Synthesis and characterization of Starch based bio-composite films and their degradation behavior--an alternative to the conventional polymer

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CERTIFICATE

This is to endorse that **Mr. Ranajit Mondal** has carried out the project work on **“Synthesis and characterization of Starch based bio-composite films and their degradation behavior--an alternative to the conventional polymer”** in the specific time. It is hereby approve that the effort given by him is a creditable study in the pasture of chemical engineering and is carried out with all the information and precisions for the completion of the Master’s in Technology in Chemical Engineering under my supervision and guidance.

Date:

Dr. Susmita Mishra
(Supervisor)

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ABSTRACT

Plastics are being used all over the world starting from drinking cups and disposable silverware to parts for automobiles and motorcycles. But in spite of its varied usages, its disposal has threatened the environment. Thus this work outlines the synthesis of a biodegradable plastic that can meet the demand and can be disposed to the environment. Synthesis of biodegradable plastics was done using starch compiled with sucrose, glycerol and PVA. Various composites of these ingredients were combined and synthesized to test the feasibility of the prepared polymer. The tensile strength, bio- degradation rate, TGA, DTA, FTIR analysis and capacity of water absorption of the films were carried out to analyze the film properties. Biodegradation study was conducted by burying the prepared polymer under the soil and the micro-organism responsible for its degradation was identified.

Key words: Starch, bio-degradation, tensile strength, polymer, disposal, micro-organism.

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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

DTA- Differential thermal analysis

TGA- Thermo gravimetric analysis

FTIR- Fourier transforms infrared spectroscopy

SEM- Scanning electron microscope

TS- Tensile strength

EB- Elongation at break

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. We were passed through the stone-age, bronze-age, iron-age and the steel age in accordance with the fact stated above. Considering that at present, the total volume of plastic production has exceeded than that of steel, the last part of the 20th century has been called the PLASTIC AGE.

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 packaging of materials all over the world. However, they have been an environmental anxiety because of the very slow rate of degradation.

They compose about 20% by volume devastate per year. Industrial development, urbanization, wrong agricultural practices, etc. are responsible for pollution and loss of environmental quality. The usage of plastics in 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 plastics synthesized using renewable resources which facilitate the straightforwardly decomposition in the atmosphere by means of microbes. Starch-based bio-plastics can manufacture from either modified starch or raw starch (e.g. TPS) otherwise the fermentation of sugar which is starch-derived (e.g. PLA). Typical starch source 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. 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 plastics. The bacteria 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.

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 produce 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 make from bio ethanol.

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. They contain hydrocarbons that form the building blocks of plastic, commonly known as monomers. 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. So, this dictates the difference that we find 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, our objective would be to prepare a biodegradable plastic from renewable sources such as starch that would be environment-friendly. Optimization of preparation condition would help us to study the feasibility and potential of this starch with other additives to obtain a biodegradable as well as high tensile strength plastic.

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. In India, plastics consumption grew exponentially in 1990s.In India, the consumption of plastics has increased many fold from 4000 tones per annum (1990) to 5 million tones per annum (2005) and is expected to rise further. The per capita plastic consumption is 4.0 kg/annum [1]. 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 affect the environment but also the individuals. 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. It is a fact that plastics will not at all degrade and remains on landscape for numerous years. The recycled plastics are too much harmful to the environment than the virgin one due to mixing of colour, additives, flame retardants, stabilizers etc. 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. 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).

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

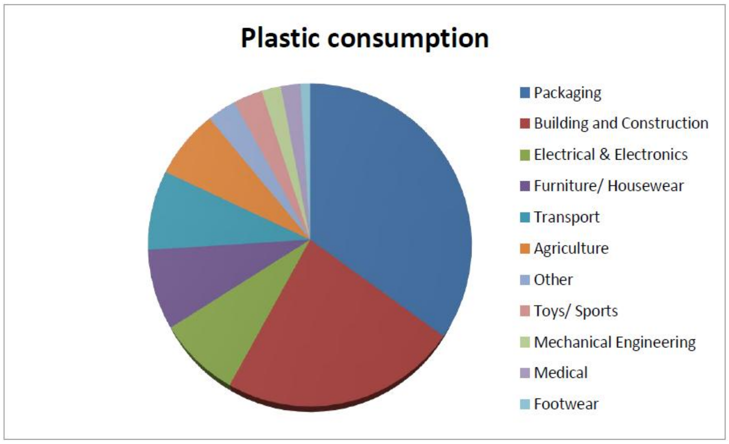


Figure 2. 1 Sector wise distribution of plastic consumption [1].

2.2 Environmental Effect of Polymers

Since 1950s, one billion tones 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. Various awareness programs should have been staged to educate the growing ignorant population to reduce the usage and proper disposal of plastics. 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 continually lost when polyethene bags enter into the soil; they chunk further passage of mineral salts and oxygen to the soil. When blocked, the soil is incapable to yield crops appropriately this can cause huge problems to farmers and consumers. Polythene bags comprise an acidic combination that with time affect the chemical formulas of soils.

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 gets more costly next to the day as we are using this non-renewable source more and more. Petroleum is essential to our contemporary way of living. Petroleum is essential for our power necessities – for factories, lighting, transport etc. Exclusive of feasible alternative resource of energy up till now on the perspective, if the availability of petroleum were to be stopped, which lead to practically the whole world grind to a halt. And to produce plastic, about 100 million barrels of oil are required each year all over the world.

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. Waste materials serve as a procreation place for various disease carriers. Female Anopheles mosquito spreads malaria. There are also exceptional germs like the cholera germ that has led to the death of millions of inhabitants in the world.

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. 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.

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. Plastic bags, once ingested cannot be digested or conceded by an animal, so it stays in the gut. Plastic in animal's gut avert food digestion and can lead to a very slow and painful death.

Figure 2. 3 Sewage plastic waste

2.3 The Prospective of Biodegradable Plastics

For better sustainability, eco-efficiency, and green chemistry has obsessed a search for renewable and environment friendly resources. Among the natural polymers, starch takes prior attention. Starch is a biodegradable polysaccharide, produced in plenty at low expenditure and exhibits thermoplastic in nature. Thus, it has become most promise alternative material to replace conventional plastics in individual market segments. As well known, synthetic polymeric material has great used in every field of human activity during last several years. These artificial macromolecular substances are usually generated from petroleum and most of are regarded as non-degradable. However, the resources of petroleum are limited, and the flourishing use of non-biodegradable polymers has caused serious environmental tribulations. In addition, the non-biodegradable polymers are not appropriate for impermanent exercise. Thus, the polymer materials that are degradable or biodegradable have great interest since 1970s. Both the synthetic and natural polymers that include hydrolytically or enzymatically liable bonds or groups are easily decomposed. The advantages of synthetic polymers are distinct, and can tailor quickly. In spite of this, they are somewhat expensive. This reminds us to focus for an alternative natural polymer, which is naturally biodegradable and can capable to meet different necessities.

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. Efforts have been made to make starch-based polymers for conserving the petroleum resources, sinking environmental impact and probing more applications.

2.4 Starch

Most of organic substance lying on earth is in attendance as the structure of polysaccharides. A significant polysaccharide is starch. Plants amalgamate and store starch in their formation as an energy preserve. 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. 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. A good number crops producing starch are very fruitful. 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. Whereas a corn seed comprises starch about 60-75 weight %, with an average capitulate of 5 ton per hectare.

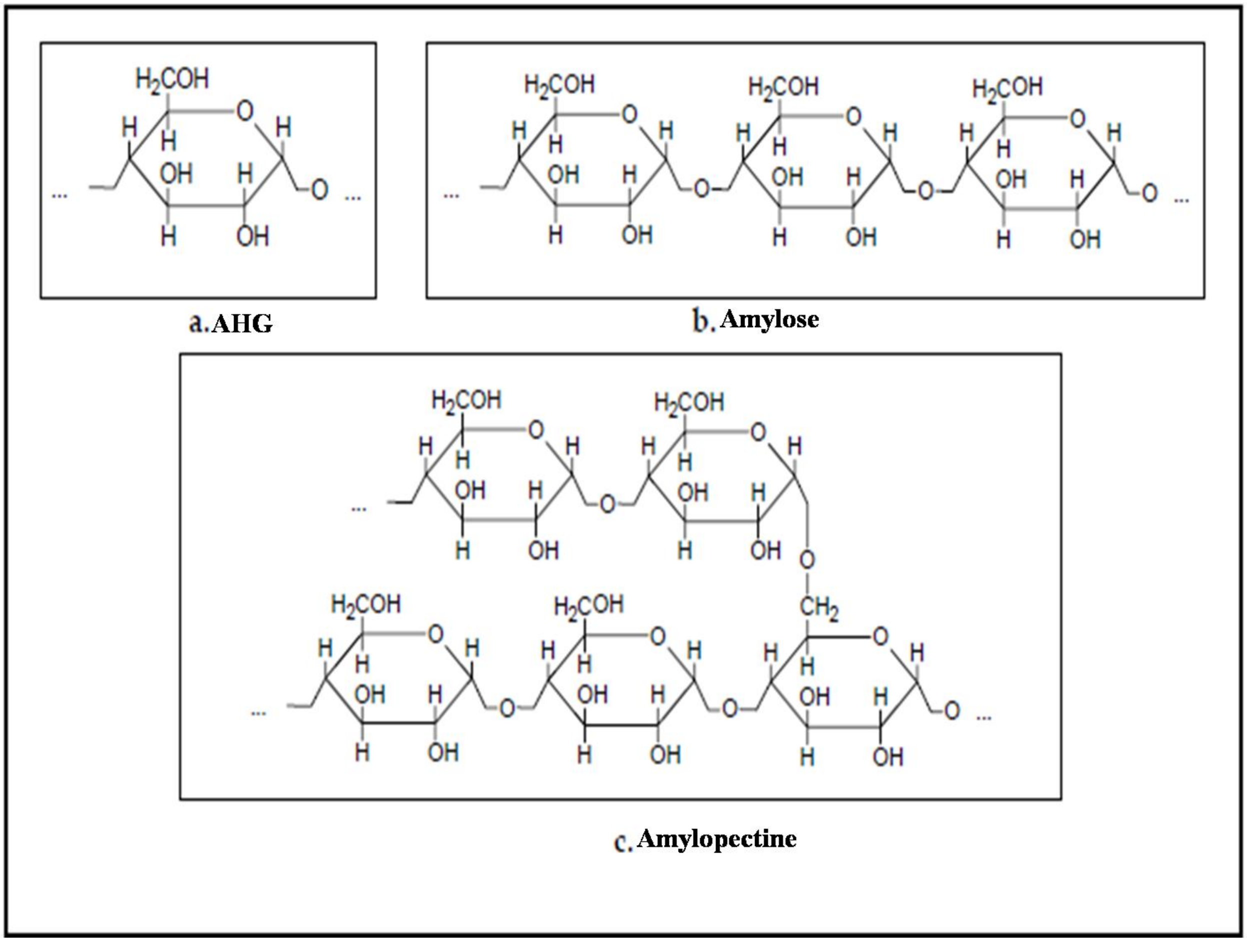
2.4.1 Arrangement and properties of starch

Starch is a polymer comprising with anhydroglucose (AHG) units (Figure 2.4 a.). Two types of AHG polymers are generally there in starch: amylose and amylopectin. Amylose is basically a linear polymer in which AHG units are principally connected all the way through α-D-(1,4)-glucosidic bonds. The molecular weight of amylose is a gathering of the plant resource and processing technique. 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. The presence of amylose and amylopectine in starch varies and mostly depends on the starch resource. 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 [4].

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. Heating a starch solution leads to thrashing of hydrogen bonding in the core of the starch grain and the starch will initiate to gelatinize. The starch grain will swell up speedily to numerous times its actual volume. The linear amylose molecules percolate the granules into the solution.



a.AHG

b.Amylose

c.Amylopectine

Figure 2. 4 Chemical Structure of Starch [4]

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.

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. The first invention of marketable plastics was derived from cellulose nitrate and is well-known as celluloid [2-3]. A. Parker in 1838 primarily prepared cellulose nitrate and J. Hyatt foremost patented celluloid in 1870 [3]. Despite the fact that celluloid is derived from usual polymer (cellulose), the oldest merely synthetic plastic is Bakelite, discovered by Baekeland in 1907 [2]. 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 [3]. 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. Plastics have lesser melting temperatures compared to glass and metals, and, therefore, require smaller amount energy to form into useful products [3].

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 able to decompose of when prearranged a proper atmosphere and adequate amount of time. Biodegradable plastics have gained great curiosity since the 1980s. Nowadays new types of biodegradable plastics with enhanced properties and lesser costs have been developed [3]. 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 [3].

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 [4]. 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 [4]. 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. 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.

2.5 Plastic in Solid Waste and it’s Disposal

Locke and Vinson have reported their concern to plastics in the solid waste through their analysis. It further reported the prospective of recycle plastics as a polymer blend of different types [5]. Property degradation was bring into being 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. Ottinger et. al devised a method to dispose of waste plastic without affecting the environment by passing it to the reactor [6]. It was then heated in the presence of gas to a decomposition temperature of plastic and recovering products from there. Hossain et. al intended an experimental program to find out the discrepancy of permeability with degradation [7]. 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.

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 [8]. 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.

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. 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 [9]. The use of yearly renewable resources, like wheat, be required to be understood in a absolute carbon cycle. This thought is based on the enlargement and the manufacture of products based on renewable and biodegradable resources: starch, cellulose. By collecting and composting biodegradable plastic wastes, we can make much-needed carbon-rich droppings: humic materials. 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.

2.7 Bio-degradability and Compostability

Bio-degradable stands for the ‘proficient of undergoing decay into methane, water, carbon dioxide, inorganic material, and biomass.’ 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. 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 [10]. It can be seen that the contrast of the outcome obtained from a variety of standards seems to be complex or unfeasible. We have to consider the quantity of mineralization also the character of the residues left behind the biodegradation [11]. The accretion [12] of contaminants with poisonous wastes might slow down plant growth. The main concern is to decide the environmental toxicity intensity for these by-products, named as ecotoxicity [13]. 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 [14].

An effort was made by Vijaya and Reddy 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 [15]. 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. Their study indicated that the biodegradation of polyethene films occur in the natural environment at a extremely slower rate.

2.8 Bio-degradable Polymers

Bio-degradable polymers stand for an emergent field [16–18]. Huge amount of bio-degradable polymers (e.g. chitin, cellulose, polylactide, starch, and other polypeptides) encompass to synthesize or to produce in normal atmosphere all through the augmentation cycle of organisms. Some microbes and enzymes able of degrading such polymers were recognized [16, 19]. Ddiverse 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. 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).

VanSoest and Knooren made stress-strain measurements in relative with starch crystallinity [20]. Starch in grainy form was made which was plasticized with diverse amounts of glycerol and water. The vague rubbery materials were pliable and feeble with high elongations. All through aging, the materials became less stretchy with privileged elastic modulus and tensile stress.

Mantia and Dintcheva 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 [21]. The macromolecules rupture 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.

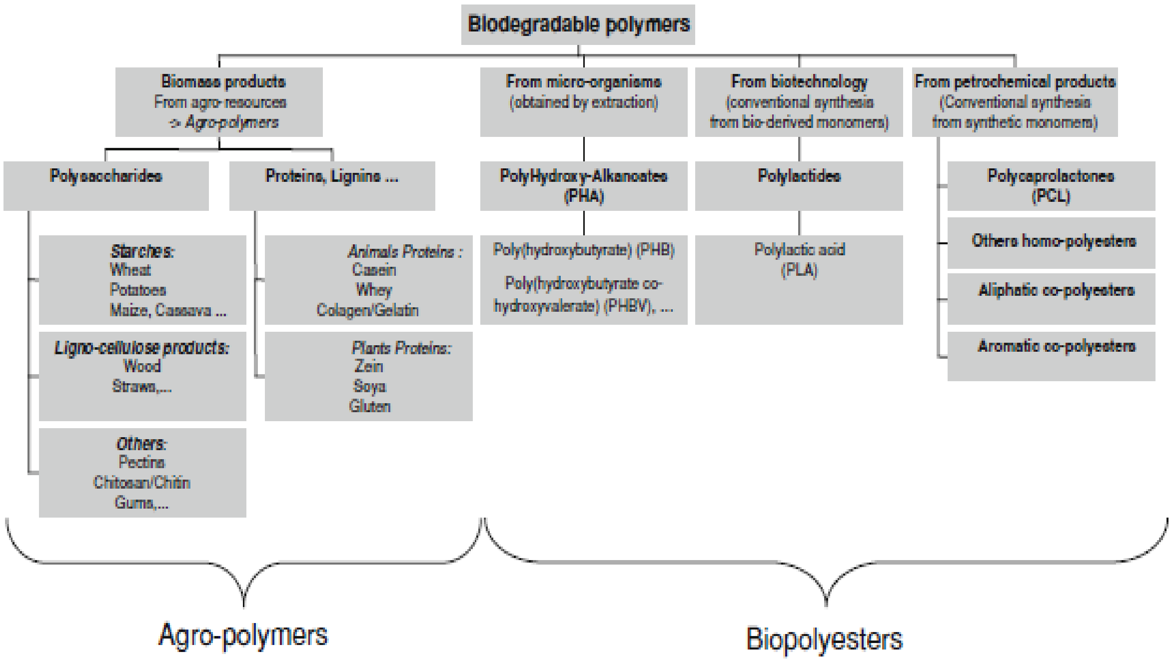


Figure 2. 5 sorting of the main bio-degradable polymers [39].

Kolybaba et. al gave an insight into how a material is created and the technique in which it is tainted [22]. A common declaration as regards the breaking down of polymer materials [23] is that it may possibly occur by microbial accomplishment, photo-degradation or chemical degradation. 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. Characteristically soil bacteria and water are first and foremost required for microbial reduced plastics [24]. Polymers that are based on naturally developed materials (such as starch) are vulnerable to degradation by microbes [23]. The material may or may not decompose quickly under aerobic conditions, depending on the formulation used, and the microorganisms present. Reuse of plastic materials is expectant and well-highlighted, but attempts at growing this 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 [25]. 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 Mulder [26] 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.

A study performed by Chaffee & Yaros compared three unlike compositions of grocery bags. The typical polyethylene grocery bags when was compared to grocery baggage prepared from compostable plastic resins [27], 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. Their conclusions suggest that biodegradable plastics are neither a clean alternative to petroleum-based traditional plastics nor grocery bags made from recycled paper.

Mohanty reported that Starch based plastics were primarily harvested from wheat, potatoes, rice, and corn [28]. 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. 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.

Takahashi suggested that Polylactic acid (PLA) is one of the major promising bio-based plastics manufactured commencing lactic acid, which is obtained from fermentation [29] 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, it could be a good suggestion to compost PLA used 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.

Joshi and Patel suggested that biodegradable polymer degrades within the body as a consequence of natural biological processes, eliminating the need to remove a drug delivery system [30] 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. 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. Biodegradable polymers mainly investigated for drug deliverance applications are of either natural or synthetic foundation.

CHAPTER 3

MATERIALS & METHODS

3. MATERIALS AND METHODS

3.1 Chemicals

All Chemical reagents used in the experiment were of analytical grade. *Starch* (P^H 6-7, sulfated ash: maximum 0.5%, lead: 0.001 %) obtained from Loba Chemie Pvt. Ltd. Mumbai, India. *Glycerol* (MW: 92.10, density: 1.25-1.26 gm/cc,) obtained from Fisher Scientific, *Polyvinyl Alcohol* (viscosity: 25-32 cP, VM: max. 5%, Ash: 0.7%, P^H: 5-7) was obtained from Loba Chemie Pvt. Ltd. Mumbai, India, *Magnesium Stearate* (precipitated fine powder, MW:591.27, heavy metals:0.002%, zinc stearate:0.5%, chloride:0.02%, sulphate:0.3%, acid number of precipitated fatty acid:195-210) and *Sucrose* (Sulphated Ash 0.01%, heavy metals 0.0012%, reducing sugar 0.5%) were obtained from Himedia Laboratories Pvt. Ltd. Mumbai, India. Prepare 0.1mol/dm^3 *Hydrochloric acid* and the distilled water used to make starch blend film after deionization.

3.2 Preparation of Films

Starch, Sucrose, Glycerol/PVA or both were properly dry mixed in a beaker; some amount of Mgst and HA were added and mixed properly. Enough water was added to the mixture and stirring at room temperature for 10-15 minutes at a moderate speed. The beaker along with its content was maintained at165^{0}Con the heater with continuous stirring for 15-20 minutes. The gelatin-like solution was formed and spread in a mold to make a film. The film prepared was kept in a hot air oven maintained at 60^{0}C for 24 hours to obtain a dry film. The film was further vacuum dried to remove all the moisture content on the film surface.

3.3 Characterization methods

3.3.1 Mechanical testing

The prepared samples were conditioned for at least a week at room temperature and 50% relative humidity (RH), before performing the mechanical testing. Tensile strength, displacement yield, Young's modulus of the films was investigated by using the Universal Testing Machine (INSTRON: Electroplus E1000 & E3000 test system). Each sample has a size specification of 50 mm in length and 10 mm wide. The rate was maintained at 2 mm/min, having 20 mm Gauge span and load capability of 250 Newton be maintained in UTM. Three replicates of each sample tested followed the ASTM D882 standards method (standardized method of testing the Tensile Properties of Plastic Sheeting). All the samples were tested at a temperature of 18^0C and 50% RH.

3.3.2 DT-TG analysis

Thermal behaviors of the composite films were investigated to ensure their thermal stability and the percentage weight loss with temperature. The transition temperatures determined from the obtained thermograms according to ASTM D-3417 (ASTM D-3417 Standard Test Method for Thermal analysis of polymers by DTA). The analysis was performed by using DTA-Thermo gravimetric analyzer (Shimadzu / DTG-60H) with microbalance type–parallel guide differential top pan with an empty pan used as the reference. Samples (weighted about10-15 mg)was first heated from 25^0C to 500^0C. Thereafter it was cooled to room temperature from 500^0C at a scanning rate of 10^0C/min in nitrogen atmosphere (flow rate about 25ml/min).

3.3.3 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}.

3.3.4 Surface Morphology

The surface topology studies of all the films were studied using a JEOL JSM-6084LV 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 film 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.

3.3.5 Water Absorption

Capacity of water absorption of the film was carried out according to ASTM D570method. Film pieces 20mm×20mm were conditioned in a hot air oven for 2 hour at a temperature of 60^0C and weighted (W_{dry}). Dried films were deep in distilled water at room temperature for 24 hours. After that, samples were removed, dried by wiping gently by blotting paper and weighted (W_{wet}) to determine the water absorbed by the films. The water absorption capacity (W_a) was determined by:

$$\% \mathrm{Wa} = \frac{\mathrm{Wwet} - \mathrm{Wdry}}{Wdry} \times 100 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 3.1$$

3.3.6 Contact Angle Measurement

Contact angle measurement on the film surface was done according to ASTM D5946-04. The polymer films were kept at room temperature for 24 hours at a 50 % RH before contact angle measurement test was done. The contact angle measurement was done by using Kruss Germany DSA/25 contact angle measurement instrument. A droplet of water was applied to the film surface, and the droplet shape upon the film surface was recorded at every time by a video camera and image analyzing software to determine the contact angle. The assessment of the angle of contact reported as average of four measurements.

3.3.7 Biodegradation Behaviors under Soil

The degradation tendency of the films under soil was studied. The soil was collected from the garden of NIT Rourkela campus and treatment of soil was done in the laboratory. The microorganism present were explored to know which microorganisms (bacteria) were responsible for the decay of the films. The humidity of the soil was maintained at approximately 20%. The samples were buried 7cm below under the soil. In every five days interval films were taken away from the soil. Later than clean-up through water and exposure to air at room temperature, changes in weight were calculated. Changes of weight (%) were calculated using the following equation:

$$\% \mathrm{Wg} = \frac{\mathrm{Wi} - \mathrm{Wf}}{Wi} \times 100 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 3.2$$

Where W_i and W_f be the weight of the samples before and after the soil action.

The appearances of physical changes were also determined by distinguishing the pictures of the film surface before and after soil treatment.

CHAPTER 4

RESULTS & DISCUSSION

4. RESULT AND DISCUSSION

Films were prepared with variable amounts of starch, sucrose, glycerol and PVA, as reported in Table 4.1. The film testing was done to characterize the different processed films.

Table 4.1: Composition of film based on starch, glycerol, PVA, Sucrose, MgSt and HA.

Sl. No.	**Formulation**	**Starch (%)**	**Sucrose (%)**	**Glycerol (%)**	**PVA[a] (%)**	**MgSt[b] (%)**	**HA[c]**
1	F1	50	48	-	-	1.5	0.5
2	F2	50	30	18	1.5	0.45	0.05
3	F3	50	20	28	1.5	0.45	0.05
4	F4	50	10	38	1.5	0.45	0.05
5	F5	50	-	48	1.5	0.45	0.05
6	F6	50	30	1.5	18	0.45	0.05
7	F7	50	20	1.5	28	0.45	0.05
8	F8	50	10	1.5	38	0.45	0.05
9	F9	50	-	1.5	48	0.45	0.05

[a] PVA- Poly (vinyl alcohol)

[b] MgSt- Magnesium Stearate

[c] HA- Hydroxy Apetite

4.1 Mechanical Properties

Polymeric films perhaps subject to a variety of stresses when used as packaging material [31]. Therefore the testing of mechanical properties (tensile strength, elongation at break etc.) is a significant factor of influential of the performance of the material. Poor strength of pure native starch composite films is the major drawbacks for their uses in commercial applications. Enhancements of mechanical properties of the films are, therefore mandatory. Studies were done by using different plasticizer (Glycerol or PVA) compile with starch and sucrose. It is estimated fact that tensile strength of composites is influenced by reinforcement agents and fillers such as MgSt and HA. Uniformly distributed particle with an adequate bond between the reinforcing agents and matrix allows effective transfer of stress by a shear mechanism from the matrix to the particle that can effectively withstand load and improve the strength of the sample. Tensile strength represents the force per unit area required to tear the film whereas elongation at break represents the ability of film to stretch.

4.1.1 Effect of Glycerol and Sucrose content on the Tensile Properties of the Film

Figure 4.1 and figure 4.2 represents the mechanical properties of the prepared film such as TS and EB. It was observed that film's TS and EB are function of both sugar content as well as glycerol content. With an increase in glycerol content and decrease in the sucrose content, TS increases up to a certain point then decreases. Fahmida Parvin et al, 2011 represented similar trend using gamma irradiated sugar [32] containing starch/PVA based films. The starch/sucrose film (without glycerol) shows lower tensile strength (1.5 MPa). The film (without glycerol) shows maximum EB (50%) and the film (without sucrose) shows minimum EB. With an increase in glycerol content and decrease in the sucrose content the EB of the films decreases. With an increase in the sucrose content increases the elongation at break of the polymer. Similar behavior was reported by researchers [33, 34]. Out of these five different starch/glycerol/sucrose based bio-composite films F_3 (50% starch/20% sucrose/ 28% glycerol) and F_4(50% starch/10% sucrose/ 38% glycerol) gives an optimum TS and EB value, these two composite films were further tested.

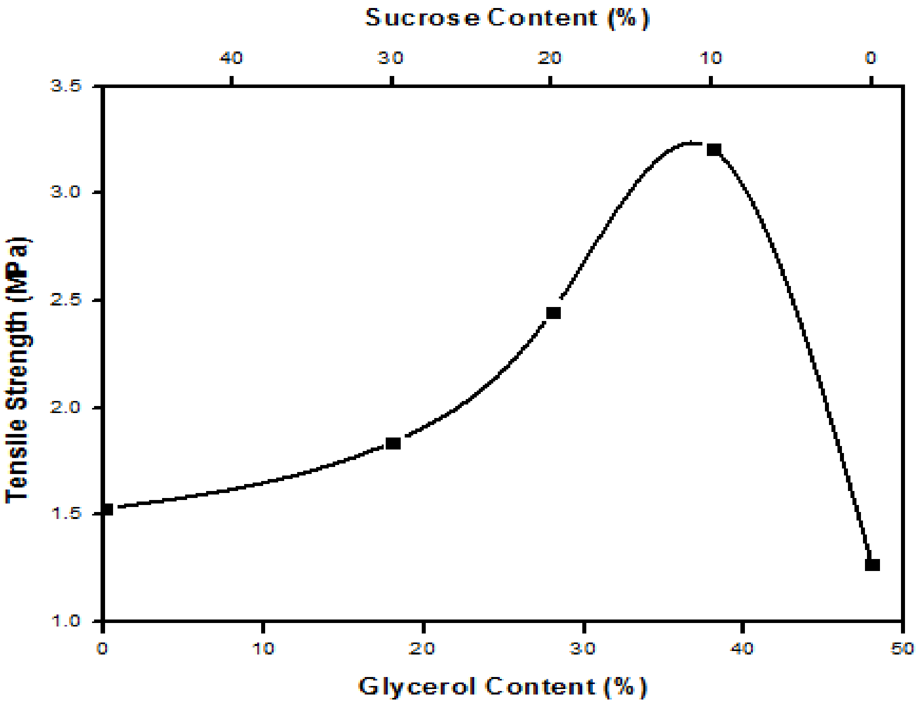


Figure 4. 1 consequence of glycerol and Sucrose on the TS of the starch/glycerol/sucrose blend film.

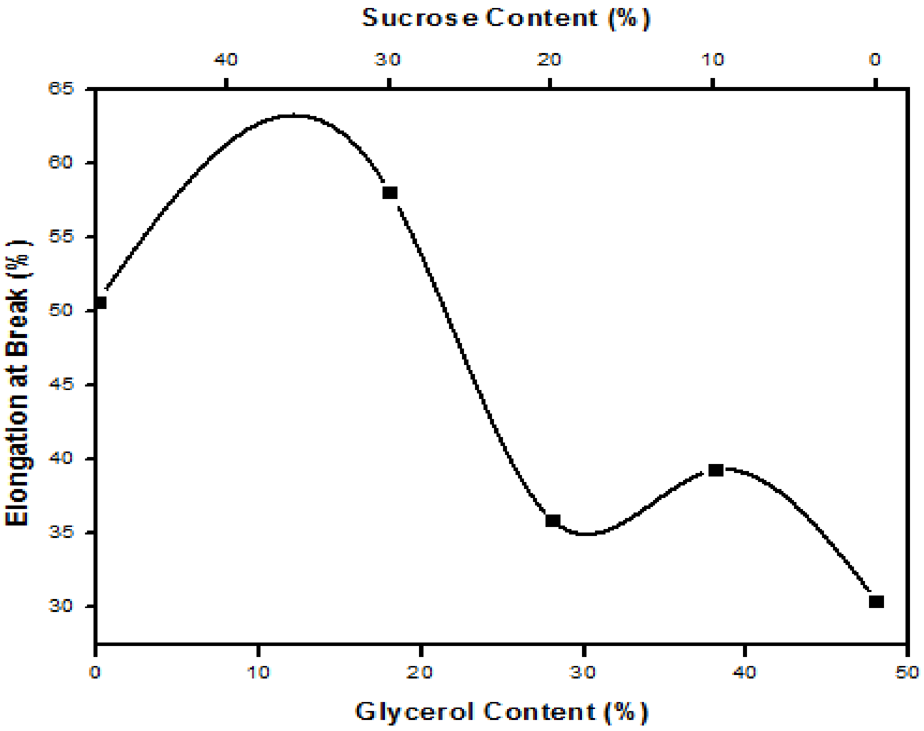


Figure 4. 2 Consequence of glycerol and Sucrose on the EB of the starch/Glycerol/sucrose blend film.

4.1.2 Effect of PVA and Sucrose content on the Tensile Properties of the Film

Figure 4.3 shows the tensile strength at break starch/PVA/sugar based film as function together PVA and sucrose content correspondingly. PVA and sucrose content shows divergent effects on TS of the films. TS of the films increase with increase in PVA content and decreases with sucrose content. In this study, TS of the F_6 (18% PVA, 30% Sucrose) film was bring into being superior to that of the film F_1 (without PVA). The increase in sucrose satisfied to decrease in the TS of the polymeric film. Figure 4.4 shows the influence of sucrose and PVA content on EB.

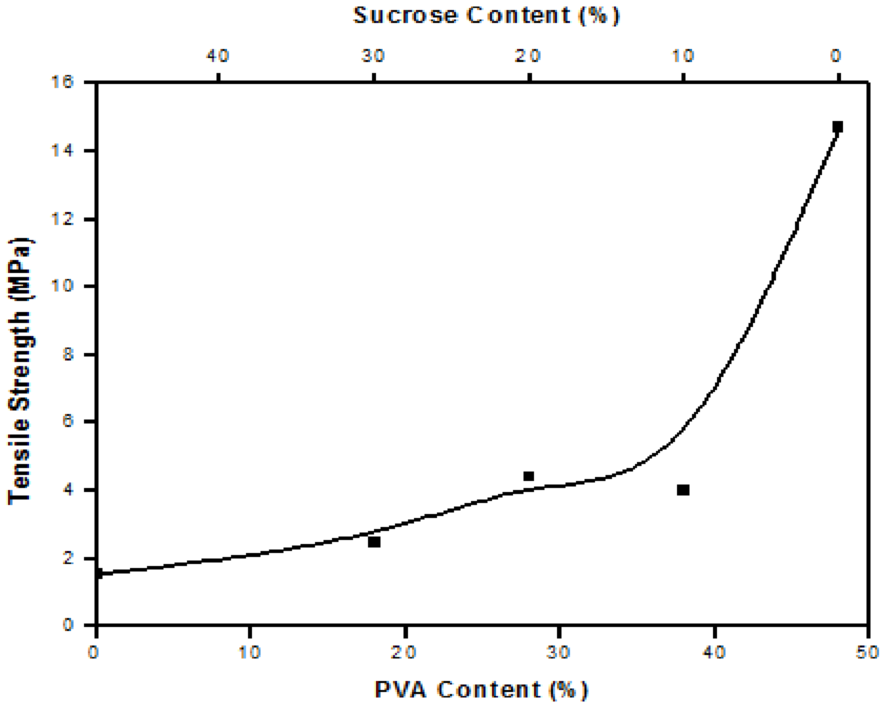


Figure 4. 3 consequence of PVA and Sucrose on the TS of the starch/PVA/sucrose based film.

An increase in sucrose content decreases the attraction of cohesive force linking PVA, starch and sucrose and thereby lowers the tensile strength [32]. Since F_7 (50% starch/20% sucrose/28% PVA) film and F_8 (50% starch/10% sucrose/38% PVA) film composition exhibit the optimum performance for both EB and TS, these composite films were used for further investigation.

TS and EB are influenced by the nature of the blend and the linkage between the sucrose, PVA or glycerol and starch. The bio-composite obtain from starch/PVA/sucrose shows better mechanical properties (TS and EB) compared to starch/glycerol/sucrose based bio-composite polymeric films.

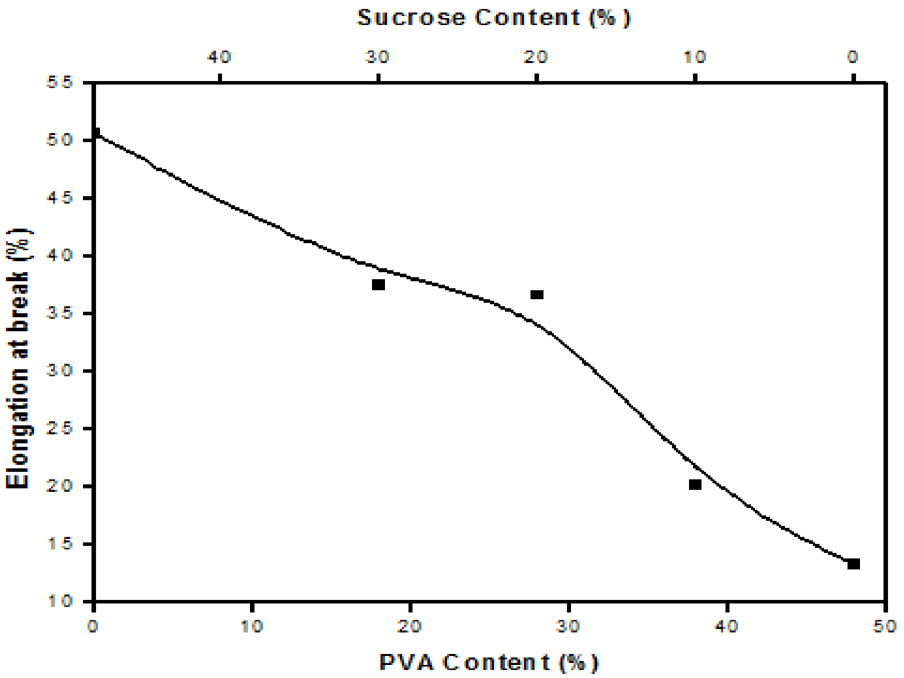


Figure 4. 4 consequence of PVA and Sucrose on the EB of the starch/PVA/sucrose based film.

4.2 Thermal analysis of the films

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

4.2.1 Differential Thermal Analysis

Figure 4.5 indicates the DTA curves of starch/sucrose; starch/sucrose/glycerol and starch/glycerol based films. Starch/sucrose based films show two endothermic peaks at about 85 and 215 ^{0}C indicating the melting temperature and the loss of moisture of the film, respectively. A further endothermic peak at 290^{0}C shows the decay of the polymeric series. The curvature of the F_3 (50% Starch/20% sucrose/28% glycerol) composite shows endothermic peaks at 80 and 240^{0}C, respectively and the curve of the F_4 (50% starch/ 10% sucrose/38% glycerol) shows endothermic peaks at 70 and 235^{0}C, respectively. These endothermic peaks indicate the melting point and the moisture loss of the film. One more endothermic peak at 350^{0}C represents the decay of the films. The curvature of the starch/glycerol is showing two endothermic peaks at 85 and 245^{0}C indicates the melting point and moisture loss of the film, respectively. Another endothermic peak at 470 ^{0}C indicates the decomposition of the film. A prominent exothermic peak at a temperature of about 360 ^{0}C indicates the cross-linking between the starch and glycerol molecules.

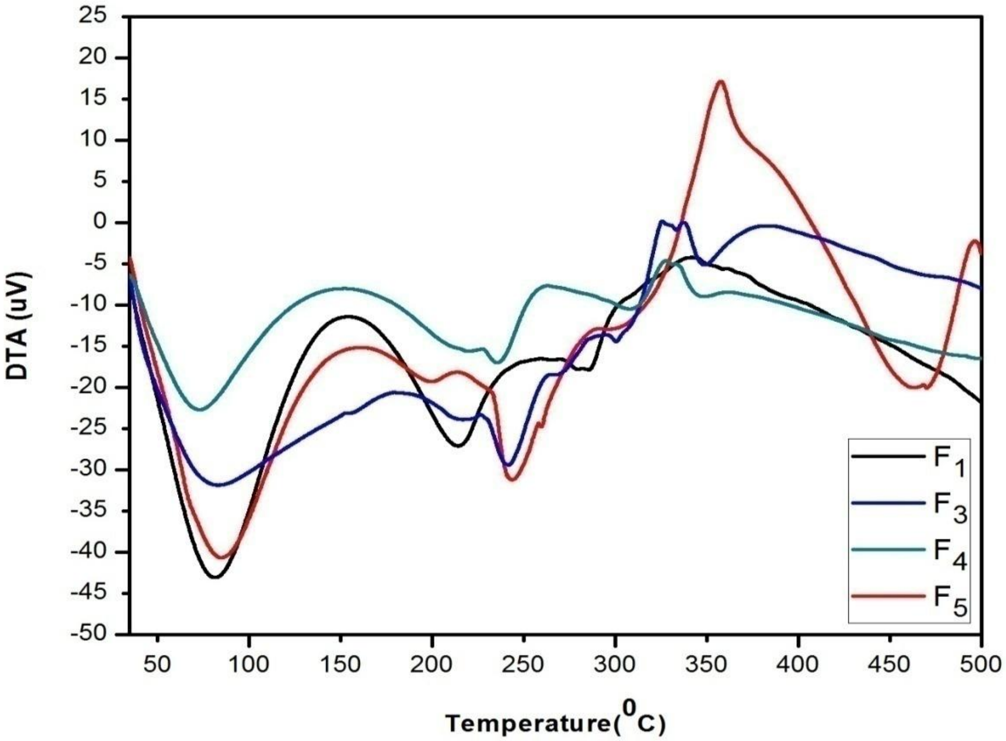


Figure 4. 5 Comparison of DTA of starch/sucrose, starch/sucrose/Glycerol and Starch/Glycerol based blend film.

Figure 4.6 indicates the DTA curves of starch/sucrose; starch/sucrose/PVA and starch/PVA based composite films. The curve of the F_6 (50% starch/30%sucrose/18% PVA) gives the two endothermic peaks at 150 and 250 ^{0}C which indicates the melting point and removal of moisture of the film. An exothermic peak at a temperature of 330 ^{0}C signifies the cross-linking between the starch, sucrose and PVA molecules. The curvature of the F_7 (50% starch/20% sucrose/28% PVA) composite gives two endothermic peaks at 190 and 240 ^{0}C that provides the measure of melting point and the moisture removal, respectively. The curve of the F_8 (50% starch/10%

sucrose/38% PVA) shows an endothermic peak at a temperature of 210 ^{0}Cindicating the

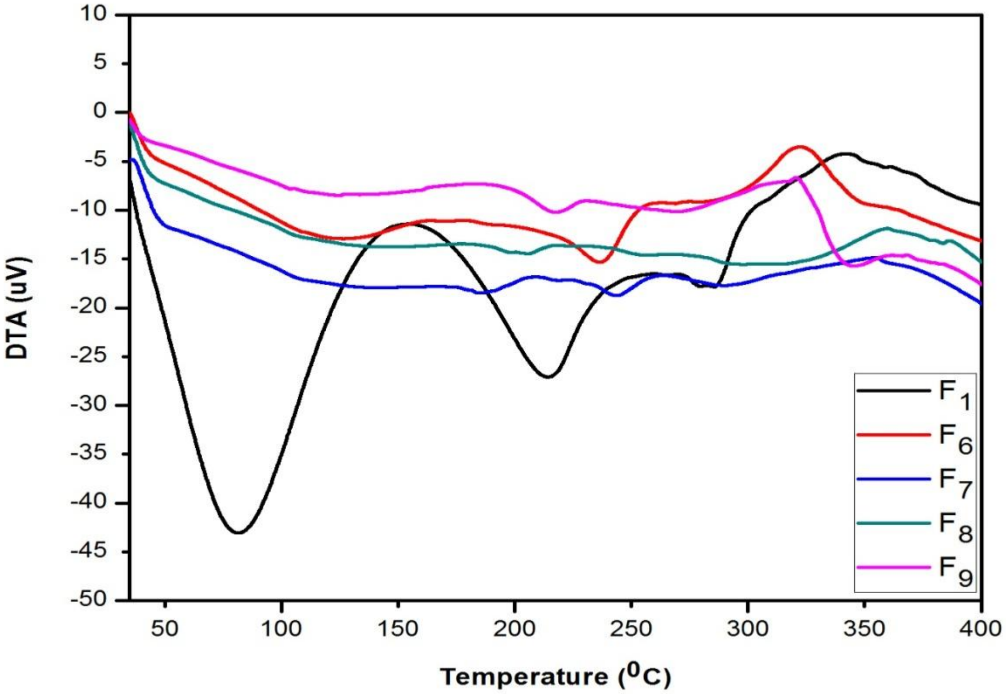


Figure 4. 6 Comparison of DTA of starch/sucrose, starch/sucrose/PVA and Starch/PVA based blend film.

melting point of the film surface. The curvature of the starch/PVA based composite films shows the endothermic peaks at 210 and 270 ^{0}C showing its melting point and the removal of its moisture content. An exothermic peak at about320 ^{0}C indicates the presence of cross-linking between starch and PVA molecules. Another endothermic peak at 340 ^{0}C gives the measure of decomposition of the film.

Significant changes in DTA plot of different composite film suggest the strong interaction between starch, sucrose, glycerol and PVA molecules [32].

4.2.2 Thermo Gravimetric Analysis

Figure 4.7 analyze the TG Analysis of starch/sucrose, starch/sucrose/glycerol and starch/glycerol based blend film. The curve of starch/sucrose based film shows a faster decomposition rate. The weight loss takes place due to loss of moisture and loosely bound volatile components. The film loses its 50% weight at 210^{0}C and gets completely degraded at a temperature of 305^{0}C. The curve of F_4 (50% starch/10%sucrose/38% glycerol) composite film shows a two-step decomposition patterns. Initially decomposition started at 175^{0}C and the next decomposition occurred at 235^{0}C as depicted in figure 4.7. The first step decomposition indicates the loss of loosely bound water, accompanied by the formation of the volatile products. The second step decomposition was mainly caused by the thermal decomposition of the products composed of small molecular carbon and hydrocarbon. The film F_3 (50% starch/20% sucrose/28% glycerol) shows the same decomposition at a temperature about 230^{0}C and 300^{0}C respectively. The starch/glycerol based film decomposes at a faster rate, loses its moisture and volatile matter

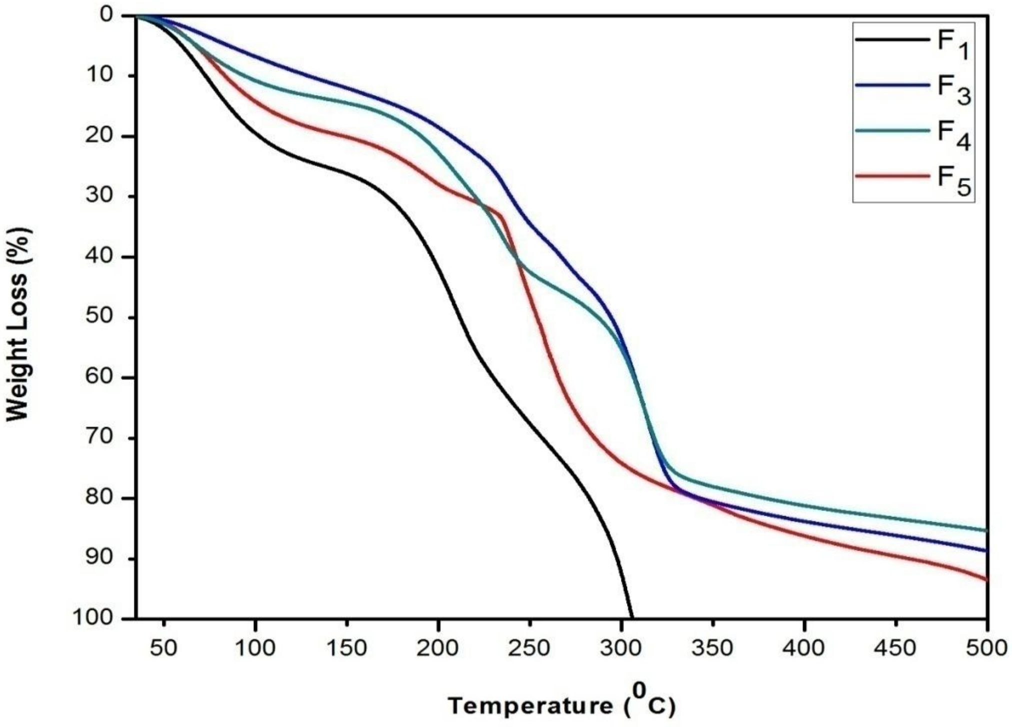


Figure 4. 7 Comparison of TG of starch/sucrose, starch/sucrose/Glycerol and Starch/Glycerol based blend film.

content at 175^{0}C. The thermal deprivation of the semi-crystalline starch occurred at about 235^{0}C. 50% decay of the film occurred approximately at 255^{0}C and losses 90% weight at 450^{0}C. The faster rate of film decomposition can be achieved due to the absence of plasticizing agent (glycerol).

The figure 4.8 represents the Thermo Gravimetric Analysis (TGA) of starch/sucrose, starch/sucrose/PVA and starch/PVA based blend films. The decomposition of the films caused by the removal of moisture, volatile disintegrated product and the semi-crystalline starch molecules. The curve of the F_6 (50% starch/30% sucrose/18% PVA) film shows its first step decomposition at about 175^{0}C where loosely bound water and volatile disintegrated product gets removed. The second step decomposition occurred due to loss of disintegrated products of carbon and hydrocarbon molecules. The F_7 (50% starch/20% sucrose/28% PVA) composite shows decomposition at about 225^{0}C and 275^{0}C due to loss of moisture and semi-crystalline starch molecules respectively. The film F_8 (50% starch/10% sucrose/38% PVA) shows same decay rate, but at a temperature about 230^{0}C and 280^{0}C respectively. The film lost 50% of its

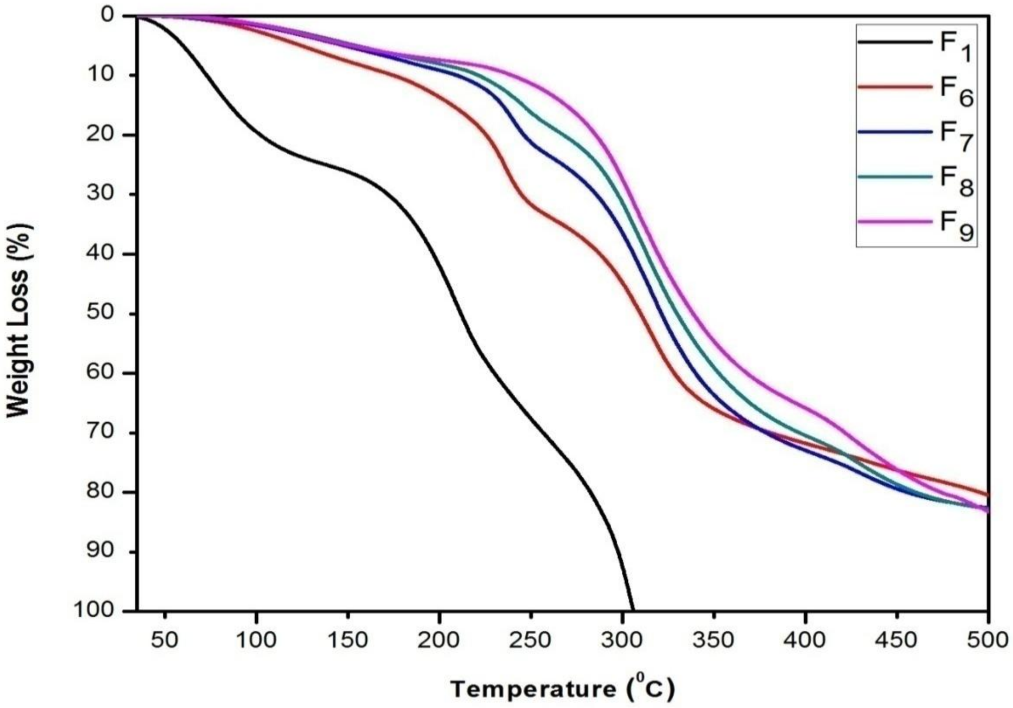


Figure 4. 8 Comparison of TG of starch/sucrose, starch/sucrose/PVA and Starch/PVA based blend film.

weight at about 325^0C and 80% weight at 400^0C. The curve of starch/PVA-based film shows first step decomposition due to loss of moisture and volatile disintegrated product at a temperature of 230^0C. The second step decomposition occurred at a temperature of 295^0C due to loss of its semi-crystalline starch molecules. The film loses its 50% weight approximately at 340^0C and losses 80% weight approximately at 440^0C. Sucrose is found to be highly sensitive to thermal degradation because of its incorporation with starch. However in presence of PVA on starch/sucrose film reduces thermal degradation of the films that results in improved thermal stability.

4.3 FTIR Analysis of the film

Figure 4.9 shows the contrast of FTIR spectrum of starch/sucrose and different composition starch/sucrose/glycerol blend film. In this examination, it was attempted to distinguish the inclusion of glycerol and sucrose into the starch-based films and then differentiate the IR spectra and shifts of the vibrations related to the sucrose, starch and glycerol interaction. Starch, Sucrose and PVA molecules in general allied with inter-molecular and intra-molecular H-bonding in the blends. The cross-linking of these blends consequences in the decrease in the inter-molecular H-bonds. The starch/sucrose composite gives broad band due to O-H vibration at 3325 cm^{-1}, C-H or C-H_2 stretching vibration at 2930 cm^{-1}, C=O stretching at 1741cm^{-1}, bending vibration of C-H or C-H_2 (asymmetric) at 1342 cm^{-1}, bending vibration of C-H or C-H_2 (symmetric) at 1236 cm^{-1}, stretching vibration of C-O between 1103-1020 cm^{-1} and bending vibration out of plane of C-H at 900 cm^{-1}, 866 cm^{-1} and 600 cm^{-1} correspondingly. In the spectra of starch/sucrose/glycerol and starch/glycerol film, the absorption band of O-H shift to 3281 cm^{-1} and 3285 cm^{-1} indicates the increase of H-bond. The shifting of bending vibration of

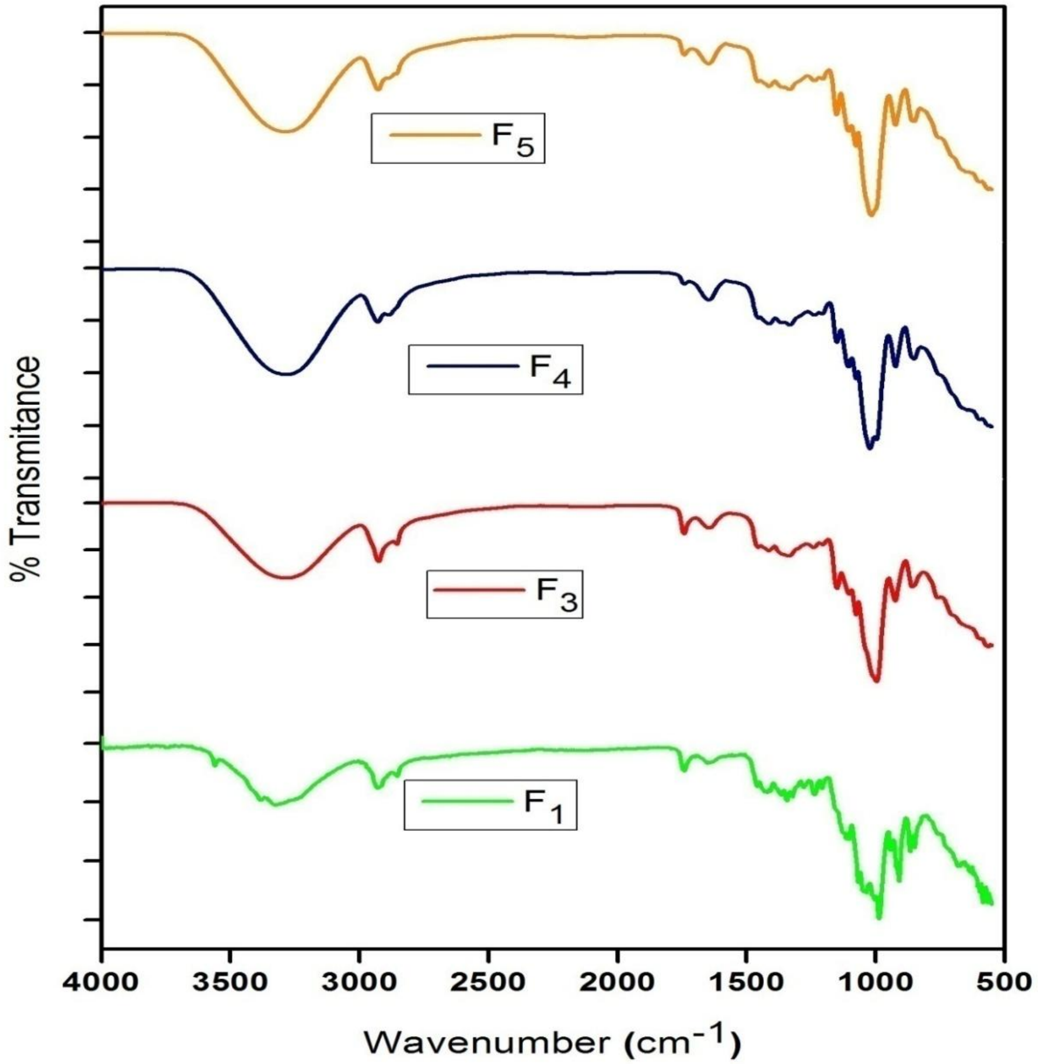


Figure 4. 9 FTIR spectrum of starch/sucrose, starch/sucrose/glycerol and starch/glycerol blend film.

C-H or C-H_2 from 1342 cm^{-1} to 1332 cm^{-1} for starch/sucrose/glycerol film and to 1336 $cm^{-1}$for starch/glycerol respectively, confirmed the formation of comparatively strong H-bond.

Figure 4.10 shows the assessment of FTIR spectra of starch/sucrose film, different composition starch/sucrose/PVA films and starch/PVA film. In this study, it was attempt to characterize the assimilation of PVA and sucrose into the starch-based films and then distinguish the IR spectra and vibrations shifts associated to the sucrose, starch and PVA interaction.

The spectrum of starch/sucrose/PVA and starch/PVA based films O-H vibration shifts to 3279-3281 cm^{-1} and broaden enough compare to starch/sucrose based films. The shifting of bending vibration of C-H or C-H_2 for both symmetric and asymmetric to 1415 cm^{-1} and 1325 cm^{-1} established the strong H-bond. Narrower peaks of stretching C-H or C-H_2 confirm the better bond strength of starch/sucrose/PVA composite films.

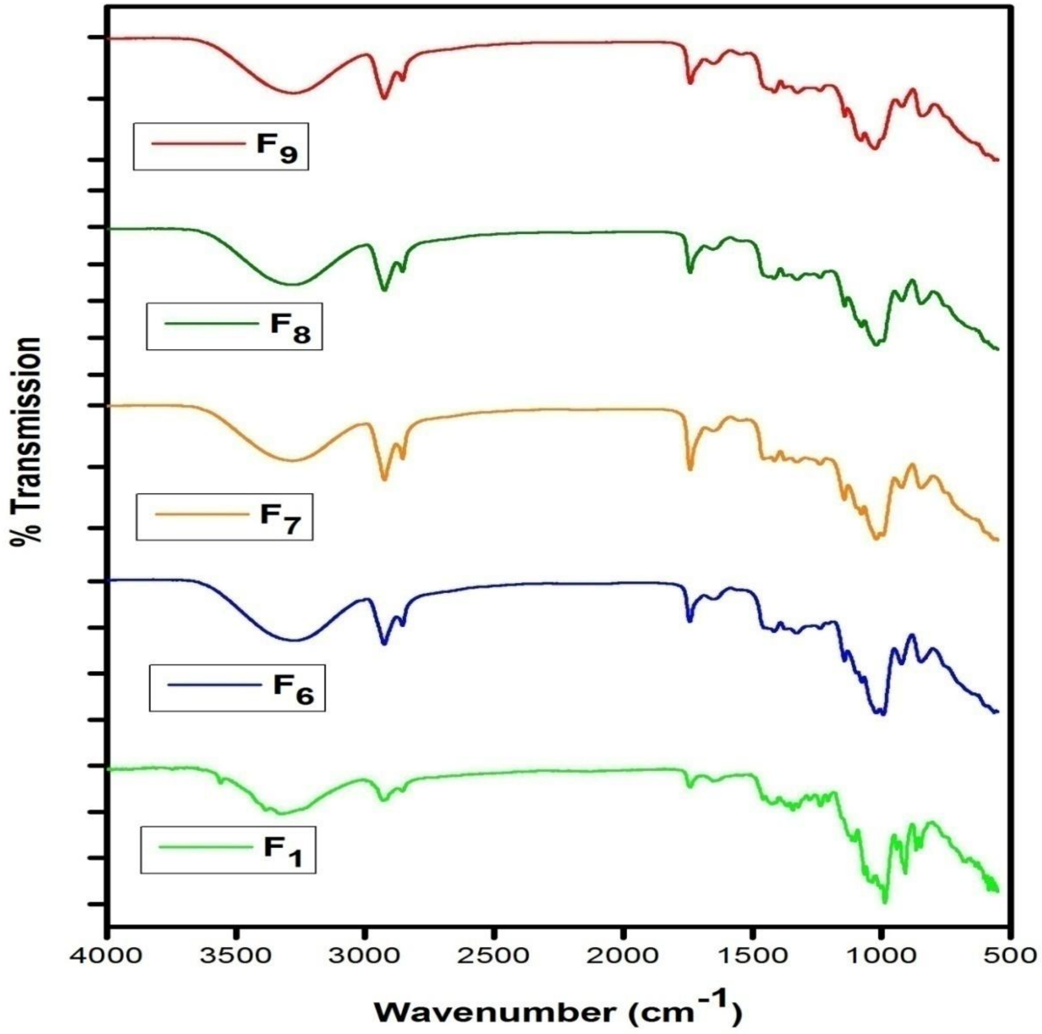


Figure 4. 10 FTIR spectrum of starch/sucrose, starch/sucrose/glycerol and starch/glycerol blend film.

4.4 Surface Morphology

The surface topography of starch/sucrose, starch/sucrose/glycerol and starch/glycerol films was studied with SEM (Figure 4.11). The starch/sucrose based film has rougher surface compared to starch/glycerol film. With increase in glycerol content the surface of the film gets smoother. The surface morphology of starch/sucrose, starch/sucrose/PVA and starch/PVA films was studied with SEM (Figure 4.12). The starch/PVA film has very smooth surface compared to the starch/sucrose and starch/sucrose/PVA films. With increase in the PVA content and decreasing sucrose content the surface of the films become smoother. The surface of the starch/sucrose/PVA film appear to comprise stripes or fibrous like topography on the face. The SEM observation seems to prop up the FTIR structural examination and provides support of enhancement of the properties of the film by cross-linking obtained between the starch/glycerol and starch/PVA films.

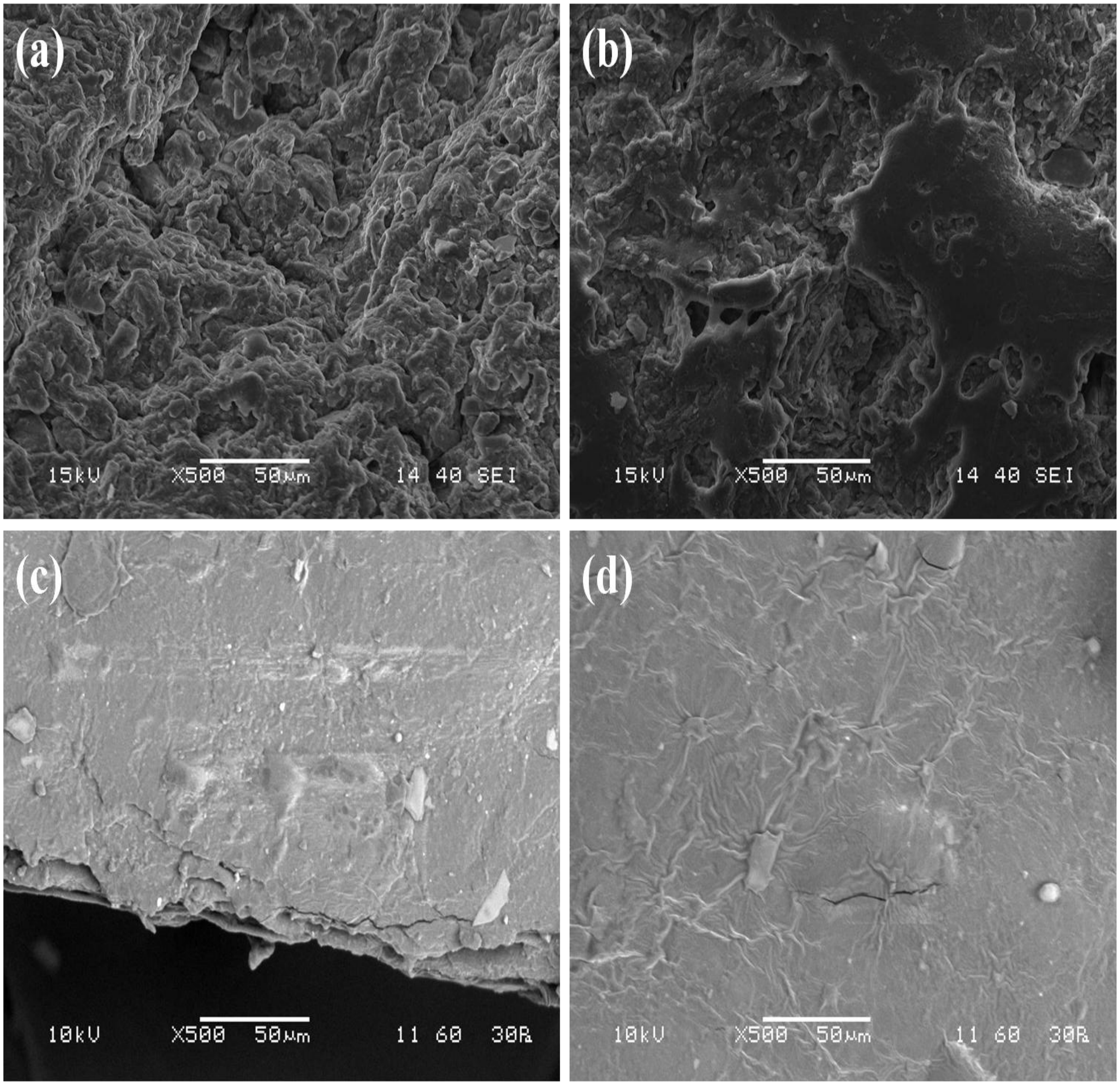


Figure 4. 11 SEM images of: a)F1, b)F3,c)F4 and d)F5 blend film.

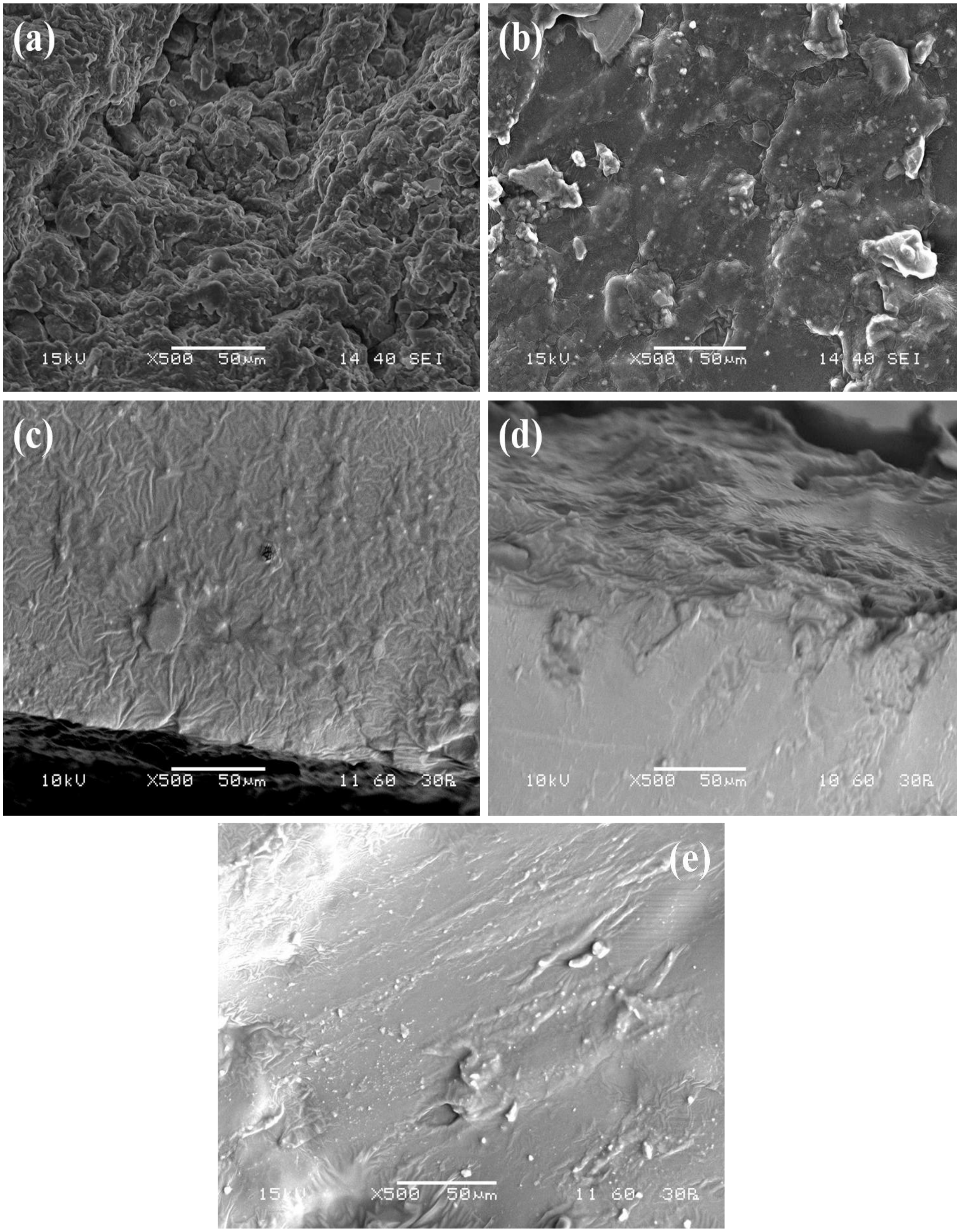


Figure 4. 12 SEM images of: a)F1, b)F6,c) F7,d) F8 and e)F9 blend film.

4.5 Water Absorption

Water absorption is a important factor for biodegradable composite material for their application [35] typically in packaging industry. The measurement hydrophilicity of polymeric film was evaluated by measuring the water absorption capacity of the film surface. The figure 4.13 represents the water absorption capacity of starch/sucrose, starch/sucrose/glycerol and starch/glycerol film. Starch/glycerol composite film shows better hydrophobic properties compared to the starch/sucrose and starch/sucrose/glycerol film. The major drawback of this starch/glycerol film is of very poor tensile properties. The F_1 (50% starch/48% sucrose) composite film shows maximum water absorption (71.35%). An increase in glycerol content the water absorption capacity minimizes. The starch/PVA based film has better tensile properties but it has maximum water absorption. Figure 4.14 indicate the water absorption capacity of starch/sucrose, starch/sucrose/PVA and starch/PVAcomposite film. More the

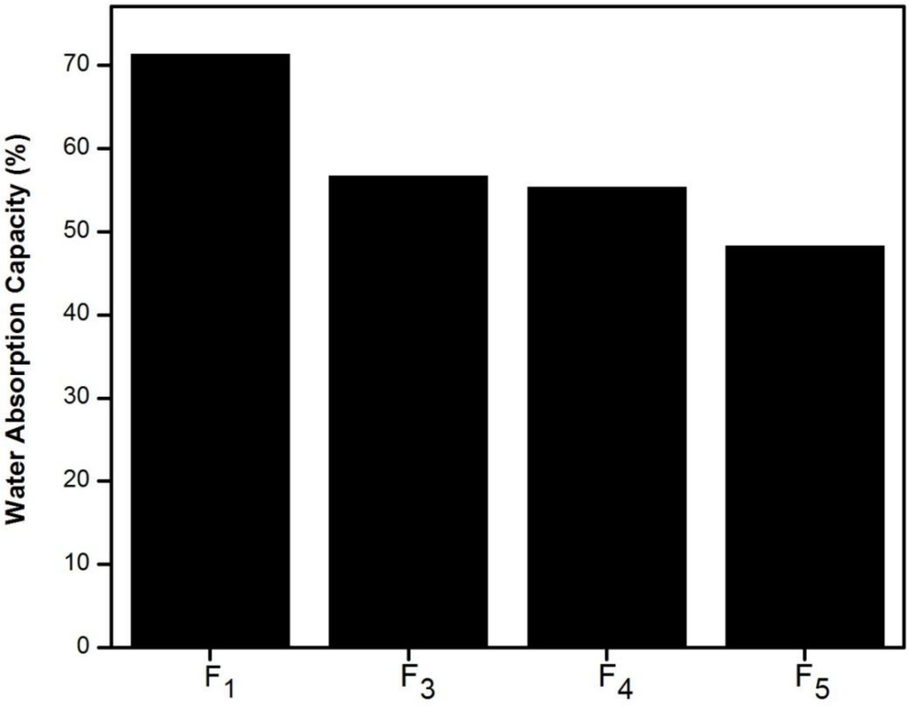


Figure 4. 13 Percent water absorption by starch/sucrose, starch/sucrose/glycerol and starch/glycerol composite film.

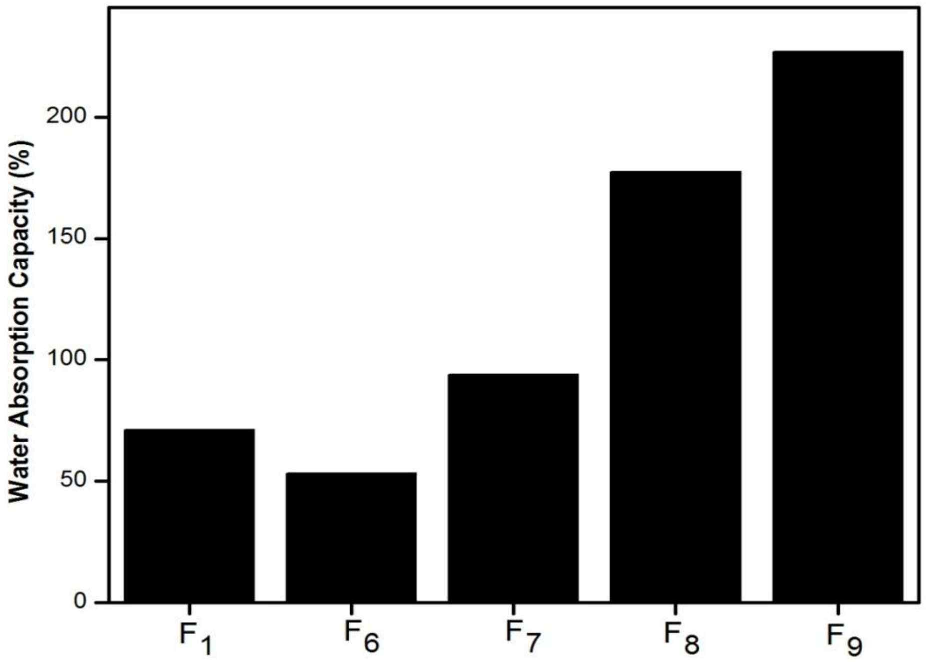


Figure 4. 14 Percent water absorption by starch/sucrose, starch/sucrose/PVA and starch/PVA composite film.

presence of hydroxil group shows more water absorption capacity [36]. The starch/PVA film shows maximum water absorption capacity, indicates the maximum number of available hydroxil group. The starch/PVA film shows 227% water absorption capacity in 24 hours time period. The starch/sucrose/PVA film better hydrophobic in nature. With increase in the sucrose content the hydrophobicity of the film is enhanced.

4.6 Contact Angle measurement

The contact angle measurement of water drop on the film surface is the indication of hydrophobic properties or the wettability of the film surface [37]. For water on a completely hydrophilic surface the contact angle is zero. The surface having contact angle less than 90^0 on water drop is hydrophilic in nature. Less the contact angle more the hydrophilic surface. Table 4.1 shows contact angle on different film surface. Starch/glycerol film shows higher contactangle than the starch/sucrose and starch/PVA film surface. The starch/PVA film has more hydrophilic surface because of more -OH rich molecules.The starch/sucrose/PVA film surface shows poor wetting properties compared to starch/sucrose/glycerol film surface.

Table 4.2: Contact angle measurement of water droplet obtained for the films

Sample	F_1	F_2	F_3	F_4	F_5	F_6	F_7	F_8	F_9
Contact angle	30.7	57.9	62.1	64.7	84.4	61.8	73.6	70.6	49.4

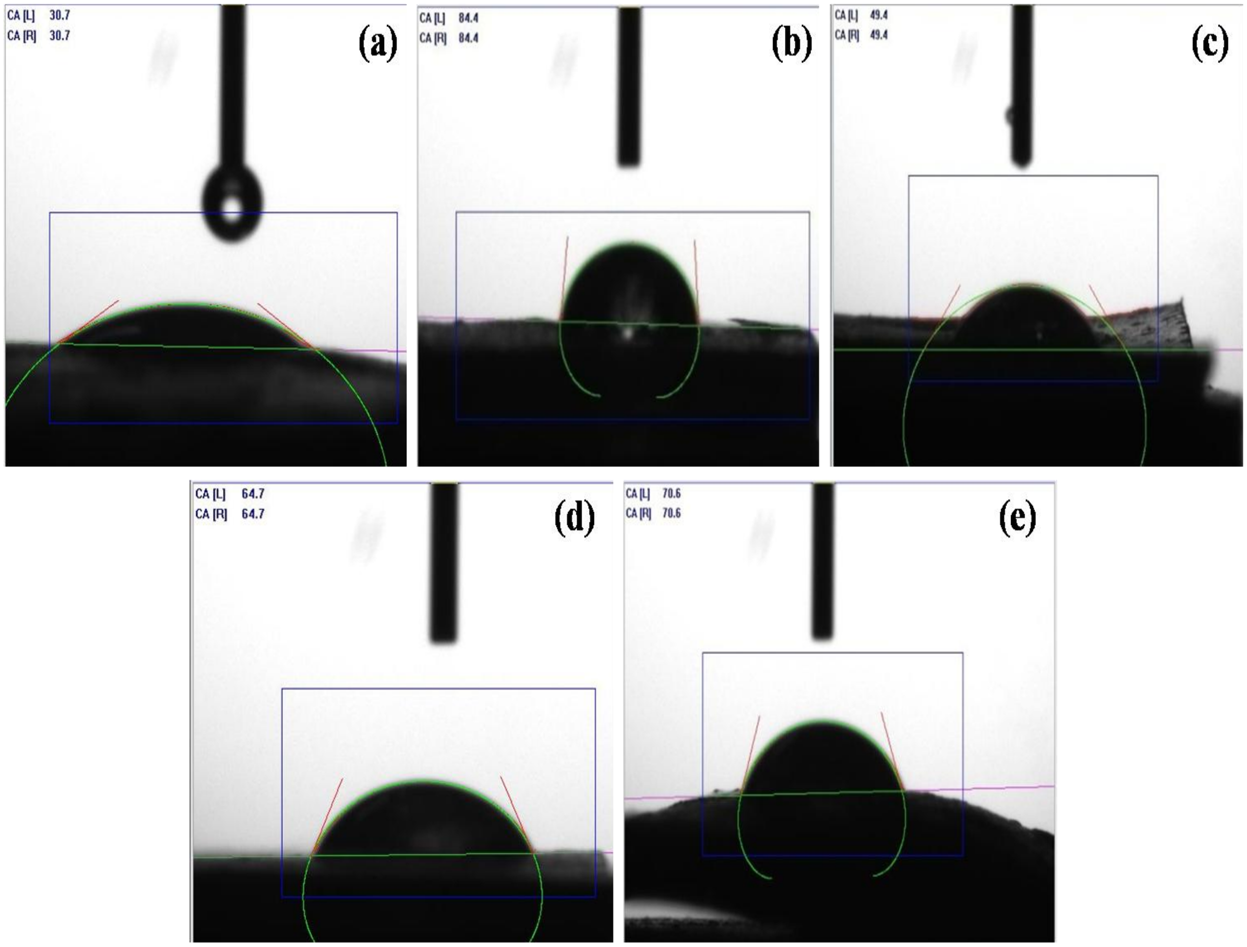


Figure 4. 15 images of contact angle measurement on a) starch/sucrose, b) starch/glycerol, c) starch/PVA, d) starch/sucrose/glycerol and e) starch/sucrose/PVA film surface.

4.7 Biodegradation Behavior

Degradability of polymers is a critical functionality for their application purpose. Biodegradation is the chemical breakdown process of material in the natural environmental condition. Soil burial method is commonly used by many researchers for the degradation study of materials [37, 38].

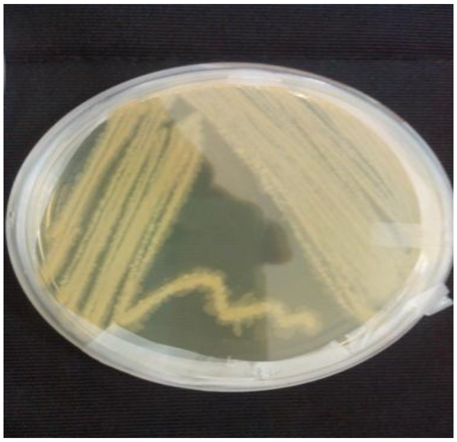


Figure 4. 16 culture of microorganism of soil sample on agar plate.

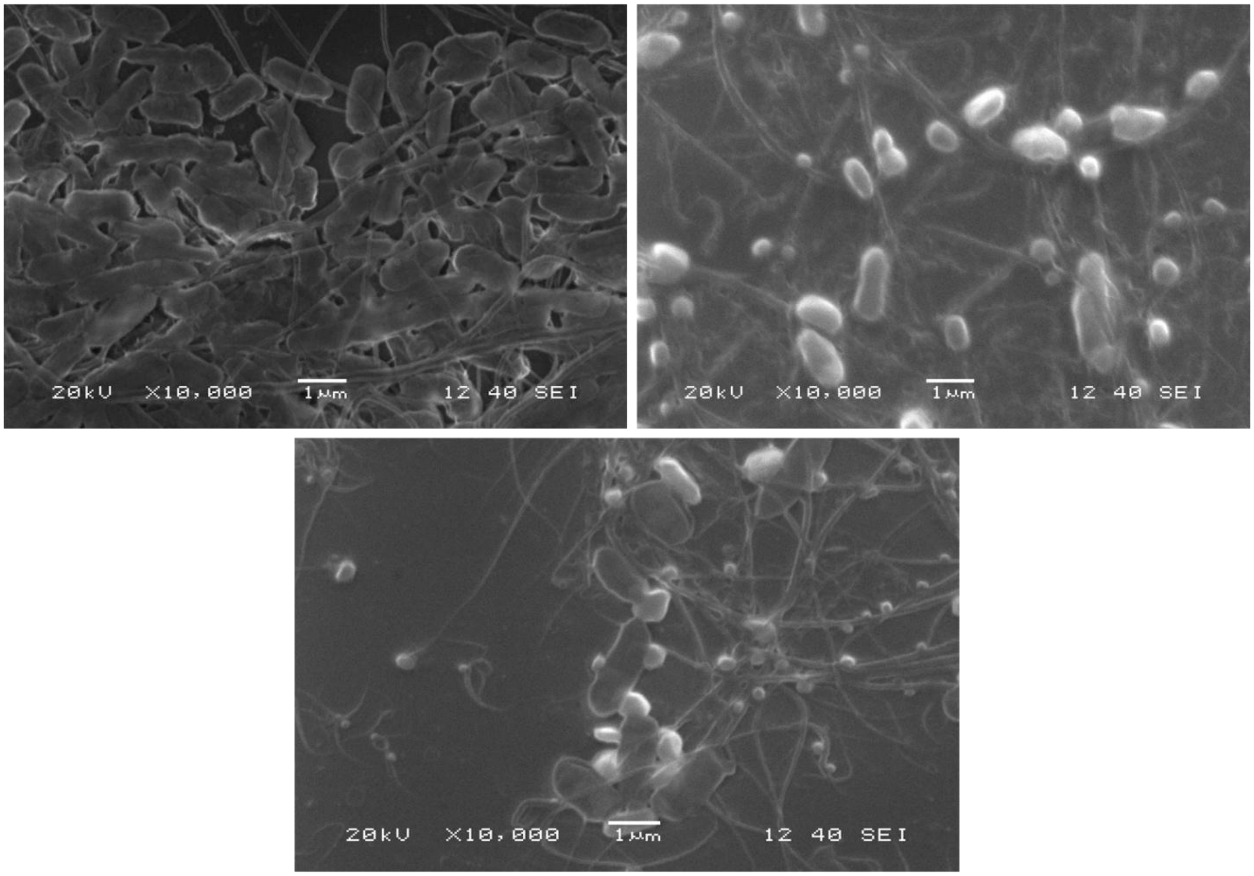


Figure 4. 17 SEM micrographs of microorganism present on the soil sample.

The degradation in soil burial method was mainly caused due to the presence of microorganism in the soil. To identify the microorganism resposible for the degradation of the polymer films, the soil testing was carried out in the laboratory. The microorganism was characterized depending upon their shapes. The rod like shape indicates the presence of bacillus, vibrios are comma shaped curved rods, coccus represents spherical or oval cells. SEM analysis shows (figure 4.17) the main dominating microorganism present in the soil were Bacillus and was reported.Besides Bacillus species other microorganism present in the soil were vibrious, coccus and fungi. These microorganism were responsible for the degradation of film surface.

Figure 4.18 indicates the degradation of starch/sucrose, starch/sucrose/glycerol and starch/glycerol films under the 7 cm layer soil. The starch/sucrose film is easily degraded underthe soil and losses about 88% weight in 30 days. The starch/sucrose/glycerol based film initialyshows faster degradationbehaviour and after certain time period the degradation becomes slower.The interaction of microorganism on starch and sucrose molecules increased initialy

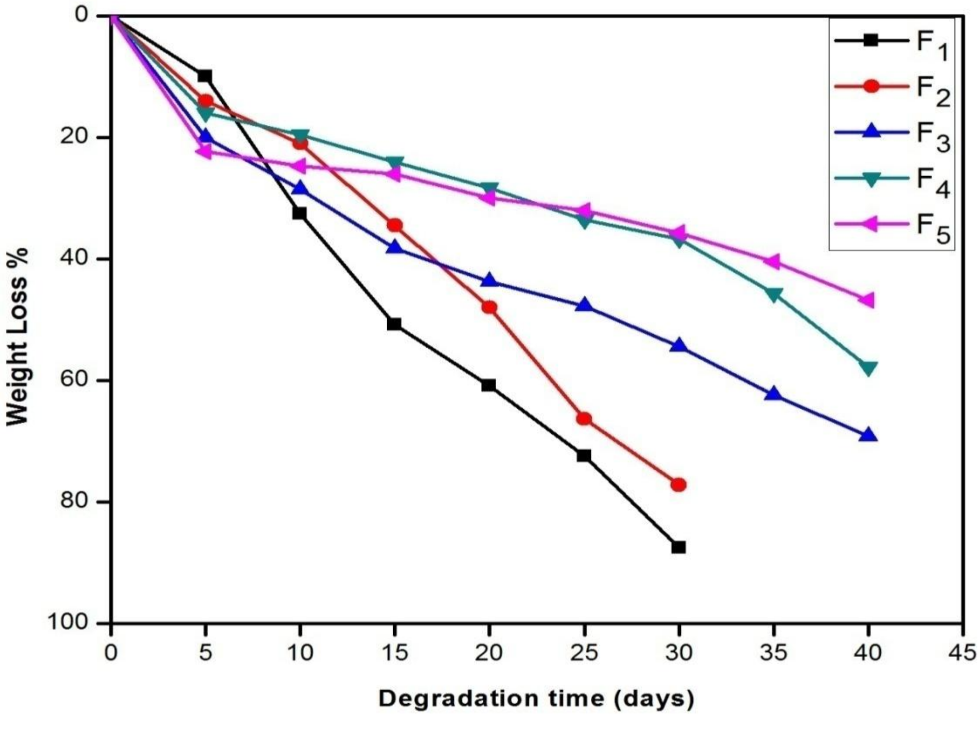


Figure 4. 18 Comparison of weight loss of starch/sucrose film, various starch/sucrose/glycerol film and starch/glycerol film at different soil burial time.

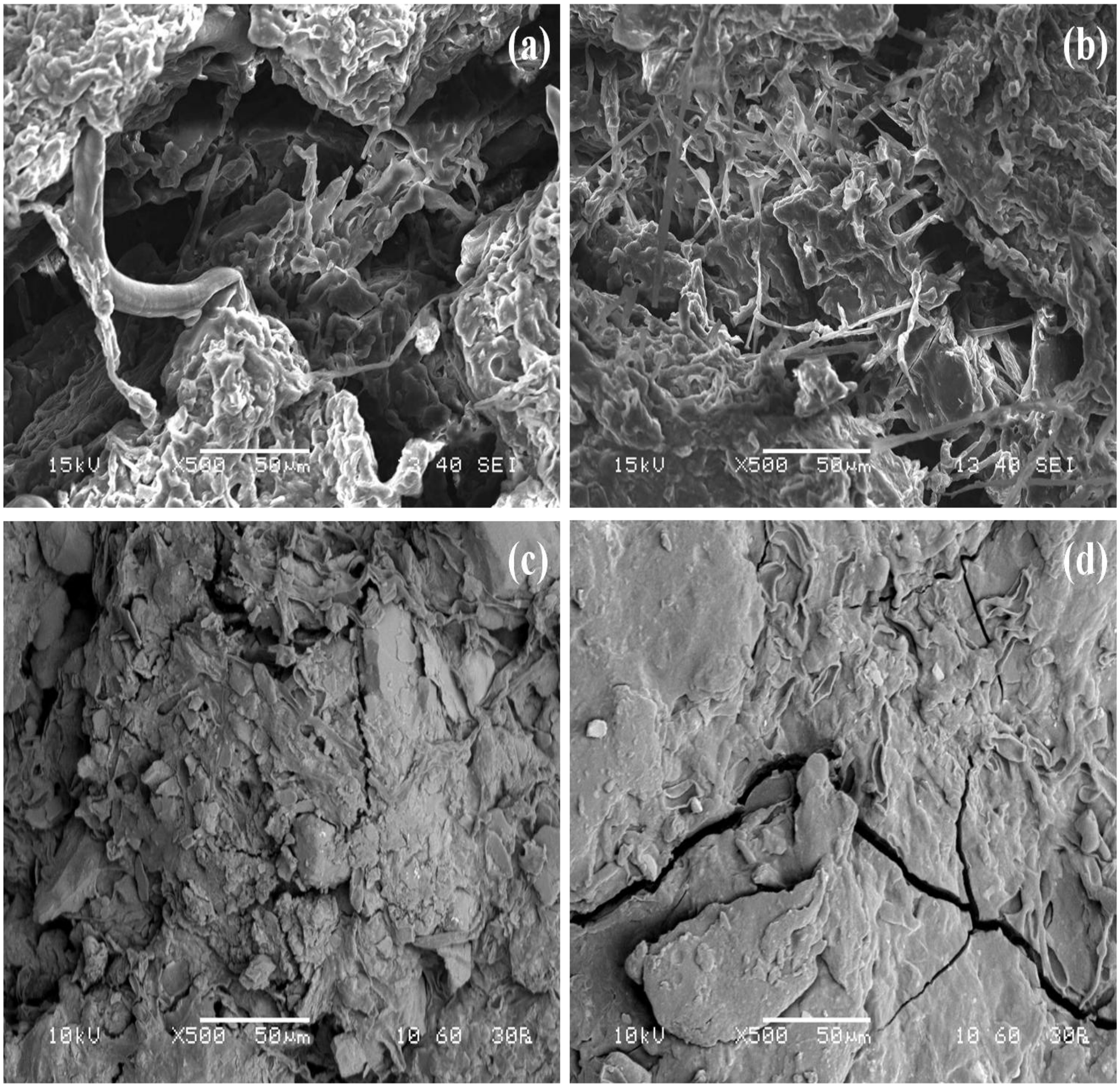


Figure 4. 19 SEM images of: a) F1, b) F3, c) F4, d) F5 blend film after soil burial test.

which leads to faster degradation rate. Aas soon as the starch and sucrose molecules was almost fully degraded, the glycerol molecules was promote to degrade which shows slower degradation behaviour. The F_3composite film losses about 70% weight in 40 days whereas F_5 (starch/glycerol) film losses about 47% weight in 40 days.

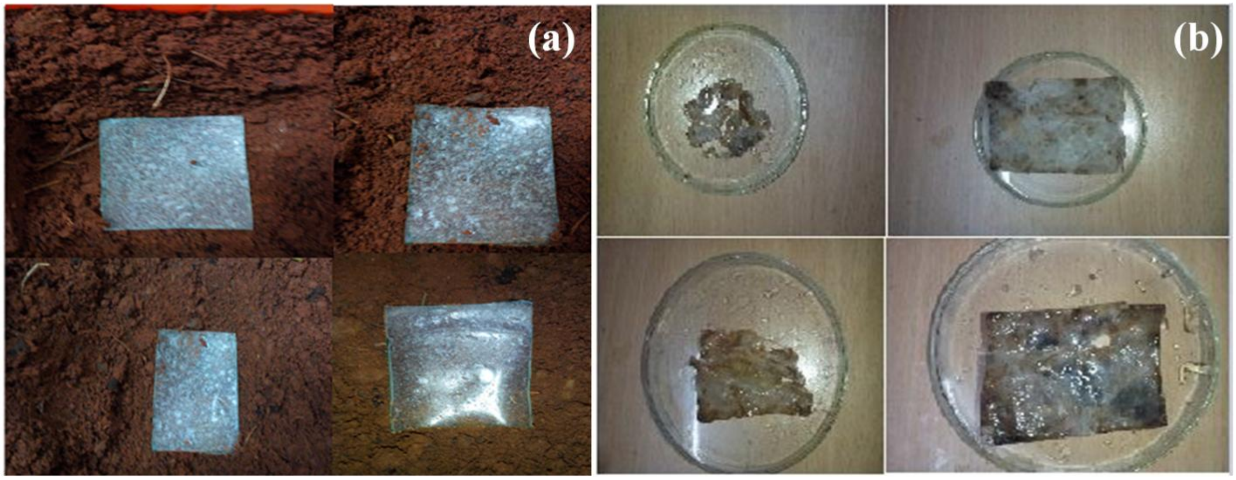


Figure 4. 20 Pictures of starch/sucrose, starch/sucrose/glycerol and starch/glycerol films. (a) before degradation, (b) after degradation (20 days) under soil.

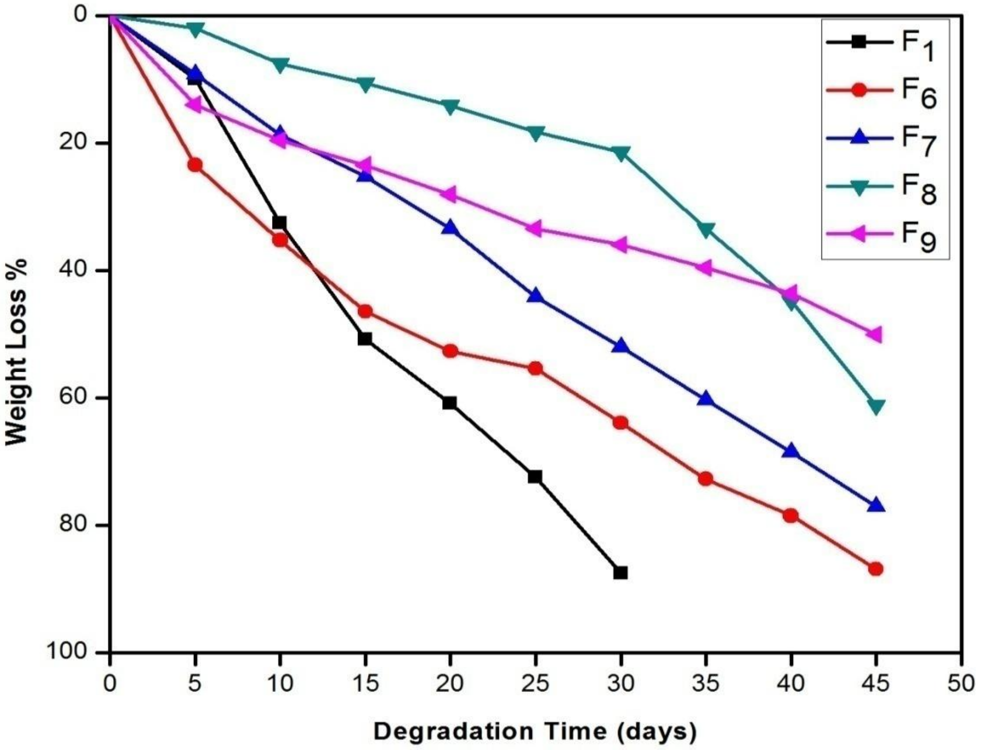


Figure 4. 21 Comparison of weight loss of starch/sucrose film, various starch/sucrose/PVA film and starch/PVA film at different soil burial time.

Figure 4.21 shows that the starch/PVA film gives slower degradation behavior compared to starch/sucrose and starch/sucrose/PVA film. The starch/sucrose/PVA film initially represented faster degradation as starch and sucrose molecules are easily degraded by the microorganism present in the soil. When starch and sucrose molecules are completely ruined, the PVA was

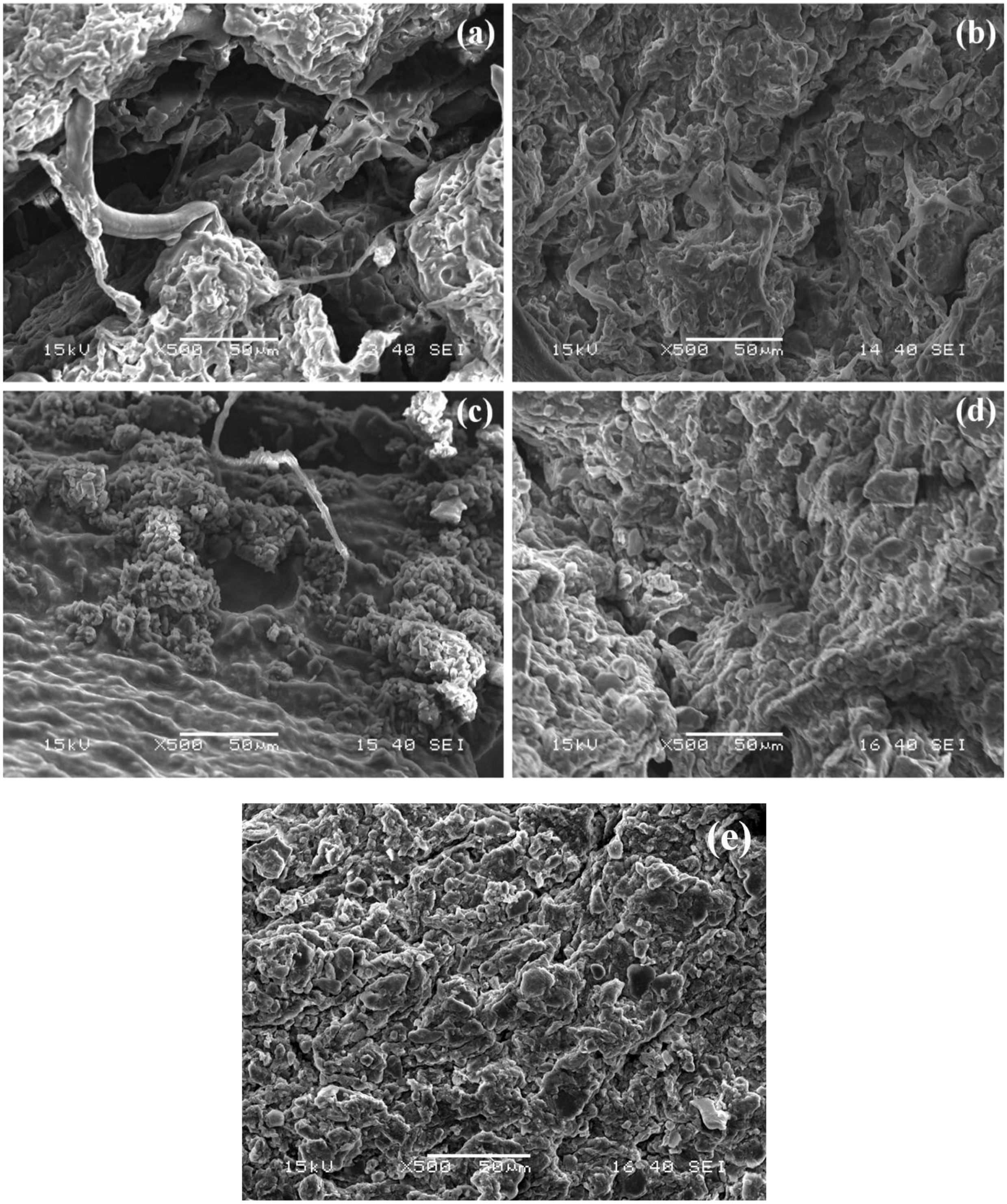


Figure 4. 22 SEM images of: a) F1, b) F6, c) F7, d) F8 and e) F9 blend film after soil burial test.

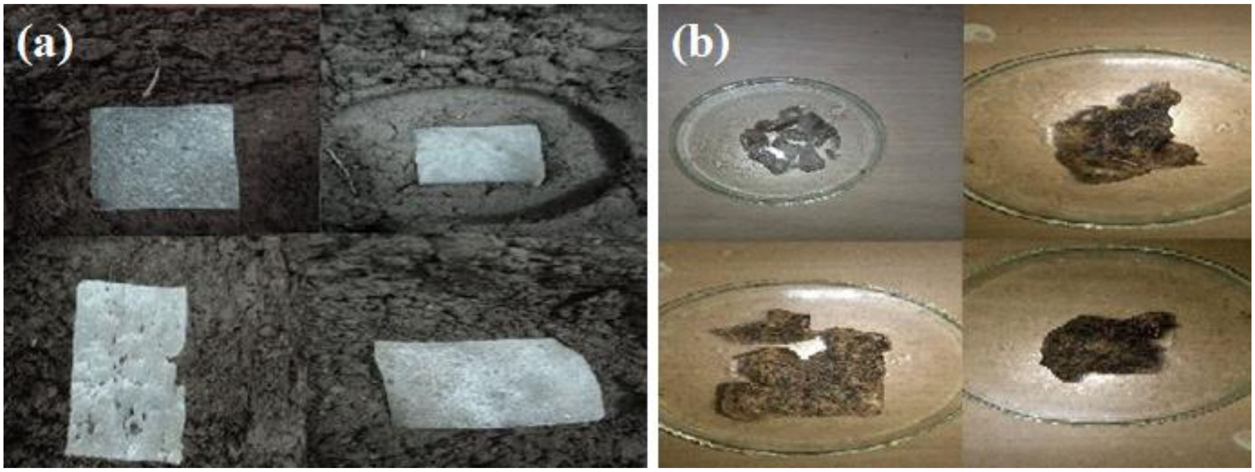


Figure 4. 23 Pictures of starch/sucrose, starch/sucrose/PVA and starch/PVA films. (a) before degradation, (b) after degradation (20 days) under soil.

-further degraded. However, degradation of PVA was slower than the starch and sucrose molecules. Starch/PVA film has very slow degradation due to the cross-linking between the starch and PVA molecules. The F_7 composite film lost about 77% weight and F_9 (starch/PVA) film lost about 50% weights in 45 days.

CHAPTER 5

CONCLUSIONS

5. CONCLUSIONS

It is a challenge before us to develop bio-degradable environment friendly materials essentially a polymer based on the natural resources and replaces the conventionally used polymers. Therefore the primary goal of this work was to synthesis a starch based film and to improve the film properties. Glycerol, PVA and sucrose were used to enhance the properties of the film. Thereafter the degradation behavior of film was investigated which is the prior concern.

- From the mechanical analysis, the starch/sucrose film shows very lower tensile properties. Addition of glycerol or PVA enhanced the TS and EB. With increase in glycerol content and decrease in sucrose content, the tensile strength increased. The F_4composite film performed enhanced tensile strength. But if we use PVA instead of glycerol, the starch/sucrose/PVA film shows comparatively better mechanical strength.
- Thermal analysis describes the stability and degradation of the film with temperature. DTA analysis shows the thermal stability of the starch based film whereas TGA analysis implies the percent loss in weight of the film as a function of temperature. The DT-TG analysis shows that the incorporation of PVA molecules in starch/sucrose composite indicated better thermal stability as compared to the glycerol incorporation.
- 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 sucrose, glycerol or PVA with the starch blend. The peaks of absorption corresponding to the hydroxyl and carbonyl group shifting, indicates the existence of strong H-bonding interaction between the starch, sucrose, PVA and glycerol molecules.
- SEM micrographs illustrates that the glycerol or PVA are able to enhance the compatibility among starch and sucrose, which is useful for the enhancement of the properties of the biopolymer products. SEM micrographs also proved the structural changes after the soil burial test of the film and helped to identify the presence of microorganism in the soil sample, which is responsible for the breakdown of the polymer film.
- Water absorption capacity and contact angle measurement proves the hydrophobic nature of the film. Starch/PVA has more water absorption capacity and low contact

angle implies that this film is very much hydrophilic in nature. The starch/sucrose/PVA film is better hydrophobic in nature than starch/sucrose/glycerol film.

- The soil burial test was done to study the degradation study of the various films which is our main concern. The starch/sucrose composite film easily degraded under the soil and lost 88% weight within 30 days while the conventional polymer takes innumerable days to decompose.

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 PROSPECTS

6. FUTURE PROSPECTS

With an ever-increasing world population, the question is not whether the global environment will be impacted by our presence but how and to what degree. The implementation of sustainable practices will help minimize our blow lying on the environment and conserve resources for future generations. To that end, there is a need to perpetuate the culture of environmental stewardship and sustainability that has grown stronger in recent years. Consumers and municipalities must continue to demand more sustainable packaging materials and practices. Retailers must continue to provide suppliers incentives for greater sustainability in their packaging choices. Although some of the starch-based materials and other biopolymers may not currently be cost-competitive with petroleum plastics, this may change as petroleum prices increase. Starch is poised to establish an even stronger role in the manufacture of sustainable plastics and other bio-products largely because it is abundant, renewable, and inexpensive. Strategies for improving the properties of starch-based plastics such as blending starch with other polymers, using starch in composite materials, and using starch as a fermentation feedstock to make other biopolymers have been successful in developing viable replacements for petroleum based plastics. The prospects for starch in the packaging sector continue to become brighter as the market for sustainable plastics drives further innovation and development.

CHAPTER 7

REFERENCES

7. REFERENCES

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