Synthesis and Characterization of CuO Nanoparticle Reinforced Starch Based Bio-Plastic

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Candidate’s Declaration

It is hereby declared that no portion of the work referred to in the thesis has been submitted in support of an application for another degree or qualification of this or any other academic institution.

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Abstract

For the last 50 years, plastics are being widely used all over the world starting from drinking cups and disposable silverware to parts for automobiles and motorcycles. These materials have brought a lot of convenience and attraction to the agro, food and packaging industry. However, increased use of plastic has created serious ecological problems to the environment because of their resistance to biodegradation, thus disposal issues along with the non-renewability of these materials. Due to the growing concern over environmental problems of these materials, interest has shifted towards the development and promoting the use of “bio-plastics”. Bio-plastic is a term used for renewable resources i.e. produced from agro/food sources, materials such as starch, cellulose, etc. and which are considered safe to be used in food packaging applications and the field of medical science. The quality of bio-plastics can be expressed in terms of different properties like physical, thermal, mechanical, antibacterial, and water barrier properties. To enhance these properties, it can be blended easily with other polymers as well as with nanoparticles. For the research purpose CuO nanoparticles was have blended in the starch based bio-plastic. Thus this work outlines the synthesis and characterization of a starch-based biodegradable plastic that can meet the demand and can be disposed to the environment. Synthesis of biodegradable plastics was done by mixing distilled water, Glycerol, 10% Acetic Acid with starch powder. Various amount of CuO nanoparticles was used as a percentage of starch in the main composition. The FTIR, XRD, SEM, EDX, DSC, TGA, tensile strength, and UV-Vis of the samples were done to measure viability of the biopolymer. The peaks shift to lower wavenumber and the decrease in area under the peaks give clear indication of CuO interaction with the functional groups (OH, CH, CH2, CO). The amorphous nature of the final products happen with the increment of the content of CuO NPs in the host matrix indicates high miscibility of CuO nanoparticles in the starch matrix leading to the increased barrier properties. According to the SEM the rigidity that replaced the gummy surface, some agglomeration and weakening of cross links indicates that after a certain level of CuO NPs addition, it deteriorates the mechanical properties after initial enhancement. The chemical analysis (EDX) graphs indicate the presence of Cu other than C, O2 and as with the increment of CuO the Cu peaks go up. Indicates thermal stability of the CuO NPs reinforced bio-plastics with temperature as the glass transition temperatures go up with approximately fixed melting temperature. The weight loss against temperature curves also support the transition temperature shift to a higher temperature and the mass losses temperature ranges have gone up that indicates thermally more stable bio-plastics reinforced CuO NPs into those bio-plastics. The standard tensile

strength for food packaging is 4MPa, which is also what the pure starch bio-plastic is showing and the 0.5% and 1% CuO NPs reinforced bio-plastics show promising results. Although the 2% and 4% CuO NPs reinforced samples have fallen below the threshold, they can be used for other purposes. The direct band gap increment, blue shift, is an indication that the final CuO reinforced products will be good contender to be used as semi-conductors in Photo amplifier and modulators for optical fiber communications.

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List of Abbreviation

TPS - Thermoplastic Starch

PLA - Polylactic acid

CA-Cellulose Acetate

PU- Polyurethane

PE- Polyethylene

TPA- Tones per Annum

TPD- Tones per Day

AHG- Anhydroglucose

MSW- Municipal Solid Waste

HDPE- High Density Polyethylene

LDPE- Low Density Polyethylene

PHA- Poly-Hydroxy-Alkanoates

PVA- Polyvinyl Alcohol

MgSt- Magnesium Stearate

HA- Hydroxiapetite

RH- Relative humidity

UTM- Universal Testing Machine

ASTM- American Society for Testing and Materials

DSC- Differential Scanning Calimetry

TGA- Thermo gravimetric analysis

FTIR- Fourier transforms infrared spectroscopy

SEM- Scanning Electron Microscope

TS- Tensile Strength

EB- Elongation at Break

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CHAPTER 1

INTRODUCTION

1. Introduction

With the very conception of this universe, we have seen the dominance of different materials at various points of time that gave their name to the eras in which they prevailed (Rochman, et al.,2013). As the time passed through the stone-age, bronze-age, iron-age and the steel age in accordance with the fact stated above (Lee, 2006). Considering that at present, the total volume of plastic production has exceeded that of steel, the last part of the 20th century has been called the PLASTIC AGE (Eriksen, M., et al., 2014).

Plastics are used worldwide, from drinking cups and disposable silverware to various parts of automobiles and motorbikes, plastics are enduring to rise. They are imperative to the trade market as well as the packaging of materials all over the world (Eriksen, M., et al., 2014). However, plastics have been environmental anxiety because of the very slow rate of degradation.

Plastics compose about 20% by volume devastate per year. Industrial development, urbanization, wrong agricultural practices, etc. are responsible for pollution and loss of environmental quality (Cozar, et al., 2014). The usage of plastics in the packaging industry and disposable products and the production of plastic waste have increased significantly, making the environment worse for living.

Depending upon their degradability plastics are classified into two groups, namely

- Biodegradable Plastic.
- Non-Biodegradable Plastic.

Biodegradable plastics are synthesized using renewable resources which facilitate the straightforward decomposition in the atmosphere utilizing microbes (Rochman, et al.,2013). Starch-based bio-plastics can manufacture from either modified starch or raw starch (e.g. TPS) otherwise the fermentation of sugar is starch-derived (e.g. PLA). Typical starch sources include wheat, maize, cassava, and potatoes. Cellulose-based bio-plastics are characteristically modified plant fiber materials such as CA. General Cellulose sources comprise cotton, hemp, and wood pulp (Eriksen, M., et al., 2014). Bio-plastics based on Lignin contain wood produced as an offshoot of the paper mill industry. Bacteria are the supplementary treatment used to create a different type of biodegradable plastic (Cozar, et al., 2014). The bacteria are harvested after they are grown-up in the culture and subsequently created into biodegradable plastics. The mechanical properties of their resins can be changed depending on the requirements of the product (Rochman, et al.,2013).

The Non-biodegradable Plastics are the derivative of renewable resources that cannot be easily broken down in the environment by micro-organisms. Usual plastic resins can be produced from plant oils and are manufactured using compounds extracted from castor, soya bean or oilseed rape oil. Examples comprise polyurethane (PU) synthesized from soya bean oil and nylon made using castor bean oil. Conventional Polyethylene (PE) can be made from bio ethanol (Eriksen, M., et al., 2014).

The fragment of this plastic is very long consisting of carbon atoms linked together to form a long chain. A large amount of the plastics are manufactured by using fossil fuels as raw materials (Eriksen, M., et al., 2014). They contain hydrocarbons that form the building blocks of plastic, commonly known as monomers (Lee, 2006). These monomers combine to form polymers. Due to this kind of complicated composition, plastics cannot be broken down into simpler substances. Thus, they are non- biodegradable (Cozar, et al., 2014). So, this dictates the difference that were found the properties of these two different kinds of polymers which in turn, has far-fetched aspects as far as various mechanical properties and degradability concerned.

Thus, the objective is to prepare a biodegradable plastic from renewable sources such as starch that would be environment-friendly. Optimization of preparation condition will help the world to study the feasibility and potential of this starch with other additives to obtain a biodegradable as well as high tensile strength plastic.

1.1 Purpose of the Study

The principal objective of this study is to develop starch based bio-plastic and enhancement of its properties by adding CuO nanoparticles as reinforcement. The specific aims of the work include:

i. Synthesis of CuO nanoparticles by sol-gel method and making starch based plastic from potato.
ii. Processing of CuO nanoparticle reinforced starch based bio-plastic.
iii. Investigation and analysis of the structural, mechanical, thermal and optical properties of the CuO nanoparticle reinforced bio-plastic.

Possible Outcome:

The possible outcome of this study is having an environment friendly bio-degradable plastic. The reinforcement of the bio-degradable plastic will make it comparable to the regular plastics used these days. Use of such bio-degradable plastic will certainly subside the hazardous effects associated with production, use and disposal of the available plastics.

1.2 *Outline of Methodology/Experimental Design*

i. CuO nanoparticles will be synthesized by sol-gel method and will be characterized using scanning electron microscope (SEM) and X-ray diffraction (XRD) analysis.
ii. Starch will be made from mashed potato in a simple solution based process and the bio-plastic will be produced from starch.
iii. CuO nanoparticle will be added at different weight percentages.
iv. The structural characterization of the synthesized bio-plastic will be carried out by SEM, XRD and Fourier Transform Infrared Spectroscopy (FTIR).
v. Mechanical properties will be studied using universal testing machine (UTM).
vi. Thermal properties will be studied by Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA).
vii. Optical properties will be studied using ultraviolet–visible spectroscopy (*UV-VIS*).

CHAPTER 2

LITERATURE REVIEW

2. LITERATURE REVIEW

2.1 Plastic Consumption Scenario

Plastics have become the key drivers of innovations and application development. Asia has been world's largest plastics consumer for several years (Lee, 2006). In India, plastics consumption grew exponentially in 1990s (Hossain, Penmethsa, and Hoyos, 2009).In India, the consumption of plastics has increased many fold from 4000 tons per annum (1990) to 5 million tons per annum (2005) and is expected to rise further (Wang et al, 2013). The per capita plastic consumption is 4.0 kg/annum (Kinnaman, 2006). With the increase of plastics consumption, plastic wastes have also attracted attention for the few years due to extensive litter on land that not just affects the environment but also the individuals (Cozar, et al., 2014). Its wide range of application is in packaging industry, wrapping materials, shopping and garbage bags, fluid containers, household clothing, toys, and industrial products, and construction material (Shen, Haufe and Patel, 2009). It is a fact that plastics will not at all degrade and remains on landscape for numerous years (Eriksen et al, 2014). The recycled plastics are too much harmful to the environment than the virgin one due to mixing of color, additives, flame retardants, stabilizers etc. (Basyooni, Shaban, and Sayed, 2017). Further, the recycling of a virgin plastic material can be done only 2-3 times, for the reason that, after every recycling, the strength of plastic material is reduced due to thermal degradation (Vinson & Locke, 1972). It is to mention that no reliable assessment is available on total generation of plastic waste in the country however, considering about 70% of total plastic consumption is discarded as waste, thus approximately 6 million tons per annum (TPA) of plastic waste is generated in country, which is about 15 kilo tones per day (TPD) (Cozar, et al., 2014).

According to industry prospective, among the factors driving this growth of plastics are increased in packaging, infrastructure, agriculture, automotive and health care segments (Narayan, 2001).

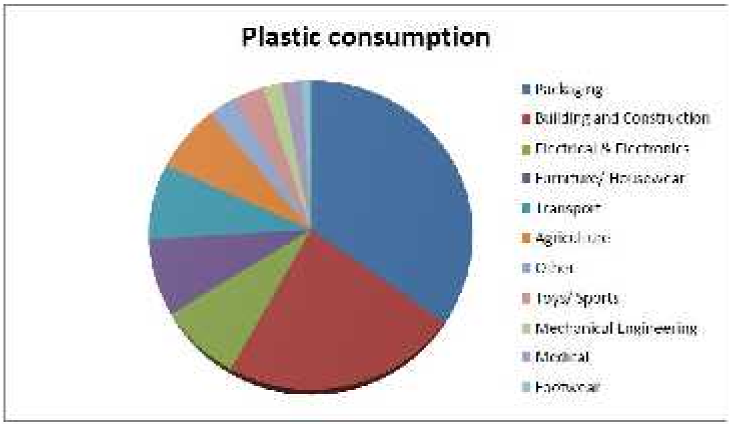


Figure 2.1: Sector wise distribution of plastic consumption (Wang et al, 2013).

2.2 Environmental Effect of Polymers

Since 1950s, one billion tons of plastic are discarded and may persist for hundreds of years. Due to lack of stringent laws and strict regulation in regards to the dumping of polyethylene bags, by the Government, India has been heavily polluted with non-biodegradable plastic (Eriksen, M., et al., 2014). Various awareness programs should have been staged to educate the growing ignorant population to reduce the usage and proper disposal of plastics (Cozar, et al., 2014). Due to this ignorance of the mass has led to the continuous inappropriate disposal of waste. Despite the fact that they are inexpensive as well as light, they are harmful in following ways:

2.2.1 Effect on Soil

A vast amount of land is continually lost when polyethene bags enter into the soil; they chunk further passage of mineral salts and oxygen to the soil (Steinbuchel, 2003). When blocked, the soil is incapable to yield crops appropriately this can cause huge problems to farmers and consumers (Tuil et al, 2000). Polythene bags comprise an acidic combination that with time affect the chemical formulas of soils (Avella, Bonadies & Martuscelli, 2001).

Figure 2.2: Solid waste

2.2.2 Consumption of Non-Renewable Resources

At the same time as, petroleum based products are losing ground and are getting costlier everyday using these non-renewable sources more and more (Fritz, Link and Braun, 2001). Petroleum is essential to the contemporary way of living (Karlsson and Albertsson, 1998). Petroleum is essential for the power that is necessary – for factories, lighting, transport etc (Eriksen, M., et al., 2014). Without feasible alternative resource of energy till now on the perspective, if the availability of petroleum were to be stopped, that might practically lead to halt the whole world grind (Vijaya and Reddy, 2008). To produce plastics, about 100 million barrels of oil are required each year all over the world (Kaplan et al, 1993).

2.2.3 Effect on Health and Hygiene

As plastics are non-biodegradable, they clog and choke on water that can act as procreation places for many of malady germs which sooner or later cause an endemic in the surrounding inhabitants (Velde and Kiekens, 2002). Waste materials serve as a procreation place for various disease carriers. Female Anopheles mosquito spreads malaria (Rouilly & Rigal, 2002). There are also exceptional germs like the cholera germ that has led to the death of millions of inhabitants in the world (Chandra and Rustgi, 1998).

2.2.4 Clogging of Drains and Sewage

Polythene bags easily block sewage and supply of water that ultimately lead to the extent of disease and flooded during rainy season (Vansoest, and Knooren, 1999). They can also grounds water clogging since water can't drip all the way through them, and this can be an excellent reproduction ground for a number of species that spread disease (Mantia & Dintcheva, 2003).

2.2.5 Effect on Wildlife

About a million animals such as dolphins, turtle's whales are killed every year due to these bags. Many animals such as cow, goat, etc. are mistaken plastic as food (Okada, 2002). Plastic bags, once ingested cannot be digested or conceded by an animal, so it stays in the gut (Selin, Oksman and Skirfvars, 2003). Plastic in animal's gut avert food digestion and can lead to a very slow and painful death (Ashwin, Karthick and Arumugam, 2011).

Figure 2.3: Sewage plastic waste

2.3 The Prospective of Biodegradable Plastics

For better sustainability and eco-efficiency, green chemistry is obsessed with a search for renewable and environment friendly resources (Baier et al., 2012). Among the natural polymers, starch takes prior attention (Chiellini et al, 2001). Starch is a biodegradable polysaccharide, produced in plenty at low expenditure and exhibits thermoplastic in nature (Mulder, 1998). Thus, it has become the most promising alternative to replace conventional plastics in individual market segments (Chaffee, and Yaros, 2007). Well-known synthetic polymeric materials has great used in every field of human activity during last several years and these artificial macromolecular substances are usually generated from petroleum and most of the synthesized plastics are regarded as non-degradable (Cozar, et al., 2014). However, the resources of petroleum are limited, and the flourishing use of non- biodegradable polymers has caused serious environmental tribulations

(Mohantya, Misraa and Hinrichsen, 2000). In addition, the non- biodegradable polymers are not appropriate for impermanent exercise (Takahashi, 2010). Thus, the polymer materials that are degradable or biodegradable have great interest since 1970s (Joshi, Patel, 2012). Both the synthetic and natural polymers that include hydrolytically or enzymatically liable bonds or groups are easily decomposed (Spiridon, Teaca and Bercea, 2013). The advantages of synthetic polymers are distinct, and can tailor quickly (Rahman and Brazel, 2004). In spite of this, they are somewhat expensive (Parvin et al, 2011). This reminds us to focus for an alternative natural polymer, which is naturally biodegradable and can capable to meet different necessities (Parvin et al, 2010).Owing to its totally biodegradable, cheap and renewability, starch is showing potential to develop sustainable resources. In view of this, starch has been getting attention since 1970s (Guohua, et al, 2006). Efforts have been made to make starch-based polymers for conserving the petroleum resources, sinking environmental impact and probing more applications (Mergaert et al, 1993).

2.4 Starch

Most of organic substance lying on earth has the structure of polysaccharides and a significant polysaccharide is starch (Xu and Hanna, 2005). Plants amalgamate and store starch in their formation as an energy preserve (Lin, 2016). It is deposited in appearance of tiny granules or cells with diameters stuck between 1-100 µm. Starch is originated in seeds (i.e. corn, maize, wheat, rice, barley, or peas) and tubers or roots (i.e. potato) of the plants (Herrera, 2017). A large amount of the starch produced worldwide is originating from corn, additional types, such as potato, wheat, cassava and sweet potato starch are moreover produced in huge amount (Ajibade and Nqombolo, 2018). A good number crops producing starch are very fruitful (Woo, 2002). Accumulation of starch by potato about 70-72 % of the bone dry mass in the tubers having capitulated up to 20 ton starch per hectare (Anandhavelu et al. 2017). Whereas a corn seed comprises starch about 60-75 weight %, with an average capitulate of 5 ton per hector (Chen et al, 2018).

2.4.1 Arrangements and Properties of Starch

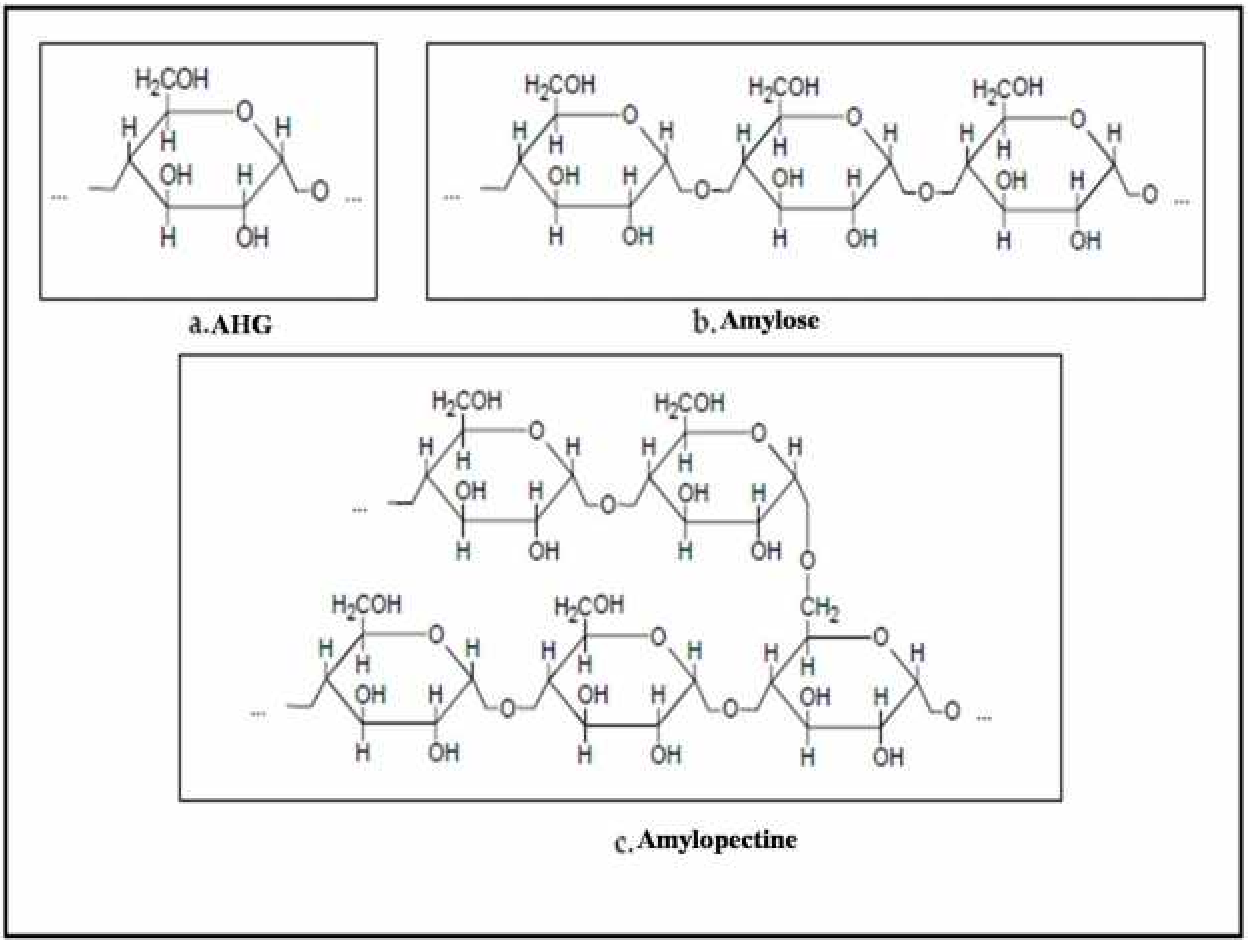
Starch is a polymer comprising with anhydroglucose (AHG) units (Figure 2.4 a.) (Dankar, et al, 2018). Two types of AHG polymers are generally there in starch: amylose and amylopectin (Marichelvam, Jawaid and Asim, 2019). Amylose is basically a linear polymer in which AHG units are principally connected all the way through α-D-(1,4)-glucosidic bonds (Mitrus, 2005).The molecular weight of amylose is the combined molecular weight of the plant resource and processing technique (Harunsyah et al,2017). Amylopectin is a linked polymer, containing periodic kindling with the backbones through α-D-(1,6)-glucosidic bonds. Every branch consists of about 20-30 anhydroglucose units. The molecular weight of amylopectin is more than that of amylase (Radhakrishnan, and Beena, 2014). The presence of amylose and amylopectine in starch varies and mostly depends on the starch resource (Eyarani et al, 2016). Typically, the amylose content is stuck between 18-28 percent. The amylose content of some frequent starches is specified in Table 2.1.

Table 2.1: Approximate content of amylose on common starches (Eyarani et al, 2016).

Starch	Amylose (%)
Oat	27
Corn	29
Hybrid amylomaize Class VII	50-52
Hybrid amylomaize Class V	70-72
Arrowroot	21
Potato	**20-22**
Rice	19

Manioc	15
Sweet potato	17
Sago	25
Wheat	25
Tapioca	16

Generally starch is not soluble in water, however it is extremely hygroscopic and binds water reversibly (Jiang et al, 2016). Heating a starch solution leads to thrashing of hydrogen bonding in the core of the starch grain and the starch will initiate to gelatinize (Xingxun et al, 2013). The starch grain will swell up fast multiple times its actual volume. The linear amylose molecules percolate the granules into the solution (Vilas et al, 2018).


a.AHG

b.Amylose

c.Amylopectine

Figure 2.4: Chemical Structure of Starch (Vilas et al, 2018)

The consequential suspension contains a combination of linear amylose molecules, inflated granules, and granule trash, and depending on the extent of water present, will form a bulky paste or gel. Gelatinization temperature assortment can be defined as the temperature at which grainy enlargement begins in anticipation of the temperature when almost 100% of the granules are gelatinized (Vilas et al, 2018).

2.4.2 Biomaterials from starch

Plastic is the common phrase for a broad range of synthetic or semi-synthetic polymerization products. Plastics are used in a broad range of applications, and the requirement is still rising every year (Sreeju, Rufus and Philip, 2017). The first invention of marketable plastics was derived from cellulose nitrate and is well-known as celluloid (Sreeju, Rufus and Philip, 2017). A. Parker in 1838 primarily prepared cellulose nitrate and J. Hyatt foremost patented celluloid in 1870 (Cozar, et al., 2014). Despite the fact that celluloid is derived from usual polymer (cellulose), the oldest merely synthetic plastic is Bakelite, discovered by Baekeland in 1907. A remarkable enlargement in demand for plastics began subsequent to Second World War when invention of polyethylene (PE) was done. PE is a very adaptable plastic as it can be wrought easily into diverse forms, for occasion, to be used in packaging and paper coatings. Plastics are very striking materials. They have a low density and can be wrought in thin films as maintaining excellent properties. The latter is important when using the matter for packaging prospect to save weight, space, and energy at some stage in carrying of goods (Sreeju, Rufus and Philip, 2017). Plastics have lesser melting temperatures compared to glass and metals, and, therefore, require smaller amount energy to form into useful products (Vilas et al, 2018).

The relevance of biodegradable plastics might be a beautiful solution for the troubles related to the use of usual plastics. Biodegradable plastics are polymeric materials that are able to decompose when prearranged a proper atmosphere and adequate amount of time. Biodegradable plastics have gained great curiosity since the 1980s (Sreeju, Rufus and Philip, 2017). Nowadays new types of biodegradable plastics with enhanced properties and lesser costs have been developed. Biodegradable plastic desecrate may be treated in composting facilities, jointly with food and yard waste as well as paper. It can also be processed in dirt sludge water management plants or obscured in the soil. The significant development of composting as a means to reserve landfill due to the diminishing dumping spaces might help the steps forward for biodegradable plastics development.

In modern years, there has been a noticeable enlargement in biodegradable materials for use in packaging, medicine, agriculture, and other areas. In particular, biodegradable polymer materials are of importance (Vilas et al, 2018). Polymers outline the backbones of plastic materials and are repeatedly being employed in a mounting range of areas. As a result, many researchers are investing time into modifying conventional materials to make them more user-friendly, and into designing original polymer composites out of physically occurring materials. A number of biological materials may be integrated into biodegradable polymer materials, with the most common being starch and fiber extracted from different types of plants (Sreeju, Rufus and Philip, 2017). The belief is that biodegradable polymer materials will diminish the requirement for synthetic polymer production (thus reducing pollution) at a low cost, thus producing an affirmative effect both environmentally and economically. Dates to the 1970s, attempts to recycle plastics was conducted on the municipal solid waste. The chemistry and technology of its pyrolysis and efforts were made to devise methods of disposing of plastic wastes without any pollution of the environment (Sreeju, Rufus and Philip, 2017). Eventually, it was realized that recycling of solid wastes must be incorporated into the existing and upcoming waste management strategy to give the remuneration of conserving natural resources and saving fossil fuels (Zhang, Wang and Cheng, 2018).

2.5 Plastic in Solid Waste and its Disposal

Locke and Vinson have reported their concern to plastics in the solid waste through their analysis (Zhang, Wang and Cheng, 2018). It further reported the prospective of recycle plastics as a polymer blend of different types. Property degradation was more severe since the blend became more complex which indicated that common municipal wastes might be reused in extremely inferior applications while definite viable wastes may comprise brighter projection. Strategies for improving blend properties be outlined in this (Kolybaba et al, 2003). Ottinger et. al devised a method to dispose of waste plastic without affecting the environment by passing it to the reactor. It was then heated in the presence of gas to a decomposition temperature of plastic and recovering products from there (Sreeju, Rufus and Philip, 2017). An experimental program was conducted to find out the discrepancy of permeability with degradation (Zhang, Wang and Cheng, 2018). The persuade of density and voids ratio on the permeability of MSW was studied which summarized that the disparity in permeability with instance and landfill depth should be consider during design of landfill rather than making an allowance for an usual value for the whole landfill height and process time (Sreeju, Rufus and Philip, 2017).

Kinnaman examined recycling and the associated costs and benefits of reducing waste sent to landfills. A municipal curb-side recycling program required households to label garbage bags. Identifying biodegradable plastics for sorting could be implemented through this collection system. By giving the consumer the option to arrange biodegradable plastics from other, non-biodegradable plastics, issues with PLA products finding their way into the waste stream could be avoided (Zhang, Wang and Cheng, 2018).

2.6 Renewability and Sustainable Development

Renewability is associated to the perception of sustainable development. The UN World Commission on "Environment and Development in Our Future" define sustainability as the development that meets the desires of the recent time exclusive of compromising the capability of future generations to gather their needs (Sreeju, Rufus and Philip, 2017). According to Narayan, the manufactured products, e.g., packaging be required to be designed and engineered as of "conception to reincarnation", the so-called "cradle-to-grave" approach. The use of yearly renewable resources, like wheat, be required to be understood in an absolute carbon cycle. This thought is based on the enlargement and the manufacture of products based on renewable and biodegradable resources: starch, cellulose (Vilas et al, 2018). By collecting and composting biodegradable plastic wastes much-needed carbon-rich droppings: humic materials can be made. These precious soil amendments can go back to the farmland and reinitiate the carbon cycle. In addition, composting is a progressively more key point to sustain the sustainability of the farming system by dropping the utilization of chemical fertilizers (Zhang, Wang and Cheng, 2018).

2.7 Bio-degradability and Compostability

Bio-degradable stands for the proficient of undergoing decay into methane, water, carbon dioxide, inorganic material, and biomass (Liu et al, 2019). A principal technique is the enzymatic act of microbes that are able to precise by usual test in excess of particular time, shiny accessible dumping state of affairs. There are diverse media to examine bio-degradability. Material's compostability is the degradability using manure intermediate. Bio-degradation is the dilapidation of an organic substance cause due to the biological act, principally microorganism's enzymatic act (Sreeju, Rufus and Philip, 2017). The yields are CO_2, water and new biomass (in the occurrence of oxygen, i.e. aerobic conditions) or else methane (in the nonappearance of oxygen, i.e., anaerobic conditions). However, a different composting environment like temperature and humidity cycle must be realized to decide about the compostability level (Zhang, Wang and Cheng, 2018). It can be seen that the contrast of the outcome obtained from a variety of standards seems to be complex or unfeasible. To consider the quantity of mineralization also the character of the residues left behind the biodegradation (Liu et al, 2019). The accretion of contaminants with poisonous wastes might slow down plant growth (Vilas et al, 2018). The main concern is to decide the environmental toxicity intensity for these by-products, named as eco-toxicity (Liu et al, 2019). A number of common regulations make certain the estimates of the biodegradability progression. As an example of raise in parameter such as the weight of macromolecules, hydrophobicity, and the size of crystalline domains or the crystallinity reduces the performance of bio-degradability (Sreeju, Rufus and Philip, 2017).

An effort was made by Vijaya and Reddy (2008) to study the biodegradation of polyethene films in the natural atmosphere. The technique recommended by ASTM standards, i.e. composting of polyethene films with MSW, was adopt to examine the biodegradation of synthetic plastic in the natural environment (Vilas et al, 2018). The samples were collected and tested for weight loss and decrease in tensile strength at two months space for twelve months of composting. Loss of weight and decrease in tensile strength of polyethene films were considered as the criterion for representing biodegradation of these materials. Composting of polyethene films for four months did not confirm any degradation. After four months of composting, the loss in weight was 2.9-4.5% for HDPE films. In the same way, the reduction in tensile strength ranges from 16-20% for HDPE and 12-13% for LDPE films (Liu et al, 2019). Their study indicated that the biodegradation of polyethene films occur in the natural environment at an extremely slower rate (Herrera, 2017).

2.8 Bio-degradable Polymers

Bio-degradable polymers stand for an emergent field (Liu et al., 2017). Huge amount of bio-degradable polymers (e.g. chitin, cellulose, polylactide, starch, and other polypeptides) are there to synthesize or to produce in normal atmosphere all through the augmentation cycle of organisms. Some microbes and enzymes are able to degrade such polymers were recognized (Liu et al., 2017). Diverse classifications of a variety of Bio-degradable Polymers have been reported in Fig 2.5. Sorting of the bio-degradable polymers according to their production method (Fig. 2.5) suggests that (i) polymers starting from biomass such as agro-polymers from agro-resources (e.g., starch or cellulose), (ii) polymers obtained by microbial creation such as the poly-hydroxy-alkanoates (PHAs), (iii) polymers traditionally and chemically synthesized from monomers obtained from agro-resources, e.g., the polylactic acid (PLA), and (iv) polymers obtained from fossil resources (Vilas et al, 2018). Only the first three categories (i–iii) were derivative from renewable resources. Further classifying these green polymers into two foremost categories: the agro-polymers (category i) and the biodegradable polyesters or bio-polyesters (categories ii–iv).

Liu et al. (2017) made stress-strain measurements in relative with starch crystallinity. Starch in grainy form was made which was plasticized with diverse amounts of glycerol and water. The dull rubbery materials were pliable and feeble with high elongations. All through aging the materials became less stretchy with high elastic modulus and tensile stress (Liu et al, 2019). Mantia and Dintcheva (2003) recommended that the major difficulty in post-consumer plastics recycling was due to the thermo-mechanical stress subjected on the melt for the period of pre-processing operations. The macromolecules ruptured because of temperature and mechanical stress. The extent of degradation was interrelated with the level of mechanical stress which in turn was proportional to the viscosity of the melt.

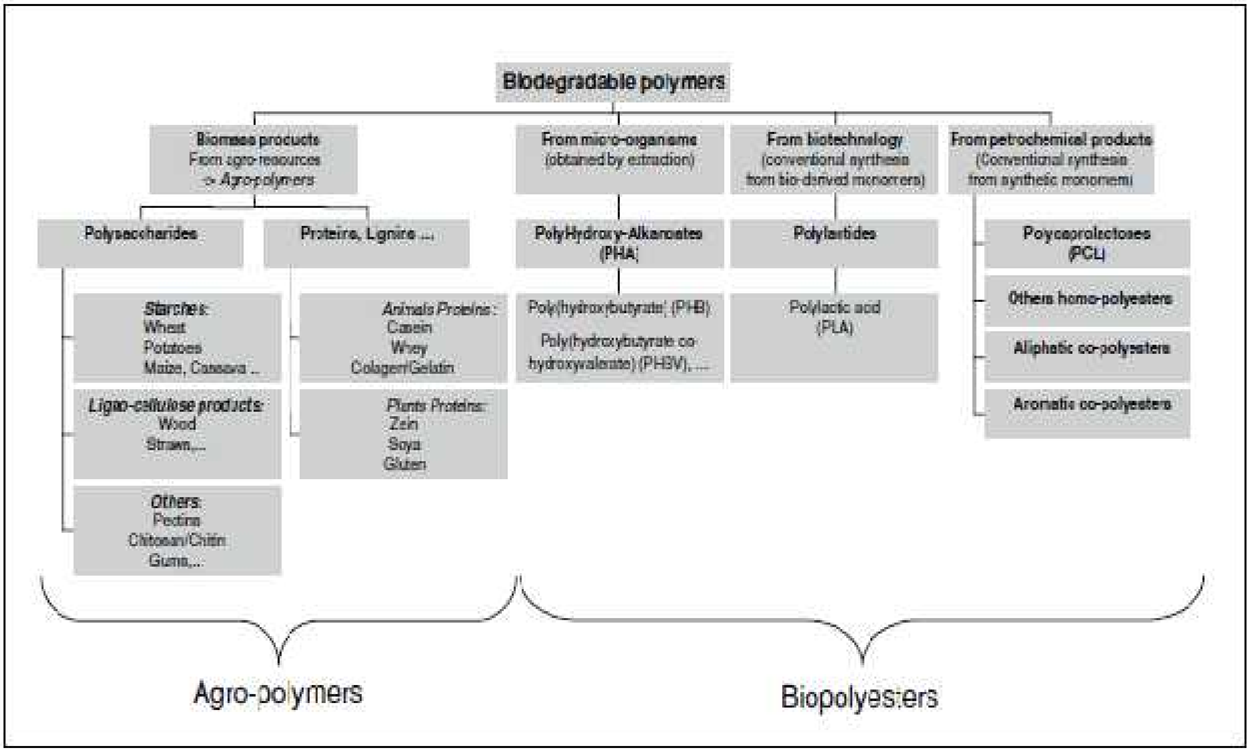


Figure 2.5: sorting of the main bio-degradable polymers (Vilas et al, 2018)

Kolybaba et al (2003) gave an insight into how a material is created and the technique in which it is tainted. A common phenomenon of the breaking down of polymer materials is that it may possibly occur by microbial accomplishment, photo-degradation or chemical degradation (Liu et al., 2017). Many biopolymers are intended to be unnecessary in landfills, composts, or top soil. The materials may perhaps be broken down, provided that the essential microorganisms were present (Fama et al., 2011). Characteristically soil bacteria and water are first and foremost required for microbial reduced plastics (Taabouche, 2014). Polymers that are based on naturally developed materials (such as starch) are vulnerable to degradation by microbes (Annual report, April, 2007). The material may or may not decompose quickly under aerobic conditions, depending on the formulation used, and the microorganisms present (Ceylan et al., 2013). Reuse of plastic materials is expected and well documented, but attempts to withhold this growing endeavor have been less than effective. In the United States, at present a reduced amount of 10 percent of plastic products were recycled at the end of their functional life (Liu et al, 2019). Recycling must be acknowledged as a disposal method, not a concluding goal for material development. An unworried attitude concerning recycling processes ignores the truth that highly developed infrastructure is necessary to properly house recycling unit. As Taabouche (2014) surveyed that, in underdeveloped countries plastics are more or less exclusively recycled, based on economic condition. Although it appears to be positive at the beginning, up till now the open systems by which the plastics are recycled permit the emanation of toxic gases at decisive levels (Herrera, 2017).

A study performed by Chaffee & Yaros (2007) compared three unlike compositions of grocery bags. The typical polyethylene grocery bags when was compared to grocery baggage prepared from compostable plastic resins, it was observed that the conventional plastic grocery bags use a smaller amount energy in terms of fuels for manufacturing, a smaller amount oil, and less potable water, and emit fewer global warming gases, less acid rain emissions, and less solid wastes (Taabouche, 2014). Their conclusions suggest that biodegradable plastics are neither a clean alternative to petroleum-based traditional plastics nor grocery bags made from recycled paper.

Mohanty (2000) reported that Starch based plastics were primarily harvested from wheat, potatoes, rice, and corn. Of these four starches, corn is the mainly used and is the cheaper one. Being an enormously adaptable product, about 20 percent of the starch is used for non-food items (Strong, 1996). Starch is used for many non-food items such as making paper, cardboard, textile sizing, and adhesives. Starched based plastics have already been processed into eating utensils, plates, cups and other products. Starch, when harvested, is turned into a white, grainy product (Herrera, 2017).

Takahashi (2010) suggested that Polylactic acid (PLA) is one of the major promising bio-based plastics manufactured commencing lactic acid, which is obtained from fermentation from corn starch and sugars. At the same time, PLA is eco-friendly and compostable. It has an outstanding mechanical strength, good process ability, and large manufacture capability compared to other biodegradable plastics. One of the distinctive points of PLA is its real compostability. Therefore, a good suggestion would be to use PLA as food containers with left food or organic waste. Organic waste accounts for about 30 wt% of domestic waste, and it is incinerated. Composting can reduce encumber of incineration on local government too (Jaber-Ansari, et al., 2014).

Ceylan et al. (2013) suggested that biodegradable polymer degrades within the body as a consequence of natural biological processes, eliminating the need to remove a drug delivery system after release of the active agent has been completed. Most biodegradable polymers are intended to degrade as a result of hydrolysis of the polymer chains into biologically satisfactory and gradually smaller compounds (Jaber-Ansari, et al., 2014). For some degradable polymers, most notably the poly-anhydrides and poly-ortho-esters, the degradation occurs only at the exterior of the polymer, resulting in a discharge rate that is proportional to the surface area of the drug delivery system (Ceylan et al., 2013). Biodegradable polymers mainly investigated for drug deliverance applications are of either natural or synthetic foundation (Liu et al., 2011).

CHAPTER 3

MATERIALS

&

METHODS

3. Materials and Methods

3.1 Chemicals and Materials:

Copper oxide powder was produced in the lab using the sol gel technique. 10% Acetic Acid made from mixing Acetic Acid and water in proportional amount. Glycerol obtained from Merck (Darmstadt, Germany). Acetone was obtained from Guangdong Chemicals and Dimethyl Sulfoxide (DMSO) purchased from Qualikems Fine Chem. Pvt. Ltd. The chemicals were used without further purifications. Deionized water (DI water) was used throughout the experiments.

3.2 Synthesis of Copper Oxide (CuO):

To produce copper oxide, Sol Gel Combustion Technique was used to produce CuO nanoparticle. The CuO was used to make by the sol-gel combustion method in the laboratory by using copper (II) nitrate trihydrate [$Cu(NO_3)_2.3H_2O$], Citric acid ($C_6H_8O_7$), distilled water and ammonia solution as raw materials.

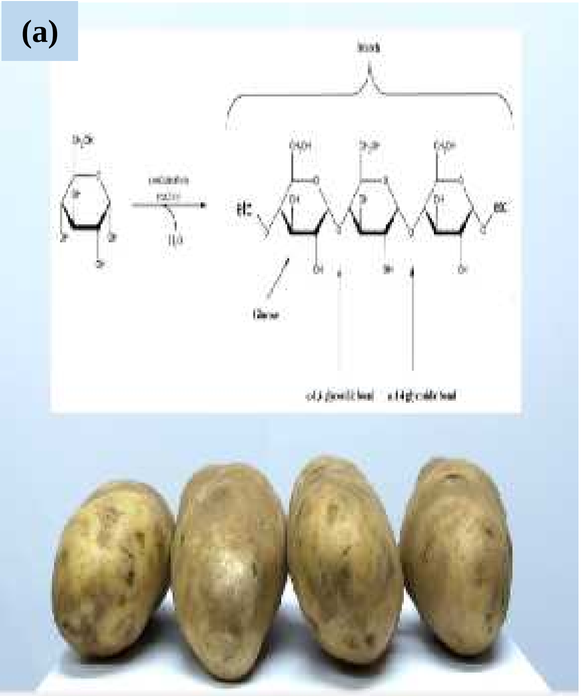
- In the gel combustion method, the raw materials, which are usually a nitrate compound and a fuel, are dissolved in water.
- After controlling the pH, by a weak base such as ammonia, the mixed solution is heated to change the sol to a high viscosity gel.
- Increasing temperature causes an exothermic combustion process and both organic materials as a reducing agent and nitrates as an oxidation agent change the gel to a very gray fine and intensively porous substance.
- Finally the nanoparticle is prepared using the grinding for sufficient amount of time.
- To check the powder characteristics SEM and XRD has carried out.

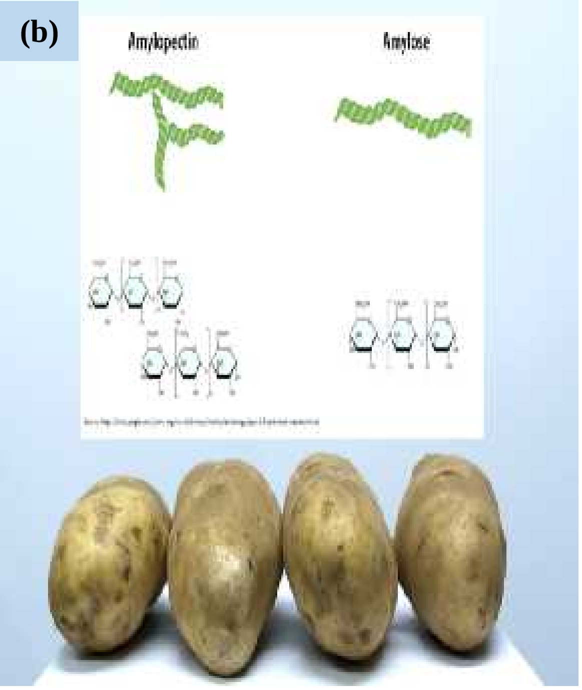
3.3 Synthesis of CuO nanoparticle reinforced Starch based Bio-plastic:

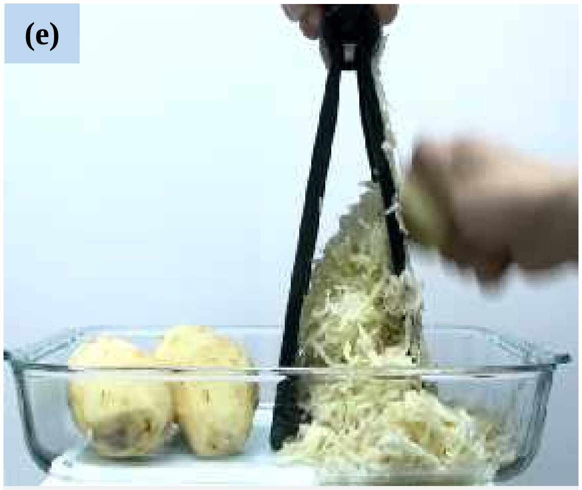
CuO nanoparticle reinforced starch was made from raw potatoes that were bought from the market following the procedure describe below:

- Potatoes were cleaned and using the grater sliced the potatoes into fine pieces and then soaked all those in distilled water in a steel bowl in standard lab environment.
- Potatoes were stirred to soak water thoroughly so that the pieces of potatoes can come in contact with the water.
- The residue was taken out using tea strainer in a beaker. Starch accumulates at the bottom of the beaker that we collected on the petri disks.
- Starch was rinsed with distilled water. The whole procedure is repeated for several times until we get the white colored starch on the petri disks.
- Then the starch was put in the petri disks in the drying oven at 60 ^{0}C for one and half hours. This is the stage we needed to be careful of as the starch is bio degradable it get affected by bacteria and rots pretty fast in the natural environment.
- Samples were measured 10 gm of starch using the balance machine. For the other ingredient, we took distilled water, Glycerol, and 10% Acetic acid in the proportion of 6 : 1/3 : 1/3 to 1/2 accordingly of starch.
- In this proportional mixture we added CuO in 0%, 0.5%, 1%, 2% and 4% of measured starch.
- All these ingredients were mixed and put the mixture on magnetic stirrer by setting the temperature at 95-100 ^{0}C. This range of temperature is suitable for the adhesive nature of glycerol.
- The 10% Acetic Acid is used to enhance the adhesive nature of the plasticizer that is the glycerol.
- The above mixture is stirred and heated at 95-100 ^{0}C for about 2-3 minutes to get the polymer that we collect on the petri disks again.
- The petri disks with different samples are then put in the drying oven at 60 ^{0}C for 1.5 hours. After oven drying the petri disks with samples are covered with ventilated foil papers (we made holes on the foil papers using needle sharp object) and put into the natural environment of the lab for 4 weeks or so depending on the conditions of the samples.
- After normal drying the samples are ready to be tested for characterization of starch based bio polymer.

3.3.1 Experimental Setup:






(e)


(f)


(g)


(h)


(i)


(j)

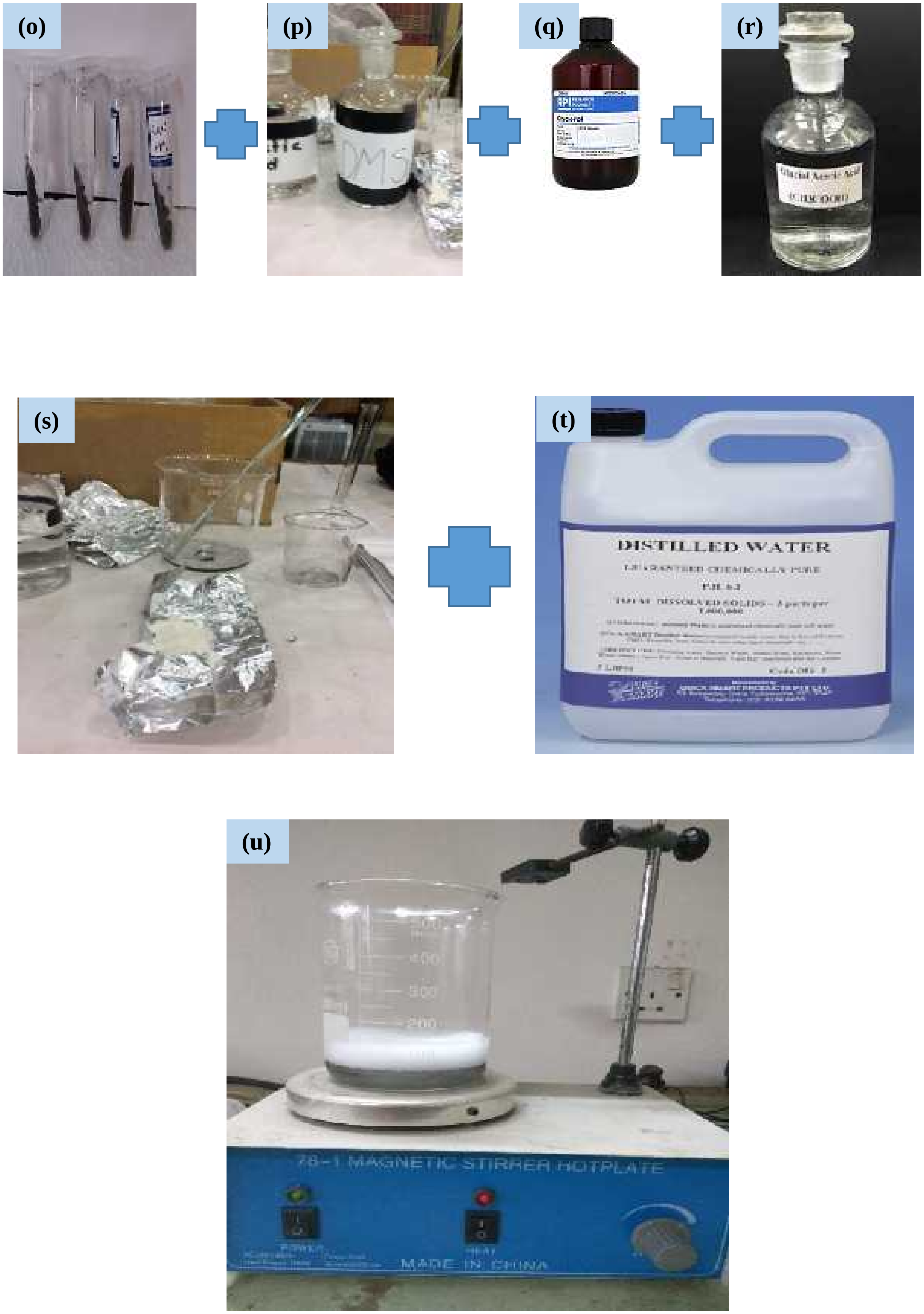
(k)

(l)

(m)

Drying in the oven for 1.5 hours at 60°C

(n)


(o)
(p)
DMS
(q)
Glycerol
(r)
Glacial Acetic Acid
CH3COOH
(s)
(t)
DISTILLED WATER
GUARANTEED CHEMICALLY PURE
(u)
78-1 MAGNETIC STIRRER HOTPLATE
POWER
HEAT
MADE IN CHINA

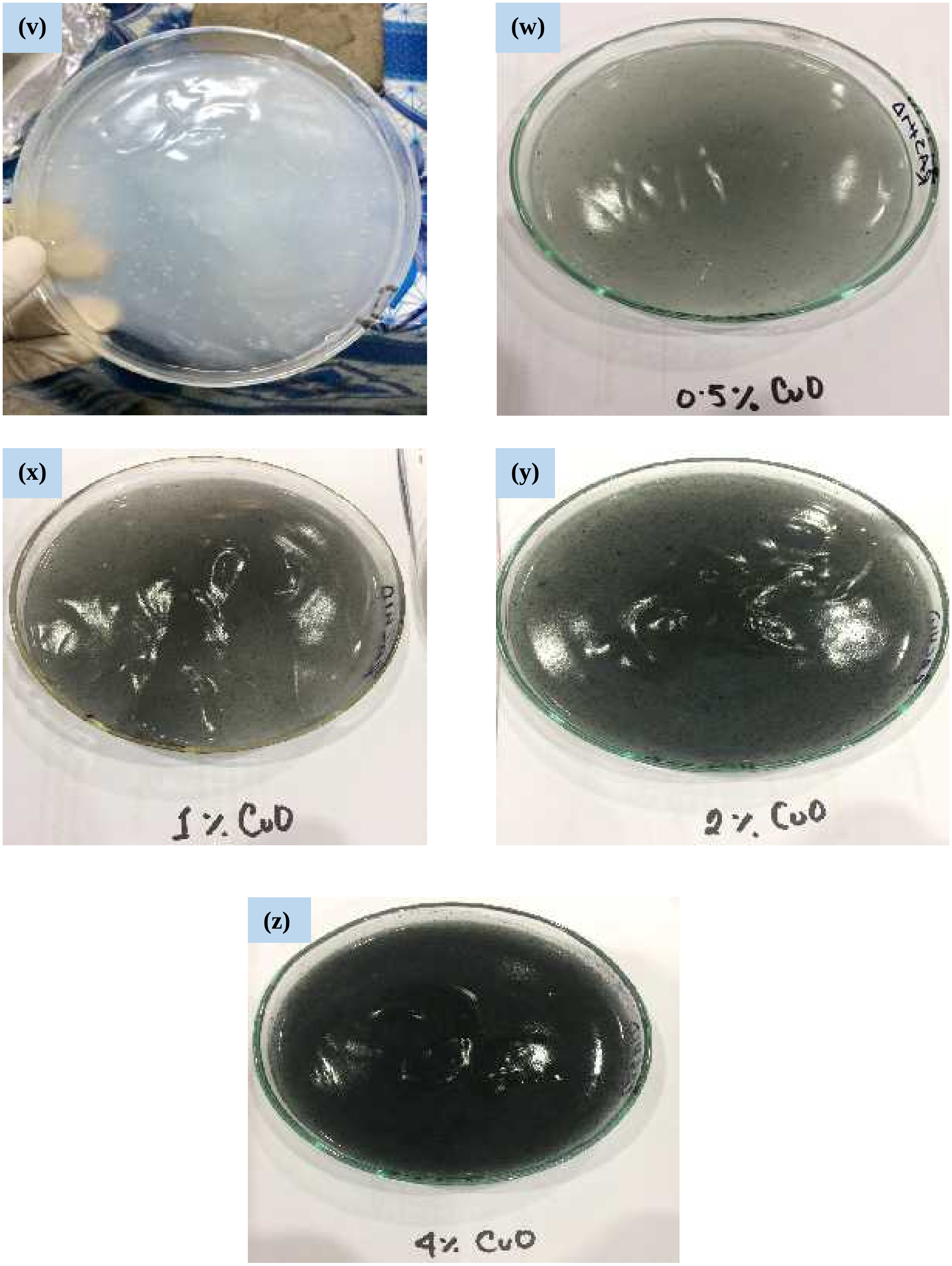


Fig 3.1: From (a) to (z) the process of producing pure and CuO nanoparticle reinforced starch based bio-plastics are shown

3.4 Characterization methods

3.4.1 FTIR Spectroscope

Infrared spectroscopy gives an idea about the molecular bonding; IR radiation passed through a sample. A few of the infrared radiations are absorbed, and a number of gets transmitted. The consequential spectrum represents the molecular absorption and transmission spectra to understand the molecular dactylogram of the sample. The Infrared Spectra (IR) of the films was measured by FTIR spectrophotometer. The infrared spectrum has taken in transmittance mode at a resolution of 5cm^{-1} ranging from 500-4000 cm^{-1}.

Fig 3.2: Cary 630 FTIR by Agilent Technologies

3.4.2 Surface Morphology

The surface topology studies of all the films were studied using a JEOL JSM-7600F Scanning Electron Microscope (SEM). SEM is a type of the electron microscope that images a sample by scanning it with a beam of electrons in a raster scan pattern. The entire sample was mounted on the aluminum stub using graphite filled tape which was vacuum coated with Platinum. SEM was run at an accelerating voltage of 10kV and 15kV.

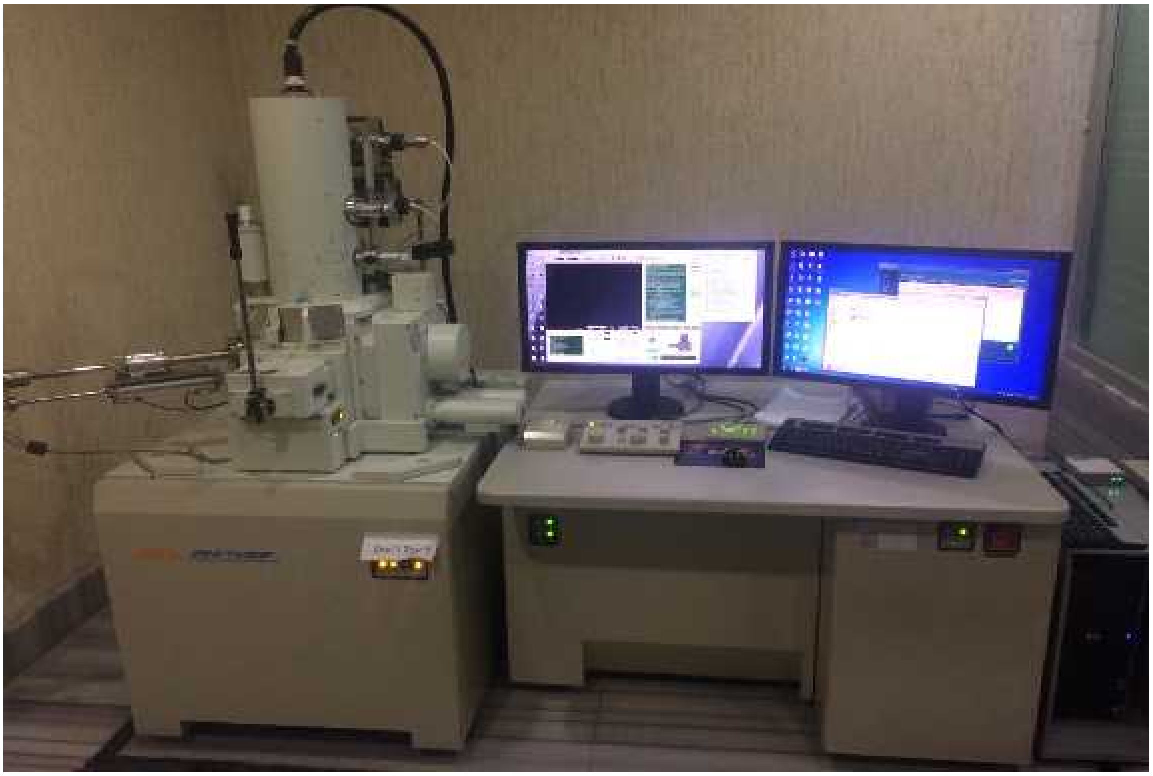


Fig 3.3: JEOL JSM-7600F Scanning Electron Microscope (SEM)

3.4.3 Chemical Analysis

The chemical analysis of all the films were studied using a JEOL JSM-7600F Scanning Electron Microscope (SEM). EDX is a type of the chemical analysis that chemical elements of any material can be studied under any certain area that has been selected by the machine. The entire sample was mounted on the aluminum stub using graphite filled tape which was vacuum coated with Platinum.

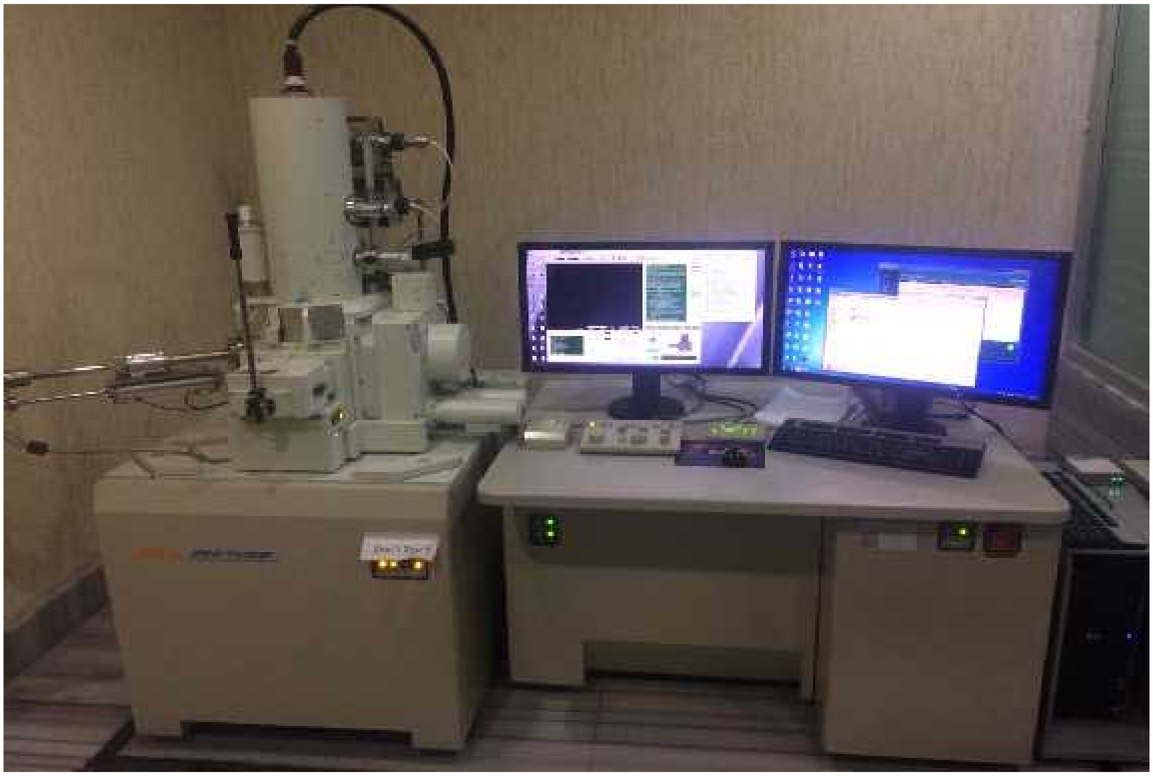


Fig 3.3: JEOL JSM-7600F Scanning Electron Microscope (SEM)

3.4.4 X-ray Diffraction (XRD) Analysis

X-ray diffraction was performed by a two circle (2θ-θ) X-ray powder diffractometer, X'Pert XRD PRO PW 3040 with high temperature attachment up to 1600°C, which is installed in Glass and Ceramics Department, BUET.

XRD is an effective method to evaluate the interlayer changes of starch base and crystalline properties of nanoparticle. The degree of crystallinity has a significant impact on the mechanical properties of CuO reinforced starch bio-plastic since starch is a semi-crystalline polymer**.**

Fig 3.4: PW 3040 X'Pert XRD PRO

3.4.4 DSC-TG Analysis

Thermal behaviors of the pure and CuO nanoparticles reinforced bio-plastics were investigated to ensure their thermal stability and the percentage weight loss with temperature by DSC and TGA respectively. The DSC & TGA were performed simultaneously by using DSC-Thermo gravimetric analyzer (Q50 STA/TG-DSC) MME department, BUET with microbalance type–parallel guide differential top pan with an empty pan used as the reference. Scanning was done in a controlled temperature over a temperature range 0^0C to 800^0C with a heating rate of 10^0C/min. TGA was performed in nitrogen medium and the heating rate of 10ºC/min is used from room temperature to 650^{O}C. The sample was placed on the platinum pan such that the surface area of the sample was maximized so as to get reasonable accuracy and repeatability.

Fig 3.5: QT 50 (STA/TG-DSC)

3.4.5 Mechanical testing

The prepared samples were cut in 3 cm length and 0.5 cm in width for the mechanical test and the test was performed at room temperature. The properties we checked is mainly the tensile strength. We have also checked the elongation or displacement yield. The tests were performed by using the Universal Testing Machine (TESTRESOUCES: Serial ID: 1608004-01A, Part No. 11000100-01) in Chemistry department, BUET. Standard test method for tensile properties of thin plastic sheeting (specification D882-02) was followed. Also in standard procedure, pneumatic grip were used to grip the sample to prevent slipping during testing, which was not followed.

Fig 3.6: TESTRESOUCES

3.4.6 UV-Vis Spectroscopy- Theoretical Principle and Experiment

When the molecules absorb energy in the form of light they excite from their ground state to a higher energy level and while they return to ground state the energy emitted can be recorded as spectra. UV-Vis spectrometer works on the principle of Beer-Lambert Law, it states that concentration of the solute is directly proportional to the absorbance of the solution. Almost all the chemical compounds absorb either visible light or UV light. When a beam with power I_0 is incident on the sample solution absorption takes place and the transmitted beam has a power of I. Then the amount of radiation absorbed can be measured by % transmittance (%T). That is,

$\%T = 100 * (I/I_0)$

The Beer-Lambert law defines absorbance as, $A = -\log$

$(I/I_0) = ECD$ Where, E= molar Absorptivity

C= concentration of the

solute M

D= path length cm

From the above equation $A = -\log(T) = ECD$

For the thin film samples equation modifies as,

$A = -\log(I/I_0) = ECD$ (where T is the thickness)

Fig 3.7: UV-VIS Spectrometer

Fig 3.8: Sample holder in UV-VIS

Therefore absorbance is more useful compared to transmittance as it has a direct linear relationship with the concentration of the solute.

UV-VIS spectroscopy was performed by HALO DB-20S UV-VIS double beam spectrometer in the Physics department of BUET.

CHAPTER 4

RESULTS
&
DISCUSSIONS

4. Results & Discussions

In this chapter the results of the study are presented and discussed with reference to the aim of the study, which was to determine the influence of using CuO nanoparticles in the starch based bio plastics that were made out of potato starch. The graphical representations of the tests FTIR, XRD, SEM, EDX, DSC, TGA, Tensile Strength and UV-Vis spectroscopy are given in the respective order. The aim of the results and discussion to explain the phenomenon that were witness during the tests. Also the interpretations of those tests are given to correlate the results and the practical use of the final product that this tests are trying to establish.

4.1 Fourier Transform Infrared spectra (FT-IR):

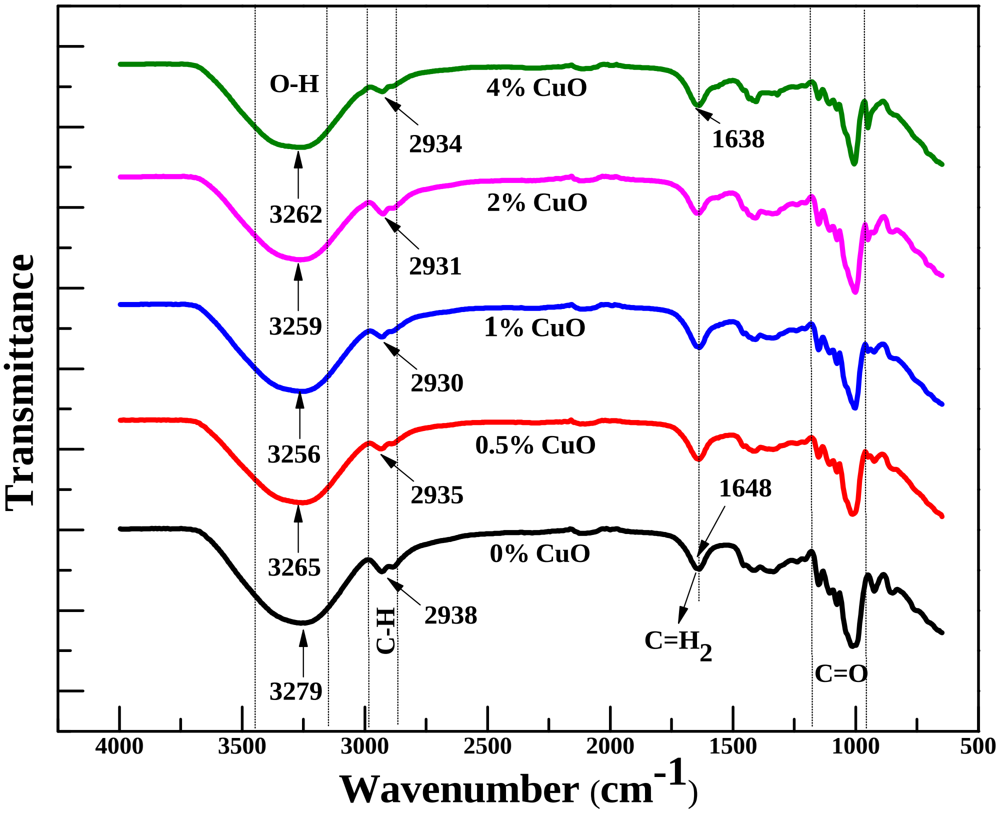


Fig 4.1: FTIR of Starch based CuO nanoparticle reinforced bio-plastics

The FTIR gives intermolecular interaction among the different molecules presents in a material.

The FTIR spectra of pure starch and starch based CuO nanoparticle reinforced bio-plastic are shown in Fig 4.1.

In the spectrum for starch bio-plastic without nanoparticles, the broadband at 3690 to 2990 cm^{-1} was the OH stretching, with the highest peak at 3279 cm^{-1}. The peak at 2938 cm^{-1} corresponded to the C–H stretching. A small peak near 1648 cm^{-1} was due to the $C=H_2$ stretching. The bands from 951 to 1183 cm^{-1} corresponded to the C–O (carbonyl) bond stretching.

In the FTIR spectrum of CuO nanoparticle reinforced bio-plastic, the absorption peaks at 3265 cm^{-1} for 0.5% CuO and 3256, 3259, and 3262 cm^{-1} for 1%, 2% and 4% respectively. It can be seen that the spectrums are moving toward lower wavenumber that means a reduction in hydrogen bonding in the OH group. The probable reason was the electrostatic interactions (O···Cu) between –OH groups of starch and Cu2+ atoms.

Moreover, the peaks the –CH zone has also shifted from 2938 to the right to 2935, 2930, 2931 and 2934 for 1%, 2% and 4% respectively. Also the intensity of the peaks and area under the pick are gradually decreasing with the increment of CuO nanoparticles.

Similar thing happened to the peaks and the area under the peaks of the carbonyl (C=O) group. For the 0% CuO the downward peak has a longer peak tip with more area under the peak. Whereas, in the 0.5%, 1%, 2% and 4% CuO nanoparticle reinforced bio-plastics are showing less sharper peaks with less area under the peaks for the respective order.

These phenomena has affected the mechanical properties of the CuO nanoparticle reinforced samples. The tensile strengths for 0.5% and 1% CuO nanoparticle are higher than the 0% CuO or pure starch sample. The tensile strengths for 2 % and 4% CuO nanoparticle are lower than the 0% CuO or pure starch sample possibly because of the ridges and grooves caused by the roughness of the surface due to higher amount of CuO agglomeration.

4.2 X-ray Diffraction (XRD) Analysis:

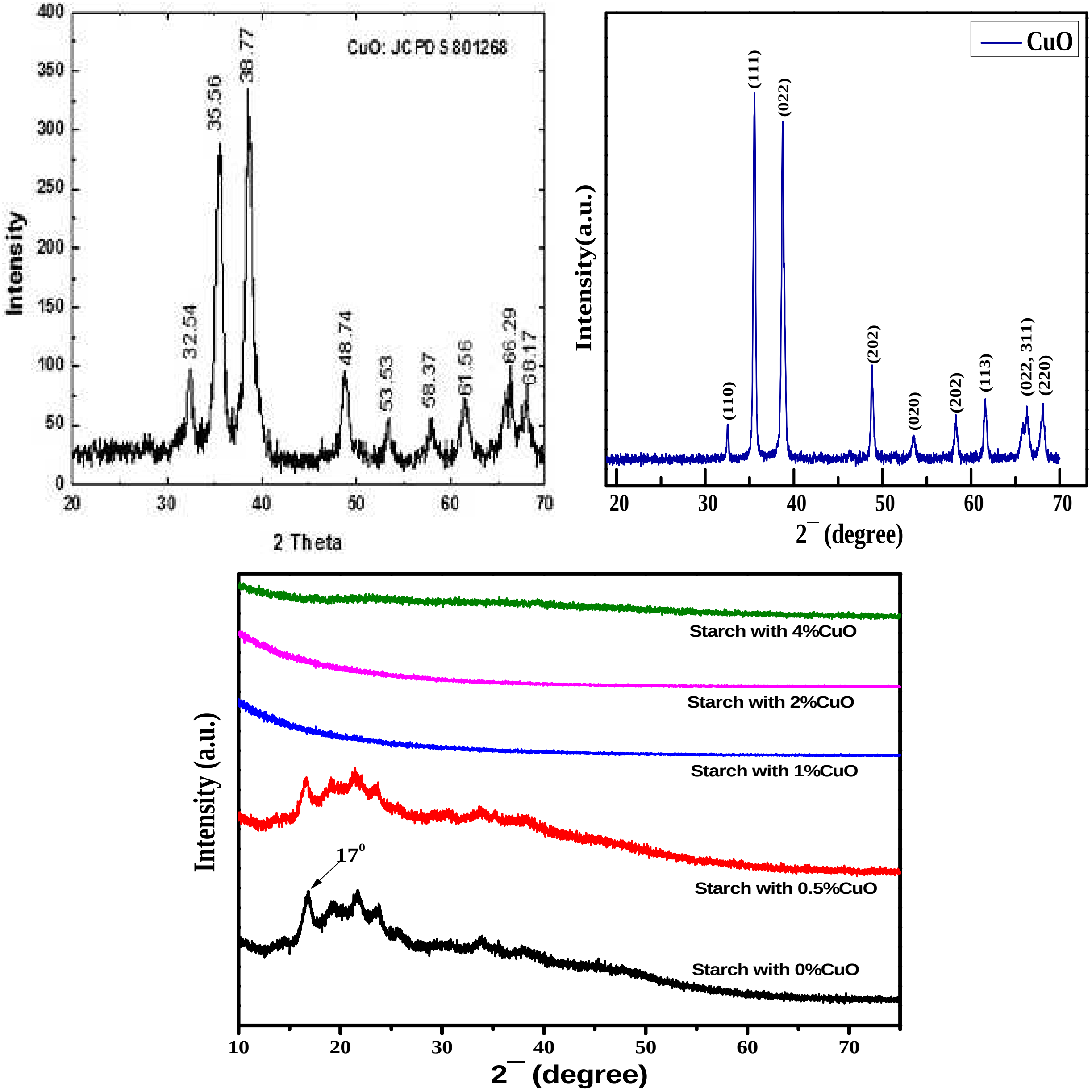


Fig 4.2: XRD patterns of CuO nanoparticles and starch based CuO nanoparticle reinforced bio-plastics

The XRD diagrams of the CuO nanoparticles resemble the JCPD standard of the CuO nanoparticles. From the XRD diagrams of CuO nanoparticles it is obvious that pure CuO was formed with no extra phase, no impurity, and with standard crystalline size of CuO NPs. CuO nanoparticles size was calculated using Derby-Scherrer formula $S = (0.9 * \lambda)/(\beta\ Cos\theta)$ where, S = crystallite size (nm) λ = 0.154 nm, β = FWHM & θ = angle (radians) and the average particle size is 26 nm.

Using the XRD analysis the compatibility of the component in the bio polymer can be characterized. When the crystalline and non-crystalline ingredients of the sample exhibit good miscibility, the crystallinity becomes lower than that of the single crystalline ingredient.

Fig 4.2 shows that the pure potato starch is semi-crystalline structure, whereas, CuO got crystalline structure. As the percentage of the CuO was increased the semi-crystalline structure of the base materials lost its crystallinity and became amorphous.

The characteristic diffraction peak of the potato starch without any nanoparticles is clearly visible at around 17^0, which could be attributed to the crystalline and amorphous fractions of the potato starch. Comparison of the patterns of the CuO reinforced starch indicated that the diffraction peaks weaken with the increase of CuO nanoparticles. The intermolecular interaction of the potato starch and CuO nanoparticles led to the dispersion of the CuO nanoparticles into the potato starch matrix. The miscibility of the CuO nanoparticles breakdown the crystalline domains of the potato starch matrix that decreases the crystallinity of the original matrix.

In 0.5% CuO sample shows that the peaks of the pure starch based bio plastics has decreased significantly. But in the cases of 1%, 2% & 4% CuO the samples have given amorphous structures.

The findings of Dr. Zhang el at. & Dr. Chen el at. confirm this phenomenon in their reports. Where in the first case Zhang el at. concluded that the crystallinity of potato starch loses its crystallinity when mixed with nanoparticles. Whereas, Chen el at. concluded that as the amount of nanoparticles increases in the base materials the crystallinity is replaced with amorphous structure.

4.3 Surface Morphology:

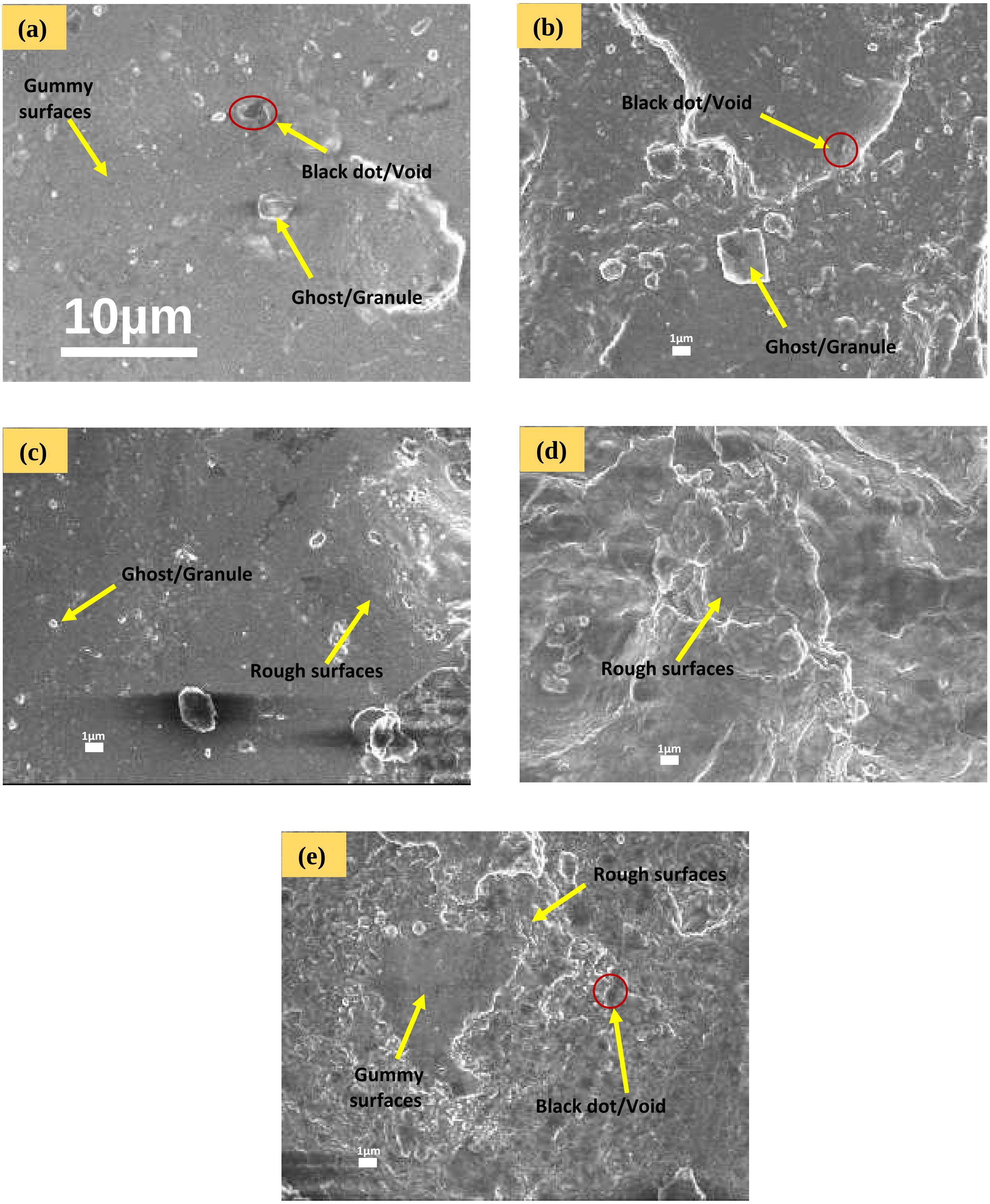


Fig 4.3: (a) Pure Starch (0% CuO) (b) 0.5% CuO reinforced starch bio plastics (c) 1% CuO reinforced starch bio plastics (d) 2% CuO reinforced starch bio plastics (e) 4% CuO reinforced starch bio plastics

The SEM of the surface structure of the starch based bio plastic and CuO reinforced starch based bio plastics was done using the Field Emission Scanning Electronic Microscope (FESEM: JEOL JSM 7600F).

From Fig 4.3 (a), the starch based bio plastic shows that the surface feature consist of granules (the remaining part of the starch particles). These are the remnant granules of starch that were not gelatinized. This outcome is similar to the reports of Hern’andez et al. It has been described that SEM images depicted contained insoluble remnants (i.e. ghosts) from starch granules swelling. Some void were also visible (black dots visualized) those contributed to the low tensile strengths.

From the later images of the reinforced starch bio plastics the smooth gummy surface are being replaced by the irregular structures, ridges and grooves [Fig 4.3 {(b), (c), (d), (c)}]. As the content of starch is increasing the roughness of the surface is also increasing. Although few granules are visible in the 0.5% CuO contained reinforced bio plastic there are almost now visible granules on the 2% CuO reinforced bio plastics and the 4% CuO reinforced bio plastics shows clustering of the CuO. This agglomeration could be the reason why the tensile strength of the higher CuO contained bio plastics are losing the strength. The finding is supported by similar finding by Selene Harunsyah et al. and concluded that the surface morphology of starch, reinforced nanoparticles, and glycerin plasticizer didn’t give homogenous surface structure with roughness along with ridges and grooves on the surface. This roughness all through the reinforced samples also ensure that the homogenous dispersion of the nanoparticles. The homogenous dispersion is a necessity for a good barrier properties and the samples have shown very good barrier properties. Therefore, the SEM ensured the barrier properties of the reinforced starch bio plastics.

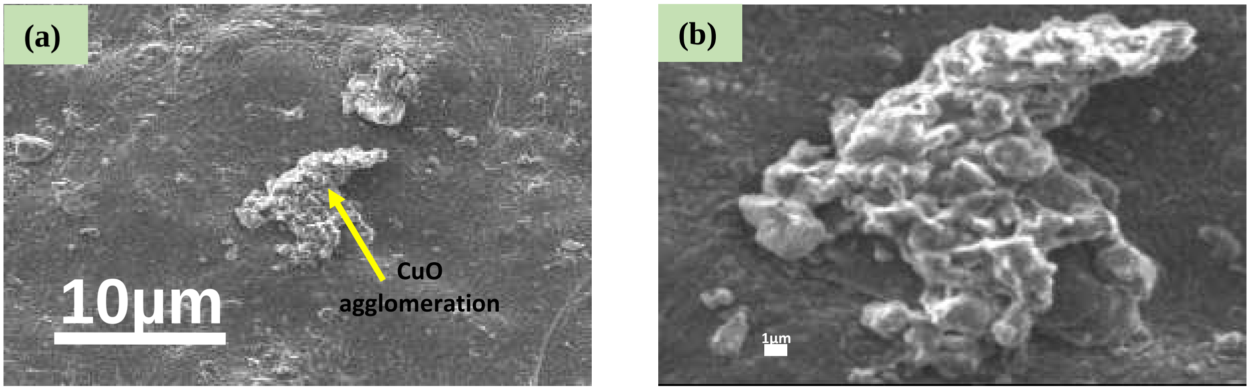


Fig 4.4: (a) is low magnification image of CuO agglomeration and (b) is the high magnification of CuO agglomeration

Both in the low and higher magnification of the 4% CuO NP reinforced sample showed the agglomeration of CuO NP, which are depicted in the Fig 4.4 (a) & (b) respectively.

4.4 Chemical analysis of CuO nanoparticle reinforced Starch

The chemical investigation frequently used to describe the chemical elements that are present in the materials that are been tested. The chemical analysis is done by finding out the percentage of the element that are present under the particular area. EDX analysis of the CuO nanoparticle reinforced starch based bio-plastics were studied. EDX analysis shows that the pure starch based bio-plastic got higher carbon, oxygen and amylose and amylopectine related elements in the sample. Whereas, in the 0.5%, 1%, 2% and 4% CuO nanoparticle including samples got increasing amount of Cu as a percentage under the area of study. Moreover, the amount of sulfur in those samples in an increasing order. This is due to the DMSO that we used in the sample to dissolve CuO nanoparticles.

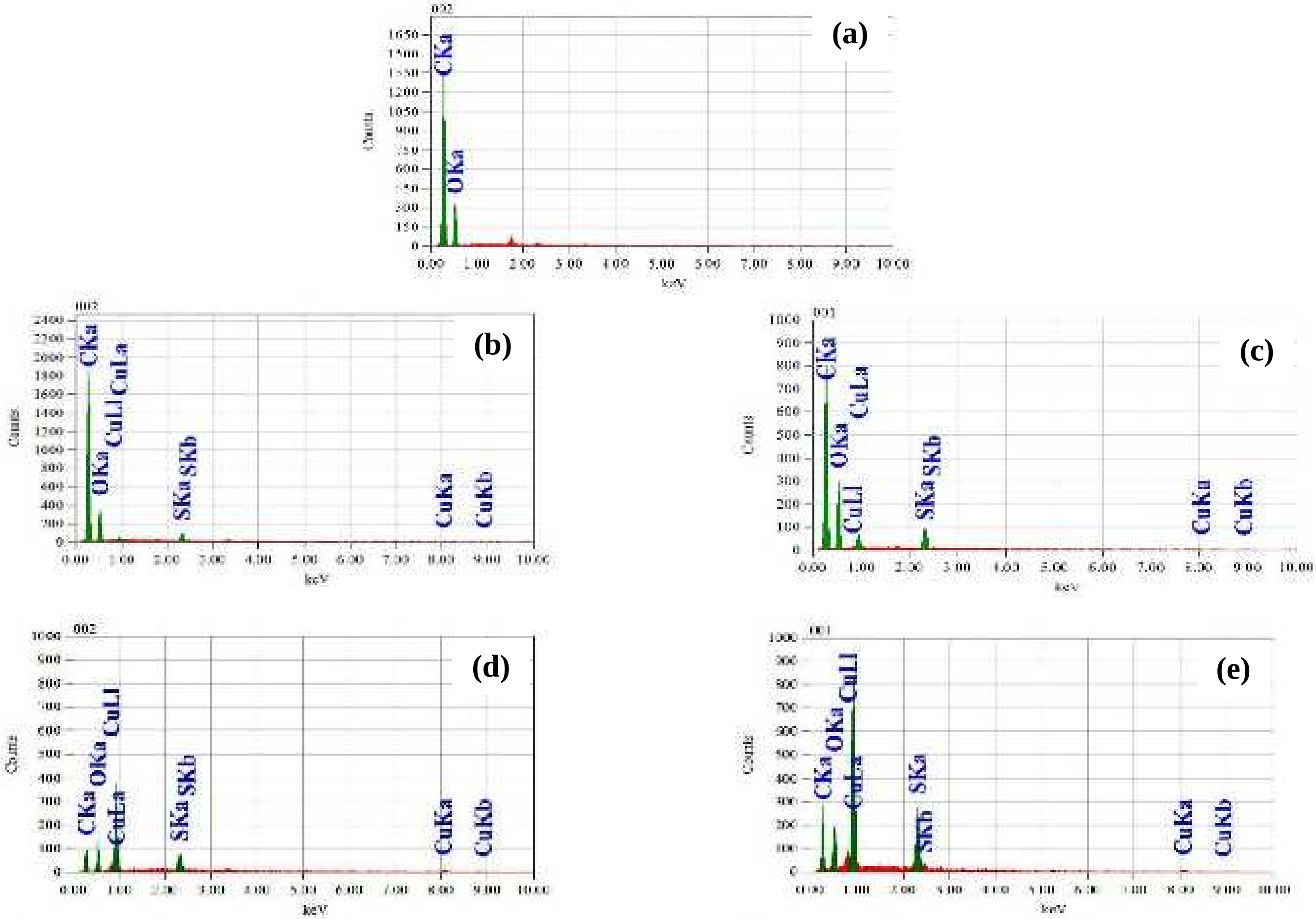


Fig 4.5: EDX of pure and CuO nanoparticle reinforced starch based bio-plastics

4.5 Thermal analysis of CuO nanoparticle reinforced Starch

The term thermal investigation frequently used to describe the analytical techniques, investigated the behaviors of a sample as a function of temperature. DSC and TG Analysis of the films were studied. DSC analysis shows the physico-chemical changes of the films with temperature and TG analysis represents the percent weight loss of the films with temperature. DSC/TG analysis gives an idea about their thermal stability, and it is an important factor of the starch for their application purpose.

4.5.1 Differential Scanning Calimetry (DSC)

The higher the barrier/permeable properties of polymers and the more desirable the polymer is for packaging, medical, cosmetics or food products. The higher the Glass Transition Temperature the higher the barrier properties of a polymer.

The Differential Scanning Calorimetry (DSC) is done by measuring how much heat is flowing into the sample or getting out of the sample when set against in a series of temperature. Heatflow into the sample is called endothermic and Heatflow out of the sample is called exothermic. Starch shows endothermic heat flow.

Two temperature that is important in the DSC analysis is the glass transition temperature (T_g) and melting temperature (T_m). Glass Transition Temperature (T_g) is the temperature where the polymers goes to rubbery state from glassy state when heated. And the Melting Temperature (T_m) is the temperature where the melting of the polymer takes place.

The higher the Glass Transition Temperature (T_g) is the higher the plasticity of the polymer. Glass transition temperature (T_g) is an important factor for the mechanical behaviors of polymers or thermo-plasts. The Melting Temperature affects the barrier/permeable properties of the polymer. The desired quality of the polymers is to have a higher glass transition temperature and a higher melting temperature to be an effective option. The desired effect that was aim in this research work is to make bio-polymer that can be used for food packing purpose.

Starch is composed of Amylose and Amylopectin and both of these compounds in dry state have higher glass temperature 227 ^{0}C. And the crystallization temperature of the starch is

216 ^{0}C. Glycerol was used as plasticizer for the experiment and the glass transition temperature of starch varies with the amount of glycerol. For 30% glycerol of the non-reinforced starch sample the glass transition temperature can be as less as 20 ^{0}C.

The plasticizer that was used is glycerol but water can also work as plasticizer.

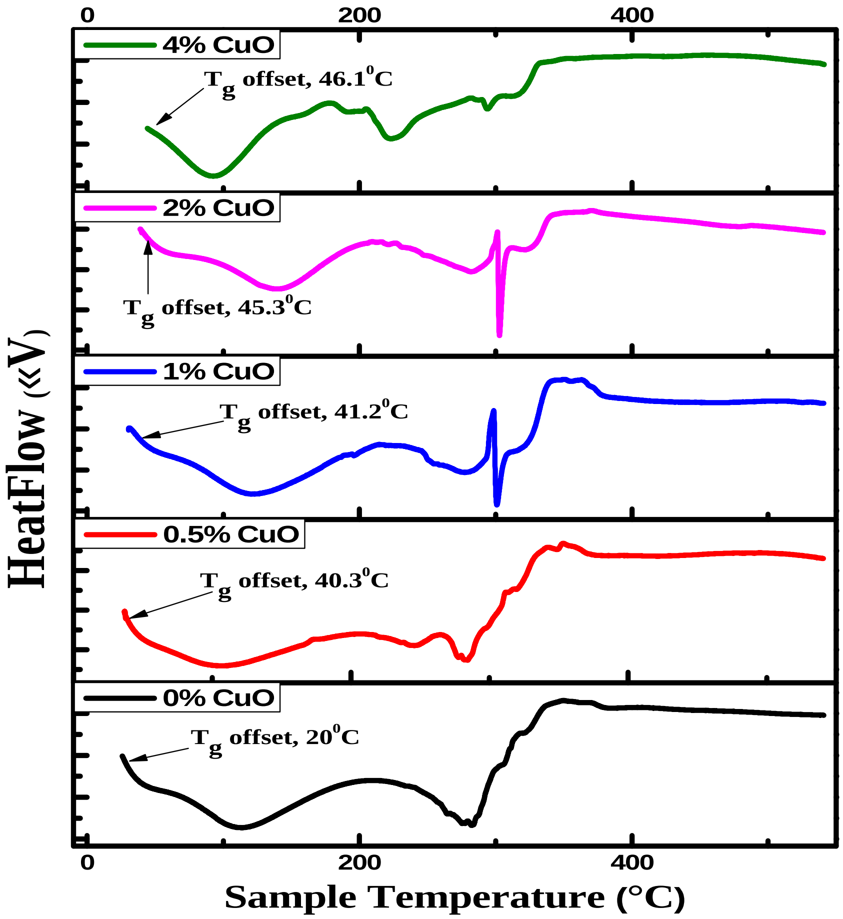


Figure 4.6: Comparison of DSC of pure starch & CuO nanoparticle reinforced bio-plastics

1. The Glass Transition Temperature (T_g) is for the Starch Based Bio-Polymer without CuO nanoparticle reinforced is approximately 20 ^{0}C and Melting Temperature is 277 ^{0}C. The Glass Transition Temperature (T_g) is for the Starch Based Bio-Polymer with CuO nanoparticle with 0.5%, 1%, 2%, and 4% are 40.3 ^{0}C, 41.2 ^{0}C, 45.3 ^{0}C, and 46.1 ^{0}C. The melting temperature of such samples in similar order are 285 ^{0}C, 302 ^{0}C, 309 ^{0}C, and 302 ^{0}C respectively.

2. The glass transition temperature of Starch Based Bio-plastic with nanoparticle is increased substantial amount as the CuO nanoparticle is reinforced.

3. On a similar note, the melting temperate of starch has also been influenced by the CuO nanoparticle reinforcement.

This increase in T_g and T_m indicates the bonding between the OH, CH, CO functional group and CuO that was observed during the FTIR analysis of the samples.

Higher glass transition temperature means improved mechanical properties.

4.5.2 Thermogravimetric Analysis (TGA)

For the experiment Dynamic Thermo-Gravimetric Analysis (TGA) was used where the weight loss of the samples are measured with respect to increasing temperature. Starch bio-plastic has a 4-step process mechanism of decompositions. In the first step, the moisture of starch bio-plastic is evaporated at 20–240 ^{0}C. In this stage, the very light volatile matter compounds (Water and vinegar or 10% Acetic Acid) are lost, and the vaporization process occurs due to evaporation of the water. The mass loss takes place due to decomposition of the organic matters in the range between 260 ^{0}C to 321 ^{0}C. In the stage 3 the second mass loss phase takes place in the temperature range 420 to 510 ^{0}C due to the carbonization of organic matters. The final stage (stage 4) takes place in the 500 to 600 ^{0}C range due to the complete carbonization of the organic matters.

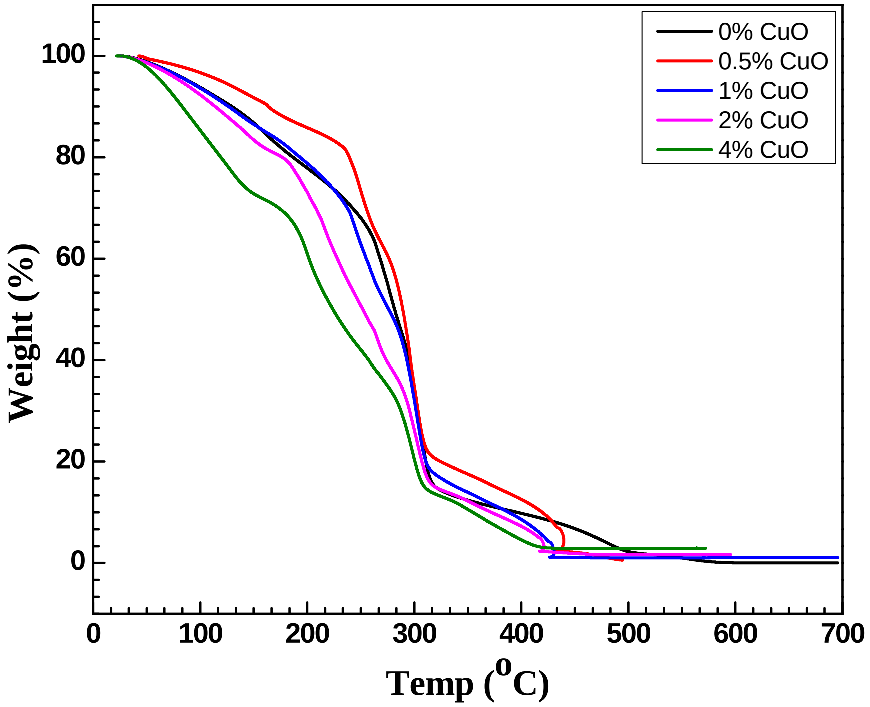


Fig 4.7: TGA plot for different percentage of CuO nanoparticles reinforced starch with

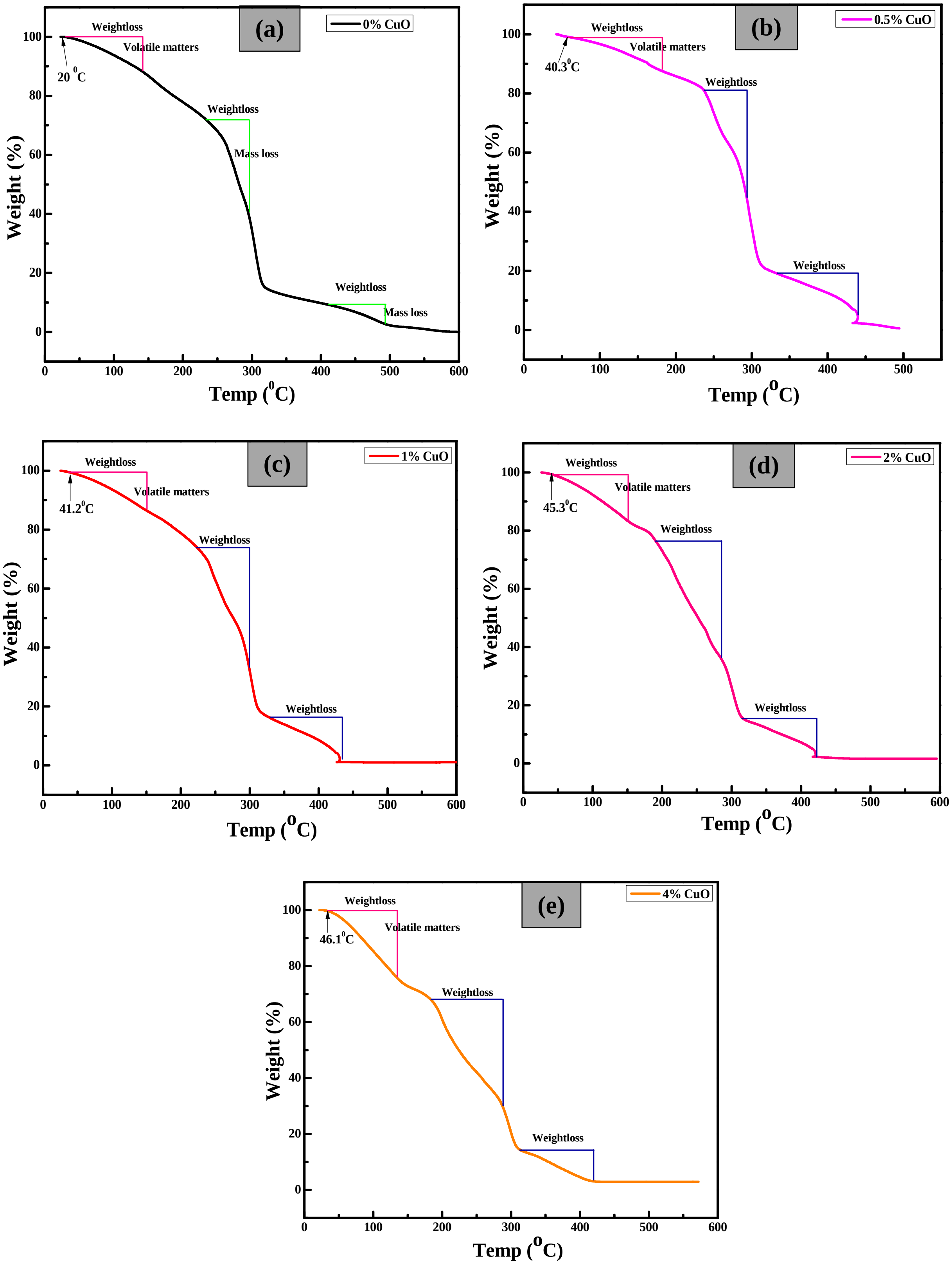


Fig 4.8: Different stage of TGA plot for (a) 0% CuO (b) 0.5% CuO (c) 1% CuO (d) 2% CuO (e) 4% CuO with Temp

- For the 0.5%, CuO nanoparticles reinforced bio-plastics the TGA shows similar 4 step thermal decomposition processes as well, where the moisture of starch bio-plastic is evaporated at 40.3–190 ^{0}C and the thermal decomposition stage takes place between 242-295 ^{0}C.
- For the 1%, CuO nanoparticles reinforced bio-plastics the moisture of starch bio-plastic is evaporated at 41.2–238 ^{0}C and the thermal decomposition stage takes place between 230-305 ^{0}C.
- For the 2%, CuO nanoparticles reinforced bio-plastics the moisture of starch bio-plastic is evaporated at 45.3–152 ^{0}C and the thermal decomposition stage takes place between 190-295 ^{0}C.
- For the 4%, CuO nanoparticles reinforced bio-plastics the moisture of starch bio-plastic is evaporated at 46.1–153 ^{0}C and the thermal decomposition stage takes place between 182-294 ^{0}C.

It is evident that the moisture evaporating temperature has changed substantially as the percentage of CuO increases in the sample. Also the percentage of the volatile matters has increased from a 16% in the pure starch sample to a 24% in the 4% CuO nanoparticles reinforced sample. As the evaporation temperature is going up that mean the starch samples are getting more stabilized with respect to temperature as the percentage of CuO is getting higher. This is due to the boding the CuO is having with the OH, CH, CH_2 & CO group. Also the weight loss is getting less stepper due to the presence of the DMSO which means a high range of weight temperatures in the nanoparticle reinforced starch samples. In addition to that, DMSO caused the decomposition to start at a lower temperature than the sample with 0% CuO nanoparticle reinforced Starch or pure starch.

The decomposition temperature range of the organic matters is getting higher. This is also due to the CuO and OH, CH, CH_2 & CO group bonding. As the starch is made up of Amylose (straight chain bonding) and Amylopectin (Cross chain bonding), having the straight chain and cross chain boing make the thermal decomposition temperature to go up. Due to the bonding between the CuO and OH, CH, CH_2 & CO group and other molecules the thermal decomposition temperatures of the nanoparticle reinforced starches have decreased from the non-reinforced starch.

4.5 Tensile properties:

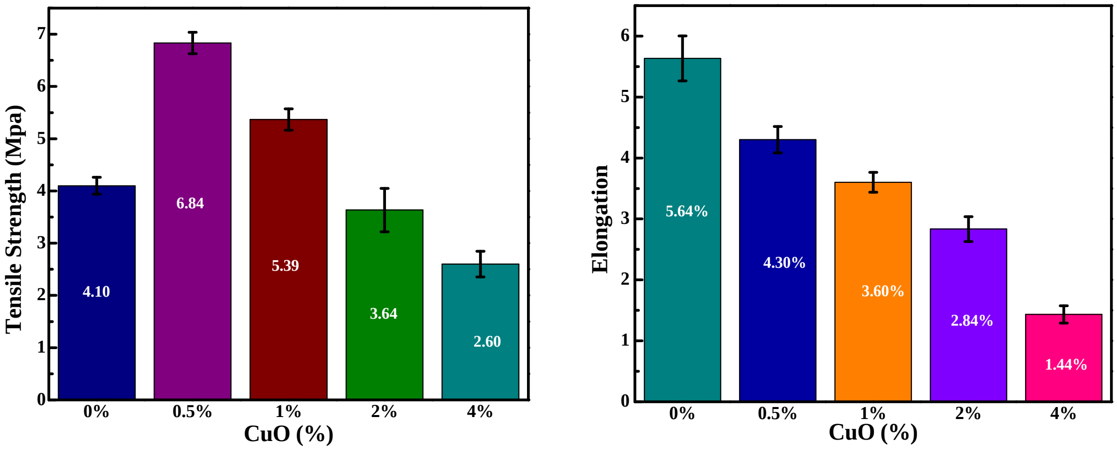


Fig 4.9: (a) Tensile strengths and (b) Elongation at break of CuO nanoparticles reinforced starch based bio-plastics

Tensile strength express the load that any material can take before it breaks down or tear of after application of stress on it. From the references we have found that the tensile strength of potato starch that are used in food packing is approximately 4 MPa.

From the graph of CuO percentage with respect to the Starch base vs. tensile strength the tensile strength of 0.5% CuO nanoparticle is approximately 6.84 MPa whereas, the tensile strength of the starch sample without nanoparticle reinforcement that is 4.1 MPa. The tensile strength of 1% CuO nanoparticle reinforcement (5.67 MPa) though decreased from the 0.5% CuO nanoparticle reinforcement is still above the tensile strength benchmark of 0% CuO starch sample. And the tensile strength of 2% & 4% CuO nanoparticle reinforcement have tensile strength of 3.64 MPa and 2.60 MPa falls below the benchmark. The decrease in the tensile strength of the samples with 2% & 4% CuO has been attributed to the agglomeration of CuO on the sites of CuO and functional group (OH, CH, CO) interaction in the starch. This agglomeration decreases the attraction of the cohesive forces between the functional groups and CuO and also the attraction forces among the different elements of the functional groups. As the amylopectin has cross liking structure and the amylose has straight structure of hydroxyl group and carbon compounds, the CuO interactions with the functional group have strengthen the initial strength to a proportional amount. But as the CuO agglomeration starts taking place after the addition of incremental CuO the tensile strength drops off.

Elongation is elasticity that a material shows before breaking down or tearing off. From the data it is obvious that the elongation of the CuO nanoparticle reinforced starch are supported by the tensile strength data. That is from 0.5% CuO up to 4% CuO nanoparticles the elongation is negatively correlated that elongation is decreasing as the nanoparticles content increases in the base matrix. The elongation of 0.5% and 1% is higher than the base starch bio-plastics. Whereas, for 2% and 4% CuO nanoparticles reinforced bio-plastics elongations went below the pure starch bio-plastic.

4.6 Optical Properties:

UV-Vis Spectroscopy- Experiment

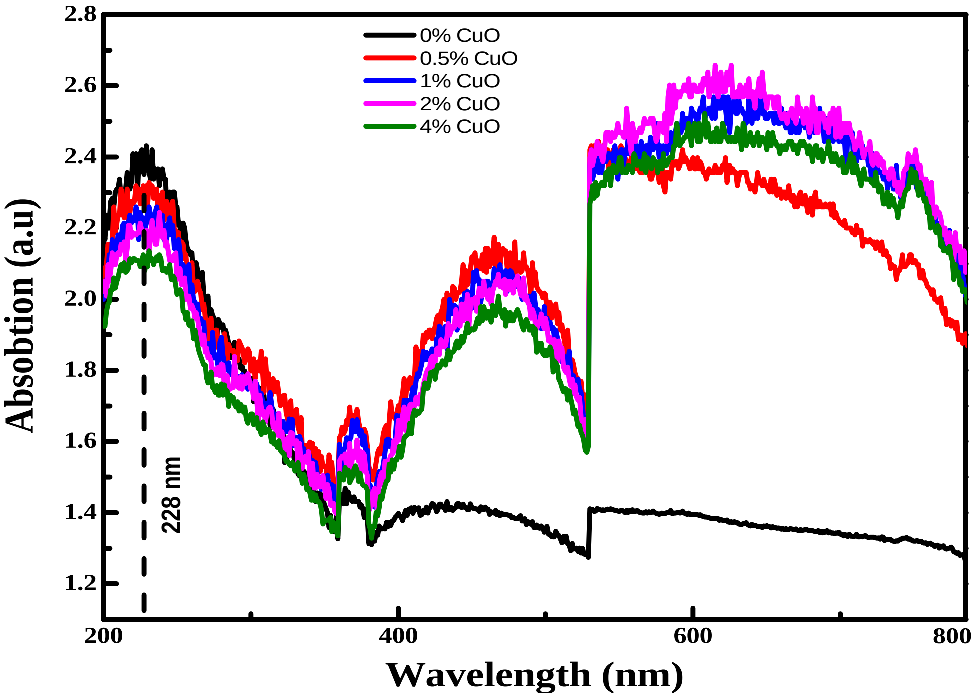
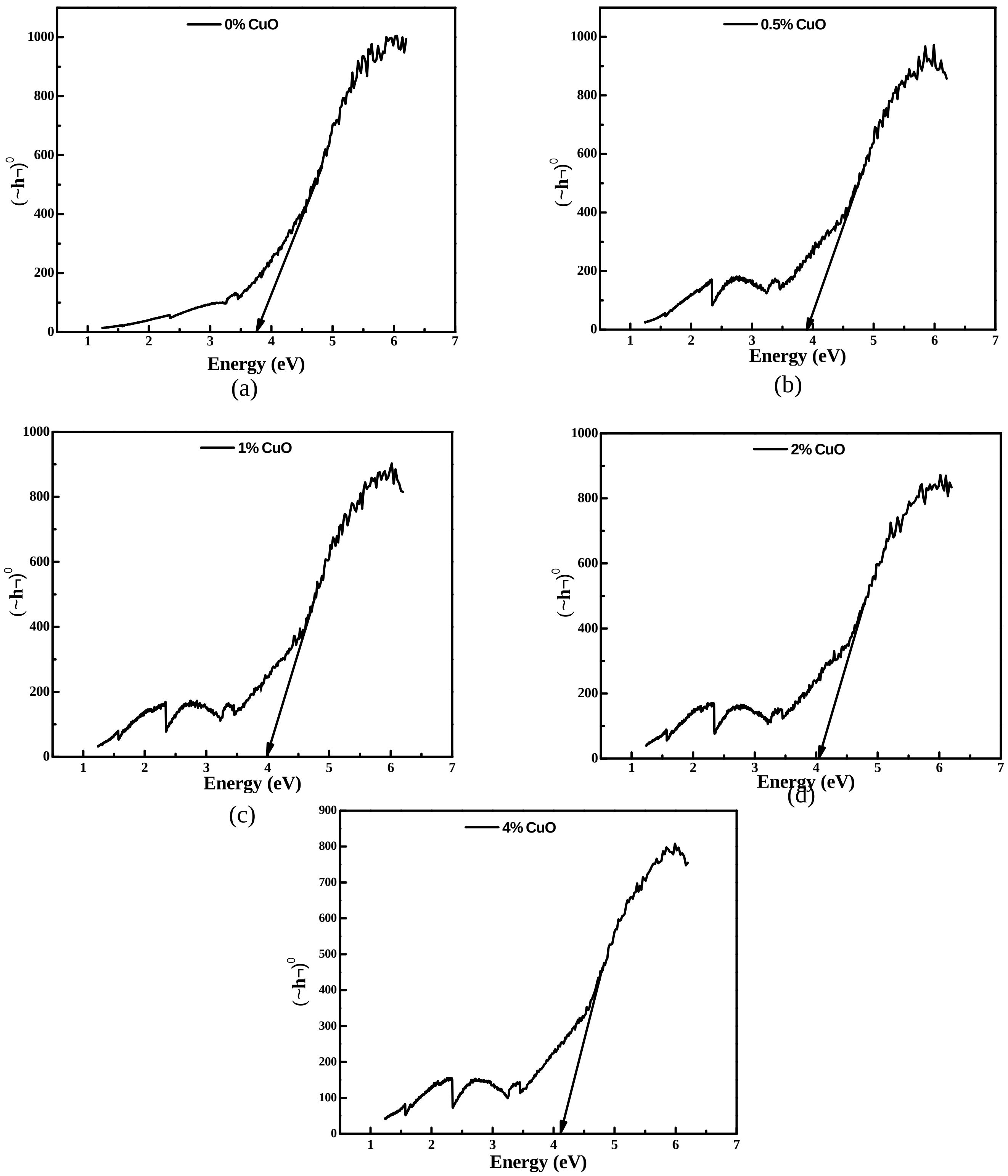


Fig 4.10: Absorption plot of pure and CuO nanoparticle reinforced starch based bio-plastic

The starch sample with no CuO nanoparticle reinforced sample show minimal absorbance when put in to the UV-VIS spectroscopy in the visible range that is 400-800 nm as it absorbs all the spectrum in the visible region but it shows an increase absorbance in the ultraviolet reason and has the highest absorbance in the 228 nm (approx.). This is due to the electron transfer from highest occupied molecular orbital or HOMO to the lowest unoccupied molecular orbital or LUMO. That mean for the pi electron transfer from non-reinforced starch needs higher energy.

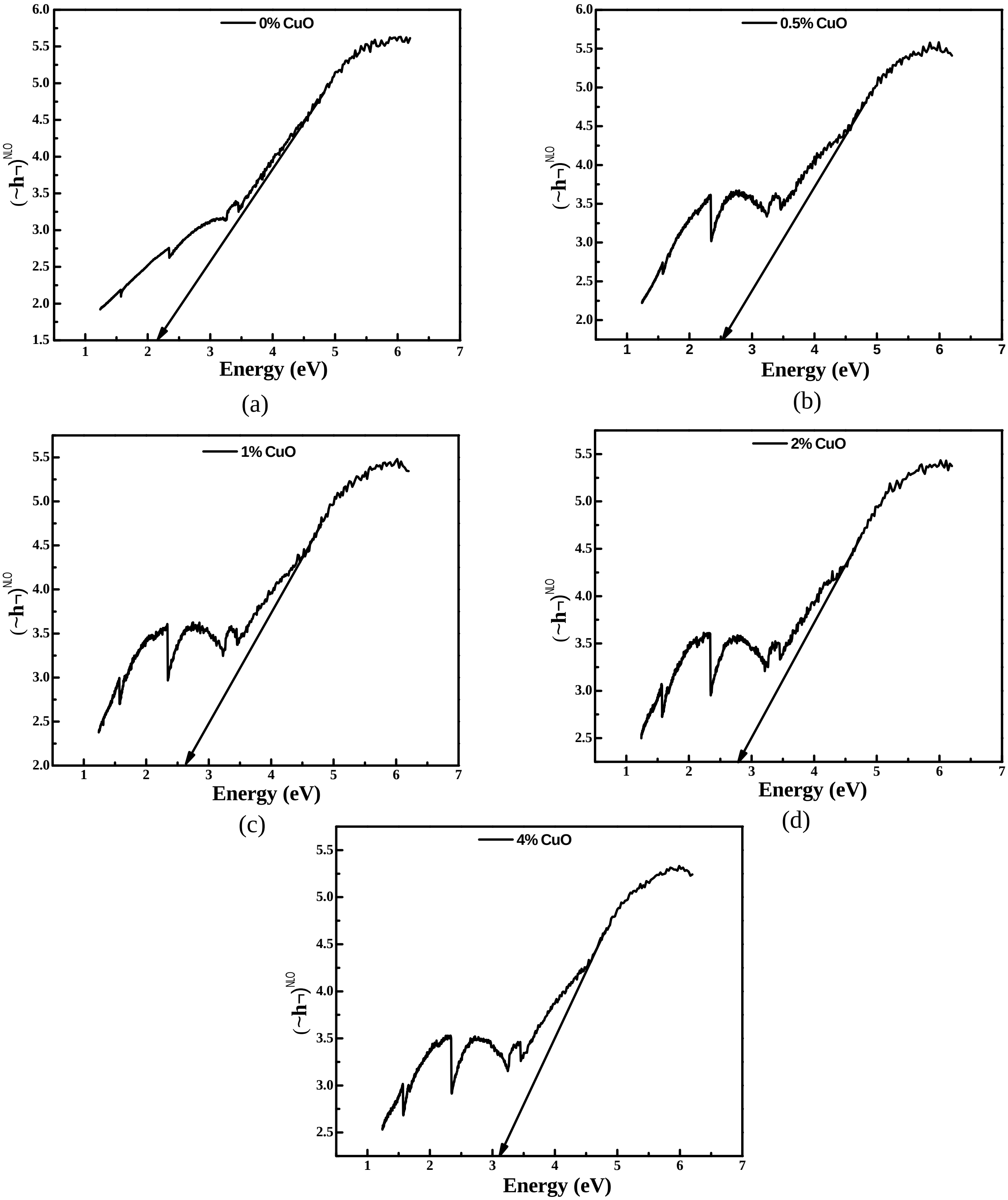
From the graph it is clear that the absorbance of Nanoparticle reinforced starch biopolymers are much higher compare to the non-reinforced starch biopolymer and this is due to the higher amount of free pi electrons that the reinforced starch samples are having because of the CuO nanoparticles. Although the non-reinforced starch is showing slightly higher absorbance in the 200-250nm region but this is due to the colorlessness of the non-reinforced starch.

There is a sharp drop in the absorbance of the samples on 528 nm (approx.) but the reason is not clearly identified. As there is a drop on the same wavelength in the non-reinforced starch as well as in the CuO nanoparticle reinforced starch it might be due to the plasticizer or Acetic Acid and it has sharpen in reinforced bio-plastics due to the additional DMSO.



(a) (b) (c) (d) (e)

Fig 4.11: Direct band gap of non-reinforced starch and reinforced starch samples are given in respective incremental order from (a) 0% CuO (b) 0.5% CuO (c) 1% CuO (d) 2% CuO (e) 4% CuO



(a)

(b)

(c)

(d)

(e)

Fig 4.12: Indirect band gap of non-reinforced starch and reinforced starch samples are given in respective incremental order from (a) 0% CuO (b) 0.5% CuO (c) 1% CuO (d) 2% CuO (e) 4% CuO

The Direct and Indirect band gaps of given in the charts below:

Table 4.1: Direct band gap of pure and CuO nanoparticle reinforced starch based bio-plastics

CuO	Direct Band Gap
0%	3.75
0.50%	3.9
1%	3.98
2%	4.05
4%	4.12

Table 4.2: Indirect band gap of pure and CuO nanoparticle reinforced starch based bio-plastics

CuO	Indirect Band Gap
0%	2.16
0.50%	2.52
1%	2.62
2%	2.78
4%	3.1

The absorbance curve for the nanoparticle reinforced samples in the UV region is showing two pics in the one small in 390 nm and another more prominent in the 228 nm due to the dipole moment oscillation of electrons. The appearance of the absorbance curve in the UV region was due to the presence of CuO nano-cluster which give rise to the dipole moment oscillation. It is clear from the UV curve that as the concentration of CuO is increased the absorbance curve becomes more stable. And as the wavelength is increasing the absorbance drops exponentially. The decrease in the absorbance indicate the increase in the band gap in the materials.

It is also evident that the CuO absorbs throughout the visible region which is in good agreement with its optical band gap. Also from the direct band gap we have seen that blue shift has taken place. This is a clear sign of concentration effect of CuO nanoparticles. Moreover, the indirect band gap is also increasing with the concentration of CuO nanoparticles. This also supports the direct band gap increase in the CuO reinforced starches.

The minimum energy gap is the difference in energy between the conduction band-edge and the valence band edge. As the direct band gaps are going up (blue shift) that means the samples could be used in semiconductor devices such as photo amplifiers and modulators for optical fiber communication system etc. Further investigation is required in this sector.

Chapter 5

CONCLUSION

5. Conclusions

It is a challenge to develop bio-degradable environment friendly materials specially a polymer based on the natural resources and replaces the conventionally used polymers. Therefore, the primary goal of this work was to synthesize a starch based bio-plastic and to characterize the bio-plastic to check the viability of such bio-plastic. Glycerol, 10% Acetic acid (Vinegar), CuO and DMSO were used to enhance the properties of the biodegradable starch based bio-plastic.

- FTIR analysis describes the structural analysis of the film. It gives an idea about the presence of functional groups or the molecular interaction changes with addition of CuO with the starch blend. The peaks of absorption corresponding to the hydroxyl (OH), Alkyne (CH) and carbonyl (CO) group shifting and changing the area under the peaks indicates the existence of strong H-bonding interaction between the starch and CuO molecules.

- Pure starch is a semi-crystalline materials under the XRD with the characterized peak on 17^0. With the increment of CuO nanoparticles the base matrix started losing its crystallinity and becomes amorphous. The intermolecular interaction of the potato starch and CuO nanoparticles led to the dispersion of the CuO nanoparticles into the potato starch matrix. The miscibility of the CuO nanoparticles breakdown the crystalline domains of the potato starch matrix that decreases the crystallinity of the original matrix.

- SEM micrographs illustrate that the pure starch bio-plastic resembles what potato starch bio-plastic surface should be when made in the way that were made in the research. The CuO was thoroughly blend in the starch matrix. This phenomenon was visible in the subsequent CuO increment starch based bio-plastics. As the percentage of CuO was increased the smooth gammy surface of pure starch was replaced by rough surfaces with ridges and grooves. Due to the increase in the CuO nanoparticles the black spots increased that caused the tensile strength of the higher CuO content samples.

- EDX analysis confirms the presence and increment of the Cu in the samples of this experiment. Moreover, as the amount of CuO is has increased with respect to the based matrix the amount of oxygen in the elemental analysis has shown a increment in the oxygen content in the CuO nanoparticle reinforced samples.

- Thermal analysis describes the stability and degradation of the bio-plastics with temperature. DSC analysis shows the thermal stability by showing the increasing in glass transition temperature of the starch based bio-plastics up with approximately fixed melting temperature.

- TGA analysis implies the percent loss in weight of the film as a function of temperature. The DT-TG analysis with higher range of weight loss temperature shows that the incorporation of CuO molecules in starch indicated better thermal stability as the decomposition and carbonization temperature ranges have increased significantly as compared to the pure starch based bio-plastic.

- From the mechanical analysis point of view, the reference bio-degradable plastic has a required tensile strength of approximately 4 MPa for food packaging purpose. The pure starch sample exhibited a 4.1 MPa. Whereas, 0.5% & 1% CuO reinforcement showed 6.84 MPa and 5.39 MPa respectively. Which have shown considerable amount of increase in mechanical strength. For the 2% and 4% CuO nanoparticle reinforcement the tensile strength have dropped below the 4 MPa threshold. After the optimal bonding of the CuO and the functional groups (O-H, C-H, C=O) the extra amount of CuO made agglomeration on the based matrix. Due to this, the mechanical strength of the bio-plastics have dropped below the standard value (3.95 MPa) for food packaging purpose.

- The optical properties of biodegradable starch based bio-plastics have potential to be used as semi-conductor. The base matrix starch is insular, whereas, the Cu is conductive in nature. When the samples were measured with the band gap energies it became clear that the direct band gaps is in the blue shift, that means the direct band gaps are increasing means an decrease in conductivity. This decrease change in the conductivity confirms that bonding among CuO and the functional groups of amylose and amylopectin have taken place. There is a good amount of chance that the final CuO reinforced products can also be used as semiconductors in cases of photo amplifiers and modulators for optical fiber communication system etc.

Thus, considering the reported data and easiness of preparation of bio-plastics, their fabrication should further be encouraged. These bio-plastics can, hence be truly considered as the environmental friendly polymer and be adopted by packaging industries.

Chapter 6

FUTURE RECOMMENDATION

6. Future Recommendations

With an ever-increasing world population, the question is not whether the global environment will be impacted by the presence mankind but how and to what degree. The implementation of sustainable practices will help minimize the detrimental effects on the environment and conserve resources for future generations. Due to the non-gradable behavior and carcinogenic effects in the food industries the starch based biodegradable bio-plastics have huge prospect. On the similar note, bio-degradable bio-plastics can help to save the natural resources and can also have a huge impact on the economy as a whole.

Starch is poised to establish an even stronger role in the manufacture of sustainable plastics and bio-products largely because it is abundant, renewable, and inexpensive. For food packing the primary requirements are barrier properties that is to have a slightly higher glass transition temperature and to keep the food safe from the environment. From the experiment it is evident that the amount of CuO has a best performance for smaller amount nanoparticles. The optimal amount can be figured out by future investigation. The prospects for starch in the food packaging sector continue to become brighter as the market for sustainable plastics drives further innovation and development.

Another promising aspect that this experiment has brought up is the optical properties. The increase in direct band gaps of the samples is a good indication of the samples to be candidates for the use of semiconductors. It is recommended that more investigation be carried out on this particular properties of CuO reinforced starch based bio-plastics to have a definite outcome.

Chapter 7

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