

PROJECT REPORT

On

**“SYNTHESIS AND CHARACTERIZATION OF STARCH-UREA
BASED BIODEGRADABLE POLYMERIC LIGAND AND ITS
COORDINATION COMPLEX WITH Zn (II) METAL”**

Submitted by

**LIZ MARIA THOMSON (AB16CHE039)
ALIDA SAIJU (AB16CHE030)
CELIN FEMINA (AB16CHE014)**

*In partial fulfillment for the award of the
B.Sc. Degree in Chemistry*



**POST GRADUATE AND RESEARCH
DEPARTMENT OF CHEMISTRY**

**ST. TERESA'S COLLEGE (AUTONOMOUS)
ERNAKULAM**

2018-2019

**POST GRADUATE AND RESEARCH
DEPARTMENT OF CHEMISTRY
ST. TERESA'S COLLEGE (AUTONOMOUS)
ERNAKULAM**



B.Sc. CHEMISTRY PROJECT REPORT

Name : LIZ MARIA THOMSON
ALIDA SAIJU
CELIN FEMINA
Register Number : AB16CHE039
AB16CHE030
AB16CHE014
Year of Work : 2018-2019

This is to certify that the project "SYNTHEIS AND
**CHARACTERIZATION OF STARCH-UREA BASED
BIODEGRADABLE POLYMERIC LIGAND AND ITS
COORDINATION COMPLEX WITH Zn (II) METAL**" is the work
done by LIZ MARIA THOMSON, ALIDA SAIJU, CELIN FEMINA.

Dr. Ushamani M
Head of the Department

Ms. Sicily Rilu Joseph
Staff-member in charge

Submitted to the Examination of Bachelor's Degree in Chemistry

Date:.....

Examiners:.....

DECLARATION

I hereby declare that the project work entitled “SYNTHESIS AND CHARACTERIZATION OF STARCH-UREA BASED BIODEGRADABLE POLYMERIC LIGAND AND ITS COORDINATION COMPLEX WITH Zn (II) METAL ” submitted to Department of Chemistry, St. Teresa’s College (Autonomous) affiliated to Mahatma Gandhi University, Kottayam, is a record of an original work done by me under the guidance of Ms. Sicily Rilu Joseph, Department of Chemistry, St. Teresa’s College (Autonomous), Ernakulam and this project work is submitted in the partial fulfillment of the requirements for the award of the degree of Bachelor of Science in Chemistry.

LIZ MARIA THOMSON
ALIDA SAIJU
CELIN FEMINA

Acknowledgements

The success and final outcome of this project required a lot of guidance and assistance from many people and we are extremely fortunate to have got this all along the completion of our project work. Whatever we have done is only due to such guidance and assistance and we would not forget to thank them.

Primarily, we thank God almighty for being with us throughout all the days and helping us complete the project successfully.

We respect and thank our project guide Ms. Sicily Rilu Joseph, Assistant Professor(guest), Department of Chemistry, St.Teresa's College(autonomous), Ernakulam for her invaluable and enlightened guidance and the support and suggestions which helped us in completing this project.

We extend our sincere gratitude to Dr. Ushamani M, Head of the department, Department of chemistry, St.Teresa's College(Autonomous),Ernakulam for providing us with all the facilities and support to meet our project requirements.

We also express our sincere gratitude to Dr. Sr. Vinitha CSST, Director, St. Teresa's College(Autonomous), Ernakulam and Dr.Sajimol Augustine, Principal,St. Teresa's College(Autonomous), Ernakulam for their extended support and co-operation during our project work.

We also like to extend our sincere thanks to Sophisticated Test and Instrumentation Centre,CUSAT for their assistance in various stages of completion of the project.We would like to express our gratitude towards our parents and friends for their kind co-operation and encouragement which helped us in completion of this project.

We thank all the teachers and non-teaching staffs of the Department of Chemistry, St.Teresa's College(Autonomous),Ernakulam for their support and cooperation during our entire project work.

*LIZ MARIA THOMSON
ALIDA SAIJU
CELIN FEMINA*

Contents

Chapter 1 Introduction	
1.1 Biodegradable Polymer	1
1.2 Biodegradable Polymer Metal Complex	5
1.3 Starch-Urea Based Biodegradable Polymer Metal Complex	6
1.4 Zinc Metal	11
1.5 Characterization Techniques	
1.5.1 Fourier Transform Infrared Spectroscopy	12
1.5.2 Scanning Electron Microscope	15
1.5.3 EDX Analysis	16
Chapter 2 Materials And Methods	
2.1 Synthesis of Starch-Urea Based Polymer	19
2.2 Synthesis of Starch-Urea-Zinc Polymer Metal Complex	20

Chapter 3 Results And Discussions	
3.1 FT-IR Spectral Studies of Starch-Urea Polymer and its Metal Complex	21
3.2 SEM Analysis of Starch-Urea Based Biodegradable Polymer and its Zinc Metal Complex	23
3.3 EDX Analysis of Starch-Urea Based Biodegradable Polymer and its Zinc Metal Complex	25
Chapter 4 Conclusion	28
References	30

INTRODUCTION

1.1 Biodegradable Polymer

Polymers are large molecules composed of many repeat units called monomers, which have been chemically bonded into long chains. Monomers, are molecules of small to moderate molecular weight, and are linked to each other during a chemical reaction called polymerization. Although most of the polymers are organic, with carbon based monomers, there are also inorganic polymers; for example, the silicones, with a backbone of alternating silicon and oxygen atoms and polyphosphazenes.[1] Polymeric materials have been used from prehistoric times. Polymers are abundant in nature, found in all living systems and materials such as wood, paper, leather, natural fibers and have found extensive use. While natural polymers retain their intrinsic importance, today synthetic materials are mostly used. With the progress of technology, people started producing materials that could withstand extreme temperatures, durable and easy to use like plastic bags, plastic bottles, tin cans etc. These are some of the things that make life easy for us. However, these products do not breakdown naturally. When we dispose them to the environment; the air, moisture, climate, or soil cannot break them down. They are not biodegradable.[2]

Biodegradable polymers are defined as materials whose chemical and physical characteristics undergo deterioration and completely degrade when exposed to microorganisms, aerobic, anaerobic processes.[3] Biodegradable polymers cover a large area of high molecular

weight compounds. Biodegradable polymer can be natural or synthetic and can be derived either from either renewable resources or non-renewable resources. Native biodegradable polymers are the result of a synthesis developed during millions of years of evolution, leading to tailor-made materials for variant applications in nature. These biopolymers include proteins, polysaccharides, nucleic acids or lipids etc.

Synthetic biopolymers are often synthesized by condensation reaction, ring opening polymerization etc. There are certain properties that a biodegradable polymer must possess. All biodegradable polymers must be stable and durable enough for use in their particular application, but upon disposal they should easily breakdown. A polymer based on C-C backbone tends to resist degradation, whereas heteroatom containing polymer backbones confers biodegradability. Biodegradability can therefore be engineered into polymers by judicious addition of chemical linkages such as anhydride, ester or amide bond, among others.

The usual mechanism for degradation is by hydrolysis or enzymatic cleavage of labile heteroatoms bonds, resulting in a scission of the polymer backbone. Extra-cellular enzymes (endo or exo-enzymes) and abiotic reactions are responsible for the polymeric chain cleavage. During this phase the contact area between the polymer and the microorganisms increases. This is followed by bio-assimilation of polymer fragments by microorganisms and their mineralization.

Synthetic polymers susceptible to biodegradation can be of different types, e.g. -polymers containing hydrolysable backbone polyesters. Recent research activity on biodegradable synthetic polymers has often been focused on the stimulation of different polymers with degradable backbones, e.g.; polyanhydride, polycarbonates, polylactones etc.

A series of pure biodegradable petroleum based synthetic polymers have been developed. However owing to concerns over environmental pollution and the depletion of fossil oils, intensive research is being conducted for developing biodegradable polymers and plastic materials from renewable natural resources such as starch, cellulose and soy protein. Biodegradable polymers are considered eco-friendly because of their biodegradability. [4]

The major advantage of biodegradable polymers are that they can be composted with organic wastes and it can be returned to enrich the soil. Their use will not only reduce harm to nature caused by dumping of conventional plastics, but will also lessen the labour cost for the removal of plastics from the environment because they are degraded naturally. They could be recycled to useful monomers and oligomers by microbial and enzymatic treatment. Although synthetic plastics are a more economically feasible choice than biodegradable ones, an increased availability of biodegradable polymers will allow many consumers to choose them on the basis of their environmental responsible disposal. [5,6,]

For economic reasons, even for health and safety reasons, biodegradable polymers with hydrolysable chemical bonds are researched extensively for biomedical, pharmaceutical, agricultural and packaging applications. Biodegradability is particularly desired in biomedical applications, in which degradation of the polymer ensures clearance from the body and eliminates the need for retrieval. Biodegradable polymers have applications in controlled or sustained release drug delivery approaches, tissue engineering scaffolds, temporary prosthetic implant etc. Many opportunities exist for the application of synthetic biodegradable polymers in the biomedical area, particularly in the fields of tissue engineering and controlled drug delivery.

Biodegradable polymers are used in medicine because of the degradation of the polymeric implant means surgical intervention may not be required in order to remove the implant at the end of its functional life, eliminating the need for a second surgery. The great benefit of a biodegradable drug delivery system is the ability of the drug carrier to target the release of its payload to a specific site in the body and then degrade into nontoxic materials that are then eliminated from the body through natural metabolic pathways. The polymer slowly degrades into smaller fragments, releasing a natural product, and there is controlled ability to release a drug. The drug slowly releases as polymer degrades. Artificial skin substitutes and wound dressings made of biodegradable polymeric materials have been developed to treat burns. Tissue engineering is the ability to regenerate tissue with the help of artificial materials. The perfection of such systems can be used to grow tissues and cells invitro or use a biodegradable scaffold to construct new structures and organs invitro. Biodegradable scaffold is preferred as it reduces the risk of immunological reaction and rejection of foreign object.

Biodegradable polymers are often used to reduce the volume of waste in packaging materials. In packaging applications, a biodegradable additive is often included as a way to promote environmental degradation e.g., starch in polyethylene. The renewable and biodegradable characteristics of biopolymers are what render them appealing for innovative use in packaging. There is also significant effort to replace materials derived from petrochemicals with those that can be made from biodegradable components.[7,8]

1.2 Biodegradable Polymer Metal Complex

A polymer metal complex mainly composed of a synthetic polymer and a metal ion. Its synthesis represents an attempt to give an inorganic function to an organic polymer. It is also known that existence of metal ions bonded to biologically active compounds may enhance their activities. The properties of coordination compounds are influenced to a considerable extent by the nature and oxidation state of central metal atom. Studies enlightened that metal complexes has received increased interest in various branches of chemistry, chemical technology and biology and the subject has been reviewed periodically. A polymer–metal complex is a coordination complex between a ligand function anchored on a polymer matrix and a metal ion in which the metal ion is attached to the polymeric ligand by a coordinate bond. Here a polymeric ligand is considered as a polymeric substance that contains coordinating groups or atoms mainly N, O and S.

In a polymer–metal complex, a complex with a specific structure results since the metal ion is surrounded by a structural polymer chain. Polymer-metal complexes show unique properties which are distinctly different from their low-molecular weight analogues. These unique properties originate from the properties of the polymer backbone. There are different approaches for the preparation of polymer metal complexes. The methods involve complexation between a ligand function anchored on a polymer matrix and metal ion, reaction of a multifunctional ligand with metal ions, reaction of a metal complex with a neutral polymer and the polymerization of low molecular weight complexes. Thus polymer-metal complex is formed by the reaction of a polymer containing coordinating groups with metal ions. [9,10]

The chelating polymers find application in collecting transition metal ions as well as alkali and alkaline earth metal ion separations, preconcentration and recovery of trace metal ions, catalysis, organic synthesis, nuclear chemistry, water and waste water management, pollution control, industrial process hydrometallurgy and polymer drug grafts. In addition polymer-metal complexes are also used as mechanochemical systems and as models of bioinorganic systems.[11]

In this work the transition metal ion Zn (II) is complexed with the synthesized Starch-Urea biodegradable polymer. The main reason for the preference of transition metal ion over the other metal ions is due to its unique feature such as flexibility to adopt more than one coordination geometries and the ability to exist in multiple oxidation states. Generally it has been observed that transition metal complexes have greater activity and lesser toxic effects. The transition metal complexes are used in various fields such as medicine, agriculture, industries etc. Use of biodegradable polymer (starch-urea) as a support for metal, instead of non-biodegradable polymer is the highlight of this work because the polymer degrades after its intended purpose.

1.3 Starch-Urea Based Biodegradable Polymer Metal Complex

Starch is a polymeric carbohydrate consisting of a large number of glucose units joined by glycosidic bonds. It is mainly composed of two homopolymers of D-glucose, amylose is mostly linear α -D[1,4']glucose and branched amylopectin having the same backbone structure as amylose but with α -1,6'- linked branch points.

Starch being a natural polymer possesses many unique properties. Of these some are biodegradable and can be tailor-made easily.

Starch based coordination polymers are found to be completely degradable in soil and water and can promote the degradation of non-biodegradable material when blended or modified. And it is one among the main natural polymers studied for the production of biodegradable materials. [12,13]

Starch can be used to reduce the carbon footprint of tradition resins because they can replace petroleum-based polymers with natural ones. It is also highly degradable, meaning it can be used alongside a compostable polymer without interfering with the degradation process. In general, starch-based plastics are more cost competitive than alternative bioplastics. They can accommodate a wide range of physical properties that alternative bioplastics lack, such as tensile strength and heat tolerance.

Starch-based materials have some drawbacks including limited long term stability caused by water absorption, aging caused by retro gradation, poor mechanical properties and bad processability. To overcome these limitations biodegradable polymers have been synthesized and modified. The purpose of this work is the modification of starch with urea for improving the properties and with some transition metals for enhancement in the characteristics.[14]

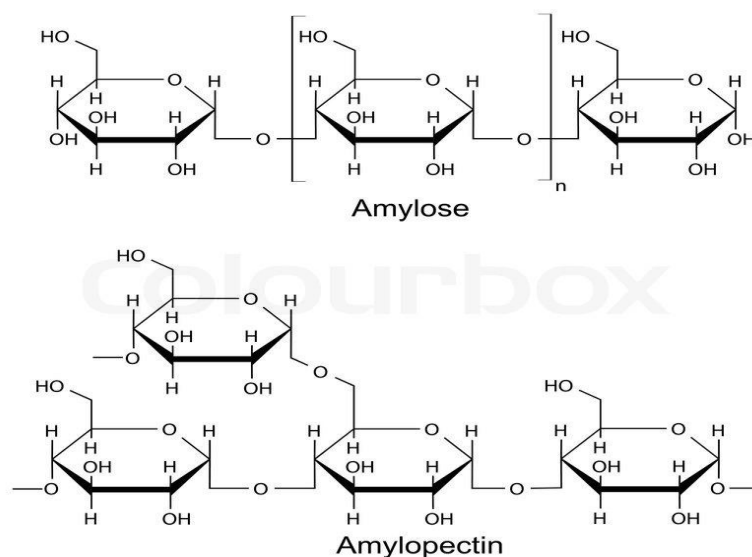


Figure 1.1: Structure of Amylose and Amylopectin

There are a lot of hydroxyl groups on starch chains, two secondary hydroxyl groups at C-2 and C-3 of each glucose residue, as well as one primary hydroxyl group at C-6 when it is not linked. Eventually starch is hydrophilic. The available hydroxyl groups of starch chains potential exhibit reactivity. Starch based polymer have been designed for conserving petrochemical resources, reducing environmental impact and other applications. It can be hydrolyzed into glucose by microorganism or enzymes, and then metabolized into carbon dioxide and water. Carbon dioxide will recycle into again by plants and sunlight. Various biopolymers such as starch and cellulose have been of increased interest due to more environmentally aware consumers, increased price crude oil and global warming. Due to various advantages like renewability, non-toxicity and biocompatibility, their bio composites are used in variety of application, like therapeutic aids, medicines, coatings, food products and packing materials. Starch based coordination polymers are known to be

completely degradable in soil and water and can promote the degradation of non-biodegradable material when blended or modified.

Starch is the major carbohydrate in plants, tubers and seed endosperm. Starch is a promising raw material because of its annual availability from many plants, its rather excessive production with regard to current need. Starch is potentially useful material because of its natural abundance and low cost. Starch is renewable from Carbon dioxide, water and sunshine. It is biodegradable, cheap and can be physically or chemically modified easily.[15] Urea which is also known as carbamide is an organic compound with chemical formula $\text{CO}(\text{NH}_2)_2$. This amide group has two NH_2 groups joined by a carbonyl functional group. Urea has important uses as a fertilizer and feed supplement as well as a starting material for manufacture of plastics and drugs. It is a colourless crystalline substance that melts at 132.7°C , soluble in water and ethanol, but insoluble in ether, and decomposes before boiling. [16]

Urea is physiologically very important. It is the chief nitrogenous product of protein metabolism. Urea is used for preparing formaldehyde-urea resin (plastics), barbiturates, and fertilizers. Urea is also extensively used in the paper industry to soften cellulose and has been used to promote healing in infected wounds and many other applications in the field of the manufacture of hydrazine in which urea is treated with alkaline sodium hypochlorite.

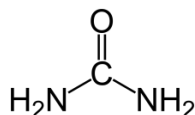


Figure 1.2 Structure of Urea

Urea is used in reactive dyeing which has an effect on the formation and cleavage of covalent bond between the reactive dye and cellulose. Complexes of urea with some metal ions are used as fertilizers. Complexes of urea with zinc sulphates and nitrate, and have very important application in the field. These complexes were found to increase the yield of product more than a dry mixture of urea-zinc salt does. Some metal complexes have pharmaceutical application, e.g., the platinum-urea complex which is used as antitumor.

In urea-metal complexes, if a nitrogen-to-metal bond is present, the vibrational spectrum of that complex differs significantly from that of the free urea molecule. Recently, urea represents not only an important molecule in biology but also an important raw material in chemical industry. [17]

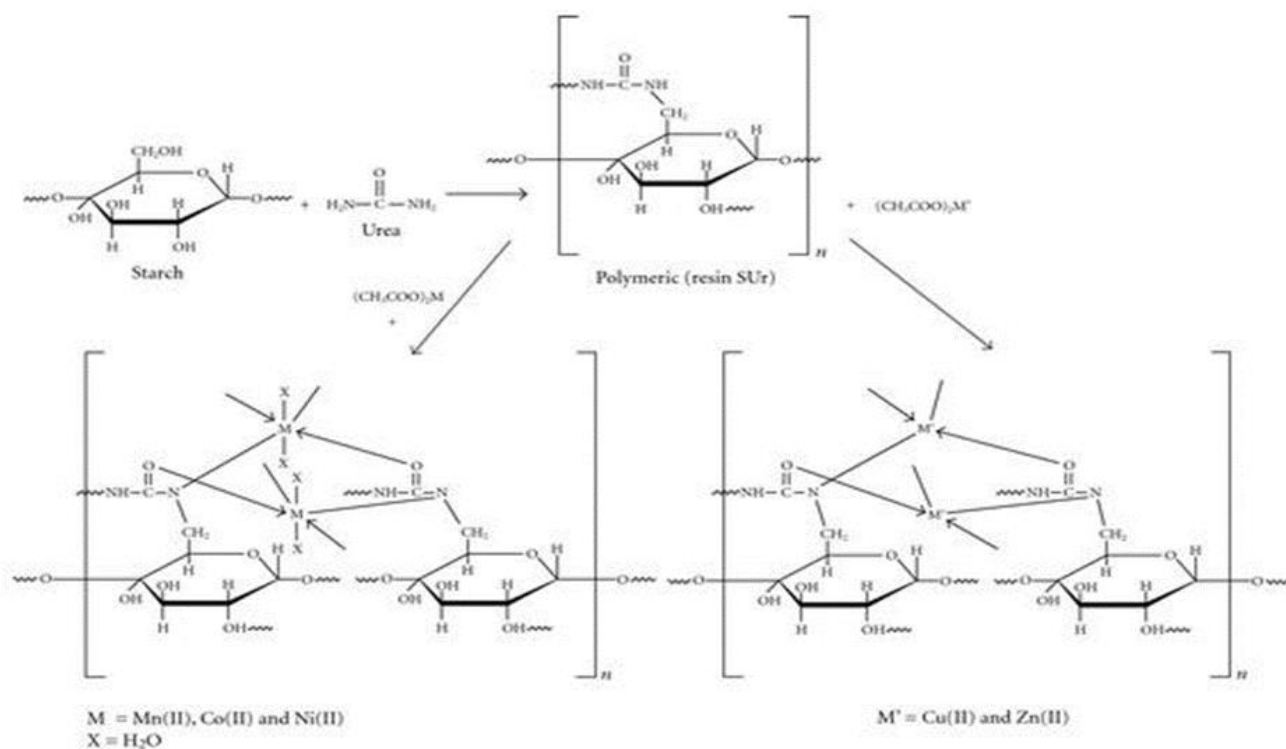


Figure 1.3 Scheme of formation of Starch-Urea polymer metal complex

Starch-Urea polymer is synthesized by polycondensation of Starch and Urea which are both easily available and biodegradable.

1.4 Zinc Metal

Zinc is a chemical element with symbol Zn and atomic number 30. It is the first element in group 12 of the periodic table. In some respects Zinc is chemically similar to Magnesium such as both the elements exhibit only one normal oxidation state (+2) and the Zn^{2+} and Mg^{2+} ions

are of similar size. Zinc is the 24th most abundant element in the earth's crust and have five stable isotopes.[18]

It burns in air with a bright bluish- green flame producing white clouds of oxide. The metal is hard and brittle at most temperatures but becomes malleable between 100 and 150°C. Above 210°C, the metal becomes brittle again and can be pulverized by heating. The metal zinc has relatively low melting point (419.5⁰C) and boiling point (907⁰C). It is a reasonable conductor of electricity. The metal has high heat capacity and and heat conductivity.Zinc also reacts with

substances like halogens, oxygen, chalcogens, alkalis, acids, ammonium, and ammonium salts, and also with weaker metals.[19]

It is also used in alloys such as brass, nickel, silver and aluminium solder. Zinc oxide is widely used in the manufacture of very many products such as paints, rubber, cosmetics, pharmaceuticals, plastics, inks, soaps, batteries, textiles and in many electrical equipments. A base metal zinc is primarily used in order to galvanize steel, a process to protect the metal against unwanted corrosion. Zinc is reported to show significant antimicrobial activity even at lower concentrations .The salts of zinc are common catalysts when used for their activity in a variety of organic reactions. [20]

1.5 Characterization Techniques

1.5.1 Fourier Transform Infrared Spectroscopy

IR radiation is passed through a sample. Some of the infrared radiation is absorbed by the sample and some of it is transmitted. The resulting spectrum represents the molecular absorption and transmission, creating a molecular fingerprint of the sample. Like a fingerprint no two

unique molecular structures produce the same infrared spectrum. This makes infrared spectroscopy useful for several types of analysis. IR can provide information about unknown materials in a sample. It can determine the quality or consistency of a sample. It can also determine the amount of components in mixture. A basic IR spectrum is essentially a graph of infrared light absorbance (or transmittance) on the vertical axis vs frequency or wavelength on the horizontal axis.

Fourier Transform Infrared (FT-IR) spectroscopy was developed in order to overcome the limitations encountered with dispersive instruments. The Fourier Transform Infrared is the preferred method of infrared spectroscopy. In dispersive IR, main difficulty was the slow scanning process. A method for measuring all of the infrared frequencies simultaneously, rather than individually was needed. A solution was developed which employed a very simple optical device called an interferometer. The interferometer produces a unique type of signal which has all of the infrared frequencies encoded into it. The signal can be measured very quickly, usually within seconds. Thus, the time element per sample is reduced to a matter of a few seconds rather than several minutes. Because the analysis requires a frequency spectrum (a plot of the intensity at each individual frequency) in order to make identification, the measured interferogram signal cannot be interpreted directly. A means of decoding the individual frequencies is required. This can be accomplished via a well-known mathematical technique called the Fourier transformation. The term Fourier transform infrared spectroscopy originates from the fact that a Fourier transform (a mathematical process) is required to convert the raw data into the actual spectrum.

Rather than shining a monochromatic beam of light at the sample, this technique shines a beam containing many frequencies of light at once, and measures how much of that beam is absorbed by the sample. Next, the beam is modified to contain a different combination of frequencies, giving a second data point. This process is repeated many times. Afterward, a computer takes all this data and works backward to infer what the absorption is at each wavelength.

The beam described above is generated by starting with a broadband light source—one containing the full spectrum of wavelengths to be measured. The light shines into a Michelson interferometer—a certain configuration of mirrors, one of which is moved by a motor. As this mirror moves, each wavelength of light in the beam is periodically blocked, transmitted, blocked, transmitted, by the interferometer, due to wave interference. Different wavelengths are modulated at different rates so that at each moment the beam coming out of the interferometer has a different spectrum. Computer processing is required to turn the raw data (light absorption for each mirror position) into the desired result (light absorption for each wavelength). The processing required turns out to be a common algorithm called the Fourier transform (hence the name, "Fourier transform spectroscopy"). The raw data is sometimes called an "interferogram". The FT-IR has made possible the development of many new sampling techniques which were designed to tackle challenging problems which were impossible by older technology. It has made the use of infrared analysis virtually limitless.

[21]

1.5.2 Scanning Electron Microscope

SEM uses a focused beam of high energy electrons to generate a variety of signals at the surface of solid specimens. The signals that derive from electron-sample interactions reveal information about the sample including morphology (texture), chemical composition, crystalline structure, orientation of materials making up the sample. In a typical SEM an electron beam is thermionically emitted from an electron gun. These electrons are then accelerated to a voltage between 1-40 kV. A series of condenser lenses focus the electron beam as it moves from source down the column. This narrow beam is used to scan in a raster fashion over the sample. Samples are mounted and placed into a chamber that is evacuated.

When electron beam comes and hits the atoms of specimen those atoms absorb their energy and give off their own electron-SE. There is a detector to pick up SE which has a positive charge on it about 300V. Secondary Electrons (SE) emitted from very close to specimen surface and can produce very high resolution image of sample surface revealing details less than 1nm. Back scattered electrons (BSE) emerge from deeper locations within specimen and consequently BSE images are poorer than SE images. We mainly use SE and BSE in SEM study. It is called SEM because the primary beam that comes down makes pixel by pixel image of the surface hit from left to right, top to bottom and every time it hits we get electrons from that particular part of specimen. Thus SEM uses beam of electrons to form image of the surface.

The detectors of the SEM collect the electrons coming off the sample and image is obtained on screen. Electronic amplifiers of various types are used to amplify the signals which are displayed as variations in

brightness on a computer monitor. The electron beam is generally scanned in a raster pattern and the beam's position is combined with the detected signal to produce an image of the surface. The composition of surface is not necessarily same as the bulk. Frequently, in otherwise homogenous solid systems, inhomogeneities occur as one approaches an interface. The distribution of surface species become an important parameter when considering chemical analysis of a surface.

Each pixel of computer video memory is synchronized with the position of the beam on the specimen in the microscope. The resulting image is therefore a distribution map of intensity of signal being emitted from the scanned area of specimen. Due to very narrow electron beams, SEM micrographs have a large depth of field yielding a characteristic three dimensional appearance useful for understanding the surface structure of the sample. [22]

1.5.3 EDX Analysis

Energy-dispersive X-ray spectroscopy (EDS, EDX, EDXS or XEDS), sometimes called energy dispersive X-ray analysis (EDXA) or energy dispersive X-ray microanalysis (EDXMA), is an analytical technique used for the elemental analysis or chemical characterization of a sample. Every atom has a unique number of electrons that reside under normal conditions in specific positions. These positions belong to certain shells, which have different, discrete energies.

The generation of the X-rays in a two step process 'in the first step, the electron beam hits the sample and transfers part of its energy to the atoms of the sample 'this energy can be used by the electrons of the "jump" to an energy shell with higher energy or be knocked off from the

atom. If such a transition occurs the electron leaves behind a hole. Holes have a positive charge and in second step of the process, attract the negatively charged electrons from higher energy shell fills the hole of the lower energy shell, the energy difference of this transition can be released in the form of an X-ray

This X – ray has energy which is characteristic of the energy difference between these two shells. It depends on the atomic number, which is unique property of every element .in this way ,X-rays are a “fingerprint” of each element can be used to identify the type of elements that exist in a sample.

Unlike BSE and TE, X rays are electromagnetic radiation just like light, and consist of photons. To detect them, the latest systems use the so called silicon drift detectors (SDDs).these are superior to the conventional Si (Li) detectors due to higher count rates, better resolution, and faster analytical capabilities.

These detectors are placed under an angle ,very close to the sample , and have the ability to measure the energy of the incoming photons that belong to the X-rays .The higher the solid angle between the detector and the sample , the higher the X-rays detection probability ,and therefore the likelihood of acquiring the best results .

The data that is generated by EDX analysis consists of spectra with peaks corresponding to all the different elements that are present in the sample. Every element has characteristic peaks of unique energy, all extensively documented. Furthermore EDX can be used for qualitative (the type of elements)as well as quantitative (the percentage of the concentration of each element of the sample)analysis. In most SEMs dedicated software enables auto identification of the peaks and calculation of the atomic

percentage of each element that is detected. One more advantage of this technique is that it is a non destructive characterization technique, which requires little or no sample preparation. Benefits from EDX analysis are improved quality control, rapid identification of contaminant and source, full control of environmental factors, emissions, higher production yield, easy to identifying the source of the problem in process chain.[23]

MATERIALS AND METHODS

All reagent used were of A.R grade .The Scanning electron micrographs were taken using a Hitachi S-2400 instrument.EDX image was obtained from EDX-800,Japan instrument. The FTIR spectra was recorded on a broker IFS – 55 spectrometer using KBr pellets

Requirements

- Starch
- Urea
- Alcohol
- NaOH
- Acetone
- DMSO
- Zinc(II) acetate tetrahydrate

2.1 Synthesis of Starch-Urea based polymer

The polymeric resin was synthesized by polycondensation of Urea and Starch in alkaline medium in 1:1 molar ratio.In a 500 ml beaker, 1.2 gram(0.02 mol) of Urea and 3.24 gram(0.02 mol) of Starch poured with minimum quantity of distilled water were taken, stirred well and dissolved.The beaker is placed on heating mantle. The pH of the above solution is adjusted to 8 using NaOH solution by pH meter. The Urea-Starch solution is then stirred at high speed using a magnetic stirrer for 4 hours at 80⁰C. The polymeric resin is then poured into a beaker containing crushed ice. To this, equal amount of ethanol and acetone is added with

constant stirring. The polymer is thus formed and it is filtered using a whatmann filter paper and then allowed to dry.

2.2 Synthesis of Starch-Urea-Zinc polymer metal complex

Metal complex of Starch-Urea polymer was prepared by dissolving about 2.22 gm (0.01mol) of the Starch-Urea polymer in minimum quantity of hot DMSO (25 ml). Also 2.194gm of (0.01 mol) Zn (II) acetate is also dissolved in minimum quantity of hot DMSO. Both these solutions are mixed together in a 250ml beaker in hot conditions itself and kept for stirring in a magnetic stirrer for 4 hours at 60⁰C. The solution is then added to a beaker containing crushed ice and washed with equal amounts of ethanol and acetone with constant stirring. The precipitate thus formed is filtered using a whatmann filter paper and then allowed to dry.

Chapter 3

RESULTS AND DISCUSSION

3.1 FT-IR Spectral Studies of Starch-Urea Polymer and its Metal Complex

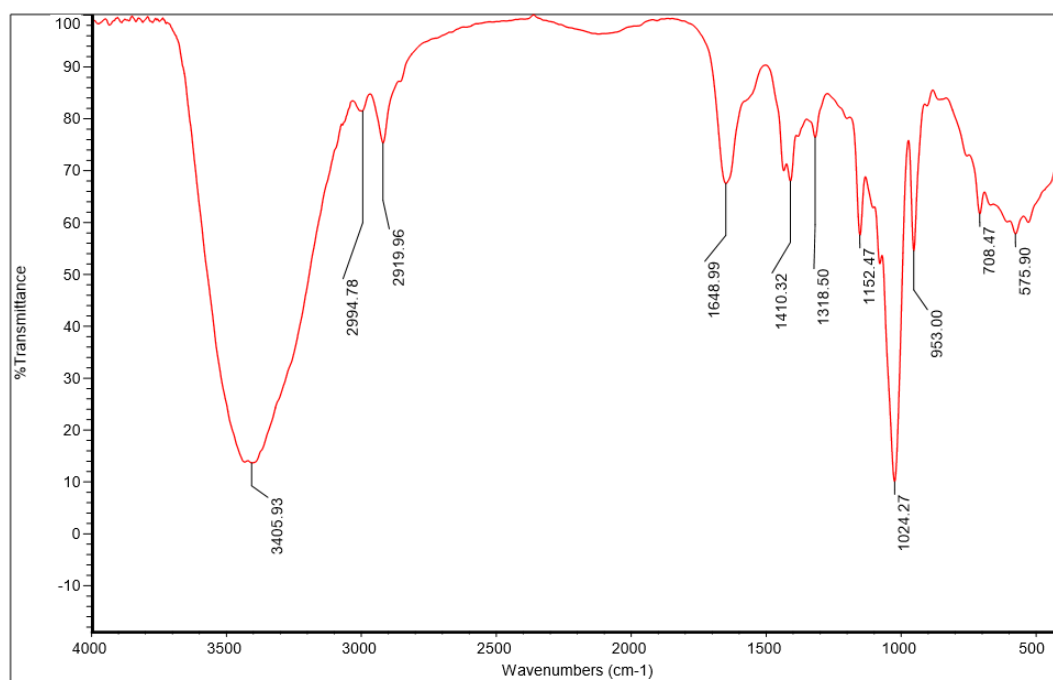


Figure: 3.1.1 IR Spectra of Starch-Urea Polymer

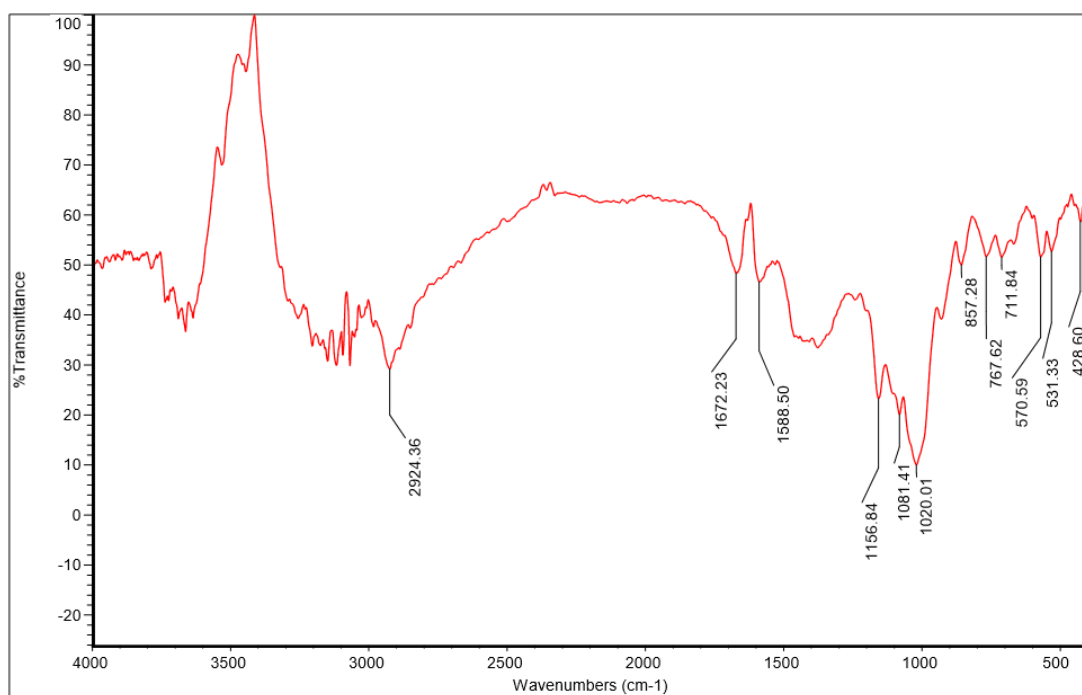


Figure 3.1.2 IR Spectra of Starch-Urea- Zinc Polymer Complex

Table 1: IR Analysis Of Starch-Urea Based Biodegradable Polymer And Its Metal Complex

COMPOUND	$\nu(\text{O-H})$ cm^{-1}	$\nu(\text{C-O})$ cm^{-1}	$\nu(\text{C-N})$ cm^{-1}	$\nu(\text{O=CNH})$ cm^{-1}	$\nu(\text{N-H})$ cm^{-1}	$\nu(\text{M-O})$ cm^{-1}	$\nu(\text{M-N})$ cm^{-1}
1. Starch-Urea Polymer (SUr)	3405.93	1024.27	1152.47	1648.99	1410.32	—	—
2. SUr-Zn(II) Polymer	2924.36	1020.01	1156.84	1672.23	1588.50	531.33	428.60

The IR spectral studies show that there has been certain variations happened in the spectra of starch-urea based polymer from its metal complex. The IR spectral studies shows $\nu(\text{O-H})$ for starch-urea polymer at 3405.93 cm^{-1} and this has lowered in the polymer to 2924.36 cm^{-1} . In polymer metal complex bands appeared in range $540\text{-}600 \text{ cm}^{-1}$ and $440\text{-}495 \text{ cm}^{-1}$ which support coordination of metal through oxygen and nitrogen. Thus proving the evidences for the attachment of the Zn metal to the SUR polymer.

3.2 SEM Analysis of Starch-Urea Based Biodegradable Polymer and its Zinc Metal Complex

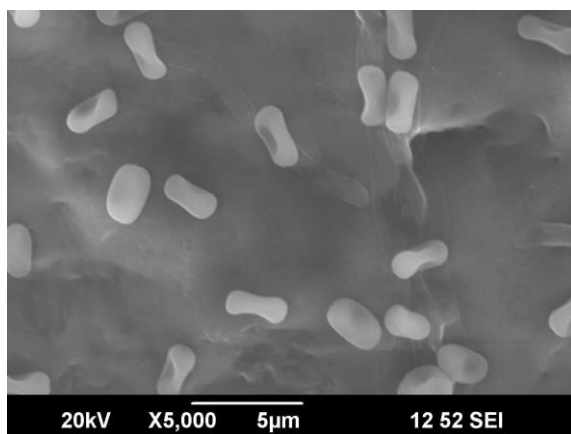


Figure: 3.2.1 SEM image of Starch-Urea Polymer

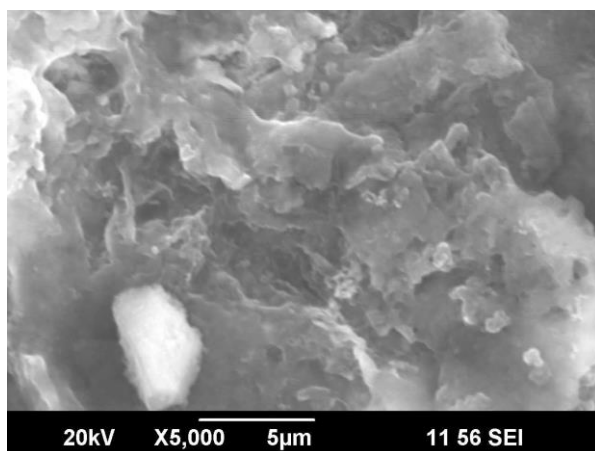


Figure:3.2.2 SEM image of Starch-Urea-Zinc Polymer Complex

The surface morphology of the biodegradable polymer and its metal complex has been examined under scanning electron microscope and their respective images have been shown above. From the figure, the starch-urea polymeric ligand shows smooth surface. Whereas in the SEM images of the zinc metal complexed polymer, the surface appears to be roughened. This roughening may be due to the cooperative contribution of the ligand for complexation with metal ions. Thus there is a clear change in the surface morphology of the polymeric ligand upon complexation with metal which is a clear evidence for the attachment of the metal on to the surface of the polymer.

3.3 EDX Analysis of Starch-Urea Based Biodegradable Polymer and its Zinc Metal Complex

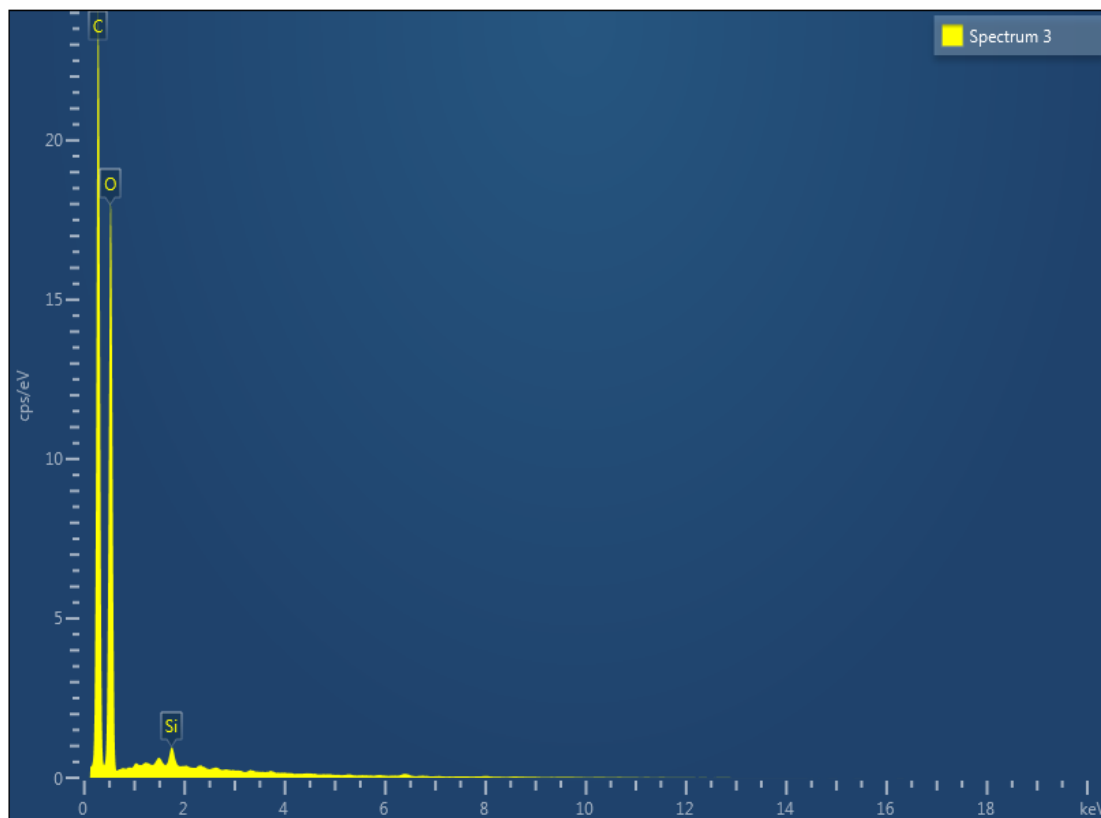


Figure: 3.3.1 EDX of Starch-Urea Polymer

Table 2: SEM EDX of Starch-Urea Polymer

ELEMENT	Wt%	ATOMIC%
C	27.18	33.24
O	72.63	66.67

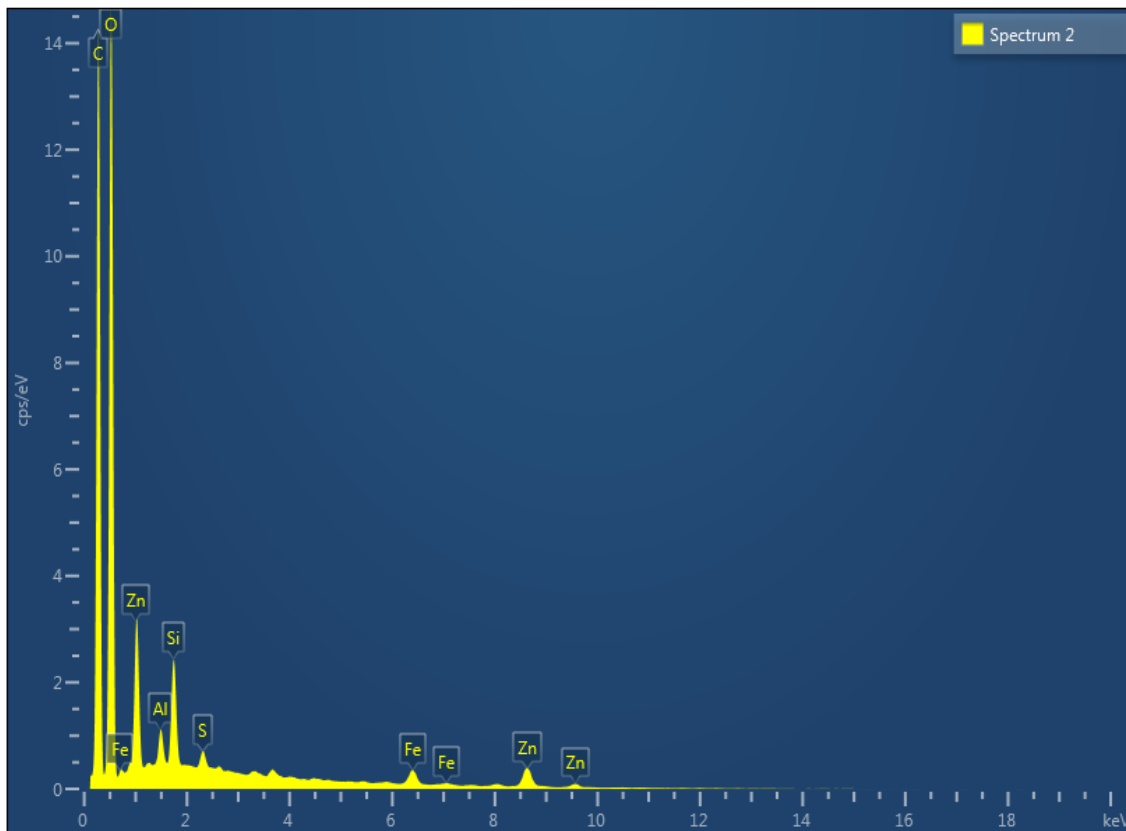


Figure: 3.3.2 SEM EDX Starch-Urea-Zinc Polymer Complex

Table 3: SEM EDX of Starch-Urea-Zinc Polymer Metal Complex

ELEMENT	Wt%	ATOMIC%
C	25.63	32.19
O	70.47	66.46
Zn	1.97	0.45

EDX spectra is used to calculate the percentage level of elements present in the metal complexes which are C, O, Al, Si, S, Fe and Zn in the starch-urea base complex. The results by energy dispersive X-ray analysis having indicated that there is a peak for Zn, which meant that there were metal attachment to the starch-urea base biodegradable polymer, and the % of metal attached to the biodegradable polymer is obtained from EDX.

CONCLUSIONS

The starch-urea based biodegradable polymers were synthesized. It was synthesized by the condensation reaction of starch and urea. The synthesized polymer was successfully complexed with Zn(II) metal ion. Modification of starch-urea polymer was carried out by using acetate salts of the metals. The synthesized polymer metal complex was found to be insoluble in water and soluble in DMSO.

The IR spectral data of starch-urea polymer metal complexes show bands appeared in 531.33cm^{-1} and 428.60cm^{-1} which support coordination of metal through oxygen and nitrogen. This shows successful complexation of metal to the polymer.

The scanning electron microscope(SEM) images of Starch-Urea biodegradable polymer shows a smooth surface, but in the SEM images of the metal complexes, the surface appears roughened. This roughening may be due to the cooperative contribution of the ligand for complexation with metal ions. There is a clear change in the surface morphology of the polymeric ligand upon complexation with metal which is a clear evidence for the attachment of the metal to the polymer.

EDX is used to calculate percentage level of elements present in the complex, shows a peak for Zn metal in the metal complexed Starch-Urea based polymer, which the peak is absent in the starch-urea based polymer alone. This compliments the attachment of Zn into the biodegradable polymer.

The main solvents used in this project are water and simple alcohols (methanol, ethanol) which are environmentally preferable

solvents. The reactants used-starch and urea, the products- starch-urea polymers are biodegradable. Hence there is lesser wastes and hazardous chemicals involved, which makes this synthesis a green chemical synthesis.

References

- 1) <https://en.wikipedia.org/wiki/polymer>
- 2) WWF: Biodegradable and Non-biodegradable Materials
- 3) Biopolymer Composites in Electronics, 2017
- 4) Ann-Christine Albertsson, Sigbritt Karlsson, in Comprehensive Polymer Science and Supplements, 1989
- 5) D.R.Lu, C.M.Xiao, S.J.Xu, *Starch based completely biodegradable polymer materials*, Express Polymer Letters Vol.3, No.6, 366–375, 2009.
- 6) A.AshwinKumar, Karthick, K.P.Arumugam, *Biodegradable polymer and its applications*, International Journal of Bioscience and Bioinformatics, Vol.1, 2011
- 7) Long Jiang, Jinwen Zhang, in Handbook of Biopolymers and Biodegradable Plastics, 2013
Adapted from a chapter in: Kutz, Applied Plastics Engineering Handbook (2011)
- 8) www.toppr.com/chemistry/polymers/biodegradable-polymers
- 9) NahidNishat ,Fahmina Zafar, synthesis, *characterization and biological activity of transition metal ions coordination polymers based on schiff base ligands*, POLYCHAR 22 World Forum on Advanced Materials, 7-11 April 2014

-
- 10) ShalinKumar,DurgaNathDhar,P.NSaxena,*Applications of metal complexes of Schiff bases-A review*,Journal of Scientific and Industrial Research Vol 68,2009
 - 11) H.N Aliyu,I.Ado,*Studies of Mn(II) and Ni(II) complexes with Schiff base derived from 2-amino benzoic acid and Salicylaldehyde*,BiokemistriVol 23,2011
 - 12) <https://en.wikipedia.org/wiki/Starch>
 - 13) Ashraf Malik, ShadmaParveen, TansirAhamad, SaadM.Alshehri ,Prabal Kumar Singh,NahidNishat,*Coordination Polymer: Synthesis, Spectral Characterization and Thermal behavior of StarchUrea Based Biodegradable Polymer and Its Polymer Metal Complexes*,Hindawi Publishing Corporation,2010
 - 14) K.P.R Chowdary,K.Krishna Chaithanya,*Preparation and Evaluation of cross-linked starch-urea-A new polymer for controlled release of Aceclofenac*,Asian Journal of Chemistry Vol 22,2010
 - 15) K.P.R Chowdary,D.Udaya Chandra,*Preparation and Evaluation of cross-linked starch-urea-A new polymer for controlled release of Diclofenac*,Int.J.Chem.Sci,2009
 - 16) <https://en.wikipedia.org/wiki/Urea>
 - 17) Omar B. Ibrahim, Moamen S. Refat, Mahmoud Salam, M.M.AL-Majthoub, International journal of material science; chemical studies on the uses of urea complexes to synthesize compounds having electrical and biological applications.
 - 18) <https://en.m.wikipedia.org/wiki/Zinc>
 - 19) <https://melscience.com/chemical> and physical properties of Zn

- 20) Virtual Chembook; Elmhurst college; Charles E. Ophardt, c.2003;
Zinc
- 21) Thermo Nicolet- introduction to fourier transform infrared
spectroscopy (pdf)
- 22) https://en.wikipedia.org/wiki/Scanning_electron_microscope
- 23) AntonisNanakoudis; blog; Thermo Fisher Scientific (2018) EDX
analysis with scanning electron microscope