

**Synthesis of MOF derived  
Nano-composites with PVA & Starch for  
Packaging application**



**By**

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# **Synthesis of MOF derived nano-composites with PVA & Starch for Packaging application**



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## **Dedication**

*Dedicated to my Beloved Parents*

*“Whoever wants to increase his rizq and to live a long life should honor ties with his  
blood relatives”*

*- [Bukhari]*

## Acknowledgments

All acclaim and eminence be to "**ALLAH**" a definitive maker of this universe, who favored us with the capacity to think and made us anxious to investigate this entire universe. Incalculable greetings upon the "**HOLLY PROPHET HAZRAT MUHAMMAD (P.B.U.H)**": the wellspring of information and blessings for whole humankind.

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## Abstract

Bio nano-composites based packaging materials have a bright future for a broad range of applications in the food and biomedical industry. In addition to innovative active and intelligent packaging, bifunctional characteristics are also being developed. Considerable efforts have been made to utilize the unique properties of MOFs as energy materials in developing high performance catalyst material. A zeolitic imidazolate framework (ZIF-67) based (loading 2-10 wt.%), pre and post pyrolysis composite of poly vinyl alcohol (PVA) is studied as a model system to investigate the role of interfacial interaction in molecular packing, glass transition process and tensile properties. Zeolitic Imidazolate Frameworks (ZIF) is one of the potential candidates as a highly conducting network with large surface area. Furthermore, it has possibility to be used as the support for the packaging material. Molecular packing is changed throughout the polymer matrix with increase in additive loading. This happens because interparticle distance and interphase width becomes comparable. At the highest loading, PVA shows bulk glass transition temperature because of the non-significant volume fraction of interphase resulting from aggregation of ZIF. The best mechanical properties are exhibited by a moderate loading of pyrolyzed ZIF-67 i.e. at 4%. By comparing the maximum stress endured by membranes containing pyrolyzed and non pyrolyzed ZIF-67, the composites containing pyrolyzed ZIF are more strong. It can attributed to the stronger interactions between the exfoliated ions and the polymer matrix.

**Keywords:** Metal Organic Framework; Zeolitic Imidazolate Framework; Solvothermal Synthesis, Room Temperature Synthesis.

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## Acronyms List

MOF	Metal Organic Framework
ZIF	Zeolitic Imidazolate Framework
IM	Imidazolate
XRD	X-ray diffraction
FTIR	Fourier Transform Infrared
SEM	Scanning Electron Microscopy
TGA	Thermal Gravimetric Analysis
PSM	Post synthetic modifications
PCN	Porous Coordination Network
SBU	Secondary building unit
CUS	Coordinative unsaturated metal site
STP	Standard temperature and pressure
DMF	Dimethylformamide
DEF	Diethylformamide
BTC	1, 3, 5-Benzenetricarboxylic acid
1D	1 Dimensional
2D	2 Dimensional
3D	3 Dimensional

# Chapter 1 Introduction

## 1.1 Background

Use of packaging over the years has increased due to the increase in international trade and the rise of e-commerce. The demand for packaging is being met by the use of various synthetic plastics like PVC, PET, Polystyrene etc. The use of these materials results in pollution of the oceans as well as an increase in greenhouse gases resulting in elevated global average temperatures [1].

Therefore, these issues demand the use of responsible packaging that can not only tackle environmental concerns but can also withstand the increasingly harsh temperature conditions faced during shipment of goods. As a result of human exploration, waste products are found in the most remote areas of Earth, which last a long time and have been shown to be a cause of concern for environmental sustainability. Development of biodegradable materials is a way forward in diminishing the impact humans have on the planet. Any idea that focuses only on sustainability and not on the reliability and functionality of a product is bound to fail in the cut throat economic conditions of present day. Environmentally responsible business decisions, therefore, require the design of materials that can not only withstand harsh conditions but can also withstand the test of time and have the ability to be easily disposed without fear of environmental damage [2].

Composite materials represent a great opportunity whereby they can bring together the positive aspects of various materials while reducing the effects of their flaws. For packaging materials, blending of plastics and complex sugars can result in products that biodegrade at a faster rate. Starch has long been considered to be a biopolymer with immense potential for use in biodegradable plastics. It is an abundant and low cost material. It can be used as a thermoplastic under high temperatures and shear. However, it is sensitive to moisture which can be countered by mixing it with plastics like PLC, PLA, PVOH and PVA etc. [3] Furthermore, in order to increase the strength

of the material, metal organic frameworks can be introduced into the mixture which can introduce stresses into the system thereby improving strength. [4]

## **1.2 Biodegradable Packaging**

Owing the intense impact of plastics on the environment, regulations have been put in place to lower the use of harmful plastics that do not biodegrade. For this reason, multiple synthetic and natural polymers have been studied as a replacement for non-biodegradable plastics. Biodegradable plastics usually have functional groups that are cleaved by hydrolytic or enzymatic processes. Most natural polymers are susceptible to enzymatic degradation. [5] Compostability is another important factor in the use of biodegradable polymers. In situations where recycling is not an option and plastic has to be put in a landfill, the material needs to be decomposed relatively easily by microbes and produce mainly water and carbon dioxide. Materials with such properties can also be used as soil conditioners and fertilizers. Under composting conditions, where temperature is controlled (50 to 70 °C) and a large number of microbes are present under humid conditions, the bioplastics are degraded in about 6 to 12 weeks. [1]

Biodegradable polymers find application in medical equipment and medicine along with food packaging. Synthetic polymers have the advantage of batch to batch uniformity as well as predictable properties, but the cost of manufacturing biodegradable synthetic plastics is prohibitive to large scale production. Therefore, natural polymers are more suitable like starch. Since, they can be formed from water and carbon dioxide by photosynthesis. Efforts are being made to use starch by blending it with traditional synthetic polymers derived from petrochemical sources.

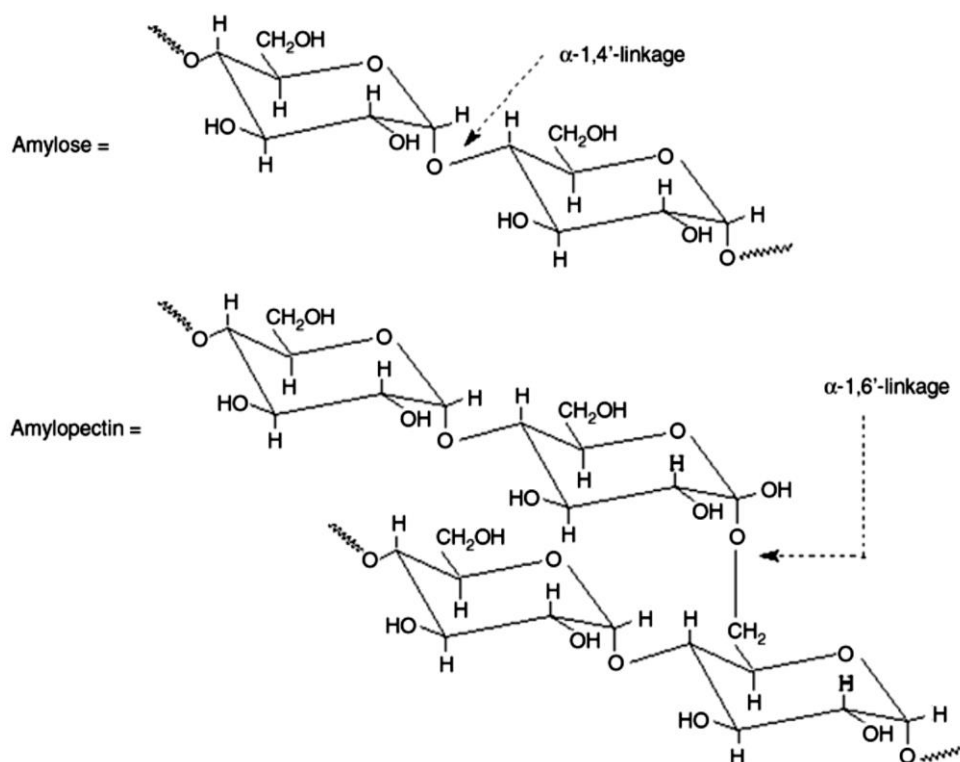


Figure 1 Molecular Structure of Starch

### 1.3 Introduction of MOFs

Metal organic frameworks (MOFs) are also known as porous coordination polymers. They are formed by the coordination of metal ions and organic binding ligands. Based on the type of metal ion used and the synthesis strategy adopted, pore size, surface chemistry and crystal structure of the resultant, MOF can be manipulated. These frameworks are crystalline materials with permanent porosity and a wide structural diversity, giving imparting multiple application opportunities. MOFs can also be used in conjunction with other materials in order to form composites with enhance the physical properties of the final product. [6, 7]

Metal organic frameworks can be built up by using two central components known as connectors and linkers. Here, the connectors take the form of transition metal ions that are versatile connectors owing to the different oxidation states they can attain. [8]

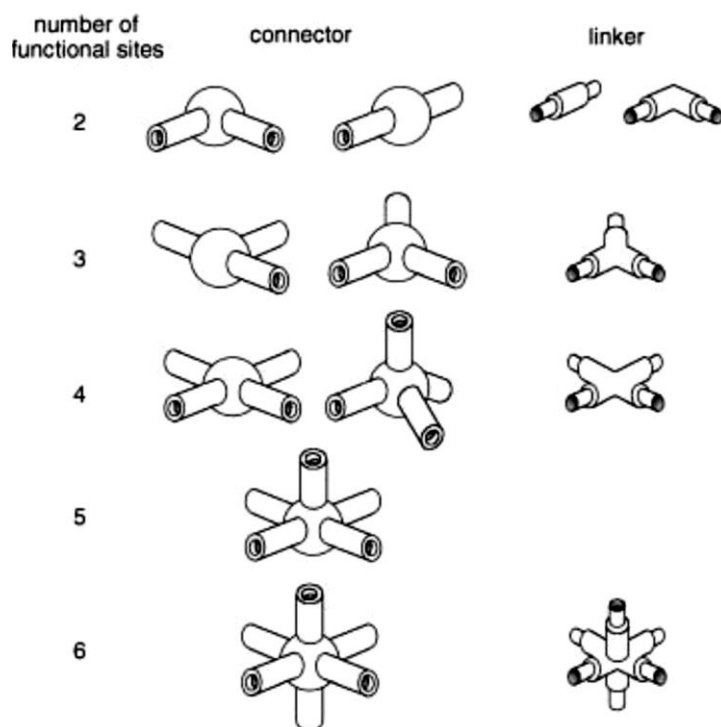
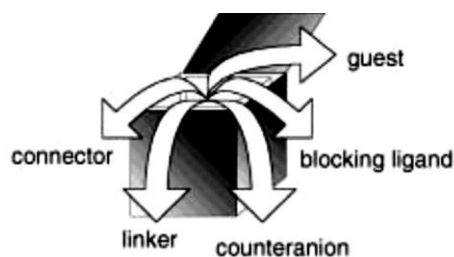


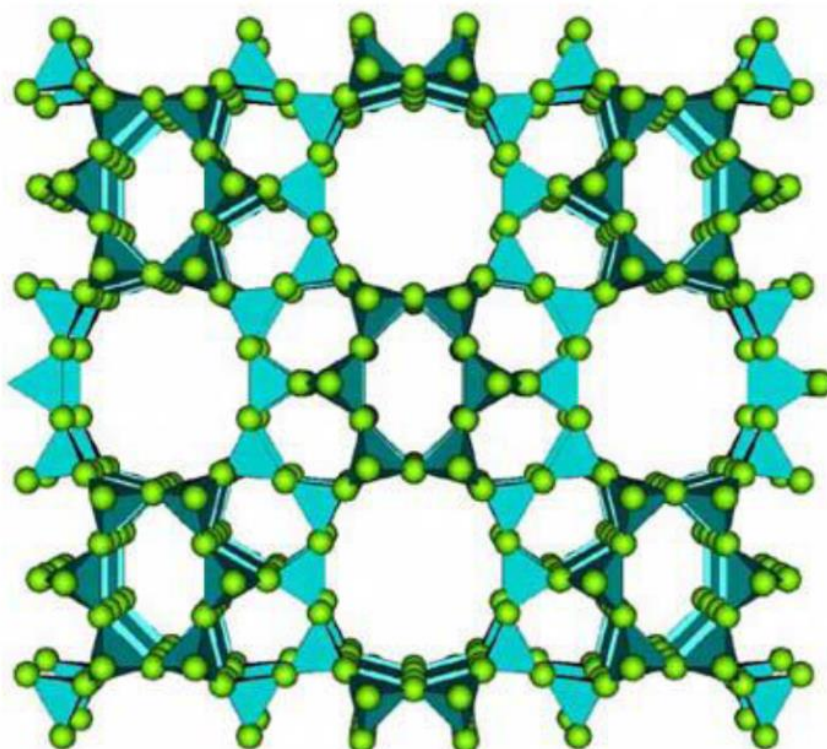
Figure 2 Components of coordination Polymers[9]

## 1.4 Effects of Thermal Treatment on MOF Structure

Metal organic frameworks provide self-sacrificing templates by pyrolysis or calcination after heat treatment. This also allows the material to gain new advantageous characteristics like high surface area and catalytic, which is useful in energy applications. [10] Under normal conditions, the degraded MOF will have the linker oxidized and therefore, the structure becomes amorphized. While under inert conditions, linker-graphitization process can occur which yields products having useful properties like high surface activity which can be taken advantage of in catalytic reactions. [11] Addition of these graphitized materials in the polymer increases the mechanical strength of the final product. This becomes essential since imparting biodegradability with addition of starch reduces strength by a certain degree.

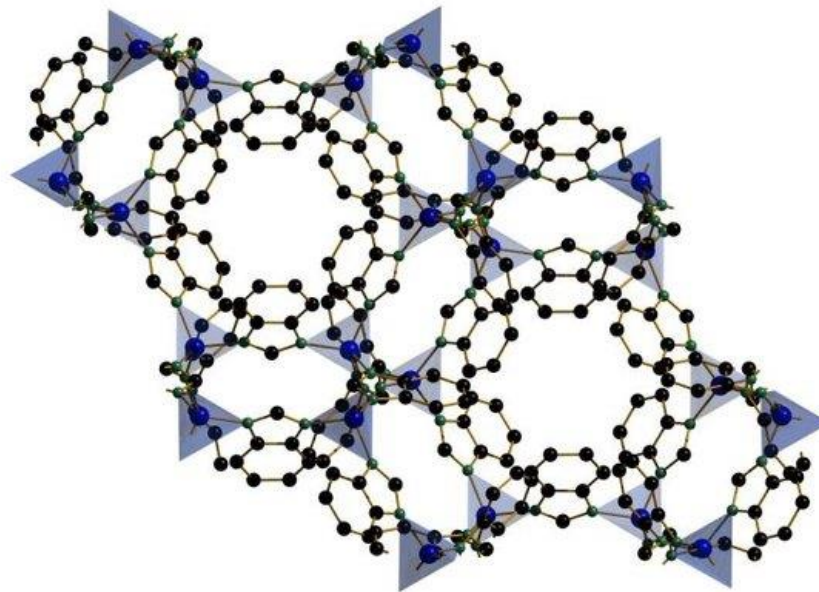
### 1.4.1 Zeolitic Imidazolate Frameworks (ZIFs)

Zeolitic Imidazolate Frameworks are a step forward in the search for structures that are similar to that of Zeolites (tetrahedral Si(Al)O<sub>4</sub> units) and made of transition metals held together by organic links. The porosity of such structures can be useful in catalytic processes because the high porosity material can provide access to transition metal sites. [12] Recently discovered Zinc based Imidazolate frameworks have shown porous structures that are symmetrical and show structural analogy to zeolites, the most notable examples of these include (ZIF)-7 and -8 [13]



*Figure 3 Structure of a complex zeolite [14]*





*Figure 4 Crystal Structure of ZIF-7[15]*

## 1.5 Aim of Present Work

- Synthesis of PVA Starch films using ZIF-67
- Characterization of synthesized films
- Evaluate the effect of concentration of pyrolysed and non pyrolysed ZIF-67

### 1.5.1 Thesis Outline

**1<sup>st</sup> Chapter** has the Metal Organic Frameworks and Zeolitic Imidazolate Frameworks introduction. It also comprises of challenges related to synthesis of MOFs. Aim of this work and outline of this work are concluded at the end.

**2<sup>nd</sup> Chapter** contains a summary of already work carried out on MOFs and ZIFs for dye adsorption applications. Different synthesis techniques for preparation of ZIFs have been discussed. In the end, various applications of MOFs and ZIFs along with their different properties are deliberated.

**3<sup>rd</sup> Chapter** comprises of experimental work along with ZIFs synthesis methodology. Moreover, it also includes the materials used for the preparation of films and characterization techniques utilized for the determination of its properties.

**4<sup>th</sup> chapter** includes the results from characterization as well as dyes adsorption study of ZIFs. The detail discussion is included in this part. It also shines light on the adsorption kinetics and comparison among ZIFs.

The thesis is concluded with a summary of the whole research work and it also discusses future recommendations.

# Chapter 2 Literature Review

## 2.1 Applications of Metal Organic Frameworks

Metal organic frameworks (MOFs) are made by connecting inorganic and natural units by solid bonds (reticular mix). The versatility with which the constituents' geometry, size, and handedness can be changed has incited more than 20,000 different MOFs being represented and thought about inside the earlier decade. The natural units are ditopic or polytopic natural carboxylates, which yield compositionally solid crystalline MOF structures with a common porosity of more prominent than half of the MOF valuable stone volume when associated with metal-containing units,. The surface locale estimations of such MOFs ordinarily go from 1000 to 10,000 m<sup>2</sup>/g, as such surpassing those of standard porous materials, for instance, zeolites and carbons. Until this point in time, MOFs with enduring porosity are more expansive in their combination and assortment than some different class of porous materials. These perspectives have made MOFs ideal possibility for capacity of invigorates (hydrogen and methane), catch of carbon dioxide, and catalysis applications, to make reference to a couple [16]. MOFs comprises of open structure containing metallic focused optional structure unit (SBU) which are joined by a few natural linkers shaping an assortment of 1-D, 2-D and 3-D structure. These structures are crystalline in nature and have long range order. They have excellent pore size which is adjusted by the dissolvable particles or the dissolvable particles during the combination procedure. As per explicit needs and wanted applications, MOFs can be built, giving them an extra trademark over the conventional zeolite or carbon systems where structure is hard to modify [17]. MOFs have various utilizations involving dye degradation, catalysis, magnetic, biomedical applications and separation. Precursor materials ought to be sensibly chosen before preparing MOFs, for accomplishing the foreseen properties. The syntheses of MOFs are genuinely similar to the production of organic polymers, where the physical attributes of the polymer are exceedingly relying on monomers nature, which succeeds the properties of MOFs. In this part a few applications of the MOFs will be discussed [18].

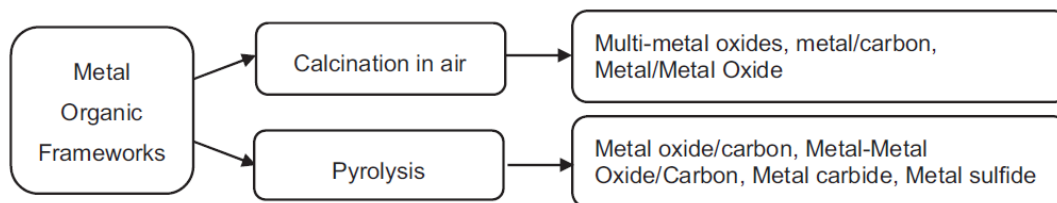


Figure 5 Overview of different types of nanostructures that can be made from MOF precursors [16]

## 2.2 Applications of MOFs in Polymer Composites

It has been demonstrated that because of the alluring interfacial cooperation, two zones of various pressing densities are made inside the polymer grid. First zone viz. interphase reached out from ZIF molecule's surface to couple of nm deep into the network and second zone comprises of mass polymer lattice. From contemplating the nanoscopic structures of metal natural systems, it has been anticipated that the impact of interfacial connections in the composite expand profound into the lattice beginning from the outside of ZIF and the pressing in both the zones is not the same as the mass network [19].

With an end goal to consider the impact of zeolite stacking on the film morphology, the glass advances of the various layers are tried (Sharma et al. 2019). The T<sub>g</sub> of the cross-connected PVA layer increments deliberately with expanding the measure of included zeolite, showing that the free volume of cross-connected PVA film diminishes with expanding the zeolite stacking (Sharma et al. 2019). This is on the grounds that segmental movements of the chains are limited by expanding the zeolite stacking. For the most part, an expansion in free volume prompts higher pervasion motion giving a lessening in selectivity. The upgrade in warm qualities propose that the nearness of zeolites in cross-connected PVA layers builds the pressing thickness, which thus, is in charge of the improvement of partition selectivity without fundamentally giving up pervasion motion [20].

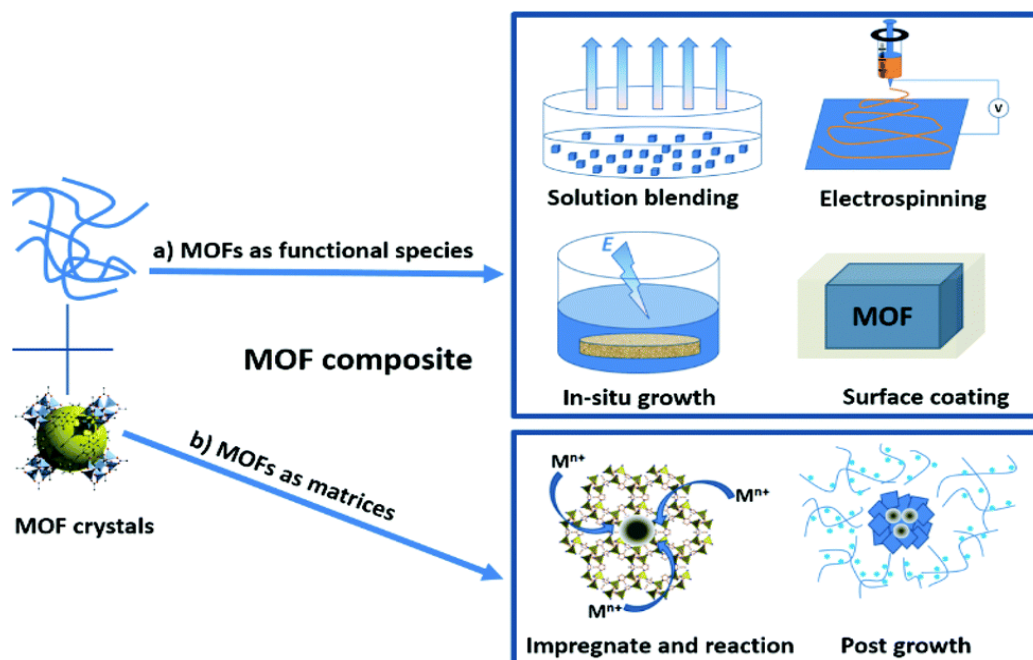


Figure 6 Different methods for achieving a blend of polymers with MOFs [21]

## 2.3 Bio Polymers in Packaging Materials

The utilization of characteristic fiber-strengthened polymer composites has expanded lately. They are considered as a conceivable answer for natural issues brought about by the utilization of oil based, non-biodegradable polymeric. Cellulose is an inexhaustible, biodegradable and the most richly accessible characteristic polymer on the planet. Cellulose comprises of Nano-sized smaller scale fibrils, which are developed by crystalline and a formless area. The cellulose chains are related to each other by hydrogen holding between hydroxyl gatherings. This interlinking outcome in high solidness and auxiliary solidarity to the material. High mechanical quality, lightweight, high length-to-measurement proportion, and enormous explicit surface territory are a couple of the outstanding attributes of Nano cellulose [22]. Because of all these promising properties contrasted with conventional cellulosic filaments and oil based materials, Nano cellulose has pulled in a lot of effort for logical and industrial research [23].

Cellulose nanostructures have been generally examined as parts of materials for an assortment of uses including sustenance bundling. They are generally consolidated as a support stage in nanocomposites (as cellulose nanocrystals or cellulose Nano fibrils). In different cases, cellulose nanostructures have been utilized as frameworks for

films—bacterial cellulose (BC) meriting an exceptional consideration in this specific circumstance. It is delivered as normally nanostructured films, which may develop in a medium containing different biopolymers (creating base up manufactured bio nanocomposites), be impregnated with different parts, or be deteriorated into nanofibrils or even nanocrystals [22].

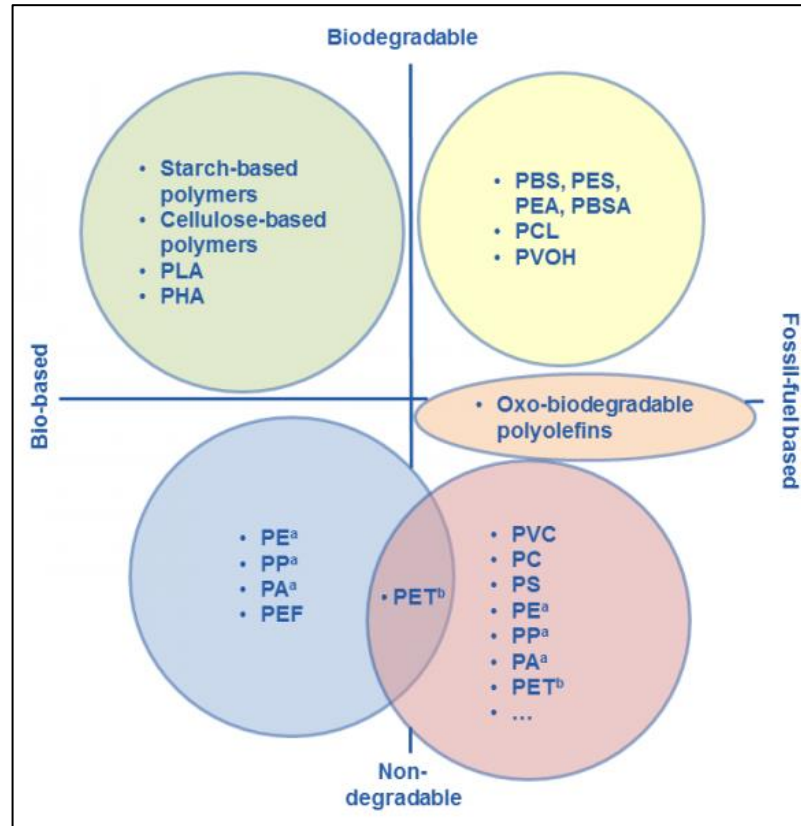


Figure 7 Sources of polymers and their biodegradability [24]

## 2.4 PVA Starch Blends

The utilization of biodegradable polymers for bundling offers an option and halfway answer for the issue of aggregation of strong waste made out of engineered dormant polymers. A wide scope of manufactured aliphatic polyesters and normally happening items are being utilized as biodegradable polymers for chose applications [1,2]. The utilization of starch is expanding in numerous applications, basically as a result of the minimal effort and accessibility of starch. Packaging films made totally out of starch, be that as it may, do not have the quality and inflexibility to withstand the stresses to which many bundling materials are oppressed. The intelligent arrangement is to consolidate starch into a film with a more strong base. Broad research has been done

to conquer a portion of the restrictions related with starch based polymer mixes. Starch mixed with the manufactured polymer polyvinyl liquor (PVA) has been contemplated as a potential biodegradable polymer [25]. Contingent upon the level of biodegradability, it appears that PVA may give a steady help medium to starch films. The mechanical properties and biodegradability of starch PVA mixed movies have been accounted for by a few scientists. Such mixed films have not been thoroughly concentrated to decide such highlights as their compound heterogeneity or surface practically [2],[5].

## **2.5 Polymer composites reinforced with nanoparticles**

Starch is a naturally existing biopolymer which is accessible in wide amount from different sources. Potato is one of the major resources, which is easily accessible and can likewise be considered as one of the economical source of starch. In any case, starch itself has certain restrictions e.g., low quality, low lengthening, high fragility and so on [26]. Subsequently it is blended with Polyvinyl alcohol (PVA) to upgrade its properties. PVA is produced however nontoxic, biodegradable and nourishment safe. Expanding utilization of manufactured polymers and insufficient reusing of the equivalent has expanded the environmental concerns [4], [27]. Subsequently alternative of the manufactured polymers with biopolymers might be considered as one stage ahead towards the green technique. Biopolymers having practical asset may solve the environmental issues all things considered. With this thought a ton of specialists worldwide are currently considering the biopolymers based mixes for different polymeric applications like food packaging and recyclable shopping bags and are attempting to supplant engineered polymers with biopolymers [24], [1].

In recent times numerous scientists are taking a shot at different renewable common/biopolymer based mixes and composites. Among various sorts of biopolymer like starch, cellulose, chitosan, polylactic corrosive and so forth., starch is one of the most effectively accessible, cost effective and sustainable biopolymer. In addition, starch is accessible from different sources like potato starch, corn starch, wheat starch and so forth. Literature study uncovers that expansion of starch to different manufactured polymers not just improves the biodegradability of the end

material yet additionally diminishes cost with better adequacy assistants of properties [18], [28].

*Table 1: Literature survey of synthesis and adsorption applications of MOFs and ZIFs*

<b>Sr. No.</b>	<b>Authors</b>	<b>Year (Journal)</b>	<b>Title</b>	<b>Findings</b>
1	S. K. Sharma, K. Sudarshan and P. K. Pujari [19]	2016 (Physical Chemistry Chemical Physics)	Unravelling the sub-nanoscope structure at interphase in Poly (vinyl alcohol)-MOF nanocomposite and its role on thermomechanical properties	A decrease in ductility and increase in rigidity was seen for the polymer chains in the tensile testing measurements due to attractive interfacial interaction.
2	A. A. Kittur et al. [20]	2003 (Applied Polymer)	Pervaporation Separation of Water–Isopropanol Mixtures Using ZSM-5 Zeolite Incorporated Poly (vinyl alcohol) Membranes	The Glass Transition Temperature ( $T_g$ ) of the cross-linked PVA membrane increased systematically with increasing the amount of zeolite, indicating that the free volume of cross-linked PVA membrane decreased with



				increasing the zeolite loading
3	M. S. Sarwar et al. [29]	2018 (Carbohydrate Polymers)	Preparation and characterization of PVA/Nano cellulose/Ag nanocomposite films for antimicrobial food packaging	By addition of silver nanoparticles the mechanical strength along with antimicrobial properties were improved which makes the end product suitable for use as a packaging material.
4	Susmita Dey Sadhu et al. [26]	2015 (Journal of Nano medicine & Nanotechnology)	Thermal Studies of the Starch and Polyvinyl Alcohol based Film and its Nano Composites	Addition of nanoparticles in blends of PVA and Starch imparts mechanical strength to the material
5	R. Jayasekara et al. [18]	2004 (Material characterization)	Preparation, surface modification and characterization of solution cast starch PVA blended films	Methods for material preparation and characterization

				(SEM, XRD, FTIR)
6	S.Ceylan et al. [30]	2018 International Journal of Polymeric Materials and Polymeric Biomaterials	Comparison of additive effects on the PVA/starch cryogels: Synthesis, characterization, cytotoxicity, and genotoxicity studies	Discussion of the effects of addition of different additives in polymer matrix and its characterization
7	J.Qian et al. [31]	2012 (Materials Letters)	Hydrothermal synthesis of zeolitic imidazolate framework-67 (ZIF-67) nanocrystals	Parameters and process for preparation of water based ZIF-67 which is conventionally made using methanol
8	Z.Wu et al.[32]	2019 (International Journal of Biological Macromolecules)	Physical properties and structural characterization of starch/polyvinyl alcohol/graphene oxide composite films	Addition of Graphene Oxide improves the mechanical properties of the polymer along with imparting moisture resistance
9	B. Guo et al. [33]	2018 (Materials)	Polyvinyl alcohol microspheres reinforced thermoplastic starch composites	Addition of small amounts of PVAMSs can enhance the mechanical strength and

				toughness of the material.
10	Noshervani et al. [34]	2016 (International Journal of Food Engineering)	Starch-PVA Nanocomposite Film Incorporated with Cellulose Nanocrystals and MMT: A Comparative Study	The study shows that the addition of Sodium Montmorillonite (MMTs) reduces the moisture affinity of the polymer
11	A. Singha et al. [35]	2015 (International Journal of Polymer Analysis and Characterization)	Cornstarch/Poly(vinyl alcohol) Biocomposite Blend Films: Mechanical Properties, Thermal Behavior, Fire Retardancy, and Antibacterial Activity	Characterization of PVA blends, methods and procedures. The blend was concluded to be biologically inert and hence safe for food use.
12	K. Kaur et al. [36]	2019 (International Journal of Biological Macromolecules)	Studies on the properties and biodegradability of PVA/Trapa natans starch (N-st) composite films and PVA/N-st-g-poly (EMA) composite films	Due to the formation of starch grafted composite increase in tensile strength of the polymer is observed.
13	Lopez et al. [37]	2018 (Carbohydrate Polymers)	Study of the behavior of biodegradable starch/polyvinyl alcohol/rosin blends	The study compare the use of resin and starch as additives in the

				polymer discussing the pros and cons of each
14	Guimarães et al. [38]	2015 (Journal of Polymer Research)	High moisture strength of cassava starch/polyvinyl alcohol-compatible blends for the packaging and agricultural sectors	Increasing the polymer content in a blend renders it more flexible and ductile.
15	Du et al. [39]	2019 (Chemistry Select)	Structure and Properties of Starch/Poly (vinyl alcohol) Film Modified by Different Inorganic Salts	The study analyzed the effect of different ions on the mechanical strength of PVA blends and concluded that MgCl yielded highest tensile strength

## 2.6 Motivation and Objectives

Owing the global impact of plastic use, the need for biodegradable packaging products has recently gained much attention. Following are the chief motivational aspects behind this work:

- Increase the mechanical strength of packaging material
- Improve the shelf life of packaged material
- Better efficiency with high surface-to-volume ratio
- Enhanced surface reactivity
- Enhanced Bifunctional properties

Besides the overall drive to attain fully biodegradable products, we chose to focus on the use of specific additives in the traditionally used PVA to test their effectiveness in achieving the ultimate goals. The prime objectives for the study are as follows:

- Synthesis of MOF based nanocomposites with PVA & Starch.
- Investigating the improvements of nanocomposites films.
- Comparison of pyrolysed and non pyrolyzed ZIF 67 based films.
- Enhanced Bifunctional properties

# Chapter 3 Experimental

## 3.1 Materials Used

Cobalt Nitrate Hexahydrate  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  was of 97% purity and purchased from DAEJUNG. The 2-Methylimidazole of 99% purity was purchased from MERCK along with Poly Vinyl Alcohol (PVA) and Starch. All these chemicals were used as per received.

Table 2: Properties of materials used in synthesis of ZIFs

Sr. No.	Chemicals	Molecular Weight ( $\text{gmol}^{-1}$ )	Boiling Point ( $^{\circ}\text{C}$ )	Melting point ( $^{\circ}\text{C}$ )
1	2-Methylimidazole $\text{C}_4\text{H}_6\text{N}_2$	82.10	270	145
2	Cobalt Nitrate Hexahydrate $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	291.03	74	55
3	Distilled Water $\text{H}_2\text{O}$	18	100	0
4	Starch	692.661	Decomposes	Decomposes
5	PVA (Poly Vinyl Alcohol)	85,000- 124,000	228	200

## 3.2 Synthesis Procedure of MOFs

The ZIF-67 samples were synthesized by room temperature method. ZIF-67 was synthesized by making a solution of 1.97 grams of 2-Methylimidazole by dissolving

it in 20ml of deionized water and 1.74 grams of cobalt nitrate was dissolved in 20 ml of deionized water as well. This is in contrary to the conventionally used ethanol or methanol as a solvent during the synthesis process, resulting in an economical product.

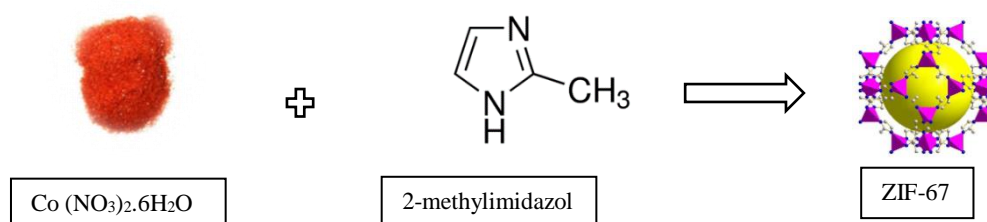


Figure 8 Formation of ZIF-67

A mixture of 20 ml of previously prepared solutions each was used as solvent for ZIF-67 synthesis. Both solutions were mixed and stirred for 20 hours at room temperature. The purple precipitates were formed which were centrifuged out and washed with water several times. The collected precipitates were dried at 80°C overnight [11,16,31].

For comparing the effect of pyrolysis on the strength of the final film, the prepared ZIF-67 was also pyrolysed in a tube furnace at an ultimate temperature of 700°C under Argon atmosphere [31,40]. The pyrolysis process involved heating from 50 to 350°C at a ramp rate of 10°C per min and then to 700°C at a ramp rate of 2°C per min. The temperature was held at 350°C for 1.5 hours and at 700°C for 2 hours. The resultant product contained less than half of the mass of the initial weight of the sample. The furnace was cooled down under inert atmosphere using Argon to avoid any oxidation of the material [41].

### 3.3 Preparation of PVA-Starch films

The polymeric films were prepared in petri dishes by combining PVA with starch along with ZIF-67. 5g of PVA was added to 50ml of water followed by the addition of 3.5g of starch in 50ml water in two separate beakers. The solutions were stirred at 80°C for 2hrs and were subsequently mixed together and stirred for another 2hrs at the same temperature. A few drops of glutaraldehyde along with glycerin were also added at this stage. Glutaraldehyde acts as a linker and promotes cross linking in the film and the latter acts as a plasticizer [39][42].

Finally, ZIF-67 was added to the resultant mixture with different weight percent according to the amount of PVA. Mixtures of 2 to 10 w.t. % concentration were prepared resulting in six different compositions. All the prepared compositions were sonicated to achieve homogenization. The detailed description of the amounts of additives is given in the table which resulted in a final volume of 30ml for each. The procedure was repeated for the pyrolyzed ZIF-67 as well making six additional films [43].

*Table 3 Concentrations of ZIF-67 in PVA-Starch films with corresponding amount of additive*

<b>w.t. %</b>	<b>Amount of ZIF-67</b>	<b>Amount of PVA</b>	<b>Amount of Starch</b>
2%	0.03g	0.91875g	0.55125g
4%	0.06g	0.9g	0.54g
6%	0.09g	0.88125g	0.52875g
8%	0.12g	0.8625g	0.5175g
10%	0.15g	0.84375g	0.50625g
Blank	0g	0.9375g	0.5625g

Each 30ml solution, containing different concentration of ZIF-67, was dried in a petri dish for 48hrs at room temperature and were then peeled off and dried in an oven at 50°C for 5hrs to ensure maximum drying.

### **3.4 Characterization Techniques**

Characterization of the synthesized ZIFs is done by various techniques including:

1. Scanning electron microscopy
2. X-Ray Diffraction
3. Thermogravimetric Analysis
4. Ultimate Tensile testing
5. Fourier Transform Infrared Spectroscopy

These techniques are discussed in detail are discussed below:



### 3.4.1 Scanning Electron Microscopy (SEM) & Energy Dispersive X-ray Spectroscopy (EDS)

SEM is used widely for characterizing and studying the morphology of materials. The microscope makes use of an electron beam which is emitted either under thermionic conditions or field emission. Samples can be resolved up to a very high magnification as the electron beam scans the surface.

The incident electron beam results in the production of various resultant electrons and emissions which can be collected to convey information about various aspects of the sample. Secondary electrons emitted from the sample are collected using a Secondary electron detector which converts the incident electron into an image.

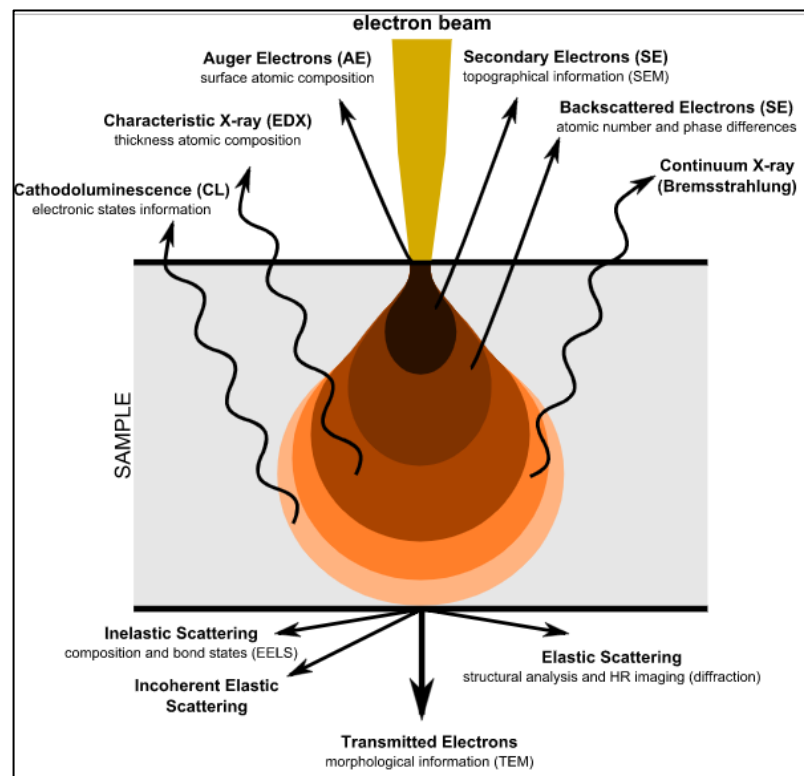
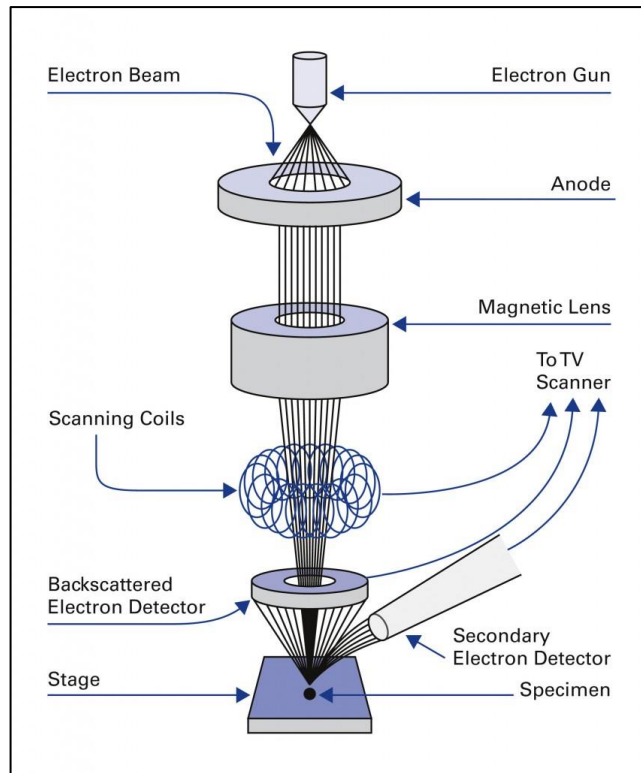


Figure 9 Emission from sample after interaction with an incident electron beam ([44])



*Figure 10 Working mechanism of Scanning Electron Microscope ([44])*

The characteristic X-rays produced as a result of electron beam bombardment can be used to infer information about the chemical composition of the sample by using Electron Dispersive X-Ray Spectroscopy. After collection of the characteristic emissions the resultant spectrum is compared to a calibrated standard and gives the weight percentage as well as the atomic percentage of the constituent elements in the sample. The only exception being the detection of Hydrogen as it does not emit any X-rays that can be detected.

### **3.4.2 X-Ray Diffraction (XRD)**

Crystallography relies on the use of X-rays in order to diagnose the structure and placement of different atoms within the crystal structure of a crystalline material. Monochromatic X-rays are used in the process whereby they fall on the sample over a range of angles, by either rotating the sample or the source. X-rays fall in-between UV rays and  $\gamma$ -rays. The diffracted rays are recorded and the intensity measured at each angle and the resultant spectrum is compared to available libraries in order to identify the material.

The source used for the production of X-rays is usually copper or molybdenum which is heated using electrical energy (usually 1200W). The interaction of these rays with the electrons of the material atoms excites them and they attain a higher energy

level and release a photon of corresponding energy that can be captured. Following equation shows the relation between the radiation energy and wavelength where  $c$  represents the speed of light in vacuum while the  $h$  is the Planck's constant. The wavelength of light  $\lambda$  typically has a value of  $1.58 \text{ \AA}$

$$E = \frac{hc}{\lambda}$$

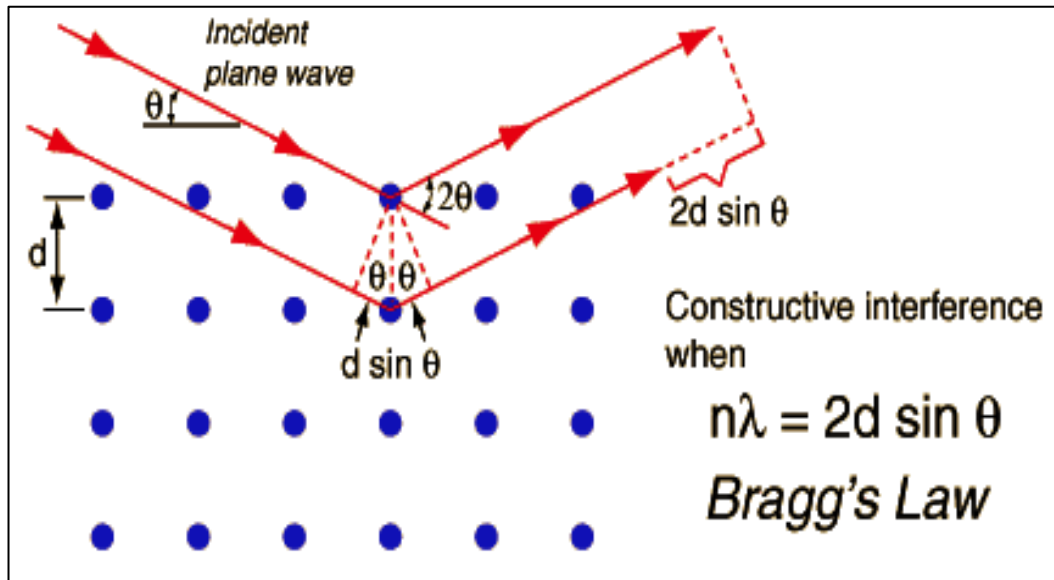


Figure 11 Bragg's Law ([45])

Bragg's law is a straightforward and well known equation to comprehend the procedure of diffraction and is broadly utilized in crystal diffraction. Utilizing Debye-Scherer equation we can ascertain the crystallite size. Every crystalline material has their own particular remarkable X-ray pattern.

### 3.4.3 Fourier Transform Infrared (FTIR) Spectroscopy

The Fourier-transform spectroscopy is a method of finding information about the absorption characteristics of a material. Multiple sets of light frequencies are shone on the sample and for each set of frequencies it is recorded which part of the incident radiation is absorbed. A broadband light source which all of the wavelengths of light that are to be tested interacts with an interferometer that sequentially blocks some of the frequencies to test the behavior of the sample in the absence of said frequencies. The process yields a set of points which is processed via software to infer information about the frequencies of light that were absorbed by the material.

The main reason for conducting this characterization is to get information about the functional groups and bonding in the material which can be used to identify

the material. The raw data is processed in a process called Fourier Transformation which transforms the raw data into a spectrum showing which wavelengths of light show maximum absorption.

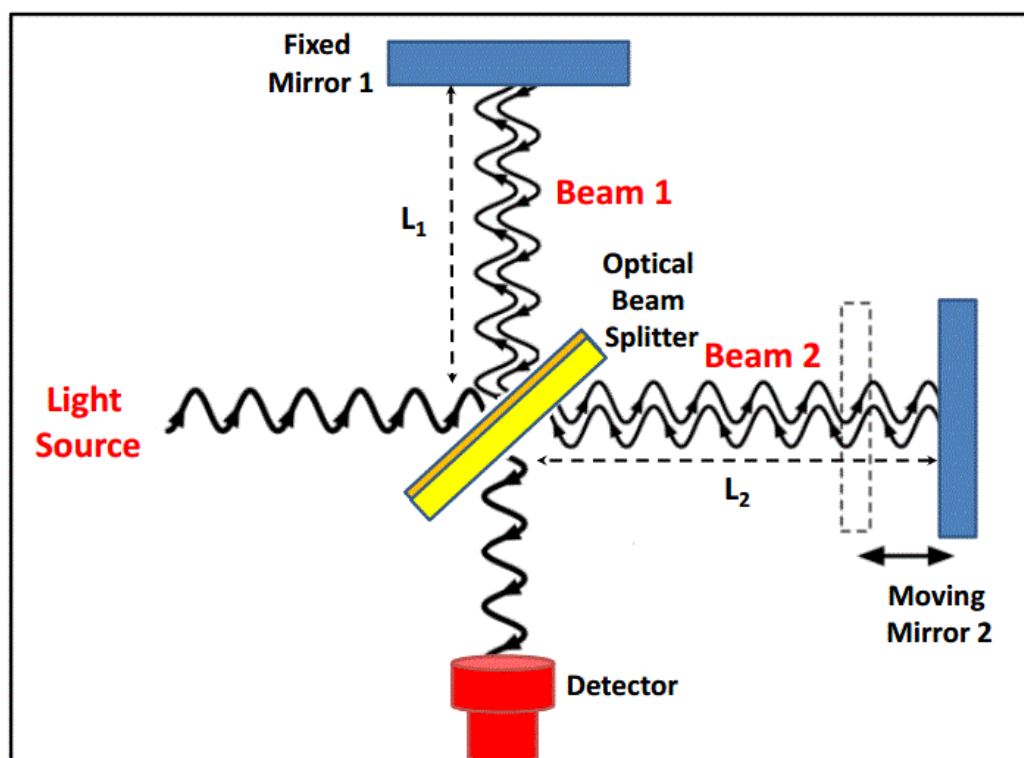


Figure 12 Working principle of FTIR([46])

#### 3.4.4 Thermogravimetric Analysis (TGA) & Differential Thermal Analysis (DTA)

Thermal gravimetric analysis involves the monitoring of the weight of a sample as it is heated in order to gather information about the thermal stability of the material along with processes like absorption, desorption and phase transformations of the material. The instrument is capable of providing a preprogrammed temperature at a ramp and record the loss or gain in the mass of the sample over the time of the analysis. Based on the type of sample and the nature of the information required, TGA is able to provide different atmosphere that can either have low or high pressure as well as either be ambient air or an inert or reactive gaseous medium. The data for mass and temperature is plotted usually with the percentage mass on the y-axis and temperature on the x-axis.

In order to gather information about the phase transitions or glass transition temperatures along with crystallization and melting points, thermal gravimetric analysis is accompanied by differential thermal analysis (DTA). This involves putting

a standard reference material under similar thermal conditions as the sample. The difference between the temperature of the sample and the reference is used to identify the changes in the sample.

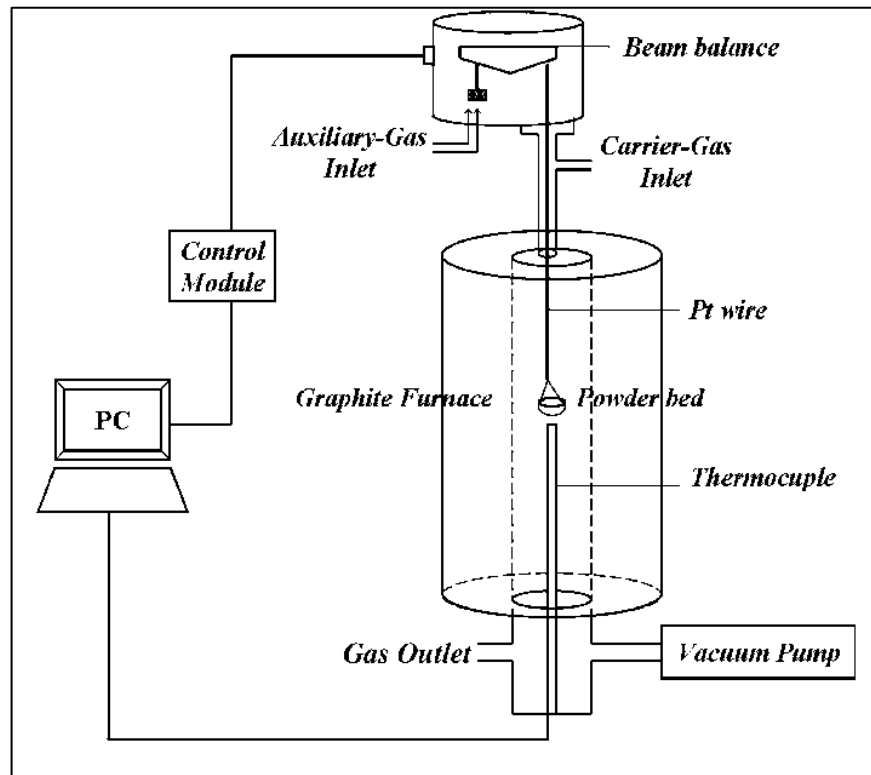


Figure 13 Schematic diagram of TGA ([47])

A steady horizontal line in the plot indicates the stability of the sample at the given temperature. As the line slopes negatively, the mass of the sample drops in coordination as well and in the case of polymers at a certain temperature under oxidizing conditions all of the mass is lost.

### 3.4.5 Ultimate Tensile Testing

In order to find the effect of tension on a material, force is applied to the sample and the strain is monitored. The point of breaking of the sample is known as the ultimate tensile strength of the material, this is the point where a material can withstand the maximum strain. The machine uses two vices to apply force to the material in opposite directions until the material fractures. Based on the amount of strain that materials can withstand prior to fracture, materials can be characterized into being ductile or brittle which lies at far ends of the spectrum of elasticity. Elasticity is the ratio of stress to strain and brittle materials are capable of withstanding a higher level of stress while exhibiting low strain before reaching their ultimate tensile strength.

$$E = \frac{\sigma}{\epsilon} = \frac{F/A}{\Delta L/L_0}$$

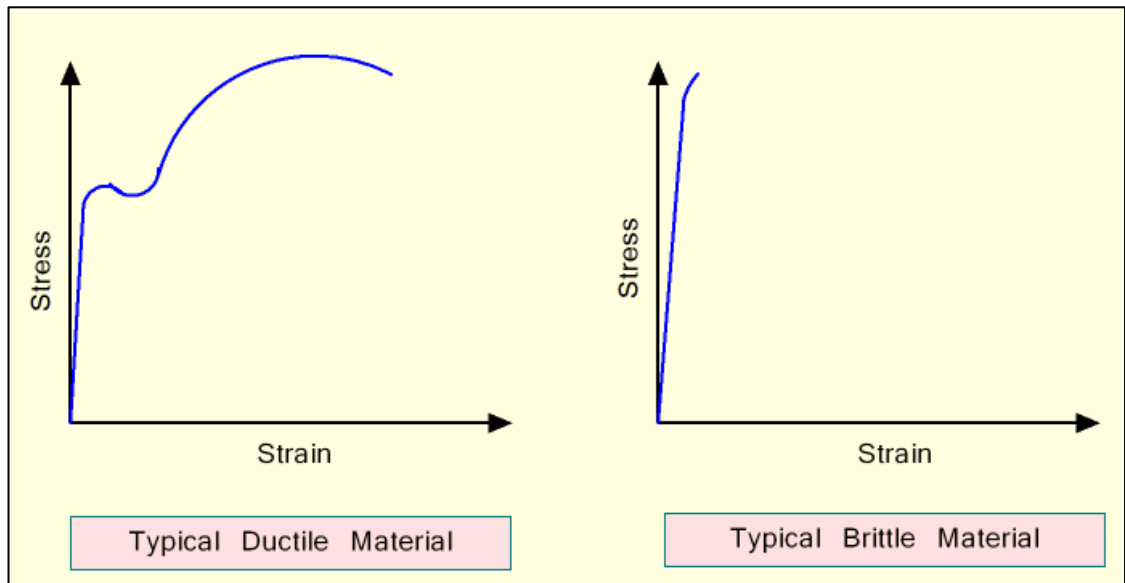


Figure 14 Stress-Strain curve for ductile and brittle materials ([48])

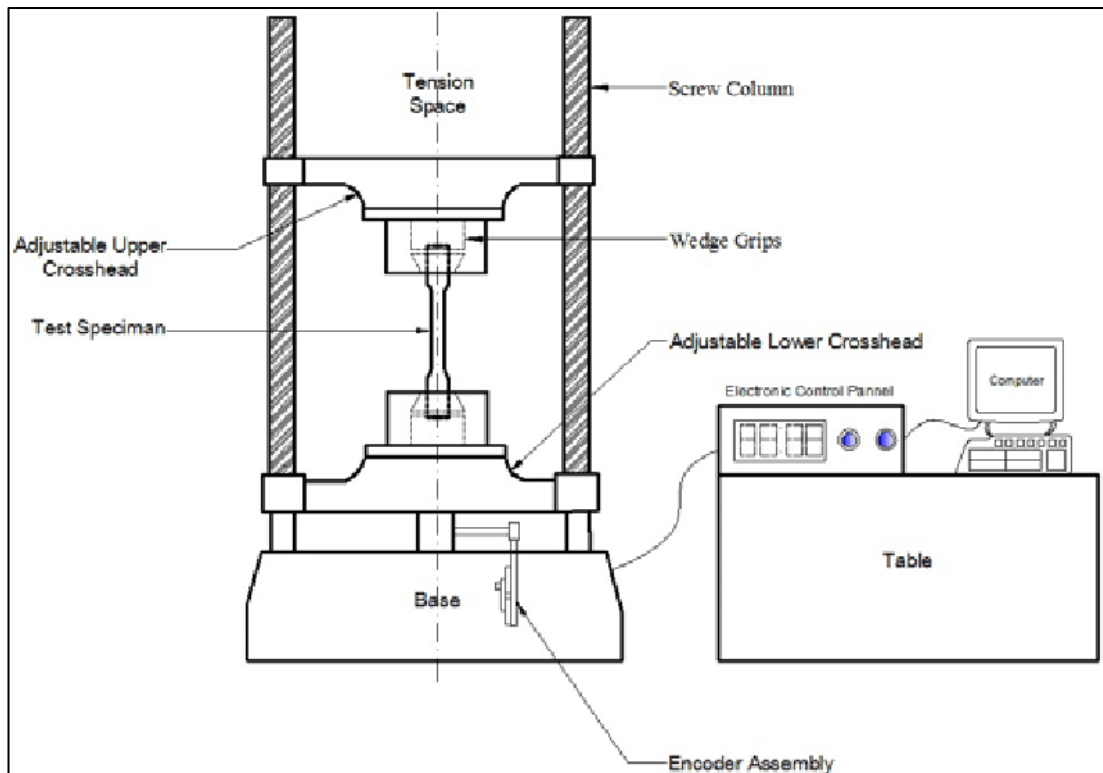


Figure 15 Schematic diagram of tensile testing machine ([48])

# Chapter 4 Results and Discussion

## 4.1 Scanning Electron Microscopy (SEM) Analysis

The micrographs of ZIF-67 are shown in figure 17. The surface area of the material is increased as the material is pyrolysed. This aspect helps in increasing the strength of the composite as the pyrolysed ZIF is able to form stronger interactions with the polymer thus imparting mechanical strength [4], [19].

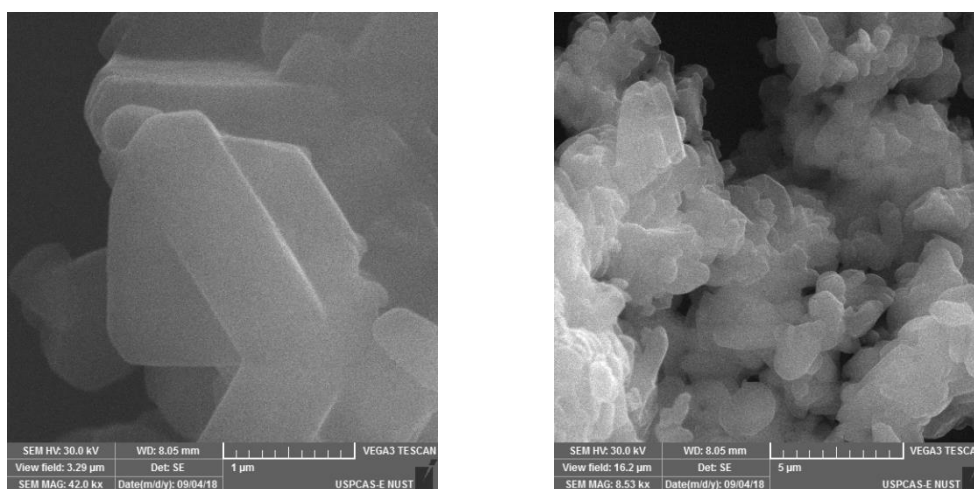


Figure 16 ZIF-67 Before Pyrolysis

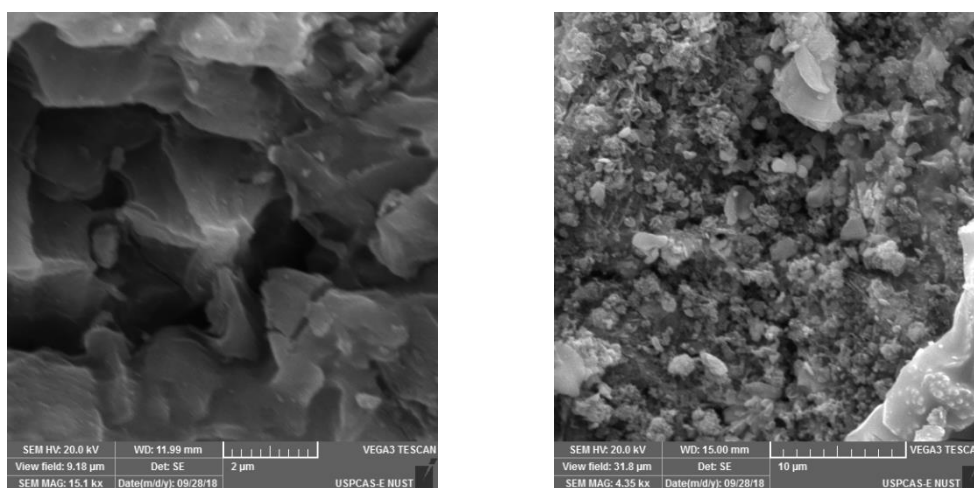


Figure 17 ZIF 67 After pyrolysis

Figure 16 and 17 represent the surface morphology of both ZIF-67 before and after pyrolysis, respectively. The images show a gradual increase in the aggregation of the added ZIF. To a certain extent the material seems to distribute itself in the PVA

starch composite but as the concentration is increased further, the added ZIF seems to aggregate and the dispersion in the material is reduced. This may be attributed to the affinity of ZIF to form aggregates at higher concentrations.

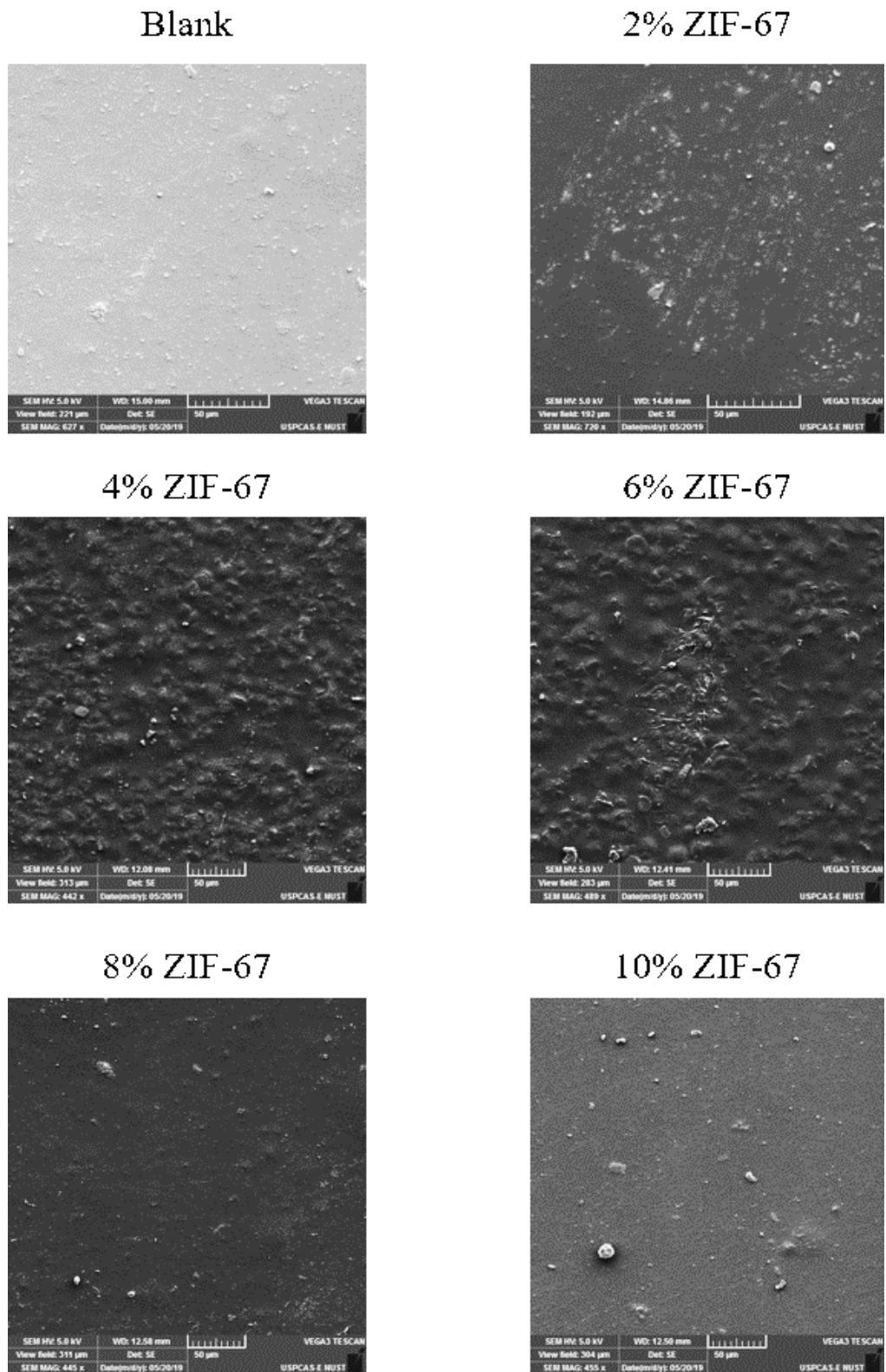


Figure 18 Scanning Electron Microscopy images of composite polymer films with different concentrations of non-pyrolysed ZIF-67



The mechanical strength of the films mirrors the dispersion of ZIF in the material. The maximum dispersion of ZIF is in the 4% sample and this is the sample which shows high mechanical strength.

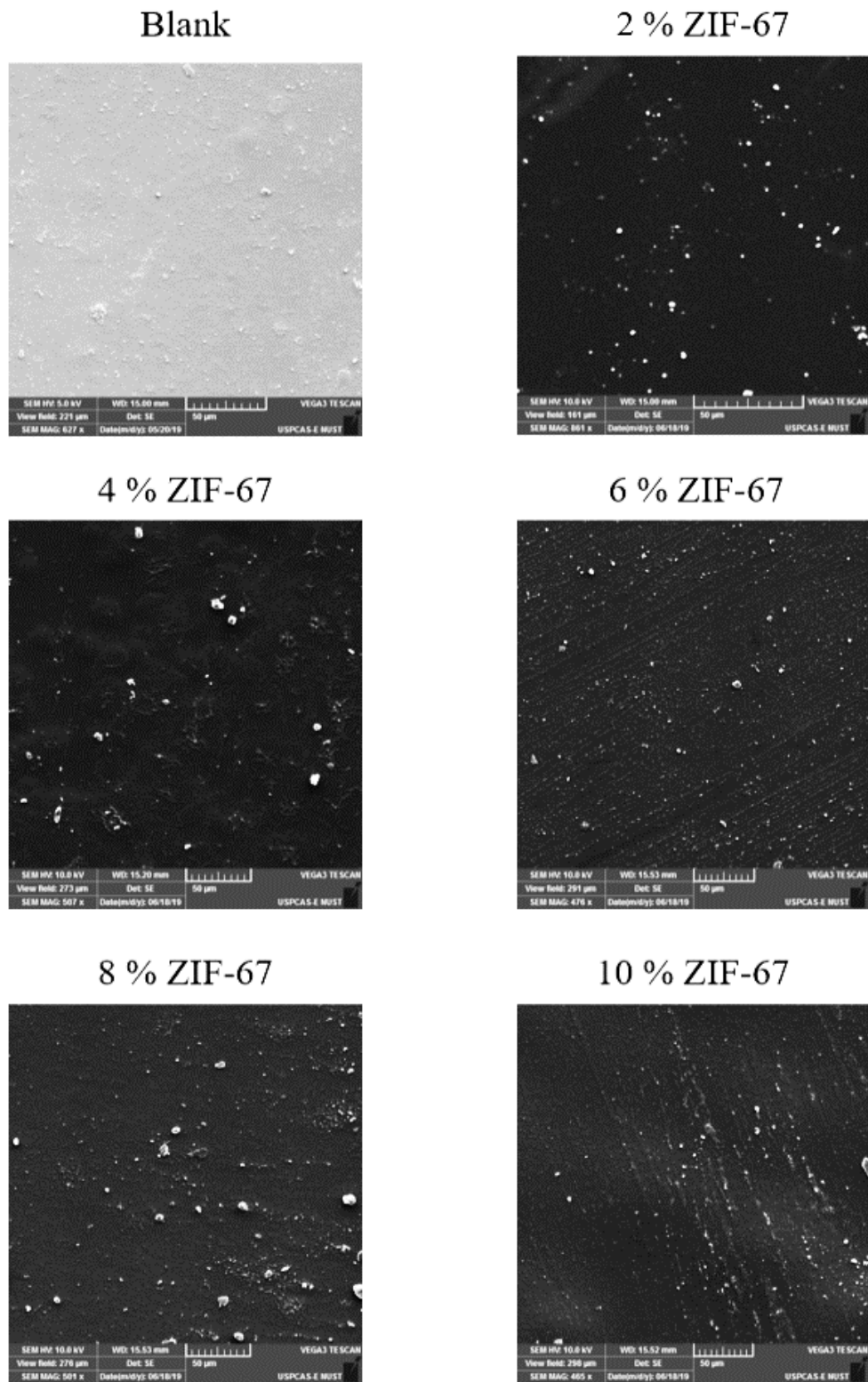


Figure 19 Scanning Electron Microscopy images of composite polymer films with different concentrations of pyrolysed ZIF-67

## 4.2 Electron dispersive spectroscopy

EDS of the samples was conducted in order to find out the amount of ZIF-67 that is dispersed in the sample. Here, Cobalt concentration is mentioned in order to show the dispersion loading rate of each film.

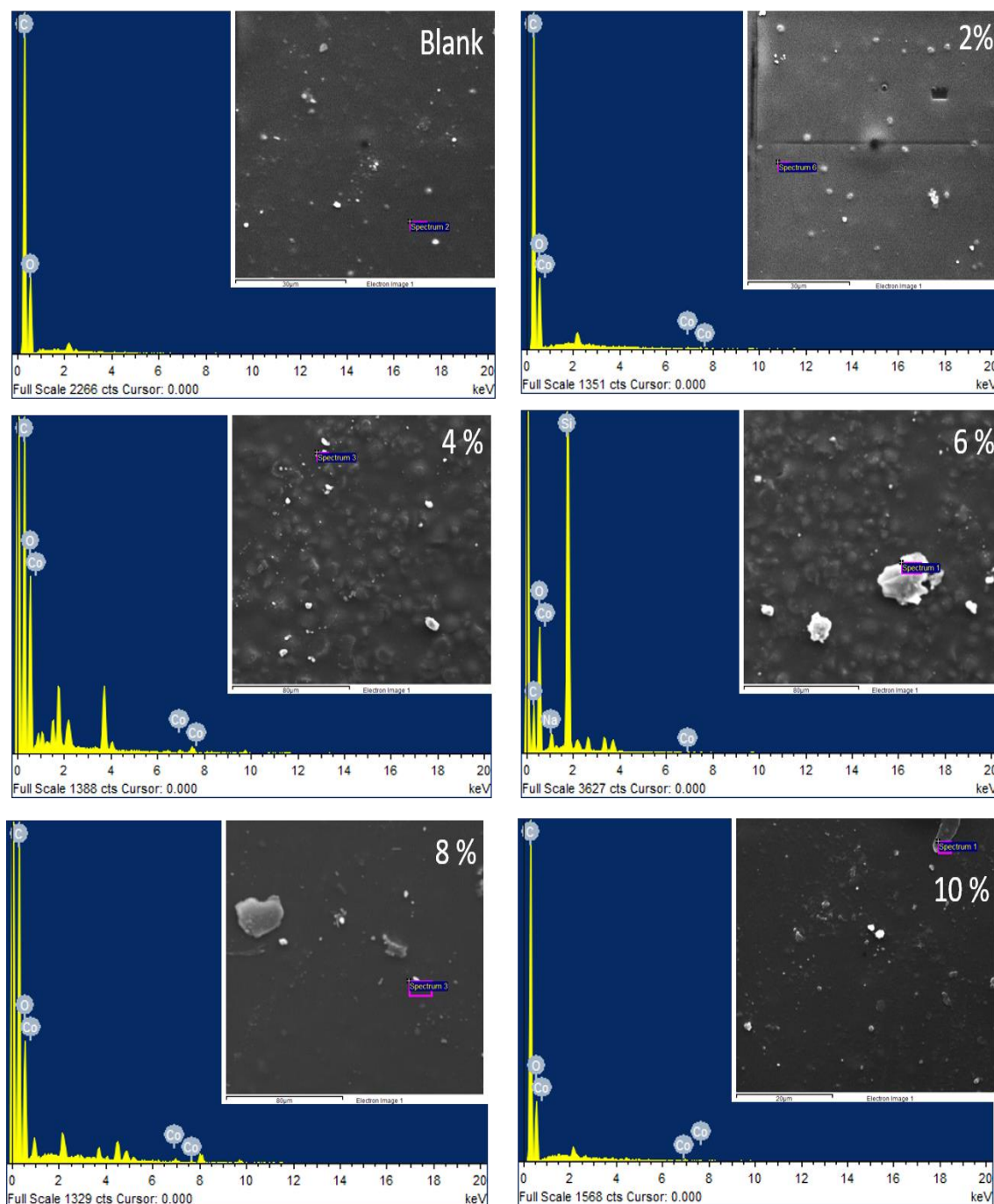


Figure 20 EDS graph's and respective images of non-pyrolysed films

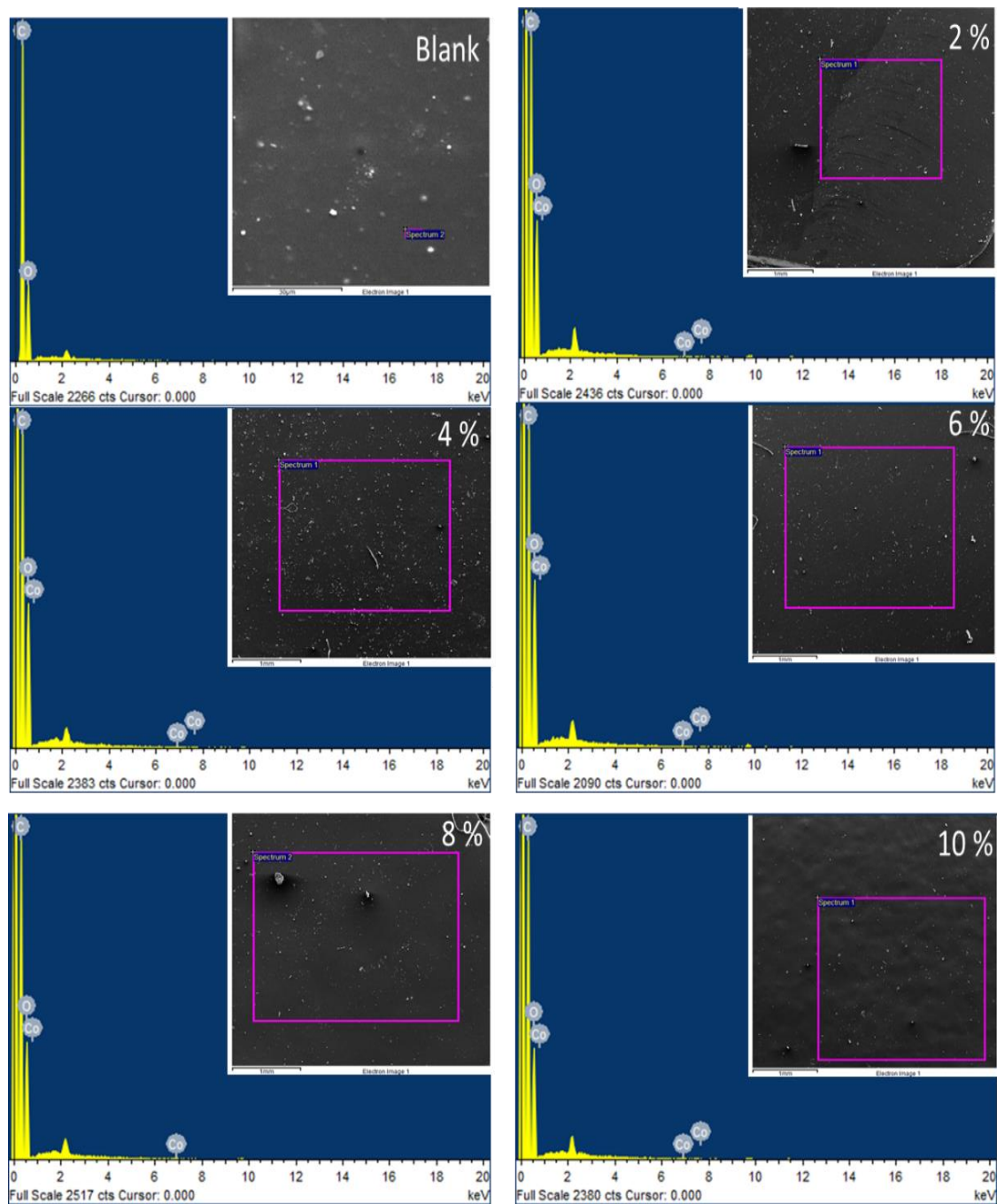


Figure 21EDS graph's and respective images of pyrolysed films

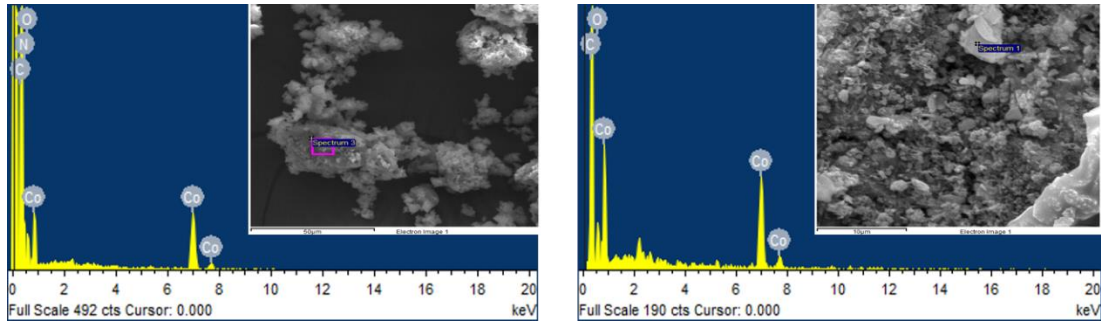


Figure 22 EDS graphs and images of Zif-67 before and after pyrolysis

Table 4 Concentration of Cobalt in Pyrolysed and Non pyrolysed ZIF-67 composites of PVA and starch

Additive concentration	Co concentration in non pyrolysed ZIF-67, PVA, Starch composites	Co concentration in pyrolysed ZIF-67, PVA, Starch composite
Blank	0%	0%
ZIF-67	22.92%	16.47%
2%	0.11%	0.01%
4%	0.25%	0.05%
6%	0.29%	0.03%
8%	0.22%	0.02%
10%	0.26%	0.10%

### 4.3 X-Ray Diffraction Analysis (XRD)

The X-ray diffraction patterns for the PVA-Starch films and ZIF-67 were obtained using D8Advance Bruker Powder X-ray diffractometer with Cu-K $\alpha$  (1.58Å) radiation. All the X-ray patterns were recorded over an angular range 10-70 degree with a step size of 0.02 degree and a time step of 0.1 second. The diffraction patterns of ZIF-67 and the composite films are shown in Figure 20. The diffraction peak of PVA can be seen in the Blank spectrum with a peak at  $2\theta \sim 18.5$  degrees. This is typical of PVA crystallites that are overlapped with a broad hump showing the characteristic of an amorphous region [49]. ZIF-67, being a crystalline substance, shows clear peaks in the diffractogram [31]. This peak get shaper in the composite films as the composition of ZIF is enhanced. This shows that the crystallinity of ZIF-67 remains unchanged when it is added to PVA-Starch films.

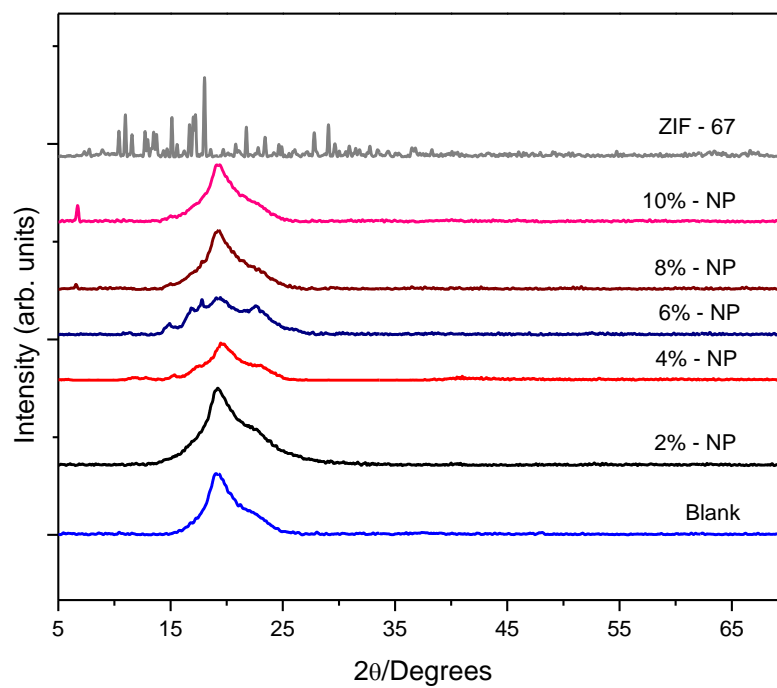


Figure 23 XRD of ZIF-67 and PVA-starch composite containing ZIF-67 in different amounts before pyrolysis

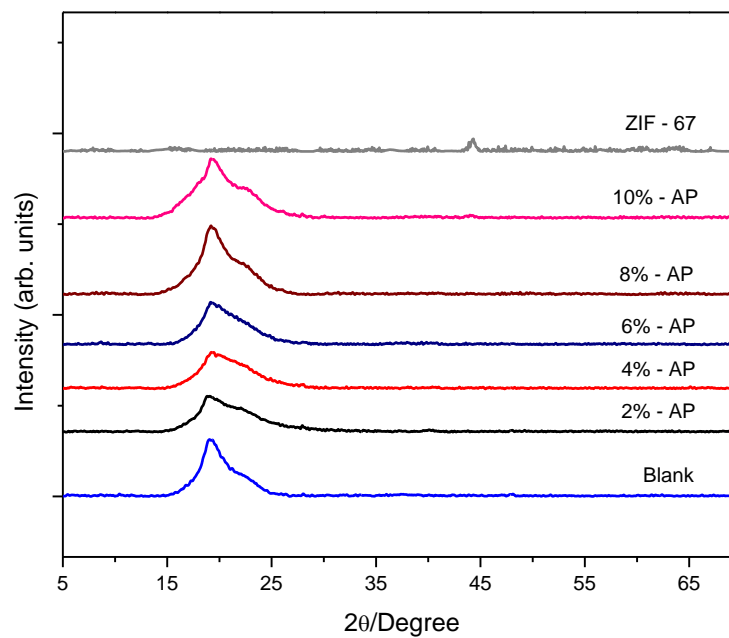


Figure 24 XRD of ZIF-67 and PVA-starch composite containing ZIF-67 in different amounts after pyrolysis

## 4.4 Fourier Transform Infra-Red (FTIR)

Cary 630 FTIR Spectrometer was used for obtaining FTIR spectrums of the PVA-Starch composite films. Zinc Selenide are used as detector along with a diffused reflectance accessory for testing the samples over a wavelength range of 4000 to 400  $\text{cm}^{-1}$ . The spectrum in the figure 25-26 provides the characteristic spectrum of ZIF-67 without pyrolysis and with pyrolysis, respectively. The absorption peaks remain same across all the samples showing that the chemical structure of the films is not affected by addition of the metal organic framework.

The stretching and bending vibration of the hydrogen bonding -OH group of PVA and PVA/starch blends occurred at 3500-3200  $\text{cm}^{-1}$  and 1653  $\text{cm}^{-1}$ , respectively. All spectra exhibit the characteristic absorption bands of pure PVA which are 3548-3211, 2041, 1745, 1456 and 1430-1275  $\text{cm}^{-1}$  [50]. The vibrational peaks are assigned to O-H stretching, C-H stretching, C=O stretching, C-H bend of CH<sub>2</sub>, and C-H wagging of PVA and they existed in the FTIR spectra of PVA/starch blends, indicating the success of blending of PVA with starch [51]. C=N Stretching is observed at 1612  $\text{cm}^{-1}$ . The C-H rocking mode of PVA was appeared at 918  $\text{cm}^{-1}$  and is shifted to 916, 926, 916 and 943  $\text{cm}^{-1}$ .

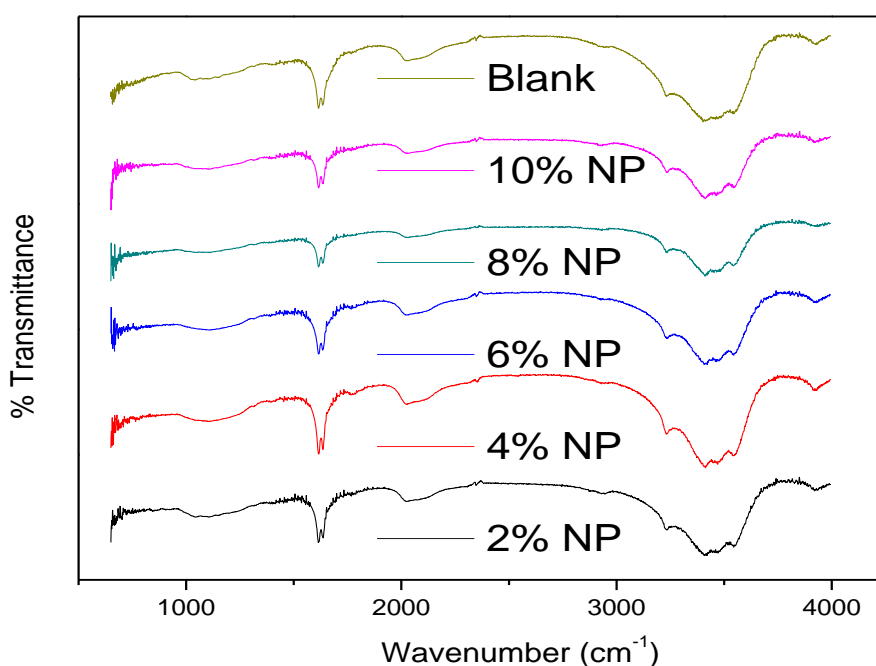


Figure 25 FTIR of PVA-starch composite films containing non pyrolysed ZIF-67

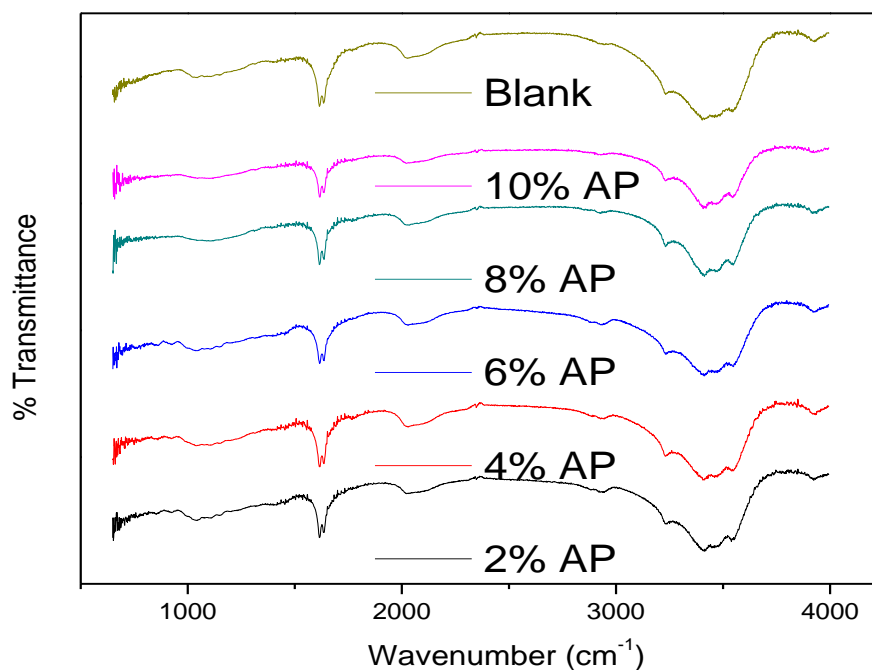


Figure 26 FTIR of PVS-starch films containing pyrolysed ZIF-67

## 4.5 Thermo gravimetric Analysis (TGA)

Thermogravimetric analysis of the films was carried out using a Thermogravimetric analyzer (SCHIMADZU DT-60) in order to study the effect of additive MOF on the thermal stability of the films. The composite films were heated from room temperature to 600 °C with a heating rate of 10 °C /min under a nitrogen atmosphere. The change in weight was recorded as a function of time. The graphs of percentage mass loss to time show three different stages of mass loss. The first stage of mass loss is from room temperature to 200 °C, where the loss is attributed to the loss of moisture which is loosely bound to the surface of the films. Around 10% of the mass is lost in this range. The second stage of mass loss is from 200 to 350 °C. This mass loss was attributed to the deterioration of the composite. This is the greatest contributing factor to decrease in mass along with dehydration and formation of volatile matter. The mass lost in this stage is around 60% of the total mass. Above this range the mass loss is because of the decomposition of carbonaceous matter.



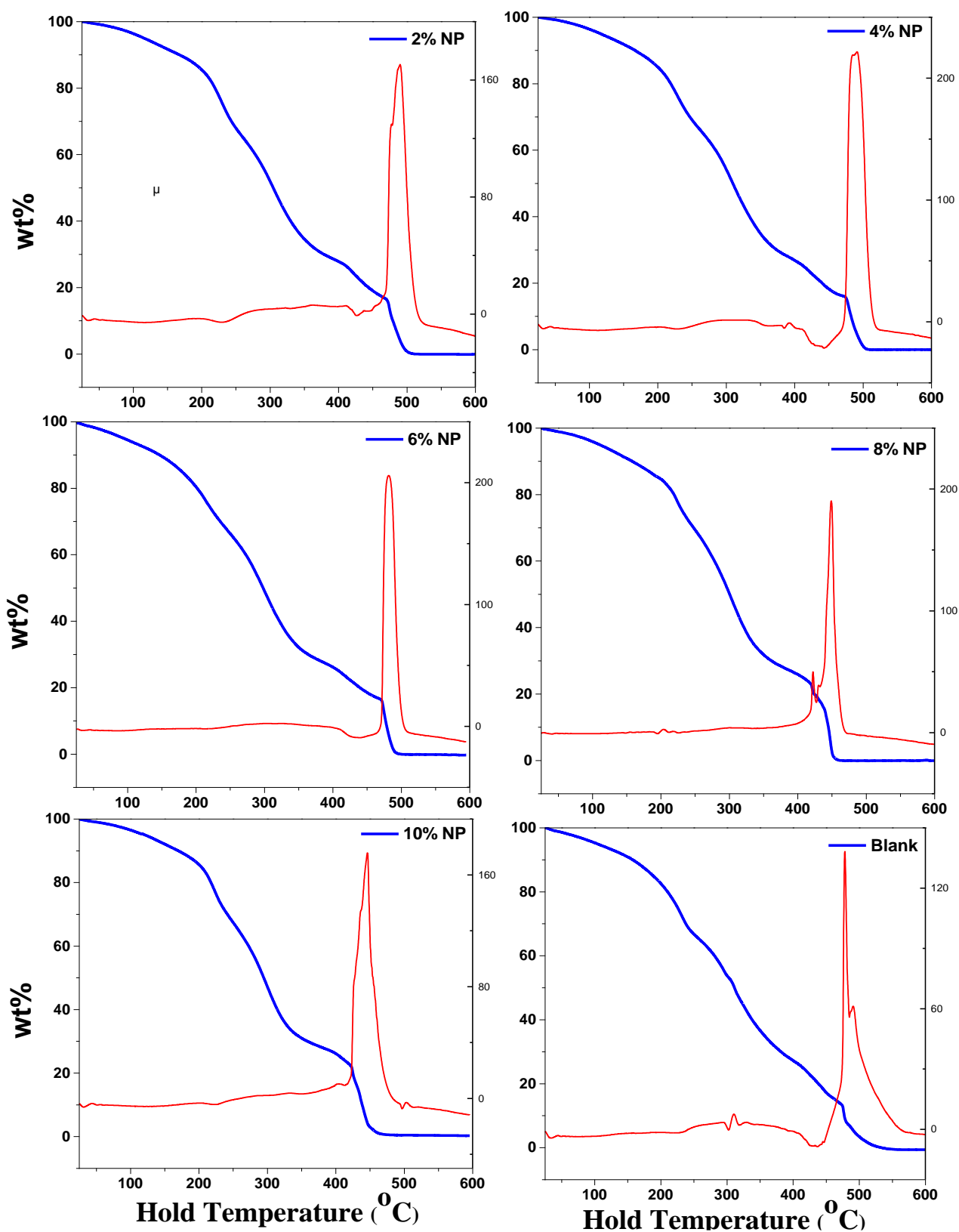


Figure 27 TG/DTA of Polymer composites containing ZIF-67 before pyrolysis



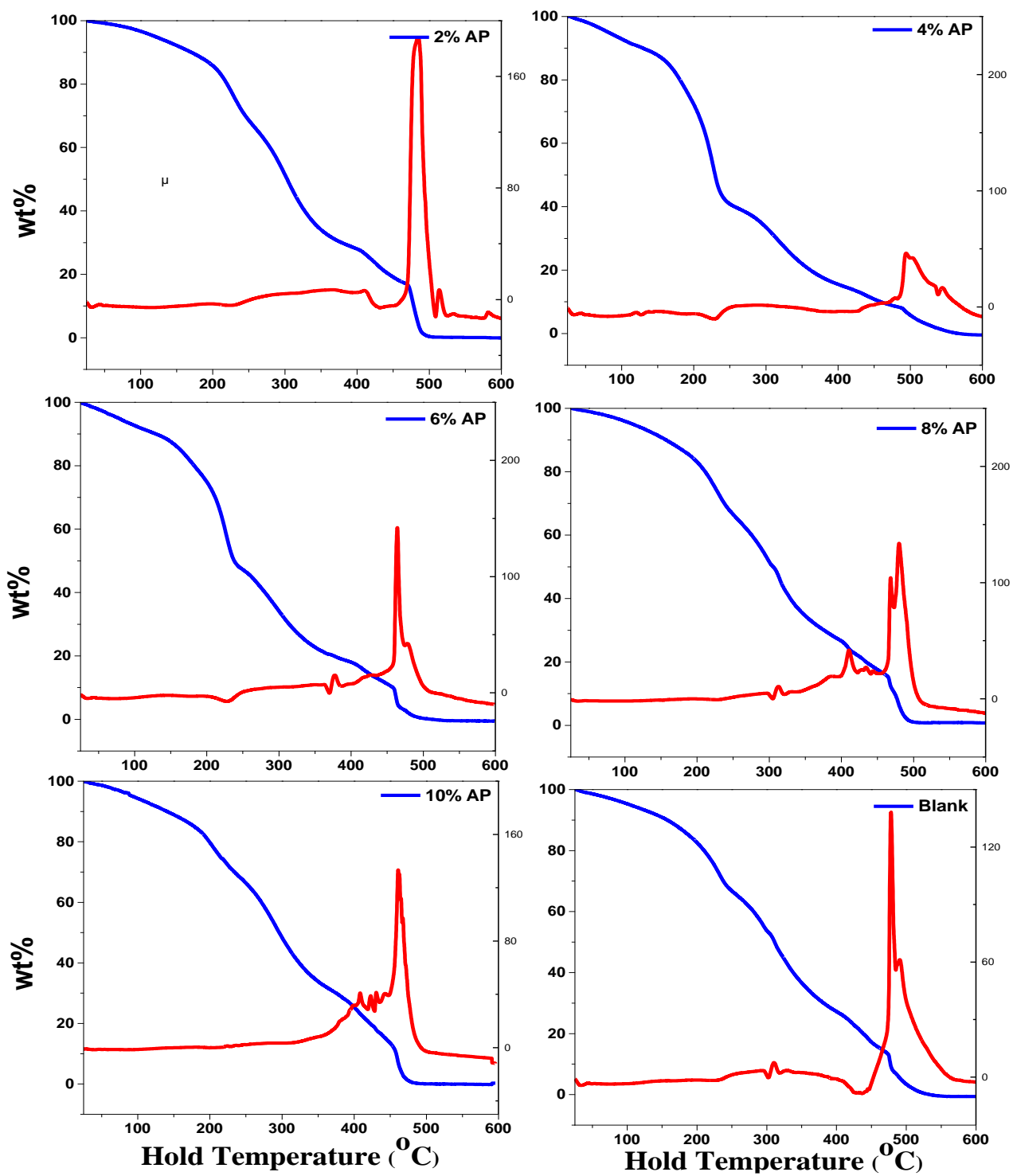


Figure 28 TG/DTA of Polymer composites containing ZIF-67 after pyrolysis

## 4.6 Ultimate Tensile Testing

The mechanical properties of food packaging films are significant to analyze their strength and durability to resist extraneous forces. The mechanical properties of the films were investigated using Universal tensile machine (UTM). The rigidity of the framework created at the interfacial region is also supported by the tensile testing measurements. Figure shows the engineering stress (MPa) vs. engineering strain (%) plots for PVA and the nanocomposite films. It is observed from the figure that the percentage strain at break is reduced as compared to neat PVA films. It indicates that the ductility of PVA film is reduced as a result of ZIF-67 loading. The tensile stress of the PVA film was increased with the addition of ZIF-67 content and the highest stress value obtained at 4 wt%. Furthermore, an increase in the ZIF-67 content resulted in the reduction of breaking stress. By comparing the maximum stress endured by membranes containing pyrolysed and non pyrolysed ZIF-67, the composites containing pyrolysed ZIF are more strong. It can attribute to the stronger interactions between the exfoliated ions and the polymer matrix.

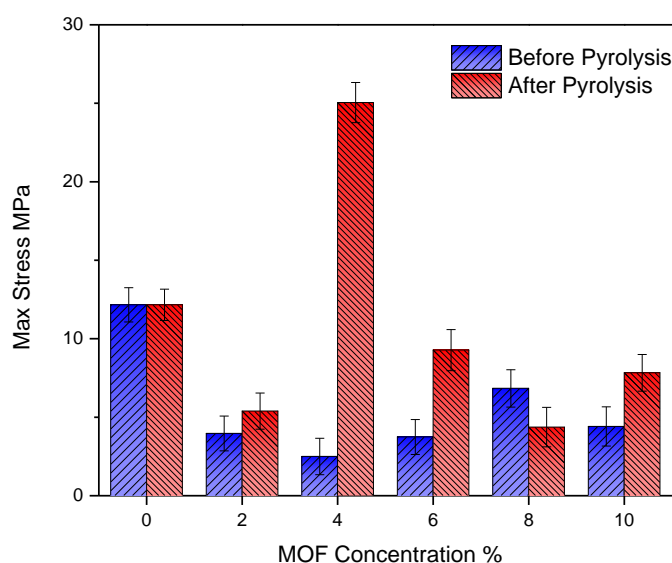


Figure 29 Comparison of the maximum stress endured by PVA-Starch films containing different concentrations of pyrolysed and non pyrolysed ZIF-67

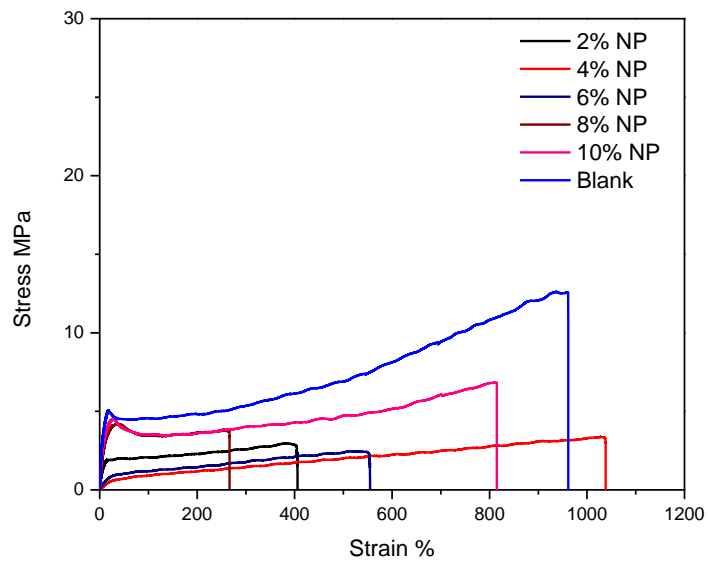


Figure 30 Stress-Strain relationship for different PVA-Starch films containing non pyrolysed ZIF-67

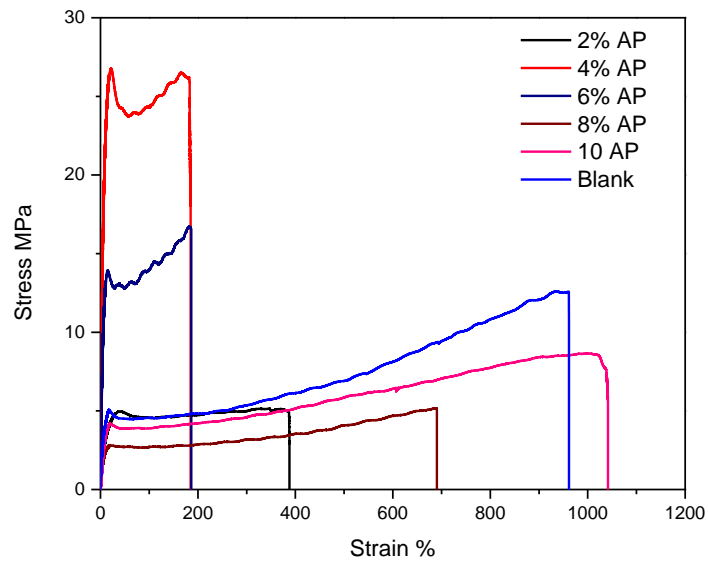


Figure 31 Stress-Strain relationship for PVS-Starch films containing different concentrations of pyrolysed ZIF-

67

# Conclusions and Recommendations

## 5.1 Conclusions

Addition of carbon based metal frameworks to PVA-starch films was studied and the ratio of additives was varied to study the change in the physical properties of the films, namely, strength and permeability. PVA-starch blends were prepared according to previously reported recipes in the literature which increases the biodegradability of the plastic. The effect of pyrolysed and non pyrolysed ZIF-67 yielded different results in for mechanical strength, which a discernable trend was also seen in the mechanical strength tests. The ratio of ZIF-67 in the PVA-starch blend was optimized for mechanical strength and it was observed that the highest mechanical strength was for 4% pyrolysed metal organic framework. The reason for increase in mechanical strength of the blend was the interfacial interaction of the metal based organic framework with the polymer matrix. Further characterization related to morphology and chemical synthesis was also carried out which showed an increase in roughness and metal content of the blend as the percentage of additive is increased.

## 5.2 Future Recommendations

- Activated carbon from different sources can be used including plants
- Different types of MOFs using alcohol formulation can be tested along with other cost effective additives
- Different ratio of PVA and starch can be used for varying degrees of biodegradability and variation of mechanical strength
- Blends containing different polymer matrices can be tested for their effect on mechanical properties
- Different nanomaterials including Graphene Oxide and nanotubes can be added to enhance directional strength of the blends.

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