate readings.

2. **Multimeter Quality**

The quality and precision of the digital multimeter defines the accuracy of the measurements.

3. **Capacitor Type**

Different types of capacitors (e.g., electrolytic, ceramic, film) may have varying tolerances and characteristics that can affect the measurement.

4. **Environmental Factors**

Temperature and humidity can influence capacitance measurements, so it's important to consider these factors for precise measurements.

Digital multimeters measure capacitance by applying a constant current to the capacitor and timing how long it takes for the voltage to reach a predetermined threshold. This time, along with the known current and voltage, is used to calculate the capacitance value, which is then displayed on the multimeter. Proper preparation, including discharging the capacitor and ensuring correct connections, is crucial for accurate measurements.

CHAPTER NO 8

RESULTS AND DISCUSSIONS

8.1. FTIR

Figure 30 presents the Fourier Transform Infrared Spectroscopy (FTIR) results of Polystyrene Maleic Anhydride (PSMA) before (black line) and after (red line) exposure to ammonia (NH_3), a component of Volatile Biogenic Amines (VBAs).

The figure's black line shows the PSMA's FTIR spectrum prior to its exposure to ammonia. The distinguishing peaks in this spectrum are those that correspond to the functional groups found in the PSMA polymer. Interestingly, there isn't a noticeable dip at some wavenumbers, which suggests that bond forms weren't present before ammonia exposure.

After being subjected to ammonia, PSMA's FTIR spectrum is depicted in the image by the red line. In theory, ammonia exposure should cause the PSMA structure to undergo chemical alterations that result in the creation of new bonds and the modification of existing ones. In the FTIR spectrum, precisely this is seen:

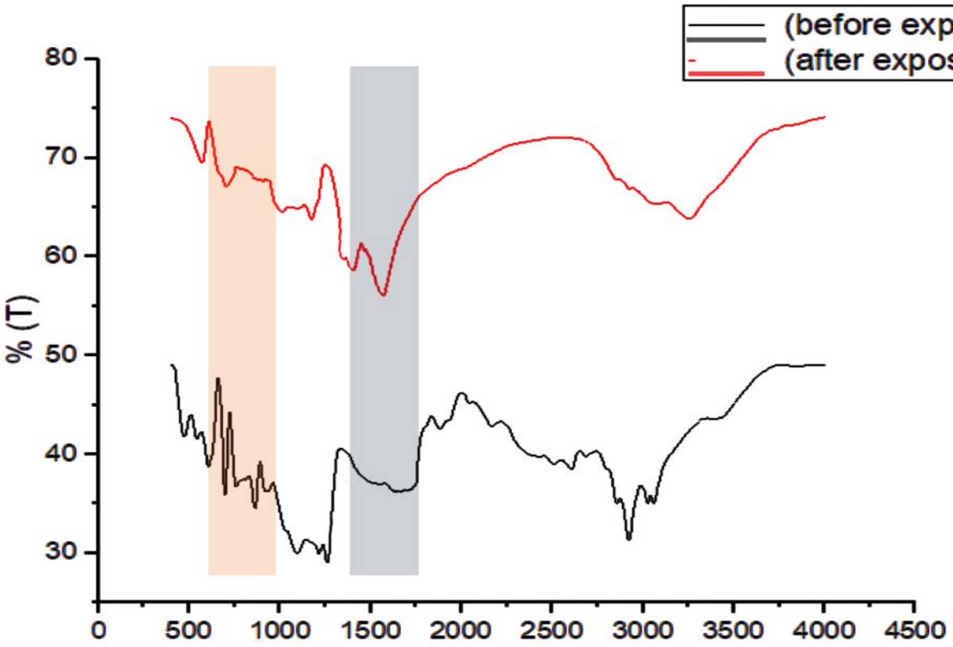


Fig.30. FTIR results before and after exposure to ammonia. At 750 cm^{-1} some peaks disappeared and at 1550 cm^{-1} a new peak is formed after exposure to ammonia.

In the red curve, there is a noticeable dip at approximately 1550 cm^{-3} that is absent in the black curve. This decline is a sign of newly formed bonds, particularly NH bonds. This alteration shows that ammonia and PSMA have interacted, resulting in the addition of NH groups to the polymer structure. It represents the change in chemical structure of the polymer.

Certain peaks that were present in the black spectrum are absent in the red spectrum. These absent peaks imply that ammonia exposure altered some of the bonds in the PSMA structure. The breaking down of these bonds is in line with ammonia's capacity for chemical reactivity, which can break existing bonds and create new chemical structures.

It is abundantly evident from the FTIR spectra that PSMA is chemically reactive with ammonia and biogenic amines. It is confirmed that PSMA experiences considerable chemical changes when exposed to ammonia by the emergence of new NH bonds and the elimination of some peaks. PSMA has the potential to be useful in a variety of chemical sensing and reactive situations, as demonstrated by its critical reactivity in applications where it is utilized to interact or detect volatile biogenic amines in protein rich food. The creation of NH bonds and the modification of preexisting chemical bonds are prominently displayed in the FTIR study, which successfully illustrates the structural alterations in PSMA brought on by exposure to ammonia. This demonstrates that PSMA is chemically sensitive to ammonia and related biogenic amines.

8.2. XRD

The physical and chemical characteristics of polymers are largely determined by their crystallinity, which also has a major impact on their reactivity. Crystalline polymers are stiff, have higher melting temperatures, and less molecular mobility due to their well organized and densely packed molecular chains. Because of its arranged structure, crystalline polymers are often less reactive because they have a limited free space that makes it difficult for gases and reactive agents to interact with the polymer. Amorphous polymers, on the other hand, have a more random and disordered structure with a higher molecular mobility and free volume due to their lack of regular arrangement. Since their disordered structure, amorphous polymers have lower melting temperatures, are more pliable, and are much more reactive since chemical agents can more easily access their molecular chains.

Our investigation required quick reactions with volatile biogenic amines (VBAs), which made the use of an amorphous polymer necessary. Luckily, our material of choice, Polystyrene Maleic Anhydride (PSMA), is amorphous, which makes it perfect for obtaining the required reactivity with VBAs. Ammonia and other biogenic amines can readily enter the polymer matrix of PSMA due to its amorphous structure, which enables them to interact with the functional groups inside and speed up chemical reactions. For applications such as sensing and detecting VBAs, where prompt and dependable response times are required, this reactivity is essential. Furthermore, amorphous PSMA's flexibility and lower melting point improve its processability and environmental applicability, making it a flexible material for a variety of reactive and chemical sensing applications.

Thus, choosing amorphous PSMA broadens its applicability in various technological fields while also ensuring appropriate responsiveness with VBAs.

It was evident from the X-ray Diffraction (XRD) investigation that PSMA is an amorphous material. The XRD pattern showed that there were hardly any of the sharp peaks that are usually found in crystalline materials; the only prominent peaks were those that might be attributed to the carbon tape that was used to prepare the sample. Its amorphous nature is confirmed by the lack of distinctive diffraction peaks, which clearly suggests that PSMA lacks a well-ordered, crystalline structure. This result is in line with previous studies that suggest amorphous polymers' reactivity is greatly increased by their disordered structure.

Chemical agents can interact with the polymer matrix more easily in amorphous polymers due to their intrinsic disorder and increased free volume, which promotes better molecular mobility and accessibility. This feature is very helpful for our Volatile Biogenic Amine (VBA) detection system, as quick reaction times are critical. Because PSMA's molecular structure is less ordered, it offers more reactive sites and interaction pathways than VBAs, enabling faster and more effective reactions.

This enhances the detection system's overall sensitivity and responsiveness by enabling quicker VBA detection. The amorphous PSMA's good detection capacity makes it a perfect material for applications that need to identify volatile biogenic amines quickly and reliably. This increases the VBA detection system's practical utility and efficacy.

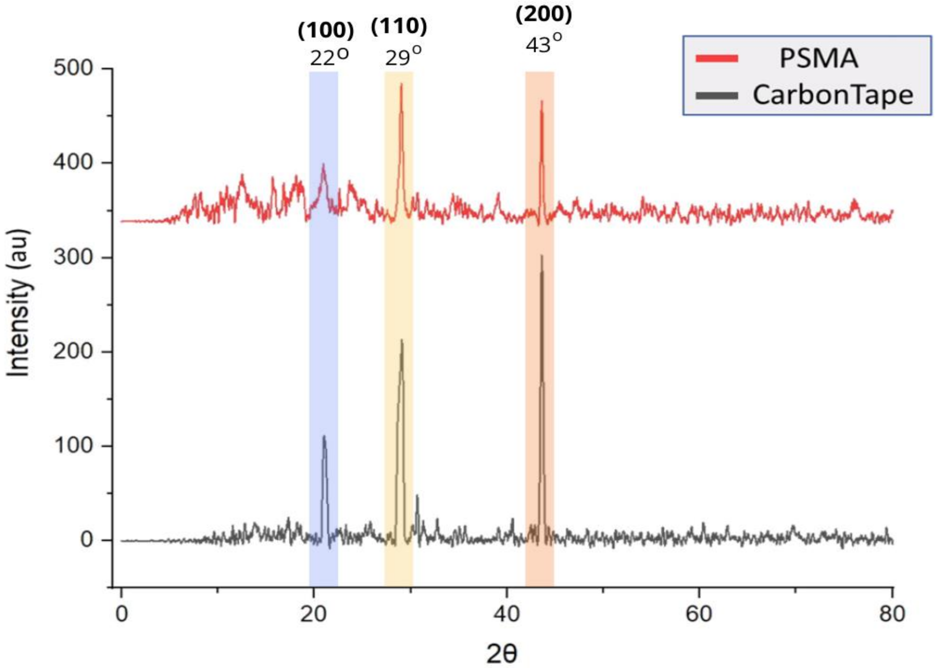


Fig.31. XRD pattern of PSMA showing amorphous nature of the sensing material.

8.3 Impedance Analysis

After XRD examination verified that PSMA was amorphous, this work used impedance analysis to look into possible alterations in the polymer's dielectric characteristics when it was exposed to volatile biogenic amines (VBAs). Ammonia (NH_3), a close derivative of VBAs, was used as a surrogate molecule for this preliminary study because of its reactivity and comparable chemical characteristics. An effective method for determining a material's electrical response to an applied alternating current (AC) field is impedance analysis. We may learn more about the capacitance (C) and electrical energy-storage capacity of the material by measuring the impedance (Z), which is the total resistance to current flow, at different frequencies.

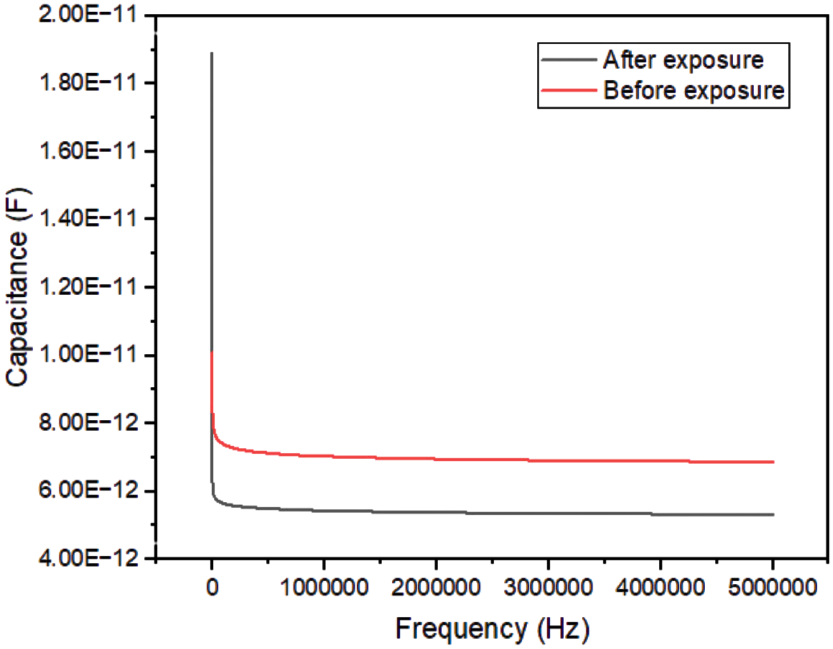


Fig.32. Change in capacitance before and after exposure of sensing material with ammonia.

The link between capacitance and dielectric (ε') is the fundamental idea behind impedance analysis. One way that dielectric affects a system's capacitance directly is by measuring the material's capacity to store electrical energy in an electric field. Modifications to the material's bonding can change its dielectric characteristics, which in turn can affect its capacitance. Thus, the purpose of this work was to identify capacitance changes that might be related to the interaction between PSMA and ammonia by examining the impedance spectra.

A PSMA sample was subjected to ammonia as part of the experiment, and its impedance was then measured at various frequencies. As expected, there was a positive association between the dielectric value and frequency, suggesting a greater capacity to store electrical energy at quicker electrical oscillations. Dielectric materials exhibit this behavior because, at higher frequencies, the dipolar polarization more successfully aligns with the alternating electric field. On the other hand, the capacitance change shown in Figure 00 was the important finding. The capacitance dropped from 8.00 x 10^{-12} F to 6.00 x 10^{-12} F after being exposed to ammonia. This drop points to a possible modification of PSMA's dielectric characteristics as a result of its interaction with ammonia, perhaps as a result of new bond creation or breakage within the polymer matrix.

Significant ramifications for the creation of a VBA detection sensor based on PSMA result from the observed capacitance shift. The sensor's ability to work depends on its ability to identify changes in capacitance when exposed to VBAs. This change in capacitance provides a quantitative indicator of the presence and concentration of VBAs since it can be directly related to the interaction between the polymer and the amines. Through the comparison of PSMA's impedance spectra before and after exposure to VBAs at different concentrations, this method provides an invaluable instrument for assessing the sensitivity and functionality of the sensor.

The data gathered from these investigations will be crucial in ensuring that the sensor's architecture is optimized and that it can effectively detect volatile biogenic amines. The method of optimization involves adjusting the structural qualities or fine-tuning the composition of the polymer to improve its interaction with VBAs, thereby improving the sensitivity and response time of the sensor. Furthermore, knowing the precise nature of the dielectric changes caused by exposure to varying VBA concentrations can help calibrate the sensor for a range of real-world uses, such as food safety and environmental monitoring. Additionally, this study offers a fundamental knowledge of how PSMA's amorphous shape enhances its appropriateness and reactivity for VBA detection. Amorphous PSMA's less structured molecular structure allows for quicker and more effective reactions with VBAs, as shown by the notable variations in capacitance seen in the impedance study. PSMA is a potential material for advanced sensor technologies because of its improved reactivity, which is essential for applications requiring quick and accurate detection of hazardous or spoilage-related amines.

Thorough knowledge of the amorphous nature of PSMA and its interaction with ammonia has been made possible by the combination of XRD and impedance investigations. These results demonstrate the capacity of PSMA-based sensors to identify volatile biogenic amines and provide important information for further study and advancement in this area. Utilizing the special qualities of amorphous PSMA, we can create extremely sensitive and effective sensors that can handle a variety of issues in food safety, environmental monitoring, and other areas.

CHAPTER NO 9

CHARACTERIZATION O CAPACITIVE SENSOR

9.1 Preparation for Measurement

Ensured that the capacitive sensor is fully discharged. This is done by briefly connecting the two terminals of the capacitor to discharge any residual charge.

9.2 Connecting the Capacitor to the Multimeter

Attached the two terminals (or joints) of the capacitive sensor to the probes of the digital multimeter. Ensure a secure and stable connection to avoid fluctuations in the measurement.

9.3 Setting Up the Multimeter

Turn the digital multimeter on and set it to the capacitance measurement mode. This is usually indicated by a symbol resembling ‖. As the multimeter has a range selection option, set it to the minimum value range to start with. This allowed for the detection of even small capacitance values accurately.

9.4 Taking the Initial Measurement

After setting the multimeter to the appropriate mode, wait for a few seconds. The multimeter charges the capacitor and stabilizes the reading. Observed the digital readout on the multimeter until a constant and stable value is displayed. This value represents the initial capacitance of the sensor before any exposure to ammonia.

9.5 Recording Baseline Capacitance

Note down the capacitance value displayed by the multimeter as 0.07nF. This is the baseline capacitance of the capacitive sensor in its initial state.

Fig.33. Capacitive sensor before exposure to ammonia

9.6 Exposure to Ammonia

Expose the capacitive sensor to ammonia in a controlled environment. Ensure that the exposure conditions are consistent, and the sensor is adequately subjected to the ammonia.

9.7 Measuring Capacitance After Exposure

After the exposure period, connect the sensor again to the multimeter probes. Wait for a few seconds until the reading stabilizes. The multimeter once again measured the capacitance, considering any changes due to the exposure to ammonia.

9.8 Recording Post-Exposure Capacitance

Note down the new capacitance value displayed by the multimeter as 0.08nF. This value represents the capacitance of the sensor after exposure to ammonia.

Fig.34. Capacitive sensor after exposure to ammonia.

9.9 Comparing Measurements

Compare the capacitance values obtained before and after exposure to ammonia. An increase in the capacitance value after exposure indicates that the capacitive sensor is responsive to the presence of ammonia.

By following this detailed procedure, the capacitance of the capacitive sensor was accurately measured before and after exposure to ammonia. The observed increase in capacitance post-exposure confirms that the sensor, utilizing PSMA, is sensitive and responsive to biogenic amines such as ammonia. This responsiveness is crucial for applications in detecting and measuring biogenic amines released during spoilage of protein rich food.

CHAPTER NO 10

CONCLUSION & FUTURE DIRECTION

10.1 Conclusion

We have synthesized material that is reactive to biogenic amines, using advanced techniques such as solution polymerization. and characterized using different techniques such as Impedance Analyzer, XRD, FTIR, and digital multimeter. Upon reacting PSMA with ammonia, we conducted the same tests to observe changes in the FTIR bond spectra and dielectric values in the Impedance Analyzer, providing insights into the capacitance variation.

For optimization, the synthesized material was created via solution polymerization. We found various parameters, including different ratios of monomers, activators, as well as altering reaction conditions such as increasing reaction time to increase yield. These adjustments aim to incorporate more reactive sites on the PSMA, enhancing its reactivity towards volatile biogenic amines (VBAs) and thereby optimizing the material's response.

Later, we integrate this advanced polymer with Interdigitated Electrodes (IDEs)to fabricate capacitive sensor and to detect material changes, as the dielectric value will alter post-reaction, leading to a change in capacitance.

10.2 Future Direction

Our long-term objective is to develop an advanced version of capacitive sensor that can be used for a mobile application. This advanced version of the device has significant potential for commercialization. By targeting food industries and entering the international market, we aim to raise awareness and address economic, health, and sustainability challenges, aligning with UN Sustainable Development Goals (SDGs) 3, 8, 12, and 15.

10.2.1. Marketing and Mass Production

To achieve mass production and broader market penetration, we plan to participate in an incubation program to refine our product and business strategy. Our efforts will focus on targeting key stakeholders in the food industry and positioning our device as a crucial tool for monitoring biogenic amines. By entering international markets, we aim to build awareness of the benefits and applications of our technology, facilitating its adoption and contributing to global health and sustainability initiatives.

10.2.2. Commercialization Strategy

A key aspect of our future direction is the commercialization of this advanced sensing technology. We plan to target food industries where monitoring biogenic amines is crucial for quality control and safety. By entering international markets, we aim to raise awareness about the benefits of our technology in detecting harmful biogenic amines. Our commercialization strategy will involve participating in incubation programs to refine our business model, product design, and market approach. These programs will provide valuable resources and mentorship to help scale our production and improve our market readiness.

10.2.3. Mass Production and Market Penetration

We will collaborate with manufacturing partners specialized in electronic sensors for mass production of the product. This will help us to scale up the manufacturing process to meet demand worldwide. Marketing efforts will mainly be focused on key stakeholders of the food industry, by demonstrating the alignment of our product with United Nations Sustainable development goals (SDGs) 3,8,12,15

10.2.4. Raising Awareness and Ensuring Impact

Our aim is to provide awareness about detection of BA in protein rich food products and innovative solution provided by our product. It will need publishing research facilities, participation in industrial conferences, and engagement with regulatory bodies to highlight the need for our technology. We hope to establish our product as standard in industry by ensuring products reliability and its impact contributing to food safety and public health worldwide.

ABBREVATIONS

PSMA - Poly Styrene Co Maleic Anhydride

IDE – Interdigitate Electrode

LOD – Line of Detection

FTIR - Fourier Transform Infrared Spectroscopy

XRD - X-ray diffraction

BA – Biogenic Amines

VBA - Volatile Biogenic Amines

TVB-N - Total Volatile Basic Nitrogen

PMMA - polymethyl methacrylate

HEMA - Hydroxyethyl methacrylate

MMA - Methyl methacrylate

MOFs - Metal-organic frameworks

Au - gold

MA – Maleic Anhydride

FSRs - Force-sensitive resistors

SDS - Sodium dodecyl sulfate

PVA - Polyvinyl alcohol

BPO - Benzoyl peroxide

KPS - Potassium persulfate

APS - Ammonium persulfate

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